Electronic Supplementary Information (ESI)

Formation of Persistent Ordered Lamellar Mesophases in Azobenzene-Containing Silver Thiolates and Their Implications for Controlled Synthesis of Silver Nanomaterials

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Supplementary Materials for Synthesis:

Synthesis of series thiol ligands 4-(10-mercaptodecyloxy)-4'-alkyloxyazobenzene (1)

4-(10-bromodecyloxy)-4'-alkoxyazobenzene employed as starting materials in this work, as representatively shown in Scheme 1 in the main text, were synthesized in our laboratory according to procedures reported previously.[S1] Synthesis of 4-(10-mercaptodecyloxy)-4'-octyloxyazobenzene (**1c**) is representatively shown here as an example, all other analogues were prepared by the same protocol.

Synthesis of intermediate 4-(10-thioacetyldecyloxy)-4'-octyloxyazobenzene: 2.28 g (20 mmol) of potassium thioacetate and 6.50 g (12 mmol) of 4-(10-bromodecyloxy)-4' -octyloxyazobenzene were dissolved in 150 mL of THF and refluxed for 24 h under vigorous stirring, the mixture was cooled to ambient temperature and filtered, the crude product was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 1) to afford the intermediate 5.90 g in yield 91.0%.

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.88 (d, 4H, J = 9.0 Hz, Ar-H), 7.00 (d, 4H, J = 9.3 Hz, Ar-H), 4.03 (t, 4H, J = 6.6 Hz, $ArOCH_2$), 2.90 (t, 2H, J = 7.5 Hz, SCH_2), 2.36 (s, 3H, CH_3CO), 1.82 (qn, 4H, J = 6.9 Hz, $ArOCH_2CH_2$), 1.25-1.39 (m, 24H, CH_2), 0.93 (t, 3H, J = 6.6 Hz, CH_3CH_2). FTIR (cm^{-1}): 2920, 2848, 1689, 1615, 1560, 1480, 1246, 1015.

Synthesis of 4-(10-mercaptodecyloxy)-4'-octyloxyazobenzene (1c): 5.90 g of 4-(10-thioaceyldecyloxy)-4'-octyloxyazobenzene (11 mmol) was dissolved in 150 mL of THF and the solution was degassed by bubbling nitrogen for 5–10 min. A solution of $NaBH_4$ (1.9 g, 53 mmol) in 15 mL distilled water was added dropwise. The resulting mixture was kept at room temperature with stirring for 24 h under nitrogen and then poured into distilled water, the mixture extracted with dichloromethane (3×50 mL). The combined organic extracts were washed with distilled water and dried under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2) to obtain the thiol ligand **1c** 4.80 g in yield 88.0%.

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.88 (d, 4H, J = 9.0 Hz, Ar-H), 7.00 (d, 4H, J = 9.3 Hz, Ar-H), 4.03 (t, 4H, J = 6.6 Hz, $ArOCH_2$), 2.50 (q, 2H, J = 7.5 Hz, SCH_2), 1.82 (qn, 4H, J = 6.9 Hz, $ArOCH_2CH_2$), 1.25-1.39 (m, 24H, CH_2), 0.93 (t, 3H, J = 6.6 Hz, CH_3CH_2). FTIR (cm^{-1}): 2922, 2847, 2560, 1635, 1510, 1474, 1230, 1015. MS(ESI): m/z 497.3 $[M]^-$.

Supplementary Tables:

Table S1. Thermal properties and assigned phases for the series silver thiolates **2** from DSC measurements in the first heating and first cooling runs scanning in the temperature range of 50-250 °C.

code	Thermal scans	Transition *T*/°C[*ΔH* (J g^{-1})][a]
2a	1st heating	Cr [b] 207.6 [123.0] I 236.6 [-5.9] Tys
	1st cooling	I 117.3 [-67.3] Cr
2b	1st heating	Cr 188.0 [83.0] SmX 196.9 [12.3] I 241.3 [-3.2] Tys
	1st cooling	I 118.2 [-5.2] SmA 99.8 [-64.0] Cr1 90.1 [-31.6] Cr2
2c	1st heating	Cr 184.1 [86.9] SmX 200.0 [13.6] I 244.7 [-3.8] Tys
	1st cooling	I 115.7 [-8.5] SmA 96.3 [-83.1] Cr1 81.8 [-54.3] Cr2
2d	1st heating	Cr 151.6[10.7] S1 168.5[7.3] S2 178.0[41.3] SmX 202.9[13.0] I 247.0[-1.9] Tys
	1st cooling	I 115.4 [-70.8] Cr

[a] The phase transition temperatures and enthalpy changes (in square brackets) obtained from DSC at 10 °C min^{-1}; [b] Abbreviations: Cr = crystal; SmA = smectic A; S1, S2 = solid-solid phase transition in the first heating of silver thiolate **2d** with long alkyloxy tail; SmX = highly ordered smectic X; I = isotropic phase; Tys = thermolysis (with a small exothermic peak in the first heating run).

Supplementary Figures:

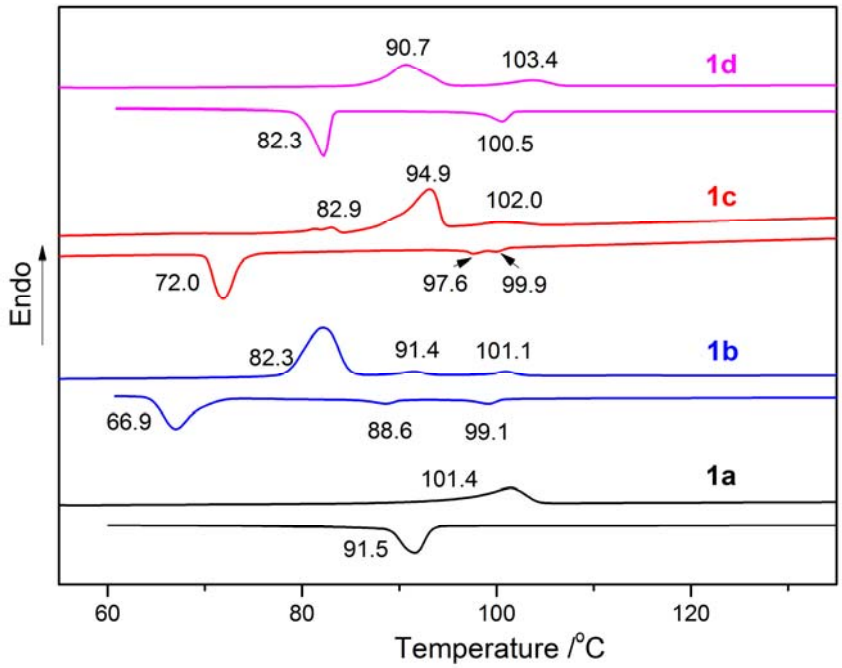

Figure S1. DSC thermograms of azobenzene-containing thiol ligands **1a**, **1b**, **1c** and **1d** during the first cooling and second heating scans in the temperature range from 50 to 140 °C at a rate of 10 °C/min.

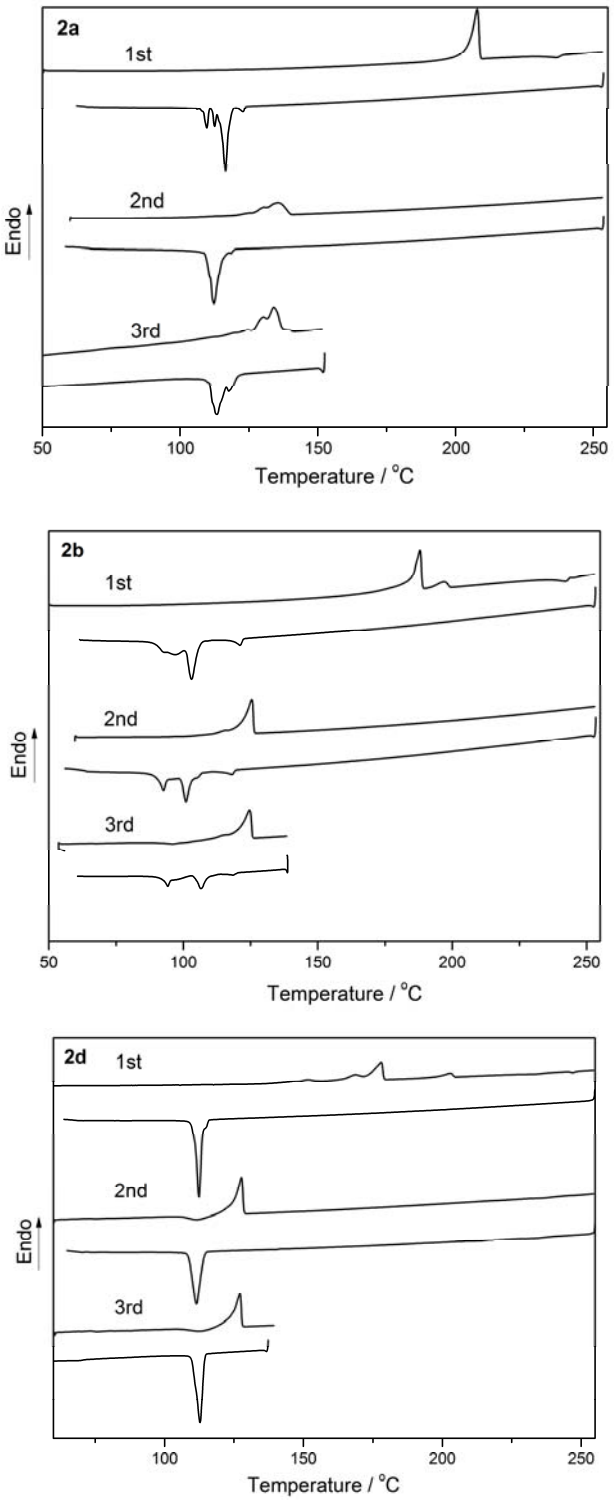

Figure S2. DSC thermograms of the series silver thiolates other than **2c** during heating and cooling scans in the temperature range of 50-255 °C (1st and 2nd cycles) or 50-150 °C (3rd cycle) at a rate of 10 °C/min. One can see that the thermolysis occurred and approached almost completion once passed through the exothermic transition temperature and then the system entered another essentially reversible process exhibited by the thermolytic byproducts which was revealed to be mainly composed of azobenzene-containing alkyl sulfide and disulfide.

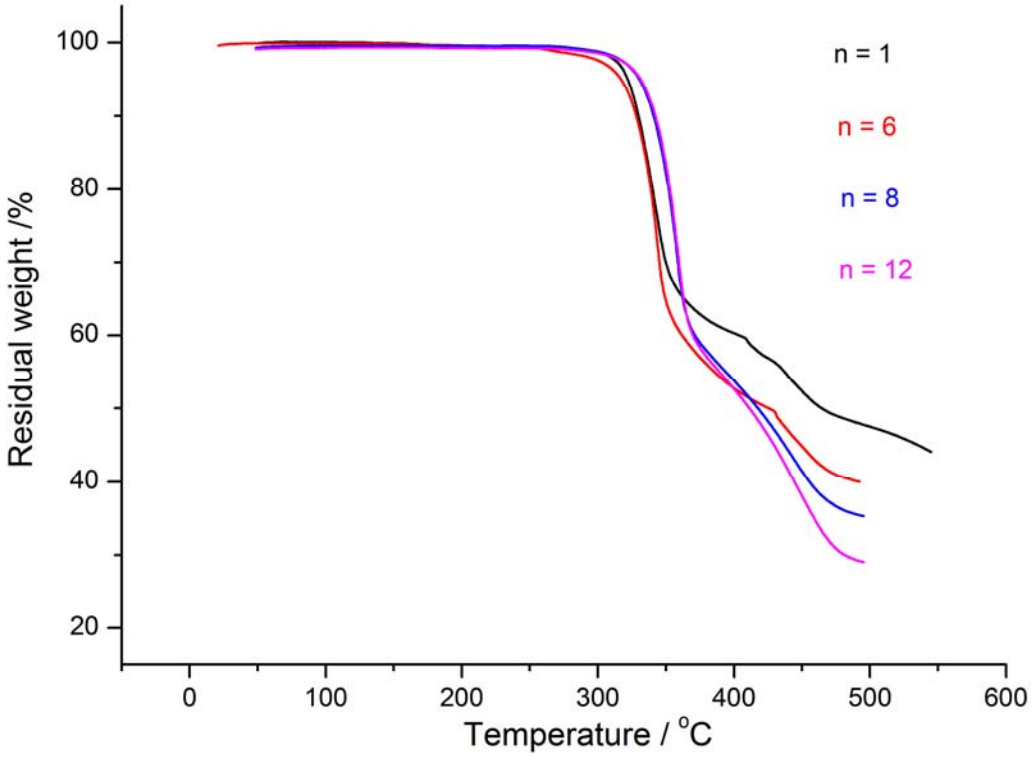

Figure S3. TGA thermograms of the series silver thiolates **2a-2d,** AgS-$C_{10}H_{21}$-Ph-N=N-Ph-OC_nH_{2n+1} with n = 1 (**2a**), 6(**2b**), 8(**2c**), and 12(**2d**).

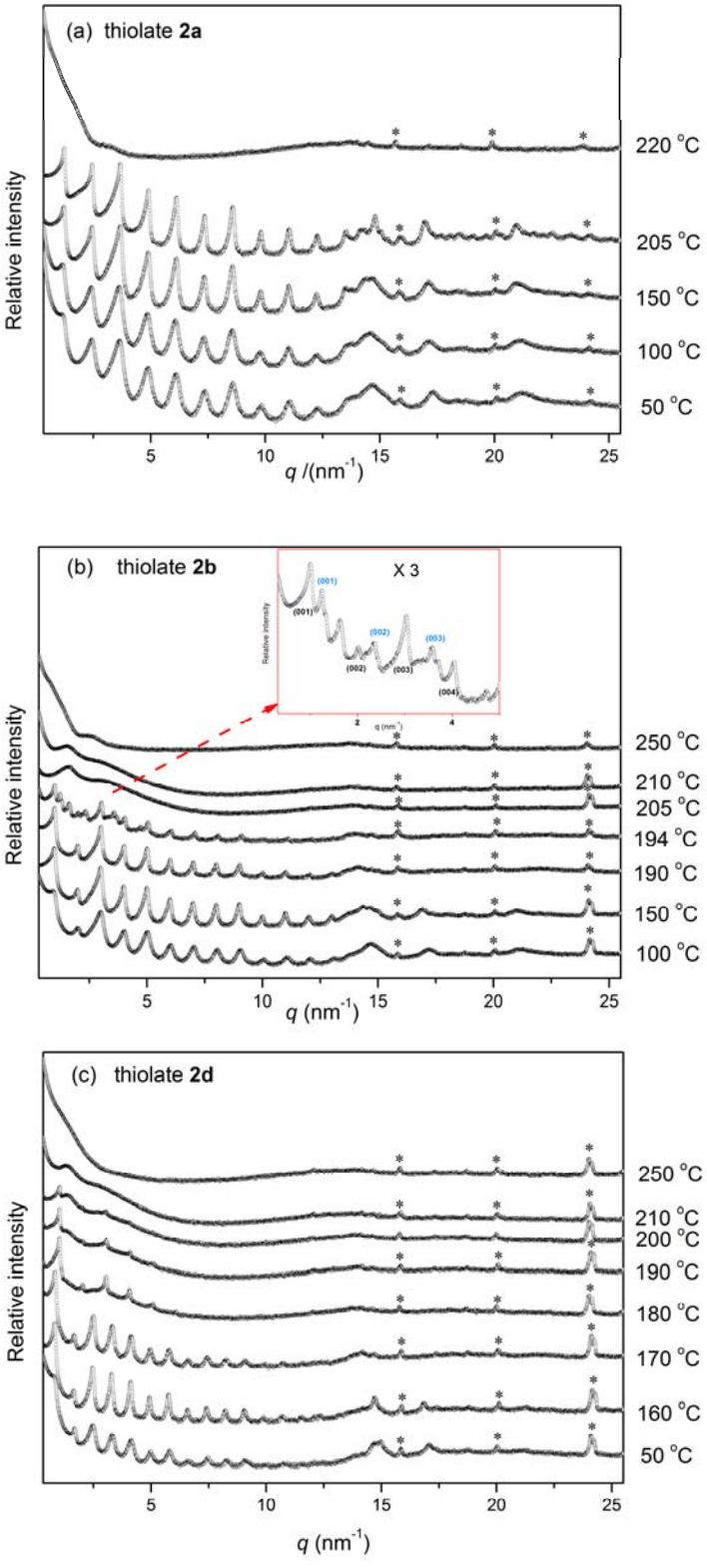

Figure S4. Variable-temperature SAXS/WAXS profiles of the series silver thiolates **2** other than **2c**. For **2b** the ordered smectic phase (enlarged in the red rectangular box) coexisting with the crystalline reflection fringes at around 194 °C due to the narrower mesophase range. The asterisk-labeled peaks are from reflections of the packing aluminum foil background. [S2]

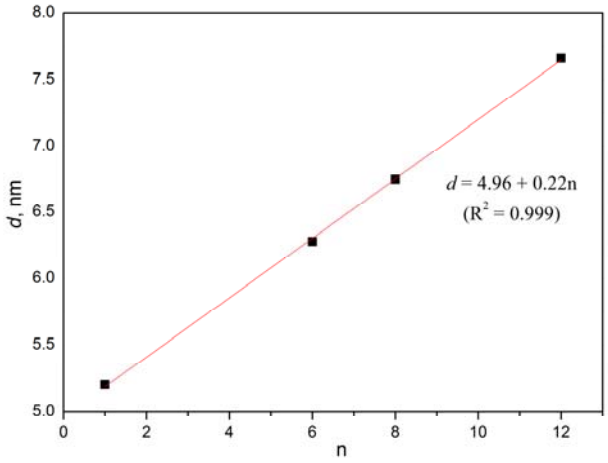

Figure S5. The linear relationship of interlayer spacing versus the alkyloxy tail carbon number *n* of the complex AgS-$C_{10}H_{21}$-Ph-N=N-Ph-OC_nH_{2n+1} in crystalline solid phase.

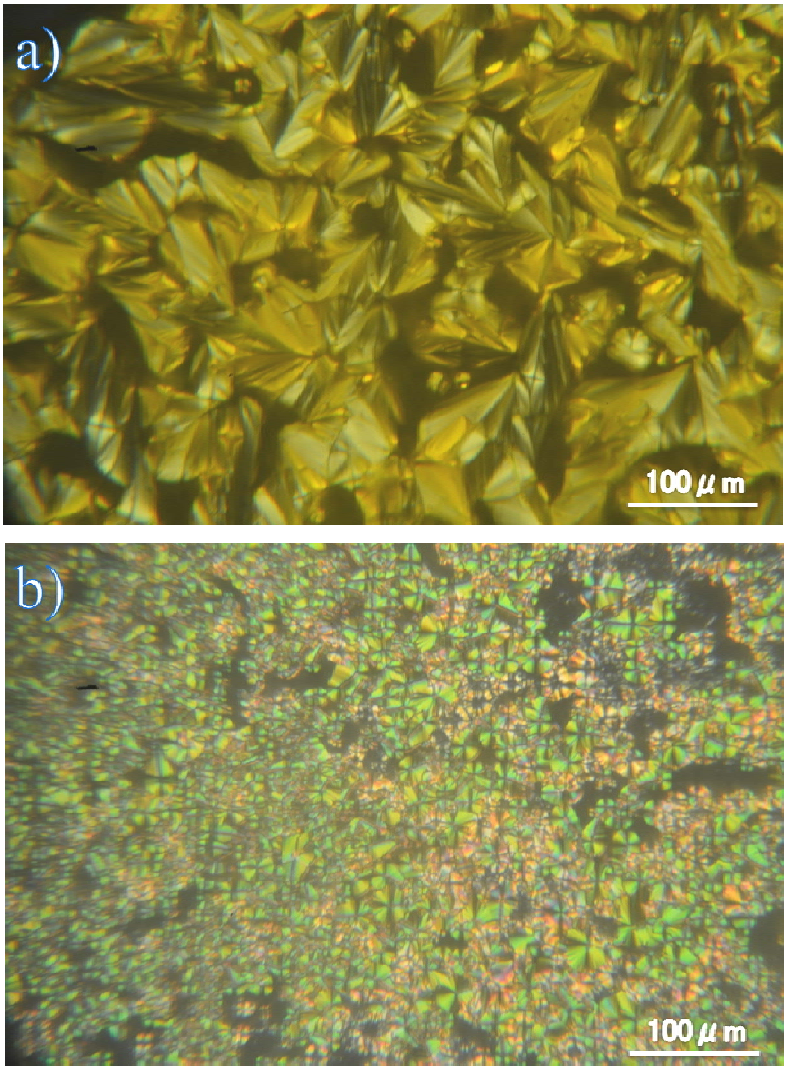

Figure S6. Representative POM images under crossed polarizers of a) **1c**, 95 °C, focal conic texture, SmA; and b) **1d**, 96 °C, diminished focal conic texture, SmA. [S3]

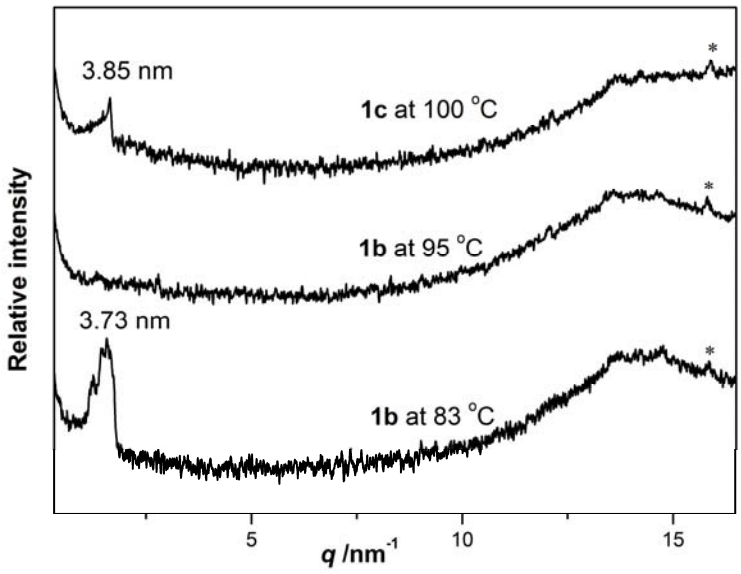

Figure S7. Representative variable-temperature SAXS/WAXS profiles of thiol ligand **1b** at 83 °C showing first order peak of SmA with layer spacing d = 3.73 nm, and at 95 °C characteristic of N phase with only a broad halo around q = 14 nm^{-1} (≈ 0.45 nm distance); and thiol **1c** heating to 100 °C showing first order peak of SmA with d = 3.85 nm (The peaks labeled by an asterisk are due to reflections of the packing aluminum foil background).[S2]

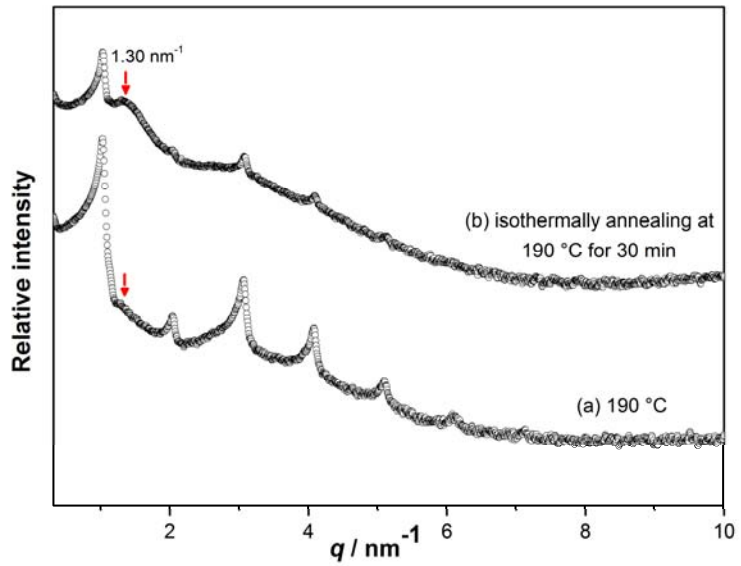

Figure S8. SAXS profiles of mesogenic silver thiolate **2d** (a) first normal measurement at 190 °C; (b) after annealing isothermally at 190 °C for 30 min.

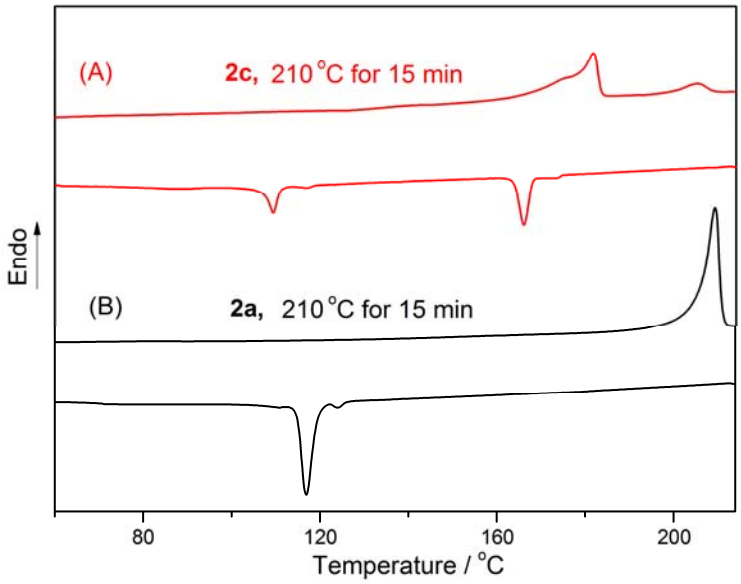

Figure S9. DSC thermograms for comparison of their thermal stability (i.e. thermolytic reaction rate) of (A) mesogenic thiolate **2c** during the first heating and the cooling scans after isothermal annealing at 210 °C for 15 min; (B) crystalline thiolate **2a** during the first heating and the cooling scans after isothermal annealing at 210 °C for 15 min.

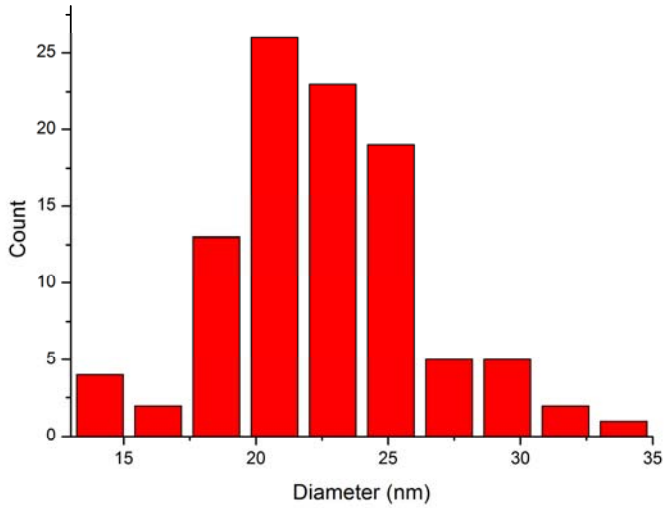

Figure S10. Particle size distribution of Ag nanodisks produced from **2c** after annealing at 210 °C for 60 min. The average diameter is 22.6 ± 2.2 nm.

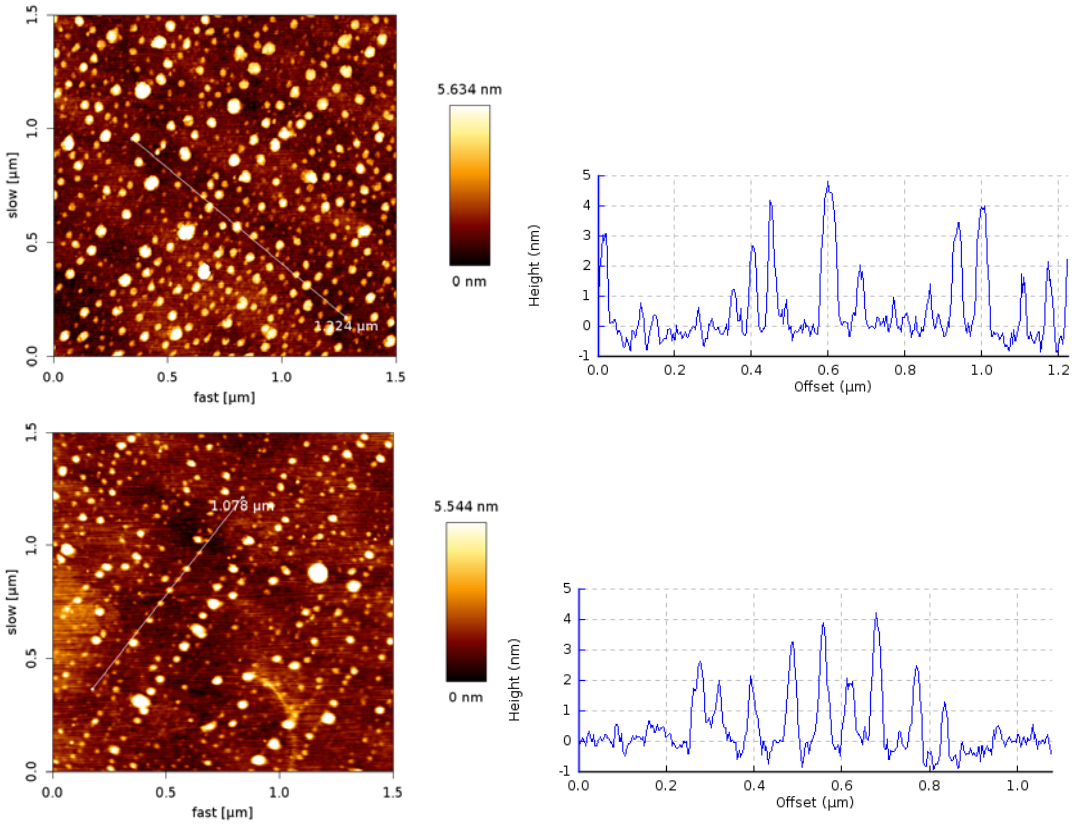

Figure S11. (left) AFM images of the Ag nanodisks (nanoparticles) produced from the thiolate **2c** thermolytic reaction at 210 °C for 1 h, and (right) the height profiles along the line labeled in the left figure. The height is around 2 ~ 4 nm.

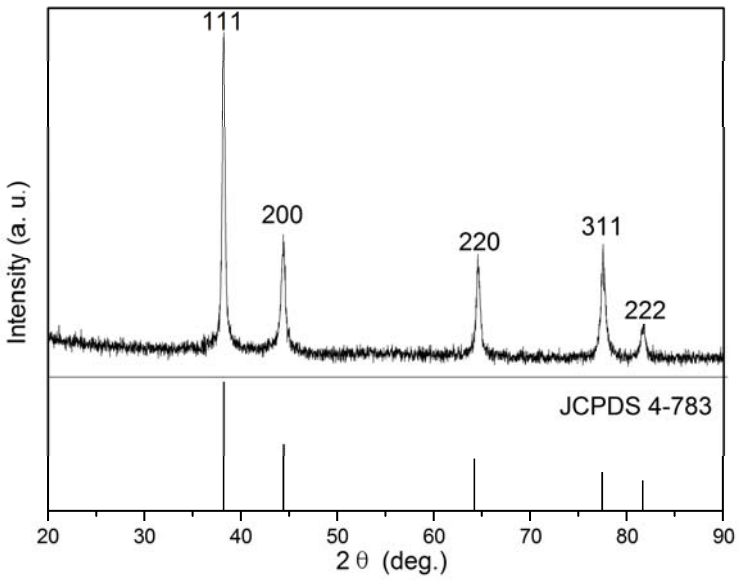

Figure S12. Comparison of XRD profile of Ag nanodisks produced from **2c** at 210 °C for 1 h with the Ag fcc cubic pattern of standard card #JCPDS 4-783.

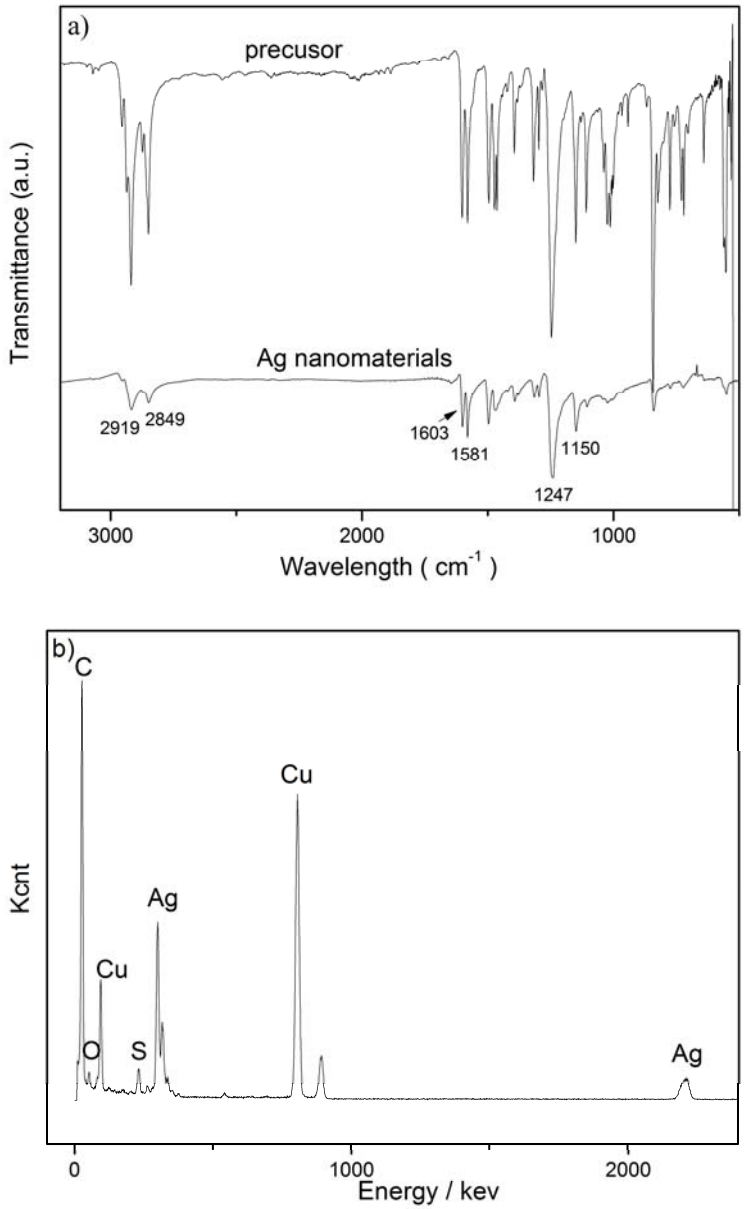

Figure S13. a) FTIR spectrum, and b) EDX profile of Ag nanodisks thermal reduced from **2c**, in the EDX profile, the signal of N was overlapped with the peak of C, and the strong peaks of Cu were from the substrate coppery grid.

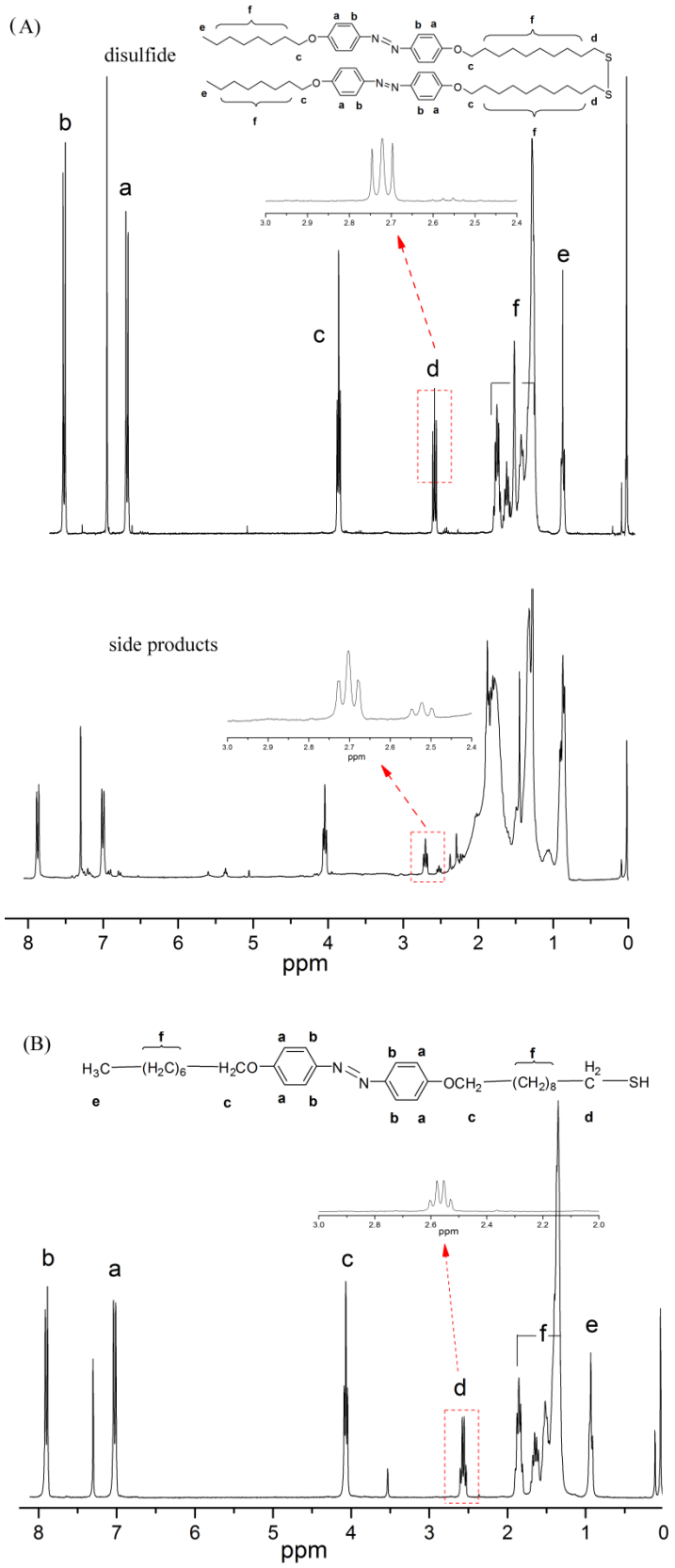

Figure S14. [1]H NMR spectra comparison of (A) disulfide and thermolytic reaction byproducts of the silver thiolates with azobenzene mesogen (taking **2c** as an example) showing double triplet peaks of alkyl sulfide and disulfide, [S4] and not the comparative quartet peaks characteristic of thiol ligand (B).

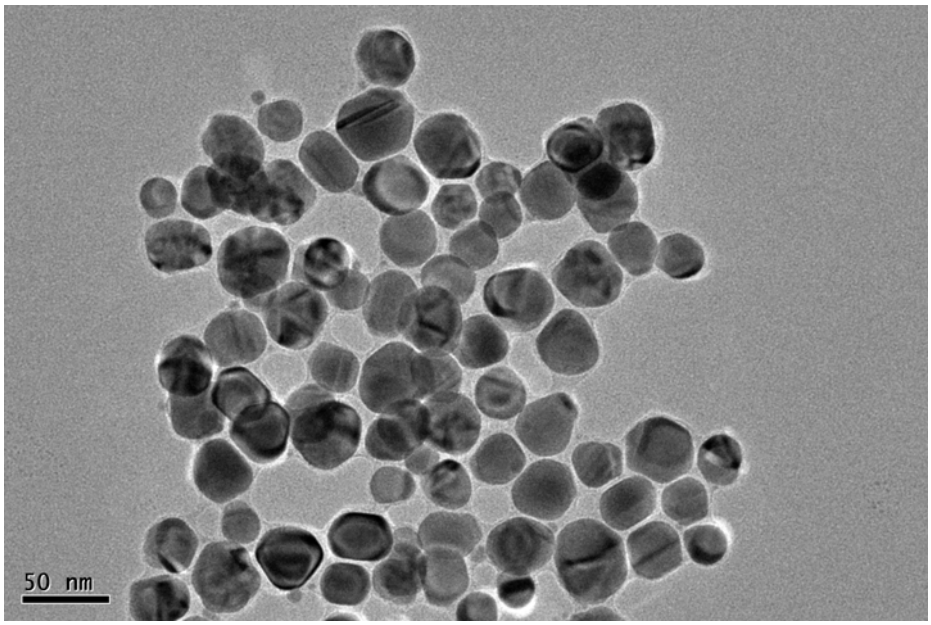

Figure S15. Typical TEM images of thermolytic products from **2a** annealing at 210 °C for 1 h.

Supplementary references

[S1] (a) Z. H. Shi, H. J. Lu, Z. C. Chen, R. S. Cheng and D. Z. Chen, *Polymer*, 2012, **53**, 359-369; (b) Z. H. Shi, D. Z. Chen, H. J. Lu, B. Wu, J. Ma, R. S. Cheng, J. L. Fang and X. F. Chen, *Soft Matter*, 2012, **8**, 6174-6184.

[S2] (a) O. Glatter and O. Kratky Eds., *Small Angle X-ray Scattering*, Academic Press Inc., London, 1982; (b) S. Kumar, *Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions*, Cambridge University Press, London, 2001.

[S3] (a) I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003; (b) G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals-Textures and Structures*, Leonard Hill, London, 1984.

[S4] S. H. Cha, K. H. Kim, J. U. Kim, W. K. Lee and J. C. Lee, *J. Phys. Chem. C.*, 2008, **112**, 13862-13868.