

*Electronic Supplementary Information for:*

**Fabrication of Multi-Charges Generable Poly(phenyl  
isocyanide)-block-Poly(3-hexylthiophene) Rod-Rod  
Conjugated Copolymer**

Wei Li,<sup>†</sup> Ya-Guang He,<sup>†</sup> Sheng-Yu Shi, Na Liu, Yuan-Yuan Zhu, Yun-Sheng Ding,

Jun Yin,\* and Zong-Quan Wu\*

Department of Polymer Material and Engineering, School of Chemistry and Chemical  
Engineering, Hefei University of Technology and Anhui Key Laboratory of Advanced Functional  
Materials and Devices, Hefei 230009, China.

E-mail: yinjun@hfut.edu.cn, zqwu@hfut.edu.cn

## Materials

2,5-Dibromo-3-hexylthiophene (3HT, 97%), isopropylmagnesium chloride (2.0 M solution in THF), Ni(dppp)Cl<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino) propane, 99%), phosphotungstic acid (99%), dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, 99%), 4-nitrobenzoic acid (99%), palladium 10% activated carbon, trifluoroacetic acid (99%; TFA), and *tert*-butyl alcohol were purchased from Aladdin and used as received. 3-Hydroxybenzaldehyde (98.5%) and 5-hydroxy-2-nitrobenzaldehyde (98%) were purchased from Aldrich and used as received. THF was dried over sodium benzophenone ketyl and further distilled just before use. Triethylamine (TEA) and chloroform (CHCl<sub>3</sub>) were distilled over CaH<sub>2</sub>. Methanol (99%), *n*-hexane (99%), and all the other solvents were purchased from Sinopharm and were used as received otherwise denoted. Water was deionized with a Milli-Q SP reagent water system (Millipore) to a specific resistivity of 18.0 MΩ cm. 5-(2'-(dimethylamino)ethoxy)-2-nitrobenzyl alcohol (DMAENBA) was synthesized according to our previous report,<sup>1</sup> the synthesis procedures were shown in Figure S3a, and corresponding chemical structures were confirmed by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR), as shown in Figure S3b.

## Sample Preparation

*Synthesis of 4-Nitro-Benzoic Acid tert-Butyl Ester (compound a in Figure S1).* This compound was synthesized according to literature procedures with little modification.<sup>2</sup> In a typical run, a 500 mL round-bottom flask was charged with 4-nitrobenzoic acid (15 g, 89.76 mmol), EDCI (16.41 g, 89.76 mmol), DMAP (366 mg, 2.964 mmol), and dry CH<sub>2</sub>Cl<sub>2</sub> (250 mL). After the reaction mixture was stirred at 0 °C for 0.5 hour under N<sub>2</sub>, the *tert*-butyl alcohol (9 mL) was injected to the mixture *via* a syringe. The reaction mixture was then allowed to stir at 0 °C for 0.5 h and warm to room temperature for another 5 hours. After removing the insoluble solids by suction filtration, the filtrate was washed with water (3 × 100 mL). The organic layers were combined and dried over anhydrous MgSO<sub>4</sub> and concentrated using a rotary evaporator. The crude product was further purified by silica gel column

chromatography using petroleum ether/ethyl acetate (5:1, v/v) as an eluent. After removing all the solvents, the compound, *a*, was obtained (6.0 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS; Figure S2a): 8.24-8.27 and 8.13-8.16 (4H, *phenyl*), 1.62 (9H, -C(CH<sub>3</sub>)<sub>3</sub>).

*Synthesis of 4-Amino-Benzoic Acid tert-Butyl Ester (compound b in Figure S1).* Into a 250 mL round-bottom flask, compound *a* (4.0 g, 17.91 mmol) and 10% palladium-activated carbon (0.5 g) were charged. After completely degassed for 30 min by H<sub>2</sub>, dry ethanol (50 mL) and dry THF (50 mL) was injected to the mixture *via* a syringe. The mixture was allowed to stir at room temperature for 12 h under an atmosphere of H<sub>2</sub>. After filtration, the solvent was removed to give the product, compound *b* (3.5 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS; Figure S2b): 7.78-7.81 and 6.61-6.63 (4H, *phenyl*), 3.99 (2H, -NH<sub>2</sub>), 1.56 (9H, -C(CH<sub>3</sub>)<sub>3</sub>).

*Synthesis of 4-Formylamino-Benzoic Acid tert-Butyl Ester (compound c in Figure S2).* A 250 mL round-bottom flask was charged with compound *b* (3.5 g, 18.13 mmol) and dry ethyl acetate (120 mL). The mixture was cooled to 0 °C in an ice-water bath, and another mixture of formic acid (13.4 mL) and acetic anhydride (6.6 mL), which had been prepared at room temperature for 2 h under N<sub>2</sub> in advance, was added dropwise. After the addition was completed, the reaction mixture was stirred at 0 °C for 0.5 hour and then allowed to warm to room temperature for another 5 hours. After the mixture was filtered, the filtrate was washed with H<sub>2</sub>O (3×30 mL) and brine (3×30 mL), and then dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed by evaporation, the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (2:1, v/v) as an eluent. After removing all the solvents, the product, compound *c*, was obtained (3.0 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS; Figure S2c): 8.76 (-NH- in *trans*, 0.35 H), 8.33 (-CHO in *trans*, 0.35 H), 8.14 (-NH- in *cis*, 0.65 H), 7.90 (-CHO in *cis*, 0.65 H), 7.88 (H<sub>m</sub> to -NH- in *trans*, 0.7 H), 7.86 (H<sub>m</sub> to -NH- in *cis*, 1.3 H), 7.53 (H<sub>o</sub> to -NH- in *cis*, 1.3 H), 7.05 (H<sub>o</sub> to -NH- in *trans*, 0.7 H), 1.54 (9H, -C(CH<sub>3</sub>)<sub>3</sub>). The *cis* and *trans* conformers are tentatively assigned based on the reported literatures.<sup>2-3</sup>

*Synthesis of 4-Isocyano-Benzoic Acid tert-Butyl Ester (compound d in Figure S1).*

This compound was synthesized according to literature procedures with little modification.<sup>2</sup> In a typical run, a 250 mL round-bottom flask was charged with compound *c* (2.0 g, 9.04 mmol), TEA (5.4 mL, 48.47 mmol), and dry THF (30 mL). The mixture was allowed to stir at 0 °C in an ice-water bath under  $N_2$  for 0.5 h. Then, a solution of  $POCl_3$  (1.5 mL, 16.1 mmol) in dry THF (20 mL) was added dropwise to the mixture. After the addition was completed, the reaction mixture was stirred at 0 °C for 0.5 hour and allowed to warm to room temperature for 8 hours, and then ethyl acetate (80 mL) was added. After filtration, the solution was washed with aqueous  $NaHCO_3$  ( $2 \times 30$  mL) and brine ( $2 \times 30$  mL) and dried over anhydrous  $MgSO_4$ . After the solvent was concentrated, the crude product was purified by silica gel column chromatography using ethyl acetate as an eluent. After removing all the solvents, the product, compound *d*, was obtained (1.5 g).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ , ppm, TMS; Figure S2d): 7.99-8.01 and 7.39-7.41 (4H, *phenyl*), 1.58 (9H,  $-C(CH_3)_3$ ).

*Synthesis of Poly(4-Isocyano-Benzoic Acid tert-Butyl Ester)-b-Poly(3-Hexylthiophene) (PPI-b-P3HT, polymer 1).* The general approaches to the preparation of PPI-*b*-P3HT using a single catalyst in a single pot are shown in Scheme 2 in main text. This polymerization was carried out in a dry glass ampule under a nitrogen atmosphere using  $Ni(dppp)Cl_2$ , acting as both initiator and catalyst, in dry THF in a similar way to that previously reported references with little modification.<sup>4</sup> A typical experimental procedure for the synthesis is described below. Into a dry glass ampule equipped with a magnetic stirring bar, 2,5-dibromo-3-hexylthiophene (3HT; 81.52 mg, 0.25 mmol) was charged. The flask was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, dry THF (3.0 mL) and isopropylmagnesium chloride (0.13 mL, 2.0 M solution in THF) were successively introduced by a syringe. The reaction mixture was allowed to stir at room temperature for further use. Then, into another dry glass ampule equipped with a magnetic stirring bar, 4-isocyano-benzoic acid *tert*-butyl ester (compound *d*, PI; 50.81 mg, 0.25 mmol) was charged, followed by the addition of  $Ni(dppp)Cl_2$  (2.81 mg, 50  $\mu$ mol) under  $N_2$  at room temperature to generate PPI block with a living chain end.

The polymerization progress was monitored by size exclusion chromatograms (SEC) until the molecular weight of PPI ceased to increase ( $M_n = 10.7$  kDa,  $M_w/M_n = 1.22$ ). Subsequently, under nitrogen atmosphere, activated 3HT mixture was added to the reaction mixture. After stirring at room temperature for another 1 h, the resulting solution was poured into an excess amount of methanol, which resulted in solid to precipitate. The solid was then collected by filtration and washed with methanol and *n*-hexane to remove residual metal salts and unreacted monomers. The final product was dried under vacuum to obtain 95 mg of the expected PPI-*b*-P3HT copolymers. SEC:  $M_n = 18.6$  kDa,  $M_w/M_n = 1.20$ . The chemical structure was confirmed by proton nuclear magnetic resonance spectroscopy ( $^1\text{H NMR}$ ), as shown in Figure S4a.

*Synthesis of Poly(4-Isocyano-Benzoic Acid)-b-Poly(3-Hexylthiophene) (PPI(-AA)-b-P3HT, polymer 2).* The general approaches were followed by reported literature procedures with little modification.<sup>5</sup> Into a 100 mL round-bottom flask, PPI-*b*-P3HT copolymers (60 mg, 3.23  $\mu\text{mol}$ ) and dry THF (4 mL) were charged. After dissolving PPI-*b*-P3HT in THF, trifluoroacetic acid (TFA; 0.6 mL, 99  $\mu\text{mol}$ ) was added. The reaction mixture was allowed to stir at room temperature for 24 h, after which the solvent was removed under reduced pressure. The resulting crude solid was then washed with cold *n*-hexane and dried under reduced pressure to afford the desired product (PPI(-AA)-*b*-P3HT, 40 mg). SEC:  $M_n = 15.7$  kDa,  $M_w/M_n = 1.21$ . The chemical structure was confirmed by proton nuclear magnetic resonance spectroscopy ( $^1\text{H NMR}$ ), as shown in Figure S4b.

*Synthesis of Poly(4-Isocyano-Benzoic Acid 5-(2-Dimethylamino-ethoxy)-2-Nitro-Benzyl Ester)-b-Poly(3-Hexylthiophene) (PPI(-DMAENBA)-b-P3HT, polymer 3).* Into a 50 mL round-bottom flask, PPI(-AA)-*b*-P3HT copolymers (30 mg, 1.91  $\mu\text{mol}$ ; -AA: 0.099 mmol), DCC (40.79 mg, 0.198 mmol), DMAP (4.89 mg, 0.04 mmol), and dry  $\text{CHCl}_3$  (5 mL) were charged. After stirring in an ice-water bath under  $N_2$  for 10 min, 5-(2'-(dimethylamino) ethoxy)-2-nitrobenzyl alcohol (DMAENBA; 40.85 mg, 0.2 mmol) was added under  $N_2$ . The reaction mixture was allowed to stir at room temperature for another 24 h, and 20 mL of methanol was poured into the mixture,

which caused solid to precipitate. The solid was then isolated *via* filtration and dried under vacuum to afford the desired PPI(-DMAENBA)-*b*-P3HT copolymers (48 mg). SEC:  $M_n = 26.1$  kDa,  $M_w/M_n = 1.22$ . The chemical structure was confirmed by proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR), as shown in Figure S4c.

*Synthesis of quaternized PPI(-DMAENBA)-b-P3HT Copolymer (PPI(-QDMAENBA)-b-P3HT, polymer 4).* The quaternization of PPI(-DMAENBA) blocks was carried out at room temperature by reacting methyl iodide with PPI(-DMAENBA)-*b*-P3HT copolymers in THF according to previously reported literature.<sup>6</sup> A typical experimental procedure for 100% quaternized is described below. Into a round-bottom flask, PPI(-DMAENBA)-*b*-P3HT (30 mg, 1.15  $\mu\text{mol}$ ; 50  $\mu\text{mol}$  DMAENBA residues), methyl iodide (6.25  $\mu\text{L}$ , 0.1 mmol), and dry THF (3 mL) were charged. The reaction was allowed to stir for 2 h at room temperature. It was then dissolved in water and thoroughly dialyzed against DI water (MW cutoff, 1000 Da) to remove impurities. After lyophilization, the cationic PPI(-QDMAENBA)-*b*-P3HT copolymer was obtained. Following the similar procedures, PPI(-QDMAENBA/DMAENBA)-*b*-P3HT copolymers with various degree of quaternization were also prepared (defined the degree of ionization of +35.9 mV to be 100%).

*Preparation of Micellar Solutions.* The two types of polymer micelles were prepared by directly dissolving the relevant block copolymers in aqueous solution at pH 8.0. About 5 milligrams of copolymers was dissolved in 10 mL of DI water. After ultrasonication for a short time period, the obtained dispersion did not exhibit any macroscopic phase separation on standing at room temperature for more than 7 days, suggesting the formation of stable aggregates. Throughout this study, unless otherwise stated, all PPI(-AA)-*b*-P3HT micellar aqueous solutions were held at pH = 8.0 to keep AA moieties in its ionized anionic state and to avoid the precipitation of negatively charged micelles.

*Preparation of Micelles Based Film.* The fabrication of film from PPI(-QDMAENBA)-*b*-P3HT and PPI(-AA)-*b*-P3HT conjugated copolymers based micelles with respective polycation and polyanion coronas was performed by a simply mixing of equal amount

of two micellar solution into a small cubic PTFE mould.

## **Characterization**

*Size Exclusion Chromatograms (SEC).* Molecular weights and molecular weight distributions were determined by SEC equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 40 °C). It used a series of three linear Styragel columns (HR0.5, HR2, and HR4; 3.6 × 300 mm) at an oven temperature of 40 °C. The eluent was THF at a flow rate of 0.3 mL/min. A series of low polydispersity polystyrene (PS) standards were employed for the SEC calibration.

*Nuclear Magnetic Resonance Spectroscopy (NMR).* All NMR spectra were recorded on a VNMRS600 NMR spectrometer (resonance frequency of 600 MHz for <sup>1</sup>H) operated in the Fourier transform mode. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual proton solvent as an internal standard. For <sup>1</sup>H NMR: CDCl<sub>3</sub>, 7.26 ppm.

*UV-Visible Spectroscopy (UV-vis).* The UV-vis measurements were performed on UNIC 4802UV/VIS Double beam spectrophotometer.

*Differential Scanning Calorimetric (DSC).* DSC measurements were carried on a Mettler-Toledo DSC821e instrument. Samples were first heated from 25 to 150 °C at a heating rate of 10 °C/min under nitrogen atmosphere and kept constant at 150 °C for 3 min, followed by cooling to 25 °C at 10 °C/min and finally heating to 220 °C again at 10 °C/min. Glass transition temperature ( $T_g$ ) was determined as the midpoint of the transition of the second heating sequence.

*Dynamic Light Scattering (DLS).* Average number distributions measurements of a series of copolymer assemblies in water (0.1 g/L) were carried on a Nano-ZS90 Zetasizer of Malvern (UK) instrument. All samples were filtered with syringe filters (0.8 μm pore size, Cellulose Acetate filter media) prior to the DLS measurements. All data were averaged over three time measurements.

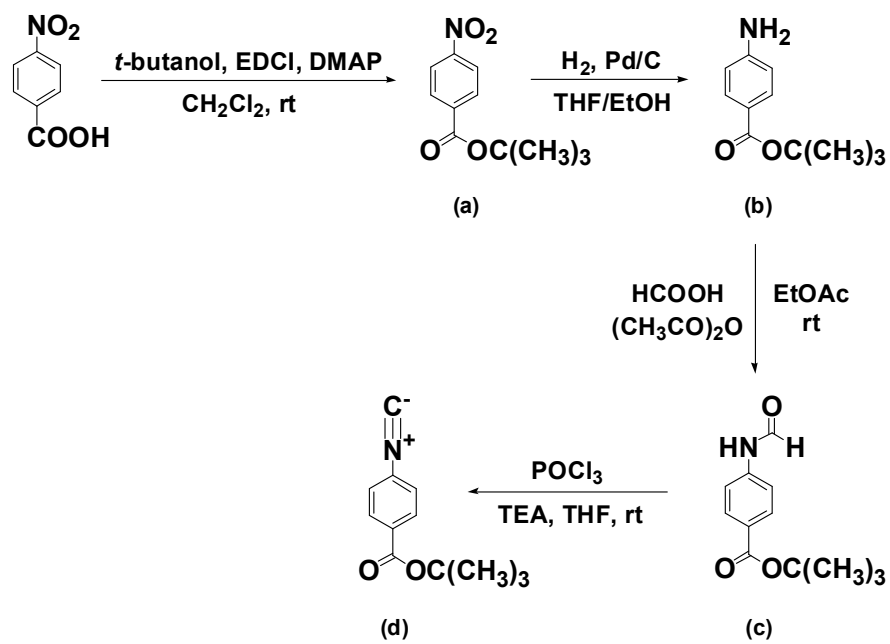
*Zeta Potential (ζ-Potential) Measurements.* The zeta potential values of the assemblies were performed by DelsaNanoC analyzer (Beckman Coulter) equipped

with a 30 mW dual laser diode. The zeta potential of the assemblies in dispersion was obtained by measuring the electrophoretic movement of charged assemblies under an applied electric field.

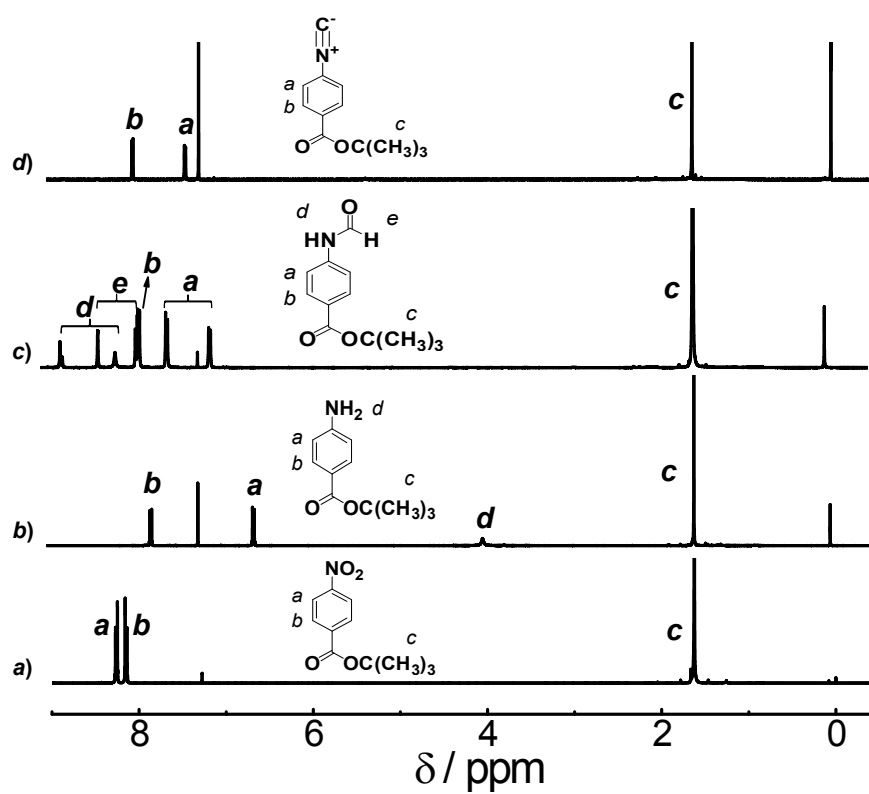
*Field-Emission Scanning Electron Microscope (FE-SEM).* FE-SEM observations were conducted on a high-resolution JEOL JSM-6700 field-emission scanning electron microscopy. The samples for SEM observations were prepared by placing 10  $\mu\text{L}$  of microgel solutions on copper grids successively coated with thin films of Formvar and carbon.

*Surface Tensiometry.* Equilibrium surface tensions were measured with a JK99B tensiometer. The instrument was calibrated against deionized water and the agreement with literature values was typically within  $\pm 0.1$  mN/m. The measurements were carried out with freshly made solutions at  $25.0 \pm 0.1$  °C.

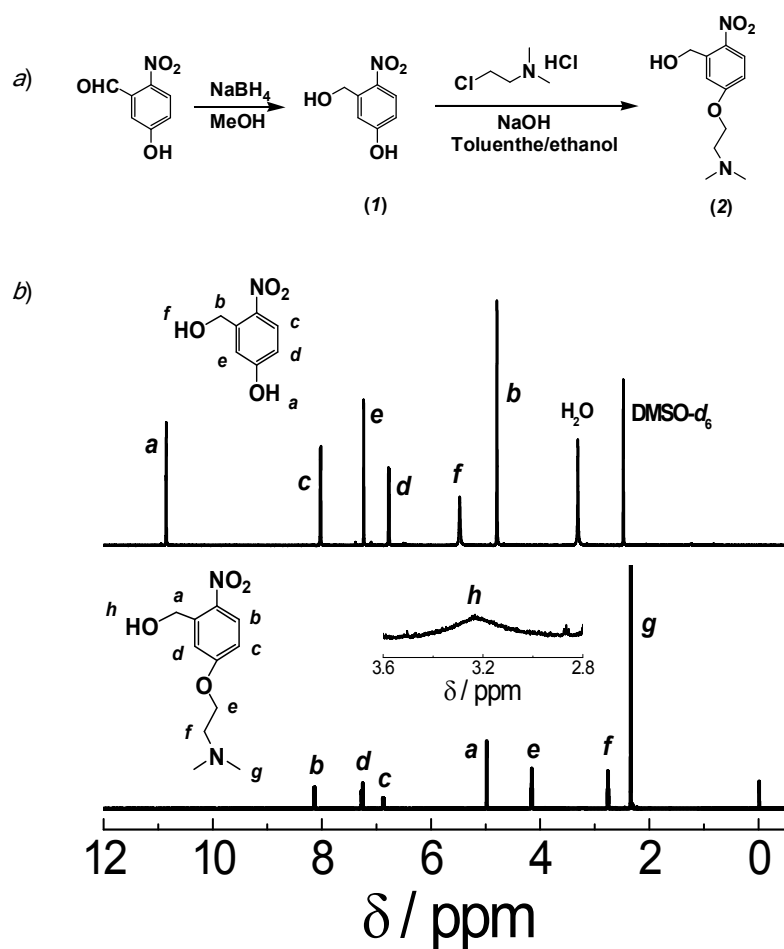


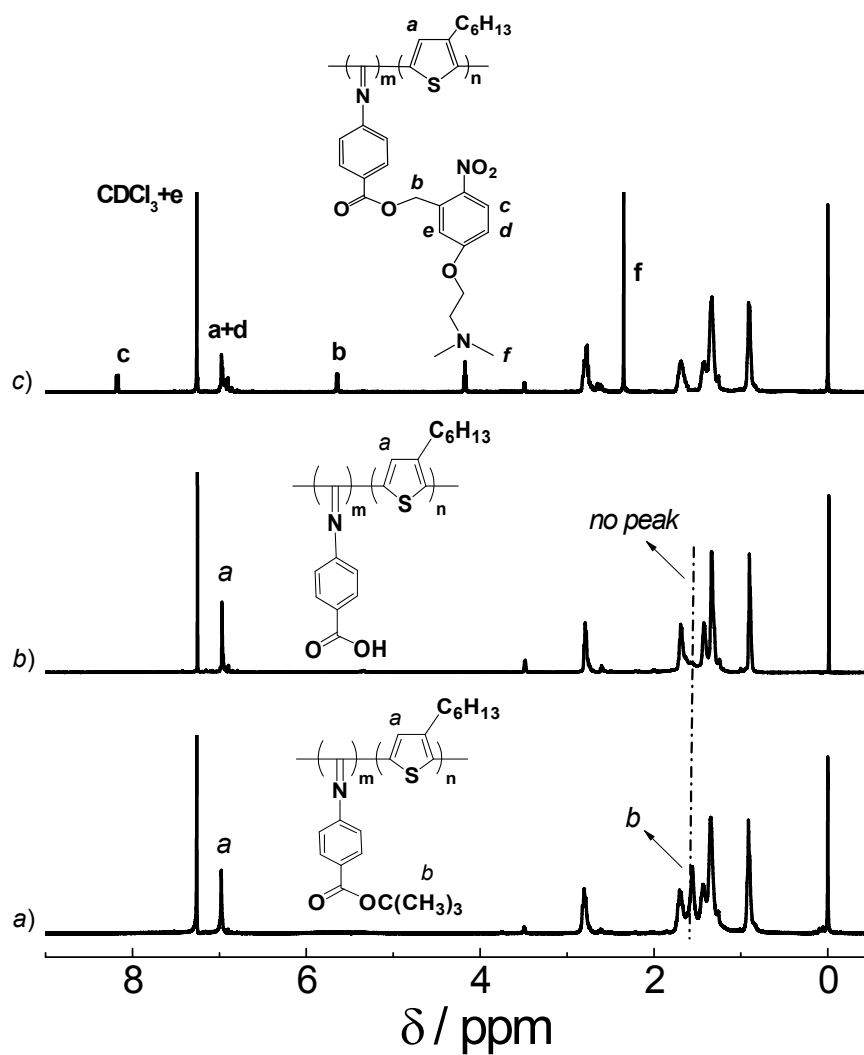


**Figure S1.** Synthetic routes employed for the preparation of 4-isocyano-benzoic acid *tert*-butyl ester (*d*).

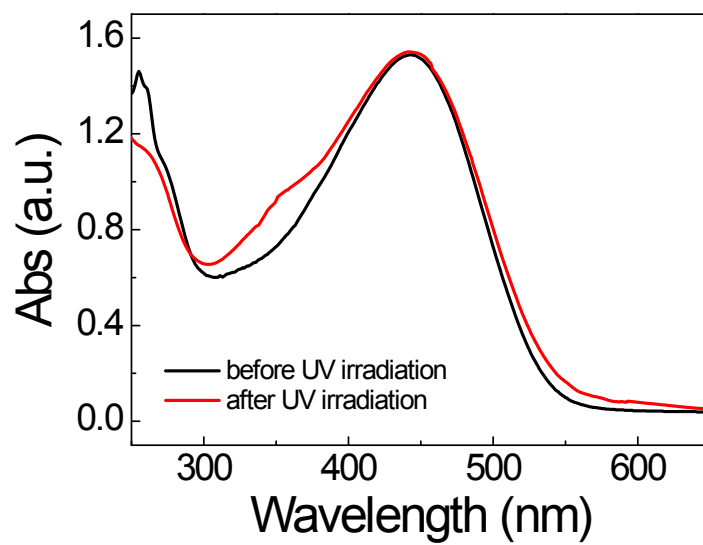


**Figure S2.** <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> for (a) 4-nitro-benzoic acid *tert*-butyl ester, (b) 4-amino-benzoic acid *tert*-butyl ester, (c) 4-formylamino-benzoic acid *tert*-butyl ester, and (d) 4-isocyano-benzoic acid *tert*-butyl ester.

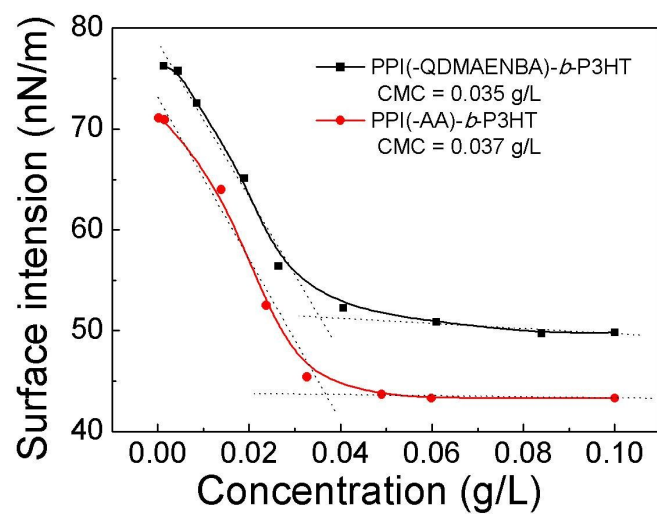




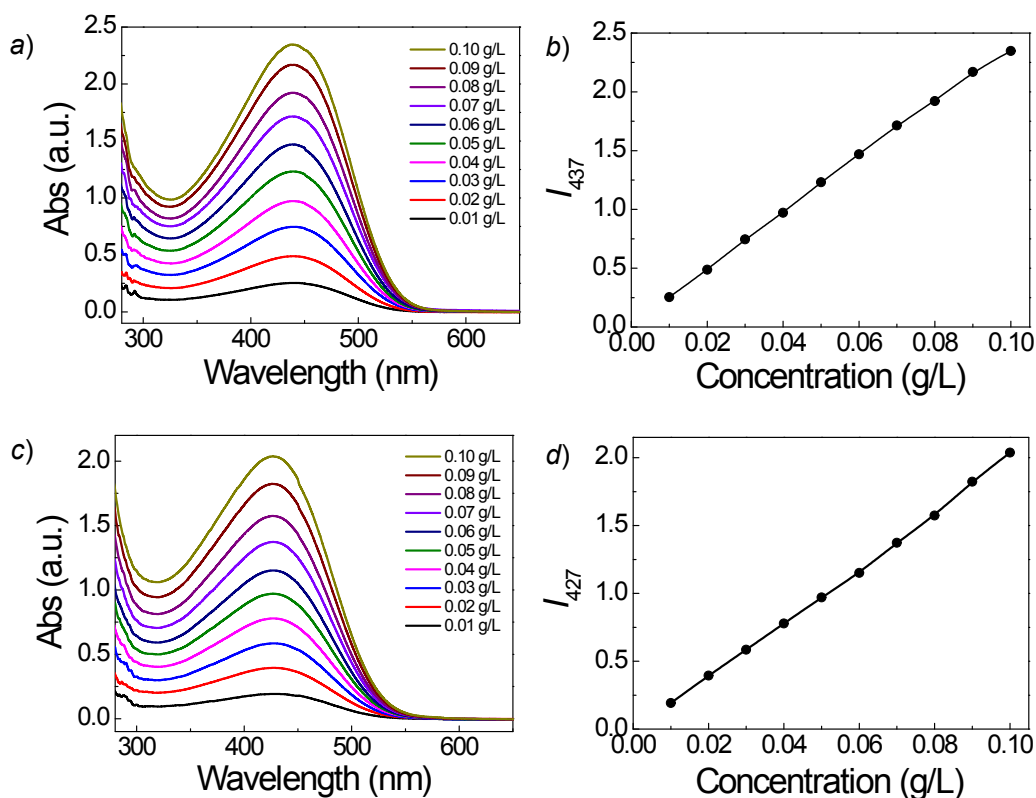
**Figure S4.**  $^1\text{H}$  NMR spectra recorded for (a) PPI-*b*-P3HT (polymer 1), (b) PPI(-AA)-*b*-P3HT (polymer 2), and (c) PPI(-DMAENBA)-*b*-P3HT (polymer 3) diblock copolymers in  $\text{CDCl}_3$ .



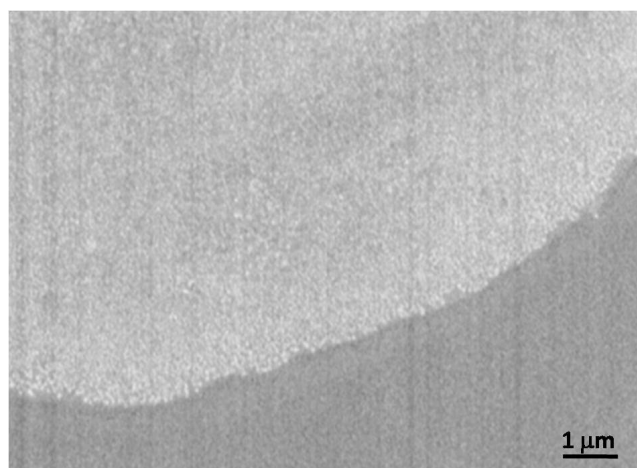
**Figure S5.** UV-vis spectra recorded for PPI(-DMAENBA)-*b*-P3HT copolymer (3) solution before and after UV irradiation (365 nm) for 2.5 h.



**Figure S6.** Surface intension of micelles prepared by PPI(-QDMAENBA)-*b*-P3HT and PPI(-AA)-*b*-P3HT diblock copolymers in water as a function of concentration at 25 °C.



**Figure S7.** UV-vis spectra recorded for (a) PPI(-DMAENBA)-*b*-P3HT and (c) PPI(-QDMAENBA/DMAENBA)-*b*-P3HT (40% degree of quaternization) in THF as a function of copolymer concentration. (b) and (d) showed the change in relative absorption intensity at  $\lambda_{em} = 437$  nm in a and  $\lambda_{em} = 427$  nm in c obtained for copolymers in THF, respectively.



**Figure S8.** SEM image obtained at a larger scale for conjugated copolymer micelles based film by directed fabrication from micelles with polycation and polyanion coronas



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