Supplementary Material (ESI) for CrystEngComm

Structural Diversity in a Series of Metal Organic Frameworks (MOFs) Composed of Divalent Transition Metals, 4,4′-bipyridine and a Flexible Carboxylic Acid

(Supporting Information: 29 pages including this page)

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Section S1: Detailed synthesis procedures for M-ADA's including multi-gram scale products, experimental and simulated PXRD patterns:

1,3-Adamantanediacetic Acid, 4,4′-bipyridine, $Cd(NO_3)_2.4H_2O$, $Zn(NO_3)_2.6H_2O$ and $Mn(NO_3)_2.xH_2O$ were purchased from the Aldrich Chemicals. *N*, *N*-dimethylformamide (DMF) was purchased from Rankem chemicals. All starting materials were used without further purification. All experimental operations were performed in air and all the stock solutions were prepared in *N*, *N*-dimethylformamide (DMF).

Synthesis of [Cd(ADA)(4,4'-bipy)$_{0.5}$]. DMF (Cd-ADA-1): 1.5 mL 1, 3-Adamantanediacetic Acid stock solution (0.20 M) and 0.5 mL $Cd(NO_3)_2{\cdot}4H_2O$ stock solution (0.20 M) were mixed in a 5 mL glass vial. To this solution was added 0.5 mL 4,4′-bipyridine solution (0.20 M). The vial was capped and heated to 85 ºC for 96 h. The mother liquor was decanted and the products were washed with DMF (15 mL) three times. Colorless crystals of Cd-ADA-1 were collected by filtration and dried in air (10 min) (yield: 58%, 0.0178 gm based on $Cd(NO_3)_2.4H_2O$).

***FT-IR* :** (KBr 4000-450cm^{-1}): 3387(br, s), 3056(w), 2897(s), 2844(m), 1680(m), 1578(s), 1489(w), 1413(s), 1220(m), 1070(m), 1007(m), 808(s), 714(w), 629(m), 569(w), 491(w).

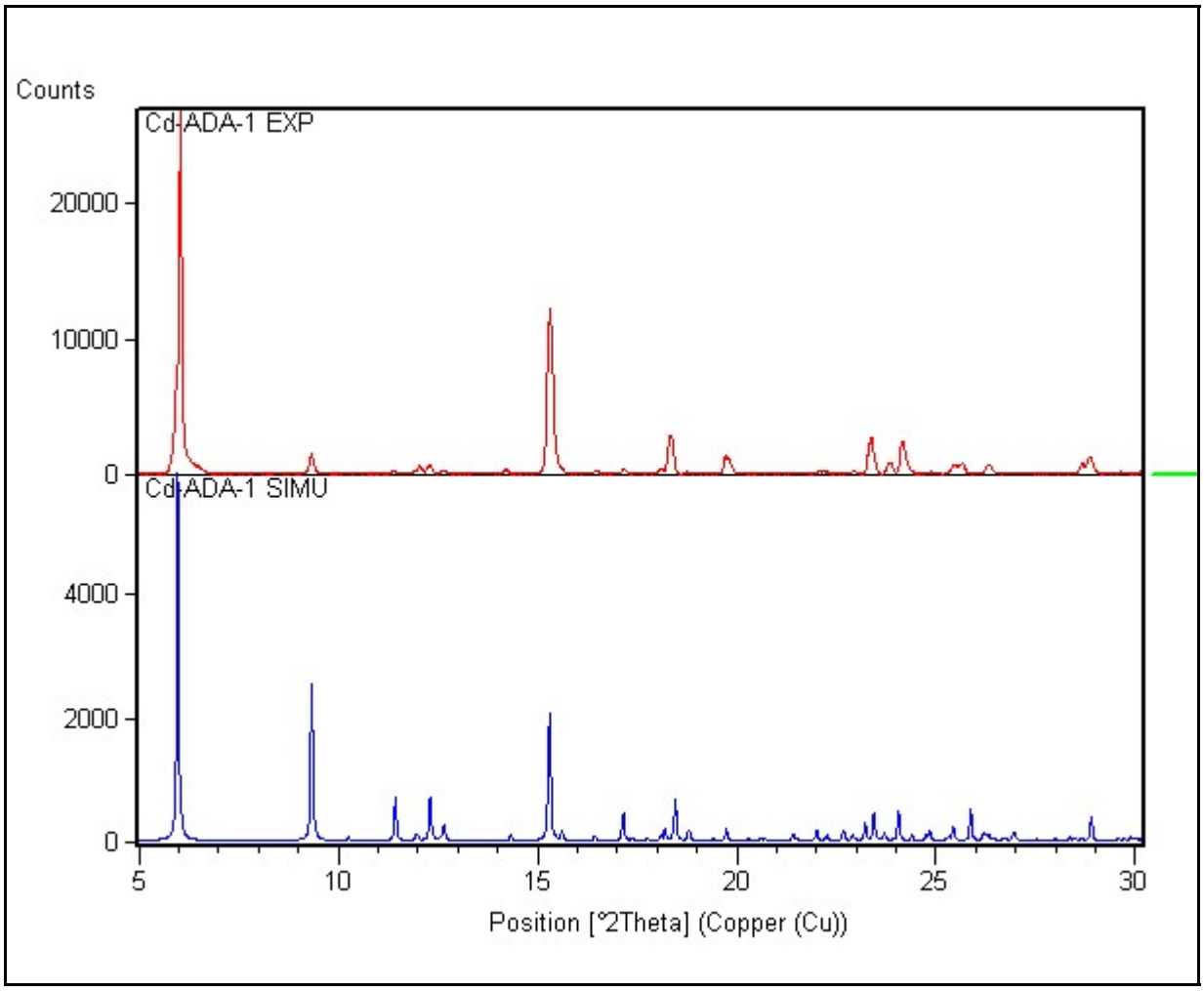

Figure S1. Comparison of the experimental PXRD pattern of as-synthesized Cd-ADA-1 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of [Mn(ADA)(4,4'-bipy)$_{0.5}$]. DMF (Mn-ADA-1): 1.5 mL 1, 3-Adamantanediacetic Acid stock solution (0.20 M) and 0.5 mL $Mn(NO_3)_2{\cdot}xH_2O$ stock solution (0.20 M) were mixed in a 5 mL glass vial. To this solution was added 0.5 mL 4,4′-bipyridine solution (0.20 M). The vial was capped and heated to 85 ºC for 96 h. The mother liquor was decanted and the products were washed with DMF (15 mL) three times. Colorless crystals of Mn-ADA-1 were collected by filtration and dried in air (10 min) (yield: 70%, 0.0200 gm based on $Mn(NO_3)_2{\cdot}xH_2O$).

FT-IR **:** (KBr 4000-450cm^{-1}): 3451(br, s), 3154(w), 2951(m), 2765(w), 1821(m), 1652(s), 1547(m), 1402(m), 1352(s), 1120(m), 1017(s), 902(s), 754(w), 654(w), 602(w), 465(w).

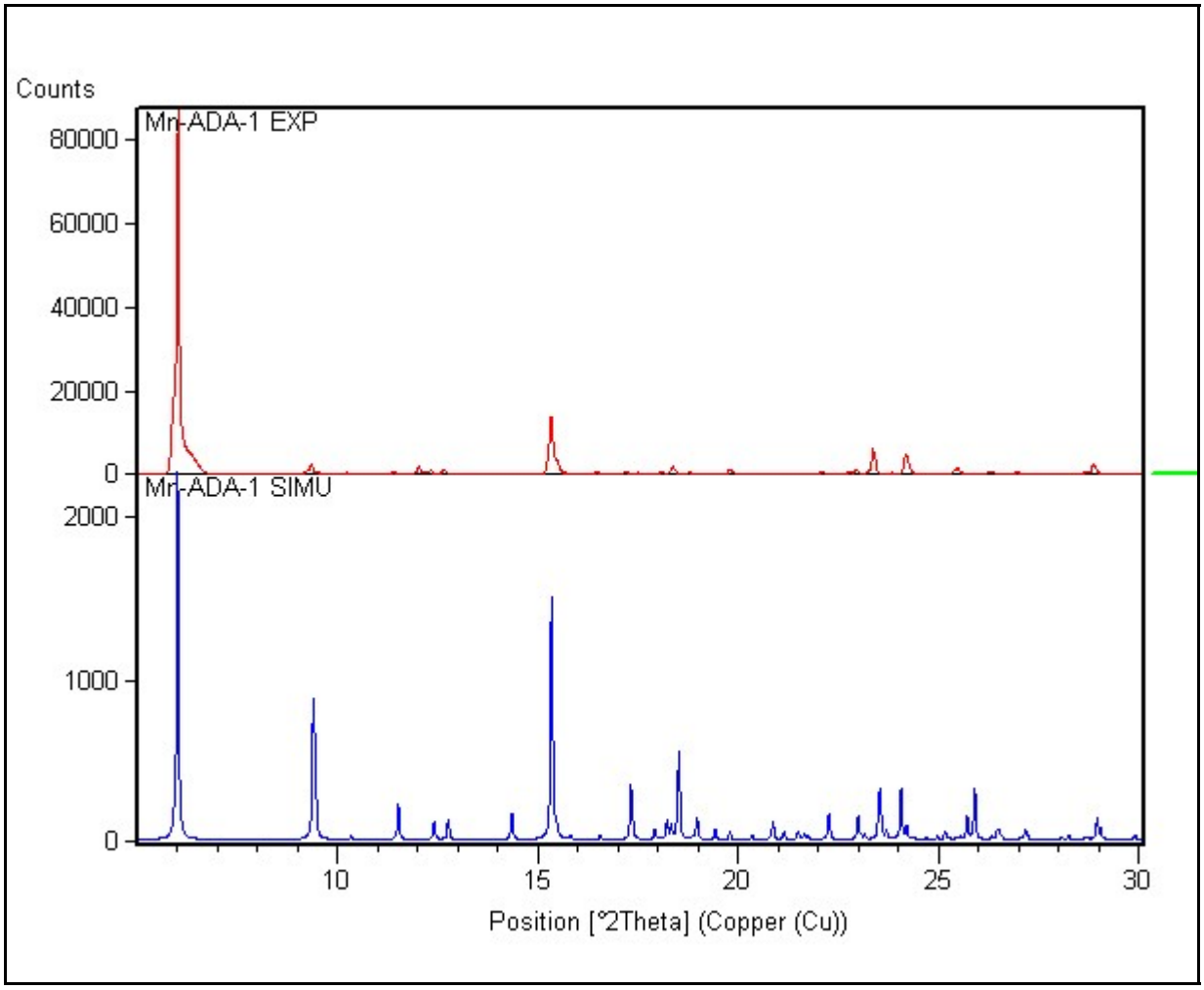

Figure S2. Comparison of the experimental PXRD pattern of as-prepared Mn-ADA-1 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of [Zn(ADA)(4,4'-bipy)$_{0.5}$] (Zn-ADA-1): 1.5 mL 1, 3-Adamantanediacetic Acid stock solution (0.20 M) and 0.5 mL $Zn(NO_3)_2 \cdot 6H_2O$ stock solution (0.20 M) were mixed in a 5 mL glass vial. To this solution was added 0.5 mL 4,4′-bipyridine solution (0.20 M). The vial was capped and heated to 85 ºC for 96 h. The mother liquor was

decanted and the products were washed with DMF (15 mL) three times. Colorless crystals of Zn-ADA-1 were collected by filtration and dried in air (10 min) (yield: 62%, 0.0184 gm based on $Zn(NO_3)_2 \cdot 6H_2O$).

***FT-IR* :** (KBr 4000-450cm^{-1}): 2897(s), 2845(w), 1618(s), 1556(w), 1423(s), 1393(w), 1223(w), 1080(w), 832(m), 755(w), 645(m), 523(m), 476(w).

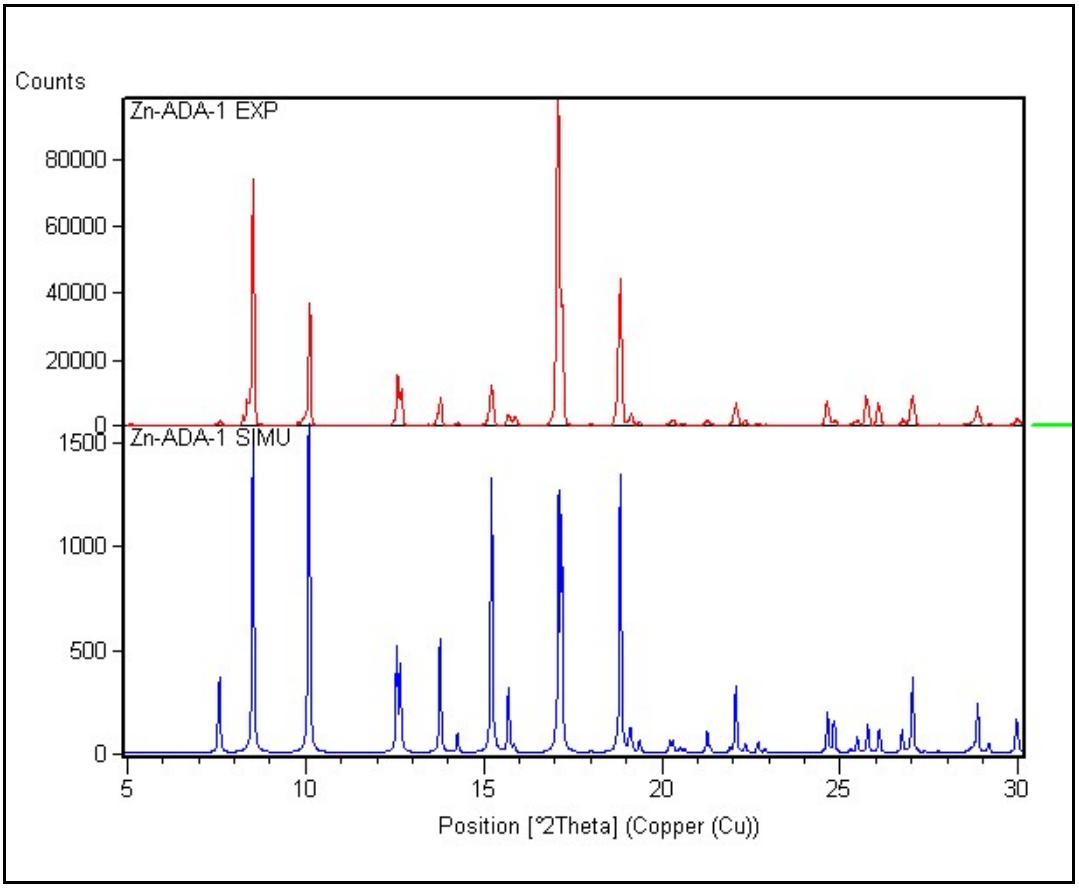

Figure S3. Comparison of the experimental PXRD pattern of as-prepared Mn-ADA-2 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of $[Mn(HADA)_2(4,4'\text{-bipy})].(H_2O)_2$ (Mn-ADA-2): Hydrothermal reaction of $Mn(NO_3)_2 \cdot xH_2O$ (0.114 g, 0.4mmol), 4,4′-bipyridine (0.0312 g, 0.2 mmol), 1, 3-Adamantanediacetic Acid (0.0252 g, 0.1mmol) and Lithium hydroxide (0.008 g, 0.2

mmol) in a 25mL acid-digestion bomb using de-ionized water (15 mL) at 120 ^{0}C for 3 days produced colorless crystals of Mn-ADA-2 in quantitative yield. Crystals were collected by filtration, washed with Ethanol and dried in air (10 min). (Yield: 49%, 0.0558 gm based on $Mn(NO_3)_2 \cdot xH_2O$).

FT-IR **:** (KBr 4000-450cm^{-1}): 3377(s), 2902(s), 2845(m), 2503(w), 1968(w), 1679(s), 1604(m), 1545(s), 1431(w), 1403(s), 1309(w), 1268(w), 1151(w), 1007(m), 822(w), 628(w), 593(w), 528(w), 492(w).

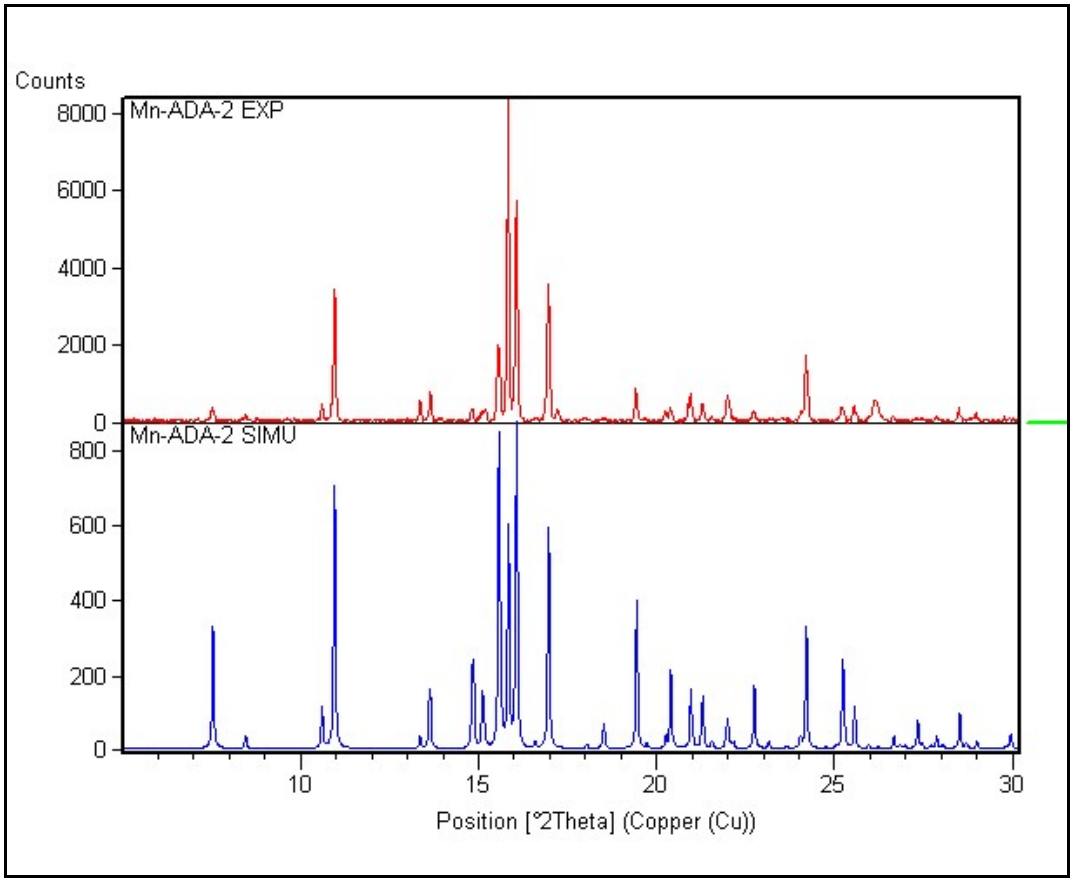

Figure S4. Comparison of the experimental PXRD pattern of as-prepared Mn-ADA-2 (top) with the one simulated from its single crystal structure (bottom).

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures.

General Data Collection and Refinement Procedures:

All single crystal data were collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo Kα radiation (λ=0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of the *F*-MOFs reported in the paper were mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Crystals were flash frozen to 100(2) K in a liquid nitrogen cooled stream of nitrogen.

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In every case frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker SMART*[1] software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using CELL_NOW[2]. In no data collection was evidence for crystal decay encountered. Following exhaustive review of the collected frames the resolution of the dataset was judged. Data were integrated using Bruker SAINT [3] software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program

SADABS[4]. The space group determinations and tests for merohedral twinning were carried out using *XPREP*[3]. In all cases, the highest possible space group was chosen.

All structures were solved by direct methods and refined using the *SHELXTL 97*[5] software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final models were refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. In some cases modeling of electron density within the voids of the frameworks did not lead to identification of recognizable solvent molecules in these structures, probably due to the highly disordered contents of the large pores in the frameworks. Highly porous crystals that contain solvent-filled pores often yield raw data where observed strong (high intensity) scattering becomes limited to ~1.0 Å at best, with higher resolution data present at low intensity. A common strategy for improving X-ray data, increasing the exposure time of the crystal to X-rays, did not improve the quality of the high angle data in these cases, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffuse scattering from the highly disordered solvent within the void spaces of the framework and from the capillary to mount the crystal contributes to the background and the 'washing out' of the weaker data. The only optimal crystals suitable for analysis were generally small and weakly diffracting. Unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize the crystal growing conditions for large high-quality specimens have not yet been fruitful.

Data were collected at 298(2) K for all the MOFs presented in this paper. This lower temperature was considered to be optimal for obtaining the best data. Electron density within void spaces has not been assigned to any guest entity but has been modeled as isolated oxygen and/or carbon atoms. The foremost errors in all the models are thought to lie in the assignment of guest electron density. All structures were examined using the *Adsym* subroutine of PLATON[7] to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. For all structures we note that elevated R-values are commonly encountered in MOF crystallography for the reasons expressed above by us and by other research groups.[8-17] Table S1 contains crystallographic data for the five MOFs.

1. Bruker (2005). *APEX2*. Version 5.053. Bruker AXS Inc., Madison,Wisconsin, USA.
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Cotton, F. A., Lin, C. & Murillo, C. A. *Inorg. Chem.* **40**, 478-484 (2001).

ADACID (Monoclinic)

Experimental and Refinement Details for ADACID

A colorless prismatic crystal (0.20 × 0.18 × 0.15 mm^3) of ADACID was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 9899 reflections were collected of which 4457 were unique and 3911 of these were greater than 2σ(I). The range of θ was from 1.47 to 25.00º. All non-hydrogen atoms were refined anisotropically. ADACID contains two 1,3-adamantanediacetic acid and in the asymmetric unit. It should be noted that other supporting characterization data (*vide infra* Section S1) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0614 (F >2σF)) and wR_2 = 0.1540 (all data) with GOF = 1.067.

Table S1. Crystal data and structure refinement for ADACID

Empirical formula	C14 H20 O4
Formula weight	252.30
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P21/n*
Unit cell dimensions	*a* = 14.7198(16) Å α = 90°
	b = 7.7386(17) Å β = 106.385(3)°
	c = 23.1799(9) Å γ = 90°
Volume	2533.2(6)
Z	8
Density (calculated)	1.323
Absorption coefficient	0.096
F(000)	1088
Crystal size	0.20 × 0.18 × 0.15 mm^3
Theta range for data collection	1.47 - 25.00
Index ranges	-17 <= h <= 16, -9 <= k <= 9, -0 <= l <= 27
Reflections collected	9899
Independent reflections	3911
Completeness to theta = 26.02°	97.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9899 / 0 / 326
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R_1 = 0.0614, wR_2 = 0.1540
R indices (all data)	R_1 = 0.0802, wR_2 = 0.1668
Largest diff. peak and hole	0.047 and -0.220 e.$Å^{-3}$

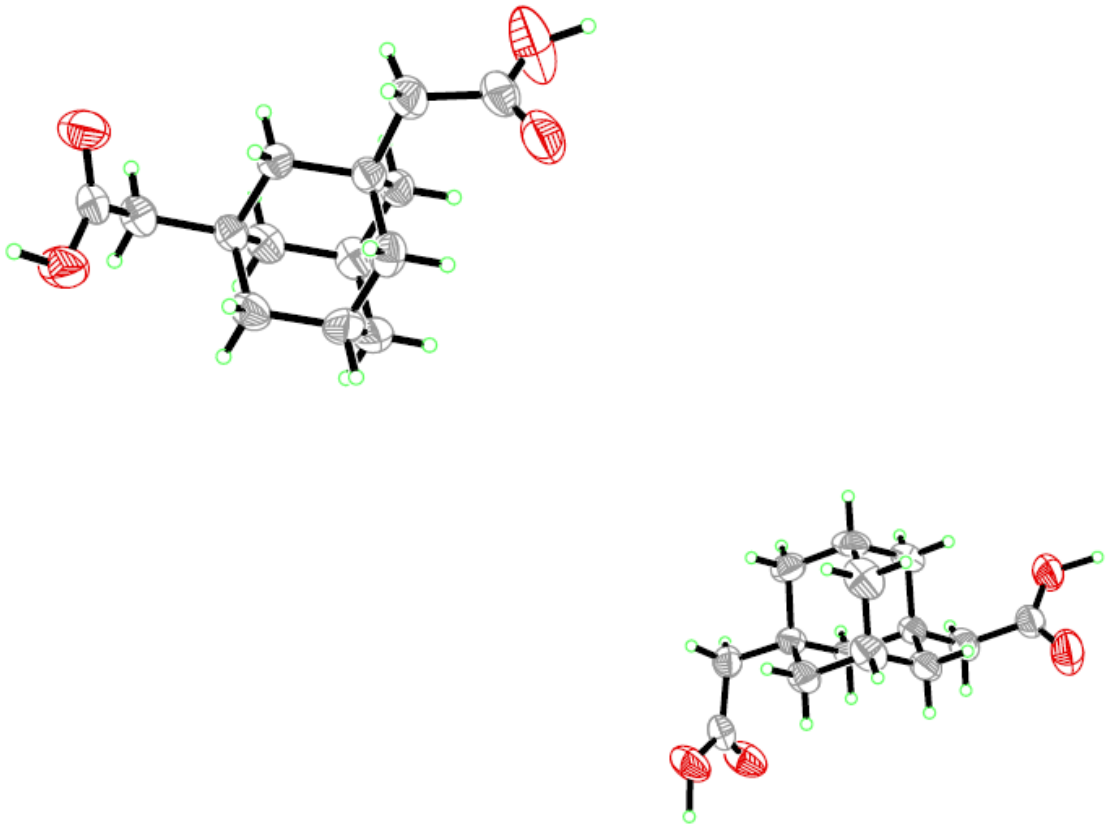

Figure S5. ORTEP drawing of the asymmetric unit of 1,3-adamantanediacetic acid (ADACID).

Cd-ADA-1 (Triclinic)

Experimental and Refinement Details for Cd-ADA-1

A colorless prismatic crystal (0.14 × 0.12 × 0.09 mm^3) of Cd-ADA-1was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 10533 reflections were collected of which 6236 were unique and 4944 of these were greater than 2σ(I). The range of θ was from 1.38 to 28.09º. All non-hydrogen atoms were refined anisotropically. Cd-ADA-1contains one 1,3-adamantanediacetic acid and two 4,4′-bipyridine in the asymmetric unit. It should be noted that other supporting characterization data (*vide infra* Section S1) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0607 (F >2σF)) and wR_2 = 0.1505(all data) with GOF = 1.067.

Table S2. Crystal data and structure refinement for Cd-ADA-1

Empirical formula	C27 H33 Cd N3 O5
Formula weight	591.97
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions	*a* = 8.924(5) Å α = 71.631(8)°
	b = 10.297(5) Å β = 89.933(8)°
	c = 15.620(8) Å γ = 75.659(8)°
Volume	1315.1(12)
Z	2
Density (calculated)	1.498
Absorption coefficient	0.877
F(000)	614
Crystal size	0.14 × 0.12 × 0.09 mm^3
Theta range for data collection	2.36 - 27.65
Index ranges	-11 <= h <= 11, -11 <= k <= 13, -19 <= l <= 20
Reflections collected	10533
Independent reflections	4944
Completeness to theta = 26.02°	88.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5636 / 1 / 327
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R_1 = 0.0607, wR_2 = 0.1505
R indices (all data)	R_1 = 0.0716, wR_2 = 0.1618
Largest diff. peak and hole	0.188 and -1.462 e.$Å^{-3}$

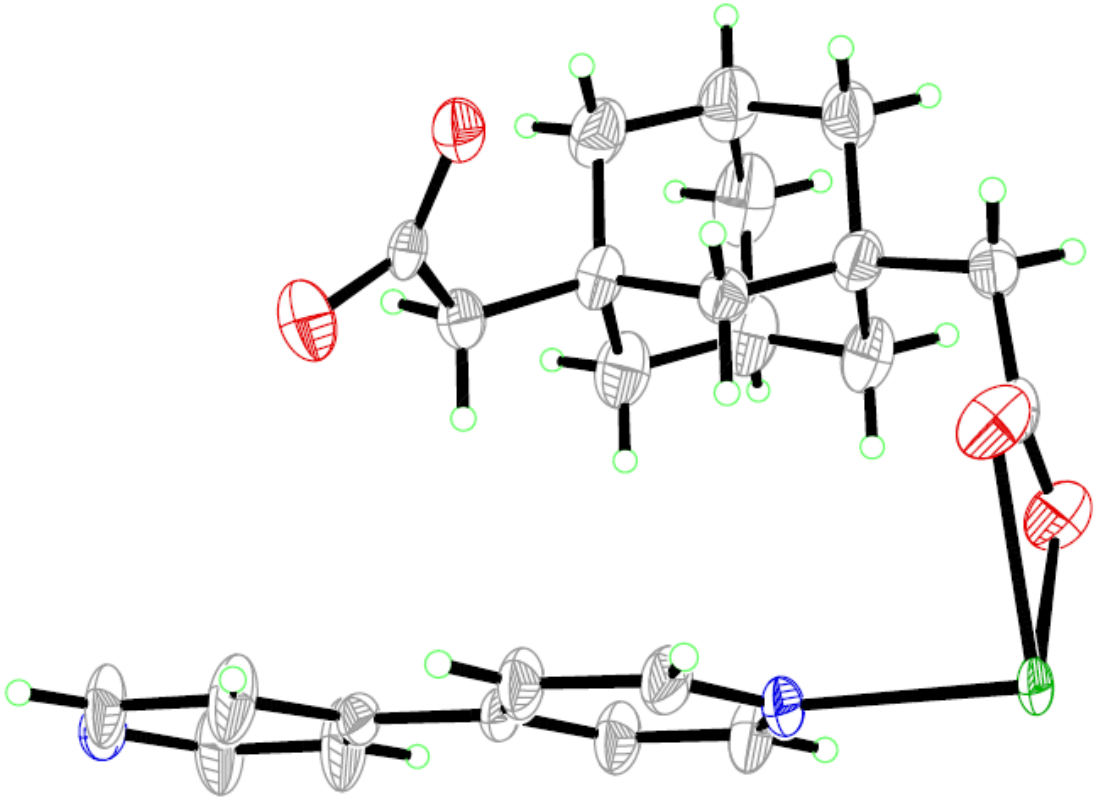

Figure S6. ORTEP drawing of the asymmetric unit of Cd-ADA-1

Zn-ADA-1 (Monoclinic)

Experimental and Refinement Details for Zn-ADA-1

A colorless prismatic crystal (0.20 × 0.18 × 0.16 mm^3) of Cd-ADA-1was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 18358 reflections were collected of which 3859 were unique and 3385 of these were greater than 2σ(I). The range of θ was from 1.22 to 26.02º. All non-hydrogen atoms were refined anisotropically. Zn-ADA-1 contains one 1,3-adamantanediacetic acid and two 4,4′-bipyridine in the asymmetric unit.. It should be noted that other supporting characterization data (*vide infra* Section S1) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0552 (F >2σF)) and wR_2 = 0.1111 (all data) with GOF = 0.948.

Table S3. Crystal data and structure refinement for Zn-ADA-1

Empirical formula	C19 H22 N O4 Zn
Formula weight	393.75
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	*a* = 22.587(4) Å α = 90.00°
	b = 14.078(3) Å β = 113.424(7)°
	c = 11.240(2) Å γ = 90.00°
Volume	3279.5(11)
Z	8
Density (calculated)	1.595
Absorption coefficient	1.523
F(000)	1640
Crystal size	0.20 × 0.18 × 0.16 mm^3
Theta range for data collection	2.33 - 28.18
Index ranges	-29 <= h <= 29, -18 <= k <= 18, -14 <= l <= 14
Reflections collected	18358
Independent reflections	3385
Completeness to theta = 26.02°	95.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3859 / 0 / 229
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R_1 0.0334, wR_2 = 0.0915
R indices (all data)	R_1 0.0374, wR_2 = 0.0934
Largest diff. peak and hole	0.081 and -0.414 e.$Å^{-3}$

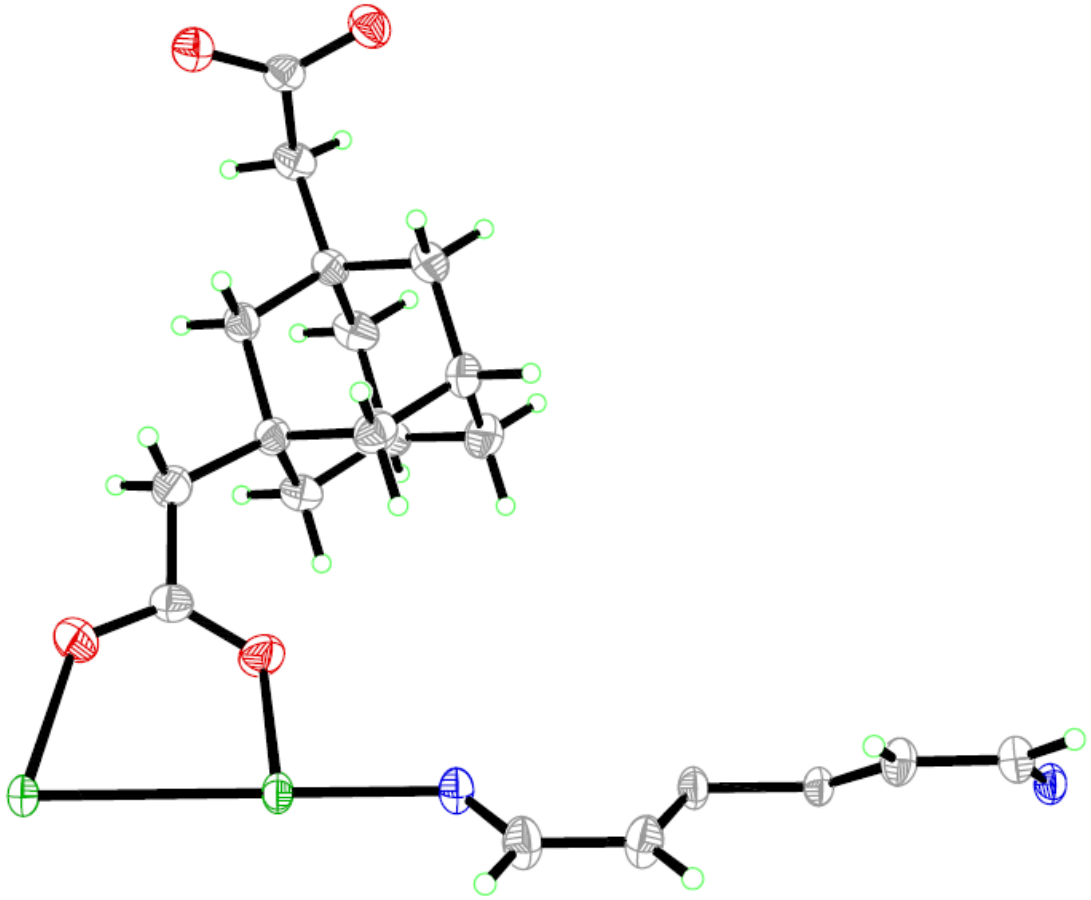

Figure S7. ORTEP drawing of the asymmetric unit of Zn-ADA-1

Mn-ADA-1 (Triclinic)

Experimental and Refinement Details for Cd-ADA-1

A colorless prismatic crystal (0.14 × 0.12 × 0.09 mm^3) of Mn-ADA-1was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 10533 reflections were collected of which 6236 were unique and 4944 of these were greater than 2σ(I). The range of θ was from 1.38 to 28.09º. All non-hydrogen atoms were refined anisotropically. Mn-ADA-1contains one 1,3-adamantanediacetic acid and one 4,4′-bipyridine in the asymmetric unit. It should be noted that other supporting characterization data (*vide infra* Section S1) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0607 (F >2σF)) and wR_2 = 0.1505(all data) with GOF = 1.067.

Table S4. Crystal data and structure refinement for Mn-ADA-1

Empirical formula	C27 H33 Mn N3 O5
Formula weight	534.50
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions	*a* = 8.8816(16) Å α = 71.530(3)°
	b = 10.2469(18) Å β = 89.774(3)°
	c = 15.551(3) Å γ = 74.903(3)°
Volume	1291.3(4)
Z	2
Density (calculated)	1.375
Absorption coefficient	0.553
F(000)	562
Crystal size	0.14 × 0.12 × 0.09 mm^3
Theta range for data collection	2.38 - 21.43
Index ranges	-11 <= h <= 11, -13 <= k <= 13, -20 <= l <= 19
Reflections collected	14927
Independent reflections	3755
Completeness to theta = 26.02°	92.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5871 / 0 / 328
Goodness-of-fit on F^2	0.948
Final R indices [I>2sigma(I)]	R_1 = 0.0552, wR_2 = 0.1111
R indices (all data)	R_1 = 0.0932, wR_2 = 0.1340
Largest diff. peak and hole	0.156 and -0.430 e.$Å^{-3}$

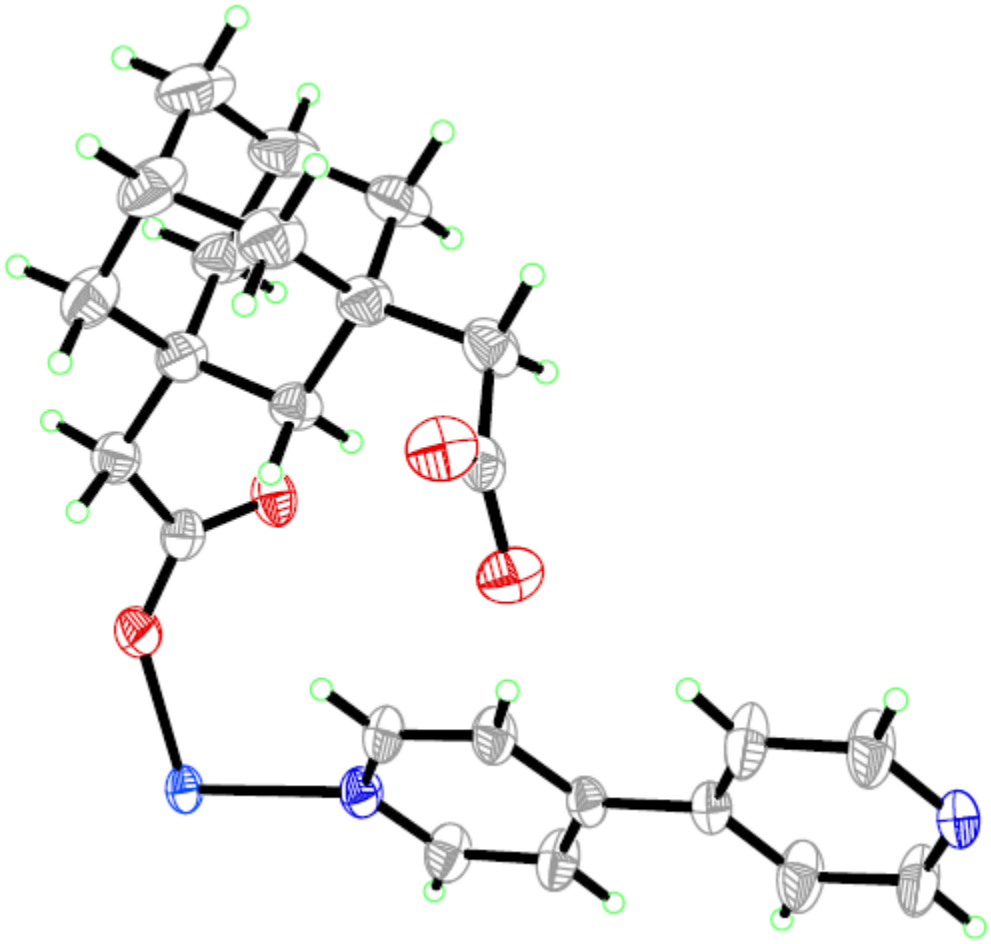

Figure S8. ORTEP drawing of the asymmetric unit of Mn-ADA-1

Mn-ADA-2 (Monoclinic)

Experimental and Refinement Details for Mn-ADA-2

A colorless prismatic crystal (0.14 × 0.12 × 0.09 mm^3) of Cd-ADA-1was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 20390 reflections were collected of which 4251 were unique and 3275 of these were greater than 2σ(I). The range of θ was from 1.22 to 26.02º. All non-hydrogen atoms were refined anisotropically. Mn-ADA-2contains one 1,3-adamantanediacetic acid and half 4,4′-bipyridine and one water molecule in the asymmetric unit. It should be noted that other supporting characterization data (*vide infra* Section S1) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0786 (F >2σF)) and wR_2 = 0.1032 (all data) with GOF = 0.945.

Table S5. Crystal data and structure refinement for Mn-ADA-2

Empirical formula	C38 H50 Mn N2 O10
Formula weight	749.80
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	*a* = 23.495(2) Å α = 90.00°
	b = 11.6667(10) Å β = 94.286(2)°
	c = 13.2885(12) Å γ = 90.00°
Volume	3632.3(5)
Z	4
Density (calculated)	1.370
Absorption coefficient	0.425
F(000)	1620
Crystal size	0.14 × 0.12 × 0.09 mm^3
Theta range for data collection	2.36 - 27.65
Index ranges	-30 <= h <= 31, -14 <= k <= 14, -16 <= l <= 17
Reflections collected	20390
Independent reflections	3275
Completeness to theta = 26.02°	94.4 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4251 / 0 / 241
Goodness-of-fit on F^2	0.945
Final R indices [I>2sigma(I)]	R_1 0.0526, wR_2 = 0.1032
R indices (all data)	R_1 = 0.0786, wR_2 = 0.1139
Largest diff. peak and hole	0.055 and -0.314 e.$Å^{-3}$

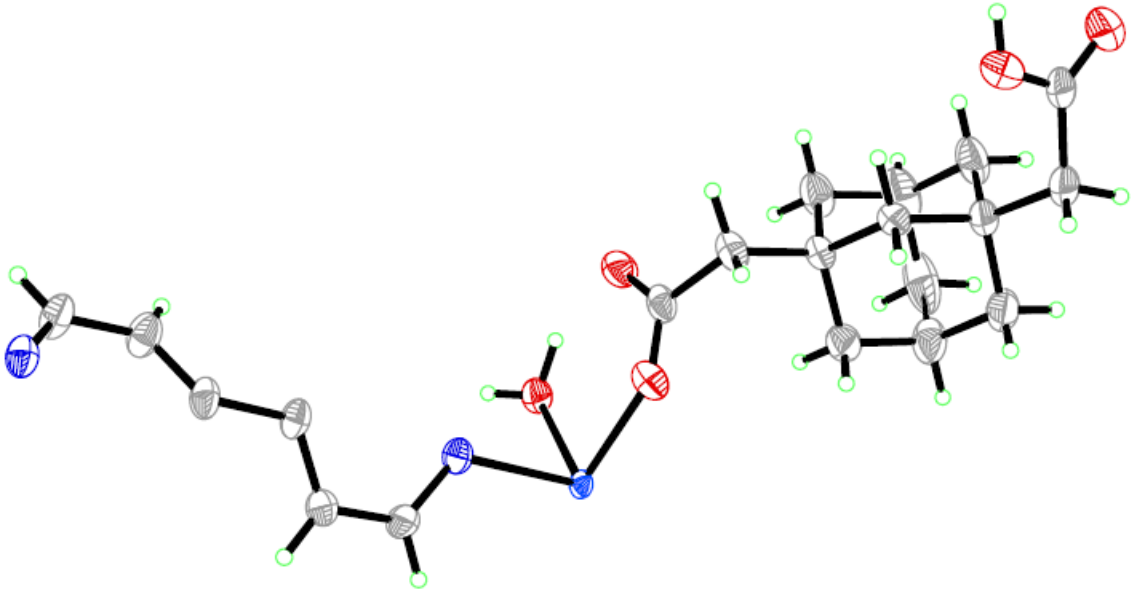

Figure S9. ORTEP drawing of the asymmetric unit of Cd-ADA-1

Section S3. Thermal stability of M-ADA's:

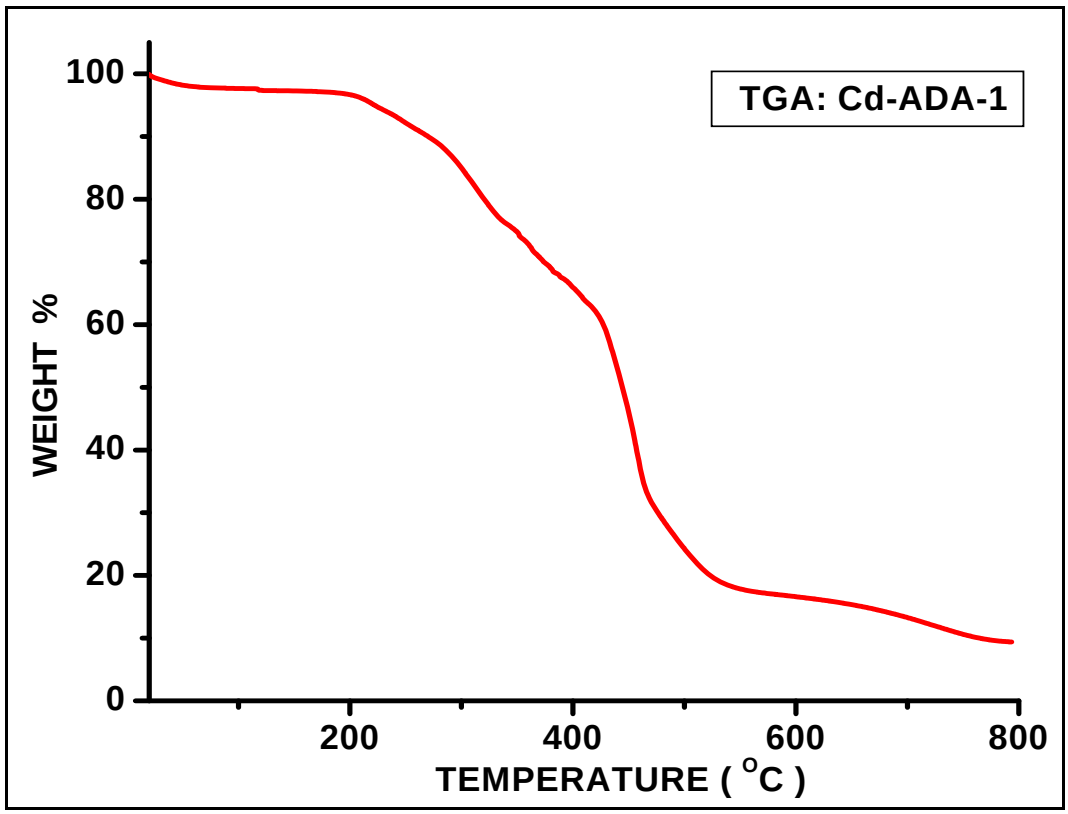

Figure S10: Thermo gravimetric analysis (TGA) plot of Cd-ADA-1.

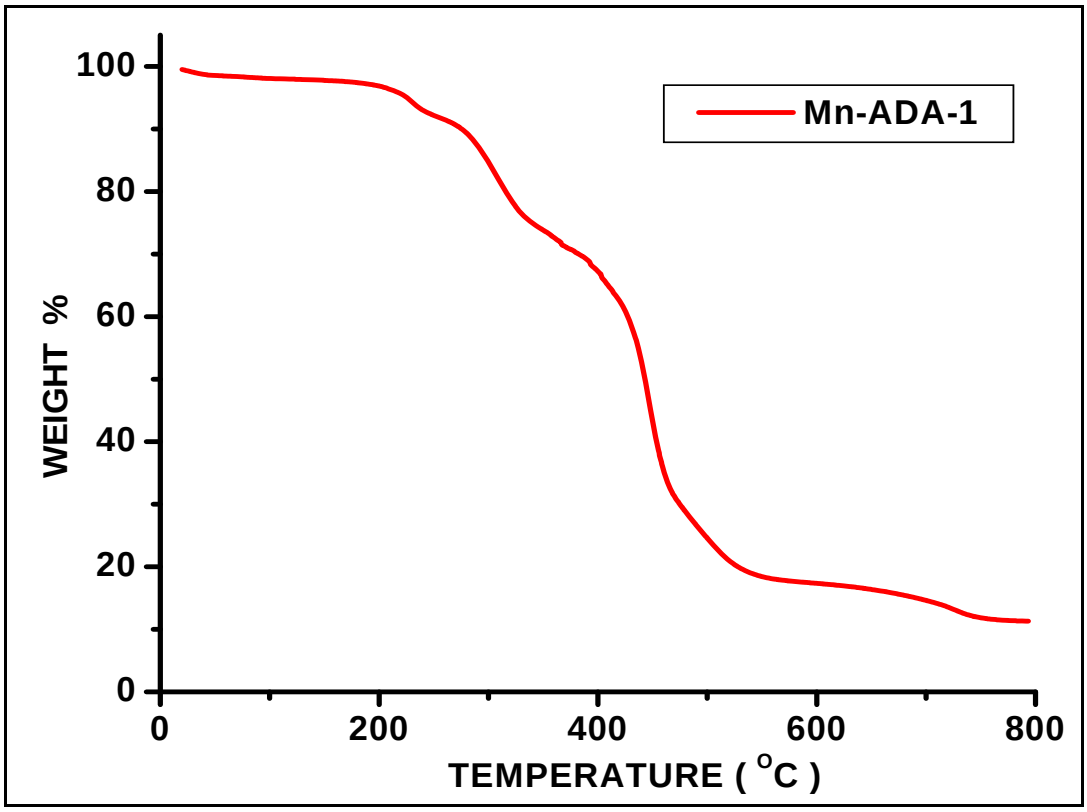

Figure S11: Thermo gravimetric analysis (TGA) plot of Mn-ADA-1.

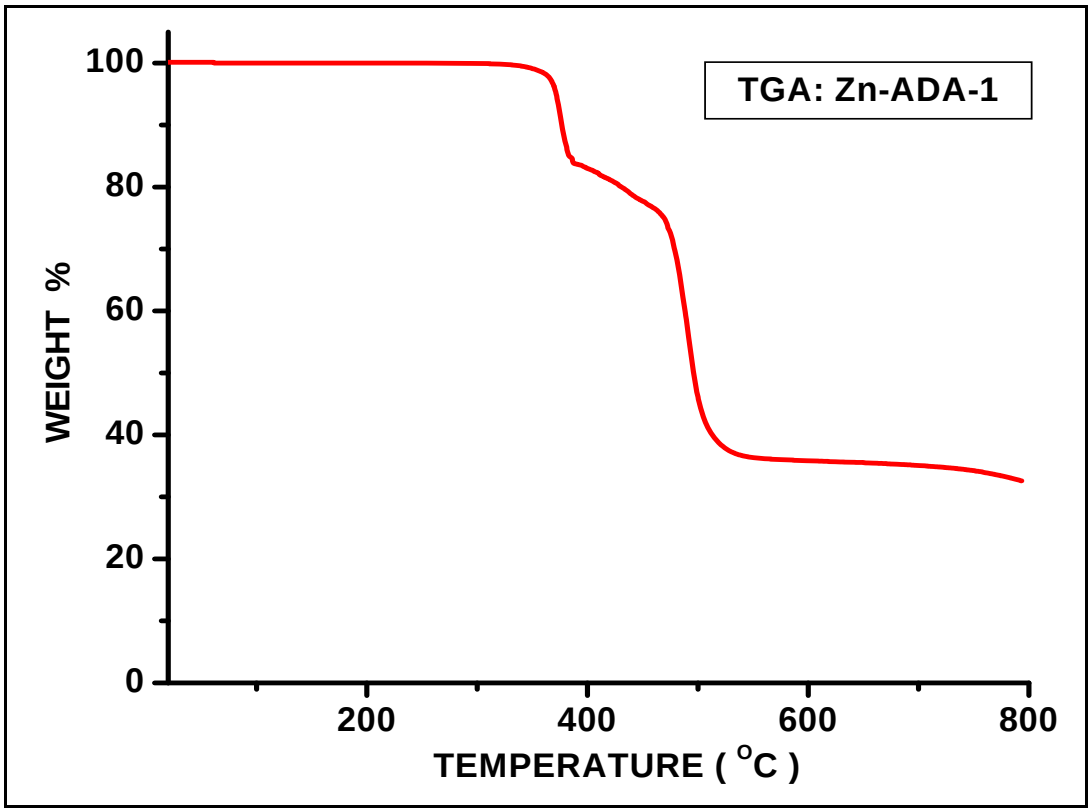

Figure S12: Thermo gravimetric analysis (TGA) plot of Zn-ADA-1.

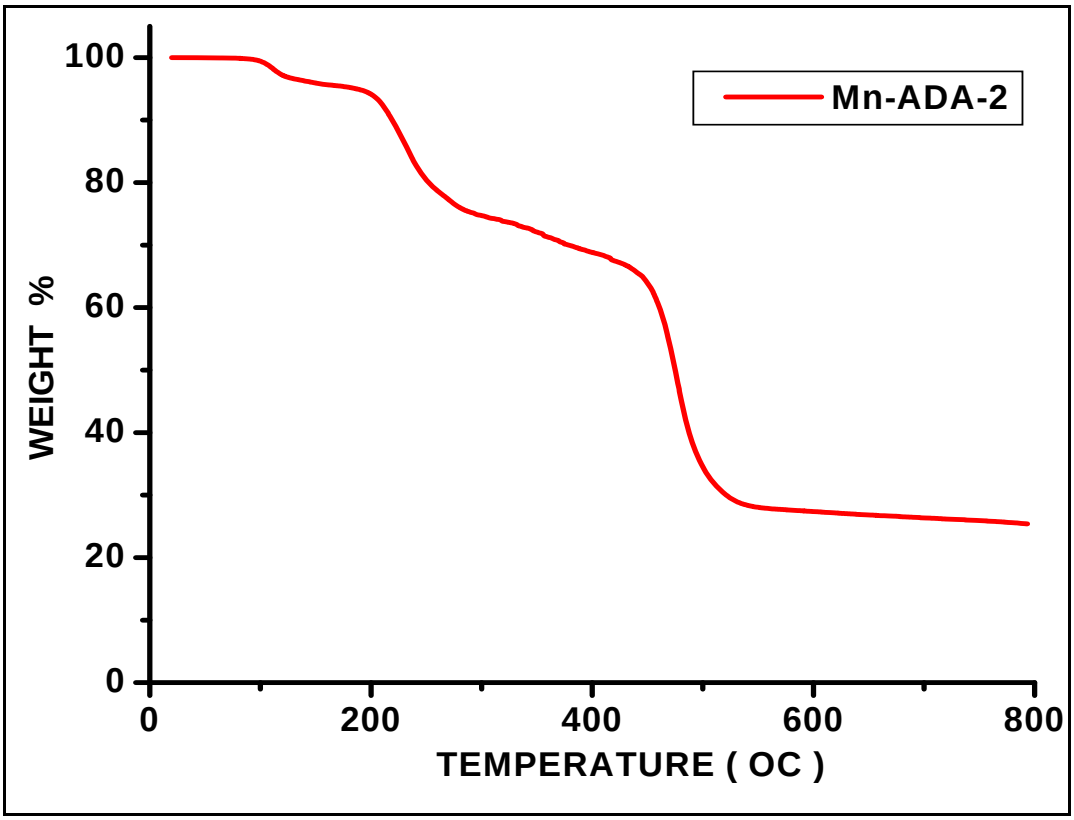

Figure S13: Thermo gravimetric analysis (TGA) plot of Mn-ADA-2.