Supplementary Material (ESI) for CrystEngComm

Supporting information for Control of the charge-transfer interaction between a flexible porous coordination host and aromatic guests by framework isomerism

Yohei Takashima, Shuhei Furukawa and Susumu Kitagawa

This PDP file includes:

General. X-ray powder diffraction data (XRPD) were collected on a Bruker D8 Discover with GADDS equipped with a sealed tube X-ray generator producing Cu-Kα radiation. Thermogravimetric (TG) analyses were peroformed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 298 K and 773 K under nitrogen atmosphere and with a heating rate of 5 K min^{-1}. Gas sorption isotherms of **2** were recorded on a BELSORP-max volumetric-adsorption instrument from BEL Japan, Inc. All measurements were performed using the samples after pretreatment at 50 °C under vaccum conditions for 2 hours. UV-Vis diffuse reflectance measurements were recorded on a JASCO V-670 spectrometer with integration sphere attachment. The samples were dispersed into aluminium oxide (5 wt%). Single crystal X-ray diffraction measurements were made on a Rigaku AFC10 diffractometer with Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing multi layer mirror monochromated MoKα radiation.

Synthesis of 1⊃DMF. *N, N'*-di(4-pyridyl)-1,4,5,8-naphthalenediimide (dpNDI) was prepared according to the literature procedure.[1] A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (59.6 mg, 0.2 mmol), H_2thdc (34.4 mg, 0.2 mmol), and dpNDI (84 mg, 0.2 mmol) was suspended in DMF (20 mL) and heated at 120 °C for 2 hours. After cooling to room temperature,

the solution was stirred for 24 hours. A slightly yellowish powder of **1⊃DMF** was formed and collected. The number of solvents in **1⊃DMF** was determined by TG and elemental analysis. Elemental analysis of **1⊃DMF** calcd (%) for $C_{48}H_{56}N_{10}O_{14}SZn$: C 52.67, H 5.16, N 12.80; found: C 53.22 H 5.20, N 12.55. Crystals suitable for single-crystal X-ray diffraction structure analysis were obtained by the following procedure. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (14.9 mg, 0.05 mmol), H_2thdc (8.6 mg, 0.05 mmol), and dpNDI (21 mg, 0.05 mmol) were suspended in DMF (5 mL) and heated at 80 ºC for 24 hours. After cooling to room temperature, rod-shaped crystals were obtained.

Synthesis of 2⊃DMF·MeOH. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (59.6 mg, 0.2 mmol), H_2thdc (34.4 mg, 0.2 mmol), and dpNDI (84 mg, 0.2 mmol) was suspended in mixed solvent (DMF/MeOH = 1/1, 20 mL) and heated at 80 ºC for 48 hours. A slightly yellowish powder of **2⊃DMF·MeOH** was formed and collected. The number of solvents in **2⊃DMF·MeOH** was determined by TG and elemental analysis. Elemental analysis of **2⊃DMF·MeOH** calcd (%) for $C_{46}H_{68}N_6O_{20}SZn$: C 49.22, H 6.11, N 7.49; found: C 49.70 H 6.00, N 7.60.

Synthesis of 1⊃anisole, 1⊃DMB and 1⊃NDMA. Powder sample of **1⊃DMF** was immersed in anisole at room temperature for 24h. the resulting sample, **1⊃anisole**, is

collected by filtration. **1ᴅDMB** and **1ᴅNDMA** were prepared in the same way by using 1,2-dimethoxybenzene and N,N-dimethylaniline, respectively.

Synthesis of 2ᴅanisole, 2ᴅDMB and 2ᴅNDMA. These samples were also prepared in the same manner as that of **1ᴅanisole** by using **2ᴅ DMF·MeOH**.

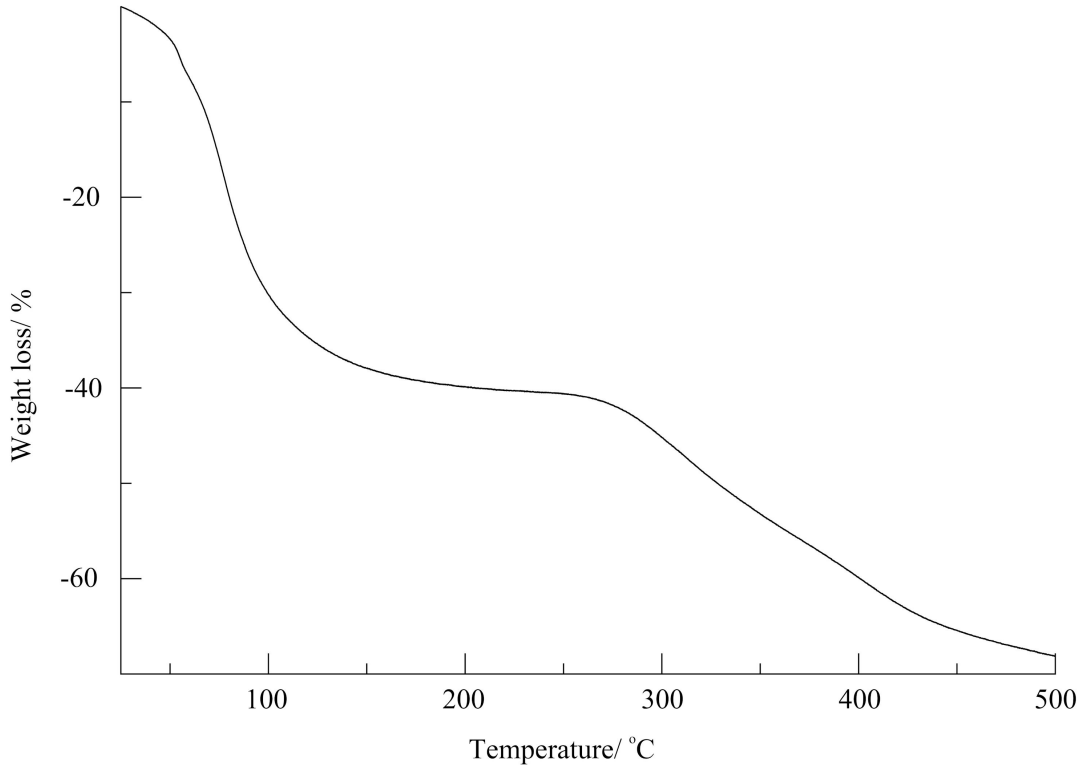

Figure S1 TG analysis showing the weight loss in **1⊃DMF**. The observed weight loss 39.9 wt% at 200 ºC is the weight of 6 DMF (calculated weight loss: 40.1 wt%).

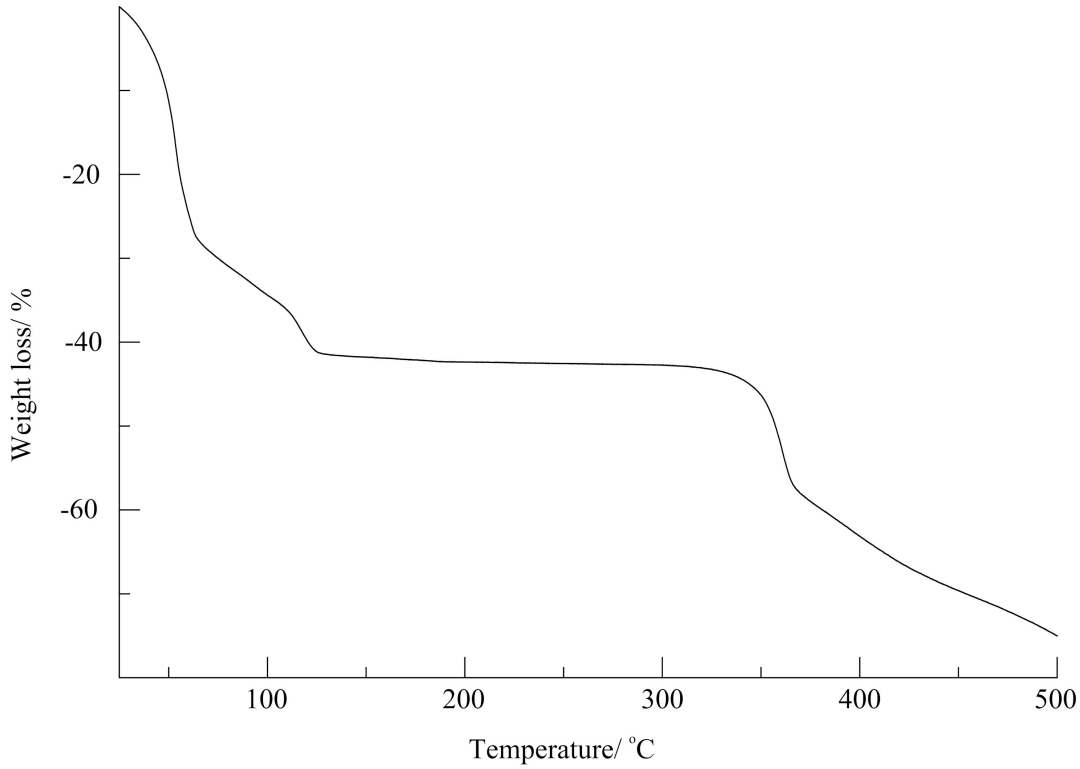

Figure S2 TG analysis showing the weight loss in **2⊃ DMF·MeOH**. The observed weight loss 41.6 wt% at 136 °C is the weight of 10 MeOH and 2 DMF (calculated weight loss: 41.6 wt%).

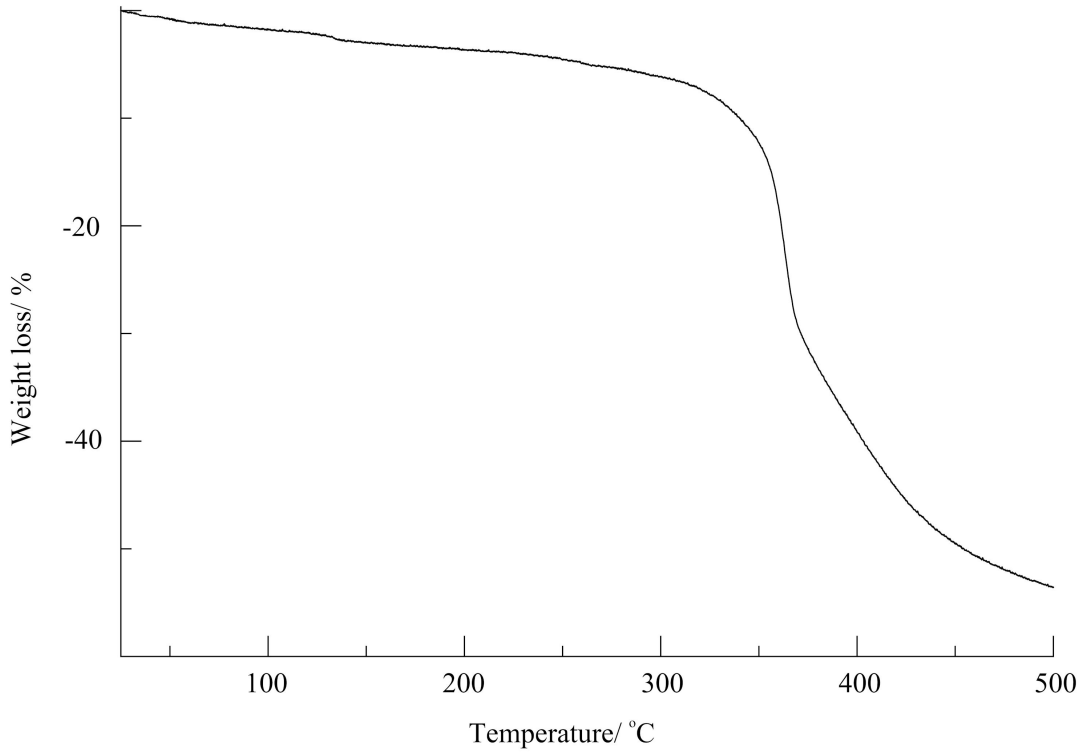

Figure S3 TG analysis of **2**.

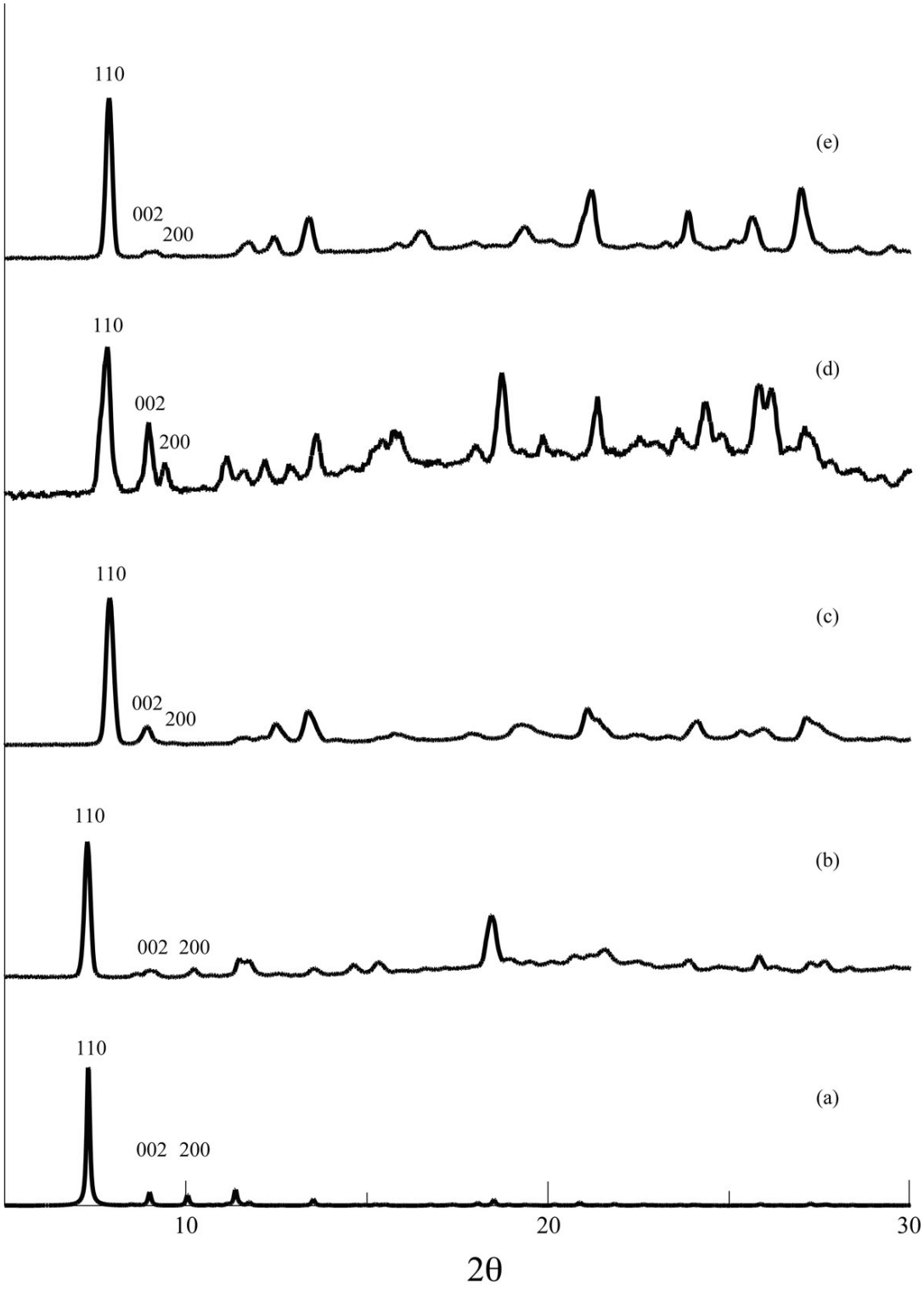

Figure S4 XRPD patterns of (a) simulated **1ᴐDMF** from single crystal, (b) experimental as synthesized form **1ᴐDMF**, (c) **1ᴐanisole**, (d) **1ᴐDMB**, and (e) **1ᴐNDMA**.

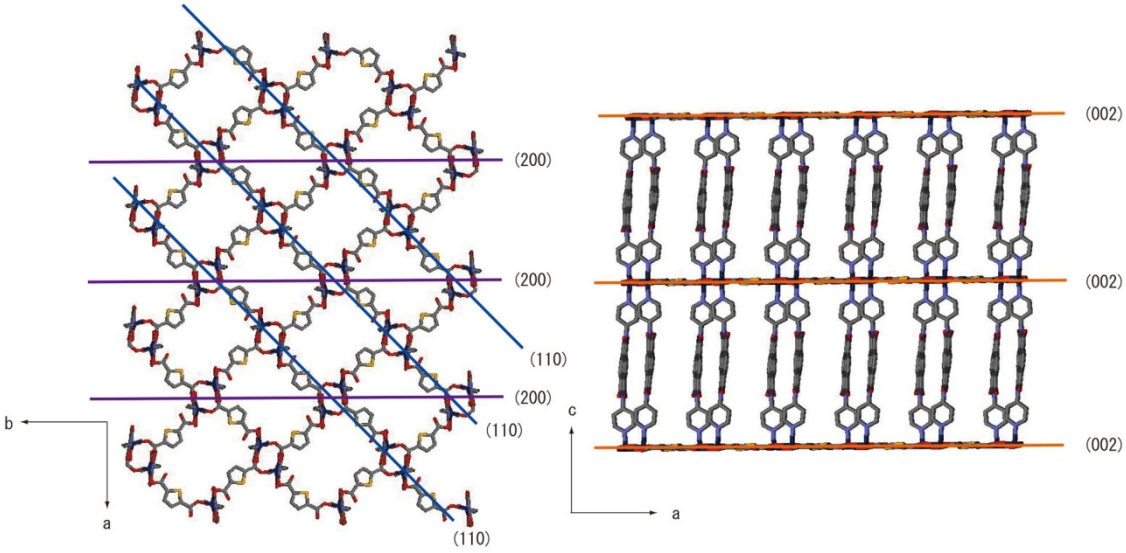

Figure S5 Three crystal faces in **1⊃DMF**.

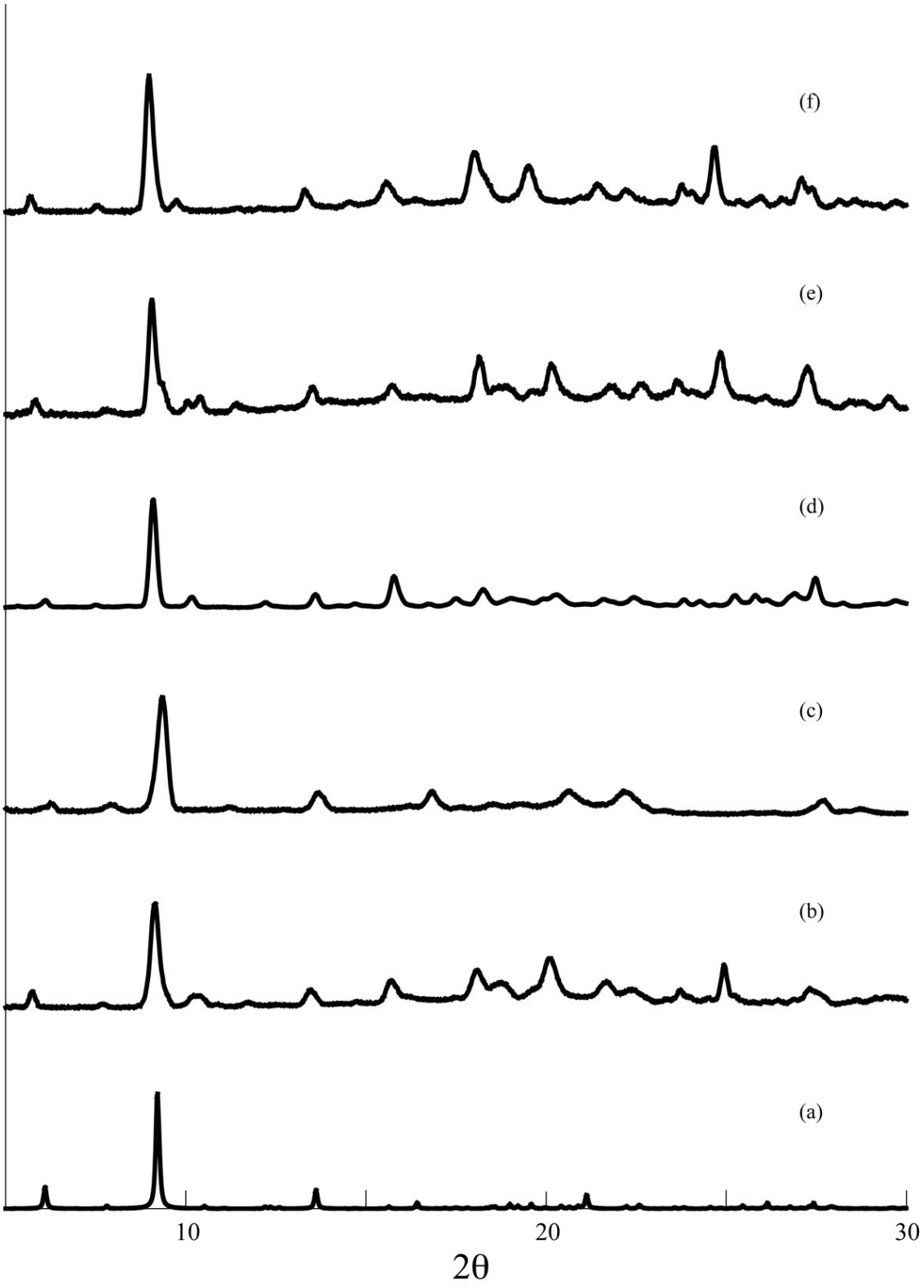

Figure S6 XRPD patterns of (a) simulated **2⊃DMF·MeOH** from single crystal, (b) experimental as synthesized form **2⊃DMF·MeOH**, (c) desolvated form **2**, (d) **2⊃anisole**, (e) **2⊃DMB**, and (f) **2⊃NDMA**

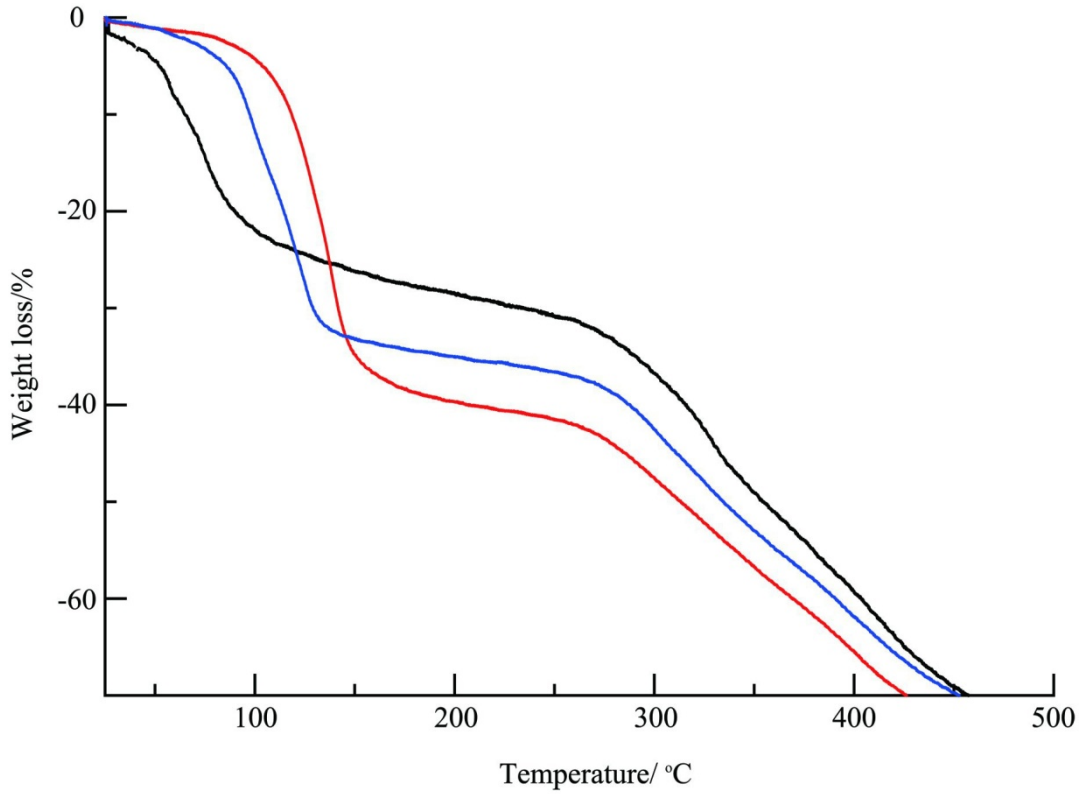

Figure S7 TG analysis showing the weight loss in **1⊃anisole** (black line), **1⊃DMB** (red line) and **1⊃NDMA** (blue line). The observed weight loss 29.2 wt% at 295 °C for **1⊃anisole** is the weight of 2.5 anisole (calculated weight loss: 29.2 wt%), 42.1 wt% at 260 °C for **1⊃DMB** is the weight of 3.5 DMB (calculated weight loss 42.4 wt%) and 35.7 wt% at 226 °C for **1⊃NDMA** is the weight of 3 NDMA (calculated weight loss 35.7 wt%).

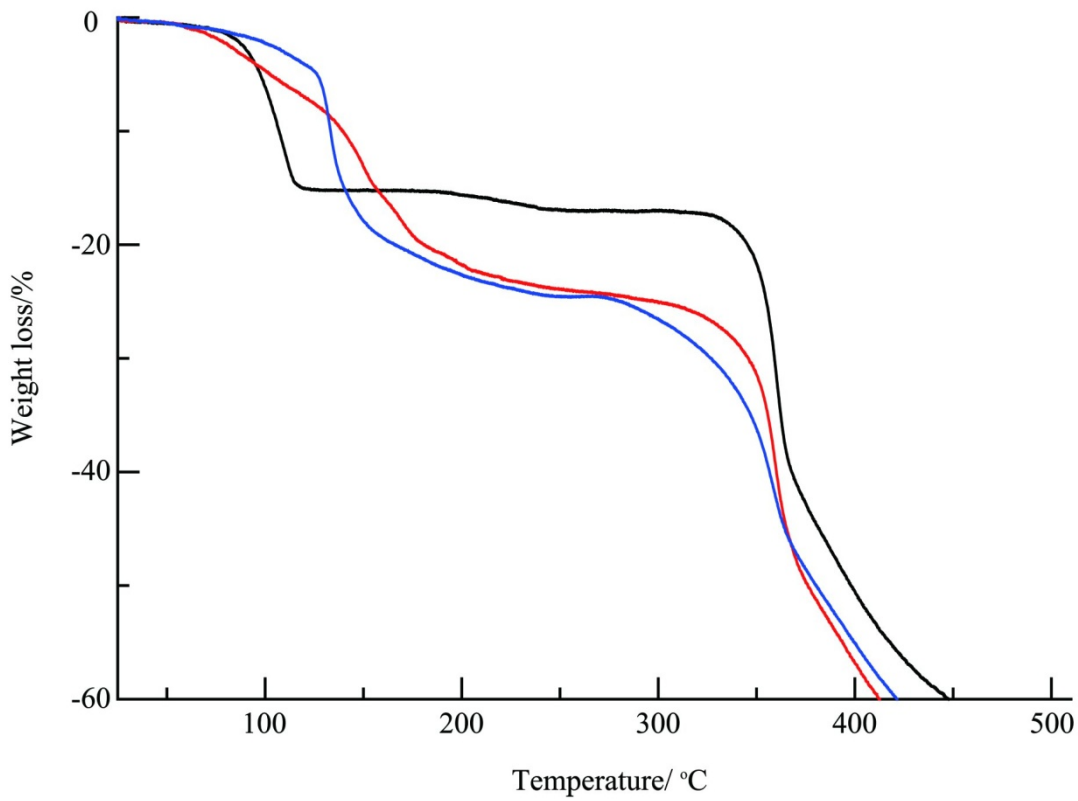

Figure S8 TG analysis showing the weight loss in **2⊃anisole** (black line), **2⊃DMB** (red line) and **2⊃NDMA** (blue line). The observed weight loss 17 wt% at 310 °C for **2⊃anisole** is the weight of 1.25 anisole (calculated weight loss: 17 wt%), 24 wt% at 255 °C for **2⊃DMB** is the weight of 1.5 DMB (calculated weight loss 24 wt%) and 24.4 wt% at 240 °C for **2⊃NDMA** is the weight of 1.75 NDMA (calculated weight loss 24.4 wt%).

Reference

(1) Dinolfo, P. H.; Williams, M. E.; Stern, C. L.; Hupp, J. T. *J. Am. Chem. Soc.* **2004**, *126*, 12989-13001.