Supporting information for

Stabilisation coordination polymer amorphous nanoparticles in a covalent organic framework

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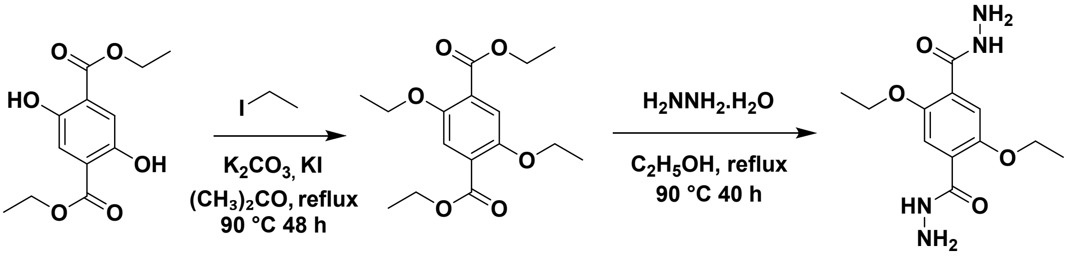
1. Experimental section

1.1. Materials

All chemicals were reagent grade and used without further purification. Diethyl 2,5-dihydroxy-terephthalate, iodoethane, hydrazine hydrate, 1,4-dioxane, and mesitylene were purchased from Sigma Aldrich. 1,3,5-Triformylbenzene and silver trifluoromethanesulfonate were purchased from Tokyo Chemical Industry Co., Ltd. Adiponitrile was purchased from Alfa Aesar. Potassium carbonate and potassium iodide were purchased from Wako pure chemical industries, Ltd. The reactions were conducted at ambient laboratory conditions unless otherwise specified.

1.2 Synthesis

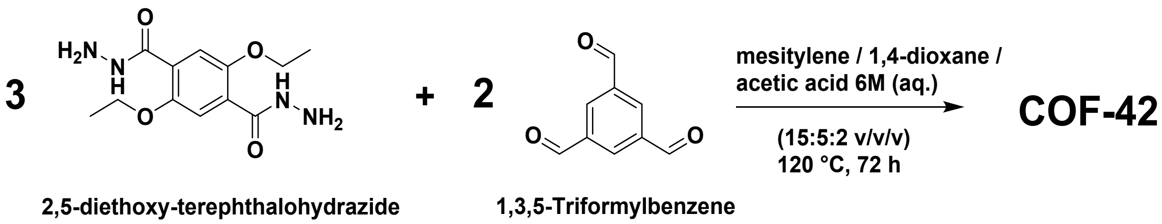
Synthesis of 2,5-diethoxy-terephthalohydrazide



Diethyl 2,5-dihydroxy-terephthalate **Diethyl 2,5-diethoxyterephthalate** **2,5-diethoxy-terephthalohydrazide**

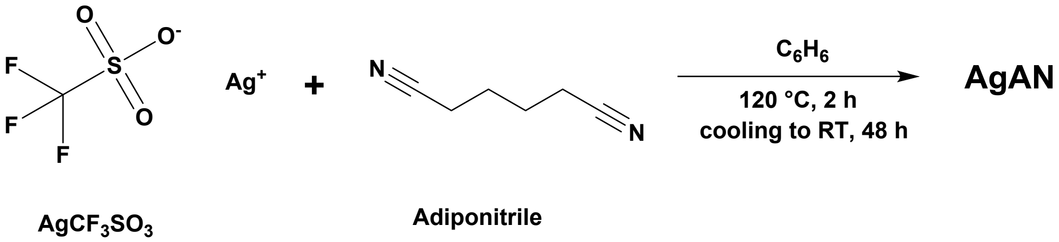
The compound 2,5-diethoxy-terephthalohydrazide was synthesised following the previous report.[1] Diethyl 2,5-dihydroxy-terephthalate (1.97 mmol, 0.5 g, 1 eq), potassium carbonate (2 g), and potassium iodide (40 mg) were suspended in 40 mL of acetone. Iodoethane (0.535 mL, 3.3 eq) was added to this mixture. The mixture was heated under reflux with continuous stirring for 48 h. Afterwards, the reaction mixture was hot-filtered, and the solid residue was washed with hot acetone, yielding a yellow solution. The solvent was evaporated under reduced pressure using a rotary evaporator, leaving behind a brownish residue. This residue was suspended in water and extracted three times with 100 mL portions of methylene chloride. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. After evaporating the solvent, a light yellow solid of diethy 2,5-diethoxyterephthalate was obtained. The intermediate was confirmed by ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (s, 2H, H_{arom}), 4.36 (q, 4H, Me-CH_2), 4.09 (t, 4H, O-C-H_2-CH_2), 1.43 (t, 6H, CO-CH_2-C-H_3), 1.38 (t, 6H, COO-CH_2-C-H_3.) ppm. The light yellow solid was then dissolved in 45 mL of ethanol along with 6 mL of hydrazine hydrate. The mixture was heated to reflux and stirred for 40 hours. After cooling, white crystals formed and were collected by filtration, followed by rinsing with ethanol. The isolated product was dried overnight at 50 °C, yielding 264 mg (48%) of 2,5-diethoxy-terephthalohydrazide. The product was confirmed by ^{1}H NMR (600 MHz, DMSOd6): δ = 9.20 (s, 2H, N-H), 7.78 (s, 2H, H_{arom}), 4.27 (q, 4H, O-C-H_2-CH_3), 4.18 (bs, 4H, N-H_2.), 1.51 (s, 12H, -CH_3.) ppm.

Synthesis of COF-42



COF-42 was synthesized by modifying the previous report.[1] 1,3,5-Triformylbenzene (16.2 mg, 0.10 mmol) and 2,5-diethoxy-terephthalohydrazide (42.3 mg, 0.15 mmol) were placed into a glass ampoule (volume of ca. 20 mL, body length of 18 cm, neck length of 9 cm). The mixture was added by 1,4-dioxane (1.0 mL) and mesitylene (3.0 mL), followed by sonication for 5 minutes using an ultrasonic bath. 0.4 mL of 6.0 M acetic acid solution was added to the mixture and continuously sonicated for 10 minutes. The ampoule was then suddenly frozen into a liquid nitrogen bath, evacuated, and flame sealed reducing the total length by ca. 10 cm. After warming to room temperature, the ampoule was placed in an oven at 120 °C for 3 days, yielding a pale-yellow solid. The pale-yellow solid was isolated by filtration and washed with 10 mL of acetone three times. The product was soaked in dried acetone overnight and dried at 80 °C under vacuum for 12 hours to yield COF-42 powder ($C_9H_9N_2O_2$) (50.2 mg, 93% yield).

Synthesis of 1D-coordination polymer of $Ag(CN(CH_2)_4CN)(CF_3SO_3)$



Silver trifluoromethanesulfonate (129 mg, 0.5 mmol) and adiponitrile (54.3mg, 0.5 mmol) were suspended in 20 mL of benzene. The mixture was stirred at room temperature for 5 minutes. The solution was transferred to a Teflon-lined vessel of 50 mL capacity, and heated to 120 °C for 2 hours. After cooling to room temperature for 48 hours, the grey crystal was isolated by filtration, washed with benzene, and dried under vacuum overnight to yield $Ag(CN(CH_2)_4CN)(CF_3SO_3)$, AgAN, (134.7 mg, 74% yield).

Preparation of 40Ag@COF

40Ag@COF was prepared in a glove box to exclude oxygen and atmospheric moisture. 36.7 mmol of AgAN was dissolved in 334 μL of anhydrous acetonitrile, followed by dispersing 20 mg of COF-42 into the solution. The mixture was stirred at room temperature for 3 hours. The acetonitrile was then removed under reduced pressure at 100 °C over 20 hours, yielding 40Ag@COF. Other *x*Ag@COF samples were prepared similarly, using 20 mg of COF-42 and varying the amount of AgAN. Here *x* represents the weight percentage of AgAN loading. The *x*Ag@COF samples were stored in an Ar-filled glove box.

Preparation of up-40Ag@COF

Up-40Ag@COF was prepared in a glove box to exclude oxygen and atmospheric moisture. 367 mmol of AgAN was dissolved in 3.34 mL of anhydrous acetonitrile, followed by dispersing 200 mg of COF-42 into the solution. The mixture was stirred at room temperature for 3 hours. The acetonitrile was then removed under reduced pressure at 100 °C for 20 hours, yielding up-40Ag@COF.

1.3 Characterization

Powder X-ray diffraction (PXRD) data were collected using a Rigaku SmartLab SE diffractometer with CuKα anode (λ = 1.540598 Å). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) data were measured at a heating rate of 10 °C min^{-1} under Ar flow, employing a Rigaku Thermo plus TG 8121 apparatus. Differential scanning calorimetry (DSC) was carried out using 20 Perkin Elmer model-lab system-8500 under a N_2 flow of 60 mL min^{-1}. Fourier transform infrared (FT-IR) spectra were collected between wavenumber from 4000 to 500 cm^{-1} under N_2 atmosphere at room temperature using a Bruker Optics ALPHA II FT-IR spectrometer with Universal ATR accessory. Scanning electron microscope (SEM) images were captured following the Osmium plasma-chemical vapor deposition for 5 seconds, using a Hitachi SU5000 instrument. High-resolution transmission electron microscopy (HR-TEM) images were obtained using the JEOL JEM-ARM 200F microscope at 120 kV equipped with a field emission gun. Energy-dispersive X-ray spectroscopy (EDX) was also applied to investigate elemental distribution. The absorption UV-Vis spectra were carried out on a UV-3600 Shimadzu UV-VIS-NIR Spectrophotometer (range 200-800). Solid-state fluorescence measurements were carried out using a JASCO FP-6600 spectrofluorometer in emission mode, with an excitation wavelength of 300 nm. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was performed to quantify the Ag^+ amount within the hybrids using an Agilent 700 series. The samples were digested in 2% nitric acid solution with a total volume of 10 mL. The solution was filtered before ICP-OES measurement.

Gas sorption isotherms: Gas adsorption isotherms were collected using BELSORP-miniX, MicrotracBEL Crop. for N_2 at 77 K and CO_2 at 195 K. Brunauer–Emmett–Teller surface areas (S_{BET}) were calculated from the N_2 adsorption isotherms. All samples were pretreated for 6 h at 120 °C before the measurements.

X-ray photoelectron spectroscopy (XPS): XPS spectra were collected with a JEOL JPS9010MC instrument using a monochromated Mg K_α X-ray source (1253.6 eV) at 12 kV and 25 mA. The chemical states of the elements and elemental compositions were analysed using JEOL software. All spectra were aligned to the adventitious carbon position (C 1s at 284.7 eV).

Solid-state ^{13}C magic-angle spinning nuclear magnetic resonance (MAS-NMR): The ^{13}C solid-state MAS-NMR were conducted using a JEOL JNM-ECZ 600R (600 MHz) solid-state NMR spectrometer at 14.1 T at 20 kHz spinning (3.2 mm rotor), measured at room temperature. The spectra were processed with Delta software (JEOL RESONANCE Inc). The percentage of AgAN within the 40Ag@COF sample was calculated by peak integration between the OCH_2 peak at 65 ppm from ethoxy (one unit of COF-42) and CH_2 peak at 24 ppm from adiponitrile (AgAN). The integrated peak area ratio between OCH_2 and CH_2 is 9:2, indicating 40% wt of aAgAN contained within the 40Ag@COF.

Solution ^1H NMR: ^1H NMR spectra were collected using a JEOL ECA-600 NMR (600 MHz). D_2O was used as the solvent. NMR sample was prepared by dissolving 10 mg of 40Ag@COF in 500 µL of D_2O with sonication. 120 µL of the filtrated solution was transferred into an NMR tube. 0.1 mmol of dimethyl sulfone (80 µL) was added as an internal standard with an overall solution volume is 600 µL.

X-ray total scattering: Each sample was filled in a borosilicate glass capillary with a diameter of 1 mm and sealed inside the Ar-filled glovebox. The synchrotron X-ray total scattering was collected on the BL04B2 beamline at the Super Photon ring-8 GeV (SPring-8, Hyogo, Japan). The energy of the incident beam is 112.9232 keV (λ = 0.109795 Å). The scattering data were collected by two CdTe 2D-detectors covering the Q range up to 25 Å. The collected scattering data were applied absorption, background, and Compton scattering corrections and normalised to give the Faber−Ziman total structure factor S(Q).[2] The pair distribution functions (PDFs) were calculated by Fourier transforming the S(Q) with a Lorch modification function using Igor Pro software.[3, 4]

X-ray absorption spectroscopy (XAS) and extended X-ray absorption fine-structure spectroscopy (EXAFS): Pellet samples with a diameter of 10 mm and a thickness of 0.5 mm were prepared by mixing the AgAN, 30Ag@COF, and 40Ag@COF with boron nitride. These samples were prepared inside an Ar-filled glovebox. Synchrotron X-ray absorption spectra with the transmission mode in the energy region of the Ag *K*-edge were collected at the BL14B2 beamline (SPring-8, Hyogo, Japan). Extended X-ray absorption fine-structure spectroscopy of the Ag K-edge was collected and Fourier transformed with k^3-weighted in the k range of 3.0 to 14 Å^{-1}. The data processing and fitting were performed with Athena and Arthemis software.

2. Supplementary figures and tables

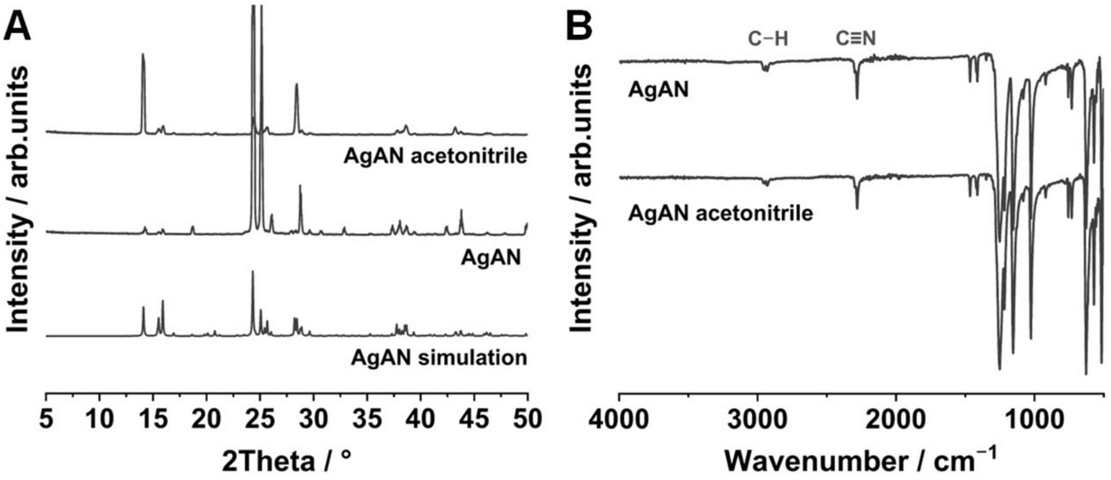


Fig. S1 (A) PXRD patterns and (B) FT-IR spectra of as-synthesised AgAN and AgAN acetonitrile, prepared by dissolving AgAN in acetonitrile followed by solvent evaporation, recrystallising to form AgAN.

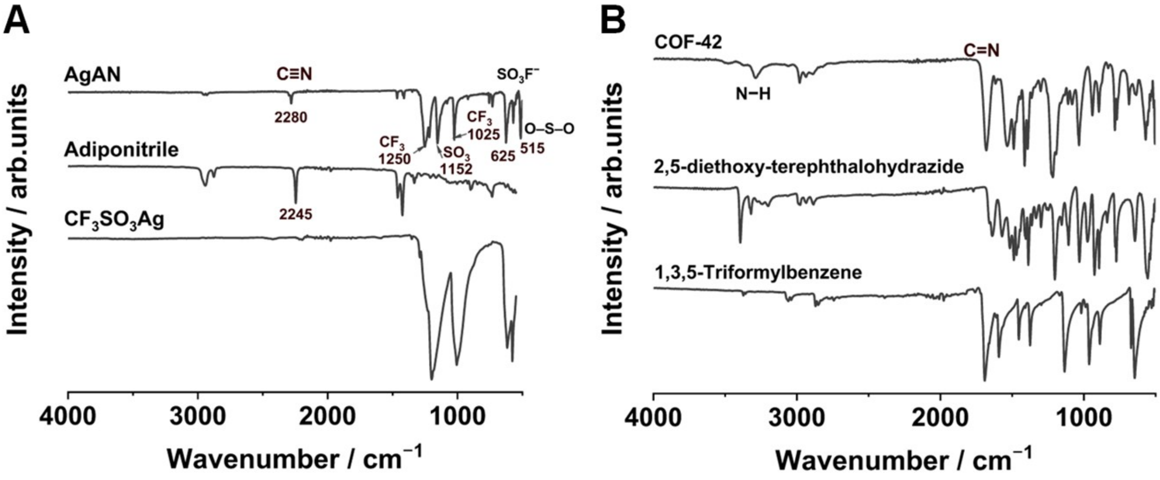


Fig. S2 FT-IR spectra of (A) AgAN, adiponitrile, and CF_3SO_3Ag and (B) COF-42, 2,5-Diethoxy-terephthalohydrazide, and 1,3,5-Triformylbenzene.

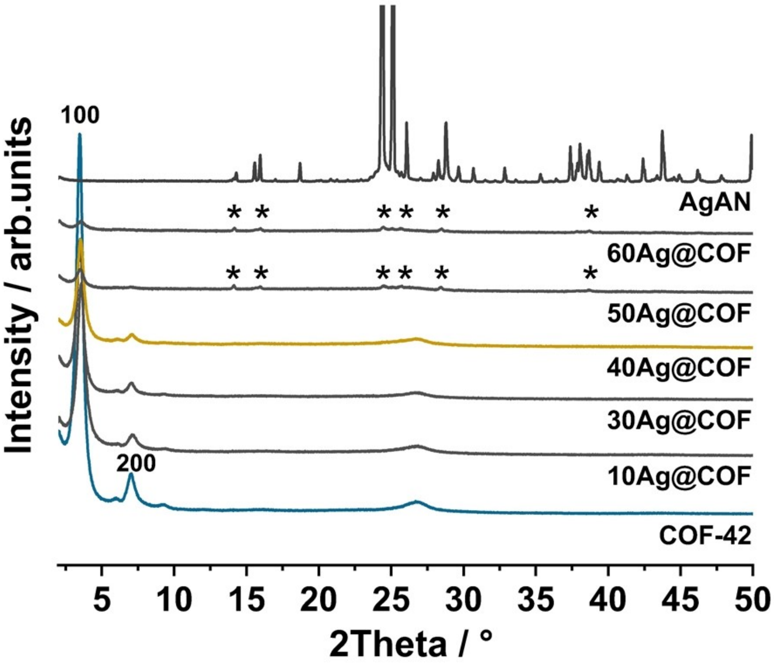


Fig. S3 PXRD patterns of COF-42, AgAN, 10Ag@COF, 30Ag@COF, 40Ag@COF, 50Ag@COF, and 60Ag@COF.

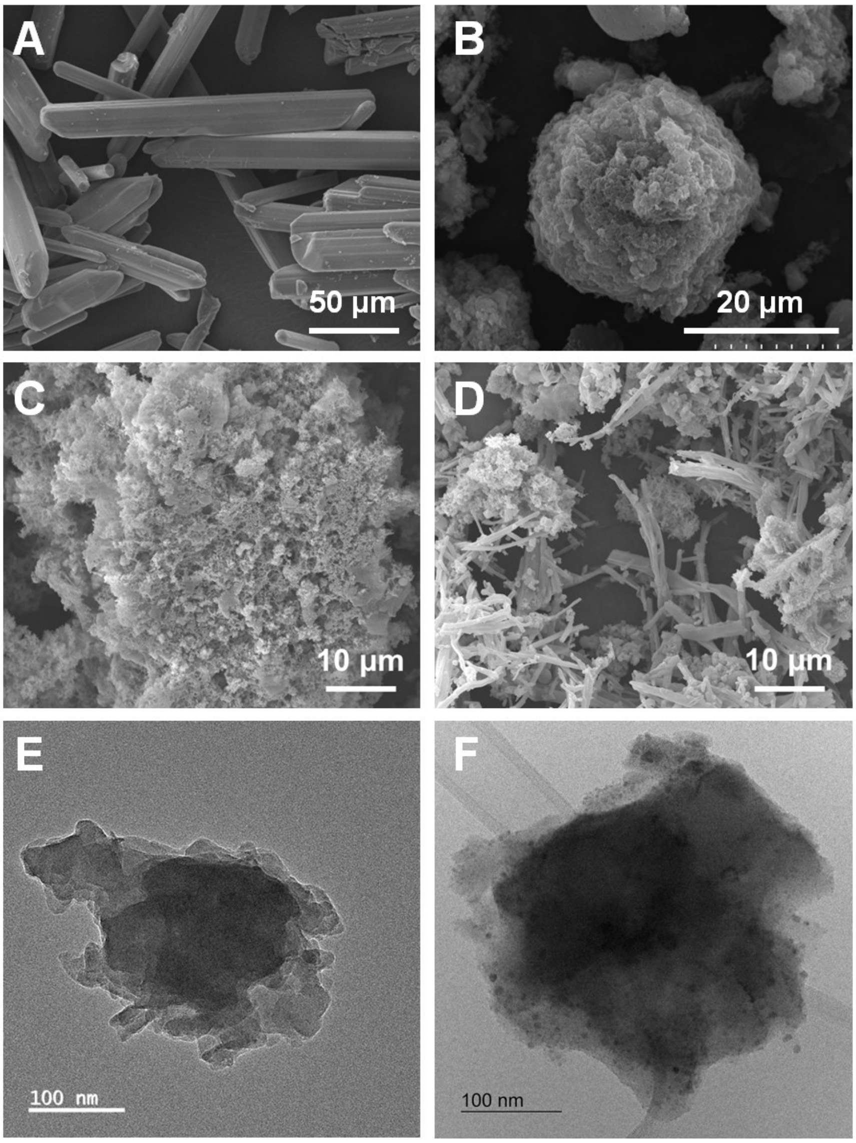


Fig. S4 SEM images of (A) AgAN, (B) COF-42, (C) 40Ag@COF, (D) 60Ag@COF. TEM images of (E) COF-42 and (F) 40Ag@COF.

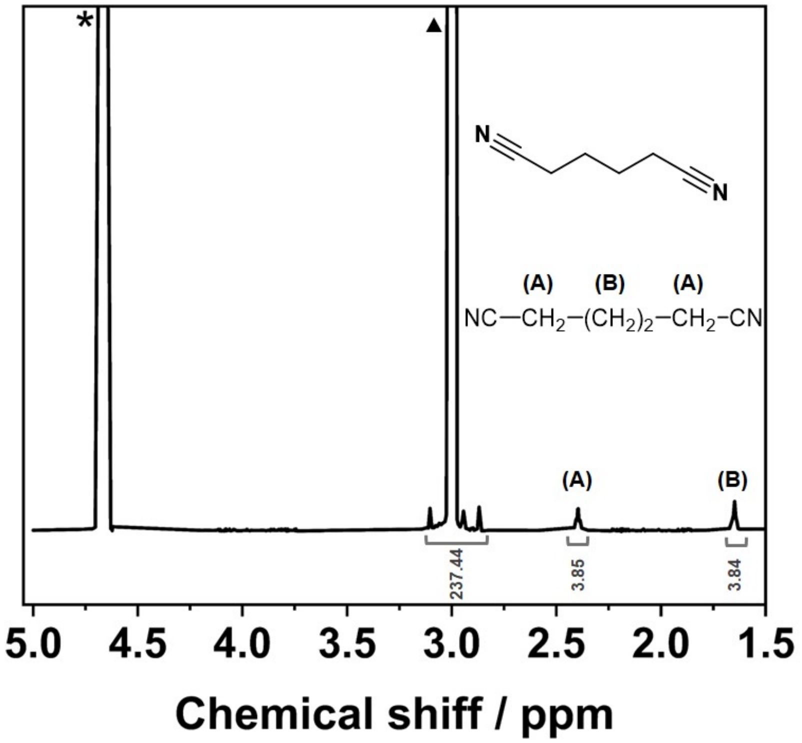


Fig. S5 Solution ^{1}H NMR spectrum of 40Ag@COF (600 MHz, D_2O at 25 °C). Dimethyl sulfone (internal standard) is noted as a triangle. * represents NMR solvent.

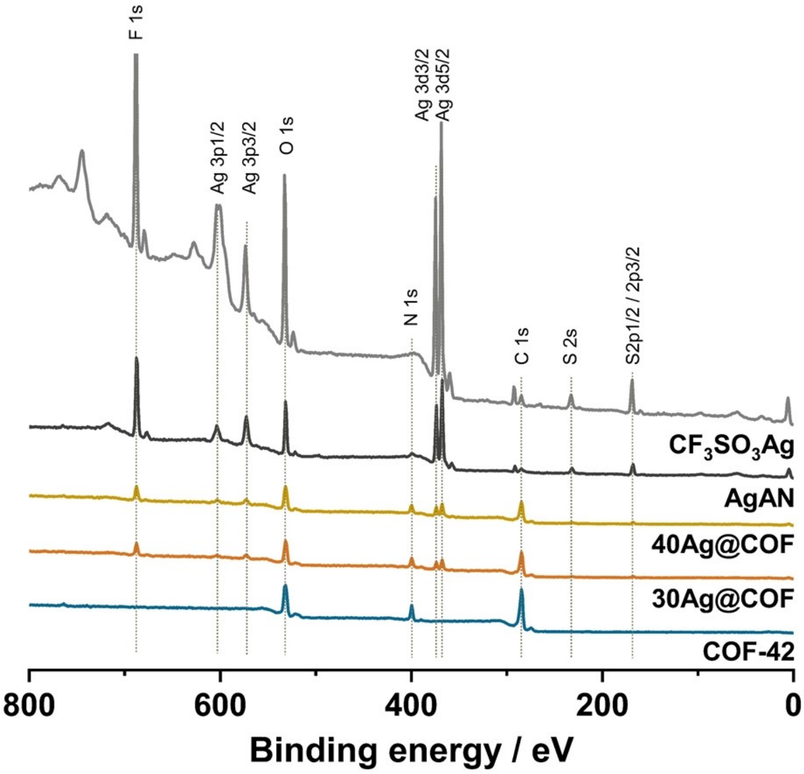


Fig. S6 XPS spectra of CF_3SO_3Ag, AgAN, COF-42, 30Ag@COF, and 40Ag@COF.

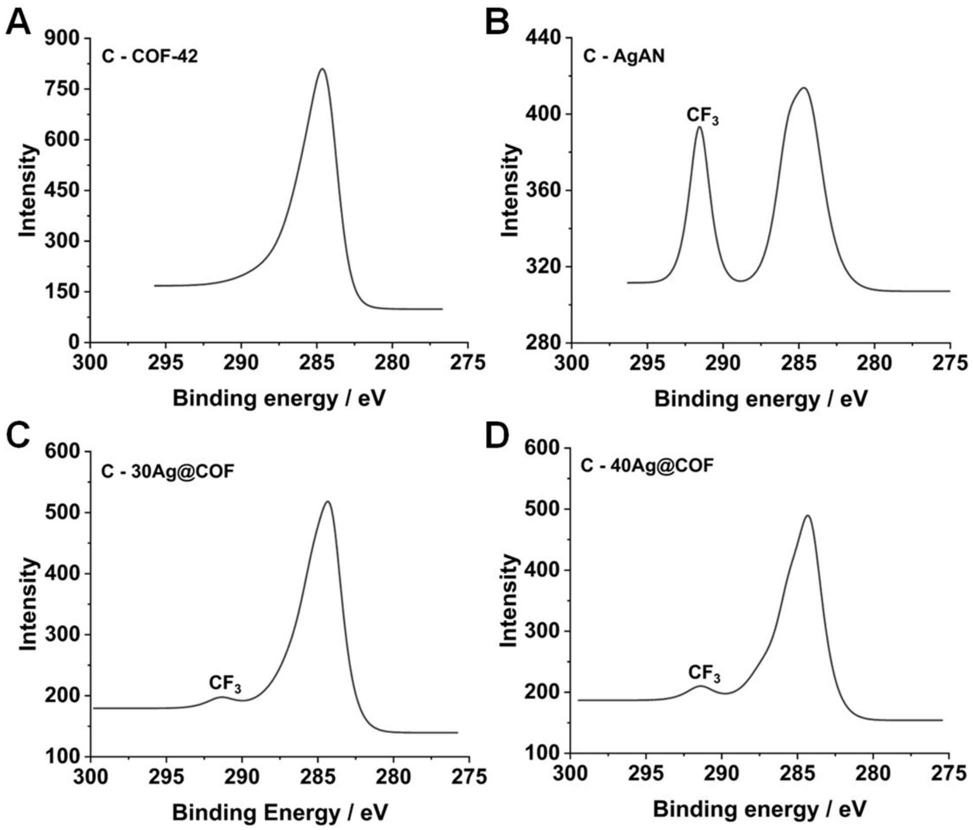


Fig. S7 The C 1s XPS spectra of (A) COF-42, (B) AgAN, (C) 30Ag@COF, and (D) 40Ag@COF.

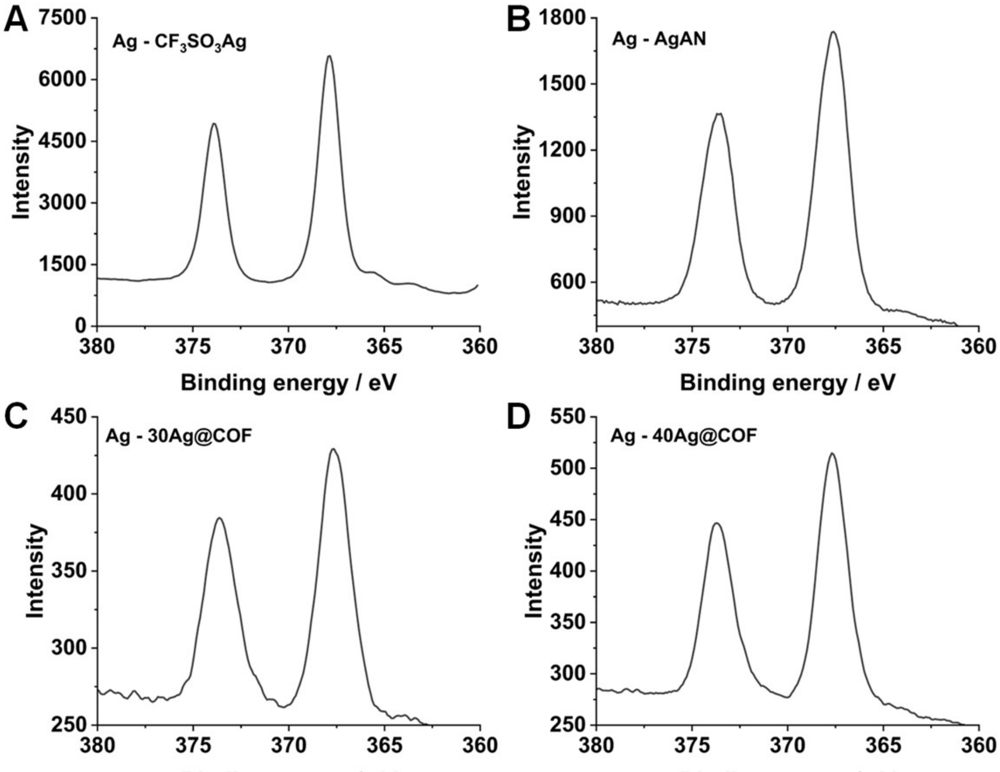


Fig. S8 The Ag 3d XPS spectra of (A) CF$_3$SO$_3$Ag, (B) AgAN, (C) 30Ag@COF, and (D) 40Ag@COF.

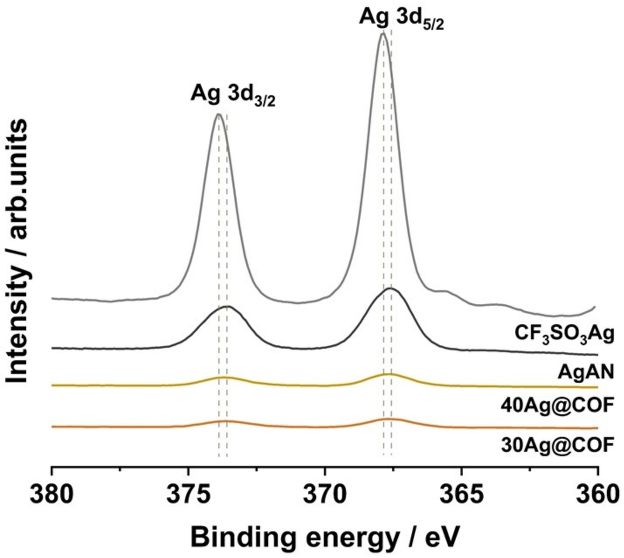


Fig. S9 Comparison of the Ag 3d XPS spectra between CF$_3$SO$_3$Ag, AgAN, 30Ag@COF, and 40Ag@COF. The Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ are located at 367.9 and 373.9 eV for CF$_3$SO$_3$Ag and 367.6 and 373.7 eV for AgAN, respectively.

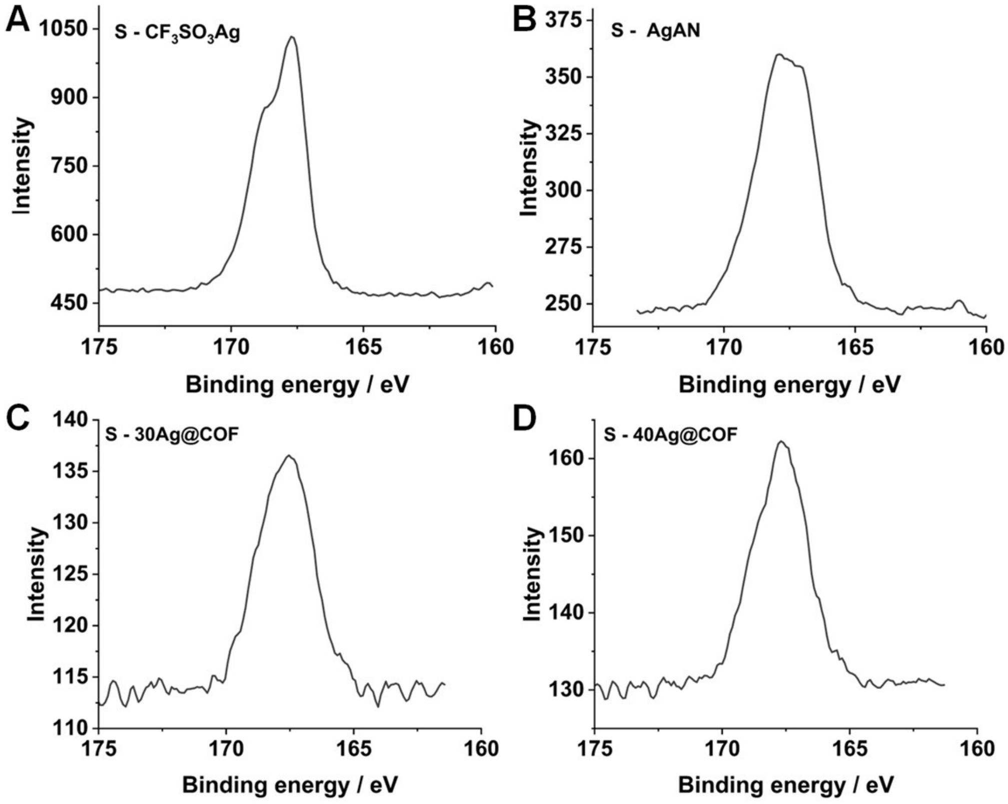


Fig. S10 The S 2p XPS spectra of (A) CF$_3$SO$_3$Ag, (B) AgAN, (C) 30Ag@COF, and (D) 40Ag@COF.

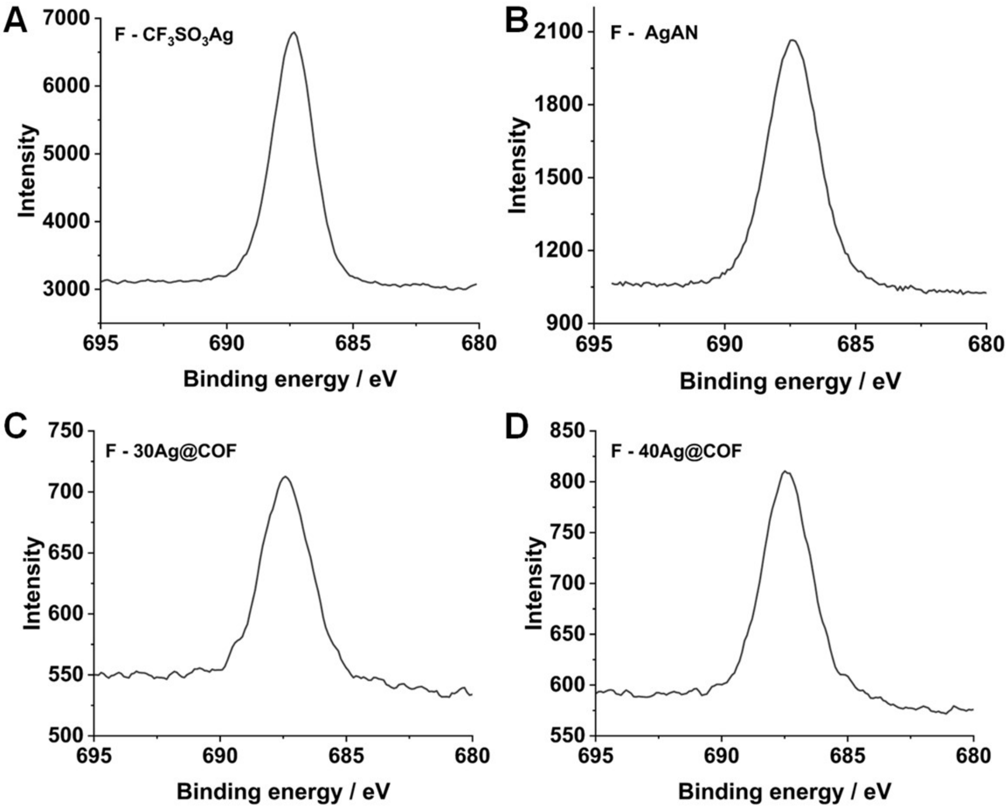


Fig. S11 The F 1s XPS spectra of (A) CF_3SO_3Ag, (B) AgAN, (C) 30Ag@COF, and (D) 40Ag@COF.

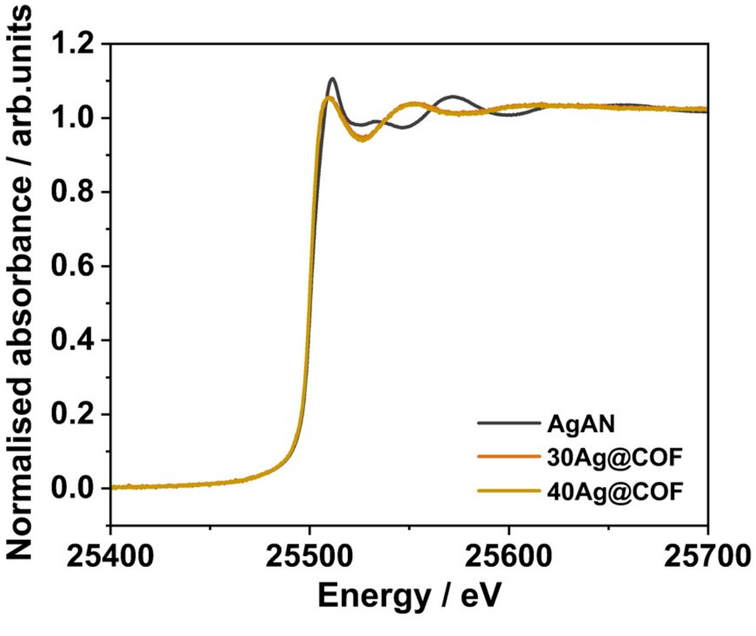


Fig. S12 The Ag K-edge XANES of AgAN, 30Ag@COF, and 40Ag@COF.

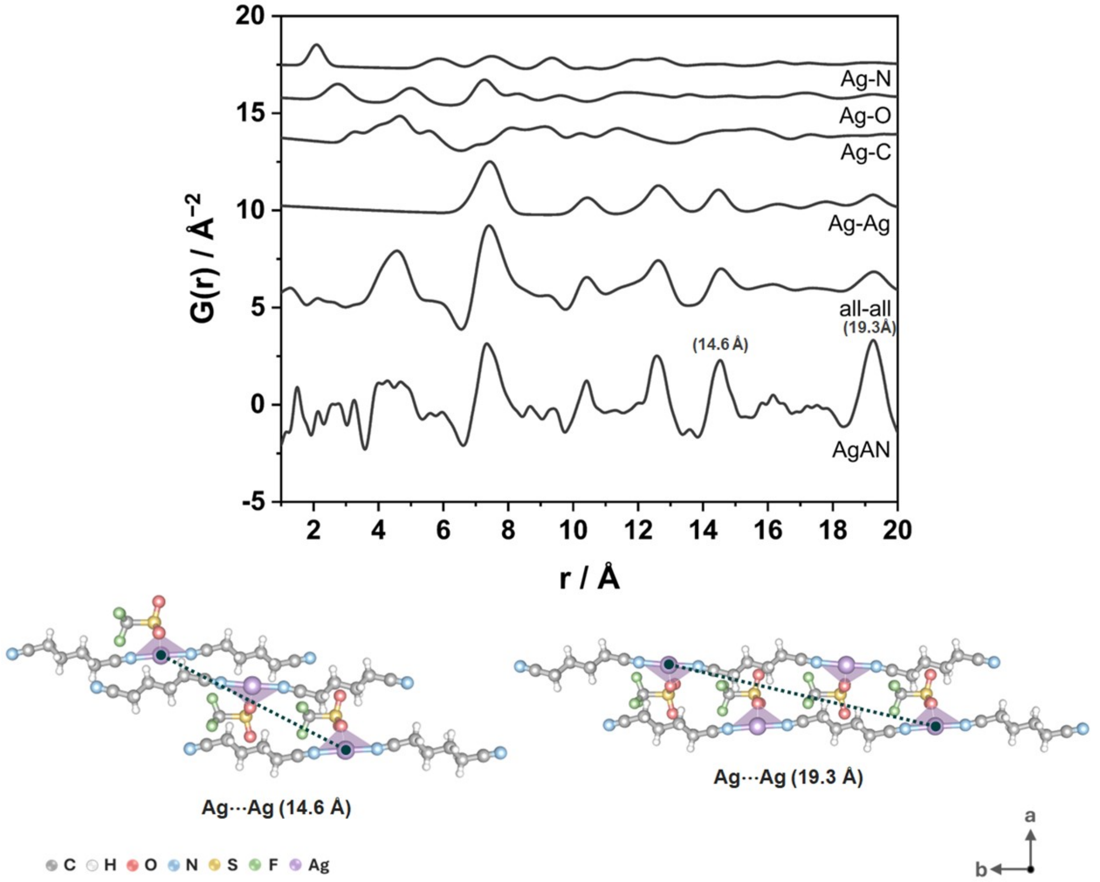


Fig. S13 Simulated PDF profile for AgAN and its partial PDF using the PDF GUI software.

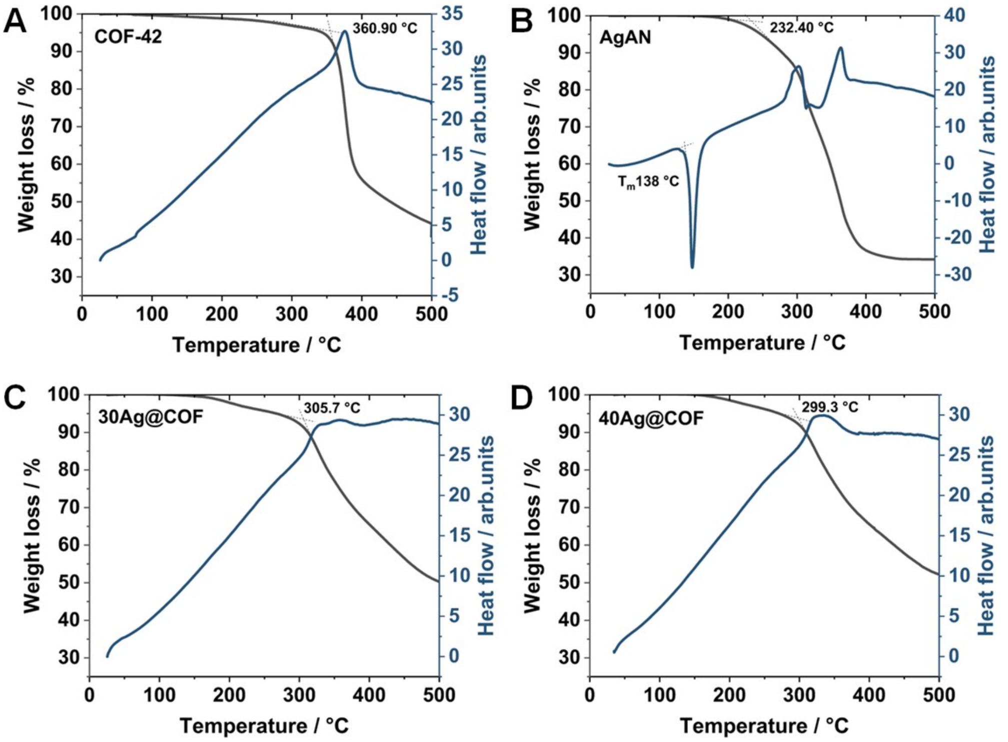


Fig. S14 TGA (black) and DTA (dark blue) profiles of (A) COF-42, (B) AgAN, (C) 30Ag@COF, and (D) 40Ag@COF.

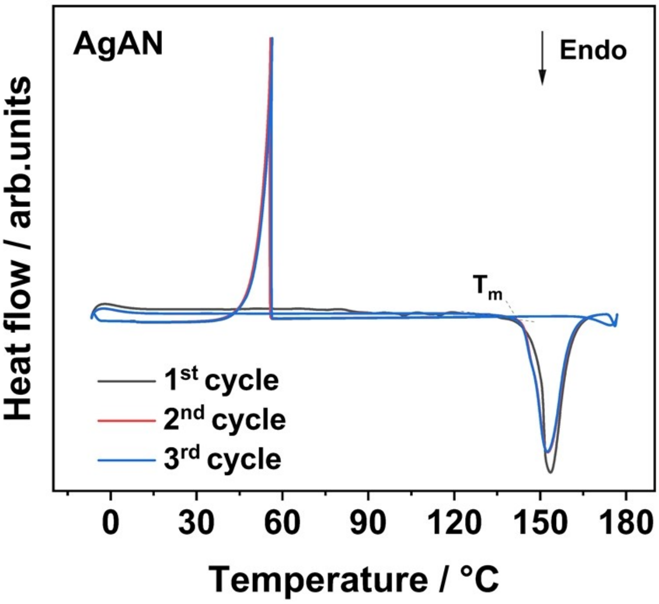


Fig. S15 DSC profiles of AgAN with $T_{m(onset)}$ at 138 °C and a T_c at 50 °C measured under N_2 flow at a ramping rate of 10°C min^{-1}.

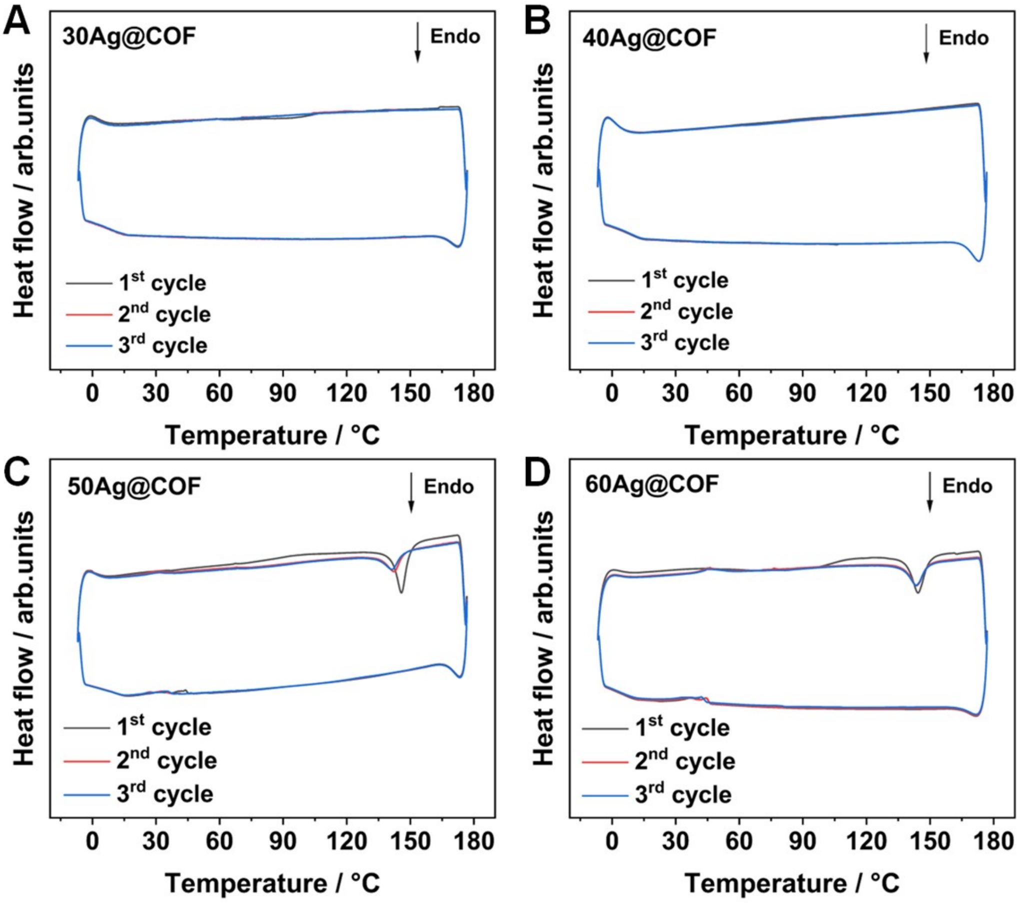


Fig. S16 DSC profiles under N_2 flow of the (A) 30Ag@COF, (B) 40Ag@COF, (C) 50Ag@COF, and (D) 60Ag@COF measured at a ramping rate of 10°C min^{-1}.

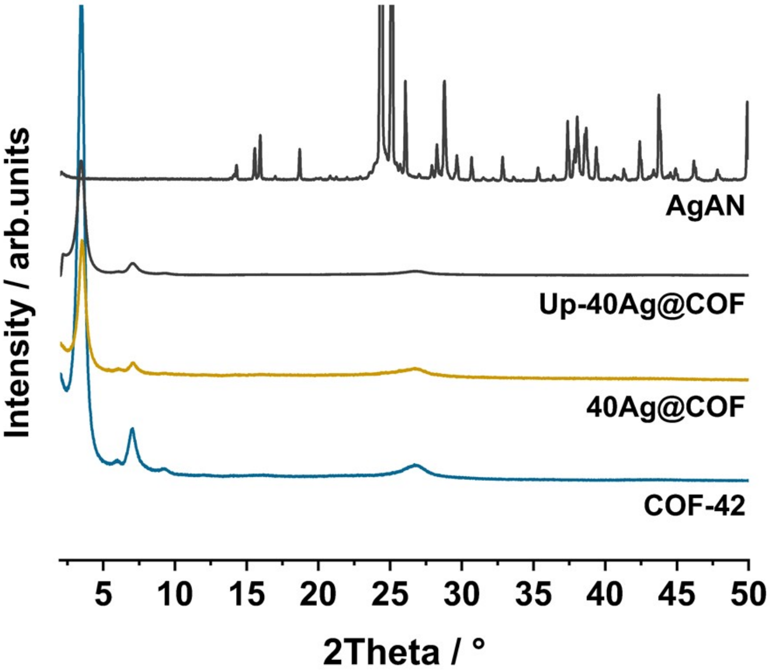


Fig. S17 PXRD patterns of COF-42, AgAN, 40Ag@COF, and up-40Ag@COF.

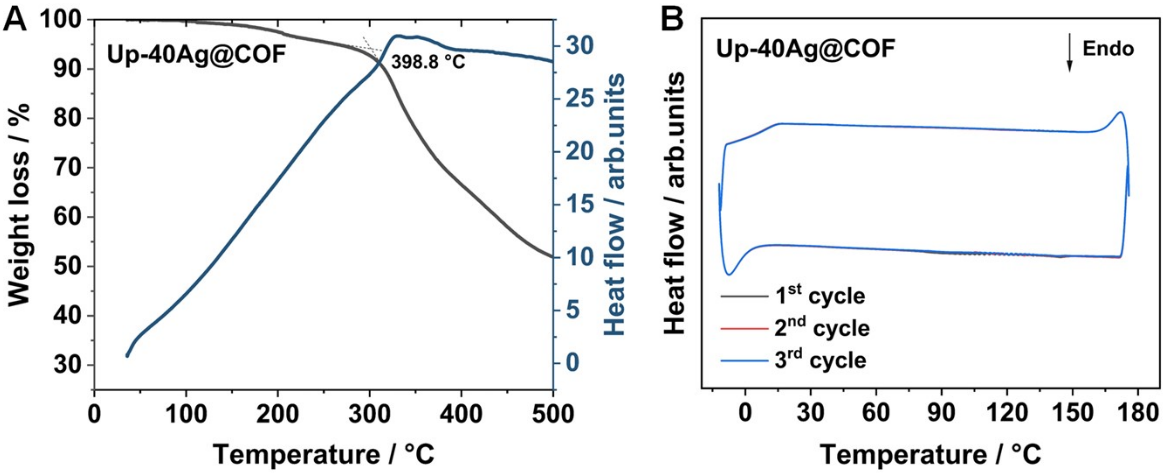


Fig. S18 (A) TGA (black) and DTA (dark blue) profiles (B) DSC profiles under N_2 flow of the up-40Ag@COF measured at a ramping rate of 10°C min^{-1}.

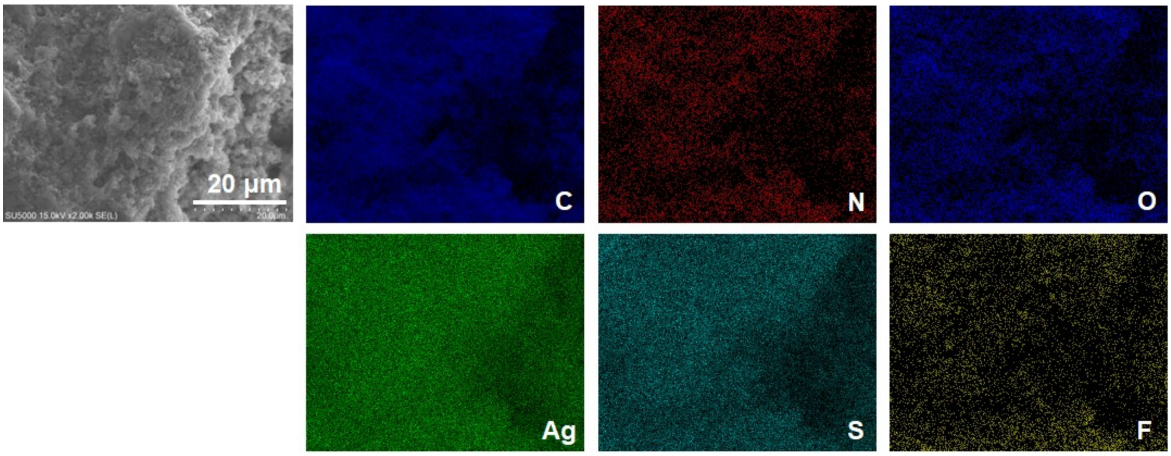


Fig. S19 SEM and EDS mapping of up-40Ag@COF.

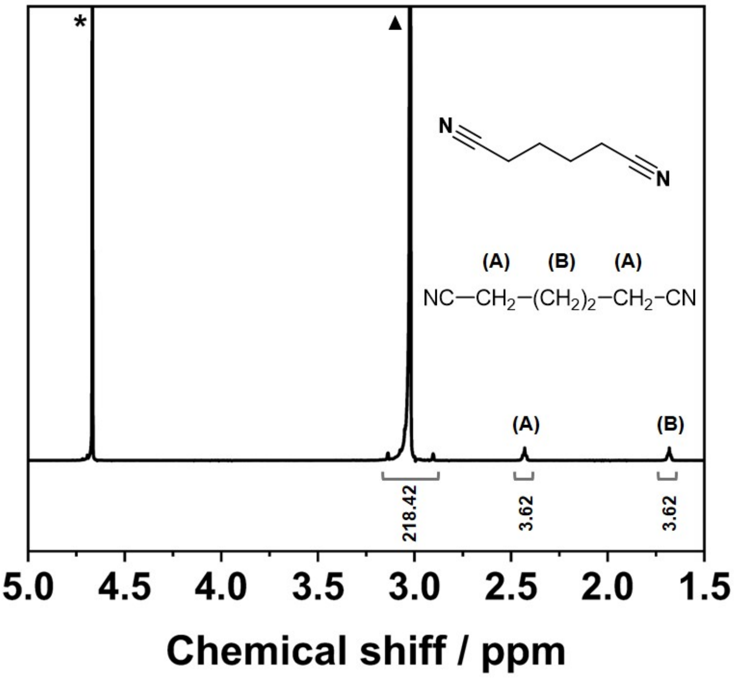


Fig. S20 Solution ^{1}H NMR spectrum of up-40Ag@COF (600 MHz, D_2O at 25 °C). Dimethyl sulfone (internal standard) is noted as a triangle. * represents NMR solvent.

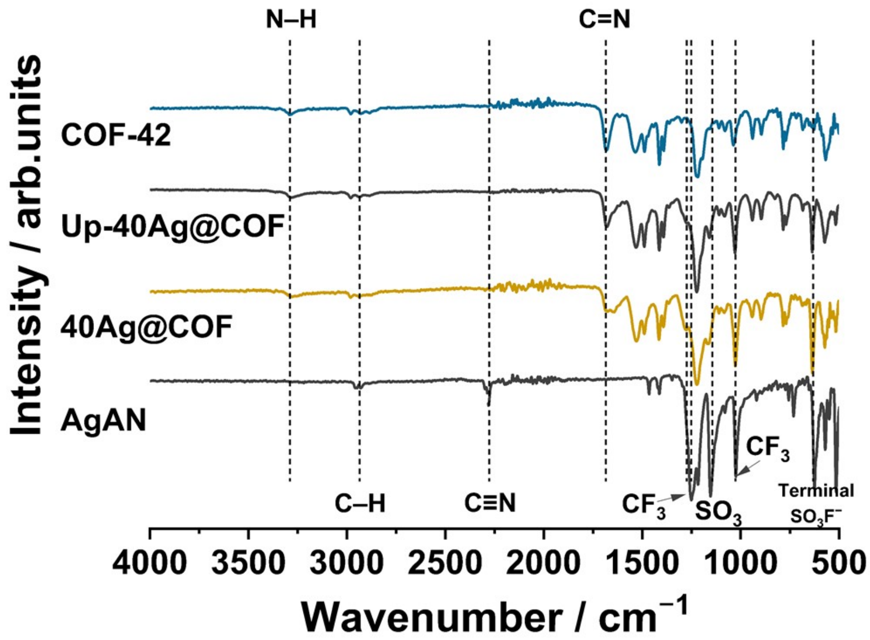


Fig. S21 FT-IR spectra of COF-42, 40Ag@COF, up-40Ag@COF, and AgAN.

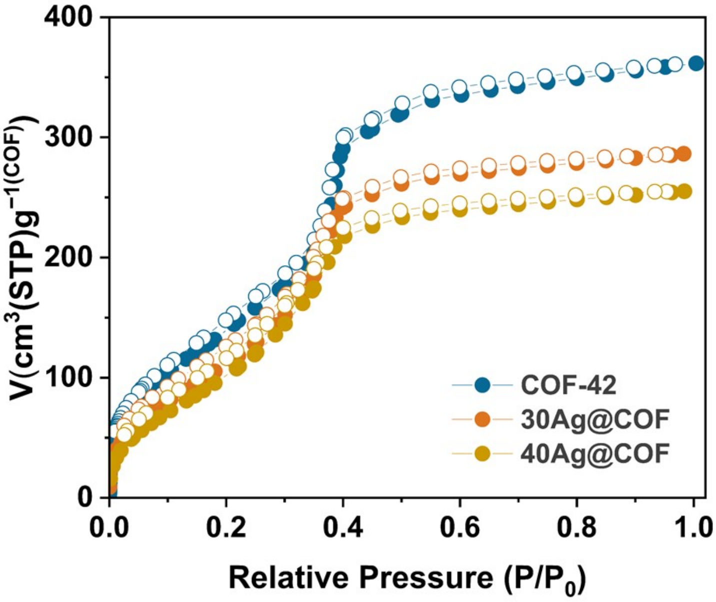


Fig. S22 CO_2 sorption isotherm at 195 K of COF-42, 30Ag@COF, and 40Ag@COF. Solid symbols are adsorption, Open symbols are desorption.

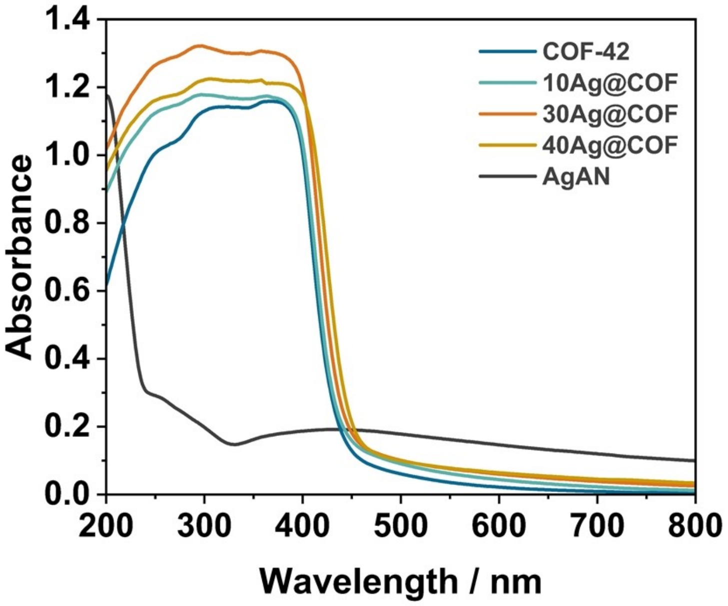


Fig. S23 UV-Vis spectra of COF-42, 10Ag@COF, 30Ag@COF, 40Ag@COF, and AgAN.

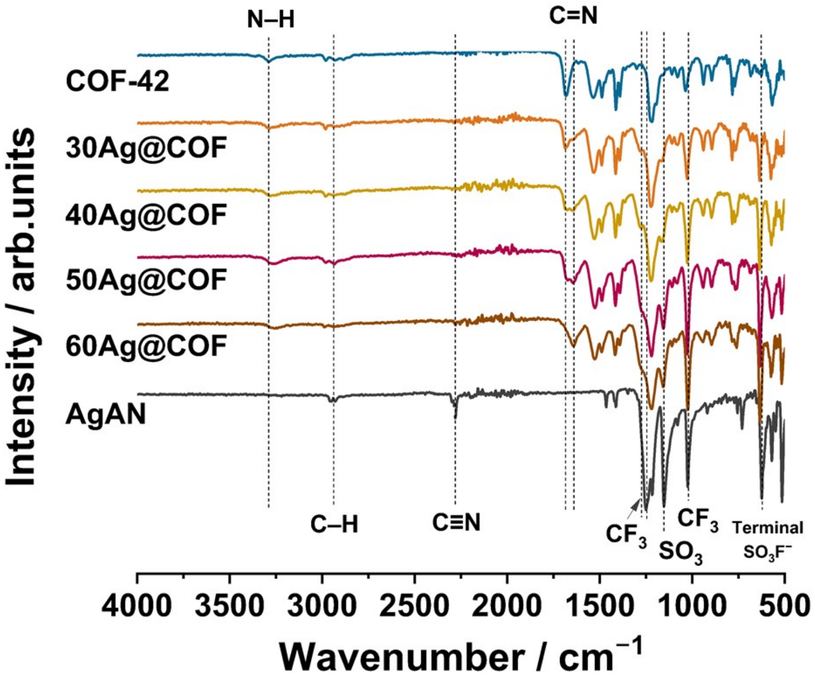


Fig. S24 FT-IR spectra of COF-42, 30Ag@COF, 40Ag@COF, 50Ag@COF, 60Ag@COF, and AgAN.

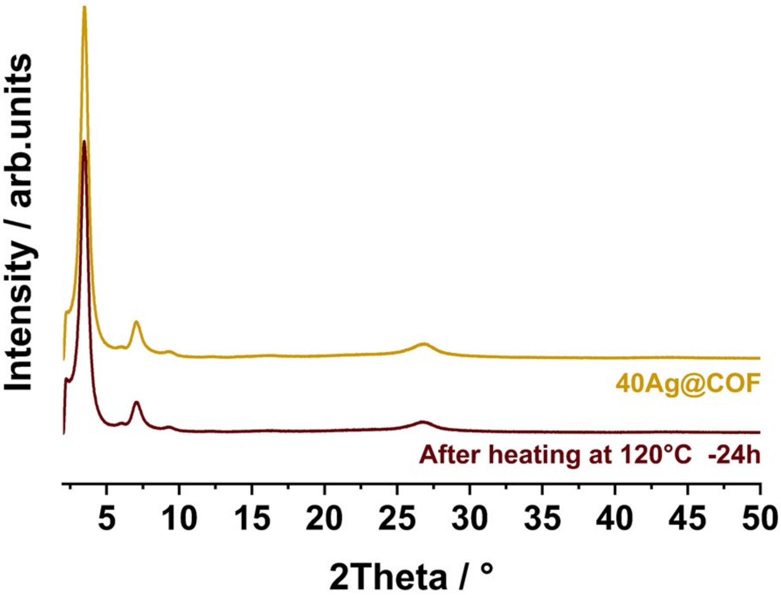


Fig. S25 PXRD patterns of 40Ag@COF before and after heating at 120°C for 24 hours.

Table S1. Comparison of synthesis methods and particle sizes for amorphous coordination polymer (CP) nanoparticles.

Amorphous CP nanoparticles	Preparation method	Size (nm)	Ref.
40Ag@COF	Dissolution and evaporation	5-20	This work
1D CP [Zn(OAc)2(bipy)]n	Block copolymer micelles	core sizes = 47 ± 5	[5]
2D CN [Zn(TFA)2(bppa)2]n		Core size = 46 ± 6	
aZIF-7 spheres	Stöber method	180–340	[6]
UiO-66	Mechanical milling	261 ± 12	[7]
glucose oxidase-aZIF-8.	Solution synthesis	~100	[8]
amorphous ZIF-8-based core@shell NPs	Core-shell	15-25 (shell)	[9]
Zn–BMSB–Zn	Solvent diffusion	190 ± 60 nm	[10]
Zn(ICA)-2	Solvent diffusion	20	[11]
Amorphous UiO-66	Mechanical milling	50	[12]

Table S2. Quantitative solution ^{1}H NMR calculation of adiponitrile within 40Ag@COF and up-40Ag@COF.

Sample	**Peak of integration**	**No. of proton**	**Integral area**	**mmol (120 µL)**	**mmol (500 µL)**	**mmol/g**
40Ag@COF						
Dimethy sulfone	3.2 ppm	6	237.44	1×10^{-1}		
Adiponitrile	2.4 ppm (peak A)	4	3.85	2.4×10^{-3}	1.01×10^{-2}	1.01
Up-40Ag@COF						
Dimethy sulfone	3.2 ppm	6	218.42	1×10^{-1}		
Adiponitrile	2.4 ppm (peak A)	4	3.62	2.4×10^{-3}	1.01×10^{-2}	1.01

Table S3. Atomic percentage obtained from the XPS analysis

Atom	**C**	**O**	**N**	**Ag**	**S**	**F**
Sample name						
AgAN	21.65	26.08	4.93	11.45	8.20	27.69
30Ag@COF	61.05	19.43	10.58	1.83	1.95	5.16
40Ag@COF	57.37	20.69	9.60	2.56	2.54	7.24

Table S4. The weight percentage of AgAN within 30Ag@COF and 40Ag@COF calculated by ICP-OES analysis.

Sample	**Content**	**Total (mg)**	**AgAN (mg)**	**Ag (mg)**	**Ag (mmol/g)***	**AgAN (%wt)**
30Ag@COF	Calculated	15	4.5	1.33	0.8	30
	Actual			1.49	0.9	33.6
40Ag@COF	Calculated	15	6	1.77	1.1	40
	Actual			2.05	1.2	46.3

* mmol of Ag per 1 gram of *x*Ag@COF

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