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Self-assembly of twisted tetrachloroperylenediimide chromophores into two dimensional brick-stone aggregates: exciton dynamics and photoconductivity[†]

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2D self-assembly has been demonstrated in perylenediimides with twisted chromophores, in which the π - π stacked units are interconnected *via* hydrogen bonding interactions. Spectroscopic measurements and theoretical calculations suggest a weak *J*-type exciton coupling in the assembly. High photoconductivity of the 2D crystal makes it a promising candidate for further opto-electronic applications.

Perylenediimides (PDIs) are particularly attractive building blocks in supramolecular self-assembly,1 because of their exceptional stability and excellent optical properties, and promising applications in opto-electronic devices such as field effect transistors,² waveguides,³ and solar cells.⁴ Chemical modifications of PDIs at either the imide or the bay positions allow versatile tunability of the supramolecular self-assembled architectures. The strong unidirectional π - π interactions in planar PDI cores generally lead to the formation of onedimensional (1D) assemblies with a face-to-face molecular arrangement, such as nanowires, nanobelts, and nanoribbons.⁵ Recently, Würthner et al. reported that core twisting of the perylene backbone by introducing substituents in the bay regions drives the self-assembly of slipped alignment, however, still gives rise to 1D morphology.⁶ On the other hand, two-dimensional (2D) crystal assemblies, which maintain a thickness comparable to their 1D counterparts and meanwhile have a side-length suitable for the device fabrication, might suggest peculiar excitonic properties and be superior for opto-electronic applications,⁷ such as carrier transport,8 electrophotography,9 and photoconductivity studies.¹⁰ To the best of our knowledge, self assembly of



Fig. 1 SEM (a) and TEM (b) images of the TCPDI microsheets (inset shows the corresponding larger magnification view and SAED pattern of microsheets). (c) Predicted morphology based on attachment energies principle, viewing perpendicular to the (002) plane. (d) XRD patterns of TCPDI microsheets and single crystal data.

PDI into 2D structures still remains seldom explored, in spite of its crucial importance in comprehensive understanding of the relationship among molecular packing, exciton dynamics and opto-electronic properties.¹¹

Herein, we synthesized twisted perylene chromophores (TCPDI) with four chlorine substituents at the bay regions (Fig. 1a, inset) and employed a colloid chemical method to induce the 2D self assembly.¹² Spectroscopic measurements and theoretical calculations have revealed distinct exciton dynamics in the assemblies, compared with those commonly observed H-type couplings in the 1D structures for those N-substituted PDIs.¹³ Moreover, these highly fluorescent single crystalline 2D microsheets demonstrate high photoconductivity, suggesting potential applications in opto-electronic devices.

TCPDI was synthesized *via* direct amination of tetrachloroperylene tetracarboxylic acid dianhydride with excess ammonium acetate in propionic acid (Scheme S1, ESI†).¹⁴ Because of the poor solubility of TCPDI in common organic solvents, di-anions that have relatively better solubility were

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used to facilitate the self-assembly of TCPDI in solution *via* a two-step reaction:¹²

$$\Gamma CPDI + Na_2S_2O_4 + 4NaOH \rightarrow Na_2TCPDI^{2-} + 2Na_2SO_3 + 2H_2O$$
(1)

In the first step, di-anions were prepared according to reaction (1) through reduction of TCPDI using dithionite as the reducing agent (Fig. S1, ESI[†]). Second, di-anions were gradually oxidized by oxygen molecules according to reaction (2) to release neutral TCPDI molecules which will undergo 2D assembly:

$$2\text{TCPDI}^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{TCPDI}(\text{s}) \downarrow + 4\text{OH}^- \quad (2)$$

Fig. 1 shows the scanning (SEM) and transmission (TEM) electron microscopy images of the obtained microstructures. 2D microsheets have been observed with tens of micrometers of the edge length (Fig. 1a) and a thickness of around 300 nm (Fig. S2, AFM image, ESI[†]). Moreover, the typical selected area electron diffraction (ED) pattern (Fig. 1b, inset) has clearly validated the single crystalline structure. On the basis of the orthorhombic single crystal data,¹⁵ the square microsheets exhibit a 2D in-plane growth along (110) and (1-10) crystal faces, as pointed out by circled and triangle sets of spots with d-spacing values of 6.2 Å. Additionally, X-ray diffraction (Fig. 1d) has confirmed the formation of single crystalline microsheets with only a sequence of peaks corresponding to (002) crystal planes. Theoretical calculation (Fig. 1c) using growth morphology algorithm also anticipates a sheet-like thermodynamic stable shape. The lowest attachment energy obtained for the (002) face (Table S1, ESI[†]) suggests that it will be prominent in the crystal morphology, since the growth rate of the crystal face is assumed to be proportional to its magnitude of attachment energy. 2D π - π stacking along (110) and (1-10) faces with larger attachment energies (*i.e.*, larger growth rates) has also been clearly revealed in this calculated morphology, in consistence with the ED result in Fig. 1b. Besides, Fig. 1c (red arrow) shows the direction of closet intermolecular contact (hydrogen bonding) between imide hydrogen and carbonyl oxygen with a separation of 2.86 Å (Fig. S3a, ESI[†]). These hydrogen bonding interactions advance the growth along a-axis and would result in different excitonic coupling behavior compared to those N-substituted PDIs, as we will discuss below. Therefore, the growth of the TCPDI microsheets demonstrates a hydrogen bonding assisted $\pi - \pi$ stacking of the twisted perylene chromophores into a 2D polymer chain like structure, which obviously will provide us with good opportunities to explore its distinctive exciton properties.

Fig. 2a shows the absorption and emission spectra of TCPDI microsheets as well as monomer tetrahydrofuran (THF) solution. The microsheets exhibit a red-shifted absorption peak centered at 603 nm, compared with that of the monomer (508 nm, Table 1). Concomitantly, they also display a strong fluorescence (Quantum yield: 5%) with small stokes shift (maximum at 650 nm) as shown in Fig. 2a. In addition, as shown in Fig. 2b and Table 1, the monomer emission can be fitted single-exponentially with a lifetime of $\tau_m = 5.44$ ns and so can be the microsheets emission with $\tau_{sheet} = 0.16$ ns. Therefore, an enhanced radiative decay rate with



Fig. 2 (a) Diffuse reflectance absorption spectrum (black line) and fluorescence spectrum (red line) of obtained TCPDI microsheets. Dashed lines show the absorption (black) and emission spectra (red) of monomer solution in THF. (b) Decay and fitted curves of TCPDI monomeric THF solution and microsheets on quartz plate.

 Table 1
 Fluorescence quantum yields and fitting results of the fluorescence decay of TCPDI monomer solution and microsheets

Sample	$\lambda_{abs,max}/nm$	$\lambda_{\rm em,max}/{\rm nm}$	τ/ns	$\Phi_{\mathrm{f}}^{~a}\left(\% ight)$	$k_{\rm f}^{\ b}(\times 10^8)$
Monomer	508	540	5.44	62	1.14
Microsheets	603	650	0.16	5	3.12

^{*a*} The fluorescence quantum yield (Φ) measurements were performed under ambient condition using a relative method for monomer solution and an absolute method for microsheets using an integration sphere (see ESI† for details). ^{*b*} $k_{\rm f}$ was calculated *via* equation: $k_{\rm f} = \Phi_{\rm f}/\tau$.

 $k_{\rm f,sheet} = 3.12 \times 10^8 \text{ s}^{-1}$ is demonstrated for the 2D crystal, compared to that of monomer: $k_{\rm f, m} = 1.14 \times 10^8 \text{ s}^{-1}$.

In order to gain a better insight into the excited states in the TCPDI 2D aggregate, the coupling of molecules is calculated using the Transition-Density-Cube (TDC) Method developed by Fleming et al.¹⁶ Single crystal data (Fig. 3, inset) were used in the calculations. Interestingly, results (Table S2, ESI⁺) show that molecular pairs (1, 1') and (3, 3') along the direction of hydrogen bonding within the same π -stacked layer give out the largest excitonic coupling strength $(-336.76 \text{ cm}^{-1})$, much larger than that of other molecular pairs, such as (1, 2) in the π - π stacking direction and (2, 3) with Van der Waals forces. As we pointed out before, the π - π stacks are interconnected by hydrogen bonding interactions along *a*-axis, thus the largest coupling strength in this direction may indicate the long "headto-tail" J-type aggregation in the crystal,¹⁷ compared to those commonly observed H-type aggregates in N-substituted PDIs. Moreover, as shown in Fig. 3, the ratio of 0-0 to 0-1 emission intensities of the microsheets increases from 1.72 to 2.87 when the temperature decreases from 300 K to 77 K. F. C. Spano demonstrated that in typical J-aggregates, the ratio of the 0-0 to 0-1



Fig. 3 Experimental emission spectra of obtained microsheets measured at 77 K and 300 K. Inset: unit cell of TCPDI single crystal.



Fig. 4 (a) I-V curves measured in dark and under different light intensities, inset shows the photograph of microsheet on two silver electrodes during the test. (b) On–off switching behavior of microsheet based device under a light density of 1.74 mw cm⁻², and an applied bias voltage 15 V.

emission intensities decreases with increasing temperature.^{18a} Thus, in combination with the enhanced radiative decay rate and red-shifted absorption, these may suggest a weak *J*-type coupling in the crystal.¹⁸

The unique photophysical properties of TCPDI microsheet have implied its promising application in photo-to-electric energy conversion. A device configuration shown in Fig. S7a (ESI[†]) was used to monitor the current change upon light illumination for the 2D microsheets. When the light intensity $(P_{\rm in})$ increases from 0.09 mw cm⁻² to 2.34 mw cm⁻², the current within the voltage sweep interval increases accordingly (Fig. 4a), which could be attributed to more photons absorbed by the photoconductor. Additionally, Fig. 4b displays the time response of single TCPDI microsheet, which exhibits a function of switcher when light ($P_{\rm in} = 1.74 \text{ mw cm}^{-2}$) was switched on and off at a constant applied voltage of $V_{\rm sd} = 15$ V, and no fatigue is observed during the whole cycle. The photocurrent $(I_{\rm ph})$ is found to switch promptly with light on and off. By using the equation: $I_{\rm ph} \propto e^{-t/\tau_{\rm d}}$, ¹⁹ we could obtain a decay time constant $\tau_d \approx 423$ ms (Fig. S8, ESI[†]) after the light was turned off. Moreover, the dark current (I_{dark}) was only 5.8 \times 10⁻¹¹ A. Upon 1.74 mw cm⁻² light illumination, the I_{ph} could approach $\sim 5.7 \times 10^{-9}$ A, indicating an on/off ratio of ~ 100 , relatively higher than that reported for a single crystalline inorganic nanowire.²⁰ Given that the average irradiation light is 550 nm, we can estimate the external responsivity (R_{ex}) of the TCPDI microsheet photoconductor to be 0.06 A W⁻¹ at an electric field of $E = 2 \text{ V} \mu \text{m}^{-1}$ via equation $R_{\text{ex}} = I_{\text{ph}}/P_{\text{in}}$,²¹ better than the single polymer-nanowire based photodetector.²² Accordingly, the corresponding external quantum efficiency was determined to be 12% under the same electric field strength (see ESI† for details). This value is larger than those reported for 1D porphyrin rods²³ and PDI based organic nanofibril heterojunctions.²⁴ The obtained high photoconductivity gain may originate from the split of excitons into free charge carriers in pristine organic crystals by bulk traps and bending of excitonic bands near the crystal surface.25

To conclude, 2D single crystalline TCPDI microsheets have been self assembled *via* a colloid chemical reaction method from its dianion. Spectral analysis and theoretical calculations have shown that synergistic 2D π - π stacking of the twisted perylene cores and orientation by the hydrogen bonding in the imide positions together advance the weak *J*-type coupling in the crystal. A high performance photodetector based on TCPDI single microsheet has been fabricated with a fast response, large on/off ratio, and an external quantum efficiency of 12%. Our results suggest a molecular design route to the crystal engineering, thus to modulate its exciton dynamic properties in the solid state to meet the specific demands of device optimization in photon-to-electrical energy conversion.

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