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Supporting Information for

Facile Non-Injection Phosphorous-Free Synthesis of Semiconductor Nanoparticles Using New Selenium Precursors

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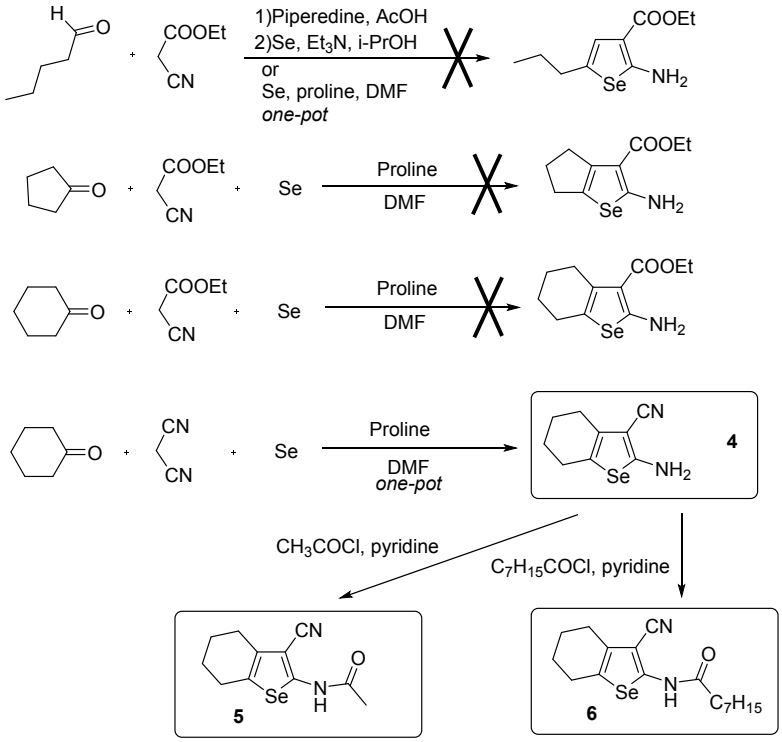
Substantial criteria for potential Se-precursors is a good solubility in non-polar and weakly polar solvents (ODE, TOPO) typically used of NPs synthesis and sufficient stability. Thus, to adjust these parameters it was first decided to vary starting carbonile- and methylene active components of base-catalyzed Gewald reaction for synthesis of selenophene derivatives (see Scheme SI-1). However, in case of ethyl cyanoacetate as methylene active component we failed to obtain selenophene derivative both in a two-step process and one-pot (Scheme S1-1, rows 1-3). This is because of a large number of by-products formed already during the Knoevenagel adduct formation. Hence, after addition (or in presence of) elemental selenium the number of by-product was further vastly increases (GCMS data and HPLC).



Scheme S1-1

Conversely, in case of malonodinitrile, as methelene active component, Knoevenagel adduct formed almost without any side reactions. By varying of different base catalyzers we found that proline gives the best results in terms of purity and yield and can be successfully applied for one-pot synthesis of aminoselenophene **4.** The obtained product can be straightforwardly purified by recrystallization and it was further used for synthesis of **5** and **6** by acylation with acetylchloride and octanoylchloride correspondingly (Scheme S1-1).

Synthesis of 1,1-diselenobisoctane (dioctyldiselenide 2)

A mixture of selenium powder (9.6 mmole, 0.76 g) and sodium borohydride (122 mmole, 12.7 eq., 4.6 g) was degassed by blowing the flask with argon during 15 min. Then 14 mL of ethanol was added to this mixture dropwise under vigorous stirring during 10 min. Dark red suspension was produced which changed to black after 17 ml of DMF was added dropwise and in 1 h the octylbromide (0.01 mole, 2.0 g) was added to the obtained suspension. The reaction was quenched in 2 h by pouring into pure water (150 mL), extracted with diethyl ether (4 x 50 ml) and the extract was washed three times with water and dried over anhydrous Na_2SO_4. The solution was filtered off; the filtrate was evaporated to dryness and dried in vacuum to give slightly yellow oil. Yield: 40% (99% purity). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 6H, CH_3), 1.21-1.45 (m, 20H, CH_2), 1.73 (m, 4H, CH_2), 2.92 (t, 4H, CH_2). GC-MS (EI, 70 eV): m/z 386 (M+, 25 %), 274 (20 %).

Synthesis of 1,1-selenobisoctane (dioctylselenide 1)

A mixture of selenium powder (6.3 mmole, 0.5 g), 15 mL of water and 15 mL of DMF was degassed by bubbling with argon during 30 min. To this suspension sodium borohydride (15.6 mmole, 0.59 g) was quickly poured. Additional portions of the same amount of $NaBH_4$ was added two times more for every 10 minutes. In 40 min and 1h additionally 0.79 g of sodium borohydride were added and the mixture was left under the stirring 12 hours at room temperature. Octylbromide (12.5 mmole, 2.4 g) was added to the reaction mixture and in 10 h the temperature of reaction was raised to 60 ^oC and left under the stirred overnight. When, according to GCMS analysis, the reaction completed the mixture was poured into pure water (150 mL), extracted with diethyl ether (4 x 50 ml), the extracts were combined, washed three times with water and dried over anhydrous Na_2SO_4. The solution was filtered off and the filtrate was evaporated to dryness and dried in vacuum. Slightly yellow oil. Yield: 52% (99.5% purity by GCMS). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6H, CH_3), 1.21-1.44 (m, 20H, CH_2), 1.65 (m, 4H, CH_2), 2.54 (t, 4H, CH_2). GC-MS (EI, 70 eV): m/z 306 (M+, 20 %).

Synthesis of 2-amino-4,5,6,7-tetrahydrobenzo[b]selenophene-3-carbonitrile (selenophene 4)

A mixture of cyclohexanone (69 mmole, 7 mL), malonodinitrile (76 mmole, 1.1 eq., 5.04 g), selenium powder (76 mmole, 1.1 eq., 5.96 g), proline (0.1 eq., 0.8 g) and 40 mL of dimethylformamide were degassed for 40 min by bubbling with argon. Then the reaction mixture was vigorously stirred at 45 ^oC for 24 hours in Argon atmosphere. After that the mixture was heated to 110 °C and left for 48 hours. After the reaction the mixture was filtered through a thin layer of silica gel (for separation of selenium), the sorbent was washed with dimethylformamide three times and the obtained solution was poured into 500 mL of water. The obtained suspension was extracted with dichloromethane (4 x 100 ml), the combined extract was washed three times with water and dried over anhydrous Na_2SO_4. After filtration, the filtrate was filtered through a pad of silica gel and washed with cold dichloromethane (5 x 50 ml). The resulting filtrate was evaporated to dryness and the obtained solid was recrystallized from benzene. The resulted precipitate was filtered off and washed with heptane (3 x 20 ml) and then with heptane/benzene mixture (1:1, 3 x 20 ml) and dried. Pale brown crystals were obtained. Yield: 26%. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.65 (m, 4H, $(CH_2)_2$), 2.25 (m, 2H, CH_2), 2.44 (m, 2H, CH_2), 9.65 (s, 2H, NH_2). MS (EI, 70 eV): *m/z* 226 (M^+, 100 %), 145 (54 %).

Synthesis of N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]selenophene-2-yl)acetamide (selenophene 5)

The flask with a mixture comprising 2-amino-4,5,6,7-tetrahydrobenzo[b]selenophene-3-carbonitrile (**4**, 1 g) and 15 mL of pyridine was placed to water bath to 20 ^0C. After that acetyl chloride (1.2 equiv.) was added dropwise under vigorous stirring in 5 minutes. After the mixture was cooled down to room temperature it was left under the stirring overnight. After completion of the reaction the mixture was poured into the mixture of iced water (100 mL) and concentrated sulphuric acid (50 mL). Obtained precipitate was filtered off, washed with water on the filter (5 x 50 mL) and recrystallized from azeotropic mixture of acetonitrile/water. The resulting precipitate was filtered off, washed with the last mixture (3 x 20 ml) and dried. Almost white crystals were obtained. Yield: 74%. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.82 (m, 4H, $(CH_2)_2$), 2.30 (s, 3H, CH_3), 2.55 (m, 2H, CH_2), 2.69 (m, 2H, CH_2), 9.65 (s, 1H, NH). MS (EI, 70 eV): m/z 268 (M+, 100 %), 225 (100 %), 198 (68 %), 145 (23 %), 118 (25 %).

Synthesis of N-(3-cyano-4,5,6,7-tetrahydrobenzo[b]selenophene-2-yl)octanoylamide (selenophene 6)

The synthesis was carried out according to the procedure of selenophene **6** synthesis (see above) using octanoyl chloride as acylated agent. As a solvent for recrystallization methanol was used. Yield: 59%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.05 (s, 3H, CH_3), 1.32 (m, 8H, $(CH_2)_4$), 1.47 (m, 2H, CH_2), 1.82 (m, 4H, $(CH_2)_2$), 2.30 (s, 2H, CH_2), 2.48 (m, 2H, CH_2), 2.68 (m, 2H, CH_2), 9.82 (s, 1H, NH). MS (EI, 70 eV): m/z 351 (M+, 100 %), 225 (82 %).

Synthesis of 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (aminothiophene 7)

A mixture of cyclohexanone (19.8 mmole, 2 mL), malonodinitrile (21.8 mmole, 1.1 eq., 1.44 g), sulphur powder (21.8 mmole, 1.1 eq., 0.7 g), proline (0.1 eq., 0.23 g) and 15 mL of dimethylformamide were degassed for 40 min by bubbling with argon. The reaction mixture was vigorously stirred for 12 h in Ar-atmosphere at 45 ^{o}C. After the reaction, the mixture was filtered through a thin layer of silica gel, washed with dimethylformamide three times and poured into 250 mL of water. Then, it was extracted with dichloromethane (4 x 100 ml), the extract was washed three times with water and dried over anhydrous Na_2SO_4. The salt was filtered off, and the filtrate was filtered through a pad of silica, washed with cold dichloromethane (5 x 50 ml). The resulting filtrate was evaporated to dryness and recrystallized from benzene. The resulting precipitate was filtered off and washed with heptane (3 x 20 ml) and then with heptane / benzene (1: 1, 3 x 20 ml), dried. Pale brown crystals. Yield: 26%. ^{1}H NMR (400 MHz, DMSO-d6): δ = 1.65 (m, 4H, $(CH_2)_2$), 2.25 (m, 2H, CH_2), 2.44 (m, 2H, CH_2), 9.65 (s, 2H, NH_2). MS (EI, 70 eV): m/z 226 (M+, 100 %), 145 (54 %).

Powder Wide-Angle X-ray Diffraction Data

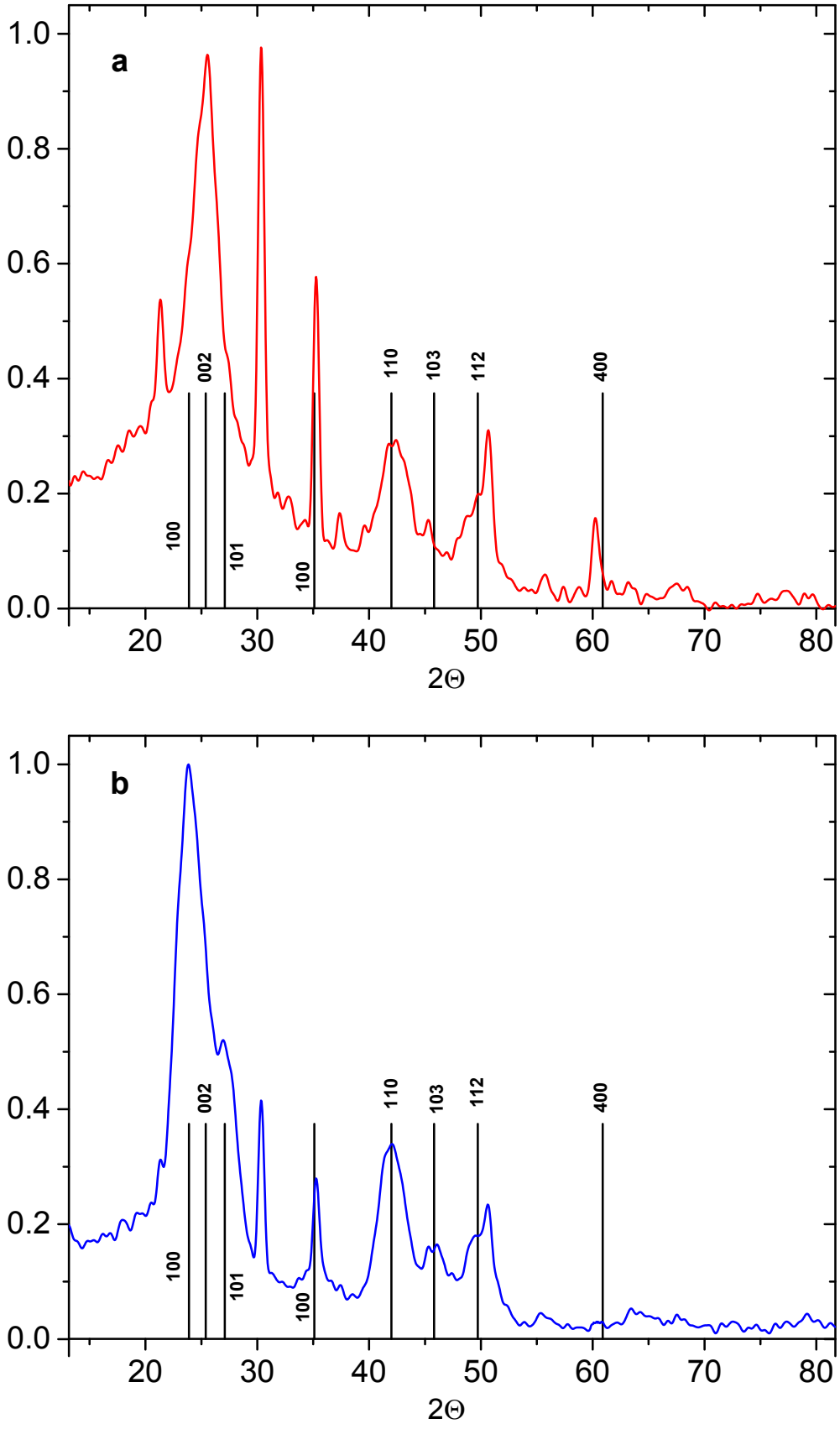


Figure SI-1. PXRD diffraction patterns for CdSe QDs synthesized: (a) using precursor **2** with OAm ligand at 200 °C; (b) using precursor **2** with HDPA ligand at 360 °C.

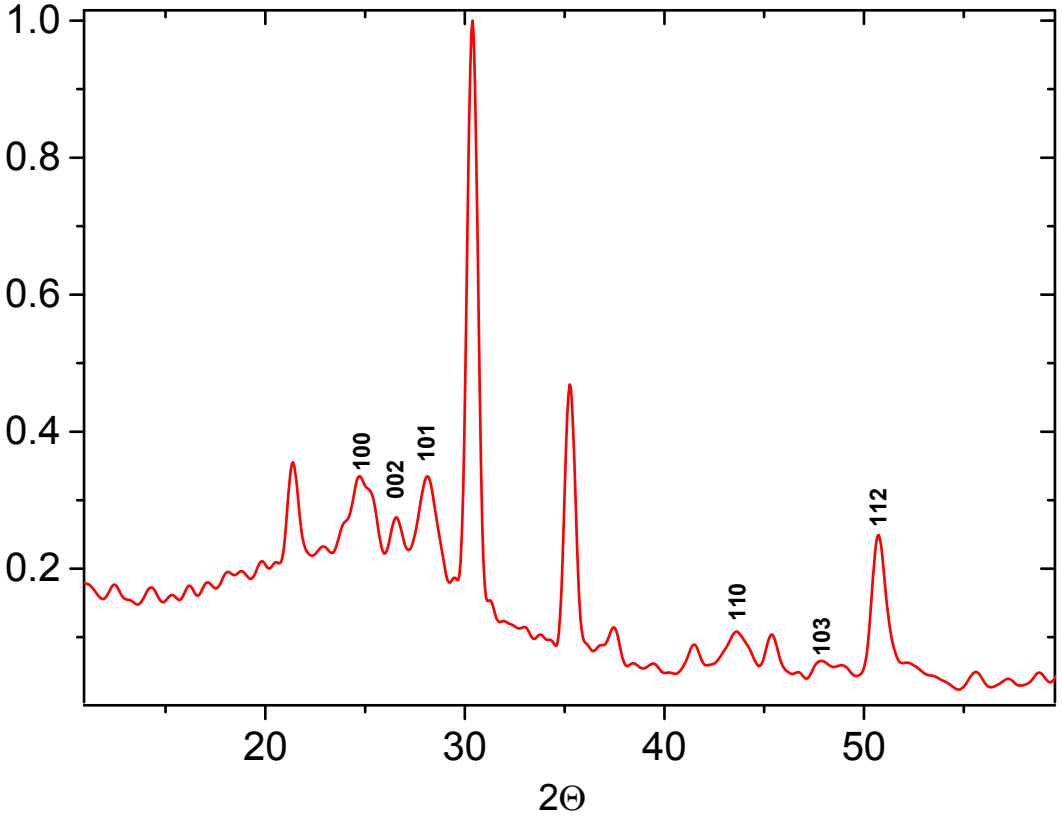
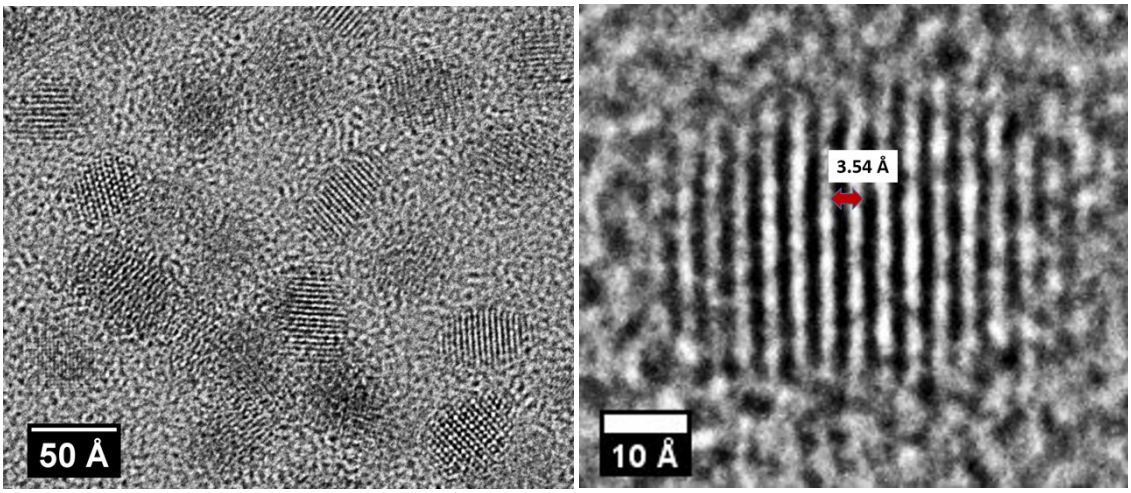


Figure SI-2. PXRD diffraction patterns for CdSe/CdS QRs synthesized using precursor **2**.

High Resolution TEM Data

a



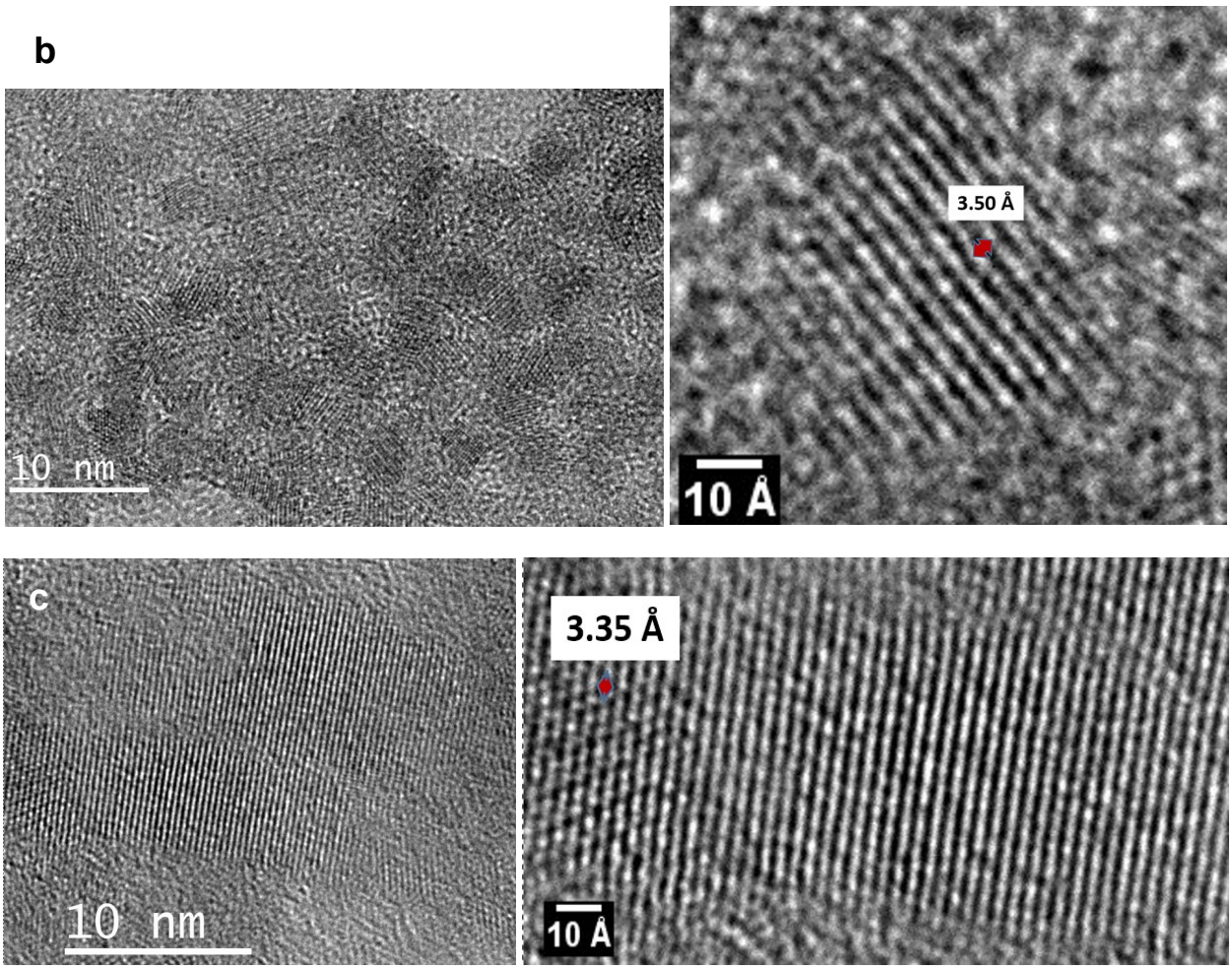


Figure SI-3. HRTEM photos for CdSe QDs synthesized (a) using precursor **2** with HDPA ligand at 360 °C and (b) using precursor **2** with OAm ligand at 200 °C; (c) HTEM photos of CdSe/CdS QRs synthesized using precursor **2**.