Supporting Information

One-Pot Synthesis of PbS NP / Sulfur-Oleylamine Copolymer Nanocomposites via the Copolymerization of Elemental Sulfur with Oleylamine

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1. Synthesis of Poly(OLA-r-S)



Figure S1. Conversion curves of solution copolymerization of oleylamine and sulfur in DCB at T = 180 °C at different reaction time. ([oleylamine : sulfur] = 1:2 (black), 1:8 (blue), and 1:33 (red)). Conversions of oleylamine with different molar ratios are shown in colored triangles, which were determined from ¹H NMR. Conversions of sulfur with different molar ratios are shown in colored circles, which were determined by SEC.



Figure S2. SEC of aliquots removed from the solution copolymerization of oleylamine and sulfur in DCB at $T=180^{\circ}C$ at different reaction time (0 to 30 min) with different feed ratios: (a) [oleylamine : sulfur] = 1:2; (b) 1:8; (c) 1:33 in molar ratio.



Figure S3. UV-Vis absorption spectra of the solution copolymerization of oleylamine and sulfur in DCB at T=180 °C for [oleylamine]:[sulfur] = 1:33 in mole ratio taken at different reaction time.



Figure S4. DSC thermograms of purified poly(OLA-r-S) with a feed molar ratio of [oleylamine]:[sulfur] = 1:33 and a PbS/poly(OLA-r-S) nanocomposite obtained by adding 0.144 M of PbCl₂, dissolved in 0.4 g of oleylamine, into poly(OLA-r-S) solution after 30 min of copolymerization.



Figure S5. ¹³C NMR spectrum of a copolymer consisting of oleylamine and sulfur polymerized in 1,2dichlorobenzene-d4 at T=180 °C for [oleylamine]:[sulfur] = 1:33 in mole ratio, after 30 min of copolymerization.

2. Model reactions

2.1. Homo-coupling reaction of 4-tert-butylbenzylamine with sulfur



Reaction was carried out by the method reported in the literature¹ with following modification. To a 5 mL vial along with a magnetic stir bar were added 4-*tert*-Butylbenzylamine (123 mg, 0.75 mmol), sulfur (792 mg, 24.75 mmol) and 1,2-dichloromethane (2 mL). The vial was placed into an oil bath preheated at T = 185 °C and the resulting solution stirred at this temperature for 30 minutes. The hot reaction mixture was added into hexanes (30 mL) and precipitate was removed by filtration. Filtrate was concentrated and purified by silica gel column chromatography using a mixture of hexanes and ethyl acetate (95:5 = v:v) as an eluent to give 4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)benzyl)benzothioamide (63 mg) in 50 % isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.60 (br, 1H), 7.43-7.36 (m, 4H), 7.34-7.30 (m, 2H), 4.95 (d, *J* = 5.0 Hz, 2H), 1.33 (s, 9H), 1.31 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 198.80, 154.77, 151.37, 138.89, 133.26, 128.22, 126.49, 125.99, 125.48, 50.86, 34.88, 34.63, 31.31, 31.12.



Figure S6. ¹H NMR spectrum of 4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)benzyl)benzothioamide synthesized from homo-coupling reaction of 4-*tert*-butylbenzylamine with sulfur



Figure S7. ¹³C NMR spectrum of 4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)benzyl)benzothioamide synthesized from homo-coupling reaction of 4-*tert*-butylbenzylamine with sulfur

2.2. Cross-coupling reaction of 4-tert-butylbenzylamine and oleylamine with sulfur

To a 24 mL vial along with a magnetic stir bar were added 4-*tert*-Butylbenzylamine (0.61 g, 3.74 mmol), sulfur (4.0 g, 125 mmol), oleylamine (1.0 g, 3.74 mL) and 1,2-dichloromethane (10 mL). The vial was placed into an oil bath preheated at T = 185 °C and the resulting solution stirred at this temperature for 30 minutes. The hot reaction mixture was added into hexanes (15 mL) and precipitate was removed by filtration. Filtrate was added into methanol (30 mL) and the resulting mixture was centrifuged at 10,000 rpm for 10 minute. Supernatant was decanted and precipitate was dried under reduced pressure at room temperature to give a dark brown colored solid (0.91g). The resulting solid material was dissolved in chlorobenzene- d_5 for ¹³C NMR characterization.



Figure S8. ¹³C NMR spectrum of reaction mixture synthesized from cross-coupling reaction of 4-*tert*butylbenzylamine and oleylamine with sulfur. NMR sample was prepared by dissolving reaction mixture in chlorobenzene- d_5 and peak at $\delta = 198.4$ ppm corresponds to a single substituted thioamide functional group.

References

1. T. B. Nguyen, L. Ermolenko and A. Al-Mourabit, Org. Lett., 2012, 14, 4274

3. Synthesis of PbS/Poly(OLA-r-S) nanocomposites



Figure S9. TEM images of PbS/poly(OLA-r-S) nanocomposites by the addition of PbCl₂-oleylamine solution (0.288 mmol of PbCl₂ dissolved in 0.4 g of oleylamine) into poly(OLA-r-S) solution (after 30 min of copolymerization) with different molar feed ratios: (a) [oleylamine]:[sulfur] = 1:2; (b) 1:8; (c) 1:33.



Figure S10. TGA curves of PbS/poly(OLA-r-S) nanocomposites obtained by adding different amount of PbCl₂ (0.288, 0.576, and 0.864 M) dissolved in 0.4 g of oleylamine into poly(OLA-r-S) solution with a molar feed ratio of [oleylamine]:[sulfur] = 1:33, after 30 min of copolymerization.