Electronic supplementary information (ESI) for:

Self-assembly of Octachloroperylenediimide into 1D Rods and 2D Plates by Manipulating the Growth Kinetics for Waveguide Applications

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Contents

1. Materials and experimental details

1) Preparation of the Cl_8-PTCDI 1D rods and 2D plates

The molecule OCPDI was synthesized and purified as previously described.[1] The 1D rods and 2D plates of Cl_8-PTCDI were prepared via a liquid phase self-assembly method. In a typical preparation, 200 μL of 10 mM Cl_8-PTCDI solution in good solvent of dimethyl formamide (DMF) was injected rapidly into 1 mL (3 mL) of methanol as poor solvent, under vigorous sonication. The turbulent mixing of DMF and methanol changes the solubility of the molecule and solvent polarity, inducing the self-assembly of Cl_8-PTCDI molecules. After cooling and aging in closed tubes at room temperature for one hour (ten hours), 1D rods (2D plates) with uniform dimensions were obtained and dispersed in the colloid solutions. The colloid solution was then used to prepare samples for further characterizations by drop-casting onto silicon wafers, copper grids and glass slides.

2) Structure characterization

The morphologies of Cl_8-PTCDI microcrystals were characterized by field-emission scanning electron microscope (HITACHI S-4800) operated at an acceleration voltage of 15 kV. A thin layer of Pt was deposited onto the samples before SEM examination. Cl_8-PTCDI microcrystals casted on copper grid were observed on a JEOL TEM-1011 transmission electron microscope with an accelerating voltage of 100 kV. AFM images and cross section profiles were taken on a Vecco Nanoscope IIIa atom force microscopy. 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 absorption spectra were measured on a Perkin-Elmer Lambda 35 spectrometer with a scanning speed of 240 nm /min and a slit width of 1 nm. The stationary fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer using a right angle configuration. Slits were set to provide widths of 5 nm for both the excitation and the emission monochromators. Cuvettes with a 1 cm path length were used. All spectroscopic measurements were carried out at room temperature.

3) Calculation using Materials Studio

The growth morphologies of Cl_8-PTCDI were calculated by using the Materials Studio software, based on the attachment energy theory[2]. The molecule structure is firstly optimized based on the experimental crystal structure using the Discover module. The geometric and energy calculation were performed using the Forcite and Morphology modules of the Material Studio software[3]. The predicted equilibrium and growth morphologies were shown in Fig. 4 in the manuscript. Moreover, the surface free energies $\gamma_{\{hkl\}}$ and attachment energies of low-index faces have been also calculated as shown in Table 1.

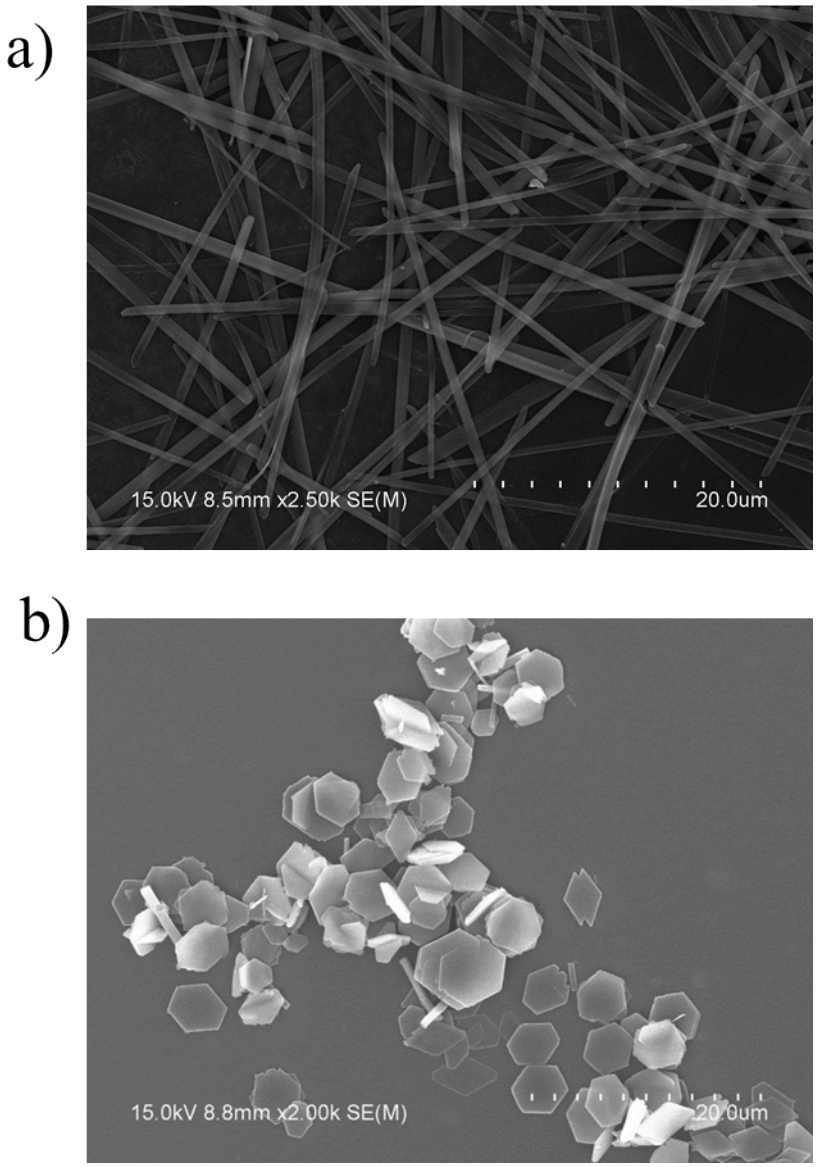
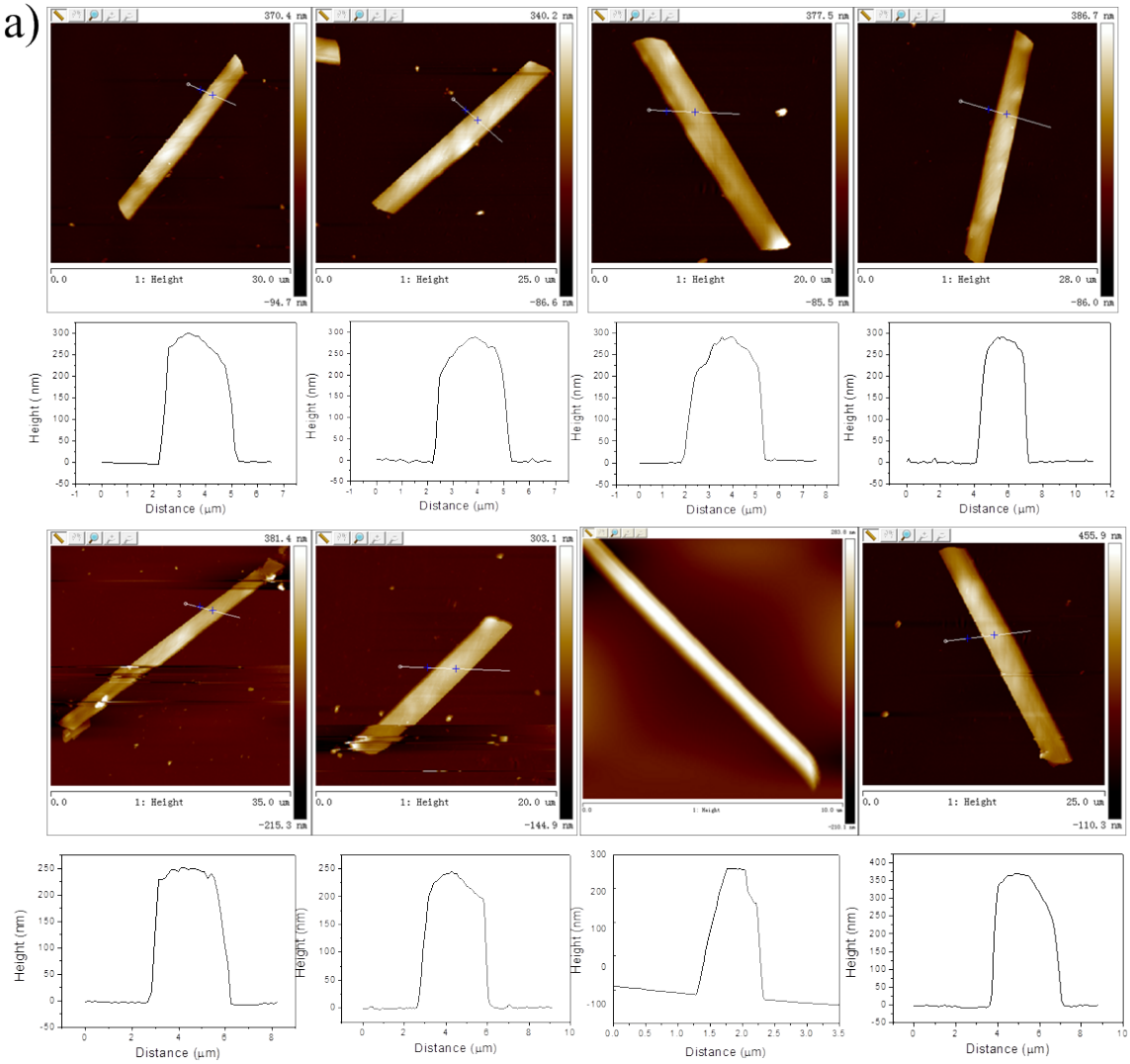


Fig S1. SEM image of Cl_8-PTCDI 1D rods and 2D plates obtained via solution self-assembly.

a)


370.4 nm
0.0
1: Height
30.0 um
-94.7 nm
340.2 nm
0.0
1: Height
25.0 um
-86.6 nm
377.5 nm
0.0
1: Height
20.0 um
-85.5 nm
386.7 nm
0.0
1: Height
28.0 um
-86.0 nm
Height (nm)
Distance (μm)
381.4 nm
0.0
1: Height
35.0 um
-215.3 nm
303.1 nm
0.0
1: Height
20.0 um
-144.9 nm
455.9 nm
0.0
1: Height
25.0 um
-110.3 nm
Height (nm)
Distance (μm)

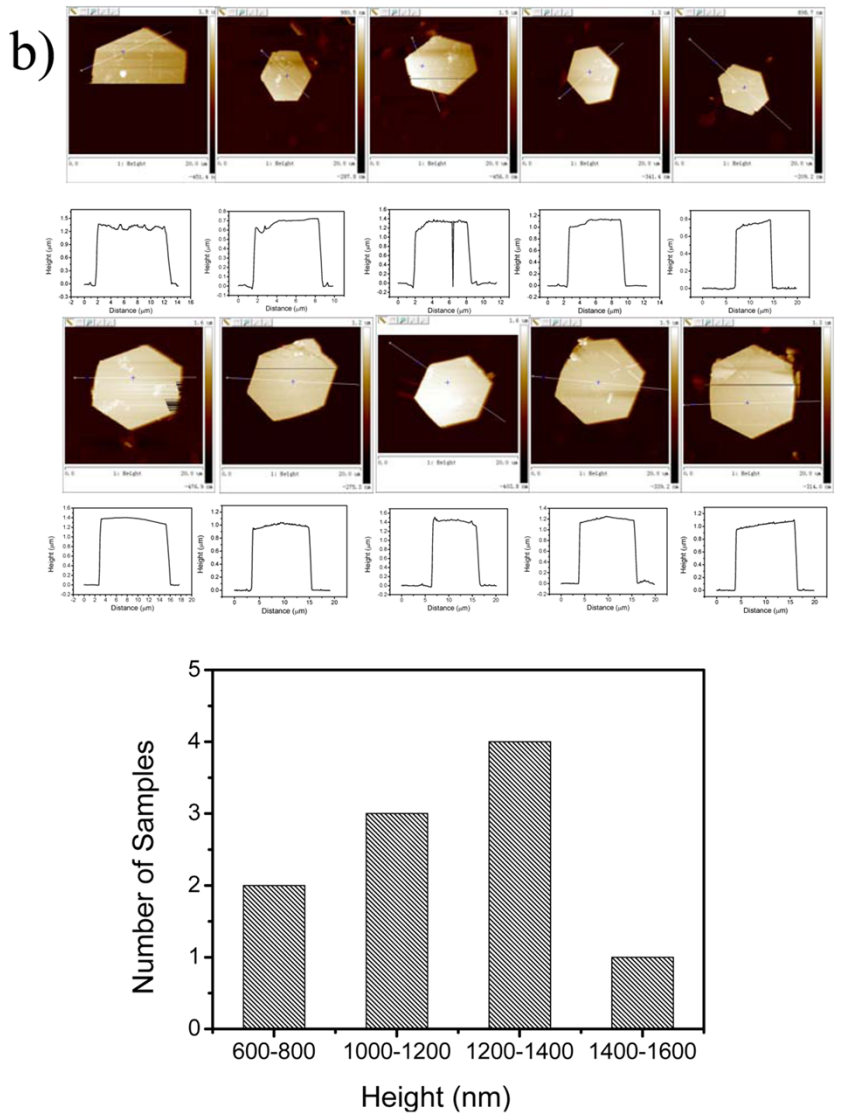


Fig. S2 Atomic force microscopy (AFM) images of a) 1D rods of Cl_8-PTCDI and corresponding cross section profiles with height of 300 ± 80 nm and b) AFM images of 2D plates and the thickness of 2D plate ranges 0.6 to 1.5 μm.

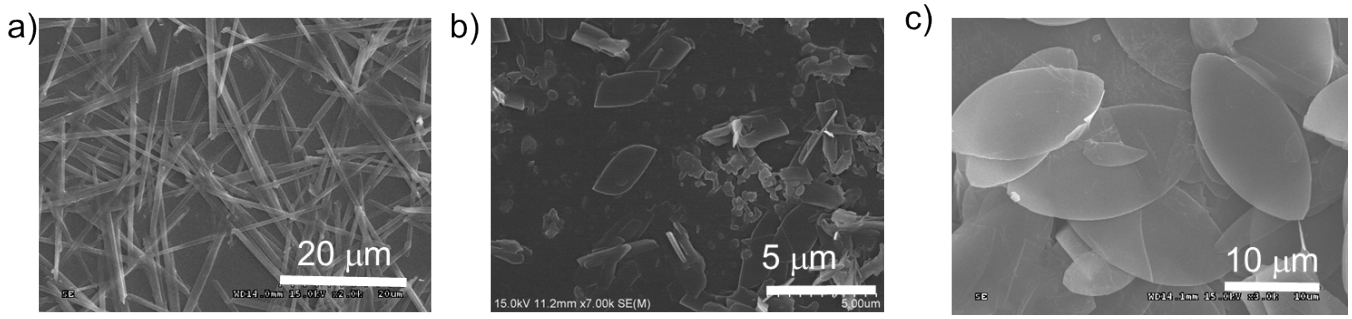


Fig. S3 The morphology evolution of 1D rods to the leaf-like 2D plates after different growth time: a) 1 h; b) 2 days; c) 5 days. Scale bars are labeled in the images.

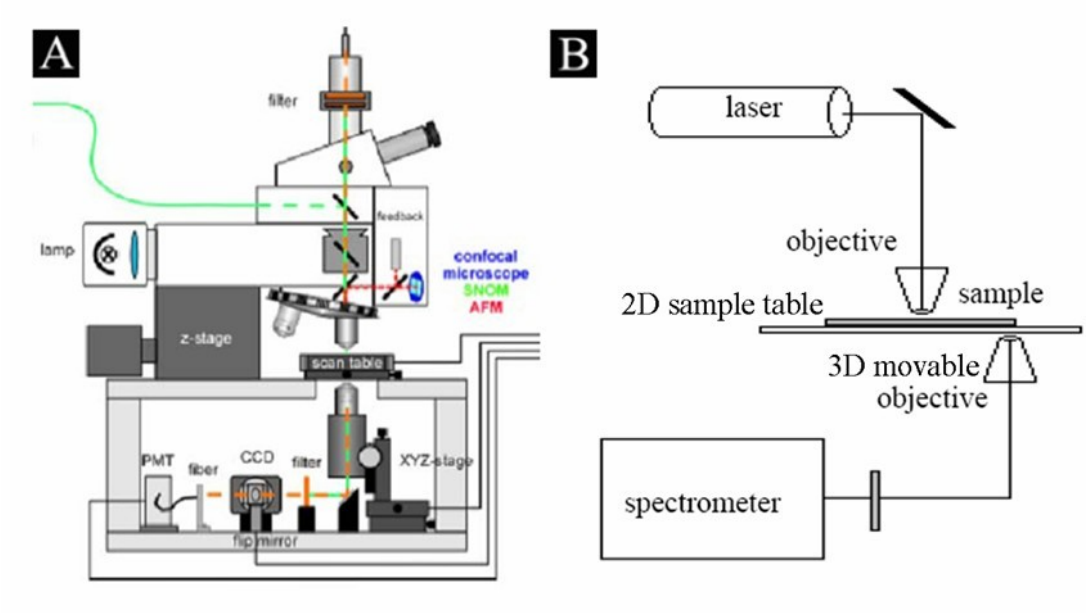


Fig. S4 Schematic demonstration of the experimental setup for the optical characterization

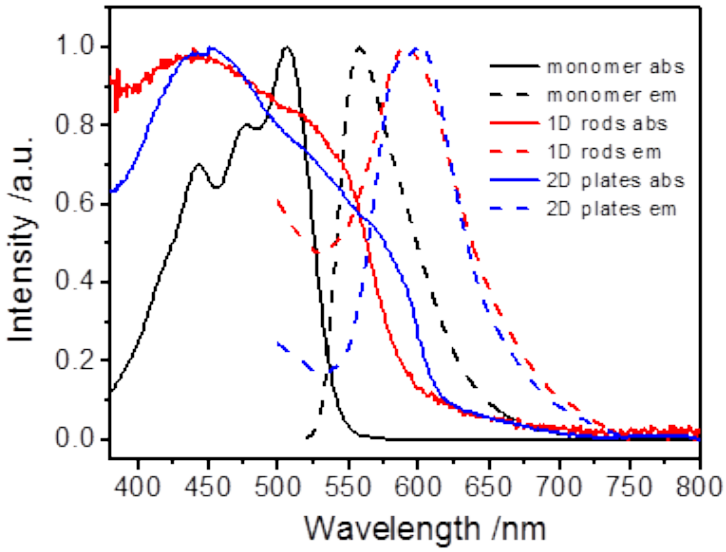


Fig. S5 Normalized steady-state UV-Vis absorption spectra (solid line) and fluorescence emission spectra (dash line) of Cl_8-PTCDI solution in THF (black), 1D rods (red) and 2D plates (blue). The absorption and PL spectra of 1D rods and 2D plates undergoes a red-shift compared to the solution, which results in a large spectral overlap between the absorption and PL spectra.

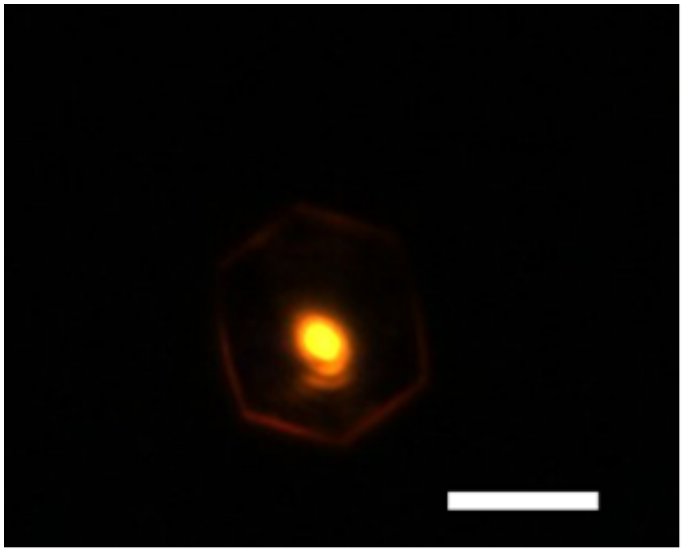


Fig. S6 Dark-field PL image for single crystals by NSOM, with white scale bar of 10 μm. The exaction wavelength of laser was set at 471 nm.

References

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