

Hybridization of Thiol-Functionalized Poly(phenylacetylene) with Cadmium Sulfide Nanorods: Improved Miscibility and Enhanced Photoconductivity

*Hai-Peng Xu,^a Bo-Yu Xie,^a Wang-Zhang Yuan,^a Jing-Zhi Sun,^{*a} Feng Yang,^a Yong-Qiang Dong,^{ab} Anjun Qin,^{ab} Shuang Zhang,^a Mang Wang^a and Ben-Zhong Tang^{*ab}*

^a Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

^b Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

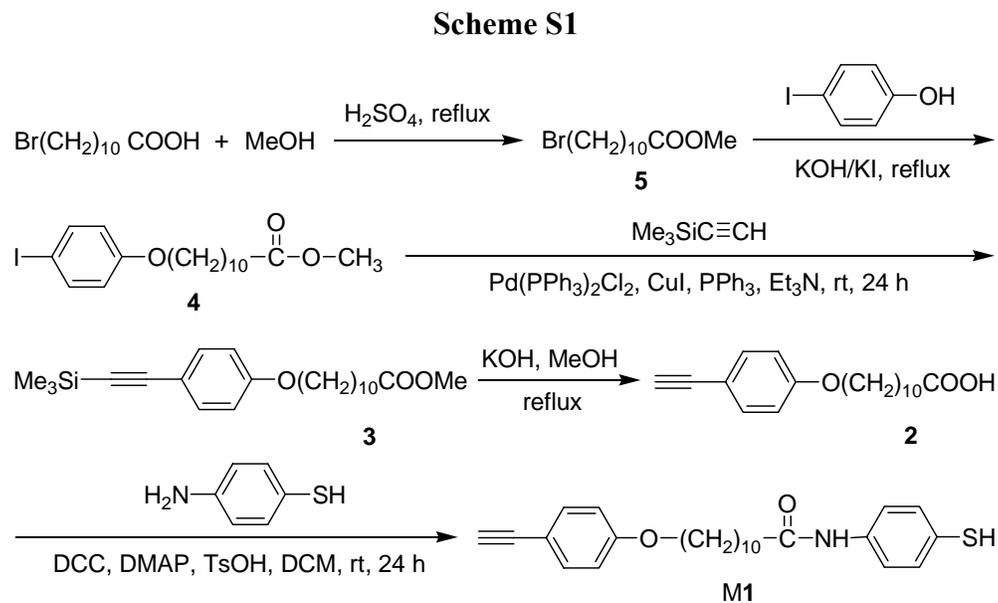
General Information. 11-Bromoundecanoic acid, bis(triphenylphosphine)palladium(II) chloride, phenylacetylene (PA), trimethylsilylacetylene, copper(I) iodide, 4-iodophenol, trimethylsilane (TMS), 4-aminothiophenol, 4-toluenesulfonic acid (TsOH), 1,3-dicyclohexylcarbodiimine (DCC), 4-(dimethylamino)pyridine (DMAP), potassium hydroxide, potassium iodide and cadmium chloride were purchased from commercial sources such as Acros, Aldrich and TCI in high purities and were used as received without further purification. Triethylamine (TEA) was distilled and dried over KOH. Dichloromethane (DCM) was dried over 4 Å molecular sieves and distilled over calcium hydride. Acetone and DMSO were dried over 4 Å molecular sieves immediately prior to use.

IR spectra were obtained on a Vector 22 Fourier transform infrared spectrometer. NMR spectra were measured on a Mercury plus NMR 300 MHz spectrometer. Mass spectra were recorded on a Bruker Daltonics Esquire 3000 plus spectrometer. UV-vis absorption spectra were taken on a Varian CARY 100 Biospectrometer. Fluorescence spectra were recorded on a Hitachi 4500 spectrophotometer.

Molecular weights (M_w and M_n) and polydispersity indexes (M_w/M_n) of the polymers were estimated in THF by a Waters Associates gel permeation chromatography (GPC) system. A set of monodisperse polystyrene standards covering molecular weight range of 10^3 – 10^7 was used for the molecular weight calibration.

Thermogravimetric analysis (TGA) was carried out on a Pyris 6 thermogravimetric analyzer (Perkin Elmer). A sample of ~3 mg was heated at the rate of 10 °C/min under a constant flow of dry nitrogen. Information about the shape and dispersion of the CdS nanorods and the hybrid were obtained from a JSM-5510 scanning electron microscopy (SEM), a JEM-200CX transmission electron microscope (TEM), and a Philips CM200 high-resolution TEM (HRTEM) coupled with an energy dispersive X-ray (EDX) analyzer.

Monomer Synthesis. The thiol-containing monomer (M1) was prepared according to the synthetic route shown in Scheme S1. Detailed experimental procedures are given below.



Preparation of Methyl 11-Bromoundecanoate (5). Into a 500mL round-bottom flask equipped with a reflux condenser were added 11-bromoundecanoic acid (13.3 g, 50 mmol) and 200 mL of methanol. With gentle stirring, 5 mL of concentrated sulfuric acid was added dropwise into the flask. The reaction mixture was refluxed for 2 h. After cooling the content to room temperature, calcium carbonate was

added gradually to neutralize the excess acid. The solvent was removed with a rotary evaporator. The residue in the flask was re-dissolved in 200 mL of chloroform and washed with deionized water. The organic layer was dried over 5 g of magnesium sulfate. After filtration of the solids and removal of the solvent, the crude product was purified on a silica gel chromatography column using chloroform as eluent. Evaporation of the solvent afforded 11.9 g of **5** as a colorless liquid (yield: 85.2%). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 3.7 (s, 3H, OCH_3), 3.4 (m, 2H, CH_2Br), 2.3 (m, 2H, $\text{CH}_2\text{CO}_2\text{CH}_3$), 1.9 (m, 2H, $\text{CH}_2\text{CH}_2\text{Br}$), 1.6 (m, 2H, $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$), 1.5–1.3 (m, 12H, $(\text{CH}_2)_6$).

Preparation of Methyl 11-(4-Iodophenoxy)undecanate (4). In a 250 mL round-bottom flask equipped with a reflux condenser, 5 g (22.7 mmol) of 4-iodophenol, 1.3 g (23.2 mmol) of potassium hydroxide, and 5.7 g (34.3 mmol) of potassium iodide were dissolved in 100 mL of acetone/DMSO mixture (9:1 by volume) with gentle stirring. To the mixture was added 6.3 g (22.6 mmol) of **5**, and the content was then refluxed for 24 h. The solids were removed by filtration, and the filtrate was evaporated under reduced pressure. The crude product was dissolved in 50 mL of DCM, and the resultant solution was washed with 50 mL of deionized water. The aqueous phase was extracted twice with 50 mL of DCM. The combined organic layers were dried over 5 g of magnesium sulfate. The crude product was condensed and purified on a silica gel column using chloroform as eluent. Evaporation of the solvent gave 7.5 g of a pale yellow solid of **4** (yield: 79.3%). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.5 (m, 2H, aromatic protons *meso* to $-\text{O}-$), 6.7 (m, 2H, aromatic protons *ortho* to $-\text{O}-$), 3.9 (m, 2H, PhOCH_2), 3.7 (s, 3H, OCH_3), 2.3 (m, 2H, $\text{CH}_2\text{CO}_2\text{CH}_3$), 1.8 (m, 2H, $\text{PhOCH}_2\text{CH}_2$), 1.6 (m, 2H, $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$), 1.5-1.3 (m, 12H, $(\text{CH}_2)_6$).

Preparation of Methyl 11-[(4-Trimethylsilylethynyl)phenoxy]undecanate (3). Into a 100 mL, two-necked, round-bottom flask were added 140 mg (0.2 mmol) of bis(triphenylphosphine)palladium(II) chloride, 10 mg (0.05 mmol) of copper(I) iodide, and 40 mL of a TEA solution of **4** (4.18 g, 10 mmol) under nitrogen. After all the catalysts were dissolved, 1.7 mL (12 mmol) of trimethylsilylacetylene was injected into the flask, and the mixture was stirred at room temperature for 12 h. The solids formed during the reaction were removed by filtration and washed with TEA. The filtrate was then evaporated

with a rotary evaporator. The residue in the flask was redissolved in 100 mL of chloroform and washed with 50 mL of hydrochloric acid (1 M) and then 50 mL of deionized water. The crude product was condensed and purified on a silica gel column using chloroform as eluent. Removal of the solvent gave 3.6 g of a light yellow solid of **3** (yield: 92.7%). IR (KBr), ν (cm⁻¹): 2158 (w, C≡C), 1733 (s, C=O). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.4 (m, 2H, aromatic protons *meso* to –O–), 3.9 (m, 2H, PhOCH₂), 3.7 (s, 3H, OCH₃), 2.3 (m, 2H, CH₂CO₂CH₃), 1.8 (m, 2H, PhOCH₂CH₂), 1.6 (m, 2H, CH₂CH₂CO₂CH₃), 1.5-1.3 (m, 12H, (CH₂)₆), 0.2 (s, 9H, (CH₃)₃Si).

Preparation of 11-(4-Ethynylphenoxy)undecanoic Acid (2). Into a 100 mL, round-bottom flask equipped with a reflux condenser were placed 2.10 g (5.4 mmol) of **3** and 50 mL of a 4% (w/v) methanol solution of potassium hydroxide. The mixture was refluxed for 4 h and was then poured into 100 mL of 1 M hydrochloric acid. The isolated product was obtained by filtration and dried in a vacuum oven at room temperature. A pale yellow solid of **2** was obtained 95.1% yield. IR (KBr), ν (cm⁻¹): 3285 (s, ≡C–H), 2105 (w, C≡C), 1700 (s, C=O). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.4 (m, 2H, aromatic protons *meso* to –O–), 6.8 (m, 2H, aromatic protons *ortho* to –O–), 3.9 (m, 2H, PhOCH₂), 3.0 (s, 1H, ≡C–H), 2.3 (m, 2H, CH₂CO₂H), 1.8 (m, 2H, PhOCH₂CH₂), 1.6 (m, 2H, CH₂CH₂CO₂H), 1.5-1.3 (m, 12H, (CH₂)₆).

Preparation of {4-[10-(4-Mercaptophenyl)aminocarbonyl]decyloxy}phenylacetylene (M1). In a 100 mL round-bottom flask, 403 mg (1.33 mmol) of **2**, 200 mg (1.6 mmol) of 4-aminothiophenol, 412 mg (2 mmol) of DCC, 33 mg (0.27 mmol) of DMAP and 51 mg (0.27 mmol) of TsOH were dissolved in 50 mL of dry DCM. The resultant solution was stirred for 12 h at room temperature under nitrogen. The byproduct was filtered from the reaction mixture. The solvent was evaporated with a rotary evaporator. The residue was purified on a silica gel column using chloroform as eluent. Removal of the solvents yielded 400 mg of a yellow solid of M1 (yield: 73.4%). IR (KBr), ν (cm⁻¹): 3288 (s, –C≡C–H), 2107 (w, C≡C), 1656 (s, amide, –NH–C=O). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.9 (d, 2H, aromatic protons *meso* to –SH), 7.4 (m, 4H, aromatic protons *meso* to –O– and aromatic protons *ortho* to –SH), 6.9 (d, 2H, aromatic protons *ortho* to –O–), 4 (t, 2H, –O–CH₂), 2.5 (s, 1H, –C≡C–H), 2.3 (m, 2H,

–CH₂CONH), 1.5-1.8 (m, 4H, –O–CH₂CH₂ and CH₂CH₂CONH), 1.2-1.4 (m, 12H, (CH₂)₆). Elemental analysis: Calcd for C₂₅H₃₁NO₂S (409.2): C, 73.31; H, 7.63; N, 3.42; Found: C, 73.33; H, 8.26; N, 3.60. MS (*m/z*): 408.1 [(M – 1)⁺].

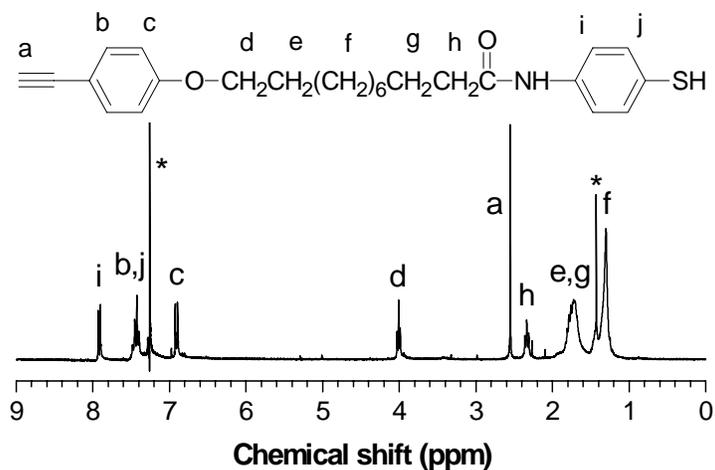


Figure S1. ¹H NMR spectrum of thiol-containing monomer M1 in chloroform-*d*. The solvent and water peaks are marked with asterisks.

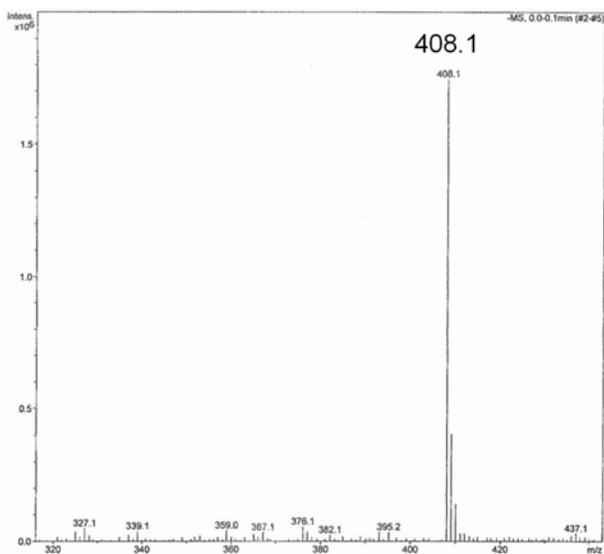


Figure S2. Mass spectrum of M1.

Fabrication of CdS Nanorods. The nanorods were prepared by a modified solvothermal method. Cadmium chloride and sulfur powders were stoichiometrically added into a mixture of deionized water and diethylamine under stirring. The contents were then transferred to a Teflon-lined stainless steel autoclave, which was airproofed and put into an oven. The solution was neither shaken nor stirred

during the period of heating process. The autoclave was gradually heated to 120–200 °C and maintained at the temperatures for 24 h and then cooled to room temperature. The product was collected by precipitation and washed with CS₂, ethanol and deionized water. A yellow powdery product was obtained after drying in a vacuum oven and treated at a temperature of ~650 °C for 1 h.

Assemblies of M1 on CdS Nanorods. In a typical run, 80 mg of M1 and 25 mg of CdS nanorods were added into 10 mL of DCM in a 20 mL tube. The mixture was gently stirred for 48 h. The product (C1) was collected by precipitation and washed with DCM several times. Thin layer chromatography (TLC) and UV-vis absorption spectroscopy were used to confirm that all the M1 molecules unattached onto the CdS nanorods had been removed thoroughly from the product. The final product was dried in a vacuum oven at 40 °C overnight.

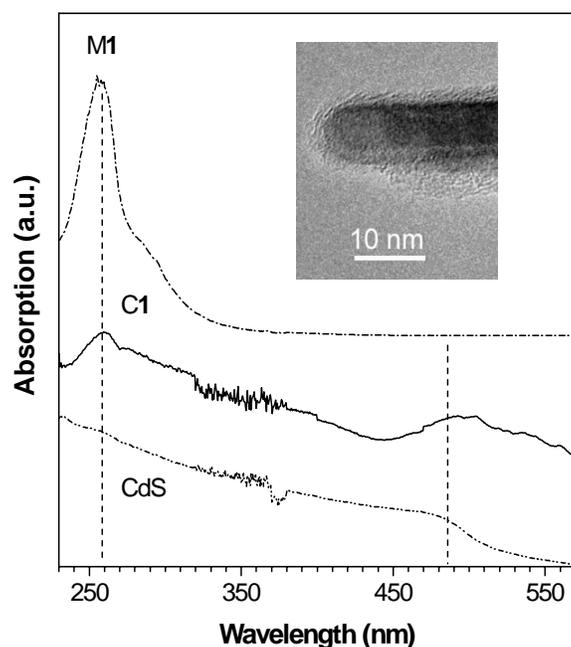


Figure S3. Absorption spectra of CdS nanorod suspension and M1 and C1 solutions (10 μM) in DCM. Inset: a typical HRTEM image of a single nanorod capped with an assembly of M1 molecules.

The absorption spectrum of C1 is shown as Figure S3. The characteristic feature of CdS crystal can be observed at ~485 nm, confirming the existence of the CdS nanorods in the solution. The TEM images of C1 reveal that the CdS nanorods retain their original shapes (Figure S4). A typical HRTEM image of C1 given in the inset of Figure S3 shows that the surface of the assembly is not as smooth as

those of the original nanorods. A rational explanation is that the clear surfaces of the original nanorods have been covered with M1 molecules. EDX analysis data are listed in Table S1, which clearly tell that C, N, Cd and S elements co-exist in the assemblies.

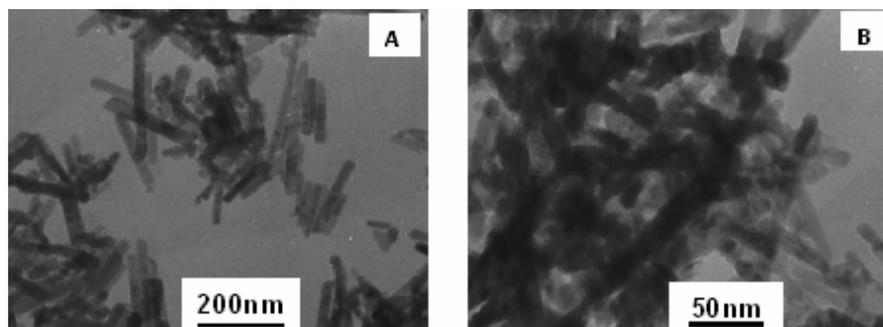


Figure S4. Typical TEM images of C1.

Table S1. EDX Analysis Data of C1^a

Element	Peak area	<i>k</i> factor	Weight content (%)	Atomic content (%)
C K	6817	2.208	23.45	57.47
N K	766	2.965	3.54	7.44
O K	429	1.810	1.21	2.23
Na K	582	1.237	1.12	1.44
S K	5377	0.940	7.87	7.23
Cl K	249	0.964	0.37	0.31
Ca K	418	0.935	0.61	0.45
Cr K	126	1.100	0.22	0.12
Fe K	140	1.170	0.25	0.13
Cu K	16017	1.366	34.08	15.79
Zn K	594	1.434	1.33	0.60
Cd L	9411	1.769	25.94	6.79

^a Recorded on a Hitachi H-900 TEM microscope, using an accelerating voltage of 300 kV.

Copolymerization of C1 with PA. The copolymerization reaction was carried out under nitrogen using the Schlenk technique in a vacuum-line system. Into a 20 mL Schlenk tube, 10 mg of purified C1 was added. The tube was evacuated under vacuum and then flushed with dry nitrogen three times, followed by injecting 50 mg of PA into the tube. DCM (1.5 mL) was then injected into the tube to dissolve the monomer. The catalyst was prepared in another tube by dissolving 2.5 mg of [Rh(cod)Cl]₂ in 0.5 mL of DCM with one drop of TEA, which was transferred to the monomer solution using a hypodermic syringe. After stirring at room temperature for 24 h, the polymerization mixture was

diluted with 5 mL of DCM and added dropwise to 500 mL of methanol under stirring. The precipitate was collected by filtration. The solid product was washed with methanol and dried under vacuum at room temperature to a constant weight.

The copolymerization of C1 and PA gave rise to the expected PPA–CdS hybrid (H1). Because the inorganic nanorods cannot penetrate through the columns in the GPC instrument, we removed the CdS nanorods in H1 by extracting it with concentric hydrochloric acid. After removal of the CdS component and drying in a vacuum oven, the yield of the polymer was calculated to be ~71%. The M_w and M_w/M_n values of the sample were estimated to be 72600 and 2.9, respectively. The ^1H NMR spectrum of H1 is shown in Figure S5. The appearance of the resonance peak for =C–H at $\delta \sim 5.8$ and the upfield shift of the resonance peaks of the aromatic protons confirm the transformation of the acetylenic triple bonds to the vinyl double bonds by the acetylene polymerization process.

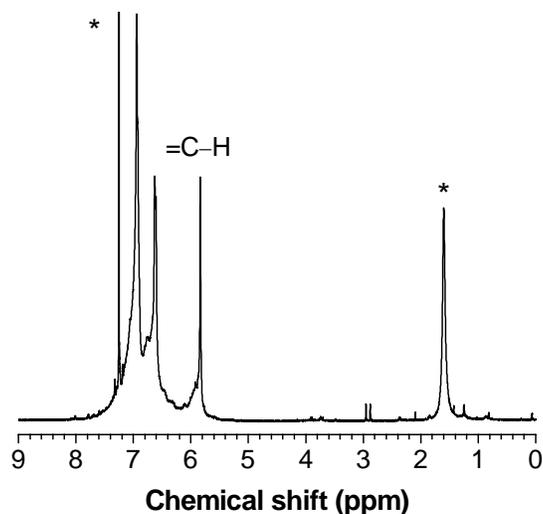


Figure S5. ^1H NMR spectra of H1 in chloroform-*d*. The solvent and water peaks are marked with asterisks.

The content of the CdS nanorods in H1 was estimated from TGA and elemental analyses. The thermograms for hybrid H1 and pure PPA are shown in Figure S6. The weight content of the CdS component was calculated by subtracting the residual carbon left by PPA from the total residual weight of H1, which was found to be ~10.8%.

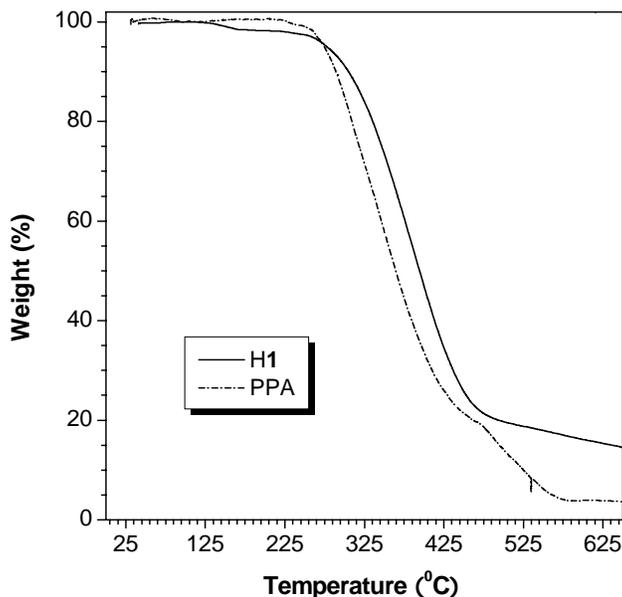


Figure S6. TGA thermograms of PPA and H1 recorded under nitrogen at a heating rate of 20 °C/min.

The elemental analysis data for M1, PPA and H1 are summarized in Table S2. The nitrogen in H1 is entirely from M1, thus the relative content of M1 in H1 can be calculated by equation 1 to be 7.78 wt %:

$$W_{M1/H1} = (W_{N/H1}) / (W_{N/M1}) \times 100\% \quad (1)$$

where $W_{M1/H1}$ is the weight percentage of M1 in H1, and $W_{N/H1}$ and $W_{N/M1}$ stand for the weight percentages of nitrogen element in H1 and M1, respectively. The weight percentage derived from the elemental analysis data is given in Table S2.

Rationally, M1 component also contributes the same percentage to the total carbon content in H1. Based on this analysis, the PA component contributes 92.22 wt % of carbon to H1, i.e., 78.28 wt % of the total 84.88 wt % in H1. Therefore, the relative content of PA in H1 can be calculated by equation 2 to be 83.21 wt %:

$$W_{PA/H1} = (W_{C/H1}) / (W_{C/PA}) \times 100\% \quad (2)$$

where $W_{PA/H1}$ is the weight percentage of PA component in H1, and $W_{C/H1}$ and $W_{C/PA}$ stand for the weight percentage of carbon element in H1 and PA, respectively. Finally, the relative content of CdS nanorods in H1 can be calculated to be 9.01 wt % by subtracting the weight percentages of M1 and PA components from 100%.

Table S2. Contents of M1, PA, and CdS in H1.

	C (%)	H (%)	N (%)	Content in H1 (%)
H1	84.88	5.58	0.28	
M1	73.33	8.26	3.60	7.78
PA	94.08	5.92	0.00	83.21
CdS				9.01

Preparation of PPA-CdS Blends. Two kinds of blends were prepared. Blend 1 or B1 was prepared by the polymerization of PA in the presence of CdS nanorods, similar to that of H1, except for that M1 was replaced by pure CdS nanorods. In another case, 10 mg of CdS nanorods and 80 mg of preformed PPA was dissolved in 4 mL of DCM. The mixture was stirred for 24 h and the solvent was evaporated with a rotary evaporator. Blend 2 or B2 was obtained after drying in vacuum oven at 40 °C overnight.

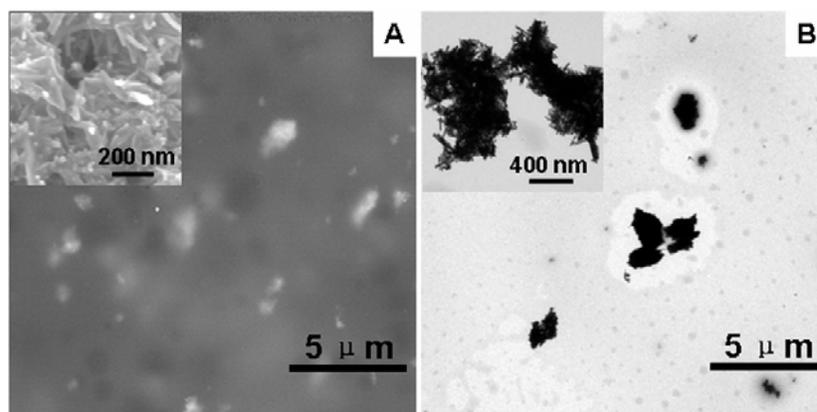


Figure S7. (A) SEM and (B) TEM images of B1. Insets: Images with high magnifications.

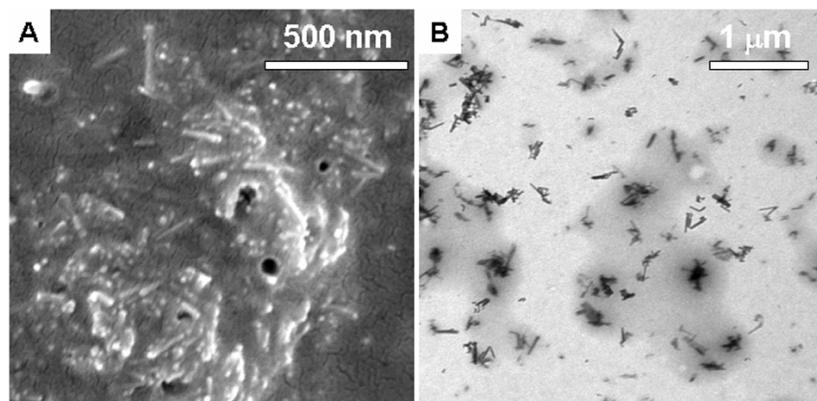


Figure S8. (A) SEM image of B2 and (B) TEM image of H1. Scale bar: (A) 500 nm, (B) 1 μm.

Photoreceptor Fabrication. Double-layered photoreceptor was prepared as follows. Stoichiometric amounts of a photogeneration material [CdS nanorods (5 mg), PPA (25 mg), H1 (30 mg), B1 (30 mg), or B2 (30 mg)], polycarbonate (0.2 g, polymer binder), and DCM (3 mL) were sequentially added into a nitrogen-flushed flask at room temperature. After stirring for 6 h, a yellow suspension was formed. An interface layer with a thickness of $\sim 1 \mu\text{m}$ was cast from a 5% ethanol solution of polyamide onto a clean surface of as-treated aluminum substrate. After the interface layer had been dried, the suspension in DCM was cast onto it to form a charge generation layer (CGL). The device was put into a vacuum oven and dried at room temperature for ~ 6 h. During the drying process, 0.6 g of a charge transport material (CTM) of α -naphthalenylphenyl-*N,N*-diethylbenzylhydrozone, 0.4 g of polycarbonate, and 4 mL of DCM were added into a nitrogen-flushed flask. The resultant yellow solution was stirred for 5 h. The CTM solution was then cast onto the CGL-coated aluminum substrate to form a charge transport layer (CTL). Drying the device in a vacuum oven at room temperature for 4–8 h gave the double-layered photoreceptor.

Photoconductivity Measurement. Photoconductivity of the obtained double-layered photoreceptor was measured using a standard GDT-II photoinduced discharge instrument, which constitutes the basis of the xerographic process in the photoimaging system. The surface of the photoreceptor was first negatively corona charged to a surface potential V_0 . After a dark discharge for 3 s, its surface potential dropped to V_i . The photoreceptor was then exposed to a light with an intensity of I ($11 \mu\text{W}/\text{mm}^2$ in this work). The light source was a halogen lamp (5 W, 24 V). The electron–hole pairs were immediately generated in the CGL upon the photon absorption and injected into the CTL. The photogenerated pairs migrated towards the negatively charged surface following the applied field through the CTL. The surface charges were thus neutralized with a low potential V_f remained. From the discharge experiment we can obtain the parameter of half-discharge exposure energy $E_{1/2}$, which equals to $t_{1/2}I$, where $t_{1/2}$ is the time from initial potential V_i to its half value under exposure to light. Photosensitivity S is defined as the reciprocal of $E_{1/2}$, or $S = 1/E_{1/2}$.