Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis, optical properties and photovoltaic applications of hybrid rod−coil diblock copolymers with coordinatively attached CdSe nanocrystals

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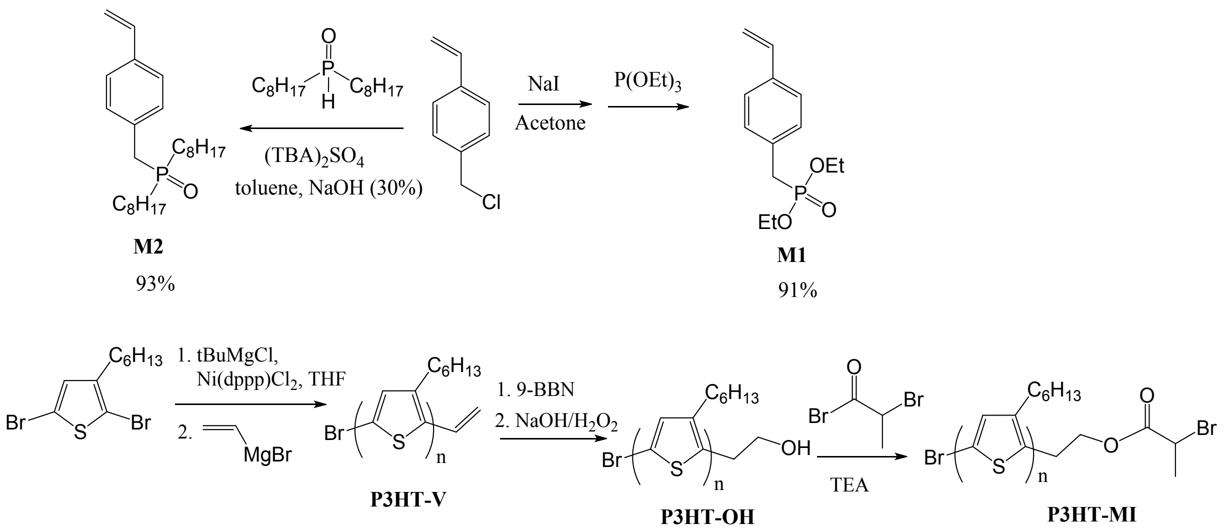
1. Synthesis of modified styrene monomers and the P3HT macroinitiator (P3HT-MI)



Scheme S1 Synthesis of M1,2 monomers and P3HT macroinitiator.

P3HT-V: Vinyl-terminated P3HT was synthesized using a one-pot Grignard metathesis polymerization (GRIM). 2,5-Dibromo-3-hexylthiophene (0.57 g, 1.75 mmol) was stirred in 2 mL of dry THF under nitrogen protection while *tert*-butylmagnesium chloride (1.0 M in anhydrous THF, 1.75 mL, 1.75 mmol) was added dropwise over a period of 20 min. The resulting mixture was stirred at r.t. for additional 2 h. After diluted with THF (20 mL), the solution was added [$Ni(dppp)Cl_2$] (18 mg, 0.036 mmol) and the reaction was continued for 30 min before vinylmagnesium bromide (1.0 M in anhydrous THF, 0.87 mL, 0.87 mmol) was added. After another 30 min, the solution was poured into methanol. The precipitates were collected by filtration and purified by Soxhlet extraction with methanol and hexane to give the vinyl-terminated P3HT in 21.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm =6.96 (br), 6.80 (m), 5.49 (d, *J* = 16.8 Hz), 5.11 (d, *J* = 11.2 Hz), 2.78 (br), 1.68 (br), 1.5-1.3 (br), 0.89 (br).

P3HT-OH: 0.5 mL of 9-BBN in THF (0.5 M, 0.25 mmol) was added dropwise into a THF (20 mL) solution of P3HT-V (0.52 g, 0.022 mmol, $M_n \approx 2400$) at r. t. under N_2. The reaction mixture was stirred at 40 ºC for 24 h, followed by the slow addition of a 30% NaOH solution (0.5 mL). The reaction was continued for another 15 min at r.t. before a 33% aqueous solution of hydrogen peroxide (1 mL) was slowly added. The resulting mixture was stirred for 24 h at 40 ºC and was then poured into methanol. The polymer precipitates were collected by filtration, washed with methanol several times and dried to give P3HT-OH in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm =6.96 (br), 3.84 (t, *J* = 5.6 Hz), 3.47 (s), 3.02 (t, *J* = 6.4 Hz), 2.78 (br), 1.69 (br), 1.5-1.3 (br), 0.89 (br).

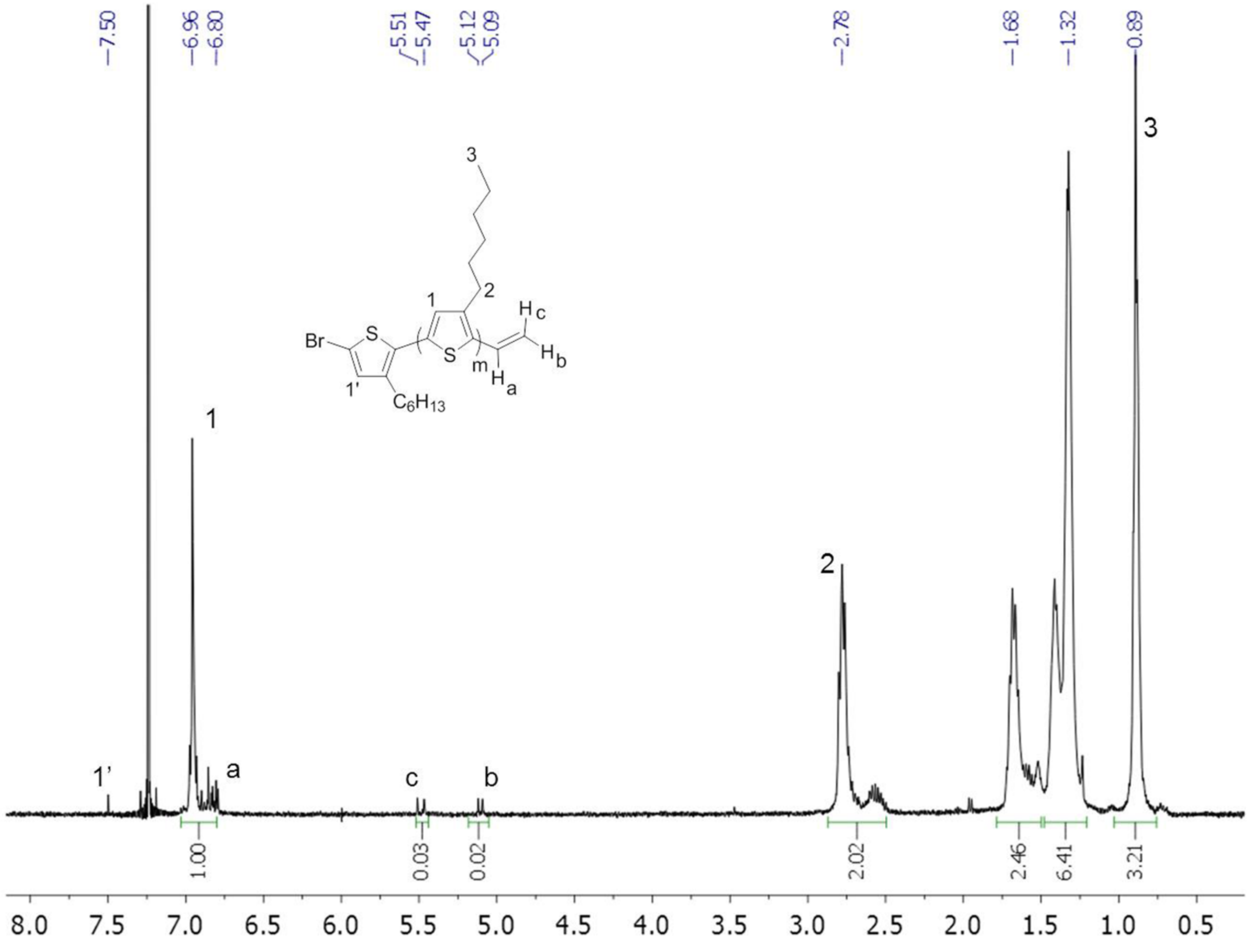


Fig. S1 ^{1}H NMR spectra of **P3HT-V** in $CDCl_3$.

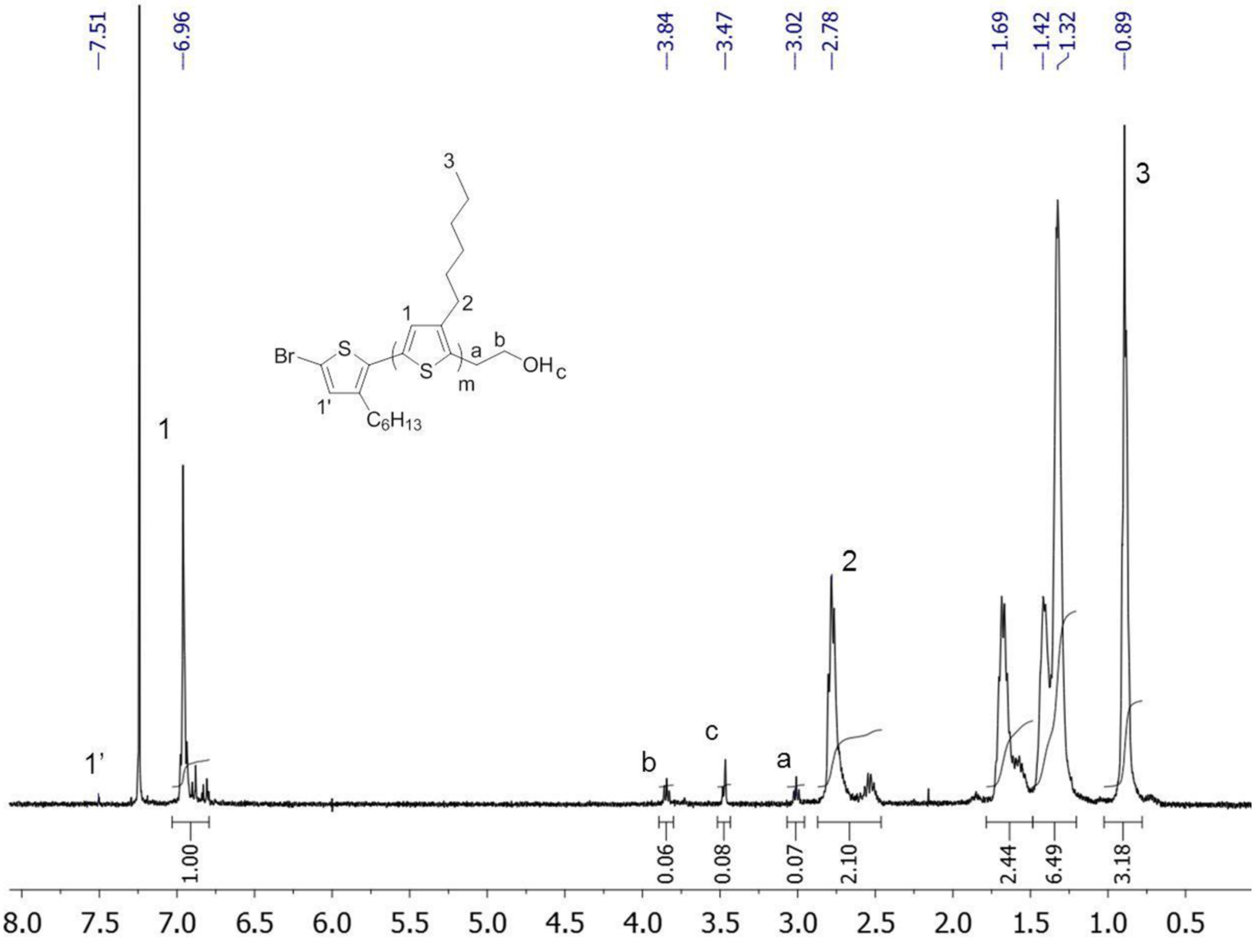


Fig. S2 ^{1}H NMR spectra of **P3HT-OH** in $CDCl_3$.

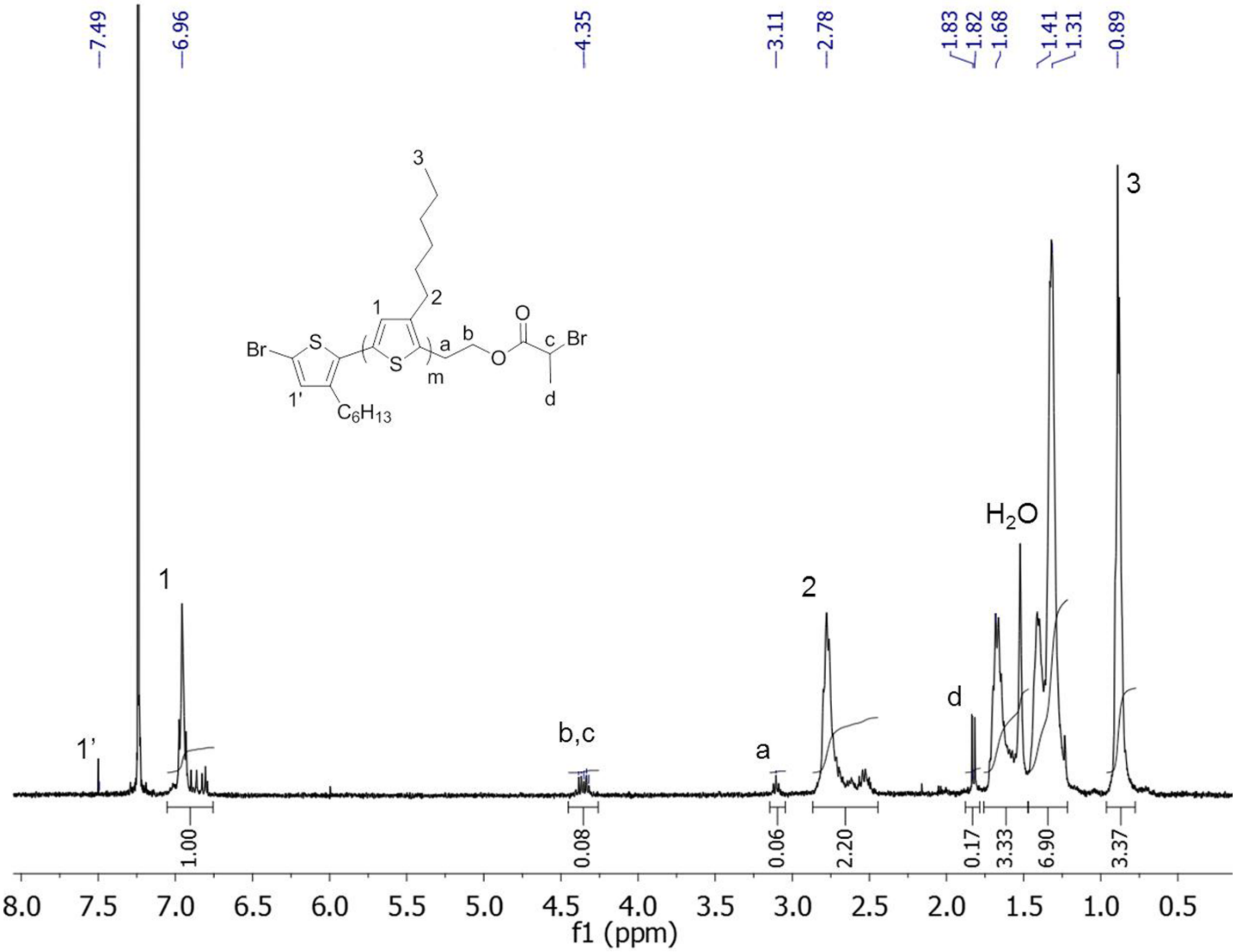


Fig. S3 ^{1}H NMR spectra of **P3HT-MI** in $CDCl_3$.

2. Synthesis of HDA/TOPO-capped CdSe Nanocrystals

CdSe nanocrystals were prepared according to well-demonstrated wet chemical method.[1] A mixture of cadmium oxide (0.512 g, 0.399 mmol) and stearic acid (2.4308 g, 8.54 mmol) was heated to 150 °C under N_2 and was stirred at 150 °C for 30 min, during which time the solid brownish mixture gradually melted into colorless liquid. The solution was cooled to room temperature, followed by the addition of trioctylphosphine oxide (TOPO, 5.028 g, 13.0 mmol) and 1-hexadecylamine (HDA, 6.149 g, 25.5 mmol). The flask was fitted with a thermometer and a condenser, and heated to ~310 °C with constant stirring. A solution of selenium (0.331 g, 4.20 mmol) in TOP (4.28 g, 11.5 mmol) was then quickly injected into the reaction flask, and the solution temperature dropped to ~270 °C. The reaction was continued at 270 °C for 3 min, and then was removed from the heating mantle and let cooled to ~60 °C. Chloroform (30 mL) was added to dissolve the nanocrystals which were then precipitated out by adding acetone. The precipitated nanocrystals were redissolved with $CHCl_3$ and reprecipitated with acetone for two additional times. Pure HDA/TOPO-capped CdSe nanocrystals were collected and dried under vacuum. The absorption and fluorescence mission spectra of the CdSe nanocrystals in chloroform were shown in Fig. S4. Based on its l_{max} (563 nm), the average size was estimated to be ~4 nm.[2,3]

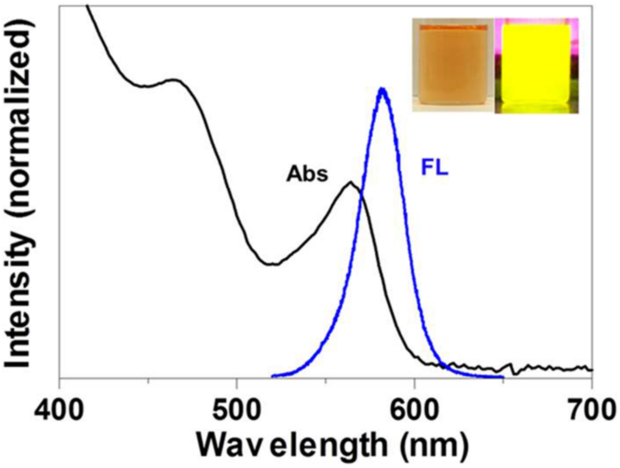


Fig. S4 Absorption and fluorescence spectra of HDA/TOPO-capped CdSe NCs in chloroform. Inset shows photographical images of the solution without/with the illumination of 365 nm UV light.

3. MALDI-TOF MS results of the vinyl-terminated P3HT and the P3HT-MI

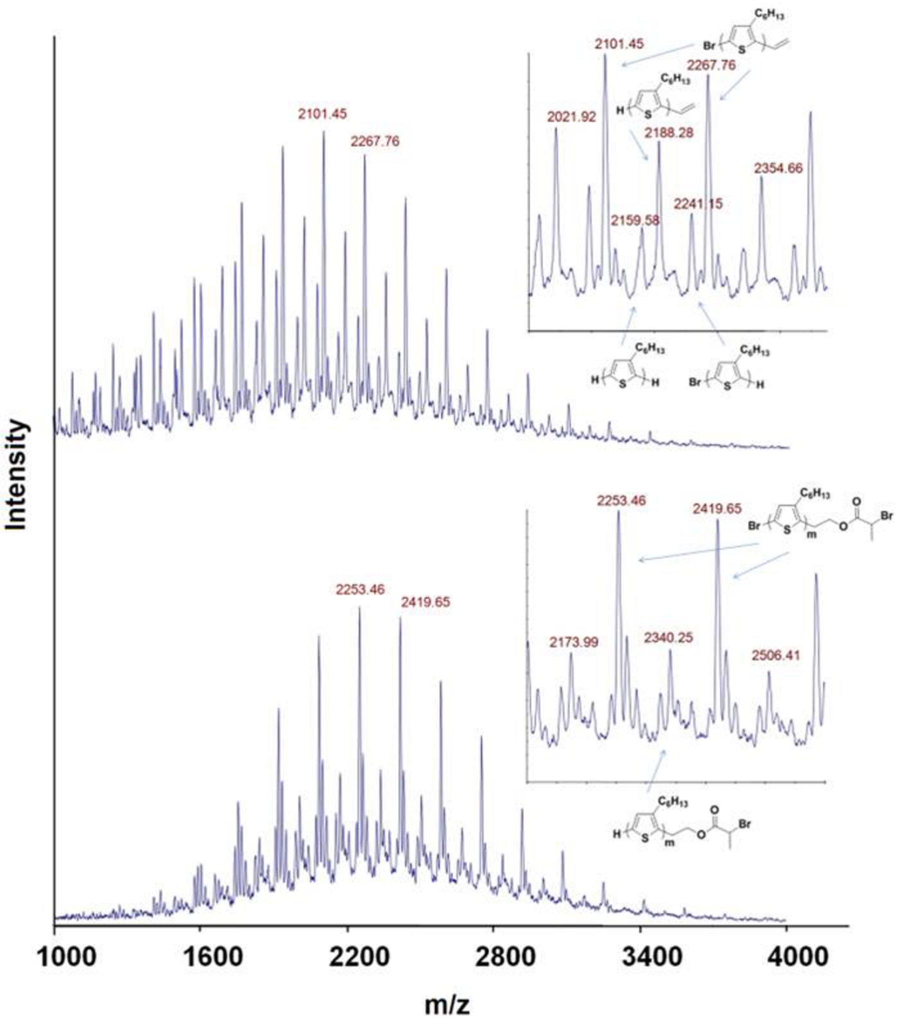


Fig. S5 MALDI-TOF MS spectra of (a) vinyl-terminated P3HT and (b) bromoester-terminated P3HT. Expanded spectra in both insets showing sets of peaks corresponding to P3HTs with different terminate group.

4. FT-IR of P3HT-PS-2 and P3HT-PS-CdSe-2

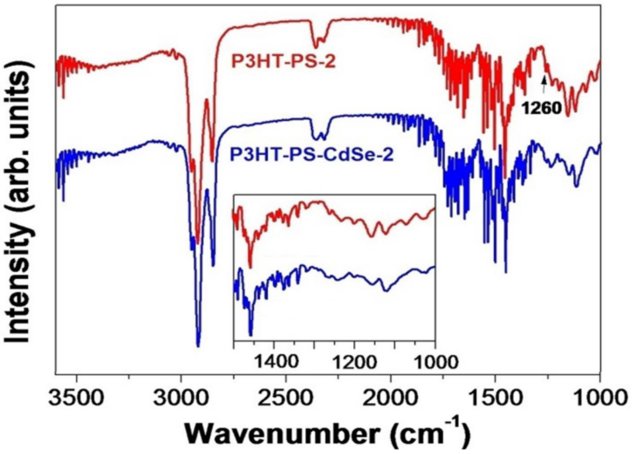
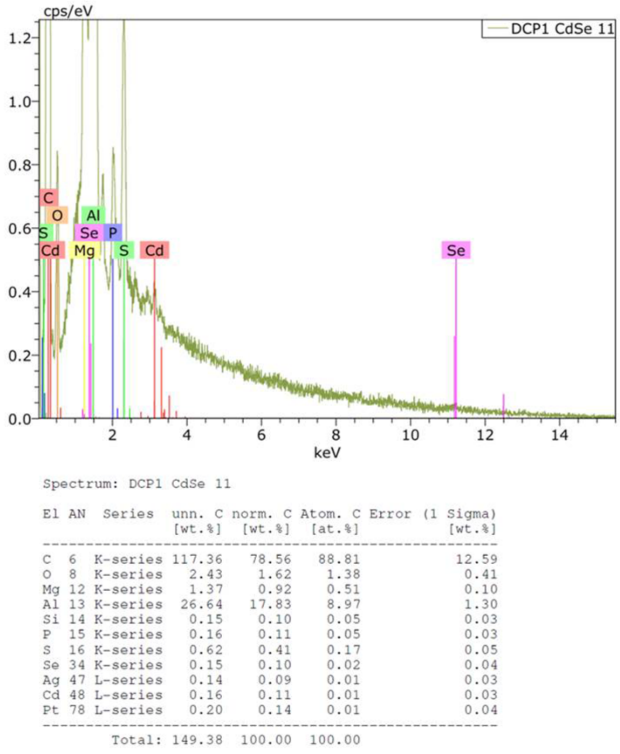


Fig. S6 FT-IR spectra of **P3HT-PS-2** and **P3HT-PS-CdSe-2**.

5. EDX analysis of P3HT-PS-CdSe-1,2,3 hybrids

The content of CdSe nanocrystals in the P3HT-PS-CdSe nanocomposites is examined by EDX analysis. EDX analysis was performed using a Tescan Vega3 scanning electron microscope integrated with energy dispersive X-ray microanalyser. The sample was placed on an aluminum stub by drop-casting the chloroform solution of the composites and dried under vacuum. All weight ratios of the two components were calculated based on the weight ratio between sulfur and cadmium. Based on the calculation, the weight ratio between P3HT-PS and CdSe was estimated to be 18:1, 19:1 and 27:1 for P3HT-PS-CdSe-1,2,3, respectively. The results confirmed the existance of CdSe content, even though in a relatively low amount, in all three hybrids.



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Spectrum: DCP1 CdSe 11

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
C   6  K-series 117.36   78.56   88.81           12.59
O   8  K-series   2.43    1.62    1.38            0.41
Mg 12  K-series   1.37    0.92    0.51            0.10
Al 13  K-series  26.64   17.83    8.97            1.30
Si 14  K-series   0.15    0.10    0.05            0.03
P  15  K-series   0.16    0.11    0.05            0.03
S  16  K-series   0.62    0.41    0.17            0.05
Se 34  K-series   0.15    0.10    0.02            0.04
Ag 47  L-series   0.14    0.09    0.01            0.03
Cd 48  L-series   0.16    0.11    0.01            0.03
Pt 78  L-series   0.20    0.14    0.01            0.04
------------------------------------------------------
        Total: 149.38  100.00  100.00
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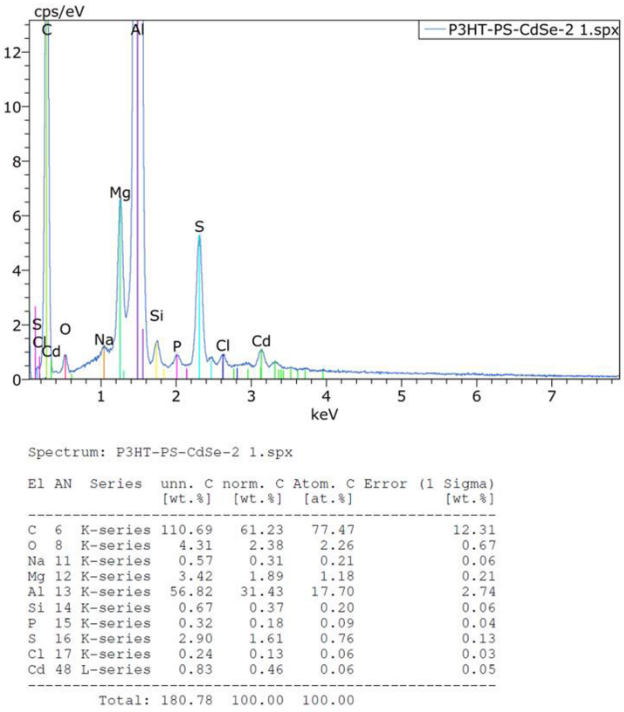
Fig. S7 EDX result of P3HT-PS-CdSe-1 sample.



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Spectrum: P3HT-PS-CdSe-2 1.spx

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
C   6  K-series 110.69   61.23   77.47           12.31
O   8  K-series   4.31    2.38    2.26            0.67
Na 11  K-series   0.57    0.31    0.21            0.06
Mg 12  K-series   3.42    1.89    1.18            0.21
Al 13  K-series  56.82   31.43   17.70            2.74
Si 14  K-series   0.67    0.37    0.20            0.06
P  15  K-series   0.32    0.18    0.09            0.04
S  16  K-series   2.90    1.61    0.76            0.13
Cl 17  K-series   0.24    0.13    0.06            0.03
Cd 48  L-series   0.83    0.46    0.06            0.05
------------------------------------------------------
        Total: 180.78  100.00  100.00
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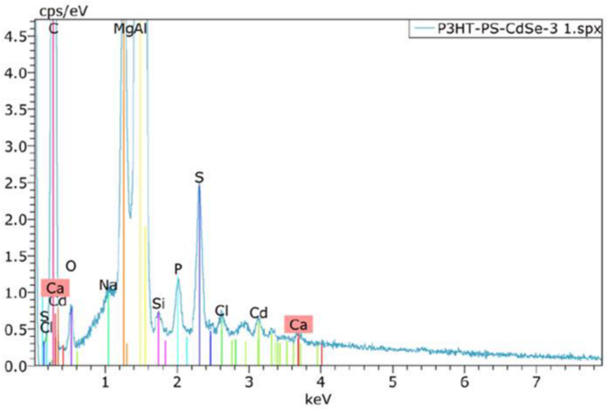
Fig. S8 EDX result of P3HT-PS-CdSe-2 sample.



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Spectrum: P3HT-PS-CdSe-3 1.spx

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
C   6  K-series 108.67   63.08   78.82            12.23
O   8  K-series   3.45    2.00    1.88             0.59
Na 11  K-series   0.35    0.20    0.13             0.05
Mg 12  K-series   3.20    1.86    1.15             0.20
Al 13  K-series  53.77   31.21   17.36             2.59
Si 14  K-series   0.15    0.09    0.05             0.03
P  15  K-series   0.48    0.28    0.13             0.05
S  16  K-series   1.31    0.76    0.36             0.07
Cl 17  K-series   0.20    0.12    0.05             0.03
Ca 20  K-series   0.17    0.10    0.04             0.03
Cd 48  L-series   0.53    0.31    0.04             0.04
-----------------------------------------------------
         Total: 172.28  100.00  100.00
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Fig. S9. EDX result of P3HT-PS-CdSe-3 sample.

6. Calculation of the weight ratio of CdSe NCs to DCP in the hybrids by solution absorption

The absorbance of pure CdSe NCs and pure DCPs in chloroform solution with known concentration are measured at certain wavelengths. The results are shown in table S1. The weight ratios of DCP/CdSe NCs are calculated based on the following equation:

$$\frac{M_{DCP}}{M_{CdSe}} = \frac{\dfrac{abs_{\ hybrids}^{\ 444\,nm}}{abs_{\ DCP}^{\ 444\,nm}} * C_{DCP}}{\dfrac{abs_{\ hybrids}^{\ 580\,nm}}{abs_{\ CdSe}^{\ 580\,nm}} * C_{CdSe}}$$

Where C_{DCP} and C_{CdSe} are the concentration of pure DCPs and CdSe NC solutions. The results are listed in Table S1.

Table S1. Weight ratios of DCP:CdSe in the hybrids, calculated based on solution absorption

n	Absorption at 444 nm (a.u.)		Absorption at 580 nm (a.u.)		Concentration of pure P3HT-PS-*n* (mg/mL)	Weight ratio of P3HT-PS-*n* to CdSe
	Hybrids (P3HT-PS-CdSe-*n*)	Pure DCPs (P3HT-PS-*n*)	Hybrids (P3HT-PS-CdSe-*n*)	Pure CdSe		
1	1.000	0.253	0.014	0.261 for 0.1mg/mL solution	0.017	≈ 12:1
2	1.000	0.626	0.017		0.031	≈ 8:1
3	1.000	0.806	0.017		0.058	≈ 11:1

7. TGA analysis of DCPs and HDCPs

The calculation of the weight percentage of NCs in the HDCPs was based on remaining weight percentage of DCPs and HDCPs. Taking P3HT-PS-1 and P3HT-PS-CdSe-1 as examples, assuming the weight ratio of CdSe:P3HT-PS-1 is *x*:1, one can calculate the remaining weight of HDCP1 at 600 °C to be $\frac{x + 1 \times 0.42}{x + 1}$, which should be equal to 0.62. In this way, the value *x* can be calculated to be 0.52, and the weight percentage of CdSe in HDCP1 can be calculated to be 34%. Using a same method, the weight percentage of CdSe in HDCP2 & 3 are calculated to be 40% and 8%, respectively.

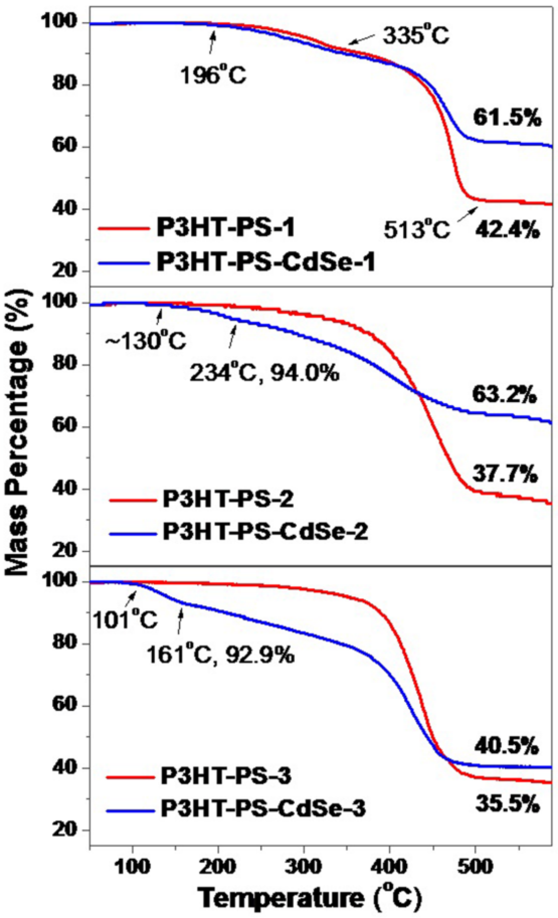

Fig. S10 TGA curves of DCPs and HDCPs at the temperature range of 50-600 °C.

8. *J–V* curves of the solar cells of HDCPs

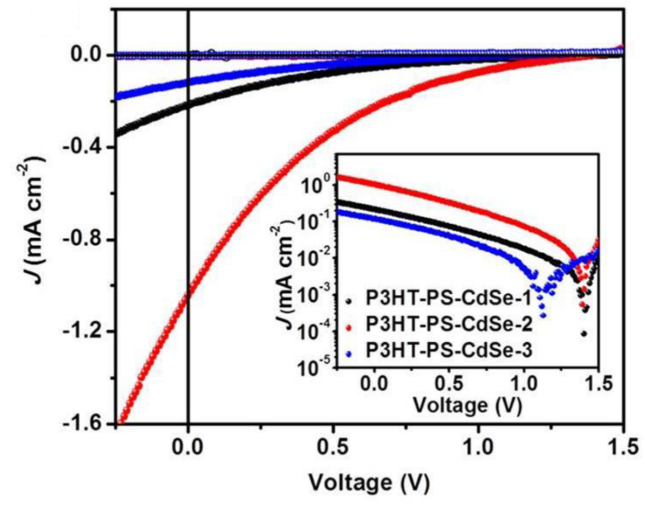

Fig. S11 Current density−voltage (*J–V*) curves (empty: dark; filled: illuminated) of the solar cells of glass/ITO/PEDOT:PSS/P3HT-PS-CdSe/Ca/Al. The illuminated curves were measured under AM 1.5 G 1-sun (100 mW/cm^{-2}) illumination. For clear identification of V_{OC}s, the inset shows the illuminated *J–V* curves of the devices with the *J*-axis plotted in log-scale.

References:

(1) Shallcross, R. C.; D'Ambruoso, G. D.; Korth, B. D.; Hall Jr., H. K.; Zheng, Z.; Pyun, J.; Armstrong, N. R. *J. Am. Chem. Soc.* **2007**, *129*, 11310-11311.

(2) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706-8715.

(3) Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1*, 333-337.