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Supporting Information of

Stable Melt Formation of 2D Nitrile-Based Coordination Polymer and Hierarchical Crystal–Glass Structuring

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Contents:

Materials and instruments

All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. $AgCF_3SO_3$ (Silver triflate, 98%) was purchased from Tokyo Chemicals Industry Co., Ltd. and super dehydrated benzene (99.5%) was purchased from Wako Pure Chemical Industries, Ltd. *m*L1 was synthesiszed by the literature method.[1]

Powder X-ray diffraction (PXRD): PXRD patterns were collected on a Rigaku MiniFlex with CuKα anode (wavelength λ = 1.5418 Å) ranging from 2θ value of 3 to 50° with a step of 0.02°, and the speed of the data collection is 5° min^{-1}.

Fourier transform infrared spectroscopy (FT-IR): FT-IR spectra were collected using a Bruker Optics ALPHA FT-IR spectrometer with Universal ATR accessory under Ar, and a Nicolet ID5 ATR under air operating at ambient temperature between 4000 to 500 cm^{-1}.

Elemental analysis: CHN elemental analysis was conducted on a MICRO CORDER JM11 (J-Science Lab Co., LTd.)

Thermogravimetric analysis (TGA): TGA-DTA profiles were collected using a Rigaku Thermo plus TG 8120 (N_2) and TG 8121 (Ar) apparatus in the temperature range of 30 °C to 500 °C at a heating rate of 10 °C min^{-1}.

Differential scanning calorimetry (DSC): The differential scanning calorimetry (DSC) was carried out with Hitachi High-Tech Science Corporation model DSC7020 at the heating rate of 10 °C min^{-1} under the N_2 atmosphere. A real-time camera is equipped with the instrument for sample observation and automatic capturing of the photograph at an interval of 2 °C min^{-1}. The melting point and glass transition temperature were determined by using a software TA7000 Standard Analysis (Ver. 5.0).

Gas and solvent sorption isotherms: CO_2 adsorption isotherms were collected using BELSORP-mini at −78.15 °C. Benzene and water adsorption isotherms were collected using BELSORP-aqua at 25 °C. Solvents were pre-dried and three cycles of freeze-pump-thaw was performed to enhance the purity of the degassed solvent. Approximately 35-40 mg of sample was taken for the gas and solvent vapor adsorption studies.

X-ray total scattering: The powder sample of **1-MIG** was sealed in a quartz glass capillary (ϕ = 2 mm) inside Ar-filled glovebox. The X-ray total scattering data were collected at 25 °C with four CdTe and two Ge detectors covering the Q range up to 25 $Å^{-1}$ at the BL04B2 beamline (61.377

keV) at the Super Photon Ring (SPring-8, Hyogo, Japan). The incident beam was monochromated at $\lambda = 0.2020$ Å. G(r) is obtained from the Fourier transformation of $S(Q)$ with a Lorch modification function through Igor Pro software.[2]

X-ray absorption spectroscopy (XAS): The samples were prepared by mixing with appropriate amounts of boron nitride (BN) and pressed into pellet of 10 mm diameter. X-ray absorption spectra were collected in the energy region of the Ag *K*-edge in transmission mode at the Aichi Synchrotron Radiation Center (Aichi SR) on beamline BL11S2. The data was processed using the IFEFFIT library.[3] Fourier transformation was k^3-weighted in the k range from 2.5-11 $Å^{-1}$. The data processing and coordination number fitting were performed with Athena and Artemis software, respectively. The RDF of **1-a**, **1** and **1-MIG** were fitted by a model in which the silver ions are surrounded by four nitrogen/oxygen atoms. The following equation was used to calculate and fit RDF of **1-a**, **1** and **1-MIG**.

$$\chi(k) = S_0^2 \sum \frac{N_j f_j(k) exp\left[-2k^2\sigma_j^2\right]}{kr_j^2} sin\left[2k_j r_j + \delta(k)\right]$$

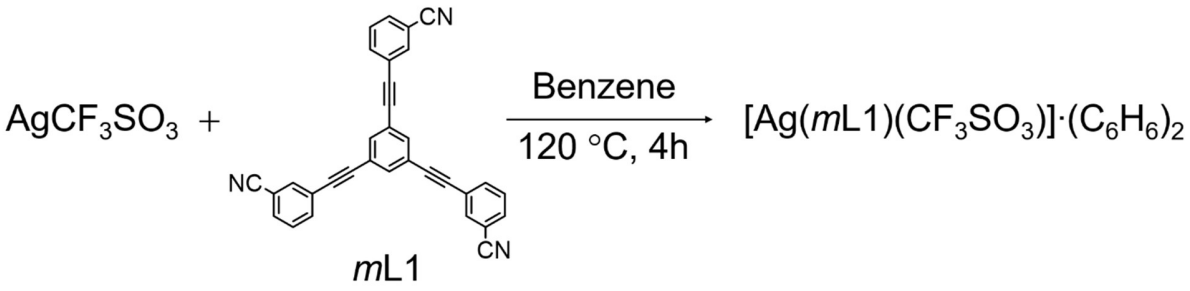
where r is distance from the target to neighboring atom, N is coordination number of the neighboring atom, and σ^2 is Debye-Waller factor. The photoelectron wavenumber k, $f(k)$ is the scattering amplitude, and $\delta(k)$ is the phase shift. S_0, amplitude reduction factor. Ag foil internal energy calibration was measured simultaneously with each sample. The energy was defined by assigning the first inflection point of the Ag foil spectrum to 25516 eV. EXAFS spectrum of **1-a**, **1** and **1-MIG** was fitted in r range from 1.2 to 2.1 Å. The final values of these parameters are summarized in Table S1.

1. Experimental methods:

1.1. Synthesis of [Ag(*m*L1)(CF_3SO_3)]·$2C_6H_6$ (1-a): The synthesis procedure was modified from the literature report.[1] [Ag(*m*L1)(CF_3SO_3)]·$2C_6H_6$ (**1-a**, *m*L1=1,3,5-tris(3-ethynylbenzonitrile)benzene) was synthesized by solvothermal method with a temperature controller oven. $AgCF_3SO_3$ and *m*L1 were transferred into an Ar-filled glovebox. $AgCF_3SO_3$ (149 mg, 0.58 mmol) and *m*L1 (59 mg, 0.13 mmol) were separately dissolved into 4 mL and 10 mL of super dehydrated benzene, respectively. Both the solutions were stirred separately for 10 mins in Ar atmosphere for complete dissolution. A white suspension was immediately formed when these two solutions were mixed together. The turbid solution was transferred into a Teflon lined

autoclave and it was fixed inside a stainless steel vessel. It was kept inside the temperature controller oven and heated at 120 °C for 4 h. It was slowly cooled down to 28 °C with a rate of 1.9 °C h^{-1} over the period of 48 h. Blcok shaped crystals were isolated after the reaction. Crystals were washed with benzene for 3 times and dried in ambient condition (0.09 g). Elemental analysis of 1-a, Calculated: C, 63.75; H, 3.14; N, 4.85. Found: C, 63.03; H,3.14; N, 4.78.

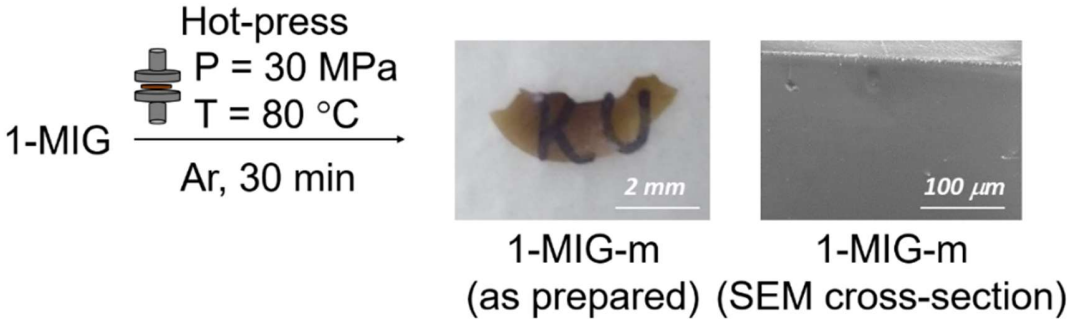
Scheme for the synthesis of 1-a:



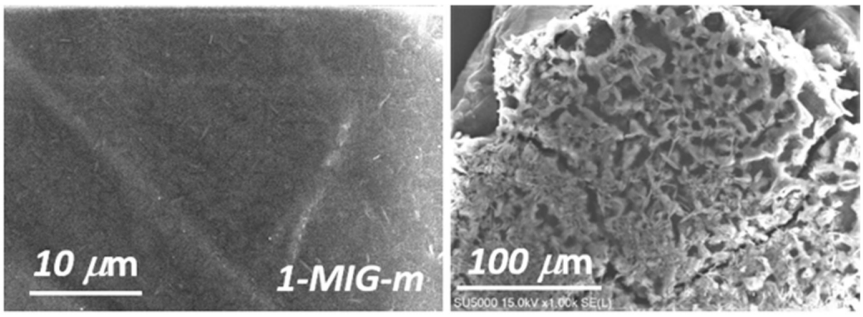
1.2. Preparation of 1: 1-a was degassed under vacuum at 140 °C for 6 h to obtain **1**. Elemental analysis of **1**, Calculated: C, 57.48; H, 2.13; N, 5.91. Found: C, 55.98; H, 2.13; N, 5.69.

1.3. Preparation of 1-MIG: 1-MIG was prepared by hand-grinding the microcrystals of **1** (0.15 g) in agate mortar under Ar atmosphere for 30 minutes. Elemental analysis of **1-MIG**, Calculated: C, 57.48; H, 2.13; N, 5.91. Found: C, 56.18; H, 2.13; N, 5.72.

1.4. Preparation of 1-MIG-m: The semi-transparent **1-MIG-m** was fabricated by hot-press instrument under Ar atmosphere. A 5 mm diameter and 1 mm thick pellet of **1-MIG** was prepared and pressed under 30 MPa at 80 °C for 30 minutes under Ar atmosphere.



1.5. Preparation of crystal-glass hierarchical structure: The crystal-glass hierarchical structure was prepared after soaking of **1-MIG-m** (2 mm diameter and 0.3 mm of thick) at 25 °C in anhydrous benzene for 24 h and dried under Ar for 12 h. Surface morphology of **1-MIG-m** before (left) and after (right) benzene soaking in Ar atmosphere characterized by SEM.



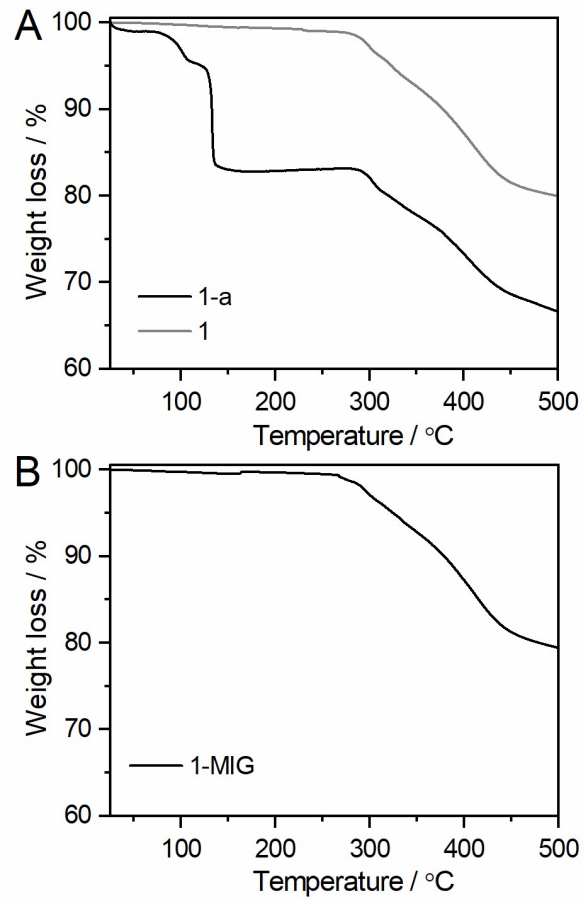


Fig. S1. (A) TGA profiles of **1-a** and **1**. (B) TGA profile of **1-MIG**. Measurements were carried out under N_2 atmosphere. Scan rates were 10 °C min^{-1}.

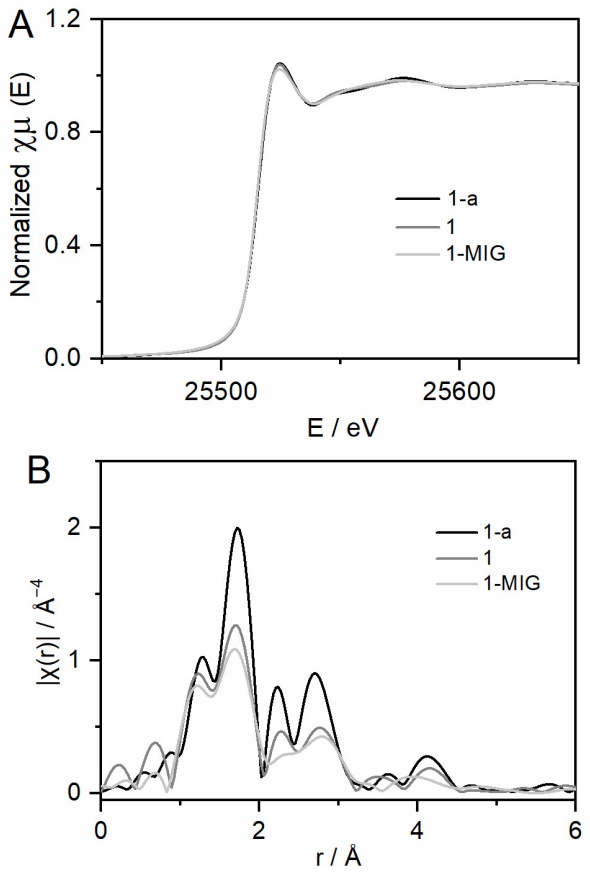


Fig. S2. (A) Ag *K*-edge X-ray near edge structure (XANES) and (B) Extended X-ray absorption fine structure (EXAFS) of **1-a**, **1**, and **1-MIG** at room temperature.

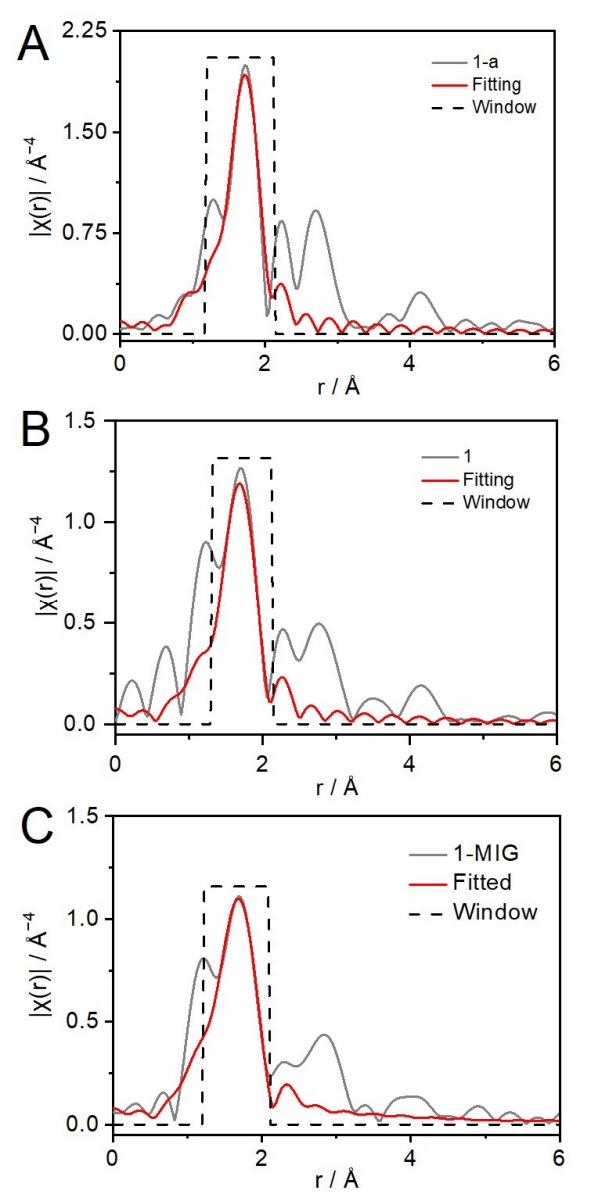


Fig. S3. Radial distribution functions of **1-a**, **1** and **1-MIG** (gray) and fitting curve (red) at room temperature.

Table S1. Parameters refined by fitting the EXAFS spectrum of **1-MIG.**

	Shell	*N*	*r* / Å	σ^2 / Å^2	E_0 / eV	*R*-factor
1-a	Ag-O/Ag-N	4.3(±0.9)	2.23655	0.008(±0.009)	2.1	0.018
1	Ag-O/Ag-N	4.1(±1.4)	2.22681	0.008(±0.004)	2.1	0.039
1-MIG	Ag-O/Ag-N	4.1(±1.2)	2.26646	0.015(±0.005)	2.1	0.019

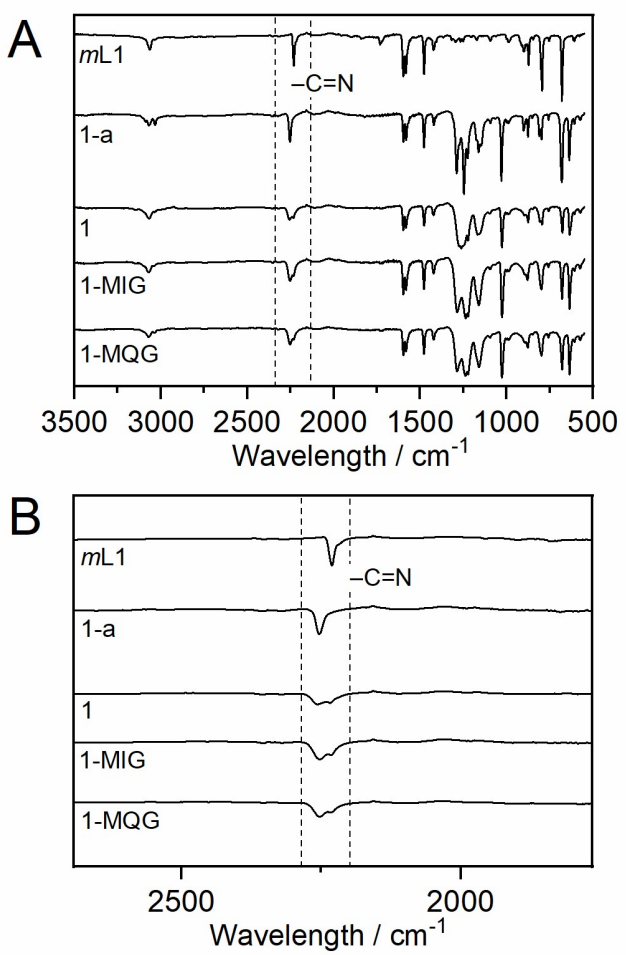


Fig. S4. (A) FT-IR spectra of *m*L1, **1-a**, **1**, **1-MIG** and **1-MQG** recorded at Ar at 25 °C. (B) The zoomed spectra of each sample.

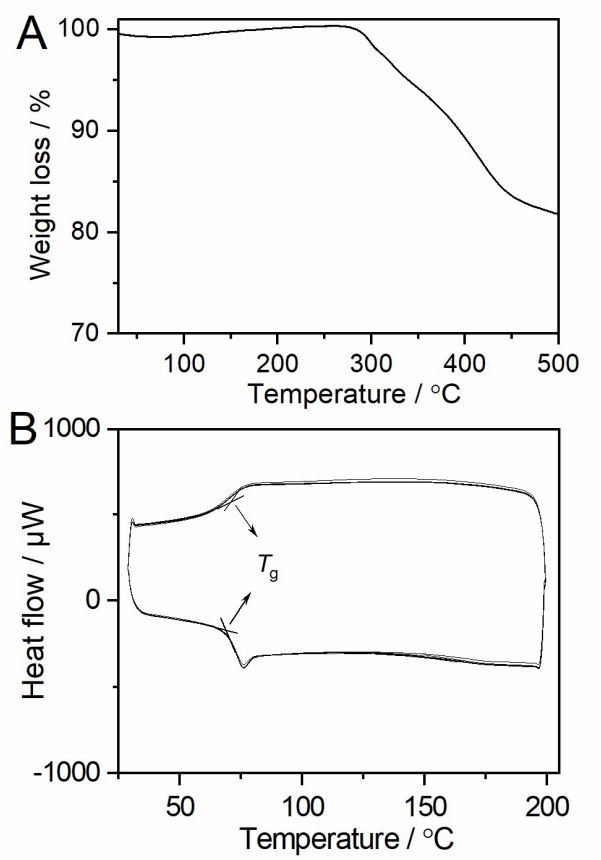


Fig. S5. (A) TGA profile of **1-MQG** under N_2. (B) DSC profiles (6 cycles) of **1-MQG**. Scan rates were 10 °C min^{-1}.

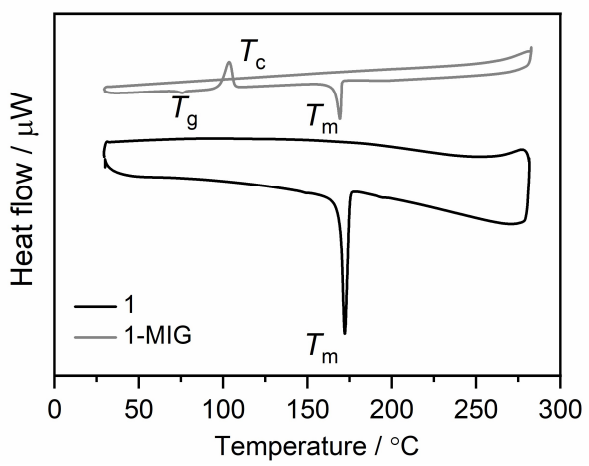


Fig. S6. DSC profiles of **1** and **1-MIG** up to 280 °C under N_2. Scan rate were 10 °C min^{-1}.

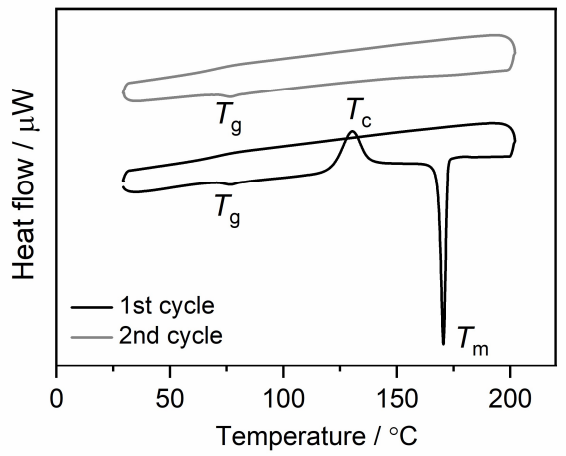


Fig. S7. DSC profiles of the hand-grinded **1-MQG** under N_2. Scan rates were 10 °C min^{-1}.

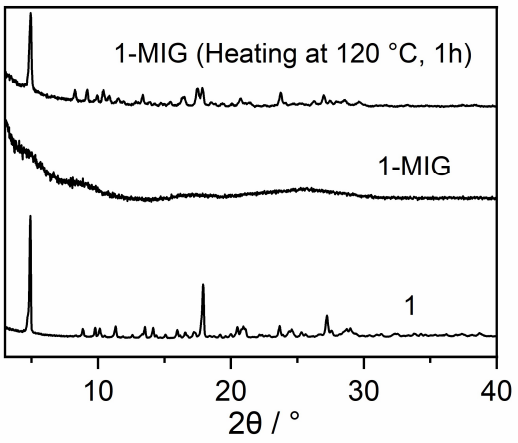


Fig. S8. PXRD patterns of **1**, **1-MIG**, **1-MIG** after heating at 120 °C for 1 h.

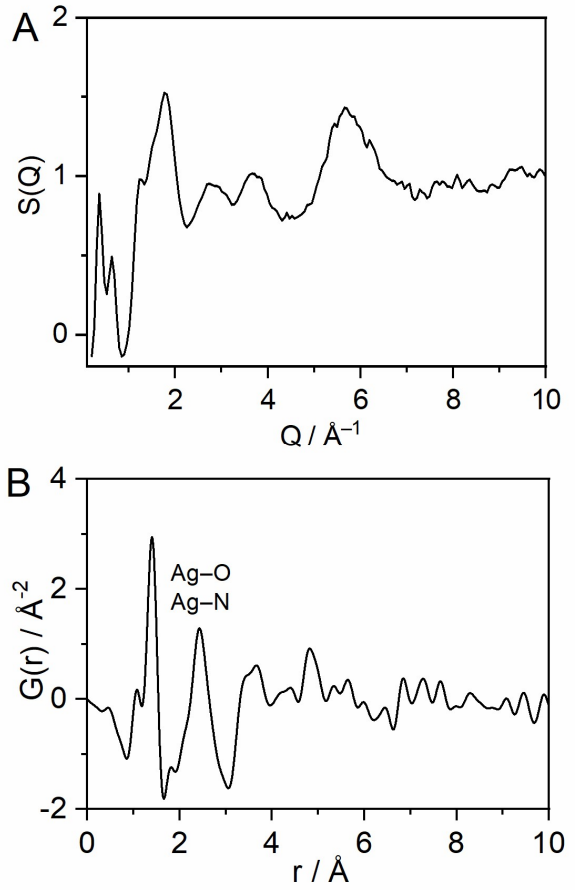


Fig. S9. (A) X-ray total structure factor *S*(Q) (B) Reduced pair distribution function (PDF) profiles of **1-MIG**.

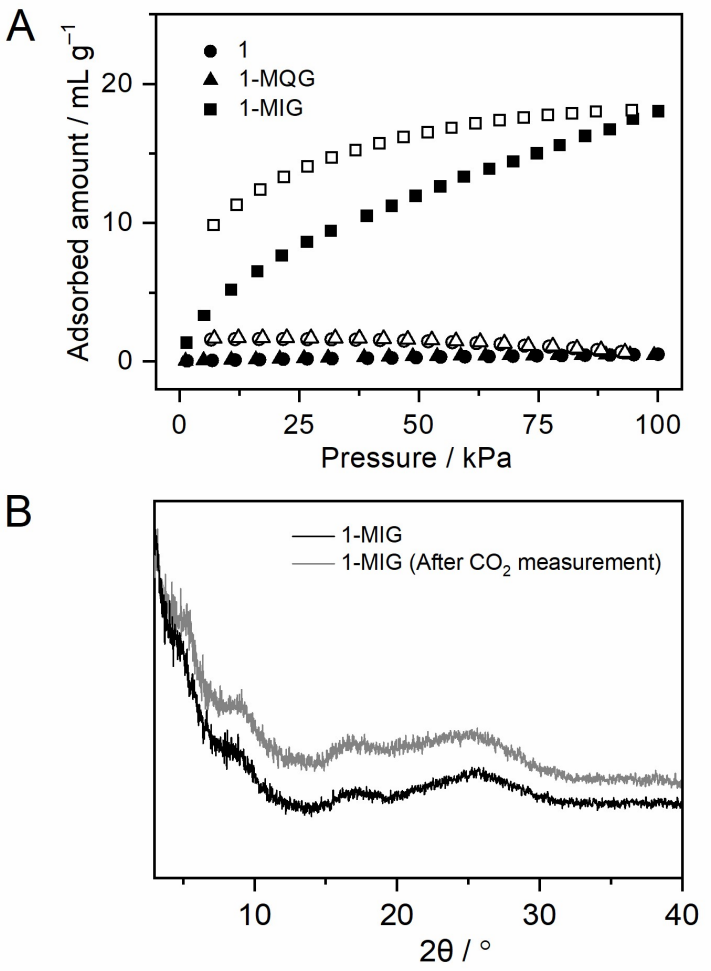


Fig. S10. (A) CO_2 adsorption and desorption isotherms of **1**, **1-MQG** and **1-MIG** at −78.15 °C. (B) PXRD patterns of **1-MIG** before and after CO_2 adsorption and desorption isotherm measurements.

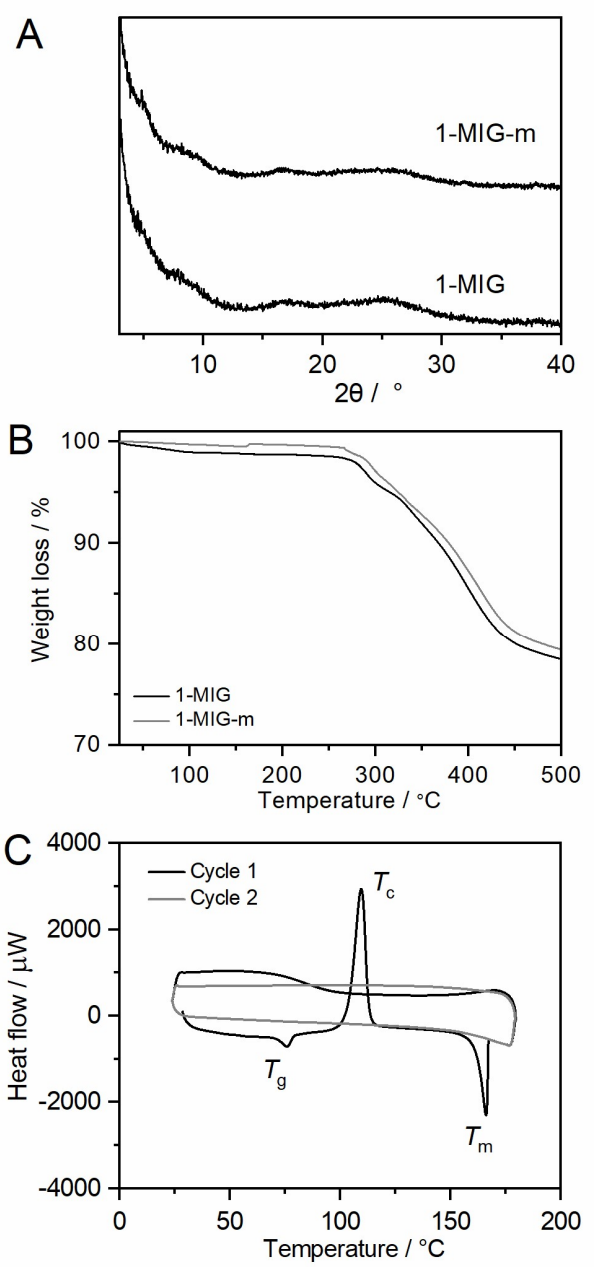


Fig. S11. (A) PXRD patterns of **1-MIG** and **1-MIG-m**. (B) TGA profiles of **1-MIG** and **1-MIG-m**. Scan rates were 10 °C min^{-1}. (C) DSC profiles for **1-MIG-m** (2 cycles). T_g, T_m and T_c represent the glass transition, crystallization and melting temperatures. Scan rates were 10 °C min^{-1}.

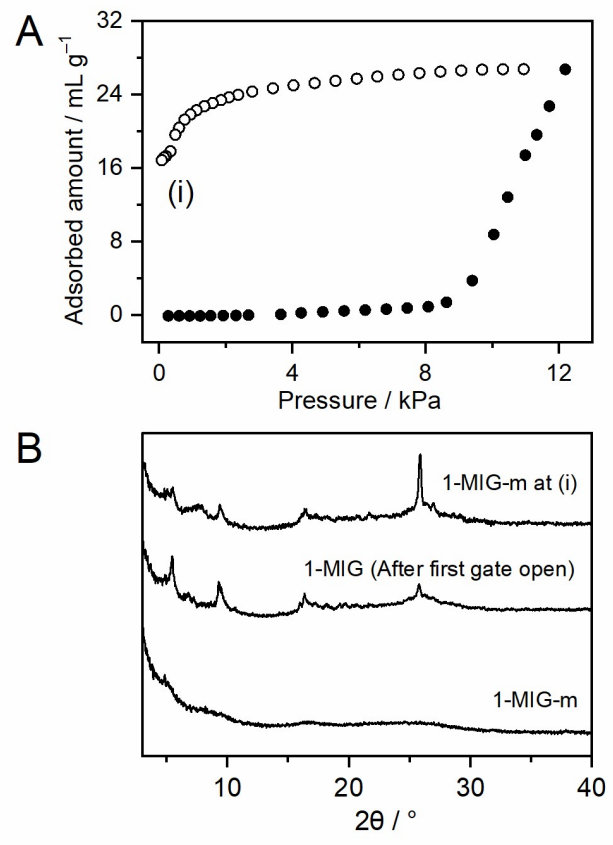


Fig. S12. (A) Benzene vapour sorption study of **1-MIG-m** at 25 °C. (B) PXRD patterns of **1-MIG-m** after benzene sorption measurement (top) and **1-MIG** after first gate open (second from top).

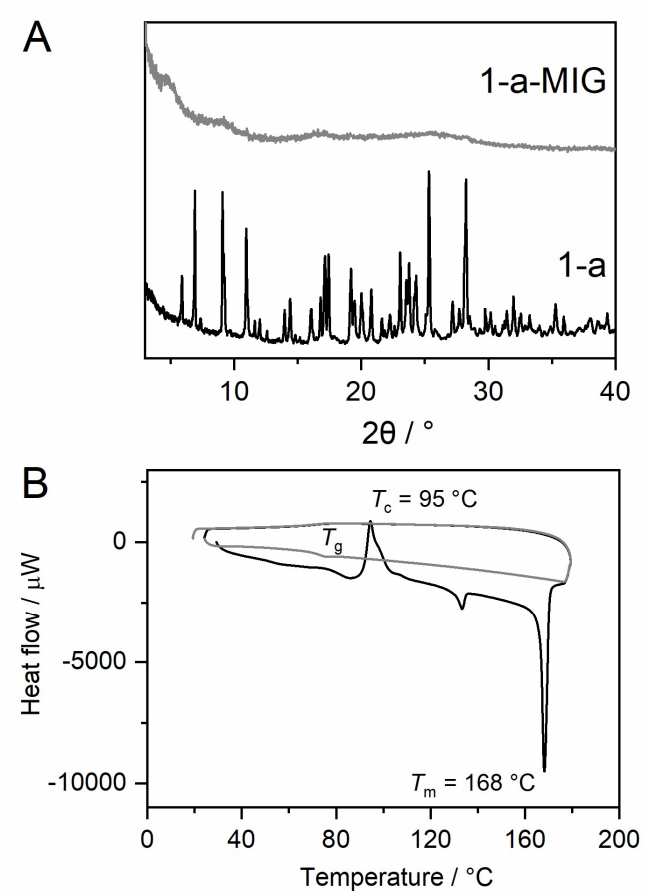


Fig. S13. (A) PXRD patterns of **1-a** and **1-a-MIG**. (B) DSC profile of **1-a-MIG** up to 280 °C under N_2. Scan rates were 10 °C min^{-1}.

References:

1. D. Venkataraman, G. B. Gardner, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 11600-11601.
2. E. Lorch, *J. Phys. C: Solid State Physics*, 1969, **2**, 229-237.
3. B. Ravel and M. Newville, *J Synchrotron Radiat.*, 2005, **12**, 537-541.