Supplementary Materials

Organic-to-Aqueous Phase Transfer of Alloyed AgInS2-ZnS Nanocrystals Using Simple Hydrophilic Ligands: Comparison of 11-Mercaptoundecanoic Acid, Dihydrolipoic Acid and Cysteine

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Preparation of $AgInS_2$-ZnS nanocrystals (R-"Red" and G-"Green")

In the synthesis of Ag-In-Zn-S nanocrystals and primary ligand exchange procedures earlier described in the literature were followed **[1,2]**. All operations were carried out under a constant dry argon flow. Silver nitrate (0.03 g, 0.17 mmol), indium(III) chloride (0.13 g, 0.59 mmol), zinc stearate (0.40g, 0.63 mmol for **R** or 0.87 g, 1.37 mmol for **G**), and DDT (0.20 g, 1.00 mmol) were mixed with ODE (15 mL) in a three-neck flask. The mixture was heated to 150 °C until a homogenous solution was formed. Then sulfur (0.015 g, 0.47 mmol) dissolved in 1 mL of OLA 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 - 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 (**R** or **G**) were separated by centrifugation (7000 rpm, 5 min) and then redispersed in toluene.

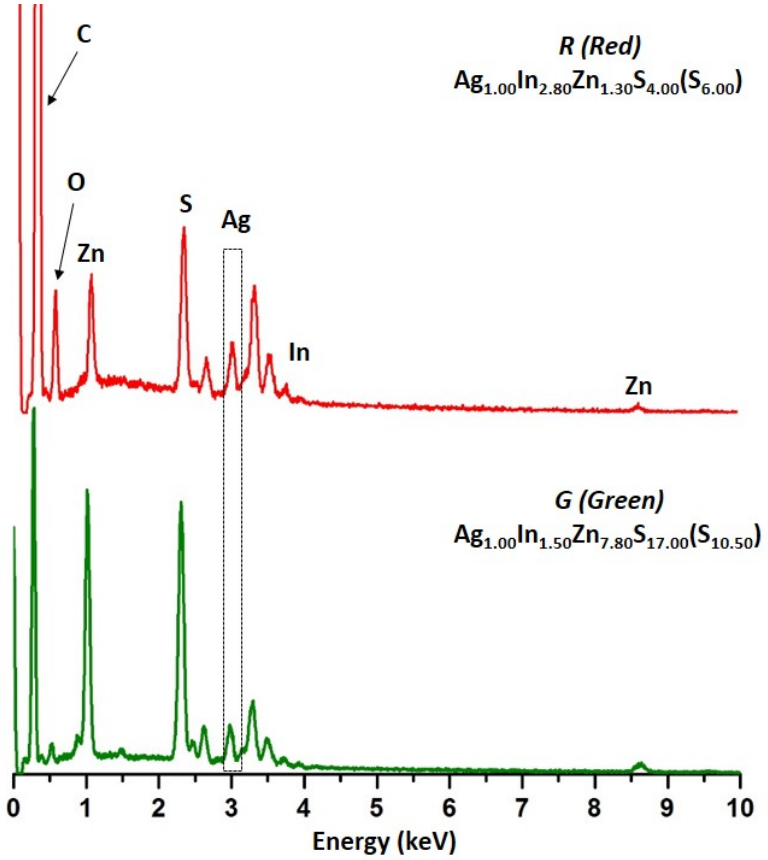
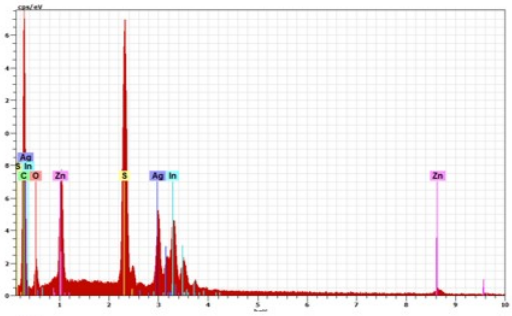
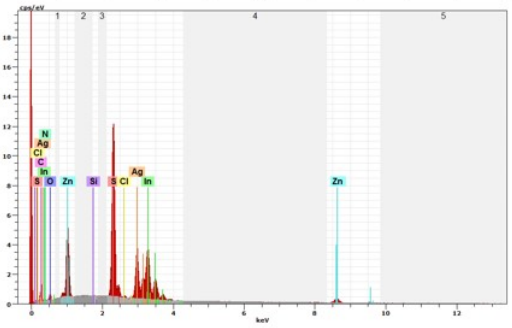


Figure S1 Energy-dispersive spectra of $Ag_{1.00}In_{2.80}Zn_{1.30}S_{4.00}(S_{6.00})$ (**R**) and $Ag_{1.00}In_{1.50}Zn_{7.80}S_{17.00}(S_{10.50})$ (**G**) nanocrystals.



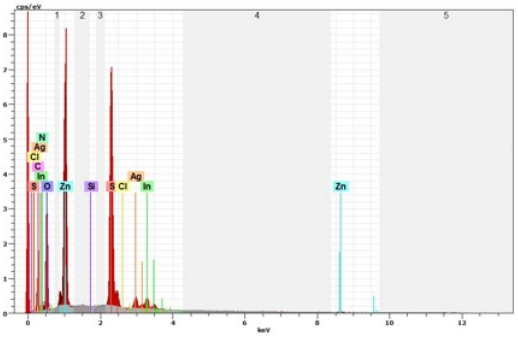
R-MUA

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Carbon	K-series	42.45	42.92	74.73	5.31
Oxygen	K-series	6.06	6.13	8.01	1.06
Sulfur	K-series	13.83	13.98	9.12	0.52
Zinc	L-series	8.96	9.06	2.90	0.61
Silver	L-series	13.35	13.50	2.62	0.46
Indium	L-series	14.25	14.41	2.62	0.47
Total:		98.91	100.00	100.00	



R-DHLA

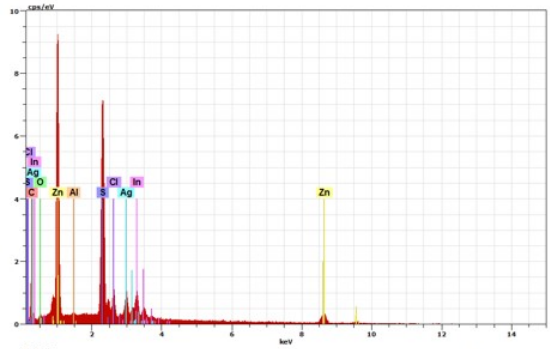
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Sulfur	K-series	19.56	22.97	30.05	0.72
Indium	L-series	22.85	26.83	9.80	0.74
Oxygen	K-series	3.29	3.86	10.13	0.70
Zinc	K-series	11.55	13.56	8.70	0.50
Carbon	K-series	7.43	8.73	30.48	1.32
Chlorine	K-series	0.00	0.00	0.00	0.00
Silver	L-series	19.98	23.46	9.12	0.67
Nitrogen	K-series	0.47	0.55	1.64	0.22
Silicon	K-series	0.04	0.05	0.07	0.03
Total:		85.18	100.00	100.00	



R-Cys

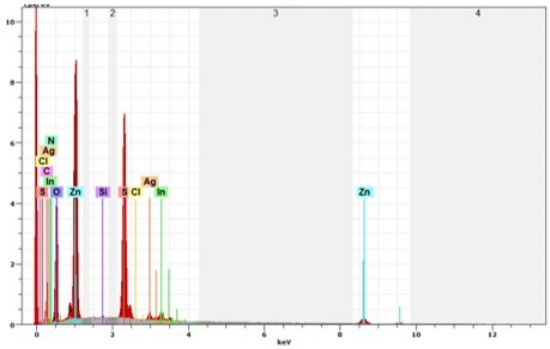
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Sulfur	K-series	14.07	22.51	12.45	0.53
Indium	L-series	2.60	4.15	0.64	0.12
Oxygen	K-series	21.57	34.52	38.25	2.81
Zinc	K-series	1.12	1.79	0.48	0.10
Carbon	K-series	16.69	26.71	39.42	2.40
Chlorine	K-series	0.00	0.00	0.00	0.00
Silver	L-series	2.44	3.90	0.64	0.11
Nitrogen	K-series	4.00	6.40	8.10	0.83
Silicon	K-series	0.01	0.02	0.01	0.03
Total:		62.50	100.00	100.00	

Figure S2. Energy-dispersive spectra of $Ag_{1.00}In_{1.00}Zn_{1.10}S_{3.50}(S_{3.10})$ (**R-MUA**), $Ag_{1.00}In_{1.00}Zn_{1.00}S_{3.30}(S_{3.00})$ (**R-DHLA**) and $Ag_{1.00}In_{1.00}Zn_{0.80}S_{19.40}(S_{2.80})$ (**R-Cys**) nanocrystals.



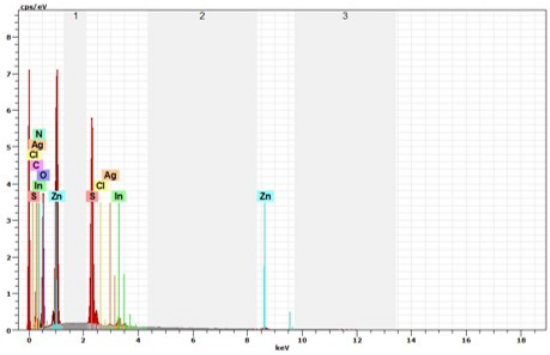
G-MUA

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Carbon	K-series	42.38	50.19	76.42	6.11
Oxygen	K-series	6.33	7.50	8.58	1.32
Sulfur	K-series	11.15	13.21	7.53	0.42
Silver	L-series	4.00	4.73	0.80	0.16
Indium	L-series	5.07	6.00	0.96	0.19
Zinc	K-series	13.53	16.02	4.48	0.54
Aluminium	K-series	0.09	0.11	0.07	0.03
Chlorine	K-series	1.90	2.25	1.16	0.09
	Total:	84.45	100.00	100.00	



G-DHLA

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Sulfur	K-series	15.64	20.73	12.86	0.58
Indium	L-series	2.30	3.05	0.53	0.11
Oxygen	K-series	27.28	36.17	44.95	3.46
Zinc	K-series	11.19	14.84	4.51	0.47
Carbon	K-series	15.81	20.95	34.69	2.40
Chlorine	K-series	0.05	0.07	0.04	0.03
Silver	L-series	2.07	2.75	0.51	0.10
Nitrogen	K-series	0.95	1.26	1.79	0.33
Silicon	K-series	0.13	0.17	0.12	0.03
	Total:	75.43	100.00	100.00	



G-Cys

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Sulfur	K-series	14.36	20.93	11.36	0.54
Indium	L-series	2.39	3.49	0.53	0.11
Oxygen	K-series	27.26	39.74	43.23	3.48
Zinc	K-series	2.81	4.09	1.09	0.17
Carbon	K-series	16.92	24.66	35.73	2.50
Chlorine	K-series	0.12	0.17	0.08	0.03
Silver	L-series	0.39	0.57	0.09	0.05
Nitrogen	K-series	4.35	6.34	7.88	0.91
	Total:	68.60	100.00	100.00	

Figure S3. Energy-dispersive spectra of $Ag_{1.00}In_{1.20}Zn_{5.60}S_{9.40}(S_{7.90})$ (**G-MUA**), $Ag_{1.00}In_{1.00}Zn_{8.80}S_{25.10}(S_{10.80})$ (**G-DHLA**) and $Ag_{1.00}In_{5.80}Zn_{12.10}S_{126.20}(S_{21.30})$ (**G-Cys**) nanocrystals.

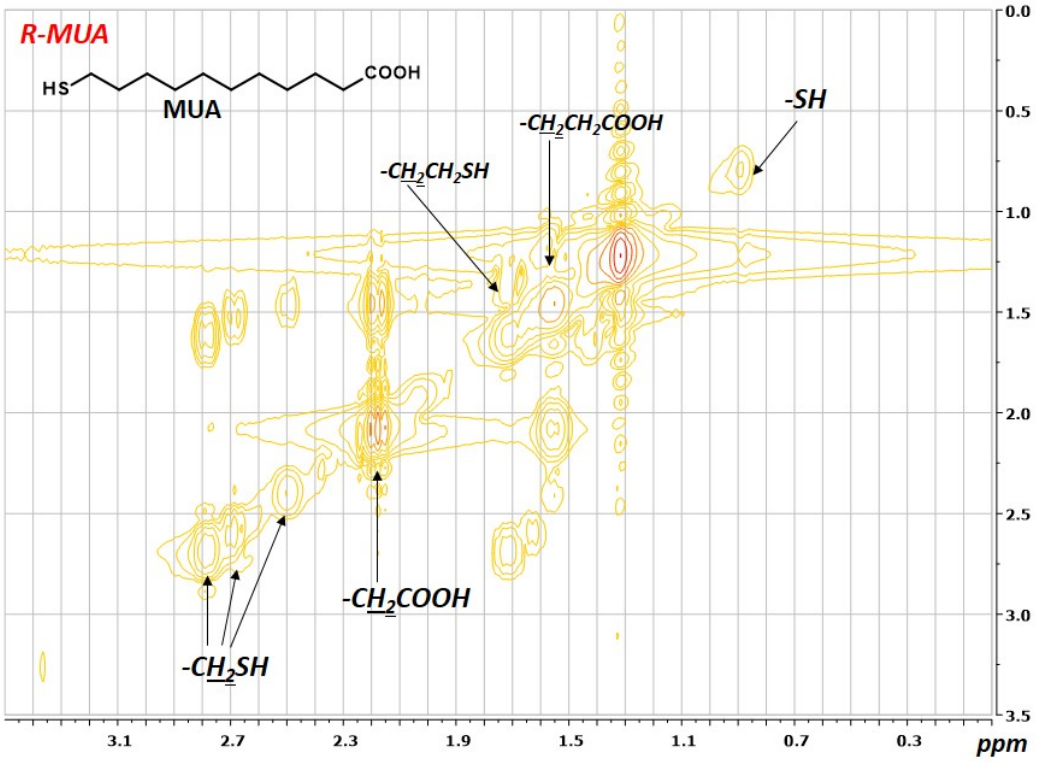


Figure S4. ^{1}H-^{1}H COSY spectrum of D_2O dispersion of $AgInS_2$-ZnS nanocrystals capped with MUA: **R-MUA**.

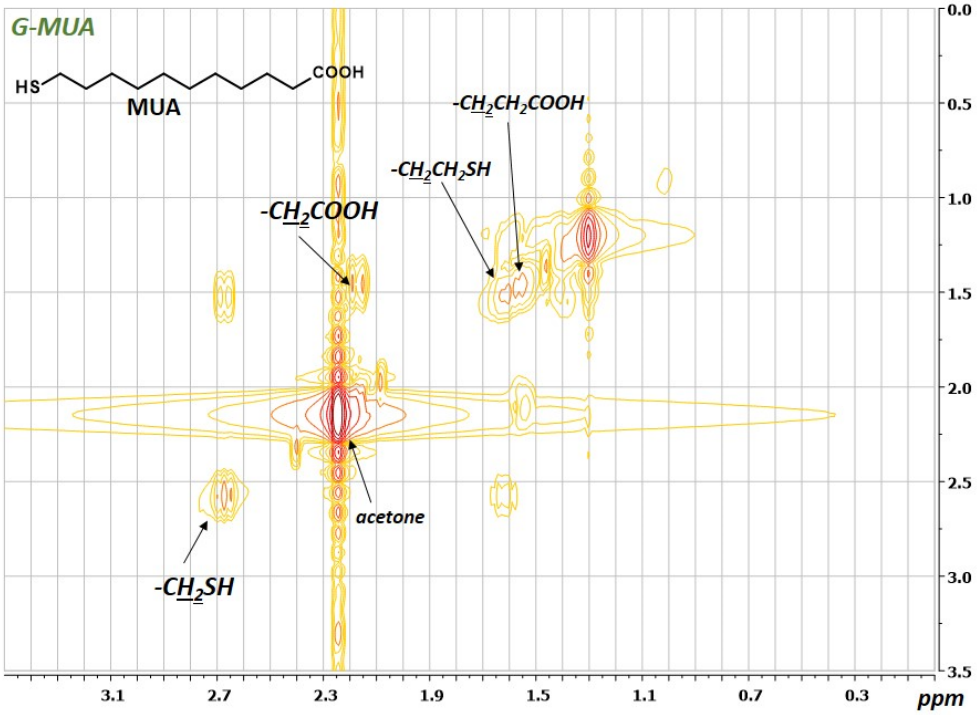


Figure S5. ^{1}H-^{1}H COSY spectrum of D_2O dispersion of $AgInS_2$-ZnS nanocrystals capped with MUA: **G-MUA**.

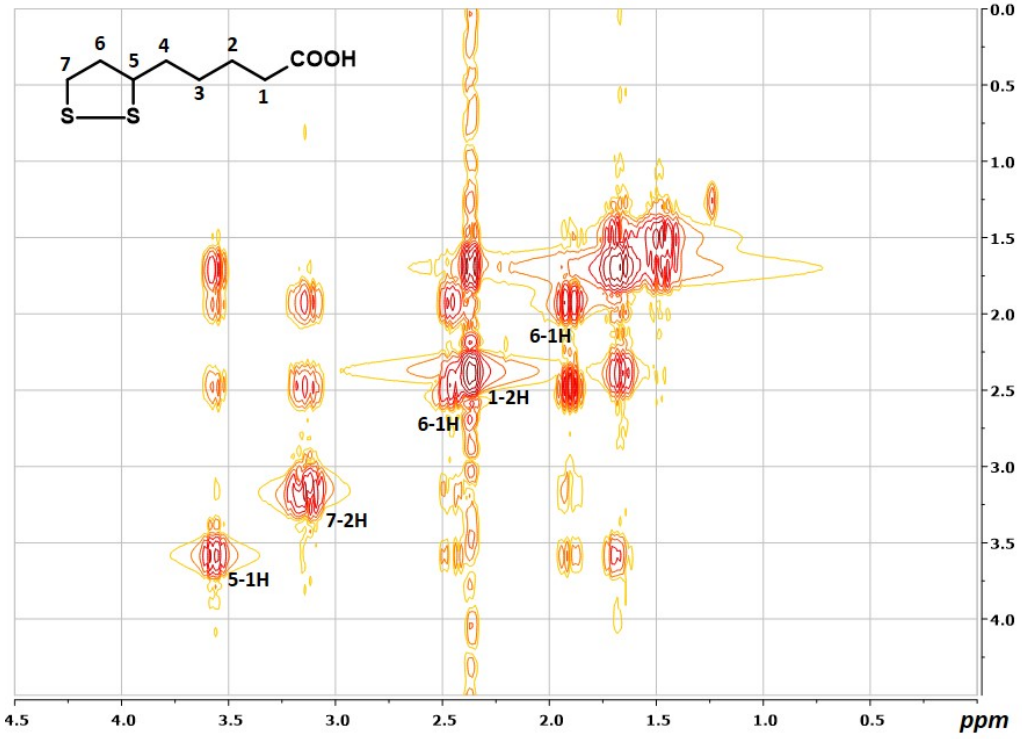


Figure S6. ^{1}H-^{1}H COSY spectrum of lipoic acid (LA) in $CDCl_3$.

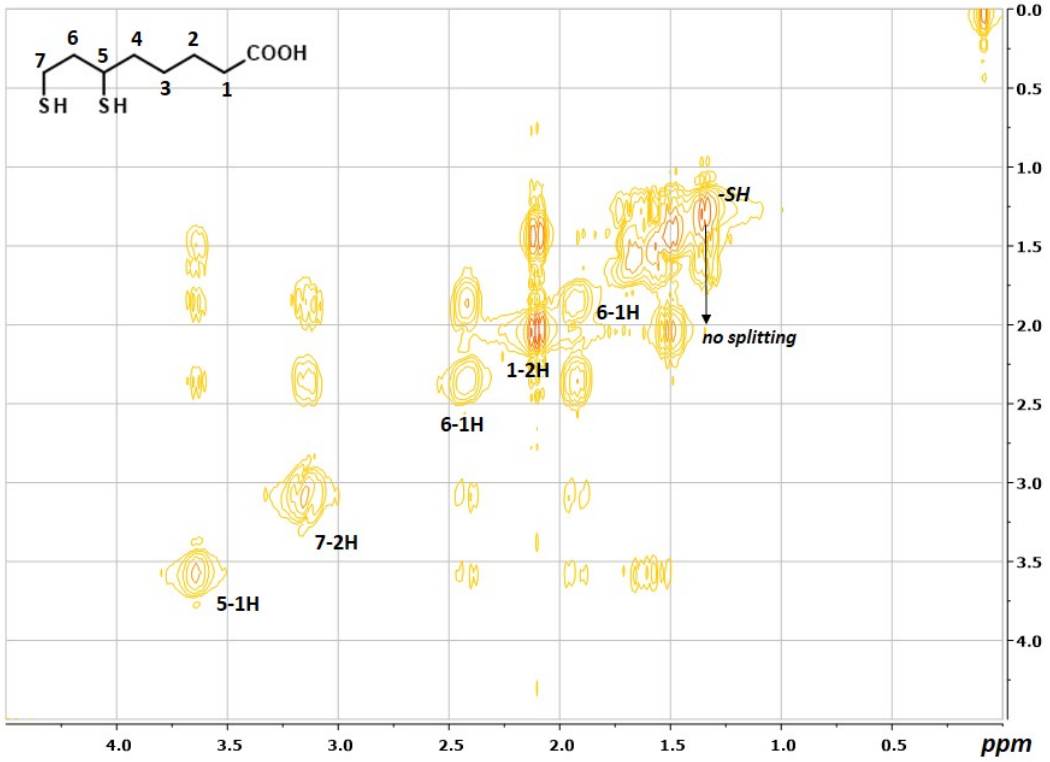


Figure S7. ^{1}H-^{1}H COSY spectrum of dihydrolipoic acid (DHLA) in D_2O.

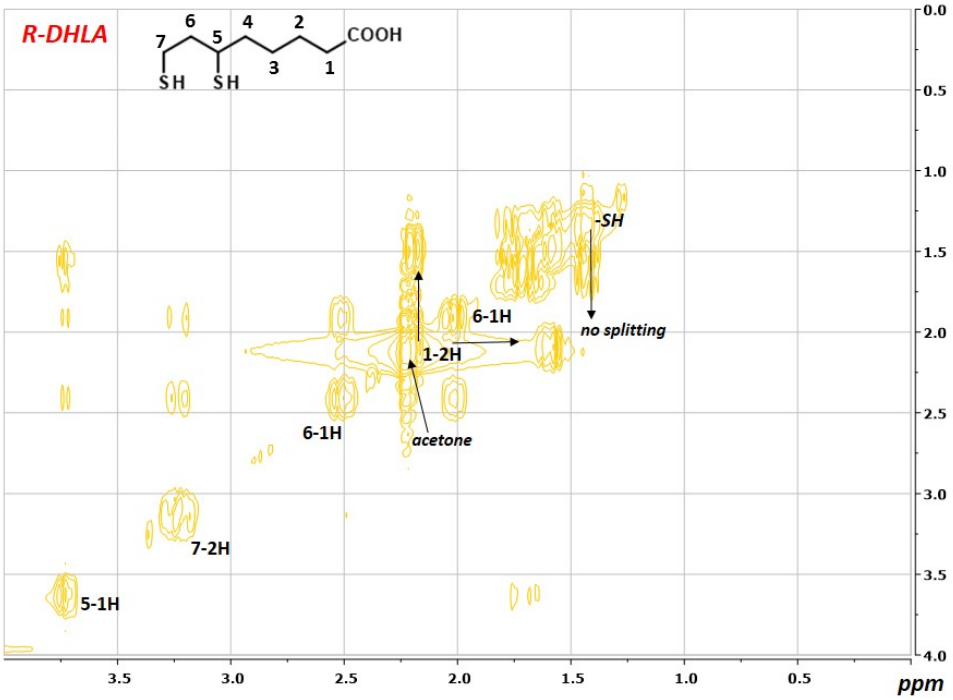


Figure S8. ^{1}H-^{1}H COSY spectrum of D_2O dispersion of $AgInS_2$-ZnS nanocrystals capped with MUA: **R-DHLA**.

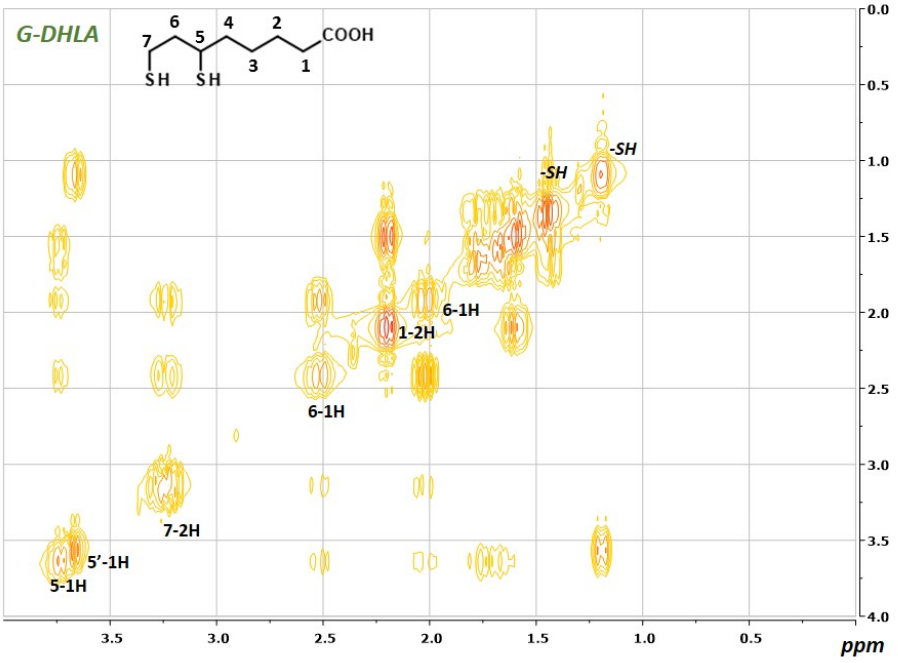


Figure S9. ^{1}H-^{1}H COSY spectrum of D_2O dispersion of $AgInS_2$-ZnS nanocrystals capped with MUA: **G-DHLA**.

Reference

1. Gabka, G.; Bujak, P.; Giedyk, K.; Ostrowski, A.; Malinowska, K.; Herbich, J.; Golec, B.; Wielgus, I.; Pron. A. A Simple Route to Alloyed Quaternary Nanocrystals Ag-In-Zn-S with Shape and Size Control. *Inorg. Chem.* **2014**, *53*, 5002-5012.

2. 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.