Band-like Transport of Charge Carriers in Oriented Two-Dimensional Conjugated Covalent Organic Frameworks

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ABSTRACT: A tunable topology and a porous network make \( \pi \)-conjugated covalent organic frameworks (COFs) a new class of organic semiconductors for optoelectronic, smart sensing, and catalytic applications. Although some of the COFs exhibit enhanced electric conductivity with a high charge carrier mobility, the nature and pathways of charge transport still remain elusive. In order to unveil the transport mechanism, herein, we have developed crystalline \( \pi \)-conjugated COFs using planar building blocks, and a wafer-scale self-supporting thin film was grown, which could be transferred onto any of the desired substrates. The COF film was found to be highly oriented and exhibited a high in-plane electronic conductivity. The conductivity was almost independent of temperature with an ultra-low activation energy of 14.3 meV, approaching a band-like transport of charge carriers within the crystalline domains. The COF films also showed a high photoresponsivity in electronic conduction against a complete visible range, demonstrated as a flexible photodetector device. This work represents a thorough investigation of the mechanism and direction of charge transport in crystalline \( \pi \)-conjugated COF semiconductors, which suggests their feasibility as key active materials in multifunctional organic electronics.

INTRODUCTION

The quest for organic two-dimensional (2D) materials has been propelled after realizing the extraordinary properties of graphene such as ballistic charge transport, high thermal and electrical conductivity, mechanical robustness, and so forth.1,2 Further interest has been escalated when theoretical studies predicted the ultra-high charge carrier mobility on a graphene layer due to the presence of a “Dirac point” in its energy diagram, where charge carriers act as massless relativistic particles: Dirac fermions.3 In spite of having such exceptional electronic properties, zero band gap and a semi-metallic nature limit its application in various electronic devices. Also, the robust chemical structure of graphene does not allow specific chemical functionalization to tune chemical and physical properties.4 These drawbacks challenged the material chemists to develop new 2D organic materials that are structural analogues of graphene.5 In this context, \( \pi \)-conjugated 2D covalent organic frameworks (COFs) emerged as a new class of organic semiconductor with lots of expectations.5-8 A large surface area, low density, a crystalline framework, and high chemical and mechanical stability make it a versatile material for gas storage and separation, as a molecular membrane, in energy harvesting and storage, in catalysis, and in sensing and biomedical applications.9,10-12 Unlike graphene, chemical connectivity, lattice geometry, electronic band gap, and optical properties can be engineered due to the tailor-made bottom-up synthesis with predesigned \( \pi \)-conjugated building blocks.13,14 Also, precise à la carte functionalization can be achieved through pre- or post- synthetic modifications.15

To date, a number of semiconducting COFs have been developed carrying \( \pi \)-conjugated building blocks and linkers and applied in the fields of photovoltaics,16,17 transistors,18 photodetectors,19 chemiresistive sensing,20 thermoelectric,21 and photo- and electrocatalysis.22-24 The performance of these devices strongly depends on the conductivity and intrinsic charge carrier mobility of the COFs. The charge carrier mobility of the COFs has been estimated using various contact (two/four probes, time-of-flight, hall effect, field effect transistors) and non-contact [time-resolved microwave conductivity (TRMC) and time-resolved terahertz spectroscopy] methods, and few of the \( \pi \)-conjugated COFs were observed to exhibit high intrinsic charge carrier mobility (\( \sim \)8.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\)),25 and high conductivity (\( \sim 10^{-2} \) S cm\(^{-1}\))26 upon doping.

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However, the mechanism or pathway of charge transport is still elusive in COFs, and fundamental questions persist regarding—(i) the nature of charge transport: thermally activated hopping or disorder-free/band-like conduction? and (ii) the direction of charge transport: in-plane versus out-of-plane? Typically, in disordered organic semiconductors, overall charge transport occurs through the hopping process, where localized charges jump from one trap site to another with the help of thermal activation. On the other hand, a few organic single crystals exhibit band transport behavior, where conductivity decreases at elevated temperatures due to lattice vibration/phonon scattering and a number of thermal activation. Most locally, the delocalization of charge carriers is restricted within few molecules, termed as “band-like” and typically suffers from the low charge carrier mobility, due to the extremely small mean free path of charge carriers. Also, narrowly overlapped molecular orbitals and weak intermolecular van der Waals interactions lead to a low carrier-density and a large thermal molecular motion, respectively. This result in a localization of charge carriers that are short-lived and typically survive up to timescale of the molecular vibrations.

The covalently linked framework structure of COFs may suppress the electron–phonon scattering and a number of theoretical calculations predict the band transport of charge carriers in COFs due to the presence of highly dispersive bands near the Fermi energy, and recently, Galeotti et al. experimentally confirmed the presence of Dirac cones in a mesoscale-ordered two-dimensional π-conjugated COF. However, the experimental charge carrier mobilities in most of the COFs are far below the theoretically predicted values (≈100 cm² V⁻¹ s⁻¹ or more). There are various possible reasons such as defects, small crystalline domains, wiggling nature of the COF layers, dramatic change in the electronic band structure owing to the possibility of multiple layer orientation, and carrier scattering by grain boundaries and impurities. Hence, it is worth investigating the mechanism of charge transport in conjugated COFs to identify the origin of discrepancy with the theoretically calculated results and furthering the COF design with an enhanced optoelectronic performance. Recently, some important studies have been performed to probe the nature of charge transport in porous framework materials.

Now, in order to have a precise optoelectronic characterization, oriented crystalline thin films of COFs are a prerequisite on desired substrates, and it will help to understand the charge migration with respect to the packing direction. Several new protocols, such as interfacial polymerization, continuous flow method, and in situ solvothermal synthesis, have been reported in recent years to prepare smooth thin films on substrates. The resulted films, however, are still unsatisfactory for uniform and planar device fabrication, which are essential for the precise characterization of charge transport properties via Hall effect/field-effect transistor measurements.

In this work, we have designed and synthesized two COFs having 9,10-bis(4-aminophenylethynyl)anthracene (AntT) as the π-conjugated building block linked with two different linkers 1,3,5-triformylbenzene (TF) and triformylphloroglucinol (TH) (Scheme 1). The resulting COFs were named AntTF and AntTTH, respectively, where anthracenes are arranged in a Kagome lattice. The rationale behind using the two different linkers is to control the electronic communication and charge carrier delocalization to access their effects on overall optical properties and charge transport. For the newly designed AntTTH, introduction of intramolecular hydrogen bonding (H-bonding) through β-ketoenamine linkage not only enhances the chemical stability but also reinforces the in-plane planarity in contrast to previously reported AntTF. It allows us to obtain wafer-scale self-supporting oriented crystalline COF films of AntTTH, which exhibit high in-plane electronic conductivity. Most captivatingly, the intrinsic photoconductivity is almost independent of temperature with an ultralow activation energy of 14.3 meV, considerably lower than k₅T (~26 meV), and the charge carrier mobility increases upon lowering the temperature. The present report shows that molecular engineering enables us to approach a band-like...
transport in metal-free COFs, thanks to the delocalized charge carriers. In addition, a photodetector operation is demonstrated using COF film-based devices with high enough photoresponsivity.

**RESULTS AND DISCUSSION**

Both AntTTH and AntTTF were synthesized by a conventional acid-catalyzed solvothermal method, using mesitylene/ dioxane as the solvent at 120 °C for 7 days (for details, see the Supporting Information), to improve the crystallinity and for bulk polymerization. Both reactions resulted in a dark red insoluble precipitate, with less than 50% yield for AntTTH and over 92% for AntTTF, indicating a lower degree of polymerization of AntTTF, probably due to the longer length of the AntTTF that causes conformational instability and strain to the imine linkage. Surprisingly, the synthesis of AntTTH resulted in the formation of a uniform self-supporting film on the wall of the reaction tube, along with the precipitate at the bottom (Figure S1). A preliminary characterization of the COF powders was performed using Fourier transform infrared (FT-IR) spectroscopy and solid-state nuclear magnetic resonance and powder X-ray diffraction (PXRD). The FT-IR spectra of both the COFs were recorded and compared with their corresponding building blocks (Figure S2a,b). The disappearance of =CHO and −NH₂ peaks and the appearance of enamine (1253 cm⁻¹) and imine (1623 cm⁻¹) stretching frequencies confirmed the network formation in AntTTH and AntTTF, respectively. 22,45 To gain further structural insight, solid-state ¹³C cross-polarization magic angle spinning (CP/MAS) NMR measurements were performed (Figure S2c,d). To distinguish and assign the peaks, quaternary carbons were selectively measured by a dipolar dephasing technique, and −CH carbon spectra were obtained by subtracting the quaternary carbon spectra from all-carbon CP/MAS spectra. For AntTTH, the quaternary carbon peaks at ~178–190 and ~108 ppm, which are characteristic of β-ketoenamine linkage, confirm the presence of the keto-form (Figure S2c). 22 In contrast, these peaks were absent in AntTTF and two new peaks appeared at ~158 (−CH) and ~149 (quaternary) ppm corresponding to the imine and α-carbon of the amino phenyl group, respectively (Figure S2d). These results are in line with FT-IR studies and confirm the complete polymerization of the building blocks.

The successful formation of crystalline frameworks was confirmed by PXRD analysis. AntTTH exhibited distinct peaks at 2.26, 3.78, 7.80, and 27.14° (Figure 1a), corresponding to the (100), (210), (420), and (001) crystal planes, respectively. Similarly, AntTTF displayed peaks at 2.29, 3.94, 4.58, 6.01, and 26.14° (Figure 1b), which can be assigned to the (100), (101), (200), (201), and (001) crystal planes, respectively. The d-spacing of the (100) and (001) planes indicates that both the COFs have a similar hexagon length and slightly different interlayer stacking distances. Compared to AntTTF (interlayer distance ~3.40 Å), AntTTH has a reduced interlayer distance of ~3.30 Å due to the strong interlayer π-stacking facilitated by the planar backbone. In order to elucidate the geometry and packing of these two isoreticular COFs, two kinds of stacking models of 2D layers, namely, AA and AB, were considered, and density functional-based tight binding (DFTB+) calculations were performed using the Materials Studio software package (details provided in the Supporting Information Figure S3a,b). Geometry optimization

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**Figure 1.** Experimental PXRD (red circle) and Pawley refined (blue line) profiles of (a) AntTTH and (b) AntTTF with minimal differences between the experimental and the refined patterns (gray line) with the simulated PXRD pattern (AA stacking). (c) SEM image with the height profile, and the inset shows the large-sized freestanding AntTTH COF film in tetrahydrofuran. (d) TEM images of the AntTTH COF film, and the inset shows the FFT filter-applied enlarged section. AntTTH COF film (e) transferred and (f) grown in situ over a quartz substrate. Adapted with the permission of Kyoto University. (g) 2D-GIXS pattern of the AntTTH COF film over a quartz substrate with a 1D in-plane profile. The inset shows the schematic in-plane hexagonal network of COF layers over the substrate.
For the crystals under the periodic boundary condition revealed that AntTTH formed a completely planar 2D π-backbone with high lattice symmetry P6/m, whereas non-planarity was observed for AntTTF with a lower lattice symmetry P2 (Scheme 1), thanks to the intramolecular H-bonding that helped AntTTH to maintain the planarity and achieve high symmetry. The experimental PXRD patterns of AntTTH and AntTTF were closely matched with the simulated PXRD profiles of the eclipsed AA stacking with a small mismatch in d-spacing; however, based on the obtained PXRD resolution, it is difficult to distinguish between eclipsed and serrated AA stacking (Figure S3c,d). The Pawley refinement was performed to confirm the cell parameters, and it matched well with the experimental PXRD patterns of both the COFs with negligible deviations. The permanent porosities of these two COFs were evaluated by nitrogen adsorption–desorption analysis at 77 K. Both AntTTH and AntTTF exhibited a type I adsorption isotherm, a typical characteristic of microporous materials, having a porosity of 940 and 544 m² g⁻¹, respectively (Figure S4a). Although AntTTH and AntTTF are isoreticular COFs, the relatively small porosity of AntTTH originated due to the lower degree of polymerization compared to AntTTF. The thermal stability of both the COFs was confirmed by thermogravimetric analysis, and AntTTH exhibited greater thermal stability than AntTTF (Figure S4b). These results confirm the successful preparation of stable, crystalline, and porous COFs.

Our next focus was the preparation of thin films of COFs for optoelectronic characterization. Unlike AntTTF, AntTTH has a unique ability to form wafer-scale COF films with a red metallic luster on the walls of the reaction tube during the solvothermal synthesis, which slowly delaminates from the wall with the progression of the reaction, leading to a self-supporting, centimeter-scale COF film (Figure S1 and inset Figure 1c, for detailed film synthesis, see the Supporting Information). These films were carefully removed from the reaction tube and washed with various organic solvents to remove the unreacted monomers. These films float as self-supported films in common organic solvents and can be easily transferred to any substrate (quartz, silicon, fluorine-doped tin oxide (FTO) etc., Figures 1e and S1, days 3 and 7). To confirm the structural integrity of the self-supporting films, FT-IR and Raman spectra were recorded and compared with the powder sample of AntTTH (Figure S5). Both spectra showed peaks at similar positions and the absence of any additional peaks, confirming the formation of expected chemical structures free of any unreacted aldehyde and amine. Also, these films can be directly grown over any desired substrate by placing the substrate vertically into the reaction mixture, and these in situ grown films were found to be chemically identical to the transferable ones (Figure S5b). Lowering the concentration of the building blocks resulted in transparent smooth films (Figure 1f, for detailed film synthesis, see the Supporting Information).

SEM and AFM analyses revealed that the surfaces of the self-supported films are smooth and free of cracks (Figures 1c and S6a). The thickness of the films can be varied from 100 nm to a few micrometers depending upon the concentration of the building blocks (see the synthesis of COF films, Supporting Information), comprising multiple COF layers. The COF film was scooped on a carbon-coated copper grid, and cryogenic transmission electron microscopy (cryo-TEM) was performed

**Figure 2.** (a) Steady-state absorption and emission spectra of AntTTH (red) and AntTTF (blue) films with the excitation at 475 nm. (b) Anisotropic FP-TRMC transient decay profile of AntTTH COF films. (c) Temperature-dependent FP-TRMC and Arrhenius plot of intrinsic photoconductivity (ϕΣμ). (d) Peak of transient photocurrent intensity vs electric field plot of the AntTTH COF film at 300, 220, and 160 K (under high electric field), showing linear relation. (e) Temperature dependence of ϕ and corresponding Σμ of AntTTH COF films. All the experiments were performed under 355 nm laser excitation with 9.1 × 10¹⁵ photons cm⁻² pulse⁻¹. (f) Wavelength dependent on–off switching of photocurrent, with a bias voltage of 1 V and a light power of 320 nW.
(Figure 1d). The film showed crystalline domains with an average size of ~30 nm (Figures 1d and S6b–d). However, due to the wiggling nature of the COF film, it is difficult to focus different areas simultaneously and quantify the crystalline and amorphous domains.46,47 High-resolution TEM revealed honeycomb structures with a pore size of ~3.9 nm in the crystalline domains, which matched well with the calculated pore size (3.94 nm). In order to confirm the crystallinity and orientation of the COF film, 2D grazing incidence X-ray scattering (2D-GIXS) measurements were performed. The film exhibited sharp and intense in-plane reflections at 2.23, 3.93, and 7.91° (Figure S7a), with negligible out-of-plane reflections (Figure S7a), reflecting a high degree of parallel orientation of the COF layers with respect to the substrate (inset Figure 1g).48,49 The broad peak at around 2θ = 20−25° arises from the quartz substrate. In-plane 1D profile of 2D-GIXS is in line with the PXRD of the powder sample as well as simulated AA1 structure

with random orientation of the COF layers (Table S1).35 Also, AntTTH films were highly oriented in nature, and therefore, anisotropic photoconductivity was measured by placing the sample parallel (ϕΣμ⊥) and perpendicular (ϕΣμ∥) to the microwave electric field vector to understand the direction of charge transport. AntTTH films exhibited a fourfold increase in anisotropic photoconductivity (ϕΣμ∥:ϕΣμ⊥), indicating a greater in-plane charge carrier mobility than the out-of-plane one.50 Moreover, no significant change in transient photoconductivity was observed upon increasing the thickness of the COF film (Figure S9b), further pointing to the major in-plane conductivity.

In order to investigate the mechanism of charge transport, temperature-dependent conductivity measurement was performed within a range of 300−190 K (see the Supporting Information). Interestingly, photoconductivity was slightly decreased upon lowering the temperature, and the activation energy was estimated using the Arrhenius relation as $E_A = 14.3$ meV, which is significantly smaller compared to other conjugated organic polymers/COFs,51 and lower than the thermal energy $k_BT (~26$ meV) at room temperature (Figure 2c). To estimate the average charge carrier mobility, $\phi$ was determined for the AntTTH film by transient photocurrent measurement (TPC) by placing the COF film over a comb-type interdigitated gold electrode on a glass substrate (Figure S9c) and was obtained as $7.2 \times 10^{-5}$. Hence, the average local charge carrier mobility was estimated as $\approx 0.1$ cm$^2$ V$^{-1}$ s$^{-1}$.60 Moreover, $\phi$ was calculated at 220 and 160 K, and its value decreased upon lowering the temperature (Figure 2cd). Substituting these $\phi$ values to the corresponding photoconductivity, an increase in the charge carrier mobility was observed upon lowering the temperature (Figure 2e), clearly indicating significant impacts of scattering by phonons/vibrational modes in planes of the COF even in the local motion of charge carriers. This is suggestive of the band-like charge transport in the AntTTH film. However, the estimated charge carrier mobility is relatively low, and probably the delocalization of charge carriers is limited to a few molecules, which is typical for band-like transport.29,30

Furthermore, to elucidate the macroscopic charge carrier transport of a COF film, temperature-dependent two-probe DC electrical conductivity was performed. AntTTH films exhibited a hysteresis-free linear $I−V$ characteristic in the dark and under light in the temperature range from 100 to 300 K (Figure S10). The estimated conductivity of the AntTTH film was $3 \times 10^{-8}$ and $1.2 \times 10^{-7}$ S cm$^{-1}$ in the dark and under light, respectively, at room temperature, which are comparable with the undoped semiconducting COFs (Table S2). The conductivity was thermally activated with quite similar values of activation energy of 229 and 222 meV in the dark and under light, respectively, using the Arrhenius relation (Figure S10c). The Arrhenius plot in a two-probe measurement shows a slight sublinear response, suggesting multiple trap-and-release mechanisms in the macroscopic measurement. Now, the large difference in the activation energy estimated from the two-probe and FP-TRMC measurement needs to be explained. Considering the difference in the probing region in these two methods, that is, macroscopic (~5 μm) for two-probe and microscopic (estimated as <10 nm in the present system) for FP-TRMC, the two-probe measurement is largely governed by the carrier transport at the grain boundary or amorphous region as the rate-determining step.36,61 TEM and XRD results showed that the average crystalite domains (~30 nm) are much smaller than the distance between two electrodes (~5 μm).

The optical and electronic properties of AntTTH and AntTTF films were then investigated to understand the structure−property relationship. The AntTTH film (thickness ~570 nm) exhibited a broad absorption compared to the AntTTF film (thickness ~200 nm) with a red-shifted absorption maximum of 34 nm (Figure 2a), and direct optical band gaps were determined as 2.10 and 2.24 eV, respectively (Figure S8a). The valence band (VB) of both the COFs was estimated using photo yield spectroscopy (Figure S8c,d). Also, AntTTH films showed low photoluminescence compared to AntTTF when excited at 475 nm (Figure 2a) where the absorbance of AntTTH is fivefold higher than AntTTF (Figure S8b), probably due to the stronger chromophoric interactions.50,51 A relatively broad absorption with a low optical band gap of AntTTH is evoked from the planar structure, which facilitates extended in-plane conjugation and strong π-stacking between the layers. These results encouraged us to investigate the charge-transporting properties in the ordered crystalline domain of AntTTH, and we compared them with those for AntTTF. Intrinsic charge carrier mobility of the COFs was estimated using the flash photolysis (FP)-TRMC measurement, which has evolved as a quick and reliable non-contact method to probe the charge dynamics at the nanoscale upon laser pulse excitation under a rapidly oscillating electric field.52−54 Unlike other contact-based measurements, this method is free from contact resistance and grain boundaries, which makes it suitable to probe the charge dynamics of different class of materials.55 Basically, FP-TRMC measures the intrinsic photoconductivity as a $\phi \Sigma \mu$ value, where $\phi$ and $\Sigma \mu$ are charge carrier generation quantum yields upon photoexcitation and the sum of charge carrier mobilities, respectively. AntTTH films (thickness ~570 nm) exhibited a maximum intrinsic photoconductivity of $7.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ upon 355 nm laser excitation (photoexcitation area 1 cm$^2$) with a photon density of $9.1 \times 10^{15}$ photons cm$^{-2}$ pulse$^{-1}$ (Figure 2b), whereas the powder samples of both the COFs showed negligible photoconductivity (Figure S9a). The poor photoconductivity of AntTTH powder probably resulted from the smaller crystal domains with random orientation of the COF layers (Table S1).55
The properties make it a potential organic material for photodetector applications. However, with the same bias voltage, no photoresponsivity was observed for the large resistance of the film. On the other hand, a small activation energy was seen in the room light, with a bias voltage of 1 V, and the on–off switching of the photocurrent can be observed many times even under very low light power in the complete UV–vis spectrum, without graphene or any other charge transporting layer (Figure 2f). These properties make it a potential organic material for photodetector applications. However, with the same bias voltage, no photoresponsivity was observed for AntTTF due to the large resistance of the film.

Finally, to support the experimentally deduced optical and electronic properties, we have calculated the band diagram of single and AA-stacked multilayers of AntTTH and AntTTF using density functional theory (DFT) (details provided in the Supporting Information). The conduction band (CB), VB, and fermi energy level ($E_F$) of the AntTTH and AntTTF single layer and multilayers are tabulated in Table S3. The CB of AntTTH showed dispersion for both the single layer and multilayers, indicating a low effective mass of electron, whereas the VB contained a flat band (Figures 3a and S11c). If we look closely, both the single layer and the AA-stacked multilayers exhibit significant in-plane band dispersion, whereas dispersion less band was observed in the out of plane direction. Hence, the in-plane effective mass of electron is much lower than the out of plane one, which justifies the anisotropic photoconductivity of AntTTH films. On the other hand, a small dispersion in CB was observed for the AA-stacked multilayer AntTTF (Figures 3b and S11d), which signifies an extremely large effective mass of the charge carriers. Also, we have calculated the electron density of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of COFs. In the case of AntTTH, both HOMO and LUMO are delocalized over the 2D $\pi$-backbone (Figure 3c,d), which may facilitate the delocalization of charge carriers, while AntTTF has localized HOMO and LUMO. Moreover, energy optimizations were performed using DFT (B3LYP-6-31G*) for the trimer (zigzag) of AntTTH and AntTTF, and the HOMO–LUMO distribution was calculated. AntTTH and AntTTF exhibited planar (H-bonded) and non-planar geometries, respectively, in line with DFTB + calculation (Figure S12). The calculated enamine bond length was 1.34 Å for AntTTH, which is slightly longer than the imine bond distance (1.28 Å) of AntTTF, however significantly smaller than the C–N single bond length (1.49 Å), indicating the partial double bond character of enamine. To further confirm, C–N bond lengths were calculated from the previously reported single structures of imine and $\beta$-ketoenamine, and they were found to be 1.27 and 1.31 Å, respectively, which matches with the theoretical results. Also, the $\beta$-ketoenamine linkage provides intramolecular H-bonding and a planar structure, which allows the lone pair on enamine $-$ to remain in conjugation with the adjacent $\pi$-electron cloud, as evident from the HOMO and LUMO orbital delocalization. In the case of AntTTF, both HOMO and LUMO were delocalized over the $\pi$-conjugated backbone, whereas these MOs are localized in AntTTF (Figure S12). Also, it was previously reported that the triple intramolecularly H-bonded system acts as a quasi-aromatic system due to the delocalization of the $\pi$-electrons. Hence, the delocalized charge carrier transport of AntTTH can be facilitated by the substantial band dispersion and delocalized orbitals. In contrast, negligible band dispersion and localized orbitals of AntTTF resulted in low photoconductivity. These results indicate that a conjugated covalent framework can be constructed through $\beta$-ketoenamine linkages, which helps to maintain the planarity as well as conjugation.
CONCLUSIONS

We have developed two anthracene-based isoreticular COFs and, by comparing their optical and electronic properties, unveiled the charge transport mechanism in conjugated COFs. In contrast to the imine-linked COF, an intramolecular H-bonded β-ketooxime-linked COF exhibited high planarity, which significantly enhanced the optoelectronic performance along with the chemical stability. Solvothermal synthesis afforded large-scale-oriented crystalline films of AntTT, which showed high photoconductivity compared to the powder, revealing a strong in-plane carrier charge mobility. The non-planar backbone restricts the charge carrier delocalization, resulting in a low photoconductivity for AntTTF, when compared to its counterpart. Notably, the intrinsic photoconductivity of AntTT films was almost independent of temperature with ultra-low activation energy, and the charge carrier mobility increased upon lowering the temperature, approaching intra-domain band-like transport of charge carriers. These results are further supported by the theoretically calculated molecular orbitals and the deduced band structures. Moreover, the COF film showed high photoconductivity, which makes it an efficient COF semiconductor for photodetectors, photocatalysis, or solar cell applications. These investigations are currently in progress in our laboratory.

EXPERIMENTAL SECTION

Synthesis of COF Powder. AntT (60.0 mg, 0.147 mM, 3 equiv) and TH (20.6 mg, 0.098 mM, 2 equiv)/TF (15.8 mg, 0.098 mM, 2 equiv) were taken in a 20 mL BIOTAGE reaction tube, followed by the addition of mesitylene (3 mL) and 1,4-dioxane (3 mL). The reaction mixture was homogenized by sonication, and aqueous acetic acid (0.5 mL, 6 M) was added, followed by 1 mL of 1,4-dioxane (caution: do not perturb the motion of charge carriers. An interdigitated comb-type gold electrode with 5 μm gaps, 50 nm height, and 2 mm width fabricated by a lithographic process in the laboratory was used for both transient photocurrent and photodetector experiments. COF films were carefully placed over the interdigitated comb-type gold electrodes. Different bias voltages were applied using a Keithley 2400 source meter, and the transient photocurrent was measured by a Tektronix model TDS3032B digital oscilloscope equipped with a termination resistance of 10 kΩ. Two-probe I–V characteristic studies under light and in the dark were performed using a Keithley 4200 semiconductor characterization system with the same interdigitated device configuration as for TPC. The sample was illuminated with monochromatic lights of different wavelengths, and the photocurrent was measured in a cryostat (Montana, Cryostation) under temperature control. The illuminating light power was measured using an optical power meter (S130VC Photodiode Power Sensor, Thorlabs).

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c03533. Synthesis of the building blocks; experimental details of the characterization, spectrometry, morphological traces, structural modeling, and band structure calculation and photoconductivity measurements; photographs of COF films; FT-IR spectra; PXRD patterns; nitrogen sorption isotherms; Raman spectra; AFM and high-resolution cryo-TEM images; GIXS patterns; Tauc plots with absorption and emission spectra; transient photoconductivity kinetic traces with temperature dependence; I–V traces from photodetector devices; calculated band structures of COFs; electron density maps of frontier orbitals; crystal sizes; electrical conductivity; and calculated energy levels (PDF)

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Author Contributions
S.G. conceived the project and wrote the manuscript with the help of S.S. and Y.T. Measurement and data analysis were done by S.N. Synthesis and characterization of the samples were performed by S.G. and T.K. The 2D-GIXS measurement and data analysis were done by S.N. Solid-state 13C CP-MAS experiments and analysis were conducted by K.S. and H.K. Y.T. performed the temperature-dependent FP-TRMC measurement and interpreted the results. TPC was conducted by W.M. All authors have given approval to the final version of the manuscript.

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