Electronic Supplementary Information

Synthesis of silica-stabilized silver clusters aided by the designed mercaptosilane ligand

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1. Experimental section

1.1 Chemicals

All chemicals were purchased from commercial sources and were directly used as received. 1,2-dibromoethane [$C_2H_4Br_2$, 99%], *o*-sulfobenzimide [saccharine, 99%], chlorotrimethylsilane [TMSCl, 98%], 1,1,1,3,3,3-hexamethyldisilazane [HMDS, 96%] and 4-(trifluoromethyl)benzenethiol [$HSPhCF_3$, 98%] were purchased from TCI, 4-bromothiophenol [HSPhBr, 98%] and cesium hydroxide solution [CsOH in water, 50 wt %] were purchased from Innochem, sodium borohydride [$NaBH_4$, 98%] was purchased from Aladdin, tetrahydrofuran [THF, 99.5%], 4-mercaptobenzoic acid [HSPhCOOH, 90%] and polyoxyethylene(4)lauryl ether [Brij®30, 99%] were purchased from Acros, magnesium turnings [Mg, 99.9%], tetraethyl orthosilicate [TEOS, A.R.], silver nitrate [$AgNO_3$, 99.9%], triethylamine [TEA, 99%], tetraphenylphosphonium bromide [PPh_4Br, 99%] and all solvents in analytical purity were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai).

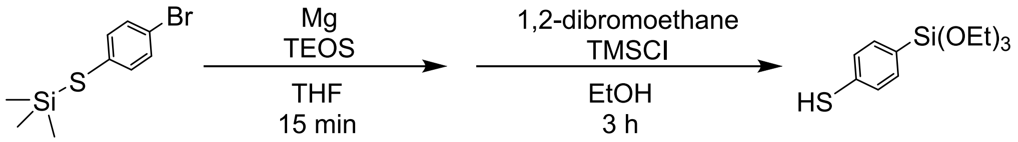
1.2 Apparatus

The UV-vis absorption spectra were recorded on a Lambda365 spectrometer of PerkinElmer. The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were conducted on a HT7700 transmission electron microscope of Hitachi with an acceleration voltage of 120 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Elemental mapping analysis were conducted on a Tecnai G2 F20 S-Twin transmission electron microscope of FEI with an acceleration voltage of 200 kV. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) were conducted on an *i*CAP7000 spectrometer of Thermo Fisher Scientific. The fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 of Thermo Fisher Scientific. The thermogravimetric analysis (TGA) were conducted on a SDT Q600 of TA Instruments. The proton nuclear magnetic resonance (^1H NMR) spectra were recorded on an AVANCE III HD of Bruker. The photoacoustic (PA) imaging were recorded on a Vevo LAZR of Fujifilm Visualsonics. The dynamic light scattering (DLS) were collected by Malvern Nanosizer. The photoluminescence (PL) spectra were recorded on a Cary Eclpse Fluorescence Spectrophotometer of Agilent. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an Axis Ultra DLD XPS of Kratos.

1.3.1 Synthesis of ((4-bromophenyl)thio)trimethylsilane

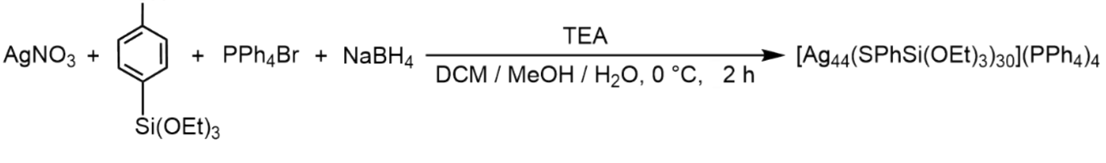
The silicon-containing mercaptan ligand and its precursor were successfully prepared according to the reported method.[1] A mixture of 4-bromothiophenol (5.0 g), saccharine (35.0 mg) and chloroform (50.0 mL) was heated to the reflux temperature in an oil bath under N_2, HMDS (6.3 mL) was added subsequently. The reaction was then refluxed for 3 h and naturally cooled to room temperature. After removing the solvent by rotary evaporation under vacuum, 6.48 g (94% yield) of ((4-bromophenyl)thio)trimethylsilane ($BrPhSSi(CH_3)_3$) as clear white crystals were obtained. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 0.27 (s, 9H) ppm. Known compound.[1]

1.3.2 Synthesis of 4-(triethoxysilyl)benzenethiol



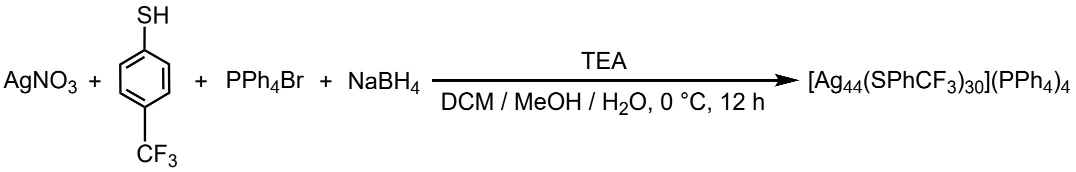
A mixture of Mg (1.0 g), TEOS (6.5 mL) and solvent THF (10.0 mL) were refluxed for 15 min under N_2 protection. Then, 1,2-dibromoethane (0.5 mL) and $BrPhSSi(CH_3)_3$ (3.5 g) which was freshly prepared were added into the mixture in sequence. After reacting 3 h and being cooled down to the room temperature, TMSCl (2.5 mL) were added. The solvent was removed under vacuum. Finally, about 10 mL ethanol (EtOH) was added and the mixture was filtered to remove residue under N_2. After removing the EtOH under vacuum, 2.9 g (79% yield) of light yellow crystalline 4-(triethoxysilyl)benzenethiol ($HSPhSi(OEt)_3$) were obtained. The impurities would be removed in the process of subsequent silver cluster synthesis. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 3.77 (m, 6H), 1.28 (t, J = 7.0 Hz, 9H) ppm. Known compound.[1]

1.3.3 Synthesis of Ag_{44}-$Si(OEt)_3$ nanoclusters



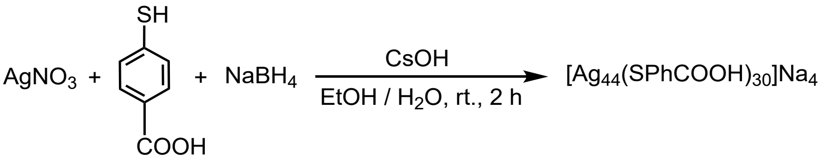
The oil-soluble $[Ag_{44}(SPhSi(OEt)_3)_{30}](PPh_4)_4$ (in short, Ag_{44}-$Si(OEt)_3$) was prepared according to the reported method with minor alteration.[2] Briefly, $AgNO_3$ (20.0 mg) was ultrasonic dissolved in methanol (MeOH, 1.0 mL). The newly compounded PPh_4Br dichloromethane (DCM) solution (1.0 mL, 12.0 mg·mL^{-1}) and the synthesized mercaptosilane ligand $HSPhSi(OEt)_3$ (200.0 mg) were added to the above solution in order. After stirring 20 min at 0 °C, TEA (50.0 μL) and $NaBH_4$ aqueous solution (1.0 mL, 45.0 mg·mL^{-1}) were added quickly. The reaction mixture was aging for 2 h at 0 °C and the color gradually changed from light yellow to purplish-red or even deeper. Then, the aqueous phase was removed and the organic phase was washed with water several times. Black powder was precipitated from DCM/hexane (about 1:20 by volume) and stored below -15 °C.

1.3.4 Synthesis of Ag_{44}-CF_3 nanoclusters



We successfully synthesized $[Ag_{44}(SPhCF_3)_{30}](PPh_4)_4$ (in short, Ag_{44}-CF_3), under the same conditions as **1.3.3** except that 10.0 μL 4-(trifluoromethyl)benzenethiol ($HSPhCF_3$) was used as the thiol ligand instead of 4-(triethoxysilyl)benzenethiol and the aging time extended to 14 h.

1.3.5 Synthesis of Ag_{44}-COOH nanoclusters



The water-soluble $[Ag_{44}(SPhCOOH)_{30}]Na_4$ (in short, Ag_{44}-COOH), was prepared according to the reported method.[3] Firstly, HSPhCOOH (154.0 mg) was dissolved into 12.0 mL ethanol and $AgNO_3$ aqueous solution (21.0 mL, 2.0 mg·mL^{-1}) was added subsequently. The pH of the solution was then raised to 12 by adding aqueous CsOH (50 wt %). After slowly dropwise adding $NaBH_4$ aqueous solution (9.0 mL, 1.1 mg·mL^{-1}), the reaction was incubated under room temperature (rt.) for 2 h. The raw product was firstly separated from the solution by centrifuging at 8000 rpm for 5 min and then precipitated with dimethyl formamide (DMF) to remove remaining soluble impurities from the reaction. The collected clusters were dissolved into DMF solution (containing 1 vol % acetic acid) for further use.

1.3.6 Synthesis of Ag_{44}-Si(OEt)$_3$@SiO$_2$

$$\text{TEOS} + \text{Ag}_{44}\text{-Si(OEt)}_3 \text{ NCs} \xrightarrow[\text{n-heptane / H}_2\text{O / DMF, rt., 24 h}]{\text{NH}_3\cdot\text{H}_2\text{O, Brij}^{\circledR}30} \text{Ag}_{44}\text{-Si(OEt)}_3\text{@SiO}_2$$

A reverse microemulsion method of coating silicon was used to synthesize the Ag_{44}-Si(OEt)$_3$@SiO$_2$ composite structure,[4] the specific operation is as follows. The mixture of oil phase n-heptane (9.4 mL) and surfactant Brij®30 (3.0 mL) was stirred rapidly for 15 min. Then H_2O (600.0 μL) and Ag_{44}-Si(OEt)$_3$ DMF solution (900.0 μL, 0.3 μmol·mL^{-1}) were dropwise added in order. After stirring for another 15 min, ammonia solution (150.0 μL) was added slowly and the mixture was stirred for 40 min. Finally, the silica precursor TEOS (20.0 μL) was added. After 24 h stirring, about 10 mL ethanol was used to destabilize the solution. The precipitation collected by centrifuging at 11000 rpm for 10 min was washed several times with ethanol and n-heptane alternately.

1.3.7 Synthesis of Ag_{44}-CF$_3$/SiO$_2$ or Ag_{44}-COOH/SiO$_2$

The Ag_{44}-CF$_3$ or Ag_{44}-COOH was used as a control and the preparation of Ag_{44}-CF$_3$/SiO$_2$ or Ag_{44}-COOH/SiO$_2$ followed the same procedures depicted above, except that Ag_{44}-Si(OEt)$_3$ DMF solution was replaced by Ag_{44}-CF$_3$ DMF solution (900.0 μL, 0.3 μmol·mL^{-1}) or Ag_{44}-COOH aqueous solution (900.0 μL, 0.3 μmol·mL^{-1}).

2. Characterizations

2.1 4-(triethoxysilyl)benzenethiol ligand

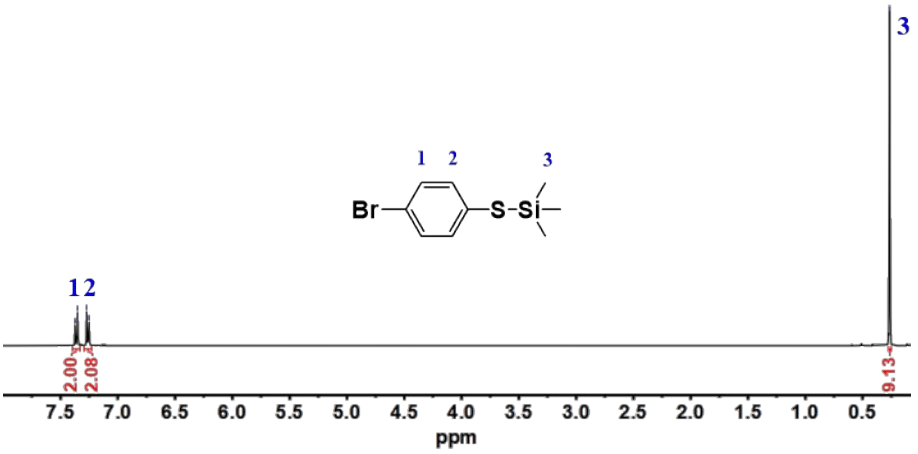


Fig. S1 ^{1}H-NMR spectrum of ((4-bromophenyl)thio)trimethylsilane in $CDCl_3$.

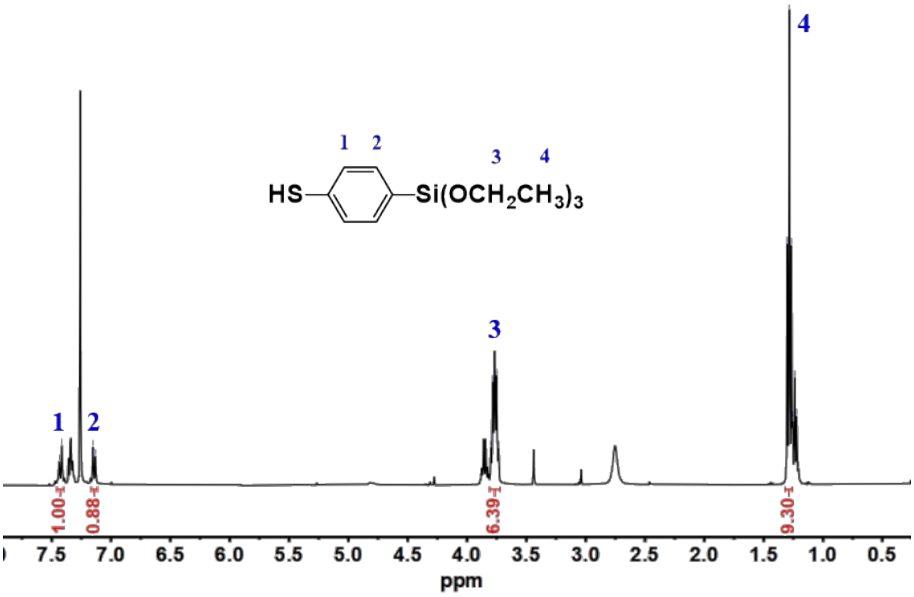


Fig. S2 ^{1}H-NMR spectrum of 4-(triethoxysilyl)benzenethiol in $CDCl_3$.

2.2 Ag_{44} nanoclusters

Table S1 The Ag/Si in Ag_{44}-Si(OEt)$_3$ NCs based on ICP-AES^a and theoretical value.

	ICP-AES	theoretical
Ag/Si	3.9	5.6

^{a}For the ICP-AES analysis, about 1 mg of Ag_{44}-Si(OEt)$_3$ was dissolved with 100 μL hydrofluoric acid (HF) plus 900 μL nitric acid (HNO_3) mixed solution and transferred to a 10 mL volumetric flask.

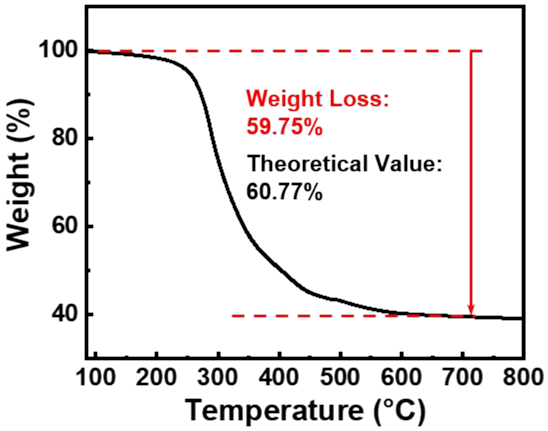


Fig. S3 TGA of Ag_{44}-Si(OEt)$_3$.

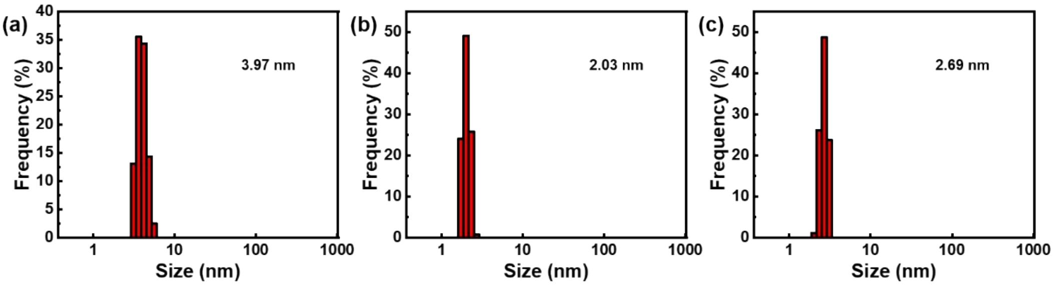


Fig. S4 DLS of **(a)** Ag_{44}-$Si(OEt)_3$ DMF solution, **(b)** Ag_{44}-CF_3 DMF solutions and **(c)** Ag_{44}-COOH DMF solution (containing 1 vol % acetic acid).

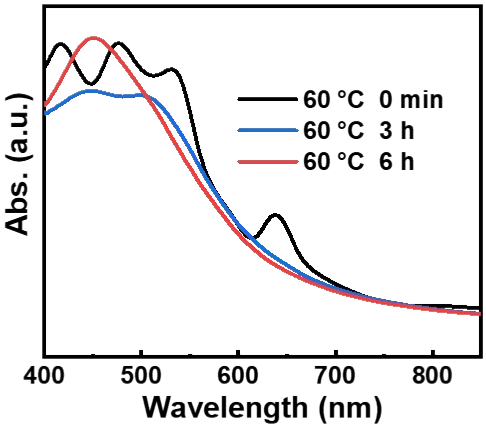


Fig. S5 UV-vis absorption spectra of Ag_{44}-CF_3 in DMF heated in air at 60 °°C for different time.

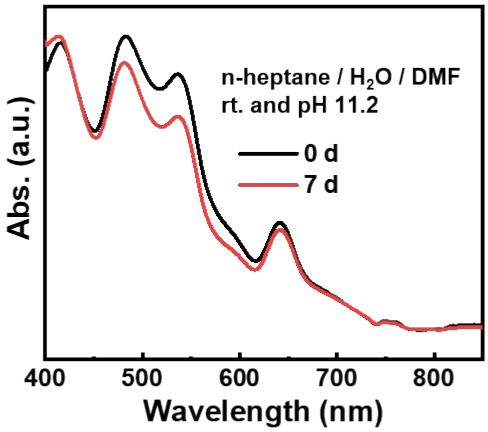


Fig. S6 UV-vis absorption spectra of Ag_{44}-$Si(OEt)_3$ dispersed in silica coating reaction solution (black line) and after 7 days (red line).

2.3 Ag_{44}-$Si(OEt)_3$@SiO_2 composite structure

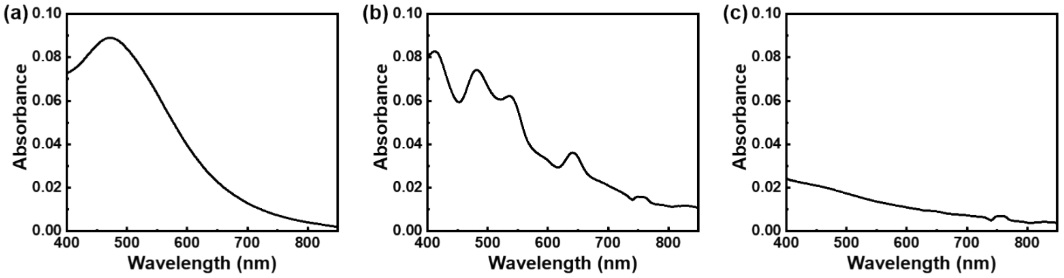


Fig. S7 UV-vis absorption spectra of reaction liquid centrifugal supernatant of the **(a)** Ag_{44}-COOH/SiO_2, **(b)** Ag_{44}-CF_3/SiO_2 and **(c)** Ag_{44}-$Si(OEt)_3$@SiO_2.

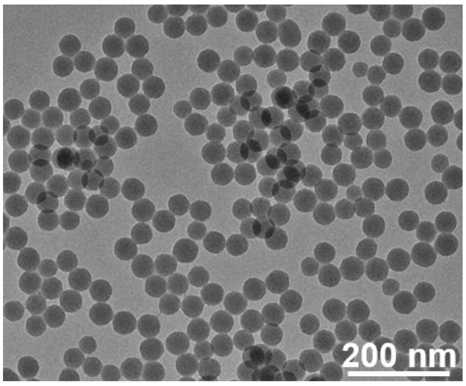


Fig. S8 TEM image of SiO_2.

Table S2 The Si/Ag in Ag_{44}-$Si(OEt)_3$@SiO_2 based on ICP-AES[a] and XPS analysis.

	ICP-AES	XPS
Si/Ag	13.9	15.9

[a]For the ICP-AES analysis, about 1 mg of Ag_{44}-$Si(OEt)_3$@SiO_2 was dissolved with 100 μL hydrofluoric acid (HF) plus 900 μL nitric acid (HNO_3) mixed solution and transferred to a 10 mL volumetric flask.

Because the size of Ag_{44}-$Si(OEt)_3$ was relatively small and the proportion of Si mass was only 6%, the number of Ag_{44}-$Si(OEt)_3$ nanoclusters in the Ag_{44}-$Si(OEt)_3$@SiO_2 composite structure (about 22.4 nm radius) was calculated as follows:

$r_{Si/Ag}$: the mass ratio of Si to Ag tested by ICP-AES;

R: the radius of Ag_{44}-$Si(OEt)_3$@SiO_2;

N_A: the Avogadro constant;

m: the mass, ***n***: the molar mass, ***M***: the relative atom or molecular mass (the corner mark stands for the corresponding atoms or molecules).

$$\mathrm{m}_{\mathrm{Ag}} = \frac{m_{\mathrm{Si}}}{r_{\mathrm{Si/Ag}}} = \frac{n_{\mathrm{SiO_2}} \cdot M_{\mathrm{Si}}}{r_{\mathrm{Si/Ag}}} = \frac{\frac{\rho_{\mathrm{SiO_2}} \cdot \frac{4}{3}\pi R^3}{M_{\mathrm{SiO_2}}} \cdot M_{\mathrm{Si}}}{r_{\mathrm{Si/Ag}}} = \frac{\frac{2.31g \cdot cm^{-3} \times \frac{4}{3}\pi \times 22.4^3\ nm^3}{60.08g \cdot mol^{-1}} \times 28.09g \cdot mol^{-1}}{13.9} = 3.658 \times 10^{-18}g$$

$$N_{\mathrm{Ag_{44}-Si(OEt)_3}} = n_{\mathrm{Ag_{44}-Si(OEt)_3}} \cdot N_A = \frac{n_{\mathrm{Ag}}}{44} \cdot N_A = \frac{m_{\mathrm{Ag}}}{M_{\mathrm{Ag}} \cdot 44} \cdot N_A = \frac{3.658 \times 10^{-18}g}{107.87g \cdot mol^{-1} \times 44} \times 6.02 \times 10^{23} mol = 464$$

2.4 The contrast experiments

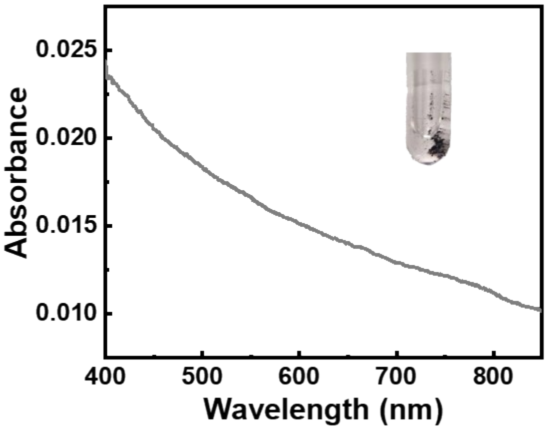


Fig. S9 UV-vis absorption spectra of Ag_{44}-$Si(OEt)_3@SiO_2$ ultrasonically dispersed in DCM (inset: the photos of the solution).

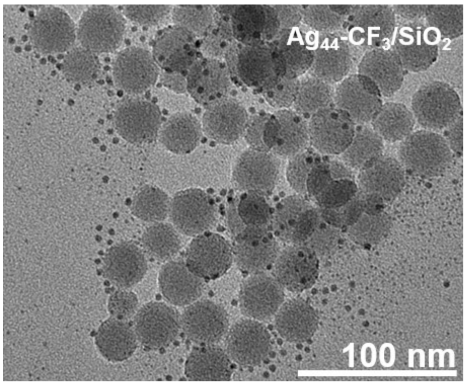


Fig. S10 TEM image of Ag_{44}-CF_3/SiO_2.

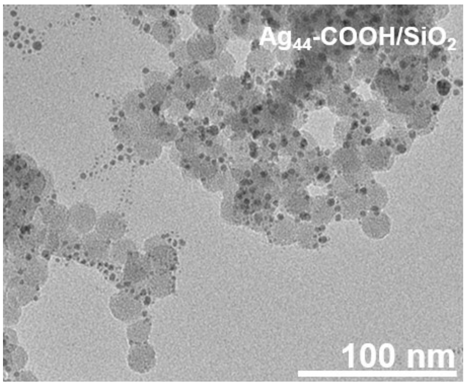


Fig. S11 TEM image of Ag_{44}-COOH/SiO_2.

2.5 The application exploration

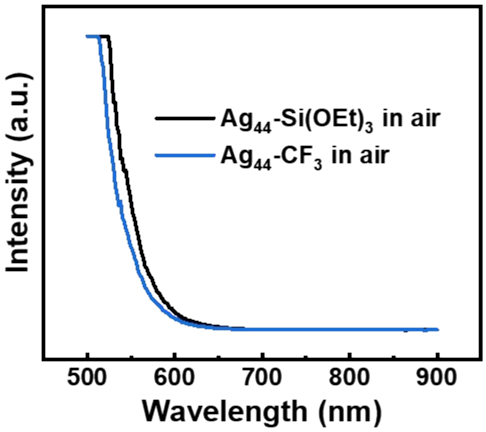


Fig. S12 PL spectra of Ag_{44}-Si(OEt)$_3$ (black line) and Ag_{44}-CF_3 (blue line) excited by 480 nm emission in air.

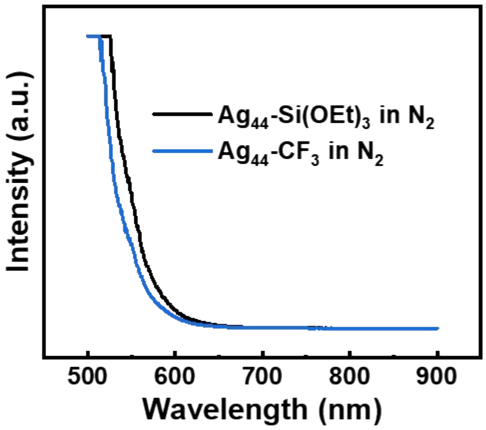


Fig. S13 PL spectra of Ag_{44}-Si(OEt)$_3$ (black line) and Ag_{44}-CF_3 (blue line) excited by 480 nm emission in N_2.

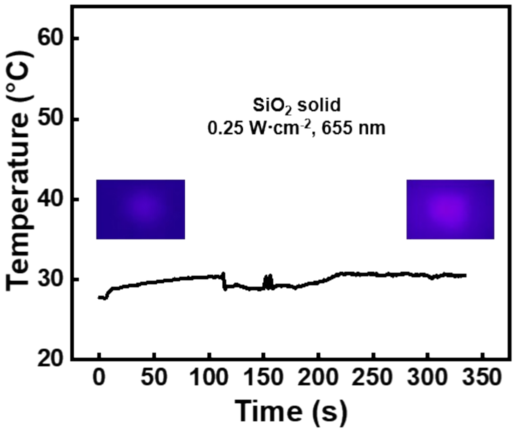


Fig. S14 PT heating curve of SiO_2 solid under laser irradiation (0.25 W·cm^{-2}, 655 nm) with images before and after irradiation (inset).

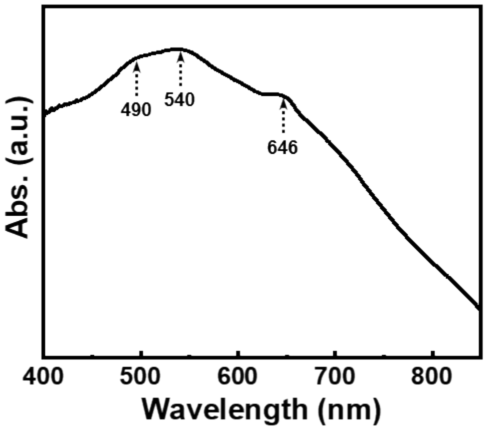


Fig. S15 UV-vis absorption spectra of Ag_{44}-$Si(OEt)_3$@SiO_2 solid after laser irradiation.

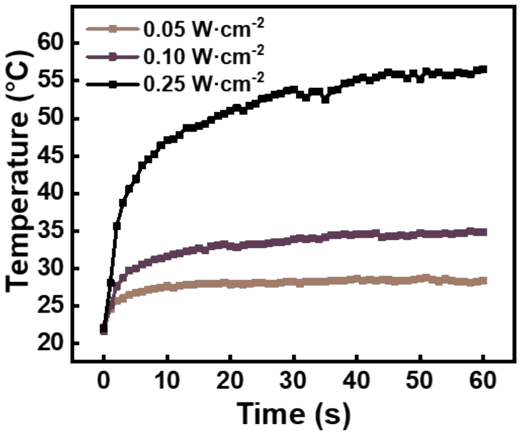


Fig. S16 PT heating curve of Ag_{44}-$Si(OEt)_3$@SiO_2 solid with different power densities (0.05, 0.10, 0.25 W·cm^{-2}, 655 nm).

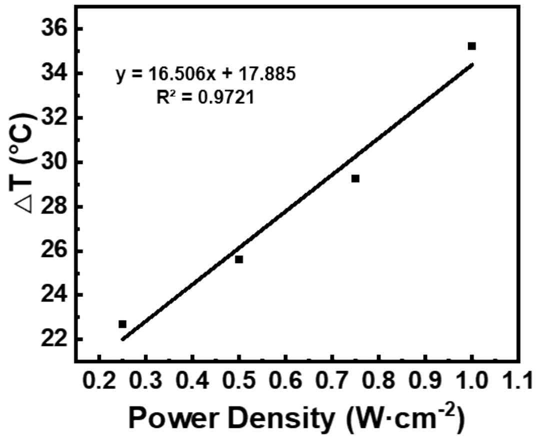


Fig. S17 Fitting curve of PT heating final temperature of 2 mg·mL^{-1} Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ in 1 vol % DMF aqueous solution with different power densities (0.25, 0.50, 0.75, 1.00 W·cm^{-2}, 655 nm).

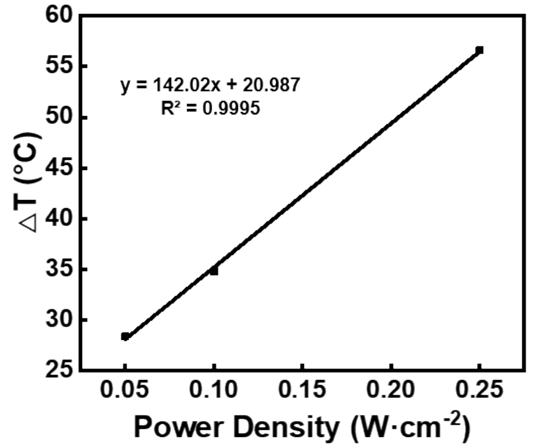


Fig. S18 Fitting curve of PT heating final temperature of Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ solid with different power densities (0.05, 0.10, 0.25 W·cm^{-2}, 655 nm).

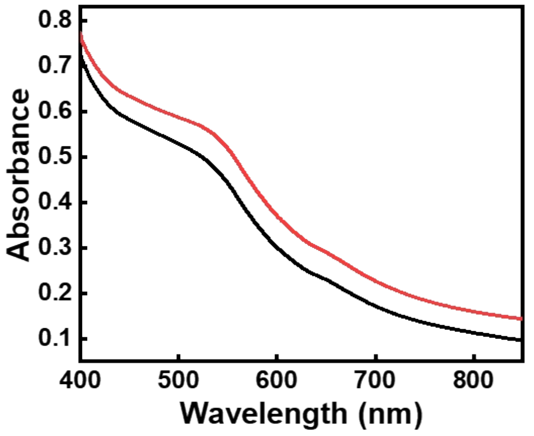


Fig. S19 UV-vis absorption spectra of 2 mg·mL^{-1} Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ in 1 vol % DMF aqueous solution before (black line) and after (red line) the ON/OFF irradiation (1.00 W·cm^{-2}, 655 nm) cycles repeated four times.

3. References

[1] Renom-Carrasco, P. Mania, R. Sayah, L. Veyre, G. Occhipinti, D. Gajan, A. Lesage, V. R. Jensen and C. Thieuleux, *Dalton Trans.*, 2019, **48**, 2886-2890.

[2] H. Yang, Y. Wang, H. Huang, L. Gell, L. Lehtovaara, S. Malola, H. Hakkinen and N. Zheng, *Nat. Commun.*, 2013, **4**, 2422-2429.

[3] A. Desireddy, B. E. Conn, J. Guo, B. Yoon, R. N. Barnett, B. M. Monahan, K. Kirschbaum, W. P. Griffith, R. L. Whetten, U. Landman and T. P. Bigioni, *Nature*, 2013, **501**, 399-402.

[4] X. Zheng, H. Zhang, Z. Wang, P. Liu, M. Du, Y. Han, R. Wei, Z. Ouyang, X. Kong, G. Zhuang, L. Long and L. Zheng, *Angew. Chem. Int. Ed.*, 2017, **56**, 11475-11479.