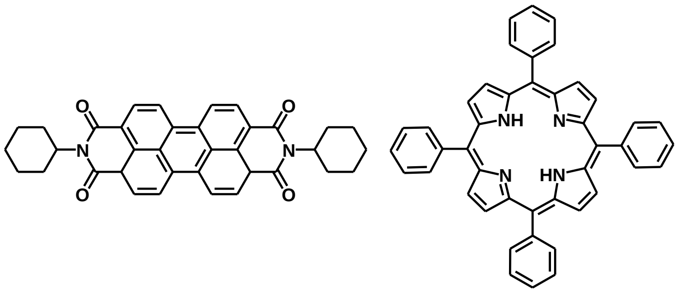
Supporting Information

S1, Fabrication of H_2TPP/CH-PTCDI (p/n) nano-heterojunctions.

The single-crystal p/n heterojunction nanostructures were synthesized by selective crystallization of tetraphenylporphyrin (H_2TPP) and N,N-(dicyclohexyl) perylene-3,4,9,10-tetracarboxylic diimide (CH-PTCDI), given that H2TPP/CH-PTCDI bilayer is a typical example of a p-like/n-like molecular organic semiconductor heterojunction, which is a common component in photocells, LEDs, and other devices. [S1-3] The synthesis of the H_2TPP/CH-PTCDI nano-heterojunctions was performed using the physical vapor transport technique in a two-zone horizontal tube furnace. H_2TPP was put at the furnace center, CH-PTCDI was located at 6 cm upstream of the center and the deposited Si substrate was located the downstream of the center. Before heated, high-purity argon was introduced into the quartz tube with a constant flowing of 60 sccm (standard cubic centimeter per minute) for 40 min to deterge the air inside. The furnace was subsequently heated to 380 °C in 8 min, and maintained at this temperature for 3-5 min. Then, the furnace cooled naturally to room temperature. High-purity argon was still kept at a constant flowing of 60 sccm and a pressure of ~45 Pa overall the preparation process. Separated H_2TPP and CH-PTCDI nanostructures were obtained respectively by putting single sample in the furnace when keeping other experimental conditions consistent.



n **p**

Fig. S1. Molecular structures of CH-PTCDI (n) and H_2TPP (p).

S2, Morphology measurements of H_2TPP/CH-PTCDI nano-heterojunctions.

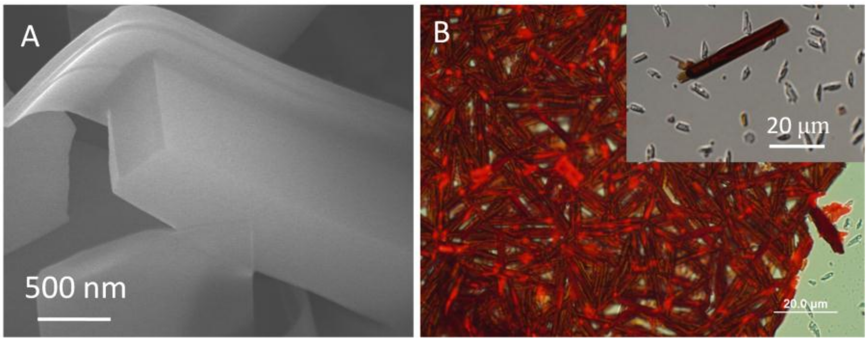


Fig. S2. A) The magnified SEM image of H_2TPP/CH-PTCDI nanostructure. B) The confocal microscopy image of H_2TPP/CH-PTCDI nanostructures, inset is the magnified image.

S3, XRD characterization of H_2TPP/CH-PTCDI nano-heterojunctions.

The XRD patterns of the as-prepared nanostructures are given in **Fig. S3**. The peaks at 2Θ values of 7.03, 8.72, and 17.57 correspond to (010), (100), and (200) crystal planes of H_2TPP single crystals[S4], while the peaks at 2Θ values of 9.62, 12.65, 14.38, 16.40, and 24.17 can be indexed to (020), (100), (030), (004), and (050) crystal planes of CH-PTCDI single crystals[S5]. The *d*-spacings deduced from the XRD spectra, 10.13 Å (100) in H_2TPP, 9.18 Å (020) and 6.98 Å (100) in CH-PTCDI, are consistent with the results obtained from the electron diffraction (inset in **Fig. 2B**). For H_2TPP/CH-PTCDI nanostructures, as its XRD spectrum showed, the (010) and (200) crystal planes belonging to H_2TPP, as well as the (020) crystal plane belonging to CH-PTCDI, were all observed to prove the coexistence of individual phases of CH-PTCDI and H_2TPP.

We expect that this single-crystal H_2TPP/CH-PTCDI nano-heterojunction is formed as a result of interfacial matching parameters such as growth a face with strong attractive interactions (e.g., along the π-π stacking direction) and similar lattice constants at interfaces of the two respect crystal faces.[S6-8] There is a limited mismatch (10.1%) between the lattice parameters of H_2TPP ($d_{020}=1/2*d_{010}=6.28$ Å) and CH-PTCDI ($d_{100}=6.99$ Å) along the π-π stacking direction of this 1D nanostructure, which is important for epitaxial crystallization of H_2TPP and CH-PTCDI.

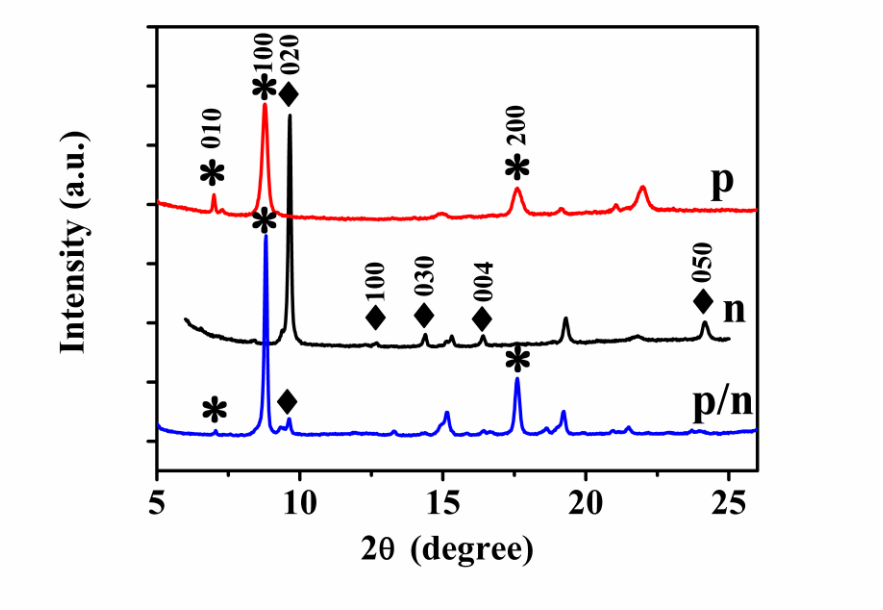


Fig. S3. X-Ray diffraction patterns of CH-PTCDI (n), H_2TPP (p), and H_2TPP/CH-PTCDI (p/n) nanostructures.

S4, Photocatalytic activity evaluation.

For the evaluation of the photocatalyst activity, the catalyst was suspended in an aqueous solution (0.05 g L^{-1}, pH=7) of MB (0.01 mM, 100 mL) and phenol (18 mg/L, 100 mL), respectively, in a Pyrex glass. Before irradiation, the suspension was stirred well in the dark overnight until an adsorption-desorption equilibrium was finally established. A Xe lamp (500 W) equipped with a cut-off filter (λ>400 nm) was used as the light source. At a given time interval of irradiation, small aliquots were withdrawn and filtered through a membrane. MB and phenol photodegradation were analyzed at 665 nm and 270 nm, respectively on a UVIKON XL spectrometer.

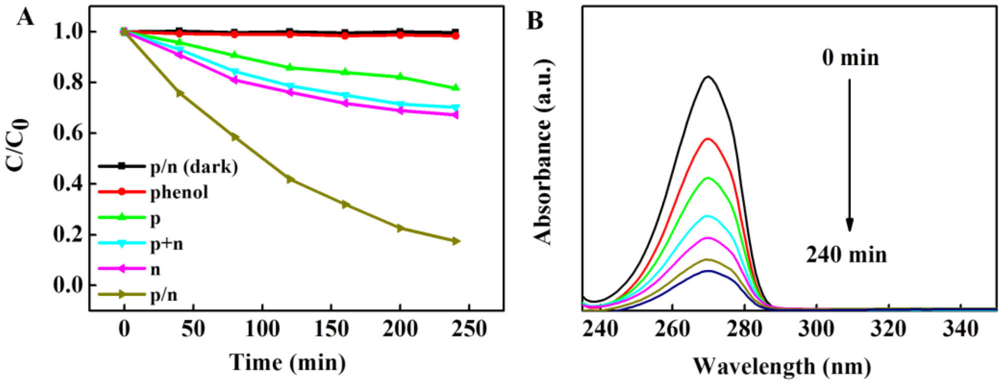


Fig. S4. A) Photocatalytic degradation of phenol with different samples under visible-light irradiation ($\lambda_{irradiation}$>400 nm). B) UV-vis absorption spectra of phenol *vs*. photoreaction time under the action of H_2TPP/CH-PTCDI catalysts ($\lambda_{irradiation}$>400 nm).

References

S1. D. Wöhrle, L. Kreienhoop, G. Schnurpfeil, J. Elbe, B. Tennigkeit, S. Hiller and D. Schlettwein, *J. Mater. Chem.*, 1995, **5**, 1819-1829.

S2. T. Abe, K. Nagai, M. Kaneko, T. Okubo, K. Sekimoto, A. Tajiri and T. Norimatsu, *ChemPhysChem*, 2004, **5**, 716-720.

S3. T. Abe, K. Nagai, S. Kabutomori, M. Kaneko, A. Tajiri and T. Norimatsu, *Angew. Chem. Int. Ed.*, 2006, **45**, 2778-2781.

S4. R. Paolesse, L. Jaquinod, F. Della Sala, D. J. Nurco, L. Prodi, M. Montalti, C. Di Natale, A. D'Amico, A. Di Carlo and P. Lugli, *J. Am. Chem. Soc.*, 2000, **122**, 11295-11302.

S5. Y. Che, X. Yang, K. Balakrishnan, J. Zuo and L. Zang, *Chem. Mater.*, 2009, **21**, 2930-2934.

S6. W. Chen, H. Huang, S. Chen, Y. L. Huang, X. Y. Gao and A. T. S. Wee, *Chem. Mater.*, 2008, **20**, 7017-7021.

S7. F. Zhu, K. Lou, L. Huang, J. Yang, J. Zhang, H. Wang, Y. Geng and D. Yan, *Appl. Phys. Lett.*, 2009, **95**, 203106-203106-203103.

S8. H. Wang, F. Zhu, J. Yang, Y. Geng and D. Yan, *Adv.Mater.*, 2007, **19**, 2168-2171.