Crystal engineering of a hybrid metal-organic host framework and its single-crystal-to-single-crystal guest exchange using second sphere coordination[†]‡

Lei Li,^a Jian Tong,^a Fang Guo*^a Javier Martí-Rujas*^b

Contents

Materials and instrumentation

Figure S1. ¹H NMR corresponding to the as synthesized SSC adduct $1 \cdot G_1$.

Figure S2. Crystal packing viewed along the *b*-axis showing the uncoordinated Br- anions forming hydrogen bonds with the cations.

Figure S3. Crystal packing viewed along the *c*-axis showing the uncoordinated Br- anions forming hydrogen bonds with the cations.

Figure S4. Experimental XRPD paters measured at rt after being heated to 100 °C, 150 °C, and 200 °C.

Figure S5. TGA curve exhibits an initial weight loss from RT to 195 °C, corresponding to the releases of methanol molecules. The following weight loss at higher temperature results from the decomposition of the complex.

Figure S6. ¹H NMR of the heated sample dipped into dichloromethane for 3 days.

Figure S7. ¹H NMR of the heated sample dipped into chloroform for 3 days.

Figure S8. ¹H NMR of the heated crystal 1 immersed into CH₃CN for 2 days.

Figure S9. ¹H NMR of the heated crystal 1 immersed into THF for 2 days.

Figure S10. ¹H NMR of the heated crystal 1 immersed into toluene for 2 days.

Figure S11. ¹H NMR of the heated crystal 1 immersed into chlorobenzene for 2 days.

Figure S12. ¹H NMR of the heated crystal 1 immersed into nitrobenzene for 2d

Figure S13. a: IR of crystal 1; b- g: IR of the heated samples dipped into different solvents for 2d: b: CH₃CN, c: THF, d: dichloromethane, e: chloroform, f: toluene, g: nitrobenzene.

Figure S14. Simulated XRPD comparison among $1 \cdot G_1$ (black) and $1 \cdot G_2$ (red). Inset: view of the shift affecting the 011 and 020 planes.

Figure S15. The heated samples dipped into different solvents: a: dichloromethane, b: chloroform, c: CH₃CN, d: THF, e: toluene.

Figure S16. ¹H NMR of the heated crystal **2** immersed into dichloromethane for different times: 5:1. a: 1d, b: 2d, c:3d, d:4d.

Figure S17. ¹H NMR of the heated crystal **2** immersed into CH₃CN for different times; a: 1d; b: 2d, c: 3d; d: 4d.

Figure S18. ¹H NMR of heated crystal 2 immersed into chlorobenzene for 2 days.

Figure S19. The heated sample dipped into nitrobenzene for 2 days.

Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purifications. IR spectra were obtained with a PerkinElmer 100 FT-IR spectrometer (USA) using KBr pellets. NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz) at 25°C with TMS as the internal reference. Dimethyl sulfoxide-d6 was used to dissolve the crystals in order to analyse the guest exchange. TGA (thermal gravimetric analysis) was collected on a TGA/SDTA851e under 15 mL min⁻¹ nitrogen gas flow.

Preparation of crystal 1.G1

0.0594 g (0.3 mmol) 4, 4'-methylenedianiline (L) was dissolved into 1 ml methanol, and 0.1032 g (0.3 mmol) CdBr₂·4H₂O was dissolved into 3 ml methanol with 5 drops hydrobromic acid. The two solutions were mixed in a 50 ml Erlenmeyer flask. The flask was allowed to stand for about one week at room temperature when colorless block crystals crystallized. M. p. 225-235°C. ¹H NMR (DMSO, 300 MHz): δ : 4.00 (2H, s, -CH₂); 9.78-10.10 (6H, m, -NH₃⁺); 7.36 (8H, m, ArH); 3.16 (1H,s, -CH₃ of CH₃OH).



Figure S1. ¹H NMR corresponding to the as synthesized SSC adduct $1 \cdot G_1$.



Figure S2. Crystal packing viewed along the *b*-axis showing the uncoordinated Br- anions forming hydrogen bonds with the cations.



Figure S3. Crystal packing viewed along the *c*-axis showing the uncoordinated Br- anions forming hydrogen bonds with the cations.



Figure S4. Experimental XRPD paters measured at rt after being heated to 100 °C, 150 °C, and 200 °C.

TGA analysis

The TGA experiment for crystal 1 was performed under a N_2 atmosphere with a heating rate of 10 °C·min⁻¹ in the temperature range of 20-800 °C, as shown in Fig. S2.



Figure S5. TGA curve exhibits an initial weight loss from RT to 195 °C, corresponding to the releases of methanol molecules. The following weight loss at higher temperature results from the decomposition of the complex.

Guest exchange experiments using $1 \cdot G_1$ as a host framework.

Crystal **1** was heated to 190°C for 2h and then cooled down to room temperature, after that the heated sample was dipped into dichloromethane and chloroform for 3 days, respectively.

As shown in Fig S3, the ¹H NMR shows there is no dichloromethane and chloroform in the spectrum which indicates that such guest molecules are not included in the channel of **1**.



Figure S6. ¹H NMR of the heated sample dipped into dichloromethane for 3 days.



Figure S7. ¹H NMR of the heated sample dipped into chloroform for 3 days.

Crystal 1 was heated to 200 °C for 1h and then cooled down to room temperature, after that the heated sample was dipped into CH_3CN , for 2 days, respectively.



Figure S8. ¹H NMR of the heated crystal 1 immersed into CH₃CN for 2 days.

¹ H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.26-7.36 (8H, m, ArH), 9.47-9.98 (6H, m, -NH₃⁺), 2.07 (0.75H, s, CH₃ of CH₃CN).

The molar ratio of the ligand and CH_3CN is 4:1. This result is in agreement with the crystallographic analysis.



Figure S9. ¹H NMR of the heated crystal 1 immersed into THF for 2 days.

¹ H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.26-7.36 (8H, m, ArH), 9.46-10.08 (6H, m, -NH₃⁺), 1.72-1.77 (1.60H, m, -CH₂ of THF), 3.57-3.62(1.60H, m, -CH₂ of THF).

The molar ratio of the ligand and THF is 5:2.



Figure S10. ¹H NMR of the heated crystal 1 immersed into toluene for 2 days.

¹ H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.27-7.37 (8H, m, ArH), 9.35-10.01 (6H, m, -NH₃⁺).

There is no toluene in the spectrum.

Figure S11. ¹H NMR of the heated crystal 1 immersed into chlorobenzene for 2 days.

¹ H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.26-7.36(8H, m, ArH), 9.45-10.01 (6H, m, -NH₃⁺).

There is no chlorobenzene in the spectrum.

Figure S12. ¹H NMR of the heated crystal 1 immersed into nitrobenzene for 2d

¹ H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.26-7.36(8H, m, ArH), 9.46-10.06 (6H, m, -NH₃⁺).

There is no nitrobenzene in the spectrum.

Figure S13. a: IR of crystal 1; b- g: IR of the heated samples dipped into different solvents for 2d: b: CH₃CN, c: THF, d: dichloromethane, e: chloroform, f: toluene, g: nitrobenzene.

Figure S14. Simulated XRPD comparison among $1 \cdot G_1$ (black) and $1 \cdot G_2$ (red). Inset: view of the shift affecting the 011 and 020 planes.

Comparison to Crystal 2.G1.

The guest behaviour of the homologous Cu SSC adduct $[4LH_2] \cdot [CuCl_{10}] \cdot (H_2O) \cdot (CH_3OH)$ (2·G₁) was monitored in the presence of different solvents. The heated sample of 2·G₁ were introduced in dichloromethane, chloroform, CH₃CN, THF and toluene, respectively. ¹H NMR shows that only dichloromethane and CH₃CN were adsorbed successfully into the structure, as shown in Figure S8.

Figure S15. The heated samples dipped into different solvents: a: dichloromethane, b: chloroform, c: CH₃CN, d: THF, e: toluene.

We also studied the saturation time of the adsorption of dichloromethane, and CH_3CN , we immersed the heated crystal **2** into dichloromethane and CH_3CN for 1d, 2d, 3d and 4d, respectively. The ¹H NMR shows that the amount of the adsorption is saturation for 1d for dichloromethane, the molar ratio of the ligand and dichloromethane is 5:1, and the saturation time of CH_3CN is 3d, the molar ratio of the ligand and CH_3CN is 5:1. As shown in the Fig. S9 and Fig. S8.

Figure S16. ¹H NMR of the heated crystal **2** immersed into dichloromethane for different times: 5:1. a: 1d, b: 2d, c:3d, d:4d.

Figure S17. ¹H NMR of the heated crystal **2** immersed into CH₃CN for different times; a: 1d; b: 2d, c: 3d; d: 4d.

Figure S18. ¹H NMR of heated crystal 2 immersed into chlorobenzene for 2 days.

¹H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.26-7.34(8H, m, ArH), 10.01-10.43 (6H, m, -NH₃⁺).

As observed there is no chlorobenzene included in the crystal.

Figure S19. The heated sample dipped into nitrobenzene for 2 days.

¹H NMR (DMSO, 300 MHz) δ: 4.00 (2H, s, -CH₂), 7.26-7.34(8H, m, ArH), 10.06-10.35 (6H, m, -NH₃⁺), 7.65-7.70 (0.14H, m, ArH of NB), 7.85 (0.07H, m, ArH of NB), 8.22-8.25 (0.14H, m, ArH of NB).

The ratio of nitrobenzene and L is 1:14. The tiny amount of nitrobenzene is probably due to small cracks in the crystal or because it was not dried properly. The size of nitrobenzene is too big to fit in the channels.