

Supporting Information

From Red to Green Luminescence *via* Surface Functionalization. Effect of 2-(5-mercaptothien-2-yl)-8-(thien-2-yl)-5-hexyl-thieno[3,4-*c*]pyrrole-4,6-dione Ligands on the Photoluminescence of Alloyed Ag-In-Zn-S Nanocrystals

Patrycja Kowalik,^{1,2*} Piotr Bujak,^{1*} Zbigniew Wróbel,³ Mateusz Penkala,⁴ Kamil Kotwica,^{1,5} Anna Maroń,⁴ Adam Pron¹

¹*Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland. E-mail: pkowalik@ch.pw.edu.pl, piotr.bujak@poczta.onet.pl*

²*University of Warsaw, Faculty of Chemistry, Pasteura 1 Str., PL-02-093 Warsaw, Poland*

³*Institute of Organic Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland*

⁴*Institute of Chemistry, Faculty of Science and Technology, University of Silesia, Szkolna 9, 40-007 Katowice, Poland*

⁵*Institute of Physical Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland*

Experimental

Materials. Silver nitrate (99%), indium(III) chloride (98%), zinc stearate (technical grade), 1-dodecanethiol (DDT, 98%), sulfur (99%), 1-octadecene (ODE, 90%), oleylamine (OLA, 70%), thiophene (99%), bromine (99.5%), zinc dust (98%), cuprous cyanide (99%), ethylene glycol (99%), acetic anhydride (98%) *n*-hexylamine (99%), thionyl chloride (99%), CDCl₃ (100%, 99.96 atom %D) and benzene-d₆ (100%, 99.6 atom %D) were supplied by Sigma-Aldrich.

Preparation of S/OLA Precursor. 15 mg (0.47 mmol) of sulfur powder and 1.0 mL of OLA were loaded into a glass vial, which was then immersed in an ultrasonic bath. The mixture was sonicated at room temperature (for about 10 min) until a clear red solution was formed.

Preparation of alloyed Ag-In-Zn-S nanocrystals^{1,2} All operations were carried out under constant dry argon flow. Silver nitrate (0.03 g, 0.17 mmol), indium(III) chloride (0.13 g, 0.59 mmol), zinc stearate (0.40 g, 0.63 mmol), and DDT (0.2 g, 1.0 mmol) were mixed with ODE (15 mL) in a three-neck flask. The mixture was heated to 150 °C until a homogeneous solution was formed. Then, 1 mL of S/OLA precursor was quickly injected into the reaction solution. The temperature was increased to 180 °C, and the mixture was kept at this temperature for 60 min. After the mixture was cooled to room temperature, toluene (20 mL) was added, and the reaction mixture was centrifuged and the isolated black precipitate was separated. The supernatant was treated with 30 mL of acetone leading to the precipitation of the desired fraction of nanocrystals. The nanocrystals were separated by centrifugation (7000 rpm, 5 min) and then redispersed in toluene (or hexane, chloroform, dichloromethane).

5-(*n*-hexyl)thieno[3,4-*c*]pyrrole-4,6-dione was obtained using a modification of procedure described in ref [3].

2,3,4,5-tetrabromothiophene (1). A solution of thiophene (7.52 g, 0.09 mol) in 10 mL of chloroform was cooled to 5 °C. With vigorous stirring bromine (20 mL, 0.39 mol) was added drop wise over 3 h. The resulting mixture was refluxed under argon atmosphere for 4 h. After cooling to room temperature, the mixture was stirred overnight. The reaction mixture was treated with 22 mL of 2 M aqueous NaOH solution then filtered and dried to afford the crude product as reddish brown crystals (30 g, 0,075 mol, 83%).

3,4-dibromothiophene (2) To a vigorously stirred mixture of glacial acetic acid (24 mL) and water (48 mL) under argon atmosphere were added 2,3,4,5-tetrabromothiophene (30 g, 0.075 mol) and zinc dust (15.5 g, 0.237 mol). The flask was equipped with a Dean-Stark trap and the mixture was heated to boiling. Reaction was carried out until the distillate no longer contained organic material. The organic fraction was isolated and then dried over anhydrous MgSO₄. Distillation afforded 3,4-dibromothiophene as colorless liquid (8 g, 0.033 mol, 44%).

Thiophene-3,4-dicarbonitrile (3). A mixture of 3,4-dibromothiophene (8 g, 0.033 mol) and cuprous cyanide (8.7 g, 0.097 mol) in 10 mL of DMF was refluxed for 4 h. After cooling to room temperature, the mixture was poured into a solution of hydrated ferric chloride (40 g, 0.148 mol) in 60 mL of 2 M hydrochloric acid and stirred vigorously for 1 h at 60-70 °C. After filtration the mixture was extracted four times with 200 mL portions of methylene chloride. Each organic extract was washed successively with two portions of 6 M hydrochloric acid, water, saturated NaHCO₃ solution and with water once more. The organic phases were combined and dried over anhydrous MgSO₄. After removal of the solvent, the obtained crude product was sublimated to afford thiophene-3,4-dicarbonitrile as white crystals (2.8 g, 0.020 mol, 63%).

Thiophene-3,4-dicarboxylic acid (4). A suspension of thiophene-3,4-dicarbonitrile (2.8 g, 0.02 mol) and sodium hydroxide (5.6 g, 0.14 mol) in 30 mL of ethylene glycol was refluxed for 3 h. After cooling to room temperature, the mixture was stirred overnight. The reaction mixture was poured into 200 mL of water, it was then washed with diethyl ether, acidified with concentrated hydrochloric acid and extracted with diethyl ether. The combined organic extracts were dried over anhydrous MgSO₄ and evaporated to afford the crude product as yellow crystals (2.5 g, 0.014 mol, 73%).

5-(*n*-hexyl)thieno[3,4-*c*]pyrrole-4,6-dione (5). A solution of thiophene-3,4-dicarboxylic acid (2.5 g, 0.014 mol) in 67 mL of acetic anhydride was refluxed for 3 h. After cooling to room temperature, the reaction mixture was subsequently concentrated to a pale brown solid. This crude product was filtered to afford thiophene-3,4-dicarboxylic anhydride (2 g, 0.013 mol, 93%). A mixture of thiophene-3,4-dicarboxylic anhydride (2 g, 0.013 mol) and *n*-hexylamine (0.69 g, 0.0068 mol) in 70 mL of toluene was refluxed for 24 h. The crude product was collected by filtration of the cold reaction mixture. Another portion of product was achieved by washing the filtrate with 5% hydrochloric acid solution and then evaporating the solvent. A solution of

crude product: 4-*n*-hexylcarbamoylthiophene-3-carboxylic acid in 150 mL of thionyl chloride was refluxed for 3 h. The reaction mixture was concentrated to a yellow oil which was thoroughly dried to pale yellow crystals. Recrystallization from toluene afforded 5-(*n*-hexyl)thieno[3,4-*c*]pyrrole-4,6-dione (1.1 g, 0.0046 mol, 33%). ¹H NMR (400 MHz, CDCl₃) δ = 0.86 ppm (t, *J* = 7.0 Hz, 3H, CH₃), 1.25-1.31 (m, 6H, 3×CH₂), 1.59-1.66 (m, 2H, CH₂CH₂N), 3.59 (t, *J* = 7.4 Hz, 2H, CH₂N), 7.79 (s, 2H C_{Ar-H}).

Characterization Methods. Elemental analysis was carried out with a multichannel Quantax 400 energy-dispersive X-ray spectroscopy (EDS) system with a 125 eV xFlash detector 5010 (Bruker) using a 15 kV electron beam energy. X-ray powder diffractograms were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with a LYNXEYE position-sensitive detector using Cu Kα radiation ($\lambda = 0.15418$ nm). The data were collected in the Bragg-Brentano ($\theta/2\theta$) horizontal geometry (flat reflection mode) between 10° and 70° (2θ) in a continuous scan, using 0.04° steps at 960 s/step. The incident-beam path in the diffractometer was equipped with a 2.5° Soller slit and a 1.14° fixed divergence slit, whereas the path of the diffracted beam was equipped with a programmable antiscatter slit (fixed at 2.20°), a Ni β-filter, and a 2.5° Soller slit. The sample holder was rotated at an angular speed of 15 rpm. The data were collected under standard conditions (temperature and relative humidity). For XPS analysis the nanocrystals were first dispersed in chloroform, then deposited on a Si(100) wafer and dried at room temperature. Survey and high-resolution (HR) XPS spectra were recorded using a PHI 5000 VersaProbe™ (ULVAC-PHI) spectrometer with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV). The HR XPS spectra were collected with the hemispherical analyzer at the pass energy of 23.5 eV, the energy step size of 0.1 eV and the photoelectron take off angle of 45° with respect to the surface plane. The CasaXPS software was used to evaluate the obtained XPS data. Deconvolution of HR XPS spectra were performed using a Shirley background and a Gaussian peak shape with 30% Lorentzian character. The binding energy (BE) scale of all detected spectra was referenced by setting the BE of C1s to 284.8eV. For quantification the PHI Multipak sensitivity factors and determined transmission function of the spectrometer were used. Transmission electron microscopy (TEM) analysis was performed on a Zeiss Libra 120 electron microscope operating at 120 kV. High-resolution images were acquired by a Tecnai TF20 X-TWIN (FEI) microscope operated at 200 kV. ¹H, ¹³C, ¹H-¹H COSY and ¹H-¹³C HMQC NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer and referenced with respect to tetramethylsilane (TMS) and solvents. Differential pulse and cyclic voltammetry investigations of the nanocrystals before and after ligands exchange (dispersion in methylene chloride) and free ligand (D-A-D-SH) ($c = 1 \times 10^{-4}$ M) were carried out in 0.1 M Bu₄NBF₄ solution in methylene chloride with a platinum working electrode of the surface area of 3 mm², a platinum wire counter electrode, and an Ag/0.1 M AgNO₃/CH₃CN reference electrode. UV-vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Steady-state PL spectra of toluene

solutions of samples were measured with FLS-980 fluorescence spectrophotometer equipped with a 450 W Xe lamp and photomultiplier (Hamamatsu, R928P) detector with a standard 10 mm cuvette ($\lambda_{\text{exc}} = 375 \text{ nm}$). The quantum yields were examined using integrating sphere absolute method with solvent used as blank. The compounds were excited with wavelengths in each case corresponding to the obtained excitations. The emission correction file was used to take into account the sensitivity of the monochromator, detector, sphere coating and optics to wavelength. Each scans were conducted with 0.25 nm steps, 0.2 Dwell time as well as repeated 2 times. The FLS-980 software was used to designate the quantum yield values. The PL lifetime measurement was performed with a time correlated single photon counting (TCSPC) method on FLS-980 fluorescence spectrophotometer. The excitation wavelength (405 nm) was obtained using the picosecond pulsed diode laser (EPL – 405 nm, Edinburgh Instruments). The system was aligned at the emission wavelengths. Additionally, for the analysis of a fluorescence decay lower than 50ns, an instrument response function (IRF) was obtained. The IRF contains the information about the time response of the overall optical and electronic system. The IRF was designated using solutions of LUDOX® as a standard at excitation wavelength. The decay components were evaluated using the FLS-980 software.

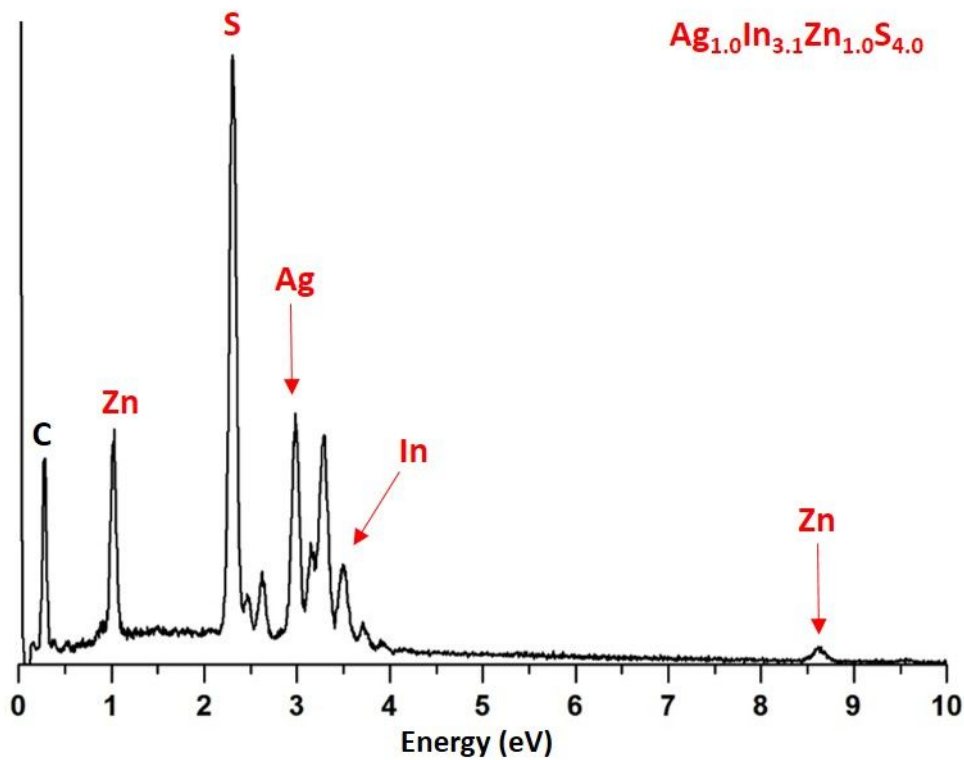


Figure S1. Energy-dispersive spectrum of $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.0}$ nanocrystals capped with initial ligands.

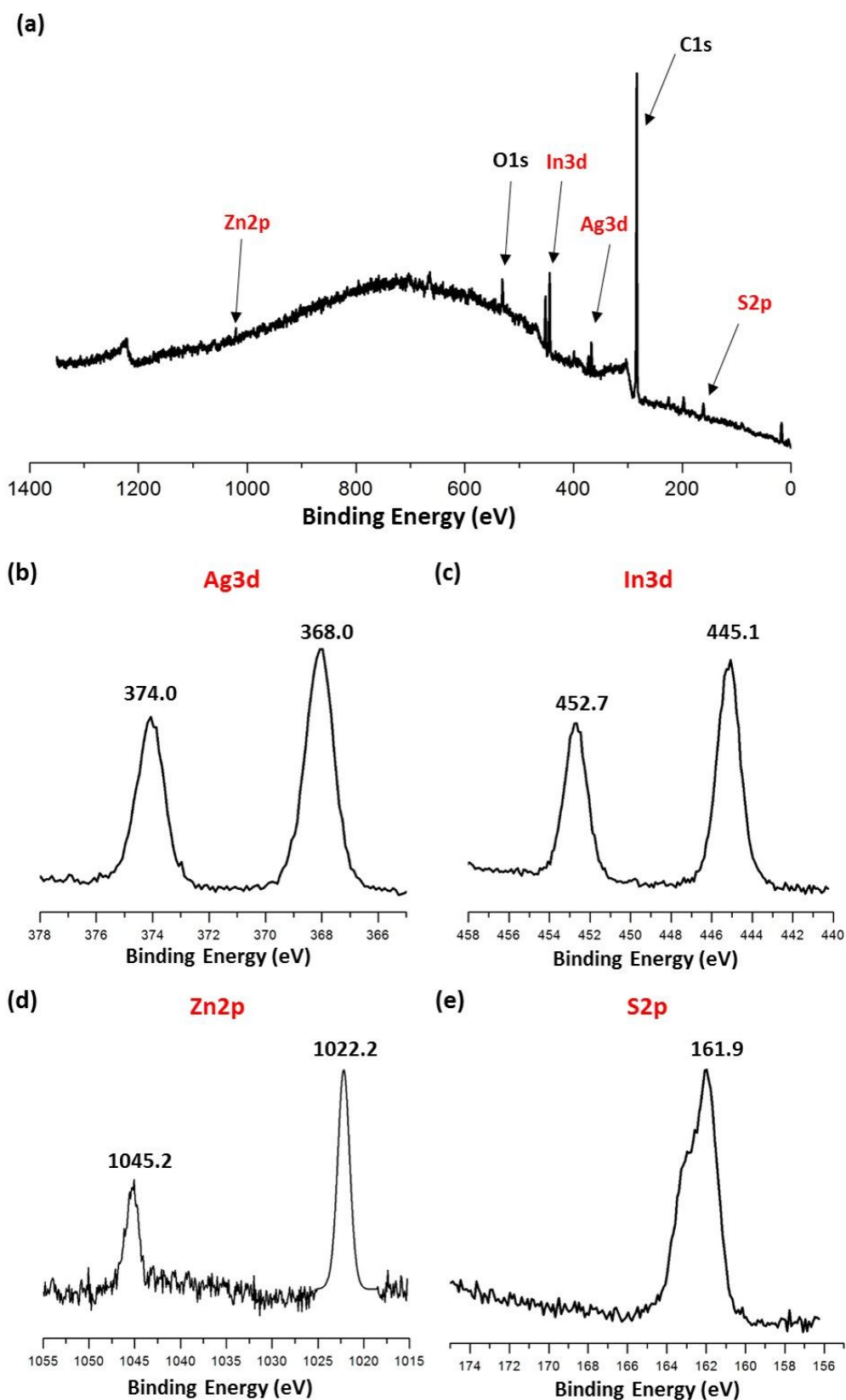


Figure S2. XPS survey spectrum (a) and high-resolution spectra of $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.0}$ nanocrystals in the Ag3d (b), In3d (c), Zn2p (d) and S2p (e) range.

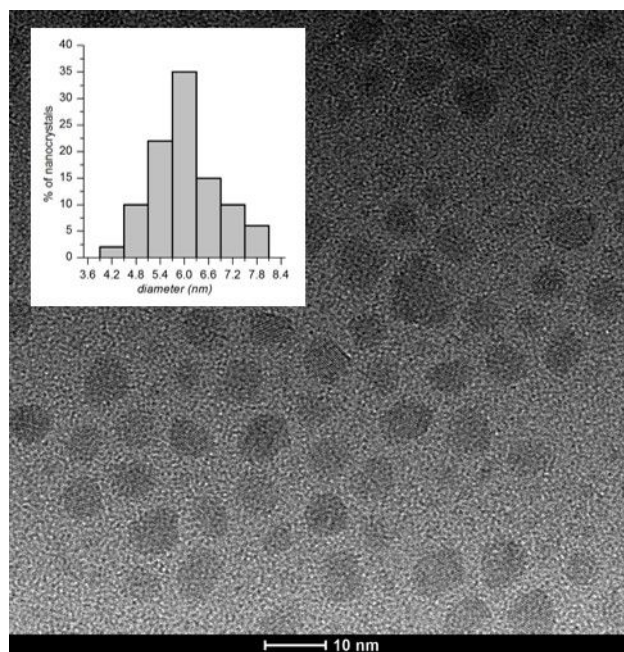


Figure S3. HR-TEM image and corresponding histogram of $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.0}$ nanocrystals.

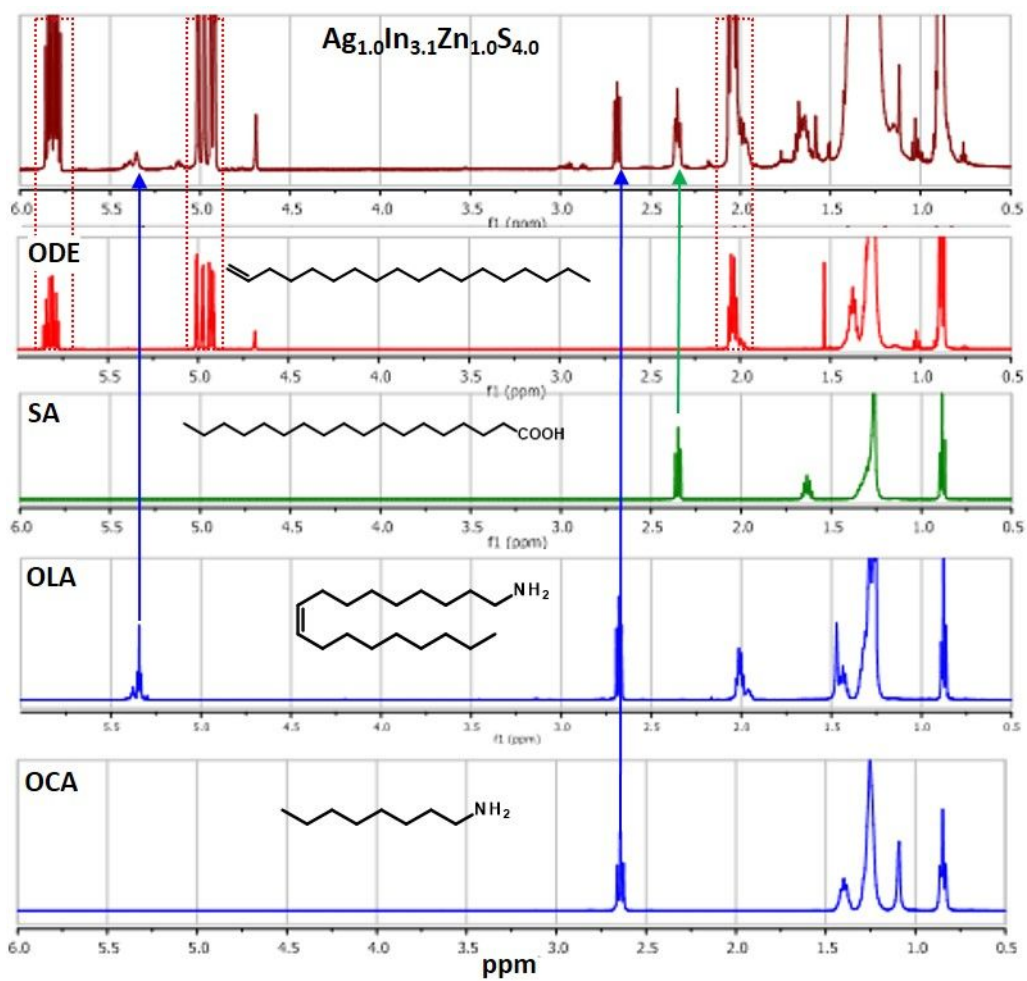


Figure S4. ^1H NMR spectra of the organic residue from $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.0}$ nanocrystals capped with initial ligands, 1-octadecene (ODE), stearic acid (SA), oleylamine (OLA) and *n*-octylamine (OCA) recorded in CDCl_3 .

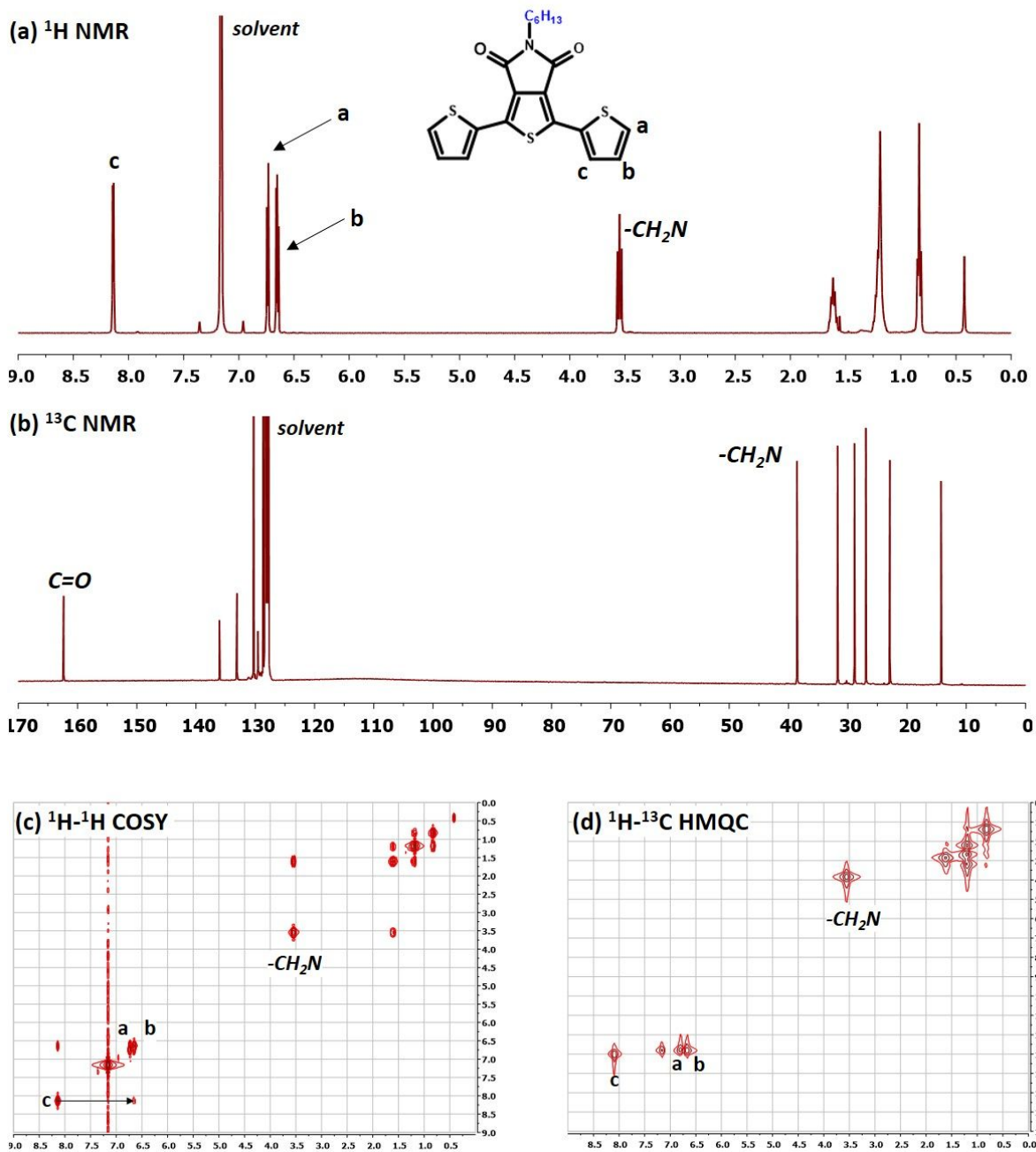


Figure S5. ^1H (a), ^{13}C (b), ^1H - ^1H COSY (c) and ^1H - ^{13}C HMQC NMR (d) spectra of 2,8-bis(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (D-A-D) recorded in benzene- d_6 at 298 K.

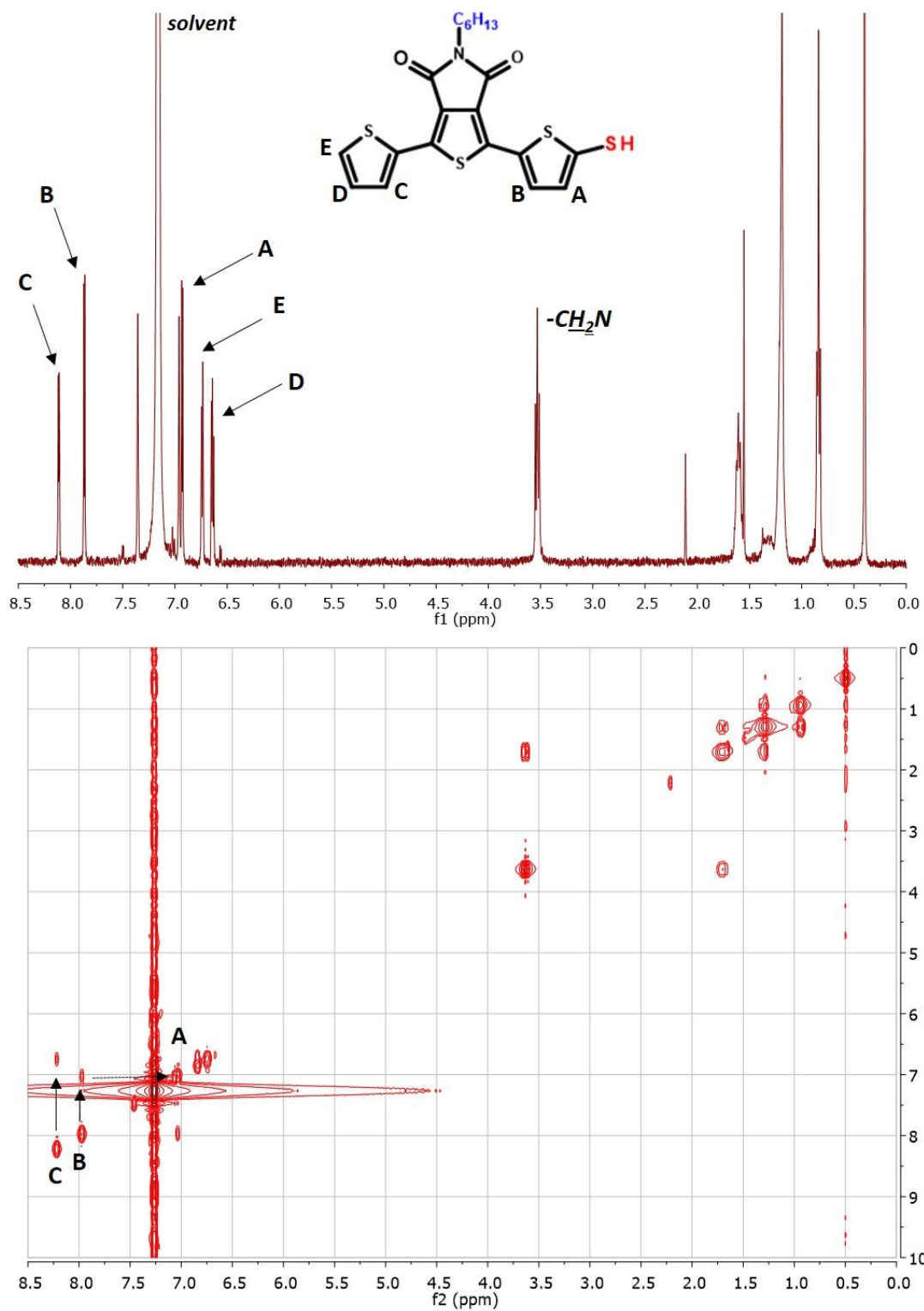


Figure S6. ¹H and ¹H-¹H COSY NMR spectra of 2-(5-mercaptothien-2-yl)-8-(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (D-A-D-SH) recorded in benzene-d₆ at 298 K.

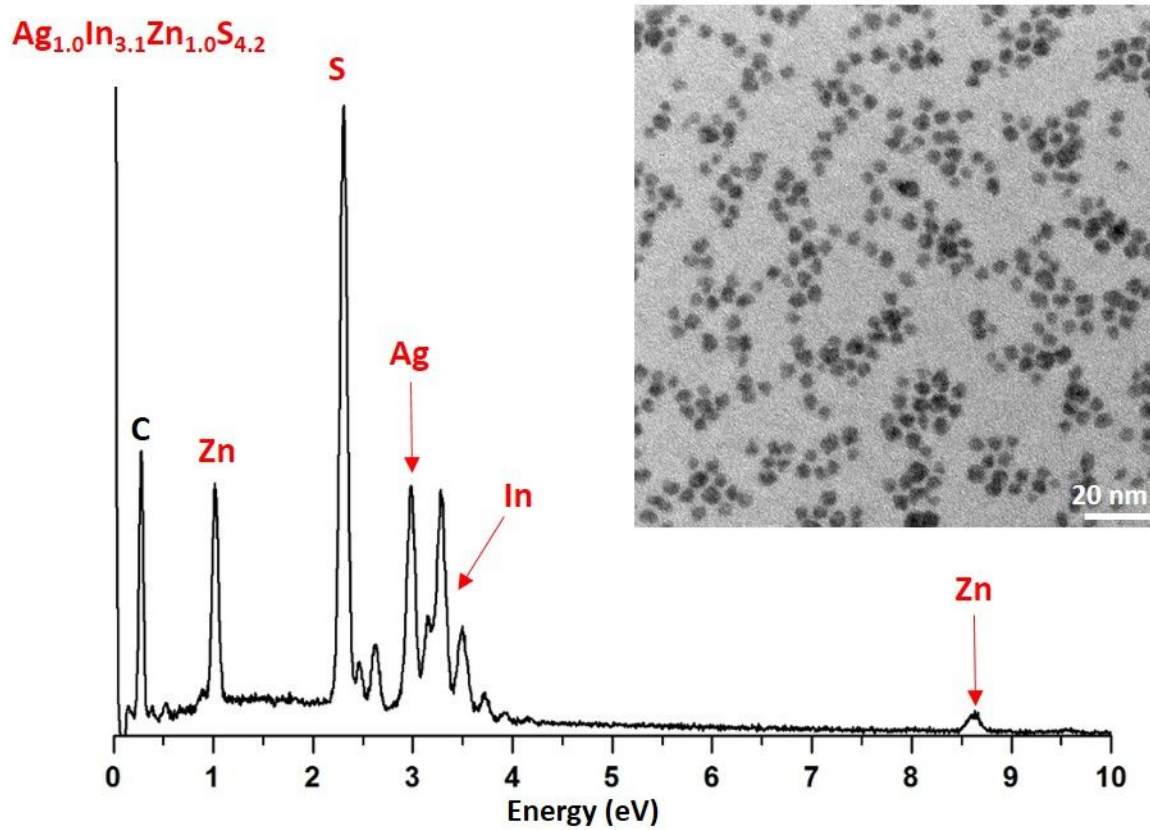


Figure S7. Energy-dispersive spectrum and TEM image of $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.2}$ nanocrystals (6.0 ± 0.8 nm, $n = 200$ nm) capped with ligand (D-A-D-SH).

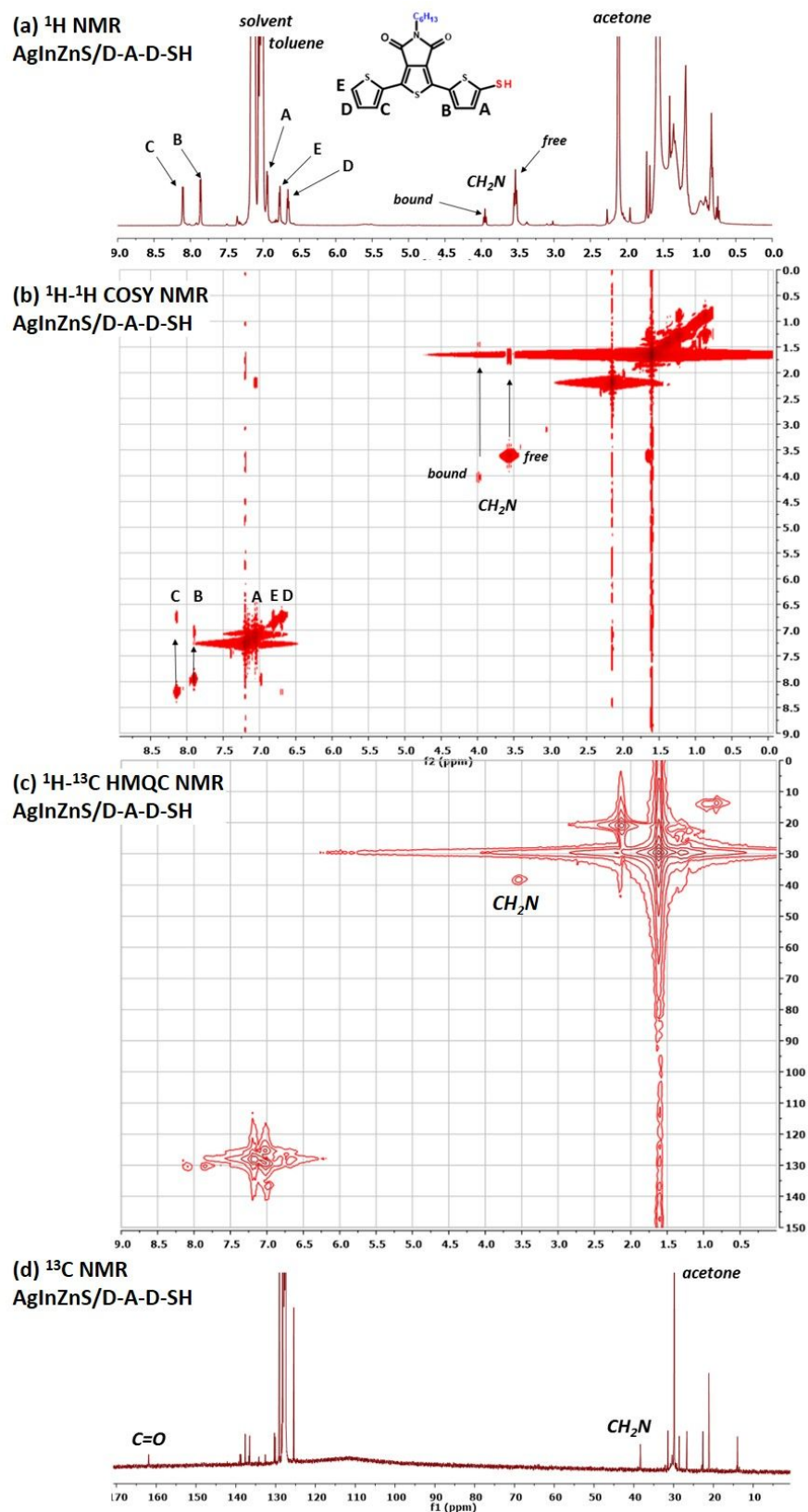


Figure S8. ^1H (a), ^1H - ^1H COSY (b), ^1H - ^{13}C HMQC (c) and ^{13}C NMR (d) spectra of $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.2}$ nanocrystals capped with ligand: 2-(5-mercaptothien-2-yl)-8-(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (D-A-D-SH) recorded in benzene- d_6 at 298 K.

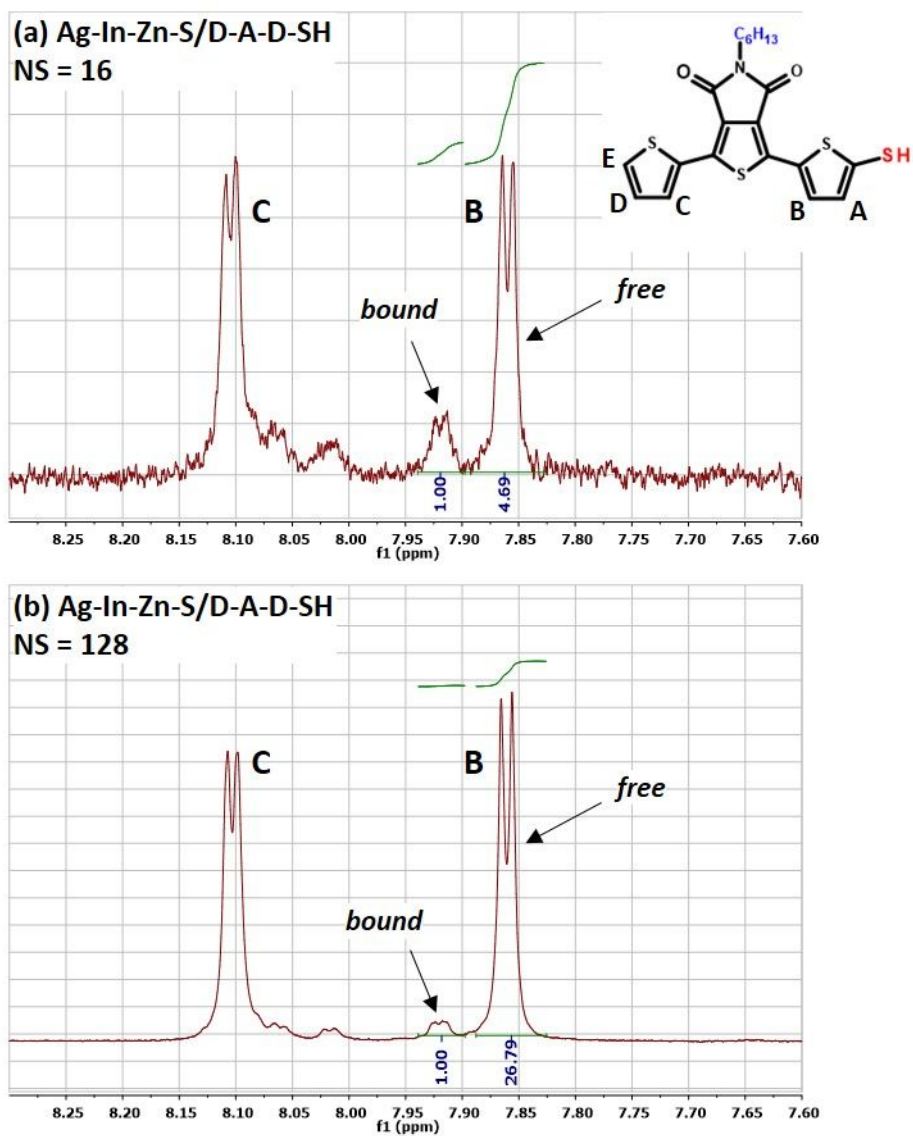


Figure S9. ^1H NMR spectra (in the range of 7.6–8.3 ppm) of the hybrid Ag-In-Zn-S/D-A-D-SH recorded with 16 scans (a) and 128 scans (b) in benzene- d_6 at 298K.

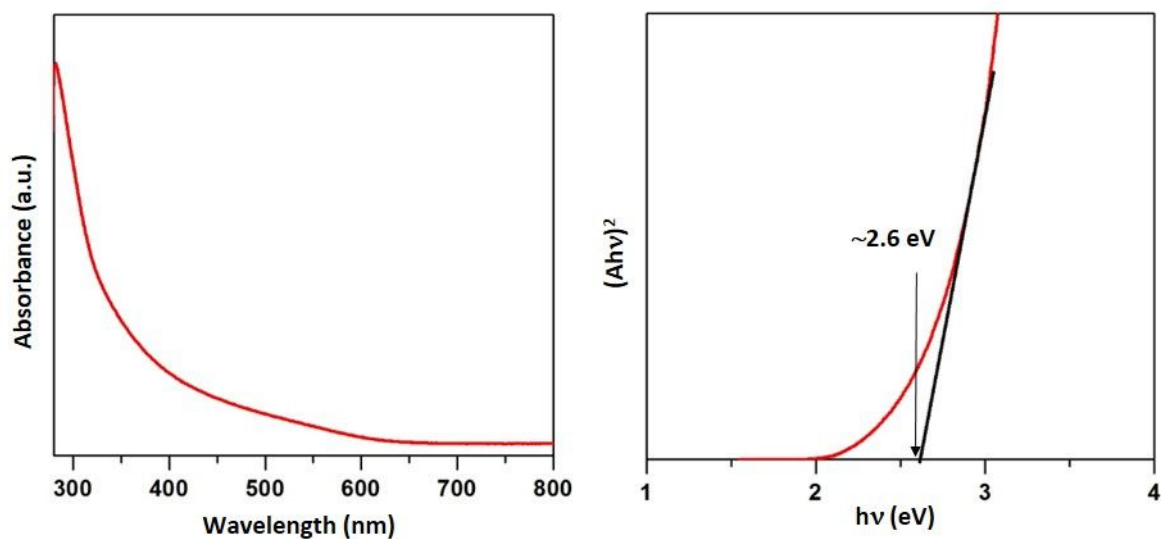


Figure S10. Room temperature UV-vis-NIR spectrum of toluene dispersion of $\text{Ag}_{1.0}\text{In}_{3.1}\text{Zn}_{1.0}\text{S}_{4.0}$ nanocrystals capped with initial ligands and the corresponding $(Ah\nu)^2$ vs $h\nu$ curve (where A = absorbance, h = Planck's constant and ν = frequency).

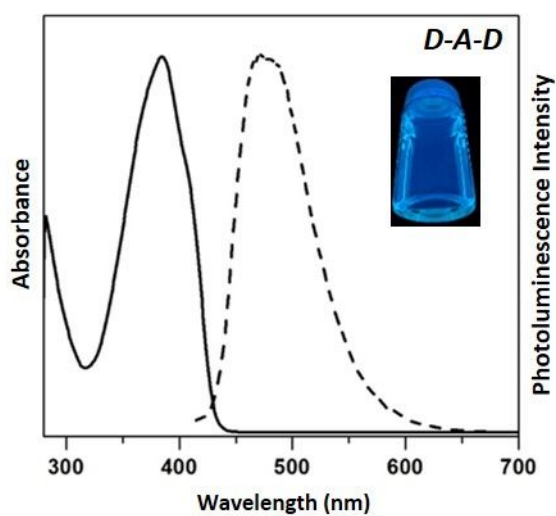


Figure S11. UV-vis-NIR (solid line) and photoluminescence (dash line) spectra of 2,8-bis(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (**D-A-D**) in toluene.

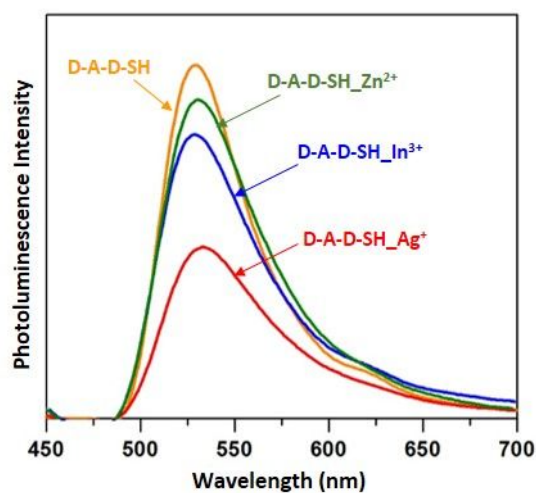


Figure S12. Photoluminescence spectra of 2-(5-mercaptothien-2-yl)-8-(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (**D-A-D-SH**) (orange line) and its complexes with the following metal ions: Ag^+ (red line), In^{3+} (blue line) and Zn^{2+} (green line) in toluene.

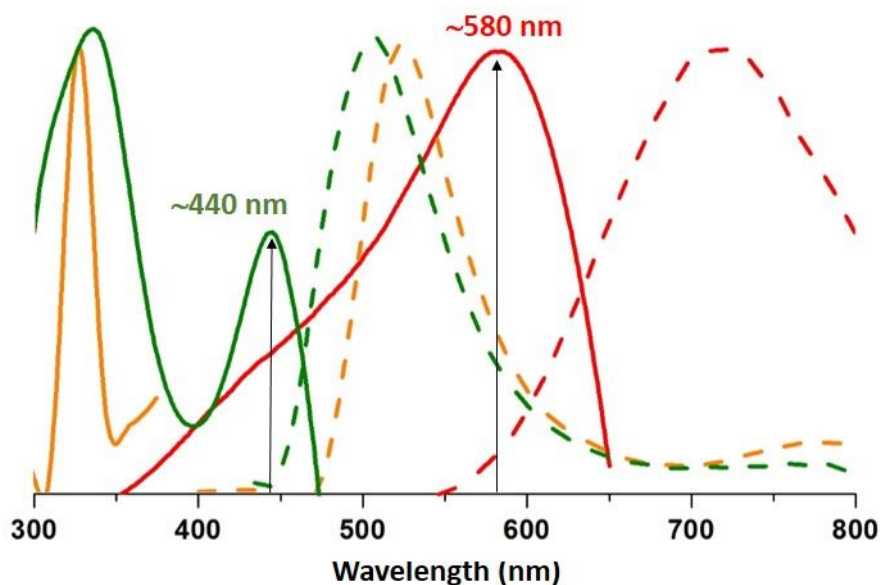


Figure S13. Photoluminescence excitation (solid lines) and emission (dash lines) spectra of 2-(5-mercaptothien-2-yl)-8-(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (**D-A-D-SH**) (orange lines), **Ag-In-Zn-S** capped with initial ligands (red lines) and ligand (**D-A-D-SH**) (green lines) in toluene.

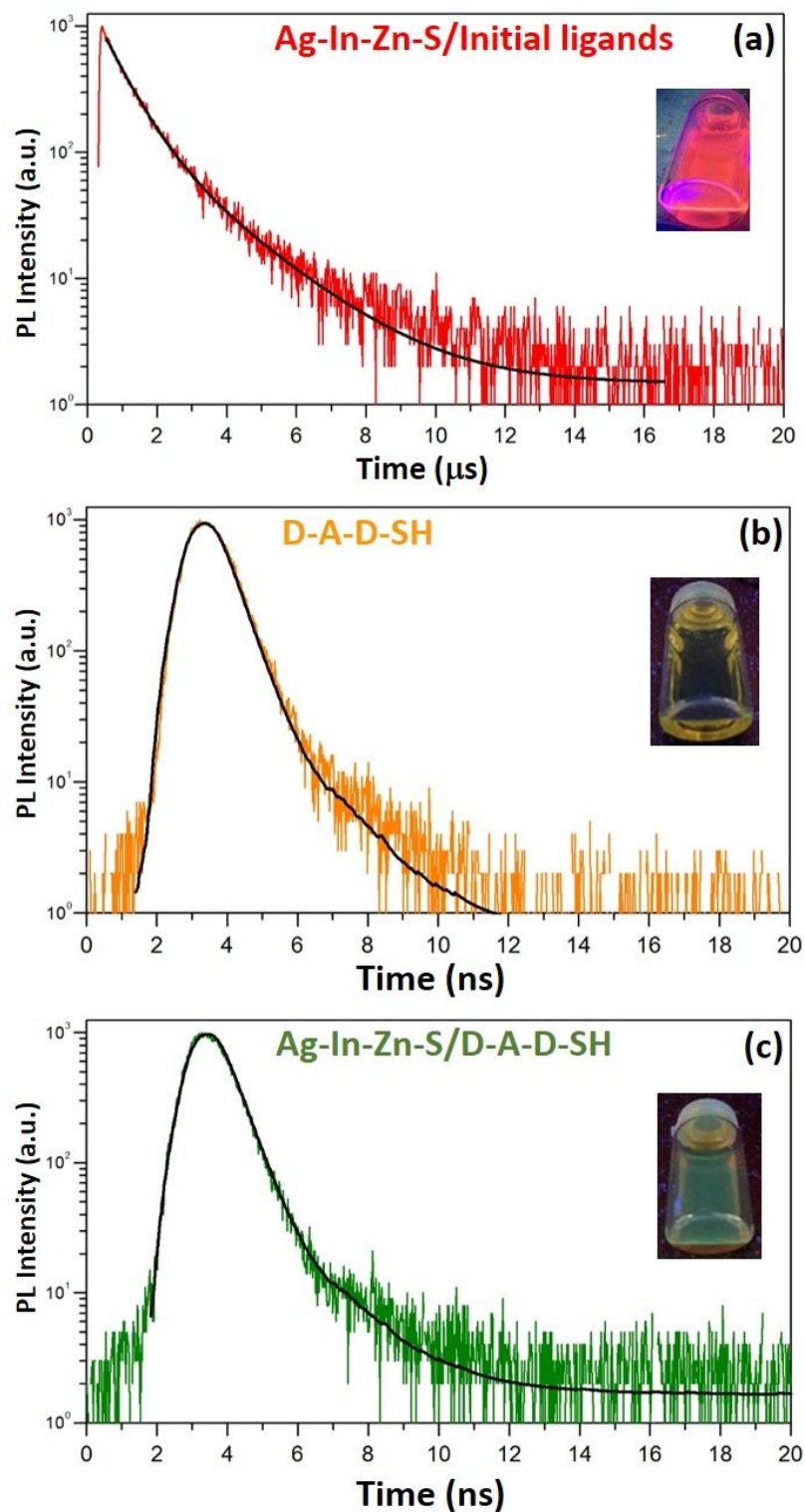


Figure S14. Photoluminescence decay curves of Ag-In-Zn-S nanocrystals capped with initial ligands (a), *2-(5-mercaptothien-2-yl)-8-(thien-2-yl)-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione* (D-A-D-SH) (b) and Ag-In-Zn-S/D-A-D-SH hybrid (c) and the corresponding biexponential fitting curves.

References

- [1] Gabka, G.; Bujak, P.; Kotwica, K.; Ostrowski, A.; Lisowski, W.; Sobczak, J. W.; Pron, A. Luminophores of Tunable Colors from Ternary Ag-In-S and Quaternary Ag-In-Zn-S Nanocrystals Covering the Visible to Near-Infrared Spectral Range. *Phys. Chem. Chem. Phys.* **2017**, *19*, 1217-1228.
- [2] Bujak, P.; Wróbel, Z.; Penkala, M.; Kotwica, K.; Kmita, A.; Gajewska, M.; Ostrowski, A.; Kowalik, P.; Pron, A. Highly Luminescent Ag-In-Zn-S Quaternary Nanocrystals: Growth Mechanism and Surface Chemistry Elucidation. *Inorg. Chem.* **2019**, *58*, 1358-1370.
- [3] Nielsen, C. B.; Bjørnholm, T. New Regiosymmetrical Dioxopyrrolo- and Dihydropyrrolo-Functionalized Polythiophenes. *Org. Lett.* **2004**, *6*, 3381-3384.