

Supporting Information

Silver thiolate coordination polymers with reversibly switchable visible-to-near infrared transitions

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Experimental section

Chemicals:

All reagents were purchased and used without further purification. Silver nitrate (Sigma-Aldrich, BioXtra, >99%), 3-mercaptopropionic acid (Aldrich, ≥99%), ethylene glycol (Acros organics, 99.5%, for analysis), 1,3-propanediol (VWR, for synthesis), 1,4-butanediol (Merk KGaA, for synthesis), 1,5-pentanediol (Merk KGaA, for synthesis) and 1,6-hexandiol (Alfa aesar, 97%), glycerol (Alfa Aesar, 99+%), acetone (Fisher Chemical, ≥99.8%), 3-mercapto-1-propanol (Aldrich Chem. Co., 95%), methyl 3-mercaptopropionate (Acros organics, 98%), 1-hexanethiol (Aldrich, 95%), 12-mercaptododecanoic acid (Aldrich, 96%), Polyglycerol polyricinoleate (Danisco, Grindsted PGPR 90 kosher), toluene (Fisher, ≥99.8%), indocyanine green (ICG, Roth, p.a.).

Methods:

Synthesis of Ag-MPA(UV): The Ag-MPA coordination polymer was prepared modifying the procedure published by Jiang et al.¹ and Kubie et al.² Briefly, 0.022 g of AgNO₃ (0.125 mmol) and 25 mL of ethylene glycol were added into a 100 mL 3-neck-flask. The mixture was degassed under vacuum while stirring at 50°C for 30 min in order to remove water and oxygen dissolved in ethylene glycol. After stopping the vacuum and putting the flask to argon, 22 μL of 3-mercaptopropionic acid (0.25 mmol) was injected into the flask and the temperature was set to 130°C. The colorless solution changed to cloudy white immediately, then started to change to orange gradually when reaching around 130°C. The reaction was allowed to proceed for 10 min at 130°C. Afterwards, the mixture was cooled to room temperature using a water bath to obtain orange sample Ag-MPA(UV). The subsequent purification steps were described in the purification section below.

Synthesis of Ag-MPA(NIR): In order to obtain stable Ag-MPA(NIR) coordination polymers with the near infrared photoluminescence, the synthesized orange Ag-MPA(UV) sample was kept at 130°C. Between the 10 to 25 min, the orange solution changed to brown gradually, if Ag-MPA solution was cooled down to room temperature during this period of time, it would come back to orange state. When keep heating for longer time, Ag-MPA solution can stay at the brown state with NIR photoluminescence. Then the solution was cooled to room temperature using a water bath. The subsequent purification steps were described in the purification section below.

Synthesis of Ag-thiolates from various solvents: The synthesis methods of the reaction in different solvents were similar to the method above. Ethylene glycol was replaced by either 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexandiol or glycerol, and the final heating temperature were set to 140°C, 150°C, 155°C, 155°C, and 130°C, respectively. The reaction proceeded at the final temperature for ~30 min. Then the heating mantle was removed and the mixture was cooled to room temperature with a water bath.

Synthesis of Ag-thiolates with various ligands: The synthesis methods of the reactions with different thiol ligands were similar to the method above. 0.022 g of AgNO₃ (0.125 mmol) and 25 mL of ethylene glycol were added into a 100 mL 3-neck-flask. After the mixture was degassed and the flask was put to argon and 0.25 mmol of different thiol ligand was injected. For 3-mercapto-1-propanol, methyl 3-mercaptopropionate, 1-hexanethiol, and 12-mercaptododecanoic acid, the temperature was set to 160°C, 130°C, 175°C and 175°C respectively. The reaction proceeded for 30 min at the corresponding reaction temperature. The mixture was then cooled to room temperature using a water bath.

Purification: 30 mL of acetone was added to 5 mL of reaction solution in a 50 mL centrifuge tube. After shaking the centrifuge tube, larger fiber-like structure flocculated from the solvent. The mixture was centrifuged for 5 min at 7000 rpm, the clear supernatant was discarded and

the precipitated was washed with acetone at least two more times. Then the precipitate was dried in a vacuum oven at 50°C for 8 h.

When needed for analysis, the purified powder was dissolved in Milli Q water to obtain a clear aqueous solution.

Preparation of Ag-MPA toluene emulsion: 0.5 g of Polyglycerol polyricinoleate (PGPR) was mixed with 30 ml toluene, then mixed with 7 mL of Ag-MPA aqueous solution (~0.1 wt%) under stirring. Then the mixture was pre-emulsified for 2 min with an Ultra-Turrax at 15000 rpm. Finally, the pre-emulsified mixture was passed through a microfluidizer (LM, Microfluidic corp) equipped with a F20Y interaction chamber with channels of 75µm at a pressure of 10000 PSI for two cycles.

Characterization:

Transmission Electron Microscopy. TEM samples were prepared by drop-casting the aqueous solution onto a carbon coated copper grid. Routine TEM imaging was done using JEOL1400 TEM with an acceleration voltage of 120 kV.

X-ray Diffraction. Purified powder was used to perform XRD. Powder XRD patterns were collected on a Rigaku SmartLab Diffractometer, operated with a Cu K α radiation source (1.540593Å) with increment steps of 0.01° and at 0.3°/min.

Absorption measurements. 200 µL original solution was dispersed in 3 mL ethylene glycol to measure the absorption spectra. The absorption spectra were conducted on an Agilent Cary 60 Spectrophotometer.

Photoluminescence Measurements. 200 µL original solution was dispersed in 3 mL ethylene glycol to measure the photoluminescence spectra. Photoluminescence spectra were recorded using J&M TIDAS, Diodenarray Spectrometer with an XBO-lamp as excitation source.

Differential Scanning Calorimetry. Purified powder was used to perform DSC on a Mettler Toledo DSC823 under N₂ flow cycling from room temperature to 150°C and back at a heating/cooling rates of 5 °C/min.

X-ray photoelectron spectroscopy. A purified aqueous solution was drop cast on a silicon wafer to perform XPS measurement on an Axis Ultra DLD by Kratos Analytical spectrometer. XPS data were collected with the anode at 10 mA and 15 kV; the analyzer was kept in hybrid mode and the resolutions was 80eV pass energy for the survey scans and 20eV pass energy for the high resolution scans. The binding energy (BE) scale was referenced to the value of 284.8 eV for the C 1s peak.

Atomic Force Microscopy. AFM samples were prepared by drop-casting the water solution onto a silicon wafer on a heating plate set to 90°C. AFM was performed on a Dimension Icon FS AFM in tapping mode with a scan rate of 0.595 Hz.

Solid state NMR. Solid state NMR measurements have been performed at 700.25 MHz ¹H Larmor frequency and 25 kHz magic angle spinning (MAS) frequency with a Bruker Avance III console using a commercial double resonance probe supporting zirconia rotors with 2.5 mm outer diameter. The radio frequency (rf) power for signal excitation and decoupling has been adjusted on both frequency channels, ¹H and ¹³C, to a nutation frequency of 100 kHz corresponding to a duration of 90° excitation pulses of 2.5 µs. The ¹³C CP-MAS NMR measurement have been performed with 10% amplitude variation on the ¹H channel and 1-3 ms CP contact time using the swf-TPPM decoupling scheme for high power ¹H decoupling

during acquisition.³ All NMR experiments have been performed under ambient conditions, corresponding to a sample temperature 45°C under the fast MAS conditions which has been determine based on the temperature dependent chemical shift of lead nitrate in separate experiments for temperature calibration.^{4,5}

Supporting Data:

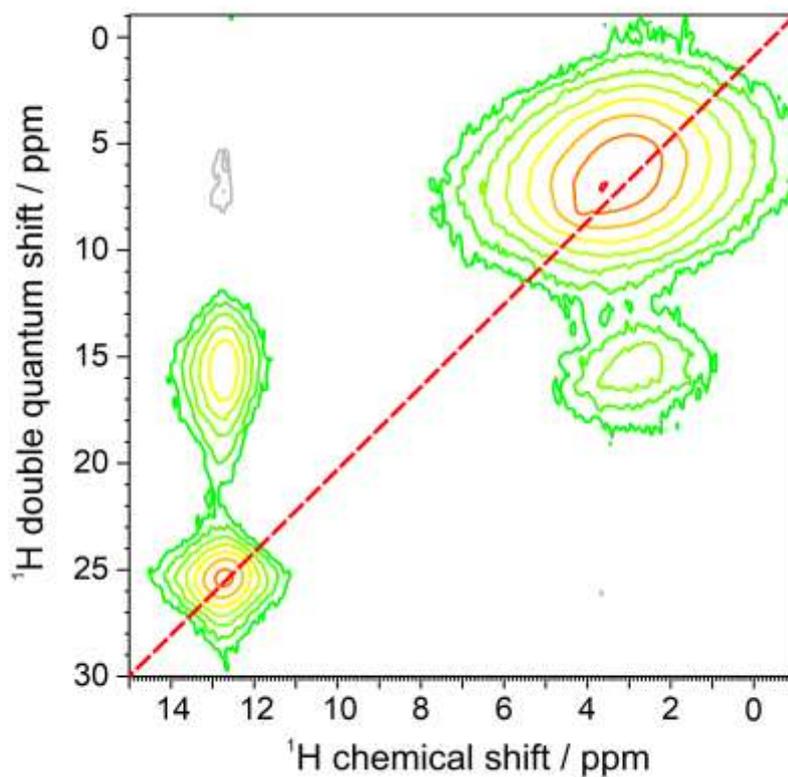


Fig. S1. 2D ^1H double quantum correlation NMR spectrum of the stage I aliquot, recorded at 700 MHz ^1H Larmor frequency and 25 kHz MAS using one rotor period of xy16-BABA for double quantum excitation and reconversion.⁶ The intense correlation signal at 12.8 ppm ^1H chemical shift and 25.6 ppm ^1H DQ shift observed with only 40 μs DQ excitation is a direct proof for the formation of stable acid dimers in the aliquot stage I.

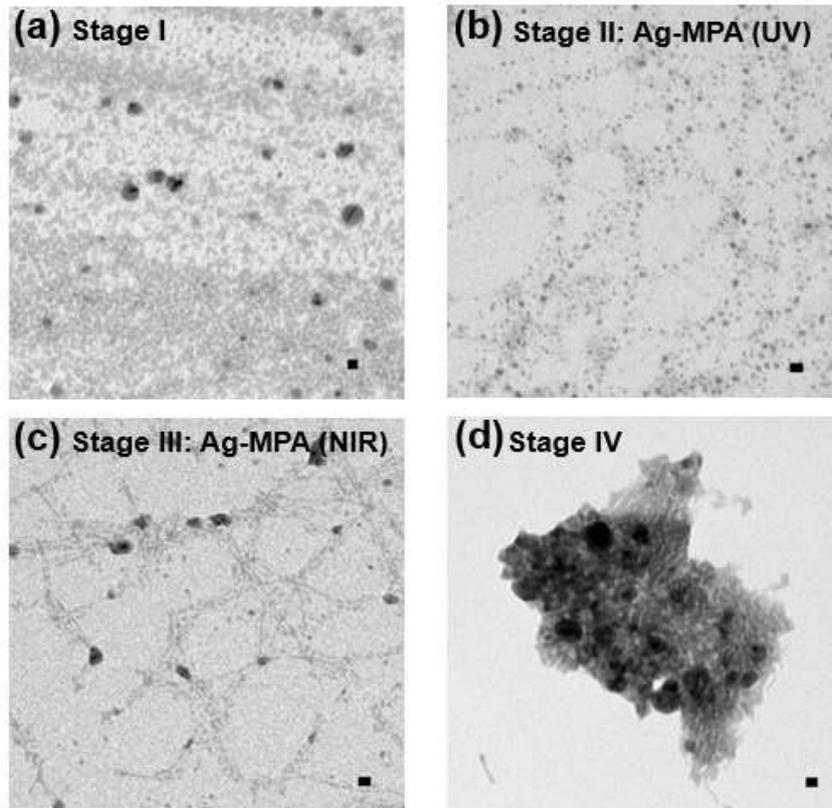


Fig. S2. TEM micrographs of Ag-MPA samples at the four stages. Scale bars are 10 nm.

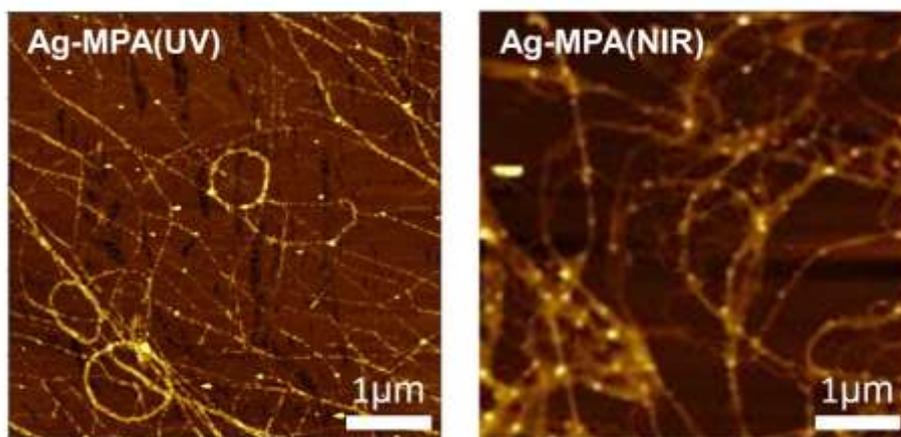


Fig. S3. AFM images for Ag-MPA(UV) and Ag-MPA(NIR)

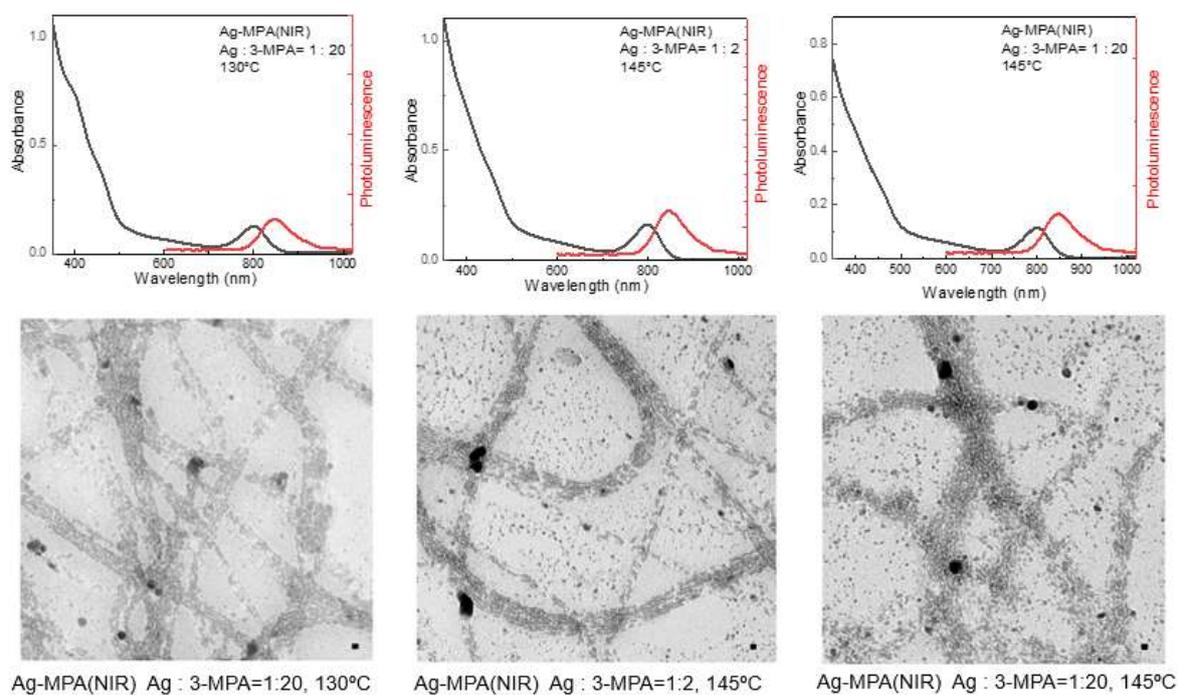


Fig. S4. Absorption spectra, photoluminescence spectra and TEM micrographs for Ag-MPA(NIR) synthesized at different temperature with different concentrations. Scale bars are 10 nm.

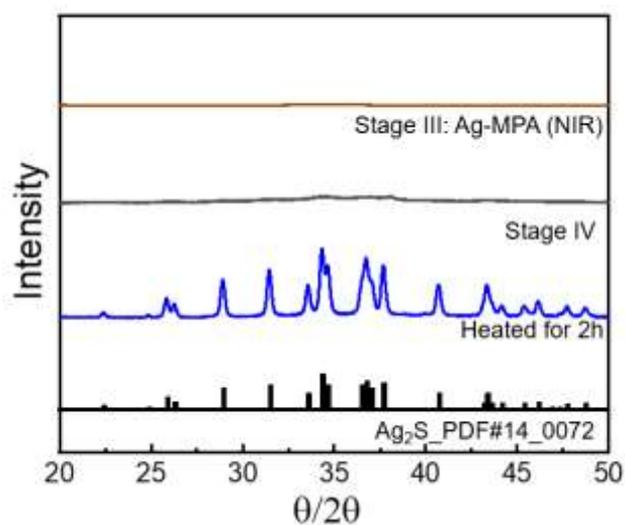


Fig. S5. PXRD patterns of samples Ag-MPA(NIR), Stage IV, 2h heated sample and Ag₂S_PDF#14_0072

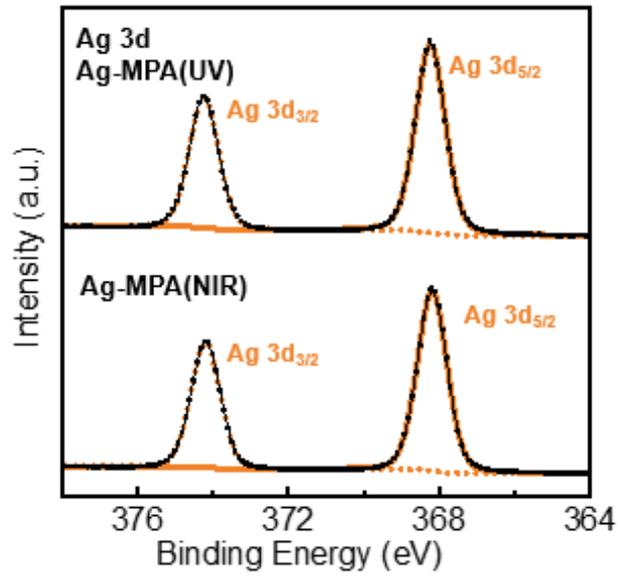


Fig. S6. High-resolution XP-spectra of Ag-MPA (UV) and Ag-MPA (NIR), Ag 3d, solid lines represent the signals stemming from Ag 3d_{5/2}, dash lines represent the signals stemming from Ag 3d_{3/2}.

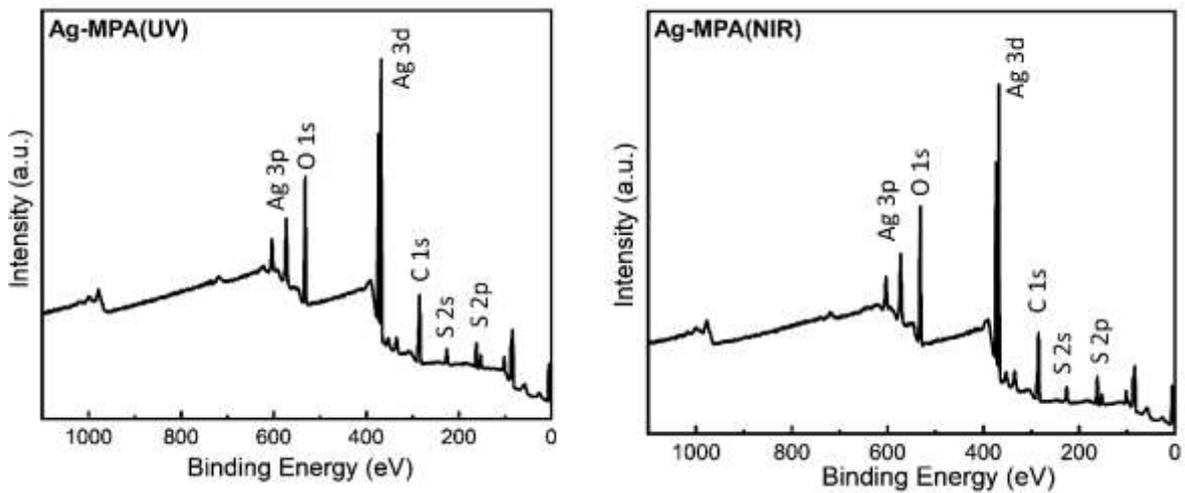


Fig. S7. Overall XPS survey spectra for Ag-MPA(UV) and Ag-MPA(NIR)

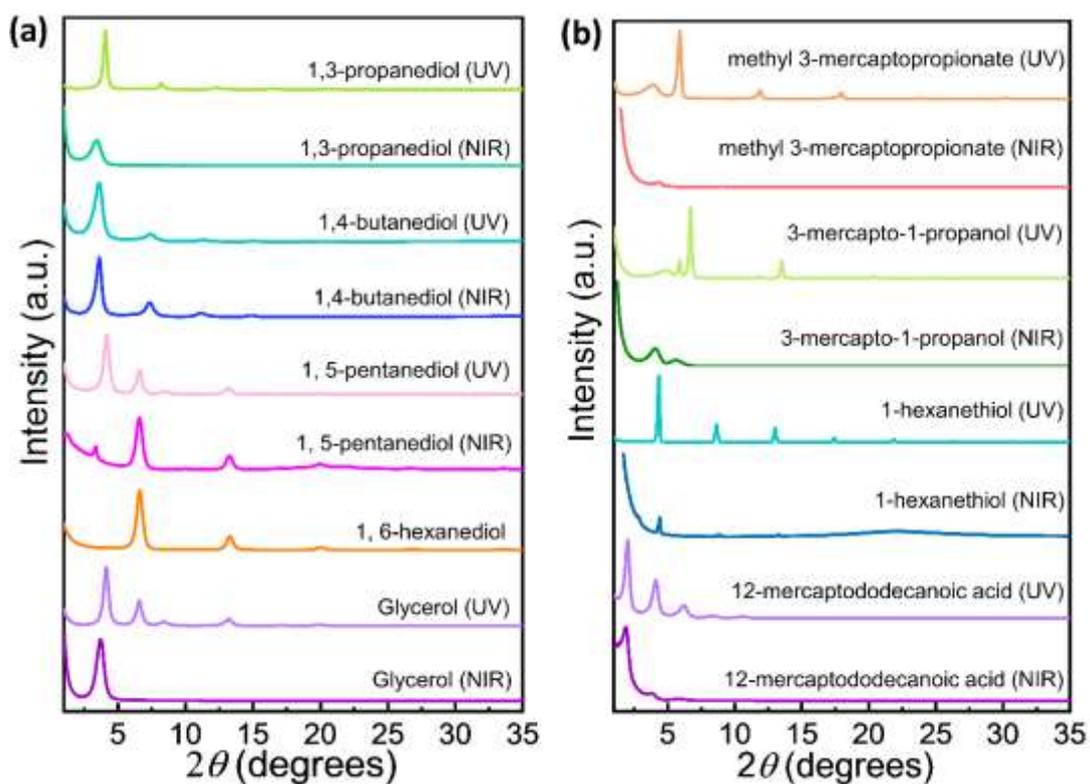


Fig. S8. PXRD of (a) silver thiolates synthesized with different thiol ligands in ethylene glycol and (b) Ag-MPA synthesized in different solvent.

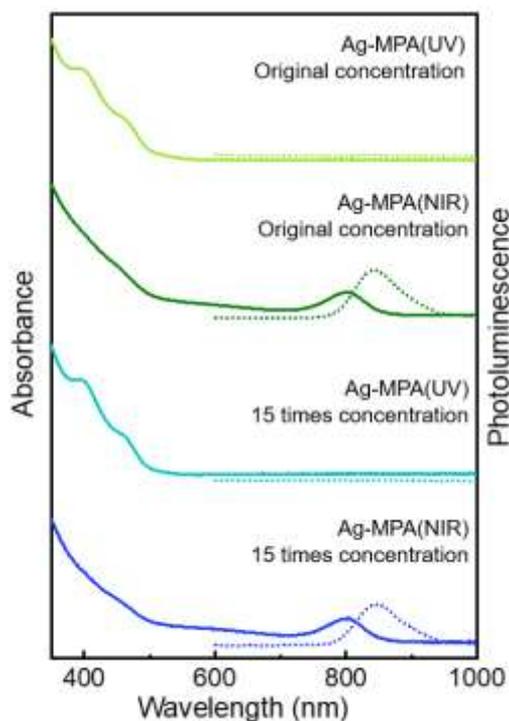


Fig. S9. Absorption spectra (solid lines) and photoluminescence spectra (dash lines) for Ag-MPA synthesized at different precursor concentrations. See method section for details.

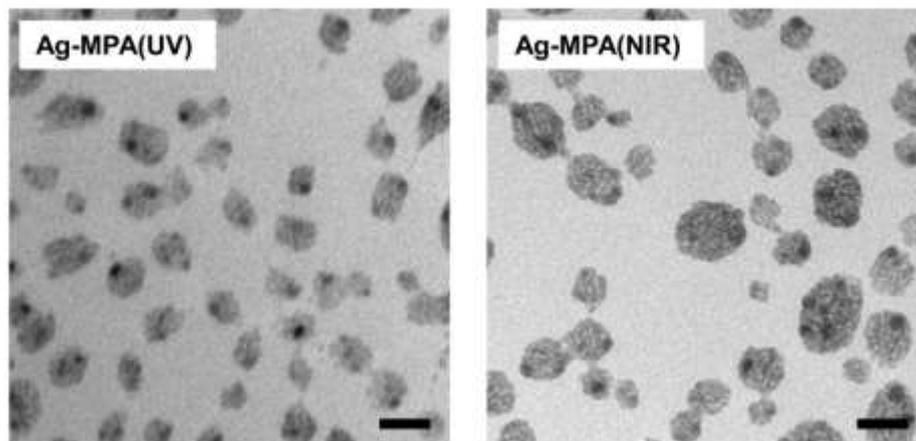


Fig. S10. TEM images of Ag-MPA(UV) and Ag-MPA(NIR) toluene emulsion. Scar bar: 50nm.

Table S1. The quantum yield(QY) of Ag thiolate with different ligands.

	Slope	Solvent	η_{solvent} (the refractive index of solvent)	QY (%)
ICG	294213	DMSO	1.479	10.6
Ag-MPA(NIR)	159596	Ethylene glycol	1.431	5.38
Ag-3-mercapto-1-propanol	158837	Ethylene glycol	1.431	5.35
Ag-methyl 3- mercaptopropionate	73385	Ethylene glycol	1.431	2.47
Ag-12- mercaptododecanoic acid	30370	Ethylene glycol	1.431	1.02
Ag-1-hexanethiol	15633	Ethylene glycol	1.431	0.53

Calculation of QYs of Ag-MPA(NIR) based on ICG and Equation S1.

$$QY_{\text{sample}} = QY_{\text{standard}} \left(\frac{\text{Slope}_{\text{sample}}}{\text{Slope}_{\text{standard}}} \right) \left(\frac{\eta_{\text{sample}}}{\eta_{\text{standard}}} \right)^2 \quad \text{S1}$$

The slope is calculated from the linear fit of integrated absorption against integrated photoluminescence of silver thiolate and ICG reference. Integrated absorption was measured between 655-665 nm, based on the excitation wavelength of 660 nm.

Reference:

1. P. Jiang, C. N. Zhu, Z. L. Zhang, Z. Q. Tian and D. W. Pang, *Biomaterials*, 2012, **33**, 5130-5135.
2. L. Kubie, L. A. King, M. E. Kern, J. R. Murphy, S. Kattel, Q. Yang, J. T. Stecher, W. D. Rice and B. A. Parkinson, *ACS Nano*, 2017, **11**, 8471-8477.
3. C. Vinod Chandran, P. Madhu, N. D. Kurur and T. Bräuniger, *Magn. Reson. Chem.*, 2008, **46**, 943-947.
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