



Supporting Information

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Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization from Unprotected Cadmium Selenide Nanoparticles

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Experimental Section

General. Selenium (99.999%), tri-*n*-octylphosphine (technical grade 90%), tri-*n*-octylphosphine oxide (technical grade), and N,N'-carbonyl diimidazole were purchased from Alfa Aesar. Cadmium acetate dihydrate, allyl alcohol, AIBN and all other reagents were purchased from Aldrich. Tetrahydrofuran, benzene, and toluene were purified by conventional distillation over sodium/benzophenone. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker-Spectrospin 300. UV/Visible spectra were recorded on a Hitachi U-3010. Photoluminescence measurements were taken on a Perkin-Elmer LS55B (excitation at 330 nm). Transmission electron microscopy (TEM) was performed on a JEOL 100CX microscope at 100 KeV. Gel permeation chromatography (GPC) measurements were performed in tetrahydrofuran (THF) using three PLgel Mixed-D columns. TEM grids were purchased from Ted Pella, Inc. and consisted of 3-4 nm amorphous carbon film supported on a 400-mesh copper grid.

Preparation of hydroxypropyl di-*n*-octylphosphine oxide (1). Di-*n*-octylphosphine oxide^[26] (15.0g, 54.7 mmol), AIBN (1.35 g, 8.23 mmol), and allyl alcohol (3.49 g, 60.2 mmol) were stirred at 80 °C under a nitrogen atmosphere for 8 hrs. The product was purified by column chromatography over silica gel, eluting with methanol:chloroform mixtures to yield **1** (15.1 g, 83%): ¹H NMR (300 MHz, CDCl₃) δ 4.75 (br, 1H, OH), 3.50 (t, 2H, CH₂-OH), 1.66-1.12 (m, 32H, alkyl), 0.73 (t, 6H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 62.0, 61.9, 31.5, 30.9, 30.7, 28.8, 27.9, 27.0, 25.3, 25.0, 22.3, 21.4, 13.7 ppm; ³¹P (121 MHz, CDCl₃) δ 52.2 ppm.

Preparation of ligand 3. Compound **2**^[27] (1.2 g, 3.3 mmol) in CH₂Cl₂ (5 mL) was stirred at room temperature under nitrogen atmosphere. A solution of 1,1'-

carbonyldiimidazole (0.53 g, 3.3 mmol) in CH₂Cl₂ (5 mL) was added, and the mixture was stirred for 1 hr. Compound **1** (1.2 g, 3.6 mmol) in CH₂Cl₂ (5 mL) was then added, and the mixture was stirred for several days until complete conversion was observed by ³¹P NMR. CH₂Cl₂ was removed, and the residue was purified by column chromatography over neutral alumina, eluting with methanol:chloroform mixtures to yield **3** (1.49 g, 67%): ¹H NMR (300 MHz, CDCl₃) δ 4.14 (t, 2H, CH₂O), 3.25 (t, 2H, CH₂S), 1.72 (s, 6H, *tert*-CH₃), 1.68-1.25 (br, 52H, alkyl), 0.88 (t, 9H, CH₂CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 221.6, 206.8, 198.3, 172.7, 135.5, 131.3, 117.7, 66.0, 55.9, 51.0, 36.9, 31.8, 31.7, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.8, 25.3, 22.6, 22.5, 21.7, 14.1, 14.0 ppm; ³¹P (121 MHz, CDCl₃) δ 49.0 ppm; HRMS calcd 678.4303, found 678.4333.

Preparation of 3-covered CdSe nanoparticles. TOPO-covered CdSe nanocrystals were prepared,^[28,29] precipitated into anhydrous methanol, and centrifuged. The supernatant was discarded and the particles were dissolved in pyridine and stirred at 50 °C for 8 hrs. Pyridine was partially removed under reduced pressure to give a viscous solution. The nanocrystals were then precipitated into hexane and isolated by centrifugation. The supernatant was discarded, and the precipitate was stirred as a suspension in dry THF. Compound **3** (ca. 250 mg) was added, and the suspension was stirred for several hours at 55 °C, during which time the mixture became homogenous. THF was removed by distillation, and the newly functionalized nanoparticles were dissolved in hexane. **3**-Covered nanoparticles were isolated from excess **3** using a centrifuge device (MWC 50,000). The isolated nanoparticles were then redissolved in toluene or benzene.

General polymerization procedure. To a solution of **3**-covered CdSe nanoparticles (20 mg) in 1 mL toluene was added the monomer (8.7 mmol) and *t*-butyl peroxide (63.0 mg, 0.43 mmol). The mixture was subjected to freeze-pump-thaw cycles. The mixture was then heated to 70 °C under nitrogen atmosphere for 24 hours. The polymer-CdSe composite material was precipitated into methanol, isolated by filtration, and dried in a vacuum oven. For GPC analysis, the polymers were removed from the nanoparticle surface by stirring the product in a THF solution of hexylphosphonic acid at 50 °C, followed by fractional precipitation.