

UNIVERSITY OF CALIFORNIA SAN DIEGO

Computational Design Principles for Functional Nanoporous Materials via Atomistic
Simulations

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requirements for the degree Doctor of Philosophy

in

Chemistry

by

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University of California San Diego

2025

DEDICATION

To my mother and father,
whose love and support made this journey possible.

To Lin,
for your love, strength, and support, even when we were far apart.

To my mentors and friends,
for making all of this more interesting and meaningful.

EPIGRAPH

“Stay hungry, stay foolish.”

“求知若饥，虚心若愚。”

Steve Jobs; the Whole Earth Catalog (1974)

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PREFACE

This dissertation reflects my journey through the intersection of theory, simulation, and materials design and discovery over the past several years. From the beginning of my PhD, I was drawn to further understanding the underlying physical and chemical mechanisms of various interesting processes and materials, especially within the context of functional nanoporous materials.

The work presented here is the result of both curiosity-driven inquiry and collaborative effort. Chapters of this thesis are focused on two major directions: (i) investigating the influence of chemical composition and structural motifs on the electronic, transport, and photophysical properties of covalent organic frameworks (COFs), and (ii) uncovering the thermodynamic and kinetic mechanisms governing water and ion uptake in metal-organic frameworks (MOFs). These systematic studies leverage a range of computational tools, including density functional theory, molecular dynamics, and enhanced sampling techniques.

Some of the chapters are based on manuscripts that have been published or submitted for publication. Where applicable, co-authors are acknowledged, and permissions have been obtained for reproduction. I have taken care to integrate these works into a cohesive narrative while maintaining the scientific integrity of the original studies.

Writing this thesis has offered a chance to reflect on not only the technical and scientific outcomes but also the process of becoming a more thoughtful, rigorous, and open-minded researcher. I hope that the ideas and findings presented here can contribute to the broader understanding and design of next-generation functional nanoporous materials for energy conversion and storage, as well as ion-mining applications.

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One of the most cherished parts of my daily routine has been our lab lunches — an hour or so of camaraderie and catharsis. These conversations, filled with research highs and lows, scientific and non-scientific gossip, doubts, ideas, and wisdom, have meant more than words can say. A special shoutout to Saswata, Hilliary, Hank, and Suman, the long-standing “lunch gang”, for making that tradition flourish. I will deeply miss those moments. Love you all!

I would also like to thank Prof. Alina Schimpf and the members of her group, including Linfeng, Jessica, Haeun, and Hang, for engaging collaborations and insightful discussions!

Through our joint projects, I gained valuable exposure to experimental research, materials synthesis, and practical applications. Thank you also for your encouragement and support during my job search.

To my friends and colleagues in the Department of Chemistry and Biochemistry and other departments — Arghadip, Javi, Yixing, Arthur, Ziran, Ming, Lisa, Yong Rui, RC, Kevin, Marc, Anqi, Emily, Xandra, Vanessa, and many others — thank you for your companionship and support. Whether through casual chats, scientific debates, or wild parties, your presence has been a vibrant part of this journey. Thank you!

I'm also grateful that I could continue enjoying one of my greatest passions — basketball — throughout these years. Playing has always helped me recharge, no matter my mood. I'm thankful for all the friends I've played with, including Qixuan ("Kuli"), Junlin ("Wu Ge"), Howie, Alvin, Ben, and others. You helped me stay grounded and energized!

Most importantly, I want to thank my parents for their unconditional love and support! As the first college and graduate student in my family, their encouragement, especially from my mother, has meant the world to me. Studying abroad is never easy, and being away from family for nearly four years has been challenging. I'm thankful for modern technology, which made staying connected just a little easier.

A special thank you goes to one of my best friends, Zheng Zeng, for his constant support in both easy and difficult times.

Finally, I am endlessly grateful for meeting Lin, who is currently my fiancée, back in 2022. Thank you for being there for me, even if mostly from afar. Though the distance has been hard, I truly believe we can overcome anything together. In love we trust! Love you!

Chapter 2, in full, is a reprint of the material as it appears in "Engineering Flat and Dispersive Bands in 2D Layered COFs via Interlayer Stacking and Donor–Acceptor Strategy", Y. Pan, C.-H. Ho, F. Paesani, and R. Ghosh, *Chem. Mater.*, 2023, 35, 6235. The dissertation author was the primary investigator and author of this paper.

Chapter 3, in full, is currently being prepared for submission for publication of the mate-

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Chapter 4, in full, has been submitted for publication of the material as it may appear in *Chem. Sci.* as “Thermodynamics of alkali metal ion uptake from aqueous solution in MOF-808”, Y. Pan, S. Saha, M. Burigana, V. Singh, O. Yaghi, and F. Paesani, 2025. The dissertation author was the primary investigator and author of this paper.

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PUBLICATIONS

Y. Pan, C.-H. Ho, F. Paesani, and R. Ghosh, “Engineering flat and dispersive bands in 2D layered COFs via interlayer stacking and donor–acceptor strategy”, *Chem. Mater.*, **2023**, 35, 6235.

S. Dasgupta, **Y. Pan**⁼, E. Palos⁼, and F. Paesani, “Balance between physical interpretability and energetic predictability in widely used dispersion-corrected density functionals”, *J. Chem. Theory Comput.*, **2023**, 20, 49.

J. Geisenhoff, **Y. Pan**, H. Yin, F. Paesani, and A. Schimpf, “Concentration-dependent layer-stacking and the influence on phase-conversion in colloiddally synthesized WSe₂ nanocrystals”, *Chem. Mater.*, **2024**, 36, 8834.

H. Chang⁼, L. Chen⁼, E. Samolova, **Y. Pan**, K. Acosta, C.E. Lemmon, M. Gembicky, F. Paesani, and A. Schimpf, “Electro-reduction-driven formation and connectivity of preyssler-based metal oxide coordination networks”, *Inorg. Chem.*, **2025**, 64, 1630.

Y. Pan⁼, S. Saha⁼, M. Burigana, V. Singh, O. Yaghi, and F. Paesani, “Thermodynamics of alkali metal ion uptake from aqueous solution in MOF-808”. *Under review*.

R. Zhou, E. Bull-Vulpe, **Y. Pan**, and F. Paesani, “Data-Driven Many-Body Simulations of Biomolecules with CCSD (T) Accuracy: I. Polyalanine in the Gas Phase”. *Under review*.

Y. Pan, S. Dasgupta, R. Ghosh, and F. Paesani, “Interplay of Intermolecular Interactions Overrides Chemical Intuition in Functionalized 2D Covalent Organic Frameworks”. *In preparation*.

L. Chen⁼, **Y. Pan**⁼, H. Jung, H. Zhang, C.E. Lemmon, F. Paesani, and A. Schimpf, “Air-stable reduction of Zn-bridged Preyssler-type polyoxometalate frameworks”. *In preparation*.

Note: “=” indicates equal contribution.

ABSTRACT OF THE DISSERTATION

Computational Design Principles for Functional Nanoporous Materials via Atomistic Simulations

by

Yuanhui Pan

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The urgent global challenges of clean energy production and sustainable resource extraction have driven the search for advanced materials capable of addressing these needs. This dissertation focuses on two classes of nanoporous crystalline materials, covalent organic frameworks (COFs) and metal–organic frameworks (MOFs), to uncover the subtle composition–structure–property relationships that govern their electronic and photophysical properties in COFs, and the thermodynamics of ion uptake behavior in MOFs. By applying various appropriate levels of theory and methods for the systems of interest, including density functional theory (DFT), molecular dynamics, and enhanced sampling techniques, this work sheds lights on the electronic

properties of COFs and the thermodynamics of ion transport in MOFs.

In the first part of the study, we investigate how interlayer stacking modulates charge transport in donor–acceptor 2D COFs. The results reveal that structural changes in stacking can result in dramatic tuning in electronic behavior, from delocalized, metallic-like transport to highly localized states with flat bands. These findings highlight the critical role of interlayer interactions in mitigating defect-induced trap states and enhancing charge mobility.

The second part expands this understanding by exploring how chemical composition, functionalization, and lattice symmetry influence stacking preferences and the resulting optoelectronic properties. We find that while van der Waals forces generally favor slipped stackings, functional group-specific electrostatics dominate the degree of slipping and symmetry breaking. Breaking lattice symmetry via backbone functionalization emerges as an effective strategy for tuning transport and photophysical properties, providing novel design principles for photocatalytic COFs.

Finally, we perform molecular dynamics simulations with enhanced sampling techniques and free energy calculations to investigate alkali metal ion uptake in MOF-808 from dilute aqueous solutions. We find that the small pore confinement leads to strong ion-specific thermodynamic and kinetic preferences, governed by a balance between dehydration penalties and confinement-driven stabilization. These insights lay the groundwork for designing MOFs with improved selectivity for critical metal recovery.

Together, this work provides a detailed electronic- and molecular-level framework for understanding and engineering the composition–structure–property relationships in COFs and MOFs, advancing their potential applications in electronics, photocatalysis, and sustainable ion capture from seawater.

Chapter 1

Introduction

1.1 Motivation

The growing global energy demand, combined with the severe environmental pollution due to the combustion of depleting fossil fuels, has made the development of renewable and sustainable energy technologies a critical priority.^{1–3} Modern civilization still relies heavily on fossil fuels — coal, petroleum, and natural gas — to meet its energy needs, accounting for approximately 80% of local or global energy consumption.¹ The combustion of these fuels not only releases vast amounts of carbon dioxide, driving climate change, but also contributes to air and water pollution, resource depletion, and geopolitical tension. As fossil fuel reserves diminish and climate goals become increasingly urgent, there is a clear imperative to transition toward clean energy sources.

In this context, solar energy represents a particularly attractive solution to this crisis.^{1,4,5} It is the most abundant renewable energy resource available, with the potential to supply global energy needs more sustainably. Advances in photovoltaic and photocatalytic technologies have significantly improved conversion efficiencies and reduced costs, making solar power a viable option for both centralized and decentralized energy systems.^{6–9} However, one of the major limitations of solar energy is its intermittency — solar power generation depends on the time of day and weather conditions. To address this issue, effective energy storage systems are essential to ensure a stable and reliable power supply.

To this end, lithium-ion batteries (LIBs) have emerged as a dominant technology for energy storage, owing to their high energy density, long cycle life, and rapidly declining costs.^{10–13} They are already widely used in portable electronics, electric vehicles, and increasingly in grid-scale storage applications. Nevertheless, further improvements are required in terms of capacity, charge/discharge rates, stability, and safety to fully realize their potential in future energy systems. The performance of both solar energy devices and batteries is intimately tied to the properties of the materials they employ. As such, discovering and optimizing new materials with enhanced functionality is central to advancing energy-related technologies.

For example, nanoporous materials, such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), have attracted considerable attention.^{14–16} These materials possess highly ordered crystalline structures with well-defined pores on the nanometer scale. Their modular architectures allow for precise control over chemical composition, pore size, surface functionality, and framework topology. Such tunability makes MOFs and COFs promising platforms for applications in gas adsorption, separation and storage, catalysis, sensing, as well as energy conversion and storage.^{17–19}

Specifically, MOFs have been proposed as hosts for solid-state electrolytes, offering pathways for ion conduction while maintaining chemical and mechanical stability.^{20,21} They have also been explored as precursors to conductive carbon composites in battery electrodes.²² COFs, on the other hand, with their extended π -conjugated systems and all-organic backbones, exhibit excellent thermal stability and can support charge transport — making them promising candidates for use in organic electronic devices, supercapacitors, and photocatalysts.^{23–25} Moreover, both MOFs and COFs offer opportunities for post-synthetic modification, allowing for further functionalization to enhance performance in various applications.^{26–29}

In addition, COFs are gaining increasing attention for their electronic and photophysical properties. Due to their extended conjugation and crystallinity, COFs often exhibit semiconducting behavior and can support efficient charge transport through their frameworks. This makes them promising candidates for applications in organic electronics, including field-effect

transistors, light-emitting diodes, and sensors.^{30,31} Furthermore, COFs have been successfully integrated into photocatalytic systems for solar fuel production and pollutant degradation, benefiting from their high surface area, tailored band structures, and visible-light absorption capabilities. By incorporating donor-acceptor units, redox-active sites, or metal complexes into the backbone, COFs can be designed to mediate photoinduced charge separation and catalyze important redox reactions.^{32,33} These features position COFs as a versatile class of materials with potential impact across energy conversion, environmental remediation, and device technologies.

Furthermore, the growing demand for lithium, driven largely by the proliferation of LIBs in electric vehicles and grid storage systems, presents additional challenges for sustainability. Lithium resources on land are geographically concentrated, with significant deposits in regions such as the Lithium Triangle in South America, China, and Australia.³⁴ This uneven distribution raises concerns about supply security, geopolitical dependency, and the environmental impact of conventional lithium mining. Moreover, traditional mining methods are water- and energy-intensive and can lead to ecological degradation.

As a result, there is growing interest in extracting lithium from unconventional sources such as seawater, which contains vast but dilute quantities of lithium ions.^{34–36} Although the total amount of lithium in seawater is practically inexhaustible, the concentration is very low (approximately 0.2 ppm). Therefore, the development of materials and technologies that can selectively capture lithium from such dilute aqueous solutions could provide a more sustainable and widely accessible alternative to land-based mining.

In this context, MOFs have shown great promise due to their high surface area, tunable functionality, and potential for ion-selective uptake.^{37,38} MOFs can be engineered with specific binding sites that preferentially coordinate lithium ions over competing cations such as sodium, magnesium, and calcium. Their modular architecture allows for both experimental tuning and computational screening to optimize performance. Thus, MOFs represent a promising platform for enabling environmentally friendly and scalable lithium recovery from seawater.

Given the vast design space and the complexity of interactions within these materials,

experimental discovery and optimization alone can be time-consuming and resource-intensive. Computational approaches play a critical role in accelerating the development of functional nanoporous materials. This thesis focuses on the application of theoretical and computational methods to gain electronic- and molecular-level insights into the behavior of COFs and MOFs for their charge transport and photocatalytic performance, as well as ion transport and mining activity, respectively. The integration of electronic structure calculations, molecular dynamics simulations, and enhanced sampling techniques enables the characterization of properties and processes that are difficult and challenging to probe experimentally, and in turn provide physical insights and design principles for next-generation of functional nanoporous materials.

The remainder of this chapter introduces the computational tools employed throughout the thesis, with consideration for balancing computational cost and the desired level of physical and chemical accuracy. Section 2 presents the foundational principles of Density Functional Theory (DFT), a quantum mechanical framework for modeling electronic structure. Section 3 describes classical molecular dynamics and the force field formalism used to model large-scale atomistic systems. Section 4 introduces enhanced sampling techniques, particularly umbrella sampling, used to probe the free energy profiles and analyze rare events. Together, these tools form a comprehensive computational toolbox for understanding and engineering nanoporous materials for clean and renewable energy applications.

1.2 Density Functional Theory

Density Functional Theory (DFT) is a first-principles quantum mechanical method used to investigate the electronic structure of atoms, molecules, and solids.^{39–41} In contrast to wavefunction-based methods, DFT reformulates the many-body Schrödinger equation using the electron density $n(\mathbf{r})$ as the fundamental variable.

The first Hohenberg–Kohn theorem establishes that, for any system of interacting particles in an external potential, the external potential is a unique functional of the electron density (up to

a constant). This implies that all ground-state observables are functionals of the electron density. The second Hohenberg–Kohn theorem introduces a variational principle for the energy functional: the correct ground-state electron density minimizes the total energy functional.⁴² Together, these theorems provide the formal foundation for replacing the many-body wavefunction with the electron density as the central variable in quantum mechanical calculations, leading to substantial simplification for many-electron systems.

Based on these, the Kohn–Sham (KS) approach further introduces a fictitious system of non-interacting electrons that produce the same ground-state density as the real interacting system.⁴³ The KS equations are:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (1.1)$$

where $v_{\text{eff}}(\mathbf{r})$ is the effective potential composed of:

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}). \quad (1.2)$$

Here ε_i is the orbital energy of the corresponding KS orbital ψ_i , and the density for the N -particle system is given as:

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2. \quad (1.3)$$

The total energy functional is expressed as:

$$E[n] = T_s[n] + E_{\text{ext}}[n] + E_H[n] + E_{\text{xc}}[n], \quad (1.4)$$

where $T_s[n]$ is the kinetic energy of non-interacting electrons, $E_H[n]$ is the classical electrostatic energy, and $E_{\text{xc}}[n]$ is the exchange-correlation (XC) energy.

The XC potential $v_{\text{xc}}(\mathbf{r})$ is expressed as the first derivative of the XC energy $E_{\text{xc}}[n]$ with

respect to the density $n(\mathbf{r})$:

$$v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (1.5)$$

Although the KS equations are exact, the exact form and expression of the XC potential $v_{\text{xc}}(\mathbf{r})$ and the corresponding XC energy $E_{\text{xc}}[n]$ are unknown, thus approximations are needed and proposed to solve the KS equations. Several levels of approximation for the XC functional exist, collectively referred to as Jacob’s ladder, with each rung incorporating increasingly sophisticated information about the electronic density:⁴⁴

- **Local Density Approximation (LDA):** Assumes the XC energy at each point depends only on the local electron density, as in a uniform electron gas.
- **Generalized Gradient Approximation (GGA):** Incorporates the gradient of the electron density to account for its spatial variation; common examples include PBE and BLYP.
- **Meta-GGA:** Builds upon GGA by including higher-order terms such as the kinetic energy density; notable examples are SCAN and TPSS.
- **Hybrid Functionals:** Combine GGA or meta-GGA with a fraction of exact exchange from Hartree–Fock theory to reduce self-interaction errors; examples include B3LYP, PBE0, and HSE06.
- **Double Hybrids:** Incorporate both exact exchange and perturbative correlation corrections, such as second-order Møller–Plesset (MP2) contributions.

In this thesis, the GGA functional of PBE⁴⁵ is often used for the calculations of two-dimensional (2D) COFs due to its good balance between accuracy and computational cost. Geometry optimizations, electronic structure calculations, and partial charge analysis are performed to investigate the complicated relationships among chemical composition, lattice structure, interlayer stacking, symmetry, and the electronic, transport, as well as photophysical properties

of 2D COFs. Usually, the van der Waals (vdW) interactions in the systems are better described by using the dispersion-corrected functionals such as DFT-D3(BJ).^{46–48} For better band gap estimation and orbital energetics, HSE06 is often used as a reference.^{49,50}

1.3 Force Fields and Molecular Dynamics

Molecular dynamics (MD) simulations provide insights into the time evolution of molecular systems based on classical Newtonian mechanics. In these simulations, atoms interact via predefined potential energy functions (PEFs) known as force fields. The total potential energy of the system is often modeled as:⁵¹

$$U = U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{vdW}} + U_{\text{elec}}. \quad (1.6)$$

Bonded terms capture covalent interactions:

$$U_{\text{bond}} = \sum k_b (r - r_0)^2. \quad (1.7)$$

$$U_{\text{angle}} = \sum k_\theta (\theta - \theta_0)^2. \quad (1.8)$$

$$U_{\text{dihedral}} = \sum v_n [1 + \cos(n\phi - \delta)]. \quad (1.9)$$

Non-bonded terms include van der Waals (vdW) and electrostatic interactions:

$$U_{\text{vdW}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1.10)$$

$$U_{\text{elec}} = \sum_{i,j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}. \quad (1.11)$$

MD trajectories are often generated by integrating Newton's equations of motion:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i U. \quad (1.12)$$

Simulation conditions are often controlled using various statistical ensembles, each characterized by the physical quantities they hold constant. In the microcanonical ensemble (NVE), the number of particles (N), the system volume (V), and the total energy (E) are conserved. This ensemble is particularly useful for studying isolated systems and serves as a reference for energy conservation in simulations. In the canonical ensemble (NVT), the number of particles (N), volume (V), and temperature (T) are kept constant. Thermostats such as Nosé–Hoover^{52,53} or Langevin dynamics⁵⁴ are employed to maintain a fixed temperature. For simulations under constant pressure (P) and temperature (T), the isothermal-isobaric (NPT) ensemble is used, often utilizing barostats like the Parrinello–Rahman⁵⁵ or Berendsen⁵⁶ algorithms. These ensembles allow for the exploration of different thermodynamic conditions relevant to experimental scenarios. Time steps are typically on the order of 1 fs, with total time scales ranging from nanoseconds to microseconds.

MD is critical for exploring dynamic behavior in nanoporous systems where size, charge, and flexibility play essential roles. Force fields used in this work include general frameworks (e.g., UFF⁵⁷ and GAFF⁵⁸) and specialized models parameterized against *ab initio* calculations. The partial atomic charges are derived from DFT using methods such as the CM5 (Charge Model 5)⁵⁹ or DDEC (Density Derived Electrostatic and Chemical Charges)⁶⁰ scheme. Simulation outputs such as mean square displacements, radial distribution functions, and ion coordination numbers are analyzed to infer diffusion, residence times, and solvation dynamics.

1.4 Enhanced Sampling and Umbrella Sampling

Standard MD simulations often fail to capture rare events due to high energy barriers. Enhanced sampling techniques, such as umbrella sampling, enable targeted exploration of specific reaction coordinates or collective variables (CVs).^{61–64}

Umbrella sampling involves applying a biasing potential (e.g., a harmonic potential) to

constrain the system near predefined values of a CV:

$$U_i(\xi) = \frac{1}{2}k_i(\xi - \xi_i)^2, \quad (1.13)$$

where ξ_i is the center of the i -th window along the CV and k_i is the biasing strength.

Independent MD simulations (windows) are run for each bias to generate histograms of the CV. The unbiased potential of mean force (PMF) is then reconstructed using techniques such as the Weighted Histogram Analysis Method (WHAM):^{65,66}

$$F(\xi) = -k_B T \ln P(\xi), \quad (1.14)$$

where $P(\xi)$ is the probability distribution of the CV from the biased simulations.

The choice of CV is crucial: distances, angles, or coordination numbers are commonly used for ion transport, ligand exchange, or guest adsorption. Window spacing and overlap ensure smooth merging of histograms.

In this thesis, umbrella sampling is used to quantify the free energy profiles associated with ion transport through nanopores within the MOF environments. The method allows identification of free energy profiles, coordination changes, and the influence of solvation environments along the pathway. Reaction mechanisms inferred from PMFs can then be used to predict macroscopic observables or validate with experiment.

References

- [1] Leif Hammarström. Overview: capturing the sun for energy production. *Ambio*, 41(Suppl 2):103–107, 2012.
- [2] Nathan S Lewis and Daniel G Nocera. Powering the planet: Chemical challenges in solar energy utilization. *Proc. National Acad. Sci.*, 103(43):15729–15735, 2006.
- [3] Steven Chu and Arun Majumdar. Opportunities and challenges for a sustainable energy future. *Nature*, 488(7411):294–303, 2012.
- [4] Nadarajah Kannan and Divagar Vakeesan. Solar energy for future world:-A review. *Renew. Sustain. Energy Rev.*, 62:1092–1105, 2016.
- [5] Ehsanul Kabir, Pawan Kumar, Sandeep Kumar, Adedeji A Adelodun, and Ki-Hyun Kim. Solar energy: Potential and future prospects. *Renew. Sustain. Energy Rev.*, 82:894–900, 2018.
- [6] Bryce S Richards, Damien Hudry, Dmitry Busko, Andrey Turshatov, and Ian A Howard. Photon upconversion for photovoltaics and photocatalysis: a critical review: focus review. *Chem. Rev.*, 121(15):9165–9195, 2021.
- [7] Zhiyi Yuan, Pin Chieh Wu, and Yu-Cheng Chen. Optical resonator enhanced photovoltaics and photocatalysis: fundamental and recent progress. *Laser & Photonics Reviews*, 16(2): 2100202, 2022.
- [8] César Clavero. Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nat. Photonics*, 8(2):95–103, 2014.
- [9] Naveen Kumar Elumalai, Chellappan Vijila, Rajan Jose, Ashraf Uddin, and Seeram Ramakrishna. Metal oxide semiconducting interfacial layers for photovoltaic and photocatalytic applications. *Mater. Renew. Sustain. Energy*, 4:1–25, 2015.
- [10] Taehoon Kim, Wentao Song, Dae-Yong Son, Luis K Ono, and Yabing Qi. Lithium-ion batteries: outlook on present, future, and hybridized technologies. *J. Mater. Chem. A*, 7(7): 2942–2964, 2019.
- [11] Matthew Li, Jun Lu, Zhongwei Chen, and Khalil Amine. 30 years of lithium-ion batteries. *Adv. Mater.*, 30(33):1800561, 2018.
- [12] Arumugam Manthiram. An outlook on lithium ion battery technology. *ACS Central Sci.*, 3(10):1063–1069, 2017.

- [13] Ghassan Zubi, Rodolfo Dufo-López, Monica Carvalho, and Guzay Pasaoglu. The lithium-ion battery: State of the art and future perspectives. *Renew. Sustain. Energy Rev.*, 89: 292–308, 2018.
- [14] Hong-Cai “Joe” Zhou and Susumu Kitagawa. Metal–organic frameworks (MOFs). *Chem. Soc. Rev.*, 43(16):5415–5418, 2014.
- [15] San-Yuan Ding and Wei Wang. Covalent organic frameworks (COFs): from design to applications. *Chem. Soc. Rev.*, 42(2):548–568, 2013.
- [16] Keyu Geng, Ting He, Ruoyang Liu, Sasanka Dalapati, Ke Tian Tan, Zhongping Li, Shanshan Tao, Yifan Gong, Qihong Jiang, and Donglin Jiang. Covalent organic frameworks: design, synthesis, and functions. *Chem. Rev.*, 120(16):8814–8933, 2020.
- [17] Ralph Freund, Orysia Zaremba, Giel Arnauts, Rob Ameloot, Grigori Skorupskii, Mircea Dincă, Anastasiya Bavykina, Jorge Gascon, Aleksander Ejsmont, Joanna Goscińska, Markus Kalmutzki, Ulrich Lächelt, Evelyn Ploetz, Christian S. Diercks, and Stefan Wuttke. The current status of MOF and COF applications. *Angew. Chem. Int. Ed.*, 60(45):23975–24001, 2021.
- [18] Tian Luo, Leisan Gilmanova, and Stefan Kaskel. Advances of MOFs and COFs for photocatalytic CO₂ reduction, H₂ evolution and organic redox transformations. *Coord. Chem. Rev.*, 490:215210, 2023.
- [19] Xing Gao, Yu Dong, Siwu Li, Junwen Zhou, Lu Wang, and Bo Wang. MOFs and COFs for batteries and supercapacitors. *Electrochem. Energy Rev.*, 3:81–126, 2020.
- [20] Satoshi Horike, Daiki Umeyama, and Susumu Kitagawa. Ion conductivity and transport by porous coordination polymers and metal–organic frameworks. *Acc. Chem. Res.*, 46(11): 2376–2384, 2013.
- [21] Wendan Xue, Christopher D Sewell, Qixing Zhou, and Zhiqun Lin. Metal–organic frameworks for ion conduction. *Angew. Chem. Int. Ed.*, 61(34):e202206512, 2022.
- [22] Minghai Shen and Hailing Ma. Metal-organic frameworks (MOFs) and their derivative as electrode materials for lithium-ion batteries. *Coord. Chem. Rev.*, 470:214715, 2022.
- [23] Hanyin Zhang, Yubo Geng, Jin Huang, Zixiao Wang, Kun Du, and Haoyuan Li. Charge and mass transport mechanisms in two-dimensional covalent organic frameworks (2D COFs) for electrochemical energy storage devices. *Energy & Environmental Science*, 16(3):889–951, 2023.
- [24] Muhammad Sajjad and Wen Lu. Covalent organic frameworks based nanomaterials: Design, synthesis, and current status for supercapacitor applications: A review. *J. Energy Storage*,

39:102618, 2021.

- [25] Yongzhi Chen and Donglin Jiang. Photocatalysis with covalent organic frameworks. *Acc. Chem. Res.*, 57(21):3182–3193, 2024.
- [26] Seth M Cohen. Postsynthetic methods for the functionalization of metal–organic frameworks. *Chem. Rev.*, 112(2):970–1000, 2012.
- [27] Timur Islamoglu, Subhadip Goswami, Zhanyong Li, Ashlee J Howarth, Omar K Farha, and Joseph T Hupp. Postsynthetic tuning of metal–organic frameworks for targeted applications. *Acc. Chem. Res.*, 50(4):805–813, 2017.
- [28] Amir Khojastehnezhad, Ali Samie, Anna Bisio, Hani M El-Kaderi, and Mohamed Siaj. Impact of postsynthetic modification on the covalent organic framework (COF) structures. *ACS Appl. Mater. Interfaces*, 2024.
- [29] Narges Abdolhossein Rejali, Mohammad Dinari, and Yong Wang. Post-synthetic modifications of covalent organic frameworks (COFs) for diverse applications. *Chem. Commun.*, 59:11631–11647, 2023.
- [30] Qi Liu, Qiang Li, Yu Li, Taotao Su, Binghan Hou, Yibo Zhao, and Youzhi Xu. Two-dimensional covalent organic frameworks in organic electronics. *Angew. Chem. Int. Ed.*, page e202502536, 2025.
- [31] H. Vignesh Babu, M. G. Monika Bai, and M. Rajeswara Rao. Functional π -conjugated two-dimensional covalent organic frameworks. *ACS Appl. Mater. Interfaces*, 11(12):11029–11060, 2019.
- [32] Lingsong Wang and Weigang Zhu. Organic donor-acceptor systems for photocatalysis. *Adv. Sci.*, 11(10):2307227, 2024.
- [33] Islam E Khalil, Prasenjit Das, and Arne Thomas. Two-dimensional covalent organic frameworks: Structural insights across different length scales and their impact on photocatalytic efficiency. *Acc. Chem. Res.*, 57(21):3138–3150, 2024.
- [34] Sixie Yang, Fan Zhang, Huaiping Ding, Ping He, and Haoshen Zhou. Lithium metal extraction from seawater. *Joule*, 2(9):1648–1651, 2018.
- [35] Juezhi Yu, Daliang Fang, Hang Zhang, Zhi Yi Leong, Jingtao Zhang, Xiaoxia Li, and Hui Ying Yang. Ocean mining: a fluidic electrochemical route for lithium extraction from seawater. *ACS Mater. Lett.*, 2(12):1662–1668, 2020.
- [36] Zhen Li, Chunyang Li, Xiaowei Liu, Li Cao, Peipei Li, Ruicong Wei, Xiang Li, Dong Guo, Kuo-Wei Huang, and Zhiping Lai. Continuous electrical pumping membrane process for

seawater lithium mining. *Energy & Environmental Science*, 14(5):3152–3159, 2021.

- [37] Jue Hou, Huacheng Zhang, Aaron W Thornton, Anita J Hill, Huanting Wang, and Kristina Konstas. Lithium extraction by emerging metal–organic framework-based membranes. *Adv. Funct. Mater.*, 31(46):2105991, 2021.
- [38] Lirong Li, Biyuan Liu, and Zhigang Li. Metal-organic framework-based membranes for ion separation/selection from salt lake brines and seawater. *Nanoscale*, 16(42):19543–19563, 2024.
- [39] Reinier M Dreizler and Eberhard KU Gross. *Density functional theory: an approach to the quantum many-body problem*. Springer Science & Business Media, 2012.
- [40] Walter Kohn, Axel D Becke, and Robert G Parr. Density functional theory of electronic structure. *J. Phys. Chem.*, 100(31):12974–12980, 1996.
- [41] Robert G Parr and Weitao Yang. Density-functional theory of the electronic structure of molecules. *Annu. Rev. Phys. Chem.*, 46(1):701–728, 1995.
- [42] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136(3B):B864, 1964.
- [43] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140(4A):A1133, 1965.
- [44] John P Perdew and Karla Schmidt. Jacob’s ladder of density functional approximations for the exchange-correlation energy. In *AIP Conference Proceedings*, volume 577, pages 1–20. American Institute of Physics, 2001.
- [45] John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77(18):3865, 1996.
- [46] Erin R Johnson and Axel D Becke. A post-hartree-fock model of intermolecular interactions: Inclusion of higher-order corrections. *J. Chem. Phys.*, 124(17):174104, 2006.
- [47] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate *Ab Initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.*, 132(15):154104, 2010.
- [48] Stefan Grimme, Stephan Ehrlich, and Lars Goerigk. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.*, 32(7):1456–1465, 2011.
- [49] Jochen Heyd, Gustavo E Scuseria, and Matthias Ernzerhof. Hybrid functionals based on a screened coulomb potential. *J. Chem. Phys.*, 118(18):8207–8215, 2003.

- [50] Aliaksandr V Krukau, Oleg A Vydrov, Artur F Izmaylov, and Gustavo E Scuseria. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.*, 125(22), 2006.
- [51] Andrew R Leach. *Molecular modelling: principles and applications*. Pearson education, 2001.
- [52] Shuichi Nosé. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.*, 81(1):511–519, 1984.
- [53] William G Hoover. Canonical dynamics: Equilibrium phase-space distributions. *Phys. Rev. A*, 31(3):1695, 1985.
- [54] Pierre Turq, Frédéric Lantelme, and Harold L Friedman. Brownian dynamics: Its application to ionic solutions. *J. Chem. Phys.*, 66(7):3039–3044, 1977.
- [55] Michele Parrinello and Aneesur Rahman. Crystal structure and pair potentials: A molecular-dynamics study. *Phys. Rev. letters*, 45(14):1196, 1980.
- [56] Herman JC Berendsen, JPM van Postma, Wilfred F Van Gunsteren, ARHJ DiNola, and Jan R Haak. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.*, 81(8):3684–3690, 1984.
- [57] Anthony K Rappé, Carla J Casewit, KS Colwell, William A Goddard III, and W Mason Skiff. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.*, 114(25):10024–10035, 1992.
- [58] Junmei Wang, Romain M Wolf, James W Caldwell, Peter A Kollman, and David A Case. Development and testing of a general amber force field. *J. Comput. Chem.*, 25(9):1157–1174, 2004.
- [59] Aleksandr V Marenich, Steven V Jerome, Christopher J Cramer, and Donald G Truhlar. Charge model 5: An extension of hirshfeld population analysis for the accurate description of molecular interactions in gaseous and condensed phases. *J. Chem. Theory Comput.*, 8(2):527–541, 2012.
- [60] Thomas A Manz and Nidia Gabaldon Limas. Introducing DDEC6 atomic population analysis: part 1. charge partitioning theory and methodology. *Rsc Adv.*, 6(53):47771–47801, 2016.
- [61] Yi Isaac Yang, Qiang Shao, Jun Zhang, Lijiang Yang, and Yi Qin Gao. Enhanced sampling in molecular dynamics. *J. Chem. Phys.*, 151(7), 2019.
- [62] Jérôme Hénin, Tony Lelièvre, Michael R Shirts, Omar Valsson, and Lucie Delemotte.

Enhanced sampling methods for molecular dynamics simulations. *arXiv preprint arXiv:2202.04164*, 2022.

- [63] Glenn M Torrie and John P Valleau. Monte Carlo free energy estimates using non-Boltzmann sampling: Application to the sub-critical Lennard-Jones fluid. *Chem. Phys. Lett.*, 28(4):578–581, 1974.
- [64] Glenn M Torrie and John P Valleau. Nonphysical sampling distributions in Monte Carlo free-energy estimation: Umbrella sampling. *J. Comput. Phys.*, 23(2):187–199, 1977.
- [65] Alan M Ferrenberg and Robert H Swendsen. Optimized Monte Carlo data analysis. 63 (12):1195, 1989.
- [66] Grossfield, Alan. WHAM: the weighted histogram analysis method. version 2.0.10. <http://membrane.urmc.rochester.edu/content/wham/>.

Chapter 2

Engineering Flat and Dispersive Bands in 2D Layered COFs via Interlayer Stacking and Donor-Acceptor Strategy

2.1 Introduction

The discovery of 2D covalent organic frameworks (COFs) in 2005 has sparked renewed interest in organic electronics research.¹ Due to a range of unique advantages such as morphological precision and positional control of diverse functional building blocks, COFs have received widespread research interest for a broad range of applications, including gas adsorption and separation,^{2–4} sensing,^{5,6} catalysis,^{7,8} energy conversion and storage^{9–11}. More recently, building upon the success of D-A copolymers for device applications, there have been reports of the synthesis of several donor-acceptor (D-A) COFs.^{12–15} For example, D-A copolymers have achieved record power conversion efficiencies (17.3%)¹⁶ and hole mobilities as high as $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported,^{17,18} thus making them ideal candidates for field-effect transistors (FETs).^{19,20} In a similar vein, the incorporation of donor and acceptor building blocks has been found to modulate the optoelectronic properties of various COF structures, thus demonstrating the potential of COFs in photoelectric^{13,14,21,22} and photocatalytic applications.^{15,23–25}

Tailoring COFs with the aforementioned targeted properties requires a deeper understanding of the factors influencing charge transport processes. Charge transport in COFs is a

multi-scale process that involves many aspects of the COF microstructure, from molecular-scale charge transfer events to nano-scale intra- and inter-layer polaron/charge delocalization.²⁶ In this context, 2D layered COFs are formed from the self-assembly of the molecular layers via interlayer π -stacking interactions. The manner in which the 2D layers stack largely influences the electronic and transport properties of COFs.^{27–34} Interlayer stacking interactions are governed by several factors such as monomer structure and planarity, crystallinity, stacking configuration (e.g., eclipsed vs. staggered vs. random), and hydrogen bonding. Different stacking arrangements such as cofacial vs. slip-stacked configurations directly influence the degree and extent of charge/energy transfer along the π -stacks.^{35–39} Although slipped and inclined stacking arrangements are usually the energetically preferred stacking patterns,^{13,21,37,40–42} various stacking patterns can be achieved under appropriate chemical and thermodynamic conditions.^{30,36,43} Common forms of interlayer stacking patterns are the eclipsed (AA) and staggered (AB) forms. In the eclipsed configuration, π -stacking maintains an “in-phase” registry where the donors and acceptors in one layer are positioned adjacent to the donors and acceptors in the neighboring layer, respectively. The staggered arrangement exhibits an “out-of-phase” registry, where the donors in one layer line up adjacent to the acceptors in the neighboring layer.²² Since there are few prior computational reports,^{35,37,38,44–46} we employ density functional theory (DFT) and simulations based on the Multiparticle Holstein Formalism (MHF) to investigate the influence of interlayer stacking on the electronic and transport properties of layered D-A COFs.

Due to remarkable photo-induced charge transfer and long-lived charge separation,²² we chose D_{CuPc}-A_{PyrDI}-COFs as a representative model COF system for our DFT simulations. In our recent studies, we have introduced the three-dimensional MHF model to investigate the effects of defects, domain size, chemical doping, and topological connectivity on the charge transport properties of COFs.^{26,47,48} Building upon good agreement with available experimental measurements of the mid-infrared spectra of doped COFs, we have gained fundamental insights and proposed new design strategies for the synthesis of 2D COFs with improved conductivity.²⁶ In this study, we combine MHF-based analysis with simulations based on DFT to investigate

how inter-layer stacking arrangements impact interlayer charge delocalization.

2.2 Results and Discussion

2.2.1 Structural Models

Figure 2.1 shows the PBE+ U -D3(BJ)-optimized structures of the D_{CuPc} - A_{PyrDI} COF monolayer, eclipsed, and staggered stacking arrangements along with the high symmetry k -point pathways in the first Brillouin zone (highlighted in orange). Our calculated lattice parameters (reported in the caption of Figure 2.1) are in good agreement with previously reported values.²² It should be noted that the optimized structures reported in Ref. 22 were obtained at the DFTB level of theory, which is possibly the reason for the small differences found with our PBE+ U -D3(BJ)-optimized unit cells.

2.2.2 Electronic Structure Calculations

In this section, we investigate the evolution of the intra- and inter-framework electronic properties of D_{CuPc} - A_{PyrDI} COFs as a function of different stacking arrangements. To begin with, we characterize the electronic properties of the individual donor and acceptor building blocks.

Figure 2.2 shows the frontier molecular orbitals (MOs) of the isolated Cu(II) phthalocyanine donor, D_{CuPc} , and pyromellitic diimide acceptor, A_{PyrDI} , which have D_{4h} and D_{2h} symmetry, respectively. The shifted energy levels between the spin-up (-5.37 eV) and spin-down (-3.43 eV) channels (labeled “Cu-induced state” in Figure 2.2) are primarily induced by the Cu(II) center. This can be confirmed by analyzing the partial density of states (PDOS) in Figure 2.3 as well as the MO symmetry associated with the two shifted states, B_{1g} , which matches the symmetry of the $3d_{x^2-y^2}$ orbital from the Cu center. For the donor building block, the singly degenerate highest occupied molecular orbital (HOMO) and the doubly degenerate lowest unoccupied molecular orbitals (LUMOs) that are induced by the organic components, exhibit slightly different energies (≈ 0.01 eV) between the spin-up and spin-down channels due to spin polarization induced by

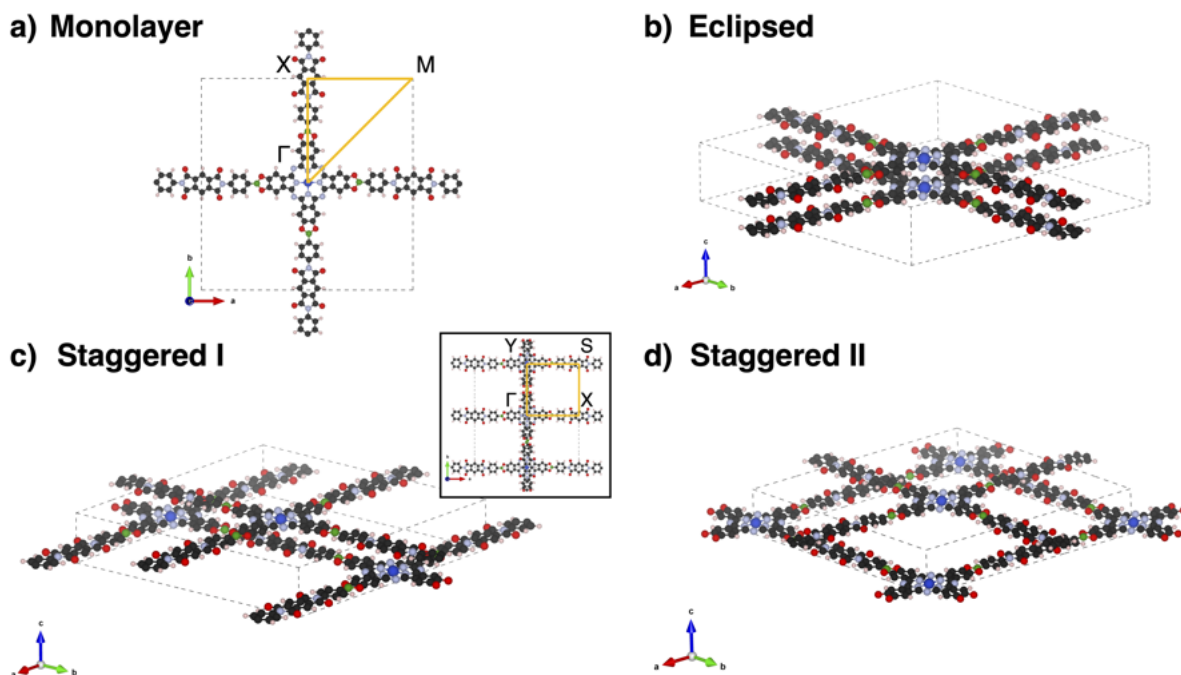


Figure 2.1. PBE+*U*-D3(BJ)-optimized structures of the D_{CuPc}-A_{PyrDI}-COFs. The optimized lattice parameters for (a) monolayer: $a = b = 35.50$ Å. (b) eclipsed: $a = b = 35.34$ Å, and $c = 3.36$ Å. (c) staggered I: $a = 35.42$ Å, $b = 35.39$ Å, and $c = 3.18$ Å. (d) staggered II: $a = b = 35.41$ Å, and $c = 3.11$ Å. The colors of the atoms are as follows: dark blue for Cu, light blue for N, red for O, black for C, green for B, and pink for H. The high symmetry k -point pathways in the first Brillouin zone (highlighted in orange) are indicated for the monolayer (similar pattern for the eclipsed and staggered II stackings) and staggered I (see inset) systems. The three stacking arrangements have one more high symmetry k -point pathway (Γ – Z) along the stacking direction, which is not shown here. The unit cell boundaries are indicated by the dashed lines.

the unpaired electron of Cu(II). The energies of the frontier MOs suggest that the predominant contributions to the valence band (VB) and conduction band (CB) in the D-A system originate from the individual donor and acceptor building blocks, respectively, which can be confirmed by analyzing the partial charge distributions in the VBs and CBs that are shown in Figure 2.4. The VB throughout this study is defined as the topmost energy band/range which originates mainly from the organic components and lies right below the Fermi level. Similarly, the CB is the lowermost energy band/range which originates from the organic components and lies right above the Fermi level (see Figure 2.3).

Monolayer: The band structure of the 2D COF monolayer (Figure 2.3a) exhibits flat bands for the (doubly degenerate) CBs and VB along the Γ -X-M- Γ (i.e. intra-framework) directions. This implies that both the electrons and holes have infinite effective masses (m^*) and are highly localized within the COF monolayer.

The partial charge distribution in Figure 2.4a shows that the contributions to the VBM and CBM are indeed dominated by the donor (D_{CuPc}) and acceptor (A_{PyrDI}) building blocks,

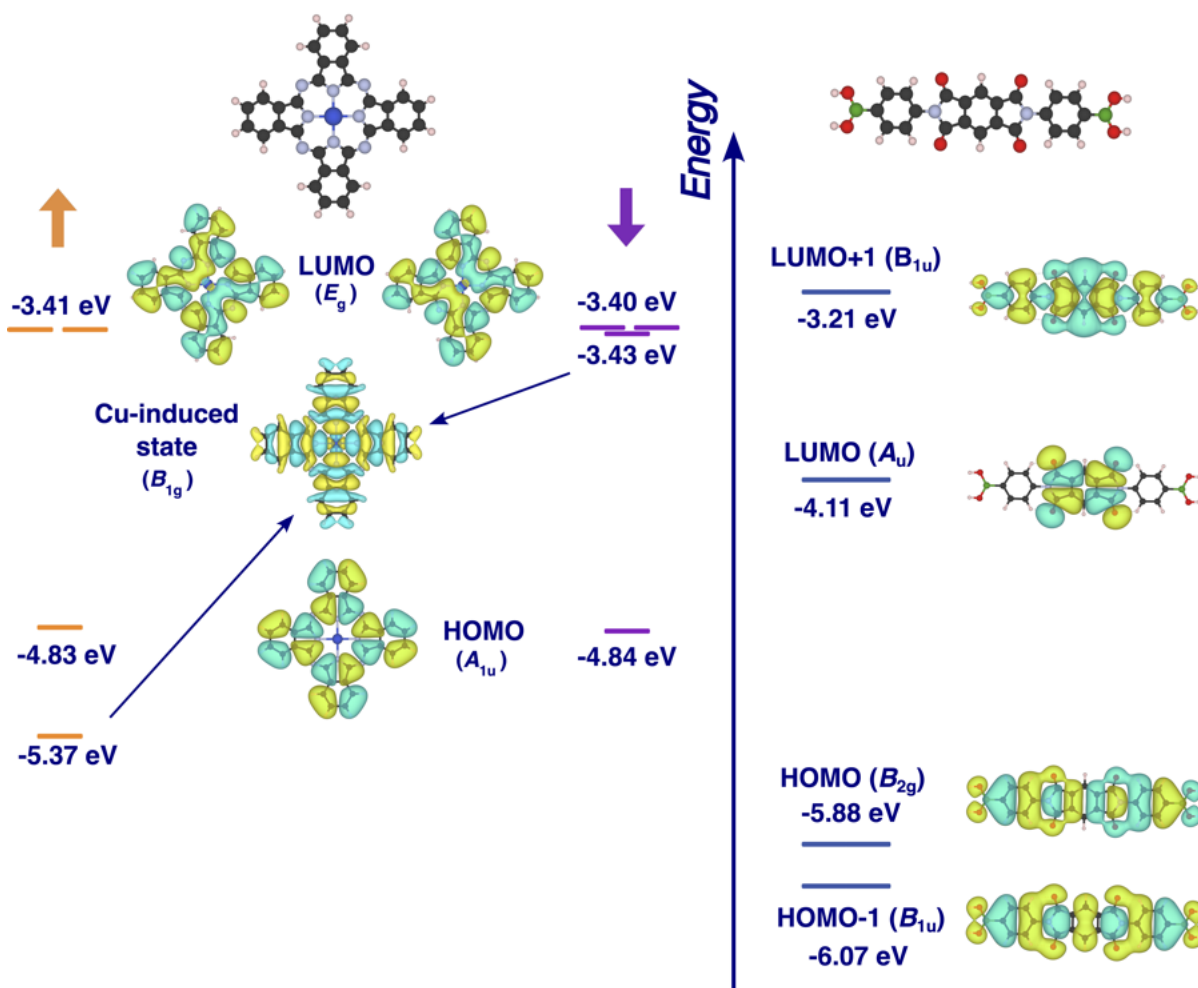


Figure 2.2. PBE+ U -optimized geometry structure of the donor (D_{CuPc}) and acceptor (A_{PyrDI}) along with the frontier MOs. The spin-polarized energy levels of the frontier MOs of D_{CuPc} are shown in orange and purple for spin-up and spin-down, respectively. The non-spin-polarized energy levels of the frontier MOs of A_{PyrDI} are shown in blue. The MO symmetries are shown in parentheses.

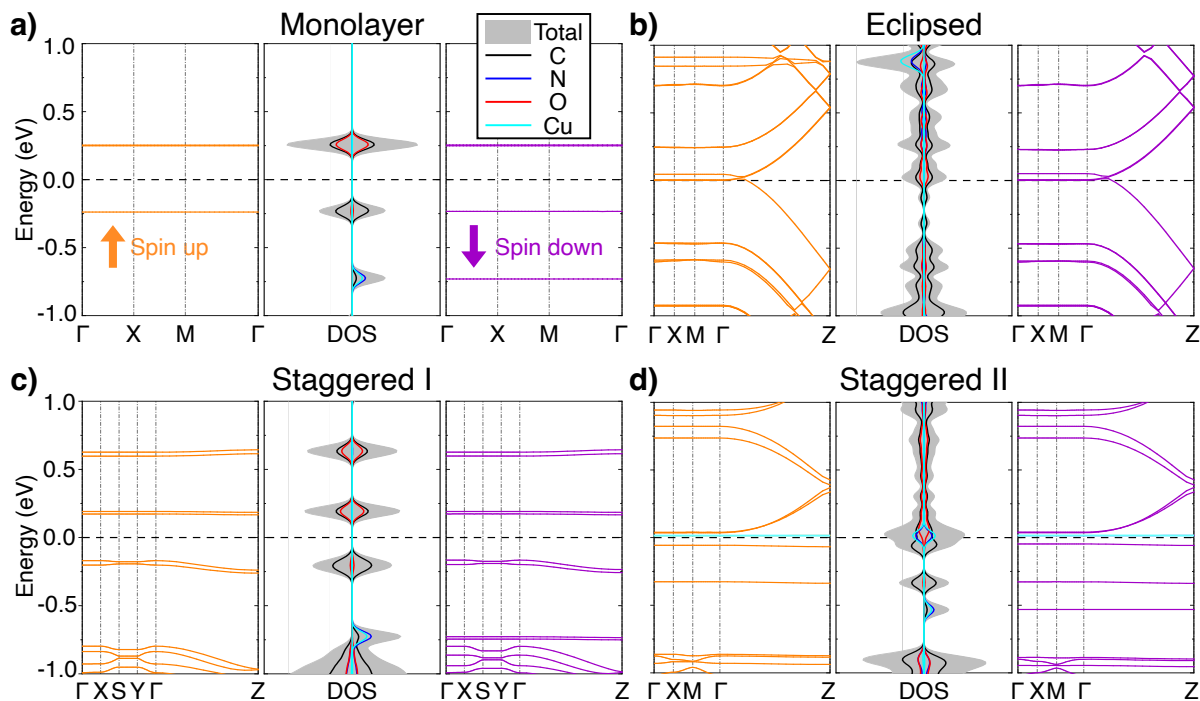


Figure 2.3. PBE+*U*-D3(BJ)-evaluated spin-polarized band structures and DOS of the D_{CuPc} - A_{PyTfDI} -COFs. (a) monolayer, (b) eclipsed, (c) staggered I, and (d) staggered II. The orange and purple band structures on the left and right columns in each sub-figure correspond to the spin-up and spin-down configurations, respectively. The left and right parts of the middle column in each subfigure show the corresponding spin-polarized total and PDOS from C, N, O, and Cu. The bands in cyan near the Fermi level in (d) represent the mid-gap bands with predominant contributions from the Cu(II) centers as indicated by the PDOS. The Fermi level is set to zero and indicated by the black horizontal dashed line.

respectively. The monolayer is semiconductive and displays direct band gaps of 0.49 eV and 0.48 eV for the spin-up and spin-down channels, respectively. It is important to mention here that this study is not focused on reporting precise band gap values and effective masses, for which hybrid functionals such as PBE0 and HSE06 may be necessary. Instead, the primary focus is on investigating how the band structure associated with the organic components evolves as a function of different interlayer stacking arrangements. More specifically, our goal is to understand how the relative position of the donor and acceptor molecular building blocks in the neighboring layers impact the dispersion of the valence and conduction bands.

Eclipsed stacking: For the eclipsed stacking arrangement (Figure 2.1b, Figure 2.5a), the

CB within the COF plane (i.e., along the Γ -X-M- Γ direction in Figure 2.3b) display flat bands which are consistent with our observation for the 2D monolayer (Figure 2.3a). However, the VBs (~ -0.46 eV) within the plane (Γ -X-M- Γ) become slightly more dispersive with lighter

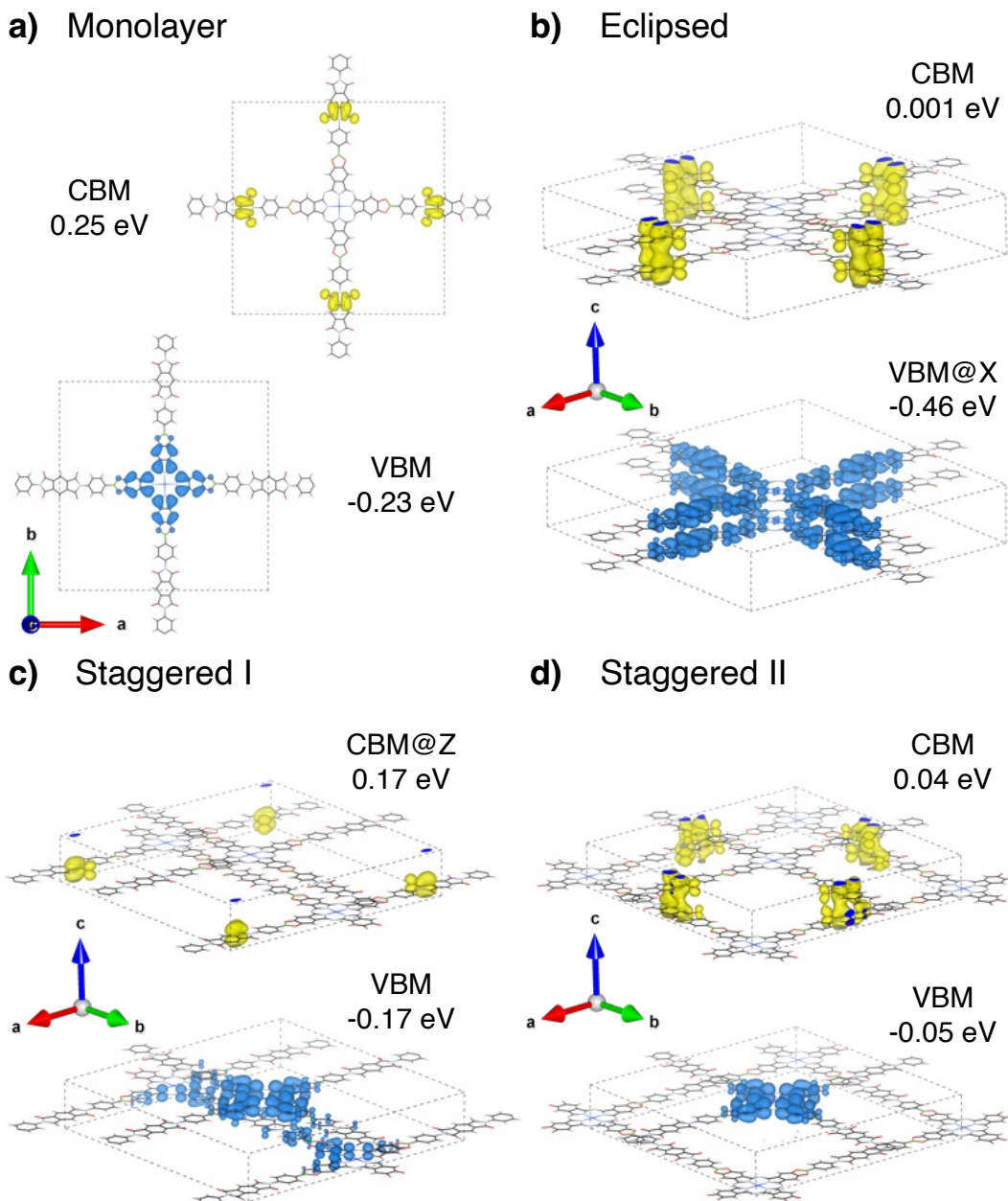


Figure 2.4. PBE+U-D3(BJ)-evaluated partial charge distribution in the CBMs (yellow) and VBMs (blue) at Γ (unless otherwise specified) of the D_{CuPc} - A_{PyrdI} -COFs. (a) monolayer, (b) eclipsed, (c) staggered I, and (d) staggered II. The unit cell boundaries are indicated by the dashed lines. More details can be found in the Appendix.

m_h^* compared to the monolayer. Dispersive bands along the intra-framework direction can be understood by analyzing the more delocalized partial charge distribution of the VBM at X (VBM@X) in Figure 2.4b, as well as a smaller value of m_h^* ($-7.493 m_0$) at X along X–M for the spin-up channel. This observation suggests that stacking-induced interlayer interactions may potentially enhance charge delocalization within the plane (i.e., intra-framework) resulting in more dispersive bands and lighter m_h^* compared to the monolayer. Overall, the eclipsed stacking arrangement exhibits intra-framework band gaps of 0.46 eV and 0.47 eV for the spin-up and spin-down channels, respectively.

In contrast to the flat CBs within the plane, the bands near the Fermi level along the c direction (Γ –Z) are significantly dispersive (Figure 2.3b). The bands crossing the Fermi level along the Γ –Z direction for the spin-up and spin-down channels suggest metallic behavior having zero band gap. The magnitude of the corresponding m^* (along Γ –Z), evaluated from the metallic band segment crossing the Fermi level, is calculated to be $0.973 m_0$ (spin-up) and $0.979 m_0$ (spin-down), respectively, suggesting lighter and more delocalized charge carriers (both electrons and holes) along the inter-framework direction. The enhanced delocalization of the charge carriers along the inter-framework stacking direction primarily arises due to effective π -overlap of the frontier orbitals and resonant electronic interactions between the donor-donor and acceptor-acceptor components, respectively, in the adjacent layers (Figure 2.4b). The dispersion along the Γ –Z direction can be confirmed by analyzing the partial charge distribution of the CBs, which originates mostly from the π orbitals of the C and O atoms located on the acceptors, allowing the charges to efficiently transfer between layers. Our analysis, therefore, suggests that highly anisotropic transport characteristics, including metallic behavior, can be potentially achieved via eclipsed stacking arrangements in 2D layered COFs.

Staggered I: Unlike eclipsed stacking, in staggered I stacking (Figure 2.1c, Figure 2.5a), the donors line up adjacent to the acceptors in the neighboring layers. Due to lower symmetry of staggered I stacking (D_{2h} symmetry) compared to monolayer and eclipsed stacking (D_{4h} symmetry), there is a change in the high symmetry k -paths along the intra-framework directions

(Figure 2.1c). The band structure (Figure 2.3c) near the Fermi level along the intra-framework direction (i.e., along Γ -X-S-Y- Γ) displays completely flat CBs, with localized partial charge distribution on the acceptors (Figure 2.4c), primarily due to the highly localized LUMO of the acceptor (Figure 2.2). However, similar to the eclipsed stacking, the VBs along the intra-framework direction (i.e., along Γ -X-S-Y- Γ) become more dispersive compared to the monolayer. The corresponding m_h^* (at Γ along Y- Γ) values are found to be $-2.076 m_0$ for both spin channels. The dispersive nature and associated enhancement in charge (hole) transport along the intraframework direction originate from interlayer interactions, which can be appreciated by looking at the delocalized partial charge distribution induced by the donor units from the neighboring layer (Figure 2.4c).

In sharp contrast to eclipsed stacking which displays metallic behavior and a vanishing band gap along the Γ -Z direction, the almost flat CBs along the Γ -Z direction in staggered I correspond to states that are highly localized ($m_e^* = 48.136 m_0$ for spin-up and $m_e^* = 45.304 m_0$ for spin-down channel) on the acceptors, with negligible overlap (see Figure 2.4c) of the partial charge distribution between the donor and acceptor units along the inter-framework direction. Unlike (almost) flat CBs, the comparatively more dispersive VBs along the Γ -Z direction (Figure 2.3c) result in effective masses of m_h^* (at Γ along Γ -Z) of $-5.067 m_0$ (spin-up) and $-5.157 m_0$ (spin-down), respectively. This is consistent with Figure 2.4c, where the partial charge distribution from the more dispersive VB is delocalized to a greater extent along the inter-framework direction, as compared to that in the CBs. Nevertheless, the calculated values of m_h^* along the inter-framework (Γ -Z) direction in staggered I are heavier than the inter-framework m_h^* values of $0.973 m_0$ (spin-up) and $0.979 m_0$ (spin-down) in eclipsed stacking. This implies that the relative arrangement of donors and acceptor units in neighboring layers has a profound impact on the extent of anisotropic through-space and through-bond electron and hole transport. Staggered I stacking exhibits semiconducting behavior with calculated band gaps of 0.34 eV and 0.33 eV for the spin-up and spin-down channels, respectively.

Staggered II: Slipping one layer relative to the neighboring layer results in a new

stacking arrangement referred to as staggered II stacking, where the donors are now positioned on top of the central pores in the neighboring layers (Figure 2.1d) and the acceptors in the neighboring layers lie adjacent to each other. The band structure displays highly flat mid-gap bands (highlighted in cyan in Figure 2.3d) that are induced by the 3d orbitals of the Cu atoms. These flat bands correspond to highly localized states (see Figure 2.8) and are referred to as “intrinsic mid-gap states”.⁴⁹ It is important to clarify that the focus of this work is not on these localized states and our definition of VB and CB remains unchanged. The VB and CBs originating from the organic components remain flat along the intra-framework direction (Γ -X-M- Γ)(Figure 2.3d). However, along the Γ -Z direction (Figure 2.3d), the CBs become more dispersive compared to the monolayer with m_e^* (at Γ along Γ -Z) values of $3.063 m_0$ for both the spin channels. The dispersive CBs along the interframework direction compared to the flat bands along the intraframework direction is a result of the effective orbital overlap between the acceptors along the interlayer direction, as indicated in the partial charge distribution at CBM (at Γ , in Figure 2.4d). In contrast, the VB along the Γ -Z direction, is almost flat with highly localized states on the donors (Figure 2.3d and Figure 2.4d). The corresponding m_h^* values (at Γ along Γ -Z) are calculated to be -46.663 and -50.552 m_0 for spin-up and spin-down channels, respectively. Staggered II stacking is therefore ideally suited to exhibit single-carrier-type behavior along the inter-framework direction, with delocalized electrons (dispersive CBs) and localized holes (flat VB), thus showing potential for applications in unipolar transistors or FETs. However, the introduction of highly flat mid-gap bands induced by the Cu centers in Figure 2.3d that lies slightly above the Fermi level modifies the band gap and transport properties. As a result, staggered II stacking is a semiconductor having a very low band gap of 0.09 (0.08) eV for the spin-up (down) channel from the organic components, and the band gap further reduces to 0.07 (0.06) eV due to the existence of the Cu-induced mid-gap states. We also note that it is possible to modify the Fermi level either by fine-tuning the externally applied electric fields or via chemical doping⁵⁰⁻⁵² to obtain fully single-carrier-type (either electron or hole) charge transport characteristics for applications in unipolar transistors or FETs.

It is important to note that the flat bands observed in our systems arise from highly localized orbitals with vanishing overlap between the atomic wavefunctions, as indicated in the corresponding PDOS (with predominant contribution coming from carbon and/or oxygen atom orbitals) and partial charge distribution.^{53,54} The flat bands observed in our systems should not be confused with nontrivial flat bands that mainly originate due to the specific symmetry of certain geometrically frustrated lattices, with potential applications in ferromagnetism⁵⁵ and superconductivity.⁵⁶ We direct interested readers to the Appendix, which provides additional details regarding the partial charge distribution for other relevant bands near the Fermi level, and results obtained from calculations using the PBE-D3(BJ) level of theory.

2.2.3 Effect of Interlayer Stacking on Intra- and Inter-framework Polaron Coherence

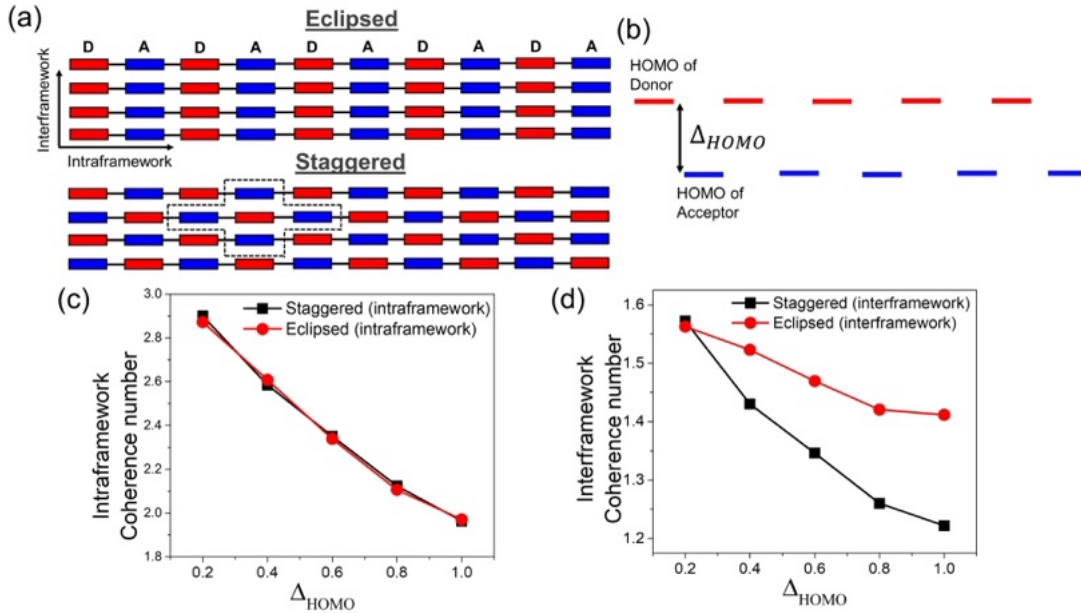


Figure 2.5. (a) Schematic illustration of the eclipsed and staggered stacking geometries with the donor and acceptor units distinguished as red and blue rectangles. (b) Schematic showing the offset of the energies of the HOMO orbitals (Δ_{HOMO}) of the donor and acceptor (black) fragment units which is referred to as the HOMO alternation energy. Simulated polaron coherence numbers for the eclipsed and stacking arrangements as a function of Δ_{HOMO} polarized along the (c) intraframework and (d) interframework directions.

In this section, we investigate the intra- and inter-framework coherence numbers in 2D

layered COFs having eclipsed and staggered interlayer stacking arrangements. Intra-framework and inter-framework polaron coherence numbers refer to the number of coherently connected repeat units over which the polaron is spatially delocalized. For our analysis, we utilize the MHF adapted to polarons in polymers and COFs as described in our previous studies.^{26,47,48,57} We construct 2D D-A COF structures where the COF backbone is taken to be along the x -axis (intra-framework) and the π -stacked layers are along the y -axis (inter-framework) (Figure 2.5a). As demonstrated in our previous studies,^{26,47,58–60} individual chromophores or repeat units can be successfully treated in a coarse-grained approximation. We retain the local HOMO level for every repeat unit.^{26,47,57} The neighboring HOMOs for the adjacent repeat units along both the COF backbone and the π -stacking direction are electronically coupled through the hole transfer integral, t_h . t_h has contributions from two components where t_{intra} (t_{inter}) governs intra-framework (inter-framework) delocalization of the hole. Hence, electronic coupling induces delocalization of the hole within the COF structure. Our primary goal is to have a qualitative understanding of how polaron coherence is impacted by the two extreme forms of stacking arrangement such as eclipsed and staggered.

Polaron coherence describing hole delocalization can be defined as the range over which the polaron maintains a wave-like property and is given by

$$C_P(r) \equiv \left\langle \langle \Psi_G | \sum_R d_R^\dagger d_{R+r} | \Psi_G \rangle \right\rangle_C \quad (2.1)$$

In Eq. 2.1, $R = (m, n)$ is a dimensionless position vector. In the limit when $r = 0$, the coherence function reduces to unity, $C_P[(0, 0)] = 1$, since $\sum_R d_R^\dagger d_R$ is the operator for the total number of holes, which is taken to be unity. The total number of coherently connected repeat units, N_{coh} , is derived from the coherence function, and is given by⁵⁷

$$N_{coh} = \sum_r |C_P(r)| \quad (2.2)$$

which reduces to unity in the limit of a strongly localized or trapped polaron.

In our coarse-grained models (Figure 2.5a), each layer in the eclipsed and stacking arrangements consists of ten repeat units along the intra-framework direction and has four π -stacked layers in the inter-framework direction (π -stacking direction). To investigate the sensitivity of polaron/charge delocalization to the interlayer stacking arrangement, we report the intra-framework and inter-framework polaron coherence numbers for the eclipsed and staggered stackings as a function Δ_{HOMO} , where Δ_{HOMO} is the difference in the HOMO energies of the donor and acceptor fragments (Figure 2.5b). For the simulations of the polaron coherence numbers reported in Figures 2.5c,d, we have used an inhomogeneous disorder width having a standard deviation of $\sigma = 0.3$ eV. This value of disorder width was successful in quantitatively reproducing the polaron-induced infrared lineshapes in TANG COF in our previous study.²⁶ A minimum of 1000 disorder configurations have been employed which is necessary to obtain converged coherence numbers.²⁶ For our calculations of the coherence numbers in Figures 2.5c,d, the intra-framework and inter-framework charge transfer integrals were set to 0.4 eV and 0.1 eV, respectively. Since the focus of the electronic structure discussion was not the localized states induced by the Cu atoms, we ignore the effect of the metal center in our modeling. We have assumed identical intra- and inter-framework electronic couplings for both the eclipsed and staggered arrangements. This is purposefully done to theoretically demonstrate how the morphology in the eclipsed and staggered arrangements impacts interlayer polaron coherence. Since we have not calculated the precise values of the electronic couplings for our model system of interest, we emphasize that the absolute values of the polaron coherence numbers reported in the Results and Discussion section are therefore irrelevant. More importantly, we focus on the relative change in the polaron coherence numbers between the eclipsed and staggered arrangements. Maintaining identical parameters (i.e., electronic couplings and disorder width) to define the Hamiltonian for both the stacking arrangements helps us better appreciate how the relative position of the donor and acceptor fragments in the neighboring layers alone impacts the polaron coherence numbers. Although precise coupling values for the model system of our

interest have not been calculated, we have used realistic electronic coupling values generally observed in 1D and 2D polymers. For example, the interchain through-space electronic couplings in 1D polymers like P3HT, lie in the range between 0.07 eV to 0.15 eV.^{57,61} The electronic couplings for similar 2D COF structures have been calculated in previous reports.⁶² Our values are in good agreement with the calculated electronic couplings (or charge transfer integrals) from previous studies.

Unlike in Figure 2.5c, where the simulated intra-framework polaron coherence numbers converge to similar values for both eclipsed and staggered stackings, the origin of much larger coherence along the π -stacking direction for the eclipsed configuration shown in Figure 2.5d can be traced back to the resonant donor-donor and acceptor-acceptor electronic interactions. The greater delocalization of the hole along the stacking axis in the eclipsed stacking can therefore be correlated to a much more dispersive band along the stacking axis.

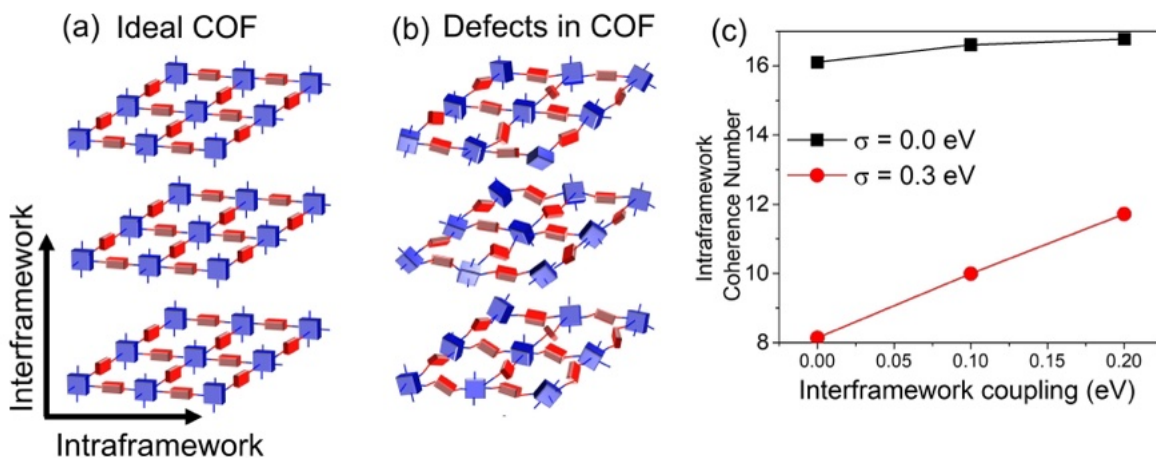


Figure 2.6. Schematic illustration of (a) ideal 3D COF structure having no defects and (b) 3D COFs with disorder width of $\sigma = 0.3$ eV (c) calculated intra-framework coherence numbers as a function of inter-framework electronic coupling.

In our discussion of the electronic structure, we showed that the completely flat bands along the intra-framework direction in the monolayer become dispersive in the eclipsed and staggered I stacking arrangements. To understand this phenomenon, we constructed 3D COF structures as schematically shown in Figure 2.6a,b. In our coarse-grained 3D models, each

layer consists of five repeat units along the x and y directions and three π -stacked layers. For our calculation of the coherence numbers in Figs 2.6c, the intra-framework charge transfer integral was set to 0.4 eV, the HOMO alternation energy (Δ_{HOMO}) was set to 0.0 eV, and the disorder width (σ) was set to 0.3 eV. We start our analysis by considering a hypothetical scenario where the inter-framework electronic coupling (t_{inter}) and inhomogeneous static disorder are neglected. A value of $t_{inter} = 0$ implies that the hole can only delocalize along the intra-framework direction, with no delocalization of the hole along the π -stacked columns. Gradual increase in the t_{inter} value is representative of better π orbital overlap, therefore, resulting in more efficient delocalization of the hole along the π -stacking direction. In the absence of disorder, the black curve in Figure 2.6c indicates that the calculated intra-framework coherence numbers exhibit slight improvement when $t_{inter} = 0.20$ eV compared to when $t_{inter} = 0.0$ eV. This analysis suggests that inter-framework interactions indeed facilitate more efficient delocalization of the hole along the intra-framework direction in good agreement with electronic structure results. This observation sheds light on why flat bands in the monolayer become dispersive upon stacking.

More interestingly, in a realistic scenario where inhomogeneous static disorder (σ) is incorporated in our modeling, the calculated intra-framework coherence numbers for $t_{inter} = 0.20$ eV show significant gradual improvement and converge to a larger number compared to when $t_{inter} = 0.0$ eV (see red curve in Figure 2.6c). This implies that interlayer interactions can play an important role in circumventing defect-induced trap sites and facilitating enhanced delocalization of the charge carriers along the intra-framework direction.

2.3 Conclusions

We employed DFT calculations and MHF simulations to demonstrate that different interlayer stacking arrangements (i.e., eclipsed, staggered I, and staggered II) can be exploited to significantly modify the electronic and transport properties of layered D-A COFs. Taking advantage of resonant donor-donor and acceptor-acceptor electronic interactions along the

stacking direction, it is possible to employ eclipsed type stacking to obtain anisotropic transport characteristics, with metallic and semiconductive behavior along the inter-framework and intra-framework directions, respectively. Unlike eclipsed stacking where the donors are stacked on top of the donors and the acceptors lie on top of acceptors in the neighboring layers, the arrangement in staggered I is different, with the donors stacked on top of the acceptors in the neighboring layers. Staggered I stacking is semiconductive in nature with rather localized charge carriers along both the intra-framework and inter-framework directions. Finally, in staggered II stacking, where the donors are positioned on top of the pores and the acceptors lie adjacent to the acceptors in neighboring layers is ideally suited to exhibit single-carrier-type behavior with predominantly delocalized electrons and localized holes. This suggests the potential of staggered II stacking arrangement for applications in unipolar FETs.

From our analyses, we believe that if the stacking-induced band dispersion is larger than the intra-framework band gap, the CBs and/or VBs along the inter-framework direction can cross the Fermi level, resulting in metallic behavior.^{38,45,63} However, if the stacking-induced band dispersion is smaller than the intra-framework band gap, the system remains semiconductive or insulative, with a smaller band gap along the stacking direction compared to the intra-framework directions.^{35,44} Based on this observation, we hypothesize that metallic charge transport along the interlayer direction can be potentially achieved in low band gap 2D layered COFs (and possibly in 2D MOFs too).

To corroborate the observations from the electronic structure calculations, we constructed coarse-grained 2D COF structures with eclipsed and staggered stackings to investigate the extent of intra-framework and inter-framework charge/polaron delocalization as a function of the difference between the HOMO energies of the donors and acceptor units. By performing MHF-based simulations on the 2D coarse-grained COF structures, we demonstrate that the extent of charge delocalization (or polaron coherence) is sensitive to the type of stacking. The simulated intra-framework coherence numbers converged to similar values for the two stacking arrangements due to similar arrangements of the donor and acceptor units along

the intra-framework direction. However, with increasing alternation energies between the HOMOs of the donor and acceptor fragments, the simulated inter-framework coherence numbers converged to a larger number for the eclipsed stacking compared to the staggered stacking. This analysis, combined with our previous observations from DFT simulations, highlights that the extent of inter-framework charge delocalization is sensitive to the type of stacking arrangement, and the precise arrangement of donor and acceptor building blocks can be exploited to engineer the functionalization of 2D layered COFs for applications in organic electronic devices. Furthermore, the combination of DFT calculations and MHF simulations demonstrates that intra-layer delocalization of the charge carriers within the plane can be enhanced by stacking-induced interlayer interactions. Importantly, our analysis using the MHF also predicts that interlayer interactions can help circumvent defect-induced trap states, which, in turn, can greatly improve overall charge delocalization in 2D layered COF structures. Future work will therefore be directed at incorporating disorder in our DFT simulations to see if it is possible to engineer defects to obtain dispersive bands along the COF backbone to further improve charge transport.

2.4 Acknowledgements

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Chapter 2, in full, is a reprint of the material as it appears in “Engineering Flat and Dispersive Bands in 2D Layered COFs via Interlayer Stacking and Donor–Acceptor Strategy”, Y. Pan, C.-H. Ho, F. Paesani, and R. Ghosh, *Chem. Mater.*, 2023, 35, 6235. The dissertation author was the primary investigator and author of this paper.

Appendix A: Supplementary Methods

Electronic Structure

Due to the presence of highly localized 3d orbitals of Cu atoms in our systems, electronic structure calculations were performed at the DFT+ U level using the Vienna ab initio simulation package (VASP).^{64,65} The Perdew-Burke-Ernzerhof (PBE)⁶⁶ exchange-correlation functional of the generalized gradient approximation (GGA) was adopted in all DFT+ U calculations.^{67,68} Specifically, for the PBE+ U calculations, the rotationally invariant approach introduced by Dudarev et al.⁶⁹ was applied. In this approach, only an effective U parameter is required. The effective Hubbard U of 4.0 eV for Cu was chosen from the study by Wang et al.,⁷⁰ in which the value reproduced the experimental oxidation energy of copper oxides. The core electrons were treated by the projector augmented wave (PAW) pseudopotential.⁷¹ A plane-wave basis set with an energy cutoff of 400 eV was used in all calculations. The convergence criteria for the energies and forces were set to 1×10^{-4} eV and $0.03 \text{ eV } \text{\AA}^{-1}$, respectively. The electron spin polarization was considered in systems containing Cu(II) since the electronic configuration of the Cu(II) is $[\text{Ar}]3d^9$ and, therefore, every Cu(II) atom has an unpaired spin. Monkhorst-Pack k -meshes⁷² of $1 \times 1 \times 1$ and $1 \times 1 \times 3$ k -point grids were used for structural optimization. $3 \times 3 \times 1$ and $3 \times 3 \times 9$ k -point grids were used for electronic structure calculations for the monolayer and multi-layered D-A COF unit cells, respectively. For the molecular donor and acceptor building blocks, Γ point k -point grid was used for the electronic structure calculations. A vacuum space of more than 15 $\text{\AA}$ along the c direction was set for the monolayer unit cell to avoid spurious interactions between the periodic replicas. The empirical correction by Grimme with the Becke-Johnson damping (D3(BJ))^{73–75} was applied to the stacking arrangements in order to describe the van der Waals interactions. The unit cell shapes and volumes were relaxed with the PBE-D3(BJ) functional. Subsequent optimization of the ionic positions with fixed unit cells was carried out at the level of PBE+ U -D3(BJ). It is known that the PBE functional, and any functional developed within GGA, systematically underestimates the values of the band gaps^{76,77} — however, reporting

precise band gap values is not the goal of this study. Since the systems of our interest are quite large, implementation of hybrid functionals such as PBE0 and HSE06 is computationally very expensive to be feasible. Visualization and post-processing were carried out using VESTA⁷⁸ and VASPKIT.⁷⁹

Effective Mass

Unless otherwise specified, the effective masses m^* for electrons (m_e^*) and holes (m_h^*) are calculated by fitting a parabola around the conduction band (CB) and valence band (VB) maximum, respectively, by using

$$m^* = \frac{\hbar^2}{\partial^2 E(\mathbf{k}) / \partial \mathbf{k}^2}, \quad (\text{A1})$$

where $\hbar$ is the reduced Planck constant. m^* is inversely proportional to the second derivative (i.e., curvature) of $E(\mathbf{k})$ over $\mathbf{k}$. Qualitatively, a flat CB or VB represents charge carriers with infinite effective masses, which corresponds to fully localized charge carriers with vanishing charge mobility. In contrast, a highly curved CB or VB corresponds to charge carriers with finite and small effective masses, which suggests higher charge mobility.

Multiparticle Holstein Formalism

We employ the MHF model introduced in our previous studies^{26,47,60} to investigate intra- and inter-framework polaron coherence in D-A COFs as a function of two different stacking arrangements. Within the MHF model, which considers electronic coupling, electron-phonon coupling, and defects on equal footing, the D-A COF is treated as a sequence of donor and acceptor fragments with a periodic variation of the local HOMO energies. In the vector subspace containing a single hole in a one-dimensional lattice with an alternate arrangement of donor and acceptor fragments, the complete Hamiltonian for single polarons in a disordered COF structure is given by

$$H_{total} = H_{FH} + H_{D-A} + H_{disorder} \quad (\text{A2})$$

where H_{FH} is the Frenkel-Holstein Hamiltonian and is defined as

$$H_{FH} = \sum_n E_n |n\rangle \langle n| + \sum_{m,n} t_{m,n} \{ |m\rangle \langle n| + |n\rangle \langle m| \} \\ + \omega_{vib} \sum_n b_n^\dagger b_n + \lambda \omega_{vib} \sum_n (b_n^\dagger + b_n + \lambda) |n\rangle \langle n| \quad (A3)$$

In Eq. A3, the first term represents the local hole energy, while the transfer integral, $t_{m,n}$, in the second term governs the transport of the polaron in the lattice. Upon electronic excitation, polarons in π -conjugated organic molecules strongly couple to the vinyl stretching or aromatic-quinoidal vibrational mode, ω_{vib} , in the range between 1200-1500 cm^{-1} . The last two terms in Eq. A3 account for the vibronic couplings, where the operator $b_n^\dagger$ (b_n) creates (annihilates) a vibrational quantum of energy on the n^{th} unit in the ground state (S_0) of the corresponding potential energy well. The Huang-Rhys factor (λ^2) represents the geometric relaxation energy experienced by a single repeat unit upon ionization (in units of $\hbar\omega_{vib}$).

The second term in Eq. A2 represents the local hole energy with the even and odd units associated with the donors and acceptors, respectively, where H_{D-A} is defined as

$$H_{D-A} = \frac{\Delta_{HOMO}}{2} \sum_n (-1)^n |n\rangle \langle n| \quad (A4)$$

The local energies of the HOMO orbitals alternate between the donor and acceptor units: $\frac{+\Delta_{HOMO}}{2}$ is assigned for the donors and $\frac{-\Delta_{HOMO}}{2}$ for the acceptors. The difference in the HOMO energies between the donor and acceptor fragments is referred to as Δ_{HOMO} . Similar to our previous studies,⁶⁰ we assume $\hbar\omega_{vib}$ and λ^2 to be the same for both donors and acceptors in order to be consistent with the vibronic terms in Eq. A3. The Huang-Rhys factor in our simulations is set to one which is consistent with our previous studies.^{57,60}

Disorder in π -stacked organic molecules such as COFs arises due to an inhomogeneous polarizing environment surrounding the hole, which includes variations in the nearest-neighbor π -stacking distances, intramolecular torsional angles within the framework backbone, and spatially

varying local electric fields. The various forms of disorder induce random changes in the hole energy, for a hole located at site n . In our model, all these sources of disorder are accounted for phenomenologically and the disorder Hamiltonian, $H_{disorder}$, is given by

$$H_{disorder} = \sum_n \Delta_n |n\rangle \langle n| \quad (\text{A5})$$

where Δ_n is selected randomly from a Gaussian distribution of width σ .

Appendix B: Supporting Data

PBE+*U* Results

Staggered I

As indicated in Figure 2.3c in the Results and Discussion section, the CBs along the intra-framework directions (Γ -X-S-Y- Γ) remain flat with very high m_e^* , consistent with the monolayer configuration. However, the VBs in the intra-framework directions become more dispersive compared to the monolayer, as confirmed by the partial charge distribution in the VBs (Figure 2.7), which is more delocalized than the CBs. This implies that enhanced charge (hole) transport along the intra-framework directions can be achieved due to inter-framework interactions, similar to our observations in eclipsed stacking. The m_h^* (at Γ along Y- Γ) value is $-2.076 m_0$ for both spin channels. The partial charge distribution of the VBM at Γ is mainly distributed along the directions parallel to the ***b*** direction, consistent with the VBs being more dispersive along X-S and Y- Γ which are parallel to ***b*** (Figure 2.1c and 2.3c).

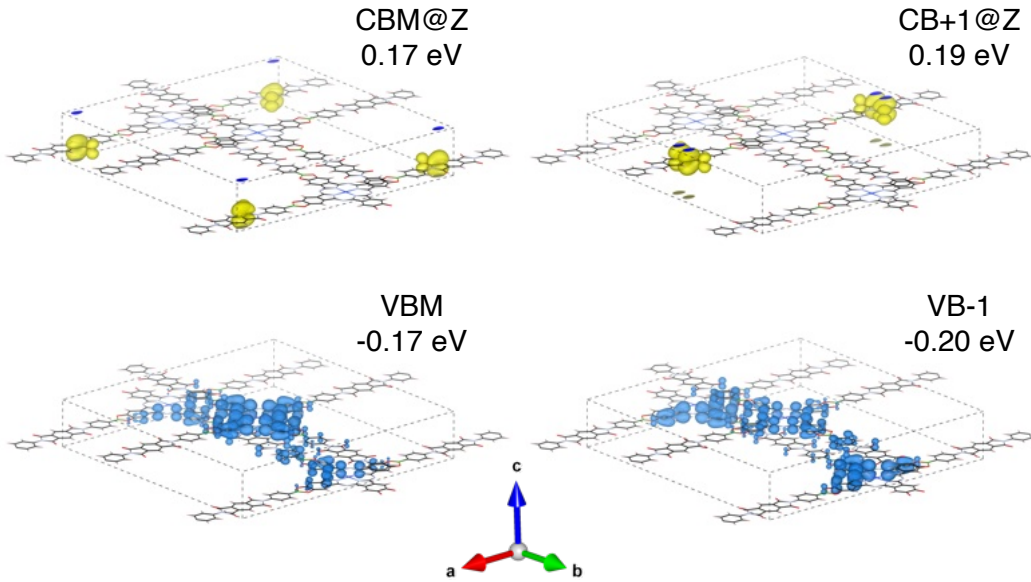


Figure 2.7. PBE+*U*-D3(BJ)-evaluated partial charge distribution in the CBs and VBs at Γ of the DCuPc-APyrDI-COF under staggered I stacking. The partial charge distribution in the unoccupied and occupied bands is presented in yellow and blue, respectively. Unit cell boundaries are indicated by the dashed lines.

Along Γ -Z, i.e., along the stacking direction, the CBs are almost flat and correspond to highly localized states with high m_e^* of 48.136 and 45.304 m_0 at Z for spin-up and spin-down channel, respectively, whereas the VBs exhibit more dispersion with m_h^* (at Γ along Γ -Z) values of -5.067 m_0 (spin-up) and -5.157 m_0 (spin-down), which are heavier than the m_h^* (at Γ along Γ -Z) in the eclipsed stacking. This is supported by the partial charge distribution in the CBs (Figure 2.7), which shows that the electrons in the CBs are highly localized on the acceptors with almost no overlap along the inter-framework directions. On the other hand, the holes in the VBs are slightly more delocalized along the inter-framework direction compared to the electrons. Overall, the staggered I stacking exhibits semiconducting behavior with calculated band gaps of 0.34 eV and 0.33 eV for the spin-up and spin-down channels, respectively.

Staggered II

Figure 2.8 illustrates the distribution of partial charges at the conduction band minimum (CBM), the mid-gap band, and the valence band maximum (VBM) at the Γ point for the DCuPc-APyrDI-COF with staggered II stacking. The flat CBs and VBs within the plane (see Figure 2.3d in the Results and Discussion section) naturally correspond to very high effective masses. This is due to the specific stacking arrangement where the donors lie on top of the pores. The CBs become more dispersive along the Γ -Z direction in the band structure (see DOS in Figure 3d), with m_e^* (at Γ along Γ -Z) values of 3.063 m_0 for both the spin channels. The dispersive bands along the inter-framework direction (compared to the flat bands along the intra-framework direction) is due to effective overlap of orbitals between the acceptors along the interlayer direction, as evidenced by the partial charge distribution at CBM (at Γ , in Figure 2.8). In addition, the mid-gap state induced by the Cu(II) centers occurs slightly above the Fermi level. The partial charge distribution of the “mid-gap” state shows highly localized charges on Cu(II) centers and the surrounding N atoms. This corresponds to highly flat mid-gap bands in the band structure, which modifies the band gap and transport properties.

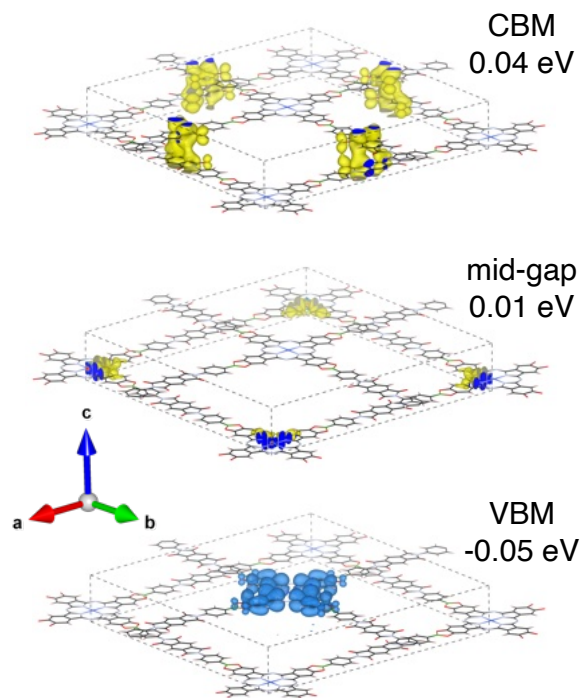


Figure 2.8. PBE+ U -D3(BJ)-evaluated partial charge distribution at CBM, mid-gap, and VBM at Γ of the D_{CuPc} - A_{PyrDI} -COF of staggered II stacking. The partial charge distribution in the unoccupied and occupied bands is presented in yellow and blue, respectively. Unit cell boundaries are indicated by the dashed lines.

PBE Results

In addition to the results at the PBE+ U level of theory discussed in the Results and Discussion section, we carried out calculations at the PBE-D3(BJ) level of theory to investigate whether the Hubbard U correction makes any changes to our final conclusions. To begin with, we characterized the electronic properties of the individual donor and acceptor building blocks.

Figure 2.9 shows the frontier MOs of the isolated Cu(II) phthalocyanine donor, D_{CuPc} , and pyromellitic diimide acceptor, A_{PyrDI} , similar to the MOs results included in the Results and Discussion section.

The shifted energy levels between the spin-up (-4.75 eV) and spin-down (-3.82 eV) channels (labeled “mid-gap Cu” in Figure 2.9) are primarily induced by the Cu(II) center. This can be confirmed by analyzing the PDOS in Figure 2.10 as well as the symmetry associated

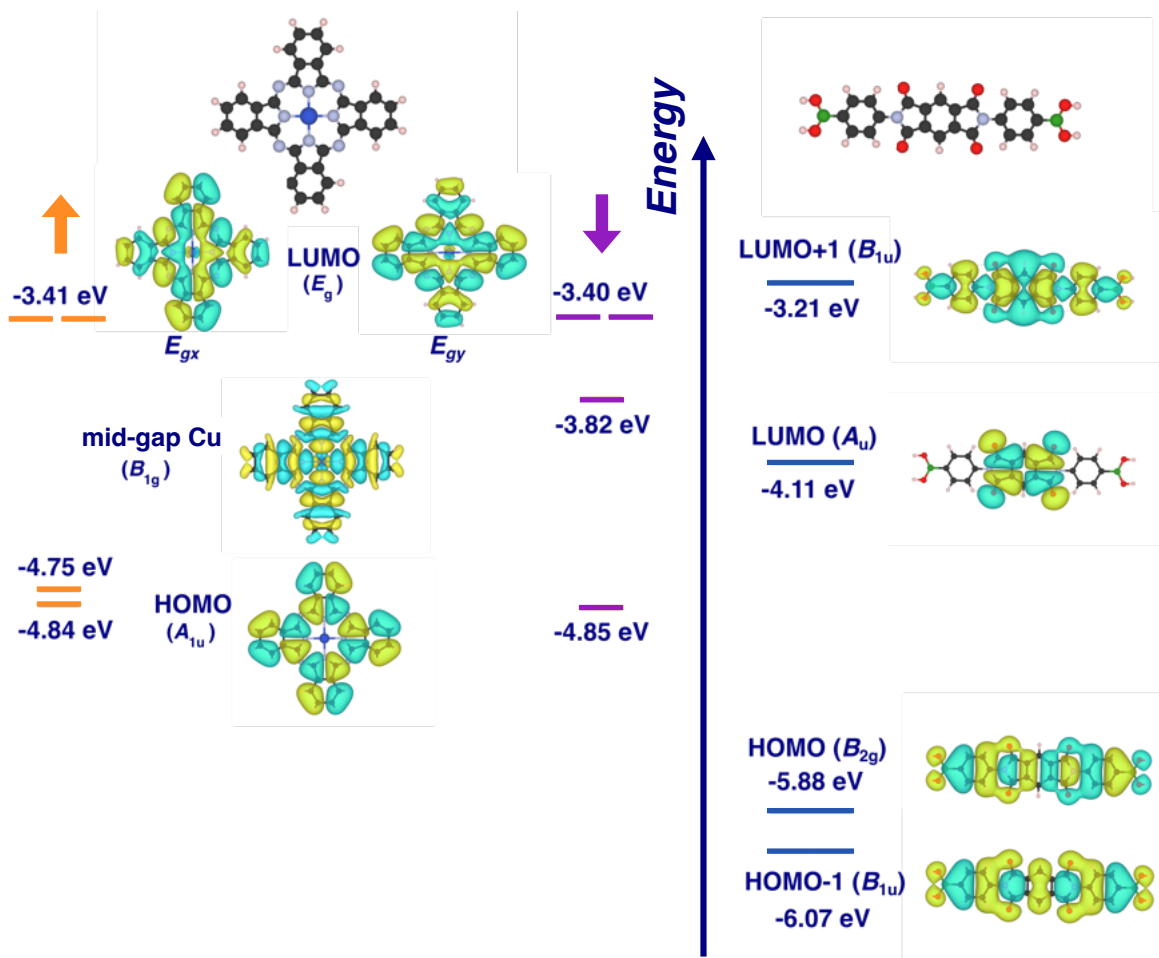


Figure 2.9. PBE-D3(BJ)-optimized geometry structure of the donor (D_{CuPc}) and acceptor (A_{PyrDI}) along with the frontier MOs. The spin-polarized energy levels of the frontier MOs of D_{CuPc} are shown in orange and purple for spin-up and spin-down, respectively. The non-spin-polarized energy levels of the frontier MOs of A_{PyrDI} are shown in blue. The MO symmetries are shown in parentheses. The E_{gx} and E_{gy} orbitals are named due to their nodal planes lying along the y and x axes, respectively.

with the two mid-gap states, B_{1g} , which matches the symmetry of the $3d_{x^2-y^2}$ orbital from the Cu center. The energies of the frontier MOs suggest that the predominant contributions to the VBs and CBs in the D-A system originate from the individual donor and acceptor building blocks, respectively, which are consistent with results upon the $+U$ correction.

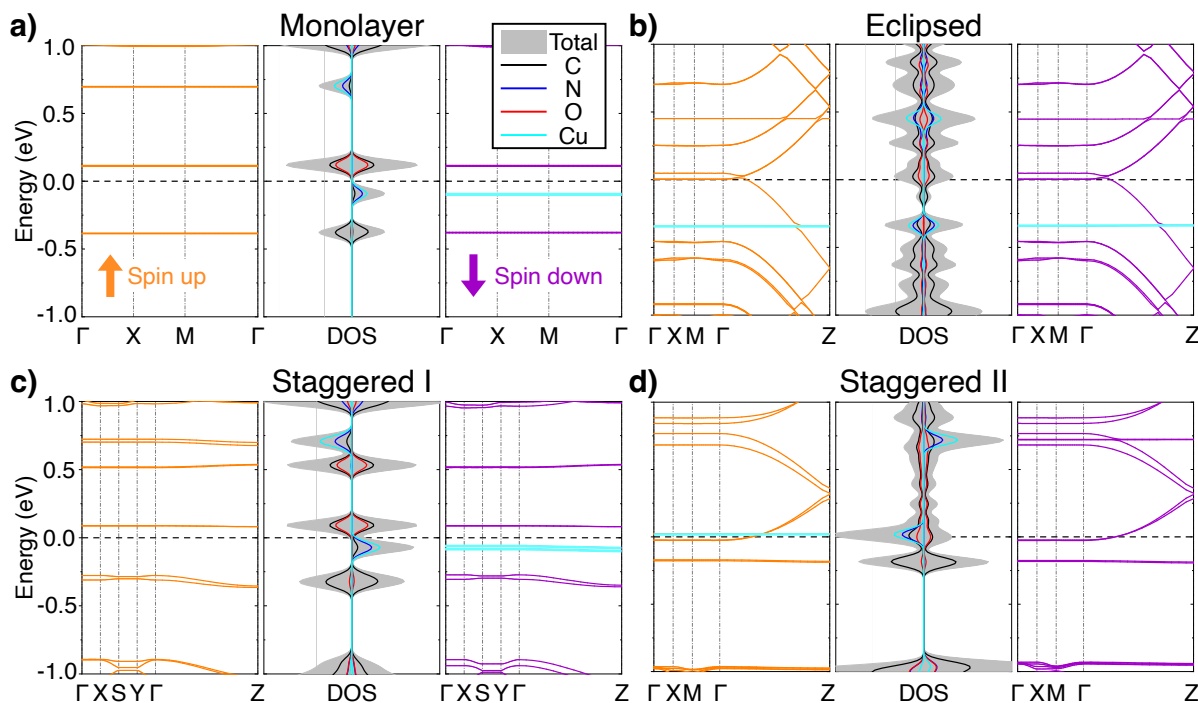


Figure 2.10. PBE-D3(BJ)-evaluated spin-polarized band structures and density of states (DOS) of the D_{CuPc} - A_{PyDI} -COFs. (a) monolayer, (b) eclipsed, (c) staggered I, and (d) staggered II. The orange and purple band structures on the left and right columns in each sub-figure correspond to the spin-up and down configurations, respectively. The left and right parts of the middle column in each subfigure show the corresponding spin-polarized total and PDOS from C, N, O, and Cu. The bands in cyan near the Fermi level represent the mid-gap bands with predominant contributions from the Cu(II) centers as indicated by the PDOS. The Fermi level is set to zero and indicated by the black horizontal dashed line.

Monolayer

The band structure and DOS of the monolayer at the PBE level (Figure 2.10a) reveal two spin-polarized shifted bands for the spin-up (at ~ 0.70 eV) and spin-down (at ~ -0.10 eV) configurations. These bands are mainly contributed by the Cu(II) centers and the neighboring N atoms, as evidenced by the partial density of states (PDOS) (Figure 2.10) and the partial charge distribution (Figure 2.11). This observation of localized Cu-induced states holds true for the PBE-evaluated electronic band structures of eclipsed, staggered I, and staggered II configurations as well. In addition, from the DOS (Figure 2.10a) and the partial charge distribution (Figure 2.11), we can find that the VB is dominated by the donor unit (D_{CuPc}) and the CBs are dominated by

the acceptor (A_{PyrDI}). This is consistent with the PBE-evaluated molecular orbital characteristics shown in Figure 2.9 and the results evaluated at the PBE+*U* level of theory.

Overall, the monolayer is semiconductive with direct band gaps of 0.50 eV and 0.21 eV for the spin-up and spin-down channels, respectively. The lower band gap for the spin-down channel at the PBE level of theory is due to the appearance of a Cu-induced mid-gap state (highlighted in cyan in Figure 2.10a). However, the position of the localized mid-gap bands shifted away from the Fermi level upon the Hubbard *U* correction (see Figure 2.3a in the Results and Discussion section), as a result of the on-site Coulomb interaction among the 3d electrons of Cu. This observation is consistent with previous reports.^{80,81} Consequently, the band gap upon including the Hubbard *U* correction is found to be 0.49 eV and 0.48 eV for the spin-up and spin-down channel, respectively.

Eclipsed

Figure 2.12 shows the partial charge distribution at CBM (at Γ , doubly degenerate), Cu-induced mid-gap band at Γ , and in the VBs (at X, almost degenerate but slightly split by ~ 0.01 eV) of the 2D extended D_{CuPc}-A_{PyrDI}-COF under eclipsed stacking. Compared to the monolayer, the VBs (~ -0.46 eV) within the plane (Γ -X-M- Γ) in eclipsed stacking are more dispersive with lighter m_h^* . The partial density distribution in the VBs at X in Figure 2.12 shows more delocalization within the plane due to enhanced charge transport from interlayer interactions. The corresponding m_h^* (at X along X-M) value is calculated to be $-1.338 m_0$ for spin-up and $-1.070 m_0$ for spin-down.

The eclipsed stacking exhibits semiconducting behavior within the COF plane, displaying a reduced band gap of 0.34 eV from 0.46 eV for both spin-up and spin-down channels due to the presence of Cu-induced mid-gap states (Figure 2.10b). In contrast, from the PBE+*U*-D3(BJ)-evaluated band structure shown in Figure 2.3b in the Results and Discussion section, we found that the highly localized Cu-induced bands are shifted away from the Fermi level, leading to intra-framework band gaps of 0.46 eV and 0.47 eV for the spin-up and spin-down channels,

respectively.

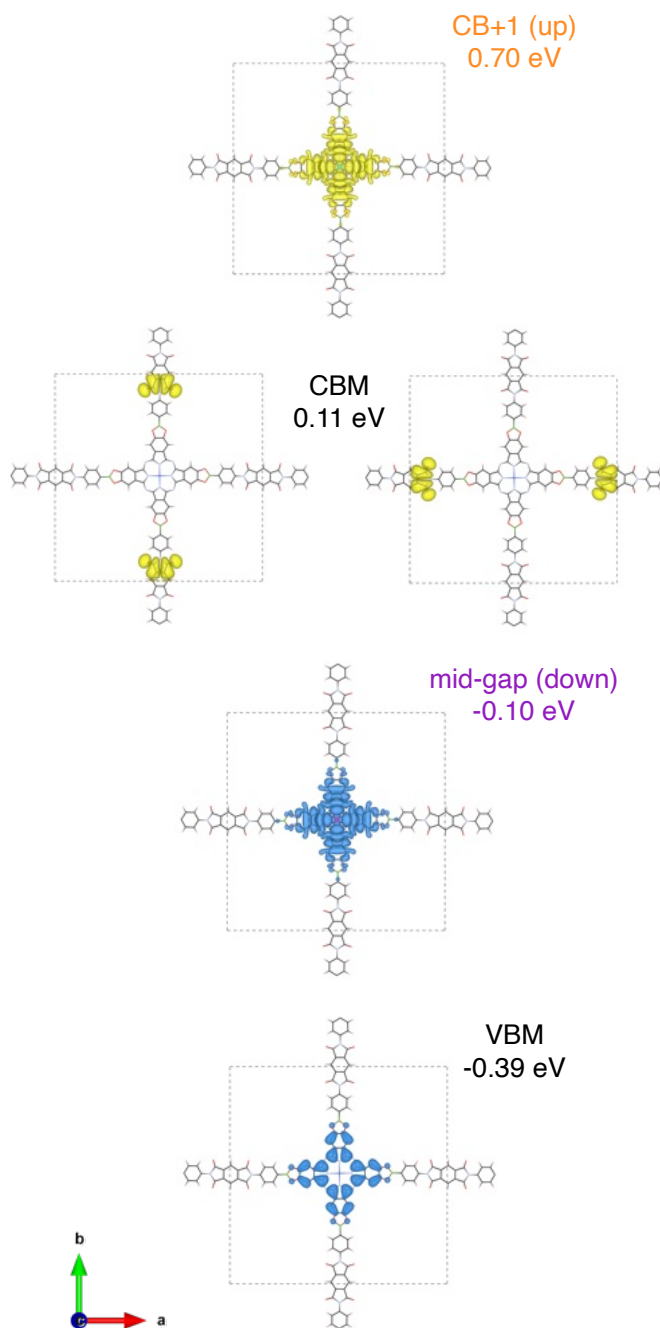


Figure 2.11. PBE-D3(BJ)-evaluated partial charge distribution in the CBs, mid-gap (spin-down), and VBM at Γ of the monolayer $D_{\text{CuPc}}\text{-}A_{\text{PyDI}}\text{-COF}$. The partial charge distribution in the unoccupied and occupied bands is presented in yellow and blue, respectively. Unit cell boundaries are indicated by the dashed lines.

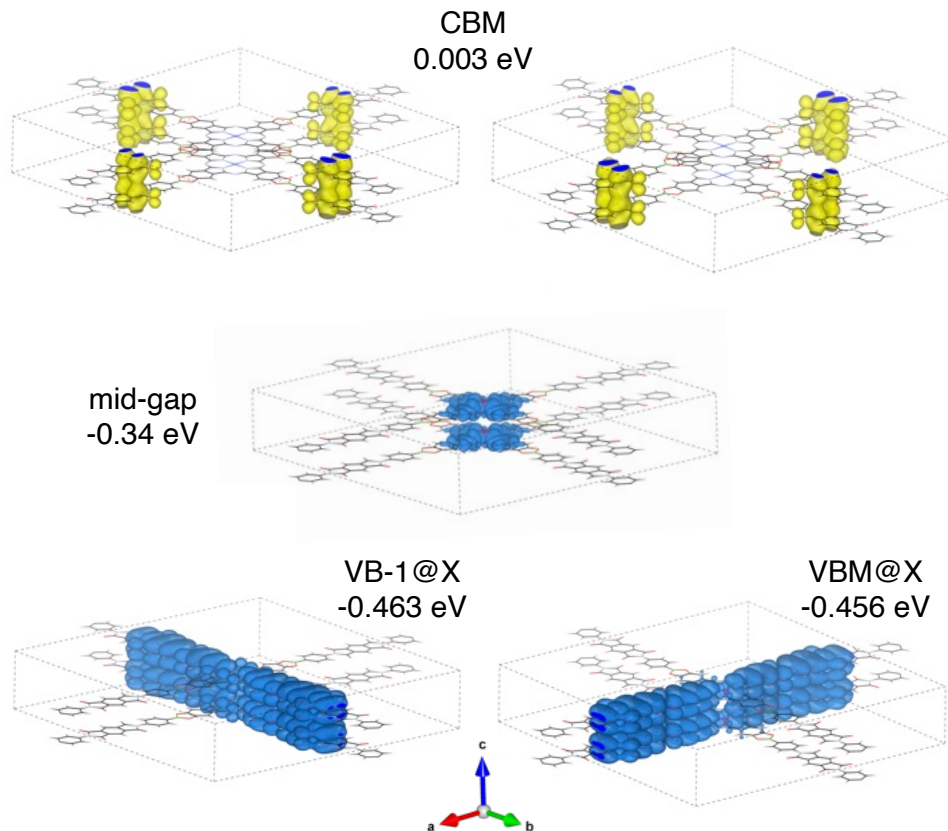


Figure 2.12. PBE-D3(BJ)-evaluated partial charge distribution at CBM (doubly degenerate at Γ), mid-gap (at Γ , spin paired), and VBs@X (almost degenerate but slightly split by ~ 0.01 eV) of the $D_{CuPc}-A_{PyDI}-COF$ under eclipsed stacking. The partial charge distribution in the unoccupied and occupied bands is presented in yellow and blue, respectively. Unit cell boundaries are indicated by the dashed lines.

Staggered I

As indicated in Figure 2.10c, along the intra-framework directions ($\Gamma-X-S-Y-\Gamma$), the CBs remain flat with very high m_e^* , consistent with the monolayer configuration. However, the VBs in the intra-framework directions become more dispersive compared to the monolayer, as confirmed by the partial charge distribution in the VBs (Figure 2.13), which is more delocalized than the CBs. This implies that enhanced charge (hole) transport along the intra-framework directions can be achieved due to inter-framework interactions, similar to our observations in eclipsed stacking.

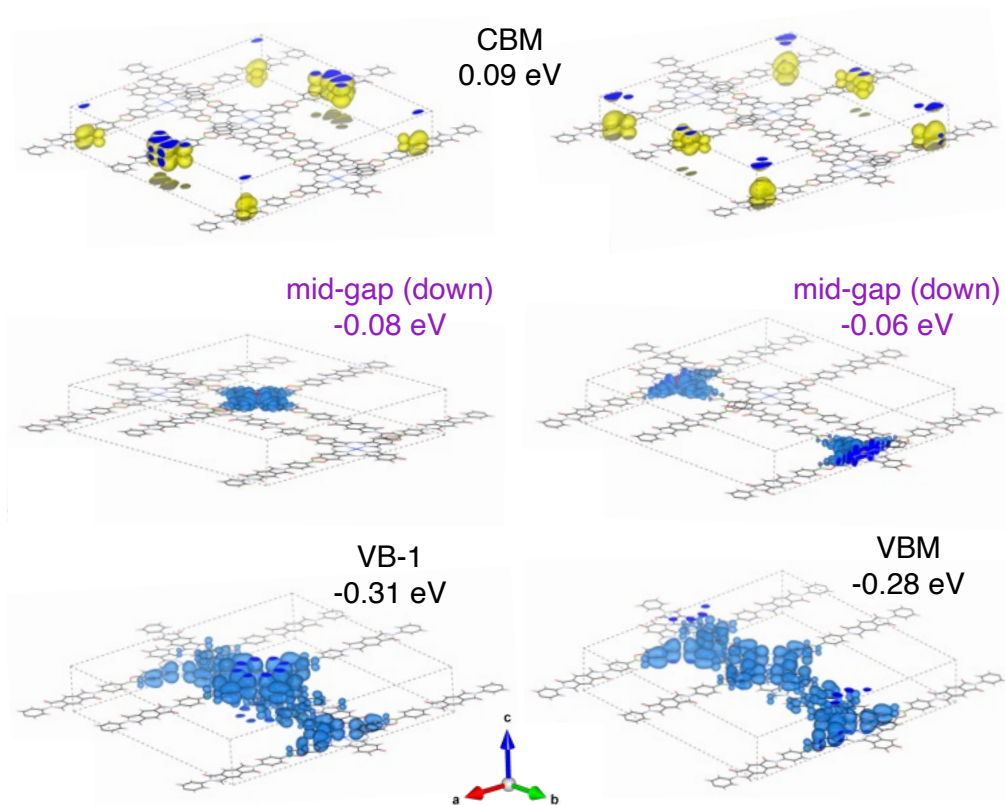


Figure 2.13. PBE-D3(BJ)-evaluated partial charge distribution at CBM, mid-gaps, and VBs at Γ of the $D_{CuPc}-A_{PyrDI}$ -COF under staggered I stacking. The partial charge distribution in the unoccupied and occupied bands is presented in yellow and blue, respectively. Unit cell boundaries are indicated by the dashed lines.

The m_h^* (at Γ along $Y-\Gamma$) values are $-2.669 m_0$ for both spin channels. The partial charge distribution in the VBs at Γ (Figure 2.13) is mainly distributed along directions parallel to the b direction, consistent with the VBs being more dispersive along $X-S$ and $Y-\Gamma$ which are parallel to b .

Along $\Gamma-Z$ (Figure 2.10c), i.e., in the stacking direction, the CBs are almost flat and correspond to highly localized states with high m_e^* of $41.254 m_0$ at Z for both spin channels, whereas the VBs exhibit slight dispersion and have m_h^* (at Γ along $\Gamma-Z$) values of $-4.715 m_0$ (spin-up) and $-4.854 m_0$ (spin-down), which are heavier than the m_h^* (at Γ along $\Gamma-Z$) in the eclipsed stacking. This is supported by the partial charge distribution at CBM (at Γ , Figure 2.13), which shows that the electrons at CBM are highly localized on the acceptors with almost no

overlap along the inter-framework directions. On the other hand, the holes in the VBs are slightly more delocalized along the inter-framework direction compared to the electrons. Staggered I stacking exhibits semiconducting behavior with calculated band gaps of 0.36 eV for the spin-up configuration and a reduced band gap of 0.15 eV for the spin-down configuration due to the existence of Cu-induced mid-gap states (see Figure 2.10c). The band gaps are calculated to be 0.34 eV and 0.33 eV for the spin-up and spin-down channels, respectively, when PBE+ U is applied.

Staggered II

The partial charge distribution in the CBs and VBs of the D_{CuPc}-A_{Pyridine}-COF under staggered II stacking is shown in Figure 2.14. Due to this specific stacking arrangement of Staggered II where the donors lie on top of the pores, the VBs and CB remain flat with highly localized charge carriers (Figure 2.14) along the intra-framework direction (Γ -X-M- Γ), as shown in Figure 2.10d. However, along the inter-framework direction (Γ -Z), the two bands near the Fermi level are dispersive and cross the Fermi level (Figure 2.10d), suggesting metallic behavior with rather delocalized charge carriers (Figure 2.14). The corresponding effective masses (along Γ -Z, for both electrons and holes) obtained from the metallic band segment crossing the Fermi level were calculated to be $3.466 m_0$ and $3.398 m_0$ for the spin-up and spin-down, respectively. Furthermore, the bands along the Γ -Z direction, which lie below the two metallic bands, are almost flat (Figure 2.10d) with high m_h^* values (calculated at Γ along Γ -Z) of $-55.144 m_0$ and $-56.426 m_0$, for the spin up and spin down configurations, respectively. In sharp contrast, along the Γ -Z direction, the two metallic bands and the bands that lie above them (except the highly flat Cu-induced bands) are dispersive (Figure 2.10d) due to the effective overlap of the frontier orbitals of the acceptor units in the neighboring layers (Figure 2.14). These bands correspond to rather light and delocalized electrons (with a small fraction of delocalized holes in the metallic bands). Staggered II stacking, therefore, demonstrates single-carrier-type behavior along the inter-framework direction, with predominantly delocalized electrons and mostly localized holes.

It should be noted that within our systems, the 3d orbitals of Cu couple with the neighboring N atoms, resulting in highly localized states. However, these localized states do not engage in hybridization with the frontier molecular orbitals (MOs) of the donors and acceptors.

Besides, it is important to mention that the focus of this work is not to report precise values of the band gaps and effective masses, instead, our focus is on understanding the influence of different interlayer stacking arrangements on the electronic and transport properties. More specifically, our goal is to explore how the arrangement of the donor and acceptor molecular building blocks in the neighboring layers impacts the dispersion of the valence and conduction bands that are *originated mainly from the organic components*. Within this context, our results using PBE+ U in the Results and Discussion section indicate that the observed trends along the intra- and inter-framework directions in the band structure for VB and CB, originating mainly from the organic components in the systems of interest, are quite similar to PBE discussed here. Finally, to determine the exact/accurate positions of the localized Cu-induced states, and values of the band gaps of the COFs upon different stacking arrangements, more sophisticated methods such as hybrid functionals (e.g., PBE0 and HSE06), and experimental measurements (e.g., optical absorption and photoluminescence spectroscopy) may be needed.

Table 2.1 and Table 2.2 provide a summary of the effective masses for the D_{CuPc}-A_{PyrDI}-COF for various configurations: monolayer, eclipsed, staggered I, and staggered II, calculated using the PBE+ U and PBE level of theory, respectively.

Table 2.1. PBE+ U -D3(BJ)-evaluated effective masses calculated at Γ unless otherwise specified, for the D_{CuPc}-A_{PyrDI}-COFs of the monolayer, eclipsed, staggered I, and staggered II configurations.

		Monolayer		Eclipsed		Staggered I		Staggered II	
		intra-framework		intra-framework	inter-framework	intra-framework	inter-framework	intra-framework	inter-framework
		–		(X–M)	(Γ –Z, metallic)	(Y– Γ)	(Γ –Z)	–	(Γ –Z)
electron m_e^*/m_0	up	–		–	-0.973	–	48.136 (at Z)	–	3.063
	down	–		–	-0.979	–	45.304 (at Z)	–	3.063
hole m_h^*/m_0	up	–		-7.493 (at X)	-0.973	-2.076	-5.067	–	-46.663
	down	–		-37.465 (at X)	-0.979	-2.076	-5.157	–	-50.552

Table 2.2. PBE-D3(BJ)-evaluated effective masses calculated at Γ unless otherwise specified, for the D_{CuPc} - A_{PyrDI} -COFs of the monolayer, eclipsed, staggered I, and staggered II configurations.

		Monolayer	Eclipsed		Staggered I		Staggered II	
		intra-framework	intra-framework	inter-framework	intra-framework	inter-framework	intra-framework	inter-framework
		–	(X–M)	(Γ –Z, metallic)	(Y– Γ)	(Γ –Z)	–	(Γ –Z, metallic)
electron m_e^*/m_0	up	–	–	-0.979	–	41.254 (at Z)	–	3.466
	down	–	–	-0.973	–	41.254 (at Z)	–	3.398
hole m_h^*/m_0	up	–	-1.338 (at X)	-0.979	-2.669	-4.715	–	3.466
	down	–	-1.070 (at X)	-0.973	-2.669	-4.854	–	3.398

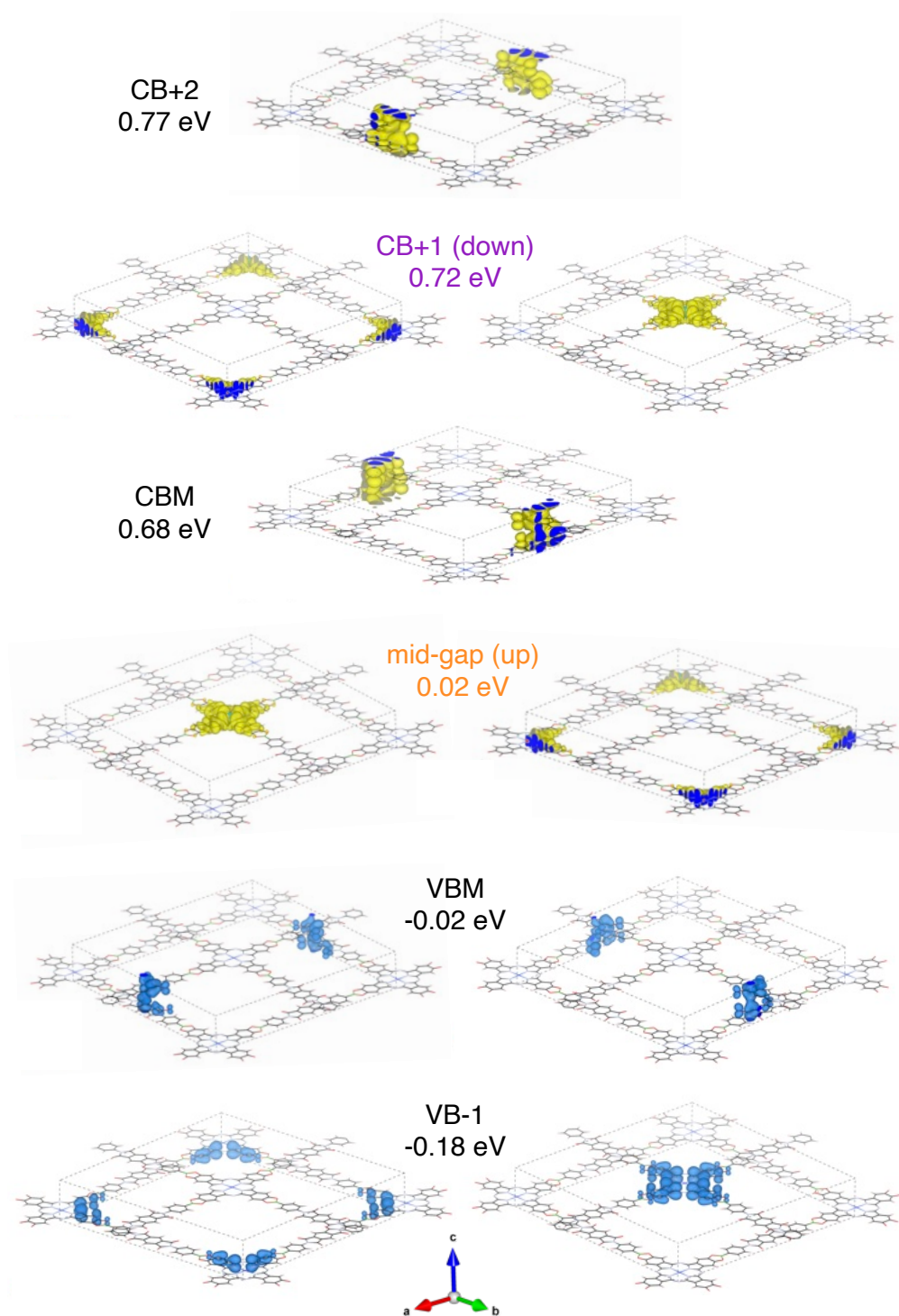


Figure 2.14. PBE-D3(BJ)-evaluated partial charge distribution in the CBs, mid-gap, and VBs at Γ of the $D_{CuPc}-A_{PyrDI}$ -COF of staggered II stacking. The partial charge distribution in the unoccupied and occupied bands is presented in yellow and blue, respectively. Unit cell boundaries are indicated by the dashed lines.

References

- [1] Adrien P Cote, Annabelle I Benin, Nathan W Ockwig, Michael O’Keeffe, Adam J Matzger, and Omar M Yaghi. Porous crystalline covalent organic frameworks. *Science*, 310(5751): 1166–1170, 2005.
- [2] Pengyuan Wang, Yuan Peng, Chenyu Zhu, Rui Yao, Hongling Song, Lun Kun, and Weishen Yang. Single-phase covalent organic framework staggered stacking nanosheet membrane for CO₂-selective separation. *Angew. Chem. Int. Ed.*, 60(35):19047–19052, 2021.
- [3] Ning Huang, Xiong Chen, Rajamani Krishna, and Donglin Jiang. Two-dimensional covalent organic frameworks for carbon dioxide capture through channel-wall functionalization. *Angew. Chem. Int. Ed.*, 54(10):2986–2990, 2015.
- [4] Zhongping Li, Xiao Feng, Yongcun Zou, Yuwei Zhang, Hong Xia, Xiaoming Liu, and Ying Mu. A 2D azine-linked covalent organic framework for gas storage applications. *Chem. Commun.*, 50(89):13825–13828, 2014.
- [5] Atanu Panda, Yanqin Yang, Sada Venkateswarlu, Younghu Son, Tae-Hyun Bae, and Miny-oung Yoon. Highly durable covalent organic framework for the simultaneous ultrasensitive detection and removal of noxious Hg²⁺. *Microporous Mesoporous Mater.*, 306:110399, 2020.
- [6] Xigui Liu, Danlian Huang, Cui Lai, Guangming Zeng, Lei Qin, Han Wang, Huan Yi, Bisheng Li, Shiyu Liu, Mingming Zhang, Rui Deng, Yukui Fu, Ling Li, Wenjing Xue, and Sha Chen. Recent advances in covalent organic frameworks (COFs) as a smart sensing material. *Chem. Soc. Rev.*, 48(20):5266–5302, 2019.
- [7] Song Lin, Christian S Diercks, Yue-Biao Zhang, Nikolay Kornienko, Eva M Nichols, Yingbo Zhao, Aubrey R Paris, Dohyung Kim, Peidong Yang, Omar M Yaghi, and Christopher J Chang. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water. *Science*, 349(6253):1208–1213, 2015.
- [8] Hui Hu, Qianqian Yan, Rile Ge, and Yanan Gao. Covalent organic frameworks as heterogeneous catalysts. *Chinese J. Catal.*, 39(7):1167–1179, 2018.
- [9] Jie Li, Xuechun Jing, Qingqing Li, Siwu Li, Xing Gao, Xiao Feng, and Bo Wang. Bulk COFs and COF nanosheets for electrochemical energy storage and conversion. *Chem. Soc. Rev.*, 49(11):3565–3604, 2020.
- [10] De-Gao Wang, Tianjie Qiu, Wenhan Guo, Zibin Liang, Hassina Tabassum, Dingguo Xia, and Ruqiang Zou. Covalent organic framework-based materials for energy applications. *Energy Environ. Sci.*, 14(2):688–728, 2021.

- [11] Shanshan Tao and Donglin Jiang. Covalent organic frameworks for energy conversions: Current status challenges and perspectives. *CCS Chem.*, 3(1):2003–2024, 2021.
- [12] Jinwei Zhao, Junyu Ren, Guang Zhang, Ziqiang Zhao, Shiyong Liu, Wandong Zhang, and Long Chen. Donor-acceptor type covalent organic frameworks. *Chem. Eur. J.*, 27(42): 10781–10797, 2021.
- [13] Xiao Feng, Long Chen, Yoshihito Honsho, Oraphan Saengsawang, Lili Liu, Lu Wang, Akinori Saeki, Stephan Irle, Shu Seki, Yuping Dong, and Donglin Jiang. An ambipolar conducting covalent organic framework with self-sorted and periodic electron donor-acceptor ordering. *Adv. Mater.*, 24(22):3026–3031, 2012.
- [14] Mona Calik, Florian Auras, Laura M. Salonen, Kathrin Bader, Irene Grill, Matthias Handloser, Dana D. Medina, Mirjam Dogru, Florian Löbermann, Dirk Trauner, Achim Hartschuh, and Thomas Bein. Extraction of photogenerated electrons and holes from a covalent organic framework integrated heterojunction. *J. Am. Chem. Soc.*, 136(51):17802–17807, 2014.
- [15] Chenxiang Lin, Xiaolin Liu, Baoqiu Yu, Chaozheng Han, Lei Gong, Chiming Wang, Ying Gao, Yongzhong Bian, and Jianzhuang Jiang. Rational modification of two-dimensional donor–acceptor covalent organic frameworks for enhanced visible light photocatalytic activity. *ACS Appl. Mater. Interfaces*, 13(23):27041–27048, 2021.
- [16] Lingxian Meng, Yamin Zhang, Xiangjian Wan, Chenxi Li, Xin Zhang, Yanbo Wang, Xin Ke, Zuo Xiao, Liming Ding, Ruoxi Xia, Hin-Lap Yip, Yong Cao, and Yongsheng Chen. Organic and solution-processed tandem solar cells with 17.3% efficiency. *Science*, 361(6407):1094–1098, 2018.
- [17] Jun Li, Yan Zhao, Huei Shuan Tan, Yunlong Guo, Chong-An Di, Gui Yu, Yunqi Liu, Ming Lin, Suo Hon Lim, Yuhua Zhou, Haibin Su, and Beng S. Ong. A stable solution-processed polymer semiconductor with record high-mobility for printed transistors. *Sci. Rep.*, 2(1): 1–9, 2012.
- [18] Yuning Li, Prashant Sonar, Leanne Murphy, and Wei Hong. High mobility diketopyrrolopyrrole (DPP)-based organic semiconductor materials for organic thin film transistors and photovoltaics. *Energy Environ. Sci.*, 6(6):1684–1710, 2013.
- [19] Mike Hambsch, Tim Erdmann, Annabel R Chew, Sigrid Bernstorff, Alberto Salleo, Anton Kiriy, Brigitte Voit, and Stefan CB Mannsfeld. Increased charge carrier mobility and molecular packing of a solution sheared diketopyrrolopyrrole-based donor–acceptor copolymer by alkyl side chain modification. *J. Mater. Chem. C.*, 7(12):3665–3674, 2019.
- [20] Weimin Zhang, Jeremy Smith, Scott E Watkins, Roman Gysel, Michael McGehee, Alberto Salleo, James Kirkpatrick, Shahid Ashraf, Thomas Anthopoulos, Martin Heeney, and Iain McCulloch. Indacenodithiophene semiconducting polymers for high-performance,

air-stable transistors. *J. Am. Chem. Soc.*, 132(33):11437–11439, 2010.

- [21] Shangbin Jin, Xuesong Ding, Xiao Feng, Mustafa Supur, Ko Furukawa, Seiya Takahashi, Matthew Addicoat, Mohamed E. El-Khouly, Toshikazu Nakamura, Stephan Irle, Shunichi Fukuzumi, Atsushi Nagai, and Donglin Jiang. Charge dynamics in a donor–acceptor covalent organic framework with periodically ordered bicontinuous heterojunctions. *Angew. Chem. Int. Ed.*, 7(52):2017–2021, 2013.
- [22] Shangbin Jin, Mustafa Supur, Matthew Addicoat, Ko Furukawa, Long Chen, Toshikazu Nakamura, Shunichi Fukuzumi, Stephan Irle, and Donglin Jiang. Creation of superheterojunction polymers via direct polycondensation: Segregated and bicontinuous donor–acceptor π -columnar arrays in covalent organic frameworks for long-lived charge separation. *J. Am. Chem. Soc.*, 137(24):7817–7827, 2015.
- [23] Pradip Pachfule, Amitava Acharjya, Jérôme Roeser, Ramesh P Sivasankaran, Meng-Yang Ye, Angelika Brückner, Johannes Schmidt, and Arne Thomas. Donor–acceptor covalent organic frameworks for visible light induced free radical polymerization. *Chem. Sci.*, 10(36):8316–8322, 2019.
- [24] Wenjing Qiu, Yajun He, Liuyi Li, Zheyuan Liu, Shenghong Zhong, and Yan Yu. Donor–acceptor pairs in covalent organic frameworks promoting electron transfer for metal-free photocatalytic organic synthesis. *Langmuir*, 37(39):11535–11543, 2021.
- [25] Haiping Yu, Jianze Zhang, Xiaorong Yan, Chuanguang Wu, Xiaoran Zhu, Bowen Li, Tengfei Li, Qiuquan Guo, Jiefeng Gao, Mingjun Hu, and Jun Yang. Donor–acceptor covalent organic framework hollow submicrospheres with a hierarchical pore structure for visible-light-driven h_2 evolution. *J. Mater. Chem. A*, 10(20):11010–11018, 2022.
- [26] Raja Ghosh and Francesco Paesani. Unraveling the effect of defects domain size and chemical doping on photophysics and charge transport in covalent organic frameworks. *Chem. Sci.*, 12(24):8373–8384, 2021.
- [27] Shiwei Wang, Anton D Chavez, Simil Thomas, Hong Li, Nathan C Flanders, Chao Sun, Michael J Strauss, Lin X Chen, Albert J Markvoort, Jean-Luc Brédas, and William R. Dichtel. Pathway complexity in the stacking of imine-linked macrocycles related to two-dimensional covalent organic frameworks. *Chem. Mater.*, 31(17):7104–7111, 2019.
- [28] Xing Li, Jingsi Qiao, See Wee Chee, Hai-Sen Xu, Xiaoxu Zhao, Hwa Seob Choi, Wei Yu, Su Ying Quek, Utkur Mirsaidov, and Kian Ping Loh. Rapid scalable construction of highly crystalline acylhydrazone two-dimensional covalent organic frameworks via dipole-induced antiparallel stacking. *J. Am. Chem. Soc.*, 142(10):4932–4943, 2020.
- [29] Niklas Keller, Mona Calik, Dmitry Sharapa, Himadri R Soni, Peter M Zehetmaier, Sabrina Rager, Florian Auras, Andreas C Jakowetz, Andreas Göring, Timothy Clark, and Thomas

- Bein. Enforcing extended porphyrin J-aggregate stacking in covalent organic frameworks. *J. Am. Chem. Soc.*, 140(48):16544–16552, 2018.
- [30] Xiaowei Wu, Xing Han, Yuhao Liu, Yan Liu, and Yong Cui. Control interlayer stacking and chemical stability of two-dimensional covalent organic frameworks via steric tuning. *J. Am. Chem. Soc.*, 140(47):16124–16133, 2018.
- [31] Yu Fan, Qiang Wen, Tian-Guang Zhan, Qiao-Yan Qi, Jia-Qiang Xu, and Xin Zhao. A case study on the influence of substitutes on interlayer stacking of 2D covalent organic frameworks. *Chem. Eur. J.*, 23(24):5668–5672, 2017.
- [32] Pablo Albacete, Jose I Martinez, Xing Li, Alejandro Lopez-Moreno, Sofiá Mena-Hernando, Ana E Platero-Prats, Carmen Montoro, Kian Ping Loh, Emilio M Perez, and Felix Zamora. Layer-stacking-driven fluorescence in a two-dimensional imine-linked covalent organic framework. *J. Am. Chem. Soc.*, 140(40):12922–12929, 2018.
- [33] Alexander M Pütz, Maxwell W Terban, Sebastian Bette, Frederik Haase, Robert E Dinnebier, and Bettina V Lotsch. Total scattering reveals the hidden stacking disorder in a 2D covalent organic framework. *Chem. Sci.*, 11(47):12647–12654, 2020.
- [34] Florian Auras, Laura Ascherl, Amir H. Hakimiyoun, Johannes T. Margraf, Fabian C. Hanusch, Stephan Reuter, Derya Bessinger, Markus Döblinger, Christina Hettstedt, Konstantin Karaghiosoff, Simon Herbert, Paul Knochel, Timothy Clark, and Thomas Bein. Synchronized offset stacking: A concept for growing large-domain and highly crystalline 2D covalent organic frameworks. *J. Am. Chem. Soc.*, 138(51):16703–16710, 2016.
- [35] Agnieszka Kuc, Maximilian A Springer, Kamal Batra, Rosalba Juarez-Mosqueda, Christof Wöll, and Thomas Heine. Proximity effect in crystalline framework materials: Stacking-induced functionality in MOFs and COFs. *Adv. Funct. Mater.*, 30(41):1908004, 2020.
- [36] Chengjun Kang, Zhaoqiang Zhang, Vanessa Wee, Adam K Usadi, David C Calabro, Lisa Saunders Baugh, Shun Wang, Yuxiang Wang, and Dan Zhao. Interlayer shifting in two-dimensional covalent organic frameworks. *J. Am. Chem. Soc.*, 142(30):12995–13002, 2020.
- [37] Binit Lukose, Agnieszka Kuc, and Thomas Heine. The structure of layered covalent-organic frameworks. *Chem. Eur. J.*, 17(8):2388–2392, 2011.
- [38] Cheng-Hao Liu, Allan Wei, Maïline Fok Cheung, and Dmytro F Perepichka. Vanishing electronic band gap in two-dimensional hydrogen-bonded organic frameworks. *Chem. Mater.*, 34(7):3461–3467, 2022.
- [39] Yingying Zhang, Miroslav Položij, and Thomas Heine. Statistical representation of stacking disorder in layered covalent organic frameworks. *Chem. Mater.*, 34(5):2376–2381, 2022.

- [40] Shangbin Jin, Ko Furukawa, Matthew Addicoat, Long Chen, Seiya Takahashi, Stephan Irle, Toshikazu Nakamura, and Donglin Jiang. Large pore donor–acceptor covalent organic frameworks. *Chem. Sci.*, 4(12):4505–4511, 2013.
- [41] Eric L Spitler, Brian T Koo, Jennifer L Novotney, John W Colson, Fernando J Uribe-Romo, Gregory D Gutierrez, Paulette Clancy, and William R Dichtel. A 2D covalent organic framework with 4.7-nm pores and insight into its interlayer stacking. *J. Am. Chem. Soc.*, 133(48):19416–19421, 2011.
- [42] Brian T Koo, William R Dichtel, and Paulette Clancy. A classification scheme for the stacking of two-dimensional boronate ester-linked covalent organic frameworks. *J. Mater. Chem.*, 22(34):17460–17469, 2012.
- [43] Wen-Qi Tang, Ying-Jie Zhao, Ming Xu, Jin-Ya Xu, Sha-Sha Meng, Yun-Dong Yin, Qing-Hua Zhang, Lin Gu, Da-Huan Liu, and Zhi-Yuan Gu. Controlling the stacking modes of metal–organic framework nanosheets through host–guest noncovalent interactions. *Angew. Chem. Int. Ed.*, 60(13):6920–6925, 2021.
- [44] Dequan Er, Liang Dong, and Vivek B Shenoy. Mechanisms for engineering highly anisotropic conductivity in a layered covalent-organic framework. *J. Phys. Chem. C*, 120(1):174–178, 2016.
- [45] Andrew J Clough, Jonathan M Skelton, Courtney A Downes, Ashley A De La Rosa, Joseph W Yoo, Aron Walsh, Brent C Melot, and Smaranda C Marinescu. Metallic conductivity in a two-dimensional cobalt dithiolene metal–organic framework. *J. Am. Chem. Soc.*, 139(31):10863–10867, 2017.
- [46] Taku Hayashi, Yuh Hijikata, Alister Page, Donglin Jiang, and Stephan Irle. Theoretical analysis of structural diversity of covalent organic framework: Stacking isomer structures thermodynamics and kinetics. *Chem. Phys. Lett.*, 664:101–107, 2016.
- [47] Raja Ghosh and Francesco Paesani. Topology-mediated enhanced polaron coherence in covalent organic frameworks. *J. Phys. Chem. Lett.*, 12(39):9442–9448, 2021.
- [48] Raja Ghosh and Francesco Paesani. Connecting the dots for fundamental understanding of structure–photophysics–property relationships of COFs, MOFs, and perovskites using a multiparticle holstein formalism. *Chem. Sci.*, 14:1040–1064, 2023.
- [49] Jikai Liu, Shuhao Wen, Xiaoxin Zou, Fan Zuo, Gregory JO Beran, and Pingyun Feng. Visible-light-responsive copper (II) borate photocatalysts with intrinsic midgap states for water splitting. *J. Mater. Chem. A*, 1(5):1553–1556, 2013.
- [50] Kaoru Hisama, Yanlin Gao, Mina Maruyama, Ryo Kitaura, and Susumu Okada. Continuous fermi level tuning of Nb-doped WSe₂ under an external electric field. *Jpn. J. Appl. Phys.*,

61(1):015002, 2021.

- [51] Zhi Ren, AA Taskin, Satoshi Sasaki, Kouji Segawa, and Yoichi Ando. Fermi level tuning and a large activation gap achieved in the topological insulator $\text{Bi}_2\text{Te}_2\text{Se}$ by Sn doping. *Phys. Rev. B*, 85(15):155301, 2012.
- [52] Xiao-Xin Gao, Qian-Qing Ge, Ding-Jiang Xue, Jie Ding, Jing-Yuan Ma, Yao-Xuan Chen, Bao Zhang, Yaqing Feng, Li-Jun Wan, and Jin-Song Hu. Tuning the fermi-level of TiO_2 mesoporous layer by lanthanum doping towards efficient perovskite solar cells. *Nanoscale*, 8(38):16881–16885, 2016.
- [53] Wei Jiang, Xiaojuan Ni, and Feng Liu. Exotic topological bands and quantum states in metal–organic and covalent–organic frameworks. *Acc. Chem. Res.*, 54(2):416–426, 2021.
- [54] Nicolas Regnault, Yuanfeng Xu, Ming-Rui Li, Da-Shuai Ma, Milena Jovanovic, Ali Yazdani, Stuart S. P. Parkin, Claudia Felser, Leslie M. Schoop, N. Phuan Ong, Robert J. Cava, Luis Elcoro, Zhi-Da Song, and B. Andrei Bernevig. Catalogue of flat-band stoichiometric materials. *Nature*, 603(7903):824–828, 2022.
- [55] Shizhong Zhang, Hsiang-hsuan Hung, and Congjun Wu. Proposed realization of itinerant ferromagnetism in optical lattices. *Phys. Rev. A*, 82(5):053618, 2010.
- [56] S Miyahara, S Kusuta, and N Furukawa. BCS theory on a flat band lattice. *Physica C Supercond.*, 460:1145–1146, 2007.
- [57] Raja Ghosh and Frank C Spano. Excitons and polarons in organic materials. *Acc. Chem. Res.*, 53(10):2201–2211, 2020.
- [58] Raja Ghosh, Christopher M Pochas, and Frank C Spano. Polaron delocalization in conjugated polymer films. *J. Phys. Chem. C*, 120(21):11394–11406, 2016.
- [59] Raja Ghosh, Annabel R Chew, Jonathan Onorato, Viktoria Pakhnyuk, Christine K Luscombe, Alberto Salleo, and Frank C Spano. Spectral signatures and spatial coherence of bound and unbound polarons in P3HT films: Theory versus experiment. *J. Phys. Chem. C*, 122(31):18048–18060, 2018.
- [60] Raja Ghosh, Christine K Luscombe, Mike Hambsch, Stefan CB Mannsfeld, Alberto Salleo, and Frank C Spano. Anisotropic polaron delocalization in conjugated homopolymers and donor–acceptor copolymers. *Chem. Mater.*, 31(17):7033–7045, 2019.
- [61] John E Northrup. Atomic and electronic structure of polymer organic semiconductors: P3HT PQT and PBTTT. *Phys. Rev. B*, 76(24):245202, 2007.
- [62] Simil Thomas, Hong Li, Raghunath R. Dasari, Austin M. Evans, Ioannina Castano, Tay-

- lor G. Allen, Obadiah G. Reid, Garry Rumbles, William R. Dichtel, Nathan C. Gianneschi, Seth R. Marder, Veaceslav Coropceanu, and Jean-Luc Brédas. Design and synthesis of two-dimensional covalent organic frameworks with four-arm cores: Prediction of remarkable ambipolar charge-transport properties. *Mater. Horizons*, 6(9):1868–1876, 2019.
- [63] Grigorii Skorupskii, Khoa N Le, Dmitri Leo M Cordova, Luming Yang, Tianyang Chen, Christopher H Hendon, Maxx Q Arguilla, and Mircea Dincă. Porous lanthanide metal-organic frameworks with metallic conductivity. *Proc. Natl. Acad. Sci. U.S.A.*, 119(34):e2205127119, 2022.
- [64] Georg Kresse and Jürgen Furthmüller. Efficient iterative schemes for *Ab Initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54(16):11169, 1996.
- [65] Georg Kresse and Jürgen Furthmüller. Efficiency of *Ab-Initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.*, 6(1):15–50, 1996.
- [66] John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77(18):3865, 1996.
- [67] David C Langreth and MJ Mehl. Beyond the local-density approximation in calculations of ground-state electronic properties. *Phys. Rev. B*, 28(4):1809, 1983.
- [68] Axel D Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, 38(6):3098, 1988.
- [69] Sergei L Dudarev, Gianluigi A Botton, Sergey Y Savrasov, CJ Humphreys, and Adrian P Sutton. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B*, 57(3):1505, 1998.
- [70] Lei Wang, Thomas Maxisch, and Gerbrand Ceder. Oxidation energies of transition metal oxides within the GGA+U framework. *Phys. Rev. B*, 73(19):195107, 2006.
- [71] Peter E Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50(24):17953, 1994.
- [72] Hendrik J Monkhorst and James D Pack. Special points for Brillouin-zone integrations. *Phys. Rev. B*, 13(12):5188, 1976.
- [73] Erin R Johnson and Axel D Becke. A post-Hartree-Fock model of intermolecular interactions: Inclusion of higher-order corrections. *J. Chem. Phys.*, 124(17):174104, 2006.
- [74] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate *Ab Initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.*, 132(15):154104, 2010.

- [75] Stefan Grimme, Stephan Ehrlich, and Lars Goerigk. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.*, 32(7):1456–1465, 2011.
- [76] John P Perdew and Mel Levy. Physical content of the exact Kohn-Sham orbital energies: Band gaps and derivative discontinuities. *Phys. Rev. Lett.*, 51(20):1884, 1983.
- [77] Paula Mori-Sánchez, Aron J Cohen, and Weitao Yang. Localization and delocalization errors in density functional theory and implications for band-gap prediction. *Phys. Rev. Lett.*, 100(14):146401, 2008.
- [78] Koichi Momma and Fujio Izumi. VESTA 3 for three-dimensional visualization of crystal volumetric and morphology data. *J. Appl. Crystallogr.*, 44(6):1272–1276, 2011.
- [79] Vei Wang, Nan Xu, Jin-Cheng Liu, Gang Tang, and Wen-Tong Geng. VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code. *Comput. Phys. Commun.*, 267:108033, 2021.
- [80] Junghyun Noh, Osman I Osman, Saadullah G Aziz, Paul Winget, and Jean-Luc Brédas. A density functional theory investigation of the electronic structure and spin moments of magnetite. *Sci. Technol. Adv. Mater.*, 15(4):044202, aug 2014.
- [81] Anna Majtyka-Piłat, Marcin Wojtyniak, Łukasz Laskowski, and Dariusz Chrobak. Structure and properties of copper pyrophosphate by first-principle calculations. *Materials*, 15(3): 842, 2022.

Chapter 3

Interplay of Intermolecular Interactions Overrides Chemical Intuition in Functionalized 2D Covalent Organic Frameworks

3.1 Introduction

The escalating threats of global warming and the increasing global energy demands have intensified the search for alternative and sustainable energy solutions, making the development of clean and renewable energy techniques more critical than ever.¹ To this end, photocatalysis has emerged as one of the central players in energy conversion technologies, offering a renewable and environmentally friendly solution.^{2–4}

As one of the most critical physical quantities governing the performance of various photoelectronic and catalytic devices, an exciton describes a bound electron–hole pair in materials.^{5–7} Recently, organic polymer semiconductors have been shown to function as alternative platforms for photocatalysis.^{8,9} However, the issue of usually strongly bound excitons in organic semiconductors makes the process of exciton dissociation more difficult compared to the inorganic counterparts, which in turn greatly hinders their photocatalytic applications.¹⁰ In this context, covalent organic frameworks (COFs), a class of crystalline porous nanomaterials composed of organic nodes and linkers connected by strong covalent bonds, present promising opportunities to address this challenge.^{11–15} Over the past two decades, COFs have garnered

significant research interest due to their high surface area and highly tunable compositions and structures, which endow them with promising electronic, transport, and photophysical properties.^{11,16} These materials have the ability to regulate electron–hole recombination through the tunability of donor–acceptor (D–A) pairs, thereby significantly modifying the photocatalytic activity.^{17–20} While in principle, a vast array of D–A COFs can be synthesized from a nearly limitless design space of organic building blocks, their actual photocatalytic performance can vary drastically due to differences in D–A interactions.^{21–31} Among these, two-dimensional (2D) COFs are particularly intriguing because they can be designed from the bottom–up approach using topological strategies, allowing for the fine-tuning of electronic and photocatalytic properties through various building blocks, including nodes and linkers.^{32–36} Furthermore, the in-plane conjugated π orbitals and out-of-plane van der Waals interactions formed *via* layered π – π stacking were found to facilitate the transfer of photogenerated charge carriers and suppress their recombination.^{37–40}

While functionalization of 2D COFs and other organic polymer materials has been widely employed as an effective strategy to tailor their electronic and photophysical properties, the underlying principles guiding these modifications remain largely underexplored.^{25,41–44} Conventionally, electron-withdrawing and electron-donating groups are expected to exert opposing effects when attached to aromatic linkers — altering local charge environment, orbital energies, and π – π interactions in predictable ways. However, in extended frameworks like 2D COFs, such intuition might fail to account for the overall photophysical performance or activity of the material, which is often a collective effect of the building blocks, the covalent and noncovalent interactions among them, and the lattice symmetry.

Moreover, while the exact stacking pattern is extremely challenging to probe experimentally due to line broadening and limited resolution,^{45–48} the detailed stacking arrangement of these 2D layered COFs can significantly influence the electronic and transport properties of COFs.^{46,49–56} Although slipped and inclined stacking patterns are typically theoretically predicted to be energetically preferred,^{57–61} a variety of stacking arrangements can be achieved

with suitable chemical and thermodynamic controls.^{52,62,63}

Overall, how different functional groups modulate the stacking patterns through different and often subtle intermolecular interactions is often largely overlooked. In turn, how these structural changes influence the electronic, charge transport, and excitonic behavior is also of significant scientific interest. In this context, we herein present a systematic analysis of the complicated and entangled effects among chemical substituent, interlayer stacking, backbone composition, as well as lattice symmetry, and how these factors collectively contribute to the composition–structure–property relationships in 2D COFs. Specifically, we investigate how the intricate molecular interaction dictates the stability and stacking arrangements of 2D COFs, and how the resulting and inherent electronic structure regulates the transport properties and excitonic characteristics in COFs. The strategy and findings presented in this work open up new and effective avenues for fine-tuning the electronic, transport, and photophysical properties of COFs, rendering novel insights into the composition–structure–property relationships, and in turn providing physical and rational design principles for functional reticular materials for their energy-related applications.

3.2 Results and Discussion

Recently, Li *et al.* showed that the incorporation of appropriate D–A pairs of organic components into COFs can significantly extend the charge carrier lifetime and achieve excellent performance in photocatalytic H₂ evolution.⁶⁴ As prototypical systems, we investigate the 2D BD-COF in their work, along with its monosubstituted derivatives, overall denoted as the –R systems, as illustrated in Figure 3.1a. Specifically, in these variants, electron-withdrawing groups such as cyano (–CN) and fluoro (–F), as well as the electron-donating hydroxyl (–OH) group, are introduced on the benzene rings of the organic linker to systematically explore the impact of functionalization.

In these frameworks, the nodes form a honeycomb sublattice, while the linkers construct

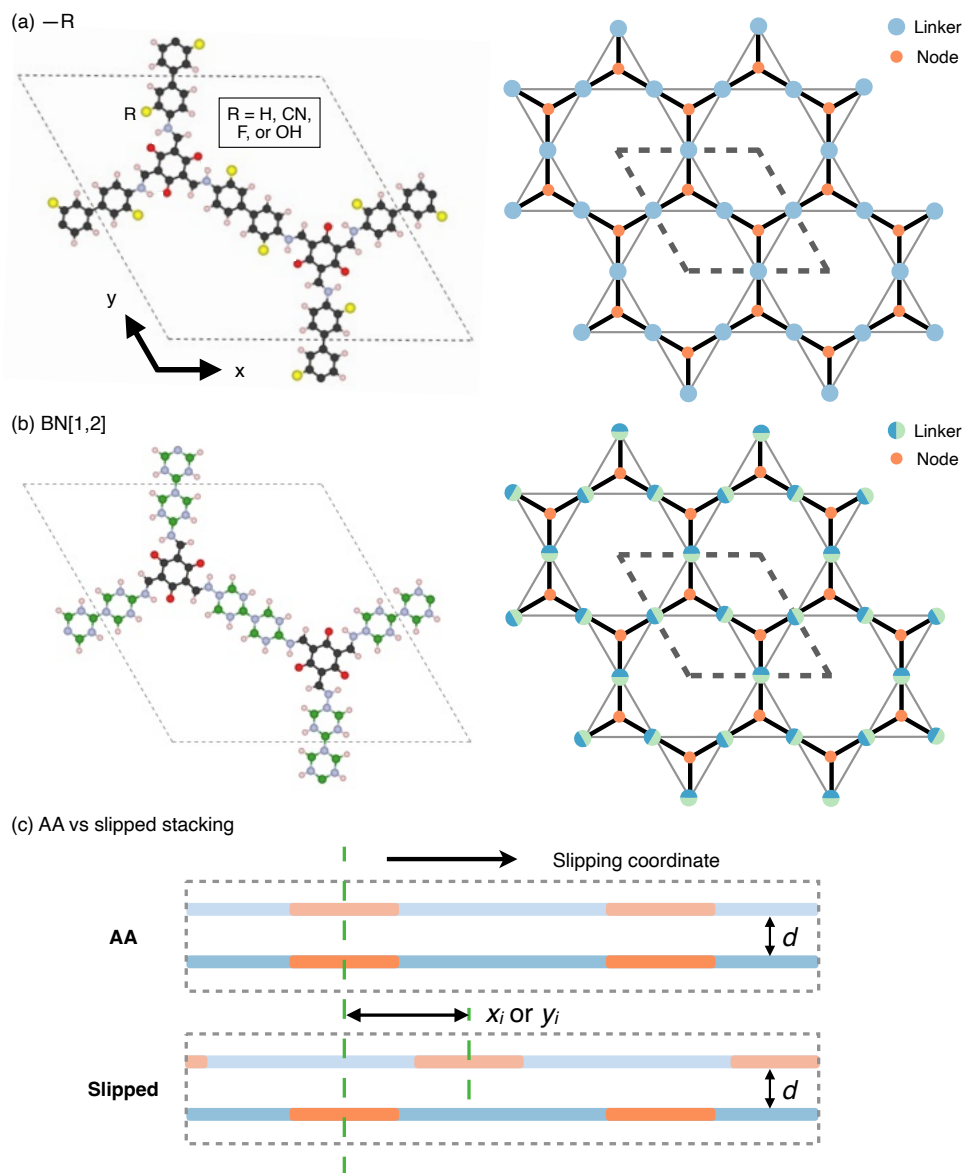


Figure 3.1. Geometry structures (left) and schematic representations of the corresponding lattices (right) for the (a) $-R$ systems exhibiting honeycomb-kagome lattice symmetry, and (b) BN[1,2] systems featuring broken lattice symmetry. Atom colors: pink (H), black (C), blue (N), red (O), and green (B). (c) Schematic depiction of the slipping coordinates (x_i or y_i) used to describe the relative lateral displacement in 2D COFs. d stands for the interlayer distance. Unit cell boundaries are marked with dashed lines.

a kagome sublattice, together giving rise to the characteristic 2D honeycomb-kagome framework (see Figure 3.1a). To elucidate the role of lattice symmetry along with the effects of functionalization, we introduce a novel design strategy that replaces the original homocyclic benzene

rings in the organic linkers of BD-COF with symmetry-broken heterocyclic borazine rings, while preserving the overall macroscopic lattice framework (see Figure 3.1b). The resulting systems are uniquely denoted as BN[m,n], where m and n indicate the number of B–N bonds connecting each node to the neighboring linkers within the unit cell. Following this convention, we investigate the structural and electronic properties of BN[1,2], BN[0,0], BN[3,3], and BN[0,3] systems (Figures 3.1b and 3.8). Importantly, BN[0,0] and BN[3,3] preserve the honeycomb-kagome lattice symmetry, akin to the –R systems (R = H, CN, F, or OH) depicted in Figure 3.1a, which was disrupted in BN[1,2] and BN[0,3].

3.2.1 Geometry and Potential Energy Surface

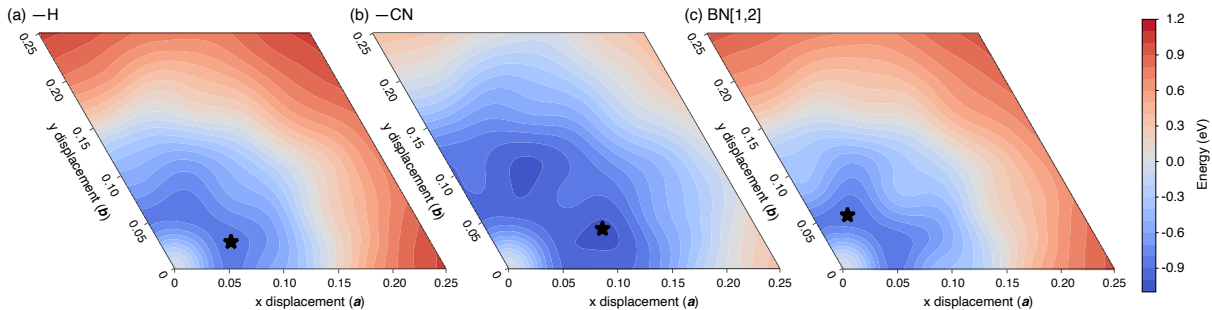


Figure 3.2. PES contours of fractional interlayer displacements of a double-layer unit cell for the (a) –H, (b) –CN, and (c) BN[1,2] systems. The black stars represent the minima in the 2D PES contours, corresponding to (0.067, 0.029) for the –H, (0.108, 0.043) for the –CN, and (0.034, 0.058) for the BN[1,2] system. For each system, the energy of the corresponding AA-stacked structure is used as the zero reference for the PES contours.

Due to the relatively weak interactions between adjacent layers, 2D COFs possess significant intrinsic flexibility in the relative positioning between the 2D layers. This flexibility can be described in two orthogonal degrees of freedom: the layer offset, a vector within the plane defining lateral shifts, and the interlayer distance, which characterizes the vertical separation between neighboring layers. Most reported 2D COFs adopt either AA (also referred to as eclipsed) stacking, where there is a zero lateral layer offset between neighboring layers, or shifted stacking structures, where small but finite lateral displacements occur. However, determining

the precise magnitude of these lateral offsets experimentally remains challenging with standard X-ray diffraction or electron diffraction techniques.^{45–48}

To investigate the electronic and transport properties of planar 2D COFs, it is first critical to identify the most energetically favorable stacking arrangements. To this end, we systematically mapped the potential energy surface (PES) as a function of interlayer slipping along the x and y directions (see Figure 3.1c).

As shown in Figure 3.2a, the 2D PES relative to the AA stacking of the –H (BD-COF) system, reveals that slightly slipped configurations — corresponding to displacements of ~ 0.02 – 0.13 fractions of the lattice constants (~ 0.6 – $3.9\text{\AA}$) — are energetically more favorable than the perfect AA stacking. From Figures 3.2a and 3.10, we observe that the COF functionalized with fluoro (–F) exhibits a PES contour similar to that of the unfunctionalized –H BD-COF. In contrast, functionalization with –CN or –OH group leads to similar and broader regions (~ 0.02 – 0.17) of stability along the slipping coordinates.

This trend suggests that –CN and –OH functional groups enhance the framework’s tolerance on slipping displacements. While all functionalized 2D COFs favor slightly displaced structures by 0.86–1.03 eV relative to the corresponding AA stacking, the stabilization effect is even more pronounced with –CN and –OH substitutions (see Figure 3.2 and Figure 3.10). Interestingly, despite their different electronic characteristics — –OH being an electron-donating group and –CN an electron-withdrawing group — both modifications similarly promote a greater propensity for a larger extent of slipping compared to the unsubstituted BD-COF. In contrast, the strongly electron-withdrawing –F substitution results in a stacking PES profile closely resembling that of the BD-COF.

Although functionalization is often used to manipulate stacking arrangements in synthesized COFs,^{65,66} our analysis reveals no straightforward/direct correlation between the electron-donating or electron-withdrawing nature of the substituents and systematic trends in interlayer stacking behavior.

As shown in Figure 3.2c, the borazine-replaced BN[1,2] system, as well as other BN

systems (See Figure 3.12), exhibit comparable PES profiles to the unfunctionalized BD-COF.

3.2.2 Energy Decomposition Analysis

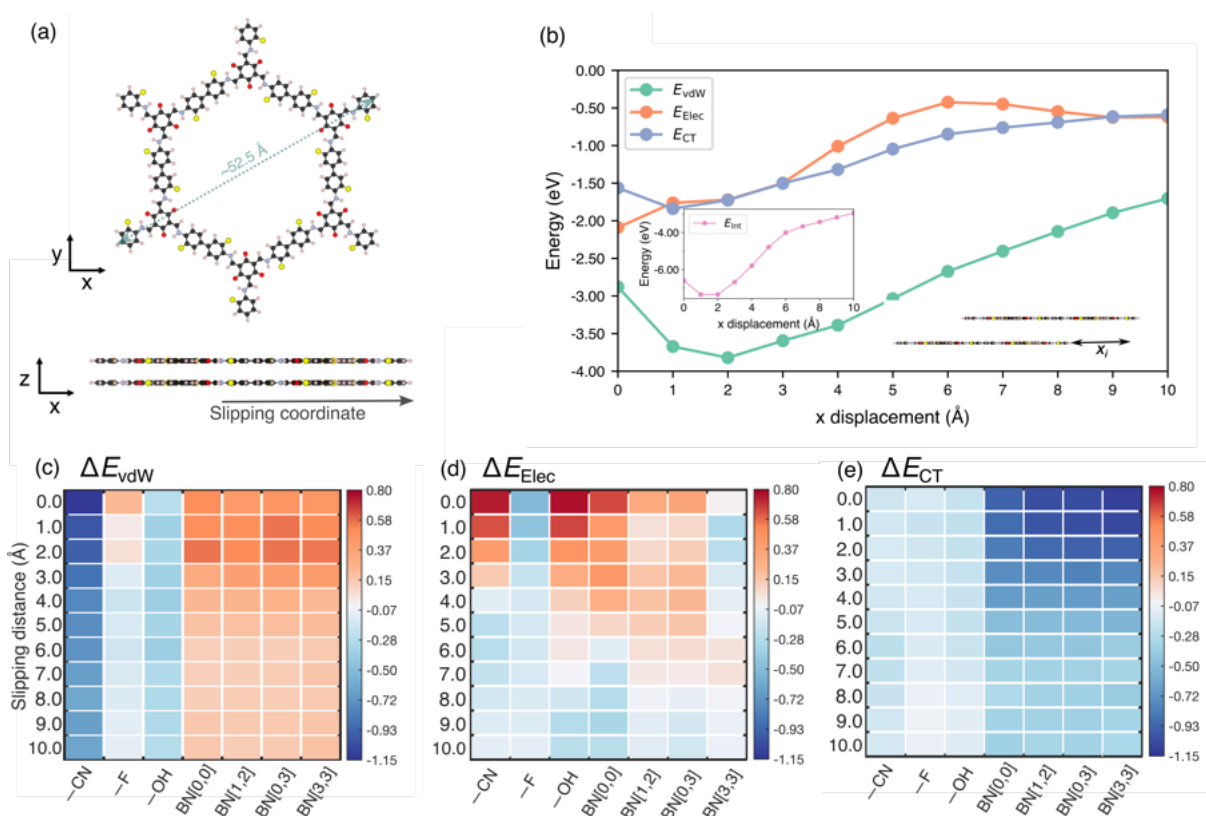


Figure 3.3. Molecular systems and results from the ALMO-EDA calculations. The (a) top and side view of the relatively large-in-size molecular ring-shape systems, using the -R systems as an example, and similar systems are used for the BN systems; (b) evolution of the E_{vdW} , E_{Elec} , and E_{CT} of the -H system as a function of slipping along x. The evolution of E_{Int} is included in the inset; and results for the (c) ΔE_{vdW} , (d) ΔE_{Elec} , and (e) ΔE_{CT} interactions, relative to the -H system included in (b). The neighboring layers are slipped along the x direction. More details for the ALMO-EDA results can be found in Figures 3.14-3.17.

To investigate the physical driving forces underlying the stacking arrangements and PES profiles shown in Figures 3.2, 3.10, and 3.12, we performed energy decomposition analysis based on absolutely localized molecular orbitals (ALMO-EDA) to dissect the interlayer interactions in 2D COFs.^{67,68} Details can be found in Appendix A. For this analysis, we employed relatively large, double-layered, ring-shaped molecular clusters with a diameter of ~ 52.5 Å (see

Figure 3.3a).

As shown in Figure 3.3b, for the –H BD-COF system, van der Waals interaction (E_{vdW}), comprising both Pauli repulsion and dispersion components, plays a dominant role in governing the offset stacking preference. This is evident from the similarity in the curvature of the E_{vdW} and the total intermolecular interaction energy (E_{Int}) along the slipping coordinate, indicating that the energetic preference on the offset stackings is largely driven by the balance between these noncovalent interactions. Specifically, while the attractive dispersion interaction favors the AA stacking, the Pauli exchange repulsion introduces a significant energetic penalty when aligning high electron density regions near atomic nuclei, ultimately destabilizing the AA configuration (Figures 3.14-3.17). This is consistent with previous studies on π – π stacked systems, which attributed the preferred offset stacking geometry to a subtle balance between these opposing interactions,^{69–71} challenging earlier interpretations that emphasized quadrupolar electrostatics as the primary driving force.

Interestingly, functionalization of BD-COF with substituents such as –CN, –F, or –OH retains the qualitatively similar preference for slipped stacking, further supporting the central role of E_{vdW} . Although the absolute magnitude of E_{vdW} varies depending on the specific functional group, the location of the energy minima remains nearly unchanged across all derivatives, mirroring that of the unfunctionalized system (see Figures 3.14-3.17). However, this fails to explain the variation in the functionalization-dependent and favorable extent of slipping, especially between the –H (or –F) and the –CN (or –OH) substituted systems. This indicates that although E_{vdW} dictates the general preference for slipped stacking, it alone cannot fully account for the variation in the extent of slipping observed across different functionalized systems, as illustrated in Figure 3.2.

As shown in Figure 3.3d, we found that the observed variations in interlayer displacement are primarily influenced by differences in electrostatic interactions (E_{Elec}) arising from the nature of functionalization. Functional groups such as –CN and –OH significantly modify electrostatic stabilization, promoting a larger extent of slipping, whereas –F substitution

yields electrostatic interaction similar to that of the unfunctionalized BD-COF, favoring the AA stacking (Figures 3.14-3.15). These findings challenge the conventional view wherein electron-withdrawing substituents decrease electron density within the aromatic π -cloud, thereby reducing quadrupolar electrostatic repulsion and enhancing π - π stacking interactions, while electron-donating substituents act oppositely, weakening such interactions.^{72,73} Studies have demonstrated that both electron-donating and electron-withdrawing substituents can stabilize aromatic dimers, indicating limitations of explanations based solely on multipolar electrostatics.^{74,75} These substituent effects are found to be highly local, predominantly involving only the atoms in local proximity rather than entire aromatic rings, suggesting minimal contributions from quadrupole-quadrupole interactions.⁷⁶ Within this local interaction description, the AA stacking arrangement might intuitively seem purely repulsive and energetically unfavorable;^{58,58} however, charge penetration significantly influences stacking energetics.⁷⁷⁻⁸⁰ Electron cloud overlap reduces repulsion compared to point charges, making electron-nuclear attraction terms slightly exceed nuclear-nuclear and electron-electron repulsions. Any substituent, irrespective of electron-donating or electron-withdrawing character, inherently possesses greater electron density than hydrogen, enhancing favorable charge penetration effects. Thus, the subtle balance between charge penetration and electron-cloud repulsion depends critically on the detailed electronic structure of the aromatic framework, which is challenging to determine a priori from chemical intuition.

As shown in Figure 3.3, a comparison of energy decomposition analysis between borazine-based COFs and the BD-COF reveals markedly distinct intermolecular interaction profiles. In particular, the E_{vdW} (see Figure 3.3c) in borazine-based systems is significantly weaker, while the charge transfer component (E_{CT} , see Figure 3.3e) is substantially enhanced. Despite similar Pauli repulsion energies between benzene- and borazine-based COFs (Figures 3.16-3.17), the differences in E_{vdW} arise from the distinct electronic structure of borazine. Specifically, the more localized π -electron cloud in borazine results in a reduced and less anisotropic molecular polarizability compared to benzene,⁸¹ thereby weakening dispersion interaction relative to the

BD-COF. Additionally, borazine features both electron-rich (nitrogen atoms with lone pairs, contributing to the HOMO) and electron-deficient (boron atoms, contributing to the LUMO) sites. In stacked configurations, this electronic asymmetry enhances D–A interactions (also referred to as charge transfer), where electron density is transferred from the nitrogen lone pairs of one layer to the empty boron orbitals of an adjacent layer. This interlayer charge transfer provides a strong attractive interaction absent in the symmetric, homonuclear benzene-based 2D COFs.

3.2.3 Electronic Transport

While the AA stacking configuration, usually possessing higher lattice symmetry than other stacking motifs, is often presumed to be the predominant structure in many studies,^{82–84} this arrangement can lead to an overestimation of interlayer charge mobility due to idealized π – π interaction. In contrast, the energetically more favorable slipped-stacked configurations would often exhibit increased band gaps and heavier effective carrier masses, reflecting reduced interlayer electronic coupling. To systematically investigate the influence of stacking arrangements and linker functionalization on the electronic properties of 2D COFs, we computed electronic band structures for both the AA-stacked and the slipped-stacked configurations, being slipped at the PES minima identified in the PES contours (Figure 3.2).

AA-stacked 2D COFs

As shown in Figure 3.4a-c and Figure 3.18, the AA-stacked systems with various –R substituents (R = H, CN, F, OH) display prominent Dirac bands in both the conduction (CBs) and valence bands (VBs), which are characteristic of honeycomb-kagome lattices.^{85–87} The CBs are highly dispersive, indicating efficient electron delocalization and low effective masses along both intra- (Γ –M–K– Γ) and inter-layer (Γ –Z) directions (see Table 3.3). In contrast, the VBs feature a flat intralayer band, signifying strong in-plane hole localization, while being more dispersive out-of-plane, suggesting enhanced interlayer hole mobility.⁸⁸ Notably, as shown in Figures 3.4d and 3.18, all AA-stacked –R systems display highly similar band structures (similarity scores, s

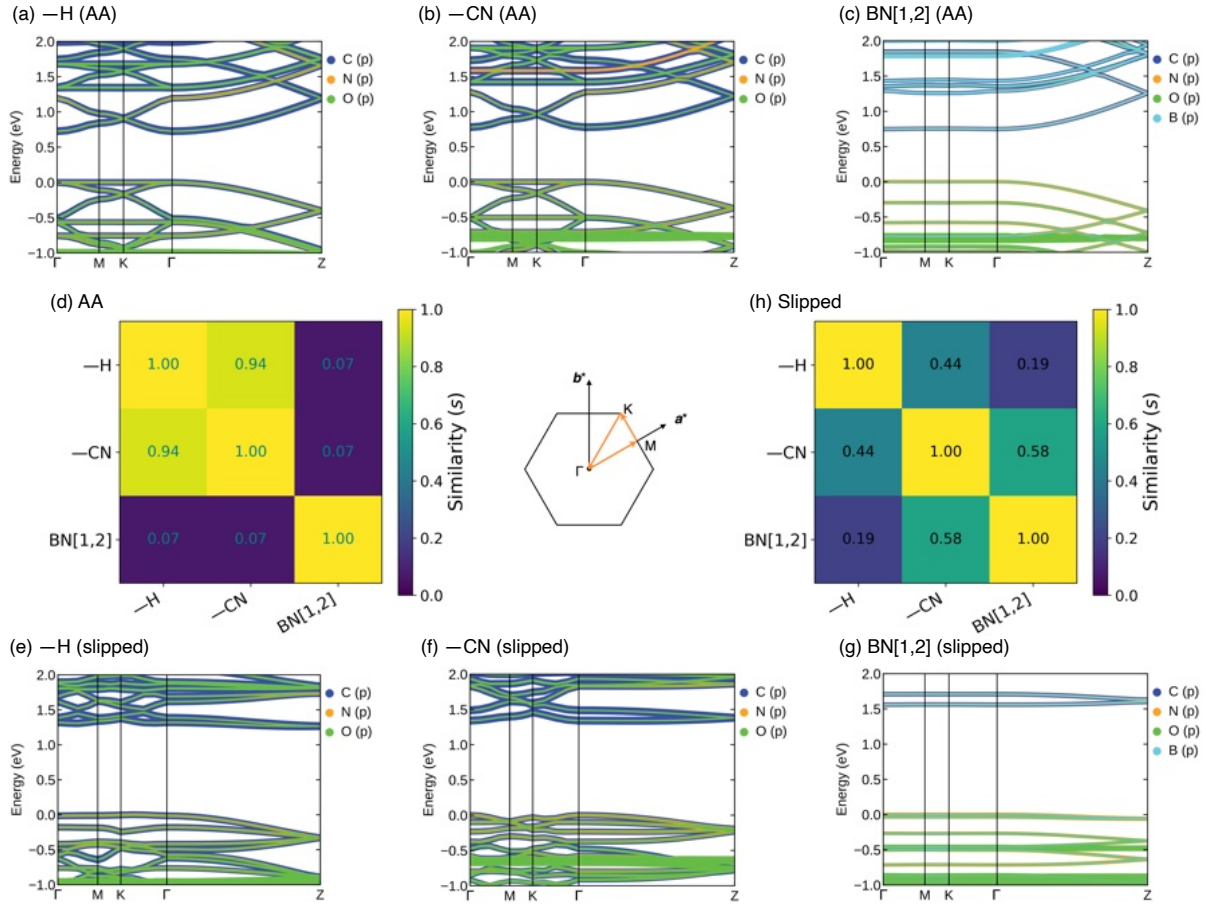


Figure 3.4. PBE-D3(BJ)-evaluated band structures (with orbital projections) and the corresponding similarity matrices. (a), (b), and (c) correspond to the -H, -CN, and BN[1,2] systems under AA stacking, while (e), (f), and (g) are from the corresponding slipped stackings which correspond to the minima in the PES contours in Figure 3.2. The high symmetry k -paths in the first Brillouin Zone are shown in the inset between the similarity matrices among the (d) AA stackings and (h) slipped stackings, where the path of Γ -Z (interlayer) is not shown. The valence band maximum (VBM) is set to zero. More details can be found in the Appendix.

> 0.85) and consistently preserve the kagome-derived features, resulting in comparable electron and hole effective masses across both substituted and unsubstituted BD-COFs. This indicates that the electronic structure for the AA-stacked substituted and unsubstituted BD-COFs is largely governed by the underlying lattice symmetry, with functionalization by substituents exerting minimal influence, as visualized in the partial charge density included in Figure 3.20. This symmetry-dominated behavior persists even in bi-substituted systems, where each phenyl ring

carries two functional groups (Figures 3.23–3.24).

The underlying symmetry-driven electronic structure is disrupted in the AA-stacked BN[1,2] system, where the homocyclic benzene rings are replaced by heterocyclic borazine groups. The resulting lowering in lattice symmetry and disruption of in-plane π -conjugation significantly alter the signature electronic bands (see Figure 3.4c and Figure 3.25e). Consequently, both the CBs and VBs become markedly less dispersive along the intralayer (Γ –M–K– Γ) direction, leading to significantly heavier effective masses due to weakened intralayer electronic coupling (Table 3.7). Although the band dispersion along the interlayer (Γ –Z) direction remains comparable to that of the AA-stacked –R systems — yielding similar out-of-plane effective masses — the CBs and VBs deviate significantly from the characteristic kagome bands. This deviation is reflected quantitatively in the much lower similarity scores between the BN[1,2] and the BD-COF (see Figure 3.4d).

Slipped-stacked 2D COFs

Compared to the AA stacking, the slipped-stacked configurations of substituted and unsubstituted BD-COFs exhibit larger and indirect band gaps (Figure 3.4e–g, Figure 3.18, Table 3.5). The indirect nature of the gap necessitates phonon participation for transitions from the valence band maximum (VBM) to the conduction band minimum (CBM), reducing the efficiency of optical absorption. Additionally, both CBs and VBs become less dispersive along the interlayer (Γ –Z) direction, resulting in heavier effective masses and indicating weakened interlayer electronic coupling. Interestingly, the hole effective masses along the intralayer direction (Γ –M–K– Γ) become significantly lighter in the slipped-stacked structures compared to the AA stackings, as shown in Figure 3.4e–f and Table 3.5. This reduction is attributed to the disappearance of the flat VB present in AA-stacked counterparts, a direct result of broken honeycomb-kagome symmetry. As the lattice symmetry is disrupted in slipped-stacked configurations, the electronic structures of different functionalized systems begin to diverge noticeably. This divergence is evident in the systematic decrease in band structure similarity

scores from AA to slipped-stacked geometries among the substituted and unsubstituted BD-COFs (see Figure 3.4h and Figure 3.22), underscoring the strong sensitivity of electronic properties to stacking arrangement and lattice symmetry (see Figure 3.11 and Figure 3.13 for slipped geometries).

We further compared the electronic band structures of the –H BD-COF and BN systems in their slipped configurations, as shown in Figure 3.4 and Figure 3.25. In slipped BN systems, the band gaps increase compared to their AA-stacked counterparts but notably remain direct (Table 3.8), allowing efficient optical transitions without momentum transfer — unlike the indirect gaps observed in slipped –R systems. Similar to the –R systems, slipping reduces the dispersion of CBs and VBs along both intra- and interlayer directions, leading to heavier charge carriers, especially for electrons along the interlayer (Γ –Z) direction.

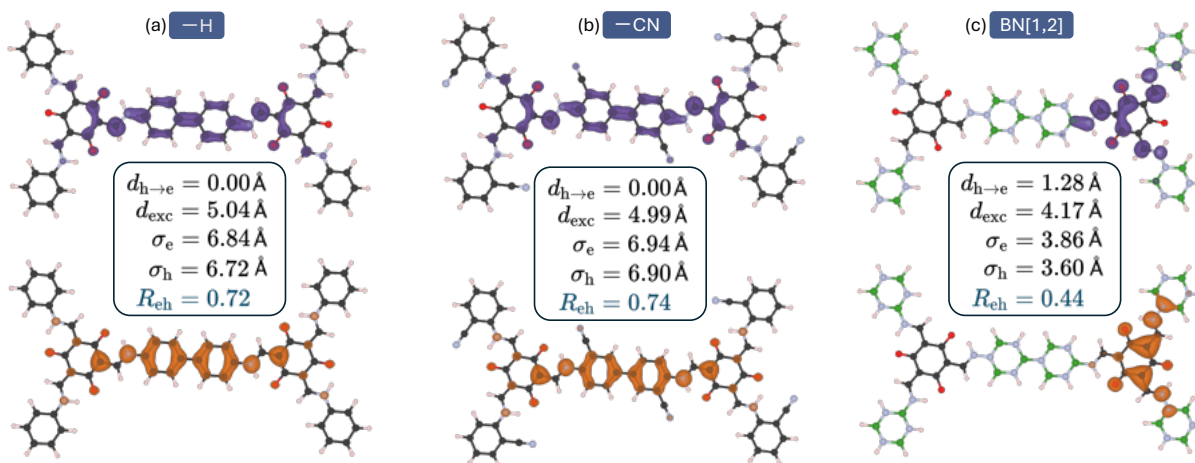


Figure 3.5. Results for the density-based excitonic analysis. Top view of the spatial distribution of the electron (top row) and hole (bottom row) and the distance between the centroids of the electron and hole, $d_{h \rightarrow e}$, exciton size d_{exc} , sizes of the electron and hole σ_e and σ_h , and the normalized electron–hole correlation coefficient R_{eh} , for the monolayer systems of the (a) –H, (b) –CN, and (c) BN[1,2] systems. Details of the methodology can be found in Appendix A.

From our analyses, we can see that when under the slipped stacking, electron-donating substituents like –OH and electron-withdrawing substituents like –CN lead to heavier interlayer electron effective masses compared to the unsubstituted BD-COF (see Table 3.5). Despite their

differing electronic characteristics, these functionalized systems (with $-\text{CN}$ or $-\text{OH}$) adopt similar slipped-stacked topologies, favoring a larger extent of slipping compared to the unsubstituted BD-COF, as discussed earlier. Increased slipping extent reduces orbital overlap and weakens interlayer electronic coupling, thereby increasing the effective mass along the out-of-plane direction. This highlights the dominant role of stacking geometry in governing interlayer charge transport. In contrast, the more localized π -electrons in borazine linkers suppress intralayer coupling, resulting in heavier effective masses and poorer transport properties than the unsubstituted BD-COF (see Table 3.7 and Table 3.8).

Although the computed band structures delineate the energetic landscape for charge carriers, they do not capture the interactions between photo-generated electrons and holes⁸⁹ that govern optical responses in materials and critically influence the performance of photoelectronic and catalytic devices.^{5–7} To address this, we computed density-based excitonic descriptors derived from the transition density matrix, following Ref. 90, which explicitly quantify the correlation between electron–hole pair, *i.e.*, the exciton.

In the intralayer direction, as shown in Figure 3.5a-b, both the unfunctionalized ($-\text{H}$) and $-\text{CN}$ functionalized BD-COFs exhibit bound excitons, with highly correlated electron–hole pairs characterized by a high positive value of the electron–hole correlation coefficient R_{eh} . In contrast, replacing the benzene backbone with borazine results in a more localized excitonic state (Figure 3.5c), with much smaller sizes for the exciton, electron and hole (d_{exc} , σ_{e} , and σ_{h}), in agreement with the electronic band structure results discussed earlier. This localization arises because borazine disrupts the extended π -conjugation network of the COF, leading to less dispersive CBs and VBs along the intralayer (Γ –M–K– Γ) direction. Consequently, the reduced effective mass in the BD-COF is smaller than in their borazine-based counterparts, which exhibit heavier carriers and more strongly localized electronic states. This localization diminishes dielectric screening and enhances Coulomb interactions between the electron–hole pairs, yielding a lower dielectric constant and stronger electron–hole attraction.^{91,92} As a result, the BN[1,2] system exhibits a larger intralayer exciton binding energy—the energy required to

separate the electron–hole pair—compared to the –H and –CN systems (see Table 3.9), indicating comparatively less favorable photocatalytic performance.

3.2.4 Effect of Defects in 2D COFs

To realistically model the properties and performance of 2D COFs, it is essential to account for the effects of disorders or defects, as perfect crystalline order is rarely achieved experimentally. Structural defects such as vacancies, substitutions, and lattice distortions can profoundly influence electronic properties, charge transport, excitonic dynamics, and optical responses by introducing localized states and scattering centers that are challenging to capture by conventional band structure calculations. To incorporate these disorder effects, we employed the Holstein Hamiltonian^{93,94} to probe how stacking arrangements impact interlayer electron delocalization in disordered 2D COFs. Further details can be found in the Appendix.

Figure 3.6a shows the calculated interlayer coherence number for both AA-stacked and slipped-stacked configurations of the –H and BN[1,2] systems as a function of increasing static disorder (σ). The interlayer coherence number or electron delocalization length describes the spatial extent over which an electron remains delocalized along the stacking direction. A larger interlayer coherence number indicates more efficient interlayer electron delocalization and consequently enhanced charge transport. We found that the slipped-stacked arrangement results in greater electron localization compared to the AA-stacked configuration across all disorder regimes, indicating that slipped stacking hinders electron transport, consistent with the electronic structure calculations (*vide supra*). However, the extent of this difference in electron delocalization between the two arrangements depends on the degree of disorder. For example, in the low-disorder regime, where σ is minimal (~ 0.02 eV), electrons in the slipped-stacked –H arrangement are delocalized over roughly 8 layers, compared to ~ 10 layers for the AA-stacked –H configuration. In the same regime, localization is more pronounced for the BN[1,2] system — electrons are delocalized over only 3 layers in the slipped-stacked arrangement, compared to 10 in the AA-stacked counterpart. In the experimentally relevant disorder regime

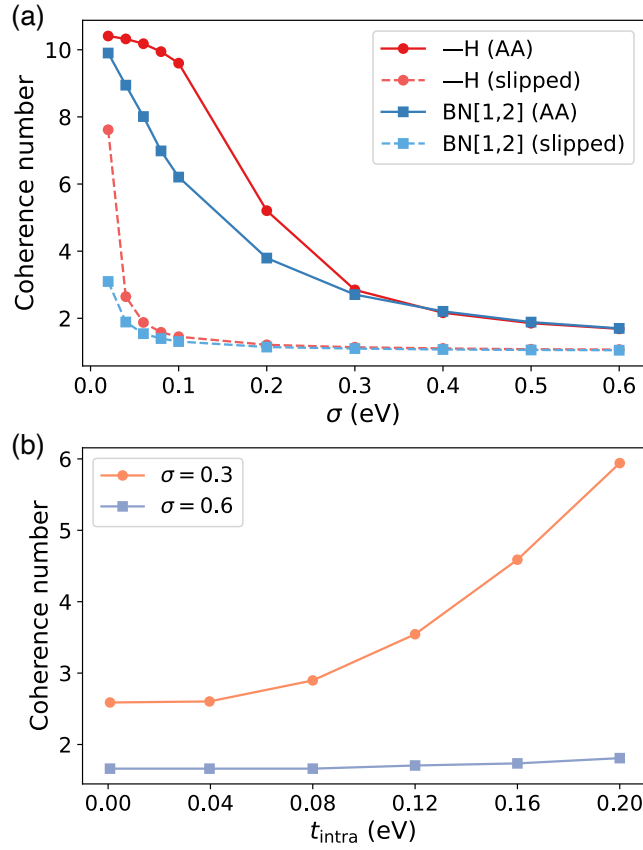


Figure 3.6. Interlayer coherence number (in layers) as a function of (a) inhomogeneous static disorder (σ) for AA- and slipped-stacked arrangements of -H and BN[1,2] systems, and (b) intralayer electron transfer integral t_{intra} when under different disorder levels ($\sigma = 0.3$ or 0.6 eV).

of $\sigma = 0.3$ eV, previously used in our studies to reproduce experimental spectra of COFs⁹⁴ and polymers⁹³, the relative difference in electron delocalization length between AA- and slipped-stacked configurations becomes more similar for these two systems. This indicates that, under such realistic disorder levels, the delocalization difference between these two stacking arrangements is becoming much less system-dependent. As disorder increases further ($\sigma > 0.4$ eV), approaching levels characteristic of nearly amorphous COFs, the difference in interlayer coherence number between the two stacking arrangements continues to diminish.

In addition, comparing the interlayer coherence number within the AA-stacked arrangement for both the -H and BN[1,2] systems in the disorder range $\sigma < 0.3$ eV, we found that despite

having similar interlayer electronic coupling values (see Table 3.1), the interlayer coherence number is higher for –H than for BN[1,2]. This difference primarily arises from the much higher computed intralayer coupling in the –H system. This observation underscores that intralayer coupling, governed by factors such as conjugation length, planarity, chemical structure, and thermal fluctuations, plays a critical role even in interlayer electron delocalization. Stronger intralayer coupling allows the electron to bypass deep traps induced by electronic disorder and explore more extended delocalization pathways. To further illustrate this effect, Figure 3.6b shows that within the regime of realistic disorder widths ($\sigma = 0.3$ eV), the simulated interlayer coherence number gradually increases as the intralayer electronic coupling (t_{intra}) strengthens. However, such an increase in interlayer coherence number is not observed in amorphous COF structures, i.e., at very high σ values (*e.g.*, $\sigma = 0.6$ eV) — where the electron is already highly localized due to disorder.

3.3 Conclusions

In this study, we systematically investigated how linker functionalization, interlayer stacking, backbone composition, lattice symmetry, and static disorder shape the structural, electronic, transport, and photophysical properties of 2D COFs. Our results reveal that slipped-stacked configurations are generally the most energetically favorable, with the degree of slipping systematically modulated by the nature of the functional groups. While van der Waals interactions primarily drive the slipping preference, variations in electrostatic interactions further tune the extent of slipping, thereby influencing the electronic structure and charge transport properties.

We find that when the electronic properties are governed by a highly symmetric lattice backbone, functionalization has limited ability to adjust electronic or transport characteristics. In contrast, modifications that disrupt lattice symmetry, such as interlayer slipping, as well as heterocyclic linker incorporation, induce pronounced and effective changes in electronic, charge transport, and photoelectronic behaviors. In the symmetry-broken configurations, the

slipped stacked pattern becomes a critical determinant of interlayer coupling and charge transport, complementing the underlying electronic structure of the framework.

Our analysis of interlayer electron coherence across different stacking arrangements and static disorder levels further shows that, although stacking topology influences interlayer coherence, these system-dependent differences largely vanish in highly disordered samples. In addition, we find that under realistic disorder levels, the intralayer electronic couplings contribute positively to the interlayer electron coherence, while this effect drops to negligible at very high disorder levels.

Importantly, our findings challenge the conventional assumption that electron-donating and electron-withdrawing substituents impose strictly opposing effects on material properties. As such, our methods offer an *in silico* design principle, guiding the targeted exploration and engineering of COFs within the large design space. Together, these insights provide valuable principles for the rational synthesis and post-synthetic modification of COFs and other reticular materials, enabling the tailored optimization of their electronic and photophysical properties for improved real-world applications.

3.4 Conflicts of Interest

There are no conflicts of interest to declare.

3.5 Acknowledgements

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Chapter 3, in full, is currently being prepared for submission for publication of the material as “Interplay of Intermolecular Interactions Overrides Chemical Intuition in Functionalized 2D Covalent Organic Frameworks”, Y. Pan, S. Dasgupta, R. Ghosh, and F. Paesani, 2025. The dissertation author was the primary investigator and author of this material.

Appendix A: Supplementary Methods

Atomistic Model: Periodic Systems

All the calculations for the periodic systems of interest were performed using the Vienna Ab initio Simulation Package (VASP).^{95,96} The core electrons were treated by the projector-augmented wave (PAW) method.^{97,98} Unless otherwise specified, the PBE functional⁹⁹ with the D3(BJ) dispersion correction^{100–102} was applied.

During the geometry optimization of the periodic systems using one-layer unit cells, the unit cell parameters and the atomic coordinates were allowed to fully relax. A plane-wave basis set with an energy cutoff of 520 eV was used in all calculations. The convergence criteria for the energies and forces were set to 1×10^{-5} eV and $0.01 \text{ eV } \text{\AA}^{-1}$, respectively. Two-layer supercells were created from the optimized one-layer unit cells for later calculations of the potential energy surface (PES) contours and band structures. Γ -centered k -point grids¹⁰³ with a k -point resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$ were used for all calculations, unless otherwise specified. The Γ -centered k -point grids were generated using VASPKIT.¹⁰⁴ The atomic geometry structure visualization is performed using VESTA¹⁰⁵.

Potential Energy Surface

The contours of the 2D PES of all the periodic structures were calculated by performing single-point energy calculations. The interlayer spacing along the c direction of each system of interest was kept the same as the corresponding AA stacking configuration. For the PES contours, we first evenly sampled 30 points between the fractional displacement of 0 to 0.5 (of $\sim 30 \text{ \AA}$ of lateral lattice constant), i.e., with a step-size of $\sim 0.5 \text{ \AA}$, along x and y directions (see Figure 3.9), respectively. After confirming the energetically more favorable regions are within fractional interlayer slipping of < 0.2 (see Figure 3.9), we effectively sample the regions within fractional interlayer displacement of $[0, 0.25]$ with similar spacing (see Figure 3.2). This allowed us to determine the most stable slipped stacking configurations for all the periodic structures.

Subsequently, we also scanned along the c direction at a regular interval of 0.01 Å in the range between 3.0 Å to 4.20 Å after the most stable slipped stackings are found for the –R systems.

Band Structure, Effective Mass, and Similarity Matrix

It is widely known that the PBE functional, and any functional developed under GGA, will systematically underestimate the electronic band gaps^{106,107}. With the benefit of the incorporation of HF exchange, hybrid functionals such as HSE06 can provide better agreements to experimental electronic band gaps^{108,109}. To provide a better quantitative comparison between the PBE-D3(BJ)-evaluated band structures in this study and results from hybrid functionals, we also calculated the band structures at the HSE06-D3(BJ) level of theory. A k -point resolution of $2\pi \times 0.05 \text{ Å}^{-1}$ was chosen for the HSE06-D3(BJ) band structure calculations due to the more expensive computational cost.

The effective masses m^* for electrons (m_e^*) and holes (m_h^*) can be used to further characterize the charge transport properties of the crystals. Generally, m_e^* and m_h^* are calculated by fitting a parabola around the conduction band (CB) and valence band (VB) maximum of the electronic band structures, respectively, via the following equation.

$$m^* = \frac{\hbar^2}{\partial^2 E(\mathbf{k}) / \partial \mathbf{k}^2}, \quad (\text{A1})$$

where $\hbar$ is the reduced Planck constant. Consequently, m^* is inversely proportional to the second derivative (i.e., curvature) of $E(\mathbf{k})$ over $\mathbf{k}$. In general, a flat CB or VB indicates charge carriers with infinite effective masses, which correspond to fully localized charge carriers with vanishing charge mobility. On the contrary, a highly curved CB or VB means that the charge carriers have finite and small effective masses, suggesting higher charge mobility.

To better quantitatively describe the similarity between the bottom CBs and top VBs among the studied systems, we adopted the method mentioned in Ref. 110 to calculate the so-called similarity matrix. Specifically, the similarity score $s_{A,B}$ between two systems ($x = A$ or

B) is calculated via the following equations.

$$\Delta E_{A,B}^2 = \frac{1}{n_v N_{\text{kp}}} \sum_v \sum_k [(E_v^A(k) - \bar{E}_v^A) - (E_v^B(k) - \bar{E}_v^B)]^2. \quad (\text{A2})$$

$$\bar{E}_v^x = \frac{1}{N_{\text{kp}}} \sum_k E_v^x(k). \quad (\text{A3})$$

$$s_{A,B} = e^{-\Delta E_{A,B}^2 / 2E_0^2}. \quad (\text{A4})$$

Here, $\Delta E_{A,B}^2$ is the mean square deviation in the bottom CBs and top VBs (v) between the A and B systems, calculated based on the differences in the bottom CBs and top VBs for each k -point with respect to the corresponding average band energy value ($\bar{E}_v^x$, over the k -points) of band v for COF x . The arbitrary constant E_0 was introduced to tune the sensitivity of the similarity score, which is taken as the same value ($\sqrt{2}k_B T$) as in Ref. 110. Therefore, similarity scores will be between 0 (*i.e.*, completely different) and 1 (*i.e.*, identical). Note that this definition of similarity matrix is used to quantify the similarity of the shape and curvature between the CBs and VBs between two systems, but not bandgap sensitive.

Specifically, for the AA-stacked systems, especially to better account for the highly symmetric honeycomb-kagome lattices and characteristic kagome bands in the –R systems, we include the two lowest CBs and the three highest VBs, resulting in $n_v = 5$ (see Figure 3.4d). For the slipped systems, where the kagome signature bands in the –R systems are significantly disrupted, only the lowest CB and the highest VB ($n_v = 2$) are considered (see Figure 3.4h), following the standard approach in Ref. 110. For comparison, we also computed similarity matrices using only the lowest CB and highest VB ($n_v = 2$) for the AA-stacked systems, providing a measure of similarity between the bottom CB and top VB across the AA-stacked systems, as shown in Figure 3.21.

We have also compared the band structures of the –H and BN systems under the stacking

configurations slipped at fractional displacements of (0.034,0.058), as they share highly similar PES contour patterns and their energetic minima are very close to (if not at) (0.034,0.058) (see Figure 3.10 and Figure 3.12). The results are included in Figure 3.25 and Figure 3.27.

As discussed in the Results and Discussion section, the AA-stacked BN[0,0] and BN[3,3] maintain honeycomb-kagome lattice symmetry, similar to the –R systems. Consequently, these systems preserve the characteristic kagome bands, as shown in Figure 3.25. In contrast, for the AA-stacked BN[1,2] (see Figure 3.4) and BN[0,3], the reduced symmetry in the linkers and linkage pattern disrupts the kagome bands entirely.

The Sumo toolkit¹¹¹ is used to calculate the effective masses and plot the orbital-projected electronic band structures.

Exciton Binding Energy

An exciton describes a bound electron–hole pair in materials and is one of the most critical physical quantities governing the performance of various photoelectronic and catalytic devices^{5–7}. In addition, it is highly desirable to accurately determine the exciton binding energy (E_b), *i.e.*, the amount of energy required to separate an excitonic electron–hole pair. This provides a direct measurement of how easy or difficult it is to break a bound electron–hole pair into free charge carriers for further redox reactions. However, we note that it is computationally extremely challenging to calculate E_b for these large systems. Recently, it has been shown that the E_b of organic or 2D monolayer inorganic semiconductors exhibits a linear relationship with the fundamental gap (E_g), *i.e.*, $E_b \approx E_g/4$.^{92,112} In consideration of computational cost, we calculated the E_b values for the 2D monolayer –H, –CN, and BN[1,2] systems using this linear scaling relationship, in an attempt to provide a general discussion about the influence of chemical composition, intermolecular interactions, and lattice symmetry on E_b . The fundamental gap, E_g , is calculated as the energy difference between the vertical ionization potential ($IP = E_{\text{cation}} - E_{\text{neutral}}$) and the electron affinity ($EA = E_{\text{neutral}} - E_{\text{anion}}$), evaluated at the HSE06-D3(BJ) level of theory. A vacuum layer of 20 Å along the out-of-plane direction is applied to avoid interlayer

coupling. Γ -centered k -point grids with a k -point resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$ were used for all calculations.

Atomistic Model: Molecular Systems

Energy Decomposition Analysis

The molecular systems used for the energy decomposition analysis (EDA) are the two-layer molecular rings, as illustrated in Figure 3.3. Using the EDA based on the absolutely localized molecular orbitals (ALMO) scheme^{67,68}, as implemented in Q-Chem¹¹³, the total intermolecular interaction energy (E_{Int}) is decomposed into physically meaningful components, as shown below.

$$E_{\text{Int}} = E_{\text{Elec}} + E_{\text{Pauli}} + E_{\text{Disp}} + E_{\text{Pol}} + E_{\text{CT}}, \quad (\text{A5})$$

$$E_{\text{vdW}} = E_{\text{Pauli}} + E_{\text{Disp}}, \quad (\text{A6})$$

where the electrostatics component (E_{Elec}) represents the classical Coulombic interaction between the total charge distributions of the interacting molecular fragments, Pauli repulsion (E_{Pauli}) is associated with the Pauli exclusion principle of electrons and corresponds to the energy penalty from the antisymmetry requirement for the wavefunctions, dispersion (E_{Disp}) describes the attractive interaction between the fragments resulting from correlated fluctuations of electron density, polarization (E_{Pol}) refers to the distortion of the electron density distribution due to the existence of electrostatic potential from other molecules, and charge transfer (E_{CT} , often referred to as donor-acceptor interactions) arises from the attractive interaction due to orbital overlapping and mixing across different molecular fragments. In addition, similar to the idea mentioned in Ref. 69, we combined E_{Pauli} (short-range repulsion) and E_{Disp} (long-range attraction) into a “van der Waals” interaction (E_{vdW}).

All ALMO-EDA calculations were carried out at the level of theory of PBE0-D3(BJ)/6-

31G*. ^{114–116} EDA scans were performed along x (zig-zag) and y (armchair) for each system of interest, from 0 to 10 Å at a step-size of 1 Å, to study the evolution of the energy components under displacements away from the AA stacking. The EDA helps us analyze the evolution and the nature of intermolecular interaction and identify the driving forces^{80,117} among the stacking patterns.

Density-based Excitonic Analysis

To further quantify the excited-state properties, density-based descriptors for the exciton analysis were adopted, as outlined in Ref. 90. A brief description is provided below.

The distance between the centroids of the electron and hole, $d_{h \rightarrow e}$, which characterizes the extent of charge transfer (CT) in the system, is calculated as

$$d_{h \rightarrow e} = |\langle \vec{x}_e - \vec{x}_h \rangle_{\text{exc}}| = |\langle \vec{x}_e \rangle_{\text{exc}} - \langle \vec{x}_h \rangle_{\text{exc}}|, \quad (\text{A7})$$

where the position of the centroids of the electron and hole of the exciton are calculated as the expectation values of the position operator $\hat{x}$.

The exciton size d_{exc} , which is defined as the root-mean-square separation between the instantaneous hole and electron positions, is evaluated using

$$d_{\text{exc}} = \sqrt{\langle |\vec{x}_h - \vec{x}_e|^2 \rangle_{\text{exc}}}. \quad (\text{A8})$$

In terms of the spatial extension of the electron and hole around their respective centers of charge, σ_e and σ_h , they are quantified as the square root of the corresponding variance, using

$$\sigma_e = \sqrt{\langle \vec{x}_e^2 \rangle_{\text{exc}} - \langle \vec{x}_e \rangle_{\text{exc}}^2}, \quad (\text{A9})$$

and

$$\sigma_h = \sqrt{\langle \vec{x}_h^2 \rangle_{\text{exc}} - \langle \vec{x}_h \rangle_{\text{exc}}^2}. \quad (\text{A10})$$

Furthermore, the covariance between the joint electron and hole positions is defined as

$$\text{COV}(r_h, r_e) = \langle \vec{x}_h \cdot \vec{x}_e \rangle_{\text{exc}} - \langle \vec{x}_h \rangle_{\text{exc}} \cdot \langle \vec{x}_e \rangle_{\text{exc}}. \quad (\text{A11})$$

With that, the normalized electron–hole correlation coefficient R_{eh} is defined as the covariance normalized by the electron and hole sizes.

$$R_{\text{eh}} = \frac{\text{COV}(r_h, r_e)}{\sigma_h \sigma_e} \quad (\text{A12})$$

This quantity describes the interdependent spatial distribution and movement of the electron–hole pair. Therefore, a positive value of R_{eh} indicates a joint motion of the electron and hole, indicating the formation of bound excitons, while a negative value implies that the electron and hole are repelling each other. $R_{\text{eh}} = 0$ suggests no linear correlation between their motions.

The density-based excitonic analysis is carried out by calculating the charge density differences between the ground and excited states of the 2D monolayer –H, –CN, and BN[1,2] systems, evaluated using Q-Chem, at the level of theory of ω B97X-D/6-31G*.¹¹⁸ The charge density analysis provides insights into the degree of charge distribution and separation upon excitation¹¹⁹.

The Coarse-grained Holstein Hamiltonian Model

A model three-dimensional (3D) π -stack is shown in Figure 3.7a. A single 2D COF layer lies in the xy-plane, with the stacking axis oriented along z. Each repeat unit is identified by the coordinate (m, n, o) , indicating the m^{th} and n^{th} unit in the o^{th} layer. As demonstrated in previous studies on excitons and polarons, individual chains can be effectively described using a coarse-grained approximation: an electron on a given repeat unit or chromophore is treated as an additional electron occupying its local LUMO. Neighboring LUMOs of adjacent repeat units within the 2D COF layer are coupled via the electron transfer integrals, $t_{\text{intra}-x}$ and $t_{\text{intra}-y}$. In a π -stack composed of such layers, wavefunction overlap also occurs between

LUMOs of neighboring units on adjacent layers. The resulting interlayer electronic coupling is described by the interlayer electron transfer integral, $t_{inter-z}$. Together, these couplings enable three-dimensional delocalization of the electron. The Holstein Hamiltonian used to model single electrons in disordered π -stacks of 3D COFs is given by

$$\begin{aligned}
H_{total} = & \sum_{m=1}^{N-1} \sum_{n=1}^N \sum_{o=1}^N t_{intra-x} \{d_{m+1,n,o}^+ d_{m,n,o} + h.c\} + \sum_{m=1}^N \sum_{n=1}^{N-1} \sum_{o=1}^N t_{intra-y} \{d_{m,n+1,o}^+ d_{m,n,o} + h.c\} \\
& + \sum_{m=1}^N \sum_{n=1}^N \sum_{o=1}^{N-1} t_{inter-z} \{d_{m,n,o+1}^+ d_{m,n,o} + h.c\} + \sum_{m=1}^N \sum_{n=1}^N \sum_{o=1}^N \Delta_{m,n,o} d_{m,n,o}^+ d_{m,n,o}
\end{aligned} \tag{A13}$$

where the first three terms in H_{total} represent the kinetic energy of the electron along the x, y (intralayer), and z (interlayer) directions. The operators $d_{m,n,o}^+$ and $d_{m,n,o}$ respectively create and annihilate an electron on the m^{th}, n^{th}, o^{th} unit in the 3D COF framework. The final term takes into account spatially uncorrelated energetic site disorder, which arises due to in- and out-of-plane fluctuations in the torsional angles, chemical defects in the framework, presence of inhomogeneous electric fields, etc. Random fluctuations in the electron's site energy, $\Delta_{m,n,o}$, when the electron is located on the (m,n,o) unit are shown in the final term. The deviations, $\Delta_{m,n,o}$, are randomly selected from a Gaussian distribution with standard deviation σ :

$$P(\Delta_{m,n,o}) = (2\pi\sigma^2)^{-1/2} \exp(-\Delta_{m,n,o}^2/2\sigma^2) \tag{A14}$$

The 3D coherence function describing electron delocalization is given by,

$$C_P(r) \equiv \left\langle \Psi_G \left| \sum_R d_R^\dagger d_{R+r} \right| \Psi_G \right\rangle_C \tag{A15}$$

Here, $R = (m, n, o)$ is a dimensionless position vector. When $r=0$ the coherence reduces to unity, $C_P[(0, 0, 0)] = 1$, since $\sum_R d_R^\dagger d_R$ is the operator for the total number of electrons, which is

taken to be one. The total number of coherently connected repeat units over which the electron is delocalized is given by

$$N_{\text{coh}} = \sum_{\mathbf{r}} |C_{\mathbf{P}}(\mathbf{r})| \quad (\text{A16})$$

The Holstein Hamiltonian incorporates 3D electron delocalization via both intra- and interlayer electronic couplings, governed by electron-transfer integrals and spatially uncorrelated (“short-range”) site-energy fluctuations arising from electronic disorder. For our simulations, we assume a 3D rectangular lattice comprising 8×8 (*i.e.*, 64) coupled chromophores per 2D layer, with 12 such layers stacked to form the complete 3D structure, as illustrated in Figure 3.7. The general trends observed regarding the impact of stacking on N_{layers} persist even when a hexagonal lattice is considered instead of a rectangular one. In our modeling, we assume the presence of free unbound electrons that can delocalize within the disordered COF structures.

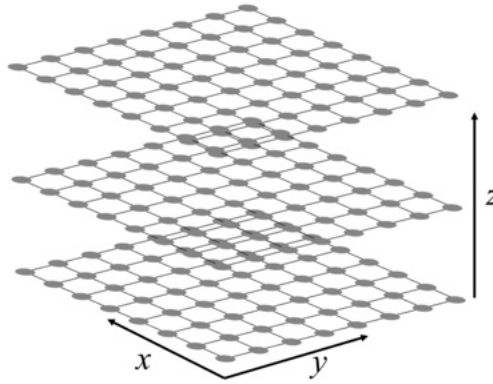


Figure 3.7. A schematic representation of a 3D π -stack system used in the coarse-grained model.

The intra- and inter-layer electron transfer integral t values used in the Holstein Hamiltonian for the –H and BN[1,2] systems, under AA or slipped-stacked stacking configurations, respectively, are estimated using the simple tight-binding picture.^{120–122} Specifically, the t values are estimated using $W = 2zt$, where W is the bandwidth of the corresponding CB as shown in the electronic band structures (see Figure 4 in the main text), z is the number of neighboring

sites, as included in Table 3.1. $z = 3$ for intra- and $z = 2$ for interlayer direction were applied, respectively. The folding of band structures along the stacking direction was taken into account for the calculations.

Table 3.1. The intra- and inter-layer electron transfer integral t values (in eV) for the –H and BN[1,2] systems, under AA or slipped-stacked stacking configurations, respectively.

System	Stacking	t_{intra}	t_{inter}
–H	AA	0.07788333	0.23395000
	Slipped	0.01131667	0.02785000
BN[1,2]	AA	0.00091667	0.25455000
	Slipped	0.00046667	0.01980000

Appendix B: Supporting Data

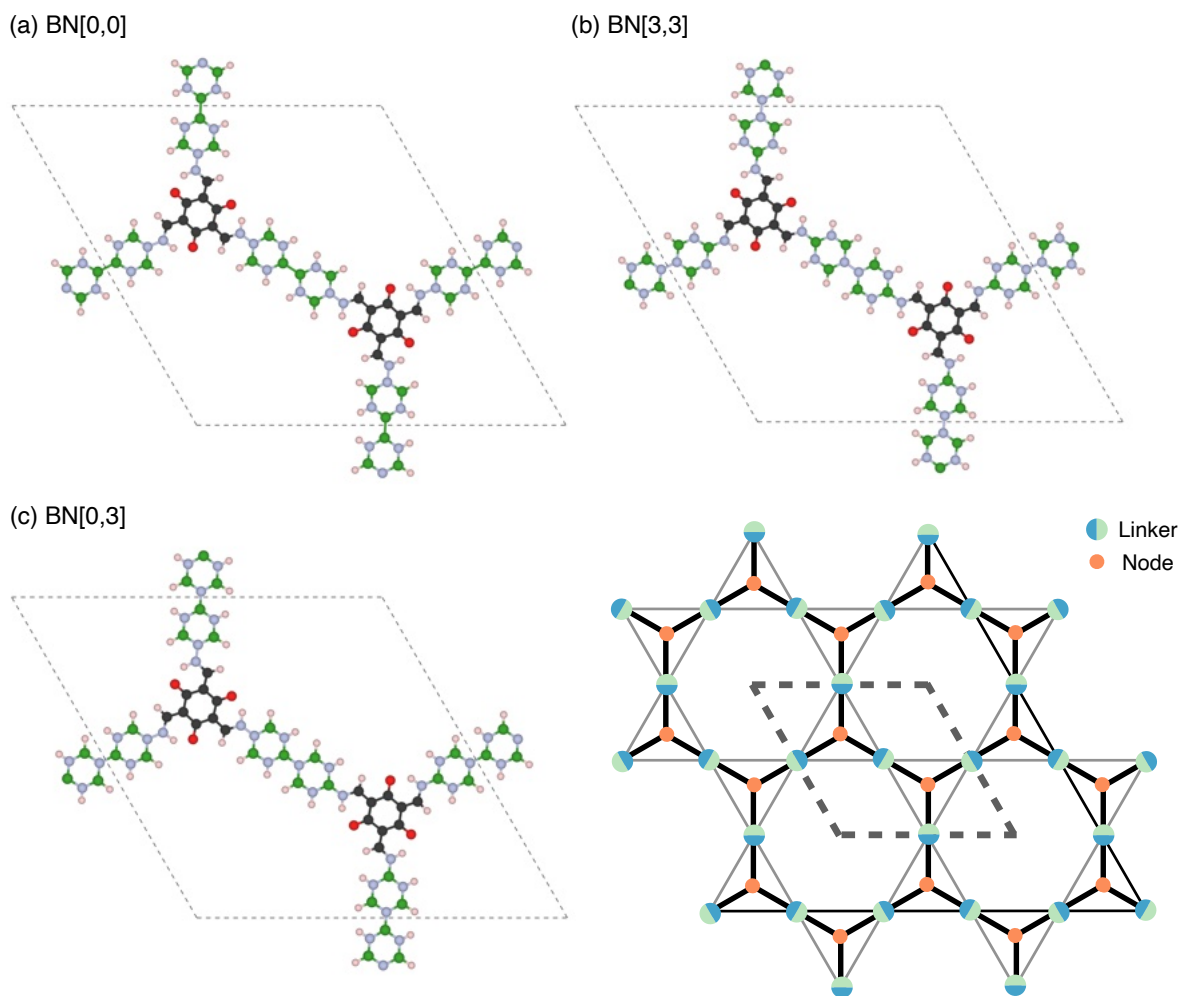


Figure 3.8. Geometry structures of (a) BN[0,0], (b) BN[3,3], and (c) BN[0,3] (left) with the schematic illustration of the corresponding honeycomb-kagome lattices (right). BN[0,0] and BN[3,3] share the same lattice symmetry as the $-R$ (where $R = H, CN, F, \text{ or } OH$) systems. The unit cell boundaries are indicated by the dashed lines. Color codes: pink for H, black for C, blue for N, red for O, green for B.

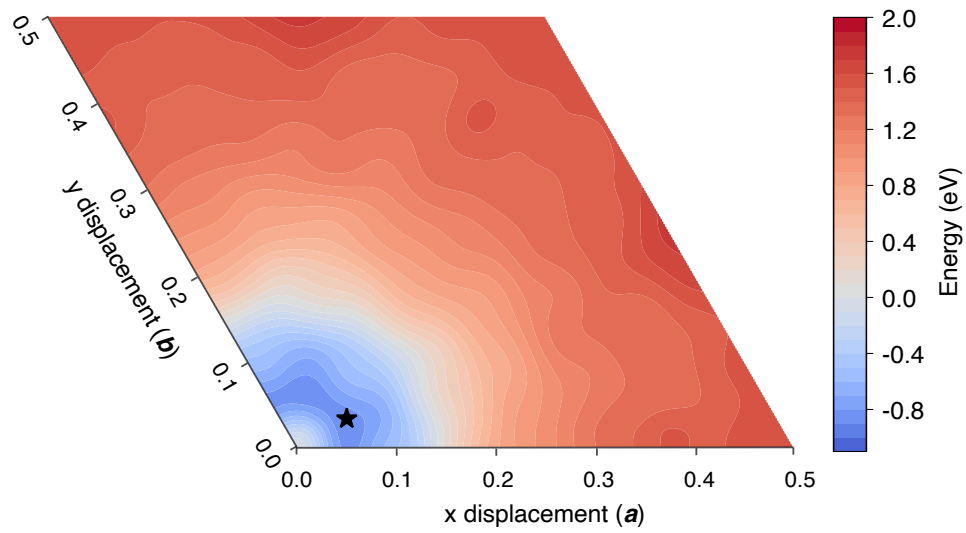


Figure 3.9. PES contours of fractional interlayer displacements from 0 to 0.5 of a double-layer unit cell for the $-H$ system. The black star represents the minimum in the PES contour, at (0.067, 0.033). The minor difference between this minimum and that at (0.067, 0.029) as shown in Figure 3.2 is due to the sampling spacing, which is relatively negligible. The energy of the AA-stacked structure is used as the zero reference.

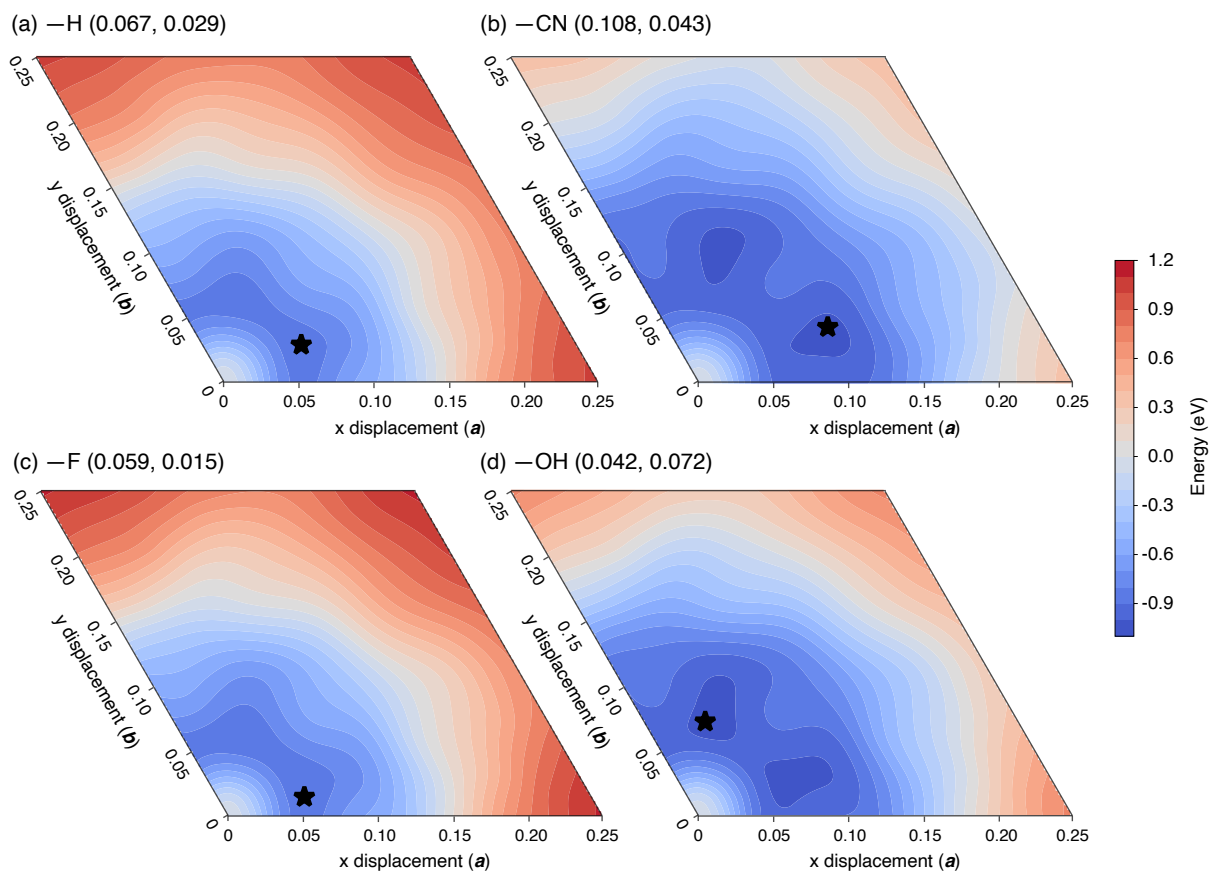


Figure 3.10. PES contours of fractional interlayer displacements of a double-layer unit cell for (a) $-H$, (b) $-CN$, (c) $-F$, and (d) $-OH$. The black stars represent the minima in the PES contours, with the corresponding displacements given in the parentheses on top of each PES contour. For each system, the energy of the AA-stacked structure is used as the zero reference.

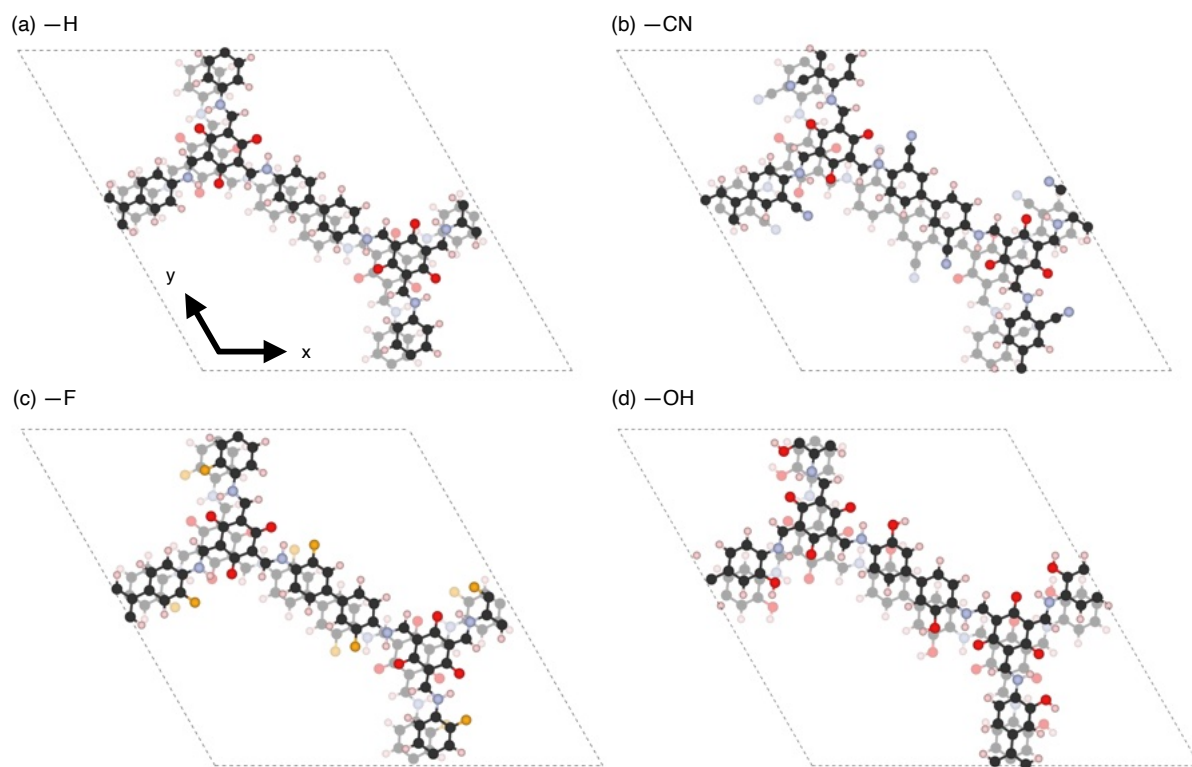


Figure 3.11. Top view of the geometry structures of the $-R$ systems under the slipped stackings which correspond to the minima in the PES contours in Figure 3.10. The colors of the atoms are as follows: pink for H, black for C, blue for N, red for O, and orange for F. The unit cell boundaries are indicated by the dashed lines.

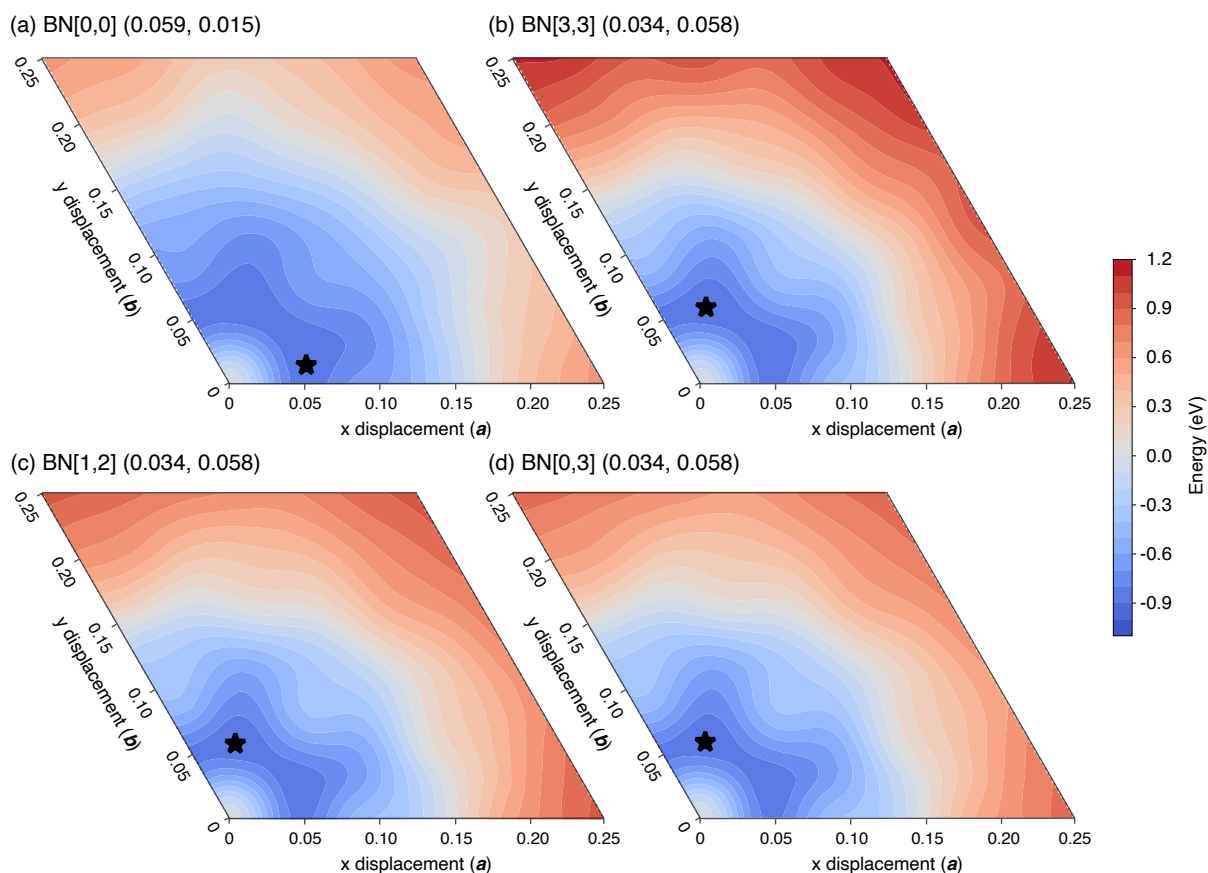


Figure 3.12. PES contours of fractional interlayer displacements of a double-layer unit cell for (a) BN[0,0], (b) BN[3,3], (c) BN[1,2], and (d) BN[0,3]. The black stars represent the minima in the PES contours, with the corresponding displacements given in the parentheses on top of each PES contour. For each system, the energy of the corresponding AA-stacked structure is used as the zero reference.

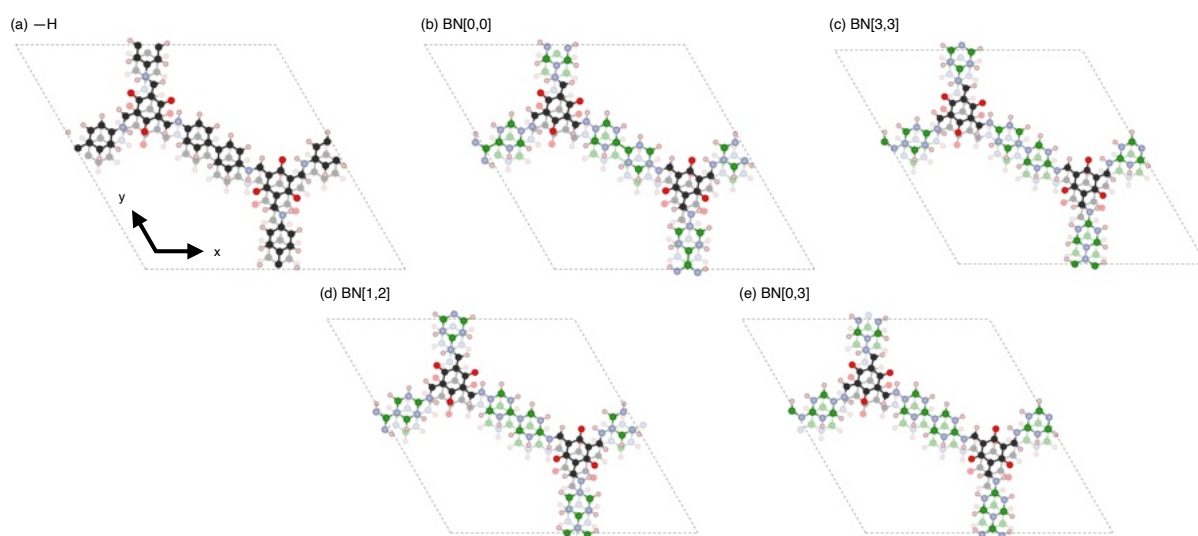


Figure 3.13. Top view of the geometry structures of the $-H$ and BN systems under the slipped stackings which correspond to fractional displacements of $(0.034, 0.058)$. The colors of the atoms are as follows: pink for H, black for C, blue for N, red for O, and green for B. The unit cell boundaries are indicated by the dashed lines.

Table 3.2. Lattice parameters a , b , and the interlayer distance d of the studies systems, including the $-R$ systems ($-H$, $-CN$, $-F$, and $-OH$) and BN systems (BN[0,0], BN[3,3], BN[1,2], and BN[0,3]). The d of the $-R$ systems at the slipped stacking which correspond to the minima in the PES contours in Figure 3.10 are also optimized *via* single-point energy scans.

System	$a/\text{\AA}$	$b/\text{\AA}$	$d/\text{\AA}$ (AA / Slipped at PES minimum)
$-H$	30.07	30.07	3.67 / 3.39
$-CN$	30.06	30.06	3.69 / 3.32
$-F$	30.08	30.09	3.63 / 3.39
$-OH$	30.05	30.07	3.65 / 3.39
System	$a/\text{\AA}$	$b/\text{\AA}$	$d/\text{\AA}$ (AA / Slipped at (0.034, 0.058))
$-H$	30.07	30.07	3.67 / 3.67
BN[0,0]	30.61	30.60	3.63 / 3.63
BN[3,3]	30.56	30.55	3.63 / 3.63
BN[1,2]	30.34	30.34	3.63 / 3.63
BN[0,3]	30.36	30.35	3.63 / 3.63

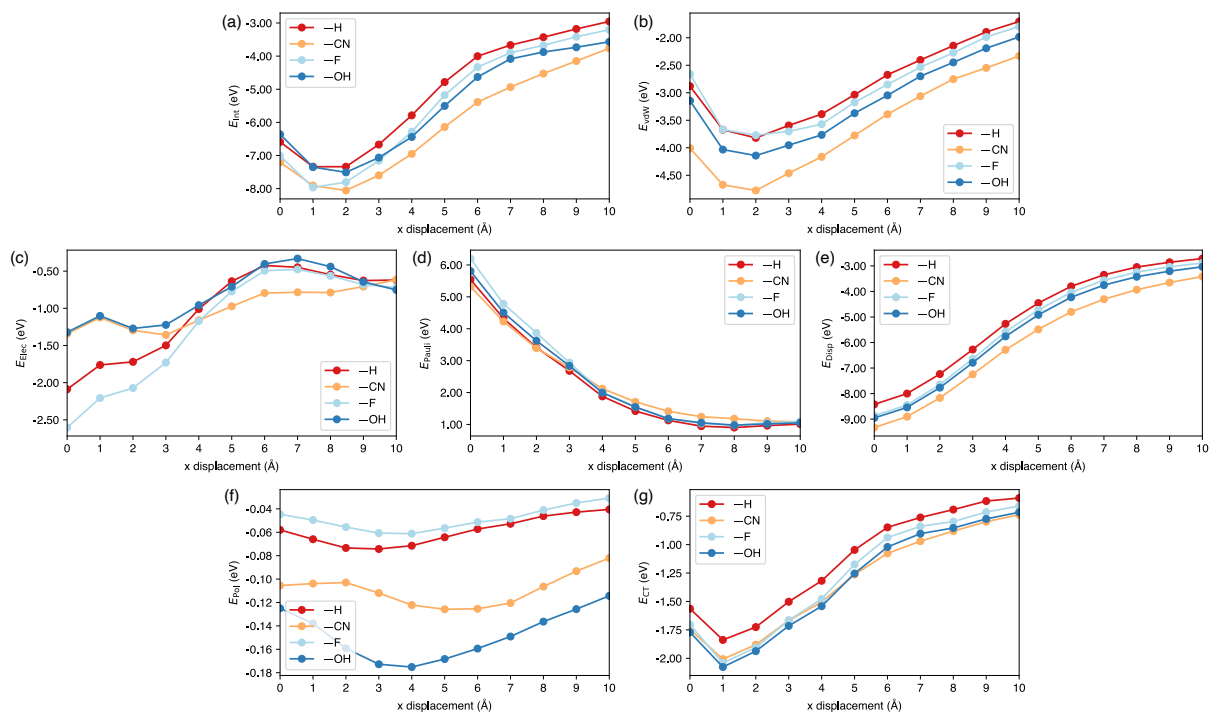


Figure 3.14. Comparisons of the evolutions of (a) E_{Int} , (b) E_{vdW} , (c) E_{Elec} , (d) E_{Pauli} , (e) E_{Disp} , (f) E_{Pol} , and (g) E_{CT} along x (zig-zag) for $-R$ systems where $R = \text{H}, \text{CN}, \text{F}, \text{or OH}$.

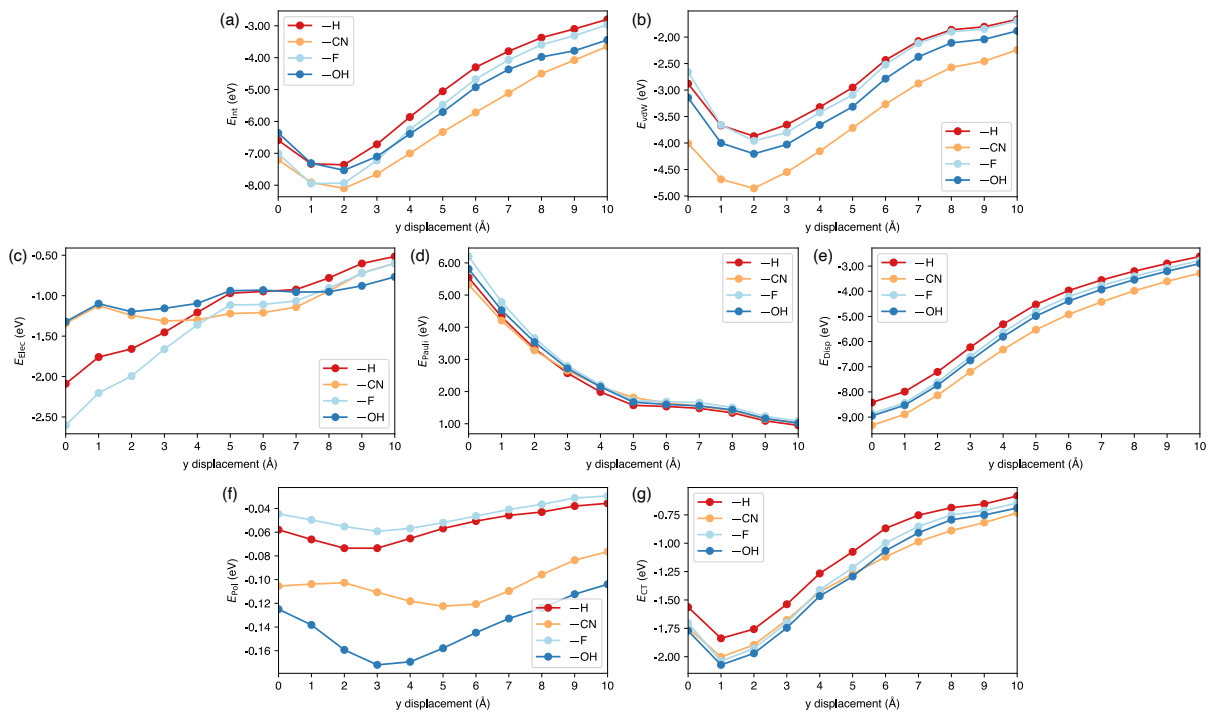


Figure 3.15. Comparisons of the evolutions of (a) E_{Int} , (b) E_{vdW} , (c) E_{Elec} , (d) E_{Pauli} , (e) E_{Dis} , (f) E_{Pol} , and (g) E_{CT} along y (armchair) for -R systems where R = H, CN, F, or OH.

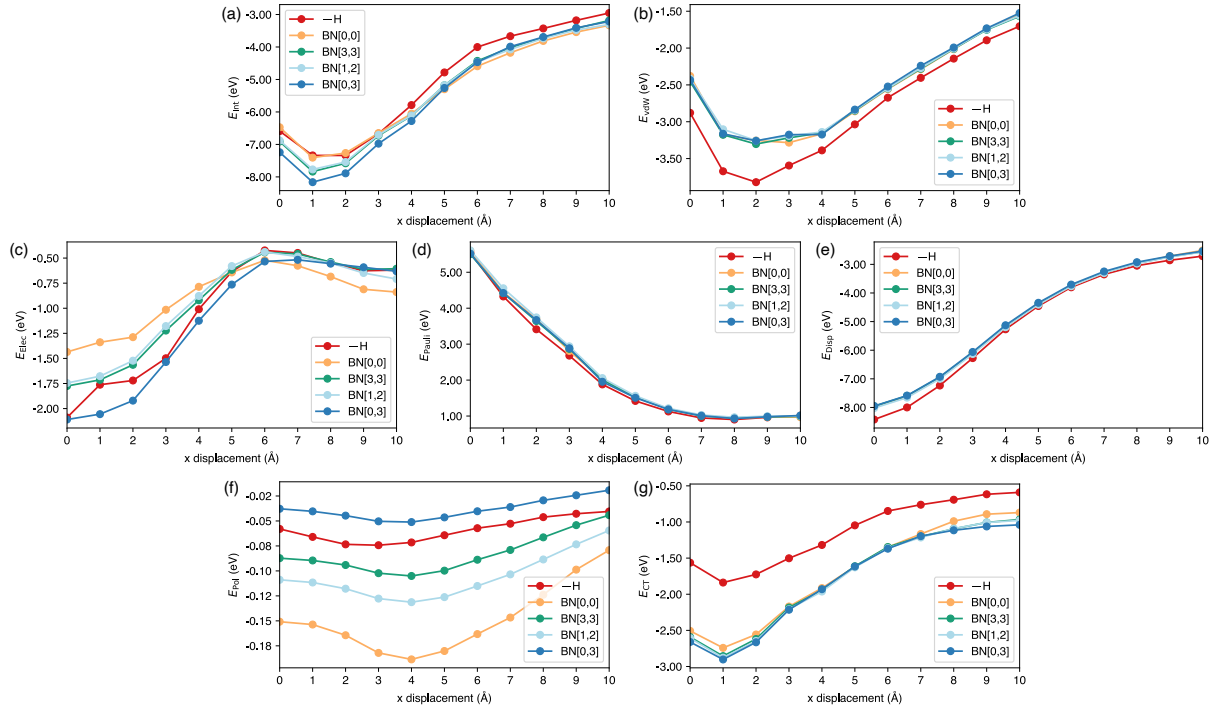


Figure 3.16. Comparisons of the evolutions of (a) E_{Int} , (b) E_{vdW} , (c) E_{Elec} , (d) E_{Pauli} , (e) E_{Disip} , (f) E_{Pol} , and (g) E_{CT} along x (zig-zag) among -H and the BN systems.

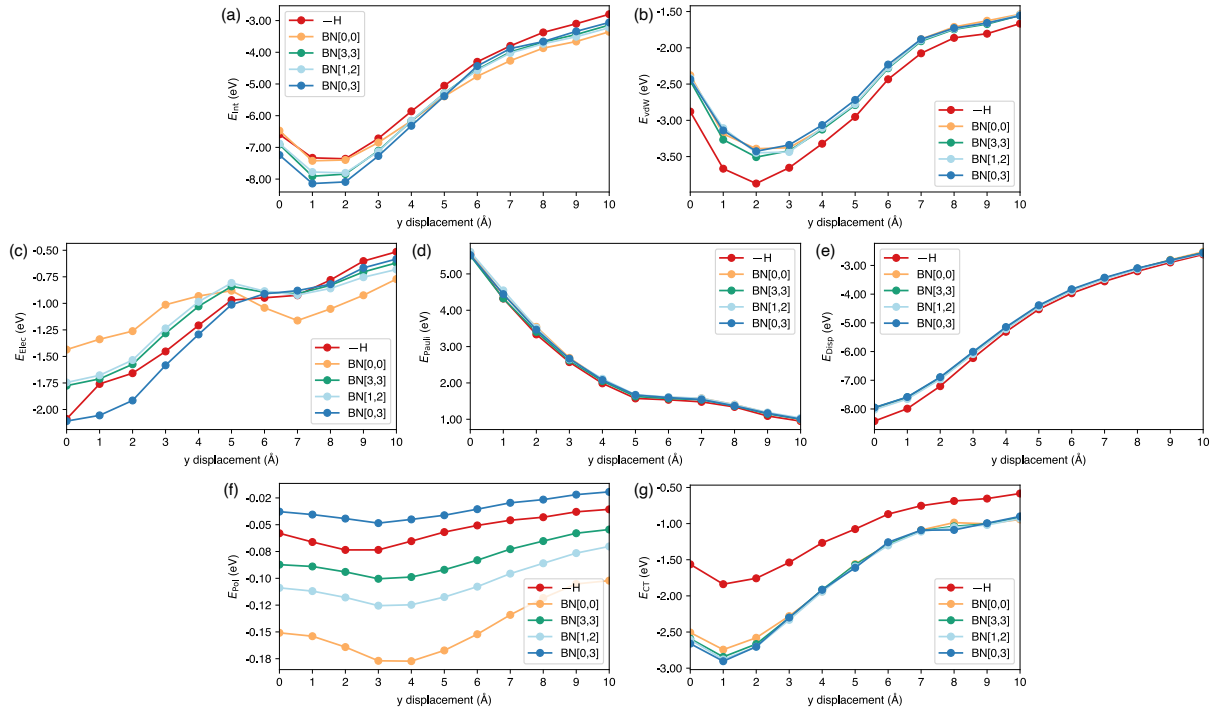


Figure 3.17. Comparisons of the evolutions of (a) E_{Int} , (b) E_{vdW} , (c) E_{Elec} , (d) E_{Pauli} , (e) E_{Disp} , (f) E_{Pol} , and (g) E_{CT} along y (armchair) among $-H$ and the BN systems.

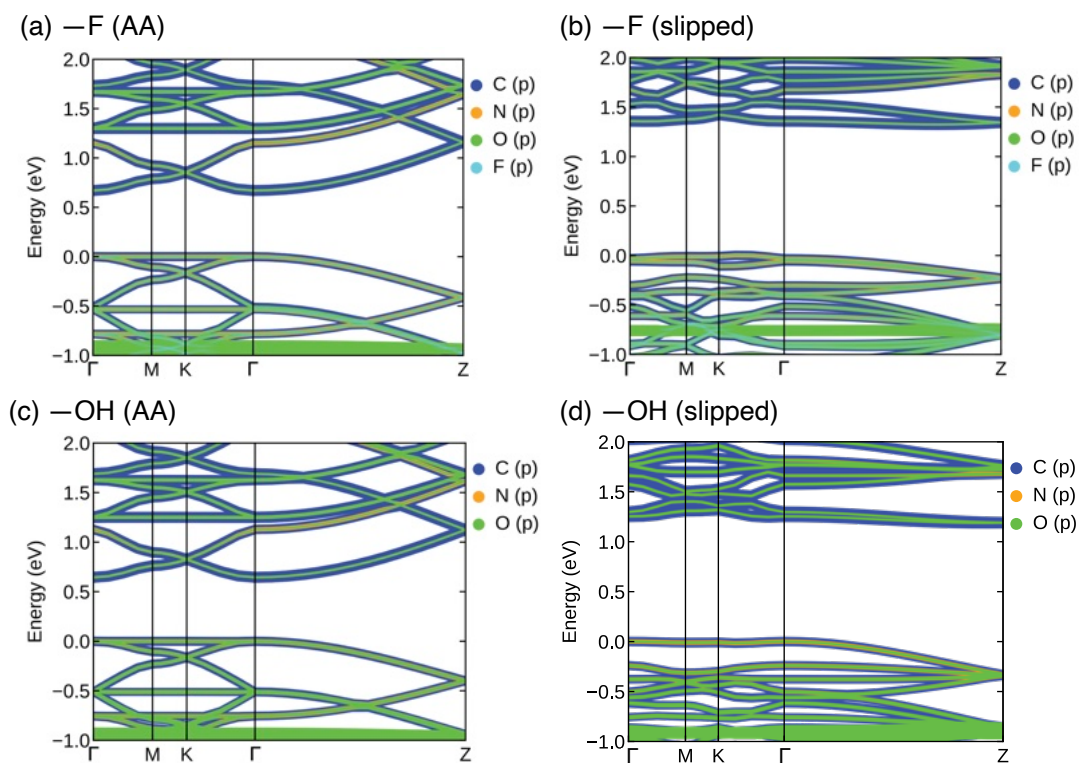


Figure 3.18. PBE-D3(BJ)-evaluated band structures for -F and -OH . (a), and (c) correspond to the results under AA stackings, while (b), and (d) are from the slipped stackings which correspond to the minima in the PES contours in Figure 3.10.

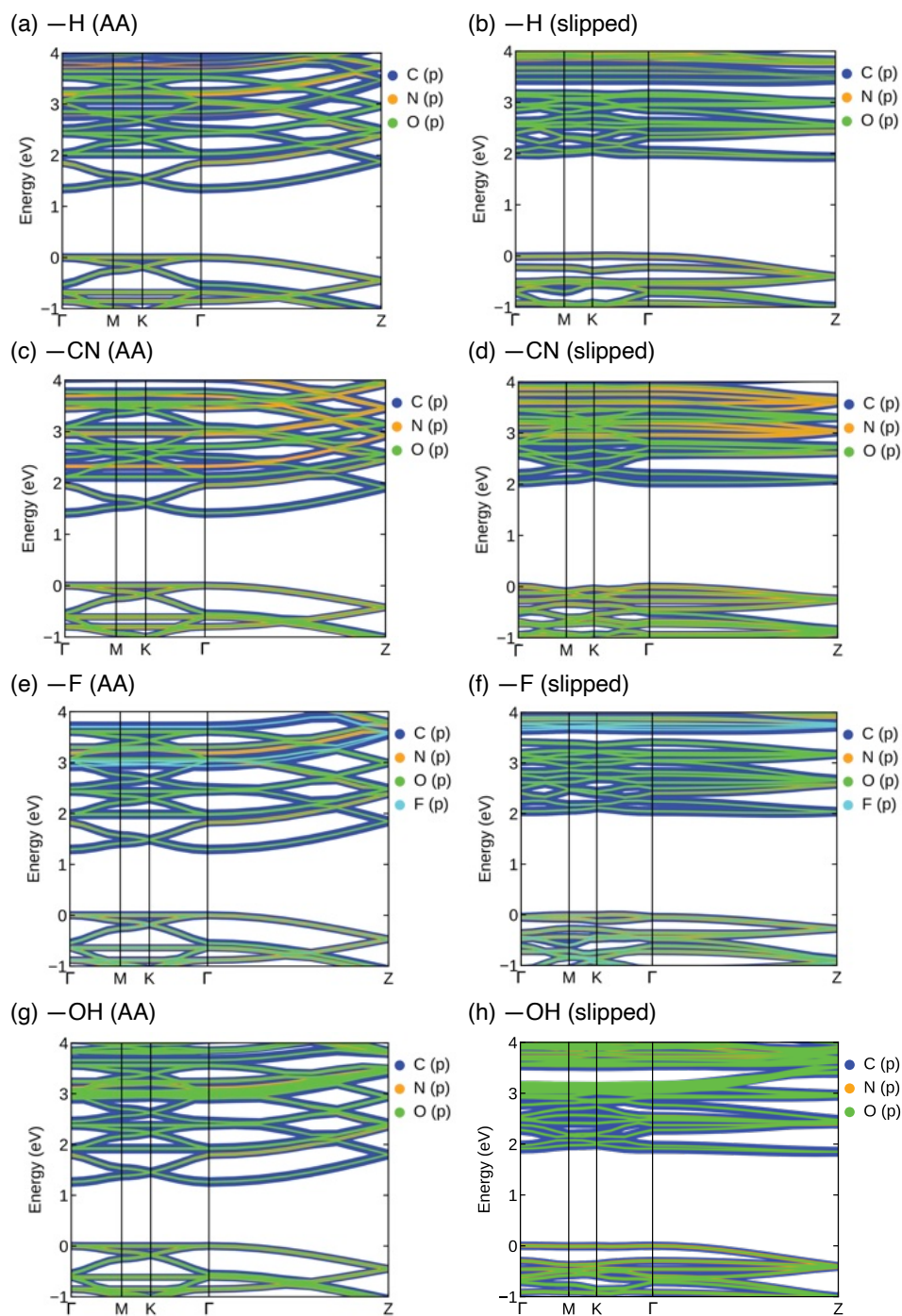


Figure 3.19. HSE06-D3(BJ)-evaluated band structures for $-R$ (where $R = H, CN, F,$ or OH). (a), (c), (e), and (g) correspond to the results under AA stackings, while (b), (d), (f), and (h) are from the slipped stackings which correspond to the minima in the PES contours in Figure 3.10.

Table 3.3. PBE-D3(BJ) evaluated bandgaps (direct) and effective masses of the D-A COFs under AA stacking, including -H, -CN, -F, and -OH.

System	bandgap/eV	m^*/m_0	$\Gamma \rightarrow M$	$\Gamma \rightarrow K$	$\Gamma \rightarrow Z$
-H	0.725	m_e^*	0.359	0.362	1.297
		m_h^*	-66.179	-37.328	-1.347
-CN	0.777	m_e^*	0.352	0.354	1.349
		m_h^*	-63.339	-102.231	-1.419
-F	0.669	m_e^*	0.351	0.354	1.268
		m_h^*	-103.878	-114.043	-1.317
-OH	0.643	m_e^*	0.354	0.358	1.276
		m_h^*	-29.754	-52.503	-1.357

Table 3.4. HSE06-D3(BJ) evaluated bandgaps (direct) and effective masses of the D-A COFs under AA stacking, including -H, -CN, -F, and -OH.

System	bandgap/eV	m^*/m_0	$\Gamma \rightarrow M$	$\Gamma \rightarrow K$	$\Gamma \rightarrow Z$
-H	1.344	m_e^*	0.351	0.350	1.177
		m_h^*	-55.997	-30.329	-1.233
-CN	1.408	m_e^*	0.341	0.341	1.224
		m_h^*	-56.031	-84.452	-1.303
-F	1.291	m_e^*	0.341	0.341	1.151
		m_h^*	-90.893	-138.481	-1.212
-OH	1.258	m_e^*	0.343	0.345	1.157
		m_h^*	-23.142	-45.177	-1.251

Table 3.5. PBE-D3(BJ) evaluated indirect (up) and direct (bottom) bandgaps and effective masses of the D-A COFs under the slipped stacking whose energy is minimal in the PES contours (as indicated by the star in Figure 3.10), including -H, -CN, -F, and -OH.

System	bandgap/eV	m^*/m_0	$\Gamma \rightarrow M$	$\Gamma \rightarrow K$	$\Gamma \rightarrow Z$
-H	1.263	m_e^*	-	-	3.921
	1.320	m_h^*	-	-2.641	-
-CN	1.339	m_e^*	-	-	12.103
	1.340	m_h^*	-0.455	-0.850	-3.006
-F	1.322	m_e^*	-	-	3.333
	1.374	m_h^*	-	-1.216	-
-OH	1.186	m_e^*	-	-	5.052
	1.248	m_h^*	-3.398	-2.691	-1.643

Table 3.6. HSE06-D3(BJ) evaluated indirect (up) and direct (bottom) bandgaps and effective masses of the D-A COFs under the slipped stacking whose energy is minimal in the PES contours (as indicated by the star in Figure 3.10), including –H, –CN, –F, and –OH.

System	bandgap/eV	m^*/m_0	$\Gamma \rightarrow M$	$\Gamma \rightarrow K$	$\Gamma \rightarrow Z$
–H	1.925	m_e^*	-	-	4.730
	1.987	m_h^*	-	-3.141	-
–CN	2.029	m_e^*	-	-	12.779
	2.029	m_h^*	-0.436	-0.745	-2.564
–F	2.011	m_e^*	-	-	4.680
	2.066	m_h^*	-	-0.933	-
–OH	1.841	m_e^*	-	-	4.415
	1.906	m_h^*	-3.226	-2.779	-1.418

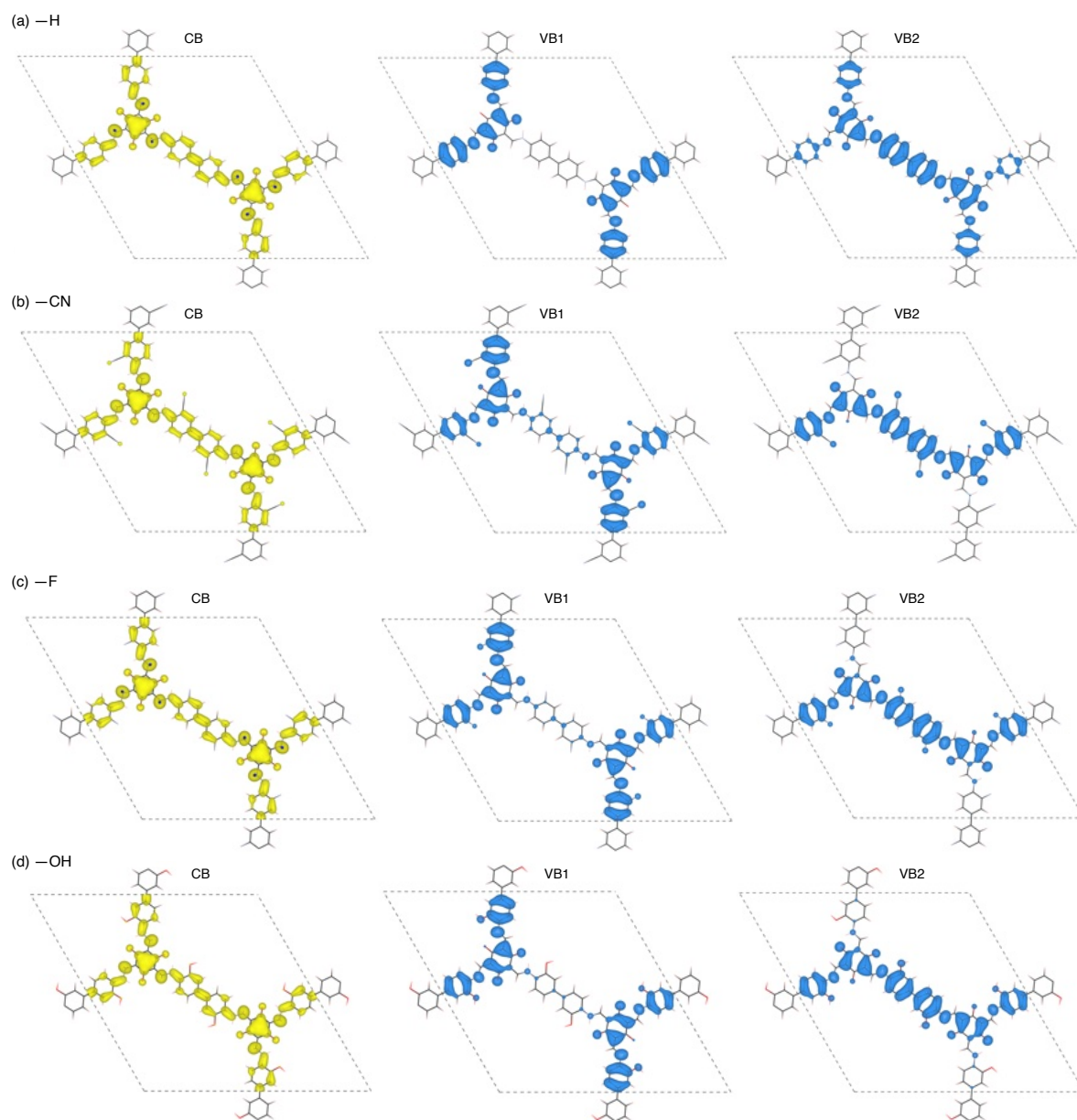


Figure 3.20. Partial charge density at the CBM and VBMs (at Γ , with isosurface level of 0.0003 e Å⁻³), respectively, for the AA-stacked systems of (a) -H, (b) -CN, (c) -F, and (d) -OH. The VBMs of these systems are doubly degenerate, thus here labeled as VB1 and VB2.

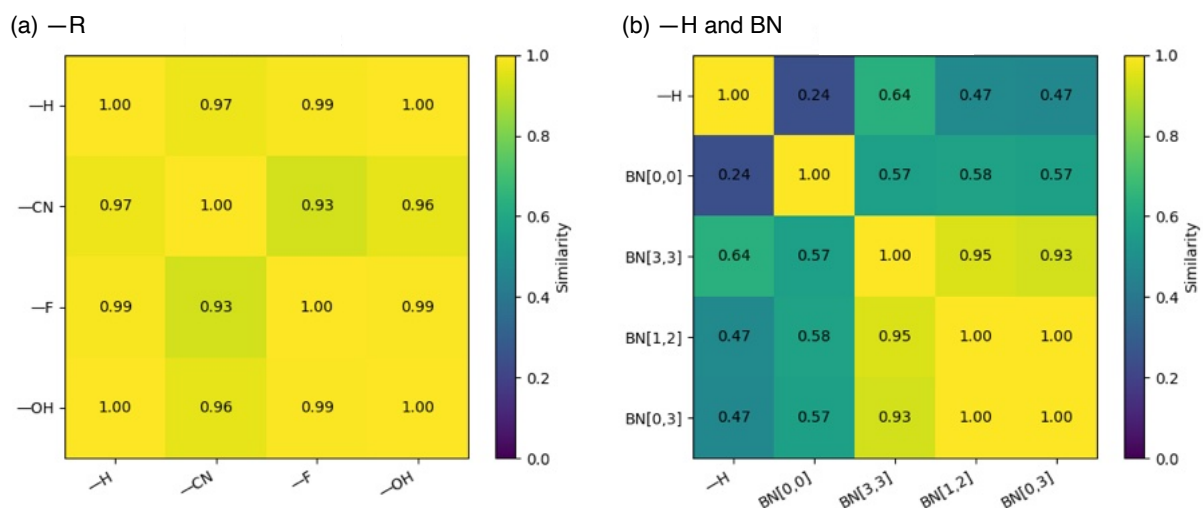


Figure 3.21. Similarity matrix among the AA-stacked (a) $-R$, and (b) $-H$ and BN systems calculated using 2 frontier bands.

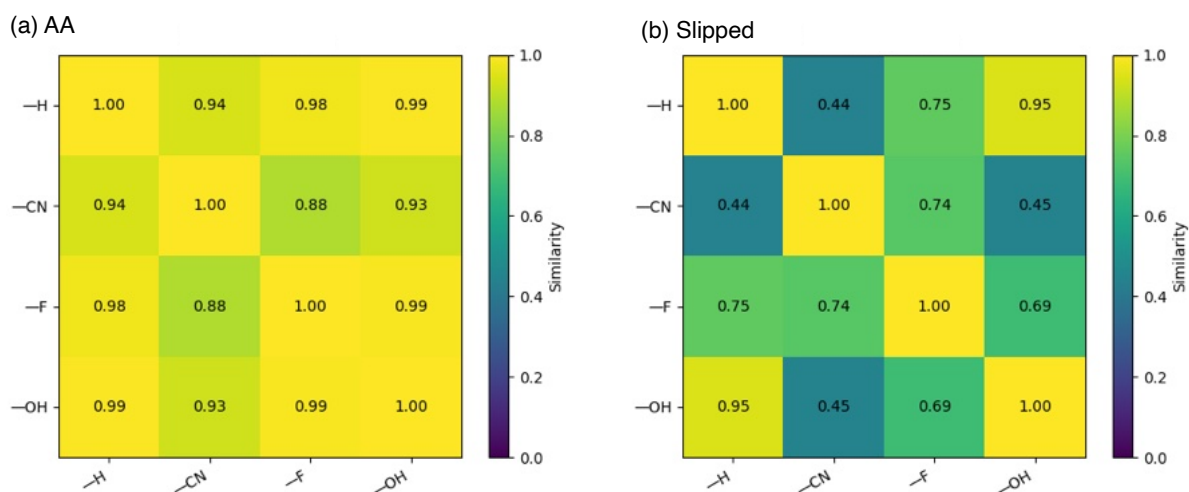


Figure 3.22. Similarity matrix among the (a) AA-stacked (using 5 frontier bands), and (b) slipped (corresponding to the minima in the PES contours in Figure 3.10; calculated using 2 frontier bands) $-R$ systems.

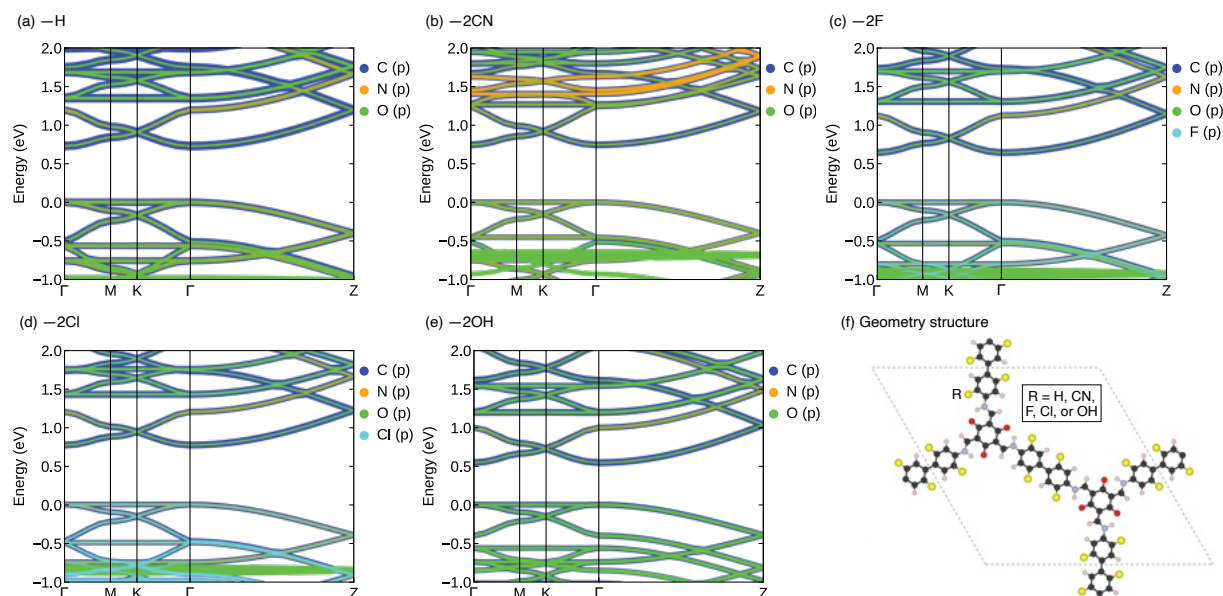


Figure 3.23. PBE-D3(BJ)-evaluated band structures for (a) -H, and systems with bi-substitution on each of the benzene rings on the linkers: (b) -2CN, (c) -2F, (d) -2Cl, and (e) -2OH. The corresponding geometry structure is illustrated in (f) where R = H, CN, F, Cl, or OH.

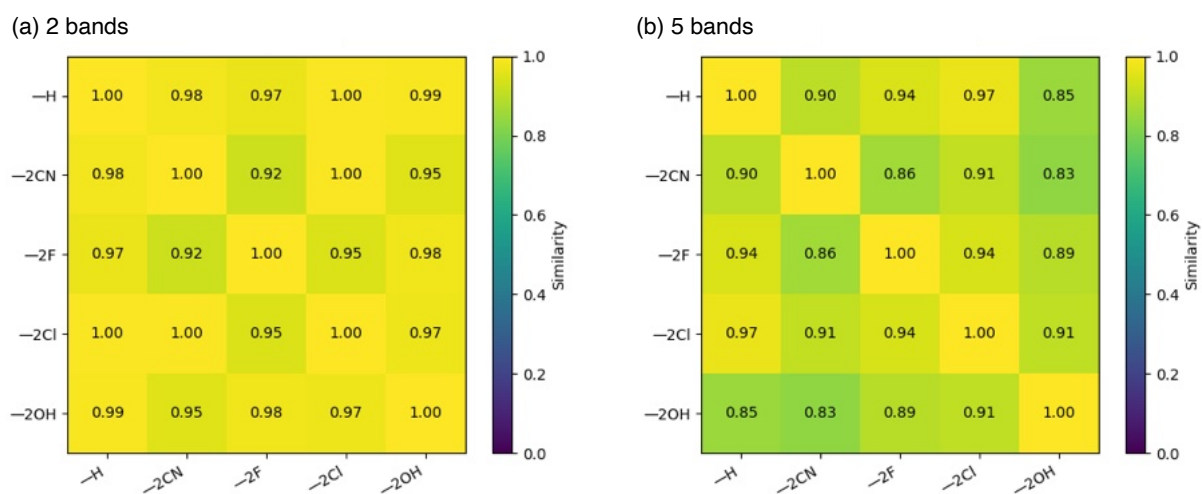


Figure 3.24. Similarity matrix for the -H and the bi-substituted systems, using (a) 2 or (b) 5 frontier bands. The geometry structure is shown in Figure 3.23f.

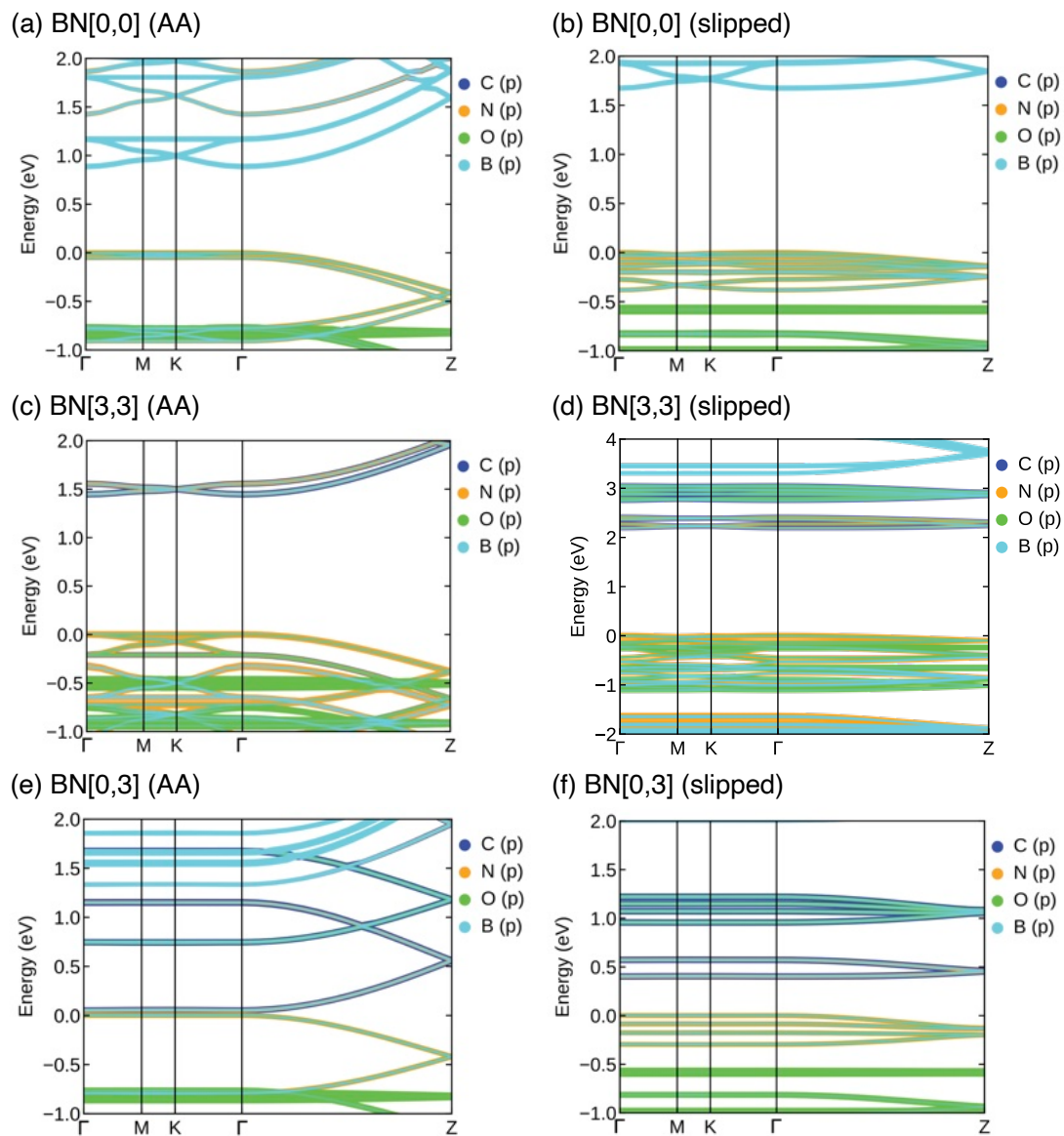


Figure 3.25. PBE-D3(BJ)-evaluated band structures for BN[0,0] (a, b), BN[3,3] (c, d), and BN[0,3] (e, f). (a), (c), and (e) correspond to the results under AA stackings, while (b), (d), and (f) are from the slipped stacking, which correspond to fractional displacements of (0.034, 0.058).

Table 3.7. PBE-D3(BJ) evaluated bandgaps (direct) and effective masses of the D-A COFs under AA stacking, including –H and the BN systems.

System	bandgap/eV	m^*/m_0	$\Gamma \rightarrow M$	$\Gamma \rightarrow K$	$\Gamma \rightarrow Z$
–H	0.725	m_e^*	0.359	0.362	1.297
		m_h^*	-66.179	-37.328	-1.347
BN[0,0]	0.885	m_e^*	0.572	0.570	0.886
		m_h^*	-200.691	-93.673	-1.328
BN[3,3]	1.445	m_e^*	1.177	1.194	1.208
		m_h^*	-201.373	-187.991	-1.429
BN[1,2]	0.747	m_e^*	7.371	8.474	1.206
		m_h^*	-119.159	-112.156	-1.326
BN[0,3]	0.050	m_e^*	11.901	13.412	1.219
		m_h^*	inf	-380.905	-1.300

Table 3.8. PBE-D3(BJ) evaluated bandgaps (direct) and effective masses of the D-A COFs under the slipped stacking which correspond to fractional displacements of (0.034, 0.058), including -H and the BN systems.

System	bandgap/eV	m^*/m_0	$\Gamma \rightarrow M$	$\Gamma \rightarrow K$	$\Gamma \rightarrow Z$
-H	1.400	m_e^*	0.424	0.512	299.503
		m_h^*	-1.093	-1.336	-3.810
BN[0,0]	1.673	m_e^*	0.617	0.685	6.945
		m_h^*	-2.158	-8.006	-3.727
BN[3,3]	2.180	m_e^*	1.428	1.910	305.714
		m_h^*	-1.412	-3.363	-4.947
BN[1,2]	1.559	m_e^*	13.240	17.654	43.591
		m_h^*	-119.159	-86.666	-6.127
BN[0,3]	0.401	m_e^*	20.698	26.824	76.588
		m_h^*	-32.458	-65.673	-3.301

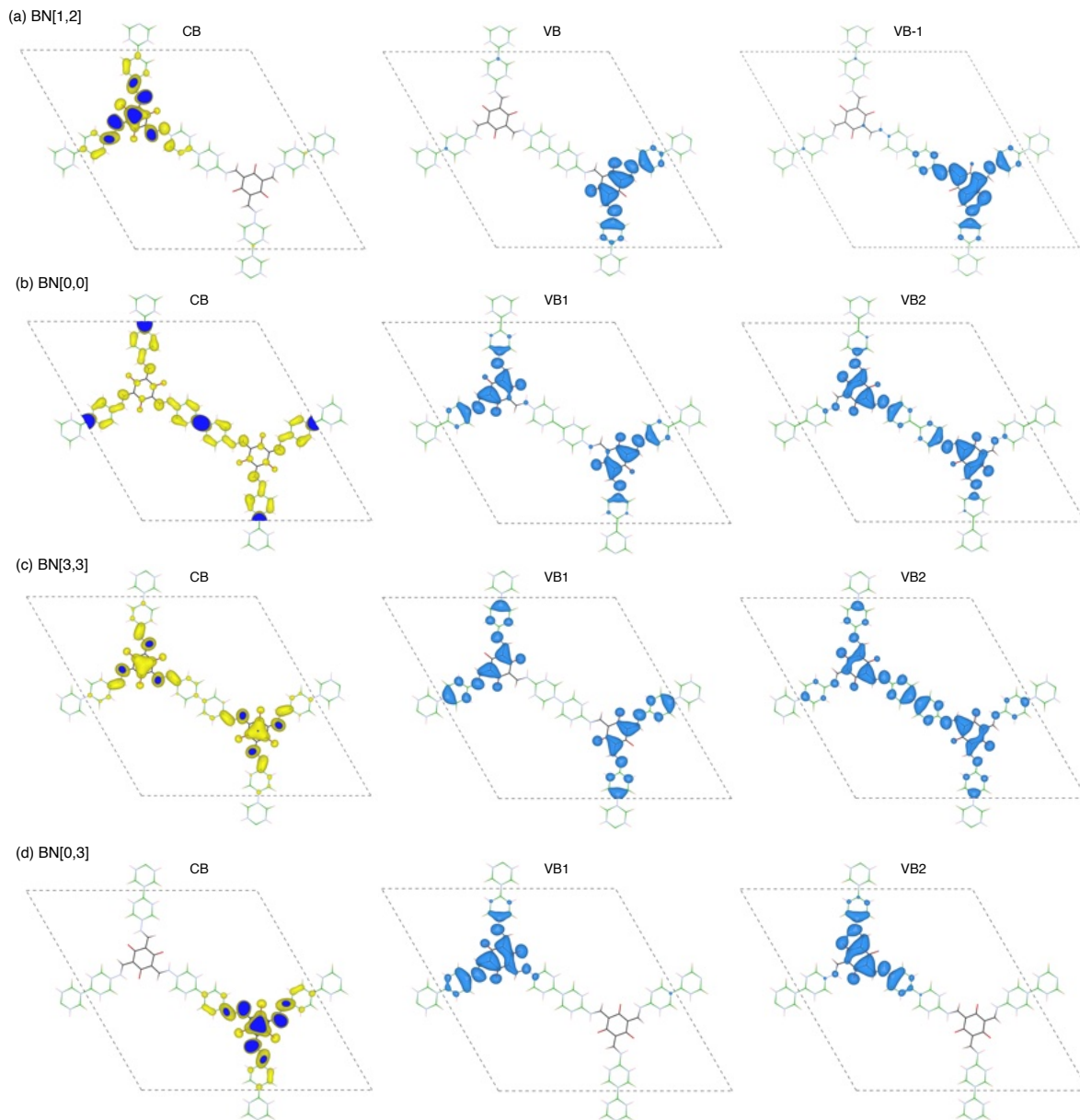


Figure 3.26. Partial charge density at the CBM and VBMs (at Γ , with isosurface level of $0.0003 \text{ e } \text{\AA}^{-3}$), respectively, for the AA-stacked systems of (a) BN[1,2], (b) BN[0,0], (c) BN[3,3], and (d) BN[0,3]. The VBMs for BN[0,0], BN[3,3], and BN[0,3] are doubly degenerate, thus here labeled as VB1 and VB2. Since the BN[1,2] system has only one VBM, for comparison, the partial charge density for its VB-1 is also provided. The dark blue part in the CBs corresponds to the interface between neighboring unit cells.

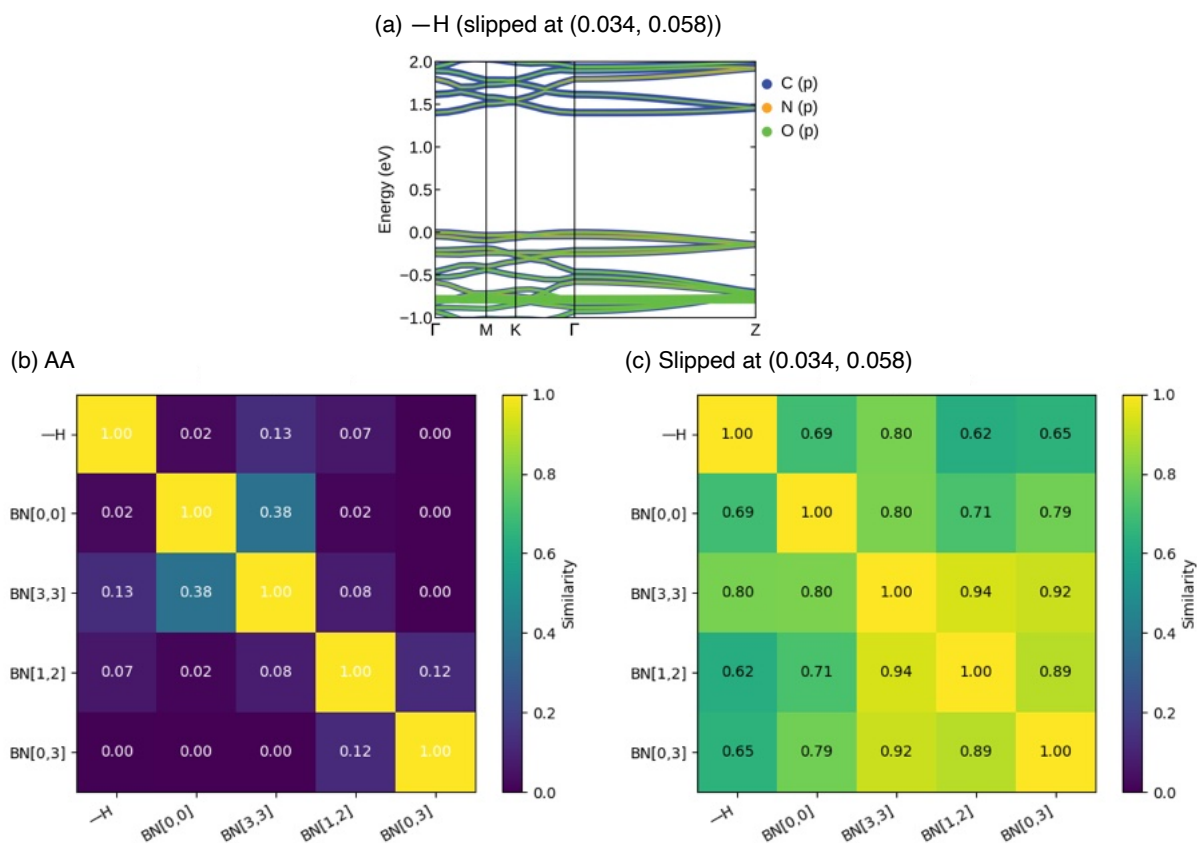


Figure 3.27. (a) Band structure of the —H system (slipped at (0.034, 0.058)) and the similarity matrices among the (b) AA-stacked (using 5 frontier bands), and (c) slipped (at (0.034, 0.058); calculated using 2 frontier bands) —H and BN systems.

Table 3.9. The estimated ionization potential (IP), electron affinity (EA), fundamental gap (E_g), and the exciton binding energy (E_b) (all in eV) for the representative monolayer systems of -H, -CN, and BN[1,2].

System	IP	EA	E_g	E_b
-H	5.265	2.392	2.873	0.718
-CN	5.856	3.011	2.844	0.711
BN[1,2]	5.509	1.798	3.712	0.928

References

- [1] Zhi Wei Seh, Jakob Kibsgaard, Colin F Dickens, IB Chorkendorff, Jens K Nørskov, and Thomas F Jaramillo. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science*, 355(6321):eaad4998, 2017.
- [2] Qian Wang and Kazunari Domen. Particulate photocatalysts for light-driven water splitting: mechanisms, challenges, and design strategies. *Chem. Rev.*, 120(2):919–985, 2019.
- [3] Hiroshi Nishiyama, Taro Yamada, Mamiko Nakabayashi, Yoshiki Maehara, Masaharu Yamaguchi, Yasuko Kuromiya, Yoshie Nagatsuma, Hiromasa Tokudome, Seiji Akiyama, Tomoaki Watanabe, Ryoichi Narushima, Sayuri Okunaka, Naoya Shibata, Tsuyoshi Takata, Takashi Hisatomi, and Kazunari Domen. Photocatalytic solar hydrogen production from water on a 100-m² scale. *Nature*, 598(7880):304–307, 2021.
- [4] Peng Zhou, Ishtiaque Ahmed Navid, Yongjin Ma, Yixin Xiao, Ping Wang, Zhengwei Ye, Baowen Zhou, Kai Sun, and Zetian Mi. Solar-to-hydrogen efficiency of more than 9% in photocatalytic water splitting. *Nature*, 613(7942):66–70, 2023.
- [5] Yuhei Miyauchi, Munechiyo Iwamura, Shinichiro Mouri, Tadashi Kawazoe, Motoichi Ohtsu, and Kazunari Matsuda. Brightening of excitons in carbon nanotubes on dimensionality modification. *Nat. Photonics*, 7(9):715–719, 2013.
- [6] Srabanti Ghosh, Dipendu Sarkar, Sweta Bastia, and Yatendra S Chaudhary. Band-structure tunability via the modulation of excitons in semiconductor nanostructures: manifestation in photocatalytic fuel generation. *Nanoscale*, 15(26):10939–10974, 2023.
- [7] Chenglong Ru, Xiaoyu Nie, Zhi-An Lan, Zhiming Pan, Wandong Xing, Sibao Wang, Jimmy C Yu, Yidong Hou, and Xinchun Wang. Regulation of exciton effects in functionalized conjugated polymers by B-N Lewis pairs for visible-light photocatalysis. *Angew. Chem. Int. Ed.*, 64(5):e202417712, 2025.
- [8] Lingsong Wang and Weigang Zhu. Organic donor-acceptor systems for photocatalysis. *Adv. Sci.*, 11(10):2307227, 2024.
- [9] Wenlong Jin, Chi-Yuan Yang, Riccardo Pau, Qingqing Wang, Eelco K. Tekelenburg, Han-Yan Wu, Ziang Wu, Sang Young Jeong, Federico Pitzalis, Tiefeng Liu, Qiao He, Qifan Li, Jun-Da Huang, Renee Kroon, Martin Heeney, Han Young Woo, Andrea Mura, Alessandro Motta, Antonio Facchetti, Mats Fahlman, Maria Antonietta Loi, and Simone Fabiano. Photocatalytic doping of organic semiconductors. *Nature*, pages 1–6, 2024.
- [10] Jingxiang Low, Jiaguo Yu, Mietek Jaroniec, Swelm Wageh, and Ahmed A Al-Ghamdi. Heterojunction photocatalysts. *Adv. Mater.*, 29(20):1601694, 2017.

- [11] Xiao Feng, Xuesong Ding, and Donglin Jiang. Covalent organic frameworks. *Chem. Soc. Rev.*, 41(18):6010–6022, 2012.
- [12] Vijay S Vyas, Vincent Wing-hei Lau, and Bettina V Lotsch. Soft photocatalysis: organic polymers for solar fuel production. *Chem. Mater.*, 28(15):5191–5204, 2016.
- [13] Torben Sick, Alexander G. Hufnagel, Jonathan Kampmann, Ilina Kondofersky, Mona Calik, Julian M. Rotter, Austin Evans, Markus Döblinger, Simon Herbert, Kristina Peters, Daniel Böhm, Paul Knochel, Dana D. Medina, Dina Fattakhova-Rohlfing, and Thomas Bein. Oriented films of conjugated 2D covalent organic frameworks as photocathodes for water splitting. *J. Am. Chem. Soc.*, 140(6):2085–2092, 2017.
- [14] Yangyang Wan, Lei Wang, Hangxun Xu, Xiaojun Wu, and Jinlong Yang. A simple molecular design strategy for two-dimensional covalent organic framework capable of visible-light-driven water splitting. *J. Am. Chem. Soc.*, 142(9):4508–4516, 2020.
- [15] Wei Zhao, Peiyao Yan, Boyu Li, Mounib Bahri, Lunjie Liu, Xiang Zhou, Rob Clowes, Nigel D. Browning, Yue Wu, John W. Ward, and Andrew I. Cooper. Accelerated synthesis and discovery of covalent organic framework photocatalysts for hydrogen peroxide production. *J. Am. Chem. Soc.*, 144(22):9902–9909, 2022.
- [16] Peter J Waller, Felipe Gándara, and Omar M Yaghi. Chemistry of covalent organic frameworks. *Acc. Chem. Res.*, 48(12):3053–3063, 2015.
- [17] Yu Jing, Zhenpei Zhou, Weixiang Geng, Xinyue Zhu, and Thomas Heine. 2D honeycomb-kagome polymer tandem as effective metal-free photocatalysts for water splitting. *Adv. Mater.*, 33(21):2008645, 2021.
- [18] Junsong Xu, Can Yang, Shuai Bi, Wenyan Wang, Yafei He, Dongqing Wu, Qifeng Liang, Xinchun Wang, and Fan Zhang. Vinylene-linked covalent organic frameworks (COFs) with symmetry-tuned polarity and photocatalytic activity. *Angew. Chem. Int. Ed.*, 59(52):23845–23853, 2020.
- [19] Liping Guo, Yingli Niu, Shumaila Razzaque, Bien Tan, and Shangbin Jin. Design of D–A₁–A₂ covalent triazine frameworks via copolymerization for photocatalytic hydrogen evolution. *ACS Catal.*, 9(10):9438–9445, 2019.
- [20] Vijay S Vyas, Frederik Haase, Linus Stegbauer, Gökçen Savasci, Filip Podjaski, Christian Ochsenfeld, and Bettina V Lotsch. A tunable azine covalent organic framework platform for visible light-induced hydrogen generation. *Nat. Commun.*, 6(1):8508, 2015.
- [21] Enquan Jin, Zhian Lan, QiuHong Jiang, Keyu Geng, Guosheng Li, Xinchun Wang, and Donglin Jiang. 2D sp² carbon-conjugated covalent organic frameworks for photocatalytic hydrogen production from water. *Chem*, 5:1632–1647, 2019.

- [22] Jintao Ming, Ai Liu, Jiwu Zhao, Pu Zhang, Haowei Huang, Huan Lin, Ziting Xu, Xuming Zhang, Xuxu Wang, Johan Hofkens, Maarten B. J. Roeloffs, and Jinlin Long. Hot π -electron tunneling of metal-insulator-COF nanostructures for efficient hydrogen production. *Angew. Chem. Int. Ed.*, 131:18458–18462, 2019.
- [23] Jin Yang, Samrat Ghosh, Jérôme Roeser, Amitava Acharjya, Christopher Penschke, Yusuke Tsutsui, Jabor Rabeah, Tianyi Wang, Simon Yves Djoko Tameu, Meng-Yang Ye, Julia Grüneberg, Shuang Li, Changxia Li, Reinhard Schomäcker, Roel Van De Krol, Shu Seki, Peter Saalfrank, and Arne Thomas. Constitutional isomerism of the linkages in donor-acceptor covalent organic frameworks and its impact on photocatalysis. *Nat. Commun.*, 13:6317, 2022.
- [24] F. Meng, S. Bi, Z. Sun, D. Wu, and F. Zhang. 2,4,6-trimethylpyridine-derived vinylene-linked covalent organic frameworks for confined catalytic esterification. *Angew. Chem. Int. Ed.*, 61:e202210447, 2022.
- [25] Zhengfeng Zhao, Yunlong Zheng, Chun Wang, Sainan Zhang, Jie Song, Yafei Li, Shengqian Ma, Peng Cheng, Zhenjie Zhang, and Yao Chen. Fabrication of robust covalent organic frameworks for enhanced visible-light-driven H_2 evolution. *ACS Catal.*, 11(4): 2098–2107, 2021.
- [26] Wenqian Li, Xiaofeng Huang, Tengwu Zeng, Yahu A. Liu, Weibo Hu, Hui Yang, Yue-Biao Zhang, and Ke Wen. Thiazolo[5,4-d]thiazole-based donor-acceptor covalent organic framework for sunlight-driven hydrogen evolution. *Angew. Chem. Int. Ed.*, 60:1869–1874, 2021.
- [27] Lishan Sun, Meng Lu, Zongfan Yang, Zhenyi Yu, Xi Su, Ya-Qian Lan, and Long Chen. Nickel glyoximate based metal-covalent organic frameworks for efficient photocatalytic hydrogen evolution. *Angew. Chem. Int. Ed.*, 61:e2022043, 2022.
- [28] Hou Wang, Cheng Qian, Jia Liu, Yongfei Zeng, Dongdong Wang, Weiqiang Zhou, Long Gu, Hongwei Wu, Guofeng Liu, and Yanli Zhao. Integrating suitable linkage of covalent organic frameworks into covalently bridged inorganic/organic hybrids toward efficient photocatalysis. *J. Am. Chem. Soc.*, 142:4862–4871, 2020.
- [29] Liang Yao, Andrés Rodríguez-Camargo, Meng Xia, David Mücke, Roman Guntermann, Yongpeng Liu, Lars Grunenberg, Alberto Jiménez-Solano, Sebastian T. Emmerling, Viola Duppel, Kevin Sivula, Thomas Bein, Haoyuan Qi, Ute Kaiser, Michael Grätzel, and Bettina V. Lotsch. Covalent organic framework nanoplates enable solution-processed crystalline nanofilms for photoelectrochemical hydrogen evolution. *J. Am. Chem. Soc.*, 144:10291–10300, 2022.
- [30] Fulai Liu, Yanyan He, Xiaopeng Liu, Zhuan Wang, Hong-Lai Liu, Xiang Zhu, Chun-Chao Hou, Yuxiang Weng, Qianfan Zhang, and Yong Chen. Regulating excitonic effects in

- covalent organic frameworks to promote free charge carrier generation. *ACS Catal*, 12: 9494–9502, 2022.
- [31] Weitao Wang, Haotian Wang, Xiaohui Tang, Jinlei Huo, Yan Su, Chuangye Lu, Yujian Zhang, Hong Xu, and Cheng Gu. Phenothiazine-based covalent organic frameworks with low exciton binding energies for photocatalysis. *Chem. Sci.*, 13:8679–8685, 2022.
- [32] Liangjun Chen, Minchu Huang, Bo Chen, Chengtao Gong, Nanjun Li, Hongfei Cheng, Ye Chen, Yongwu Peng, and Guodong Xu. Two-dimensional covalent organic framework nanosheets: Synthesis and energy-related applications. *Chin. Chem. Lett.*, 33(6):2867–2882, 2022.
- [33] Rong-Ran Liang, Shu-Yan Jiang, A Ru-Han, and Xin Zhao. Two-dimensional covalent organic frameworks with hierarchical porosity. *Chem. Soc. Rev.*, 49(12):3920–3951, 2020.
- [34] Hesham R Abuzeid, Ahmed FM EL-Mahdy, and Shiao-Wei Kuo. Covalent organic frameworks: Design principles, synthetic strategies, and diverse applications. *Giant*, 6: 100054, 2021.
- [35] Mingchao Wang, Marco Ballabio, Mao Wang, Hung-Hsuan Lin, Bishnu P. Biswal, Xiaocang Han, Silvia Paasch, Eike Brunner, Pan Liu, Mingwei Chen, Mischa Bonn, Thomas Heine, Shengqiang Zhou, Enrique Cánovas, Renhao Dong, and Xinliang Feng. Unveiling electronic properties in metal–phthalocyanine-based pyrazine-linked conjugated two-dimensional covalent organic frameworks. *J. Am. Chem. Soc.*, 141(42):16810–16816, 2019.
- [36] P Zhu and V Meunier. Electronic properties of two-dimensional covalent organic frameworks. *J. Chem. Phys.*, 137(24):244703, 2012.
- [37] Jia Guo, Yanhong Xu, Shangbin Jin, Long Chen, Toshihiko Kaji, Yoshihito Honsho, Matthew A. Addicoat, Jangbae Kim, Akinori Saeki, Hyotcherl Ihee, Shu Seki, Stephan Irle, Masahiro Hiramoto, Jia Gao, and Donglin Jiang. Conjugated organic framework with three-dimensionally ordered stable structure and delocalized π clouds. *Nat. Commun.*, 4(1):2736, 2013.
- [38] Soyoung Kim and Hee Cheul Choi. Recent advances in covalent organic frameworks for molecule-based two-dimensional materials. *ACS Omega*, 5(2):948–958, 2019.
- [39] Tae Wu Kim, Sunhong Jun, Yoonhoo Ha, Rajesh K. Yadav, Abhishek Kumar, Chung-Yul Yoo, Inhwon Oh, Hyung-Kyu Lim, Jae Won Shin, Ryong Ryoo, Hyungjun Kim, Jeongho Kim, Jin-Ook Baeg, and Hyotcherl Ihee. Ultrafast charge transfer coupled with lattice phonons in two-dimensional covalent organic frameworks. *Nat. Commun.*, 10(1):1873, 2019.

- [40] Lei Zhang, Qiu-Hong Zhu, Yue-Ru Zhou, Shuang-Long Wang, Jie Fu, Jia-Ying Liu, Guo-Hao Zhang, Lijian Ma, Guohua Tao, Guo-Hong Tao, and Ling He. Hydrogen-bonding and π - π interaction promoted solution-processable covalent organic frameworks. *Nat. Commun.*, 14(1):8181, 2023.
- [41] Jae Woong Jung, Feng Liu, Thomas P Russell, and Won Ho Jo. Anthracene-based medium bandgap conjugated polymers for high performance polymer solar cells exceeding 8% pce without additive and annealing process. *Adv. Energy Mater.*, 5(11):1500065, 2015.
- [42] Jae Woong Jung, Feng Liu, Thomas P Russell, and Won Ho Jo. Medium bandgap conjugated polymer for high performance polymer solar cells exceeding 9% power conversion efficiency. *Adv. Mater.*, 27(45):7462–7468, 2015.
- [43] Pierre M Beaujuge, Wojciech Pisula, Hoi Nok Tsao, Stefan Ellinger, Klaus Müllen, and John R Reynolds. Tailoring structure–property relationships in dithienosilole–benzothiadiazole donor–acceptor copolymers. *J. Am. Chem. Soc.*, 131(22):7514–7515, 2009.
- [44] Weiben Chen, Lei Wang, Daize Mo, Feng He, Zhilin Wen, Xiaojun Wu, Hangxun Xu, and Long Chen. Modulating benzothiadiazole-based covalent organic frameworks via halogenation for enhanced photocatalytic water splitting. *Angew. Chem. Int. Ed.*, 59(39):16902–16909, 2020.
- [45] Yanpei Song, Qi Sun, Briana Aguila, and Shengqian Ma. Opportunities of covalent organic frameworks for advanced applications. *Adv. Sci.*, 6(2):1801410, 2019.
- [46] Alexander M Pütz, Maxwell W Terban, Sebastian Bette, Frederik Haase, Robert E Dinnebier, and Bettina V Lotsch. Total scattering reveals the hidden stacking disorder in a 2D covalent organic framework. *Chem. Sci.*, 11(47):12647–12654, 2020.
- [47] Zhehao Huang, Erik Svensson Grape, Jian Li, A Ken Inge, and Xiaodong Zou. 3D electron diffraction as an important technique for structure elucidation of metal-organic frameworks and covalent organic frameworks. *Coord. Chem. Rev.*, 427:213583, 2021.
- [48] Chao Gao, Jian Li, Sheng Yin, Guiqing Lin, Tianqiong Ma, Yi Meng, Junliang Sun, and Cheng Wang. Isostructural three-dimensional covalent organic frameworks. *Angew. Chem. Int. Ed.*, 58(29):9770–9775, 2019.
- [49] Shiwei Wang, Anton D. Chavez, Simil Thomas, Hong Li, Nathan C. Flanders, Chao Sun, Michael J. Strauss, Lin X. Chen, Albert J. Markvoort, Jean-Luc Brédas, and William R. Dichtel. Pathway complexity in the stacking of imine-linked macrocycles related to two-dimensional covalent organic frameworks. *Chem. Mater.*, 31(17):7104–7111, 2019.
- [50] Xing Li, Jingsi Qiao, See Wee Chee, Hai-Sen Xu, Xiaoxu Zhao, Hwa Seob Choi, Wei

- Yu, Su Ying Quek, Utkur Mirsaidov, and Kian Ping Loh. Rapid scalable construction of highly crystalline acylhydrazone two-dimensional covalent organic frameworks via dipole-induced antiparallel stacking. *J. Am. Chem. Soc.*, 142(10):4932–4943, 2020.
- [51] Niklas Keller, Mona Calik, Dmitry Sharapa, Himadri R Soni, Peter M Zehetmaier, Sabrina Rager, Florian Auras, Andreas C Jakowetz, Andreas Görling, Timothy Clark, and Thomas Bein. Enforcing extended porphyrin J-aggregate stacking in covalent organic frameworks. *J. Am. Chem. Soc.*, 140(48):16544–16552, 2018.
- [52] Xiaowei Wu, Xing Han, Yuhao Liu, Yan Liu, and Yong Cui. Control interlayer stacking and chemical stability of two-dimensional covalent organic frameworks via steric tuning. *J. Am. Chem. Soc.*, 140(47):16124–16133, 2018.
- [53] Yu Fan, Qiang Wen, Tian-Guang Zhan, Qiao-Yan Qi, Jia-Qiang Xu, and Xin Zhao. A case study on the influence of substitutes on interlayer stacking of 2D covalent organic frameworks. *Chem. Eur. J.*, 23(24):5668–5672, 2017.
- [54] Pablo Albacete, Jose I Martinez, Xing Li, Alejandro Lopez-Moreno, Sofiá Mena-Hernando, Ana E Platero-Prats, Carmen Montoro, Kian Ping Loh, Emilio M Perez, and Felix Zamora. Layer-stacking-driven fluorescence in a two-dimensional imine-linked covalent organic framework. *J. Am. Chem. Soc.*, 140(40):12922–12929, 2018.
- [55] Florian Auras, Laura Ascherl, Amir H. Hakimiooun, Johannes T. Margraf, Fabian C. Hanusch, Stephan Reuter, Derya Bessinger, Markus Döblinger, Christina Hettstedt, Konstantin Karaghiosoff, Simon Herbert, Paul Knochel, Timothy Clark, and Thomas Bein. Synchronized offset stacking: A concept for growing large-domain and highly crystalline 2D covalent organic frameworks. *J. Am. Chem. Soc.*, 138(51):16703–16710, 2016.
- [56] Yuanhui Pan, Ching-Hwa Ho, Francesco Paesani, and Raja Ghosh. Engineering flat and dispersive bands in 2D layered COFs via interlayer stacking and donor–acceptor strategy. *Chem. Mater.*, 35(16):6235–6245, 2023.
- [57] Eric L Spitler, Brian T Koo, Jennifer L Novotney, John W Colson, Fernando J Uribe-Romo, Gregory D Gutierrez, Paulette Clancy, and William R Dichtel. A 2D covalent organic framework with 4.7-nm pores and insight into its interlayer stacking. *J. Am. Chem. Soc.*, 133(48):19416–19421, 2011.
- [58] Binit Lukose, Agnieszka Kuc, and Thomas Heine. The structure of layered covalent-organic frameworks. *Chem. Eur. J.*, 17(8):2388–2392, 2011.
- [59] Brian T Koo, William R Dichtel, and Paulette Clancy. A classification scheme for the stacking of two-dimensional boronate ester-linked covalent organic frameworks. *J. Mater. Chem.*, 22(34):17460–17469, 2012.

- [60] Shangbin Jin, Xuesong Ding, Xiao Feng, Mustafa Supur, Ko Furukawa, Seiya Takahashi, Matthew Addicoat, Mohamed E. El-Khouly, Toshikazu Nakamura, Stephan Irle, Shunichi Fukuzumi, Atsushi Nagai, and Donglin Jiang. Charge dynamics in a donor–acceptor covalent organic framework with periodically ordered bicontinuous heterojunctions. *Angew. Chem. Int. Ed.*, 7(52):2017–2021, 2013.
- [61] Shangbin Jin, Ko Furukawa, Matthew Addicoat, Long Chen, Seiya Takahashi, Stephan Irle, Toshikazu Nakamura, and Donglin Jiang. Large pore donor–acceptor covalent organic frameworks. *Chem. Sci.*, 4(12):4505–4511, 2013.
- [62] Chengjun Kang, Zhaoqiang Zhang, Vanessa Wee, Adam K Usadi, David C Calabro, Lisa Saunders Baugh, Shun Wang, Yuxiang Wang, and Dan Zhao. Interlayer shifting in two-dimensional covalent organic frameworks. *J. Am. Chem. Soc.*, 142(30):12995–13002, 2020.
- [63] Wen-Qi Tang, Ying-Jie Zhao, Ming Xu, Jin-Ya Xu, Sha-Sha Meng, Yun-Dong Yin, Qing-Hua Zhang, Lin Gu, Da-Huan Liu, and Zhi-Yuan Gu. Controlling the stacking modes of metal–organic framework nanosheets through host–guest noncovalent interactions. *Angew. Chem. Int. Ed.*, 60(13):6920–6925, 2021.
- [64] Chunzhi Li, Jiali Liu, He Li, Kaifeng Wu, Junhui Wang, and Qihua Yang. Covalent organic frameworks with high quantum efficiency in sacrificial photocatalytic hydrogen evolution. *Nat. Commun.*, 13(1):2357, 2022.
- [65] F Haase, K Gottschling, L Stegbauer, LS Germann, R Gutzler, V Duppel, VS Vyas, K Kern, RE Dinnebier, and BV Lotsch. Tuning the stacking behaviour of a 2D covalent organic framework through non-covalent interactions. *Mater. Chem. Front.*, 1(7):1354–1361, 2017.
- [66] Xiong Chen, Matthew Addicoat, Stephan Irle, Atsushi Nagai, and Donglin Jiang. Control of crystallinity and porosity of covalent organic frameworks by managing interlayer interactions based on self-complementary π -electronic force. *J. Am. Chem. Soc.*, 135(2): 546–549, 2013.
- [67] Rustam Z Khaliullin, Erika A Cobar, Rohini C Lochan, Alexis T Bell, and Martin Head-Gordon. Unravelling the origin of intermolecular interactions using absolutely localized molecular orbitals. *J. Phys. Chem. A*, 111(36):8753–8765, 2007.
- [68] Paul R Horn, Yuezhi Mao, and Martin Head-Gordon. Probing non-covalent interactions with a second generation energy decomposition analysis using absolutely localized molecular orbitals. *Phys. Chem. Chem. Phys.*, 18(33):23067–23079, 2016.
- [69] Montgomery Gray and John M Herbert. Origins of offset-stacking in porous frameworks. *J. Phys. Chem. C*, 127(5):2675–2686, 2023.

- [70] Kevin Carter-Fenk and John M Herbert. Electrostatics does not dictate the slip-stacked arrangement of aromatic π - π interactions. *Chem. Sci.*, 11(26):6758–6765, 2020.
- [71] Kevin Carter-Fenk, Meili Liu, Leila Pujal, Matthias Loipersberger, Maria Tsanai, Robert M Vernon, Julie D Forman-Kay, Martin Head-Gordon, Farnaz Heidar-Zadeh, and Teresa Head-Gordon. The energetic origins of pi-pi contacts in proteins. *J. Am. Chem. Soc.*, 145(45):24836–24851, 2023.
- [72] Christopher A Hunter, Kevin R Lawson, Julie Perkins, and Christopher J Urch. Aromatic interactions. *J. Chem. Soc., Perkin Trans. 2*, (5):651–669, 2001.
- [73] Franco Cozzi, Rita Annunziata, Maurizio Benaglia, Kim K Baldrige, Gerardo Aguirre, Jesús Estrada, Yongsak Sritana-Anant, and Jay S Siegel. Through-space interactions between parallel-offset arenes at the van der waals distance: 1,8-diarylbiphenylene syntheses structure and qm computations. *Phys. Chem. Chem. Phys.*, 10(19):2686–2694, 2008.
- [74] Mutasem Omar Sinnokrot and C David Sherrill. Unexpected substituent effects in face-to-face π -stacking interactions. *J. Phys. Chem. A*, 107(41):8377–8379, 2003.
- [75] Steven E Wheeler and KN Houk. Substituent effects in the benzene dimer are due to direct interactions of the substituents with the unsubstituted benzene. *J. Am. Chem. Soc.*, 130(33):10854–10855, 2008.
- [76] Steven E Wheeler. Understanding substituent effects in noncovalent interactions involving aromatic rings. *Acc. Chem. Res.*, 46(4):1029–1038, 2013.
- [77] Sean M Ryno, Chad Risko, and Jean-Luc Bredas. Noncovalent interactions and impact of charge penetration effects in linear oligoacene dimers and single crystals. *Chem. Mater.*, 28(11):3990–4000, 2016.
- [78] Ganna Gryn’ova and Clemence Corminboeuf. Implications of charge penetration for heteroatom-containing organic semiconductors. *J. Phys. Chem. Lett.*, 7(24):5198–5204, 2016.
- [79] C David Sherrill. Energy component analysis of π interactions. *Acc. Chem. Res.*, 46(4):1020–1028, 2013.
- [80] Christian Winkler, Tomas Kamencek, and Egbert Zojer. Understanding the origin of serrated stacking motifs in planar two-dimensional covalent organic frameworks. *Nanoscale*, 13(20):9339–9353, 2021.
- [81] National Institute of Standards and Technology (NIST). Computational chemistry comparison and benchmark database: Experimental data for B₃N₃H₆ (borazine). <https://cccbdb.nist.gov/exp2x.asp?casno=6569513>, 2022. Standard Reference Database 101,

Release 22 (May 2022). Accessed: 2025-05-09.

- [82] YS Meng, G Ceder, CP Grey, W-S Yoon, M Jiang, J Bréger, and Y Shao-Horn. Cation ordering in layered O₃ Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ ($0 \leq x \leq 1/2$) compounds. *Chem. Mater.*, 17(9):2386–2394, 2005.
- [83] Christian J Doonan, David J Tranchemontagne, T Grant Glover, Joseph R Hunt, and Omar M Yaghi. Exceptional ammonia uptake by a covalent organic framework. *Nat. Chem.*, 2(3):235–238, 2010.
- [84] Hui Yang, Mengjie Hao, Yinghui Xie, Xiaolu Liu, Yanfang Liu, Zhongshan Chen, Xiangke Wang, Geoffrey IN Waterhouse, and Shengqian Ma. Tuning local charge distribution in multicomponent covalent organic frameworks for dramatically enhanced photocatalytic uranium extraction. *Angew. Chem. Int. Ed.*, 62(30):e202303129, 2023.
- [85] H-M Guo and M Franz. Topological insulator on the kagome lattice. *Phys. Rev. B*, 80(11):113102, 2009.
- [86] Daniel J. Rizzo, Qingqing Dai, Christopher Bronner, Gregory Veber, Brian J. Smith, Michio Matsumoto, Simil Thomas, Giang D. Nguyen, Patrick R. Forrester, William Zhao, Jakob H. Jørgensen, William R. Dichtel, Felix R. Fischer, Hong Li, Jean-Luc Bredas, and Michael F. Crommie. Revealing the local electronic structure of a single-layer covalent organic framework through electronic decoupling. *Nano Lett.*, 20(2):963–970, 2020.
- [87] Xiaojuan Ni, Hong Li, Feng Liu, and Jean-Luc Brédas. Engineering of flat bands and dirac bands in two-dimensional covalent organic frameworks (COFs): relationships among molecular orbital symmetry, lattice symmetry, and electronic-structure characteristics. *Mater. Horiz.*, 9(1):88–98, 2022.
- [88] Simil Thomas, Hong Li, Cheng Zhong, Michio Matsumoto, William R Dichtel, and Jean-Luc Bredas. Electronic structure of two-dimensional π -conjugated covalent organic frameworks. *Chem. Mater.*, 31(9):3051–3065, 2019.
- [89] Diana Y Qiu, Galit Cohen, Dana Novichkova, and Sivan Refaely-Abramson. Signatures of dimensionality and symmetry in exciton band structure: Consequences for exciton dynamics and transport. *Nano Lett.*, 21(18):7644–7650, 2021.
- [90] Stefanie A Mewes and Andreas Dreuw. Density-based descriptors and exciton analyses for visualizing and understanding the electronic structure of excited states. *Phys. Chem. Chem. Phys.*, 21(6):2843–2856, 2019.
- [91] Marc Dvorak, Su-Huai Wei, and Zhigang Wu. Origin of the variation of exciton binding energy in semiconductors. *Phys. Rev. Lett.*, 110(1):016402, 2013.

- [92] Zeyu Jiang, Zhirong Liu, Yuanchang Li, and Wenhui Duan. Scaling universality between band gap and exciton binding energy of two-dimensional semiconductors. *Phys. Rev. Lett.*, 118(26):266401, 2017.
- [93] Raja Ghosh and Frank C Spano. Excitons and polarons in organic materials. *Acc. Chem. Res.*, 53(10):2201–2211, 2020.
- [94] Raja Ghosh and Francesco Paesani. Unraveling the effect of defects domain size and chemical doping on photophysics and charge transport in covalent organic frameworks. *Chem. Sci.*, 12(24):8373–8384, 2021.
- [95] Georg Kresse and Jürgen Furthmüller. Efficient iterative schemes for *Ab Initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54(16):11169, 1996.
- [96] Georg Kresse and Jürgen Furthmüller. Efficiency of *Ab-Initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.*, 6(1):15–50, 1996.
- [97] Peter E Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50(24):17953, 1994.
- [98] Georg Kresse and Daniel Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59(3):1758, 1999.
- [99] John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77(18):3865, 1996.
- [100] Erin R Johnson and Axel D Becke. A post-Hartree-Fock model of intermolecular interactions: Inclusion of higher-order corrections. *J. Chem. Phys.*, 124(17):174104, 2006.
- [101] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate *Ab Initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.*, 132(15):154104, 2010.
- [102] Stefan Grimme, Stephan Ehrlich, and Lars Goerigk. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.*, 32(7):1456–1465, 2011.
- [103] Hendrik J Monkhorst and James D Pack. Special points for Brillouin-zone integrations. *Phys. Rev. B*, 13(12):5188, 1976.
- [104] Vei Wang, Nan Xu, Jin-Cheng Liu, Gang Tang, and Wen-Tong Geng. VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code. *Comput. Phys. Commun.*, 267:108033, 2021.
- [105] Koichi Momma and Fujio Izumi. VESTA 3 for three-dimensional visualization of crystal,

- volumetric and morphology data. *J. Appl. Crystallogr.*, 44(6):1272–1276, 2011.
- [106] John P Perdew and Mel Levy. Physical content of the exact Kohn-Sham orbital energies: Band gaps and derivative discontinuities. *Phys. Rev. Lett.*, 51(20):1884, 1983.
 - [107] Paula Mori-Sánchez, Aron J Cohen, and Weitao Yang. Localization and delocalization errors in density functional theory and implications for band-gap prediction. *Phys. Rev. Lett.*, 100(14):146401, 2008.
 - [108] Joachim Paier, Martijn Marsman, K Hummer, Georg Kresse, Iann C Gerber, and János G Ángyán. Screened hybrid density functionals applied to solids. *J. Chem. Phys.*, 124(15): 154709, 2006.
 - [109] Aliaksandr V Krukau, Oleg A Vydrov, Artur F Izmaylov, and Gustavo E Scuseria. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.*, 125(22):224106, 2006.
 - [110] Antonios Raptakis, Alexander Croy, Arezoo Dianat, Rafael Gutierrez, and Gianaurelio Cuniberti. Exploring the similarity of single-layer covalent organic frameworks using electronic structure calculations. *Rsc Adv.*, 12(20):12283–12291, 2022.
 - [111] Alex M Ganose, Adam J Jackson, and David O Scanlon. sumo: Command-line tools for plotting and analysis of periodic *ab initio* calculations. *J. Open Source Softw.*, 3(28):717, 2018.
 - [112] Ai Sugie, Kyohei Nakano, Keisuke Tajima, Itaru Osaka, and Hiroyuki Yoshida. Dependence of exciton binding energy on bandgap of organic semiconductors. *J. Phys. Chem. Lett.*, 14(50):11412–11420, 2023.
 - [113] Evgeny Epifanovsky, Andrew T. B. Gilbert, Xintian Feng, Joonho Lee, Yuezhi Mao, Narbe Mardirossian, Pavel Pokhilko, Alec F. White, Marc P. Coons, Adrian L. Dempwolff, Zhengting Gan, Diptarka Hait, Paul R. Horn, Leif D. Jacobson, Ilya Kaliman, Jörg Kussmann, Adrian W. Lange, Ka Un Lao, Daniel S. Levine, Jie Liu, Simon C. McKenzie, Adrian F. Morrison, Kaushik D. Nanda, Felix Plasser, Dirk R. Rehn, Marta L. Vidal, Zhi-Qiang You, Ying Zhu, Bushra Alam, Benjamin J. Albrecht, Abdulrahman Aldosary, Ethan Alguire, Josefine H. Andersen, Vishikh Athavale, Dennis Barton, Khadiza Begam, Andrew Behn, Nicole Bellonzi, Yves A. Bernard, Eric J. Berquist, Hugh G. A. Burton, Abel Carreras, Kevin Carter-Fenk, Romit Chakraborty, Alan D. Chien, Kristina D. Closser, Vale Cofer-Shabica, Saswata Dasgupta, Marc de Wergifosse, Jia Deng, Michael Diedenhofen, Hainam Do, Sebastian Ehlert, Po-Tung Fang, Shervin Fatehi, Qingguo Feng, Triet Friedhoff, James Gayvert, Qinghui Ge, Gergely Gidofalvi, Matthew Goldey, Joe Gomes, Cristina E. González-Espinoza, Sahil Gulania, Anastasia O. Gunina, Magnus W. D. Hanson-Heine, Phillip H. P. Harbach, Andreas Hauser, Michael F. Herbst, Mario Hernández Vera, Manuel Hodecker, Zachary C. Holden, Shannon Houck, Xunkun Huang,

[114] Carlo Adamo and Vincenzo Barone. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.*, 110(13):6158–6170, 1999.

[115] Warren J Hehre, Robert Ditchfield, and John A Pople. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.*, 56(5):2257–2261, 1972.

[116] Praveen C Hariharan and John A Pople. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta*, 28(3):213–222, 1973.

[117] AD Dinga Wonanke and Matthew A Addicoat. Effect of unwanted guest molecules on the

- stacking configuration of covalent organic frameworks: a periodic energy decomposition analysis. *Phys. Chem. Chem. Phys.*, 24(25):15494–15501, 2022.
- [118] Jeng-Da Chai and Martin Head-Gordon. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.*, 10(44): 6615–6620, 2008.
- [119] Yuniang Qian, Yulan Han, Xiyuan Zhang, Ge Yang, Guozhen Zhang, and Hai-Long Jiang. Computation-based regulation of excitonic effects in donor-acceptor covalent organic frameworks for enhanced photocatalysis. *Nat. Commun.*, 14(1):3083, 2023.
- [120] Zhou Li, D Baillie, C Blois, and F Marsiglio. Ground-state properties of the holstein model near the adiabatic limit. *Phys. Rev. B*, 81(11):115114, 2010.
- [121] Hongde Yu and Dong Wang. Metal-free magnetism in chemically doped covalent organic frameworks. *J. Am. Chem. Soc.*, 142(25):11013–11021, 2020.
- [122] Shengdan Tao, Xuanlin Zhang, Jiaojiao Zhu, Pimo He, Shengyuan A Yang, Yunhao Lu, and Su-Huai Wei. Designing ultra-flat bands in twisted bilayer materials at large twist angles: Theory and application to two-dimensional indium selenide. *J. Am. Chem. Soc.*, 144(9):3949–3956, 2022.

Chapter 4

Thermodynamics of Alkali Metal Ion Uptake From Aqueous Solution in MOF-808

4.1 Introduction

Conventional metal extraction primarily relies on solid ores and salt lake brines, which are geographically unevenly distributed and finite in supply.¹ Moreover, these extraction processes are typically energy-intensive and inefficient, generating significant solid and liquid waste and contributing to environmental contamination.² In contrast, seawater presents a vast and underutilized source of valuable metals, including lithium, cobalt, nickel, uranium, gold, and rare earth elements.^{3,4} Given the abundance of these resources, seawater offers a promising alternative for metal extraction.

Among valuable metals, lithium has gained increasing attention due to its critical role in energy storage technologies. The growing demand for electric vehicles and mobile electronic devices has recently led to a sharp increase in industrial lithium consumption.^{1,5,6} Although extracting lithium from seawater is promising, its concentration is extremely low – approximately 0.1–0.2 ppm (0.01–0.03 mM).⁷ Thus, developing highly efficient sorbent materials capable of selectively capturing Li^+ from seawater is crucial for enabling efficient and sustainable lithium extraction.

Metal-organic frameworks (MOFs) have emerged as promising materials for selective ion transport,^{8–13} separation,^{14–19} and uptake.^{20–25} Composed of metal ions or clusters, known

as secondary building units (SBUs), coordinated with organic linkers, MOFs form diverse structures by adopting different topologies.^{26,27} Their high surface area, along with exceptional compositional and structural tunability, has enabled applications in gas adsorption, separation, and storage, as well as sensing, drug delivery, fuel cells, supercapacitors, and catalysis.^{28–30} Given their intrinsic properties, MOFs present a compelling opportunity for selective uptake of metal ions, such as Li^+ , from seawater.

Ion selectivity in porous materials is primarily governed by the thermodynamic balance between ion hydration in bulk water and ion uptake within the material, where ions may undergo partial or complete dehydration. In solution, ion–water interactions influence both enthalpy – through the competition between ion–water and water–water interactions – and entropy, as ion hydration may disrupt the surrounding hydrogen-bond network.³¹ The magnitude of these effects is determined by the ion’s intrinsic properties, such as size and charge density. However, upon entering the porous material, enthalpic contributions are further shaped by ion–host and water–host interactions, which collectively govern the stabilization of the ion within the confined environment.³²

Along the ion uptake pathway, an energy penalty or exclusion effect typically regulates ion transport into porous materials. The primary rejection mechanisms include steric (size-based) exclusion and Donnan (charge-based) exclusion.^{33–35} For example, steric exclusion prevents larger ions, such as K^+ , from entering narrow pores that can accommodate only smaller ions like Li^+ . Similarly, Donnan exclusion occurs when the porous material carries a net charge, repelling ions of the same charge while attracting counterions.

More recently, ion dehydration has been identified as a significant factor contributing to the overall energy barrier for ion transport.^{36–39} Ions with stronger hydration shells, such as Li^+ , require greater energy to shed water molecules, which is necessary for entry into small confined spaces within porous materials, leading to slower uptake rates compared to less hydrated ions like K^+ .^{36,38,40,41} Along ion permeation pathways, specific binding sites within the porous material may help offset dehydration energy costs through stabilizing ion–host interactions, facilitating ion

retention and transport.^{14,15,42–44} Thus, selectivity arises from the balance between dehydration energy costs and specific ion–host interactions, ultimately favoring the uptake of some ions over others.³⁹ Similar mechanisms govern ion selectivity in biological ion channels.^{39,45–47}

A detailed understanding of the driving forces and molecular-level mechanisms governing metal ion uptake from dilute aqueous solutions in MOFs remains largely unexplored, primarily due to the complexity of their confined porous environments. Additionally, disentangling the effects of local hydration structures along ion permeation pathways from the subtle interplay of ion–water and ion–framework interactions presents a significant challenge. In this study, we focus on pristine MOF-808, a prototypical MOF known for its hydrothermal stability,⁴⁸ to investigate the driving forces underlying alkali metal ion (Li^+ , Na^+ , and K^+) uptake and to examine the molecular mechanisms that govern ion and water transport within the framework. The fundamental insights gained from our simulations offer valuable guidance for designing MOFs with enhanced selectivity for metal ion extraction from dilute solutions.

4.2 Results and Discussion

Pristine MOF-808 consists of zirconium (Zr) oxide SBUs coordinated by 1,3,5-benzenetricarboxylate (BTC) linkers.⁴⁸ As shown in Figure 4.1, for pristine MOF-808, the inorganic SBUs are bonded to six organic BTC linkers, while each of the linkers is bonded with three SBUs. In addition, each SBU is also coordinated with six formate groups. As a result, the framework features large adamantane-shaped pores (*LPs*, diameter ~ 18.4 Å) and small tetrahedral-shaped pores (*SPs*, diameter ~ 4.8 Å), as illustrated in Figure 4.1.^{48–50} For each of the tetrahedral-shaped *SPs*, four inorganic SBUs are located at the vertices, with four organic BTC linkers positioned in the faces of the tetrahedron. We note that the *LPs* are interconnected to each other, while the *SPs* are well separated, with narrow windows formed between the nearby BTC linkers connecting each *SP* and the neighboring *LPs*. In this study, we focused on pristine MOF-808 as a prototypical system to elucidate the fundamental thermodynamic and molecular-level mechanisms governing

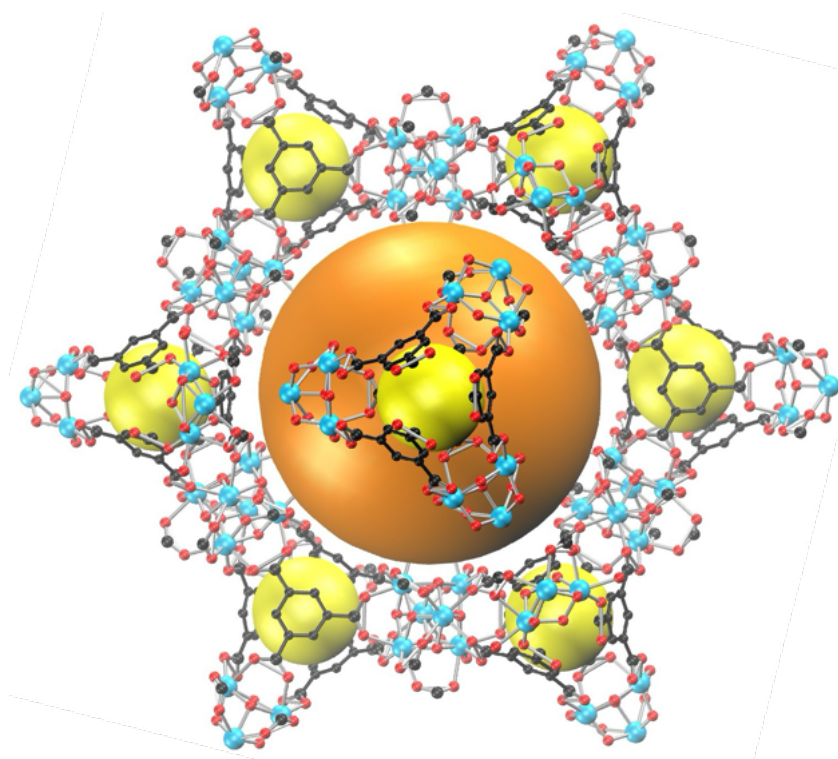


Figure 4.1. Schematic illustration of the structure of MOF-808. The large adamantane-shaped pores (*LPs*) and small tetrahedral-shaped pores (*SPs*) are indicated by the orange and yellow balls, respectively. Color code: C, black; O, red; Zr, cyan. Hydrogen atoms are omitted for clarity.

ion uptake. However, it is well established that MOF-808 can exhibit structural defects, such as missing formate ligands or BTC linkers. Introducing such defects offers a promising strategy to modulate the ion uptake capacity and selectivity of MOF-808. These structural changes result in coordinatively unsaturated Zr sites within the SBUs, which can substantially alter both water–framework and ion–framework interactions. Consequently, defect engineering may significantly affect not only the thermodynamics but also the kinetics of ion transport and uptake in MOF-808, offering promising directions that will be explored in future studies.

To systematically investigate the thermodynamics of hydrated alkali metal ions in MOF-808, the first step is to determine whether these ions preferentially reside within the framework’s *LPs* or *SPs*, compared to remaining fully hydrated in bulk water. Additionally, exploring the free-energy landscapes governing the transport of ions and water molecules between an *LP*

and an *SP* through the narrow connecting window is crucial for understanding the kinetic and thermodynamic barriers involved. Finally, analyzing the local hydration structures of ions upon uptake into MOF-808 provides key insights into the molecular-level interactions that dictate their stability within the framework.

4.2.1 Thermodynamics of Ion Uptake: From Bulk Water to MOF-808

To evaluate the thermodynamic stability of alkali metal ions within the MOF-808 framework relative to bulk water, we performed hydration free-energy calculations for ions located in different pore environments. Recognizing that the change in free energy (ΔG) is a state function, we employed the thermodynamic cycle (a) illustrated in Figure 4.2 to determine the free-energy change associated with transferring an ion from bulk water to an *LP* ($\Delta G_{\text{Bulk} \rightarrow \text{LP}}^{\text{ion}}$) of MOF-808. It is important to note that the effect of confinement on ion hydration is highly system-dependent. Factors such as pore size, surface chemistry, and ion–host and water–host interactions can enhance or weaken hydration under confinement.^{51–53} Our results reveal that all alkali metal ions considered in this study (Li^+ , Na^+ , and K^+) exhibit comparable $\Delta G_{\text{Bulk} \rightarrow \text{LP}}^{\text{ion}}$ values of ~ -4.1 kcal/mol (details in Table 4.7 in the Appendix). This negative value indicates a relative thermodynamic preference for the ions to reside within the *LPs* of MOF-808 compared to bulk water. We note that these results are derived from simulations performed under conditions corresponding to an ion uptake of approximately 0.046 mmol/g (details available in Appendix B), closely matching recent experimental measurements for Li^+ uptake in MOF-808.⁵⁴ A systematic decomposition of the free-energy changes for each step of the thermodynamic cycle for all ions is reported in Table 4.7 in the Appendix.

The structural and dynamic differences in water organization surrounding the ions in bulk water versus the confined environment of an *LP* provide insight into their thermodynamic stability. Alkali metal ions such as Li^+ , Na^+ , and K^+ are known to interact differently with bulk water due to their varying sizes and charge densities. Understanding how these behaviors change under confinement is therefore essential for designing porous materials with enhanced

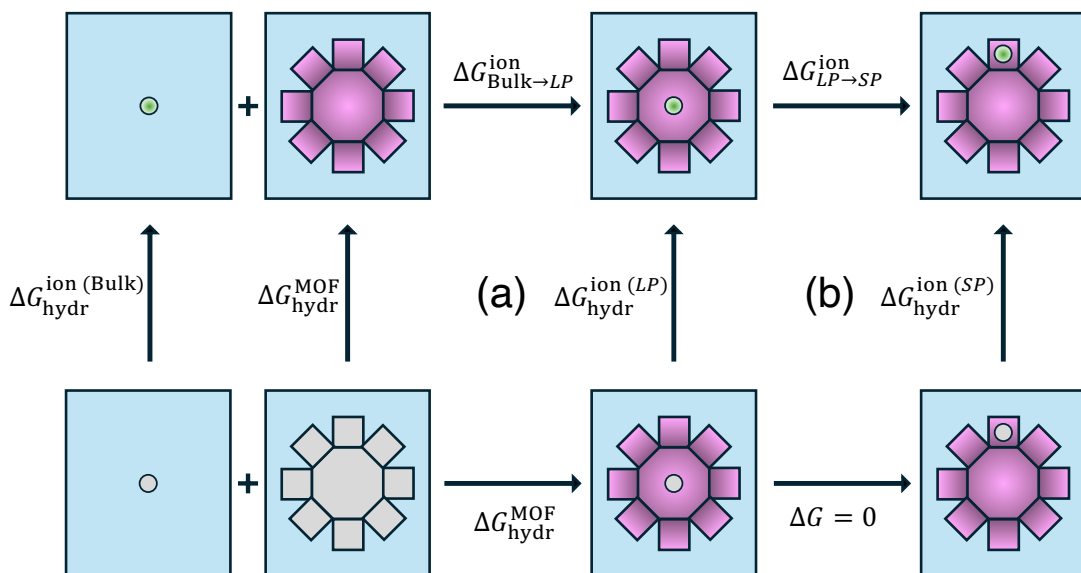


Figure 4.2. Thermodynamic cycles illustrating ion hydration in different environments. Cycle (a) shows that the free-energy change for transferring an ion from bulk water to a large pore (LP) of MOF-808 is given by $\Delta G_{\text{Bulk} \rightarrow \text{LP}}^{\text{ion}} = \Delta G_{\text{hydr}}^{\text{ion (LP)}} - \Delta G_{\text{hydr}}^{\text{ion (Bulk)}}$. Cycle (b) shows the free-energy change for transferring an ion from a large pore (LP) to a small pore (SP) is given by $\Delta G_{\text{LP} \rightarrow \text{SP}}^{\text{ion}} = \Delta G_{\text{hydr}}^{\text{ion (SP)}} - \Delta G_{\text{hydr}}^{\text{ion (LP)}}$. In all panels, species (either the ion or framework components) shown in gray do not interact with their surrounding environment.

ion uptake and selectivity. Given its relevance for selective extraction from dilute solutions, the following analyses focus on Li^+ , while results for Na^+ and K^+ , which show similar changes from bulk to confined environments, are presented in Figure 4.10 and Figure 4.11 in the Appendix, respectively. The radial distribution functions (RDFs) between Li^+ and water oxygen atoms (Figure 4.3a) reveal a more pronounced first peak under confinement, indicating a tighter first hydration shell within the LP compared to bulk water. This suggests a higher probability of water molecules residing in close proximity to Li^+ inside the LP of MOF-808. Notably, the position of the first peak remains unchanged across both environments, implying that confinement primarily influences the local structuring of water around Li^+ without significantly altering the average ion–water distance. These structural differences influence water dynamics, as reflected in the significantly longer residence time of water molecules around Li^+ in the LP of MOF-808 compared to bulk water (Figure 4.3b). Moreover, water dynamics are significantly slower under confinement, as indicated by the slower decay of the orientational correlation function ($C_2(t)$) for

water molecules in the *LP* of MOF-808 compared to bulk water (Figure 4.3c). This slowdown is primarily due to water molecules near the pore surface, where interactions with the framework restrict molecular motion, consistent with previous findings.⁵⁵ While the hydration structures and dynamics around Li^+ , Na^+ , and K^+ remain distinct under confinement, we found that the magnitude of change from bulk water to the *LP* environment is comparable for all three ions. This observation is consistent with the similar values of $\Delta G_{\text{Bulk} \rightarrow \text{LP}}^{\text{ion}}$ across the series, underscoring the dominant influence of confinement effects. Further differences arise in the spatial arrangement of water molecules, as captured by the tetrahedral order parameter (q_{tet}) distributions in both environments (Figure 4.3d). Within an *LP* of MOF-808, the q_{tet} distribution exhibits two distinct peaks: the peak at $q \sim 0.75$, similar to the main peak in bulk water, corresponds to water molecules near the center of the *LP*, where they retain a tetrahedral-like arrangement akin to that in bulk water. In contrast, the peak at $q \sim 0.50$ corresponds to water molecules near the framework, where interactions with the surface disrupt the hydrogen-bond network, leading to a more disordered local structure compared to bulk water.

To determine the driving forces underlying the thermodynamic preference of alkali metal ions for the *LPs* of MOF-808 compared to bulk water, additional hydration free-energy calculations were performed. In particular, to disentangle the contributions of ion–water interactions from those of ion–framework interactions, all direct interactions between the ions and the framework (both van der Waals and electrostatic) were explicitly removed in these calculations. Notably, the hydration free energies remain virtually unchanged (Table 4.7) compared to cases where all ion–framework interactions are present, indicating that MOF-808 does not provide strong binding sites for alkali metal ions. This finding, consistent with previously reported ordered water structures in confined environments,^{55,56} confirms that the observed thermodynamic preference of alkali metal ions within the *LP* arises primarily from the unique water organization and structural ordering induced by confinement, rather than direct ion–framework interactions.

Using the thermodynamic cycle (b) illustrated in Figure 4.2, we then calculated the free-energy change associated with ion transfer from an *LP* to an *SP* ($\Delta G_{\text{LP} \rightarrow \text{SP}}$). To account

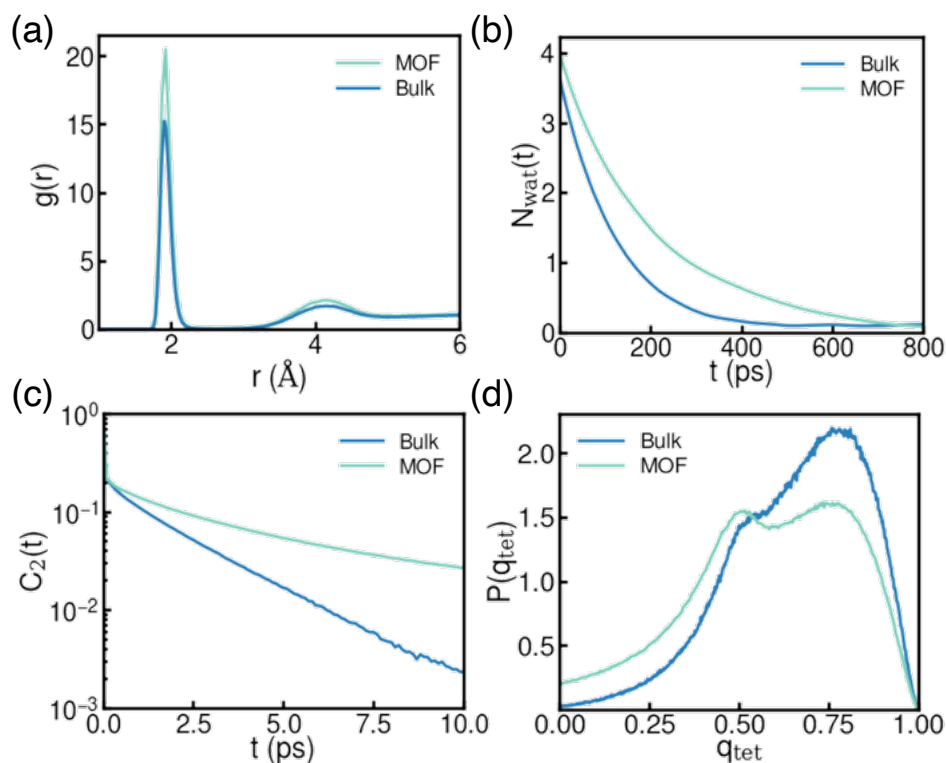


Figure 4.3. Structural and dynamical properties of water molecules with Li^+ ion in bulk water (Bulk) and confined within the *LP* of MOF-808 (MOF). (a) Radial distribution function describing the spatial correlation between Li^+ and water oxygen atoms; (b) Time evolution of the number of water molecules that remain in the first hydration shell, considering those initially present at time zero; (c) Water orientational correlation function; (d) Probability distribution of the tetrahedral order parameter. See Appendix A for additional details on the calculations of these properties.

for variations in local environments, we examined multiple scenarios differing in both the number of water molecules present within the *SP* and the extent of ion hydration, i.e., the coordination number of ions with surrounding water molecules (specific details are reported Table 4.7 in the Appendix). In the following analyses, we focus on two representative cases: the completely dehydrated *SP* and the most thermodynamically stable hydrated *SP*. As shown in Figure 4.4a, distinct trends emerge in $\Delta G_{LP \rightarrow SP}$ for ions transferring from a fully hydrated *LP* to a dehydrated *SP*. The observed trend $-\text{Li}^+ < \text{Na}^+ < \text{K}^+$ – indicates that K^+ exhibits the greatest thermodynamic stability within a dehydrated *SP*, likely due to the closer match between the ionic radius of K^+ and the size of the *SP*, thereby promoting stronger ion–framework interactions

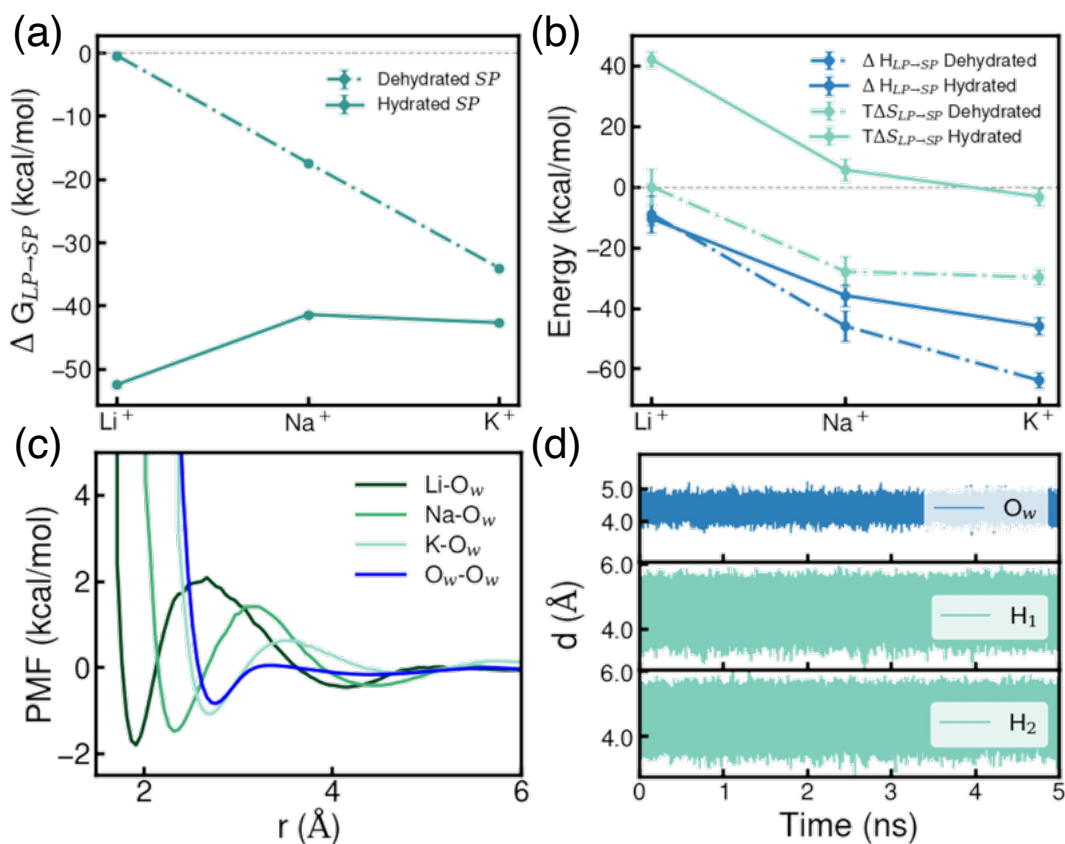


Figure 4.4. (a) Free-energy change ($\Delta G_{LP \rightarrow SP}$) for the transfer of a single Li^+ , Na^+ , and K^+ ion from an LP to an SP. (b) Decomposition of $\Delta G_{LP \rightarrow SP}$ into enthalpic ($\Delta H_{LP \rightarrow SP}$) and entropic ($T\Delta S_{LP \rightarrow SP}$) contributions for both dehydrated and hydrated SP. (c) Potential of mean force (PMF) profiles for ion–water and water–water interactions in the LP calculated using Li-O_w , Na-O_w , K-O_w and $\text{O}_w\text{-O}_w$ distances as collective variables, respectively. Here, O_w refers to the oxygen atoms of any water molecule. (d) Time evolution of the oxygen and hydrogen distances of a water molecules within an SP containing a Li^+ relative to a carbon atom of a BTC benzene ring.

compared to Li^+ and Na^+ . These findings suggest that designing MOF pore structures with dimensions that more closely match the size of Li^+ could enhance both the uptake capacity and selectivity for Li^+ over larger ions. In contrast, within a hydrated SP, the trend is effectively reversed – $\text{Li}^+ > \text{Na}^+ \approx \text{K}^+$ – indicating that Li^+ is the most thermodynamically stable in this environment. This stability arises from its strong hydration shell and the favorable ion–water interactions facilitated by the confined space of the SP.

To further elucidate these trends, $\Delta G_{LP \rightarrow SP}$ was decomposed into enthalpic (ΔH) and

entropic ($T\Delta S$) contributions, following the procedure detailed in Appendix A. As shown in Figure 4.4b, for a dehydrated *SP*, the process is primarily enthalpically driven, with K^+ exhibiting the most negative enthalpy change. This stabilization arises from the favorable size of K^+ relative to the dehydrated *SP*, which enables optimal interactions with the benzene rings of the BTC linker while allowing the ion to remain centrally positioned within the pore—a point further explored in the following section. For a hydrated *SP*, although the enthalpic trend remains similar, the entropic contribution becomes more pronounced, ultimately reversing the free-energy trend as shown in Figure 4.4a.

The transfer of an ion from an *LP* to an *SP* is generally accompanied by a decrease in entropy (ΔS) from the perspective of the ion, as its translational mobility is reduced within the confined environment of the *SP*. This effect is evident from the diffusion coefficients of ions in different environments, as reported in Table 4.10. To better understand the overall entropic trend, we examined the behavior of each ion within a dehydrated *SP*. The observed decrease in ΔS from Li^+ to Na^+ to K^+ (Figure 4.4b) can be attributed to each ion's ability to structure surrounding water molecules within the *LP*. The potential of mean force (PMF) profiles shown in Figure 4.4c, constructed using ion–water distances as collective variables, reveal that the energy barriers for removing a water molecule from the ion's first hydration shell follow the order $Li^+ > Na^+ > K^+$. This trend is further supported by the analysis of water residence times in the first shell, which shows that water molecules remain longest in the hydration shell of Li^+ , followed by Na^+ and then K^+ (Table 4.9). For an ion confined within an *SP*, removing a water molecule from the first hydration shell of K^+ requires less energy than for Na^+ or Li^+ , highlighting the weaker ion–water interaction for the larger ion.^{57,58} As a result, Li^+ exhibits the most ordered first hydration shell, followed by Na^+ and K^+ . When an ion transitions from a fully hydrated *LP* to a dehydrated *SP*, this structured hydration environment is disrupted, leading to an entropy increase for water molecules remaining in the *LP*. This disruption creates a subtle competition between the entropy gain of water molecules and the entropy loss of the ion itself. For Li^+ , these two effects nearly cancel each other out, resulting in $\Delta S \approx 0$. In contrast, for Na^+ and K^+ , the

loss of ion entropy becomes increasingly dominant, leading to progressively more negative ΔS values, as illustrated in Figure 4.4b.

In contrast, the transfer of each alkali metal ion from a fully hydrated *LP* to a fully hydrated *SP* is associated with a positive shift in $T\Delta S$, as shown in Figure 4.4b. This entropic gain can be attributed to the rotational degrees of freedom of water molecules confined within the *SP*. Figure 4.4d shows the time evolution of distances between water oxygen and hydrogen atoms relative to a reference atom in the SBU for Li^+ . Analogous plots for Na^+ and K^+ are provided in Figure 4.13 in the Appendix. These results demonstrate that while water molecules maintain relatively fixed spatial positions within the *SP*, they retain rotational freedom, contributing to an increase in rotational entropy, which is absent in a dehydrated *SP*. This gain in rotational entropy leads to a comparable positive shift in $T\Delta S$ for both Li^+ and Na^+ , each of which accommodates four water molecules within a hydrated *SP*. The smaller shift observed for K^+ , which accommodates only three water molecules in its most stable hydrated structure (Table 4.7), further supports this interpretation, highlighting the role of hydration shell size in modulating entropic contributions.

4.2.2 Thermodynamics of Ion Uptake: From Large to Small Pores

Beyond hydration free-energy calculations, which determine the relative preference of alkali metal ions for different environments (i.e., bulk water and MOF-808 confinement within *LPs* and *SPs*), we investigated the free-energy profiles associated with the transport of water molecules and alkali metal ions from an *LP* to an *SP*. The activation behavior of single-ion transport through confined pores is primarily dictated by ion dehydration and closely follows hydration energy trends.^{37,38,40,41} However, a detailed molecular-level understanding of the mechanisms governing this process remains incomplete. To address this gap in the case of MOF-808, we employed enhanced sampling simulations to compute the free-energy changes experienced by water molecules and alkali metal ions along a chosen collective coordinate (ξ), offering mechanistic insights into the transport pathways and energy barriers involved (further

details are provided in Section 9 in the Appendix).

Although porous materials immersed in aqueous environments typically reach equilibrium with water occupying their pores, this assumes that water infiltration is both thermodynamically favorable and kinetically accessible. In MOF-808, the *LPs* (diameter ~ 18.4 Å) are sufficiently open to allow rapid hydration, and our study assumes that these *LPs* are fully hydrated. However, the *SPs* (diameter ~ 4.8 Å) are connected to the *LPs* via narrow windows (~ 4 Å wide, see Table 4.12), which can impose significant steric and energetic barriers, particularly for water molecules. Moreover, under confinement, the thermodynamic preference for ion and water uptake may differ drastically between hydrated and dehydrated environments. To explore these effects, we investigated the free-energy profiles for the stepwise transfer of water molecules and alkali metal ions from a fully hydrated *LP* into a fully dehydrated *SP*. This approach allowed us to systematically probe the differences in thermodynamic and kinetic barriers during early-stage pore filling, prior to the establishment of equilibrium.

Given the large excess of water molecules in dilute aqueous solutions, we first evaluated the PMF for a single water molecule entering a dehydrated *SP* from a fully hydrated *LP*. As shown in Figure 4.5 (and further supported by Figure 4.15 and Figure 4.16 in the Appendix), the PMF profile indicates a slight thermodynamic preference for a water molecule to enter a dehydrated *SP* from a fully hydrated *LP*, with $\Delta G_{LP \rightarrow SP}$ being marginally negative. However, this process is hindered by a high energy barrier – exceeding 26 kcal/mol – located near the window along the path connecting an *LP* and an *SP*, indicating that the transfer is kinetically slow. This barrier arises from a combination of steric hindrance and dehydration effects, as the narrow pore window restricts water transport. Further analyses demonstrate that the insertion of a second water molecule into an *SP* already occupied by a water molecule becomes thermodynamically unfavorable (Figure 4.15 and Figure 4.16), due to the inability of the second water molecule to have optimal interactions with both the first water molecule and the benzene rings of the BTC linkers. It should be noted that, as shown in Figure 4.15 and Figure 4.16, the PMFs for the transfer of water molecules from an *LP* to an *SP*, which were obtained from simulations of a

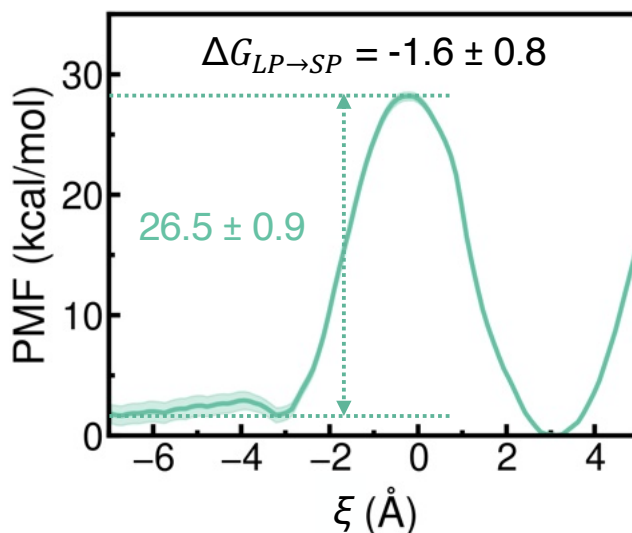


Figure 4.5. Potential of mean force (PMF) for a water molecule transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ). Statistical errors were calculated as 95% confidence intervals and are shown as a colored shaded area. See Appendix A for additional details.

single alkali metal ion in MOF-808 performed with the TIP4P-Ew water model⁵⁹ and associated models for ions in water,⁶⁰ are independent of the presence of the ion, the type of the ion, and the presence of a counterion. Importantly, Figure 4.16 demonstrates that these PMFs are also in qualitative agreement with those obtained from simulations performed with the more realistic MB-pol^{61–65} data-driven many-body potential.

Since the first water molecule encounters a significant free-energy barrier when entering a dehydrated *SP*, we subsequently investigated the PMFs associated with transferring a single Li^+ , Na^+ , or K^+ ion from a fully hydrated *LP* into a dehydrated *SP*. These simulations build on previous findings that ions permeate through porous materials independently.⁶⁶ By comparing the free-energy landscapes of water and ion transfer into dehydrated *SP*s, we assess which species is more kinetically and thermodynamically favored during the initial stages of uptake. To complement this analysis, we also monitored changes in the coordination number (CN) of each ion, enabling us to quantify the extent of ion dehydration along the transport pathway — a process that remains challenging to characterize experimentally.

As shown in Figure 4.6, the PMFs indicate that the transfer of an alkali metal ion into

a dehydrated *SP* is generally favorable. However, distinct differences are apparent in the PMF profiles for Li^+ , Na^+ , and K^+ . Specifically, the PMF for Li^+ displays the highest energy barrier and the steepest profile, followed by Na^+ and then K^+ , indicating progressively easier ion transfer as the ionic radius increases. Additionally, due to its smaller ionic size, Li^+ preferentially localizes near the vertices of the tetrahedral *SP*, corresponding to two distinct free-energy wells along the PMF ($\xi \approx 1 \text{ \AA}$ and $\xi \approx 5 \text{ \AA}$, respectively). In contrast, the larger Na^+ and K^+ ions exhibit a single free-energy minimum near the center of the tetrahedral *SP* ($\xi \approx 3 \text{ \AA}$), reflecting their size matching with the *SP* dimensions. The free-energy well for Na^+ is notably broader than that for K^+ , suggesting increased rattling of Na^+ within the dehydrated *SP*, consistent with the RDF analysis presented in Figure 4.12 in the Appendix.

In all cases, the free-energy barriers are located near the window along the path connecting an *LP* to an *SP*, consistent with observations for ion transport through model pores.^{37,38,40,67} As highlighted by the gray-shaded region in Figure 4.6a, these energy barriers arise before dehydration of the first hydration shell. This early onset of barriers may result from the reorientation or partial loss of outer hydration shells, as suggested in previous studies.⁴⁰ We note that the energy barriers associated with entry into the *SP* are largely due to the dehydration energy penalty and potentially the structural constraint of opening the narrow window through which ions pass. In contrast to the three-stage model of ion transport proposed in Ref. 66 – comprising dehydration, stabilization, and diffusion – our analyses of ion transfer from a hydrated *LP* to a dehydrated *SP* of MOF-808 show no clear separation between dehydration and stabilization stages. Instead, these processes appear convoluted and overlapping. First, as shown in Figure 6, the PMF begins to decrease while dehydration is still ongoing, indicating that ion–framework interactions begin to stabilize the ion even before full dehydration. These interactions arise from favorable electrostatic interactions between the ions and the negatively charged aromatic carbon atoms of the BTC linkers near the window. Second, although the ions undergo complete dehydration ($\text{CN} = 0$), the associated free-energy barriers are significantly lower than their corresponding dehydration energies, which range from approximately 70 kcal/mol for K^+ to

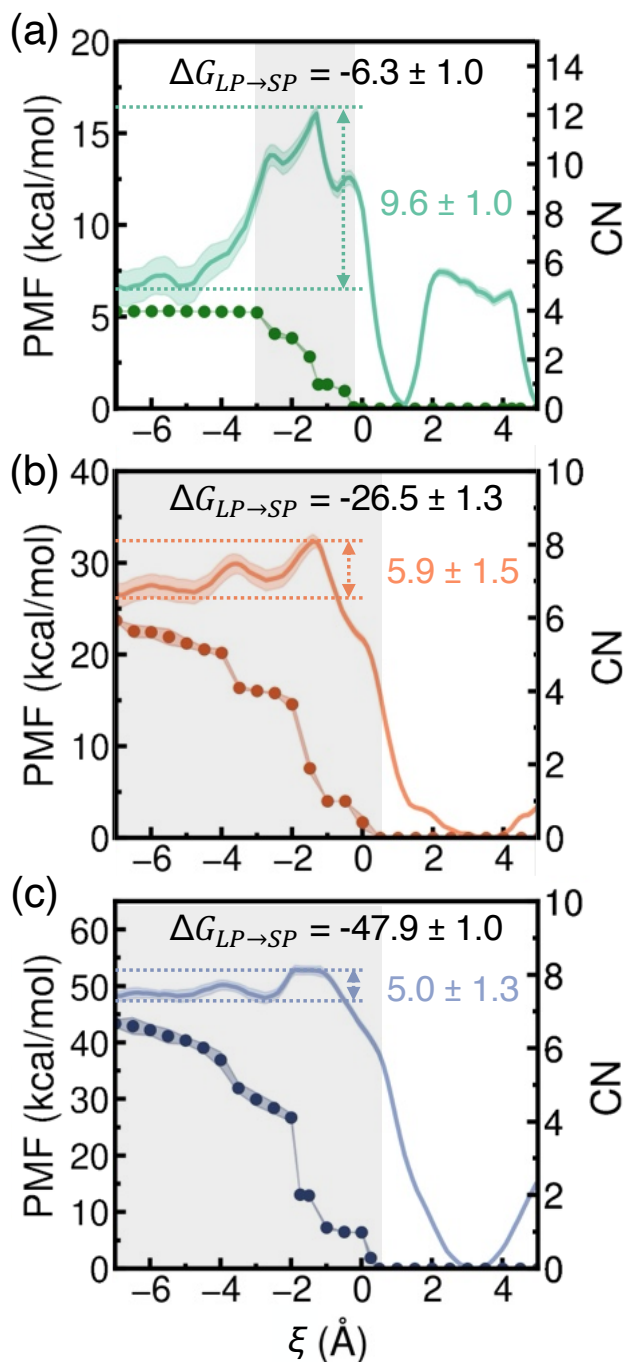


Figure 4.6. Potentials of mean force (PMFs) (solid lines, left y-axis) and corresponding coordination numbers (CNs) (filled circles, right y-axis) for a single Li^+ (a), Na^+ (b), and K^+ (c) ion transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ). Statistical errors were calculated as 95% confidence intervals and are shown as colored shaded areas. The regions of first-shell dehydration are shown as gray-shaded areas.

120 kcal/mol for Li^+ .^{41,68,69} This finding indicates that ion–framework interactions play an important role in stabilizing the ion during dehydration. The computed free-energy barriers for Na^+ and K^+ are consistent with previous studies (7–10 kcal/mol).^{41,66} However, earlier investigations did not characterize the corresponding hydration states. It should also be noted that both energy barriers and hydration states depend on the specific ion type and the nature of the porous material. After full dehydration, the PMF continues to decrease, indicating further stabilization due to ion–framework interactions. Specifically, as shown by the RDF results in the middle column of Figure 4.12, Li^+ , due to its small ionic size, is able to position near the vertices of the tetrahedral *SP*, where it is stabilized by electrostatic interactions with the oxygen atoms of the SBUs and carboxylate groups of the BTC linkers. In contrast, Na^+ and K^+ tend to localize near the center of the *SP*, where stabilization is primarily mediated by cation– π interactions with the aromatic carbon atoms of the BTC linkers. While further investigations into the influence of formate ligands and structural defects on ion transport would be highly valuable, we note that the formate ligands are not directly positioned along the transport pathway considered in this study, suggesting that their effects would be primarily indirect. Consistent with previous studies,⁴¹ the energy barriers for ion transfer from a hydrated *LP* to a dehydrated *SP* in MOF-808 follow the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, reflecting the trend in ion size and hydration strength. In contrast, the barriers for ion exit from a dehydrated *SP* follow the reverse order: Li^+ (15.9 kcal/mol) $<$ Na^+ (32.3 kcal/mol) $<$ K^+ (52.8 kcal/mol), providing further evidence that K^+ experiences stronger stabilization within a dehydrated *SP* due to favorable interactions with the *SP*, compared to being fully hydrated in the *LP*.

Based on the analysis of $\Delta G_{LP \rightarrow SP}$, the propensity of an ion to enter a dehydrated *SP* from a hydrated *LP* follows the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$. These results are consistent with findings for ion-exchange membranes, which show that ions with lower hydration free energies are adsorbed more readily.⁴¹ In MOF-808, this trend arises from the interplay between ion–water and ion–framework interactions, which are influenced by the ion’s size and corresponding charge density. As shown in Table 4.12 in the Appendix, the uptake of a single Li^+ , Na^+ , or K^+ ion

in a dehydrated *SP* does not appreciably change its size. The same trends and similar PMF features were observed with the more realistic MB-pol^{61–65} and MB-nrg^{57,58,70–73} data-driven many-body potentials for water and alkali metal ions (Figure 4.17 in Appendix B), though with consistently higher energy barriers for entering a dehydrated *SP*. It has been established that these differences are due to the inability of empirical force fields like TIP4P-Ew⁵⁹ and associated ion–water⁶⁰ models to quantitatively capture many-body effects in water⁷⁴ as well as alkali metal ion hydration.^{57,58,70–73} Overall, our simulations indicate that Li^+ , Na^+ , and K^+ ions face relatively low free-energy barriers when transitioning from a hydrated *LP* to a dehydrated *SP* – significantly lower than those predicted for water molecules – suggesting that ion uptake into a dehydrated *SP* occurs at a higher rate than water uptake. Moreover, the more negative $\Delta G_{LP \rightarrow SP}$ values for ions compared to water molecules suggest a stronger thermodynamic driving force for ion entry into a dehydrated *SP*.

Building on the process where a single ion transfers from a hydrated *LP* into a dehydrated *SP*, we next examined the PMF associated with a water molecule entering an *SP* that already contains one ion. As shown in Figure 4.7, the presence of the ion enhances the thermodynamic driving force for water uptake, making it more favorable for a water molecule to enter compared to the case of a dehydrated *SP* (Figure 4.5). Two key trends emerge when comparing Li^+ , Na^+ , and K^+ . First, the free-energy barriers for water entry into the *SP* are similar for Li^+ and Na^+ (~ 24 kcal/mol) but rise significantly for K^+ (32.7 kcal/mol). This suggests that accommodating K^+ imposes greater structural constraints within the *SP* due to its larger ionic size, making it more challenging to open the window between the *LP* and *SP* compared to the smaller alkali metal ions. This trend reflects the influence of ion–framework interactions within the *SP* environment and mirrors the barrier pattern observed in Figure 4.6 for ion exit from the *SP*. Second, the free-energy barriers for water molecules to exit the *SP* systematically decrease from Li^+ to Na^+ to K^+ . This trend arises from the combined effects of water–ion interactions within the *SP* and the increasing size of the confined ion, which modulates the structural stability and hydration dynamics of the surrounding water molecules.

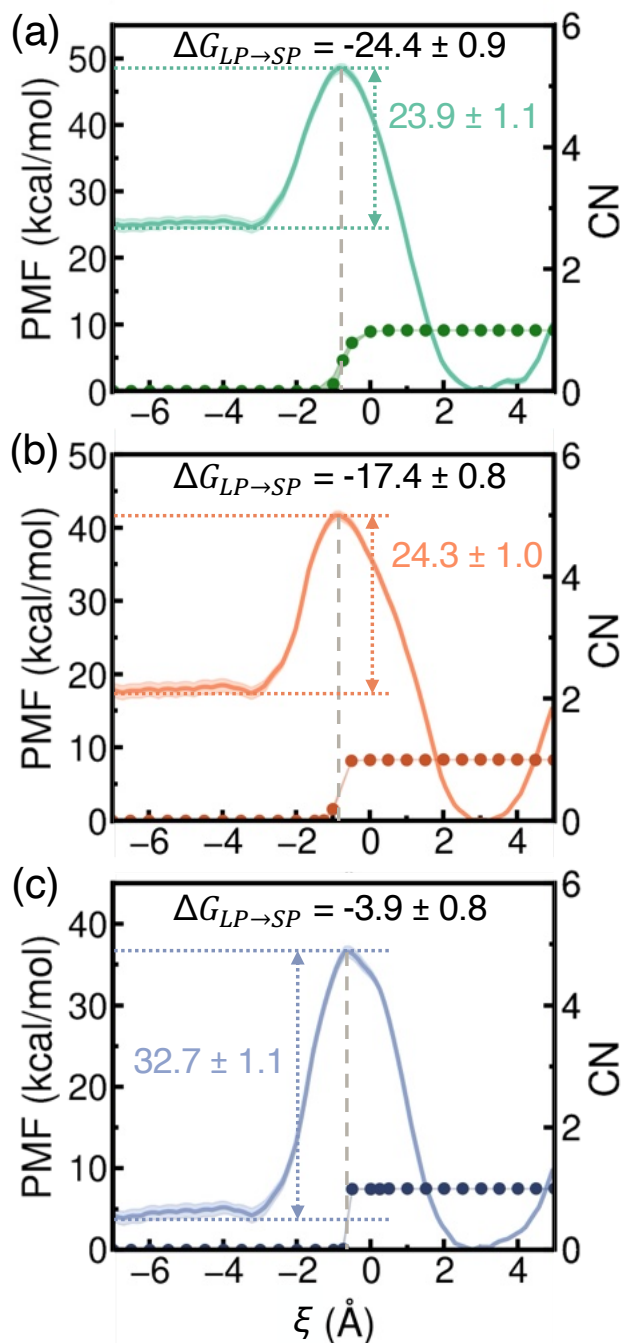


Figure 4.7. Potentials of mean force (PMFs) (solid lines, left y-axis) for a water molecule transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ) containing a single Li^+ (a), Na^+ (b), and K^+ (c) ion. Statistical errors were calculated as 95% confidence intervals and are shown as colored shaded areas. Also shown are the ion's coordination numbers (CNs) (filled circles, right y-axis) within the *SP*. The gray dashed lines indicate the positions of the corresponding PMF maxima.

Our simulations predict that the propensity of a water molecule to enter an *SP* already containing a single ion follows the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. This trend is primarily governed by ion–water interactions and the confined environment within the *SP*. As shown in Figure 4.7, the peak of each PMF curve (marked by the gray dashed line) consistently aligns with the hydration state of the alkali metal ion inside the *SP*. Once hydration occurs, the free energy decreases, suggesting stabilization driven by water–framework and water–ion interactions. Despite this stabilization, the free-energy barriers for water entry into an ion-occupied *SP* remain high, exceeding 23 kcal/mol. Consistent with the analyses reported in Figures 4.5 and 4.6, the same trends and similar features are observed in analogous PMFs calculated from simulations carried out with the more realistic MB-pol^{61–65} and MB-nrg^{57,58,70–73} data-driven many-body potentials for water and alkali metal ions, respectively (Figure 4.18 in Appendix B). However, the MB-pol and MB-nrg potentials systematically predict higher energy barriers for water entry into the *SP*, likely due to a more quantitative description of many-body interactions.⁷⁴

4.3 Conclusions

Through free-energy calculations and enhanced sampling simulations, we have provided a detailed molecular-level characterization of alkali metal ion uptake in MOF-808 from dilute aqueous solutions. Our findings indicate that while the large pores of MOF-808 provide a similarly favorable environment for different ions, the small pores exhibit distinct thermodynamic and kinetic properties that influence ion selectivity. Specifically, dehydrated ions are stable within the small pores. Further hydration – although thermodynamically favorable – requires water molecules to overcome significant energy barriers to transfer from the large to the small pores.

Based on systematic thermodynamic analyses, all the alkali metal ions considered in this study are predicted to face lower energy barriers for entering the small pores of MOF-808 than water molecules, indicating that ion uptake occurs at a higher rate than water uptake. Among these ions, Li^+ faces the highest energy barrier due to its strong hydration shell, whereas K^+

shows the greatest thermodynamic propensity for uptake into the small pores in its dehydrated state. However, within hydrated small pores, Li^+ becomes the most thermodynamically stable among the alkali metal ions studied, illustrating a strong interplay between hydration structure and confinement effects. Specifically, when the *SP* is dehydrated, uptake is driven by size compatibility and ion–framework interactions, favoring larger ions such as K^+ . In contrast, in the hydrated *SP*, strong ion–water interactions and enhanced rotational entropy of water molecules favor Li^+ uptake. This reversal in thermodynamic preference underscores the importance of the local hydration environment in modulating confinement effects.

The insights gained from this study underscore the critical role of ion dehydration, ion–water interactions, and ion–framework interactions in governing ion uptake mechanisms in MOFs. These findings provide fundamental guidance for the design and optimization of MOFs with enhanced selectivity for metal ion extraction from seawater. Future studies should explore tailored functionalization strategies, such as modifying pore chemistry to introduce selective binding sites or optimizing pore size to enhance confinement effects for target ions, such as Li^+ . Several experimental efforts have demonstrated that incorporating functional groups, such as carboxyl or amino groups, into MOF linkers can significantly enhance uptake capacity for multivalent ions.^{24,43} More recently, high Li^+ uptake with notable $\text{Li}^+/\text{Mg}^{2+}$ selectivity has been achieved by integrating ion-specific adsorption motifs into MOFs with suitably narrow pore windows.⁵⁴ Additionally, incorporating many-body effects into computational models of water–framework and ion–framework interactions could further refine the description of ion behavior in MOFs at the molecular level.

4.4 Conflicts of Interest

There are no conflicts to declare.

4.5 Data Availability

All data, along with the molecular dynamics trajectories, are available from the authors upon request.

4.6 Acknowledgements

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Chapter 4, in full, has been submitted for publication of the material as it may appear in *Chem. Sci.* as “Thermodynamics of alkali metal ion uptake from aqueous solution in MOF-808”, Y. Pan, S. Saha, M. Burigana, V. Singh, O. Yaghi, and F. Paesani, 2025. The dissertation author was the primary investigator and author of this paper.

Appendix A: Supplementary Methods

Models and Molecular Dynamics Simulations

Force Field for MOF-808

The flexible force field used for MOF-808 in this study is based on our previous work.⁷⁵ The corresponding structures for the SBU and the benzene-1,3,5-tricarboxylate (BTC) organic linker, along with the atom types adopted in the force field, are shown in Figure 4.8. The oxygen atoms in the carboxylate groups in the BTC linkers belong to “o1” type. It is noteworthy to mention that multiple reference angles for the O–Zr–O angles (if present) among the same specific atom types are taken into account during the re-fitting process using the genetic algorithm,^{76,77} considering the specific bonding pattern of Zr and O in the SBU. Further details can be found below in Table 4.3.

A complete list of force field parameters developed for MOF-808 in this work is reported in Tables 4.1–4.5.

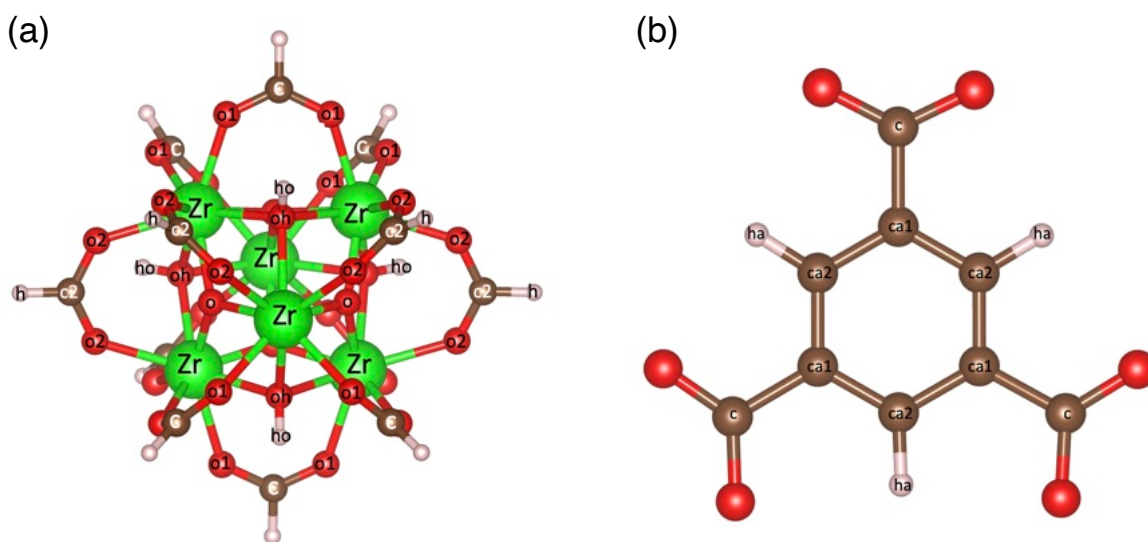


Figure 4.8. Structural illustration of the MOF-808 (a) SBU and (b) benzene-1,3,5-tricarboxylate (BTC) organic linker with specific atom types used for force field parameters indicated. Color scheme: Zr = green, O = red, C = brown, H = white. Figures are adapted from Ref. 75.

Non-bonded Interactions

The interactions between MOF-808 and guest species (i.e., water and ions), as well as among the guest species, were described by Coulomb and van der Waals interactions, with the latter represented by Lennard-Jones (LJ) potentials. The water molecules are described by the TIP4P-Ew model,⁵⁹ while the LJ parameters for the metal ions are obtained from those optimized for the TIP4P-Ew water model, as reported in Ref. 60. The cross LJ terms were calculated using the Lorentz–Berthelot mixing rules.⁷⁸

We also performed simulations using the more realistic MB-pol^{61–65} as well as the MB-nrg^{57,58,70–73} data-driven many-body potentials for water and alkali metal ions, respectively, as implemented in MBX.^{79,80} To describe the framework–water interactions in these simulations, we used the effective LJ parameters for the oxygen and hydrogen atoms recommended in Ref. 79: $\sigma_{\text{O}}=3.26393$ Å, $\epsilon_{\text{O}}=0.26948$ kcal/mol, $\sigma_{\text{H}}=2.68354$ Å, and $\epsilon_{\text{H}}=3.7 \times 10^{-10}$ kcal/mol. The effective LJ parameters for the alkali metal ions were obtained from fits to ion–dimer scans calculated using corresponding MB-nrg potentials: $\sigma_{\text{Li}}=1.70872$ Å, $\epsilon_{\text{Li}}=0.04945$ kcal/mol, $\sigma_{\text{Na}}=2.25973$ Å, $\epsilon_{\text{Na}}=0.16504$ kcal/mol, $\sigma_{\text{K}}=2.96667$ Å, and $\epsilon_{\text{K}}=0.40727$ kcal/mol. To use a relatively large time step of 1 fs for the simulations with the MB-pol and MB-nrg potentials, the water molecules were kept fixed at average geometry ($r(\text{O–H})=0.98823$ Å, $\theta(\text{H–O–H})=105.50896^\circ$) obtained from path-integral molecular dynamics (PIMD) simulations carried out for bulk water in the isothermal-isobaric (*NPT*: constant number of particles, pressure, and temperature) at 298 K and 1 atm.⁶³

Table 4.1. Partial charge and Lennard-Jones parameters.

Atom name	Atom type	Charge	ϵ (kcal · mol ⁻¹)	$\sigma/2$ (Å)
Zr	Zr	1.565694	0.069000	1.391500
c	c	0.143236	0.086000	1.700000
c2	c2	0.262510	0.086000	1.700000
ca1	ca	-0.066223	0.086000	1.700000
ca2	ca	-0.127265	0.086000	1.700000
ha	ha	0.061341	0.015000	1.300000
ho	ho	0.335613	0.000000	0.000000
h	h	0.247635	0.015000	1.210700
o1	o1	-0.389495	0.210000	1.480000
o2	o2	-0.260281	0.210000	1.480000
oh	oh	-0.703638	0.210000	1.480000
o	o	-0.813039	0.210000	1.480000

Table 4.2. Bond potentials: $U(r) = \frac{1}{2}K_{ij}(r - r_0)^2$.

Bond type	K_{ij} (kcal · mol ⁻¹ · Å ⁻²)	r_0 (Å)
Zr-o1	151.029	2.428
Zr-o2	151.029	2.428
Zr-oh	150.014	2.328
Zr-o	152.172	2.328
oh-ho	742.800	0.973
c-ca	691.800	1.491
c2-h	639.400	1.105
c-o1	1275.000	1.218
c2-o2	1275.000	1.218
ca-ca	922.200	1.398
ca-ha	691.600	1.086

Table 4.3. Angle bending potentials: $U(\theta) = \frac{1}{2}K_{jik}(\theta - \theta_0)^2$.

Angle type	K_{jik} (kcal · mol ⁻¹ · rad ⁻²)	θ_0 (°)
Zr-o1-c	101.29	123.42
Zr-o2-c2	101.29	123.42
Zr-oh-ho	127.70	95.23
Zr-oh-Zr	112.70	109.52
Zr-o-Zr	103.20	93.90
o1-Zr-o1	104.81	67.06
o2-Zr-o2	104.81	67.06
o1-Zn-o2, 60° < θ < 85°	104.81	67.06
o1-Zn-o2, 105° < θ < 125°	107.85	115.33
o1-Zr-o, 67° < θ < 95°	106.53	67.29
o1-Zr-o, 130° < θ < 155°	103.32	134.72
o2-Zr-o, 67° < θ < 95°	106.53	67.29
o2-Zr-o, 130° < θ < 155°	103.32	134.72
o1-Zr-oh, 67° < θ < 95°	101.25	74.98
o1-Zr-oh, 130° < θ < 155°	100.20	130.04
o2-Zr-oh, 67° < θ < 95°	101.25	74.98
o2-Zr-oh, 130° < θ < 155°	100.20	130.04
o-Zr-oh	100.17	57.33
oh-Zr-oh	100.82	92.91
o-Zr-o	103.18	102.02
c-ca-ca	128.60	120.30
ca-c-o1	137.40	122.60
h-c2-o2	107.40	123.65
ca-ca-ca	133.20	120.00
ca-ca-ha	96.40	119.90
o1-c-o1	155.80	130.20
o2-c2-o2	155.80	130.25

Table 4.4. Dihedral angle potentials: $U(\phi) = K_{ijkl} [1 + \cos(N\phi - \chi)]$.

Dihedral type	K_{ijkl} (kcal · mol ⁻¹)	χ (°)	N
Zr-o2-c2-h	0.0000	0.00	2
Zr-o1-c-ca	0.0000	0.00	2
Zr-o1-c-o1	0.0000	0.00	2
Zr-o2-c2-o2	0.0000	0.00	2
Zr-o-Zr-oh	0.0000	0.00	2
Zr-o-Zr-o	0.0000	0.00	2
Zr-oh-Zr-o	0.0000	0.00	2
Zr-oh-Zr-oh	0.0000	0.00	2
o1-Zr-o1-c	0.0000	0.00	2
o1-Zr-o2-c2	0.0000	0.00	2
o1-Zr-oh-ho	0.0000	0.00	2
o2-Zr-o2-c2	0.0000	0.00	2
o2-Zr-o1-c	0.0000	0.00	2
o2-Zr-oh-ho	0.0000	0.00	2
o1-Zr-o-Zr	0.0000	0.00	2
o2-Zr-o-Zr	0.0000	0.00	2
o1-Zr-oh-Zr	0.0000	0.00	2
o2-Zr-oh-Zr	0.0000	0.00	2
o-Zr-oh-ho	0.0000	0.00	2
oh-Zr-oh-ho	0.0000	0.00	2
o-Zr-o1-c	0.0000	0.00	2
o-Zr-o2-c2	0.0000	0.00	2
oh-Zr-o1-c	0.0000	0.00	2
oh-Zr-o2-c2	0.0000	0.00	2
c-ca-ca-ca	3.6250	180.00	2
c-ca-ca-ha	3.6250	180.00	2
ca-ca-ca-ca	3.6250	180.00	2
ca-ca-ca-ha	3.6250	180.00	2
o1-c-ca-ca	1.0000	180.00	2

Table 4.5. Improper dihedral angle potentials: $U(\phi) = K_{ijkl} [1 + \cos(N\phi - \chi)]$.

Dihedral type	K_{ijkl} (kcal · mol ⁻¹)	χ (°)	N
c-ca-o1-o1	1.1000	180.00	2
ca-c-ca-ca	1.1000	180.00	2
ca-ca-ca-ha	1.1000	180.00	2

Molecular Dynamics Simulations

All molecular dynamics (MD) simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package⁸², which was interfaced with the MBX C++ library^{79,80} for simulations with the MB-pol^{61–65} and MB-nrg^{57,58,70–73} potentials.

MOF-808 was simulated in periodic boundary conditions, considering a $1 \times 1 \times 1$ unit cell. The lattice parameters are listed in Table. 4.6. All properties were calculated from MD simulations performed in the *NPT* ensemble at 298 K and 1 atm. The temperature was controlled *via* Nosé–Hoover thermostat chains⁸³ (length of 4) with a characteristic time of 0.1 ps, while the pressure was controlled *via* Nosé–Hoover thermostat chains on barostat (length of 3) with a characteristic time of 1 ps. The equations of motion were propagated according to the velocity-Verlet algorithm, using a time step of 1 fs.^{84,85} In the simulations with the TIP4P-Ew water model⁵⁹ and associated models for ions in water,⁶⁰ the non-bonded interactions were treated using a cutoff distance of 12 Å and 10 Å for the LJ and Coulomb interactions,

Table 4.6. Comparison of experimental (measured at 100.15 K) and simulated lattice parameters with 95% confidence interval (*NPT* at 100.15 K).

	Experiment ^{48,81}	Simulation
a (Å)	35.0764(10)	35.0803 ± 0.0001
b (Å)	35.0764(10)	35.0803 ± 0.0001
c (Å)	35.0764(10)	35.0803 ± 0.0001
α (°)	90	90
β (°)	90	90
γ (°)	90	90

respectively. The long-range Coulomb interactions were treated by the particle-particle-particle mesh method,⁸⁶ as implemented in LAMMPS. In the simulations with the MB-pol and MB-nrg potentials, the LJ and Coulomb cutoffs were both set to 9 Å, with the long-range interactions treated by the particle mesh Ewald method⁸⁷ as implemented in MBX.^{79,80}

To determine the number of water molecules in the MOF-808 pores under equilibrium conditions, we calculated the volume of the MOF-808 available to water (31,110.21 Å³) using the Materials Studio package.^{88,89} Assuming the same density as in bulk water (0.997 g/cm³), we estimated that ~1,040 water molecules are present in a unit cell of MOF-808.

The initial configurations of both water molecules and ions inside the MOF-808 model were generated using PACKMOL.^{90,91} For each system, the positions of the water molecules and ions were further randomized *via* a three-step process, using the TIP4P-Ew model. The process includes sequential *NPT* simulations at 1000 K (20 ps), 500 K (20 ps), and 298 K (100 ps). Simulations with the MB-pol and MB-nrg potentials were started from the corresponding equilibrated configurations obtained from simulations with the TIP4P-Ew water model and associated models for ions in water, followed by further equilibration in the *NPT* ensemble for 100 ps. The potentials of mean force (PMFs) were calculated from 1-2 ns-long *NPT* simulations thereafter, with the length of trajectories dependent on the requirement to achieve desired convergence on PMF curves.

Hydration Free Energies

All hydration free-energy calculations were performed using the free-energy perturbation (FEP) package of LAMMPS,⁸² patched with PLUMED.⁹² The `fix adapt/fep` and `compute fep` commands in LAMMPS were used to calculate the hydration free energies using the finite difference thermodynamic integration (FDTI) method.⁹³ The FDTI method combines the FEP⁹⁴ and thermodynamic integration (TI)⁹⁵ methods. A brief description of the FDTI method is provided below.

Consider the change in Helmholtz free energy (A) as a function of an order parameter λ ,

where $\lambda = 0$ corresponds to state A and $\lambda = 1$ corresponds to state B. The change in free-energy can be expressed as:

$$\Delta A_{A \rightarrow B} = \int_0^1 \left(\frac{\partial A}{\partial \lambda} \right) d\lambda \quad (\text{A1})$$

For a small perturbation δ , this equation can be rewritten as:

$$\Delta A_{A \rightarrow B} = \frac{1}{\delta} \int_0^1 (A(\lambda + \delta) - A(\lambda)) d\lambda = \frac{1}{\delta} \int_0^1 \Delta A_{\lambda \rightarrow \lambda + \delta} d\lambda \quad (\text{A2})$$

From FEP, it is known that:

$$\Delta A_{A \rightarrow B} = -\frac{1}{\beta} \ln \left\langle e^{-\beta(U_B - U_A)} \right\rangle_A \quad (\text{A3})$$

where $\langle \dots \rangle_\lambda$ represents the ensemble average over λ . Combining the above equations leads to:

$$\Delta A_{A \rightarrow B} = -\frac{1}{\beta \delta} \int_0^1 \ln \left\langle e^{-\beta[U(\lambda + \delta) - U(\lambda)]} \right\rangle_\lambda d\lambda \quad (\text{A4})$$

For the *NPT* ensemble, this equation can be rewritten as⁹⁶:

$$\Delta G_{A \rightarrow B} = -\frac{1}{\beta \delta} \int_0^1 \frac{\ln \left\langle V \cdot e^{-\beta[U(\lambda + \delta) - U(\lambda)]} \right\rangle_\lambda}{\langle V \rangle_\lambda} d\lambda \quad (\text{A5})$$

Numerical integration is performed to obtain the ΔG . The value of δ was set to 0.002 and the λ values were chosen based on the simulation step, as described below.

VdW-Recharge Method

The alchemical transformation was performed in two steps^{97–99}: **vdW**: van der Waals interactions were changed, followed by **recharge**: Coulomb interactions were changed. For the vdW step, 11 λ points (0.0, 0.1, 0.2, ..., 1.0) were used, and for the recharge step, 6 λ points

(0.0, 0.2, 0.4, ..., 1.0) were used. To avoid endpoint catastrophe¹⁰⁰, softcore potentials¹⁰¹ were employed.

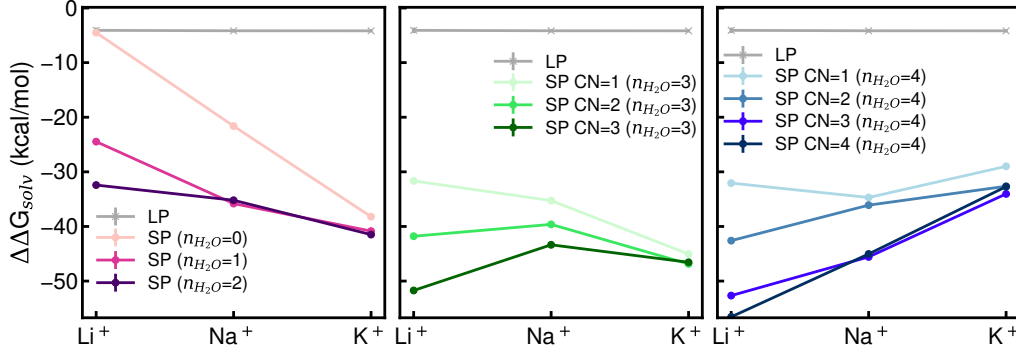


Figure 4.9. Comparison of the change in Gibbs free energy of hydration ($\Delta\Delta G_{\text{solv}}$), taking the $\Delta G_{\text{solv}}^{\text{bulk}}$ as a reference, for different ions (Li^+ , Na^+ , and K^+) in various pore environments. The environments include large (*LP*) and small (*SP*) pores with different numbers of water molecules ($n_{\text{H}_2\text{O}}$) along with coordination numbers $\text{CN} = 1, 2, 3$, and 4. Error bars represent the 95% confidence interval.

Coordination Number

In order to model various environments for a single ion within a small pore, the definition of the collective variable was implemented using the COORDINATIONNUMBER in PLUMED,⁹² following the method described in Ref. 102. The coordination number, CN, was calculated using the following equation:

$$\text{CN} = \frac{1 - \left(\frac{r+0.22}{r_0} \right)^{22}}{1 - \left(\frac{r+0.22}{r_0} \right)^{88}} \quad (\text{A6})$$

Where r_0 is derived from the radial distribution function (RDF) and represents the first hydration shell boundary ($r_0 = 2.70 \text{ \AA}$ for Li^+ , $r_0 = 3.18 \text{ \AA}$ for Na^+ , and $r_0 = 3.53 \text{ \AA}$ for K^+), a harmonic potential was applied to maintain a specific coordination number.

Table 4.7. Hydration free energies (kcal/mol) of various cations in different environments. The environments include bulk water as well as large (*LP*) and small (*SP*) pores. Hydration free energies calculated in bulk water are consistent with the values reported in Ref. 60. For the *SP* environment, the hydration free energies are provided for different numbers of water molecules ($n_{\text{H}_2\text{O}}$) and coordination numbers (CN). The bold numbers are considered as the most stable environments for dehydrated ($n_{\text{H}_2\text{O}} = 0$) and hydrated ($n_{\text{H}_2\text{O}} > 0$) *SP*.

Environment	Li^+	Na^+	K^+
Bulk Environment			
Bulk Water	-113.61 ± 0.09	-88.73 ± 0.08	-70.82 ± 0.06
Large Pore (<i>LP</i>)			
<i>LP</i>	-117.70 ± 0.50	-92.90 ± 0.30	-75.00 ± 0.27
<i>LP</i> (no ion-MOF interaction)	-118.06 ± 0.17	-92.95 ± 0.23	-74.92 ± 0.12
Small Pore (<i>SP</i>)			
$n_{\text{H}_2\text{O}} = 0$	-118.12 ± 0.14	-110.35 ± 0.05	-109.03 ± 0.06
$n_{\text{H}_2\text{O}} = 1$	-138.08 ± 0.24	-124.54 ± 0.11	-111.67 ± 0.11
$n_{\text{H}_2\text{O}} = 2$	-146.03 ± 0.15	-123.93 ± 0.17	-112.31 ± 0.11
<i>SP</i> ($n_{\text{H}_2\text{O}} = 3$)			
CN = 1	-145.27 ± 0.16	-123.99 ± 0.13	-115.87 ± 0.05
CN = 2	-155.40 ± 0.21	-128.35 ± 0.09	-117.68 ± 0.08
CN = 3	-165.33 ± 0.28	-132.09 ± 0.09	-117.38 ± 0.09
<i>SP</i> ($n_{\text{H}_2\text{O}} = 4$)			
CN = 1	-145.67 ± 0.12	-123.43 ± 0.12	-99.81 ± 0.13
CN = 2	-156.21 ± 0.24	-124.83 ± 0.17	-103.46 ± 0.17
CN = 3	-166.27 ± 0.26	-134.31 ± 0.21	-104.86 ± 0.09
CN = 4	-170.17 ± 0.10	-133.77 ± 0.14	-103.53 ± 0.09

Residence Time

The residence time calculations were performed following the method introduced in Ref 103. Briefly, a function $P_j(t_n, t; t^*)$ was defined to describe the behavior of individual water molecules (indexed by j) in relation to a center ion. This function is binary, taking the value 1 if the water molecule j resides within the desired coordination shell of the ion at both time steps t_n and $t + t_n$, and does not leave that coordination shell for any continuous period longer than t^* during the intervening time. Otherwise, $P_j(t_n, t; t^*)$ is 0.

The number of water molecules that initially lie within the desired coordination shell and

remain in the same shell after time t was then calculated as

$$N_{\text{wat}}(t) = \frac{1}{N_t} \sum_{n=1}^{N_t} \sum_j P_j(t_n, t; t^*) \quad (\text{A7})$$

Here, N_t is the number of time steps considered. It follows that $N_{\text{wat}}(0)$ corresponds to the average number of water molecules ($N_{\text{wat}}^{\text{avg}}$) in the hydration shell. The parameter t^* was introduced to account for water molecules that might temporarily leave the desired coordination shell and return without fully entering the bulk solvent. The parameter t^* is obtained from the average interchange time of the water molecules in the desired hydration shell. The t^* values used in these simulations are listed in Table 4.8.

The function $N_{\text{wat}}(t)$ exhibits a similar behavior for the three alkali metal ions considered in this study, with an exponential decay at long time:

$$N_{\text{wat}}(t) \approx N_{\text{wat}}^{\text{avg}} \exp(-t/\tau_{\text{ion}}) \quad (\text{A8})$$

The quantity τ_{ion} represents a correlation time, quantifying the persistence of the desired coordination shell surrounding the ion. It serves as a straightforward definition of the residence time for water molecules within a given shell. The τ_{ion} values for Li^+ , Na^+ , and K^+ are listed in Table 4.9, while $N_{\text{wat}}(t)$ is shown in Figure 4.2b of the main text for Li^+ , and in Figures 4.11b and 4.12b for Na^+ and K^+ , respectively.

Table 4.8. Calculated t^* values for various ions for first hydration shell in bulk water.

Ion	t^* (ps)
Li^+	1.3
Na^+	0.4
K^+	0.2

Table 4.9. Residence time for water molecules in the first hydration shells of Li^+ , Na^+ , and K^+ in bulk water and MOF-808.

Ion	Bulk Water		MOF	
	τ_{ion} (ps)	$N_{\text{wat}}^{\text{avg}}$	τ_{ion} (ps)	$N_{\text{wat}}^{\text{avg}}$
Li^+	115	3.7	206	4.0
Na^+	63	5.6	99	5.8
K^+	12	6.2	53	5.6

Orientalional Correlation Function

The orientational correlation functions, $C_2(t)$, was calculated from long MD trajectories (10 ns) using the following equation¹⁰⁴:

$$C_2(t) = \langle P_2[\vec{u}(0) \cdot \vec{u}(t)] \rangle \quad (\text{A9})$$

Here, $\vec{u}$ is a unit vector along an OH bond of a water molecule, $P_2(x) = \frac{1}{2}(3x^2 - 1)$ is the second-order Legendre polynomial, and $\langle \dots \rangle$ denotes an ensemble average over all OH bonds at time t . This equation quantifies the time-dependent correlation of OH bond orientations within the water system.

Tetrahedral Order Parameter

The tetrahedral order parameter, denoted as q_{tet} , was computed following the method outlined in Ref 105. This parameter quantifies the degree of tetrahedrality in the local arrangement of water molecules and is defined as:

$$q_{\text{tet}} = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \theta_{ijk} + \frac{1}{3} \right)^2, \quad (\text{A10})$$

Here, θ_{ijk} represents the angle formed between the oxygen atom of a central water molecule, designated by index i , and the oxygen atoms of two neighboring water molecules, identified by indices j and k . Only neighboring water molecules within a distance of 3.5 Å from the central

molecule were considered.

Radial Distribution Function

The radial distribution functions (RDFs) describing spatial correlations between the Li^+ , Na^+ , and K^+ ions and the surrounding water molecules reveal distinct structural arrangements in the *LP*, dehydrated *SP*, and hydrated *SP* environments (Figure 4.13).

In the *LP*, a dominant peak is observed for all three alkali metal ions with the water oxygen atoms (O_w), indicating that the ions are likely to be located within a solvated environment. For K^+ , a strong peak is also observed with the aromatic carbon (C_a) of the BTC benzene ring, suggesting that K^+ is frequently located near the framework.

In the dehydrated *SP*, dominant peaks are observed for Li^+ with the oxygen (O) atoms of the SBUs, indicating that Li^+ is likely located near the vertices of the tetrahedral *SP*. Na^+ and K^+ exhibit broader peaks with C_a , indicating that they are more delocalized near the center of the *SP*. In addition, the dominant peak is sharper in the RDF of K^+ than of Na^+ , suggesting that K^+ is more confined in the dehydrated *SP*, in agreement with the PMF analyses shown in Figure 5b-c of the main text.

In the hydrated *SP*, the peaks at a relatively short distances in the ion–water RDFs of all three alkali metal ions confirm the presence of water molecules within the *SP*. The $\text{Li}^+ - C_a$ RDF exhibits a sharp peak, indicating that Li^+ is likely found at the center of the *SP*. Na^+ and K^+ exhibit multiple peaks with the C_a atoms, indicating the presence of several preferred positions within the *SP*, including near the benzene rings of the BTC linker, the carboxylate groups, and the central region of pore.

Diffusion Coefficients

The diffusion coefficient (D) was calculated using the mean squared displacement (MSD) according to Einstein's relation:

$$\langle r^2(t) \rangle = 6Dt, \quad (\text{A11})$$

where $\langle r^2(t) \rangle$ is the MSD and t is time. The MSD for each ion was computed from a long MD trajectory (10 ns), which was divided into multiple 400 ps-long intervals to calculate the corresponding average value of the diffusion coefficient and associated statistical uncertainty. The D values for each alkali metal ion inside MOF-808 are listed in Table 4.10.

Table 4.10. Diffusion coefficients of ions in different environments

Diffusion Coefficient ($\times 10^{10}$ m ² /s)	<i>LP</i>	Dehydrated <i>SP</i>	Hydrated <i>SP</i>
Li ⁺	2.9 ± 0.3	0.025 ± 0.003	0.017 ± 0.004
Na ⁺	3.24 ± 0.04	0.020 ± 0.003	0.003 ± 0.001
K ⁺	3.1 ± 0.9	0.017 ± 0.003	0.0157 ± 0.0013

Enthalpy and Entropy Analyses

The enthalpy change (ΔH) is related to the internal energy change (ΔU) by the following equation:

$$\Delta H = \Delta U + P\Delta V, \quad (\text{A12})$$

where P is pressure and ΔV is the change in volume. In our simulations, the pressure was held constant at 1 atm. The observed fluctuations in volume were on the order of 10-100 Å³. Considering the conversion factor 1 atm·Å³ = 1.46 × 10⁻⁵ kcal/mol, the contribution of the $P\Delta V$ term to ΔH is negligible. Therefore, for all systems studied, we approximated ΔH by ΔU . The internal energy change, ΔU , was calculated directly from long MD trajectories, employing block averaging to estimate statistical uncertainties.

Knowing ΔG (obtained from the free-energy calculations) and approximating ΔH by ΔU , the entropic contribution ($T\Delta S$) to the free energy were evaluated using the following equation:

$$\Delta G = \Delta H - T\Delta S, \quad (\text{A13})$$

where $T = 298$ K. This allows for a decomposition of the free energy into its enthalpic and entropic components, as included in Table 4.11.

Table 4.11. Change in different thermodynamic quantities (ΔG , ΔH and $T\Delta S$) for the ions going from LP to (de)hydrated SP .

Ion	Dehydrated SP			Hydrated SP		
	$\Delta H_{LP \rightarrow SP}$ (kcal/mol)	$\Delta G_{LP \rightarrow SP}$ (kcal/mol)	$T\Delta S_{LP \rightarrow SP}$ (kcal/mol)	$\Delta H_{LP \rightarrow SP}$ (kcal/mol)	$\Delta G_{LP \rightarrow SP}$ (kcal/mol)	$T\Delta S_{LP \rightarrow SP}$ (kcal/mol)
Li^+	$0. \pm 6.$	-0.4 ± 0.5	$0. \pm 6.$	-10.5 ± 2.3	-52.5 ± 0.5	42.0 ± 2.4
Na^+	$-46. \pm 5.$	-17.4 ± 0.3	$-28. \pm 5.$	-35.9 ± 3.6	-41.4 ± 0.4	5.5 ± 3.6
K^+	-63.9 ± 2.5	-34.03 ± 0.28	-29.9 ± 2.5	-46.0 ± 2.8	-42.7 ± 0.3	-3.3 ± 2.8

Enhanced Sampling Simulations

The potentials of mean force (PMFs) were calculated using the umbrella sampling method (as implemented in PLUMED⁹²) and analyzed with the weighted histogram analysis method (WHAM).^{106,107} The reaction coordinate or collective variable, ξ , was chosen to be the projection of the center of mass (COM) of the water molecules and the position of the alkali metal ions, respectively, along the vector connecting the large (LP) and the small pore (SP) through the window (W , as shown in Figure 4.10a. As shown in Figures 4.10b and 4.10c, the configurations with negative ξ values (from -7 to 0) correspond to the path of water molecules or ions going to the W from the large pore (LP), while those with positive ξ values (from 0 to 5) are moving through the W into the center of SP . Since the LP s are interconnected in MOF-808, an upper wall bias potential was applied at 2.5 Å to ensure that the dehydration process of water molecules and alkali metal ions was accurately simulated as they moved into the SP through the narrow W . Specifically, this bias was applied to the extension of the projection component perpendicular to the vector in the negative ξ region (i.e., when the water molecules or metal ions were still outside the SP), as illustrated in Figure 4.10. When the water molecules or metal ions are inside the SP , there is no restraint on the extension component.

Since the SP is tetrahedral-shaped (see Figure 4.10), and the W is along the edges of the tetrahedral pore, the PMFs are ideally symmetric at the center ($\xi \sim 3 \text{ \AA}$) of the SP , as shown in Figure 4.15. However, we note that the PMFs for a second water molecule entering an SP already containing one water molecule are not symmetry around $\xi \sim 3 \text{ \AA}$, as shown in the second row of Figure 4.15 and Figure 4.16. This is because the equilibration process is kinetically very slow when the second water molecule in the SP moves into the region where $\xi > 3 \text{ \AA}$. However, the region where $\xi < 3 \text{ \AA}$ is expected to be well converged and equilibrated.

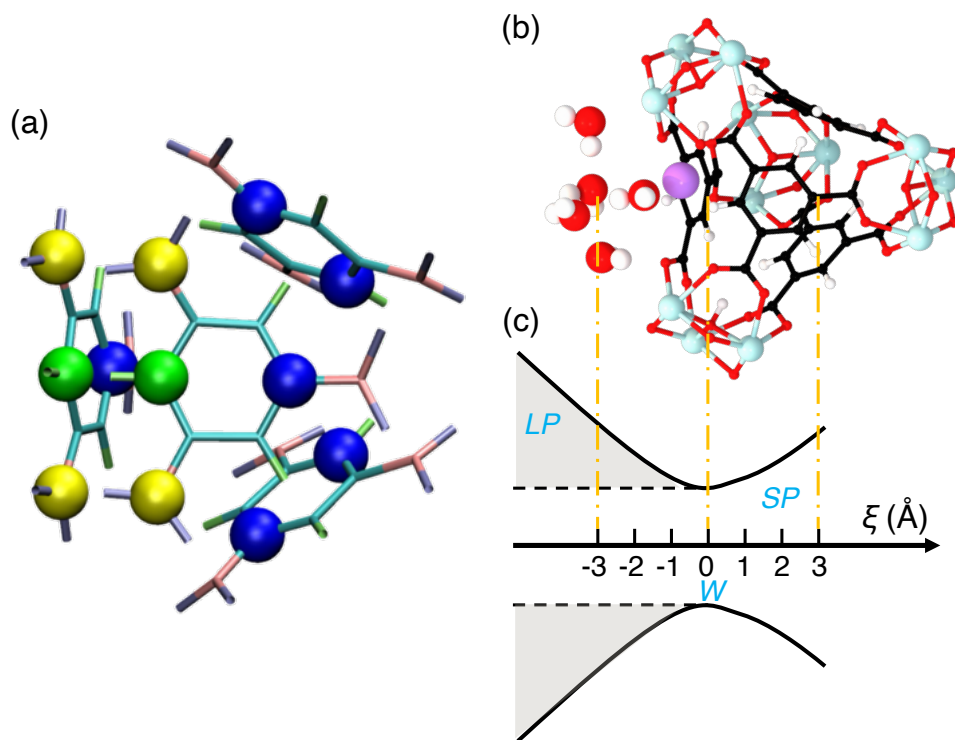


Figure 4.10. (a) Truncated structure of the target *SP* (only BTC linkers are shown for clarity) where the carbon atoms that are highlighted in yellow and green are used to define the position of the *W*, while those in blue and green are used to define the center of the target *SP*. (b) Truncated geometry of the local structure with water molecules and one of the studied alkali metal ions (Li^+ , Na^+ , or K^+) near the *W*, with the *SP* being empty. Extended framework atoms and other water molecules in the unit cell are omitted for clarity. Color code: white: H; red: O; black: C; purple: alkali metal ion; cyan: Zr. (c) Schematic illustration of the chosen reaction coordinate ξ for the PMF. ξ is chosen to be the projection of the *COM* of water molecules and the position of the ions, respectively, along the vector connecting the *W* and the *SP*. The shaded area depicts the forbidden region with an upper wall bias potential applied when the target water molecule or alkali metal ion is out in the *LP*. The orange dashed lines provide a visual idea of the umbrella sampling process along the chosen ξ .

Appendix B: Supporting Data

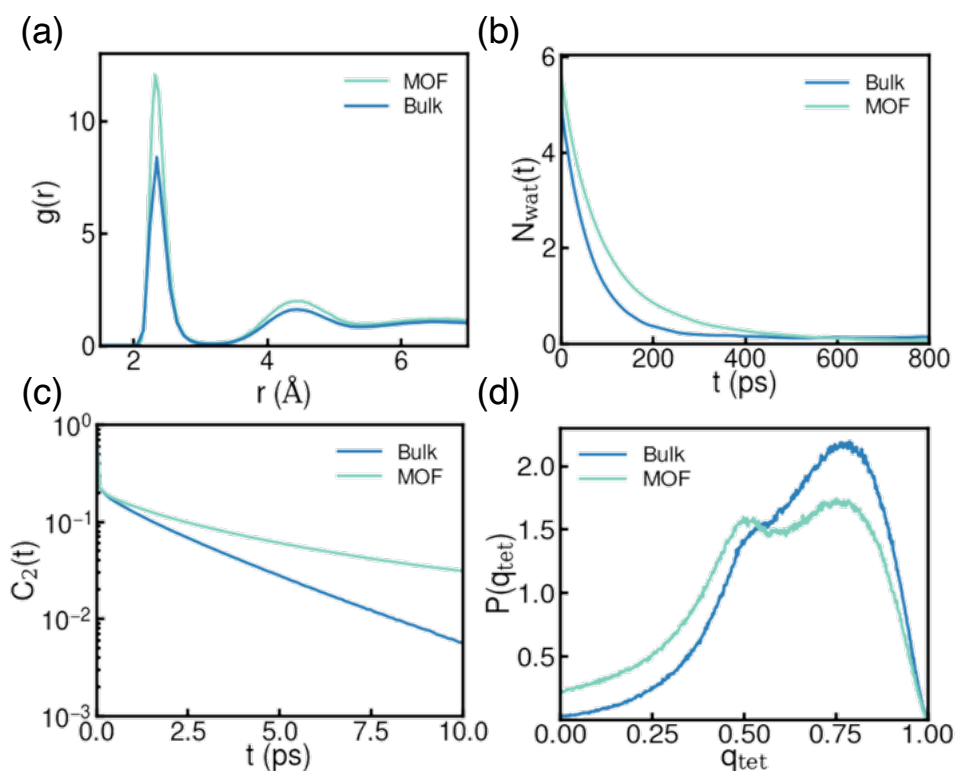


Figure 4.11. Structural and dynamical properties of water molecules with Na^+ ion in bulk water (Bulk) and confined within the *LP* of MOF-808 (MOF). (a) Radial distribution function describing the spatial correlation between Na^+ and water oxygen atoms; (b) Time evolution of the number of water molecules that remain in the first hydration shell, considering those initially present at time zero; (c) Water orientational correlation function; (d) Probability distribution of the tetrahedral order parameter.

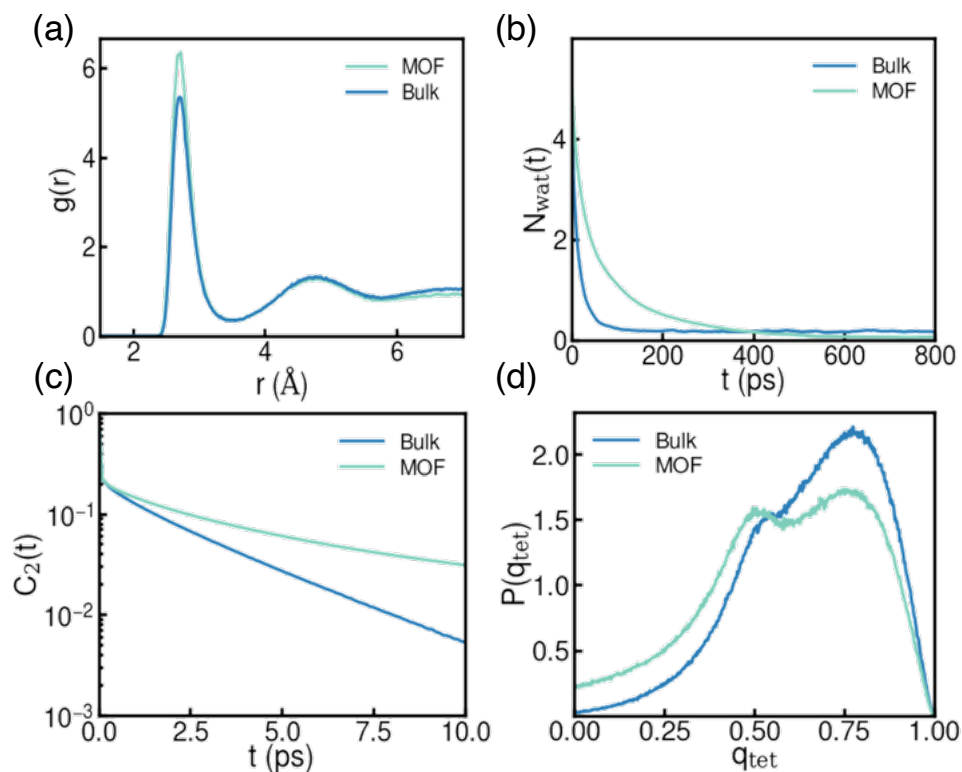


Figure 4.12. Structural and dynamical properties of water molecules with K^+ ion in bulk water (Bulk) and confined within the *LP* of MOF-808 (MOF). (a) Radial distribution function describing the spatial correlation between K^+ and water oxygen atoms; (b) Time evolution of the number of water molecules that remain in the first hydration shell, considering those initially present at time zero; (c) Water orientational correlation function; (d) Probability distribution of the tetrahedral order parameter.

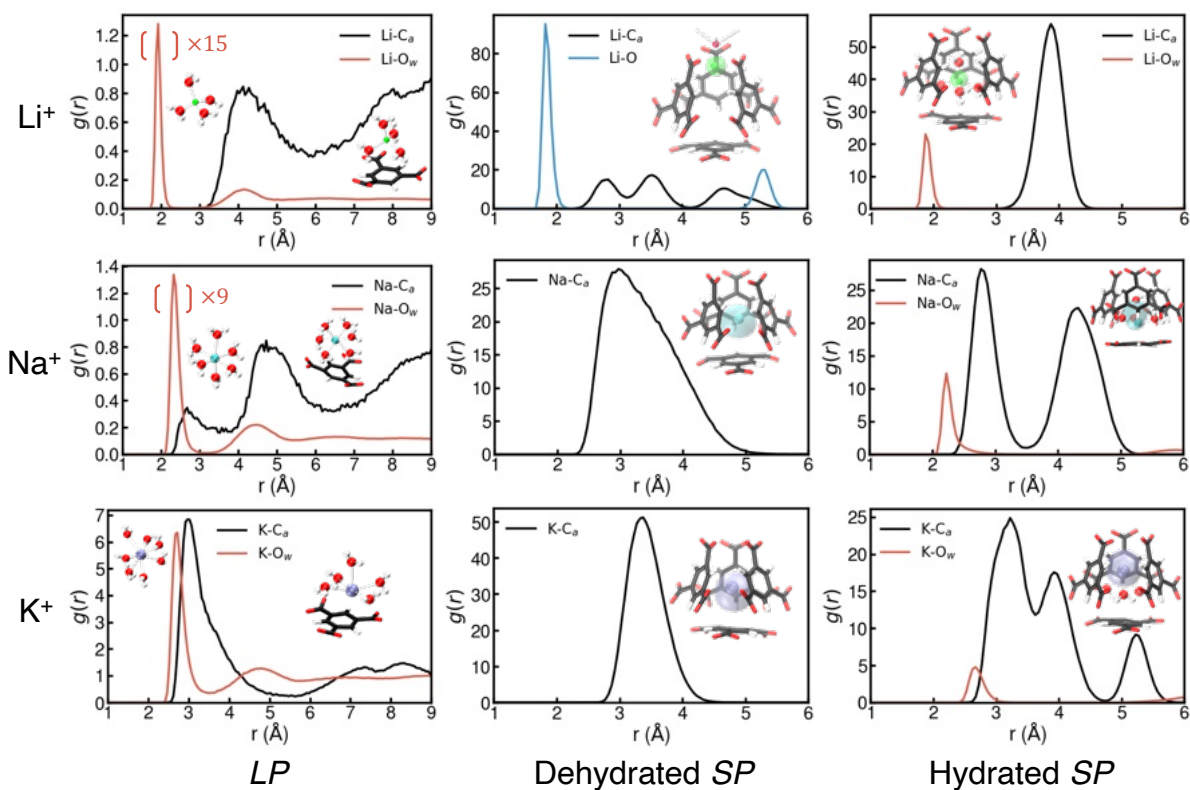


Figure 4.13. Radial distribution functions (RDFs), $g(r)$, for Li^+ , Na^+ , and K^+ interactions with different MOF atoms under varying environments: Large Pore (LP, left column), Dehydrated small pore (Dehydrated SP, middle column), and hydrated small pore (hydrated SP, right column). Each row corresponds to a specific ion, highlighting their spatial distribution relative to the MOF coordination sites and water molecules under these different confinement conditions. Representative snapshots from the trajectories are provided for the dominant peaks in the RDFs, as shown in the insets. The shaded volumes near the ions in the insets of the second and third columns (green for Li^+ , cyan for Na^+ , and purple for K^+) represent the trajectory-averaged accessible volumes for these ions in the dehydrated and hydrated SP, respectively.

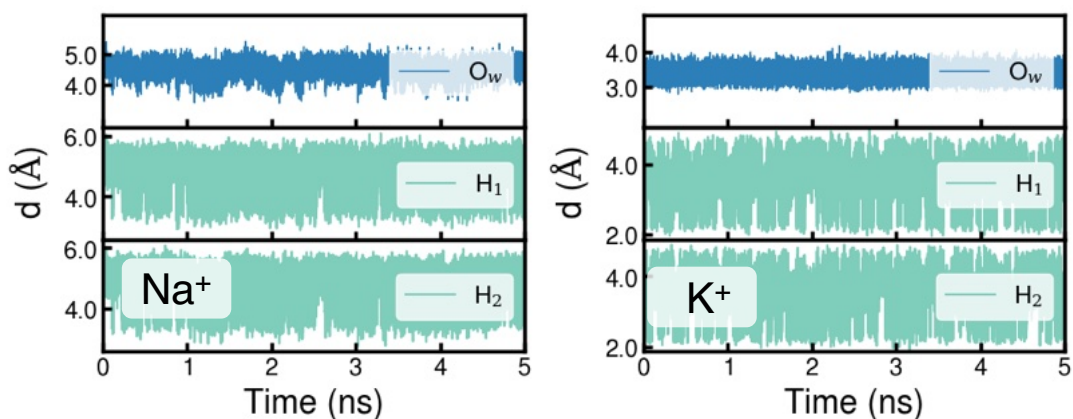


Figure 4.14. Time evolution of the oxygen and hydrogen distances (d) of the water molecules within an *SP* containing a Na^+ (left) and K^+ (right) relative to a carbon atom of a BTC benzene ring.

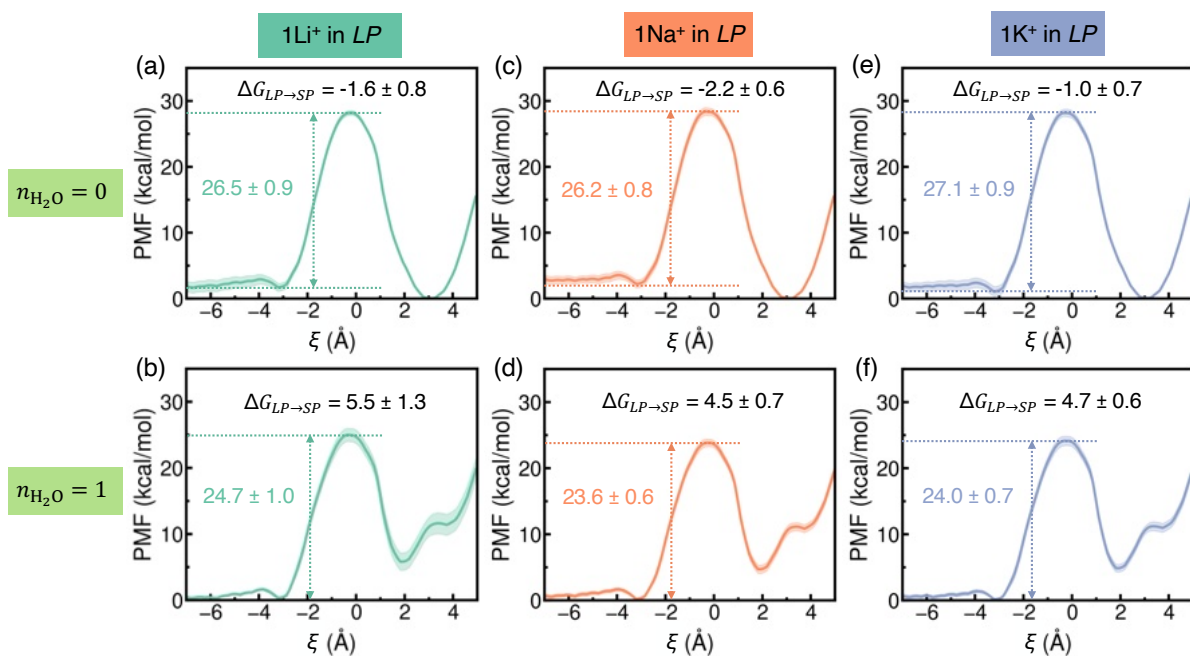


Figure 4.15. Potentials of mean force (PMFs) for water molecules transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ). Statistical errors were calculated as 95% confidence intervals and are shown as a colored shaded area. The first row ((a), (c), and (e)) corresponds to the results for a first water molecule entering a dehydrated *SP* ($n_{\text{H}_2\text{O}} = 0$), while the second row ((b), (d), and (f)) corresponds to a second water molecule entering a hydrated *SP* with one water molecule inside ($n_{\text{H}_2\text{O}} = 1$). The first column ((a) and (b)) is calculated from the system where there is one Li^+ , in addition to 1040 water molecules, while the second ((c) and (d)) and third ((e) and (f)) columns are from systems with one Na^+ and one K^+ , respectively, in addition to 1040 water molecules.

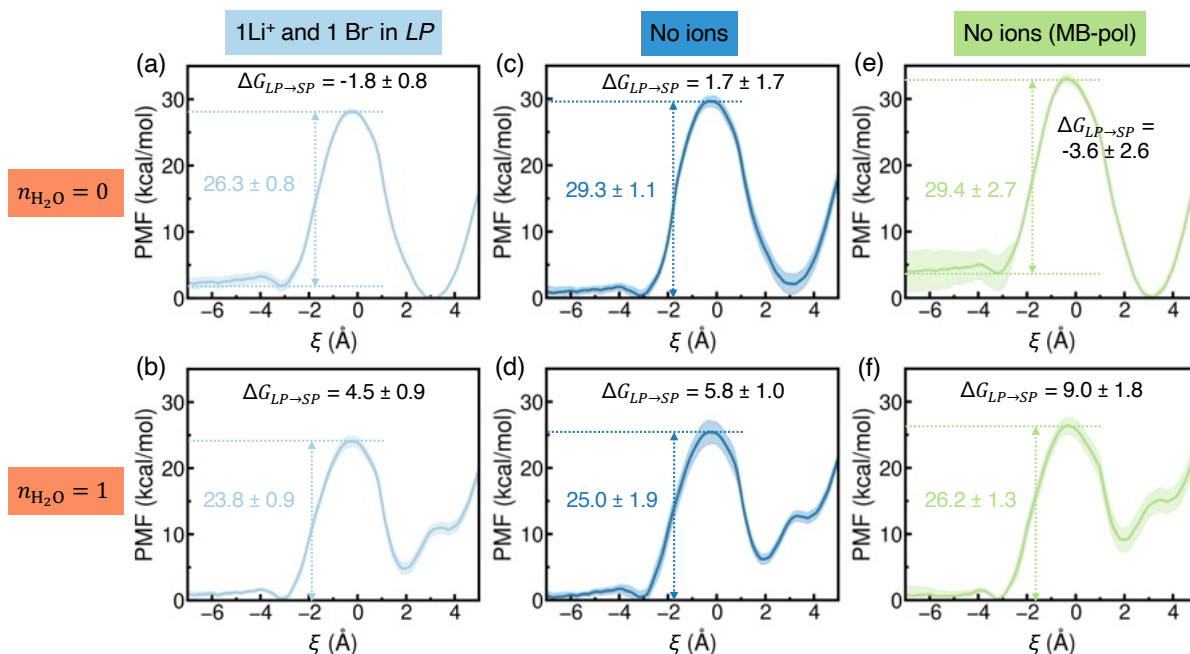


Figure 4.16. Potentials of mean force (PMFs) for water molecules transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ). Statistical errors were calculated as 95% confidence intervals and are shown as a colored shaded area. The first row ((a), (c), and (e)) corresponds to the results for a first water molecule entering a dehydrated *SP* ($n_{H_2O} = 0$), while the second row ((b), (d), and (f)) corresponds to a second water molecule entering a hydrated *SP* with one water molecule inside ($n_{H_2O} = 1$). The first column ((a) and (b)) is from the system where there is one cation Li^+ and one counterion Br^- , in addition to 1040 water molecules, while the second ((c) and (d)) and third ((e) and (f)) columns are from the system with 1040 water molecules inside but with no ions, with the third column calculated using the rigid MB-pol model.

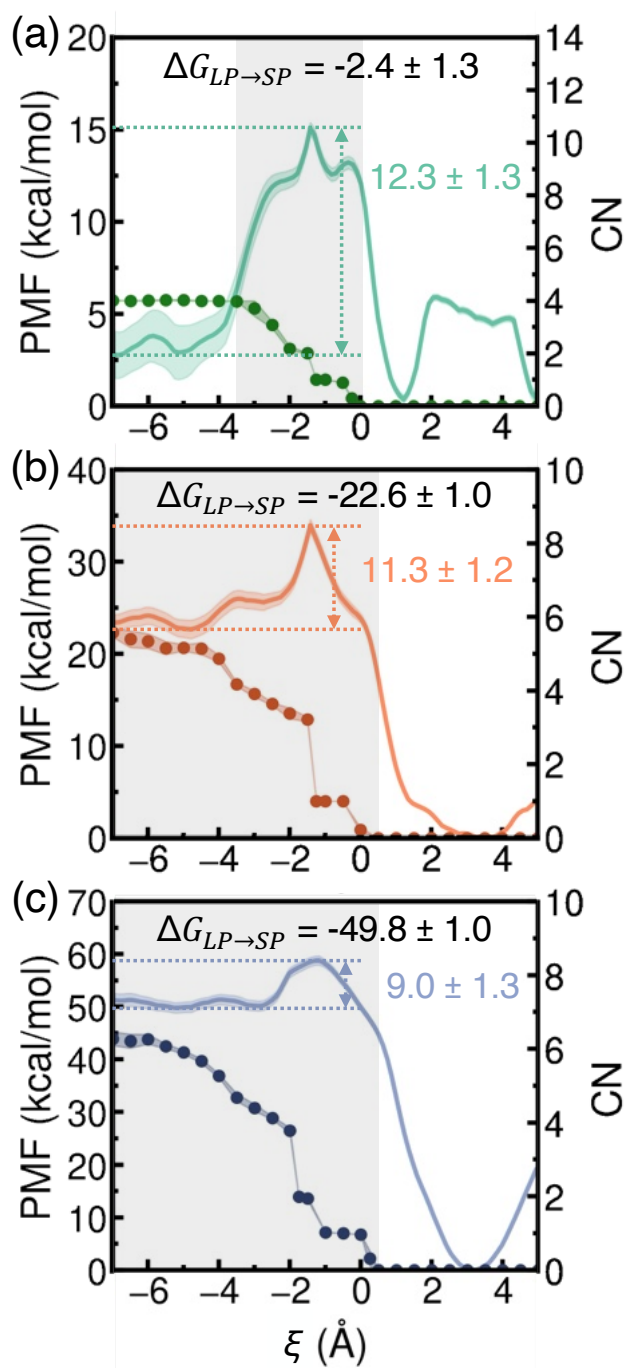


Figure 4.17. Potentials of mean force (PMFs) (solid lines, left y-axis) and corresponding coordination numbers (CNs) (filled circles, right y-axis) for a single Li^+ (a), Na^+ (b), and K^+ (c) ion transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ). Statistical errors were calculated as 95% confidence intervals and are shown as colored shaded areas. The regions of first-shell dehydration are shown as gray-shaded areas. These results are calculated using the rigid MB-pol model.

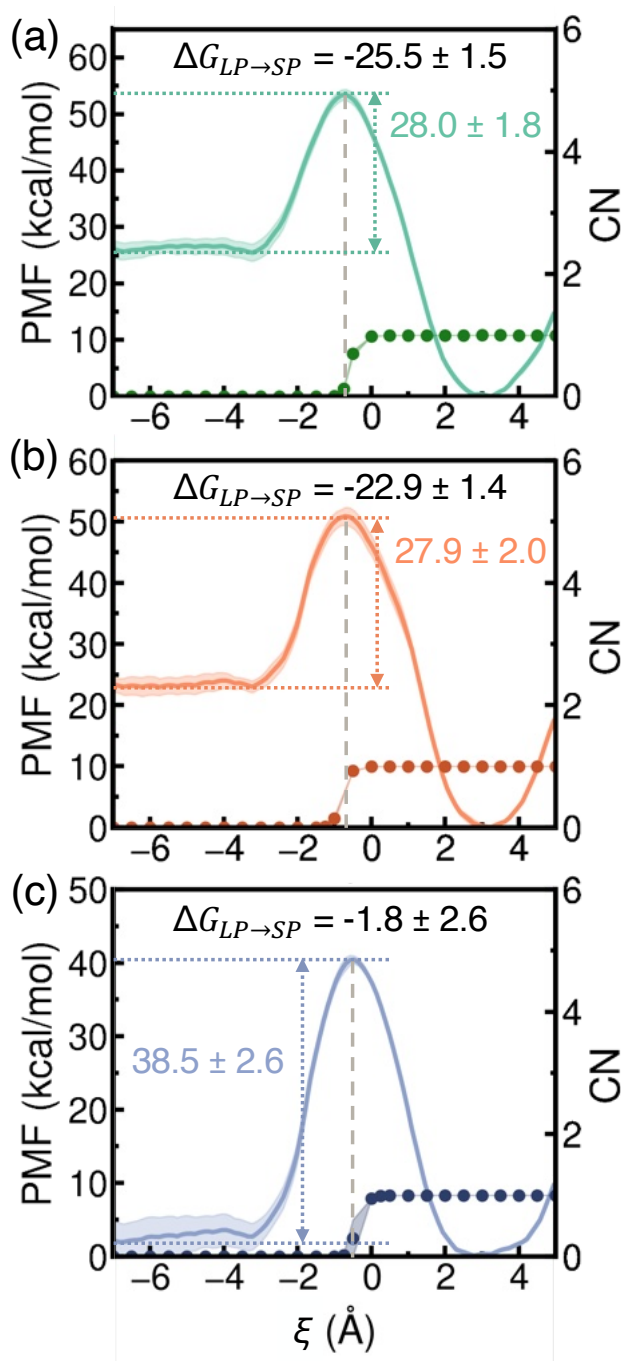


Figure 4.18. Potentials of mean force (PMFs) (solid lines, left y-axis) for a water molecule transferring from a hydrated *LP* (negative ξ) to a dehydrated *SP* (positive ξ) containing a single Li^+ (a), Na^+ (b), and K^+ (c) ion. Statistical errors were calculated as 95% confidence intervals and are shown as colored shaded areas. Also shown are the ion's coordination numbers (CNs) (filled circles, right y-axis) within the *SP*. The gray dashed lines indicate the positions of the corresponding PMF maxima. These results are calculated using the rigid MB-pol model.

In Table 4.12, we report the results for the relaxed size of an *SP*, which is defined as the average distance between the atoms used to determine the *COM* for the *SP* (atoms in blue and green as in Figure 4.10a) and the *COM* itself. Also reported In Table 4.12, is the size of the *W*, which is defined as the average distance between the atoms pairs (top two atoms in yellow, two atoms in green, and bottom two atoms in yellow, as shown in Figure 4.10a) used to determined the position of *W*.

Table 4.12. The relaxed sizes of the target *SP* and *W* (in parentheses), with sample standard deviation, in Å.

	Empty <i>SP</i>	1 Li ⁺ in <i>SP</i>	1 Na ⁺ in <i>SP</i>	1 K ⁺ in <i>SP</i>
TIP4P-Ew	3.56±0.04 (3.86±0.08)	3.54±0.05 (3.84±0.10)	3.45±0.05 (3.75±0.08)	3.46±0.04 (3.72±0.08)
Rigid MB-pol	3.55±0.05 (3.84±0.10)	3.54±0.05 (3.83±0.10)	3.45±0.04 (3.73±0.09)	3.46±0.04 (3.73±0.09)

References

- [1] Sixie Yang, Fan Zhang, Huaiping Ding, Ping He, and Haoshen Zhou. Lithium metal extraction from seawater. *Joule*, 2(9):1648–1651, 2018.
- [2] National Research Council, Division on Earth, Life Studies, Board on Earth Sciences, Committee on Earth Resources, and Committee on Critical Mineral Impacts of the US Economy. *Minerals, critical minerals, and the US economy*. National Academies Press, 2008.
- [3] Paripurnanda Loganathan, Gayathri Naidu, and Saravanamuthu Vigneswaran. Mining valuable minerals from seawater: a critical review. *Environ. Sci.: Water Res. Technol.*, 3(1):37–53, 2017.
- [4] Mamadou S Diallo, Madhusudhana Rao Kotte, and Manki Cho. Mining critical metals and elements from seawater: opportunities and challenges. *Environ. Sci. Technol.*, 49(16):9390–9399, 2015.
- [5] Xin He, Sumanjeet Kaur, and Robert Kostecki. Mining lithium from seawater. *Joule*, 4(7):1357–1358, 2020.
- [6] Zhen Li, Chunyang Li, Xiaowei Liu, Li Cao, Peipei Li, Ruicong Wei, Xiang Li, Dong Guo, Kuo-Wei Huang, and Zhiping Lai. Continuous electrical pumping membrane process for seawater lithium mining. *Energy Environ. Sci.*, 14(5):3152–3159, 2021.
- [7] Pankaj K Choubey, Kang-Sup Chung, Min-seuk Kim, Jae-chun Lee, and Rajiv R Srivastava. Advance review on the exploitation of the prominent energy-storage element lithium. part II: From sea water and spent lithium ion batteries (LIBs). *Miner. Eng.*, 110:104–121, 2017.
- [8] Jun Lu, Xiaoyi Hu, Kevin M Ung, Yinlong Zhu, Xiwang Zhang, and Huanting Wang. Metal–organic frameworks as a subnanometer platform for ion–ion selectivity. *Acc. Mater. Res.*, 3(7):735–747, 2022.
- [9] Wendan Xue, Christopher D Sewell, Qixing Zhou, and Zhiqun Lin. Metal–organic frameworks for ion conduction. *Angew. Chem., Int. Ed.*, 61(34):e202206512, 2022.
- [10] Ruby A Kharod, Justin L Andrews, and Mircea Dincă. Teaching metal-organic frameworks to conduct: ion and electron transport in metal-organic frameworks. *Annu. Rev. Mater. Res.*, 52(1):103–128, 2022.
- [11] Masaaki Sadakiyo and Hiroshi Kitagawa. Ion-conductive metal–organic frameworks. *Dalton trans.*, 50(16):5385–5397, 2021.

- [12] Huacheng Zhang, Jue Hou, Yaoxin Hu, Peiyao Wang, Ranwen Ou, Lei Jiang, Jefferson Zhe Liu, Benny D Freeman, Anita J Hill, and Huanting Wang. Ultrafast selective transport of alkali metal ions in metal organic frameworks with subnanometer pores. *Sci. Adv.*, 4(2): eaaq0066, 2018.
- [13] Xingya Li, Gengping Jiang, Meipeng Jian, Chen Zhao, Jue Hou, Aaron W. Thornton, Xinyi Zhang, Jefferson Zhe Liu, Benny D. Freeman, Huanting Wang, Lei Jiang, and Huacheng Zhang. Construction of angstrom-scale ion channels with versatile pore configurations and sizes by metal-organic frameworks. *Nat. Commun.*, 14(1):286, 2023.
- [14] Xingya Li, Huacheng Zhang, Peiyao Wang, Jue Hou, Jun Lu, Christopher D. Easton, Xiwang Zhang, Matthew R. Hill, Aaron W. Thornton, Jefferson Zhe Liu, Benny D. Freeman, Anita J. Hill, Lei Jiang, and Huanting Wang. Fast and selective fluoride ion conduction in sub-1-nanometer metal-organic framework channels. *Nat. Commun.*, 10(1): 2490, 2019.
- [15] Jun Lu, Huacheng Zhang, Jue Hou, Xingya Li, Xiaoyi Hu, Yaoxin Hu, Christopher D. Easton, Qinye Li, Chenghua Sun, Aaron W. Thornton, Matthew R. Hill, Xiwang Zhang, Gengping Jiang, Jefferson Zhe Liu, Anita J. Hill, Benny D. Freeman, Lei Jiang, and Huanting Wang. Efficient metal ion sieving in rectifying subnanochannels enabled by metal-organic frameworks. *Nat. Mater.*, 19(7):767–774, 2020.
- [16] Chengyi Zhang, Yingxin Mu, Wen Zhang, Song Zhao, and Yuxin Wang. PVC-based hybrid membranes containing metal-organic frameworks for $\text{Li}^+/\text{Mg}^{2+}$ separation. *J. Membr. Sci.*, 596:117724, 2020.
- [17] Yi Guo, Hubiao Huang, Zhuoyi Li, Xiaobin Wang, Peipei Li, Zheng Deng, and Xinsheng Peng. Sulfonated sub-nanochannels in a robust MOF membrane: Harvesting salinity gradient power. *ACS Appl. Mater. Interfaces*, 11(38):35496–35500, 2019.
- [18] Ri-Jian Mo, Shuang Chen, Li-Qiu Huang, Xin-Lei Ding, Saima Rafique, Xing-Hua Xia, and Zhong-Qiu Li. Regulating ion affinity and dehydration of metal-organic framework sub-nanochannels for high-precision ion separation. *Nat. Commun.*, 15(1):2145, 2024.
- [19] Tian-Yin Liu, Hao-Ge Yuan, Yuan-Yuan Liu, Dan Ren, Yi-Cheng Su, and Xiaolin Wang. Metal-organic framework nanocomposite thin films with interfacial bindings and self-standing robustness for high water flux and enhanced ion selectivity. *ACS nano*, 12(9): 9253–9265, 2018.
- [20] Jue Hou, Huanting Wang, and Huacheng Zhang. Zirconium metal-organic framework materials for efficient ion adsorption and sieving. *Ind. Eng. Chem. Res.*, 59(29):12907–12923, 2020.
- [21] Mengyu Tang, Qian Guan, Yilei Fang, Xu Wu, Jiajie Zhang, Hao Xie, Xin Yu, and

- Ranwen Ou. Rational design of metal organic frameworks towards toxic ion adsorption properties modulation. *Sep. Purif. Technol.*, page 127059, 2024.
- [22] Jie Li, Xiangxue Wang, Guixia Zhao, Changlun Chen, Zhifang Chai, Ahmed Alsaedi, Tasawar Hayat, and Xiangke Wang. Metal–organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chem. Soc. Rev.*, 47(7): 2322–2356, 2018.
- [23] Lei Wang, Xinhua Zhao, Jinmiao Zhang, and Zhenhu Xiong. Selective adsorption of Pb(II) over the zinc-based MOFs in aqueous solution-kinetics, isotherms, and the ion exchange mechanism. *Environ. Sci. Pollut. Res.*, 24:14198–14206, 2017.
- [24] Nan Zhang, Li-Yong Yuan, Wen-Lu Guo, Shi-Zhong Luo, Zhi-Fang Chai, and Wei-Qun Shi. Extending the use of highly porous and functionalized MOFs to Th(IV) capture. *ACS Appl. Mater. Interfaces*, 9(30):25216–25224, 2017.
- [25] Karen Leus, Jeffrey Paulo H Perez, Karel Folens, Maria Meledina, Gustaaf Van Tendeloo, Gijs Du Laing, and Pascal Van Der Voort. UiO-66-(SH)₂ as stable, selective and regenerable adsorbent for the removal of mercury from water under environmentally-relevant conditions. *Faraday Discuss*, 201:145–161, 2017.
- [26] Omar M Yaghi, Michael O’Keeffe, Nathan W Ockwig, Hee K Chae, Mohamed Eddaoudi, and Jaheon Kim. Reticular synthesis and the design of new materials. *Nature*, 423(6941): 705–714, 2003.
- [27] Hiroyasu Furukawa, Kyle E Cordova, Michael O’Keeffe, and Omar M Yaghi. The chemistry and applications of metal-organic frameworks. *Science*, 341(6149):1230444, 2013.
- [28] U Mueller, M Schubert, F Teich, H Puetter, K Schierle-Arndt, and J Pastre. Metal–organic frameworks—prospective industrial applications. *J. Mater. Chem.*, 16(7):626–636, 2006.
- [29] Hong-Cai “Joe” Zhou and Susumu Kitagawa. Metal–organic frameworks (MOFs). *Chem. Soc. Rev.*, 43(16):5415–5418, 2014.
- [30] Xu Zhang, An Chen, Ming Zhong, Zihe Zhang, Xin Zhang, Zhen Zhou, and Xian-He Bu. Metal–organic frameworks (MOFs) and MOF-derived materials for energy storage and conversion. *Electrochem. Energy Rev.*, 2:29–104, 2019.
- [31] Yizhak Marcus. *Ions in Solution and their Solvation*. John Wiley & Sons, 2015.
- [32] Razi Epsztein, Ryan M DuChanois, Cody L Ritt, Aleksandr Noy, and Menachem Elim-elech. Towards single-species selectivity of membranes with subnanometre pores. *Nat. Nanotechnol.*, 15(6):426–436, 2020.

- [33] Johan Schaep, Bart Van der Bruggen, Carlo Vandecasteele, and Dirk Wilms. Influence of ion size and charge in nanofiltration. *Sep. Purif. Technol.*, 14(1-3):155–162, 1998.
- [34] Razi Epsztein, Wei Cheng, Evyatar Shaulsky, Nadir Dizge, and Menachem Elimelech. Elucidating the mechanisms underlying the difference between chloride and nitrate rejection in nanofiltration. *J. Membr. Sci.*, 548:694–701, 2018.
- [35] Chanhee Boo, Yunkun Wang, Ines Zucker, Youngwoo Choo, Chinedum O Osuji, and Menachem Elimelech. High performance nanofiltration membrane for effective removal of perfluoroalkyl substances at high water recovery. *Environ. Sci. Technol.*, 52(13):7279–7288, 2018.
- [36] Mao Wang, Wenhao Shen, Siyuan Ding, Xue Wang, Zhong Wang, Yugang Wang, and Feng Liu. A coupled effect of dehydration and electrostatic interactions on selective ion transport through charged nanochannels. *Nanoscale*, 10(39):18821–18828, 2018.
- [37] Laura A Richards, Bryce S Richards, Ben Corry, and Andrea I Schäfer. Experimental energy barriers to anions transporting through nanofiltration membranes. *Environ. Sci. Technol.*, 47(4):1968–1976, 2013.
- [38] Laura A Richards, Andrea I Schäfer, Bryce S Richards, and Ben Corry. Quantifying barriers to monovalent anion transport in narrow non-polar pores. *Phys. Chem. Chem. Phys.*, 14(33):11633–11638, 2012.
- [39] Eric Gouaux and Roderick MacKinnon. Principles of selective ion transport in channels and pumps. *Science*, 310(5753):1461–1465, 2005.
- [40] Laura A Richards, Andrea I Schäfer, Bryce S Richards, and Ben Corry. The importance of dehydration in determining ion transport in narrow pores. *Small*, 8(11):1701–1709, 2012.
- [41] Razi Epsztein, Evyatar Shaulsky, Mohan Qin, and Menachem Elimelech. Activation behavior for ion permeation in ion-exchange membranes: Role of ion dehydration in selective transport. *J. Membr. Sci.*, 580:316–326, 2019.
- [42] Leili Esrafil, Vahid Safarifard, Elham Tahmasebi, MD Esrafil, and Ali Morsali. Functional group effect of isorecticular metal–organic frameworks on heavy metal ion adsorption. *New J. Chem.*, 42(11):8864–8873, 2018.
- [43] Zhi-Qiang Bai, Li-Yong Yuan, Lin Zhu, Zhi-Rong Liu, Sheng-Qi Chu, Li-Rong Zheng, Jing Zhang, Zhi-Fang Chai, and Wei-Qun Shi. Introduction of amino groups into acid-resistant MOFs for enhanced U(VI) sorption. *J. Mater. Chem. A*, 3(2):525–534, 2015.
- [44] Meiqin Zha, Jie Liu, Yan-Lung Wong, and Zhengtao Xu. Extraction of palladium from nuclear waste-like acidic solutions by a metal–organic framework with sulfur and alkene

- functions. *J. Mater. Chem. A*, 3(7):3928–3934, 2015.
- [45] Declan A Doyle, Joao Morais Cabral, Richard A Pfuetzner, Anling Kuo, Jacqueline M Gulbis, Steven L Cohen, Brian T Chait, and Roderick MacKinnon. The structure of the potassium channel: molecular basis of K^+ conduction and selectivity. *Science*, 280(5360): 69–77, 1998.
 - [46] Yufeng Zhou, Joao H Morais-Cabral, Amelia Kaufman, and Roderick MacKinnon. Chemistry of ion coordination and hydration revealed by a K^+ channel–Fab complex at 2.0 Å resolution. *Nature*, 414(6859):43–48, 2001.
 - [47] Atsuko Yamashita, Satinder K Singh, Toshimitsu Kawate, Yan Jin, and Eric Gouaux. Crystal structure of a bacterial homologue of Na^+/Cl^- -dependent neurotransmitter transporters. *Nature*, 437(7056):215–223, 2005.
 - [48] Hiroyasu Furukawa, Felipe Gándara, Yue-Biao Zhang, Juncong Jiang, Wendy L Queen, Matthew R Hudson, and Omar M Yaghi. Water adsorption in porous metal–organic frameworks and related materials. *J. Am. Chem. Soc.*, 136(11):4369–4381, 2014.
 - [49] Shan Dai, Charlotte Simms, Iurii Dovgaliuk, Gilles Patriarche, Antoine Tissot, Tatjana N Parac-Vogt, and Christian Serre. Monodispersed MOF-808 nanocrystals synthesized via a scalable room-temperature approach for efficient heterogeneous peptide bond hydrolysis. *Chem. Mater.*, 33(17):7057–7066, 2021.
 - [50] Ignacio Romero-Muñiz, Carlos Romero-Muñiz, Isabel del Castillo-Velilla, Carlo Marini, Sofía Calero, Félix Zamora, and Ana E Platero-Prats. Revisiting vibrational spectroscopy to tackle the chemistry of Zr_6O_8 metal-organic framework nodes. *ACS Appl. Mater. Interfaces*, 14(23):27040–27047, 2022.
 - [51] Nicholas S Gould, Sha Li, Hong Je Cho, Harrison Landfield, Stavros Caratzoulas, Dionisios Vlachos, Peng Bai, and Bingjun Xu. Understanding solvent effects on adsorption and protonation in porous catalysts. *Nat. Commun.*, 11(1):1060, 2020.
 - [52] Ruirui Liu, Zhuanfang Jing, Yifan Shao, Yongquan Zhou, Fayan Zhu, and Hongyan Liu. The hydration of Li^+ and Mg^{2+} in subnano carbon nanotubes using a multiscale theoretical approach. *Front. Chem.*, 11:1103792, 2023.
 - [53] Ateeque Malani, Sohail Murad, and KG Ayappa. Hydration of ions under confinement. *Mol. Simulat.*, 36(7-8):579–589, 2010.
 - [54] Xu Wu, Huacheng Zhang, Xinyu Zhang, Qian Guan, Xiaocong Tang, Hao Wu, Mingbao Feng, Huanting Wang, and Ranwen Ou. Sustainable lithium extraction enabled by responsive metal-organic frameworks with ion-sieving adsorption effects. *Proc. Natl. Acad. Sci. USA*, 121(6):e2309852121, 2024.

- [55] Adam J Rieth, Kelly M Hunter, Mircea Dincă, and Francesco Paesani. Hydrogen bonding structure of confined water templated by a metal-organic framework with open metal sites. *Nat. Commun.*, 10(1):4771, 2019.
- [56] Aran Lamaire, Jelle Wieme, Sander Vandenhoute, Ruben Goeminne, Sven MJ Rogge, and Veronique Van Speybroeck. Water motifs in zirconium metal-organic frameworks induced by nanoconfinement and hydrophilic adsorption sites. *Nat. Commun.*, 15(1):9997, 2024.
- [57] Marc Riera, Narbe Mardirossian, Pushp Bajaj, Andreas W Götz, and Francesco Paesani. Toward chemical accuracy in the description of ion–water interactions through many-body representations. Alkali-water dimer potential energy surfaces. *J. Chem. Phys.*, 147(16):161715, 2017.
- [58] Marc Riera, Sandra E Brown, and Francesco Paesani. Isomeric equilibria, nuclear quantum effects, and vibrational spectra of $M^+(H_2O)_{n=1-3}$ clusters, with $M = Li, Na, K, Rb,$ and Cs , through many-body representations. *J. Phys. Chem. A*, 122(27):5811–5821, 2018.
- [59] Hans W Horn, William C Swope, Jed W Pitera, Jeffry D Madura, Thomas J Dick, Greg L Hura, and Teresa Head-Gordon. Development of an improved four-site water model for biomolecular simulations: Tip4p-ew. *J. Chem. Phys.*, 120(20):9665–9678, 2004.
- [60] In Suk Joung and Thomas E Cheatham III. Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations. *J. Phys. Chem. B*, 112(30):9020–9041, 2008.
- [61] Volodymyr Babin, Claude Leforestier, and Francesco Paesani. Development of a “first principles” water potential with flexible monomers: Dimer potential energy surface, VRT spectrum, and second virial coefficient. *J. Chem. Theory Comput.*, 9(12):5395–5403, 2013.
- [62] Volodymyr Babin, Gregory R Medders, and Francesco Paesani. Development of a “first principles” water potential with flexible monomers. II: Trimer potential energy surface, third virial coefficient, and small clusters. *J. Chem. Theory Comput.*, 10(4):1599–1607, 2014.
- [63] Gregory R Medders, Volodymyr Babin, and Francesco Paesani. Development of a “first-principles” water potential with flexible monomers. III. Liquid phase properties. *J. Chem. Theory Comput.*, 10(8):2906–2910, 2014.
- [64] Sandeep K Reddy, Shelby C Straight, Pushp Bajaj, C Huy Pham, Marc Riera, Daniel R Moberg, Miguel A Morales, Chris Knight, Andreas W Götz, and Francesco Paesani. On the accuracy of the MB-pol many-body potential for water: Interaction energies, vibrational frequencies, and classical thermodynamic and dynamical properties from clusters to liquid water and ice. *J. Chem. Phys.*, 145(19):194504, 2016.

- [65] Etienne Palos, Ethan F Bull-Vulpe, Xuanyu Zhu, Henry Agnew, Shreya Gupta, and Francesco Paesani. Current status of the MB-pol data-driven many-body potential for predictive simulations of water across different phases. *J. Chem. Theory Comput.*, 20(21):9269–9289, 2024.
- [66] Xuechen Zhou, Zhangxin Wang, Razi Epsztein, Cheng Zhan, Wenlu Li, John D Fortner, Tuan Anh Pham, Jae-Hong Kim, and Menachem Elimelech. Intrapore energy barriers govern ion transport and selectivity of desalination membranes. *Sci. Adv.*, 6(48):eabd9045, 2020.
- [67] Ben Corry. Designing carbon nanotube membranes for efficient water desalination. *J. Phys. Chem. B*, 112(5):1427–1434, 2008.
- [68] Derek W Smith. Ionic hydration enthalpies. *J. Chem. Educ.*, 54(9):540, 1977.
- [69] Jens Carlsson and Johan Åqvist. Absolute hydration entropies of alkali metal ions from molecular dynamics simulations. *J. Phys. Chem. B*, 113(30):10255–10260, 2009.
- [70] Marc Riera, Justin J Talbot, Ryan P Steele, and Francesco Paesani. Infrared signatures of isomer selectivity and symmetry breaking in the $\text{Cs}^+(\text{H}_2\text{O})_3$ complex using many-body potential energy functions. *J. Chem. Phys.*, 153(4):044306, 2020.
- [71] Debbie Zhuang, Marc Riera, Gregory K Schenter, John L Fulton, and Francesco Paesani. Many-body effects determine the local hydration structure of Cs^+ in solution. *J. Phys. Chem. Lett.*, 10(3):406–412, 2019.
- [72] Debbie Zhuang, Marc Riera, Ruihan Zhou, Alexander Deary, and Francesco Paesani. Hydration structure of Na^+ and K^+ ions in solution predicted by data-driven many-body potentials. *J. Phys. Chem. B*, 126(45):9349–9360, 2022.
- [73] Roya Savoj, Henry Agnew, Ruihan Zhou, and Francesco Paesani. Molecular insights into the influence of ions on the water structure. I. Alkali metal ions in solution. *J. Phys. Chem. B*, 128(8):1953–1962, 2024.
- [74] Gerardo Andrés Cisneros, Kjartan Thor Wikfeldt, Lars Ojamäe, Jibao Lu, Yao Xu, Hedieh Torabifard, Albert P Bartók, Gábor Csányi, Valeria Molinero, and Francesco Paesani. Modeling molecular interactions in water: From pairwise to many-body potential energy functions. *Chem. Rev.*, 116(13):7501–7528, 2016.
- [75] Hilliary O Frank and Francesco Paesani. Molecular driving forces for water adsorption in MOF-808: A comparative analysis with UiO-66. *J. Chem. Phys.*, 160(9):094703, 2024.
- [76] D.L. Carroll’s FORTRAN Genetic Algorithm Driver v1.7a. <https://cuaerospace.com/products-services/genetic-algorithm>, 2001.

- [77] David E. Goldberg. *Genetic algorithms in search, optimization and machine learning*. Addison-Wesley Longman Publishing Co., Inc., USA, 1st edition, 1989. ISBN 0201157675.
- [78] Andrew R Leach. *Molecular modelling: Principles and applications*. Pearson education, 2001.
- [79] Marc Riera, Christopher Knight, Ethan F Bull-Vulpe, Xuanyu Zhu, Henry Agnew, Daniel GA Smith, Andrew C Simmonett, and Francesco Paesani. Mbx: A many-body energy and force calculator for data-driven many-body simulations. *J. Chem. Phys.*, 159(5):054802, 2023.
- [80] Shreya Gupta, Ethan F Bull-Vulpe, Henry Agnew, Shishir Iyer, Xuanyu Zhu, Ruihan Zhou, Christopher Knight, and Francesco Paesani. MBX v1.2: Accelerating data-driven many-body molecular dynamics simulations. *J. Chem. Theory Comput.*, 21(4):1838–1849, 2025.
- [81] Colin R Groom, Ian J Bruno, Matthew P Lightfoot, and Suzanna C Ward. The cambridge structural database. *Struct. Sci.*, 72(2):171–179, 2016.
- [82] Aidan P. Thompson, H. Metin Aktulga, Richard Berger, Dan S. Bolintineanu, W. Michael Brown, Paul S. Crozier, Pieter J. in ’t Veld, Axel Kohlmeyer, Stan G. Moore, Trung Dac Nguyen, Ray Shan, Mark J. Stevens, Julien Tranchida, Christian Trott, and Steven J. Plimpton. LAMMPS – A flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput. Phys. Commun.*, 271:108171, 2022. doi: 10.1016/j.cpc.2021.108171.
- [83] Glenn J Martyna, Michael L Klein, and Mark Tuckerman. Nosé–hoover chains: The canonical ensemble via continuous dynamics. *J. Chem. Phys.*, 97(4):2635–2643, 1992.
- [84] Loup Verlet. Computer “experiments” on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.*, 159(1):98, 1967.
- [85] William C Swope, Hans C Andersen, Peter H Berens, and Kent R Wilson. A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters. *J. Chem. Phys.*, 76(1): 637–649, 1982.
- [86] Roger W Hockney and James W Eastwood. *Computer simulation using particles*. crc Press, 2021.
- [87] Tom Darden, Darrin York, and Lee Pedersen. Particle mesh Ewald: An $N \cdot \log(N)$ method for Ewald sums in large systems. *J. Chem. Phys.*, 98(12):10089–10092, 1993.

- [88] Dassault Systèmes Biovia. Materials studio, 2017.
- [89] Marc Meunier and Struan Robertson. Materials studio 20th anniversary. *Mol. Simul.*, 47(7):537–539, 2021.
- [90] José Mario Martínez and Leandro Martínez. Packing optimization for automated generation of complex system’s initial configurations for molecular dynamics and docking. *J. Comput. Chem.*, 24(7):819–825, 2003.
- [91] Leandro Martínez, Ricardo Andrade, Ernesto G Birgin, and José Mario Martínez. PACK-MOL: A package for building initial configurations for molecular dynamics simulations. *J. Comput. Chem.*, 30(13):2157–2164, 2009.
- [92] Gareth A Tribello, Massimiliano Bonomi, Davide Branduardi, Carlo Camilloni, and Giovanni Bussi. PLUMED 2: New feathers for an old bird. *Comput. Phys. Commun.*, 185(2):604–613, 2014.
- [93] M Mezei. The finite difference thermodynamic integration, tested on calculating the hydration free energy difference between acetone and dimethylamine in water. *J. Chem. Phys.*, 86(12):7084–7088, 1987.
- [94] Robert W Zwanzig. High-temperature equation of state by a perturbation method. I. nonpolar gases. *J. Chem. Phys.*, 22(8):1420–1426, 1954.
- [95] John G Kirkwood. Statistical mechanics of fluid mixtures. *J. Chem. Phys.*, 3(5):300–313, 1935.
- [96] Michael P Allen and Dominic J Tildesley. *Computer simulation of liquids*. Oxford university press, 2017.
- [97] Yuqing Deng and Benoît Roux. Hydration of amino acid side chains: Nonpolar and electrostatic contributions calculated from staged molecular dynamics free energy simulations with explicit water molecules. *J. Phys. Chem. B*, 108(42):16567–16576, 2004.
- [98] Levi N Naden, Tri T Pham, and Michael R Shirts. Linear basis function approach to efficient alchemical free energy calculations. 1. Removal of uncharged atomic sites. *J. Chem. Theory Comput.*, 10(3):1128–1149, 2014.
- [99] Levi N Naden and Michael R Shirts. Linear basis function approach to efficient alchemical free energy calculations. 2. Inserting and deleting particles with Coulombic interactions. *J. Chem. Theory Comput.*, 11(6):2536–2549, 2015.
- [100] Thomas C Beutler, Alan E Mark, René C van Schaik, Paul R Gerber, and Wilfred F Van Gunsteren. Avoiding singularities and numerical instabilities in free energy calcula-

- tions based on molecular simulations. *Chem. Phys. Lett.*, 222(6):529–539, 1994.
- [101] M Zacharias, TP Straatsma, and JA McCammon. Separation-shifted scaling, a new scaling method for Lennard-Jones interactions in thermodynamic integration. *J. Chem. Phys.*, 100(12):9025–9031, 1994.
 - [102] Andrew D White and Gregory A Voth. Efficient and minimal method to bias molecular simulations with experimental data. *J. Chem. Theory Comput.*, 10(8):3023–3030, 2014.
 - [103] RW Impey, PA Madden, and IR McDonald. Hydration and mobility of ions in solution. *J. Phys. Chem.*, 87(25):5071–5083, 1983.
 - [104] HJ Bakker and JL Skinner. Vibrational spectroscopy as a probe of structure and dynamics in liquid water. *Chem. Rev.*, 110(3):1498–1517, 2010.
 - [105] Jeffrey R Errington and Pablo G Debenedetti. Relationship between structural order and the anomalies of liquid water. *Nature*, 409(6818):318–321, 2001.
 - [106] Alan M Ferrenberg and Robert H Swendsen. Optimized Monte Carlo data analysis. *Phys. Rev. Lett.*, 63(12):1195, 1989.
 - [107] Grossfield, Alan. WHAM: the weighted histogram analysis method. version 2.0.10. <http://membrane.urmc.rochester.edu/content/wham/>.

Chapter 5

Conclusion

The rising demand for clean and renewable energy technologies and sustainable resource recovery has amplified the need for rationally designed materials with tunable and improved properties. Among such candidates, reticular materials such as covalent organic frameworks (COFs) and metal–organic frameworks (MOFs) have garnered significant attention due to their modular architectures, high porosity, and chemical tunability. COFs are particularly promising for applications in organic electronics and photocatalysis, while MOFs offer promising potential in selective ion uptake and environmental remediation. However, an electronic-level understanding of how subtle variations in composition and structure influence functional behavior in COFs remains largely underdeveloped, as well as the detailed mechanisms underlying the ion transport and uptake processes in MOFs. This dissertation aims to address these knowledge gaps through a series of computational investigations into the composition–structure–property relationships that govern the electronic, photophysical, as well as ion uptake characteristics and behaviors in these reticular materials.

In this dissertation, we have advanced a deeper electronic-level understanding of how compositional and structural features, such as chemical functionalization, interlayer stacking, and lattice symmetry, tune the electronic, transport, photophysical properties of two-dimensional (2D) COFs, and molecular-level insights on the thermodynamics of ion uptake behaviors in MOFs.

Our investigations into 2D layered donor–acceptor COFs using density functional theory and multiparticle Holstein formalism reveal that interlayer stacking arrangements profoundly affect charge delocalization and transport behavior. Specifically, the eclipsed stacking configuration enables anisotropic charge transport with potential metallicity along the stacking direction, whereas staggered configurations display more localized charge character, with staggered II offering unipolar transport properties favorable for single-carrier devices. These findings suggest that band dispersion induced by interlayer interactions can be leveraged to engineer 2D COFs with directionally tuned conductivity, particularly in low-band-gap systems.

Complementing these results, our second study demonstrates that chemical functionalization, stacking slipping, and symmetry breaking in COFs modulate their composition–structure–property relationships in a highly nontrivial manner. While van der Waals interactions dictate the general preference for slipped stacking, variations in electrostatic interactions lead to nuanced differences in the extent of slipping, and in turn, in the charge transport and photoelectronic properties. Notably, breaking lattice symmetry via heterocyclic or asymmetric functional groups in the backbone emerges as an effective strategy to tune COFs’ electronic and photophysical behavior. These insights provide practical guidelines for the rational design of photocatalytically active COFs.

To further understand the microscopic ion uptake process in MOFs, we employed free-energy calculations, molecular dynamics, and enhanced sampling techniques to unravel the mechanisms governing alkali metal ion uptake in MOF-808 from dilute aqueous environments. Our results highlight the dominant role of pore confinement, hydration shell structures and environments, and ion–framework interactions in determining ion uptake and selectivity. We observe a dynamic interplay between dehydration penalties and spatial confinement, with different ions exhibiting contrasting preferences in dehydrated vs. hydrated environments. These findings establish a foundation for tuning pore chemistry and confinement to achieve improved selective ion capture, particularly for critical metals such as lithium, from seawater.

Together, these studies offer a unified computational framework to decode complex

composition–structure–property relationships in reticular materials such as COFs and MOFs, and guide the targeted design and development of COFs and MOFs for improved electronic, photocatalytic, and ion uptake applications.