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Interfacial Synthesis of Layer-Oriented 2D Conjugated Metal-Organic Framework Films towards Directional Charge Transport

Zhiyong Wang1,4, Lisa S. Walter2,7,5, Mao Wang3,4, Petko S. Petkov4, Baokun Liang5, Haoyuan Qi1,5, Nguyen Ngan Nguyen1, Mike Hambsch1, Haixia Zhong1, Mingchao Wang1, SangWook Park1, Lukas Renn2,7, Kenji Watanabe6, Takashi Taniguchi6, Stefan C. B. Mannsfeld1, Thomas Heine1,9,10, Ute Kaiser5, Shengqiang Zhou1, Ralf Thomas Weitz2,7,*, Xinliang Feng1,8,* and Renhao Dong1,5

1Center for Advancing Electronics Dresden (cfaed) and Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany
2I. Physical Institute, Faculty of Physics, Georg-August-University Göttingen, 37077 Göttingen, Germany
3Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, 01328 Dresden, Germany
4Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria
5Central Facility for Electron Microscopy, Electron Microscopy of Materials Science Central, Facility for Electron Microscopy, Ulm University, 89081 Ulm, Germany
6National Institute for Materials Science, 305-0047 Tsukuba, Japan
7Physics of Nanosystems, Department of Physics, Ludwig-Maximilians-University München, 80799 Munich, Germany
8Max Planck Institute for Microstructure Physics, Weinberg 2, Halle (Saale), D-06120 Germany
9Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Leipzig Research Branch, 04316 Leipzig, Germany
10Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 03722 Korea

ABSTRACT: The development of layer-oriented two-dimensional conjugated metal-organic frameworks (2D c-MOFs) enables an access to direct charge transport, dial-in lateral/vertical electronic devices and unveil transport mechanisms, but remains a significant synthetic challenge. Here we report the novel synthesis of metal-phthalocyanine-based p-type semiconducting 2D c-MOF films (Cu₂[PcM-OH]₈, M=Cu or Fe) with an unprecedented edge-on layer-orientation at the air/water interface. The edge-on structure formation is guided by the pre-organization of metal-phthalocyanine ligands, whose basal plane is perpendicular to the water surface due to their π-π interaction and hydrophobicity. Benefiting from the unique layer orientation, we are able to investigate the lateral and vertical conductivities by DC methods, and thus demonstrate an anisotropic charge transport in the resulting Cu₂[PcCu-OH]₈ film. The directional conductivity studies combined with theoretical calculation identify that the intrinsic conductivity is dominated by charge transfer along the interlayer pathway. Moreover, a macroscopic (cm²-size) Hall-effect measurement reveals a Hall mobility of ~4.4 cm²V⁻¹s⁻¹ for the obtained Cu₂[PcCu-OH]₈ film. The orientation control in semiconducting 2D c-MOFs will enable the development of various optoelectronic applications and the exploration of unique transport properties.

INTRODUCTION

Layered two-dimensional conjugated metal-organic frameworks (2D c-MOFs) have emerged as a new generation of MOF materials featured with strong in-plane conjugation and weak out-of-plane van der Waals force.1-4 The current development of 2D c-MOFs with conjugated redox-active ligands (e.g., benzenes, triphenylene, coronene, and phthalocyanine (Pc) derivatives) and square-planar metal-complex linkages (e.g., MNH₃, MO₄, MS₄ and M₂S₄, M is metal)5-7 has demonstrated, that the electrical conductivities and charge mobilities could reach up to 10⁵ S cm⁻¹ and ~220 cm² V⁻¹ s⁻¹ at room temperature, respectively.8-9 These results highlight the potential for high electrical conductivity or high mobility 2D c-MOFs as attractive active layers in electronic and spintronic devices, such as field-effect transistors (FETs),10 superconductors,11 chemiciresistive sensors,12 thermoelectromics,13 photodetectors,14 battery electrodes,15 capacitor electrodes,16 ferromagnetic semiconductors,17,18 as well as nonmagnetic spacer in spin valves.19

Despite extensive progress in this field, the nature of charge transport that mainly refers to the structure and electrical property relationship has remained elusive.20-21 Particularly, the fundamental understanding of the anisotropic transport mechanism in these van der Waals conducting materials is still ambiguous. In the previous reports, a great effort was devoted to exploring electronic properties via the intralayer (basal plane) pathway because it was believed that the high conductivity of 2D c-MOFs depended critically on the full π-electron delocalization in the 2D conjugated plane.5,22-25 In this context, the contribution from interlayer coupling (π-π stacking) received much less attention. However, recent advances demonstrated that long-range charge transport in these layer-stacked framework materials could be primarily mediated via π-π stacking order.6,26 Therefore, the observation of π-π stacking contributions to efficient charge transport in 2D c-MOFs has opened yet other pathways to explore the nature of charge transport and improve their electronic properties.27-29 Nevertheless, the control of the layer orientation in 2D c-MOF film by exploiting the anisotropic character, is urgently needed to direct the charge transport along the interlayer or intralayer pathway and dial-in lateral/vertical electronic devices as well as further unveil the transport mechanism, but has so far remained unexplored due to the challenge in synthesis.30,31

In this work, we demonstrate a novel strategy for the synthesis of unprecedented edge-on layer-oriented Cu₂[PcM-OH]₈ (M=Cu or Fe) 2D c-MOF films at an air/water interface by employing (2,3,9,10,16,17,23,24-octahydroxy phthalocyaninato) metal (PcCu-OH₅ or PcFe-OH₅) as ligands and square planar metal-bis(dihydroxy) complex as linkage. The π-π stacking and hydrophobic interaction could induce an ordered pre-organization of the ligands with an edge-on geometry on the water surface, which is crucial to enable the 2D coordination to the water
surface. The resulting Cu$_2$[PcCu-O$_8$] film with edge-on structure exhibits a thickness of ~20 nm and ~600 nm-sized crystal domains, and shows a room temperature conductivity of $\sim$5.6x10$^{-4}$ S cm$^{-1}$ and a Hall mobility of $\sim$4.4 cm$^2$ V$^{-1}$ s$^{-1}$ based on macroscopic van der Pauw pattern. Lateral and vertical measurements further reveal the directional charge transport feature in this edge-on 2D c-MOF film, i.e., the lateral conductivity ($\sim$2x10$^{-3}$ S cm$^{-1}$ by two-probe) is 2-3 orders of magnitude higher than the vertical one (10$^{-6}$-10$^{-5}$ S cm$^{-1}$) by conducting atomic force microscopy and two-probe). The theoretical calculation for Cu$_2$[PcCu-O$_8$] shows that higher dispersion of the valence bands is determined along the interlayer pathway compared with that along the intralayer pathway, supporting that the intrinsic conductivity is dominated by the charge transfer along the interlayer pathway. This work sheds light on controlling the crystalline orientation of 2D c-MOF films towards future high-performance optoelectronic devices as well as exploring unique charge transport properties.

RESULTS AND DISCUSSION

Design, synthesis and characterization. The first step in our study was to select suitable organic ligands to fulfill the criteria that their molecular orientations can be controlled on the water surface. In principle, the molecular packing of metal-phthalocyanine (PcM) on the water surface can be precisely controlled by considering the intermolecular distance and molecular orientations through the modification of the substituents.\textsuperscript{32-33} Thereby, we consider that the combination of supramolecular chemistry of PcM with the interface-assisted polymerization,\textsuperscript{9, 34} would provide a possible strategy to prepare oriented 2D c-MOFs films. Towards this end, a ligand of (2,3,9,10,16,17,23,24-octahydroxy phthalocyaninato) copper (PcCu-OH$_8$) was employed for the synthesis of edge-on layer-oriented Cu$_2$[PcCu-O$_8$] film at the air/water interface, as illustrated in Figure 1a. The surface pressure-mean molecular area ($\pi$-A) isotherm was firstly recorded by the Langmuir-Blodgett (LB) technique to understand the molecular packing of PcCu-OH$_8$ through compression on the water surface. As shown in Figure S1, through the compression, we observed a sharp rising of surface pressure when the mean molecular area reaches ~36 Å$^2$, revealing a transformation of molecular packing from the gas phase to the crystal phase.\textsuperscript{35} To our delight, this achieved average space per molecule is consistent with the theoretical cross-section area per PcCu-OH$_8$ (35.7 Å$^2$),\textsuperscript{33} which strongly suggests that the PcCu-OH$_8$ molecules are arranged with the basal plane perpendicular to the water surface.\textsuperscript{36-37} One would expect that part of the hydrophilic (-OH) groups orient towards the water surface, while the hydrophobic phthalocyanine macrocycles tend to leave out of the subphase, thereby enforcing the PcCu-OH$_8$ molecules to energy-favourably stand on the water surface.\textsuperscript{38-39}
Subsequently, we explored the self-assembly of PcCu-OH$_2$ ligands at higher density on the water surface. Typically, a volume of 200 μl freshly prepared solution of PcCu-OH$_2$ (0.47 mM) in chloroform/DMF (2:1 in volume) was spread onto the water surface in a 28 cm$^2$-sized beaker under ambient condition. The density of PcCu-OH$_2$ molecules in the beaker reached ~3.4×10$^4$ mmol cm$^{-2}$, which is ~7.8-fold higher than that of the LB monolayer (4.37×10$^3$ mmol cm$^{-2}$). After 30 min self-assembly of PcCu-OH$_2$, a green film was formed on the water surface, which could be readily transferred onto other substrates (Figure S2a). Remarkably enough, transmission electron microscopy (TEM) images reveal an ordered 2D network with linear lattice (Figure 1b and S2b). The selected-area electron diffraction (SAED) patterns display diffraction dots with the nearest reflection at 0.58 nm$^{-1}$ and diffusive arcs at 3.0 nm$^{-1}$, corresponding to ~1.73 nm and 0.33 nm in real space, respectively (Figure 1c). These results manifest that, before the coordination polymerization, the PcCu-OH$_2$ ligands were pre-organized into ordered 2D networks with edge-on stacking on the water surface.

Encouraged by the above result, we then performed the coordination polymerization of pre-organized PcCu-OH$_2$ ligands on the water surface by adding the solution of copper (II) acetate and sodium acetate into the water subphase. The coordination polymerization was kept at 20 °C under ambient conditions for 18 h, affording a black film on the water surface. The achieved Cu$_2$[PcCu-O] film on the water surface was transferred horizontally onto various substrates (e.g., h-BN, Si/SiO$_2$, TEM grid) for morphological and structural characterizations. The scanning electron microscopy (SEM) and optical microscopy (OM) images show a macroscopically homogenous film with a size over cm$^2$ (Figure 1d and S3). Atomic force microscopy (AFM) (Figure 1e) and TEM images (Figures 2a and S4) demonstrate that the resultant films are composed of flat crystalline nanosheets with a thickness of ~20 nm and the lateral size of hundreds of nanometers (Figure 1f).

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy of the Cu$_2$[PcCu-O]$_2$ film reveals a full vanishing of the OH modes (~3200 cm$^{-1}$) from PcCu-OH$_2$, indicating high conversion of the monomer (Figure S5a). The Raman spectra of Cu$_2$[PcCu-O]$_2$ manifest the absence of OH peaks in the range of 2900-3200 cm$^{-1}$, which suggests the efficient coordination between Cu and O ions (Figure S5b). The high degree of copper-oxygen coordination was further demonstrated by X-ray photoelectron spectroscopy (XPS) and SEM-energy dispersed X-ray spectroscopy mapping (SEM-EDX) studies, which show a Cu:O ratio of 1:2.6 (Figure S6) and 1:2.5 (Figure S7), respectively, corresponding to the ideal composition (Cu:O = 1:2.67). X-ray absorption near-edge structure (XANES) was employed to further analyze the chemical state of Cu atoms in Cu$_2$[PcCu-O]$_2$ (Figure S8a). The Cu K-edge of Cu$_2$[PcCu-O]$_2$ is different from those of CuO, Cu$_2$O, and Cu foil. The pre-edge feature in Cu$_2$[PcCu-O]$_2$ originates from the transition of 1s core electrons to hybridized orbitals of 3d. The recorded extended X-ray absorption fine structure (EXAFS) spectra show that there is one prominent peak at the energy of 800 nm corresponding to the Cu-O bond.

![Figure 2](https://doi.org/10.1021/jacs.1c05051)  
Figure 2. Structural characterization of the Cu$_2$[PcCu-O]$_2$. (a) TEM image of Cu$_2$[PcCu-O]$_2$ film. The yellow circle marks the position of the selected-area aperture. (b) SAED pattern from the circular region. (c) AC-HRTEM image of Cu$_2$[PcCu-O]$_2$. Inset: fast Fourier transform (FFT) image. (d) Enlarged image of (c) with the structure model overlaid. (e) GIWAXS diffraction pattern of Cu$_2$[PcCu-O]$_2$ film. (f) Experimental and calculated GIWAXS intensity profiles of Cu$_2$[PcCu-O]$_2$. (g) The proposed model, and GIWAXS measurement geometry. α: exit angle; β: in-plane angle. The model shows the preferential edge-on orientation and AA-inclined stacking of Cu$_2$[PcCu-O]$_2$ on the substrate.
~1.52 Å from the Cu-O contribution in Cu$_2$[PcCu-O$_8$] (Figure S8b). Another contrast sample CuO exhibits two different predominant peaks at ~1.56 Å and ~2.49 Å, which arise from Cu-O and Cu-Cu bonds, respectively. These results prove the formation of square planar complexes through the coordination of PcCu-OH$_4$ and Cu ions, and the presence of metal oxides (such as CuO) in the Cu$_2$[PcCu-O$_8$] can be excluded. The UV/vis spectra of the Cu$_2$[PcCu-O$_8$] film on a quartz substrate reveal an optical band gap of ~1.17 eV (also see Tauc plots of (ahv)$^2$ vs. hv, Figure S9).

**Crystallinity and molecular orientation.** Detailed insight into the local crystallinity and molecular orientation of the Cu$_2$[PcCu-O$_8$] film was achieved from the SAED and aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) imaging. The SAED pattern displays a line of sharp reflections and two diffusive arcs (Figure 2a, b). The nearest reflections were found at 0.57 nm$^{-1}$ corresponding to 1.75 nm in real space, agreeing with the AA-inclined atomic models of Cu$_2$[PcCu-O$_8$] derived by density functional theory (DFT) calculations (Figure S10 and S11). The diffusive arcs fit nicely into a ring with a radius of 3.0 nm$^{-1}$, i.e., 0.33 nm, which is in agreement with the π-π stacking distance. The SAED patterns acquired on isolated flat domains illustrate well-defined crystallographic orientation (Figure S12), revealing the crystalline nature of the ~600 nm-sized nanosheets. As shown in Figure 2c, the AC-HRTEM image presents a highly ordered linear arrangement with a lattice distance of 1.75 nm. In the enlarged image, fine fringes with a distance of 0.33 nm have been observed, corresponding well to the π-π stacking distance (Figure 2d). The FFT pattern is in excellent agreement with the SAED patterns measured on different crystal domains, suggesting that there is a preferential interlayer π-π stacking direction with an angle of 75° relative to the intralayer conjugation direction.

To probe the layer orientation and stacking of the Cu$_2$[PcCu-O$_8$] film on a macroscopic scale, we further performed a grazing incidence wide-angle X-ray scattering (GIWAXS) analysis. Figure 2e shows the 2D GIWAXS pattern of a Cu$_2$[PcCu-O$_8$] film. The in-plane intensity profile reveals a π-π stacking peak (001) at 1.90 Å$^{-1}$ (Figure 2f), indicating a preference of Cu$_2$[PcCu-O$_8$] for the edge-on orientation (Table S1). Furthermore, in the out-of-plane direction, three Bragg diffraction peaks with higher scattering intensities are observed at Q$_z$=0.36 Å$^{-1}$, 0.72 Å$^{-1}$, and 1.43 Å$^{-1}$ ((100), (200) and (400)). The intensity profile resolved in the samples supports the AA-inclined stacking (Figure 2g). Thus, the measured GIWAXS data combined with DFT calculations confirm that the Cu$_2$[PcCu-O$_8$] has the square unit cells with a = b = 1.81 nm (1.75/sin (75°)) and an interlayer distance of ~0.33 nm.

Inspired by the above success, we further extended the synthetic strategy towards another edge-on layer-oriented Cu$_2$[PcFe-O$_8$] film using the (2,3,9,10,16,17,23,24-octahydroxy phthalocyaninato) iron (PcFe-OH$_8$) ligand. The preparation condition is identical to the synthesis of Cu$_2$[PcCu-O$_8$] film. As shown in Figure S13, the measured π-A isotherm for PcFe-

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**Figure 3.** Directional charge transport measurement of Cu$_2$[PcCu-O$_8$] films using different configurations of measurement techniques. (a) Schematic diagrams of electrical conductivity measurements on Cu$_2$[PcCu-O$_8$] in macroscopic devices via van der Pauw geometry (left) and in vertical direction (right). The lateral contact separation for van der Pauw device was ~1 cm, and the contact area in vertical device was ~1.3×10$^{-3}$ cm$^2$. (b) Electrical conductivity of Cu$_2$[PcCu-O$_8$] as a function of temperature ranging from 256 to 310 K measured by the van der Pauw method. (c) Magnetic field dependence of the Hall resistance by measuring the changes of the electrical resistance in an applied field (from -4 T to 4 T) at 300 K. (d) Conductivity derived from the vertical device. (e) A plot of the conductivity vs. film thickness for vertical devices. (f) Schematic diagram of the device for local lateral (left) and vertical c-AFM measurements (right). (g) Conductivity derived from the local measurements. (h) Direction-dependent electrical conductivity of Cu$_2$[PcCu-O$_8$] at 300 K.
OH₃ is consistent with PcCu-OH₃, revealing that the molecules are vertically oriented on the water surface. The crystallinity and preferred orientation of the as-prepared Cu₂[PcFe-O₃] film are confirmed from the analysis by TEM imaging and SAED pattern (Figure S14). The results elucidate unambiguously that the crystalline Cu₃[PcFe-O₃] film exhibits a preferred edge-on orientation with a π-π stacking distance of 0.31 nm.

**Charge transport properties.** Benefiting from the achieved edge-on orientation in the layered Cu₃[PcCu-O₃] film, we investigated the charge transport properties along the lateral and vertical directions. Figure 3a presents the electrical measurements performed on a macroscopic Cu₃[PcCu-O₃] film (thickness, ~100 nm) along the lateral direction through the van der Pauw method (Schemes S1 and S2). The linear I-V curve was recorded to verify the Ohmic contact (Figure S15). From those measurements, the lateral conductivity was derived to be 5.6×10⁴ S cm⁻¹ at 300 K (Figure 3b). Variable-temperature conductivity measurements show a non-linear increase of electrical conductivity from 256 to 310 K. The conductivity (σ) plotted versus T⁺ presents a nonlinear relationship at this temperature range (Figure S16), which reveals thermal activation contributions to the conductivity. Activation energies (Eₐ) were derived from fitting the Arrhenius plot, which is expressed as

\[ \sigma(T) = \sigma_0 \exp \left(-\frac{E_a}{k_B T}\right) \]

( \( k_B \) is the Boltzmann constant). The fitted result for Eₐ of the measurement is determined to be ~285 meV, indicating a typical semiconducting feature of Cu₃[PcCu-O₃] films. The charge carrier mobility was further evaluated by measuring the Hall resistance (R₉₅) under magnetic field (H) based on the van der Pauw pattern (method seen in the Supporting Information and Schemes S3 and S4). As shown in Figure 3c, the Hall effect measurement shows a linear relationship of the Hall resistance R₉₅ vs. the perpendicular magnetic field H. Moreover, the polarity of the Hall coefficient indicates a p-type semiconducting behavior of Cu₃[PcCu-O₃]. The hole concentration is calculated as ~7.33×10¹⁴ cm⁻³, and the corresponding Hall mobility reaches 4.4±0.7 cm² V⁻¹ s⁻¹. Note that the arrangement of the edge-on oriented Cu₃[PcCu-O₃] nanosheets in the horizontal direction is random. To elucidate the influence of such anisotropic nature on the charge transport in the lateral direction, we measured 10 two-probe devices with a channel length of 300 μm. As shown in Figure S17, all the contrast samples display consistent conductivity values (~3×10⁻⁵ S cm⁻¹).

We further fabricated vertical devices and investigated the charge transport along the vertical direction as shown in Figure 3a (right) and S18. For better comparability, the contact resistance was determined by transmission line measurements to ~2600 Ω cm and extracted from the detected data. The resulting conductivity of the Cu₃[PcCu-O₃] film in the vertical direction is in the order of ~10⁻⁶ S cm⁻¹ and therefore two orders of magnitude smaller than in the lateral direction as detected by the van der Pauw measurements (Figure 3d). Besides, to exclude that shorts are measured between the top and bottom contacts with a contact area of 1.3×10⁻³ cm², the film thickness was varied between 20 and 250 nm, and all the contrast samples provided consistent conductivity values (Figure 3e).

To reduce the impact of grain boundaries on long-range transport, we built devices with smaller dimensions (sub-μm). For the analysis of transport in the lateral direction, FET devices were fabricated with h-BN as part of the gate dielectric as shown in Figure 3f (left). Here, the contacts with distances between 100 and 500 nm and widths of 8 μm were patterned using electron-beam lithography (Figure S19 and Scheme S5). Figure 3g (red circles) shows the resulting conductivity of one representative contact pair (400 nm) in the order of 2×10⁻⁵ S cm⁻¹, representing charge transport through only very few domains and grain boundaries.

For the analysis of local charge transport in the vertical direction, conductive AFM (c-AFM) was conducted on 20 nm thick Cu₃[PcCu-O₃] films applied on a silver substrate (Figure 3f right, Schemes S6 and S7). Again, this technique was chosen to prevent short currents from being measured. Voltages of 1.2, 3.4 V were applied to the tip and resulting local current in the contact area of ~100 nm² [ref.40] was recorded simultaneously with the film topography (Figure S20). To estimate an upper value for the conductivity, only the highest positions within a scan were evaluated. Here, the least steep curvature

![Figure 4. Modeling of the electronic structures of Cu₃[PcCu-O₃]. Calculated electronic band structure of a monolayer (a) and multi-layered Cu₃[PcCu-O₃] (b). (c) Calculated electrical conductivity within the constant-relaxation-time approximation of the Boltzmann transport equation using the BoltzTraP2 code. The k grid of the VASP calculations was interpolated onto a 7-times denser grid. (d) Schematic illustration of the correlation between Cu₃[PcCu-O₃] structure and the anisotropic charge transport.](image-url)
guarantees good contact and the film thickness can be determined by the detected height with a smaller uncertainty compared to lower-lying positions. The resulting vertical conductivities are in the order of $10^{4} \text{ to } 10^{5} \text{ S cm}^{-1}$ (Figure 3g, green balls). The local measurements, while including contact resistances, are consistent with the macroscopic measurements, as both suggest that the lateral conductivity is $10^{2} \sim 10^{3}$-fold higher than that along the vertical direction (Figure 3h). Therefore, it can be concluded that neither grain boundaries nor contact resistance is the main limiting factor for determining the charge transport of Cu$_{2}$[PcCu-O$_{8}$] film, but stems from its intrinsic anisotropic charge transport feature. Clearly, we can attribute such anisotropic behavior to the preferential charge transport along the layer-stacking direction. These results highlight the importance of controlling the stacking direction in MOF-films for the implementation in electrical devices.

**Theoretical calculation of electronic structures.** To further understand the charge transport nature and the structure-charged transport correlation, we employed DFT to calculate the electronic structures of Cu$_{2}$[PcCu-O$_{8}$]. The density difference map of monolayer and multi-layer Cu$_{2}$[PcCu-O$_{8}$], combined with Bader charge analysis demonstrate that the main density difference redistribution happens at the Cu-O moiety (Figure S21 and S22). As shown in Figure 4a and 4b, the calculated electronic band structures for the monolayer and multi-layer Cu$_{2}$[PcCu-O$_{8}$] present notable differences along the intralayer and interlayer directions. The band structure of a monolayer Cu$_{2}$[PcCu-O$_{8}$] with optimized geometry shows no dispersion in both conduction and valence bands near the Fermi level, implying that charge transport for monolayer is practically null because of an extremely large effective mass for charge carriers. The $\pi$-electrons are trapped within the PcCu-OH$_2$ moiety. In addition, the presence of defects originating from the uncoordinated Cu-site at the edge of Cu$_{2}$[PcCu-O$_{8}$] also contributes to breaking the electron delocalization (Figure S23). The localization of electron density causes flat bands and thus hampers the charge transport within the monolayer. Besides, the bands near to the Fermi level could be easily thermally-populated with holes, indicating a typical $n$-type semiconducting behavior with a bandgap of $\sim 0.35 \text{ eV}$. Contrary to the monolayer, the energy band diagram of the AA-sided stacking Cu$_{2}$[PcCu-O$_{8}$] shows a small bandgap of $0.03 \text{ eV}$ and a band dispersion of $0.19 \text{ eV}$ along the interlayer direction ($\Gamma$-$Z$ direction). The higher dispersion of the valence bands indicates the higher hole mobility along the interlayer direction compared with the intralayer direction. As shown in Figure 4c, the plot of the conductivity at constant relaxation time reveals that the intralayer conductivity is much lower than the interlayer one, thus further supporting the anisotropic transport property. In association with the DFT calculations and the experimental finding, we conclude that the charge transport of the Cu$_{2}$[PcCu-O$_{8}$] film is preferential along the interlayer direction and essentially limited along the intralayer direction, as illustrated in Figure 4d.

**CONCLUSION**

In summary, we have demonstrated a novel strategy for the synthesis of edge-on layer-oriented 2D c-MOF films employing the pre-organized PcM ligands at the air/water interface. Macroscopic Hall-effect and vertical device measurements as well as local charge transport studies by two-probe and c-AFM methods were employed for unveiling the anisotropic charge transport feature of Cu$_{2}$[PcCu-O$_{8}$]. Notably, a Hall mobility of $4.4 \pm 0.7 \text{ cm}^{2} \text{ V}^{-1} \text{s}^{-1}$ was determined, and the resolved lateral conductivity was 2~3 orders of magnitude higher than the vertical one, revealing that the electrical transport of Cu$_{2}$[PcCu-O$_{8}$] is dominated primarily by the stacking direction. The strategy of combining the ligand design and interface-assisted synthesis provides a unique route to control the layer orientation in conducting 2D c-MOFs, which can allow directional charge transport studies and the development of specific optoelectronic devices.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org)

Experimental methods, SAED patterns, TEM images, XPS spectra, XANES spectra, EXAFS spectra, DFT calculations, conductivity measurements, and c-AFM experiments (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Ralf Thomas Weitz—J. Physical Institute, Faculty of Physics, Georg-August-University Göttingen, 37077 Göttingen, Germany; Email: thomas.weitz@uni-goettingen.de

Xinliang Feng—Center for Advancing Electronics Dresden (cfaed) and Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany; Email: xinliang.feng@tu-dresden.de

Renhao Dong—Center for Advancing Electronics Dresden (cfaed) and Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany; Email: renhao.dong@tu-dresden.de

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

**Notes**

The authors declare no competing financial interest.

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