Electronic Supporting Information

Facile synthesis of 2,5-dihydroxyterephthalic acid-based charge transfer cocrystal for photoelectric applications

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A. Experimental Section.

1. Materials and general procedures.

Without additional purification, all of the chemicals were of analytical grade and were acquired from commercial sources. Powder X-ray diffraction analysis (PXRD) patterns were collected using Cu K radiation (λ = 1.5418 Å) on a Bruker D8-ADVANCE X-ray diffractometer. Measurements were performed in a 2θ range of 5−50° at room temperature, with steps of 0.02° (2θ) and counting intervals of 0.2 s/step. 40 KV and 40 mA of operational power were used. The C, H, and N elements were analyzed using a Perkin-Elmer 240 elemental analyzer. FT-IR spectrometer by incorporating the samples in KBr disks. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. Thermogravimetric analysis (TGA) experiments were carried out using SII EXStar6000 TG/DTA6300 thermal analyzer from room temperature to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. An UV-3600 plus UV-vis-NIR spectrophotometer from Shimadzu was used to analyze UV-vis absorption spectra. In order to obtain room temperature photoluminescence (PL) spectra and time-resolved lifetime measurements, an Edinburgh FLS1000 fluorescence spectrometer equipped with a xenon arc lamp (Xe900) and a nanosecond flash-lamp (nF900) was used.

Optoelectronic measurements were performed with a CHI 660E electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China) by using Phen-DTPA modified indium tin oxide (ITO) as the working electrode (working area 1.0 cm^2), Ag/AgCl as a reference electrode, platinum wire electrode as a counter electrode. All electrochemical tests were performed at room temperature in 0.5 M Na_2SO_4 solution. The system was conducted in a quartz glass reactor about 50 cm^3, and irradiated by a 300 W Xe lamp. All the cyclic voltammograms (CV) with a scan rate of 50 mV/s, electrochemical impedance spectroscopy (EIS) measurements recorded at the

potential of 0 and -0.5 V potential in the frequency range of 100 kHz to 100 mHz. Transient photocurrent responses with the on–off cycle's illumination and constant potential electrolysis curves with bias potential of 0 and -0.5 V were tested in three-electrode system at ambient pressure and room temperature.

2. Synthesis of Phen-DTPA

Upon mixing equimolar (0.1 mmol) ethanol solutions (2 mL) of DTPA and Phen, light-yellow layered crystals of Phen-DTPA can be obtained in a few minutes. Elemental analysis calcd. (%) for $C_{20}H_{14}N_2O_6$: C 63.49, H 3.73, N 7.40; Found: C 62.92, H 3.91, N 7.73.

3. X-ray crystal structure

Single-crystal X-ray diffraction data for Phen-DTPA was collected at room temperature (293K) on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å). CrysAlisPro[1] was used for the data collection, data reduction and empirical absorption correction. The crystal structure were solved by direct methods, using SHELXS-2014 and least-squares refined with SHELXL-2014 using anisotropic thermal displacement parameters for all non-hydrogen atoms.[2] The crystallographic data for **1** are listed in Table S1 and 2. The CIF file of **1** (CCDC No. 2340776) can be downloaded free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

4. Preparation of working electrode

The ITO (1 × 4 cm^2) substrate was washed by ethanol, and water under ultrasonic processing for about 30 min then dried in natural environment. The powder of the cocrystal complex (10 mg) were added into 1 mL anhydrous ethanol and ultrasonicated for 30 min to form suspension liquid. The working electrodes were prepared by

dropping the above suspension (0.2 mL) onto the surface of the pre-treated ITO by controlling the coating area about 1 cm^2, and allowing it to dry at room temperature.

5. Fabrication of LED device

The powder of the Phen-DTPA cocrystal complex (20 mg) was evenly dispersed in epoxy resin. The mixture was coated on a commercial 365 nm diode chip attached with two electrode, then heated at 100 ^{o}C for 1 hour.

6. Theoretical calculations.

The density functional theory (DFT) calculations were performed based on the crystallographic information file (cif) of the title complex. Perdew-Wang (PW91)[5] generalized gradient approximation (GGA) method was used for the full optimization of initial configuration. The self-consistent field (SCF) converged criterion was within 1.0×10^{-5} hartree atom^{-1} and the converging criterion of the structure optimization was 1.0×10^{-3} hartree bohr^{-1}.

The density functional theory (DFT) and charge density distribution were carried out using Dmol3[3] and CASTEP[4] module in Material Studio software package[5], respectively. The DFT calculations were calculated by the crystallographic information file (cif) of Phen-DTPA directly. While the calculations for CASTEP were performed by removing the symmetry of the crystallographic information file (cif) for the cocrystal. Perdew-Wang (PW91)[5] generalized gradient approximation (GGA) method was used for the full optimization of initial configuration. The self-consistent field (SCF) converged criterion was within 1.0×10^{-5} hartree atom^{-1} and the converging criterion of the structure optimization was 1.0×10^{-3} hartree bohr^{-1}.
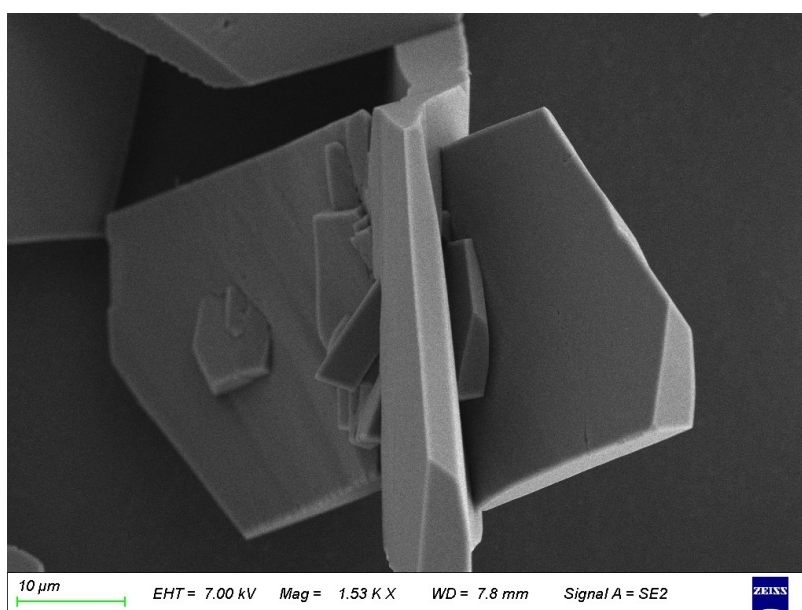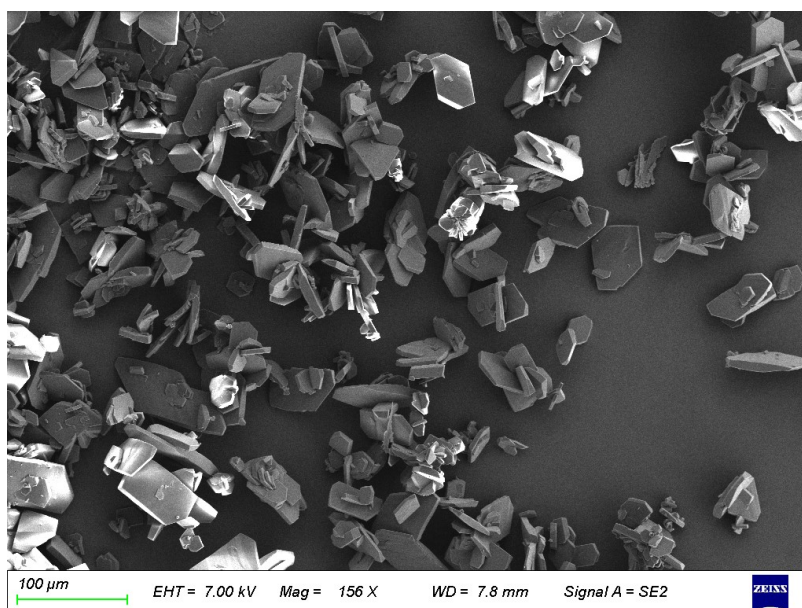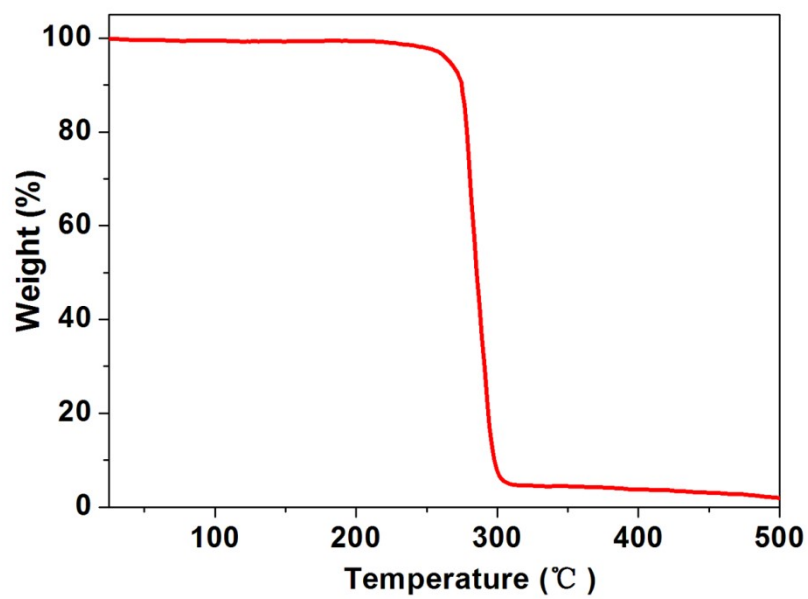
B. Supporting Figures
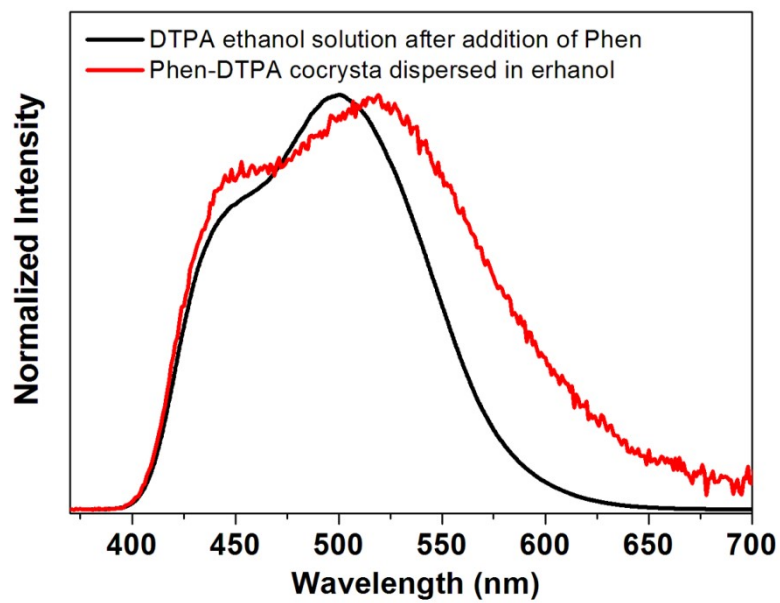
Figure S1. Normalized fluorescence spectra of DTPA ethanol solution after addition of Phen (black) and Phen-DTPA cocrystal dispersed in ethanol.
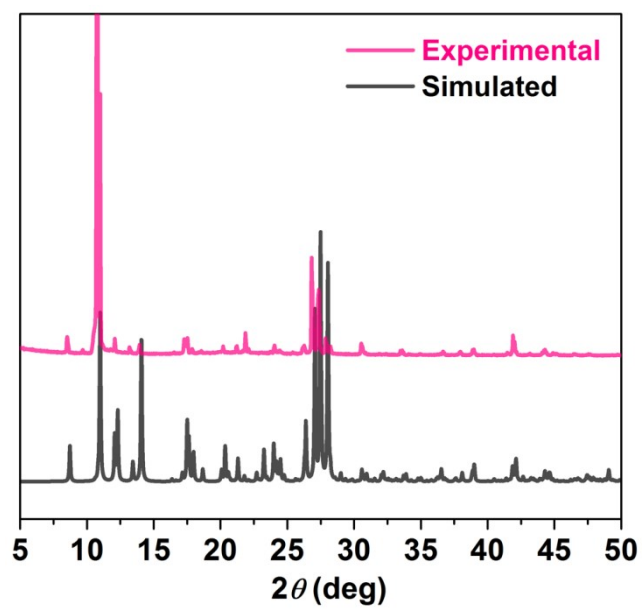
Figure S2. Powder X-ray diffraction patterns (PXRD) of the simulated (black) and as-synthesized (red) title Phen-DTPA cocrystal.
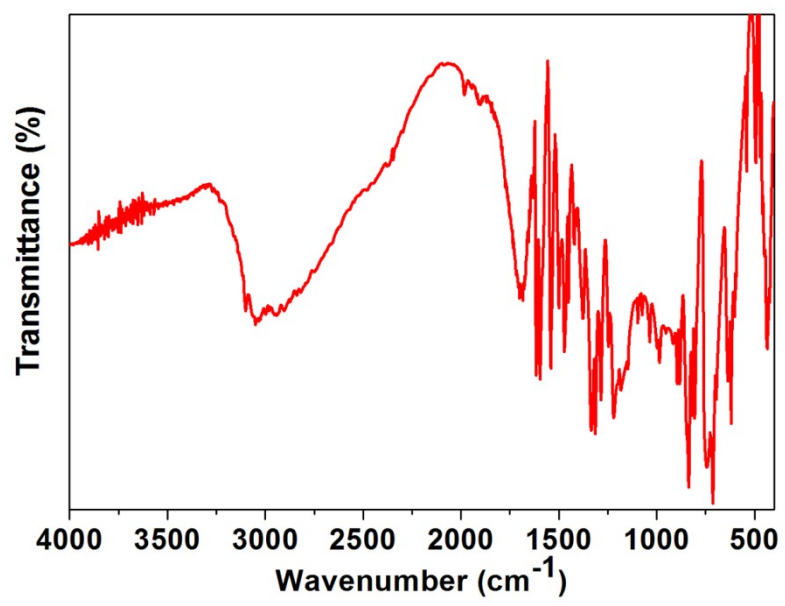
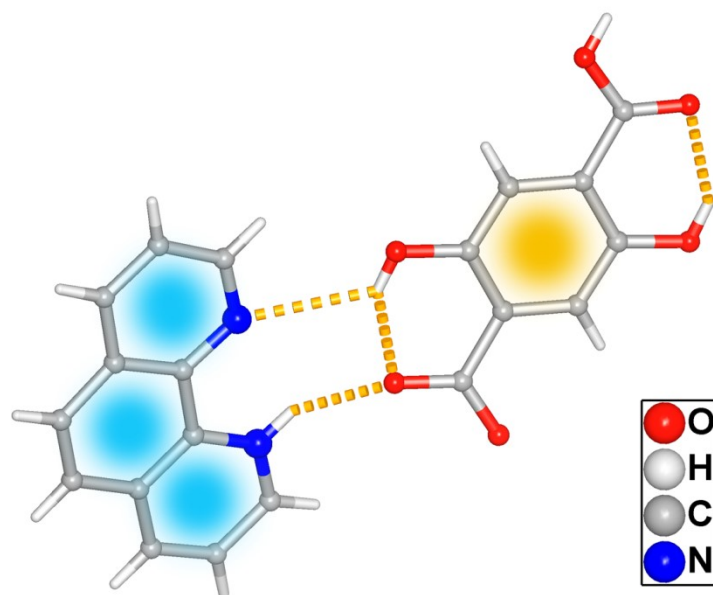**Figure S3.** SEM images of the as-prepared Phen-DTPA cocrystal.

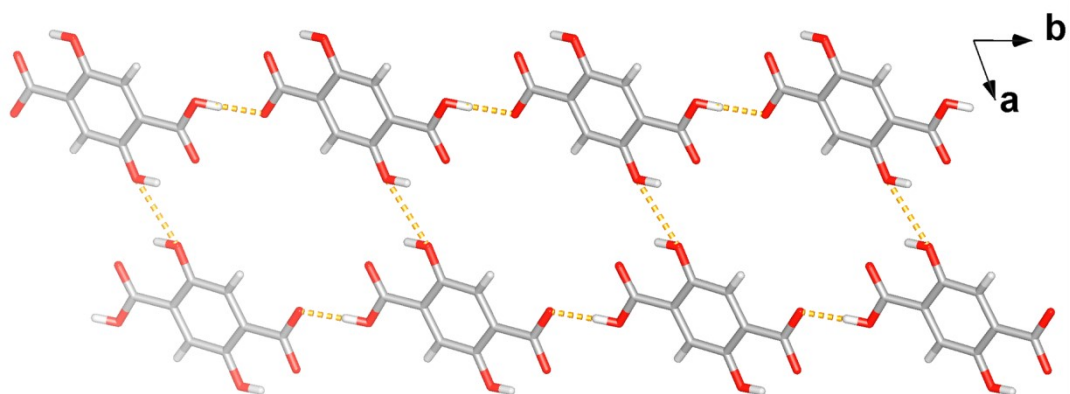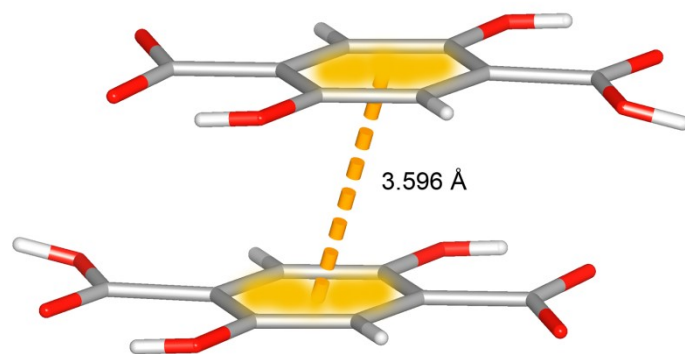**Figure S4.** Thermogravimetric analysis (TGA) curve of Phen-DTPA.
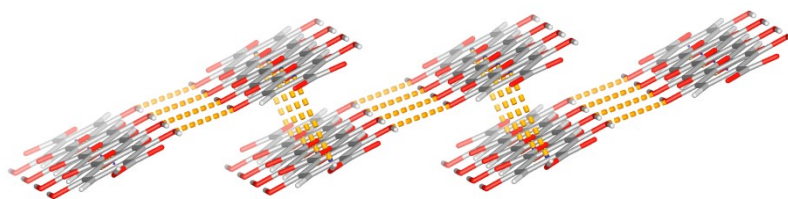
Figure S5. FT-IR spectrum of Phen-DTPA.

Figure S6. View of the asymmetric unit of Phen-DTPA showing inter- and intra-molecular hydrogen bonds.
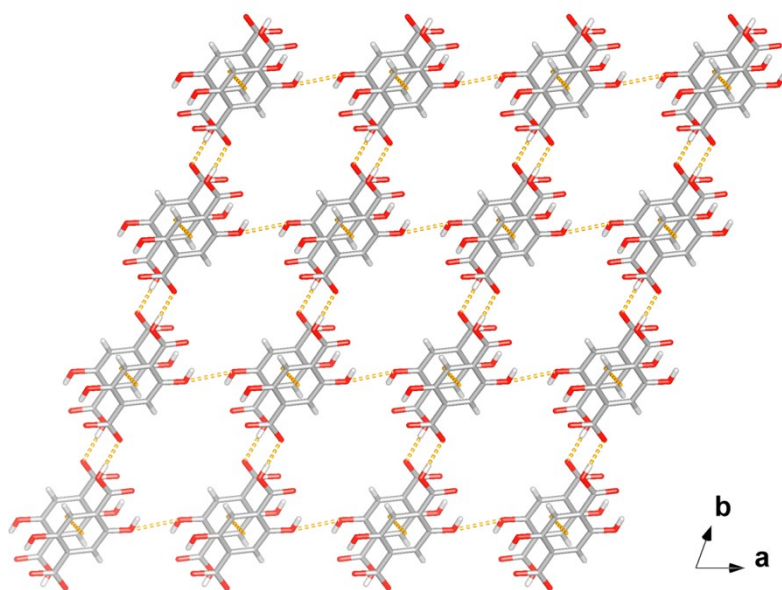
Figure S7. View of 1D chain along *b* direction consisting O-H···O hydrogen bonds interactions between DTPA molecules.

Figure S8. π···π interactions between the phenyl ring of DTPA.
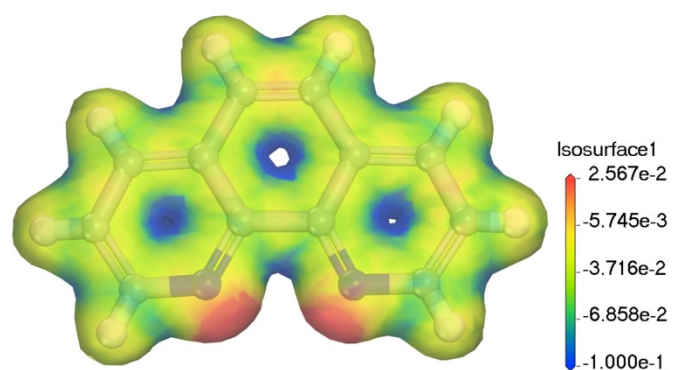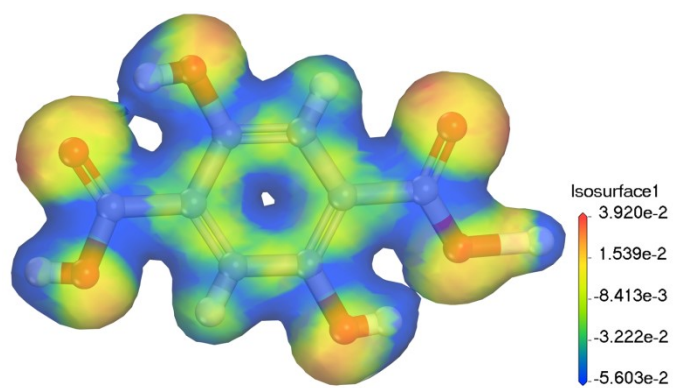
(a)

(b)

Figure S9. View of 2D double layer along *b* (a) and *c* (b) direction via inter-chain π···π interactions between the phenyl ring of DTPA.
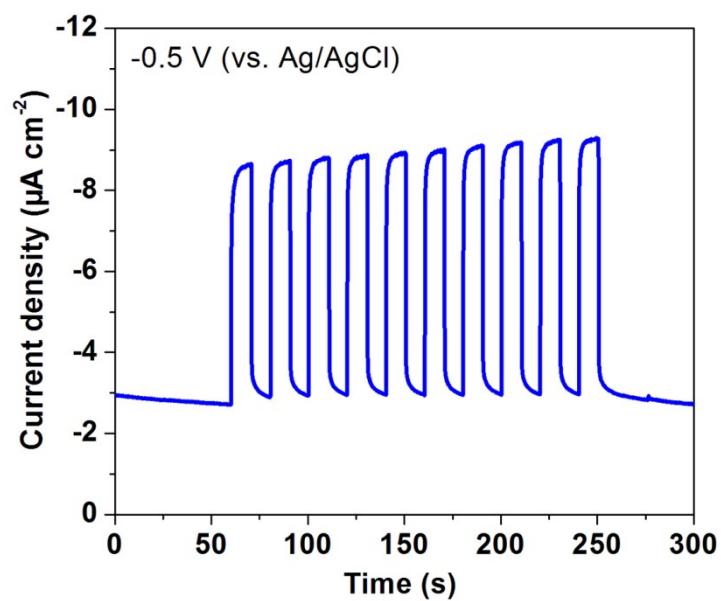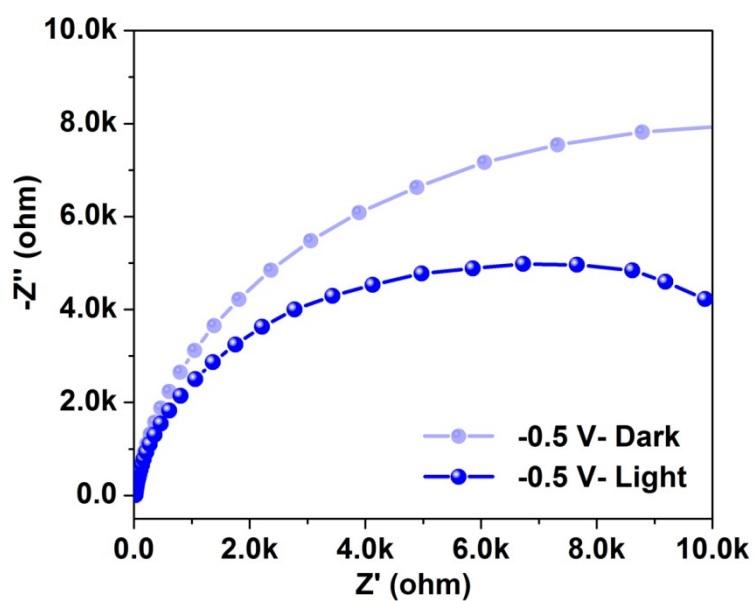
(a)

(b)

Figure S10. Electron density distribution of Phen (b) and DTPA (b). Red and blue iso-surface presents electron accumulation and depletion, respectively.

(a)

(b)

Figure S11. (a) Transient current density-time curve of Phen-DTPA under -0.5 V bias potential. (b) Electrochemical impedance spectroscopy (EIS) Nyquist plots of Phen-DTPA under light and dark states with the addition of -0.5 V bias potential.

C. Supporting Table

Table S1. Crystallographic data and experimental details for **Phen-DTPA**.

Sample	Phen-DTPA
Chemical formula	$C_{20}H_{14}N_2O_6$
Formula weight	378.33
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.0499(8)
b (Å)	9.5985(10)
c (Å)	11.2088(11)
V (Å³)	808.51(16)
$\alpha/\,°$	64.656(10)
$\beta/\,°$	78.043(8)
$\gamma/\,°$	66.903(9)
Z	2
D (g cm⁻³)	1.554
μ (mm⁻¹)	0.117
T (K)	293(2)
R_{int}	0.0244
Goof	1.058
$R_1{}^a (I>2\sigma\,(I))$	0.0594
$wR_2{}^b (I>2\sigma\,(I))$	0.0869

$^aR_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $^bwR_2 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$

D. Supporting References

1. CrysAlisPro, Rigaku Oxford Diffraction, Version 1.171.39.6a.

2. (*a*) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112; (*b*) G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3–8.

3. B. Delley, *J. Chem. Phys.* 2000, **113**, 7756–7764.

4. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne, *Zeitschrift füer Kristallographie* 2005, **220**, 567–570.

5. B. Delley, *J. Chem. Phys.* 1990, **92**, 508–517.