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ARTICLE

Non-hydrothermal synthesis, structural characterization and thermochemistry of water soluble and neutral coordination polymers of Zn(II) and Cd(II): precursors for the submicron-sized crystalline ZnO/CdO

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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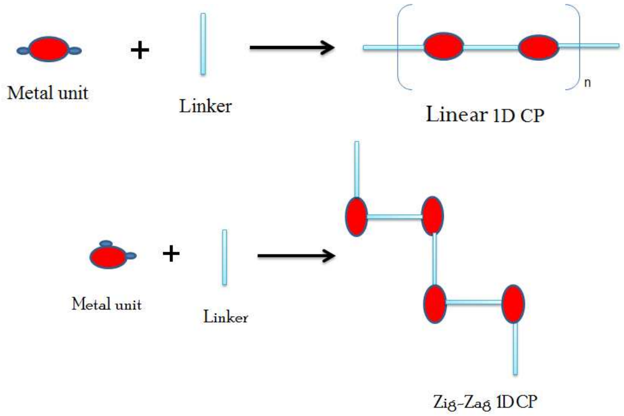
Eight new water soluble and neutral one dimensional V-shaped coordination polymers (CPs) of Zn(II) (**1**-**4**) and Cd(II) (**5**-**8**) with a general formula $\{[M_2(bpxa)_2(adc)_2]\cdot xH_2O\}_n$ (where M = Zn(II) or Cd(II); bpxa = N,N-bis(pyridylmethyl)alkyl amine; adc = acetylene dicarboxylate; x = 0 or 2) are reported. These are synthesized in good yields from the self-assembly reaction of $M(OAc)_2$ (where M = Zn or Cd), bpxa and the corresponding acid in methanol at ambient conditions. Based on the crystal structures of **1**-**3** and **6**-**8** by single crystal X-ray diffraction studies, a subtle change in the N-alkyl group in the tridentate ligands has provided structural diversity in these CPs with respect to binding differences of the adc linker and the presence (or absence) of $\pi-\pi$ interactions as well as the presence (or absence) of lattice water molecules that further shows hydrogen bonding interactions between the CP chains forming supramolecular networks. These features are unique for the CPs reported in this work. All these are characterized by elemental analysis and FTIR spectroscopy. Thermal stabilities of these CPs are studied by thermogravimetric analysis and variable temperature (-100 °C to +150 °C) PXRD experiments. For a proof of concept, using field-emission scanning electron microscopy (FESEM) and X-ray energy dispersive spectroscopy (EDS) one CP of each metal (**3** and **7**, respectively) has been shown to be a suitable precursor for generating submicron-sized crystalline ZnO or CdO, at 400 °C and 250 °C, respectively. Some of the CPs were also studied for their photoluminescence properties in the solid state at room temperature.

Introduction

In the last 15 years, the field of crystal engineering to develop materials synthesized from the coordination driven self-assembly of metal ions with organic linkers is growing steadily for their potential applications in magnetochemistry, chemical technology and host-guest chemistry.[1-4] In particular coordination polymers (CPs) with varied dimensionality have been the targets in recent times.[5-8] The use of metal centers or metal atom clusters as the building blocks gives advantages due to different binding abilities of the metal centers. The selection of ancillary ligands and the multitopic organic linkers is crucial in making such CPs. The role of ancillary ligands that surround and protect the metal cores leaving open sites for the linkers is of great importance. Depending on the orientation of the open sites at the metal center, there are two possible structural types for the 1D CPs containing a linear bi-functional linker as shown in Scheme 1, linear (for two open sites at the metal center with an angle of ~180°) and zigzag or V-shaped (for two open sites at the metal center with an angle of ~90°). This structural difference is sometimes of great importance in making nanomaterials, such as metal oxides, with diverse morphological and photophysical properties.

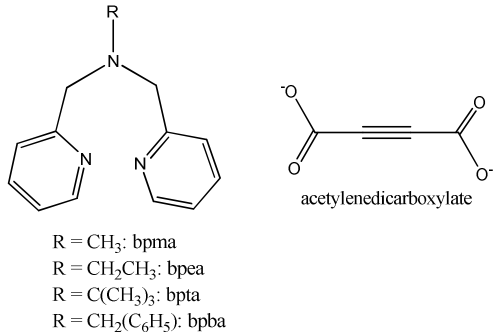
On the other hand, the use of water soluble CPs is sought in many applications, such as catalysis, luminescence, magnetism, biological activities, etc. Thus, there is a growing interest in recent years to study the nature of interactions of these polymers with water,[9] particularly for homogeneous catalysis and carrying out their biological activities (protein binding and DNA interaction), in aqueous media. However, there are not many such examples reported in the literature.[10-14] In order to make water soluble CPs, strategies reported in the literature include the use of linkers bearing highly polar functional groups, such as ether groups, amino acids (aspartic acid, glycine, asparagines, or histidine), perhalogenated aromatic dicarboxylic acids, etc. For example, compared to the Ag(I) coordination polymer with non-fluorinated phthalate, which is insoluble in water, those with tetrafluorophthalate are water soluble.[14]



Scheme 1 Two possible structural types for 1D CPs.

We have found that the use of flexible tridentate ancillary ligands shown in Scheme 2 provides a way to have better solubility of the CPs than those with mostly carboxylates. Furthermore, neutral CPs that are water soluble are rare in the literature.[10-14] Among the numerous carboxylates under consideration in our laboratory, for this work we have selected a linear bi-functional dicarboxylate such as acetylene dicarboxylate (adc) for it having much smaller steric hindrance compared to other carboxylates with organic moieties with a double bond, such as fumarate or maleate, or with an aromatic ring and being suitable for post-synthesis chemical modifications, such as attaching other molecules to it or performing photochemical reactions within the polymers through the reactive triple bond. However, it requires non-hydrothermal conditions due to its poor stability at high temperatures, which is clearly evident from the fact that there are only a few examples with adc prior to this work.[15] Thus our focus on acetylene dicarboxylate as a linker is currently in one-pot self-assembly reactions of various combinations of raw materials under ambient conditions.

In this article, we report synthesis at ambient conditions and structural characterization of eight new water soluble and neutral one dimensional V-shaped coordination polymers (CPs) of Zn(II) and Cd(II) with a general formula $\{[M_2(bpxa)_2(adc)_2]\cdot xH_2O\}_n$ (where M = Zn(II) or Cd(II); bpxa = N,N-bis(pyridylmethyl)alkyl amine; adc = acetylene dicarboxylate; x = 0 or 2). Thermal stabilities of these CPs are studied by thermogravimetric analysis, and variable temperature (-100 °C to +150 °C) PXRD experiments with one CP of each metal showed the crystalline phase change. Using field-emission scanning electron microscopy (FESEM) and X-ray energy dispersive spectroscopy (EDS) these have been shown to be good precursors for generating submicron-sized crystalline ZnO or CdO, at 400 °C and 250 °C, respectively, via the direct thermal decomposition technique. Three of these have also been studied for their photoluminescent properties in the solid state at room temperature.



Scheme 2 Structure of ligands and dicarboxylate linker used in this study.

Experimental section

Materials and methods. All chemicals and solvents used for synthesis were obtained from commercial sources and were used as received, without further purification. All reactions were carried out under aerobic conditions. All ligands were prepared by modifying the literature procedure.[16]

Physical measurements. The ^{1}H NMR spectra of the ligands were obtained in $CDCl_3$ solution at 25 °C on a Bruker ARX-400 spectrometer; chemical shifts were reported relative to the residual solvent signals. The elemental analysis (C, H, N) was carried out using a Mettler CHNS analyzer, and thermogravimetric analysis was carried out from 25 to 500 °C (at a heating rate of 10 °C/min) under dinitrogen atmosphere on a Mettler 851 E. IR spectra were measured in the 4000-400 cm^{-1} range on a Perkin-Elmer Spectrum I spectrometer with samples prepared as KBr pellets. The morphology and chemical composition of the as-prepared samples were examined using field-emission scanning electron microscopy (FE-SEM, JEOL, 15 kV) and energy dispersive X-ray spectroscopy (EDX, HORIBA EX-250, 15 kV) associated with FE-SEM, respectively. Solid state fluorescence spectra were measured using HORIBA Fluorolog-3 spectrofluorometer. Each data set was analyzed with FluorEssence™ software.

General method for synthesis. All eight polymers reported here are synthesized following this general method. Upon addition of 0.125 mmol of the dicarboxylic acid to a clear methanolic (3 mL) solution of 0.125 mmol of $M(OAc)_2$ (M = Zn or Cd) and 0.125 mmol of the tridentate ligand, a white precipitate appeared immediately. The reaction mixture was stirred for another 3 to 4 hours at room temperature (RT). The resulting slurry was evaporated to dryness and then treated with 2 mL of acetonitrile-toluene mixture (50:50 v/v) to completely remove the acetic acid affording a pure solid.

$[Zn_2(bpma)_2(adc)_2]_n$ (1). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 27.5 mg (0.125 mmol) of $Zn(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 26.5 mg (0.125 mmol) of bpma. A colorless solid was obtained. Yield: 24 mg (53%). Single crystals were grown by slow evaporation of its aqueous solution. Anal. Calcd (%) for $C_{34}H_{30}N_6Zn_2O_8$ (MW 781.4): C, 52.30; H, 3.84; N, 10.76. Found: C, 51.70; H, 3.85; N, 10.74. Selected FTIR peaks (KBr, cm^{-1}): 3421, 1639, 1619, 1603, 1489, 1441, 1351, 1320, 1023, 781, 762, 695, 677.

$[Zn_2(bpea)_2(adc)_2]_n$ (2). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 27.5 mg (0.125 mmol) of $Zn(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 28 mg (0.125 mmol) of bpea. A colorless solid was obtained. Yield: 35 mg (71%). Single crystals were grown by slow evaporation of its aqueous solution. Anal. Calcd (%) for $C_{36}H_{34}N_6Zn_2O_8$ (MW 809.4): C, 53.39; H, 4.40; N, 10.38. Found: C, 53.55; H, 3.99; N, 10.14. Selected FTIR peaks (KBr, cm^{-1}): 3420, 1636, 1606, 1346, 1314, 1024, 781, 761, 693, 674.

$\{[Zn_2(bpta)_2(adc)_2]\cdot 2H_2O\}_n$ (3). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 27.5 mg (0.125 mmol) of $Zn(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 32 mg (0.125 mmol) of bpta. A colorless solid was obtained. Yield: 38 mg (67%). Single crystals were grown by slow evaporation of its aqueous solution. Anal. Calcd (%) for $C_{40}H_{46}N_6Zn_2O_{10}$ (MW 901.6): C, 53.27; H, 5.10; N, 9.33. Found: C, 53.47; H, 4.77; N, 9.33. Selected FTIR peaks (KBr, cm^{-1}): 3451, 2977, 1634, 1609, 1587, 1366, 1321, 1026, 779, 768, 679.

$[Zn_2(bpba)_2(adc)_2]_n$ (4). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 27.5 mg (0.125 mmol) of $Zn(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 36.5 mg (0.125 mmol) of bpba. A colorless solid was obtained. Yield: 35 mg (61%). Anal. Calcd (%) for $C_{44}H_{38}N_6Zn_2O_8$ (MW 918): C, 58.02; H, 4.17; N, 9.23. Found: C, 57.92; H, 4.14; N, 8.76. Selected FTIR peaks (KBr, cm^{-1}): 3436, 1632, 1606, 1573, 1332, 1312, 1024, 769, 756, 681.

$[Cd_2(bpma)_2(adc)_2]_n$ (5). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 33.5 mg (0.125 mmol) of $Cd(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 26.5 mg (0.125 mmol) of bpma. A colorless solid was obtained. Yield: 36 mg (67%). Anal. Calcd (%) for $C_{34}H_{30}N_6Cd_2O_8$ (MW 875.5): C, 46.64; H, 3.43; N, 9.59. Found: C, 46.44; H, 3.46; N, 9.31. Selected FTIR peaks (KBr, cm^{-1}): 3438, 1611, 1594, 1528, 1349, 770.

$[Cd_2(bpea)_2(adc)_2]_n$ (6). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 33.5 mg (0.125 mmol) of $Cd(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 28 mg (0.125 mmol) of bpea. A colorless solid was obtained. Yield: 49 mg (88%). Single crystals were grown by slow evaporation of its aqueous solution. Anal. Calcd (%) for $C_{36}H_{34}N_6Cd_2O_8$ (MW 903.5): C, 47.89; H, 3.76; N, 9.31. Found: C, 47.43; H, 3.79; N, 9.14. Selected FTIR peaks (KBr, cm^{-1}): 3441, 1605, 1582, 1346, 1018, 761, 690, 641.

$\{[Cd_2(bpta)_2(adc)_2]\cdot 2H_2O\}_n$ (7). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 33.5 mg (0.125 mmol) of $Cd(OAc)_2.2H_2O$ in 3 mL methanol and 32 mg (0.125 mmol) of bpta. A colorless solid was obtained. Yield: 58 mg (93%). Single crystals were grown by slow evaporation of its aqueous solution. Anal. Calcd (%) for $C_{40}H_{46}N_6Cd_2O_{10}$ (MW 995.6): C, 48.24; H, 4.62; N, 8.44. Found: C, 48.06; H, 4.54; N, 8.39. Selected FTIR peaks (KBr, cm^{-1}): 3570, 3475, 3071, 2971, 1630, 1605, 1560, 1377, 1340, 1328, 1096, 775, 765, 690.

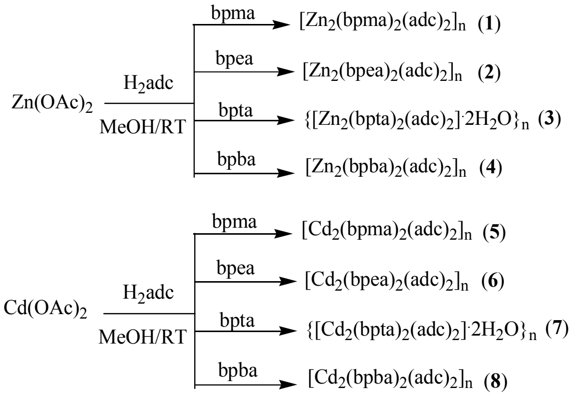
$[Cd_2(bpba)_2(adc)_2]_n$ (8). It was prepared using 14 mg (0.125 mmol) of acetylene dicarboxylic acid, 33.5 mg (0.125 mmol) of $Cd(OAc)_2\cdot 2H_2O$ in 3 mL methanol and 36.5 mg (0.125 mmol) of bpba. A colorless solid was obtained. Yield: 45 mg (57%). Single crystals were grown by slow evaporation of its aqueous solution. Anal. Calcd (%) for $C_{50}H_{38}N_6Cd_2O_{12}$ (MW 1250): C, 48.00; H, 3.04; N, 6.72. Found: C, 48.65; H, 3.40; N, 6.99. While the crude product was found to contain equal amount of [Cd(adc)], crystals grown from water contained the title compound only. Selected FTIR peaks (KBr, cm^{-1}): 3444, 1621, 1600, 1562, 1378, 1344, 1017, 776, 768, 755, 688.

Single crystal X-ray structure analysis. Initial crystal evaluation and data collection were performed on a Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealed-tube monochromated MoKα radiation.[17] By using the program SAINT[18] for the integration of the data, reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained. Data were also corrected for Lorentz and polarization effects. The subroutine XPREP[18] was used for the processing of data that included determination of space group, application of an absorption correction (SADABS),[18] merging of data, and generation of files necessary for solution and refinement. The crystal structures were solved and refined using SHELX 97.[19] In each case, positions of most of the non-hydrogen atoms were obtained from a direct methods solution. Several full-matrix least-squares/difference Fourier cycles were performed, locating the remainder of the non-hydrogen atoms. In the final difference Fourier map there was no other significant peaks >1 e/Å^3 except for **6** where the 1.761 e/Å^3 peak is 1.06 Å away from one of the Cd. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms of **1-3** and **6-8**, except those for one of the disordered ethyl groups over two positions in **6**, were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. Crystallographic parameters and basic information pertaining to data collection and structure refinement for all compounds are summarized in Table 1. All figures were drawn using Mercury V 3.0[20], OLEX2[21] and hydrogen bonding parameters were generated using Platon.[22] The final positional and thermal parameters of the non-hydrogen atoms for all structures are listed in the CIF files (Electronic Supplementary Information).

Powder X-ray Studies. Data were recorded on a Rigaku Ultima IV diffractometer equipped with a 3 kW sealed tube Cu Kα X-ray radiation (generator power settings: 40 kV and 40 mA) and a DTex Ultra detector using parallel beam geometry. Each sample ground into a fine powder using a mortar and pestle was placed on the sample holder for the variable temperature (VT) attachment. The data were collected over an angle range of 5° to 40° or 60° with a scanning speed of 1° per minute with 0.02° steps.

Results and discussion

Synthesis. Compounds **1-8** were prepared and isolated from the one pot self-assembly of the metal salt, ligand and dicarboxylic acid (1:1:1 ratio) in methanol under ambient conditions (see Scheme 3). Acetic acid that is the by-product in all reactions is removed completely with a mixture of toluene:acetonitrile (1:1) added to the reaction mixture. This general method established for these compounds has enabled us to make the water soluble CPs utilizing tridentate ancillary ligands.



Scheme 3. Synthesis of **1-8**.

The FTIR spectra of **1-8** were measured in the solid state using KBr pellets. For Zn(II) compounds, the peaks at 1639 and 1320 cm^{-1} (**1**); 1636 and 1314 cm^{-1} (**2**); 1634 and 1321 cm^{-1} (**3**); 1632 and 1312 cm^{-1} (**4**) correspond to the asymmetric and symmetric stretches of the carboxylate group, respectively. For Cd(II) compounds, the corresponding peaks are at 1594 and 1349 cm^{-1} (**5**); 1582 and 1346 cm^{-1} (**6**); 1630, 1560, 1377 and 1340 cm^{-1} (**7**); 1621, 1562, 1378 and 1344 cm^{-1} (**8**), respectively. While one set of asymmetric and symmetric stretching frequencies is observed for **1-6**, there are two sets of such frequencies observed for **7** and **8**, out of which the second set is for the chelating mode of adc with differences of 220 and 218 cm^{-1}, respectively, between the asymmetric and symmetric stretching frequencies. For the monodentate binding of adc to the Zn(II) in **1-4**, the differences of 319, 322, 313 and 320 cm^{-1}, respectively, between the asymmetric and symmetric stretching frequencies show a uniform pattern. Similarly, the differences of 245, 253 and 243 cm^{-1}, respectively, for **5**, **7** and **8** fall in the range for monodentate binding mode of a carboxylate group. In case of **6**, the value of 236 cm^{-1} can be explained due to the presence of a combination of monodentate and asymmetric chelating binding modes of the carboxylate group. These binding modes of the carboxylate groups of adc in these compounds are confirmed by single crystal X-ray diffraction studies (*vide infra*). The peaks at 1603, 1489, 1023, 781, 695 and 677 cm^{-1} are for the ligand, which are common in all compounds with a shift of few wave numbers.

Single crystal X-ray structures. Crystals of all Zn(II) and Cd(II) compounds suitable for the single crystal X-ray study were grown from slow evaporation of aqueous solution of the respective compounds.

Compounds **1** and **2** are isostructural and crystallize in the monoclinic $P2_1/n$ space group. Both are 1D V-shaped CPs with one adc bridging the Zn(II) centers. In the polymeric structure, Zn(II) centers are pentacoordinated and surrounded by three nitrogens of the ligand and two oxygens from two ends of two adc linkers (see Fig 1). The adc binds in a bis(monodentate) syn-anti fashion. The Zn-O distances are 2.013(4) and 1.974(4) Å for **1** and 2.0315(16) and 1.9833(16) Å for **2**. The C-C triple bond varies from 1.175(11) to 1.177(11) Å for **1** and 1.188(5) to 1.192(4) Å for **2**. The other selected bond distances and bond angles are listed in Table S1. Many CPs with Zn(II) have been reported in the literature with rigid dicarboxylates and/or neutral linkers, such as 4,4-bphdc, 1,10-phenanthroline, bpe, imidazole containing ligands, etc., but most of these polymers are cationic and/or insoluble in common organic solvents.[23,24] Recently, Ruschewitz et al. has reported the first CP of Zn and Tl containing adc, $[Tl_2Zn(adc)_2(H_2O)_2]_n$.[25]

Unlike **1**, moderate π–π interactions are present in **2** resulting in a chair type supramolecular assembly as shown in Fig 2. The centroid–centroid distance is 3.879 Å.[26] This could be due to subtle change in the N-alkyl group of the tridentate ligand.

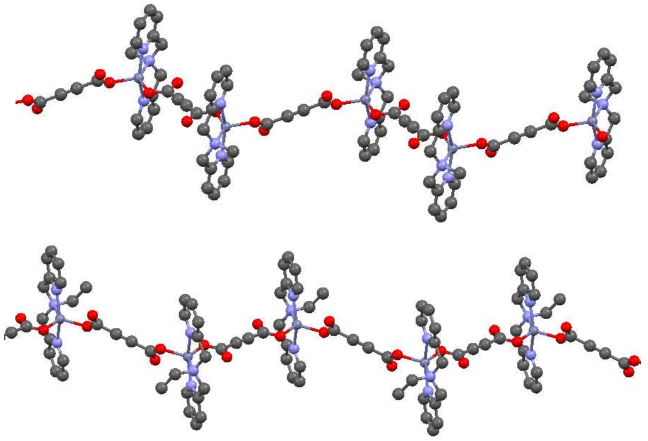


Fig 1. Perspective views of **1** (top) and **2** (bottom).

Compound **3** is a 1D CP similar to bpma (**1**) and bpea (**2**) analogs but in this case the adc linker binds in a bis(monodentate) syn-syn fashion to Zn(II) (see Fig 3). The presence of two lattice water molecules in the crystal structure also makes it different from **1** and **2**. It is clear that only the bpta analog has more affinity for lattice water molecules over the others (*vide infra* for **7**). The selected bond distances and angles for **3** are listed in Table S1. The lattice water molecules connect two 1D CP chains to form a 2D supramolecular assembly (Fig 4). For example, the oxygen of one water molecule, O5, connects the two layers together via hydrogen bonding with uncoordinated oxygen atoms of the linker. All other hydrogen bonding parameters are listed in Table 2.

Table 1. Crystal Structure Data and Refinement Parameters for **1**, **2**, **3**, **6**, **7** and **8**.

	1	**2**	**3**	**6**	**7**	**8**
Chemical formula	$C_{34}H_{30}N_6O_8Zn_2$	$C_{36}H_{34}N_6O_8Zn_2$	$C_{40}H_{46}N_6O_{10}Zn_2$	$C_{36}H_{34}N_6O_8Cd_2$	$C_{40}H_{46}N_6O_{10}Cd_2$	$C_{46}H_{38}N_6O_8Cd_2$
Formula Weight	781.38	809.45	901.57	903.49	999.66	1027.65
Temperature (K)	296(2)	296(2)	296(2)	100(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	*Pbca*	*P-1*	*Pbca*	*Pbca*
a (Å)	8.7929(7)	8.7267(7)	13.330(2)	15.3785(18)	14.056(5)	13.1609(5)
b (Å)	13.7425(11)	14.1120(13)	13.669(3)	16.5020(9)	13.731(4)	17.9462(6)
c (Å)	14.3194(11)	14.2172(14)	22.655(4)	16.6992(10)	22.565(8)	18.4789(7)
α (°)	90	90	90	117.123(2)	90	90
β (°)	99.284(5)	98.500(4)	90	97.071(3)	90	90
γ (°)	90	90	90	94.552(3)	90	90
Z	2	2	4	4	4	4
Volume ($Å^3$)	1707.6(2)	1731.6(3)	4127.9(13)	3698.8(5)	4355.0(3)	4364.5(3)
Density (g/cm^3)	1.52	1.56	1.451	1.622	1.525	1.485
μ (mm^{-1})	1.465	1.448	1.226	1.208	1.037	1.035
Theta range	2.07 to 25.07°	2.04 to 25.13°	1.80 to 25.21°	1.35 to 25.09°	1.80 to 25.12°	2.20 to 25.10°
F(000)	800	840	1888	1808	2032	1976
Reflections collected	9982	19975	25380	45426	24391	27800
Independent reflections	3013	3071	3652	13099	3791	3869
Reflections with I >2σ(I)	1551	2474	2223	11223	2165	2833
R_{int}	0.0811	0.0511	0.0947	0.0269	0.0913	0.0338
Number of parameters	228	236	268	934	268	280
GOF on F^2	0.96	1.053	0.949	1.104	0.869	1.033
Final $R_1{}^a/wR_2{}^b$ (I > 2σ(I))	0.0548/0.1115	0.0301/0.0767	0.0421/0.0971	0.0440/0.1094	0.0429/0.0789	0.0273/0.0546
Final $R_1{}^a/wR_2{}^b$ (all data)	0.1323/0.1409	0.0411/0.0825	0.0952/ 0.1205	0.0523/0.1134	0.0889/0.0924	0.0487/0.0616
Largest diff. peak and hole (eÅ-3)	0.690 and -0.483	0.450 and -0.382	0.375and -0.507	1.761 and -1.128	0.464 and -0.912	0.295 and -0.276

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[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$, where $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$, $P = (Fo^2 + 2Fc^2)/3$.

Table 2. Hydrogen bonding parameters for **3**.[a]

D–H...A	r (D-H) (Å)	r (H…A) (Å)	r(D…A) (Å)	∠D-H…A (deg)	Symmetry
O(5)--H(5A)...O(2)	0.85	1.99	2.834(5)	175	1/2+x,y,1/2-z
O(5)--H(5B)...O(3)	0.85	1.96	2.806(5)	173	1+x,y,z
C(6)--H(6)...O(5)	0.93	2.54	3.329(6)	143	
C(7)--H(7)...O(4)	0.93	2.57	3.487(5)	168	-x,1/2+y,1/2-z
C(13)--H(13)...O(4)	0.93	2.54	3.135(5)	122	-1/2-x,1/2+y,z
C(16)--H(16)...O(4)	0.93	2.51	3.407(5)	161	-x,-y,-z
C(19)--H(19A)...O(1)	0.96	2.45	3.348(5)	155	

[a]Numbers in parenthesis are estimated standard deviations in the last significant digits.

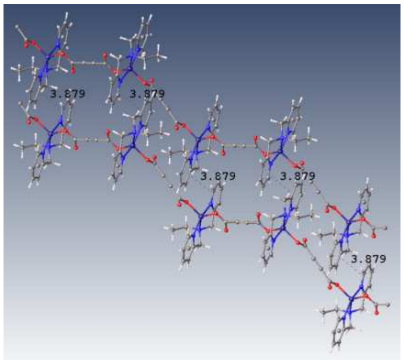

Fig 2. Chair-shaped supramolecular assembly in **2**.

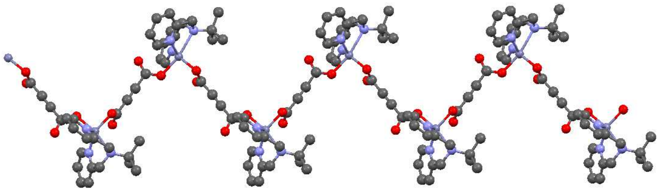

Fig 3. A perspective view of **3**.

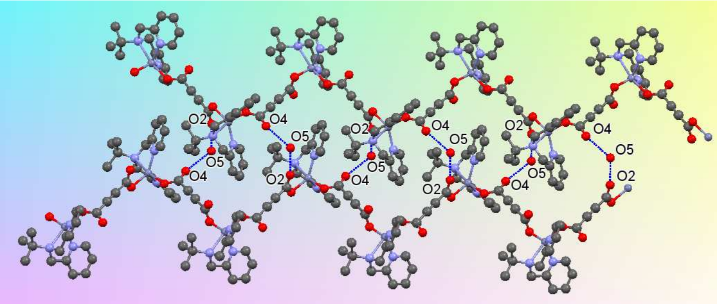

Fig 4. 2D supramolecular assembly in **3** via hydrogen bonding interactions.

Compound **6** crystallizes in the triclinic *P-1* (No. 2) space group. There are two independent 1D CP chains in the asymmetric unit (see Fig 5). In one of the polymeric chain Cd(II) centers are heptacoordinated surrounded by three nitrogens of the ligand, four oxygen atoms from the two chelated adc. In second polymeric chain one Cd(II) center is hexacoordinated surrounded by three nitrogens of the ligand and three oxygens from one chelated and one monodentate adc whereas second Cd(II) center is heptacoordinated having similar coordination environment as found in the first polymeric chain. The Cd-O distances for chelated carboxylate in this polymeric chain are 2.241 and 2.616 Å. The selected bond distances and angles are listed in Table S2. Compound **6** can be compared to $\{[Cd(adc)(H_2O)_3]{\cdot}H_2O\}_n$[15a] or $\{[Cd(adc)(py)_2(H_2O)]\}_n$[15b] where three water molecules or two pyridine and one water molecules have been replaced by the tridentate ligand bpea except **6** has no water of hydration. On the other hand, the compound $[Cd(adc)(phen)]_n$ (where phen = 1,10-phenanthroline)[15c] with a bidentate rigid pyridyl ligand has a very different structure. The Cd-O distance for the chelated carboxylate in this polymeric chain ranges from 2.268-2.616 Å. The two layers of the polymeric chain 1 in **6** are stacked together with moderate π–π interactions found in one plane (Fig 6). The centroid-centroid distance is 3.903 Å.[26] Similar π–π interactions are found in polymeric chain 2 of **6**. It appears that only the bpea analogue shows π–π interactions.

On the other hand, compounds **7** and **8** are isostructural and crystallize in the orthorhombic *Pbca* space group. In these two 1D CPs (see Fig 7), one end of adc is chelating while the other end is monodentate. Cd(II) centers are hexacoordinated surrounded by three nitrogens of the ligand and three oxygens of the two adc linkers. Thus **7** differs from **3** in coordination environment around the metal centers while both **7** and **8** differ from **6** showing diversity in changing the N-alkyl groups in the tridentate ligands. The selected bond distances and angles for **7** and **8** are listed in Tables S3 and S4, respectively.

Effect of N-donor ligands. In this study, four tridentate polypyridyl ancillary ligands differing in the N-alkyl groups have been used to investigate the formation of products in the M(II)-dicarboxylate (M = Zn or Cd) system under similar reaction conditions. This subtle change in the N-alkyl group in the tridentate ligands has provided structural diversity in these CPs with respect to binding differences of the adc linker and the presence (or absence) of π–π interactions as well as the presence (or absence) of lattice water molecules that further shows hydrogen bonding interactions between the CP chains forming supramolecular networks. For example, only in case of CPs containing the bpea ligand, π–π interactions are present; however, the formation of 2D supramolecular assembly between the CP chains is dependent on the N-alkyl substitution not on the metal center. Similarly, unlike other alkyl groups the t-butyl group allows the two CP chains of **3** and **7** get further connected through the lattice water molecules. These features are unique for the CPs reported in this work. This clearly indicates that the diversity of these structures of the Zn(II) and Cd(II) compounds are due to both the ability of adc providing different binding modes and the subtle change in the N-alkyl group of the tridentate ligands.

Thermochemistry by TGA and PXRD. Thermal stability of all these polymers was studied by thermogravimetric analysis from 50 to 500 °C under a nitrogen atmosphere. All Zn(II) CPs (**1-4**) are stable up to 175 °C followed by loss of acetylene dicarboxylic acid (Fig 8, left). On the other hand, there is a difference in the thermal stability for the Cd(II) polymers. In particular, compound **5** is found to be less stable and shows a different thermal degradation profile from others (**6-8**); furthermore, unlike other CPs in case of **5** and **7** the initial loss of lattice water molecules are observed. Both **6** and **8** are found to be stable up to 150 °C. In all the Cd(II) CPs, the loss of acetylene dicarboxylic acid is also observed (Fig 8, right).

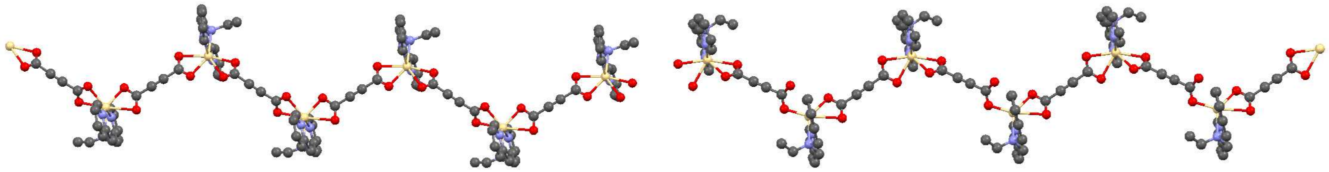

Fig 5. Perspective views of the polymeric chains 1 and 2 in **6**.

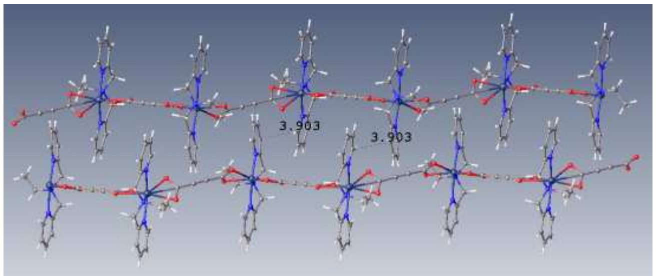

Fig 6. 2D Supramolecular assembly in **6** via π–π interactions.

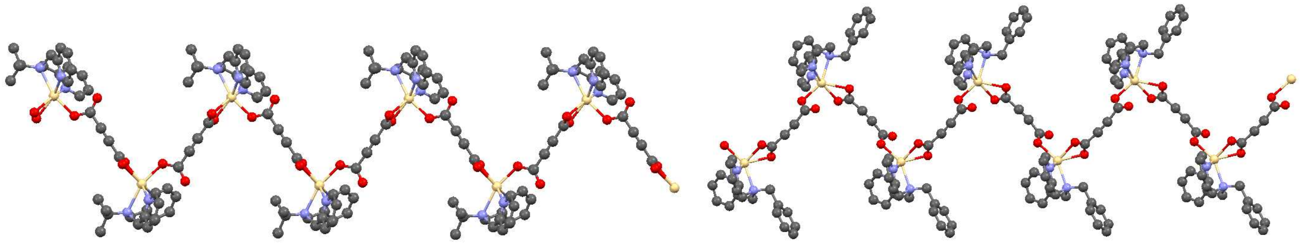

Fig 7. V-shaped 1D CPs, **7** (left) and **8** (right).

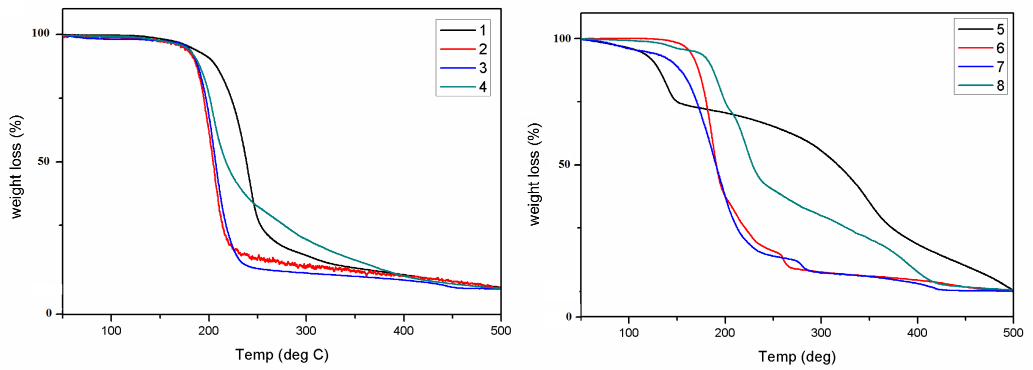

Fig 8. TGA scans for **1-4** (left) and **5-8** (right).

Based on the distinct thermal behavior described above, the bpta analogs of Zn(II), **3**, and Cd(II), **7**, were further investigated to provide inside into their crystalline properties at different temperatures (with a profile from 25 °C to -100 °C and then 50 °C to 100 °C to 150 °C followed by back to 25 °C). As can be seen from Fig 9, compound **3** retains its structure and crystallinity for this cycle. On the other hand, as shown in Fig 10 compound **7** is found to be stable up to 100 °C and decomposes to submicron-sized CdO at 150 °C.

Generation and characterization of metal oxides. A powdered sample of **3** (20 mg) was placed in a crucible and heated to 400 °C for 1 h in a forced air programmable oven. After cooling the crucible to room temperature, a white crystalline material was collected. The PXRD pattern of the white material (Fig S1, ESI) confirms it to be ZnO showing an agreement with the typical wurtzite ZnO structure (hexagonal phase, space group $P6_3mc$); the (110), (002), (101), (102) and (110) reflections are clearly seen, JCPDS reference no. 36-1451). Sharp diffraction peaks indicate good phase pure crystallinity of the ZnO isolated from **3**. For **7**, a yellow crystalline material was obtained in a similar fashion except the oven temperature was 250 °C. The PXRD pattern of the yellow material (Fig S2, ESI) confirms the formation of the cubic phase of the CdO; the (111), (200) and (220) reflections are clearly seen and closely match the reference pattern for CdO (JCPDS reference no. 05-0640). Both white and yellow materials were further characterized by EDS (see Fig S3, ESI) as ZnO and CdO, respectively.

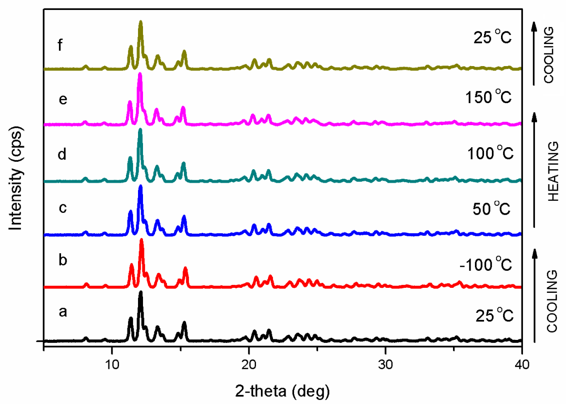

Fig 9. Variable temperature powder diffraction patterns for **3**: (a) sample at 25 °C; (b) sample cooled to -100 °C; (c) sample heated to 50 °C, (d) sample heated to 100 °C, (e) sample heated to 150 °C, and (f) sample cooled back to 25 °C.

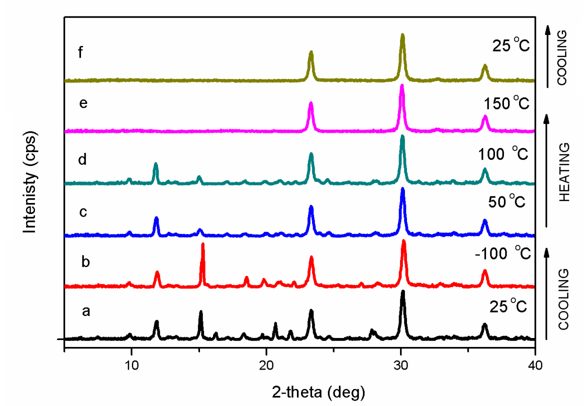

Fig 10. Variable temperature powder diffraction patterns for **7**: (a) sample at 25 °C; (b) sample cooled to -100 °C; (c) sample heated to 50 °C, (d) sample heated to 100 °C, (e) sample heated to 150 °C, and (f) sample cooled back to 25 °C.

FE-SEM images of the as-synthesized metal oxides from **3** and **7**, respectively, are presented in Fig 11. The average size (diameter) of an isolated ZnO and CdO particle is about 85 nm and 420 nm, respectively. These images clearly suggest that the CPs can be considered as suitable precursors for obtaining nanoparticles of ZnO and CdO with uniform size and size distribution. Due to the presence of the polypyridyl ligands, the as-synthesized nuclei do not come close enough to form an array. Therefore, it can be deduced that the steric hindrance present in the novel precursor acts like a protecting agent that prevents the particles from further aggregation. Furthermore, compared to the conditions applied to get such materials in earlier studies,[27] the use of these CPs provide a great opportunity as the sacrificial organic ligands are lost easily under mild conditions. Thus application of these precursors that require no solvent like oleic acid or any surfactant makes this route a cost-effective one. Additionally, these materials in large quantities are easily prepared within few hours.

Photoluminescence studies. Due to their potential applications in photovoltaic materials, CPs have been investigated for the photoluminescence properties.[28] Thus, there is a huge interest in building a database of such CPs showing photoluminescent properties. In order to contribute to this database, few of the compounds described above have been tested for photoluminescence in the solid state at room temperature (see Fig S4). Compound **3** shows an intense fluorescence with an emission maximum at ca. 450 nm upon excitation at 400 nm. On the other hand, compound **6** shows a broad emission red-shifted to 550 nm upon an excitation at 350 nm and compound **7** shows an emission at 550 nm upon excitation at 380 nm. While the free tridentate ligands have very weak fluorescence, the free H_2adc is reported to have moderate fluorescent emissions at 292 nm and 389 nm (λ_{ex} = 245 nm).[29] For compounds with Zn(II) and Cd(II), which are d^{10} ions (difficult to oxidize or reduce), the observed enhancement of the emission peaks may be attributed to the chelation of the ligand to the metal center which causes the ''rigidity" of the ligand and the linker reducing the loss of energy through a radiationless pathway.[30,31] The difference in emission behaviour of these compounds can be due to the difference in the coordination of the adc linker as well as in the rigidity of solid state crystal packing. Some of these compounds may be used as a potential material for light-emitting diode devices and may be candidates for thermally stable fluorescent material.

Conclusions. Using Zn(II) and Cd(II), eight neutral 1D CPs have been obtained with adc as a linker and four flexible tridentate ligands differing in the N-alkyl group. Compared to the corresponding adc compounds of these ions reported earlier, these CPs are water soluble due to the presence of the tridentate ligands. Our strategy to use the tridentate ligands to make water soluble CPs of Zn(II) and Cd(II) has provided a new path forward to conduct application oriented research. Furthermore, diverse binding of adc is one of the reasons to have structural differences in these CPs. For example, Zn(II) centers are pentacoordinated and surrounded by three nitrogens of the ligand and two oxygens from two ends of two adc linkers which bind in a bis(monodentate) *syn-anti* fashion. On the other hand, in the Cd(II) analogs each hexacoordinated Cd(II) center is surrounded by three nitrogens of the ligand and three oxygen atoms (from one monodentate carboxylate group of an adc and one chelated carboxylate group of another adc) except in one case where Cd(II) centers are heptacoordinated due to chelation of both carboxylate groups of adc. In combination of variable temperature PXRD and TGA, their thermal stabilities are evaluated. This encouraged us to do further studies to use these as the precursors for making submicron-sized crystalline ZnO or CdO via the direct thermal decomposition technique under relatively mild conditions. A few of these Zn(II) and Cd(II) polymers has been evaluated for their photoluminescence properties in the solid state to show their potential for ligand-based fluorescent materials. Based on the isolation and characterization of the crystalline metal oxides, further work continues in our laboratory to pursue the corresponding sulphides and selenides.

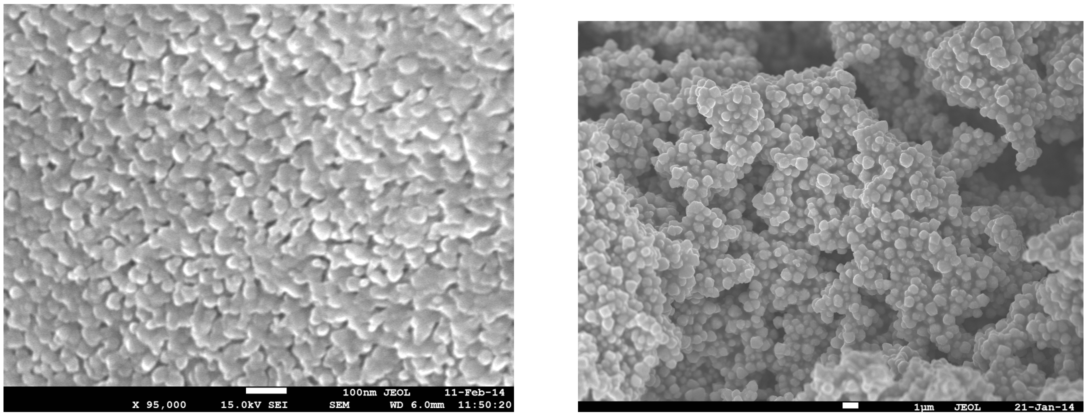

Fig 11. SEM images of ZnO prepared from **3** at 400 °C (left) and CdO prepared from **7** at 250 °C (right).

Acknowledgements

Funding for this work was provided by IISER, Mohali. S.K. is grateful to CSIR, India for a research fellowship. X-ray, NMR and Raman facilities at IISER, Mohali, and CIL, NIPER, Mohali for CHN and TGA analysis are gratefully acknowledged.

Notes and references

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†Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Crystallographic data of the structures **1-3** and **6-8** in CIF format (CCDC 975383-975388), selected bond distances and angles of **1-3** and **6-8** (Tables S1-S4), and PXRD patterns for ZnO and CdO (Figs S1 and S2), EDS plots for **3** and **7** (Fig S3) and emission spectra of **3**, **6** and **7** (Fig S4). For ESI and crystallographic data in CIF format or any other electronic format See DOI: 10.1039/b000000x/

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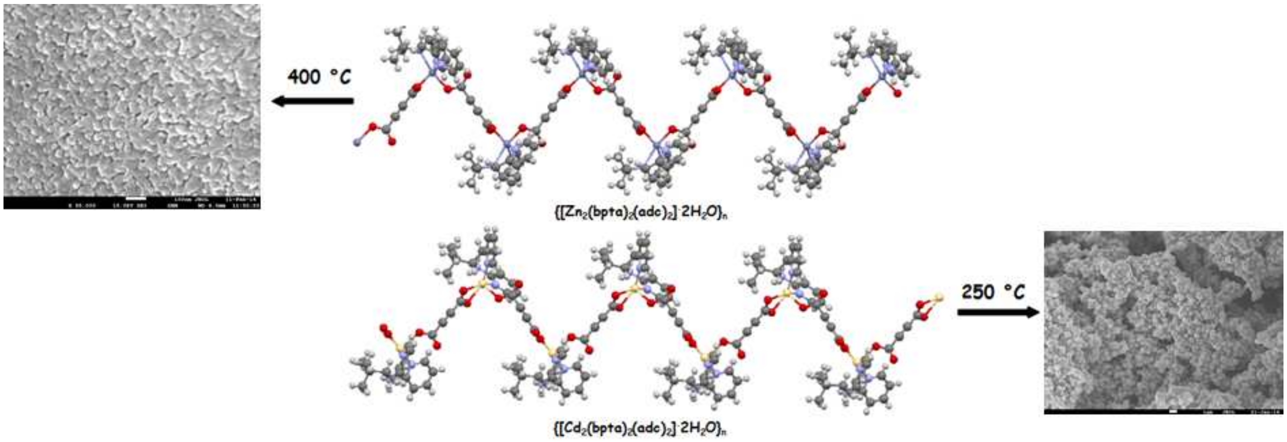
Table of contents – artwork and abstract



Utilizing flexible tridentate ancillary ligands and the acetylene dicarboxylate linker eight new water soluble neutral coordination polymers (CPs) of Zn(II) and Cd(II) are synthesized at ambient conditions. Their single crystal structures, thermal and luminescent properties are established by various analytical techniques. One CP of each metal has been shown to be a good precursor for generating submicron-sized ZnO or CdO, at 400 °C and 250 °C, respectively.