# Electronic Supplementary Information for:

# From Discrete Molecule, to Polymer, to MOF: Mapping the Coordination Chemistry of $Cd^{II}$ Using $^{113}Cd$ Solid-State NMR

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# Experimental Section

**General Considerations**: All manipulations were performed under aerobic conditions using materials as received from commercial suppliers (Sigma Aldrich, Strem Chemical). The ligand 2,4,6-tris(2-pyrimdyl)-1,3,5-triazine (TPymT)[1] and **1**[2] were prepared according to previously published procedures.

**Synthesis of 2**: TPymT (0.05 mmol, 15.6 mg) and $Cd(NO_3)_2$•$4H_2O$ (0.15 mmol, 40.0 mg) were placed in 20 ml scintillation vial. MeCN (10 ml) was added and the resulting mixture sonicated for 10 minutes. The mixture was heated from room temperature to 90 °C over a period of 2 hours, followed by heating at 90 °C for 24 hours. Cooling to room temperature over a period of 2 hours, resulted in small yellow block-like crystals suitable for single crystal X-ray diffraction in approximately 76% yield.

**Synthesis of 3**: TPymT (0.05 mmol, 15.6 mg) and $Cd(OAc)_2$•$2H_2O$ (0.15 mmol, 40.0 mg) were placed in 20 ml glass scintillation vial. MeCN/DMF (10 ml, 1:1) was added and the resulting mixture sonciated for 10 minutes. The mixture was heated from room temperature to 90 °C over a period of 2 hours, followed by heating at 90 °C for 24 hours. Subsequent cooling to room temperature over a period of 2 hours, resulted in small yellow block-like crystals suitable for single crystal X-ray diffraction in approximately 4% yield.

**Single Crystal X-ray Diffraction**

Single crystal X-ray diffraction data were collected at 200(2) K on Bruker Smart and Kappa Apex II CCD diffractometers with graphite-monochromatised Mo-$K_\alpha$ radiation. Data collection and processing were performed with the Bruker APEX II software package.[3] Semi-empirical absorption corrections based on equivalent reflections were applied.[4] The structures were solved by direct methods and refined with fullmatrix -least-squares procedures using SHELXL[5] and WinGX.[6] All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated based on the geometry of related non-hydrogen atoms. No constraints or restraints were applied during the refinement of **2** and **3**. The SQUEEZE routine of Platon[7] was used to account for disordered solvent in the lattice of **3**. While a large solvent volume (accounting for about 57% of the structure) was located, the main part of the structure was stable during the refinement and in the absence of SQUEEZE the solvent could not be easily modelled in a conventional way. See the cif. file for full details. In all cases analysis of intermolecular interactions was performed using the PLATON.[7]

**Powder X-ray Diffraction**

Data for **2** and **3** were collected using a RIGAKU Ultima IV equipped with a Cu-$K_\alpha$ radiation source, over a $2\theta$ range = 0 - 40°, and compared with calculated patterns from single crystal X-ray data.

**Solid-State NMR spectroscopy**

Solid-state NMR spectra were recorded at 9.4 T and 11.7 T using Bruker AVANCE III HD and AVANCE II spectrometers at Larmor frequencies of $\nu(^{1}H)$ = 400.130 and 500.130 MHz, $\nu(^{13}C)$ = 100.613 and 125.758 MHz, $\nu(^{113}Cd)$ = 88.802 and 110.995 MHz, respectively. Triple resonance 4 mm CP/MAS probes were used and spinning speeds were set as described in the corresponding figures, at either 10 kHz or 11 kHz. The $^{113}$Cd-$^{113}$Cd CP/MAS COSY and $^{113}$Cd-$^{113}$Cd homonuclear *J*-resolved CP/MAS pulse programs were adopted from the literature.[8] The $^{1}$H NMR and $^{13}$C NMR isotropic chemical shifts were calibrated using external secondary references; adamantane (1.85 ppm; central signal) and glycine (176.03 ppm; carbonyl signal) respectively, with respect to TMS. The $^{113}$Cd isotropic chemical shift was calibrated with respect to cadmium nitrate as an external standard (-100 ppm; central signal).[9,10] Contact times of

2000 μs and 4500 μs were used for the transfer of proton magnetization in the $^{13}C$ CP/MAS NMR and $^{113}Cd$ CP/MAS NMR spectra, respectively. $^{15}N$ CP/MAS NMR spectra were measured at 5 kHz spinning speed with contact times of 5000 and 10000 μs for MOF and polymer system, respectively. $^{15}N$ chemical shifts were calibrated using glycine at 33.4 ppm, as an external standard. During the signal acquisition of $^{13}C$, $^{15}N$ and $^{113}Cd$ CP/MAS NMR spectra, high-power decoupling (SPINAL64) was used to eliminate strong heteronuclear dipolar couplings. The recycle delays for $^{1}H$ and $^{13}C$ CP/MAS NMR measurements were 4 s. $^{15}N$ and $^{113}Cd$ CP/MAS NMR experiments were measured with 10 s recycle delays. The samples were all placed into 4 mm $ZrO_2$ rotors and all NMR experiments were performed at room temperature.

**DFT Calculations**

DFT calculations were performed on an isolated unit of **2** obtained using crystallographic coordinates as a starting point. A structure similar to **2** (Fig 1b) of the main text was used, however, in order to model the Cd-Cd core, only the two core Cd atoms were kept, while the others were removed. In addition, the furthest pyrimidine rings were replaced with hydrogen atoms to increase the computational feasibility. The Amsterdam Density Functional (ADF) software, version 2016.101, was used to perform both geometry optimizations and NMR calculations on the model unit. First, the Cd and H positions were geometry optimized using the GGA PW91 functional with a triple zeta basis set (TZP). Experimental NMR coupling was best reproduced using the revPBE functional with the TZP basis set. The CPL program of ADF was used to obtain *J*-coupling values.[11] In each case, scalar relativistic effects were accounted for using the zeroth order regular approximation (ZORA).

**Table S1:** Pertinent crystallographic data for complex **2**.

| | | |
|---|---|---|
| Empirical formula | C15 H9 Cd2 N13 O12 | |
| Formula weight | 788.15 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | *Pccn* | |
| Unit cell dimensions | a = 9.1873(8) Å | alpha = 90°. |
| | b = 12.5692(11) Å | beta = 90°. |
| | c = 20.0824(18) Å | gamma = 90°. |
| Volume | 2319.1(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.257 $Mg/m^3$ | |
| Absorption coefficient | 1.929 $mm^{-1}$ | |
| F(000) | 1528 | |
| Crystal size | 0.478 x 0.262 x 0.076 $mm^3$ | |
| Theta range for data collection | 2.028 to 27.881°. | |
| Index ranges | -12<=h<=12, -16<=k<=16, -26<=l<=26 | |
| Reflections collected | 26009 | |
| Independent reflections | 2775 [R(int) = 0.0318] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2775 / 0 / 192 | |
| Goodness-of-fit on $F^2$ | 1.111 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0297, wR2 = 0.0692 | |
| R indices (all data) | R1 = 0.0361, wR2 = 0.0721 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.791 and -0.502 e.$Å^{-3}$ | |

**Table S2:** Pertinent crystallographic data for complex **3**.

| | | |
|---|---|---|
| Empirical formula | C10 H6 Cd N4 O4 | |
| Formula weight | 358.59 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Cubic | |
| Space group | *Im-3m* | |
| Unit cell dimensions | a = 30.1172(7) Å | a= 90°. |
| | b = 30.1172(7) Å | b= 90°. |
| | c = 30.1172(7) Å | g = 90°. |
| Volume | 27317.7(19) $Å^3$ | |
| Z | 48 | |
| Density (calculated) | 1.046 $Mg/m^3$ | |
| Absorption coefficient | 0.968 $mm^{-1}$ | |
| F(000) | 8352 | |
| Crystal size | 0.242 x 0.240 x 0.192 $mm^3$ | |
| Theta range for data collection | 1.656 to 27.913°. | |
| Index ranges | -39<=h<=39, -35<=k<=39, -39<=l<=39 | |
| Reflections collected | 107139 | |
| Independent reflections | 3118 [R(int) = 0.0515] | |
| Completeness to theta = 25.242° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7456 and 0.6655 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3118 / 0 / 96 | |
| Goodness-of-fit on $F^2$ | 1.191 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0342, wR2 = 0.0770 | |
| R indices (all data) | R1 = 0.0493, wR2 = 0.0977 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.525 and -0.339 e.$Å^{-3}$ | |

| **Table S3:** Bond lengths (Å) and angles (°) measured in respect of complex **2**. | |
|---|---|
| Cd(1)-O(20) | 2.317(2) |
| Cd(1)-O(15) | 2.351(2) |
| Cd(1)-N(9) | 2.352(2) |
| Cd(1)-N(1) | 2.411(2) |
| Cd(1)-O(15)#1 | 2.423(2) |
| Cd(1)-O(19) | 2.470(2) |
| Cd(1)-N(12) | 2.546(2) |
| N(1)-C(6) | 1.324(4) |
| N(1)-C(2) | 1.344(4) |
| C(2)-C(3) | 1.378(4) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.371(5) |
| C(3)-H(3) | 0.9500 |
| C(4)-N(5) | 1.340(4) |
| C(4)-H(4) | 0.9500 |
| N(5)-C(6) | 1.327(4) |
| C(6)-C(7) | 1.496(4) |
| C(7)-N(8) | 1.330(3) |
| C(7)-N(9) | 1.339(3) |
| N(8)-C(7)#2 | 1.330(3) |
| N(9)-C(10) | 1.317(3) |
| C(10)-N(9)#2 | 1.317(3) |
| C(10)-C(11) | 1.488(5) |
| C(11)-N(12) | 1.327(3) |
| C(11)-N(12)#2 | 1.327(3) |
| N(12)-C(13) | 1.347(3) |
| C(13)-C(14) | 1.369(4) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(13)#2 | 1.369(4) |
| C(14)-H(14) | 0.9500 |
| O(15)-N(18) | 1.288(3) |
| O(15)-Cd(1)#1 | 2.423(2) |
| O(16)-N(18) | 1.233(4) |
| O(17)-N(18) | 1.213(4) |

| | |
|---|---|
| O(19)-N(22) | 1.261(3) |
| O(20)-N(22) | 1.276(3) |
| O(21)-N(22) | 1.222(3) |
| | |
| O(20)-Cd(1)-O(15) | 151.90(8) |
| O(20)-Cd(1)-N(9) | 116.27(8) |
| O(15)-Cd(1)-N(9) | 86.27(8) |
| O(20)-Cd(1)-N(1) | 114.85(8) |
| O(15)-Cd(1)-N(1) | 88.33(7) |
| N(9)-Cd(1)-N(1) | 67.96(7) |
| O(20)-Cd(1)-O(15)#1 | 101.48(7) |
| O(15)-Cd(1)-O(15)#1 | 64.64(8) |
| N(9)-Cd(1)-O(15)#1 | 138.72(7) |
| N(1)-Cd(1)-O(15)#1 | 81.87(8) |
| O(20)-Cd(1)-O(19) | 53.55(8) |
| O(15)-Cd(1)-O(19) | 98.37(8) |
| N(9)-Cd(1)-O(19) | 143.44(8) |
| N(1)-Cd(1)-O(19) | 147.90(8) |
| O(15)#1-Cd(1)-O(19) | 73.04(7) |
| O(20)-Cd(1)-N(12) | 82.27(8) |
| O(15)-Cd(1)-N(12) | 92.76(8) |
| N(9)-Cd(1)-N(12) | 66.60(7) |
| N(1)-Cd(1)-N(12) | 134.36(7) |
| O(15)#1-Cd(1)-N(12) | 138.55(7) |
| O(19)-Cd(1)-N(12) | 76.94(7) |
| C(6)-N(1)-C(2) | 116.7(2) |
| C(6)-N(1)-Cd(1) | 119.06(17) |
| C(2)-N(1)-Cd(1) | 124.14(19) |
| N(1)-C(2)-C(3) | 121.2(3) |
| N(1)-C(2)-H(2) | 119.4 |
| C(3)-C(2)-H(2) | 119.4 |
| C(4)-C(3)-C(2) | 117.0(3) |
| C(4)-C(3)-H(3) | 121.5 |
| C(2)-C(3)-H(3) | 121.5 |
| N(5)-C(4)-C(3) | 122.9(3) |
| N(5)-C(4)-H(4) | 118.6 |

| | |
|---|---|
| C(3)-C(4)-H(4) | 118.6 |
| C(6)-N(5)-C(4) | 115.3(3) |
| N(1)-C(6)-N(5) | 126.9(3) |
| N(1)-C(6)-C(7) | 116.3(2) |
| N(5)-C(6)-C(7) | 116.8(3) |
| N(8)-C(7)-N(9) | 124.1(2) |
| N(8)-C(7)-C(6) | 120.3(2) |
| N(9)-C(7)-C(6) | 115.6(2) |
| C(7)-N(8)-C(7)#2 | 115.3(3) |
| C(10)-N(9)-C(7) | 116.1(2) |
| C(10)-N(9)-Cd(1) | 122.56(18) |
| C(7)-N(9)-Cd(1) | 120.96(17) |
| N(9)#2-C(10)-N(9) | 124.2(3) |
| N(9)#2-C(10)-C(11) | 117.90(16) |
| N(9)-C(10)-C(11) | 117.90(16) |
| N(12)-C(11)-N(12)#2 | 128.0(3) |
| N(12)-C(11)-C(10) | 116.01(16) |
| N(12)#2-C(11)-C(10) | 116.02(16) |
| C(11)-N(12)-C(13) | 115.3(3) |
| C(11)-N(12)-Cd(1) | 116.14(18) |
| C(13)-N(12)-Cd(1) | 127.7(2) |
| N(12)-C(13)-C(14) | 121.5(3) |
| N(12)-C(13)-H(13) | 119.3 |
| C(14)-C(13)-H(13) | 119.3 |
| C(13)#2-C(14)-C(13) | 118.4(4) |
| C(13)#2-C(14)-H(14) | 120.8 |
| C(13)-C(14)-H(14) | 120.8 |
| N(18)-O(15)-Cd(1) | 127.78(19) |
| N(18)-O(15)-Cd(1)#1 | 114.70(18) |
| Cd(1)-O(15)-Cd(1)#1 | 115.28(8) |
| O(17)-N(18)-O(16) | 123.1(3) |
| O(17)-N(18)-O(15) | 119.3(3) |
| O(16)-N(18)-O(15) | 117.6(3) |
| N(22)-O(19)-Cd(1) | 91.34(16) |
| N(22)-O(20)-Cd(1) | 98.17(17) |
| O(21)-N(22)-O(19) | 122.7(3) |

| | |
|---|---|
| O(21)-N(22)-O(20) | 120.5(3) |
| O(19)-N(22)-O(20) | 116.8(2) |

**Table S4:** Bond lengths (Å) and angles (°) measured in respect of complex **3**.

| | |
|---|---|
| Cd-N(4) | 2.388(3) |
| Cd-N(4)#1 | 2.388(3) |
| Cd-O(1)#1 | 2.402(2) |
| Cd-O(1) | 2.402(2) |
| Cd-O(11) | 2.424(2) |
| Cd-O(11)#1 | 2.424(2) |
| Cd-N(14)#1 | 2.428(3) |
| Cd-N(14) | 2.428(3) |
| O(1)-C(2) | 1.240(3) |
| C(2)-O(1)#2 | 1.240(3) |
| C(2)-C(3) | 1.529(6) |
| C(3)-N(4) | 1.316(3) |
| C(3)-N(4)#2 | 1.316(3) |
| N(4)-C(5) | 1.349(4) |
| C(5)-C(6) | 1.368(5) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(5)#2 | 1.368(5) |
| C(6)-H(6) | 0.9500 |
| O(11)-C(12) | 1.241(3) |
| C(12)-O(11)#3 | 1.241(3) |
| C(12)-C(13) | 1.517(6) |
| C(13)-N(14) | 1.328(3) |
| C(13)-N(14)#3 | 1.328(3) |
| N(14)-C(15) | 1.347(4) |
| C(15)-C(16) | 1.369(4) |
| C(15)-H(15) | 0.9500 |
| C(16)-C(15)#3 | 1.369(4) |
| C(16)-H(16) | 0.9500 |
| | |
| N(4)-Cd-N(4)#1 | 97.94(15) |
| N(4)-Cd-O(1)#1 | 80.67(9) |
| N(4)#1-Cd-O(1)#1 | 68.18(8) |
| N(4)-Cd-O(1) | 68.18(8) |
| N(4)#1-Cd-O(1) | 80.67(9) |

| | |
|---|---|
| O(1)#1-Cd-O(1) | 132.02(11) |
| N(4)-Cd-O(11) | 141.21(8) |
| N(4)#1-Cd-O(11) | 76.81(9) |
| O(1)#1-Cd-O(11) | 129.26(8) |
| O(1)-Cd-O(11) | 73.06(7) |
| N(4)-Cd-O(11)#1 | 76.81(9) |
| N(4)#1-Cd-O(11)#1 | 141.21(8) |
| O(1)#1-Cd-O(11)#1 | 73.05(7) |
| O(1)-Cd-O(11)#1 | 129.26(8) |
| O(11)-Cd-O(11)#1 | 130.35(11) |
| N(4)-Cd-N(14)#1 | 93.57(10) |
| N(4)#1-Cd-N(14)#1 | 150.92(9) |
| O(1)#1-Cd-N(14)#1 | 140.41(8) |
| O(1)-Cd-N(14)#1 | 79.00(9) |
| O(11)-Cd-N(14)#1 | 77.51(9) |
| O(11)#1-Cd-N(14)#1 | 67.52(8) |
| N(4)-Cd-N(14) | 150.92(9) |
| N(4)#1-Cd-N(14) | 93.57(10) |
| O(1)#1-Cd-N(14) | 79.00(9) |
| O(1)-Cd-N(14) | 140.41(8) |
| O(11)-Cd-N(14) | 67.51(8) |
| O(11)#1-Cd-N(14) | 77.51(9) |
| N(14)#1-Cd-N(14) | 89.04(14) |
| C(2)-O(1)-Cd | 119.4(2) |
| O(1)-C(2)-O(1)#2 | 125.9(4) |
| O(1)-C(2)-C(3) | 117.0(2) |
| O(1)#2-C(2)-C(3) | 117.0(2) |
| N(4)-C(3)-N(4)#2 | 126.6(4) |
| N(4)-C(3)-C(2) | 116.7(2) |
| N(4)#2-C(3)-C(2) | 116.7(2) |
| C(3)-N(4)-C(5) | 116.8(3) |
| C(3)-N(4)-Cd | 117.2(2) |
| C(5)-N(4)-Cd | 125.5(2) |
| N(4)-C(5)-C(6) | 120.5(4) |
| N(4)-C(5)-H(5) | 119.8 |
| C(6)-C(5)-H(5) | 119.8 |

| | |
|---|---|
| C(5)-C(6)-C(5)#2 | 118.9(5) |
| C(5)-C(6)-H(6) | 120.6 |
| C(5)#2-C(6)-H(6) | 120.6 |
| C(12)-O(11)-Cd | 120.8(2) |
| O(11)-C(12)-O(11)#3 | 126.0(4) |
| O(11)-C(12)-C(13) | 117.0(2) |
| O(11)#3-C(12)-C(13) | 117.0(2) |
| N(14)-C(13)-N(14)#3 | 124.8(4) |
| N(14)-C(13)-C(12) | 117.60(19) |
| N(14)#3-C(13)-C(12) | 117.60(19) |
| C(13)-N(14)-C(15) | 117.3(3) |
| C(13)-N(14)-Cd | 117.0(2) |
| C(15)-N(14)-Cd | 125.7(2) |
| N(14)-C(15)-C(16) | 121.7(4) |
| N(14)-C(15)-H(15) | 119.1 |
| C(16)-C(15)-H(15) | 119.1 |
| C(15)#3-C(16)-C(15) | 117.2(5) |
| C(15)#3-C(16)-H(16) | 121.4 |
| C(15)-C(16)-H(16) | 121.4 |

**Table S5:** $^{113}$Cd-$^{14}$N Bond distances obtained from X-ray Crystallography and Calculated ($^{113}$Cd,$^{14}$N) Dipolar Coupling Constants

| Nitrogen atoms in compound | $r_{Cd\text{-}N}$(Å) | $D(^{113}Cd,^{14}N)$(Hz) |
|---|---|---|
| MOF ($N_1$) | 2.428 | -135.3 |
| MOF ($N_2$) | 2.338 | -142.2 |
| Polymer ($N_1$) | 2.546 | -117.4 |
| Polymer ($N_2$) | 2.411 | -138.2 |
| Polymer ($N_3$) | 2.352 | -148.9 |

The $^{113}$Cd-$^{14}$N dipolar coupling constants were calculated using the following equation: $D(Cd;N) = \frac{\mu_0 \gamma_N \gamma_{N'} \hbar}{8\pi^2 {r_{Cd-N}}^3}(Hz)$, where $\mu_0$ is vacuum permeability ($4\pi*10^{-7}$ N.A$^{-2}$), $\gamma_N$ and $\gamma_{N'}$ are the gyromagnetic ratios of coupled nuclei ($\gamma(^{113}Cd)$ = -5.9609153*10$^7$ rad.T$^{-1}$.s$^{-1}$, $\gamma(^{14}N)$ = 1.9337792*10$^7$ rad.T$^{-1}$.s$^{-1}$, respectively, $\hbar$ is the reduced Planck constant (1.055*10$^{-34}$ J.s), and $r_{Cd\text{-}N}$ is the distance between cadmium and nitrogen nuclei obtained from X-ray diffraction measurement.

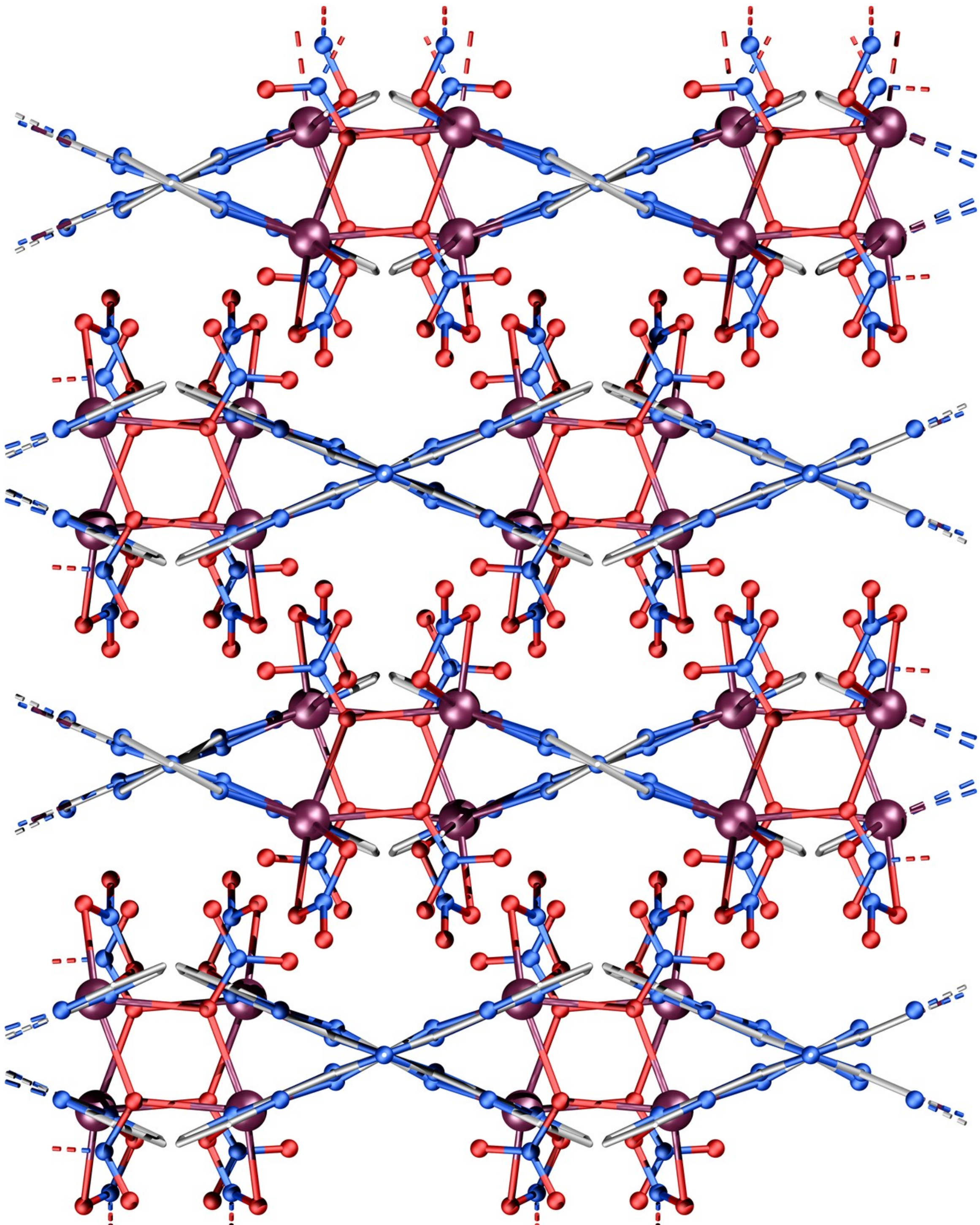


**Fig S1:** Packing of **2** as viewed along the *c*-axis.

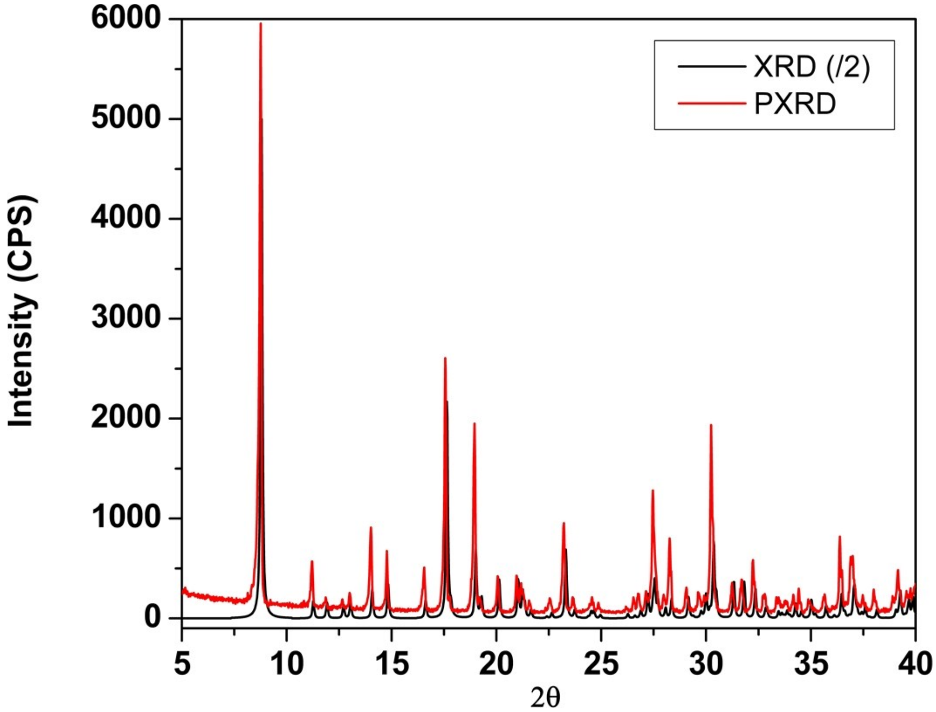



**Fig S2:** Comparison of calculated (black) and experimental (red) PXRD data obtained for **2**. Calculated pattern is scaled by a factor of 5 for comparative purposes.

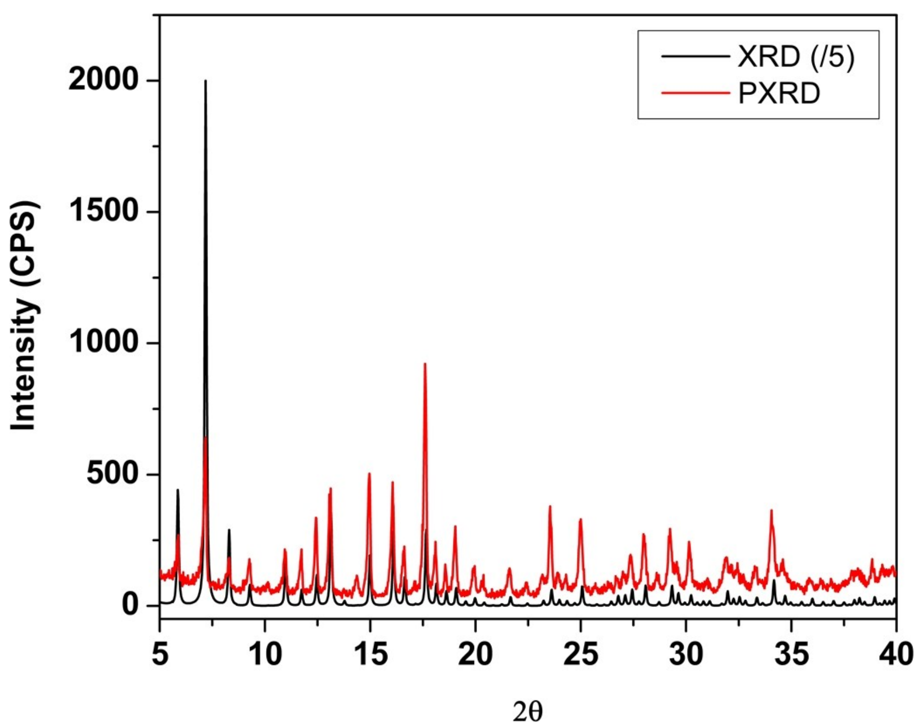
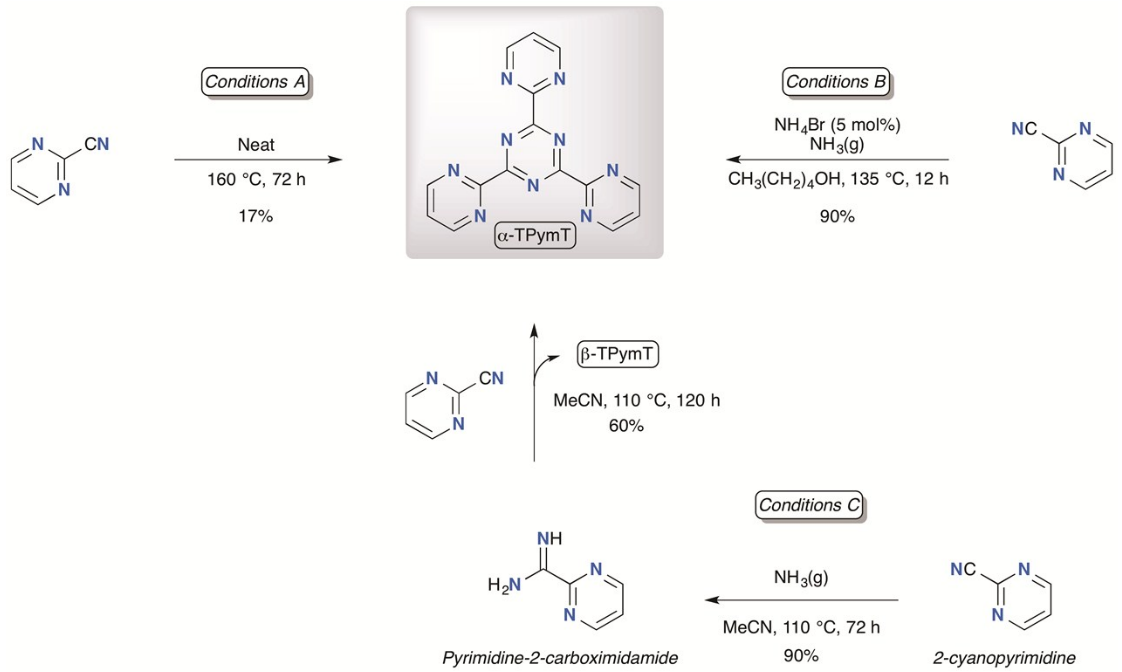



**Fig S3:** Comparison of calculated (black) and experimental (red) PXRD data obtained for **3**. Calculated pattern is scaled by a factor of 5 for comparative purposes.




**Scheme S1:** Known synthetic routes for the preparation of TPymT.

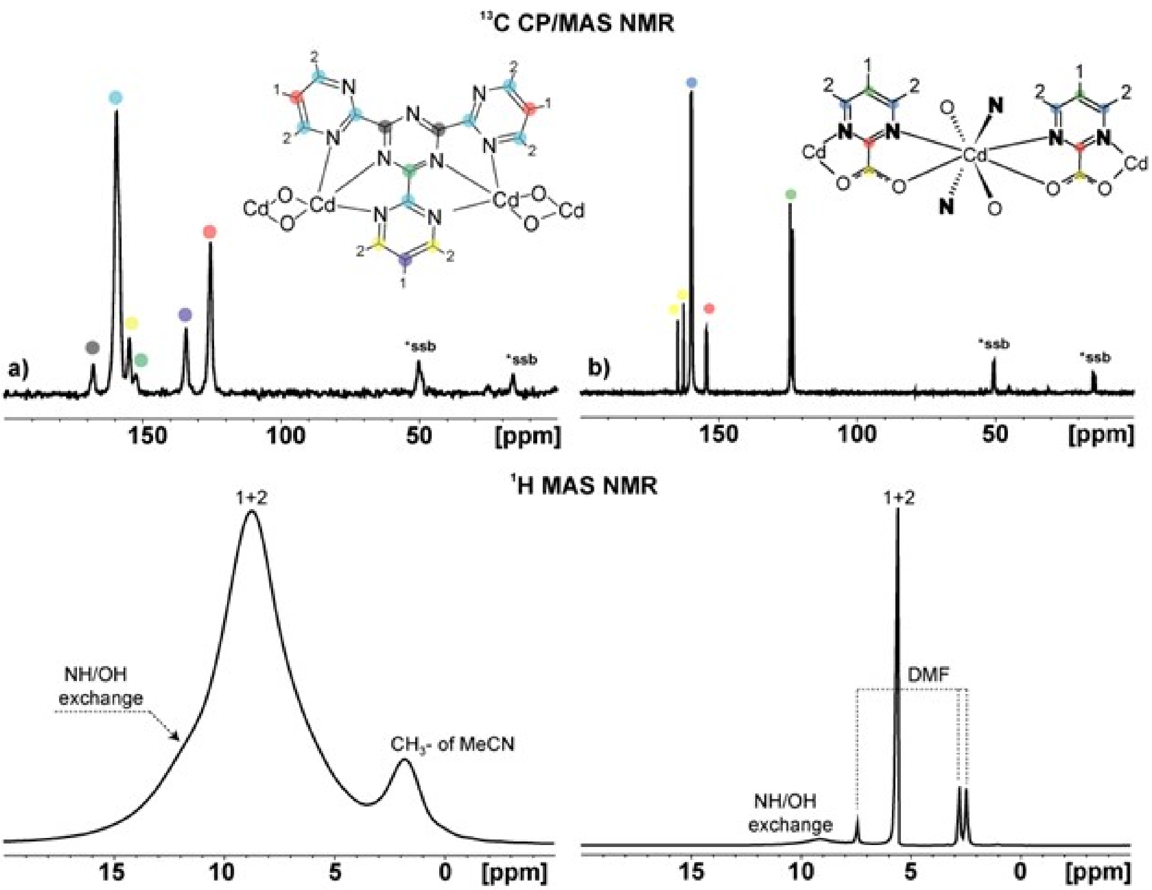



**Fig S4:** $^{13}$C CP/MAS NMR (top) and $^{1}$H MAS (bottom) and spectra of **2** (a) and **3** (b) recorded at 11 kHz on a 9.4 T spectrometer.

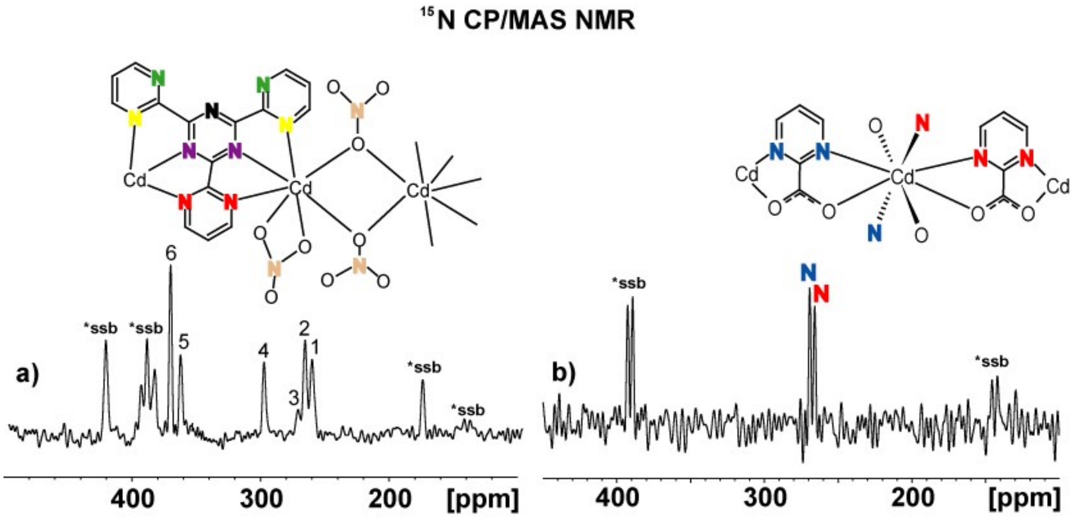



**Fig S5.** $^{15}N$ CP/MAS NMR spectra of **2** (a) and **3** (b) systems, recorded at 5 kHz on a 9.4 T spectrometer. The $^{15}N$ CP/MAS NMR spectrum of **3** (Fig 2b) reveals two signals at 265.8 ppm and 269.1 ppm corresponding to nitrogen atoms in two non-equivalent 2-PmC ligands.[12,13] In the $^{15}N$ CP/MAS NMR spectrum of **2** (Fig 2a) were observed six peaks corresponding to six distinct nitrogen atoms in the polymer structure.

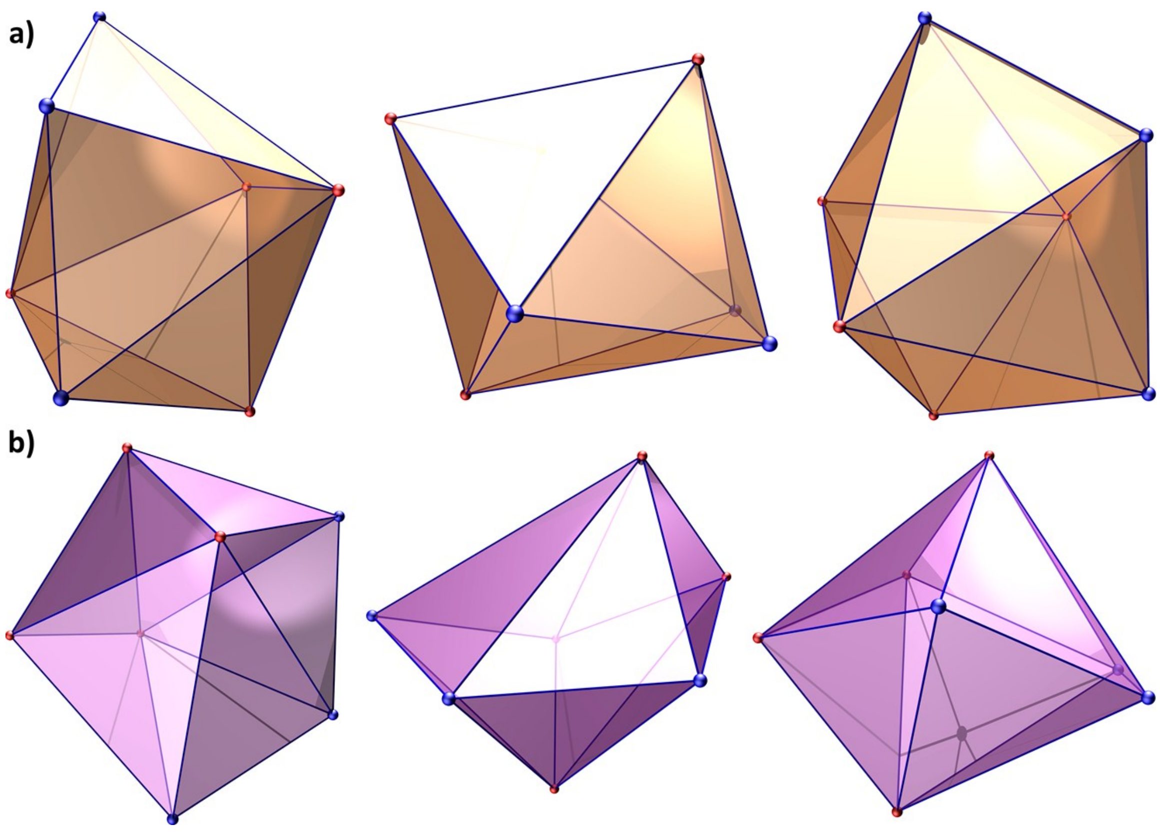



**Fig S6.** Comparison of polyhedral coordination shapes for complexes **1** (a) and **2** (b), which are both 7-coordinate and feature $O_4N_3$ coordination spheres.

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