

Supporting Information

Cu-Fe-S Nanocrystals Exhibiting Tunable Localized Surface Plasmon Resonance in the Vis to NIR Spectral Ranges

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Experimental

Materials

$\text{CuCl}_2 \times 2\text{H}_2\text{O}$ (99%), $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (97%), sulfur (99%), sodium oleate (99%), stearic acid (98%), oleic acid (OA, 90%), oleylamine (OLA, 70%), 1-octadecene (ODE, 90%), 1-dodecanethiol (DDT, 98%), 1-bromododecane (97%), Aliquat® 336, $\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$ (97%) were purchased from Aldrich.

Synthesis of copper(II) oleate^{1,2}

Copper(II) oleate was prepared by reacting CuCl_2 with sodium oleate. Sodium oleate (80 mmol, 29.7 g) and $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ (40 mmol, 6.9 g) were dissolved in a mixed solvent composed of 80 mL of ethanol, 60 mL of water and 140 mL of hexane. The mixture was heated to 70 °C and then kept at this temperature for four hours. The organic layers containing the desired product was washed three times with 30 mL of water in a separatory funnel. After washing hexane layer was evaporated and the resulting product (copper(II) oleate) was recovered in a form of a green waxy solid. The content of the salt was determined by iodometric titration of copper. The copper(II) oleate content was 96.0% (10.0% calculated as copper).

Synthesis of iron(III) stearate

Iron(III) stearate was prepared by reacting iron(III) hydroxide with stearic acid. Ammonium solution 25% (20 mL) was added drop-wise to a solution of 21.6 g $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (80 mmol) in 100 mL of water at 50 °C. The precipitate was separated by centrifugation (7000 rpm, 5 min), suspended in distilled water and centrifuged again. This step was repeated three more times. The as obtained iron(III) hydroxide was quantitatively transferred into a 500 mL flask equipped with a Dean-Stark trap, then 200 mL of toluene and stearic acid (68.3 g, 240 mmol) were added. The stirred mixture was heated to boiling. Distillation was carried out until the distillate no longer contained water. The resulting solid was filtered and dried under reduced pressure. The content of the salt was determined by complexometric titration of iron using EDTA and salicylic acid as an indicator. The iron(III) stearate weight content was 90.3% (6.2% calculated as iron).

Synthesis of didodecyl sulfide

A mixture of 1-dodecanethiol (3.0 g, 14.8 mmol), 1-bromododecane (3.7 g, 14.8 mmol), 30 mL of hexane and 20% NaOH (30 mL) was stirred at reflux for 12 h. After cooling to room temperature, the resulting mixture was acidified with hydrochloric acid (5%) solution and extracted with hexane. The combined organic extracts were washed with water, sodium hydroxide (2%) solution and water once more, evaporated and dried under reduced pressure. Crude product was recrystallized from acetonitrile to give didodecyl sulfide (5.35 g, 97%). ¹H NMR (500 MHz, CDCl₃) δ = 0.88 ppm (t, *J* = 7.0 Hz, 6H, 2×CH₃), 1.18-1.38 (m, 36H, 18×CH₂), 1.54-1.60 (m, 4H, 2×CH₂), 2.49 ppm (t, *J* = 7.5 Hz, 4H, 2×CH₂).

Synthesis of dioctadecan-2-yl sulfide

A mixture of 1-octadecene (10.0 g, 39 mmol), 25 mL of concentrated (40%) hydrobromic acid and 1.0 mL of Aliquat 336 was stirred and heated at 80 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with hexane. The organic phase was washed with water, sodium carbonate solution and water once more, evaporated and dried under reduced pressure. A mixture of crude 2-bromooctadecane (13.2 g, 39 mmol), Na₂S×9H₂O (6.7 g, 27.8 mmol), 1.0 mL of Aliquat 336, 20 mL of water and 10 mL of hexane was stirred and heated at 70 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with hexane. The organic phase was washed with water, sodium hydroxide (5%) solution and water once more, evaporated and dried under reduced pressure. The crude product was chromatographed over silica gel using hexane as eluent to give dioctadecan-2-yl sulfide (3.3 g, 33%). ¹H NMR (500 MHz, CDCl₃) δ = 0.85 ppm (t, *J* = 7.0 Hz, 6H, 2×CH₃), 1.16-1.30 (m, 58H, 26×CH₂ + 2×CH₃), 1.33-1.55 (m, 8H, 4×CH₂), 2.72-2.79 (m, 2H, 2×CH).

Table S1. Summary of the synthesis conditions and compositions of Cu-Fe-S nanocrystals

	Cu-oleate (mg)	Fe-stearate (mg)	Sulfur precursor (mg/mL)		Cu/Fe/S ^a	Cu/Fe/S ^b
A-1	653	1000	S/OLA	64/2.0	1.0/1.0/2.0	1.0/1.0/1.8
A-2	1044	803	S/OLA	64/2.0	2.0/1.0/2.5	1.0/0.5/0.9
A-3	1631	502	S/OLA	64/2.0	5.0/1.0/4.0	1.0/0.3/0.9
A-4	1827	445	S/OLA	64/2.0	6.0/1.0/4.5	1.0/0.1/0.6
B-1	653	1000	S/ODE	51/2.0	1.0/1.0/1.6	1.0/0.6/0.7
B-2	653	1000	S/ODE	77/3.0	1.0/1.0/2.4	1.0/0.7/1.2

^amolar ratio of precursors, ^bratio of elements in the nanocrystals from EDS

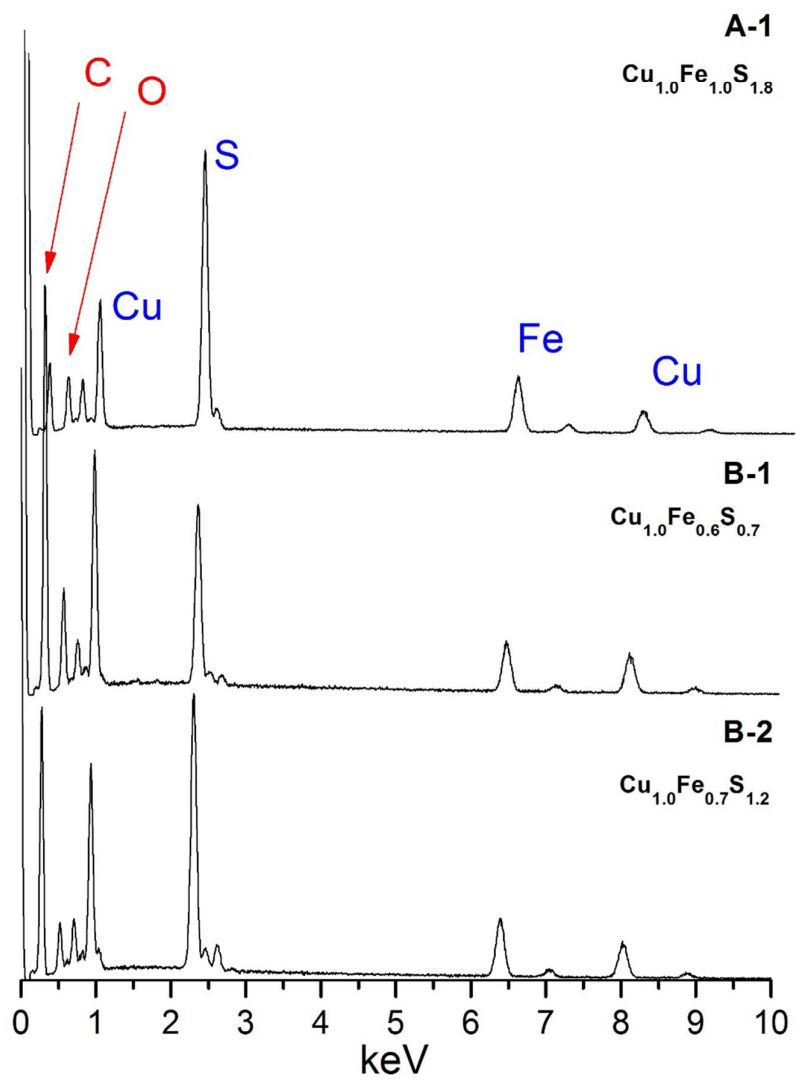


Figure S1. Energy-dispersive spectra of Cu-Fe-S nanocrystals of batches: **A-1**, **B-1**, **B-2**.

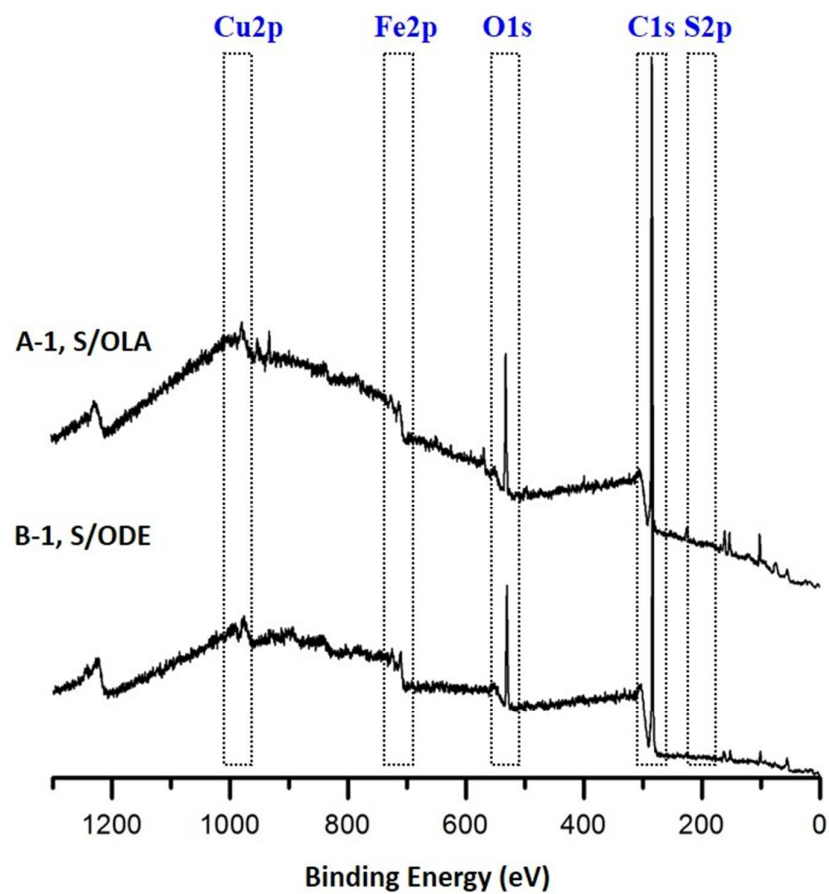


Figure S2. XPS survey spectra of Cu-Fe-S nanocrystals (**A-1** and **B-1**).

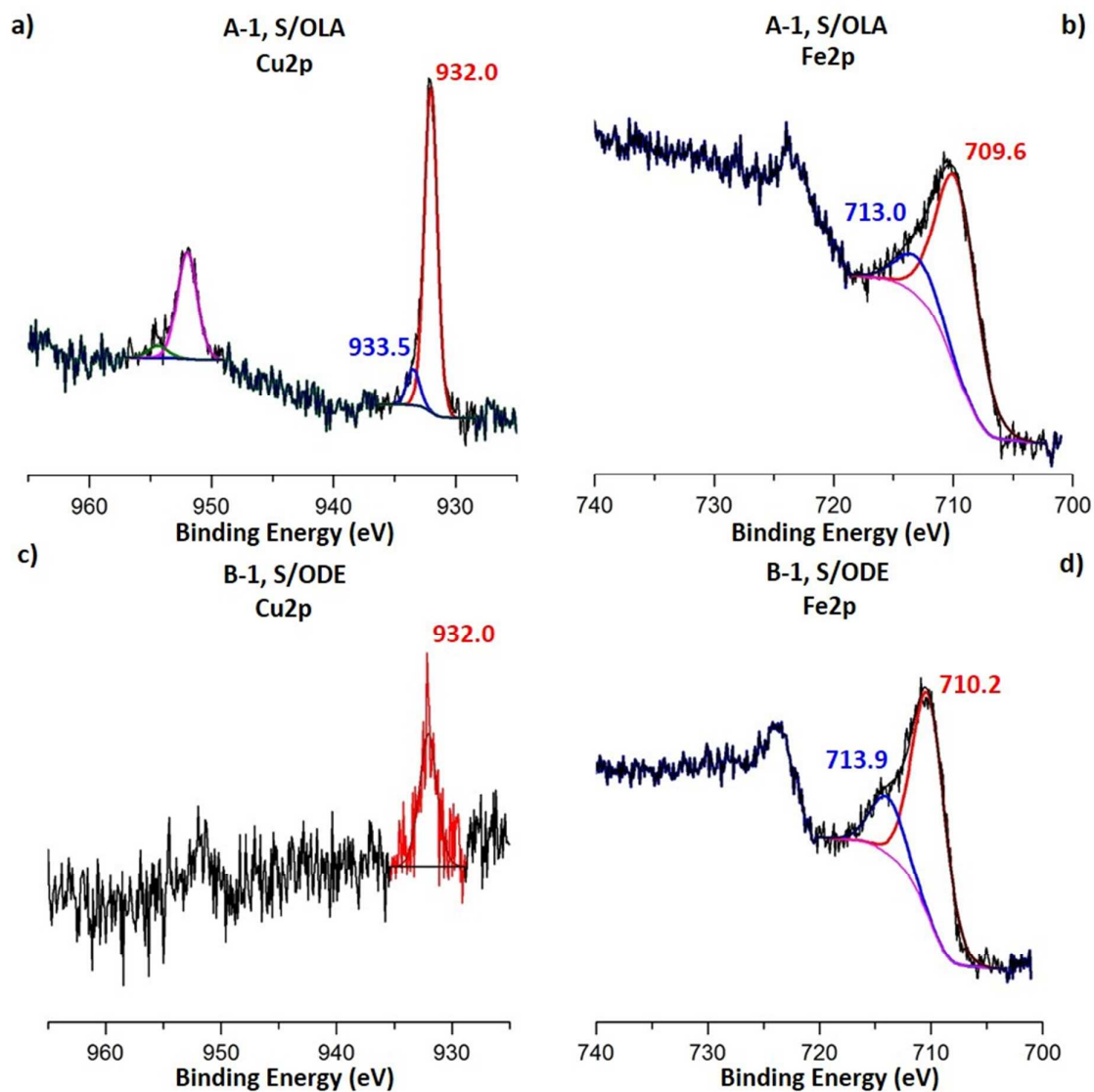


Figure S3. High-resolution Cu2p and Fe2p spectra of **A-1** (a,b) and **B-1** (c,d) Cu-Fe-S nanocrystals.

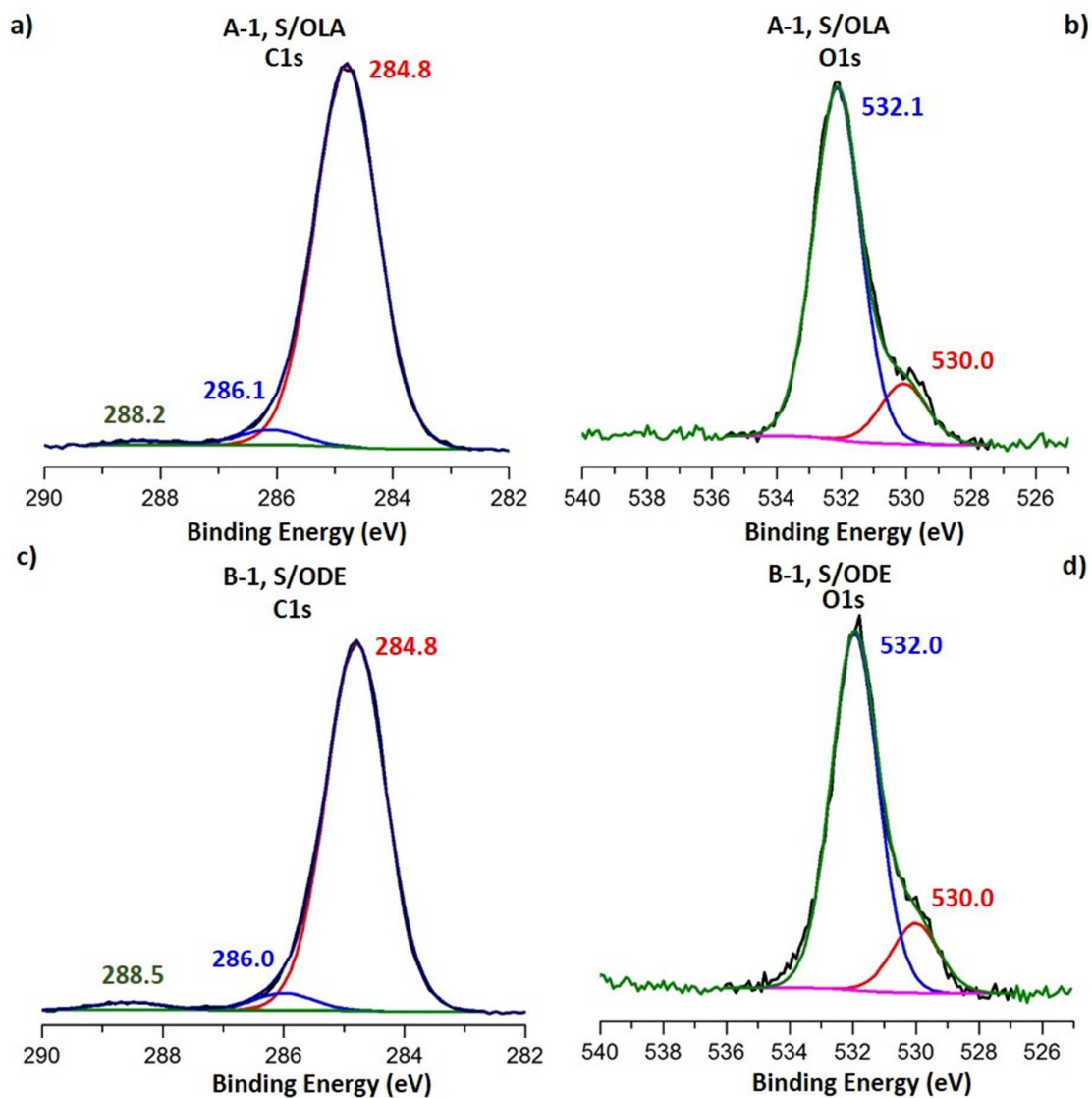


Figure S4. High-resolution C1s and O1s spectra of **A-1** (a,b) and **B-1** (c,d) Cu-Fe-S nanocrystals.

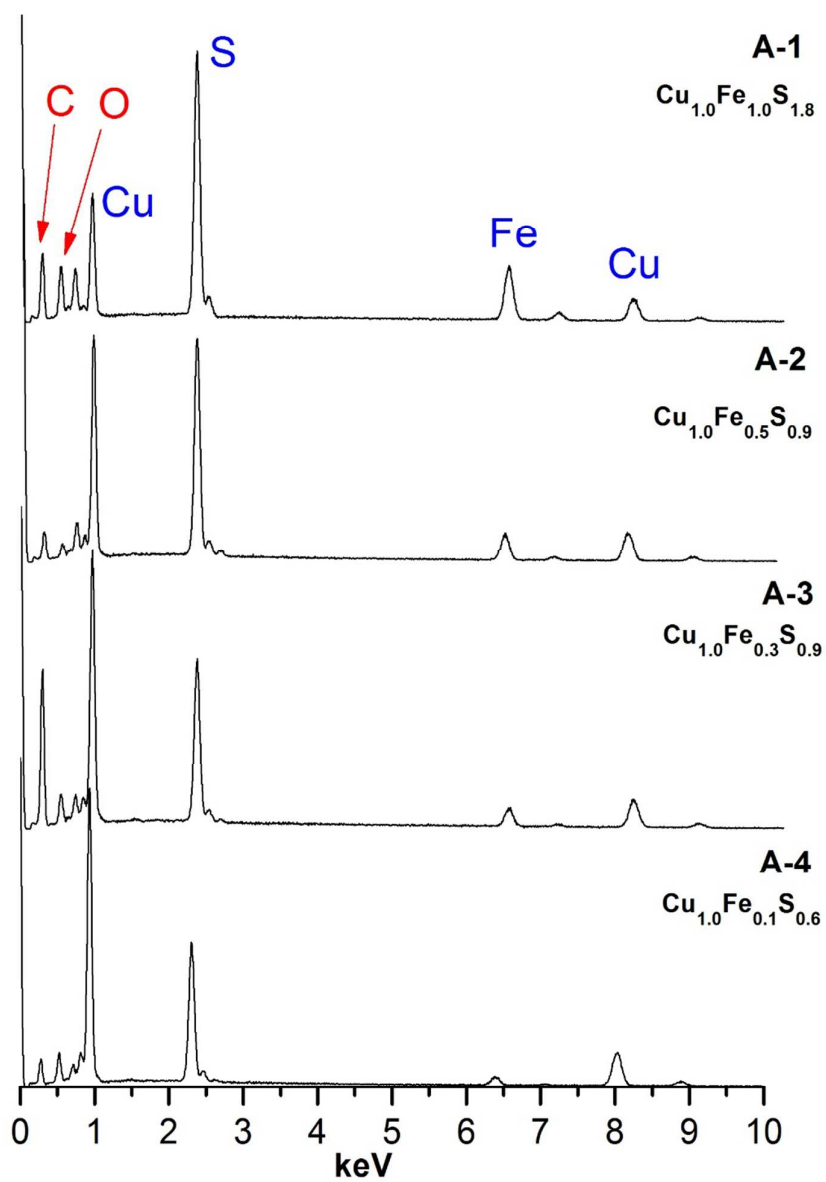


Figure S5. Energy-dispersive spectra of Cu-Fe-S nanocrystals of batches: **A-(1-4)**.

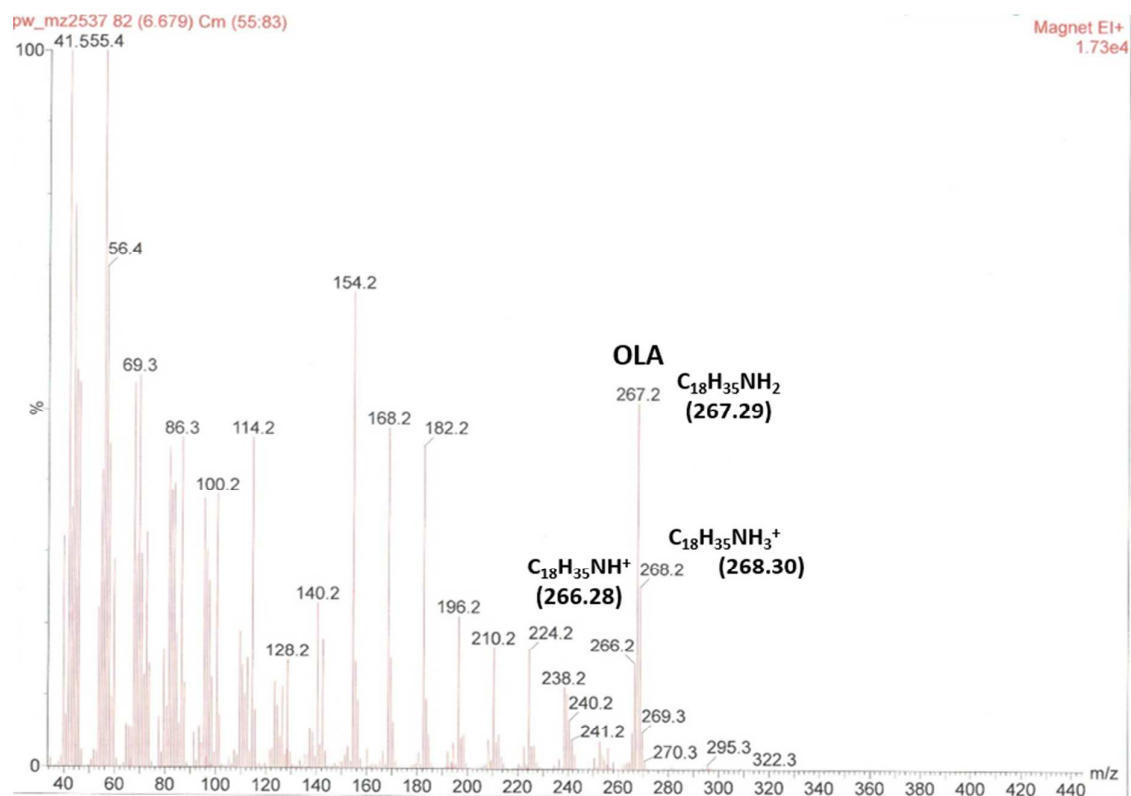


Figure S6. Mass spectrum (EI⁺) of S/OLA solution.

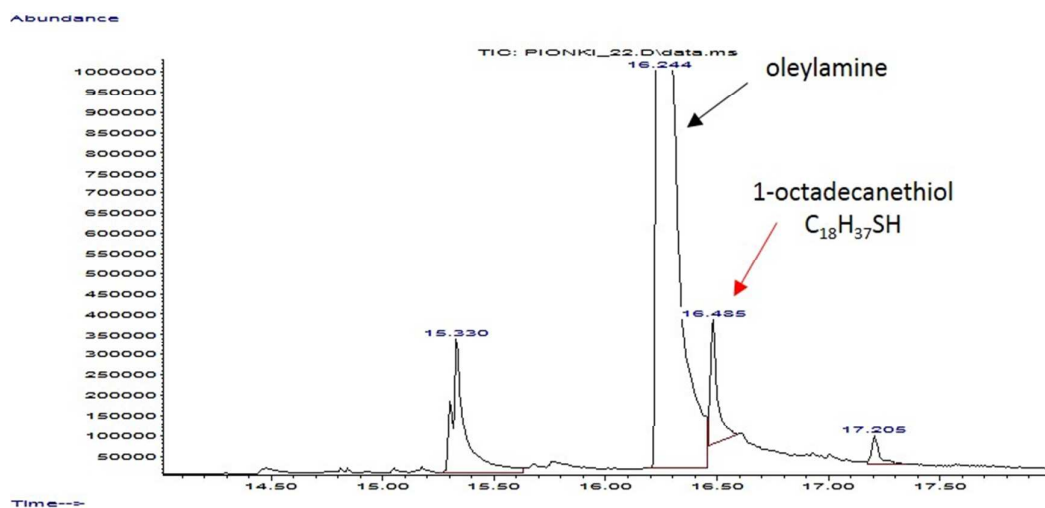


Figure S7a. GC chromatogram of S/OLA solution.

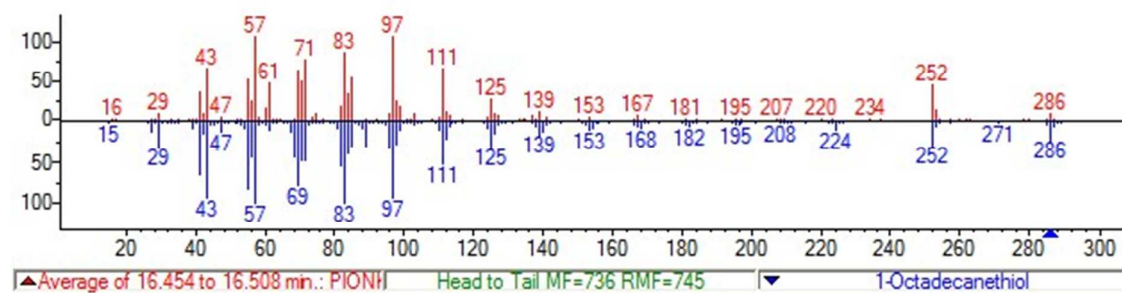


Figure S7b. EI-MS spectrum of fraction (peak 16.485) from S/OLA.

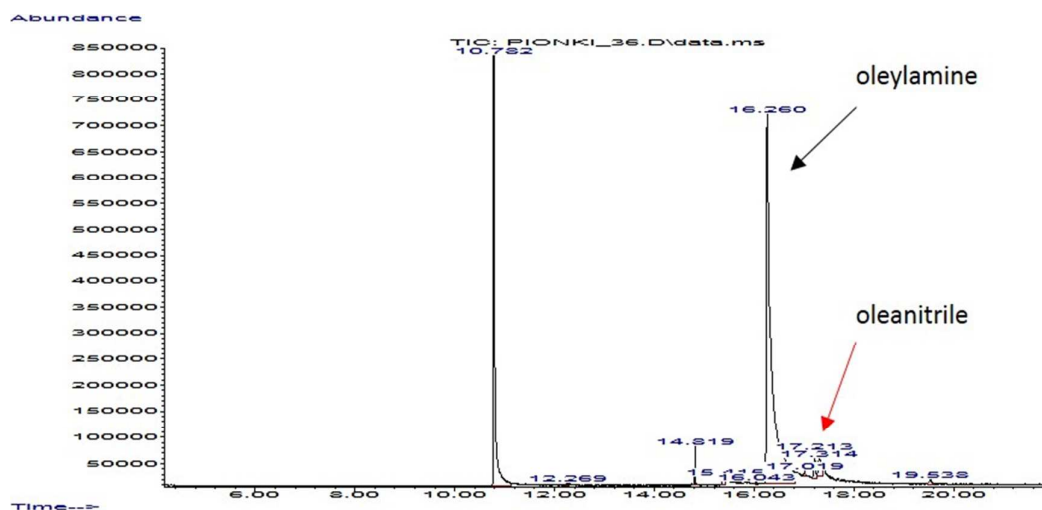


Figure S8a. GC chromatogram of organic residue from reaction mixture without metal precursor.

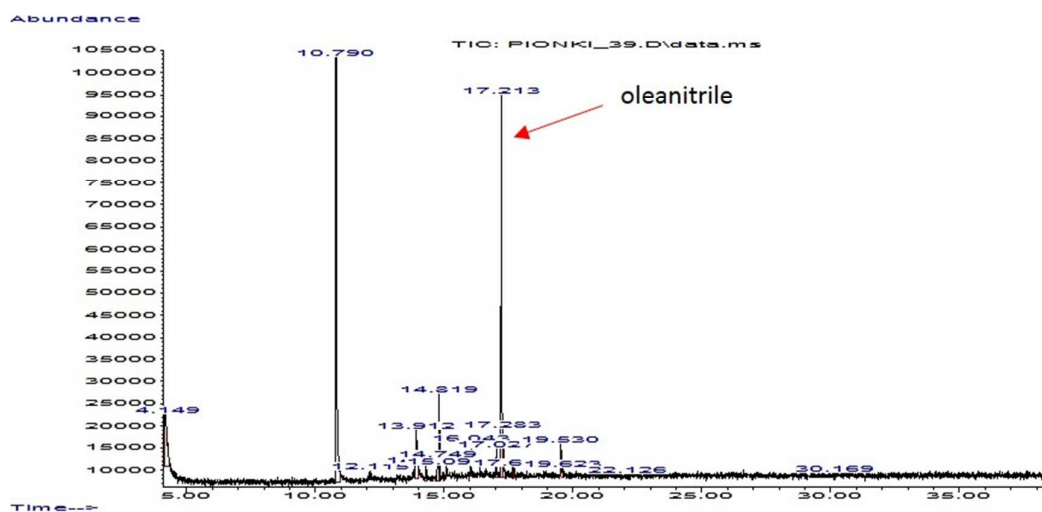


Figure S8b. GC chromatogram of organic residue from the synthesis of Cu-Fe-S nanocrystals.

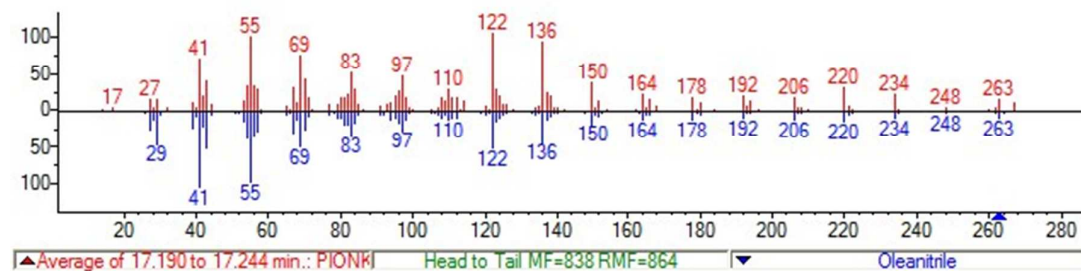


Figure S8c. EI-MS spectrum of fraction (peak 17.190-17.244) from organic residues.

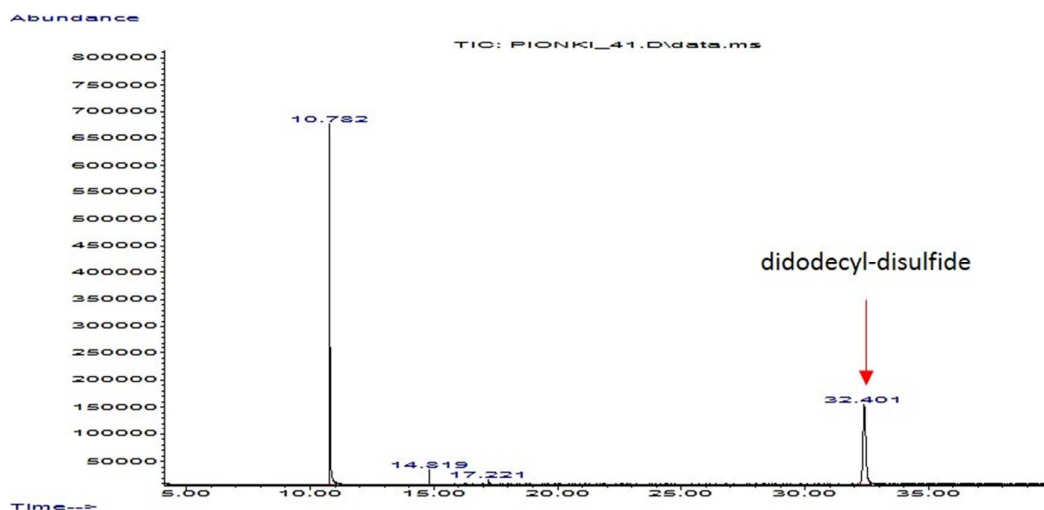


Figure S9a. GC chromatogram of organic residue from the synthesis of Cu-Fe-S nanocrystals with the addition of 1-dodecanethiol.

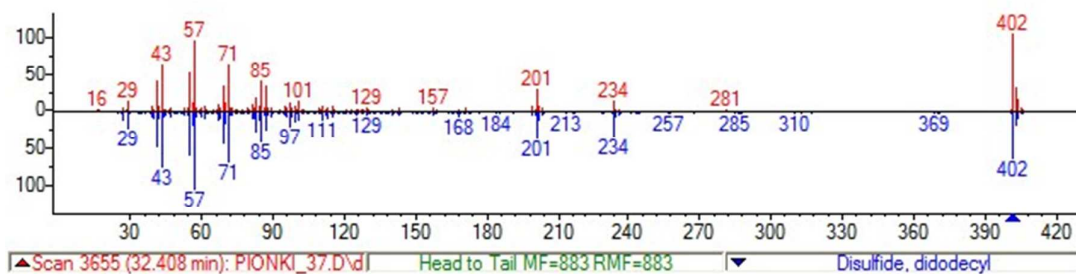


Figure S9b. EI-MS spectrum of fraction (peak 32.408) from organic residue.

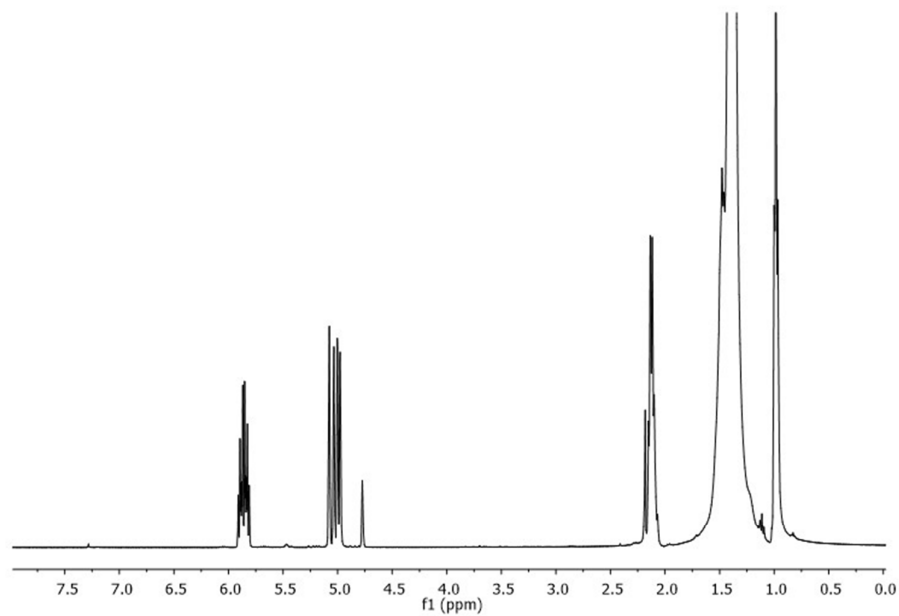


Figure S11. ^1H NMR spectrum of S-ODE-3 solution in CDCl_3 .

References

- (1) Park, J.; An, K.; Hwang, Y.; Park, J.-G.; Noh, H.-J.; Kim, J.-Y.; Park, J.-H.; Hwang, N.-M.; Hyeon, T. *Nat. Mater.* **2004**, *3*, 891-895.
- (2) Wang, J.-J.; Wang, Y.-Q.; Cao, F.-F.; Guo, Y.-G.; Wan, L.-J. *J. Am. Chem. Soc.* **2010**, *132*, 12218-12221.