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Los Angeles

Organic Semiconductor Aggregates:
from Molecular Designs to Device Applications

A dissertation submitted in partial satisfaction of the requirements
for the degree Doctor of Philosophy
in Materials Science and Engineering

by

Ran Zheng

2024

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ABSTRACT OF THE DISSERTATION

Organic Semiconductor Aggregates:
from Molecular Designs to Device Applications

by

Ran Zheng

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2024

Professor Yang Yang, Chair

Organic semiconductors built on π -conjugated structures have attracted significant attention due to their distinctive optical, electronic, and mechanical properties. These characteristics position them as ideal materials for various electronic devices. Notably, their strong light absorption and efficient charge transport capabilities mark organic semiconductors as promising solutions for addressing the global energy crisis through solar energy conversion. However, precise control of “soft” nanostructures formed by the noncovalently aggregated organic semiconductors for achieving desired optoelectronic properties is challenging, compared to

covalently or ionically inorganic semiconductors with rigid architectures. In Chapter 1, I will introduce basic structures and properties of organic semiconductors, especially on their molecular packing behavior. The structure-property relationship of organic semiconductors will be discussed in terms of device applications, such as the development of near-infrared donor and acceptor materials for organic photovoltaics. From molecular designs to device applications, in the following chapters, I will introduce the chemistry of several organic semiconductor aggregates constructed from twisted and nonplanar π -systems and their performances in various solar energy fields, such as photocatalytic hydrogen reaction, organic photovoltaics and perovskite solar cells.

In Chapter 2, I will show the self-assembly of noncovalent π -stacked organic frameworks that shows a higher activity for photocatalytic hydrogen evolution. I will first introduce the background of noncovalent π -stacked organic frameworks, which are a subclass of porous materials that consist of crystalline networks formed by self-assembly of organic building blocks through π - π interactions. π -stacked organic frameworks based on spirofluorene as central units and 3-(dicyanomethylidene)indan-1-one as end groups demonstrate strong visible light absorption from 500 nm to 700 nm and high surface area ($248 \text{ m}^2 \text{ g}^{-1}$) with 1.8 nm hydrophilic micropores, rendering them well-suited for applications in photocatalysis. The fabricated π -stacked organic frameworks nanoparticles exhibit hydrogen evolution rate up to $152 \text{ mmol h}^{-1} \text{ g}^{-1}$ at room temperature and $618 \text{ mmol h}^{-1} \text{ g}^{-1}$ at 70°C . Cryo-transmission electron microscopy further reveal the native morphology of these nanoparticles and the cocatalyst Pt loading status on them.

In Chapter 3, I will discuss the singlet fission property of pentacene polymer and its application in organic photovoltaics. Singlet fission is a process that converts one singlet exciton into two triplet excitons while conserving spin. This exciton multiplication process has the

potential to overcome the Shockley-Queisser limit of solar power conversion efficiency. Pentacene with high mobility has proved to be ideal organic semiconductors for singlet fission organic photovoltaics. Nevertheless, the cost-intensive vacuum deposition process and the propensity of molecular aggregation in the solid state to prematurely quench triplet excitons pose challenges for their application in photovoltaics. To address these issues, a pentacene polymer is engineered with pentacene units arranged orthogonally to the polymer backbone. This design facilitates the use of pentacene-based materials in organic photovoltaics as donor materials through solution processing. Rapid conversion of photoexcited singlets into triplet pairs, occurring on a picosecond time scale (495 ps) and further dissociate into two “free” triplet excitons in 9.8 μ s are observed in the pentacene polymer via transient absorption spectroscopy. The resulting photovoltaic devices based on pentacene polymer and nonfullerene acceptors demonstrate 1.92% power conversion efficiency.

In Chapter 4, I will focus on a helicene-based organic semiconductor and its application as electron transport layer in inverted perovskite solar cells. Electron transport layer materials based on fullerene tend to form large clusters and undergo dimerization when exposed to light, leading to a deterioration in electron transport capability and device degradation. The nonplanar geometry of helicenes proves effective in preventing such aggregation issues, thereby enhancing device stability. We have successfully synthesized a small-molecule n-type organic semiconductor utilizing [6]helicene. This compound was employed as the electron transport layer, n-doped by organic amines, in an inverted perovskite solar cell, achieving an impressive power conversion efficiency of over 16%.

The dissertation of Ran Zheng is approved.

Richard B. Kaner

Jaime Marian

Yuzhang Li

Yang Yang, Committee Chair

University of California, Los Angeles

2024

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Selected Publications

1. **Zheng, R.**, Meng, D., Yang, Y., **Noncovalent π -stacked organic frameworks (π OFs): A promising class of porous materials.** *Mater. Today*, In revision.
2. Tan, S., Huang, T., Yavuz, I., Wang, R., Yoon, T., Xu, M., Xing, Q., Park, K., Lee, D.-K., Chen, C.-H., **Zheng, R.**, Yoon, T., Zhao, Y., Wang, H.-C., Meng, D., Xue, J., Song, Y., Pan, X., Park, N.-G., Lee, J.-W., Yang, Y., **Stability-limiting Heterointerfaces of Perovskite Photovoltaics.** *Nature* 2022, 605, 268.
3. Meng, D., **Zheng, R.**, Zhao, Y., Zhang, E., Dou, L., Yang, Y., **Near-Infrared Materials: The Turning Point of Organic Photovoltaics.** *Adv. Mater.* 2022, 34, 2107330.
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Chapter 1 Introduction to organic semiconductors

Organic semiconductors, characterized by π -conjugated chemical structures, have become a focal point of research, particularly after the 2000 Nobel Prize in Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa for their groundbreaking work on conductive polymers¹. The adaptability of carbon-based structures, in contrast to silicon, allows for the customization of organic semiconductors with desired optoelectronic properties, making them integral components in various electronic devices. These include organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs)². In contrast to their individual molecular states in dilute solutions, organic semiconductors exhibit diverse nanostructures in the solid state due to supramolecular interactions, influenced by both molecular structures and processing conditions. The optoelectronic properties are intricately linked to the aggregated morphology, significantly impacting device applications. Different applications necessitate specific material designs. For example, organic field-effect transistors (OFETs) demand efficient charge transport horizontally, favoring planar π -conjugated units for stronger aggregation. On the other hand, organic photovoltaics (OPVs) benefit from proper phase separation in the vertical direction to enhance charge transport and extraction. Hence, a meticulous exploration of the structure-property relationship in organic semiconductor aggregates is imperative to achieve optimal device performances.

The distinctive feature of organic semiconductors lies in the delocalization of π electrons throughout a π -conjugated backbone, contributing to their excellent performance³. This characteristic has fueled the continuous exploration of novel organic semiconductor materials, primarily achieved by connecting organic building blocks through covalent bonds. Simultaneously, noncovalent intermolecular interactions, such as π - π interactions, also play a crucial role⁴. These

interactions guide individual molecules to self-assemble into aggregates with various packing patterns, introducing increased structural dimensionality. The property of aggregates is distinguished from their organic semiconductor monomer due to electronic coupling between adjacent molecules⁵. As shown in **Figure 1.1a**, two organic semiconductor molecules in neighbors can form 4 different dimers with various structural deviations from ideal face-on geometry through π - π interactions. Specifically, H-aggregate is defined as arrangements of molecules with face-on packing that promotes strong electronic coupling between them while J-aggregate refers to the eclipsed arrangement with strong fluorescence. These dimer aggregates will further self-assemble into various 3D structures (**Figure 1.1b**), which will ultimately determine the operational performances of electronic devices⁶.

To optimize device performance, the optoelectronic properties of organic semiconductors must be precisely modulated through molecular engineering. Different devices have diverse requirements for material design, influenced by the device mechanism, processing method, application scenario, and commercialization concerns. For example, organic photovoltaics (OPVs) based on donor-acceptor heterojunctions have gained prominence in the field of renewable energy due to their non-toxic nature, lightweight, low cost, and flexibility. The goal of OPVs is to convert light into electricity, and their working mechanism involves exciton generation, diffusion, charge separation, transport, and collection (**Figure 1.2a**). Prof. Yang Yang has been a pioneer in enhancing solar spectrum utilization by designing near-infrared (NIR) organic semiconductors⁷. Traditionally, active materials like poly(3-hexylthiophene) (P3HT), poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene, and phenyl-C61-butyric acid methyl ester (PCBM) could only absorb UV-visible light up to 650 nm, resulting in a low power conversion efficiency (PCE) of less than 5%. However, the infrared (IR) absorption region holds 52% of the total energy in the

solar spectrum (**Figure 1.2c**). Prof. Yang's group started investigating NIR-absorbing organic materials in 2008⁸, achieving the first OPV device with a certified PCE surpassing 10% in 2013 through the rational design of p-type NIR polymer⁹. In the era dominated by fullerene acceptors, efforts focused on developing NIR-absorbing p-type polymer donors. However, nonfullerene acceptors (NFAs) emerged as a new trend in 2012, allowing more flexibility in chemical structure modification¹⁰. This made it considerably simpler to shift NFAs' absorption window to the near infrared. The focus then shifted to developing NIR NFAs, leading to high-efficiency devices. In 2019, Prof. Yang's group designed and synthesized NIR NFAs, Y1 and Y2, with optical bandgaps smaller than 1.4 eV (900–950 nm window)¹¹. Subsequent modifications in molecular structures yielded Y3, achieving a PCE of over 14%¹². This inspired the design of the well-known acceptor, Y6, leading to a rapid advancement of the Y-series NIR NFAs, with a PCE exceeding 19%¹³⁻¹⁶. The critical criterion for assessing novel NIR materials is the absorption window. The most successful method for tuning the absorption window is intramolecular charge transfer (ICT), based on the electron push–pull effect between an electron-donating unit and an electron-withdrawing unit (D–A effect)¹⁷. Adjusting the strength of a single ICT or introducing multi-ICT can fine-tune the material's absorption (**Figure 1.2b**).

The potential of semiconductors is yet to be fully exploited, particularly in the context of photovoltaic applications, where the Shockley-Queisser limit defines the theoretical boundary¹⁸. Addressing challenges in charge transport and device stability in photovoltaics applications also requires interfacial engineering with suitable materials. Besides photovoltaics, while inorganic semiconductors dominate solar-energy conversion technologies like photocatalysis, their use raises concerns about environmental pollution and is often limited to specific structures¹⁹. Organic semiconductors, characterized by unique configurations of π -conjugated units (**Figure 1.3**) to

control aggregation behavior and their optoelectronic properties, present promising solutions. Specifically, spirofluorene units with their unique 3D extended configuration are well-suited for constructing 3D π -stacked porous networks with a high surface area. This characteristic enables effective accumulation of active sites, particularly beneficial in photocatalytic applications. Linear and planar configurations like pentacene ensure superior charge transport but often lead to significant aggregation, compromising the solution processability and thermal stability of organic semiconductors²⁰. Moreover, the singlet-fission feature of pentacene, which can generate two excitons from the absorption of one photon is expected to overcome the Shockley-Queisser limit²¹. Conversely, nonplanar structures, such as orthogonal or twisted designs like spirofluorene, maintain comparable charge transport properties with π -conjugation while enhancing solubility and thermal stability²². For instance, spiro-OMeTAD is widely used for hole-transport material in perovskite solar cells due to its superior optoelectronic properties such as proper energy-level alignment with perovskite absorbers, high mobility, good solubility in common solvents for facile processing and excellent thermal stability²³. Twisted structures like helicene introduce structural asymmetry, such as chirality, imparting unique optoelectronic properties like circular dichroism and circular photoluminescence²⁴. The structural versatility of organic semiconductors provides a platform for in-depth investigation into the relationship between molecular structures, aggregation behaviors, and optoelectronic properties. This exploration is fundamental for constructing the next generation of high-performance electronic devices.

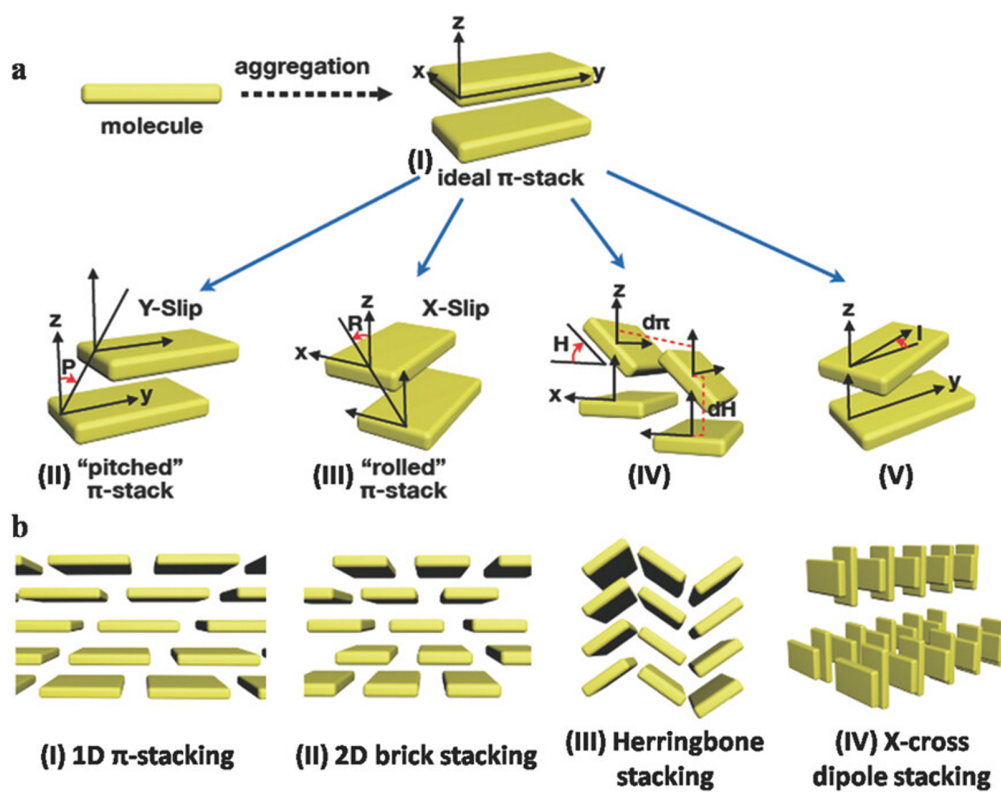


Figure 1.1 | (a) Schematics of aggregated dimers of organic semiconductors. (b) Schematics of 3D packing patterns of organic semiconductors.⁶

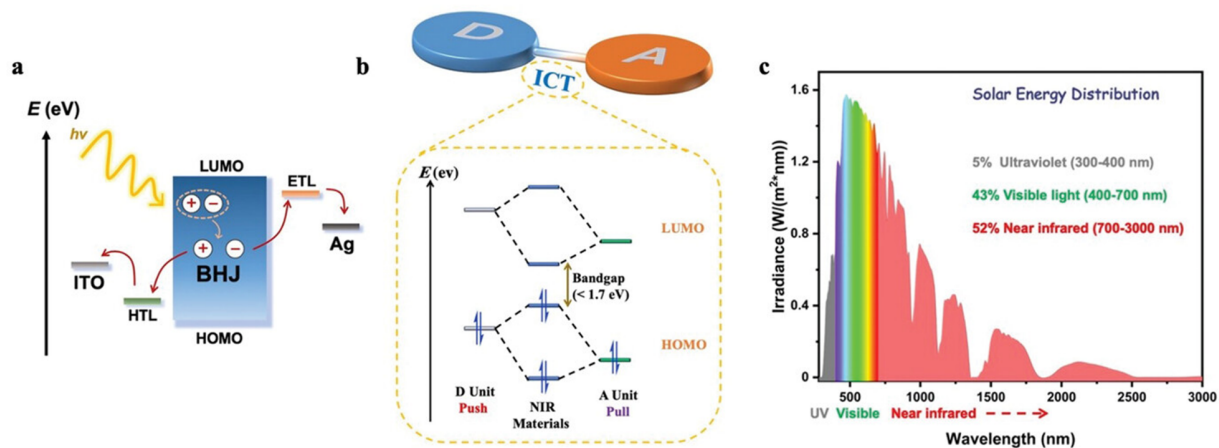


Figure 1.2 | (a) Schematics of operational mechanism of OPVs. (b) Schematics of ICT effect between donor-acceptor units in organic semiconductors. (c) Solar radiation spectrum.⁷

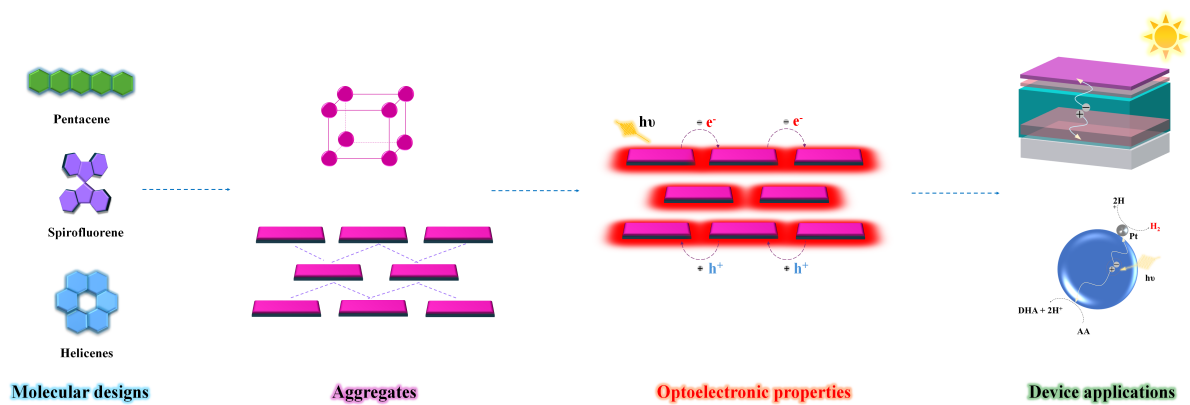


Figure 1.3 | Relationship between molecular designs, aggregation behavior, optoelectronic properties, and device applications.

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Chapter 2 Noncovalent π -stacked organic framework for photocatalytic hydrogen evolution

2.1 Introduction of noncovalent π -stacked organic framework

Over the past two decades, researchers in both scientific and industrial fields have extensively explored functional porous materials, including zeolites, metal–organic frameworks (MOFs), and covalent organic frameworks (COFs)¹⁻⁵. These intricate frameworks, characterized by their diverse chemical compositions, sizes, topologies, and porosities, have found wide-ranging applications in gas separation and storage, heterogeneous catalysis, sensing, and energy conversion. Zeolites, initially discovered as naturally occurring porous aluminosilicates, were subsequently synthesized in laboratories. Despite their inherent stability and cost-effectiveness, achieving ordered porous structures with specific pore sizes in zeolites, along with modifying their topology and functionality, remains a challenge.

In contrast, MOFs and COFs, self-assembled from meticulously designed building blocks, have garnered significant attention due to their permanent porosity, customizable structures, and diverse range of functionalities. In addition to MOFs and COFs, which are self-assembled through strong coordinative or covalent bonds, novel porous organic molecular materials comprising reversible and weak noncovalent interactions have gained significant attention owing to their utilization of simple building blocks and the soft nature of supramolecular assemblies⁶⁻⁹. These noncovalent interactions include hydrogen bonds, π - π interactions, electrostatic interactions, hydrophobic interactions, van der Waals forces, and so on.

These extended porous frameworks demonstrate many unique advantages owing to the reversible and flexible nature of noncovalent interactions. For instance, complicated porous

structures can be synthesized from functionalized single-component small molecules, which can be readily synthesized and purified by recrystallization. Furthermore, these flexible and dynamic porous lattices can exhibit responsiveness and alterability in terms of various physical properties, such as shape memory¹⁰ and light emission¹¹.

To delve into the realm of weaker non-covalent interactions, a novel category of porous crystalline solids, known as noncovalent π -stacked organic frameworks (π OFs), has recently emerged as an advancing research field. These frameworks are assembled from organic building blocks through π - π interactions, which involve the interactions between aromatic rings containing π orbitals. These interactions are renowned for their significance in both synthetic and natural systems, such as DNA base-pairing, protein folding, and molecular recognition.

A brief timeline of π OFs highlights the key milestones achieved during their development from the initial concept of π - π interactions (**Figure 2.1**). In 1990, Hunter and Sanders first introduced the concept of π - π interactions, highlighting the influence of electrostatic effects on the geometry of π -stacking patterns⁵. They proposed that van der Waals interactions, driven by the extent of π overlap between aromatic units, primarily dictate the strength of these interactions. When considering unsubstituted aromatic units, a simplified treatment involves depicting them as a quadrupole moment. This is with a “ σ -framework” positively charged and ensconced between negatively charged π -electron clouds. An electrostatic repulsion effect between these π -electron clouds favors a slipped or edge-on (T-shape) geometry.

Conversely, aromatic units influenced by electron-withdrawing (EWGs) or electron-donating groups (EDGs) exhibit polarization effects. These can either stabilize or destabilize face-on π - π interactions, depending on how they adjust the electrostatic repulsion. Subsequent research by Siegel and co-workers explored the through-space polar/ π interactions involving substituted

benzene rings in 1,8-diarylnaphthalenes, which was characterized through the utilization of two-dimensional nuclear magnetic resonance spectroscopy (2D-NMR)¹². The outcomes of their research suggested that Coulombic forces exerted a dominant influence on the interactions between two benzene rings. This is attributed to their limited π -overlap areas, which results in relatively minor contributions from the van der Waals term.

Furthermore, when one of the benzene rings is substituted with an EWG, this modification leads to a reduction in repulsion forces between the two phenyl groups. This proposition is corroborated by observed changes in the energy barriers for rotation of naphthalene derivatives. Contrarily, Sherrill and co-workers contested that relying solely on electrostatic effects does not yield precise predictions of binding energies and substituent effects within π - π interactions. Through theoretical analysis, they determined that all substituents, regardless of being electron-donating or electron-withdrawing, lead to heightened binding energies for dimers adopting sandwich configurations. This observation emerged after taking dispersion and exchange-repulsion contributions into account. Subsequently, they conducted an energy component analysis using symmetry-adapted-perturbation theory (SAPT), providing further insight into the impacts of substituents and heteroatoms on π - π interactions¹³. Later, Houk and co-workers introduced a novel model formulated by computational methods that posits direct interactions between substituents and the unsubstituted benzene ring, as opposed to inducing polarization of the π -system¹⁴.

While the model and mechanism governing π - π interactions remain subjects of ongoing debate¹⁵, numerous studies have showcased the potential to finely adjust the geometry and strength of these interactions by incorporating substituent groups into aromatic systems. This exploration has been conducted from both experimental and computational viewpoints. Notably, π - π interactions have been harnessed for constructing a diverse array of intricate supramolecular

architectures, including alloy helices¹⁶ and triaxial supramolecular weaves¹⁷. Moreover, the capacity of nanostructures to react to external stimuli through π - π interactions and subsequently produce output signals paves the way for practical applications, such as rapid DNA sequencing¹⁸, in various devices.

Given the distinctive attributes of π - π stacking interactions and their pervasive presence in supramolecular chemistry, we leveraged these interactions to engineer a novel organic framework, coining the concept " π OFs" in 2020¹⁹. Due to the inherent characteristics of π - π interactions, including reversibility, flexibility, and lack of directionality, π OFs exhibit superior recyclability, a unique self-healing property, and remarkable thermostability. Moreover, their π -stacking nature imparts excellent carrier mobility, rendering them viable candidates for high-performance organic electronics. The concept of π OFs has garnered widespread acknowledgment since our initial report²⁰⁻²⁶. The exploration of novel chemical building blocks and topologies for π OFs construction has led to the emergence of novel properties and applications in this field. Noteworthy among these are selective gas separation, molecular structure determination techniques, and electrocatalysis.

2.2 Synthesis and characterizations of noncovalent π -stacked organic framework

Creating enduring porosity in porous organic crystals is challenging due to the tight packing tendency of distinct molecules, limiting the formation of void spaces²⁷. Additionally, weak non-covalent interactions, such as π - π interactions, often result in insufficient intermolecular connections and poor structural stability in the entire framework. While various π -conjugated molecules in the field of organic semiconductors can assemble into diverse 2D and 3D motifs via π - π interactions, these configurations typically lack porosity²⁸⁻³¹. Remarkably, π -stacked organic

frameworks (π OFs) overcome this limitation, achieving significant porosity while maintaining a stable 3D framework structure after guest removal. The key to this success lies in molecular design strategies involving multiple π -conjugated units and the extension of π -conjugated contact areas. Implementing such strategies enables the stabilization of π -stacked porous structures, leading to impressive permanent porosity, especially when central units remain rigid and fully conjugated through covalent bonds with sp^3 carbon in spiro units.

Hence, our monomer structures are meticulously designed for self-assembly into π OFs based on several key principles, ensuring the creation of a robust porous network ideal for photocatalytic hydrogen evolution applications. First, we employ spirofluorene units as core structures to guarantee a three-dimensional assembly topology. Second, we utilize single bonds to connect the end groups to the core structures, imparting high flexibility to the entire structure and facilitating the formation of a soft network. Third, we introduce polar groups (oxygen atoms) into the side chains to form hydrogen bonds with water, enhancing the materials' hydrophilicity. Finally, the Intramolecular Charge Transfer (ICT) effect between the electron-donating spirofluorene and electron-withdrawing 3-(dicyanomethylidene)indan-1-one (IC) end groups imparts the organic semiconductor with strong light absorption. These design strategies collectively render our π OF materials as ideal candidates for photocatalytic hydrogen evolution due to their high surface areas, hydrophilicity, strong light absorption, and efficient charge transport.

The target monomer SFOEHIC was obtained via a two-step organic synthesis. Intermediate 1 was obtained through Suzuki-coupling. SFOEHIC was synthesized via Knoevenagel condensation between 1 and IC in 86% yield (**Figure 2.2**). The structures of compound 1 and SFOEHIC were confirmed by ^1H NMR (**Figure 2.3**, **Figure 2.4**). The thermal properties were evaluated using thermal gravimetric analysis under nitrogen. SFOEHIC showed high thermal

stability with a 5% weight loss at a decomposition temperature of over 339 °C (**Figure 2.5**). The bandgap and optical absorption were investigated by ultraviolet-visible spectrum and electrochemical cyclic voltammetry. The optical bandgap obtained from the edge of absorption spectra in the film was calculated to be 1.65 eV (**Figure 2.6a**). The energy level and electrochemical bandgap are estimated to be -5.75 eV for the highest occupied molecular orbital (HOMO), -3.94 eV for the lowest unoccupied molecular orbital (LUMO), and 1.81 eV for the bandgap, which are obtained from the onset oxidation and reduction potentials and the difference of HOMO and LUMO, respectively (**Figure 2.6b**). The narrow bandgap is attributed to the strong electron-withdrawing end group IC and endows the system with ambipolar characteristics.

The 3D-assembly porous structures of π OF-SFOEHIC are confirmed by single-crystal X-ray diffraction. The single crystal is obtained by slow vapor diffusion (toluene/hexane). As shown in **Figure 2.7**, each crisscrossed SFOEHIC molecule is connected to four adjacent SFOEHIC molecules through four pairs of π - π interactions through antiparallel end groups. Such packing forms a 2D reticular quadrangular array that undergoes perpendicular slipped one-dimensional (1D) stacking through $\text{CH}\cdots\pi$ interactions and hydrogen bonding, forming a final 3D lamellar structure. Closer investigation of the structure reveals that four discrete SFOEHIC molecules of each layer form a dimetric micropore, which has a diameter of 1.75 nm. As shown in **Figure 2.8a**, the powdery sample of guest-free π OF-SFOEHIC presented a typical type I sorption isotherm for N_2 bearing a steep slope in the high relative pressure (P/P_0) range for microporous structure within the 1-to-2-nm range. The corresponding Brunauer-Emmett-Teller (BET) surface area was over $248 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of π OF-SFOEHIC based on the nonlocal density functional theory (NLDFT) model showed a single peak at 1.8 nm (**Figure 2.8b**), which is consistent with the uniform dimetric pores of the crystal packing structure. The microporous structures with high

surface areas are fundamental to the photocatalytic hydrogen evolutions since they provide more interfacial contact with water and enhance the cocatalyst Pt loading.

2.3 Synthesis, characterizations of π -stacked organic framework@Pt nanoparticles and their applications in photocatalytic hydrogen evolution

To disperse π OF-SFOEHIC more effectively in the water phase for subsequent photocatalytic applications, we fabricated them into aqueous nanoparticles using the mini-emulsion method³². The nanoparticle fabrication procedure is illustrated in **Figure 2.9**. The π OF-SFOEHIC was dissolved in the organic solvent (chloroform) and added dropwise to a surfactant (sodium 2-(3-thienyl)ethoxybutylsulfonate (TEBS)) aqueous solution under stirring. Emulsification was then conducted using an ultrasonic probe. Chloroform was evaporated, and a nanoparticle dispersion was formed. The photodeposited Pt cocatalyst decorated the surface of the π OF-SFOEHIC nanoparticles, facilitating electron transfer from the photocatalyst to protons in the aqueous phase by providing sites for proton adsorption and electron accumulation.

The nanoparticle morphologies were investigated by cryo-transmission electron microscopy (cryo-EM). This technique was chosen to image samples in an environment close to their native state, preserving their morphology. Cryo-EM revealed that the π OF-SFOEHIC nanoparticles had a spherical shape (**Figure 2.10a**). After the photodeposition of Pt, the morphology of the π OF-SFOEHIC nanoparticles did not change significantly (**Figure 2.10b**). Magnified pictures showed that Pt is dispersed both on the surface and in the internal regions of π OF-SFOEHIC nanoparticles, with a 1.8 nm radius and 2.3 Å lattice spacing in the Pt (111) surface (**Figure 2.10c**). Elemental mapping images displayed a highly uniform dispersion of C, N, S, and

Pt elements throughout the entire π OF-SFOEHIC. Particularly, it confirmed that Pt has been evenly loaded on the π OF-SFOEHIC nanoparticles (**Figure 2.10d**).

Photocatalytic hydrogen evolution experiments were carried out to assess the activity of π OF-SFOEHIC, using ascorbic acid as a sacrificial electron donor and Pt as a cocatalyst. The photodeposited Pt cocatalyst decorated the surface of the π OF-SFOEHIC and facilitated electron transfer from the photocatalyst to protons in the aqueous phase by providing sites for proton adsorption and electron accumulation. Ascorbic acid, a sacrificial donor, was employed to scavenge the photogenerated holes, maintaining photocatalyst stability. We optimized the hydrogen evolution performance of π OF-SFOEHIC@Pt nanoparticles by adjusting the ratio of surfactant TEBS (**Figure 2.11**) and cocatalyst Pt loading (**Figure 2.12**). Furthermore, we conducted hydrogen evolution measurements for π OF-SFOEHIC@Pt nanoparticles at various concentrations using the optimized TEBS and Pt ratio loadings (**Figure 2.13**). Under the optimized conditions, the average hydrogen evolution rate reached $152 \text{ mmol h}^{-1} \text{ g}^{-1}$ and $618 \text{ mmol h}^{-1} \text{ g}^{-1}$ at room temperature and 70°C , respectively (**Figure 2.14**), which is one of the highest mass-normalized photocatalytic hydrogen evolution rates reported to date compared to various benchmark photocatalytic materials under similar conditions³³⁻³⁸ (**Table 2.1**).

2.4 Conclusion

Organic semiconductors are attractive photocatalysts, but their activity is limited by the intrinsic low surface areas due to their 2D packing patterns. High surface area organic frameworks such as COF and MOF are fascinating catalytic candidate materials, but they lack strong light absorption, which leads to low photocatalytic activities. Organic frameworks assembled from organic semiconductors offer a novel strategy for production of solar fuels from water due to their

high surface areas and strong light absorption. Here we develop a strategy to achieve a noncovalent π -stacked organic frameworks (π OFs) that show a higher activity for photocatalytic hydrogen evolution. We attribute the high photocatalytic activity to the superior charge transport via π - π interactions, strong visible light absorption, high surface area ($248 \text{ m}^2 \text{ g}^{-1}$) and 1.8 nm hydrophilic micropores. These pores functionalized with heteroatoms demonstrate high affinity to Pt clusters, leading to the hydrogen evolution rate up to $152 \text{ mmol h}^{-1} \text{ g}^{-1}$. Optimization of reaction temperature further promotes the hydrogen evolution rate up to $618 \text{ mmol h}^{-1} \text{ g}^{-1}$. The cryo-EM also confirms the uniform Pt distribution over the π OF-SFOEHIC nanoparticles. Our results provide a novel materials design strategy for achieving high-performance photocatalytic hydrogen evolutions.

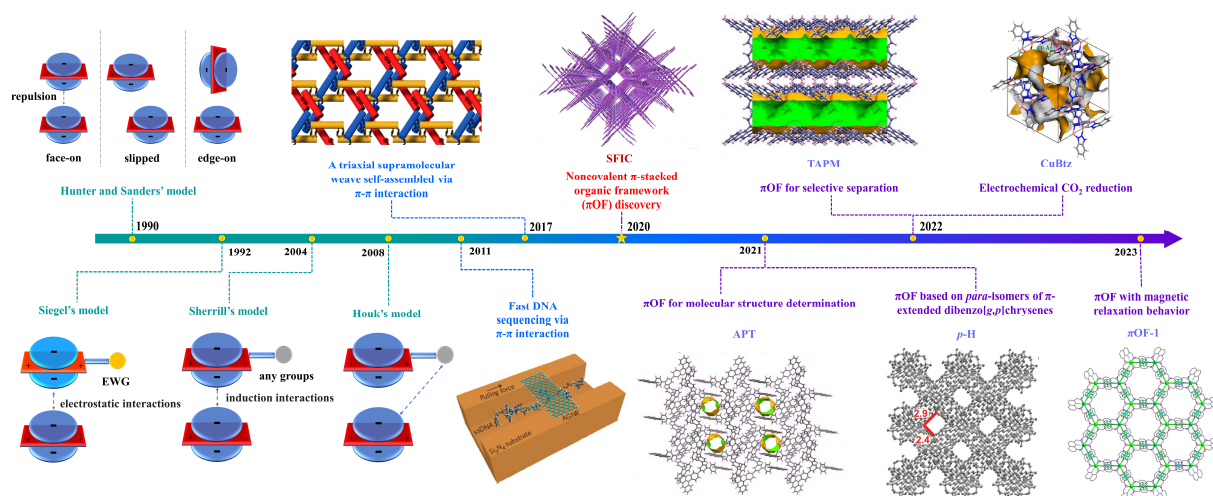


Figure 2.1 | Timeline of key milestones towards π OFs from the evolution of π - π stacking interactions models.

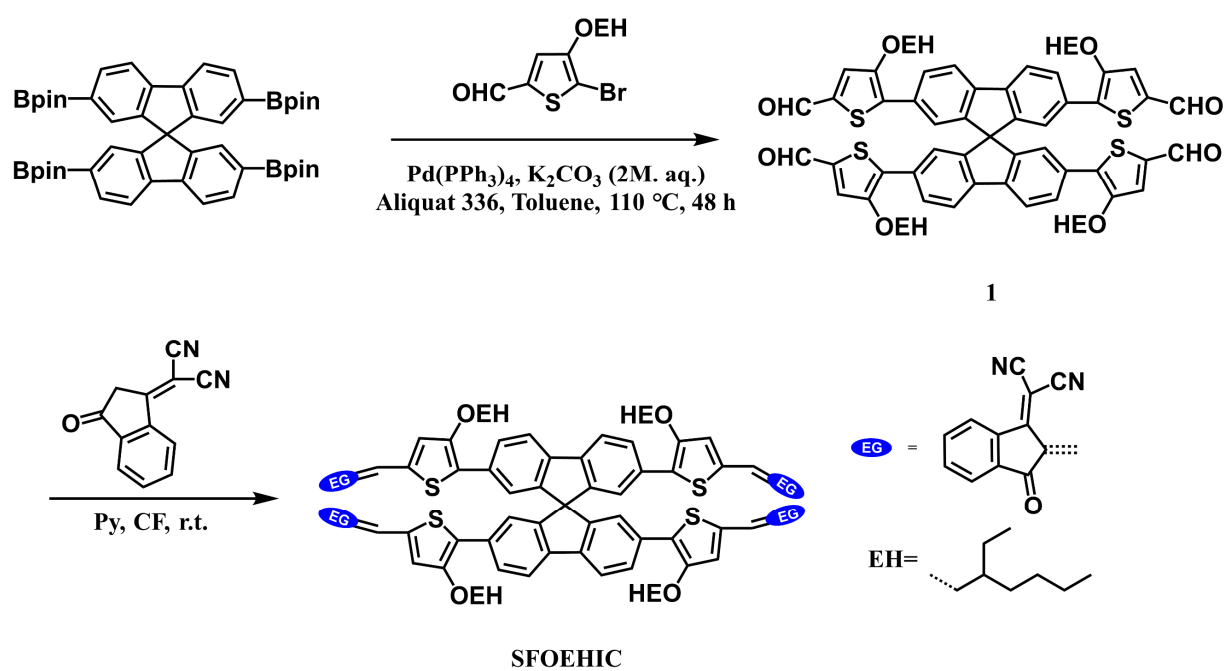


Figure 2.2 | Synthetic route for SFOEHIC.

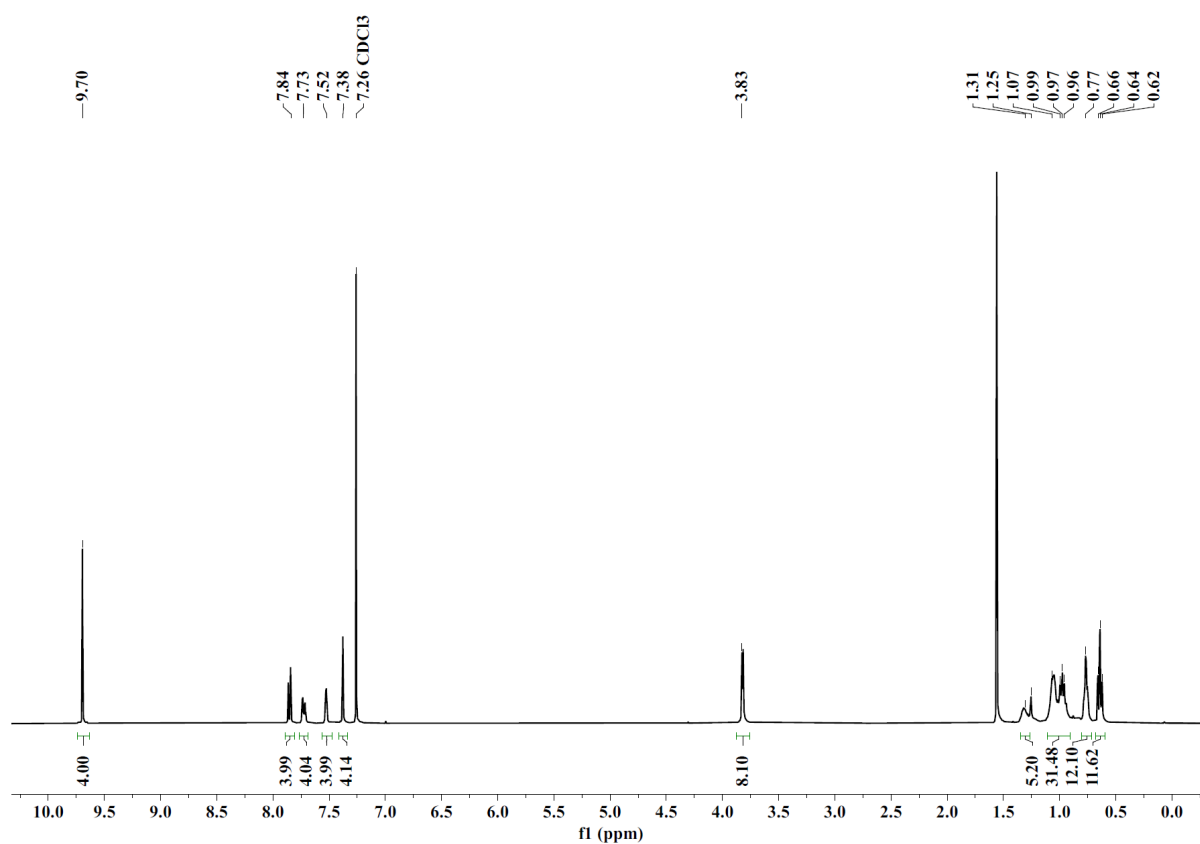


Figure 2.3 | ^1H NMR spectra of SFOEHIC. (400 MHz, CDCl_3 , 298.5 K)

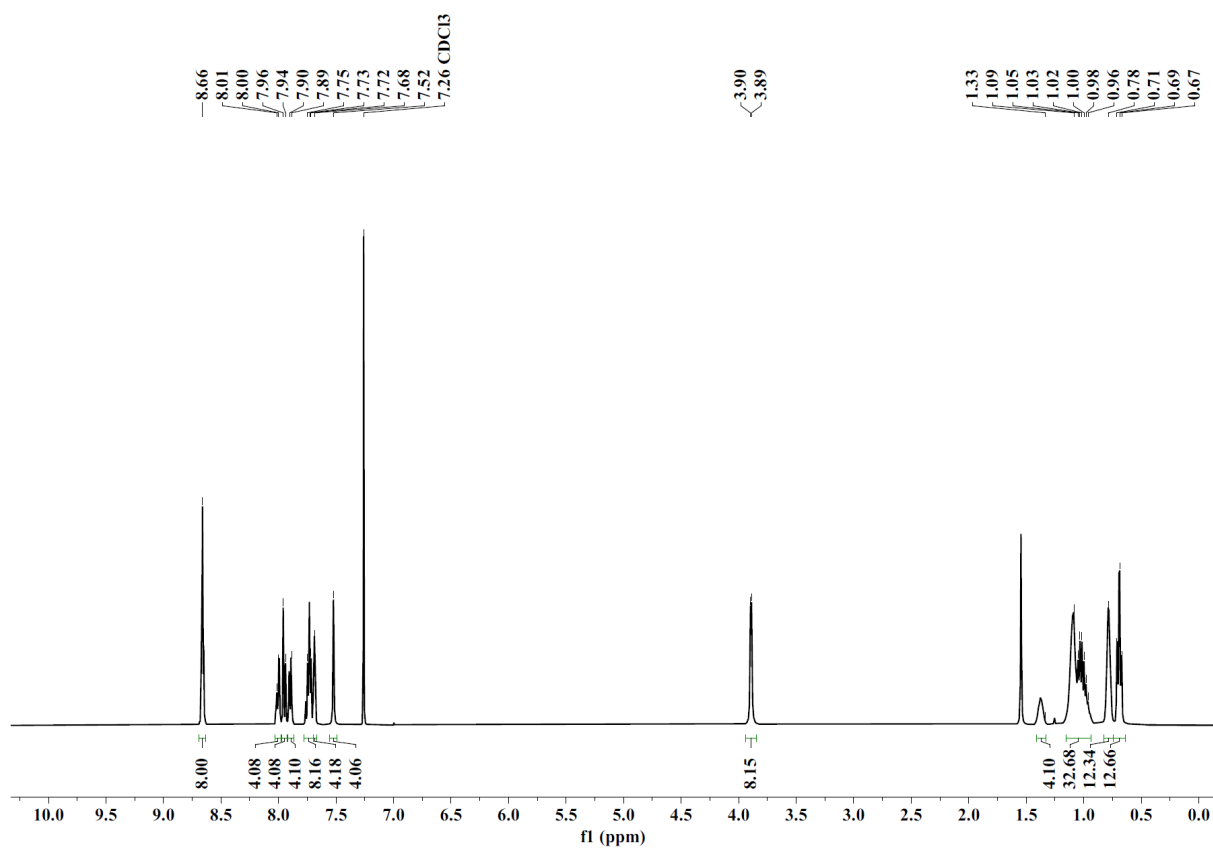


Figure 2.4 | ¹H NMR spectra of compound 1 (400 MHz, CDCl₃, 298.5 K).

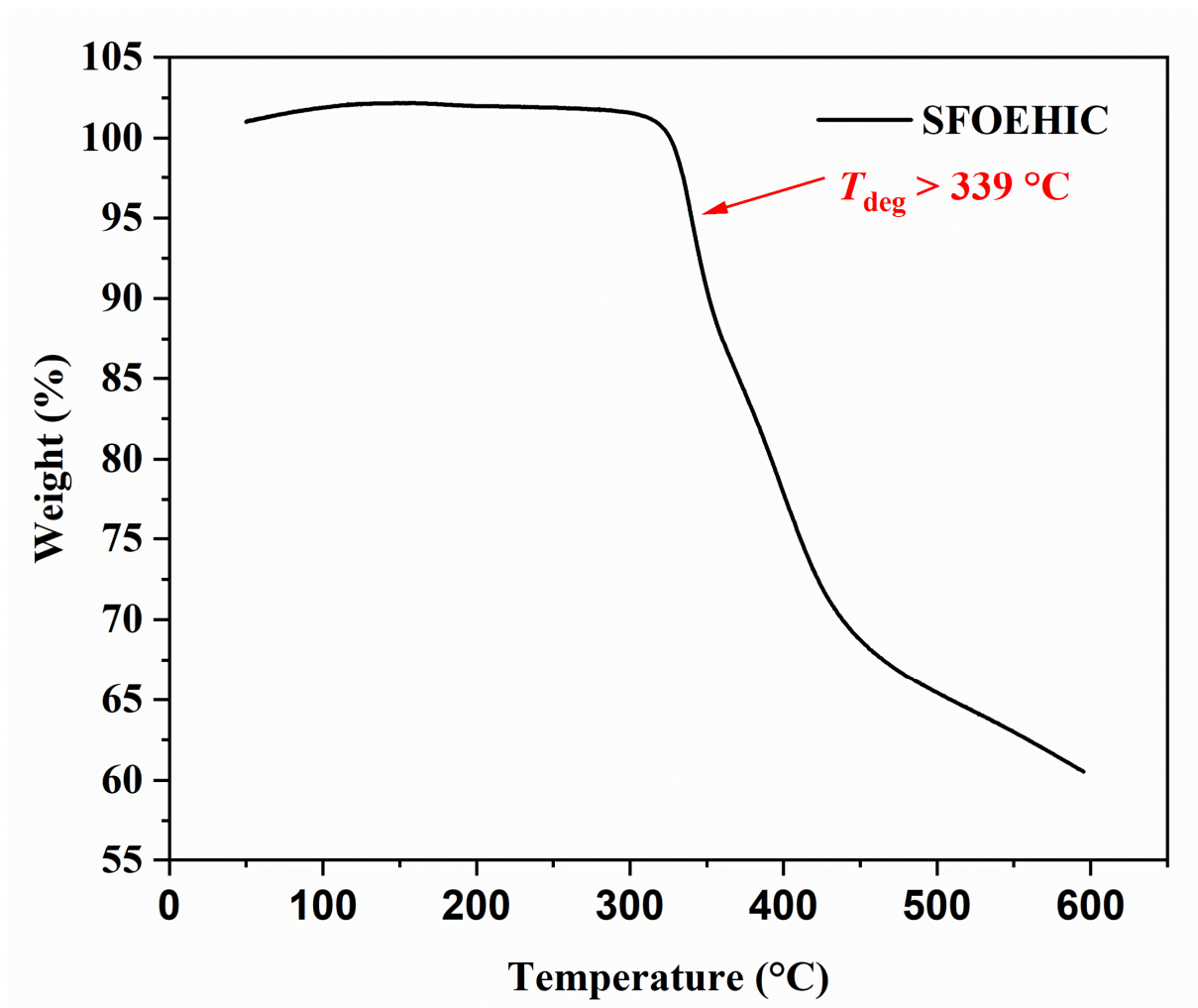


Figure 2.5| TGA curve of SFOEHIC.

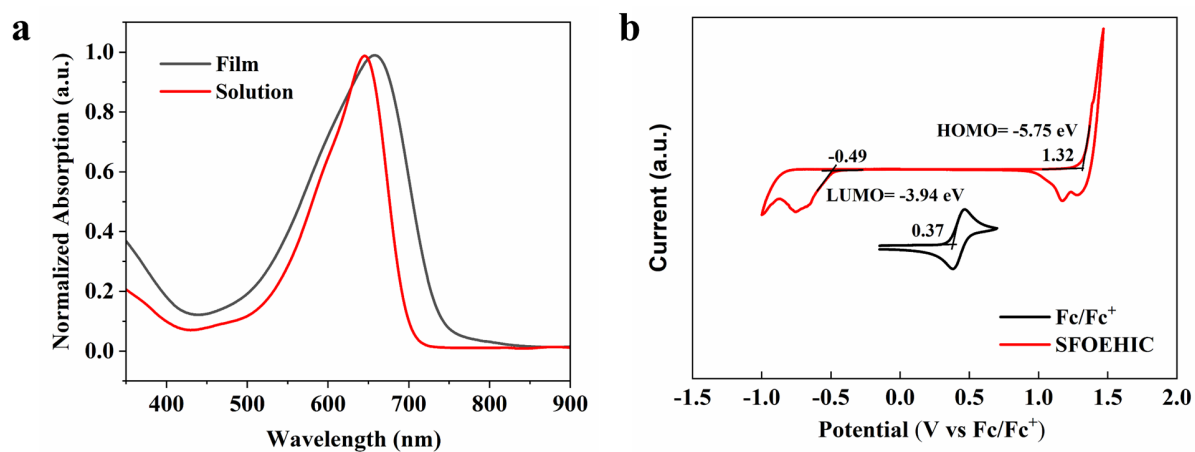


Figure 2.6 | (a) UV-vis absorption spectra of SFOEHIC in CHCl₃ (red) and film (black). (b) Cyclic voltammogram of SFOEHIC film.

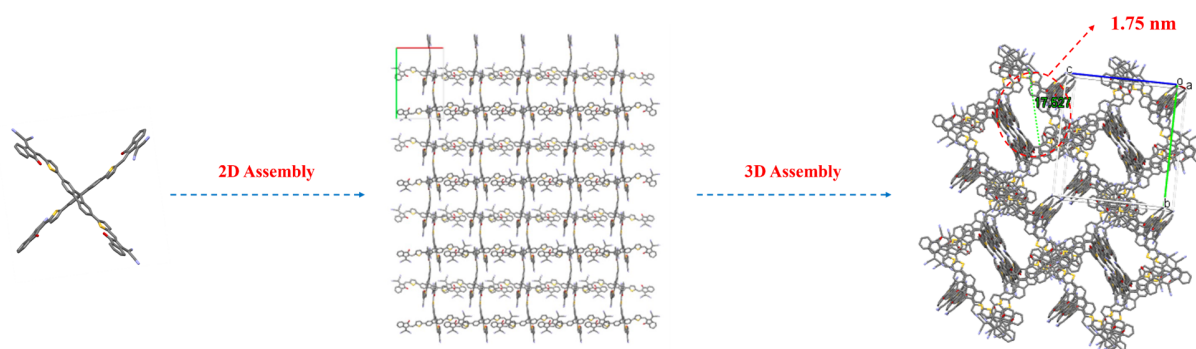


Figure 2.7 | The 2D and 3D crystal assembly of π OF-SFOEHIC.

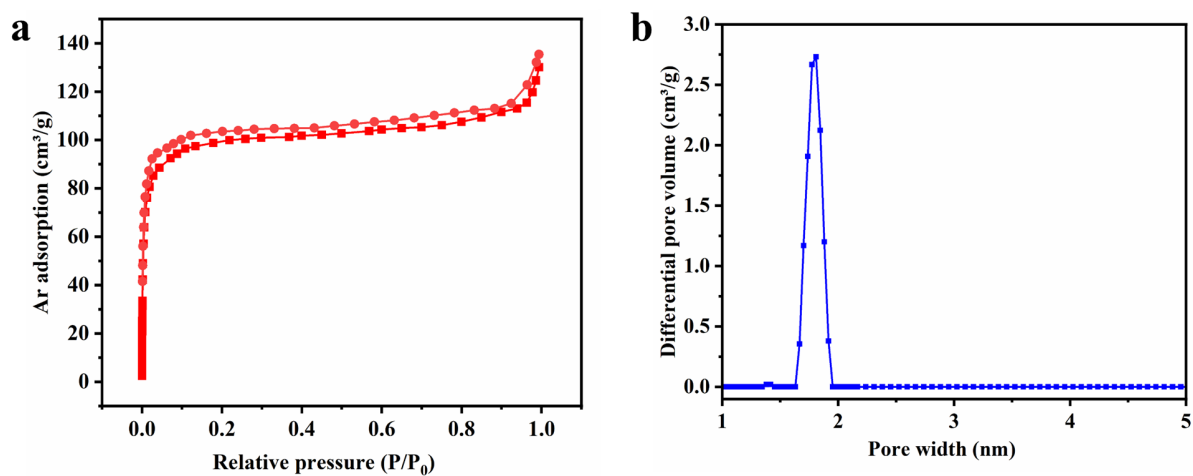


Figure 2.8 | (a) N₂ adsorption–desorption (77 K) isotherms of π OF-SFOEHIC. (b) The pore size distribution analysis of π OF-SFOEHIC film based on the NLDFT model.

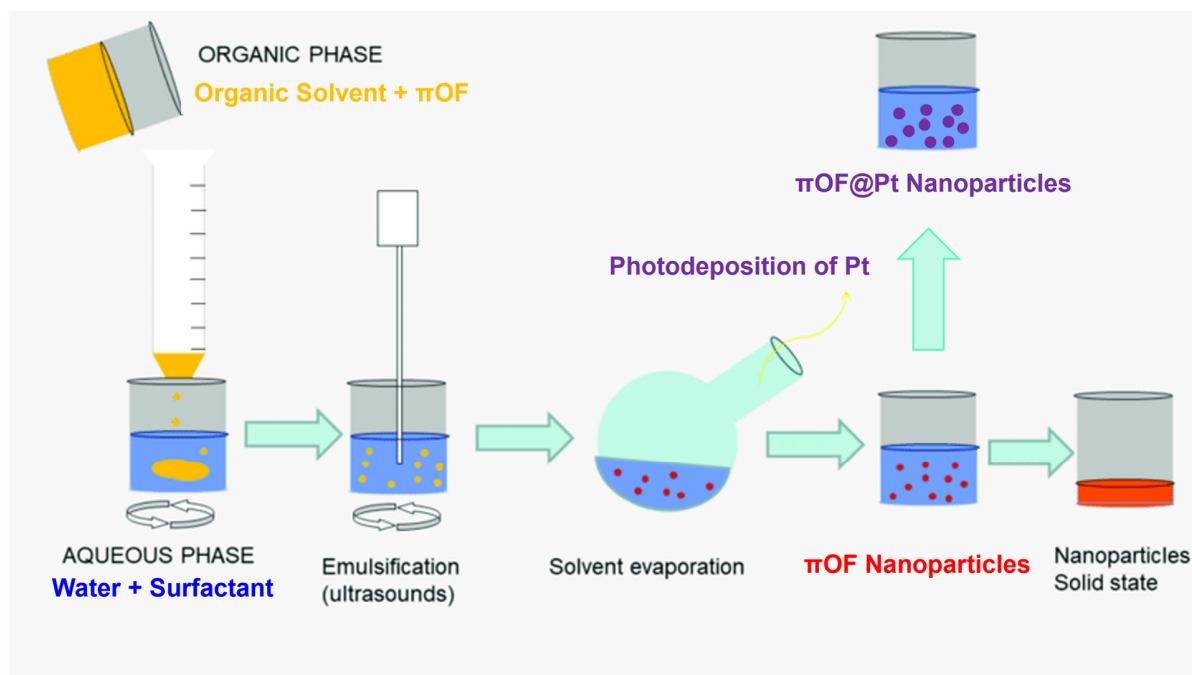


Figure 2.9 | $\pi\text{OF-SFOEHIC@Pt}$ nanoparticles fabrication procedure.³²

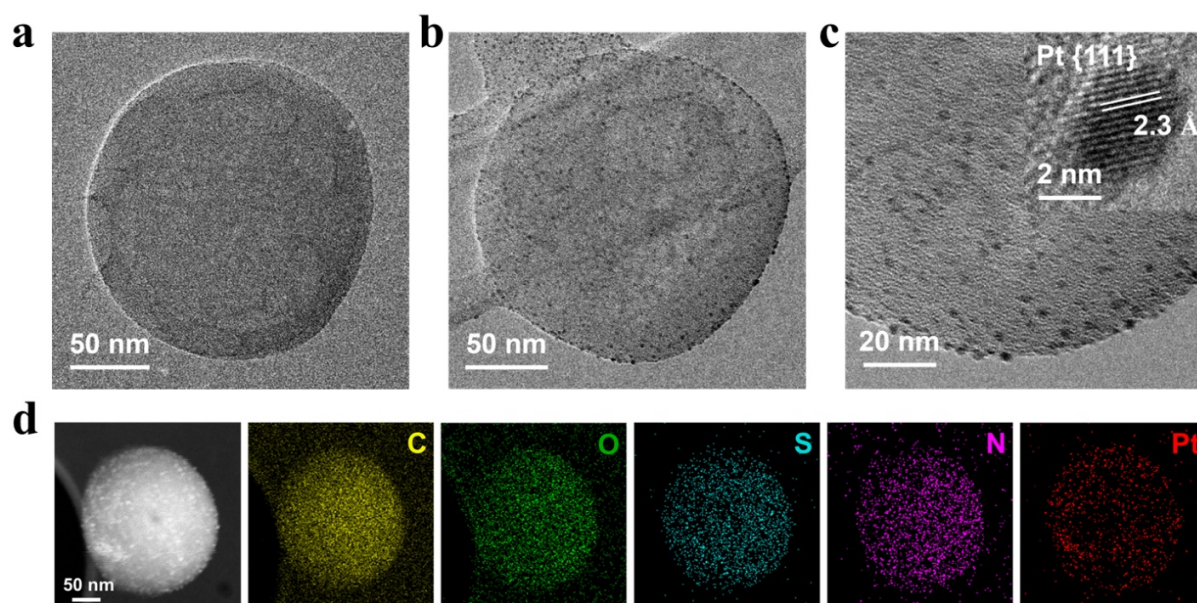


Figure 2.10 | Cryo-EM images of π OF-SFOEHIC nanoparticles (a) before photodeposition of Pt; and (b) after photodeposition of Pt. (c) Magnified images of π OF-SFOEHIC@Pt nanoparticles. (Inset) Pt (111) planes with 2.3 Å lattice spacing. (d) Energy-dispersive X-ray element mappings of π OF-SFOEHIC@Pt nanoparticles.

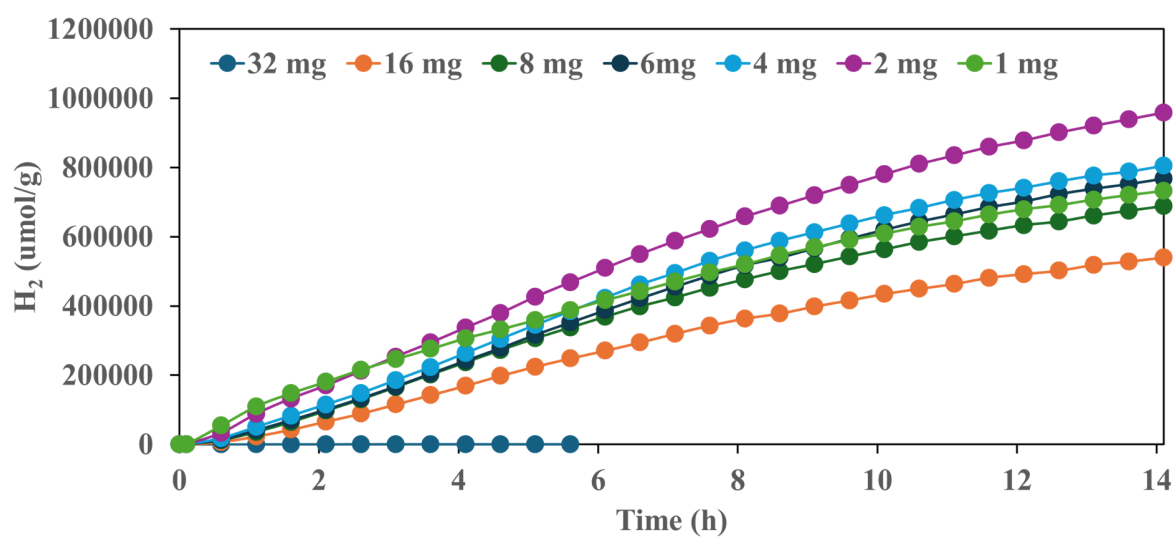


Figure 2.11 | The hydrogen evolution activity of $\pi\text{OF-SFOEHIC@Pt}$ nanoparticles with different TEBS ratios.

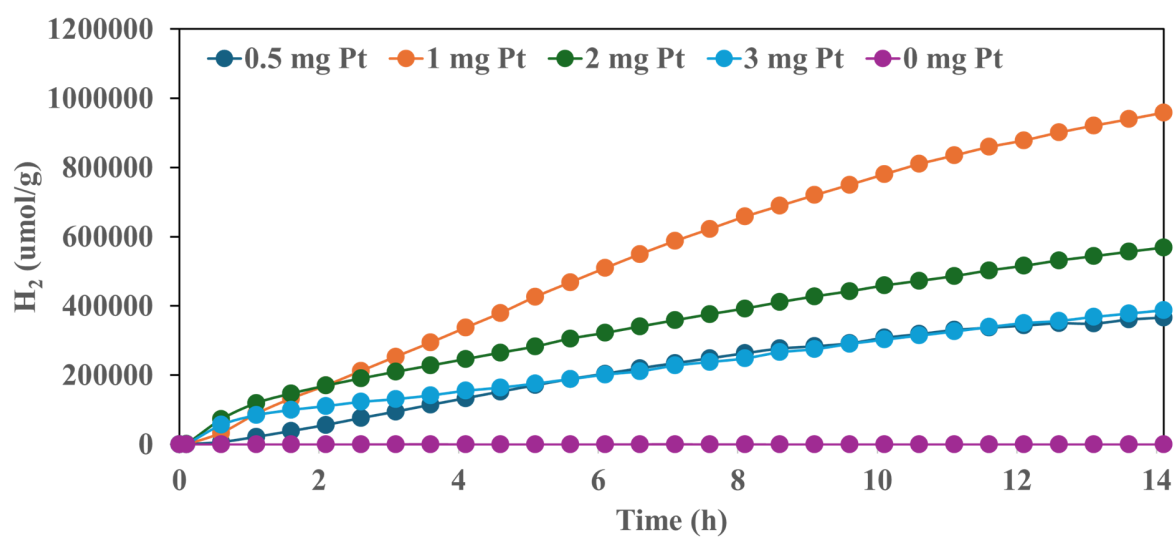


Figure 2.12 | The hydrogen evolution activity of π OF-SFOEHIC@Pt nanoparticles with different Pt loading ratios.

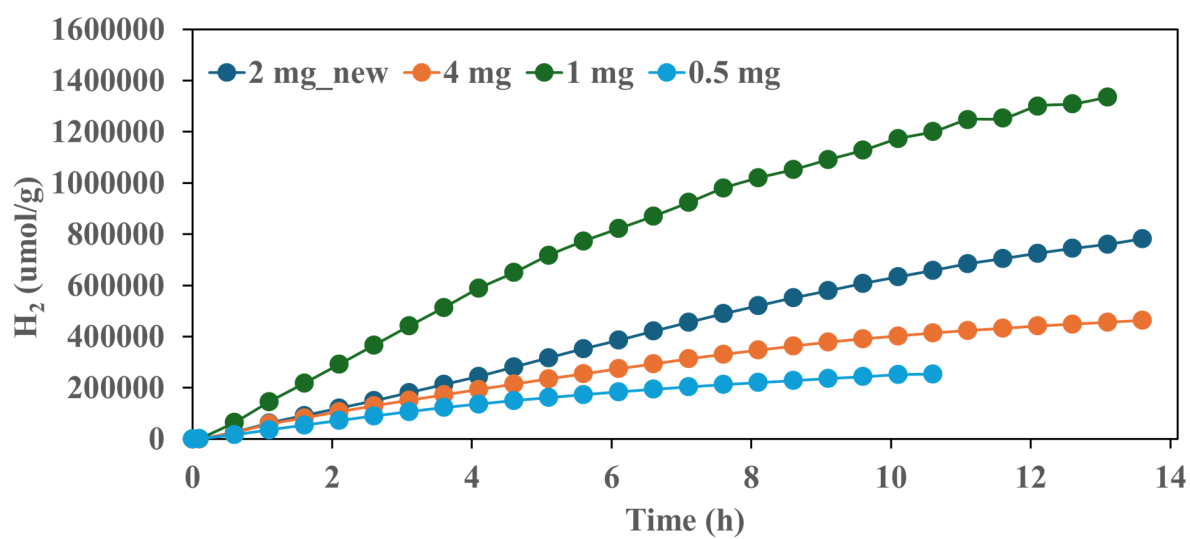


Figure 2.13 | The hydrogen evolution activity of π OF-SFOEHIC@Pt nanoparticles with different π OF-SFOEHIC concentrations.

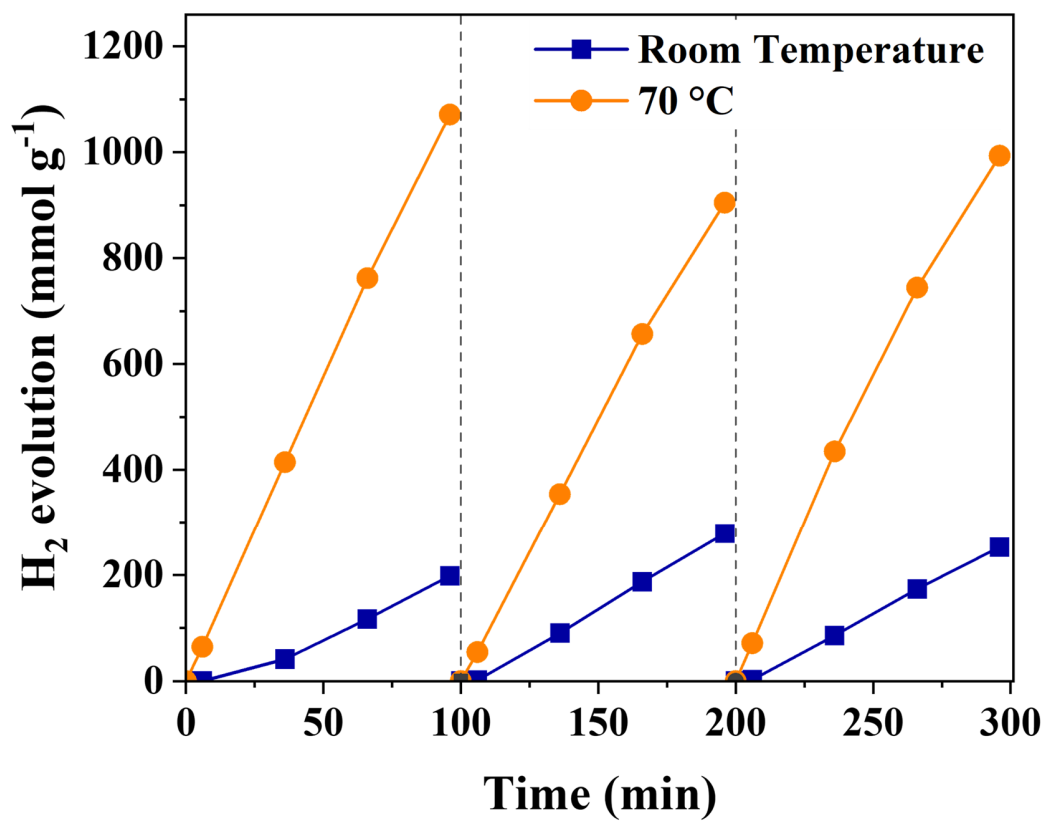


Figure 2.14 | The stable hydrogen evolution activity of π OF-SFOEHIC@Pt nanoparticles.

Catalysts	Cocatalyst	Sacrificial agent	Light Source	HER rate (mmol h ⁻¹ g ⁻¹)	Ref.
HOF-H ₄ TBAPy	Pt	Ascorbic acid	Full-arc	357.93	33
ZnSe NR	Ni-(BF ₄) ₂	Ascorbic acid	AM 1.5G	149.00	34
PTB7-Th:EHIDTBR	Pt	Ascorbic acid	Full-arc	64.00	35
FS-COF	Pt	Ascorbic acid	$\lambda > 420$ nm	10.10	36
TPPS/C ₆₀ -NH ₂	Pt	TEA	Full-arc	34.57	37
PM6:PCBM	Pt	Ascorbic acid	AM 1.5G	73.7	38
π OF-SFOEHIC	Pt	Ascorbic acid	AM 1.5G	152 at RT 618 at 70 °C	This work

Table 2.1 | The summary of the photocatalytic hydrogen evolution performances of benchmark photocatalytic materials.³³⁻³⁸

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Chapter 3 Orthogonally arranged pentacene polymers for singlet-fission organic photovoltaics

3.1 Introduction of singlet-fission organic photovoltaics

Photovoltaic technologies, designed to harness solar energy for electricity generation, present a promising solution to the global energy crisis and the pursuit of carbon neutrality. Amid various solar cell technologies like conventional, quantum dot, and perovskite cells, organic photovoltaics (OPVs) stand out due to their advantages such as cost-effectiveness, ease of fabrication (especially for large-area devices), flexibility, light weight, and potential semi-transparency¹. Conventional OPVs typically rely on blends of electron-donor materials forming bulk heterojunctions (BHJs) within the devices (**Figure 3.1a**). The BHJ structure facilitates the efficient absorption of light, critical for OPVs as they operate on excitonic principles. In BHJ OPVs, excitons move to the donor-acceptor interface, creating charge-transfer states that can dissociate into free holes and electrons. These charge carriers are then transported through the donor-rich and acceptor-rich phases, ultimately being extracted to the relevant electrode (**Figure 3.1b**)².

Despite these advantages, OPVs face challenges, especially in terms of efficiency compared to technologies like perovskite or silicon-based photovoltaics. Research efforts focus on reducing fabrication costs and improving power conversion efficiency (PCE). However, the efficiency is constrained by the Shockley-Queisser (SQ) limit, which sets a theoretical maximum efficiency of around 33% for single-junction solar cells, as shown in **Figure 3.1c**³. A promising avenue to overcome this efficiency barrier is multiple exciton generation (MEG), a process where a single photon absorption leads to the creation of multiple electron-hole pairs. Single fission, a

specific type of MEG, involves the conversion of a high-energy singlet exciton into a pair of low-energy triplet excitons (**Figure 3.1d**)^{4,5}.

Pentacene is often used as a model system for studying single fission due to its ultrafast kinetics and suitable thermodynamic properties. The ultrafast nature of single fission in pentacene, occurring in about 80 femtoseconds with a yield of 200%, makes it a favorable candidate for singlet-fission OPVs^{5,6}. Various spectroscopic techniques, including transient absorption spectroscopy (TAS), are employed to study single fission⁷. TAS can detect the rapid conversion of singlet excitons into triplet excitons, providing insights into the efficiency of singlet fission⁸. Magnetic field-dependent measurements, leveraging the magnetic field effect, offer additional tools to understand singlet fission kinetics and triplet yield⁹. Through organic chemistry and polymer chemistry, various pentacene-based structures have been constructed, such as dimers¹⁰, dendrimers¹¹, and diblock copolymers¹², to reveal the singlet fission mechanism in multichromophore systems.

In addition to spectroscopic studies, singlet fission in pentacene-based materials has been applied in photovoltaic devices. The fundamental idea is that the extra excitons generated through singlet fission contribute to the photocurrent in photovoltaics, resulting in a peak external quantum efficiency (EQE) above 100%. For example, Congreve et al. developed a singlet fission OPV using pentacene as the donor and fullerene (C₆₀) as the acceptor¹³. They strategically introduced regio-regular poly(3-hexylthiophene) (P3HT) between the hole-transport layer and the active layer to inhibit exciton diffusion (**Figure 3.2a**). The peak EQE at 670 nm reached 109% for a 15 nm thick pentacene layer, ensuring both complete singlet fission and triplet exciton diffusion (**Figure 3.2b**). Semonin et al. explored tuning the bandgap of PbSe quantum dots as active layers in photovoltaics (**Figure 3.2c**), demonstrating a MEG process with a peak EQE value of 114% (**Figure 3.2d**)¹⁴.

Instead of directly engineering the active layer, using pentacene or tetracene as an interfacial layer to sensitize the absorber without singlet fission has expanded the application scenarios. Einzinger et al. introduced an electric-field-effect passivation layer between tetracene and silicon to facilitate efficient energy transfer of triplet excitons formed in tetracene to silicon (**Figure 3.2e**). They calculated a maximum combined yield of fission in tetracene and energy transfer to silicon of around 133%, with 76% attributed to triplet transfer yield (**Figure 3.2f**)¹⁵. Hence, fine-tuning the energy levels of pentacene-based materials, especially the triplet energy level, and device engineering, such as controlling pentacene layer thickness and interfacial engineering between pentacene and charge transport layers, are crucial for maximizing the utilization of triplet excitons generated by singlet fissions. Pentacene-based materials have applications beyond being used as the active layer in OPVs. They can also function as a sensitization layer for silicon or perovskite photovoltaics. This highlights the versatility of singlet fission as a general tool for achieving high efficiency in various photovoltaic technologies.

3.2 Synthesis and characterizations of pentacene polymers

While pentacene has been successfully integrated into singlet fission photovoltaics through vacuum deposition, its insolubility restricts its application in solution-processing BHJ OPVs¹⁶. Additionally, the fixed structure of the monomeric pentacene hinders the tuning of its energy levels and optical absorption, which is suboptimal for BHJ OPVs that require aligned energy levels and complementary optical absorption between donor and acceptor materials¹⁷. The design strategy of donor-acceptor (D-A) copolymers has been extensively employed to tune the optoelectronic properties of materials in OPVs¹⁸. A unique aspect of these polymers is that their Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels are

significantly influenced by the HOMO energy level of the donor and the LUMO energy level of the acceptor, respectively. This enables the tuning of polymer energy levels by separately engineering the donor and acceptor units. For singlet fission OPVs, proper energy alignment of the triplet energy level of pentacene-based donor materials with the acceptor is crucial for efficiently utilizing triplet excitons. Considering the superior performance demonstrated by Y-series acceptors with near-infrared absorption and deep energy levels, it is anticipated that pentacene-based donors can be chemically modified to accommodate Y-series acceptors¹⁹⁻²¹. Beyond optoelectronic properties, controlling the morphology of donor/acceptor BHJ structures is key to achieving high efficiency and stability in photovoltaics^{22,23}. Monomeric pentacene, due to its highly planar structure, tends to form strong and dense face-on packing, which is detrimental to proper phase separation. To address this, we designed an orthogonally arranged pentacene polymer (PP) with pentacene units aligned vertically to the polymer backbone as donor materials in BHJ OPVs. This orthogonal arrangement helps break the strong packing of pentacene units and controls the diffusion of triplet excitons along the polymer chains²⁴. In contrast to the traditional D-A copolymer design strategy, we introduced another donor unit, benzodithiophene (BDT), to form a copolymer with the pentacene units. This special design with a donor-donor' (D-D') structure aims to prevent the strong intramolecular charge transfer (ICT) effect formed in D-A copolymers from quenching the triplet exciton.

PP was synthesized through Stille-coupling polymerization (**Figure 3.3**). The structures of precursor 1 and dibromide pentacene monomer 2 were confirmed by ¹H NMR (**Figure 3.4**, **Figure 3.5**). Comparisons of steady-state absorption spectra and photoluminescence spectra of PP with pentacene monomer revealed a 20 nm redshift of PP from the monomer in the 550-650 nm absorption band, characteristic of pentacene units. An additional absorption band between 325 and

500 nm in PP, resulting from orbital mixing across multiple pentacene units, is favorable for solar cell applications (**Figure 3.6a**). Absorption bands of PP exhibited broadening and a tail to the red of the absorption maxima in thin film compared to their solution-state counterparts due to the aggregation of conjugated polymers (**Figure 3.7b**). The photoluminescence of PP in dilute solution was significantly quenched compared to its monomeric counterpart (**Figure 3.8c**). This suggests the presence of intramolecular singlet fission (iSF) because photoluminescence is spin-allowed for singlet excitons but spin-forbidden for triplets.

Further characterization of PP with transient absorption confirmed its singlet fission properties. We observed a rapid conversion of photoexcited singlets into triplets, occurring on a picosecond time scale (495 ps) in PP. These two distinct populations of photoexcited singlets around 450 nm and triplets around 510 nm can be clearly seen in 2D pseudocolor (ΔA) plots of transient absorption spectra as a function of probe wavelength and delay time (**Figure 3.9a**). We deconvoluted the transient absorption spectra of individual species and modeled the population evolution with time using global target analysis (**Figure 3.9b**). The bound triplet pairs in PP will dissociate into two “free” triplet excitons in 9.8 μ s, as compared to free triplets generated from sensitization with anthracene (**Figure 3.9c**). These results provide evidence of the singlet fission features in PP materials, a prerequisite for fabricating singlet fission OPVs.

3.3 Device performance of singlet-fission organic photovoltaics based on pentacene polymers

The photovoltaic performance of PP was investigated using a standard device architecture of ITO/PEDOT:PSS/BHJ/PFN-Br/Ag (**Figure 3.10a**). Acceptors for PP, including the small molecule BTP-eC9 and the polymeric PY-IT, were selected (**Figure 3.10b**). PY-IT, a polymer

acceptor, shares a similar skeleton structure, low bandgap, and strong near-infrared absorption with the small-molecule BTP-eC9. Polymerization enhances the glass transition temperature and improves morphological stability compared to their small-molecule counterparts. To ensure sufficient driving forces for efficient exciton dissociation, a staggered gap (type II) heterojunction energy level alignment was targeted. The LUMO energy levels of BTP-eC9 (-4.10 eV) and PY-IT (-3.79 eV) are lower than that of PP (-3.58 eV), and their HOMO energy levels are also lower than that of PP (-5.60 eV) (**Figure 3.10c**). Additionally, the visible range absorption of PP and the near-infrared absorption of BTP-eC9 and PY-IT create a complementary absorption for better photon utilization.

The best performance was achieved with a Power Conversion Efficiency (PCE) of 1.61% based on the PP: BTP-eC9 blend, yielding a J_{sc} of 6.73 mA/cm², a V_{oc} of 0.710 V, and a FF of 33.74% (**Figure 3.11a**). For PP:PY-IT systems, the PCE was further improved to 1.92%, with a J_{sc} of 5.46 mA/cm², a V_{oc} of 0.825 V, and a FF of 42.60% (**Figure 3.11b**). The peak External Quantum Efficiency (EQE) value around 600 nm for the PP-based OPVs is all below 15% (**Figure 3.11c, d**), indicating that triplet excitons may not have completely dissociated in the BHJ to contribute to additional photogenerated carriers. This phenomenon could be attributed to the misalignment of triplet energy levels with acceptor materials.

3.4 Conclusion

In summary, we successfully synthesized a pentacene polymer as a donor material for singlet fission OPVs, aiming to surpass the SQ limit and achieve high efficiency. The orthogonal arrangement of pentacene units along the polymer backbone proves effective in preventing aggregation between pentacene units, thereby enhancing efficient triplet exciton diffusion. TAS

revealed the dynamics of singlet fission, illustrating the photoinduced split of singlets into triplet excitons. To harness these singlet fission properties, the pentacene polymer was solution-processed into BHJs with BTP-eC9 or PY-IT as acceptors, resulting in a near 2% PCE in OPVs. Our findings underscore the potential of pentacene polymers for solution-processible singlet fission OPVs.

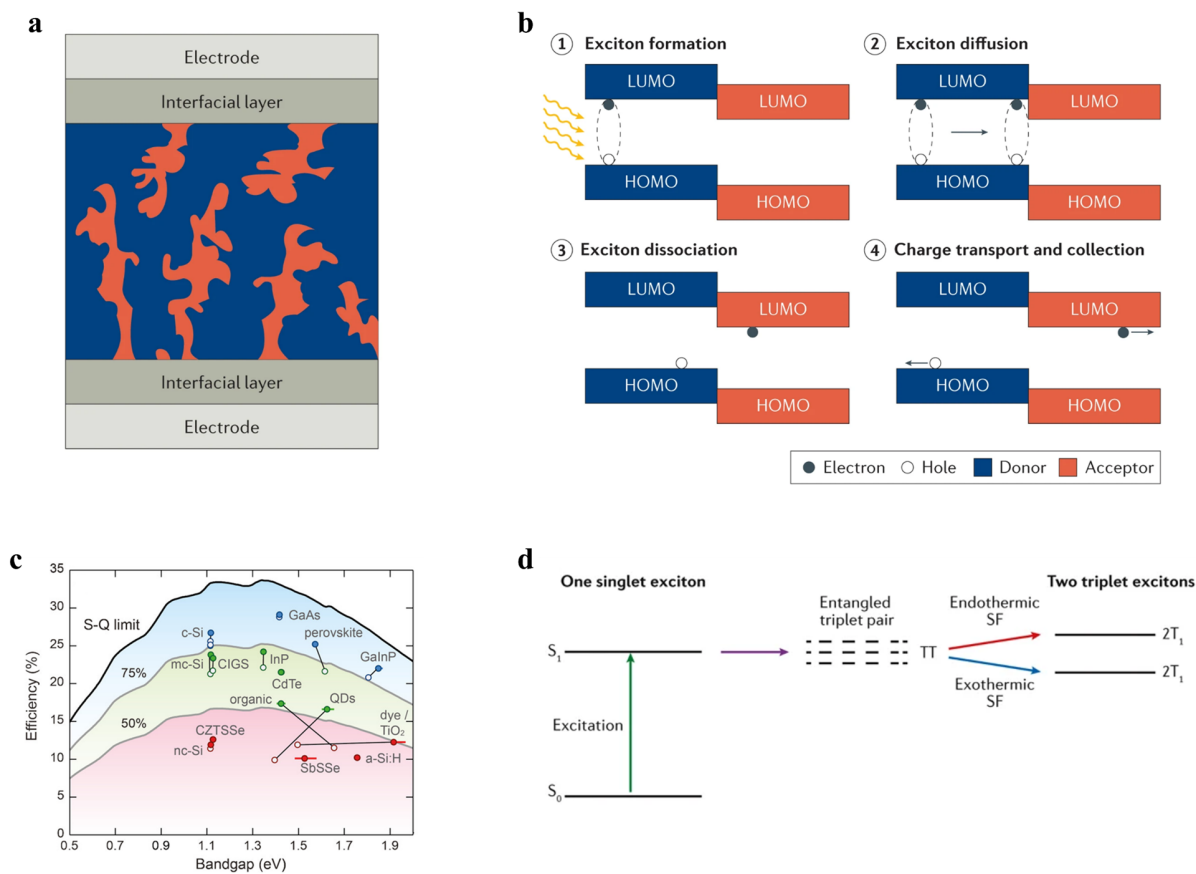


Figure 3.1 | (a) Schematics of BHJ device structure of OPVs. (b) Schematics of device mechanism of OPVs. (c) Comparison of solar cell efficiencies across various materials relative to bandgap, contrasted with the theoretical SQ limit. (d) Schematics of singlet fission.²⁻⁴

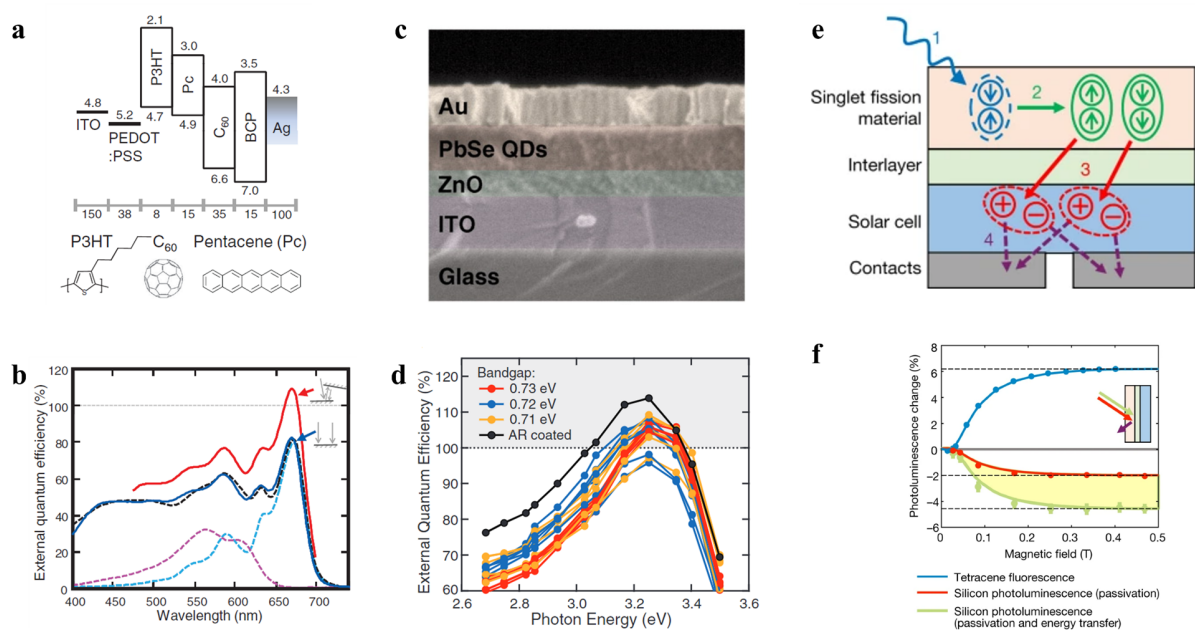


Figure 3.2 | (a) Schematics of pentacene/C₆₀ bi-layer device structure of singlet fission OPVs. (b) EQE of singlet fission OPVs. (c) Schematics of device structure of PbSe quantum dots PVs. (d) EQE of PbSe quantum dots PVs with different bandgaps. (e) Schematics of device structure of tetracene-sensitized silicon PVs. (f) Magnetic-dependent photoluminescence of tetracene-sensitized silicon PVs with interfacial passivation.¹³⁻¹⁵

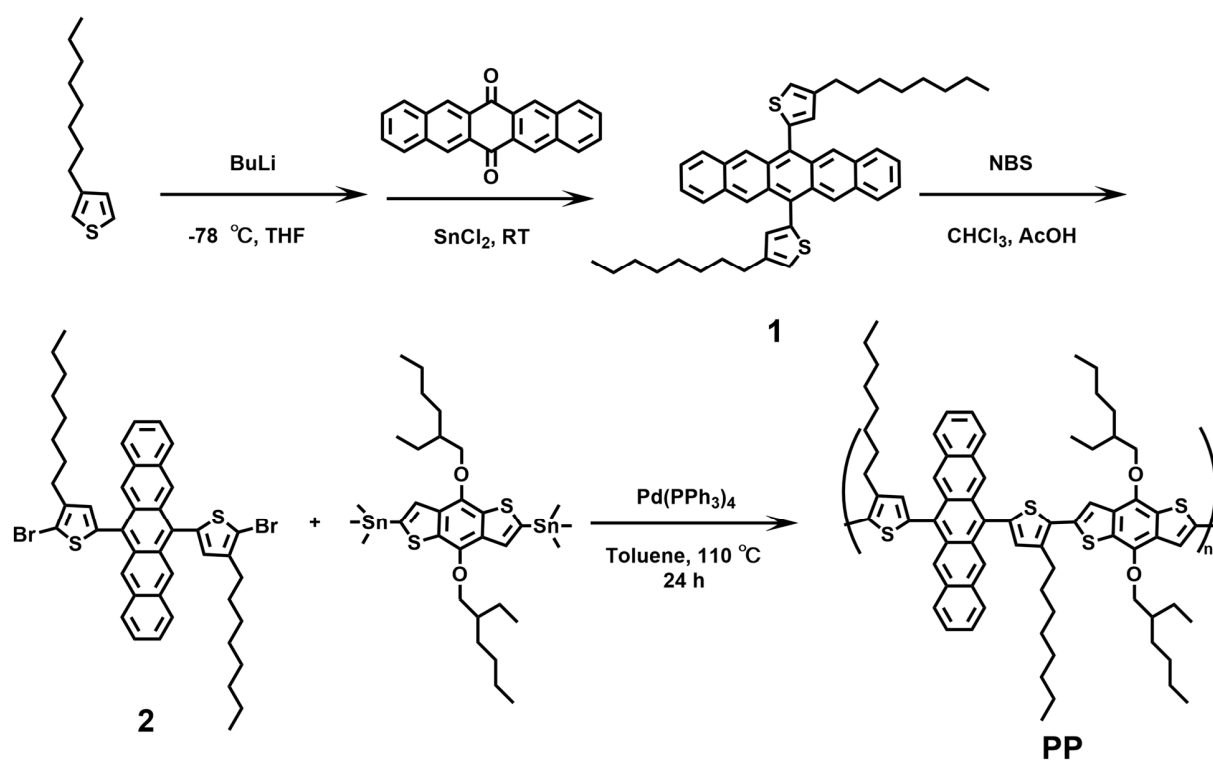


Figure 3.3 | (a) Synthetic route of PP via Stille-coupling polymerization.

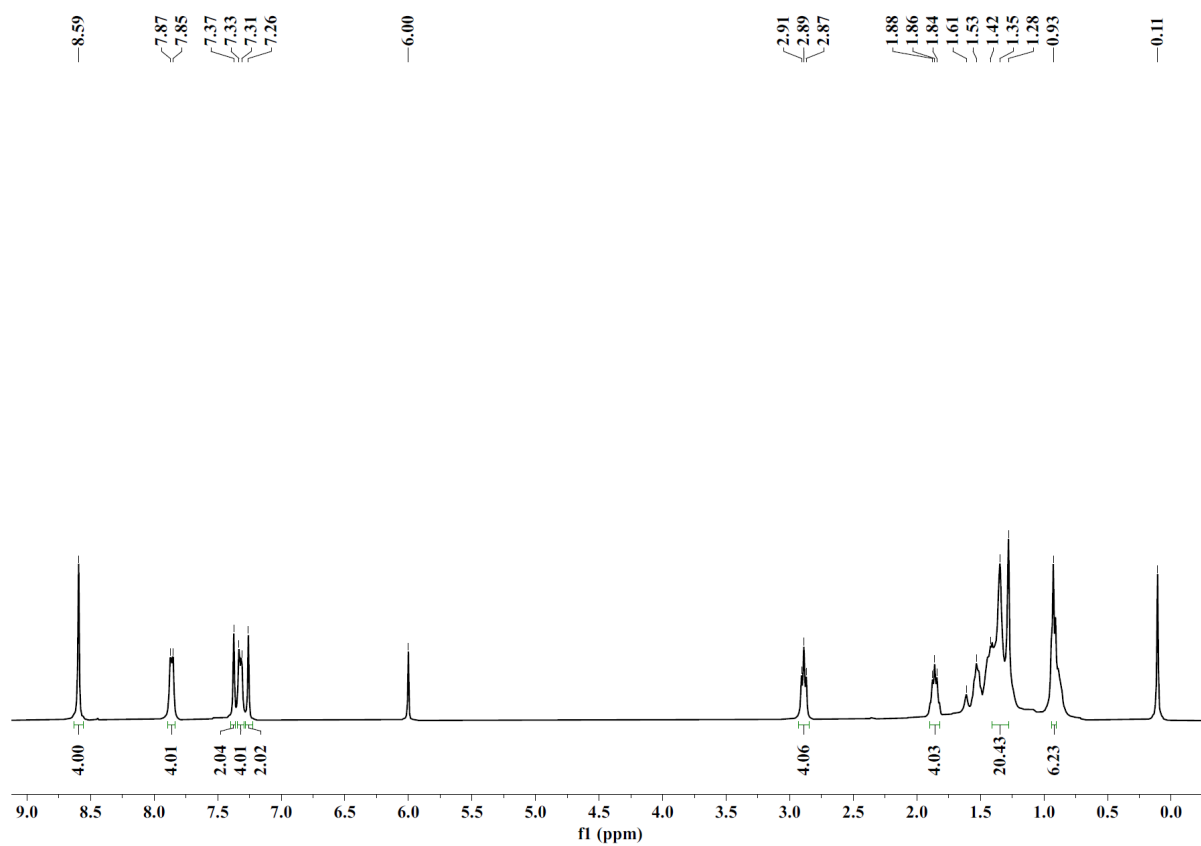


Figure 3.4 | ^1H NMR spectra of compound 1 (400 MHz, CDCl_3 , 298.5 K).

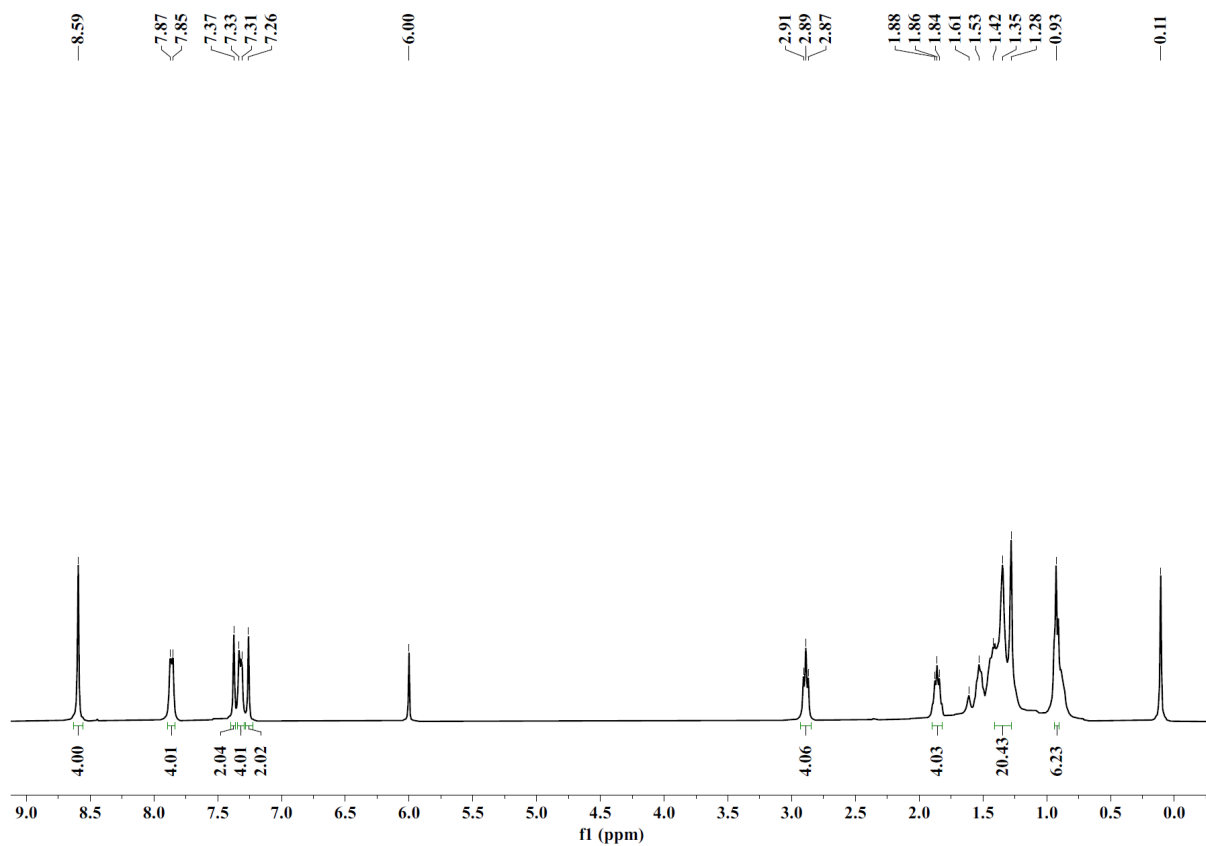


Figure 3.5 | ^1H NMR spectra of compound 2 (400 MHz, CDCl_3 , 298.5 K).

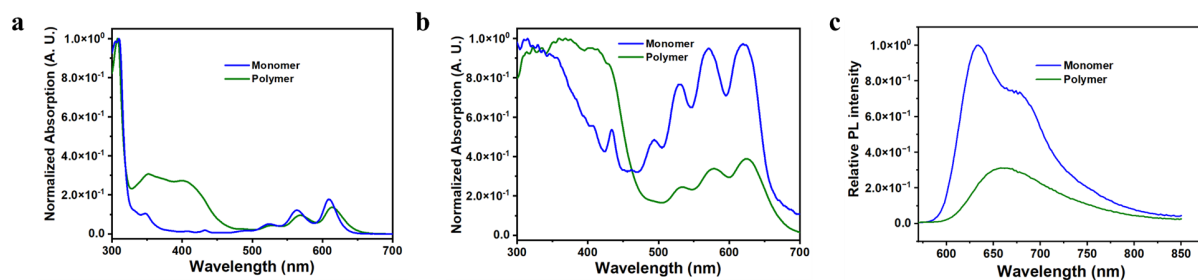


Figure 3.6 | (a) Steady-state absorption profiles of PP and monomer dissolved in chloroform solution. (b) Steady-state absorption profiles of PP and monomer in thin-film state. (c) Photoluminescence spectra of PP and monomer dissolved in dilute chloroform solutions.

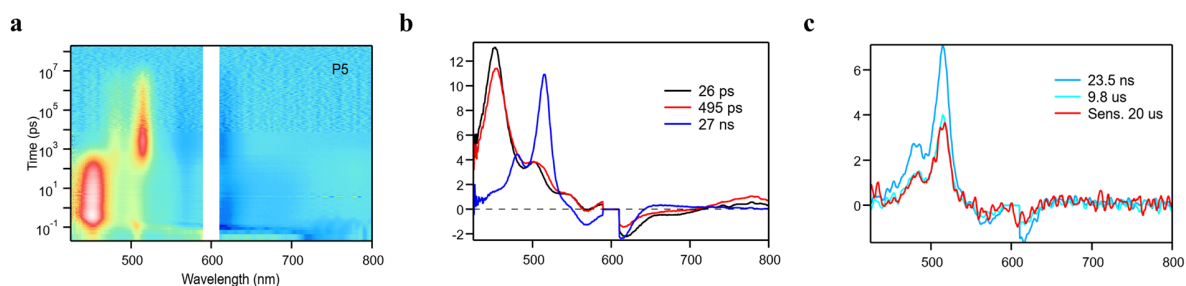


Figure 3.7 | (a) TAS of PP as a function of time and wavelength excited at 600 nm ($\sim 25 \mu\text{J cm}^{-2}$) as a dilute solution in toluene. (b) Deconvoluted transient spectra of singlet and triplet species as solved by global analysis. (c) Comparison of transient spectra of triplet pairs generated via direct excitation at 600 nm followed by singlet fission and free triplets generated from sensitization with anthracene for PP.

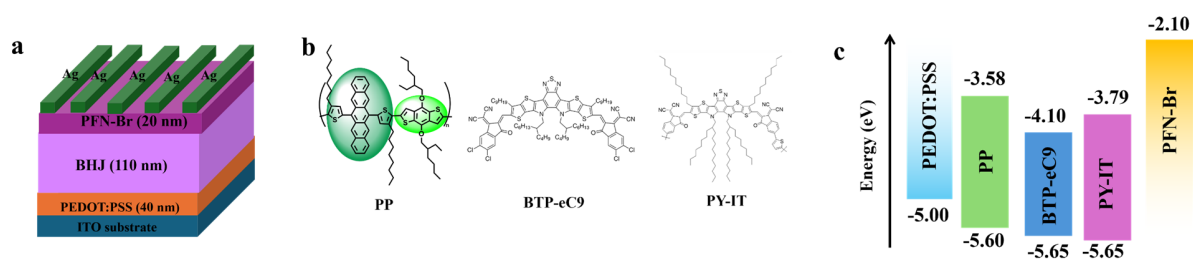


Figure 3.8 | (a) Schematics of singlet fission BHJ OPVs. (b) Chemical structures of PP, BTP-eC9 and PY-IT. (c) Energy levels of materials used in singlet fission BHJ OPVs.

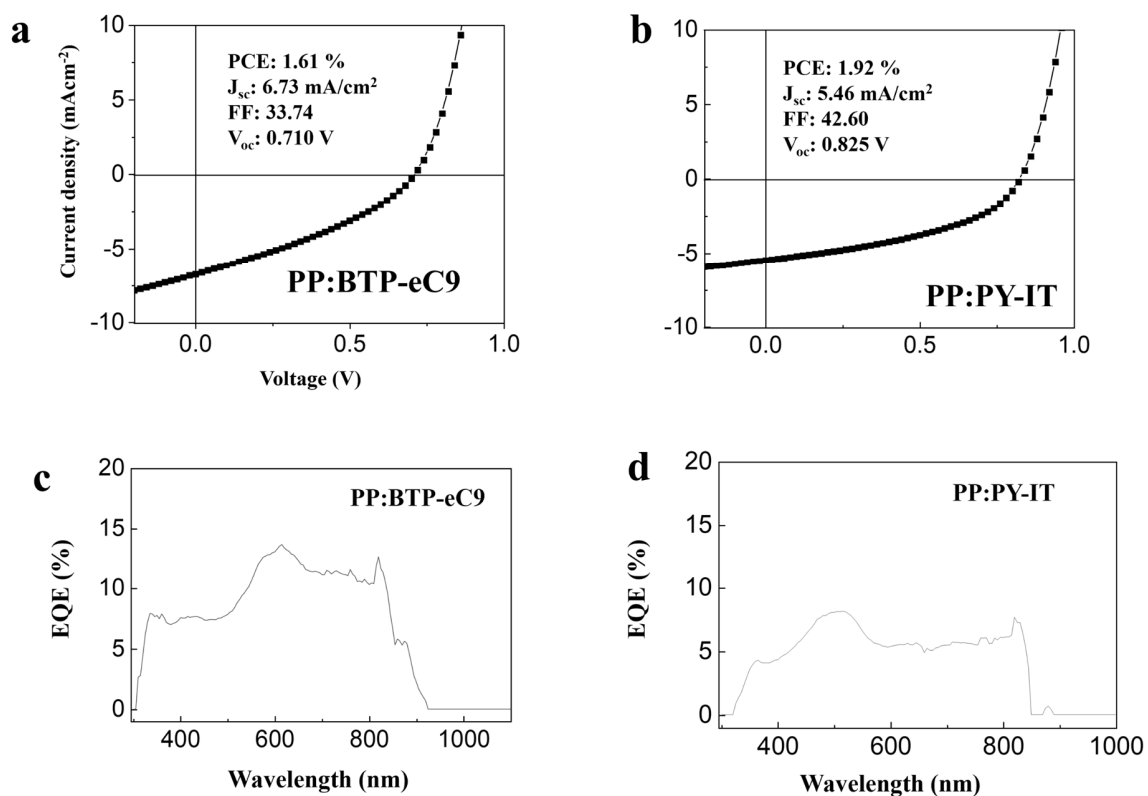


Figure 3.9 | (a) J - V curves of singlet fission BHJ OPVs based on PP: BTP-eC9. (b) J - V curves of singlet fission BHJ OPVs based on PP:PY-IT. (c) EQE of singlet fission BHJ OPVs based on PP: BTP-eC9. (d) EQE of singlet fission BHJ OPVs based on PP:PY-IT.

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Chapter 4 Helicene-based electron-transport materials for inverted perovskite solar cells

4.1 Introduction of electron-transport materials for inverted perovskite solar cells

The surging global demand for energy, combined with mounting concerns over climate change and environmental pollution from fossil fuel usage, has garnered significant public attention. In the quest to replace fossil fuels, renewable and carbon-neutral energy sources, particularly solar energy, emerge as pivotal and abundant solutions scalable to meet future energy needs through photovoltaic technology. Perovskite solar cells (PSCs) have recently taken center stage in both scientific and industrial spheres due to their potential for scalable applications. Metal halide perovskite materials, key players in third-generation photovoltaic technologies, owe their prominence to versatile chemical composition, easy processing methods, and tunable optoelectronic properties^{1,2}.

The chemical structure of these organic–inorganic hybrid perovskites can be denoted as ABX_3 , where A represents a monovalent cation (e.g., methylammonium, formamidinium, or cesium), B is a divalent cation (e.g., Pb^{2+} or Sn^{2+}), and X is a halide anion (e.g., Cl^- , Br^- , or I^-) (**Figure 4.1a**). The distinctive chemical structure contributes significantly to their superior optoelectronic properties, including a substantial absorption coefficient, adjustable band gap, and prolonged carrier lifetime due to their defect tolerance³. These characteristics enhance their photovoltaic applications, offering advantages like cost-effectiveness, straightforward device manufacturing, and impressive power conversion efficiencies (PCEs). Over the past decade, PCEs of perovskite solar cells have skyrocketed from 3.8% to over 25% for single-junction and over 30% for silicon-perovskite tandem solar cells^{4,5}. PSCs are typically constructed by sandwiching an

ambipolar perovskite semiconductor layer between an electron-transport layer (ETL) and a hole-transport layer (HTL). Depending on the physical location of ETLs and HTLs, PSCs can be generally classified into two types: n-i-p (conventional) and p-i-n (inverted) structures (**Figure 4.1b**)⁶. Different properties and processing procedures are required for charge transport materials in n-i-p and p-i-n-based devices, respectively⁷.

PSCs based on the p-i-n (inverted) architecture exhibit longer operational lifetimes than the n-i-p (conventional) structure, as their charge transport layers do not require doping. Additionally, organic charge transport layers in p-i-n PSCs allow for low-temperature processing, while many metal-oxide-based counterparts demand high-temperature annealing in n-i-p PSCs, limiting their applications. Therefore, the p-i-n structure holds promise for commercialized PSCs⁸⁻¹⁷. For p-i-n PSCs, a good ETL should provide sufficient electron collection efficiency, be capable of hole blocking, and stabilize the perovskite active layer through defect passivation. This necessitates that the ETL has a matched lower unoccupied molecular orbital (LUMO) level with the perovskite conduction band, a lower highest occupied molecular orbital (HOMO) level than the perovskite valence band, high carrier mobility, and good film morphology. Fullerene acceptors, PCBM and C₆₀, are the most common ETL materials for inverted PSCs due to their Lewis acidity to passivate negatively charged perovskite surface defects. However, fullerene-based ETLs have been shown to lead to non-radiative recombination and V_{OC} loss at the perovskite/ETL interface, resulting in lower PCEs compared to n-i-p PSCs¹⁸. Therefore, there's a need for ETL materials that can boost the PCE of p-i-n PSCs. Novel ETL material designs with easily tunable HOMO and LUMO levels, high charge mobility, and good film morphology are crucial for high performance and stable inverted PSCs. Several design concepts for ETLs in p-i-n PSCs are proposed, as shown in **Figure 4.2**: (1) Starting from reported structures like PDI, NDI, and their derivatives, or

exploring novel molecular structures with rigid and extended π -skeletons via “twisted fusion” or polymerization to promote electron mobility for efficient charge extraction. (2) Side-chain engineering to adjust the relative solubility of the ETLs in antisolvents, maintaining the energy levels and electron extraction ability of the molecules. (3) Ensuring negligible light absorption in the visible region to minimize photo consumption in the ETL layer, especially for n-i-p structure. Candidates with large bandgaps are favorable for meeting this demand. (4) Simple synthetic routes and outstanding stability to heat, moisture, and light are required for potential industrial applications. (5) Introduction of stronger hydrogen bonds into molecular structures for stability improvement. Molecules with lone-electron-pair heteroatoms are favorable for their ability to increase intermolecular interactions and passivate defects on the surface and in grain boundaries of perovskite¹⁹⁻²⁵.

4.2 Synthesis and characterizations of the helicene-based electron-transport material

We designed a novel n-type organic small molecule, named PCBM-2, to serve as the electron transport layer (ETL) in inverted perovskite solar cells (PSCs). While PCBM is commonly used as an ETL in inverted PSCs, it tends to aggregate into large clusters and form dimers under light exposure, compromising its electron transport capabilities and leading to device degradation. Additionally, modifying PCBM chemically to control its optoelectronic properties is challenging. To address these issues, we chose helicene units as building blocks for our novel ETL, PCBM-2, aiming to replace PCBM. Helicenes are polycyclic aromatic compounds with ortho-condensed aromatic rings, forming a nonplanar screw-shaped geometry. Their unique helical arrangement enhances solubility in common organic solvents while maintaining excellent charge transport capabilities. The nonplanar structure of helicenes effectively prevents aggregation issues, thereby

improving device stability. Moreover, optoelectronic properties, such as energy level and absorption, can be easily tuned due to the structural versatility of helicene-based small molecules²⁶⁻

31.

PCBM-2 was synthesized from compound 1 through photochemical ring-closing reaction, Suzuki coupling and finally Knoevenagel condensation (**Figure 4.3**). The structure of 2, 3, and PCBM-2 was confirmed by ¹H NMR (**Figure 4.4, Figure 4.5, Figure 4.6**). In chloroform solution, PCBM-2 exhibits absorption in the range of 400-650 nm, while its thin-film counterpart shows a redshift of 40 nm. The optical bandgap of the PCBM-2 films, calculated from the absorption edge (660 nm), is 1.88 eV (**Figure 4.7a**). The energy levels of PCBM-2 were determined using cyclic voltammetry (CV), with estimated HOMO and LUMO energies of -5.88 eV and -3.97 eV, respectively. The LUMO of PCBM-2 aligns well with that of the perovskite (PVSK) layer, facilitating electron extraction (**Figure 4.7b**). After initial testing of PCBM-2 as an ETL in inverted PSCs, we observed that its low intrinsic conductivity resulted in inferior carrier transport, leading to low J_{SC} and FF. To address this, we considered doping PCBM-2 with dopants to enhance its conductivity. Thermal activated doping typically requires proper energy level alignment between the dopant and the matrix. For n-doping, the ionization potential of the dopant should be smaller than the electron affinity of the host, necessitating a LUMO of the n-dopant higher than the LUMO of the matrix. Conversely, for p-doping, the electron affinity should be larger than the ionization potential of the matrix, requiring the LUMO of the p-dopant to be lower than the HOMO of the matrix (**Figure 4.8**). Various tetracyano-quinodimethane (TCNQ)-based p-dopants and metal complexes n-dopants have been widely used for organic doping processes^{32,33}. We employed the organic amine 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as n-dopant for PCBM-2. PCBM-2 doped with DBU exhibited higher conductivity than undoped PCBM-2, as detected by conductive

atomic force microscopy (C-AFM), providing a foundation for further device applications (**Figure 4.9a, b**).

4.3 Device performance of inverted perovskite solar cells based on the helicene-based electron-transport material

Inverted perovskite solar cells (PSCs) were fabricated with a device structure of ITO/2PACz/perovskite/PCBM-2/BCP/Ag (**Figure 4.10a**). Notably, PCBM-2 without doping exhibited low conductivity, resulting in a modest PCE of approximately 9.97%. To enhance the charge transport of PCBM-2, we investigated two promising n-dopants, namely 4-(2,3-dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine (N-DMBI)³⁴ and DBU³⁵ (**Figure 4.10b, c**). DBU, known for its room temperature doping capability, proved effective in doping PCBM-2 for improved device performance in inverted PSCs. PCBM-2 doped with 0.1% DBU exhibited a significantly increased PCE of 15.30%, whereas PCBM-2 doped with N-DMBI showed a comparable PCE to the reference (undoped PCBM-2) (**Figure 4.11, Table 4.1**). Having identified the suitable dopant category, we further optimized the doping conditions to enhance device performance. Excessive dopants, exceeding 0.5%, were found to be detrimental to the device's performance. Contrary to expectations, heating, and lighting, believed to promote doping, did not significantly improve device performance (**Figure 4.12, Table 4.2**). Concentration tuning the PCBM-2 concentrations and the addition of additives also failed to improve PCE (**Figure 4.13, Table 4.3**). Considering the passivation of interfaces between perovskite and PCBM-2 through quasi-2D treatment, we used phenethylammonium iodide (PEAI) and observed its effective enhancement of the PCE of PCBM-based devices. However, in PCBM-2 based devices, the J_{sc} and FF decreased after passivation (**Figure 4.14, Table 4.4**). We hypothesize that the passivation

effect is not evident, possibly due to a reaction between the acidic ligand salt and the basic dopant DBU. Further exploration of passivation methods compatible with the basic surface of doped PCBM-2 is needed for continued device optimization.

4.4 Conclusion

In conclusion, we designed and synthesized a novel ETL, PCBM-2, as a replacement for the commonly used fullerene-based ETL in inverted PSCs. The nonplanar helical structure of PCBM-2 is anticipated to enhance the morphological and thermal stability of inverted structures. PCBM-2 was successfully synthesized through a facile two-step process involving Suzuki coupling and Knoevenagel condensation. Its excellent solubility, processability, and well-aligned energy levels with perovskite layers position PCBM-2 as an ideal candidate for ETL materials in inverted perovskite solar cells. Following the selection of a suitable n-dopant and optimization of doping conditions, we achieved a PCE of over 16% in inverted structures without requiring any passivation treatment. This work introduces novel strategies for designing high-performance organic ETLs, paving the way for advanced inverted perovskite solar cells.

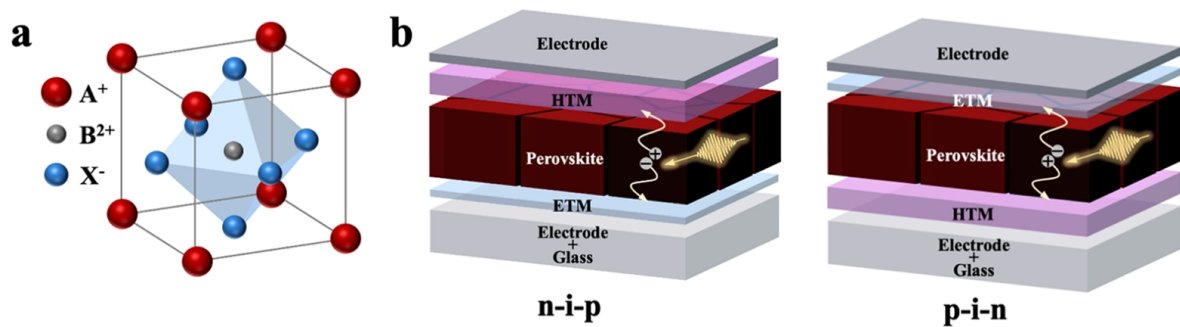


Figure 4.1 | (a) Schematics of crystal structure of metal halide perovskite. (b) Schematics of device structures of PSCs.⁶

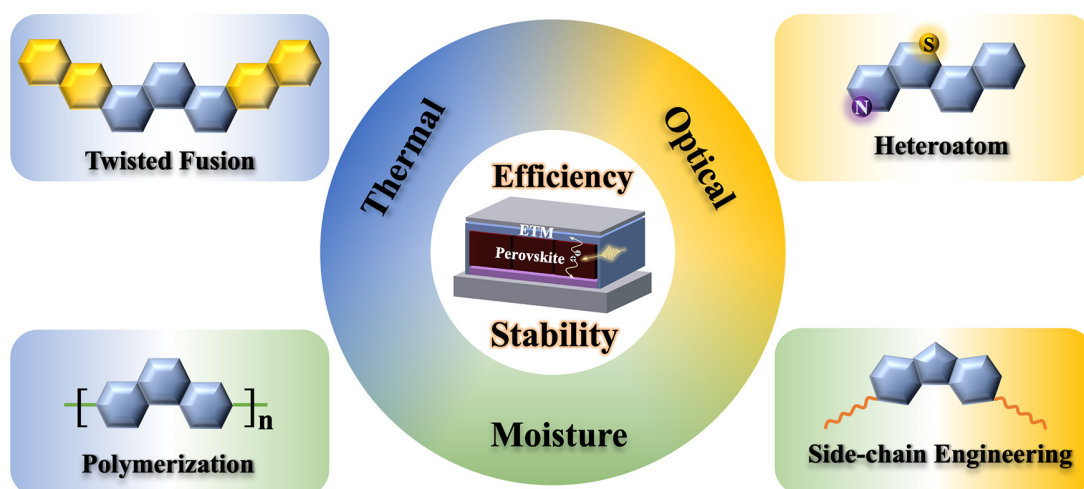


Figure 4.2 | ETL design strategies in inverted PSCs.⁶

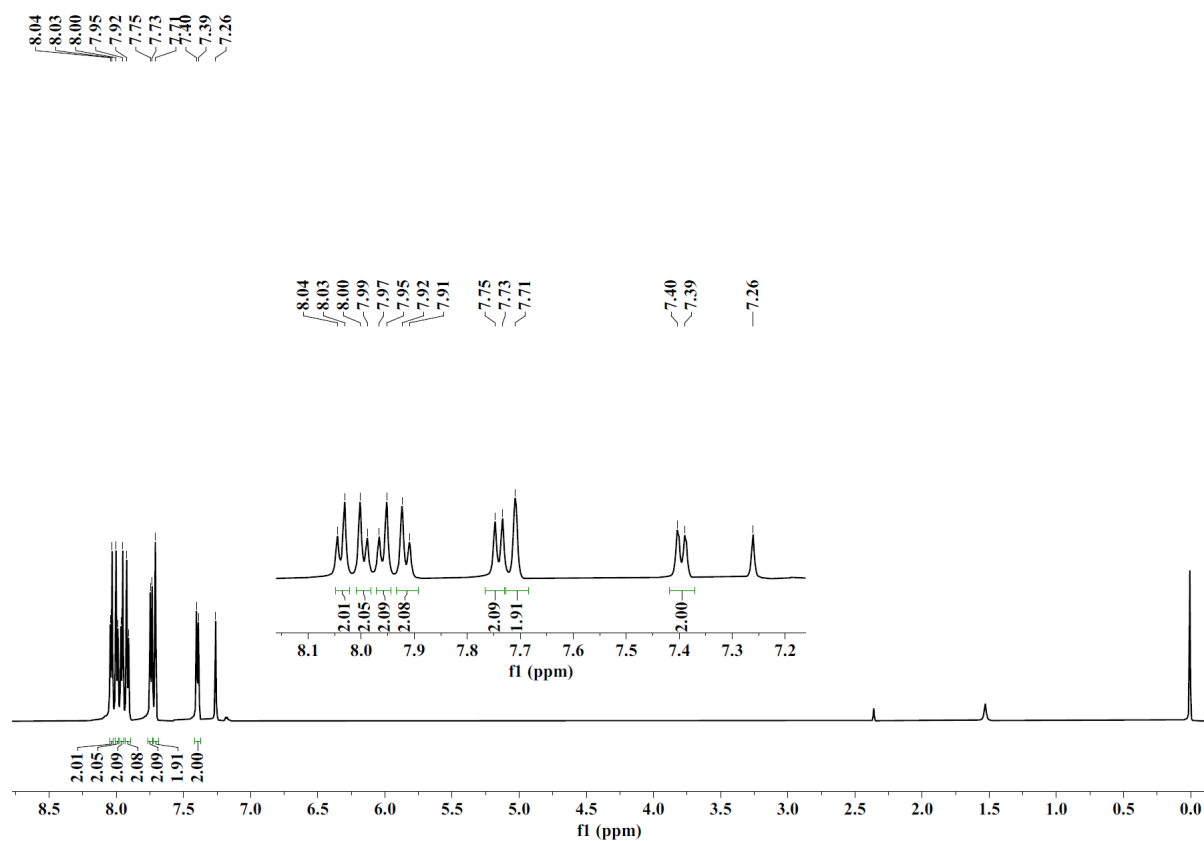


Figure 4.4 | ^1H NMR spectra of compound 2 (400 MHz, CDCl_3 , 298.5 K).

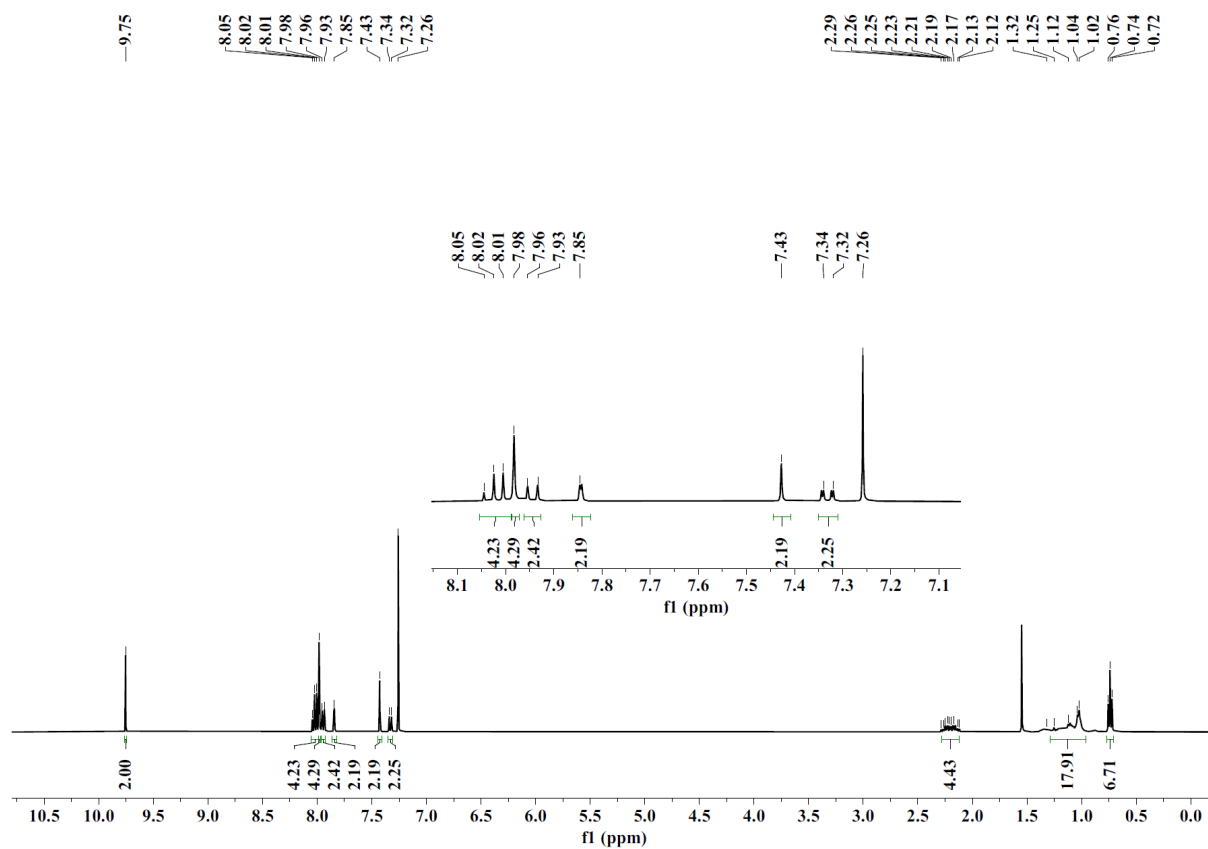


Figure 4.5 | ^1H NMR spectra of compound 3 (400 MHz, CDCl_3 , 298.5 K).

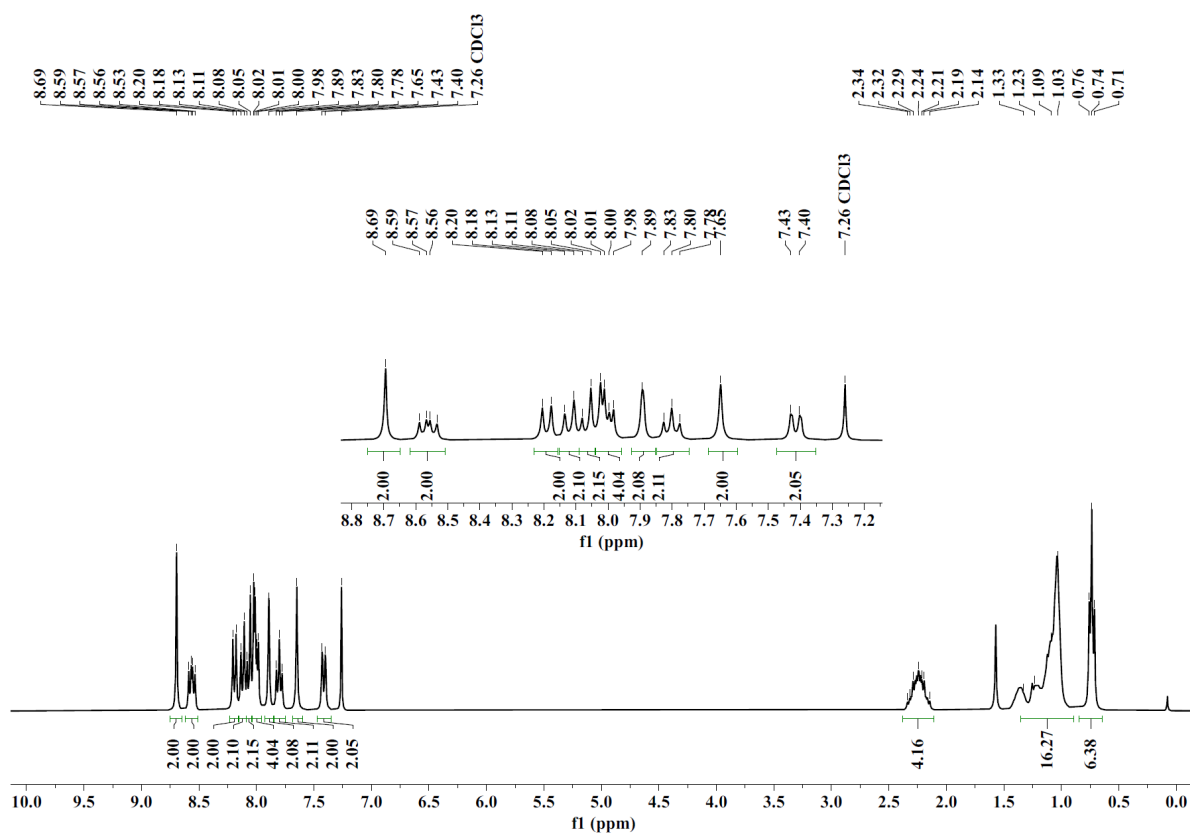


Figure 4.6 | ^1H NMR spectra of PCBM-2 (400 MHz, CDCl_3 , 298.5 K).

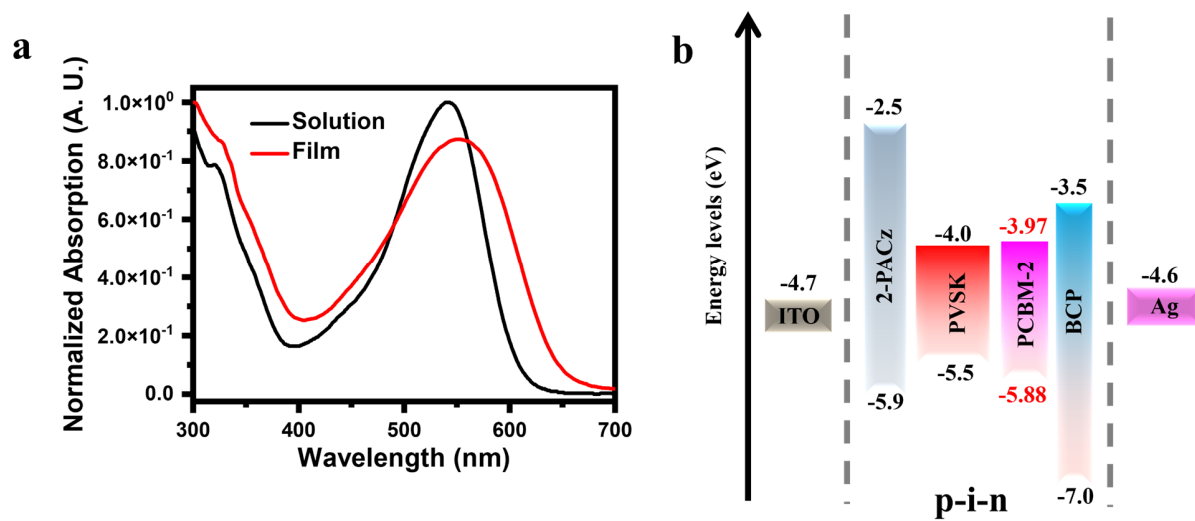


Figure 4.7 | (a) UV-vis absorption spectra of PCBM-2 in CHCl₃ solution (black) and film (red).
(b) Energy levels of PCBM-2 and other materials used in the inverted PSC.

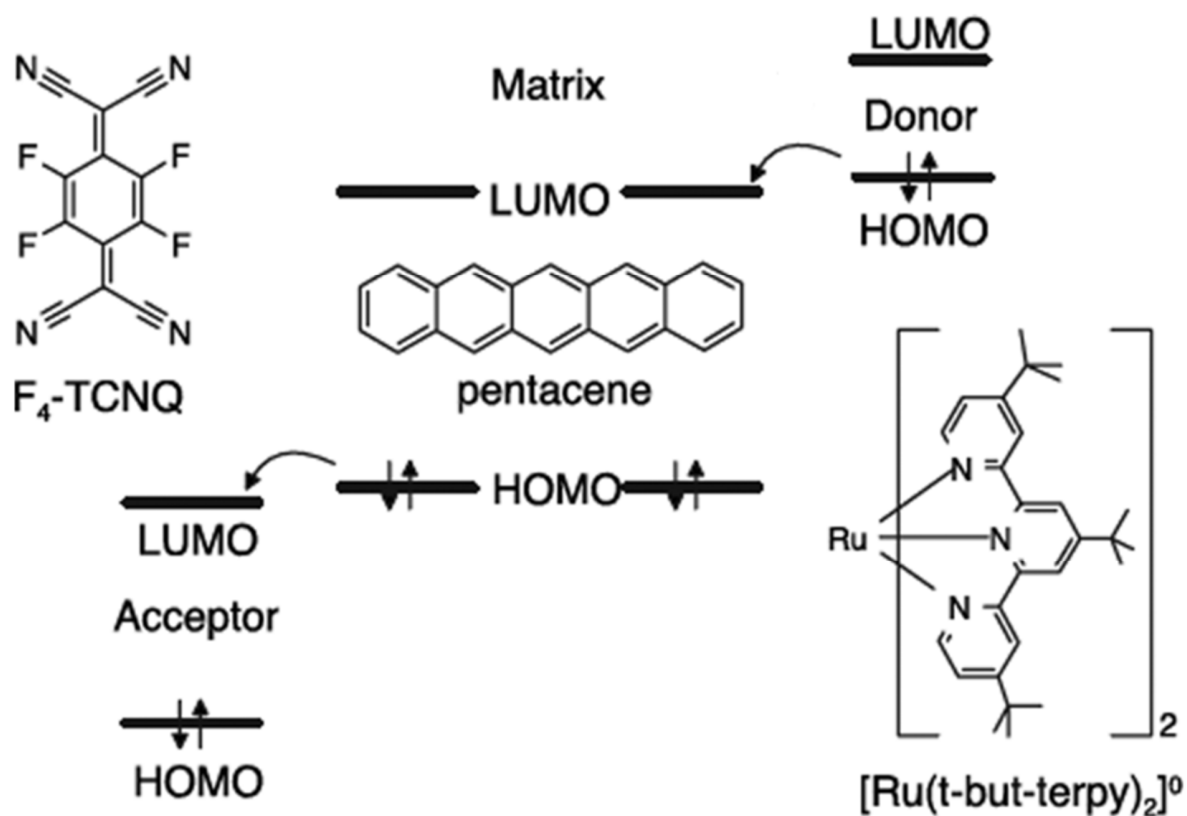


Figure 4.8 | Organic doping mechanism of pentacene.³²

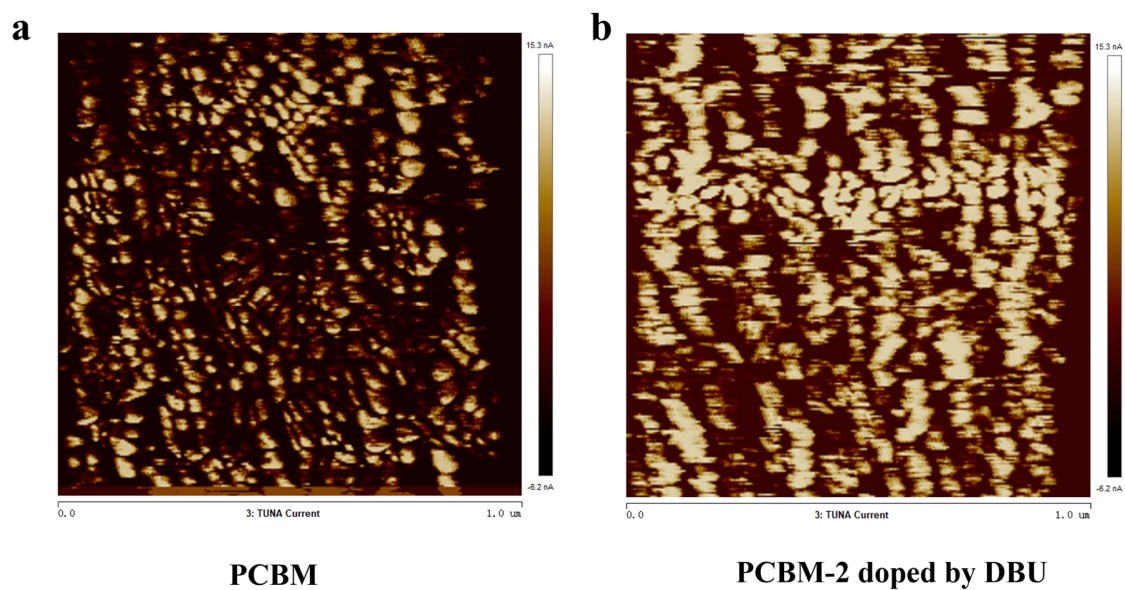


Figure 4.9 | C-AFM of (a) film of PCBM and (b) film of PCBM-2 doped by DBU.

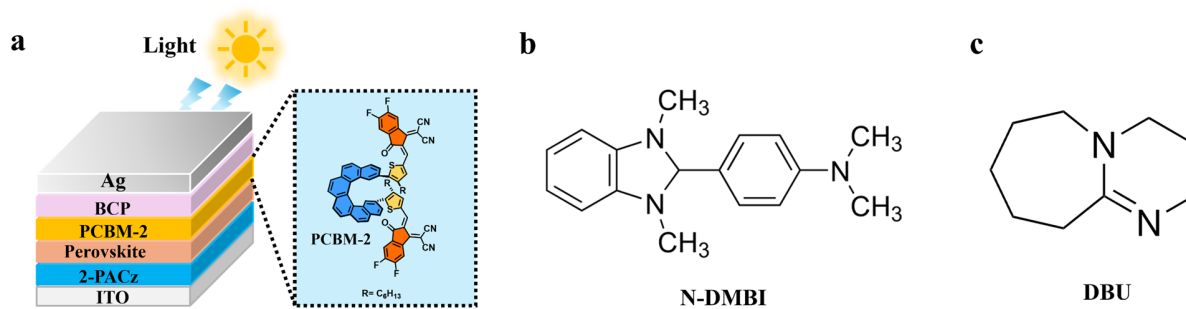


Figure 4.10 | (a) Schematics of device structure of the inverted PSC based on PCBM-2. (b) Chemical structure of N-DMBI. (c) Chemical structure of DBU.

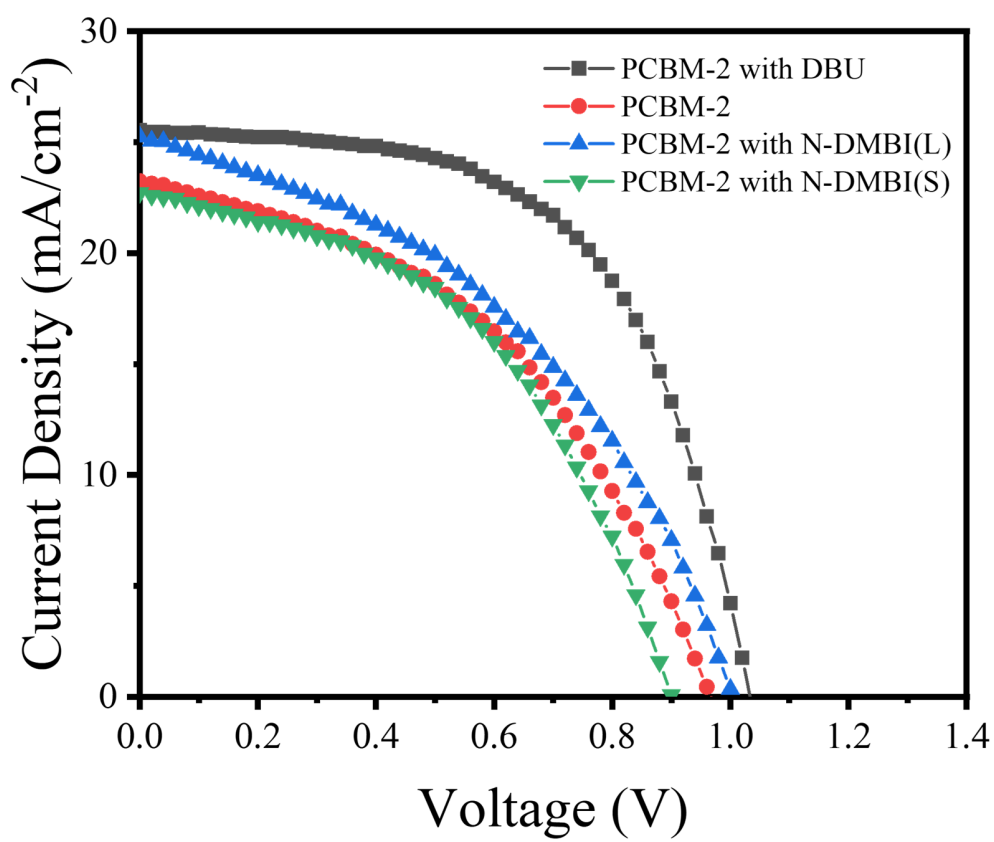


Figure 4.11 | J - V curves of inverted PSCs based on PCBM-2 doped by DBU or N-DMBI.

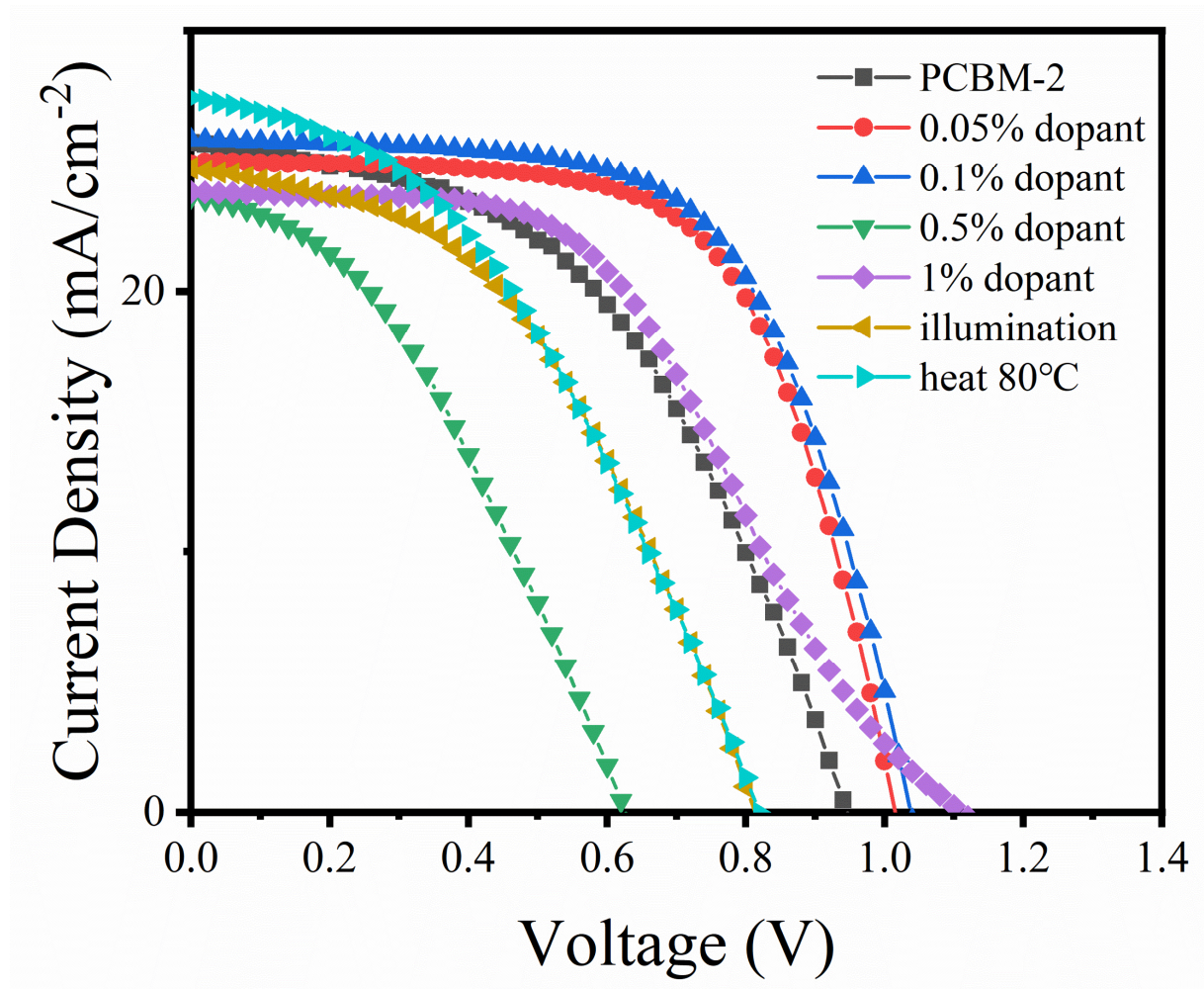


Figure 4.12 | $J-V$ curves of inverted PSCs based on PCBM-2 doped by DBU with different doping conditions.

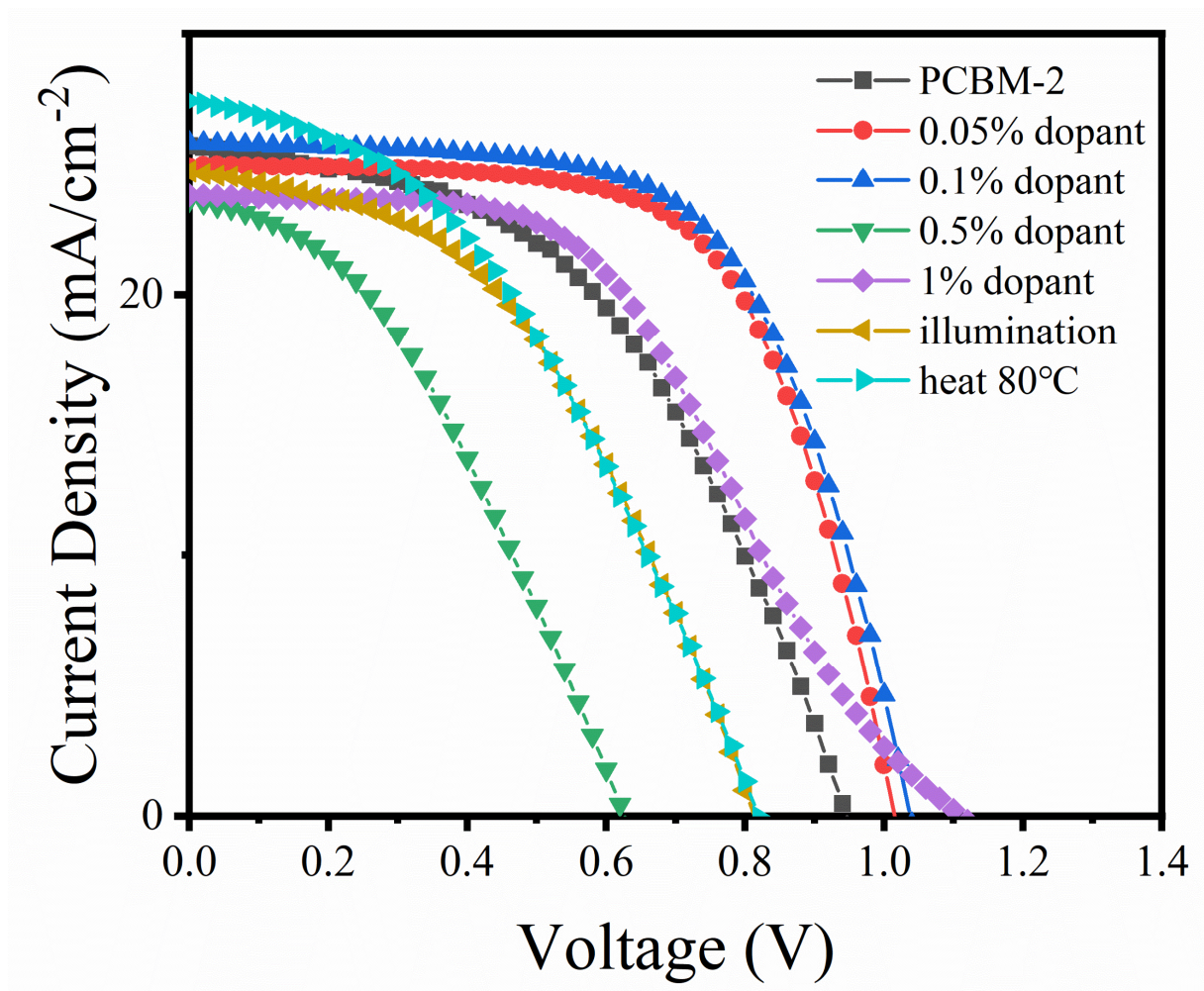


Figure 4.13 | J - V curves of inverted PSCs based on PCBM-2 with different concentrations or additives doped by DBU.

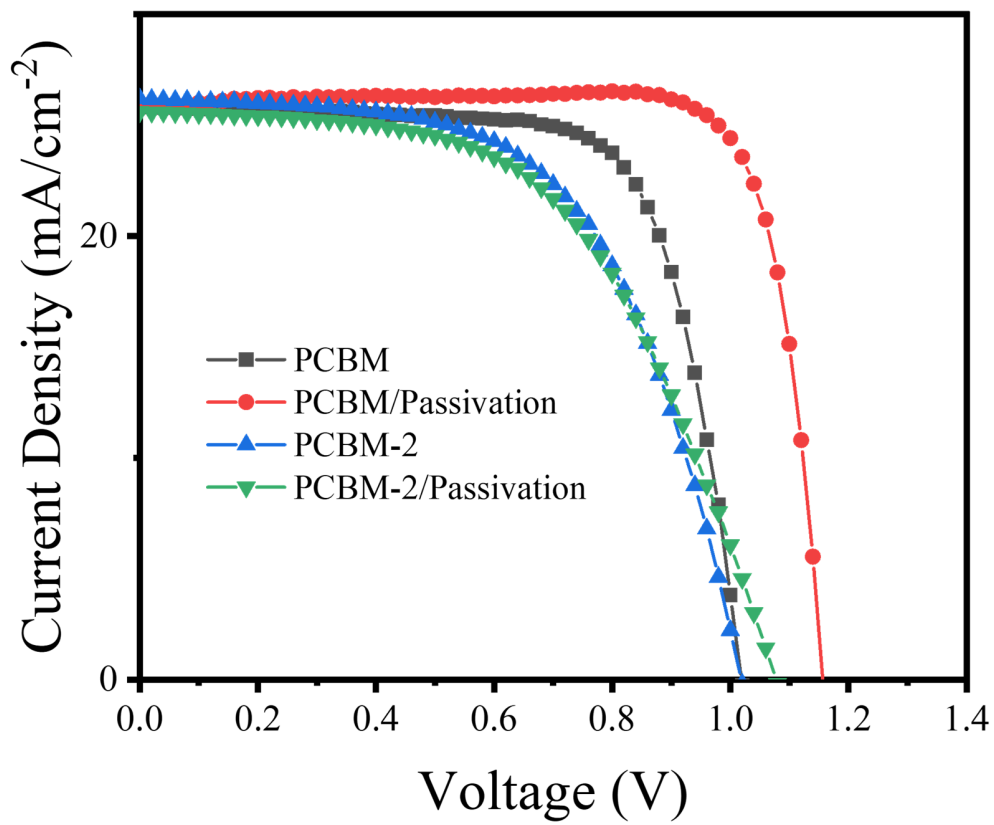


Figure 4.14 | J - V curves of inverted PSCs based on PCBM-2 doped by DBU with or without interfacial passivation.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PCBM-2 with N-DMBI (L)	1.005	25.25	42.07	10.67
PCBM-2 with N-DMBI (S)	0.901	22.73	46.98	9.62
PCBM-2	0.967	23.24	44.38	9.97
PCBM-2 with DBU (0.1%)	1.033	25.53	58.00	15.30

Table 4.1 | Detailed device parameters of inverted PSCs based on PCBM-2 doped by DBU or N-DMBI.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE(%)
PCBM-2	0.946	25.72	48.07	11.70
0.05% dopant	1.015	24.89	64.21	16.23
0.1% dopant	1.038	25.82	62.42	16.72
0.5% dopant	0.626	23.61	38.65	5.71
1% dopant	1.111	23.80	47.41	12.54
Glovebox illumination	0.813	24.72	45.42	9.13
80°C heat	0.819	27.43	41.13	9.54
PCBM	1.073	25.95	79.64	22.18

Table 4.2 | Detailed device parameters of inverted PSCs based on PCBM-2 doped by DBU with different doping conditions.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PCBM-2 (5mg/ml)	1.059	25.14	59.17	15.75
PCBM-2 (4mg/ml)	1.003	25.37	52.86	13.45
PCBM-2 (3mg/ml)	0.670	25.18	47.46	8.00
w /DIO	1.006	25.25	62.45	15.87
w /CN	1.009	24.02	61.47	14.90
PCBM	1.073	25.95	79.64	22.18

Table 4.3 | Detailed device parameters of inverted PSCs based on PCBM-2 with different concentrations or additives doped by DBU.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PCBM-2	1.018	26.20	58.76	15.68
PCBM-2/passivation	1.078	25.91	55.10	15.39
PCBM	1.019	25.81	72.28	19
PCBM/passivation	1.157	25.94	81.59	24.48

Table 4.4 | Detailed device parameters of inverted PSCs based on PCBM-2 doped by DBU with or without interfacial passivation.

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