Fast Crystallization-Deposition of Orderly Molecule Level Heterojunction Thin Films Showing Tunable Up-Conversion and Ultrahigh Photoelectric Response

Xiao-Gang Yang, Zhi-Min Zhai, Xiao-Min Lu, Lu-Fang Ma,* and Dongpeng Yan*

**ABSTRACT:** Molecular cocrystals have received much attention for tuning physicochemical properties in pharmaceutics, luminescence, organic electronics, and so on. However, the effective methods for the formation of orderly cocrystal thin films are still rather limited, which have largely restricted their photofunctional and optoelectronic applications. In this work, a fast crystallization-deposition procedure is put forward to obtain acridine (AD)-based cocrystals, which are self-assembled with three typical isophthalic acid derivatives (IPA, IPB, and TMA). The obtained donor−acceptor cocrystal complexes exhibit an adjustable energy level, wide range of photoluminescence color, and rotational angle-dependent polarized emission. The orderly and uniform cocrystal thin films further present tunable one-/two-photon up-conversion and different semiconductor properties. Particularly, AD-TMA cocrystal thin film shows a rare example of a molecule level heterojunction with the alternating arrangement of AD electronic acceptor layers and TMA electronic donor layers, and thus, provides a way for efficient mobility and separation of electron−hole pairs. A large on−off photocurrent ratio of more than 10⁴ can be achieved for the AD-TMA thin film, which is higher than state-of-the-art molecular semiconductor systems. Therefore, this work extends the application scopes of orderly cocrystal thin film materials for future luminescent and optoelectronic micro-/nanodevices.

**INTRODUCTION**

Recently, the rational design and controlled synthesis of molecule-based optoelectronic materials have attracted great attention owing to their potential applications in the fields of solar cells, photodetectors, photoswitches, phototransistors, and optical data storage.¹⁻⁶ To obtain a high performance of optoelectronic materials, several key factors need to be considered, such as a broad light harvesting range, tunable band gap, high charge carrier mobility, and efficient dissociation of photogenerated excitons, particularly for those of solution-processed thin films.⁷⁻⁸ In this context, molecular cocrystals, assembled by two or more molecular components via hydrogen bonds, halogen bonds, π−π, and/or charge transfer interactions, have recently received increasing attention due to the advantages of a facile synthesis route, adjustable molecular arrangement, easy functionality, and low cost.⁹⁻¹⁵

Among different types of cocrystals, donor−acceptor (D−A) complexes can be regarded as crystalline heterojunction materials, which are constructed by the alternating arrangement of an electron-rich donor and electron-deficient acceptor at the molecule level. The strategy to integrate advantages of D−A cocrystals has provided a platform for the development of photofunctional materials and molecular optoelectronics.¹⁶ For example, our previous work showed that the introduction of the coformers can change the geometric arrangement of the 1,4-bis-p-cyanostyrylbenzene chromophore within cocrystals, resulting in tuned fluorescence.¹⁷ To achieve large circular polarization, Duan and co-workers demonstrated a chiral charge-transfer (CT) cocrystal system with chiral electron donor and acceptor by various approaches.¹⁸ By crafting a periodic molecular barrier into cocrystal matrices, Zhang and co-workers provided a new approach to preventing the formation of dark triplet states in organic semiconductors.² To date, tremendous effects have been paid on the development of macrosized bulk cocrystal systems and the study of the basic mechanism on structure−properties relationship. However, the construction of cocrystals at the micro-/nanoscale, and particularly their orderly thin films, is still rather limited.¹² From the
fundamental and practical application perspectives, it is of significance to explore novel crystalline micro-/nanoscaled thin films by the organization of D–A assembled units, which would greatly extend the scope for the optoelectronic application based on the facile cocystal designs. Therefore, the development of an effective procedure to fabricate orderly cocystal thin films is still highly desired.

The π-conjugated acridine (AD) compound is a well-known chromophore, which plays an important role in molecular luminescence and optoelectronic materials. For example, an AD-based hybrid microbelt could exhibit an excellent optical waveguide performance due to a close and alternating arrangement of protonated AD layers, as stabilized through electrostatic and hydrogen bond interactions. The modification of molecular stacking and potential protonation of AD may further tailor its electronic structures and photophysical properties. To date, at least five AD polymorphs have been found with different packing motifs and physicochemical properties. It has also been found that the approach of template-assisted crystallization can result in different molecular packing and thus forms a new polymorph. In this work, the AD molecule is selected as the electron acceptor to construct cocystals with different electronic donors, since the AD with the coordinate nitrogen atom can potentially self-assemble with different coformers as molecular templates by strong hydrogen bonds. The coformers, isophthalic acid (IPA) modified by 5-position substituents with a di-π-conjugated acridine (AD) compound is a well-known molecule containing carboxylic groups and halogen atoms (IPA = isophthalic acid, IPB = 5-bromoisophthalic acid, TMA = trimesic acid) were selected as coformers to assemble with AD through supramolecular interactions (Scheme S1 and Figure 1a). In contrast to the low crystalline quality of the pristine AD, high-grade single crystals of AD-based two-component complexes (AD-IPA, AD-IPB, AD-TMA) can be readily obtained by a solvothermal process or slow evaporation of ethanol solutions containing AD and the coformers with a 1:1 (AD-IPA and AD-TMA) or 2:1 (AD-IPB) stoichiometry. Their crystallographic details are listed in Table S2. Powder X-ray diffraction (PXRD) patterns indicate that all of the diffraction peaks are well indexed to the simulated results, implying the high purity of the AD precursor and corresponding cocrystallized samples (Figure S1a–d). Both AD-IPA and AD-TMA are organic salt forms with protons transferring from carboxylic groups to N atoms of AD, while the AD-IPB cocystal consists of neutral AD and IPB molecules. The FT-IR spectra (Figure S1e) of the samples reveal strong bands at 1683 and 1695 cm−1 for the protonated carboxylate groups, indicating the deprotonation of IPA and TMA. The characteristic bands at 1730 cm−1 can be attributed to the protonated carboxylic groups of IPB. Thermogravimetric differential thermal analysis (TG-DTA) measurements (Figure S2) show that the melting points of all these multicomponent complexes occur at higher temperatures (214–285 °C) than the pure AD (110 °C), confirming that the thermal stability of the AD can be improved by the formation of the cocystal.

The pristine crystalline sample of AD is commercially available, which shows the III form (Figure S1a) and crystallizes in the monoclinic crystal system P21/c space group. Its asymmetric unit contains two independent AD molecules with a dihedral angle of 67.09° (Figure S3a). A pair of AD molecules are joined together to form a dimer through C–H⋯N hydrogen bonds, which is further stabilized by C–H⋯π and π⋯π stacking interactions (Figure S3b), giving rise to a 3D

**Figure 1.** (a) Chemical structures of AD, IPA, IPB, and TMA molecules in this work. Supramolecular interactions between AD and IPA (b), IPB (d), and TMA (f). Template-assisted crystallization results in structure diversity of AD motifs in AD-IPA (c), AD-IPB (e), and AD-TMA (g).
supramolecular architecture (Figure S3c,d). By assembly with the isophthalic acid (IPA) unit modified by different 5-position substituents, obviously different stacking patterns of AD can be obtained compared with its typical polymorphs. Upon formation of the AD-IPA two-component crystal, proton transfer occurs from the carboxylic acid of IPA to the nitrogen atom of AD. In AD-IPA, the dihedral angle between AD and IPA is 62.11° (Figure S4a). The IPA molecule shows a plane conformation, and the neighboring IPA molecules connect to each other through O⋯H−O and C−H⋯O hydrogen bonds and π⋯π stacking interactions (with the centroid−centroid distances of 4.00 Å) to form a 1D double stand chain along the a direction (Figure 1b and Figure S4b). The AD molecules arranging in an antiparallel packing mode are fixed together by double-standing IPA chains through N−H⋯O and C−H⋯O hydrogen bonds, giving rise to a 2D layered structure (Figure 1c). Analysis of the crystal packing shows that the AD-IPA exhibits an alternating arrangement of AD cations and IPA anions (Figure S4c).

Single-crystal X-ray diffraction analysis reveals that AD-IPB forms a neutral cocystal, which crystallizes in the monoclinic C2/c space group, and the asymmetric unit consists of one AD and half of IPB molecules. The dihedral angle between AD and IPB is 84.69° (Figure S5a). In AD-IPB, the IPB molecule exhibits a nonplane conformation with the dihedral angles between carboxylic groups and the benzene ring of 12.95°. Such a twisty conformation can provide a greater chance for the formation of hydrogen bonds. Each IPB molecule is surrounded by eight AD molecules through N−H⋯O and C−H⋯O hydrogen bonds (Figure 1d), generating a 2D double layer structure with Br atoms hanging on two sides (Figure S5b,c). The AD molecules display face-to-face antiparallel π⋯π stacking interactions, with centroid−centroid distances of 3.77 and 3.97 Å, respectively (Figure 1e). Adjacent layers are further extended to a 3D supramolecular framework through C−H⋯Br hydrogen bonds. Viewed along the c direction, the IPB guests are closely encapsulated within the AD host (Figure S5d).

When the 5-position −Br substituent is instead −COOH under the same conditions, a distinct structure of AD-TMA can be obtained. Similar to AD-IPA, proton transfer is also observed in the AD-TMA system. Within TMA, carboxylic groups form the dihedral angles of 13.07° and 4.84° with the central benzene ring plane for −COO− and −COOH, respectively. A pair of TMA molecules interact with each other in a head-to-tail arrangement to form a dimer through O⋯H−O hydrogen bonds (Figure 1f), which is further extended by guest water molecules through O⋯H−O hydrogen bonds, generating a 2D TMA-H2O layer (Figure S6b). Strictly different from those of the discrete AD dimer in AD-IPA (Figure 1c) and AD-IPB (Figure 1e), the AD molecules in AD-TMA are arranged into an infinite π-conjugated chain featuring compact H-aggregation (Figure 1g), which is expected to benefit the migration of charge carriers. Among the reported AD-based polymorphs and multicomponent complexes, only one example of organic−inorganic hybrid perovskite [(AD)Pb2Cl5] possesses such a packing arrangement, in which the orderly arrangement of the organic AD cation layers is confined between the rigid lead chloride inorganic layer (Figure S7). In AD-TMA, the infinite AD chains are fixed between TMA-H2O layers via N−H⋯O and C−H⋯O hydrogen bonds. Viewing from the b direction (Figure S6c), AD-TMA shows an alternating arrangement of the AD π-conjugated system and TMA-H2O anionic layer. Therefore, it is concluded that the packing mode and intermolecular interactions of AD can be completely alternated after cocrystallization through the introduction of different aromatic carboxylic acid coformers. The structural diversity of these compounds would further result in different luminescence and photoelectric performances.
Absorption and Photoluminescence Analyses. The photophysical properties of cocrystals AD-IPA, AD-IPB, AD-TMA, and pristine AD were investigated by UV−vis absorption, photoluminescence (PL) spectra, PL quantum yield (PLQY), and lifetime measurements. As shown in Figure 2a, AD exhibits absorption ranging from 200 to 450 nm, whereas its cocrystal samples can effectively extend the absorption band to the visible region in a wide range. Upon excitation at 310 nm, AD exhibits a weak blue fluorescence emission at 396 nm with low PLQY of 0.97%. In comparison with the pristine samples of AD, IPA, IPB, and TMA (Figure 2b and Figure S8), the three cocrystal complexes AD-IPA, AD-IPB, and AD-TMA emerge with a longer wavelength photoemission (maxima at 542, 502, and 612 nm, respectively) and higher PLQY of 17.49%, 15.74%, and 1.75%, respectively. Herein, the red-shifted PL of these cocrystals may originate from the charge-transfer interaction between two components. Upon irradiation with 365 nm UV, these well-defined bright yellow (under daylight) cocrystal samples reveal different emission colors: light-green for AD-IPA, cyan for AD-IPB, and orange-yellow for AD-TMA (Figure 2c). Thus, the emission color of AD can be vastly adjusted from blue to orange-yellow (Figure S9) via cocrystallization with different assembled units.

To further investigate the nature of the excited states, the PL lifetimes (τ) of these cocrystal samples were measured as shown in Figure 2d. The τ value for AD is 2.88 ns, while that of the AD-IPA, AD-IPB, and AD-TMA is largely enhanced to 21.19, 15.80, and 10.22 ns, respectively. A comparison of the photophysical properties (Table S1) reveals that the photoemission performances of AD can be modified obviously by coassembly with suitable coformers. The large enhancement of PLQY and PL lifetime for AD-IPA and AD-IPB can be assigned to the fact that the orderly AD molecules are highly restricted and stabilized in the cocrystal matrices through strong hydrogen bonds and/or electrostatic interactions, inhibiting the molecular thermal vibration and nonradiative relaxation. In addition, the isolation of coformers could minimize the serious aggregation-caused quenching AD chromophores. The large separation of AD in AD-IPA leads to the prolonged lifetime. The relatively high concentration of AD in AD-IPB results in a decrease of lifetime compared with AD-IPA. The alternating arrangement of AD layers and TMA layers in AD-TMA shows the shortest lifetime among three cocrystals; this can be attributed to the quenching from guest water molecules. By contrast, the higher degree of overlap of π-conjugation in AD-TMA provides much denser crystal packing, resulting in the H-aggregation of AD chromophores, leading to an obvious red-shift in the PL emission and visible light absorption. In spite of the relatively low PL performance, it can be predicted that the infinite 1D AD π-conjugation chains in AD-TMA may afford a platform of efficient charge carrier mobility for potential optoelectronic applications.

Theoretical Calculations. To better understand the variable photophysical properties of these crystalline compounds, density functional theory (DFT) based on the generalized gradient approximation (GGA) was used to calculate the molecular orbital and energy levels of cocrystals and their components. As shown in Figure 3a−c, it is observed that the electron density of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is mainly localized on the IPA/IPB/TMA and AD molecules, respectively. The calculated HOMO, LUMO, and HOMO−LUMO energy gaps are summarized in Figure 3d, which indicate that the introduction of coformers can reduce the HOMO (−4.904 eV) and LUMO (−2.462 eV) energy level of AD to a large extent: −5.660 and −3.291 eV for AD-IPA, −5.516 and −3.115 eV for AD-IPB, and −5.973 and −3.946 eV for AD-TMA. This can be attributed to the lower energy level of IPA (−6.521 and −3.167 eV), IPB (−6.497 and −3.351 eV), and TMA (−6.547 and −3.046 eV) coformers. Meanwhile, the HOMO−LUMO energy gap of AD can also be decreased from 2.442 to 2.369 eV for AD-IPA, 2.361 eV for AD-IPB, and 2.027 eV for AD-TMA. In particular, AD-TMA shows the lowest HOMO and LUMO energy level and the smallest energy gap. In all, the three cocrystals have a reduced energy gap and red-shifted wavelength of emission as compared to that of the pristine IPA, IPB, and TMA coformers and AD. The trend of these results are well consistent with their optical performances in experiment.

Angle-Dependent Polarized Fluorescence Emission. Based on different alignment fashions of AD chromophores in three cocrystal complexes, their angle-dependent polarized fluorescence spectra were measured on a microspectrometer by rotating the polarizer at different polarization angles. Figure 4 and Figures S10 and S11 illustrate the relationship between the polarization fluorescence intensity of the individual single crystal and the polarization angle (θ) irradiated under unfocused UV light. It is observed that three cocrystals present obviously different maximum (I_{max}) and minimum (I_{min}) fluorescence intensity values. AD-IPA has the maximum and minimum values at 60° and 150°, respectively. AD-IPB shows the maximum at 0° and the minimum at 90°, while AD-TMA displays the opposite values compared with those of AD-IPB. To evaluate the polarization performance, the emission dichroic ratio R_θ and polarization anisotropy σ were calculated by R_θ = I_{max}/I_{min} and σ = (R_θ − 1)/(R_θ + 1). The polarization anisotropy values of 0.50, 0.26, and 0.32 are obtained for AD-IPA, AD-IPB, and AD-TMA, respectively.
The diversity in polarization emission for these cocrystals can be assigned to the different packing mode of AD molecules. Interestingly, AD-IPB exhibits a remarkable fluorescence color transformation from cyan (maxima at 485 nm) to green (maxima at 530 nm) measured at 0° and 90°, as shown in Figure 4c,d. To the best of our knowledge, such alternant photoemission between different polarized directions has been seldomly reported, particularly in molecular crystals.30 The cyan to green color switching of AD-IPB is an instantaneous and completely reversible process, which endows it as potential candidates for display, data storage, color filters, and so on. The emission switching demonstrated in the AD-IPB cocrystal system is assigned to the nearly perpendicular arrangement of molecule packing between AD and IPB (with a dihedral angle of 84.69°).

Fabrication and Photophysical Properties of Cocry stall Thin Films. To make molecular cocrystals into potential luminescent and optoelectronic applications, it is important to fabricate well-defined thin films. Herein, thin films of AD and its cocrystals were obtained by a fast crystallization-deposition (FCD) method using thermal evaporation at 100 °C deposited on indium tin oxide (ITO) substrate. To regulate the crystallization process and produce high-quality films with a controllable morphology, several key factors are worth noting. First, the two-component raw materials should be completely dissolved in the selected solvents with relatively low boiling point. Second, the volatilization rate or the control of temperature has a great influence on film morphology. Slow evaporation of solvent coated on the ITO substrate could only provide large-scale crystal samples. Thermal evaporation of fast crystallization-deposition could obtain micro-/nanoscaled cocrystal thin films. The temperature should be higher than the boiling point of solvent to generate instantaneous evaporation of solvent. The airflow formed by solvent vapor favors the crystallization of uniform micro-/nanostructures. Generally, increasing the temperature is conducive to the formation of high-quality micro-/nanostructures. However, a phase transition would occur when the temperature is higher than the melting point of AD (110 °C). Finally, it is found that the organic salt form of AD-IPA and AD-TMA shows a higher crystallinity than the neutral AD-IPB two-component crystal and pure AD.

These thin films show strikingly different morphologies as observed by scanning electron microscopy (SEM). Figure 5a reveals that the fast evaporation of AD and AD-IPB solution could lead to the formation of uniform and orderly thin films with pinholes. By contrast, thin films of AD-IPA and AD-TMA are highly crystalline. It is worth noting that the block nanocrystals can be observed for AD-IPA, while the thin film of AD-TMA exhibits a nanorod morphology with the length and width distributed in the ranges 500−800 and 100−120 nm, respectively. The atomic force microscopy (AFM) topographical images also show uniform and continuous film surfaces with root-mean-square (RMS) roughness values of 15.5−23.8 nm over a 2 μm × 2 μm area (Figure S12). Side-view SEM images (Figure S12) suggest that the average thicknesses of these thin films are in the range 1−3 μm. The PXRD patterns of the three cocrystal thin films (Figure 5c and Figure S13) match well with their simulated ones. The differentiation peaks are narrow and strong for AD-IPA and AD-TMA, indicating their high crystallinity. The thin film of AD-IPB shows a relatively lower crystallinity compared with those of AD-IPA and AD-TMA, which is in accordance with the morphology analysis. This can be assigned to the high concentration distribution of AD (with AD-IPB stoichiometry of 2:1). Irradiated under UV light, distinct dark blue, cyan,
green, and orange emission can be observed for thin films of AD, AD-IPA, AD-IPB, and AD-TMA, respectively (Figure 5d). Fluorescence spectra (Figure S14a) of these thin films show a slight blue-shift compared with their bulk crystal samples, which can be assigned to the decrease in the size of the nano-cocrystals. The formation of thin films also leads to a decrease of PL lifetime for AD, AD-IPA, and AD-IPB films, while a slight enhancement for the film of AD-TMA (Figure S14b).

**Up-Converted Fluorescence Emission of Cocrystal Thin Films.** By changing the power of the long-wavelength femtosecond pulse laser at 980 nm, short wavelength up-conversion emissions for all these thin films are observed except for AD. Compared with the fluorescence emission for those of large-scale crystal samples, the as-prepared thin film samples also show a blue-shifted emission, which may be related to the fact that the PL performances of organic materials are highly affected by their size, shape, and morphology. Insets show the changes in up-conversion emission intensity with increasing pump powers. It can be observed that all of these samples exhibit a nearly linear relationship between the up-conversion intensity and pump powers with the slopes of 1.956, 0.837, and 0.983 for AD-IPA,
AD-IPB, and AD-TMA, respectively, indicating that the emission process involves two-photon excited states to the ground state for AD-IPA, while a one-photon process for AD-IPB and AD-TMA. These results reveal that the optical gain can be highly enhanced by the formation of orderly cocrystal thin films.

Optoelectronic Performance of Cocrystal Thin Films. It is well recognized that the efficient separation of photo-generated electron–hole pairs plays a key role in organic semiconductors for optoelectronic applications. Thus, photoelectric responses of AD-IPA, AD-IPB, and AD-TMA were tested in 0.5 M sodium sulfate aqueous solution at a standard three-electrode system, in which the three cocrystal thin film modified ITO serves as the working electrode with a working area of 1.0 cm², a platinum wire electrode as a counter electrode, and Ag/AgCl as a reference electrode. Figure 7a and Figure S15 are the transient photocurrent–time curves with the on–off cycle’s illumination (30 s) in a three-electrode system. It can be observed that photocurrent density \( I_{\text{light}} \) for the AD-TMA thin film electrode sharply increases to 27.79 μA/cm² when the light source is turned on without applying an external potential. The value is 81 and 5 times higher than those of AD-IPB (0.34 μA/cm²) and AD-IPA (5.16 μA/cm²), respectively. By switching off the irradiation, the photocurrent density returns to nearly zero with low dark current \( I_{\text{dark}} = 0.002 \) μA/cm². Generally, the on–off current ratio reveals the

Figure 6. Up-conversion fluorescence spectra of AD-IPA, AD-IPB, and AD-TMA thin films excited by a 980 nm laser under different pump powers. Insets show the changes in intensity with increasing pump powers.
sensitivity of the photoelectric materials to certain irradiation.\(^{31}\) Herein, the maximal current on/off ratio (\(I_{\text{light}}/I_{\text{dark}}\)) is calculated as high as 13 895 for AD-TMA, indicating the extremely high sensitivity of the thin film to light. This value is 2.7 times higher than those of carbon nitride nanotube membrane (5000),\(^{32}\) and 3 orders of magnitude in comparison with the metal–organic framework (MOF) material in electrolyte.\(^{33}\) Meanwhile, this value is also higher than those of inorganic perovskite\(^{34}\) and organic single crystal-based\(^{35}\) state-of-the-art optoelectronic devices. The better photocurrent efficiency of AD-TMA makes it a potential candidate for efficient photoswitches and photodetectors. Despite the photocurrent densities gradually decreasing for AD-IPA and AD-TMA as time increases, the stability test suggests that the maximal photocurrent density presenting in the first on-off cycle can also reappear by additional recycling tests, which exhibit the same decay tendency (Figure S16). Differently, the photocurrent density for AD-IPB keeps constant during the on-off cycle’s illumination. The largest photocurrent of AD-IPA/TMA in the first impulse stems from the existence of the donor–acceptor (D–A) heterojunction, which highly promotes the separation of electron–hole pairs. With the increase in the illumination time, the gradually decreased photocurrent can be related to an electron accumulation balance process. Under the inner electric field, more and more electrons migrate from IPA/TMA to AD. With the accumulation of more electrons, the inner electric field is in turn weakened. Hence, it exhibits inefficient separation of photogenerated carriers, showing decreasing photocurrent. After a long-term release of electrons, it recovers a strong inner electric field for efficient electron migration again. As a result, a large photocurrent can still be observed in the first on-off cycle.

Incident photon-to-current efficiency (IPCE) was measured by monochromatic light irradiation (Figure 7b). AD-TMA shows the highest IPCE value of 3.6% (at 380 nm) among the three cocrystal thin films. Further electrochemical impedance spectroscopy (EIS) performed at the potential of −0.5 V vs Ag/AgCl (Figure 7c) reveals that the charge transfer resistance of AD-TMA is significantly lower than those of AD-IPA and AD-IPB, suggesting the fastest charge transfer rate for AD-TMA. The semiconductor types of three cocrystal thin films were further conducted by Mott–Schottky (M–S) curves. A V-shaped M–S plot indicates a \(p-n\) junction characteristic for AD-TMA thin film, while the positive slope of the M–S plot suggests an \(n\)-type semiconductor for both AD-IPA and AD-IPB (Figure S17). To the best of our knowledge, the fabrication of the molecule level heterojunction cocrystal thin film conducting both holes and electrons has rarely been reported.

From the above results, it is concluded that the high optoelectronic performance of AD-TMA can be assigned to the following aspects: (a) The infinite \(\pi-\pi\) stacking between AD molecules results in a narrow band gap (2.027 eV), decreasing the energy levels for both HOMO and LUMO. Therefore, the solar-energy-harvesting can be extended from the UV to visible region for high photon-to-current transfer ability. (b) The large Stokes’ shift of fluorescence emission from absorption rules out the probability of self-absorption. (c) The high crystallinity of the AD-TMA thin film also benefits the efficient transfer of charge carriers. (d) As for the D–A cocrystals, the integration of electron-donating/electron-accepting molecules provide a way for the effective migration and separation of electron–hole pairs, since the electric field between carboxyl groups of TMA and AD molecules can highly enhance the separation efficiency of charge carriers. The
photogenerated electrons migrate along the continuous AD π-conjugated chains with long-range π electron delocalization, while the holes transfer along the outside TMA molecules.\textsuperscript{36,37} As a result, it presents an alternating arrangement of electron and hole transport layers at the molecule level (Figure 7d). The charge density distribution (Figure S18) reveals that the deprotonated carboxyl anions of TMA are electron accumulation, and protonated AD cations are electron depletion. The photogenerated electron can directly transfer from the carboxyl groups to the AD π-conjugated chain. The holes prefer to migrate between the carboxyl groups. Herein, the high-order π-conjugated chains provide a large electron channel for efficient charge transport; the internal electric field formed between the TMA anion layer and AD cation layer promotes the separation efficiency of charge carriers. Therefore, the rational design and construction of cocrystals could effectively tailor the semiconductor behaviors and types for molecule-based thin films.

\section*{CONCLUSION}

In summary, new types of acridine (AD) cocrystals were fabricated as models to illustrate the tuning of photofunctional and electronic properties of molecular solids. The template effect of different substituents on the coformer IPA derivatives could highly modify the molecular arrangement of AD in the cocrystals, resulting in an adjustable energy level and multicolor emission from blue to orange-yellow. The instantaneous and reversible angle-dependent polarized emission of AD-IPB can be potentially used in displays, data storage, and color filters. Furthermore, a facile and fast crystallization-deposition process has been developed to construct orderly thin films of cocrystals, which show tunable up-conversion luminescence and semiconductor properties. The AD-TMA thin film exhibits an obvious enhancement of optoelectronic performance, by virtue of molecular heterojunction assembled by the alternating arrangement of π-conjugated AD electronic acceptor layers and TMA electronic donor layers, which provides an efficient way for mobility and separation of electron–hole pairs. To the best of our knowledge, this work highlights the first examples of cocrystal thin films with tunable p/n semiconductor performances for photon-to-current conversion. It is anticipated that the fast crystallization-deposition of cocrystal thin films can vastly open up their practical applications in various luminescent and optoelectronic fields.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acscentsci.0c00447.

Materials, methods, experimental details, characterization of new compounds, crystal structures, PXRD, TGA, photoluminescent spectra, and photoelectric performance (PDF)

\subsection*{AUTHOR INFORMATION}

\textbf{Corresponding Authors}

Dongpeng Yan — College of Chemistry, Beijing Normal University, Beijing Key Laboratory of Energy Conversion and Storage Materials, Beijing 100875, P. R. China; \textsuperscript{a}orcid.org/0000-0001-8261-154X; Email: yandp@bnu.edu.cn

Lu-Fang Ma — College of Chemistry and Chemical Engineering, Luoyang Normal University, Henan Province Function-Oriented Porous Materials Key Laboratory, Luoyang 471934, P. R. China; \textsuperscript{b}orcid.org/0000-0002-5601-6437; Email: mazhuxp@126.com

\textbf{Authors}

Xiao-Gang Yang — College of Chemistry and Chemical Engineering, Luoyang Normal University, Henan Province Function-Oriented Porous Materials Key Laboratory, Luoyang 471934, P. R. China; College of Chemistry, Beijing Normal University, Beijing Key Laboratory of Energy Conversion and Storage Materials, Beijing 100875, P. R. China; \textsuperscript{a}orcid.org/0000-0002-0690-0355

Zhi-Min Zhai — College of Chemistry and Chemical Engineering, Luoyang Normal University, Henan Province Function-Oriented Porous Materials Key Laboratory, Luoyang 471934, P. R. China

Xiao-Min Lu — College of Chemistry and Chemical Engineering, Luoyang Normal University, Henan Province Function-Oriented Porous Materials Key Laboratory, Luoyang 471934, P. R. China

\textbf{Complete contact information is available at:} https://pubs.acs.org/10.1021/acscentsci.0c00447

\section*{Notes}

The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}

This work was supported by the National Natural Science Foundation of China (Grants 21971100, 21771021, 21771097, and 21822501), the Key Scientific Research Projects of Higher Education of Henan Province (Grant 20A15000S), the Fok Ying-Tong Education Foundation (Grant 171008), and Beijing Nova Program (xx2018115).

\section*{REFERENCES}

(1) Dong, H.; Zhu, H.; Meng, Q.; Gong, X.; Hu, W. Organic Photoresponse Materials and Devices. \textit{Chem. Soc. Rev.} 2012, 41, 1754–1808.

(2) Ye, H.; Liu, G.; Liu, S.; Casanova, D.; Ye, X.; Tao, X.; Zhang, Q.; Xiong, Q. Molecular Barrier Enhanced Aromatic Fluorophores in Co- Crystals with Unity Quantum Efficiency. \textit{Angew. Chem., Int. Ed.} 2018, 57, 1928–1932.

(3) Day, R. W.; et al. Single Crystals of Electrically Conductive Two- Dimensional Metal-Organic Frameworks: Structural and Electrical Transport Properties. \textit{ACS Cent. Sci.} 2019, 5 (12), 1959–1964.

(4) Chen, R. X.; Aquino, A. J. A.; Sue, A. C. H.; Niehaus, T.; Lischka, H. Characterization of Charge Transfer in Excited States of Extended Clusters of \textpi-Stacked Donor and Acceptor Complexes in Lock-Arm Supramolecular Ordering. \textit{J. Phys. Chem. A} 2019, 123, 4532–4542.

(5) Han, J.; Yang, D.; Jin, X.; Jiang, Y.; Liu, M.; Duan, P. Enhanced Circularly Polarized Luminescence in Emissive Charge-Transfer Complexes. \textit{Angew. Chem., Int. Ed.} 2019, 58, 7013–7019.

(6) Wang, Y.; Sun, L.; Wang, C.; Yang, F.; Ren, X.; Zhang, X.; Dong, H.; Hu, W. Organic Crystalline Materials in Flexible Electronics. \textit{Chem. Soc. Rev.} 2019, 48, 1492–1530.

(7) Wang, C.; Dong, H.; Jiang, L.; Hu, W. Organic Semiconductor Crystals. \textit{Chem. Soc. Rev.} 2018, 47, 422–500.

(8) Sun, L.; Wang, Y.; Yang, F.; Zhang, X.; Hu, W. Cocryltron Engineering: A Collaborative Strategy Toward Functional Materials. \textit{Adv. Mater.} 2019, 31, 1902328.

(9) Yu, W.; Wang, X. Y.; Li, J.; Li, Z. T.; Yan, Y. K.; Wang, W.; Pei, J. A Photoconductive Charge-Transfer Crystal with Mixed-Stacking Donor-Acceptor Heterojunctions within the Lattice. \textit{Chem. Commun.} 2013, 49, 54–56.
(10) Yan, D.; Evans, D. G. Molecular Crystalline Materials with Tunable Luminescent Properties: from Polymorphs to Multi-Component Solids. *Mater. Horiz.* 2014, 1, 46–57.

(11) Li, S.; Yan, D. Two-Component Aggregation-Induced Emission Materials: Tunable One/Two Photon Luminescence and Stimuli-Responsive Switches by Co-Crystal Formation. *Adv. Opt. Mater.* 2018, 6, 1870076.

(12) Sun, L.; Zhu, W.; Yang, F.; Li, B.; Ren, X.; Zhang, X.; Hu, W. Molecular Cocrysals: Design, Charge-Transfer and Optoelectronic Functionality. *Phys. Chem. Chem. Phys.* 2018, 20, 6009–6023.

(13) Jin, J.; Long, G.; Gao, Y.; Zhang, J.; Ou, C.; Zhu, C.; Xu, H.; Zhao, J.; Zhang, M.; Huang, W. Supramolecular Design of Donor-Acceptor Complexes via Heteroatom Replacement Towards Structure and Electrical Transporting Property Tailoring. *ACS Appl. Mater. Interfaces* 2019, 11, 1109–1116.

(14) Cui, Q.; Jiang, L.; Zhang, C.; Zhao, Y.; Hu, W.; Yao, J. Coaxial Organic p-n Heterojunction Nanowire Arrays: One-step Synthesis and Photoelectric Properties. *Adv. Mater.* 2012, 24, 2332–2336.

(15) Chu, M.; Qiu, B.; Zhang, W.; Zhou, Z.; Yang, X.; Yan, Y.; Yao, J.; Li, Y. J.; Zhao, Y. S. Tailoring the Energy Levels and Cavity Structures toward Organic Coocrystal Microlasers. *ACS Appl. Mater. Interfaces* 2018, 10, 42740–42746.

(16) Zhang, J.; Jin, J.; Xu, H.; Zhang, Q.; Huang W. Recent Progress on Organic Donor-Acceptor Complexes Active elements in Organic Field-Effect Transistors. *J. Mater. Chem. C* 2018, 6, 3485–3498.

(17) Yan, D.; et al. A Cocystal Strategy to Tune the Luminescent Properties of Stilbene-Type Organic Solid-State Materials. *Angew. Chem., Int. Ed.* 2011, 50, 12483–12486.

(18) Zhou, B.; Yan, D. Hydrogen-Bonded Two-Component Ionic Crystals Showing Enhanced Long-Lived Room-Temperature Phosphorescence via TADF-Assisted Förster Resonance Energy Transfer. *Adv. Funct. Mater.* 2019, 29, 1807599.

(19) Yan, D. Micro-/Nanostructured Multicomponent Molecular Materials: Design, Assembly, and Functionality. *Chem. - Eur. J.* 2015, 21, 4880–4896.

(20) Salzillo, T.; Campos, A.; Mas-Torrent, M. Solution-Processed Thin Films of a Charge Transfer Complex for Ambipolar Field-Effect Transistors. *J. Mater. Chem. C* 2019, 7, 10257–10263.

(21) Yang, X. G.; Ma, L. F.; Yan, D. F. Facile Synthesis of 1D Organic-Inorganic Perovskite Micro-Belts with High Water Stability for Sensing and Photonic Applications. *Chem. Sci.* 2019, 10, 4567–4572.

(22) Mei, X.; Wolf, C. Formation of New Polymorphs of Acridine Using Dicarboxylic Acids as Crystalization Templates in Solution. *Cryst. Growth Des.* 2004, 4, 1099–1103.

(23) Lemmerer, A.; Admond, D. A.; Esterhuyzen, C.; Bernstein, J. Polymorphic Co-Crystals from Polymorphic Co-Crystal Formers: Competition between Carboxylic Acid···Pyridine and Phenol···Pyridine hydrogen Bonds. *Cryst. Growth Des.* 2013, 13, 3935–3952.

(24) Miao, H.; Yang, J.; Peng, G.; Li, H.; Zhu, Y. Enhancement of the Degradation Ability for Organic Pollutants via the Synergistic Effect of Photoelectrocatalysis on a Self-Assembled Perylene Diimide (SA-PDI) Thin Film. *Science Bulletin* 2019, 64, 896–903.

(25) Dmol³ Module, MS Modeling, Version 2.2; Accelrys Inc: San Diego, 2003.

(26) Penfold, T. J.; Worth, G. A. The Effect of Molecular Distortions on Spin-Orbit Coupling in Simple Hydrocarbons. *Chem. Phys.* 2010, 375, 58–66.

(27) Yang, X.; Lin, X.; Zhao, Y.; Zhao, Y. S.; Yan, D. Lanthanide Metal-Organic Framework Microrods: Colored Optical Waveguides and Chiral Polarized Emission. *Angew. Chem., Int. Ed.* 2017, 56, 7853–7857.

(28) Yan, D.; Yang, H.; Meng, Q.; Lin, H.; Wei, M. Two-Component Molecular Materials of 2,5-Diphenylxazole Exhibiting Tunable Ultraviolet/Blue Polarized Emission, Pump-Enhanced Luminescence, and Mechanochromic Respose. *Adv. Funct. Mater.* 2014, 24, 587–594.

(29) Fan, G.; Yan, D. Two-Component Orderly Molecular Hybrids of Diphenylanthracene: Modulation of Solid-State Aggregation toward Tunable Photophysical Properties and Highly Enhanced Electrochemiluminescence. *Adv. Opt. Mater.* 2016, 4, 2139–2147.

(30) Martínez-Martínez, V.; García, R.; Gómez-Hortigüela, L.; Llano, R. S.; Pérez-Pariante, J.; López-Arbela, I. Highly Luminescent and Optically Switchable Hybrid Material by One-Pot Encapsulation of Dyes into MgAPO-11 Unidirectional Nanopores. *ACS Photonics* 2014, 1, 205–211.

(31) Bucsema, M.; Island, J. O.; Groenendijk, D. J.; Blanter, S. L.; Steele, G. A.; Van der Zant, H. S.; Castellanos-Gomez, A. Photocurrent Generation with Two-Dimensional van der Waals Semiconductors. *Chem. Soc. Rev.* 2015, 44, 3691–3718.

(32) Xiao, K.; Tu, B.; Chen, L.; Hei, T.; Wen, L.; Jiang, L. Photo-Driven Ion Transport for a Photodetector based on an Asymmetric Carbon Nitride Nanotube Membrane. *Angew. Chem., Int. Ed.* 2019, 58, 12574–12579.

(33) Qin, J. H.; Huang, Y. D.; Zhao, Y.; Yang, X. G.; Li, F. F.; Wang, C.; Ma, L. F. Highly Dense Packing of Chromophoric Linkers Achievable in a Pyrene-based Metal-Organic Framework for Photoelectric Response. *Inorg. Chem.* 2019, 58, 15013–15016.

(34) Wang, Y.; Yang, F.; Li, X.; Xu, R.; Liu, P.; Wang, L.; Ji, W.; Xia, J.; Meng, X. Epitaxial Growth of Large-Scale Orthorhombic CsPbBr3 Perovskite Thin Films with Anisotropic Photoresponse Property. *Adv. Funct. Mater.* 2019, 29, 1904913.

(35) Wang, C.; Liu, Y.; Wei, Z.; Li, H.; Xu, W.; Hu, W. Biphase Micro/Nanometer Sized Single Crystals of Organic Semiconductors: Control Synthesis and Their Strong Phase Dependent Optoelectronic Properties. *Appl. Phys. Lett.* 2010, 96, 143302.

(36) Wang, J.; Shi, W.; Liu, D.; Zhang, Z.; Zhu, Y.; Wang, D. Supramolecular Organic Nanofibers with Highly Efficient and Stable Visible Light Photooxidation Performance. *Appl. Catal, B* 2017, 202, 289–297.

(37) Militchko, V. A.; Makarov, S. V.; Yulin, A. V.; Vinogradov, A. V.; Krasilin, A. A.; Ushakova, E.; Dzyuba, V. P.; Hey-Hawkins, E.; Pidko, E. A.; Belov, P. A. Van der waals Metal-Organic Framework as an Excitonic Material for Advanced Photonics. *Adv. Mater.* 2017, 29, 1606034.