Supporting information for

Self-Assembly of Twisted Tetrachloroperylenediimide Chromophores into Two Dimensional Brick-Stone Aggregate: Exciton Dynamics and Photoconductivity

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All solvents and materials used in the experiments were purchased from common commercial sources and used without further purification unless otherwise stated.

1. Synthesis of the Tetrachloroperylenediimide (TCPDI)

TCPDI was synthesized via direct amination of tetrachloroperylene tetracarboxylic acid dianhydride with excess ammonium acetate in propionic acid as shown in Scheme S1. To a 500ml propionic aicd solution, 2.0 g tetrachloroperylene tetracarboxylic acid dianhydride (3.78 mmol) and 29.0 g ammonium acetate (0.38 mol) were added, and stirred under 140°C for 18h. Maroon precipitates were collected via filtration and washed with dilute hydrochloric acid and DI water for several times, then subjected to vacuum dry. Then powder was transferred to sodium carbonate solution, stirred for 4h to remove excess non-reacted dianhydride. After completely washing away excess sodium carbonate solution with water, the resulted powder was again vacuum-dried overnight. Yield: 1.8g. (90%).

Recrystallization in chloroform and subsequent gradient sublimation in vacuum (350° C) were used to purify the obtained TCPDI raw powder. The collected product in the low temperature region was used for the following experiments and characterization. ¹HNMR (400 MHz, [D₆] DMSO, r.t.): δ 12.19 ppm (s, 2H, NH), 8.50 ppm (s, 4H, Ar-H); MALDI-TOF: 527.8 (calculated 527.9 for C₂₄H₆Cl₄N₂O₄); Elemental analysis: Calculated C 54.58%, H 1.15%, N 5.30%, Cl 26.58%; Found C 53.26%, H 1.15%, N 5.20%, Cl 27.60%

Scheme S1. Synthesis of the Tetrachloroperylenediimide via direct amination



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2. Synthesis of the TCPDI Microsheets

A mixture of 10.0 mg TCPDI powder (0.019 mmol), 174 mg Sodium dithionite (1.0 mmol, excess) and 400 mg solid NaOH pellets (10 mmol) in a 50ml flask were first degassed using Schlenk line, and then filled with argon. After 2~3 cycles, argon was filled in the bottle and 20 ml degassed Acetonitrile was added to the system. The dispersed solution was stirred for 20min under argon protection, and then 5 ml of degassed water was added to the reaction system. Perylenediimides (especially that substituted with chlorine atoms at the bay regions) are fairly electron-deficient dyes and easy to undergo two reversible reductions especially with sodium dithionite, which is capable of donating two electrons. UV-Vis spectrum of di-anion in Figure S1 mainly shows electronic transitions at 650 nm and 590 nm. Partial oxidization of the di-anion shows the presence of the anion with absorption peaks at 750 nm, 910 nm and 1006 nm. These spectral characteristics are in consistence with previous experimental reports and theoretical calculations.¹⁻²



Figure S1. UV-vis spectrum of the as-prepared TCPDI di-anion acetonitrile solution (red line). As for comparison, absorption spectrum of TCPDI monomer THF solution is shown in black line. Blue line corresponds to the absorption spectrum of TCPDI anion which is obtained by first step of oxidation of TCPDI di-anion.

After stopping the agitating, the solution will finally separate into two layers. The upper THF layer containing di-anion was used as stock solution for the following preparation of TCPDI microsheets. Electronic transitions at 590 nm and 650 nm in the absorption spectra are in consistence with typical features of PDI di-anions reported elsewhere.¹ 0.5 ml 0.95 mM di-anion stock solution in acetonitrile was injected to 5 ml ethanol saturated with oxygen under shaking, and after keeping standing still in the dark for several hours, microsheets were obtained respectively as shining yellow precipitates in the tube bottom, and washed with ethanol and collected by centrifugation.



Figure S2. a). Atomic force microscopic (AFM) image of obtained microsheet; b). Corresponding cross-section profile of three pairs (1, 2, 3) indicated in a); c). Step figure of AFM image of the obtained TCPDI microsheets (Note: the Chinese character in Figure S2c should be μm).

3. Theoretical Calculation

The Morphology Growth Calculation:

The morphology growth calculations³ of orthorhombic TCPDI single crystal were performed using the Materials Studio software. The molecular structure is firstly optimized based on the crystal structure using the discover module, and then, the growth morphology with the lattice energy and attachment

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energies of low-index faces were calculated using the method given in reference.⁴ The force fields of COMPASS⁵⁻⁶ are used during the calculation. The growth morphology algorithm is based on the attachment energy method. It relates the growth rate of a given surface to the potential energy per unit cell gained if a new layer of material attaches to the surface in vacuum. The attachment energy, E_{atts} is defined as the energy released on attachment of a growth slice to a growing crystal surface. Thus, the growth rate of the crystal face is assumed to be proportional to its attachment energy by a layer-by-layer mechanism. That is to say, surfaces with attachment energies smaller in magnitude have slower growth rates and will be morphologically important. In this case, (002) face with smaller attachment energy in magnitude will have slower growth rates and be prominent in final crystal morphology. In contrast, (110), (1-10) faces with larger attachment energies in magnitude will have larger growth rates, and therefore be less present in the final crystal surface.

Table S1. Calculated Attachmen	t Energies of D	Different Crystal Faces.
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hkl	d_{hkl}/\AA	$E_{att}(Total)/kcal\cdot mol^{1}$	% Total facet area
{ 0 0 2}	9.44	-51.34	60.07
{ 2 0 0}	7.10	-199.48	8.92
{ 1 1 0}	6.20	-146.10	27.87



Figure S3. a). Packing diagram of single crystal TCPDI via viewing onto the a, b plane, showing one layer within a, b plane. b). Packing diagram of TCPDI single crystal showing the shortest Chlorine-Chlorine contact along the c axis.



Figure S4. FT-IR spectrum of TCPDI crystal powder and single crystalline microsheets.



Figure S5. a). Measurement of torsion angle associated with carbon atoms in the bay region (C12, C11, C8, and C9), and b). dihedral angle in the TCPDI single crystal.



Figure S6. Pitch angle measurement in the single crystal.

Figure S3 indicates the closet intermolecular contact (hydrogen bonding) between imide hydrogen and carbonyl oxygen with a separation of 2.86 Å, as evidenced by large bathochromic shifts of N-H stretch and bend, and C=O stretch in the FTIR spectra (Figure S4). Similar case with other bay substituted perylene diimides,⁷⁻⁸ TCPDI molecule also shows a highly twisted perylene backbone with a dihedral angle of 32.8°, and a torsion angle of 32.1° associated with bay carbon atoms (Figure S5). According to the method of Curtis *et al.*,⁹ the pitch angle was calculated to be 63.4° in the molecular π stacks, while no transverse shift was observed (Figure S6). This twisted PDI backbone induces a 2D π - π stacking within the microsheet plane. Moreover, Figure S3b shows the shortest Chlorine-Chlorine contact (3.33)

Å) in the crystal, smaller than the "sum of the vdw radii" as revealed by commercial available software "Mercury". This would advance the growth along the [001] direction which assembles the in-plane 2D π -stacked layers together. Therefore, the 2D self-assembly of TCPDI reveals a synergistic effect of different weak intermolecular forces in the crystal.

The Coupling Calculation:

The excitonic coupling of molecules is calculated using Transition-Density-Cube(TDC) Method, developed by Flemming.¹⁰ The cube files are calculated by Q-chem4.0 program. In this method, the coupling term is a sum of coulombic interaction between transition densities, as shown in the following equation:

$$J_{coub} = \int d\mathbf{r} \int d\mathbf{r}' \rho_D * (\mathbf{r}) \frac{1}{|r-r'|} \rho_A(\mathbf{r}')$$

Where $\rho_D^{*(r)}$ and $\rho_A^{(r')}$ are the transition density charges at **r** of donor molecule and **r**' of acceptor molecule. Based on this method, we can visualize transition charges distribution map by GaussView 5.0, as shown in Figure S7a. It is obvious that transition charges are not equally distributed over the molecule, but with a positive part (red color) and a negative part (green color) along the long molecular axis (the direction of hydrogen bonding interaction). More importantly, as in the case of other core-tetrasubstituted PDIs⁸ and tetrachlorinated PDIs,¹¹ the twisted perylene core of TCPDI induces conformational chirality, which will induce different directions of transition charges between molecules "1" and "2", "3" and "4" as indicated in Figure S7c. Based on the calculation results, several conclusions can be made as the following:

First, the largest coupling (-336.76cm⁻¹) of molecular pair along the hydrogen bonding direction (i.e., molecular pair (1, 1') with the shortest intermolecular distance) far outweighs others, and would be more useful in helping us understand the exciton dynamics in the aggregates.

Second, as shown in Figure S7b and S7c, although the intermolecular distance between (2, 3) is slightly larger than that of (1, 2), its coupling is slightly larger than that of (1, 2). This is because the

transition charges of molecules "2" and "3" align in the same direction, while opposite for molecules "1" and "2" (Figure S7c). In the opposite configuration, the total negative coupling strength would be partly offset by electronic repulsion from the nearest intermolecular contacts with the same charge.



Figure S7. a). Distribution map of transition charges for TCPDI molecule. b). Single crystal Cell of TCPDI with labeled molecules, and c). Arrows indicate the directions of transition charges defined in the unit cell.

Table S2. Calculated excitonic coupling strength between different adjacent molecules as indicated in Figure 3, Inset in the unit single crystal cell.

Molecular pairs	(1,2)	(3,4)	(1,1')	(3,3')	(2,3)
			(2,2')	(4,4') ^a	
Coupling Strength/cm ⁻¹	-53.45		-336.76		-83.85

^a 2', 4' refer to the identical molecules with 2, 4 along the *a* axis in the neighboring unit cell.

4. Structural and Spectral Characterization:

X-ray diffraction patterns were obtained by measuring samples filtered on 20nm AAO membrane (Whatman, Inc.) using Bruker D8 Focus X-ray powder diffraction photometer.

The steady-state fluorescence measurements were carried out in a 1-cm quartz cell with a HORIBA Jobin Yvon FluoroMax-4 equipped with a red-sensitive R928P photomultiplier. The emission spectra were corrected with instrument factors.

The fluorescence lifetime measurements were carried out on the picosecond time-resolved fluorescence spectrometer. The 800-nm laser pulses generated from a Ti:sapphire regenerative amplifier (Spitfire, Spectra Physics) were sent to an optical parametric amplifier (Spectra Physics, OPA-800CF) and used as the excitation at 488 nm. The pulse energy was about 100 nJ/pulse at the sample. Fluorescence gathered with the 90° geometry was dispersed by a polychromator (250is, Chromex) and collected with a photon-counting type streak camera (C5680, Hamamatsu Photonics). The data detected by digital camera (C4742-95, Hamamatsu) were routinely transferred to PC for analysis with HPDTA software. The spectral resolution was 2 nm, and the temporal resolution was 2-100 ps, depending on the delay time range setting.

The fluorescence quantum yields (Φ_F) of TCPDI THF solution ($\Phi_{mono} = 62\%$) were calculated with dilute solutions (A < 0.05) by the steady-state comparative method using Rhodamine 6G (Ex: 488 nm, 94% in ethanol) as a standard.¹² The following equation was used for the calculation of fluorescence

quantum yield:
$$\Phi = \Phi_s \cdot \frac{I}{I_s} \cdot \frac{OD_s}{OD} \cdot \left(\frac{n}{n_s}\right)^2$$
. For microsheets emission at 650 nm, absolute quantum yield

measurement (LabSphere®, FluoroMax-4, HORIBA Jobin Yvon, PLQY software package) was used and a repeatable value of 5% was obtained. In this experimental setup, it is possible to measure the Photoluminescence Quantum Yields (PLQY) via using the integrating sphere in combination with a commercial fluorimeter. Emission Spectrum including the scattering region of excitation light were measured for both blank and test samples, and these spectra were corrected with instrumental factors to calculate the quantum yield.¹³ Low temperature emission spectrum was obtained by the same fluorimeter using HORIB-FL-1013[®] complete Liquid Nitrogen Dewar Accessory.

Scanning electron microscopy was conducted on Hitachi S4300. Mircosheets casted on copper grid were used for TEM and corresponding SAED measurements (Tecnai G2 F20, FEI). AFM images and height profiles were taken on a Vecco Nanoscope IIIa atom force microscopy. Fourier transform infrared (FT-IR) spectroscopy was carried out on TENSOR-27, BRUKER.

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5. Electric Measurements:

Thermally evaporated silver (50 nm) was chosen as the source and drain electrodes, and 300 nm thermally grown silicon dioxide acts as the dielectric layer with the underlying n doped silicon as the gate electrode. The device was prepared by simply drop-casting microsheets ethanol solution onto the electrode surface and then subjected to vacuum dry. Previously, the SiO₂ surface was modified by a self-assembled monolayer of n-octadecyl trimethoxysilane (OTS) as reported by literature.¹⁴ Photoconductivity measurements were carried out on the device with 5 μ m channel lengths (L) and 50 μ m channel widths (W). The SiO₂ gate dielectric was 300 nm thick with the capacitance per unit area of 10 nF • cm⁻². All measurements were performed at room temperature using a Keithley 4200-SCS semiconductor parameter analyzer. Tungsten lamp was chosen as the light source, and the optical flux can be measured by placing a power meter in the place of the sample. The input optical power is therefore calculated according to the actual area of the tested photoconductor. The external responsivity (*R*_{ex}) is calculated via the following equation at a given voltage bias:

$$R_{ext} = \frac{I_{ph}}{P_{in}}$$

where I_{ph} , P_{in} respectively represent the photocurrent and the input light power density. Therefore, the external quantum efficiency (i.e., the number of excess carriers produced per incident photon) is calculated by the following equation under the same electric field strength:¹⁵

$$\eta_{ext} = R_{ext} \frac{hc}{e\lambda}$$

where *h* is Planck's constant, *c* is the speed of light, *e* is the electronic charge, λ is the wavelength.



Figure S7 a). Schematic illustration of single microsheet based device. b). Plot of photocurrents versus light densities under applied voltage bias 20 V (black), 15 V (red) and 10 V (blue). Inset shows the corresponding fitting of photocurrent versus incident light density under applied constant voltage of 15V using equation: $ln(L) \propto C_2 \times ln(P)$. (C_2 represents the photo-capture coefficient)

The relationship between photocurrent (defined as $I_{ph} = I_{illume} - I_{dark}$) and incident light density (P_{in}) under different applied voltage bias (Figure S7b), can further demonstrate simple power law dependence,¹⁶ $I_{ph} = C_1 \times P^{C2}$, where C_2 corresponds to the photocapture coefficient.¹⁷ Typical fitting of I_{ph} against P_{in} under 15 V applied voltage bias gives C_2 values of 1.16 (Figure S7b Inset), indicating an excellent photocapture in the device.

Photoconductivity involves several processes, including incident light absorption, exciton photogeneration, exciton transport, dissociation and free carriers transportation (carrier trapping, detrapping and recombination). Subsequent to photo-excitation from ground state S_0 to an upper excited state, and rapid radiationless decay to the first excited state S_1 , the formation of geminate pair (charge carrier generation) occurs in competition with radiative (fluorescence) and nonradiative conversion to S_0 . This kind of ionization of the exciton is called intrinsic charge generation, which is responsible for the photoconductivity in the TCPDI microsheet. Bulk traps¹⁸ and bending of excitonic bands near the crystal surface¹⁹ together advance the split of excitons into free charge carriers in pristine organic crystals.



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Figure S8. Single Exponential fitting of the photocurrent decay after turning off the outside

illumination.

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