

Supporting Information

Controlled Synthesis of Multi-armed P3HT Star Polymers with Gold Nanoparticle Core

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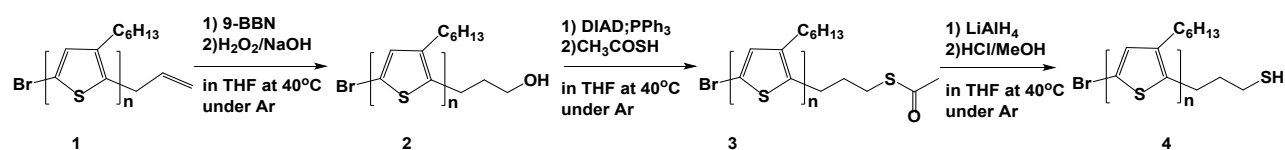
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General synthetic procedure for end-functionalized P3HT-SH (4) (Typically for Low MW P3HT-SH)



Scheme S1. Synthesis of allyl and thiol end group functionalized poly(3-hexylthiophene) (P3HT) based on GRIM method followed by end-group modification.

(a) Synthesis of allyl terminated poly(3-hexylthiophene) (P3HT-allyl) (1):^[1] The mole ratio of various components were [monomer]: [t-BuMgCl]: [Ni(dppp)Cl₂]: [AllylMgBr] = 1 : 1 : 0.022 : 0.24. To an oven dried one-neck 250 mL r.b. flask equipped with a stirring bar was introduced monomer (4.0g, 12.27 mmol) and 24 mL of dry THF. Required amount of tert-butyl magnesium chloride (6.13 mL in 2.0 M in diethylether, 12.27 mmol) was added to the flask via degassed syringe and mixture was stirred for 3 h. Thereafter, solution mixture was diluted by 95 mL of dry

THF followed by addition of Ni(dppp)Cl₂ (0.15 g, 0.276 mmol). Immediately the color of reaction mixture turned bright orange and changed dark after the addition of 1.0 M of allyl magnesium bromide (6 mL, in 1.0 M in diethylether 3 mmol) via degassed syringe. The mixture was stirred for an additional 10 min; removed reaction flask and precipitated into five-fold excess of methanol. The polymer (purple color) was filtered, using Millipore (1.0 μm) PTFE filter paper, and purified using Soxhlet extraction using n-pentane for 12 h. Finally, polymer (yield = 1.2 g) was dried under vacuum at 40 °C for 24 h and analyzed by ¹H NMR. SEC ($M_n = 7100$; $M_w/M_n = 1.1$) and MALDI-TOF-MASS ($M_n = 4,200$; $M_w/M_n = 1.08$) (see Fig. S1A(a), Fig. S2A(a) and Fig. S3(a) for more details).

(b) Synthesis of hydroxypropyl terminated poly(3-hexylthiophene) (P3HT-OH) (2):^[2] To a one-neck oven dried r.b. flask equipped with stirring bar was transferred allyl terminated P3HT (1) (1.1 g, $M_n = 7100$, 0.155mmol) followed by addition of dry THF (500 mL) in two-neck 1000 mL round bottom flask. After the addition of 9-BBN (0.378 g, 1.55 mmol), the reaction flask was taken outside and stirred for 48 h in an oil bath maintained at 40 °C. Thereafter, 6 M solution of NaOH (0.77 mL) was added to the reaction flask, followed by removal of oil bath and stirring continued for an additional 30 min. Upon cooling, added 33 % aqueous solution of hydrogen peroxide (0.72mL), and reaction stirred for 12 h at 40 °C. The polymer was precipitated in five-fold excess of methanol-water (10:1) mixture. The polymer was filtered using Millipore (1.0 μm) PTFE filter paper and purified using Soxhlet extraction using methanol for 12 h. Finally, polymer (Yield = 1.1 g) was dried under vacuum at 40 °C for 24 h and analyzed by ¹H NMR. SEC ($M_n = 7,100$; $M_w/M_n = 1.11$) and MALDI-TOF-MASS ($M_n = 4,100$ Da; $M_w/M_n = 1.05$) (see Fig. S1A(b), Fig. S2A(b) and Fig. S3(b) for more details).

(c) Synthesis of propylthioacetyl terminated poly(3-hexylthiophene) (P3HT-TA) (3):^[3] A 100 mL three neck flask was placed in a dry ice bath at -30 °C and charged with 15 mL anhydrous THF, triphenylphosphine (1.4 mmol, 0.369 g), and diisopropyl azodicarboxylate (DIAD) (1.4 mmol, 0.27 mL). A pale yellow precipitate, corresponding to the DIAD-PPh₃ adduct formed within 30 minutes. At this point the reaction flask was removed from the dry ice bath and make warm to room temperature. A solution of 1.0 g (0.14 mmol) of hydroxypropyl-terminated P3HT in 30 mL anhydrous THF and 0.1 mL thioacetic acid (1.5 mmol) were added drop-wise to the DIAD-PPh₃ adduct. The reaction mixture was stirred for 8 hrs at 40 °C, followed by precipitation of polymer in

methanol. The polymer was filtered and purified by sequential Soxhlet extractions with methanol, hexane. The polymer was isolated from the chloroform solution. Polymer was characterized by ¹H NMR. SEC ($M_n = 7,200$; $M_w/M_n = 1.2$) and MALDI-TOF-MASS ($M_n = 4,110$ Da; $M_w/M_n = 1.08$) (see Fig. S1A(c), Fig. S2A(c) and Fig. S3(c) for more details for more details).

(d) Synthesis of propylthiol terminated poly(3-hexylthiophene) (P3HT-SH) (4): ^[3] Propylthioacetyl-terminated P3HT (1.5 g, 0.15 mmol) was dissolved in anhydrous THF (100 mL) under argon. To this reaction mixture, 0.07 mL of 1.0 M solution of lithium aluminium hydride was added via a syringe. The reaction mixture was stirred for 4 h at 40 °C, followed by precipitation in methanol/HCl mixture. The polymer was filtered and purified by sequential Soxhlet extractions with methanol, and chloroform. The polymer was isolated from the chloroform solution. Polymer was characterized by ¹H NMR. . SEC ($M_n = 7,400$; $M_w/M_n = 1.3$) and MALDI-TOF-MASS ($M_n = 4,100$ Da; $M_w/M_n = 1.06$) (see Fig. S1A(d), Fig. S2A(d) and Fig. S3(d) for more details).

General synthetic procedure for gold NP ^[4]

The reaction solution of 0.45 g (1.0 mmol) of HAuCl₄, 25 mL (10.8 g, 40 mmol) of oleylamine in a 100 mL three-necked flask was slowly heated to about 120 °C. Growth of nano particles was carried out at 120 °C for 1 h. After growth of gold nanoparticles, the reaction solution was rapidly cooled to room temperature. After cooling to room temperature, ethanol was added into the solution and the nanoparticle was separated from a reaction solution by centrifuge. The precipitate was re-dispersed in hexane, repeated 3 times.

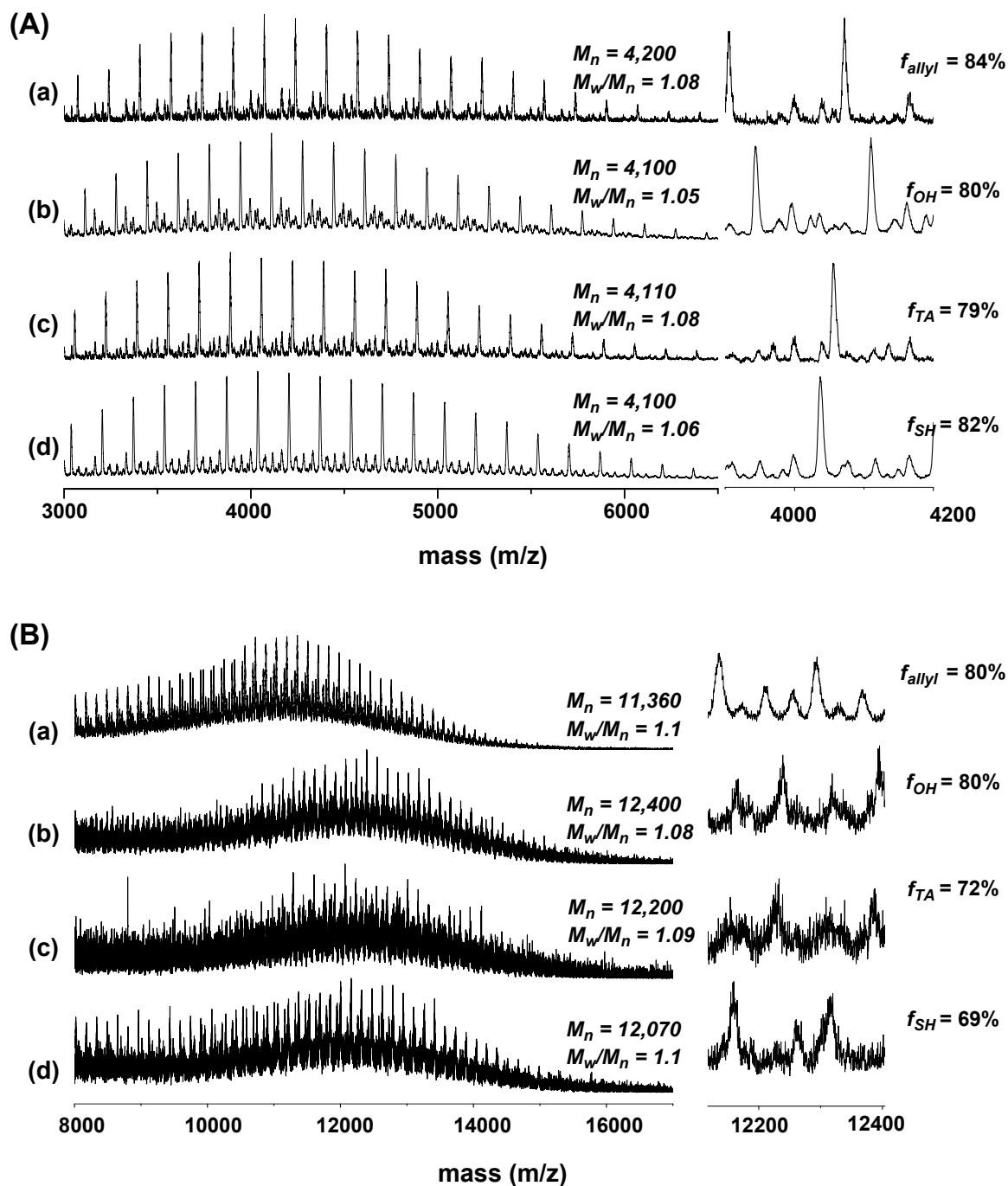


Fig. S1 MALDI-TOF MASS of end-functionalized P3HT with low (A) and high (B) molecular weights: (a) P3HT-allyl, (b) P3HT-OH, (c) P3HT-TA, (d) P3HT-SH.

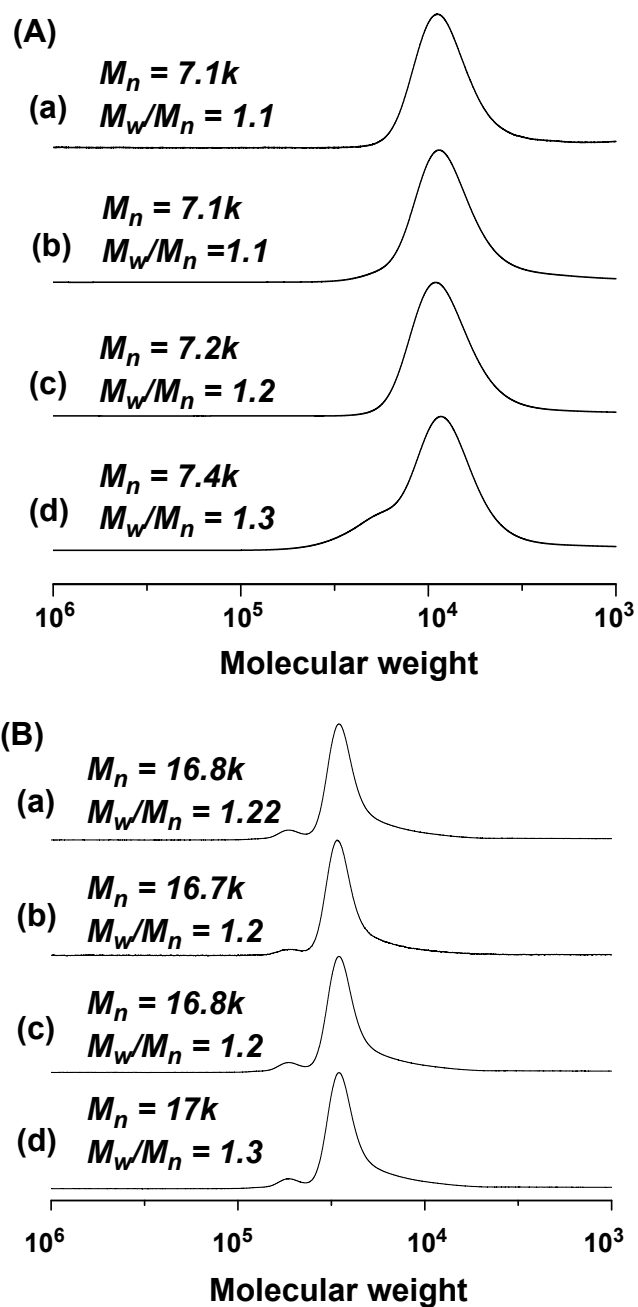


Fig. S2 SEC curves of end-functionalized P3HT with low (A) and high (B) molecular weights: (a) P3HT-allyl, (b) P3HT-OH, (c) P3HT-TA, (d) P3HT-SH.

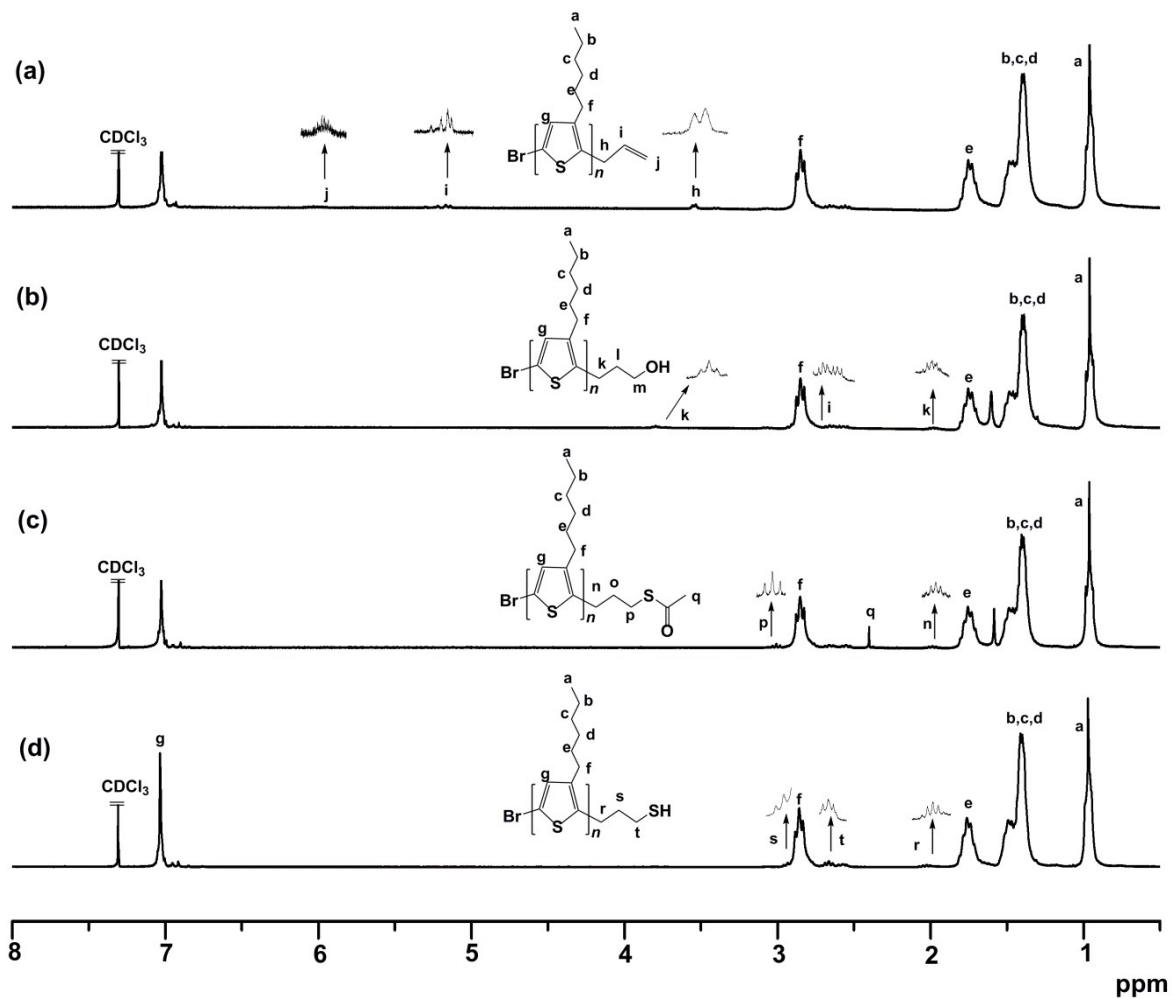


Fig. S3. ^1H NMR spectra of end-functionalized poly(3-hexylthiophene)s with low molecular weight in CDCl_3 : (a) P3HT-allyl, (b) P3HT-OH, (c) P3HT-TA, (d) P3HT-SH.

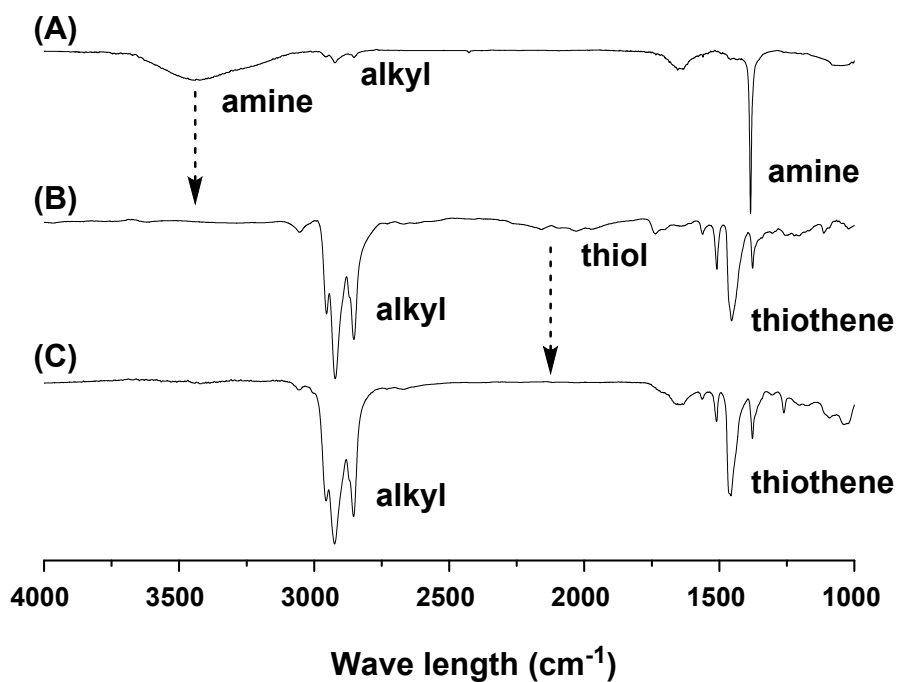


Fig.S4. (A) Gold NP with oleyl amine, (B) P3HT-SH, and (C) P3HT star polymer with gold NP core.

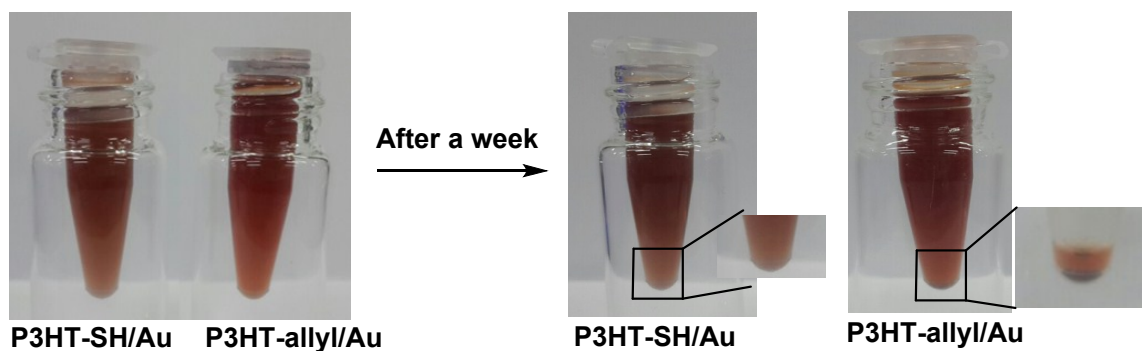


Fig.S5. Pictures of the products by ligand exchanges with P3HT-SH and P3HT-allyl (in THF solution).

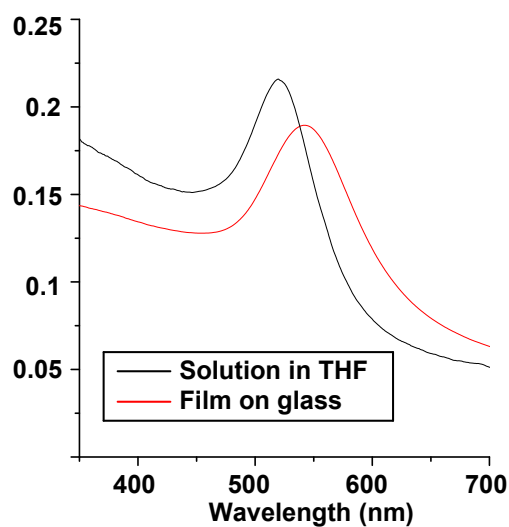


Fig. S6. Optical properties gold nanoparticle in solution state and film of UV-Vis absorption spectra.

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