A soft coordination polymer derived from container molecule ligands

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Contents:

General Experimental Details

All solvents were used as received from Fisher (Pittsburgh, PA). All reagents were used as received from Acros (Pittsburgh, PA) or Aldrich (Milwaukee, WI) and used without further purification. ^{1}H NMR were recorded on a Mercury Varian 300MHz NMR spectrometer and ^{13}C NMR were recorded on the same instrument at 79.1 MHz. All NMR spectra were collected at 25°C and referenced to the residual solvent peaks. Elemental Analyses were performed with a Perkin Elmer 2400 microanalyzer. Uncorrected melting points were determined on a Thomas Hoover capillary melting point apparatus. Infrared spectroscopy was performed using a Perkin-Elmer Spectrum One FT-IR, scanning from 4500 cm^{-1} to 500 cm^{-1}. Thermogravimetric analyses were performed using a TA Instruments TGA 2050 under a constant stream of dry nitrogen gas. Powder X-ray diffraction was performed using a Rigaku RAPID powder diffractometer (Cu$_{K\alpha}$ radiation) equipped with a curved image plate area detector. Single crystal X-ray diffraction was performed using a Siemens SMART 1K diffractometer (-100°C) using Mo$_{K\alpha}$ radiation. (±)-**1** was synthesized according to a reported literature procedure.[1]

Syntheses

(±)-H$_3$**2**

(±)-**1** (289mg, 0.223 mmol) was dissolved in 22mL DMF. 10 % NMe$_4$OH in H$_2$O (4.1 mL, 5.5 mmol) was added in one portion. The solution was heated to 80°C for 2.5 hours, and reaction was monitored by TLC (8:1 CH$_2$Cl$_2$/Et$_2$O). Solvent was removed under reduced pressure and the remaining solid was dissolved in 30 mL of 1:1 H$_2$O/acetone solution. 12M HCl was added to the solution and the resulting precipitate was filtered and washed with distilled H$_2$O. Crude (±)-H$_3$**2** was recrystallized by dissolving in an acetone/methanol mixture and allowing the slow evaporation of the acetone. Yield: 252 mg, 87%. M.P. 240°C (dec). ^{1}H NMR (300MHz, DMSO[D$_6$], 298K) δ 7.96 (s, 6H, Ar-*H*), δ 7.33 (s, 3H, Ar-*H*), δ 6.90 (s, 6H, Ar-*H*), δ 6.70 (s, 6H, Ar-*H*), δ 5.12 (d, 6H, Ar-CH_2O, ^2J(H-H) = 12.6 Hz), δ 5.02 (d, 6H, ^2J(H-H) = 12.6 Hz, Ar-CH_2O), δ 4.60 (d, 6H, ^2J(H-H) = 12.5 Hz), Ar-CH_{2a}Ar), δ 3.39 (s, 18H, *OCH$_3$*), δ 3.39 (d, 6H, ^2J(H-H) = 12.5 Hz). ^{13}C NMR (75.5 MHz, DMSO[D$_6$], 298K) δ 167.94, 148.00, 146.85, 139.21, 132.77, 132.36, 131.84, 127.68, 115.21, 114.98, 69.57, 56.55, 55.05, 35.73. ^{1}H NMR (300MHz, Acetone[D$_6$], 298K) δ 8.12 (s, 6H, Ar-*H*), δ 7.54 (s, 3H, Ar-*H*), δ 7.02 (s, 6H, Ar-*H*), δ 6.82 (s, 6H, Ar-*H*), δ 5.15 (s, 12H, Ar-CH_2O), δ 4.73 (d, 6H, ^2J(H-H) = 13.3 Hz, Ar-CH_2O), δ

3.56 (s, 18H, *OCH_3*), δ 3.51 (d, 6H, ^2J(H-H) = 13.3 Hz), Ar-CH_{2a}Ar). IR (cm^{-1}, selected bands) 3448, 2927, 1706, 1607, 1509, 1479, 1448, 1398, 1375, 1261, 1214, 1144, 1086, 1027, 948, 883, 852, 774, 740, 618, 530. Anal. calcd. for $C_{75}H_{66}O_{18}$ + 2 C_3H_6O: C, 70.94; H, 5.73. Found: C, 70.66 H 5.80.

3·*solvent*
(±)-H_3**2** (103 mg, 0.082 mmol) and $Cu(NO_3)_2\cdot 2.5H_2O$ (72 mg, 0.31 mmol) were dissolved in 2:1 DMF:MeOH (36 mL) and pyridine (3.6 mL). The solution was heated to 110˚C for 13 hours in a Parr bomb. The solution was subsequently cooled at 0.1˚C/min to 90˚C, and held at 90˚C for 1 hour. The solution was further cooled at 0.1 ˚C/min to 60˚C, held at 60˚C for 1 hour, and then cooled at 0.1˚C/min to 40˚C. Dark blue crystals were filtered and weighed (129 mg, yield = 90% (yield based on a formulation of **3**·DMF·MeOH, as estimated for partially desolvated-**3**). M.P. 220°C (dec). IR (cm^{-1}, selected bands) 3431, 2932, 2866, 1663, 1608, 1580, 1510, 1482, 1449, 1398, 1372, 1216, 1195, 1146, 1088, 1045, 944, 929, 884, 853, 789, 748, 700, 662, 639, 618, 532, 485. Due to its variable solvent composition, the material resisted agreeable elemental analyses. Powder X-ray diffraction experiments verify that the bulk material possesses the same structure as that established from the single crystal structure determination.

Crystal Structure of (±)-1$\subset$DMF·2DMF·Et_2O

Crystal data for [(±)-**1**$\subset$DMF]·2DMF·Et_2O: $C_{91}H_{103}N_3O_{22}$, M = 1590.76, colorless prism, 0.42 × 0.22 × 0.20 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 20.862(4), b = 17.512(3), c = 24.050(4) Å, β = 108.469(3)°, V = 8334(2) Å^3, Z = 4, D_c = 1.268 g/cm^3, F_{000} = 3384, Siemens SMART 1K CCD, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\theta_{max}$ = 50.0º, 61481 reflections collected, 14666 unique (R_{int} = 0.0693). Final *GooF* = 0.941, *R1* = 0.0599, *wR2* = 0.1494, *R* indices based on 7690 reflections with I >2sigma(I) (refinement on F^2), 1036 parameters, 80 restraints. Lp and absorption corrections applied, μ = 0.090 mm^{-1}. The molecule of diethyl ether was highly disordered and modeled with the SQUEEZE, which estimates, per formula unit, a residual electron density of 43.5 e$^-$ (42 e$^-$ calc.) within a void volume of 162 Å^3.

Unit Cell Analyses

The unit cells of two single crystals of **3**·solvent were monitored in real time. The crystals were removed from the mother liquor and quickly (5-20 seconds) placed into the cold temperature stream (-100°C) of the X-ray diffractometer's low temperature apparatus (LT-2, Siemens). Unit cell determinations were accomplished by the default "matrix" procedure, which collects three sets of twenty images (60 seconds/image) from orthogonal wedges of reciprocal space, harvests the images for reflections, and indexes the reflections to a unit cell. The crystals were then removed from the low temperature stream, allowed to stand for a defined period of time, and then reintroduced to the low temperature stream for subsequent unit cell determinations. The figure below plots the determined unit cell volumes as a function of cumulative time spent at ambient conditions for two crystals. The results for the two crystals are superimposed. Note that the deceleratory rate of contraction in unit cell volumes.

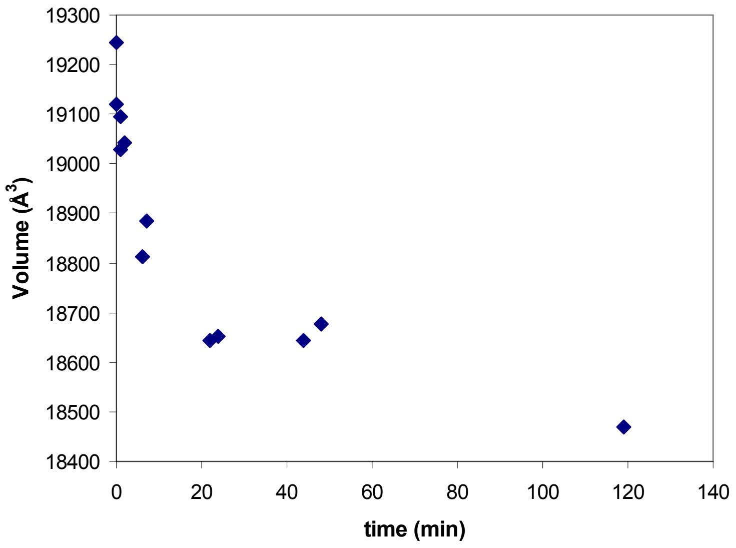

Figure S1. Experimentally determined unit cell volumes for two crystals as a function of cumulative time at ambient conditions.

Powder X-ray Diffraction (PXRD) of 3.

The PXRD specimen was mounted in a doubly open-ended glass capillary (0.5 mm).

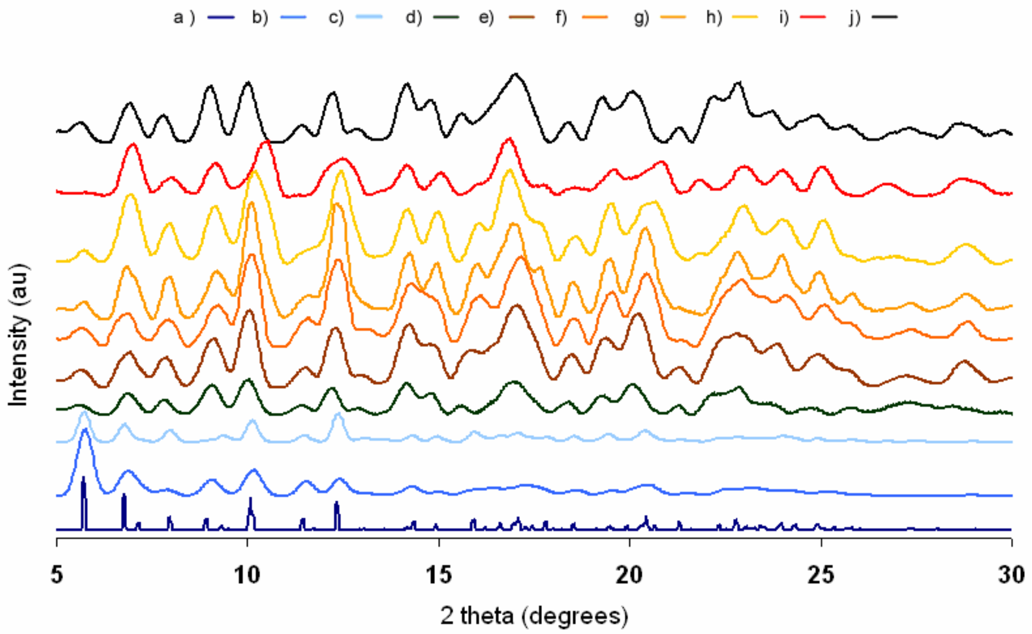

Figure S2. a) Calculated powder X-ray diffraction (PXRD) pattern of fully solvated **3**·solvent as determined (using Lazy-Pulverix) from the experimentally determined room temperature unit cell of **3**·solvent (sealed capillary, surrounded with solvent) and the low temperature atomic coordinates from the single crystal structure of **3**·solvent; b) Exactly as for a), but with artificial broadened peaks; c) As for a), but using the room temperature unit cell determined from a single crystal of desolvated-**3**; d) Experimental PXRD pattern of **3**·solvent, initially moist with mother liquor; e)-i) Experimental PXRD patterns of **3** monitoring the desolvation process occasionally at over a period of three weeks at room temperature; j) Experimental PXRD pattern of the material in i), but after moistening the material with a drop of mother liquor.

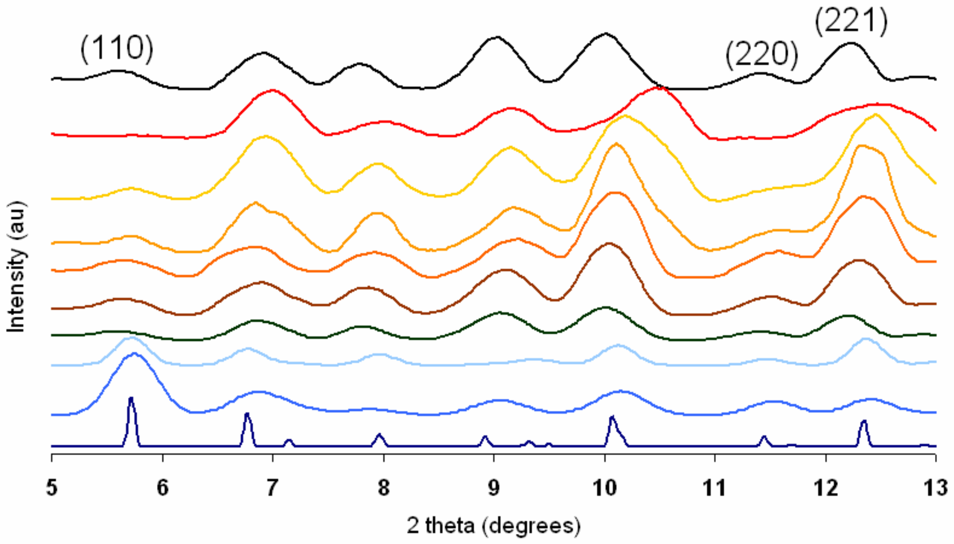

Figure S3. Magnified view of Figure S2, with selected reflections labelled.

Thermal Gravimetric Analysis of 3·*solvent*

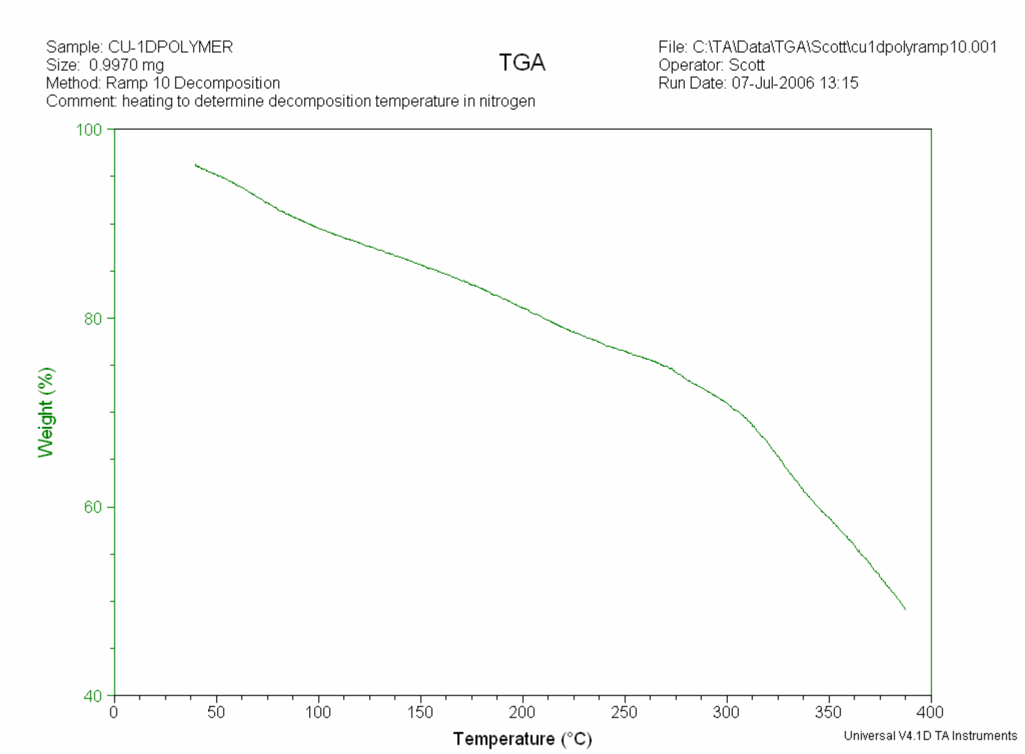

Figure S4. Freshly prepared **3**·*solvent* was heated 10°C/min from room temperature to 380°C. Although mass loss is continuous, three pseudo-transitions can be discerned: a low temperature mass loss from room temperature to *ca.* 100°C, a second transition from 150°C to 220°C and a third starting near 260°C. The third mass loss coincides with decomposition.