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Dual interfacial H-bonding enhanced deep-blue hybrid Copper Iodide LEDs

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Abstract

Solution-processed light-emitting diodes based on non-toxic copper–iodide hybrids¹ are a compelling solution for efficient and stable deep-blue lighting, attributed to their tunability, high photoluminescence efficiency, and environmental sustainability². Here we present a new hybrid copper iodide that exhibits near-unity photoluminescence quantum yield (99.6%) with an emission wavelength of 449 nm and color coordinates (0.147, 0.087), alongside its emission mechanism and charge transport characteristics. We use the thin film of this hybrid as the sole active emissive layer (EML) to fabricate deep-blue LEDs and subsequently enhance the device performance via a unique dual interfacial hydrogen bond passivation strategy. This synergetic surface modification approach, integrating a new H-bond donor self-assembled monolayer with an ultra-thin PMMA capping layer, effectively passivates both heterojunctions of the copper–iodide hybrid EML and optimizes charge injections. We achieve a maximum external quantum efficiency of 12.57%, maximum luminance of 3970.30 cd·m⁻² with color coordinates (0.147, 0.091), and an excellent operational stability (T_{50}) of 204 hours under ambient conditions. We further showcase a large-area device of 4 cm² that maintains high efficiency. Our findings reveal the potential of copper iodide-based hybrid materials for applications in solid-state lighting³ and display technologies⁴, offering a versatile strategy for enhancing device performances.

Main

Solution-processed light-emitting diodes (LEDs) are emerging as a promising technology for solid-state lighting (SSL) and displays, offering energy-efficient, low-cost fabrication⁵⁻⁷. In this realm, lead-halide perovskites⁸, organic semiconductors⁹, and colloidal core-shell quantum dots (QDs)¹⁰ have shown strong performance in green and lower-energy LEDs. However, developing efficient blue, especially deep-blue LEDs that meet the Rec. 2020 compliance in full-color displays remains challenging¹¹. Blue organic LEDs (OLEDs) and perovskite LEDs (PeLEDs) suffer from poor structural and spectral stability under high bias^{12,13}, while lead-based perovskites¹⁴ and Cd-based QDs¹⁵ raise toxicity and environmental concerns. Low-toxicity alternatives (e.g., phosphorescence organic emitters¹⁶, InP/ZnSe QDs¹⁷) face high cost and synthetic complexity. These limitations hinder full-color coverage and practical development. Thus, cost-effective, eco-friendly, and efficient emitters are urgently needed for solution-processed deep-blue LEDs to advancing SSL and display technologies.

Copper halide-based emitters have attracted increasing attention for their earth abundance, low toxicity, air/moisture stability, optical tunability, and high luminescence efficiency¹⁸⁻²¹. Efforts to use them as EML in LEDs —via ligand design for solution processability^{1,3,22-24} and host-dopant optimization^{4,25}—have significantly improved device efficiency and stability. In deep-blue LEDs, 0D-Cs₃Cu₂I₅ stands out for its ideal emission (445 nm), high photoluminescence quantum yield (PLQY) of 87-95%, and excellent thermal/moisture resistance²⁶. However, its maximum external quantum efficiency (EQE_{max}) is limited to 1.02%²⁷ due to inefficient carrier injection, an inherent issue of molecular (0D) copper-iodide clusters. Addressing this challenge calls for new emitters with higher dimensionality and advanced interface engineering.

Herein, we report a new one-dimensional (1D) hybrid copper iodide, 1D-Cu₄I₈(*Hdabco*)₄ [CuI(*Hda*), *Hdabco* = 1,4-diazabicyclo-[2.2.2]octane-1-ium], synthesized using a bifunctional cationic ligand (*Hdabco*)I. It exhibits strong deep-blue photoluminescence at 449 nm with nearly unity PLQY (99.6 %). We fabricated high-quality polycrystalline thin films of CuI(*Hda*) via solution-process, with preferred out-of-plane orientation and a high PLQY of 94.7%. Comprehensive photophysical studies on CuI(*Hda*) unveil a complex emission mechanism combining fluorescence, thermally activated delayed fluorescence (TADF), and phosphorescence. Additionally, its excitonic nature, anisotropic charge carrier dynamics and electronic structure were elucidated by time-resolved microwave conductivity (TRMC) techniques and photoelectron spectroscopy.

We fabricated high-performance deep-blue LEDs using CuI(*Hda*) thin film as the sole EML, implementing a dual interfacial hydrogen-bond passivation (DIHP) strategy. Our approach adopted a newly-designed functionalized carbazole-phosphonic acid-based self-assembled monolayer (SAM)^{28,29} and an ultrathin PMMA capping layer³⁰ as H-bond donors at the HTL/EML and EML/ETL (HTL: hole-transport layer; ETL: electron-transport layer) interfaces, respectively. The coverage/thickness and interfacial H-bonding were confirmed by angular-resolved X-ray photoelectron spectroscopy (ARXPS) and Fourier-transform infrared (FTIR) spectroscopy. The synergetic interface engineering effectively boosts LED performances by passivating defects and optimizing charge injection via H-bonded heterojunctions. DIHP-treated CuI(*Hda*) devices outperform pristine and non-H-bonded SAM controls, achieving an impressively high EQE_{max} of 12.57% and maximum luminance (L_{max}) of 3970.30 cd/m², with color coordinates (0.147, 0.091), closely approaching the Rec. 2020 standard. Furthermore, these devices exhibit remarkable operational stability, achieving a half-lifetime (T_{50}) of 204 hours under ambient conditions.

Furthermore, the robustness and high scalability of DIHP-CuI(*Hda*) enables formation of large-area (4 cm²) deep-blue LED that maintains high EQE_{max} of 7.87%.

Design, thin film fabrication, and characterization of CuI(*Hda*)

We designed a mono-protonated aliphatic ligand, (*Hdabco*)I, featuring a monodentate coordination site and high LUMO level, aiming at enhanced solution-processibility²⁰ and an optimal band gap of the resultant hybrid material for deep-blue emission. High-quality single crystals of CuI(*Hda*) (Fig. 1a) were grown from a precursor solution using a facile recrystallization method. Single crystal X-ray diffraction (SCXRD; Fig. 1a, Supplementary Figs. S1-S2 and Table S1) reveals that 1D-Cu₄I₈(*Hdabco*)₄ consists of anionic 1D-(Cu₄I₈)⁴⁻ inorganic chains and organic cationic ligand (*Hdabco*)⁺ connected via both coordinate and ionic bonds. Each Cu(I) atom is coordinated by three iodine atoms and one nitrogen atom from (*Hdabco*)⁺, forming a distorted tetrahedron of (CuI₃N). Each tetrahedron shares edges and corners with its adjacent tetrahedra, resulting in an infinite 1D chain. The organic cations form H-bonded dimers, (*Hdabco*)₂²⁺, owing to the unique bifunctional nature of (*Hdabco*)⁺, where non-protonated and protonated N atoms are engaged in Cu-N bonding and intermolecular H-bonding, respectively (Fig. 1a).

We performed first-principles DFT calculations to understand the electronic structure of CuI(*Hda*). The result suggests a direct bandgap semiconductor (Fig. 1b), with relatively flat valence band (VB) but a pronounced conduction band (CB) dispersion, implying a smaller effective mass and favorable transport of electron. To correctly estimated the DFT band gap, we used the screened hybrid functional of Heyd, Scuseria and Ernzerhof (HSE). The HSE band gap of CuI(*Hda*) was calculated to be 3.8 eV. The projected density of states (PDOS) analysis (Fig 1b) indicates that the atomic contributions to its valence band maximum (VBM) are primarily from the inorganic components, specifically Cu 3d and I 5p atomic orbitals, while the conduction band minimum

(CBM) is populated by atomic orbitals from both the inorganic motif (specifically Cu 4s, I s and p orbitals) and the organic ligand (C 2p and N 2s orbitals). Different from most reported hybrid copper halides with either a metal/halide-to-ligand charge transfer [(M/X)LCT]^{3,20,21,31} or a triplet cluster-centered transition (³CC)^{2,19,20,32}, or a mixture of both^{23,24,33}, the relatively long Cu-Cu distances (>3.3 Å) and the high lying LUMO energy of the organic ligand result in substantial orbital overlap of inorganic (Cu and I) and organic (C and N) orbitals at the CBM region in CuI(*Hda*), giving rise to a unique excited-state transition based on both (M/X)LCT and all-inorganic-transition processes^{34,35}. Time-dependent DFT (TDDFT) calculations consolidate this dual-character excited-state model and manifest significant exciton localization on the spatially and electronically confined 1D-Cu₄I₈N₄ structure, with the holes primarily localized on Cu 3d orbitals and the electrons delocalized over Cu 4s, I s, C 2p, and N 2s orbitals (Supplementary Fig. S3 and Table. S2). This distinct electronic configuration underlies the complex photophysical behavior observed in CuI(*Hda*).

We fabricated CuI(*Hda*) thin films via single-step spin-coating of the precursor solution on ITO and large-area quartz substrates (Fig. 1c), followed by antisolvent dripping to initiate the crystallization and slow annealing at room temperature for a relatively long time of 36 hours (Supplementary Fig. S4). Pin-hole free thin-film samples were obtained with a thickness of 90 nm and R_a of 0.177 nm, as measured by atomic force microscopy (AFM, Fig. 1c and Supplementary Fig. S5). Top-view scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) images (Supplementary Figs. S6-S10) demonstrate the good compactness, surface smoothness, and even elemental distribution of the as-fabricated CuI(*Hda*) thin films. Powder X-ray diffraction (PXRD) analysis of the film shows a dominant (200) peak at 2θ = 12.9°, whereas powder scraped from the film reproduces the full simulated pattern (Fig. 1d), confirming

a phase-pure CuI(*Hda*) thin film with strong preferred orientation. The GIWAXS patterns reveal the polycrystalline nature of the CuI(*Hda*) thin film and confirm the preferred orientation of (200) plane (perpendicular to the 1D-(Cu₄I₈)⁴⁻ chain) in out-of-plane scattering profile (Fig. 1e and Supplementary Figs. S11-S12). The combination of low surface roughness, high crystallinity, and a high PLQY (94.7%, Supplementary Fig. S13-S15) affirms the high-quality of the thin film samples, which is attributed to the excellent solution processability of this type of materials.

Photophysical properties of CuI(*Hda*)

Steady-state optical absorption and diffuse reflectance spectra of polycrystalline thin film (90 nm) and powder samples of CuI(*Hda*) show nearly identical sharp absorption edges, confirming its direct band gap of ~3.7 eV (Fig. 2a and inset), consistent with the DFT results. Room temperature PL of the thin film sample reveals a strong single-band emission peak centered at 449 nm with a full width at half maximum (FWHM) of 97 nm and color coordinates (0.147, 0.091) (Fig. 2a). CuI(*Hda*) features a large Stokes shift and relatively broad emission band arising from nearly degenerate excited states (Supplementary Table. S2), characteristic of other reported copper halides. The single crystals and thin film samples of CuI(*Hda*) exhibit near-unity PLQY values of 99.6% and 94.7% by the de Mello method³⁶ when excited at 280 nm, marking the highest value for blue emitters³⁷.

Insight into the emission mechanism of CuI(*Hda*) comes from the temperature dependent time-resolved photoluminescence (TRPL) decay profiles carried out on thin film sample (Fig. 2b). Tri-exponential fittings of the TRPL decay curves (Supplementary Table. S3) identify three distinct emissive pathways: a) a nanosecond-lived channel (τ_1) that is essentially temperature-independent, assignable to prompt fluorescence, b) a sub-microsecond channel (τ_2) whose contribution grows

slightly with increasing temperature, consistent with TADF reported in hybrid copper halides³⁸,
 and c) a microsecond-lived channel (τ_3) whose relative weight diminishes at higher temperature,
 characteristic of phosphorescence in copper halides³⁸. Meanwhile, the high fractional intensity of
 τ_3 indicates that phosphorescence dominates the overall emission, likely due to the strong spin-
 orbit coupling that facilitates the T_1 - S_0 transition in hybrid copper-iodide systems (Supplementary
 Figs. S16-17). A small $\Delta E_{S_1-T_1}$ of 50.8 meV (Supplementary Figs. S18) supports reverse
 intersystem crossing (RISC) transition for TADF. These three distinct decay pathways are further
 validated by TRPL decay comparison of thin film and single crystal (Supplementary Figs. S19),
 time-resolved emission spectroscopy (TRES, Extended Data Fig. 1) and a low-temperature (10 K)
 phosphorescence spectrum (Supplementary Fig. S20). The identical decay curves and tri-
 exponential fittings confirm that the prompt fluorescence is an intrinsic radiative decay pathway,
 independent of substrate emission or variations in surface/interface trap density across sample
 morphologies^{39,40}, thus ruling out trap-assisted recombination. TRES analysis reveals both S_1 and
 T_1 bands whose fractional intensities evolve over time; notably, the T_1 band becomes increasingly
 dominant at longer delay times, corroborates proposed fluorescence, TADF, and phosphorescence
 decay pathways. The 10 K phosphorescence spectrum underpins a redshift of 43 meV consistent
 with $\Delta E_{S_1-T_1}$. The TADF and phosphorescence pathways align with the established $^3(M/X)LCT$
 transition mechanism in hybrid copper halides, while the additional all-inorganic transition
 associated with delocalized CBM likely increases the singlet oscillator length²², resulting in the
 additional prompt fluorescence channel. Total radiative (k_r) and non-radiative decay rate (k_{nr}) at
 298K were calculated as $3.05 \times 10^5 \text{ s}^{-1}$ and $1.84 \times 10^3 \text{ s}^{-1}$, respectively, quantitatively manifesting
 the efficient radiative decay of $\text{CuI}(\text{Hda})$ (Supplementary note 1).

Temperature dependent (78 to 298 K, Fig. 2c) and power-dependent (Supplementary Figs. S21-S22) steady-state PL spectra were measured on a thin-film CuI(*Hda*) sample on quartz. No significant shift in the emission peak or FWHM was observed across varying temperatures and pump powers, indicating moderate electron-phonon coupling (Supplementary Fig. S23, note 2). This is attributed to the higher structural rigidity of the 1D-(Cu₄I₈)⁴⁻ chain compared to molecular (0D) copper halides. Compared with other copper halides (Supplementary Table. S4), the exciton binding energy (E_b) of 107 meV derived from Arrhenius plots of PL intensity as a function of temperature (Supplementary Fig. S24), highlights the localized exciton and reveals the excitonic nature of CuI(*Hda*).

We employed femtosecond (fs-TA) and nanosecond (ns-TA) transient absorption spectroscopy to investigate the excited-state dynamics of CuI(*Hda*) films. The fs-TA spectra (Fig. 2d and 2e and Supplementary Fig. S25) disclose a ground state bleaching band at 381 nm and an excited-state absorption band that shifts from 601 nm to 624 nm with increased delay time (Supplementary note 3, Figs. S26-S27 and Tables S5-S6). Complementary ns-TA experiments, extending beyond the 4.5 ns delay limit of fs-TA, confirm the same bleaching feature and yield decay times in quantitative agreement with the TRPL results (Supplementary Figs. S28-S29 and Table S7). Collectively, we propose a comprehensive kinetic model for the multi-channel excited-state decay processes in CuI(*Hda*) (Fig. 2f and Supplementary note 4).

Electrical properties and electronic structure of CuI(*Hda*)

We explored the anisotropic charge carrier dynamics, mobility, equilibrium doping density and dielectric constant in CuI(*Hda*) single crystals and thin films by TRMC and dark microwave conductivity (DMC) techniques. A bi-exponential fit of the TRMC transient for a polycrystalline

thin film of CuI(*Hda*) on quartz (Fig. 3a) disclosures two lifetime components: a primary 4.6 ns and a secondary 250 ns decay, corresponding to a maximum yield-mobility of $1.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

We performed additional TRMC measurements on a CuI(*Hda*) single crystal (1×1×4 mm) to investigate potential birefringence and/or mobility anisotropy attributable to its markedly anisotropic crystal structure (Fig. 3b). Analysis of the power reflectance curves for two different orientations of a CuI(*Hda*) single crystal relative to the microwave electric field (Fig. 3c) indicates nearly isotropic conductivity at $5.5 \times 10^{-5} \text{ S/cm}$ and a dielectric constant of 4.75 ± 0.5 . While no pronounced birefringence is observed, the carrier mobility appears slightly anisotropic. TRMC transients for the CuI(*Hda*) single crystal, excited by both parallel and perpendicular pump laser polarizations relative to each crystal orientation with the microwave electric field, were examined (Fig. 3d). Charge carrier mobility (at 9 GHz) measured $4.4 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ perpendicular to the *a*-axis, approximately twice that measured parallel to it, substantiating the anisotropic charge carrier properties. Such anisotropic charge carrier properties are further supported by polarized PL measurements of CuI(*Hda*) single crystals (Extended Data Fig. 1 and Supplementary note 5).

As a complement to the TRMC mobility, space charge-limited current (SCLC) measurements were performed on single-carrier devices of CuI(*Hda*). We extracted a hole-mobility of $\mu_h = 5.9 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, an electron-mobility of $\mu_e = 8.8 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ alongside a trap state density (η_{trap}) of $8.2 \times 10^{16} \text{ cm}^{-3}$ (Fig. 3e), as an overall contribution from mobilities of CuI(*Hda*), transport materials, heterojunctions and band alignments. The noted higher electron mobility correlates well with the DFT-calculated BS. The observed SCLC mobilities surpass those from TRMC, aligning with the expected lower free charge yield upon photoexcitation in TRMC assays. Notably, the charge carrier mobilities in CuI(*Hda*) thin films are comparable to those of high-

quality perovskite films for analogous applications⁸ and are approximately an order of magnitude higher than those reported for metallic copper halides¹⁰.

X-ray photoelectron spectroscopy (XPS, Supplementary Figs. S30-S34, Table S8, note 6) and reflected electron energy loss spectroscopy (REELS, Supplementary Fig. S35) experiments confirm the correct composition of CuI(*Hda*) and indicate an absorption onset 3.6 eV below the elastic peak matching the optical and DFT band gap. Ultraviolet photoelectron spectroscopy (UPS, Supplementary Fig. S36) data show a sharp valence band edge located 0.7 eV below the Fermi level, suggesting a p-type semiconductor and the calculated electronic structure dominated by Cu 3d and I 5p orbitals. The energy difference between the valence band and vacuum level is determined to be 5.8 eV (Supplementary Fig. S37).

Interfacial H-bonds on CuI(*Hda*) heterojunctions

We selected NiO_x as HTL (Supplementary Fig. S38) and Ca(*acac*)₂ (calcium acetylacetonate) as the ETL³² for CuI(*Hda*) deep-blue LEDs based on the energy diagram derived from photoemission spectroscopy for optimized electron-hole injection. To address interfacial trap-assist carrier recombination and unbalanced charge injection, we implemented the DIHP approach on both heterojunctions of the CuI(*Hda*) EML (Fig. 4a).

At the HTL/EML interface, we designed a new tri-functional 2PACz-based SAM (Ac2PACz) for HTL functionalization, and compared its performance with three reported bi-functional SAMs^{28,41} from the same class (Fig. 4b, Supplementary Figs. S39-S46, note 7). 2PACz-based SAMs provide dual functionalities of surface passivation via phosphonic acid anchoring and enhanced hole transport via carbazole group. The new SAM, featuring additional electron-withdrawing acetyl (Ac) substituent, showing both a high electrostatic potential (ESP) on the C=O group as effective H-bond donor and a suitable HOMO level for band alignment (Fig. 4b).

At the EML/ETL interface, we introduced an ultrathin PMMA layer as an electron-blocking buffer to primarily compensate for CuI(*Hda*)’s higher electron mobility and to protect the EML during solution processing of Ca(*acac*)₂ from polar protic solvent. This insulating PMMA interlayer allows fine tuning of electron injection through thickness control, while its carbonyl groups form H-bonds with surface (*Hdabco*)₂²⁺ cations (Fig. 4c), passivating surface defects without adversely affecting optical transmission.

First-principles calculations predicted the favorable surface adsorption modes of four SAMs on the NiO (111) surface (Supplementary Fig. S47), and assess the adsorption/H-bonding and charge density difference between the conformation-optimized SAMs and CuI(*Hda*) (200) plane (Extended Data Fig. 3, Supplementary Table. S9). The highest H-bond energy of 2.99 eV was calculated between Ac2PACz and CuI(*Hda*), demonstrating strong interfacial H-bonding. Likewise, modeling the EML/ETL junction reveals that compared to bare CuI(*Hda*)-Ca(*acac*)₂ heterojunction, additional PMMA capping layer increases the H-bonding energy by 1.37 eV with stronger charge density delocalization across the interface (Extended Data Fig. 4). In both cases, H-bonded heterojunctions facilitate stronger charge density relocation to the (*Hdabco*)₂²⁺ ligand, implying improved charge injection at the interface.

Kelvin probe force microscopy (KPFM) images of SAMs-treated NiO_x confirmed uniform morphologies and homogeneous surface potentials (Fig. 4c). Surface coverage of SAMs on NiO_x surface was quantitatively assessed by ARXPS (Fig. 4d, Supplementary Figs. S48-S55, Supplementary note 8), unveiling near-optimal monolayer adsorption. H-bonding between NiO_x/Ac2PACz and CuI(*Hda*) was experimentally validated via FTIR spectra (Fig. 4e), where a red shift in $\nu_{\text{C=O}}$ from 1675 cm⁻¹ to 1668 cm⁻¹ provided clear evidence of H-bond formation on the Ac2PACz-CuI(*Hda*) interface^{42,43}.

We confirmed optimized band alignments (Supplementary Fig. S56, Table S10) at the functionalized HTL/EML heterojunctions, along with a low surface-energy (Supplementary Fig. S57) and hole-selective interface (Supplementary Figs. S58-S61, note 9). Among tested SAMs, Ac2PACz-functionalized HTL exhibits the lowest contact angle, longest TRPL lifetime (Supplementary Fig. S62), lowest trap density, and highest hole-mobility, demonstrating the superior effectiveness of H-bonded interfaces (Extended Data Table 1).

ARXPS (Extended Data Fig. 5, Supplementary Figs. S63-S74, Supplementary note 10) verify the PMMA interlayers thickness across samples prepared with varying spin rates. Decreases in the $C1s_{(C=O)}/C1s_{(C-C, C-H)}$ ratio with increasing incident angle in thinner PMMA overlayers elucidates C=O enrichment at the interface, consistent with directional CuI(*Hda*)-PMMA interfacial H-bonding. We also observed systematic shifts in the O 1s and N 1s core-level spectra, indicating electron transfer from PMMA carbonyl oxygen atoms to the protonated *Hdabco* nitrogen atoms, in agreement with our computed charge-transfer results (Fig. 4f). This H-bond coupling at the EML/ETL interface correlates with an increase in overall PL intensity (Supplementary Figs. S75-S76) and characteristic $\nu_{(C=O)}$ shifts in FTIR (Supplementary Fig. S77). At both interfaces, the H-bond-enhanced strong charge redistribution creates surface dipoles oriented toward CuI(*Hda*), promoting h^+ -injection while reinforcing e^- -blocking. Together with the HTL/ETL interface, these findings validate the DIHP approach: strong dual interfacial primarily promote balanced charge injection while passivate defects at both heterojunctions.

Deep-blue CuI(*Hda*) LEDs based on DIHP approach

The pristine device featured a structure of ITO(185 nm)/NiO_x(40 nm)/CuI(*Hda*)(90 nm)/Ca(*acac*)₂(35 nm)/LiF(1 nm)/Al(60 nm) (Fig. 5a, b). Cross-sectional helium-ion microscope imaging of deep-blue LEDs demonstrates pinhole-free CuI(*Hda*) EML with uniform thickness and well-

defined interfaces(Fig. 5c). These untreated devices achieved a EQE_{max} of 3.09% and L_{max} of 1714.21 $cd \cdot m^{-2}$ at 450 nm (Fig. 5d-f). In contrast, PMMA-capped LEDs (without SAM functionalization of HTL) showed a 2-fold EQE_{max} , accompanied by a 0.8-fold reduction in current density but a 1.3-fold luminance increasement, suggesting the surface passivation and electron-blocking effect of H-bonded PMMA-capping layer. Control devices (Extended Data Fig. 6) confirmed that the PMMA interlayer systematically reduces current density by impeding electron injection. In ITO/ NiO_x /CuI(*Hda*)/PMMA/Corannulene/LiF/Al devices, the J-V and L-V showed minimal changes due to PMMA-dissolution during chloroform-based ETL processing and formation of a PMMA-corannulene mix layer, emphasizing the prominence of intact capping layer for sufficient electron blocking. In ITO/PEDOT:PSS/CuI(*Hda*)/PMMA/Ca(*acac*)₂/LiF/Al devices, the PMMA layer acted as an effective electron-blocking buffer when paired with a less efficient HTL, yielding higher efficiency than the uncapped control. For devices with TPBi (2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) as the ETL, the PMMA interlayer further impeded poor electron injection due to energy-level mismatch, resulting in reduced performance.

We observed pronounced performance gains in deep-blue DIHP-treated CuI(*Hda*) LEDs with the structure: ITO/Ac2PACz (monolayer)- NiO_x /CuI(*Hda*)/PMMA/Ca(*acac*)₂/LiF/Al, stemming from synergistic H-bonded heterojunctions that suppress interfacial trap-assisted nonradiative losses and establish interfacial dipoles oriented toward CuI(*Hda*), thereby facilitating hole-injection from the Ac2PACz- NiO_x side while simultaneously enhancing electron-blocking at the EML/ETL interface. The DIHP device achieved a L_{max} of 3970.30 $cd \cdot m^{-2}$ with CIE coordinates of (0.147, 0.091) (Figs. 5d, e). It delivered EQE_{max} of 12.57%, with an average EQE of $10.0 \pm 1.5\%$ across multiple devices (Figs. 5f,g), representing a ~4-fold improvement over the pristine device and

setting a new performance benchmark among metal halide-based deep-blue LEDs with peak emission <460 nm. Compared to control devices incorporating other, non-H-bonded SAMs (Extended Data Fig. 7), the Ac2PACz-modified heterojunction delivers significantly enhanced performance across all metrics. Notably, a large-area (2 cm × 2 cm) LED with DIHP-treatment retained a high EQE_{max} of 7.87% (inset of Fig. 5h), evidencing the scalability and robustness of the solution-processed hybrid copper iodide and the DIHP approach.

We evaluated the operational stability of deep-blue CuI(*Hda*) LEDs ($L_0 \approx 100$ cd/m²) under ambient conditions. Figure 5h shows the durability of both unprotected (pristine, PMMA-capped and DIHP) and encapsulated devices. DIHP-based devices demonstrate significantly enhanced lifetimes due to reduced defect recombination and lower operating current density from optimized charge injection. T_{50} values reached 113 h (unprotected) and 204 h (encapsulated) under ambient conditions, surpassing all reported blue PeLEDs and rivaling best performing all-inorganic copper halides, yet with an EQE 10 times higher. A performance and operational stability comparison across metal halide-based BLEDs is provided in Supplementary Table S9. DIHP-CuI(*Hda*) outperforms existing deep-blue emitting compounds in both EQE and half-lifetime, with strong thermal and long-term stability confirmed under accelerated stress (Supplementary Figs. S78-80, note 11).

Conclusion

In conclusion, we developed a deep-blue emitting copper iodide hybrid material with exceptional optical properties. Comprehensive structural, optical, electrical and computational analyses revealed its emission mechanism and charge transport behavior. We introduced a synergetic dual H-bonding passivation strategy to fabricate CuI(*Hda*)-based deep blue LED by integrating a new H-bond donor SAM at the HTL/EML interface and H-bond donor PMMA at the EML/ETL

interface. This DIHP approach effectively passivates both heterojunctions, optimizes charge injection, and achieve a maximum EQE of 12.57%, maximum luminance of 3970.30 cd·m⁻² and color coordinates (0.147, 0.091), with a *T*₅₀ lifetime of 204 hours under ambient conditions. These results underscore the potential of copper halide hybrids as stable EML materials and highlight interfacial H-bonding as a versatile strategy for high-performance LEDs (Supplementary Table S12, note 12).

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Legends of the main text figures

Fig. 1| Structural characterization and DFT analysis of CuI(*Hda*). **a**, Structure units, crystal image (under UV light) and structure plot of a unit cell of CuI(*Hda*) single crystals. **b**, Calculated

BS and DOS of CuI(*Hda*). Inset is the isosurface plots of $|\Psi|^2$ of the lowest and highest energy level of CB and VB, respectively. **c**, Photographs of CuI(*Hda*) thin film samples under excitation and atomic force microscopy (AFM) surface morphology profile. **d**, PXRD patterns of powders scratched from thin films, as-made thin film and simulated from single crystal data (from top to bottom). **e**, Grazing-incidence wide-angle X-ray scattering (GIWAXS) pattern of a CuI(*Hda*) thin film grown on ITO substrate.

Fig. 2| Photophysical characteristics of CuI(*Hda*). **a**, Room temperature optical absorbance and steady state PL spectra of CuI(*Hda*) thin film on a quartz substrate. Inset is the Kubelka–Munk (K-M) function converted from optical absorption spectrum of a powder sample. **b**, Time-resolved photoluminescence (TRPL) decay profiles of CuI(*Hda*) at different temperatures ($\lambda_{\text{ex}} = 285$ nm). Dash lines are fitting curves from the tri-exponent model. **c**, Pseudocolor map of temperature-dependent PL spectra of the CuI(*Hda*) thin film sample ranging from 78 to 298 K. **d** and **e**, Femtosecond transient absorption (fs-TA) spectra of CuI(*Hda*) thin film sample recorded at selected delay times. **f**, Proposed kinetic model for the photophysical processes of CuI(*Hda*) at 293 K determined from TRPL and TA spectroscopic studies.

Fig. 3| Charge transport properties of CuI(*Hda*). **a**, Microwave conductivity transients recorded for a thin film of CuI(*Hda*) (90 nm) on a quartz substrate (300 nm, $3 \times 10^{14} \text{ cm}^{-2}$). **b**, Schematic of time-resolved microwave conductivity setup for the anisotropic measurement on CuI(*Hda*) single crystals. **c**, Microwave cavity resonances for a cavity containing only a quartz substrate (black), and that with a large single crystal of CuI(*Hda*) introduced with the *a*-axis of the crystal oriented either parallel or perpendicular to the microwave electric field (light and deep blue). The solid traces are Lorentzian fits. The extracted sample properties are shown in the inset. **d**, Microwave conductivity transients recorded for single crystals of a single CuI(*Hda*) mounted on a quartz

substrate excited at 300 nm ($1 \times 10^{15} \text{ cm}^{-2}$), electric field of microwave and linearly polarized laser was aligned at both perpendicular and parallel geometries to the a-axis of the single crystal to explore the anisotropic photoconductivity of CuI(*Hda*). **e**, Space charge-limited current (SCLC) measurements for hole-only and electron-only devices of CuI(*Hda*).

Fig. 4| Design and characterization of dual interfacial H-Bonds. **a**, Schematic diagram of the DIHP approach on CuI(*Hda*) deep-blue LED. **b**, DFT calculated electrostatic potential (ESP) and energy levels of SAM molecules. **c**, Work function (WF) from KPFM of SAMs-functionalized NiO_x surfaces. **d**, PMMA as a H-bonding electron balancing layer. **e**, ARXPS of absorbed monolayer of Ac2PACz on NiO_x. **f**, Infrared spectra of CuI(*Hda*) thin film on Si/NiO_x/Ac2PACz versus reference spectra, suggesting an interfacial H-bonding induced redshift of $\nu_{\text{C=O}}$. **g**, ARXPS of ultra-thin PMMA layers on CuI(*Hda*), suggesting H-bonding induced binding energy shifts in O1s and N1s core levels.

Fig. 5| Performance and operating stability comparison of pristine and H-bonded deep-blue LEDs. **a**, UPS energy levels of NiO_x and Ac2PACz-functionalized NiO_x. **b**, Overall energy band diagram and a schematic illustration of the CuI(*Hda*) deep-blue LED. **c**, Cross-sectional HeIM image of the LED. **d**, EL spectra of the LED device operated under increasing voltages from 5 to 8 V. Inset is a working deep-blue LED under 7.5 V bias and the CIE1931 coordinates of the electroluminescence (EL). **e**, Current density and luminance as a function of voltage for pristine, PMMA-capped and DIHP deep-blue LEDs. **f**, EQE-J curves for pristine (bottom), PMMA-capped (middle) and DIHP deep-blue LEDs (top). The filled symbol indicates the maximum EQEs of 3.09%, 6.17% and 12.57%, respectively. **g**, Statistics of peak EQEs measured from 6 types of CuI(*Hda*) blue LEDs with different interfacial functionalization, each with a batch number of 50. Plots of the box-chart graphs containing the mean value, maximum/minimum values, bounds of

box, whiskers and percentile. **h**, Operational half-lifetime (T_{50}) of three types of blue LEDs w/wo encapsulation under ambient conditions with an initial luminance (L_0) of $100 \text{ cd}\cdot\text{m}^{-2}$. L/L_0 is the ratio between luminance at a given time and L_0 . Inset is a $2 \text{ cm} \times 2 \text{ cm}$ large area DIHP-CuI(*Hda*) deep blue LED.

Methods

Materials

All materials were used as received without further purification. Copper(I) iodide ($\geq 99.999\%$ (Cu basis), STREM CHEMICALS INC MS); copper(I) iodide (98%, Alfa Aesar); 1,4-diazabicyclo[2.2.2]octane ($>98.0\%$ (GC), TCI); hydroiodic acid (57% (w/w), BTC); ethanol (190 proof, VWR; 200 proof, anhydrous, KOPTEC); acetone (99.5%, VWR); N,N-dimethylformamide ($\geq 99.8\%$, anhydrous, Alfa Aesar); ethyl acetate (anhydrous, 99.8%, Sigma-Aldrich); carbazole ($\geq 95\%$ (GC), Sigma-Aldrich); N-Bromosuccinimide (NBS, Oakwood Chemical); acetyl chloride ($>98.0\%$, TCI); sodium methoxide ($\geq 98\%$, Thermo Scientific); sodium hydride (60%, dispersion in Paraffin Liquid, TCI); diethyl-2-bromoethyl-phosphonate (97%, Aldrich); bromotrimethylsilane (TMSBr, $\geq 97\%$, stabilized, BTC); nickel oxide (99.99%, $3.0'' \times 0.125''$, indium bonding on Cu backing plate, MSE Supplies LLC); PMMA ($M_w = 35000 \text{ Da}$, ACROS Organics); $\text{Ca}(\text{acac})_2$ (calcium acetylacetonate, anhydrous, Sigma-Aldrich Inc); PEDOT:PSS (Clevios P VP AI 4083); TPBi (99.5+%, Sigma-Aldrich); Corannulene ($>97.0\%$ (GC), TCI).

Preparation of 1,4-diazabicyclo[2.2.2]octan-1-ium iodide (*HdabcoI*)

1,4-Diazabicyclo[2.2.2]octane (11.22 g, 0.1 mol) was dissolved in DI water (100 ml) under nitrogen (N_2) protection, and hydroiodic acid aqueous solution (13.21 ml, 0.1 mol) was added

dropwise at room temperature in dark condition. The reaction mixture was stirred for 3 hours. The solvent was then evaporated under reduced pressure. The crude product was purified by recrystallization in methanol. The yield was 97%.

Preparation of 1D-Cu₄I₈(Hdabco)₄ precursor solution

In an Ar-filled glovebox, CuI (88.4 mg, 0.465 mmol) and HdabcoI (111.6 mg, 0.232 mmol) were dissolved in DMF (2 mL) and stirred at 75 °C overnight to yield a transparent solution. This solution was filtered through a PVDF filter (pore size of 0.2 μm) and kept at 75 °C before being used as the precursor solution for the subsequent fabrication of CuI(Hda) thin films.

Crystal growth of 1D-Cu₄I₈(Hdabco)₄

The single crystals of 1D-Cu₄I₈(Hdabco)₄ were grown using a facile low-temperature vapor-assist recrystallization method. 2 mL of the precursor solution was added to an open vial (4 mL) and was placed in a sealed 20 mL vial with 5 mL of ethyl acetate as anti-solvent. The system was kept at 50 °C for three days. Rod-shaped transparent single crystals were obtained with a yield of 62%.

Device fabrications

Patterned ITO glasses (20 mm × 15 mm) were sonicated sequentially in detergent-deionized water solution, deionized water, ethanol, acetone and isopropanol for 15 min each, then dried with compressed N₂. The ITO glasses were then transferred into an Ar-plasma sputter (Denton Explorer) in cleanroom. The substrates were heated to 250 °C and NiO_x was deposited at a constant power of 120 W. After cooling to room temperature, the substrate was then transferred to an Ar-filled glove box and heated to 100 °C. The CuI(Hda) EML (90 nm) was fabricated by spin-coating the precursor solution (60 μL) at 4,000 r.p.m. for 60 s on 100 °C substrates to preventing uneven crystallization or phase separation of CuI(Hda). Ethyl acetate (100 μl) was used as antisolvent. The colorless film was kept in glovebox at room temperature for 36 hours for slow

recrystallization. The electron transport layer was then fabricated by spin-coating 0.2 wt% of $\text{Ca}(\text{acac})_2$ in methoxyethanol and annealed at 80°C for 15 min. The as-fabricated film samples were attached to deposition mask and transferred to an E-beam evaporator (Nexdep System, Angstrom Engineering Inc). After the chamber was pumped down to 1.8×10^{-8} Torr, 1 nm LiF and 60 nm of Al were deposited sequentially. For PMMA-capped devices, 60 μL of PMMA solution in chloroform (1 mg/mL) was spin-coated on at 2,000 r.p.m for 45 s, followed by annealing at 100°C before the electron transport layer was deposited. For all devices with SAM (2PACz, Br2PACz, MeO2PACz and Ac2PACz) functionalized NiO_x HTL, 100 μL SAM solution (0.1 mmol/mL) in anhydrous ethanol was dropped onto the as-made ITO- NiO_x substrate at room temperature in Ar-filled glove box for 30s, then spin coating at 3,000 r.p.m for 60 s, followed by annealing at 100°C for 30 min, then washed 2 times with anhydrous ethanol (100 μL each) while spinning at 6,000 r.p.m for 60s to remove unbonded SAM molecules, which could directly follow the same EML deposition method stated above. Encapsulation was done by capping the device with a 1 cm $\times$ 1.5 cm glass slide, using UV adhesive (Norland Optical Adhesive 65) as the sealant. For reference devices, PEDOT: PSS was spin-coated on the ITO glass at 4,000 r.p.m. for 60 s and annealed at 150 °C for 30 min. Corannulene thin film was fabricated by spin coating a filtered (0.2 μm PTFE) corannulene solution in chloroform (5 mg/mL) at 1,500 r.p.m for 60 s. TPbi was deposited in a high vacuum thermal evaporator.

For single carrier devices, hole-only device with a structure of ITO/ NiO_x (w/o SAM-functionalization)/ $\text{CuI}(\text{Hda})/\text{MoO}_3/\text{Au}$ was applied, while electron-only device of ITO/corannulene/ $\text{CuI}(\text{Hda})/\text{Ca}(\text{acac})_2/\text{LiF}/\text{Al}$ was adopted. MoO_3 (40 nm) and Au (40nm) were deposited sequentially by thermal evaporation in the same Nexdep system. $\text{CuI}(\text{Hda})$ thin film

samples for other structural and optical measurements were fabricated as described above without deposition of other layers, on either ITO or quartz substrates.

Determination of single crystal structure of 1D-Cu₄I₈(Hdabco)₄

Single crystal structure analysis was carried out by single crystal X-ray diffraction method. A high-quality single crystal of 1D-Cu₄I₈(Hdabco)₄ was selected and mounted on MicroMesh (MiTeGen) with paraton oil. The data were collected on a single crystal X-ray diffractometer (Bruker D8 VENTURE) equipped with Mo micro-focus X-ray sources ($\lambda = 0.71073 \text{ \AA}$) at 298 K. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. The hydrogen atoms on carbon atoms were located at geometrically calculated positions and refined by riding. The refinement results are summarized in Table S1. Crystallographic data for the crystal structure in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-2261492. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

Surface morphology characterizations of CuI(Hda) thin film

The AFM study was done using an Asylum Research Cypher ES Atomic Force Microscope. The measurements were carried out under ambient conditions in the sealed AFM enclosure to reduce noise at a set sample temperature of 25 °C. Topography images were acquired by operating the AFM in tapping mode. Silicon cantilevers, HQ-300-Au (Asylum Research) and TAP300 (Ted Pella) were used each with a nominal spring constant of $k = 40 \text{ Nm}^{-1}$ and nominal tip radius of $r < 10 \text{ nm}$. A digital resolution of 512 lines $\times$ 512 points with a scan area of $5 \text{ }\mu\text{m} \times 5 \text{ }\mu\text{m}$ and a scanning rate of 1.6 Hz were used. The oscillation frequency of the probe was set at or near

resonance at 253 kHz. The spring constant of the tip was determined to be 25.26 Nm^{-1} using thermal tune method. Kelvin probe force microscope was carried out with the EFM mode. Both samples were measured by a conductive tip with a work function of 5.1 eV.

SEM experiments were performed on a Zeiss-Sigma Field-emission scanning electron microscope (FE-SEM), while EDS data were collected on an Oxford-XmaX80 detector coupled to the FE-SEM. The elemental maps were obtained at an operating voltage of 5 kV.

Structural characterizations of CuI(*Hda*) thin film

PXRD analysis was carried out on both powder and thin film samples using a Rigaku Ultima-IV diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Specifically, the PXRD pattern of the thin film sample was taken on powders scratched and collected from 15 thin film samples fabricated on ITO. The data were collected at room temperature in a 2θ range of $3\text{--}50^\circ$ with a scan speed of $0.5^\circ/\text{min}$ under the operating power of 44 kV/40 mA.

Grazing-incident wide-angle X-ray scattering pattern with an incident angle of 0.16° were obtained at Advanced Light Source beamline 7.3.3 in LBNL.

Characterizations of photophysical properties

Optical absorption spectra of the CuI(*Hda*) thin film and powders were recorded at room temperature on a Shimadzu UV-3600 UV–vis–NIR spectrometer, using transmittance and reflectance mode, respectively. The diffuse reflectance data were converted to Kubelka–Munk function, $\alpha/S = (1 - R)^2/2R$ (α is absorption coefficient, S is scattering coefficient and R is reflectance), and used to estimate the optical bandgap. The scattering coefficient (S) was treated as a constant as the average particle size of the samples used in the measurements was significantly larger than $5 \text{ }\mu\text{m}$.

Room temperature PL measurements of a CuI(*Hda*) thin film on quartz substrate were performed on a Horiba Duetta fluorescence spectrophotometer. The PLQY measurements were carried out at room temperature on a C11347 absolute quantum yield measurement system (Hamamatsu Photonics) with 150 W xenon monochromatic light source and 3.3 in. integrating sphere. Powder samples for PLQY measurements were prepared by spreading fine powder samples evenly on the bottom of a quartz sample holder. Sodium salicylate was chosen as the standard with reported PLQY value of 60% at an excitation energy of 280 nm. Film samples were directly set on the PTFE base in the integrating sphere, using an uncoated quartz as blank to extract the optical absorption of the substrate.

Temperature dependent PL spectra and TRPL decay profiles were recorded on a 90 nm thin film sample on quartz with a home-built time-correlated single photon counting instrument using the 285 nm pulsed light from a frequency doubled femtosecond solid state laser (Maitai-Spectra Physics, 100 fs pulse, 10 kHz repetition rate), a Janis cryostat model V500, and an optical detection system consisting of a single photon counting avalanche photodiode (PMD50, Picoquant, 45 ps response time), a time analyzer (TimeHarp 260 nano, Picoquant Germany) and an Ocean Optics FL65000 fiber optics spectrometer. The PL signals emitted by the sample were collected by a 50 mm biconvex lens and split by a 50/50 non polarizing beam splitter cube between the photodiode and PL fiber spectrometer. PL signals were acquired using an average power of 0.055 mW, with decays recorded in at least 1,000 channels using a 355 nm long-pass filter (Semrock). Additional TRPL were measured using same setup on thin film samples (60 nm) on different substrates, while TRES were recorded on both a 10 mm × 3mm × 3mm single crystal and a 90 nm thin film sample on quartz.

Femtosecond and nanosecond transient absorption measurements were performed using a pump-probe system based on a Pharos (Light Conversion) regenerative amplifier (285 nm pump delivered by an Orpheus OPA, 350fs pulses at 1 kHz repetition rate) and a Helios Fire spectrometer/microscope (Ultrafast Systems) with the white light generated by a Ti:Sapphire crystal. TA spectra and decays were analyzed by the Surface Xplorer software from Ultrafast Systems.

Polarized photoluminescence measurements were carried out in a Horiba Fluorolog-3 spectrofluorometer using a 290 nm excitation light and a 360 nm long-pass filter in the collection path. The spectrofluorometer was equipped with a 450 W xenon lamp source; a double monochromator was used on the excitation side and the PL emission was collected through an iHR 320 emission monochromator and a Hamamatsu R928P photomultiplier tube (PMT) detector. Excitation and emission slits widths were set to 3 nm (bandpass). The single crystal of CuI(*Hda*) was positioned with its (100) (011) and (0-11) faces perpendicular to the excitation and collection directions. Polarizers were added to the excitation and collection paths to analyze the polarization of the emitted light from the crystal. Polarization bias in the equipment was quantified using an amorphous conjugated polymer sample to give an instrument correction factor. Subsequently, the polarized PL spectra from CuI(*Hda*) crystals were corrected for polarization bias in the measurement using the instrument correction factor.

TRMC and DMC measurements

Time-resolved microwave conductivity (TRMC) and dark microwave conductivity (DMC) measurements were performed using a system that has already been thoroughly described⁴⁴. Thin films were mounted as usual by depositing material on a 25 × 11 × 1 mm UV fused silica substrate, and measurements were conducted in our standard rectangular microwave cavity with a sensitivity

factor of $K=23,000$. Single-crystal measurements required explicit electromagnetic modeling of the cavity response for both orientations of the individual crystal studied. In addition, the complex dielectric constant of the double-sided tape used to mount these samples to the quartz substrate was also explicitly included. Separate effective sensitivity factors⁴⁵ were calculated for each crystal orientation. These were $K_e = -159$ for the perpendicular orientation of the crystal and $K_e = -368$ for the parallel orientation. Care was taken in these measurements to ensure that there was no variation in the optical excitation intensity received by the crystal when its orientation was changed.

Excitation light was provided by a Spectra-Physics Quanta-Ray laser operating at 30 Hz repetition rate, and pumping an OPO (GWU Premi-Scan), which in turn pumps a doubler (GWU UV-Scan) to generate the final 300 nm pump beam. The spot diameter and delivered power were measured at the sample position before and after measurements to ensure there was no unacceptable drift in laser output over the course of the experiment. Specific excitation intensities are reported in each figure where transient data appears.

SCLC measurements

SCLC measurements were done on single carrier devices of $\text{CuI}(\text{Hda})$ with a Keithley 2400 source meter.

Photoemission measurements

To obtain band-edge alignment information experimentally, thin film samples were transferred from the glove box to a purged glove bag attached to a Thermo ESCALAB 250xi system, in a sealed container. Core levels are measured with an $\text{Al-K}\alpha$ line ($h\nu = 1486.7$ eV) with an energy resolution of 0.6 eV, while the valence band is measured with a 40.8 eV photon energy and the work function with a 21.2 eV photon energy, both with an energy resolution better than 0.1 eV.

The distance between the VB edge and the VL was measured in UPS by applying a -10V bias to the sample and is given as $h\nu - (\text{SECO edge} - \text{VB edge})$. All photoemission spectra were referenced to the Fermi level of a clean metallic surface in contact with the measured samples. REELS was performed in the ESCALAB 250xi using a 30 eV electron source of 0.6 eV full width half maximum in order to measure the optical absorption onset.

Fourier Transform Infrared Spectroscopic Study

The film samples of CuI(*Hda*) (85 nm) and CuI (50 nm, serve as reference) with different contact layer were fabricated on double side polished Si wafers for reducing substrate IR absorption and measured using Bruker Equinox 55 FTIR spectrometer with an DTGS detector, capable of achieving a resolution of up to 0.5 cm^{-1} . Transmission IR spectra were collected at silicon Brewster angle ($\sim 74^\circ$) using blank Si wafer as background reference. Each spectrum was collected over 100 scans, with an acquisition time of ~ 2 mins for both the background and fabricated film samples. To mitigate interference from ambient moisture the system was continuously purged with dry air for 300 secs prior to data acquisition. For comparison, the freshly prepared crystalline Ac2PACz and PMMA power samples were also measured through attenuated total reflectance (ATR).

Imaging of the LED device

Imaging of the cross-section of the LED devices was done on a Carl Zeiss Orion Plus Helium Ion Microscope (Carl Zeiss Microscopy, Peabody, MA) operating at 30 KeV acceleration voltage with a beam current of about 1 pA. Electron flood gun was not used for charge neutralization. The vacuum reading in the analysis chamber during imaging was 2×10^{-7} torr.

Performance evaluation of the LED devices

A Keithley 2400 apparatus was used to measure J-V curve of the as-fabricated LED devices from 0 to 9 V with a step voltage of 0.1 V; at the same time, luminance was collected using a luminance meter (Konica Minolta, CS-200). Electroluminescence data were recorded concurrently with a home-made fiber-coupled spectrometer (GlacierTM X, BWTEK Inc) with an integrating sphere (IS200-4, THORLABS). Other parameters used to characterize LEDs were all calculated from the L-J-V and electroluminescence measurements under the assumption that the emission of the LED exhibits a Lambertian pattern. The operational lifetime (T_{50}) was conducted using the same set-up, but under a constant current density condition in ambient air.

DFT calculations

The DFT calculations for 1D-Cu₄I₈(*Hdabco*)₄ were performed using the VASP code⁴⁶ with projector-augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) functional⁴⁷ including the Grimme's DFT-D3 dispersion corrections⁴⁸. We employed a kinetic energy of 520 eV in planewave basis sets. The initial configuration of 1D-Cu₄I₈(*Hdabco*)₄ was imported from the SCXRD refined structure. A 2×3×2 Monkhorst-Pack k-point grid was used to sample Brillouin zones. All atoms were allowed to relax until the changes in force and energy were less than 0.01 eV/Å and 10⁻⁶ eV, respectively. The final structure was in good agreement with that of experimentally determined, with the difference in the lattice constants less than 1% and was used for further electronic property calculations. To obtain more accurate density of state and band structure, HSE06 functional was used, with a 25% Hartree-Fock exact exchange.

For adsorption calculations, we created a CuI(*Hda*) (200) slab based on a 1×2×1 supercells of the crystal structures with 30 Å vacuum along the *a*-axis. The NiO (111) slab is built by a 6×6×1 supercells of the primitive NiO cell with 20 Å vacuum along the *c*-axis. The slab models are charge neutral and have more than 10 Å vacuum above the SAM molecule on the surface. The geometry

optimizations of the slabs, isolated molecules and molecules on slabs used the PBE functional in the VASP code with a kinetic energy cutoff of 520 eV and the Grimme's DFT-D3 dispersion corrections at the Gamma point. We froze the CuI chain and the bottom layer of NiO during the optimization to reduce the computational cost and maintain the bulk structures. The calculations with the NiO (111) slab also applied the Hubbard U corrections (U = 8.00 eV, J = 0.95 eV) and antiferromagnetic initial magnetic moments on Ni atoms with spin-polarization. All adsorption calculations applied the dipole corrections along with the vacuum direction. The HOMO and LUMO energy of SAM molecules are computed by aligning the VBM and CBM to the vacuum level using Equation (1):

$$E_{HOMO/LUMO} = E_{VBM/CBM} - E_{vacuum} \quad (1)$$

The adsorption energy is calculated following Equation (2):

$$E_B = E(molecule + slab) - E(molecule) - E(slab) \quad (2)$$

where $E(molecule + slab)$ and $E(slab)$ represent the total energies of the slab with and without the adsorbed molecule, respectively. $E(molecule)$ is the total energy of the isolated molecule.

The geometries of the SAM molecules were reoptimized with B3LYP/ def2TZVP method using the Gaussian 09 package⁴⁹ to compute the ESP. Frequency calculations confirmed the local minima with no imaginary frequency. We used the Multiwfn program for ESP visualization⁵⁰.

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Data availability

Source data are provided with this paper. Other datasets collected and/or analyzed during the
current study are available from the corresponding author upon request.

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Author contributions

K.Z. and J.L. conceived and designed the experiments. K.Z. grew single crystals of 1D-
 $\text{Cu}_4\text{I}_8(\text{Hdabco})_4$. K.G.Z. collected single crystal data and solved crystal structure. K.Z. developed
thin-film fabrication method. K.Z. performed PXRD, AFM, SEM/EDS experiments as well as the
DFT calculation and related data analysis. C.Y. conducted the GIWAXS experiment. K.Z.
collected and analyzed the steady state absorption (UV-vis), PL and PLQY data. K.Z., M.L. and
M.C. measured the TPL, TRPL, TRES, fs-TA, nsTA. O.G.R conducted the TRMC and DMC
experiments, analyzed the data, and wrote associated sections of the manuscript. K.Z. and S.R.

performed XPS, UPS and REELS measurements and data analysis. O.G.R conducted the TRMC and DMC experiments, analyzed the data, and wrote associated sections of the manuscript. K.Z. and N.J. conducted the polarized PL measurements, K.Z. and Y.S. synthesized the SAMs. L.W. performed the DFT calculations and Jingbai L. supervised the computational work. K.A.J.D. and K.T. performed the FTIR measurements and data analysis. K.Z. fabricated and characterized the LED devices. L.K. and L.F. did HeIM work. Y. L., D.M.O. and Kai. Z. guided part of the characterization work. J.L. supervised the experimental work. K.Z. and J.L. wrote the paper. All authors read and commented on the manuscript.

Conflict of Interest

The authors declare no competing interests.

Extended Data Figure Legends

Extended Data Fig. 1| TRES of CuI(*Hda*). **a** and **d**, 3D TRES plot of CuI(*Hda*) single crystal and thin film (on quartz), respectively. Insets are the decay profiles of CuI(*Hda*) single crystal and thin film, suggesting three identical decays as observed in TRPL decay. **b** and **e**, TRES of CuI(*Hda*) single crystal and thin film, respectively. Red dash arrows indicate the tendencies of fluorescence decay at <50 ns timescale. **c** and **f**, Bi-Gaussian fit of the TRES spectra at different timescale, incorporating a 50.8 meV singlet-triplet gap, to isolate the S₁ and T₁ components.

Extended Data Fig. 2| Polarized PL of a CuI(*Hda*) single crystal. **a**, Diagram illustrating measurement geometry with the excitation source and detection polarized parallel and perpendicular to the crystallographic (100) face. **b**, Polarized emission spectra from (100) face of CuI(*Hda*) single crystal. **c**, Diagram illustrating measurement geometry with the excitation source and detection polarized parallel and perpendicular to the crystallographic (0 $\bar{1}$ 1) face. **d**, Polarized

emission spectra from (0 $\bar{1}$ 1) face. **e**, Diagram illustrating measurement geometry with the excitation source and detection polarized parallel and perpendicular to the crystallographic (011) face. **f**, Polarized emission spectra from (011) face.

Extended Data Fig. 3| Adsorption configuration/energy and charge density difference for SAMs/CuI(*Hda*) (200) heterojunctions. a, view (along the *b*-axis) of the surface adsorption mode, charge density relocation and adsorption/H-bonding energy. **b**, view (along the *c*-axis) of the surface adsorption mode and charge density relocation.

Extended Data Fig. 4| Adsorption configuration/energy and charge density difference for CuI(*Hda*) (200)/ETLs heterojunctions. a, view (along the *b*-axis) of surface adsorption mode, charge density relocation and adsorption/H-bonding energy. **b**, view (along the *c*-axis) of surface adsorption mode and charge density relocation.

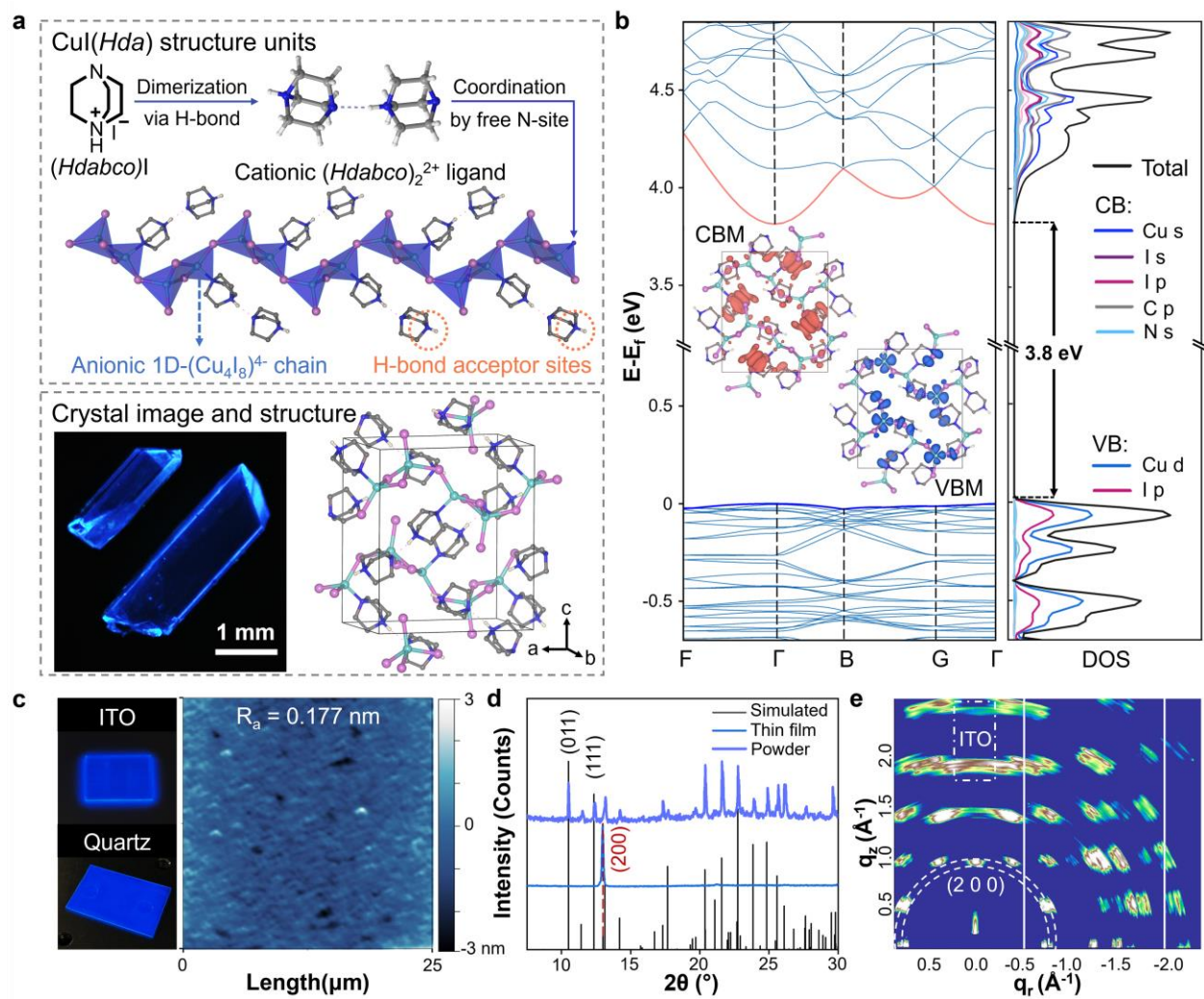
Extended Data Fig. 5| Angular-resolved C1s core level of PMMA thin films on CuI(*Hda*). a, ARXPS C1s spectra of a 500 rpm PMMA thin film (3.8 nm) on CuI(*Hda*). **b**, ARXPS C1s spectra of a 3000 rpm PMMA thin film (2.1 nm) on CuI(*Hda*). **c**, ARXPS C1s spectra of a 6000 rpm PMMA thin film (1.7 nm) on CuI(*Hda*). Ratios of integrated C1s_(C=O)/C1s_(C-C, C-H) peak intensity at normal emission angle (0°) remain constant at 1:3 in all PMMA thin films, precisely reflecting the polymer's chemical environment. However, thinner PMMA overlayers exhibit a more rapid decrease in the C1s_(C=O)/C1s_(C-C, C-H) ratio with increasing incident angle, suggesting a higher concentration of C=O groups at the CuI(*Hda*)-PMMA interface due to interfacial H-bonding.

Extended Data Fig. 6| Reference LED devices w/o PMMA capping layer using various HTL/ETL selection. a-c, Energy diagram, J-L-V curves and EQE-J curves of pristine and PMMA-capped ITO/NiO_x/CuI(*Hda*)/Corannulene/LiF/Al blue LEDs. **d-f**, Energy diagram, J-L-V curves and EQE-J curves of pristine and PMMA-capped

ITO/PEDOT:PSS/CuI(*Hda*)/Ca(*acac*)₂/LiF/Al blue LEDs. **g-i**, Energy diagram, J-L-V curves and EQE-J curves of pristine and PMMA-capped ITO/NiO_x/CuI(*Hda*)/TPBi/LiF/Al blue LEDs. **j-l**, Energy diagram, J-L-V curves and EQE-J curves of pristine and PMMA-capped ITO/PEDOT:PSS/CuI(*Hda*)/TPBi/LiF/Al blue LEDs.

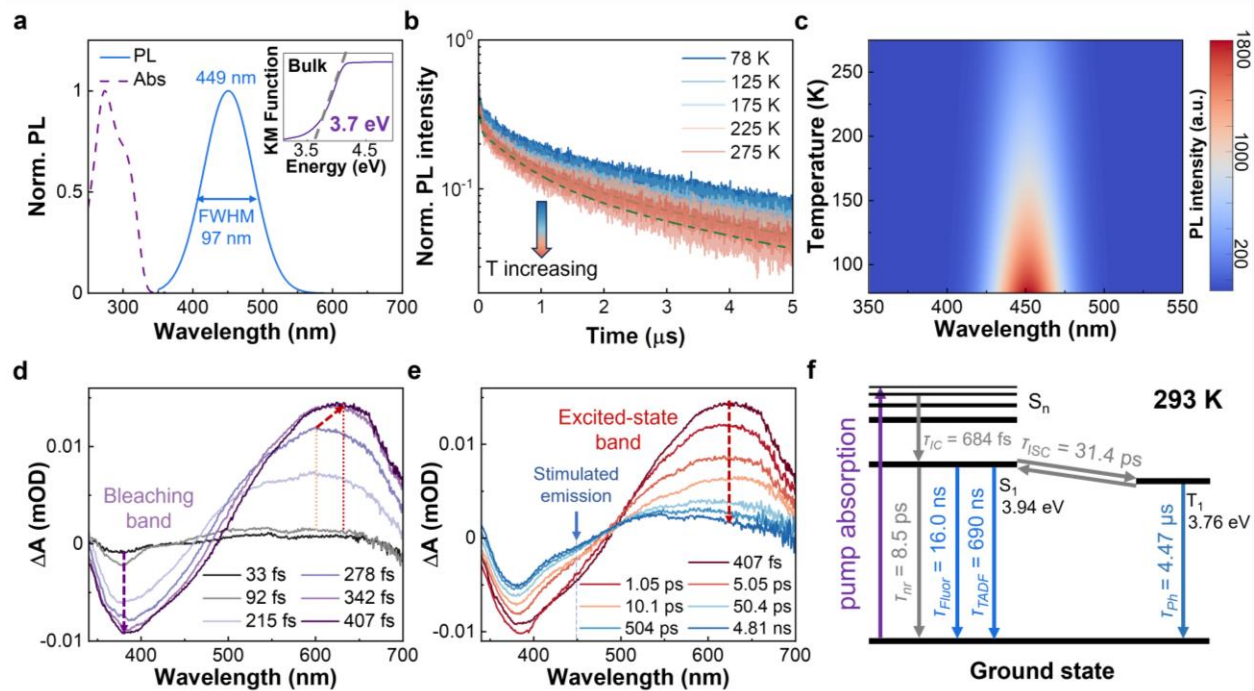
Extended Data Fig. 7| Control CuI(*Hda*) LEDs with non-H-bonded SAMs. a, UPS energy levels of 2PACz, Br2PACz and MeO2PACz-functionalized NiO_x. **b**, Current density and luminance as a function of voltage for 2PACz, Br2PACz, and MeO2PACz functionalized deep-blue LEDs. **c**, EQE-J curves for 2PACz (bottom), Br2PACz (top), and MeO2PACz (middle) functionalized deep-blue LEDs.

Extended Data Table. 1| Summary of surface adsorption and H-bonding properties of four SAMs, along with contact angle measurements, charge carrier mobilities, and trap densities for NiO_x functionalized with different SAMs.

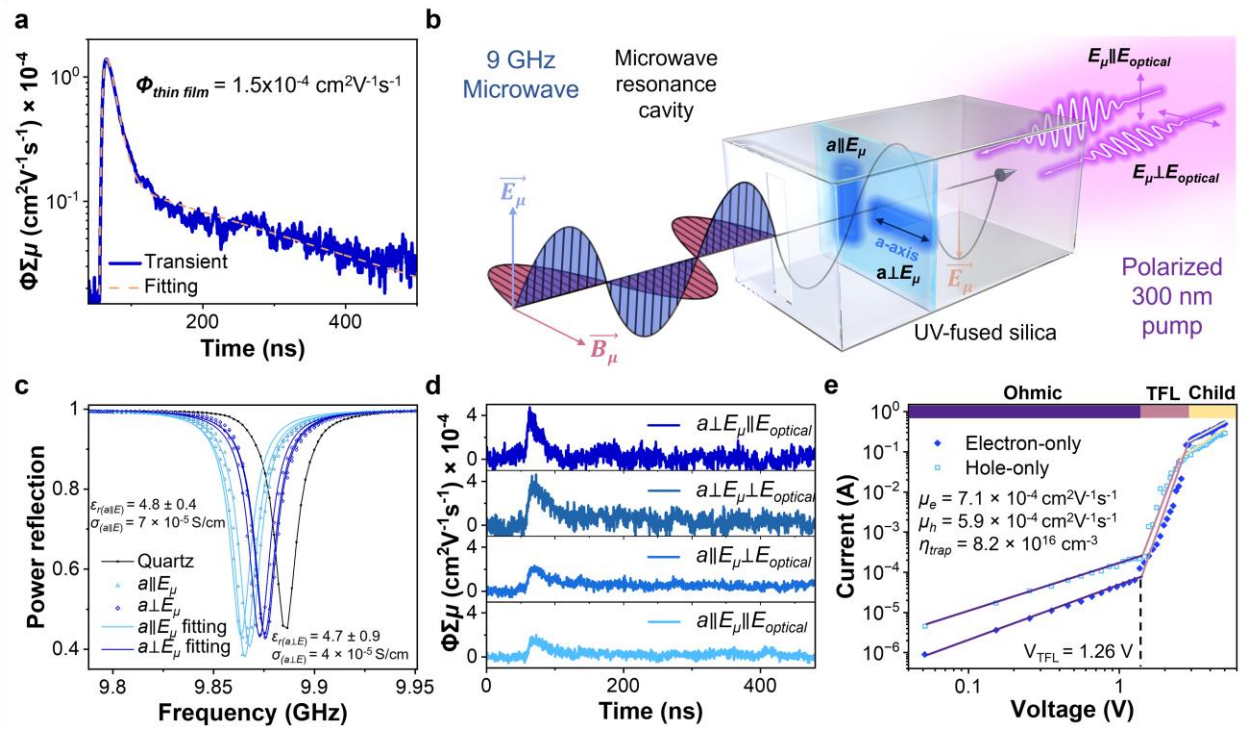


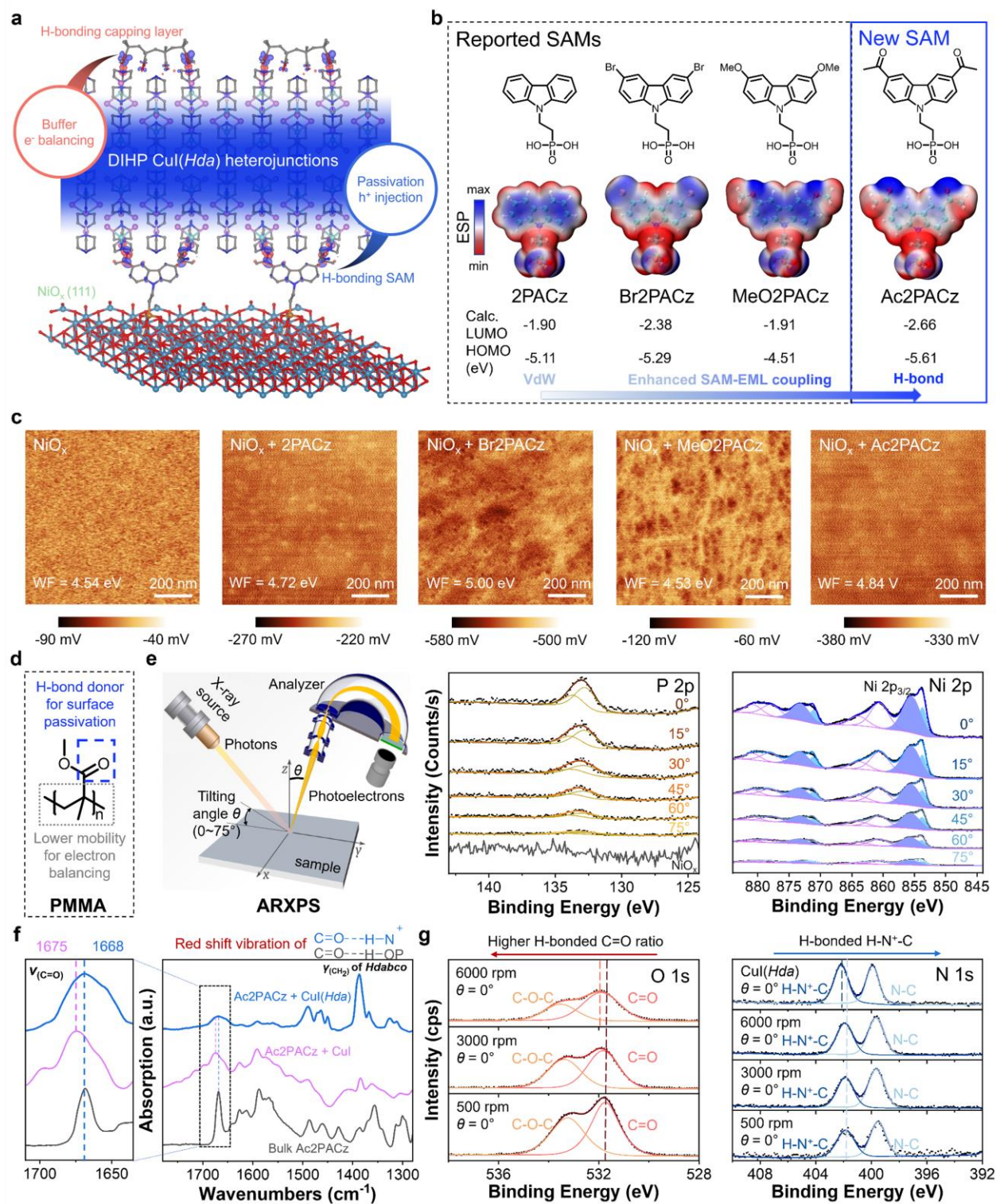
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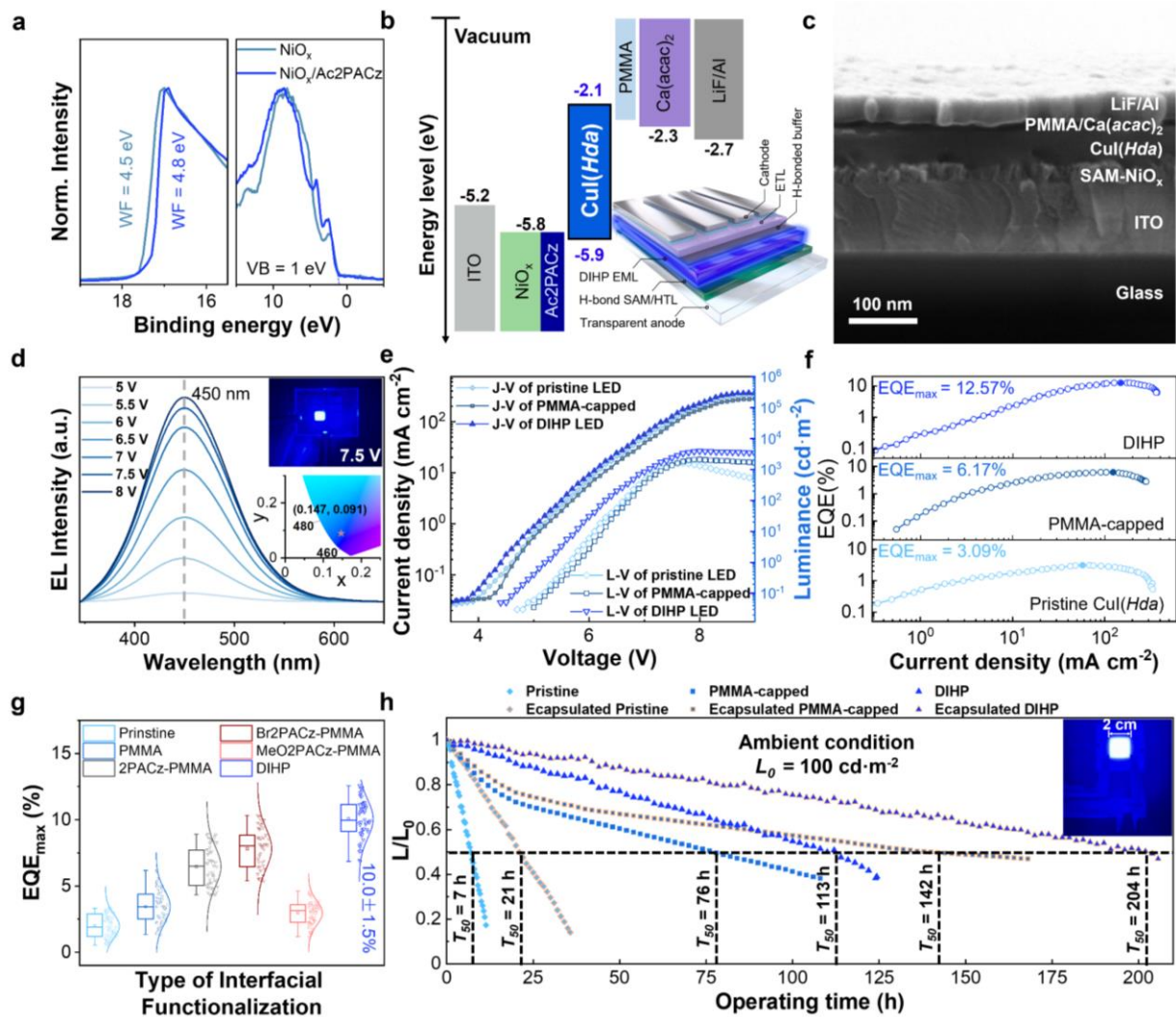
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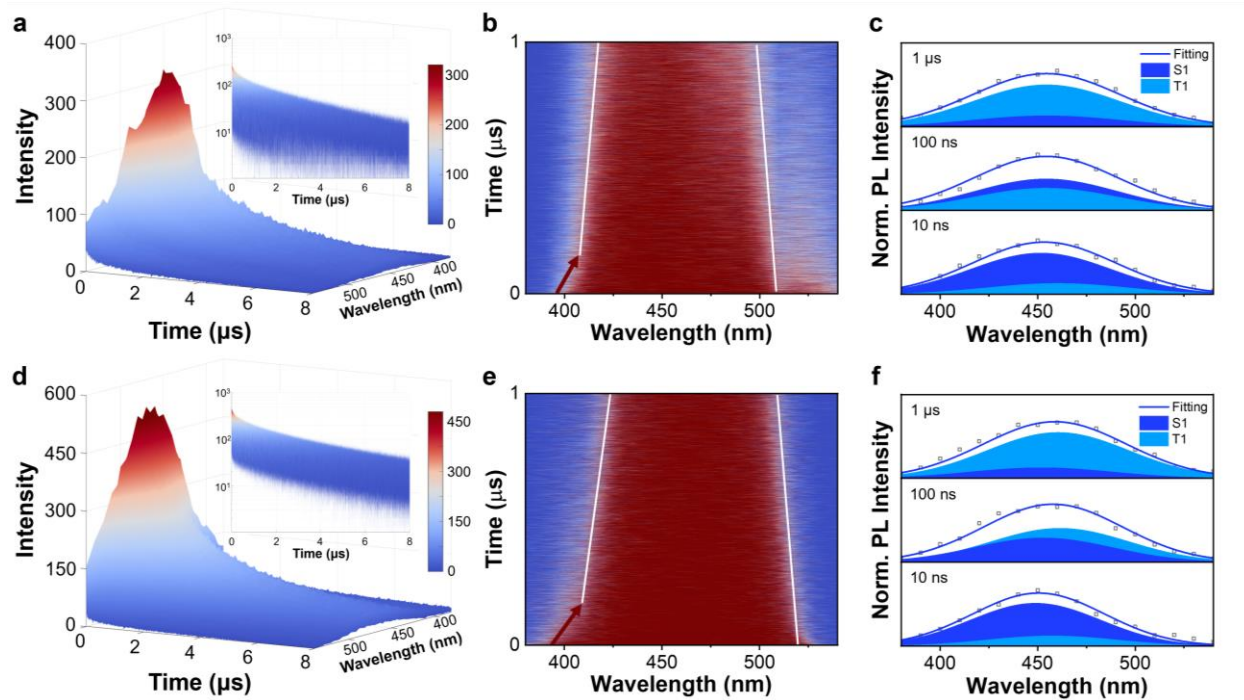
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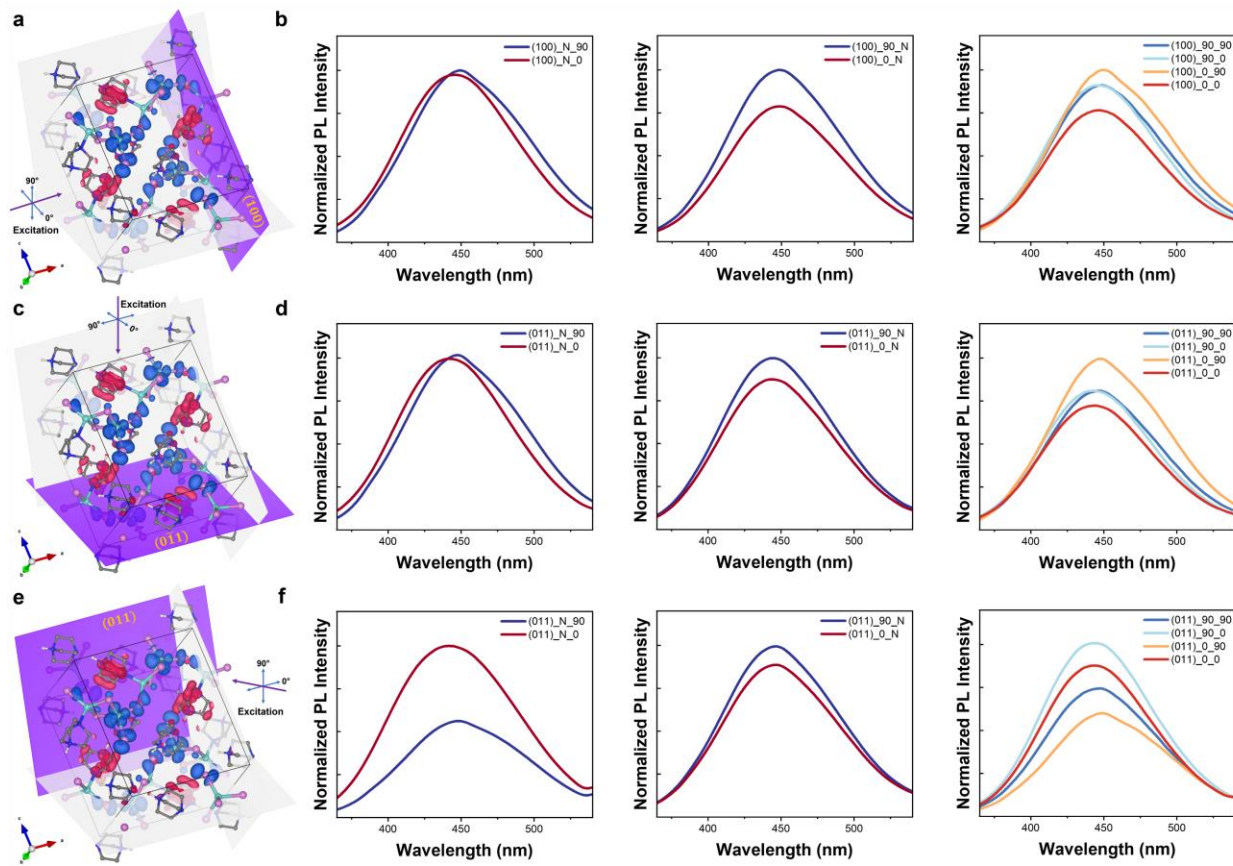




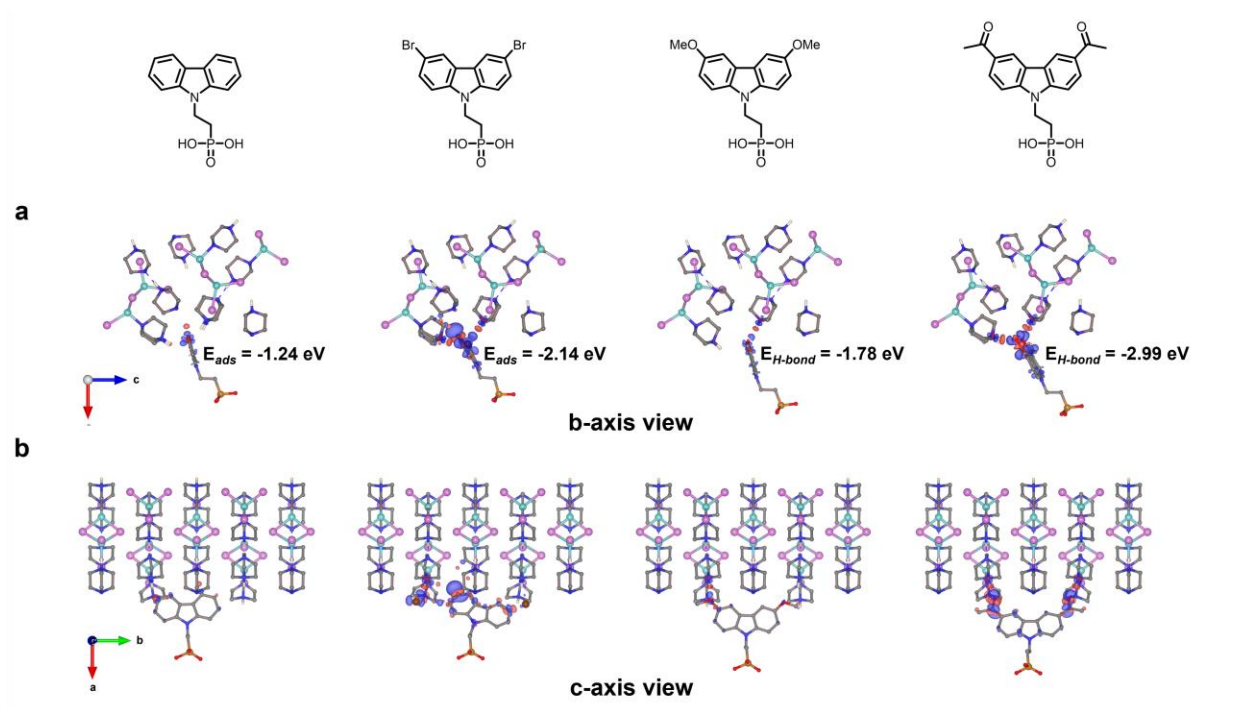
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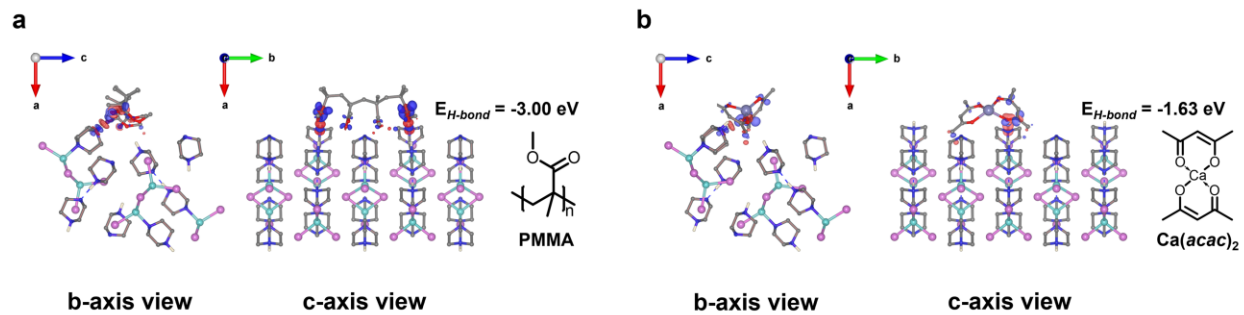
Extended Data Fig. 1



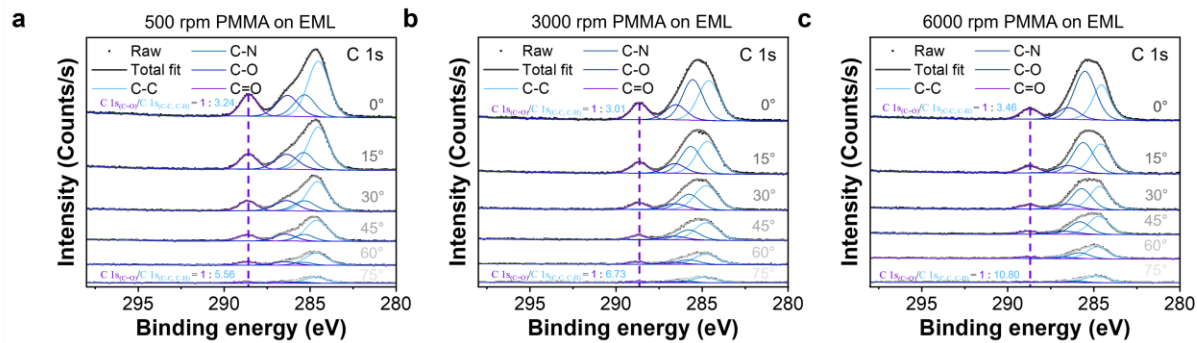
Extended Data Fig. 2



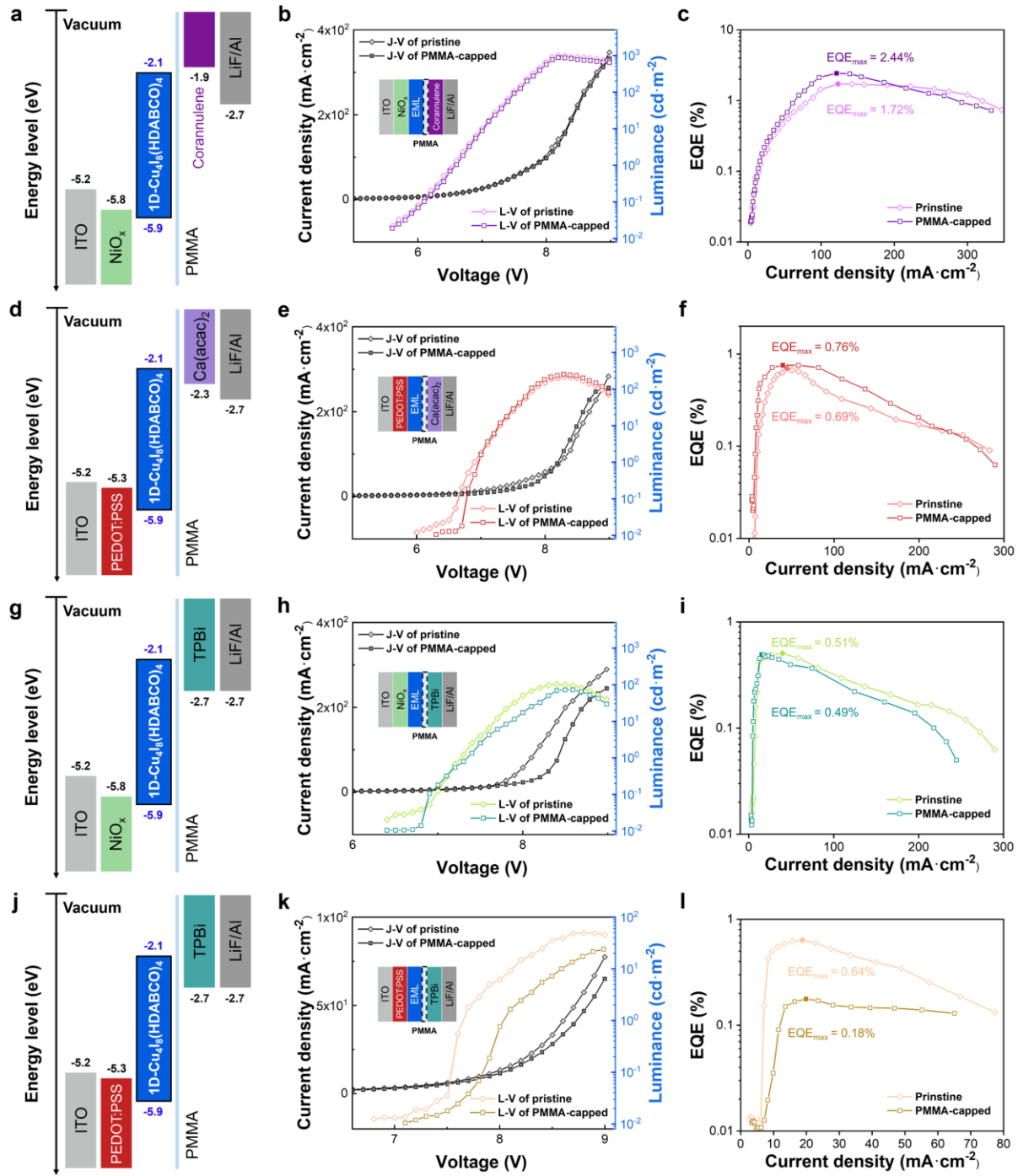
Extended Data Fig. 3



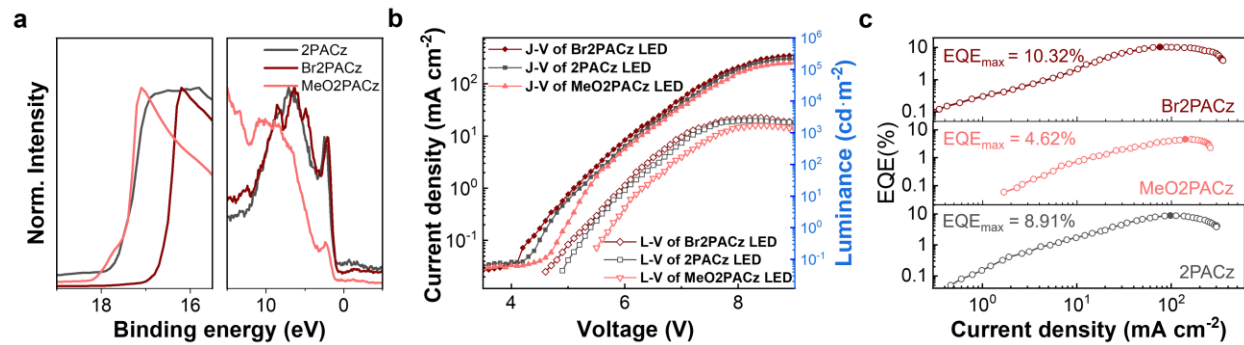
Extended Data Fig. 4



Extended Data Fig. 5



Extended Data Fig. 6



Extended Data Fig. 7

Extended Data Table 1

SAM	Preferred Adsorption mode ^a	Adsorption energy on NiO _x (eV)	Adsorption energy on CuI(<i>Hda</i>) (eV)	Contact angle (deg)	Hole mobility (cm ² V ⁻¹ s ⁻¹)	Trap density (cm ⁻³)
2PACz	E	-7.22	-1.24	35	7.2×10^{-4}	6.3×10^{16}
Br2PACz	A	-7.49	-2.14 ^b	29	7.3×10^{-4}	6.3×10^{16}
MeO2PACz	D	-7.92	-1.78	21	4.3×10^{-4}	6.3×10^{16}
Ac2PACz	A	-7.66	-2.99	13	9.0×10^{-4}	6.3×10^{16}

^a Geometries of the adsorption modes are available in Supplementary Information Fig S43.

^b The adsorption of Br2PACz on CuI(*Hda*) induced the dissociation of the Br atom.