

Electronic Supplementary Information

Controlled Growth of Conjugated Polymer-Quantum Dot Nanocomposites via a Unimolecular Templating Strategy

Guoxiao Yuan,^{a§} Tianci Liang,^{a§} Yachao Liang,^a Xinchang Pang,^{a*} and Zhongfan Jia^{b*}

a. Henan Joint International Research Laboratory of Living Polymerizations and Functional Nanomaterials, Henan Key Laboratory of Advanced Nylon Materials and Application, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China.

b. Institute for Nanoscale Science and Technology, College of Science and Engineering, Flinders University, Bedford Park, South Australia 5042, Australia.

Experimental Section

Materials. 2-Bromoisobutyryl bromide (98%), N,N,N',N'',N''-pentamethyldiethylene triamine (PMDETA, 99%), anhydrous 1-methyl-2-pyrrolidinone (99.5%), sodium azide ($\geq 99.5\%$), 2,5-dibromo-3-hexyl-thiophene (97%), tert-butyl magnesium chloride (2.0 M solution in diethyl ether), [1,3-bis(diphenyl phosphino) propane] dichloronickel(II), ethynyl magnesium bromide (0.5 M solution in tetrahydrofuran) and trifluoroacetic acid (TFA, 99.9%) were purchased from Sigma-Aldrich, and used as received. CuBr (98%, Sigma-Aldrich) was stirred overnight in acetic acid, filtrated, washed with ethanol and diethyl ether successively, and dried in vacuum. β -Cyclodextrine (β -CD, Sigma-Aldrich) was used as received. tert-Butyl acrylate (tBA, Sigma-Aldrich 98%), methyl ethyl ketone (Fisher Scientific, 99.9%), and N,N-dimethyl formamide (DMF, Fisher Scientific, 99.9%) was distilled over CaH₂ under reduced pressure before use. Tetrahydrofuran (THF, 99%) was refluxed over potassium wire and distilled from potassium naphthalenide solution. Cadmium acetylacetonate (Cd(acac)₂, $\geq 99.9\%$) and selenium powder (Se, 99.99%) were purchased from Sigma-Aldrich and used as starting materials without further purification. All other reagents were purified by common purification procedures.

Synthesis of Heptakis[2,3,6-tri-O-(2-bromo-2-methylpropionyl)]- β -Cyclodextrin (β -CD-Br₂₁).⁵¹ β -CD (6.82 g, 6 mmol, vacuum dried at 80°C over calcium oxide overnight immediately prior to use) was dissolved in 60 mL anhydrous N-methyl-2-pyrrolidione (NMP) and cooled to 0°C. 2-Bromoisobutyryl bromide (58.0 mL, 252 mmol, 2eq. per -OH) was then added dropwise to the β -CD solution under magnetic stirring. The reaction temperature was maintained at 0°C for 2 h and then slowly increased to ambient temperature, after which the reaction continued for 22 h. The brown solution was concentrated under vacuum to remove most of the NMP. The resulting syrup-like mixture was dissolved with 100 mL dichloromethane and then washed sequentially with saturated NaHCO₃ aqueous solution (3 \times 200 mL) and DI water (3 \times 200 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated. The residual was recrystallized in n-hexane to produce a white powder (18.21 g, yield = 71.2%). The chemical compositions of β -CD-Br₂₁ were confirmed by FTIR: 2931 cm⁻¹ (ν_{C-H}), 1737 cm⁻¹ ($\nu_{C=O}$), 1158 cm⁻¹ (ν_{C-O-C}), 1039 and 1105 cm⁻¹ (coupled ν_{C-C} and ν_{C-O}); ¹H-NMR in CDCl₃: δ =1.8 (broad s, 126H, CH₃), 3.5-5.4 (49 H, sugar protons).

Preparation of 21-Arm Star-like PtBA with Azide End Group (PtBA-N₃). Briefly, an ampoule charged with CuBr (0.0707 g, 4.93 $\times 10^{-4}$ mol), PMDETA (0.1707 g, 9.85 $\times 10^{-4}$ mol), β -CD-Br₂₁ (0.1 g, 4.95 $\times 10^{-4}$ mol of initiator), tBA (42.9 mL, 0.293 mol), and 43 mL methyl ethyl ketone was degassed by three freeze-pump-thaw cycles, then sealed and placed in an oil bath at 60°C. The ampoule was taken out from the oil bath and dipped in liquid N₂ at a different time to terminate the polymerization. The polymerization time and conversion (determined by H NMR) was shown in below table. The solution was then diluted with acetone, passed through a neutral alumina column to remove the catalyst, and the solution was

precipitated in the mixed solvents of methanol/water (v/v=1/1). After filtration, the product was purified by dissolution-precipitation twice with acetone and methanol/water and dried at 40°C in a vacuum for 2 days. ¹H NMR (CDCl₃, δ, ppm): 2.05-1.30 (CH₂CH, the repeat unit of PtBA), 2.56-2.06 (CH₂CH and -(CO)-OC(CH₃)₃, repeat units of PtBA), and 1.21 (-(CO)-C(CH₃)₃). Initiating efficiency was calculated according to $E_{init} = \frac{M_{n,theo}}{21 \times M_{n,PtBA}} \times 100\%$, where $M_{n,theo}$ is the theoretical value of star-like PtBA and $M_{n,PtBA}$ is the M_n of each PtBA arm calculated based on the ¹H NMR spectra in Table 1 in the main text.

Entry	Polymers	t (h)	Conv. (%)
1	PtBA ₁₆ -Br(N ₃)	0.5	3.1
2	PtBA ₂₉ -Br(N ₃)	1	5.4
3	PtBA ₄₇ -Br(N ₃)	2	8.7
4	PtBA ₆₂ -Br(N ₃)	3	11.2
5	PtBA ₁₁₇ -Br(N ₃)	8	19.4

The star-like PtBA-Br (3.60 g) was dissolved in DMF (15 mL), and sodium azide (0.16g, Br in star-like PtBA: sodium azide= 1: 10; molar ratio) was added to the solution. The reaction mixture was stirred for 24 h at room temperature. Dichloromethane (25 mL) was added to the mixture which was then washed with DI water three times. The organic layer was dried with anhydrous MgSO₄, and the solvent was removed by rotary evaporation. The final product of star-like PtBA with azide end group (i.e., PtBA-N₃), was collected and dried at 40°C in a vacuum oven for 4 h (yield = 95.4%).

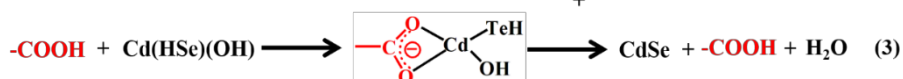
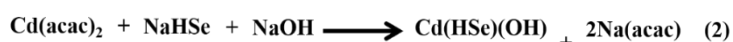
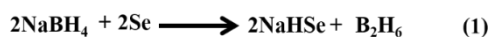
Preparation of Ethynyl-Terminated P3HT (P3HT-ethynyl). Ethynyl-terminated P3HT was synthesized by a quasi-living Grignard metathesis (GRIM) method.⁵² Briefly, 2,5-dibromo-3-hexylthiophene (0.815g, 2.5 mmol) was dissolved in THF (5 mL) in a three-neck flask and stirred under Ar. t-Butylmagnesium chloride (1.25 mL, 2.5 mmol) was added with a syringe. The mixture was stirred for 2 h at room temperature. Subsequently, it was diluted to 25 mL with THF, and Ni(dppp)Cl₂ (22.5 mg, 0.041 mmol) was added. The resulting mixture was first stirred for 10 min at room temperature, producing intermediate P3HT, which was then reacted with ethynylmagnesium bromide (2mL, 1mmol) in THF for 30 min. After precipitating the reaction mixture in methanol, filtering in an extraction thimble, and washing by Soxhlet extraction with methanol, hexanes, and chloroform sequentially, ethynyl-terminated P3HT (i.e., P3HT≡) was obtained. The final pure P3HT≡ was recovered after complete dry of the chloroform (Yield = 40.8%). The regioregularity of P3HT was greater than 98% as determined by ¹H NMR. The M_n of ethynyl-terminated P3HT was 5100 based on ¹H NMR calculation, 4100 from SEC, and Đ of 1.18 (SEC), respectively. ¹H NMR (CDCl₃, δ, ppm): 6.98 (s, 1H), 3.05 (s, 1H), 2.8 (t, 2H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), 0.92 (t, 3H).

Synthesis of Star-like Diblock Copolymers, PtBA-b-P3HT by CuAAC 'Click' Reaction. Star-like PtBA-N₃ (1.00 g) and linear P3HT≡ (2.23 g) were dissolved in DMF (10 mL) in a dry ampule, the solution was

degassed by N₂. Then CuBr (0.1414 g, 9.86x10⁻⁴ mol) and PMDETA (0.3414 g, 1.97x10⁻³ mol) were added under N₂ flow, and the reaction mixture (P3HT≡/star-like PtBA-N₃/CuBr/PMDETA = 1.2/1/10/10; molar ratio) was immersed in an oil bath at 90°C for 24 h. The reaction mixture was then cooled down, diluted with THF, and passed through an alumina column to remove the copper salt. The product was precipitated in cold methanol to remove unreacted P3HT≡ and dried in a vacuum oven at 40°C for 4 h, yielding star-like diblock copolymer, PtBA-b-P3HT. Click reaction efficiency was calculated according to $E_{Click} = \frac{9 \times 166.3 \times A_g \times M_{n,PtBA}}{128.17 \times A_h \times M_{n,P3HT}} \times 100\%$, where A_g and A_h are the integral area of protons from thiophene group at 6.98 ppm and the integral area of methyl protons from *t*-butyl group (-C(CH₃)₃) at 1.45 ppm, respectively; 128.17 and 166.3 are the molecular weights of *t*BA monomer and 3HT monomer, respectively. (Figure S5)

Synthesis of Star-like Diblock Copolymer PAA-b-P3HT. In a typical process, star-like diblock copolymer, PtBA-b-P3HT (0.3 g), was dissolved in 30 mL CH₂Cl₂, and then 10 mL trifluoroacetic acid was added. The reaction mixture was stirred at room temperature for 24 h. After the hydrolysis, the resulting star-like diblock copolymer, PAA-b-P3HT, was gradually precipitated in CH₂Cl₂. The final product was purified, washed with CH₂Cl₂, and thoroughly dried under vacuum at 40°C overnight (yield: 67.21%).

Fabrication of CdSe nanoparticles capped with P3HT (i.e., CdSe@P3HT nanocomposites)^{S3}

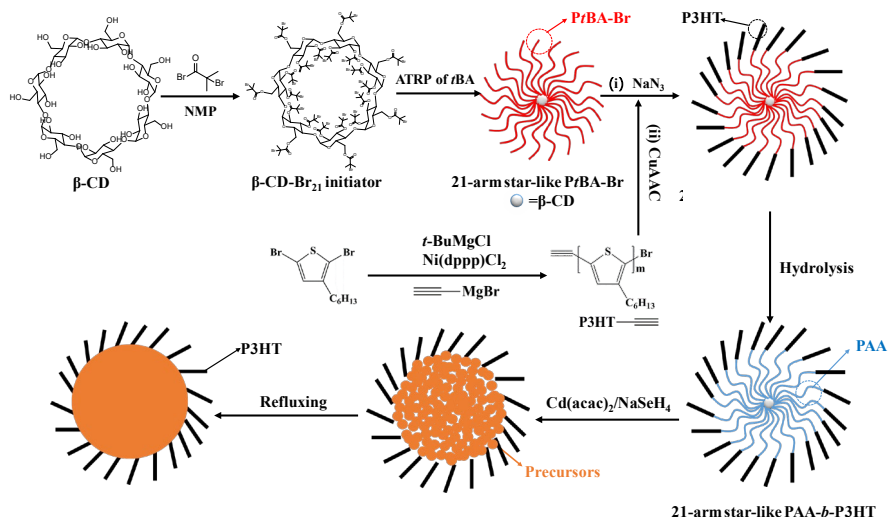


(a) Preparation of NaHSe NaHSe was prepared by reacting sodium borohydride and selenium powder in DI water. In a typical process, 1 mmol of selenium powder was introduced into 50 mL of DI water in a three-neck flask. After that, 3 mmol of NaBH₄ was added into the reaction system under argon. The reaction was then carried out at room temperature for 8h under argon. The solvent was removed by vacuum, and NaHSe was re-dispersed in dry DMF to yield the NaHSe DMF solution.

(b) Synthesis of CdSe@P3HT nanocomposites (Scheme 1) In a typical process, 10 mg of the star-like diblock copolymer, PAA-b-P3HT, was dissolved in 10 mL of DMF at room temperature, followed by the addition of an appropriate amount of precursor Cd(acac)₂ (0.2156 g) that was selectively incorporated into the compartment space containing the inner PAA template phase. The molar ratio of acrylic acid (AA) units in PAA blocks to precursors was set at 1:10 to maximize the loading of precursors into the PAA compartment. The mixture was then stirred under argon for 1h to ensure that all precursors were dissolved in DMF and the PAA blocks-containing compartment containing compartment was fully loaded by Cd(acac)₂ as one of the precursors. Subsequently, an equimolar amount of freshly-prepared

NaHSe (0.0715g) DMF solution was added dropwise at room temperature, the mixture as stirred under argon for 1h to make all precursors well dissolved in DMF and the PAA-containing compartment also fully loaded by NaHSe. The reaction system was then slowly heated to the boiling point of DMF and refluxed for 2h. The purification process was performed by low-speed centrifugation at 1000 rpm for 5 mins to remove the precipitates. 50 mL ethanol was then added into the DMF solution to ensure the complete precipitation of P3HT-capped CdSe nanoparticles from solution. The final product was obtained by centrifuging at 5000 rpm for 5 min to remove the solvent and the precipitant, followed by re-dispersing in chloroform, yielding final purified CdSe@P3HT nanocomposites (0.0712 g; yield = 53.2%).

Characterizations. Molecular weights of polymers were characterized by size exclusion chromatography (SEC, Waters) equipped with a Waters 1515 HPLC pump and a refractive index detector (RID-0.65A, 220 V). THF was used as the mobile phase at a flow rate of 1.0 ml/min at 35°C. Three Styragel HR4 5 μ m 7.8 \times 300mm (THF) columns were calibrated with 10 monodisperse PS standard samples with molecular weights ranging from 500 to 2.4 \times 10⁶ g/mol. All ¹H NMR spectra were acquired by a Bruker 400MHz spectrometer, and CDCl₃ and d₇-DMF were used as the solvent. FT-IR spectra were recorded by a Magna-550 Fourier transform infrared spectrometer. The morphologies of star-like PAA-b-P3HT unimolecular micelles were characterized by transmission electron microscopy (TEM) (JEOL TEM 100CX; operated at 100kv), dynamic light scattering (DLS) in DMF at 1 mg mL⁻¹, atomic force microscopy (AFM) on a Bruker Dimension Icon operated in the tapping mode at 0.5Hz scanning rate. The AFM samples were prepared by spin-coating the DMF solution (1mg mL⁻¹) onto Si substrate at 2000 rpm for 1 min (Headway PWM32 spin coater). The characterization of corresponding CdSe@P3HP nanocomposites were characterized by TEM, scanning electron microscopy (SEM, LEO 1530, Zeiss) equipped with energy-dispersive x-ray spectroscopy (EDS) analysis. TEM samples were prepared by applying a drop of CdSe@P3HP nanocomposites chloroform solution (1mg mL⁻¹) onto a carbon-coated copper TEM grid (300 mesh) and allowing chloroform to evaporate under ambient conditions; SEM samples were prepared by spin-coating the chloroform solution (1mg mL⁻¹) onto Si substrate at 1000 rpm for 1 min (Headway PWM32 spin coater). Shimadzu UV-2600 UV-vis spectrophotometer in solution and Perkin-Elmer LS 55 spectrofluorometer in a dry state. Crystalline structures of CdSe@P3HT were characterized by X-ray diffraction (XRD, X'Pert PRO, Netherlands).



Scheme S1. Schematic illustration of the synthesis route for CdSe@P3HT nanocomposites by using amphiphilic star-like PAA-*b*-P3HT diblock copolymers as nanoreactors.^{S1} The CdSe@P3HT nanocomposites were composed of inner CdSe nanoparticle (yellow) intimately and permanently capped with rod-like P3HT chains (black).

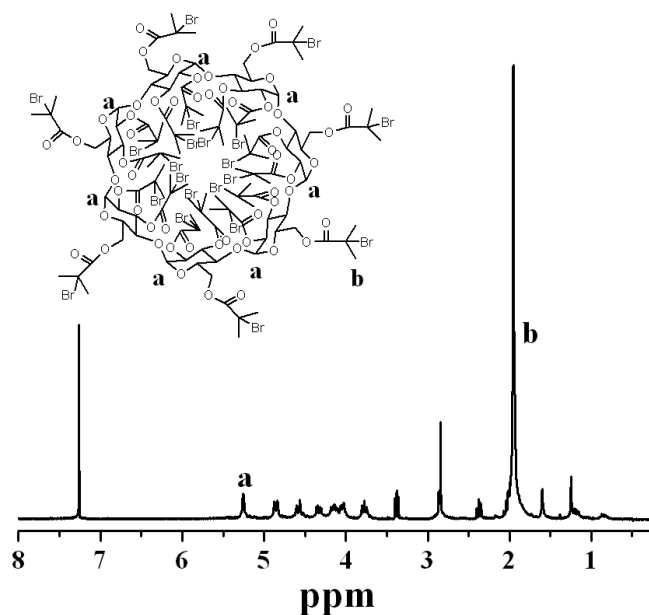


Figure S1. ¹H NMR spectrum of the multifunctional initiator, β -CD-Br₂₁ in CDCl₃.

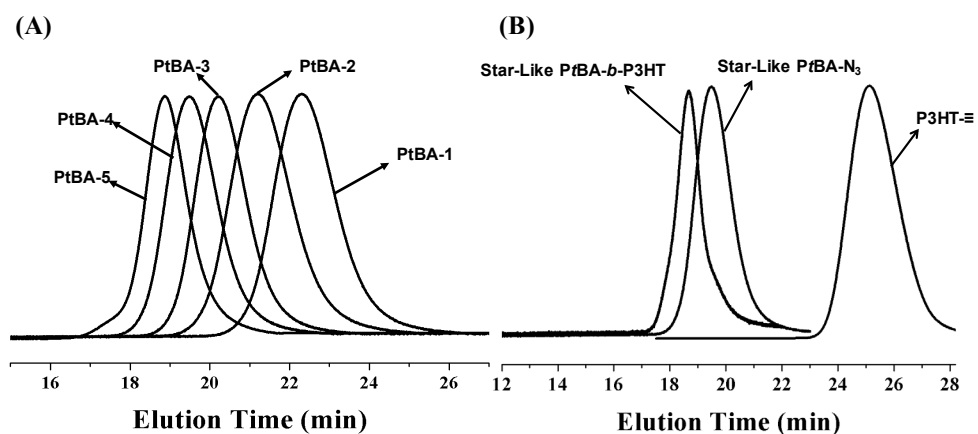


Figure S2. (A) SEC traces of 21-arm, star-like PtBA with different chain length (Entry 1-5 in Table 1) and (B) A comparison of SEC traces of P3HT-≡, star-like PtBA-N₃ (Entry 4 in Table 1) and their 'click' reaction product PtBA-*b*-P3HT (Entry 9 in Table 1).

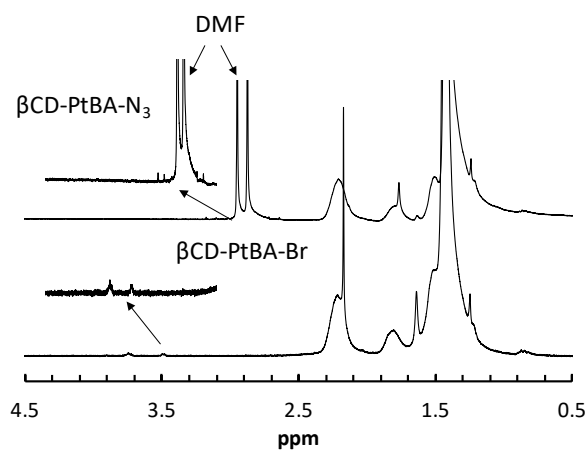


Figure S3. ¹H NMR spectra of star-like PtBA-Br and PtBA-N₃ in CDCl₃ (Entry 4 in Table 1).

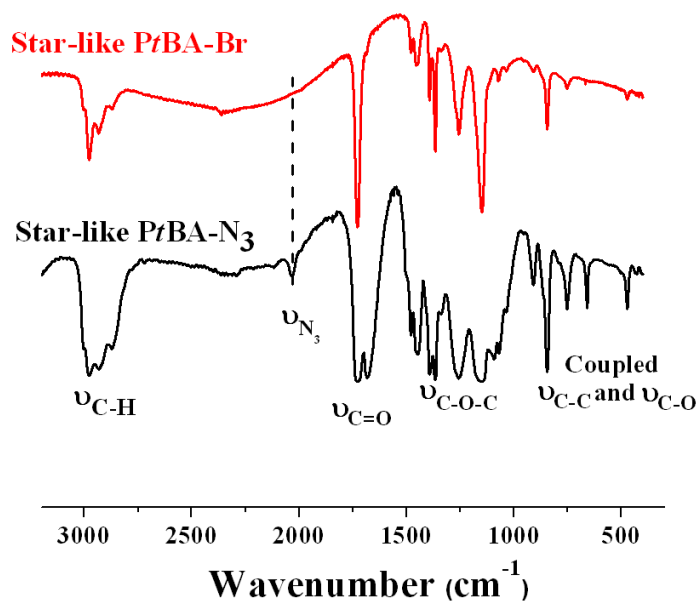


Figure S4. Typical FT-IR spectra of star-like PtBA-Br and the corresponding PtBA-N₃ (Entry 4 in Table 1).

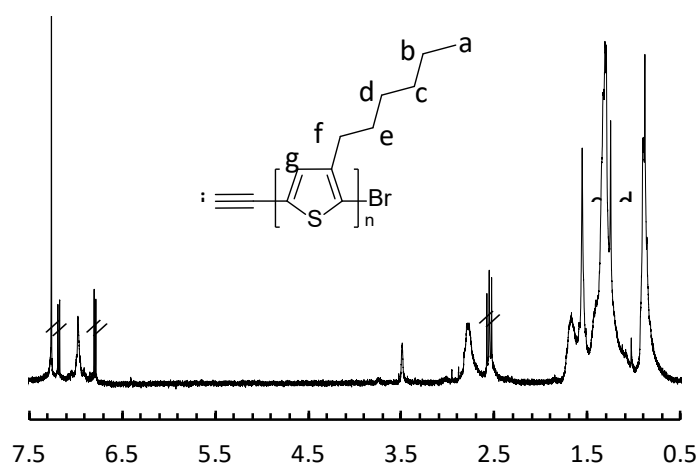


Figure S5. ¹H NMR spectrum of ≡-P3HT in CDCl₃. // marks for the impurities that can be easily removed after the ‘click’ reaction and purification (as shown in Figure S6).

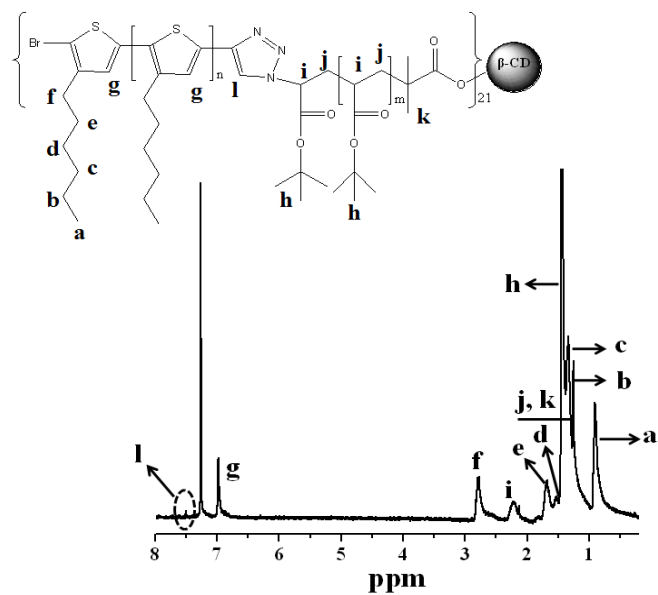


Figure S6. Typical ^1H NMR spectrum of star-like diblock copolymer, PtBA-*b*-P3HT in CDCl_3 (Entry 9 in Table 1).

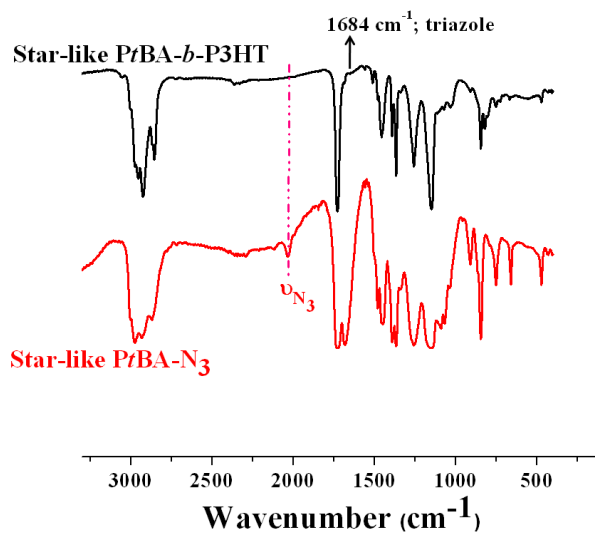


Figure S7. Typical FT-IR spectra of star-like PtBA- N_3 (Entry 4 in Table 1) and PtBA-*b*-P3HT (Entry 9 in Table 1).

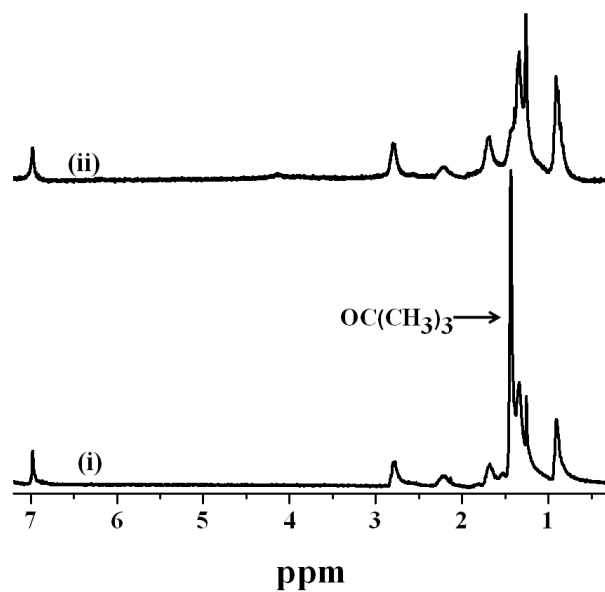


Figure S8. ^1H NMR spectra of star-like diblock copolymer (i) PtBA-*b*-P3HT (Entry 4 in Table 1) in CDCl_3 , and (ii) the corresponding PAA-*b*-P3HT ((Entry 9 in Table 1) in d_7 -DMF).

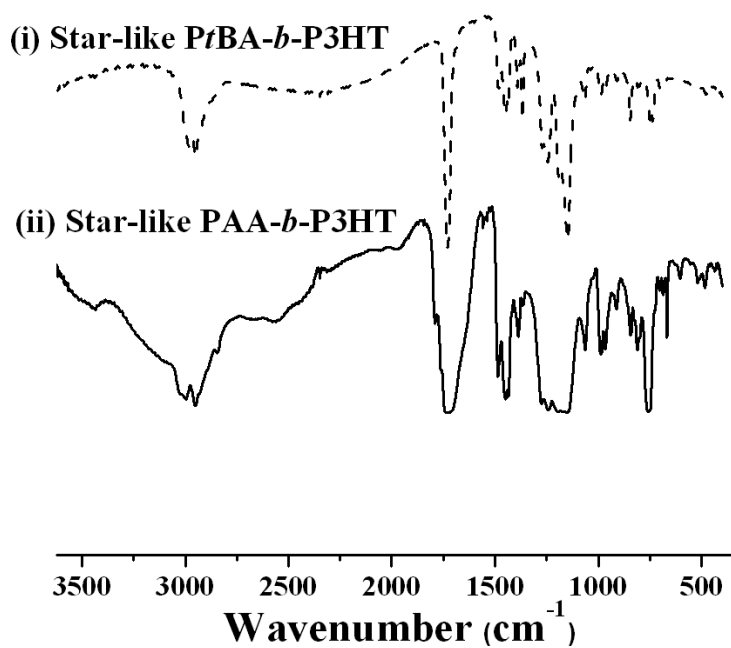


Figure S9. FTIR spectra of star-like diblock copolymers (i) PtBA-*b*-P3HT (Entry 4 in Table 1), and (ii) PAA-*b*-P3HT (Entry 9 in Table 1).

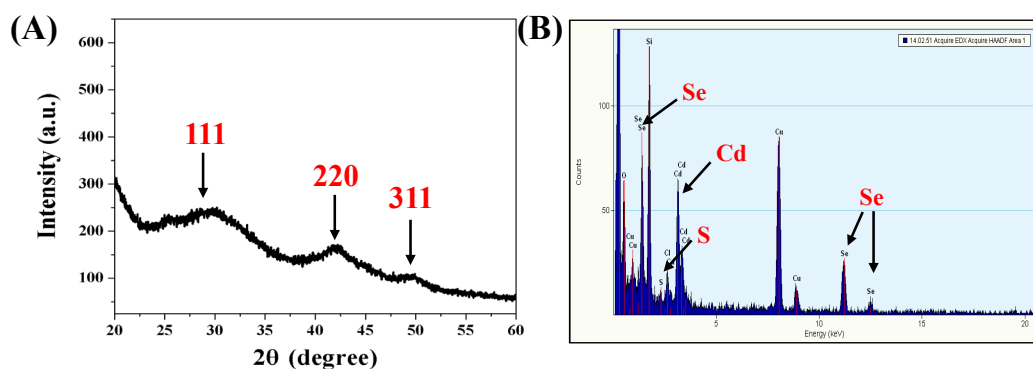


Figure S10. (A) XRD pattern (wurtzite structure, JCPDS 77-2307), and (B) EDS spectrum of CdSe@P3HT nanoparticles. All samples were prepared using star-like PAA-*b*-P3HT as a nanoreactor (Entry 9 in Table 1).

Table S1: EDS elemental analysis of CdSe@P3HT nanocomposite using star-like PAA-*b*-P3HT (Entry 9 in Table 1) as nanoreactor.

Element	Weight (%)	Atomic (%)
C K	42.04	63.47
Si K	8.06	6.02
S K	4.52	3.26
Se L	18.16	13.30
Cd M	27.22	13.95
Totals	100	100

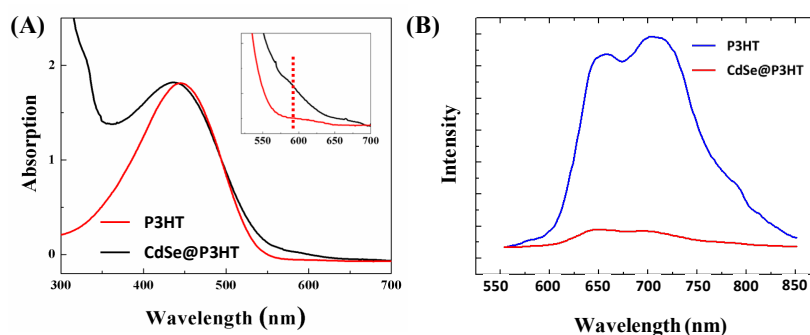


Figure S11. (A) Absorption spectra in THF and (B) emission spectra in the dry state of P3HT and CdSe@P3HT nanocomposites synthesized using star-like PAA-*b*-P3HT as nanoreactor (Entry 9 in Table 1).

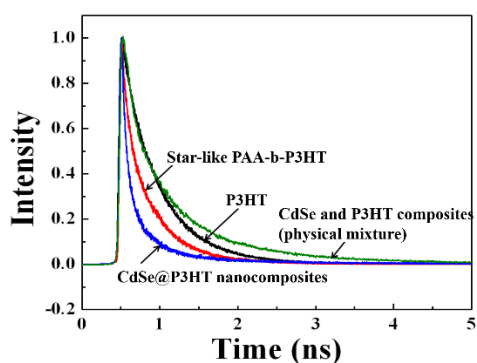


Figure S12. Normalized time-resolved photoluminescence lifetime for the samples of CdSe@P3HT nanocomposites (—), P3HT (—), Star-like PAA-b-P3HT (—) and physical mixture of CdSe with P3HT (—) with $\lambda_{\text{exc}} = 410$ nm and $\lambda_{\text{em}} \geq 550$ nm.

Reference

- S1. X. Pang, L. Zhao, M. Akinc, J. K. Kim and Z. Lin, *Macromolecules*, 2011, **44**, 3746-3752.
 S2. M. Jeffries-El, G. Sauve and R. D. McCullough, *Macromolecules*, 2005, **38**, 10346-10352.
 S3. X. Pang, L. Zhao, W. Han, X. Xin and Z. Lin, *Nat. Nanotechnol.*, 2013, **8**, 426-431.