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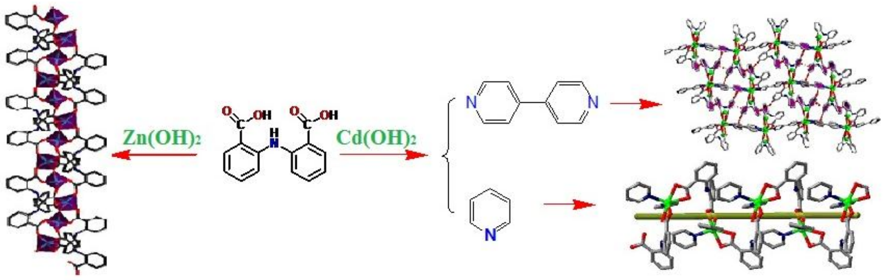
Graphical Abstract Figure



Graphical Abstract Legend

A new flexible multicarboxylate ligand and M(OH)$_2$ in the presence of different N-donor ancillary ligands afford three novel coordination polymers. These polymers show great differences in regard to their structures and properties originated from the variation of second ligands and coordination geometry of the metal ions.

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Solvothermal Synthesis, Structure, and Fluorescence Property of Three d^{10} Polymers Assembled From Semi-rigid V-shaped Aza-Bridged Multicarboxylate

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Hydro(solvo)thermal reactions between a new flexible multicarboxylate ligand of 2,2'-azanediyldibenzoic acid (H_2L) and $M(OH)_2$ (M= Cd, Zn) in the presence of different N-donor ancillary ligands: 4,4'-bipyridine (bpy) and pyridine (py) afford three novel coordination polymers $[Cd_2(L)_2(bpy)_{1.5}(H_2O)]_n$ (**1**), $[Cd_2(L)(Py)_2]_n$ (**2**), $[Zn_2(L)_2]_n$ (**3**). These polymers show great differences in regard to their structures and properties originated from the variation of second ligands and coordination geometry of the metal ions. Compound **1** exhibits a 3D supramolecular network assembled from 2D layered architecture composed of dinucelar cadmium subunits via intermolecular $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions. The supramolecular structure of compound **2** is built from the packing of two homochiral helical chain. Compound **3** possesses two crystallographical nonequivalent metal atoms with Zn1 in four-coordinated tetrahedron geometry and Zn2 in five-coordinated trigonal bipyramid geometry. Five different coordination modes of H_2L ligand ranging from μ_2, μ_3 and μ_4 have been observed respectively. The solid-state fluorescence spectra show that complexes **1** and **2** exhibit tiny blue shifts while **3** presents red shift compared to free ligand.

1. Introduction

In the field of supramolecular chemistry and crystal engineering, the design and synthesis of coordination polymers have been emerging as an ongoing field owing to their structural aesthetics and topologies as well as diverse functional properties.[1-3] Among various kinds of complexes fabricated, those with intriguing fluorescent property attracts great attention due to their potential applications in light-emitting diodes (LEDs).[4-5] The section of the special ligands is very important in the construction of these coordination polymers.

As an important family of multidentate O-donor ligands, organic aromatic polycarboxylate ligands have been extensively employed in the preparation of such metal–organic complexes for their versatile coordination modes. What's more, in comparison with the rigid aromatic multicarboxylate ligands with one benzene ring as central molecular framework, the so-called semi-rigid V-shaped multicarboxylate ligands with two benzene rings bridged by an nonmetallic atom (C, O, S, or N atom) as central molecular framework are of increasing flexibility and therefore able to lead to metal complexes with diverse structures because of the free rotation of two benzene rings around the bridged non-metallic atom.[1, 6]

The current research are concerned on the semi-rigid V-shaped multicarboxylate ligands with the two aromatic motifs bridged by '–CH_2 –' or '–O–',[2, 6, 7] there are relatively rare reports on the V-shaped multicarboxylate ligands which the two benzene ring arms are connected by '– NH –'.[5-8] With the aim of understanding the coordination chemistry of V-shaped aza-bridged multicarboxylate ligands, we synthesized 2,2'–azanediyldibenzoic acid and implemented solvothermal reactions on it.

Fortunately, three structural different coordination polymers were obtained with different second ligands and d^{10} metal salts (Cd, Zn). Here in, we report the syntheses, crystal structures, and fluorescent properties of these title intermediates.

2. Experimental Section

2.1. Materials and synthesis

All reagents and solvents employed in the present work were obtained from commercial source and used directly without further purification. 2, 2'-azanediyldibenzoic acid (H_2L) was synthesized according to the literature as detailed below[9]: A mixture of 2-chlorobenzoic acid (3.130 g, 20 mmol), 2-aminobenzoic acid (5.486 g, 40 mmol), anhydrous K_2CO_3 (1.382 g, 10 mmol) and Cu (0.1 g) combined in 15 mL N,N-dimethylformamide (DMF) was refluxed at 150 ºC for 2h. Cooling down to room temperature, 50 mL aqueous HCl (1:1) was added to the reaction slowly, light-yellow precipitate was produced. The mixture was filtered after stewed for 12 h; the crude product was washed with water (20 mL) and then dried in air, recrystallization in tetrahydrofuran yielded the final product (45.5%). Anal. Calcd. for $C_{14}H_{11}NO_4$: C 65.37, H 4.31, N 5.45. Found: C 65.12, H 4.28, N 5.50. IR/cm-1 (KBr): 3331(m), 1667 (s),1515 (s), 1447 (s), 1411 (s), 1322 (s), 1165 (s), 1044 (m), 989 (m), 924 (m), 751(s).

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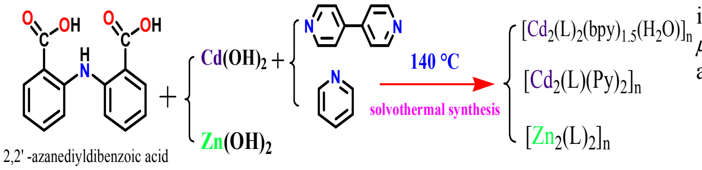
Hydrothermal reaction isolated the crystals of compounds **1**, **2** and **3**. The synthesis route was shown in scheme 1. A heavy walled Pyrex tube containing a mixture of H_2L (0.0516 g, 0.2 mmo1), 4,4'-bipyridine (0.0312 g, 0.2 mmol), $Cd(OH)_2$ (0.0292 g, 0.2 mmol), water (2 mL) and ethanol (1 mL) was frozen and sealed under vacuum, then placed it inside an oven at 140℃ for 72 h and then cooled to room temperature at a rate of 5℃·h^{-1}. The yellow block crystals for **1** yield 0.035 g, 35% (based on ligand). Calc. for **l**: C 51.32, H 3.38, N 6.96; Found for **l**: C 51.30, H 3.39, N 6.97. IR (KBr, cm^{-1}) 3256 (m), l604 (m), l549 (s), l496 (s), l392 (s), l275 (m), l159 (m), 682 (m). Complex **2** was synthesized by a similar procedure as that of complex **1** except pyridine (0.2 mL) was used instead of 4,4'-bipyridine, colorless needle-like crystals for **2** yield 0.056 g, 53% (based on ligand). Calc. for **2**: C 54.77, H 3.61, N 7.99; Found for 2: C 54.75, H 3.62, N 8.01. IR (KBr, cm^{-1}): 3251 (m), 1580 (s), l501 (s), l394 (s), l281 (m), 756 (m). Complex **3** was prepared by the solvothermal reaction between H_2L (0.0516 g, 0.2 mmo1) and $Zn(OH)_2$ (0.0198 g, 0.2 mmol) in the solvent of water (2 mL) and ethanol (1 mL) without any second ligands. Isolated yield of the yellow crystals of **3** was 0.055 g, 86% (based on ligand), Calc. for **3**: C 52.40, H 2.81, N 4.37; Found for **3**: C 52.35, H 2.80, N 4.38. IR (KBr, $cm^{-1)}$ 3332 (m), l667 (s), l575 (s), l516 (s), l448 (s), l410 (m), l321 (m), 1248 (s), 750 (s).



Scheme 1 The preparation of coordination complexes **1-3**

2.2. Characterizations

The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. The room-temperature X-ray powder diffraction spectra (XRPD) were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. Simulation of the XRPD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the internet at http://www.iucr.org. Absorption spectra were carried out on a Jasco-1500 CD spectrometer with DRCD-574 integrating sphere at ambient temperature. The solid absorption spectra were measured on the resulting complexes as crystals (ca. 0.5mg) in 100 mg of oven-dried KBr. The baseline correction was performed with the spectrum of a pure KBr disk. Spectra were recorded for the wavelength range 250–700 nm for all the disks the data pitch was 0.1 nm. PL emission spectra were measured on the resulting grinded crystals powder at room temperature using a spectro fluorophotometer (JASCO, FP-6500) with a xenon lamp (150 W) as a light source and PMT Voltage at 500V.

2.3. Single-crystal Structure Determination

X-ray single crystal structures were determined with a Bruker Smart APEX II CCD diffractometer, The diffraction data were collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were located from the successive difference Fourier syntheses. Detailed information about the crystal data and structure determination for the title compounds is summarized in Table SI. The selected intra-atomic distances and bond angles are given in Table SII. CCDC NO.: 1048011 for **1**, 1048012 for **2** and 1048013 for **3**.

3. Results and Discussion

3.1. Description of the structure

$[Cd_2(L)_2(bpy)_{1.5}(H_2O)]_n$ (1). Compound **1** crystallized in triclinic crystal system and *P*-1 space group. As shown in Figure 1, the asymmetric unit contains two independent Cd(II) ions, two 2,2'-azanediyldibenzoic acid molecules, one and a half bpy, and two solvated water molecules. Compound **1** features an unusual 2D two-layered structure constructed by a binuclear cadmium unit with Cd1···Cd2 distance of 3.8367 Å, both Cd1 and Cd2 atoms can be described as distorted octahedral geometry, each Cd1 atom is coordinated to four oxygen atoms of three ligands (by two monodentate carboxylic groups and one chelating carboxylic group) in the equatorial plane and two nitrogen atoms from bpy molecules along axial position. Cd2 atom is coordinated to five oxygen atoms of three L ligands (by two chelating carboxylic groups and one monodentate carboxylic group) and one nitrogen atom from bpy. All the Cd-O and Cd-N distances are range from 2.222(4) to 2.389(4) Å and 2.267(4) to 2.355(4) Å respectively, which are similar to that found in other Cd(II) complexes.[10-12] The Cd1–O6 distance is 2.9172 Å, suggests a nonnegligible interaction.[13] It is worth noting that H_2L in **1** adopts two different coordination modes (μ_3-*k*O:*k*O,O′:*k*O″,O‴; μ_3-*k*O:*k*O′:*k*O″,O‴) to bridge three Cd(II) atoms in O,O′-chelating, and monodentate fashions (Figure 4 A ,B).

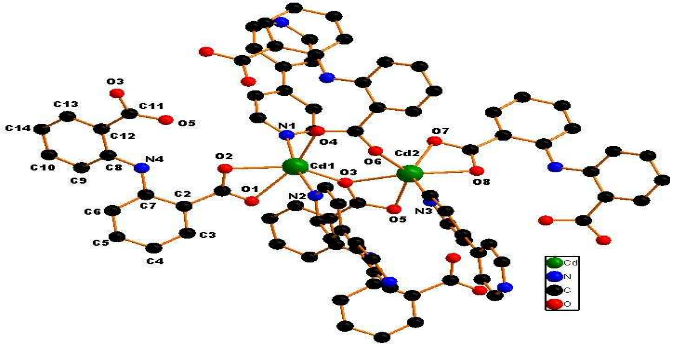


Figure 1 Asymmetric unit of **1** (H atoms of ligand are omitted for clarity)

The infinite 2D wave-like layer structure of **1** is assembled from two kinds of ladder-like chains (A and B). The ligands L connecting adjacent binuclear cadmium units with distance of 6.050 Å (orange line, the red line means binuclear cadmium unit) in mode A and B the vertical ladder armrest chain. The bpy molecules connecting Cd1 and Cd2 with distance of 11.710 Å (blue line) constitute the ladder cleats of ladder A, the other bpy molecules connecting adjacent Cd1

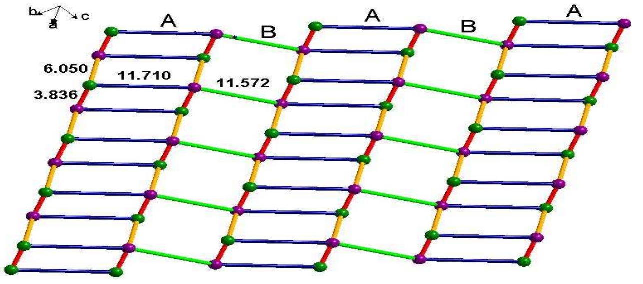


Figure 2 The 2D wave-like layer structure assembled from two kinds of ladder-like structure of **1**, the violet dots indicate Cd1 atoms, and green dots indicate Cd2 atoms.

atoms with distance of 11.572 Å (light green) form the ladder cleats of ladder B (Figure 2). Abundant $\pi\cdots\pi$ (3.699 Å, 3.719 Å) and C-H$\cdots\pi$ (2.931 Å, 3.020 Å) interactions further assemble the 2D layer to a 3D supermolecule structure in slipped AAAA stacking fashion (Figure 3).[14]

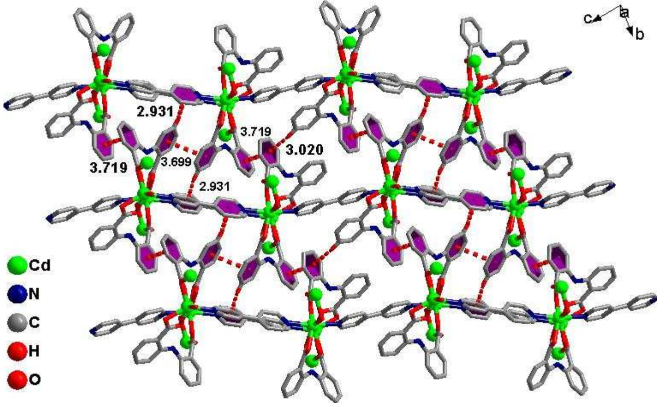


Figure 3 $\pi\cdots\pi$、C–H$\cdots\pi$ interactions and AAAA stacking fashion for **1**.

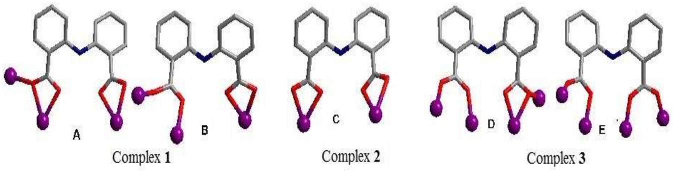


Figure 4 Five coordination modes from μ_2- to μ_4-forms in complexes **1-3**

[Cd$_2$(L)(Py)$_2$]$_n$ (2). The supermolecule of **2** can be best described as 1D structure built. X-ray diffraction study for **2** reveals that it crystallized in monoclinic crystal system with space group $P2_1/c$, and each asymmetric unit consists of one L ligand, one cadmium atom, and two pyridine molecules. As shown in Figure 5, each Cd^{II} ion is coordinated to four oxygen atoms of two ligands in chelating mode and two nitrogen atoms of two pyridine molecules to furnish a distorted octahedral geometry. The coordinated L and pyridine molecules are arranged in a trans-conformation. Different from complex **1**, each L ligand adopts μ_2- kO,O′:kO″,O‴ chelating mode coordinated with Cd^{II} ion to generate one-dimensional structures (Figure 4 C). The dihedral angle between two phenyl rings is 53.7º, 2-carboxylate groups are almost coplanar to the plane of corresponded linking phenyl rings with the dihedral angles between them being 10.6º, 2'-COO groups have the dihedral angles of 29.1º to the corresponding phenyl rings.

The combination of these twists and the non-linear flexility around the bridging nitrogen atom (N3) result in the formation of two paralle homochiral Zn-L helical chains along the b axis (Figure 6). The homochiral right-handed (P) and left-handed helices (M) arrayed alternatively constitutes an achiral 3D supermolecule structure by C–H$\cdots\pi$ interactions with distances of 3.042 Å and 3.469 Å respectively (Figure 7).[15]

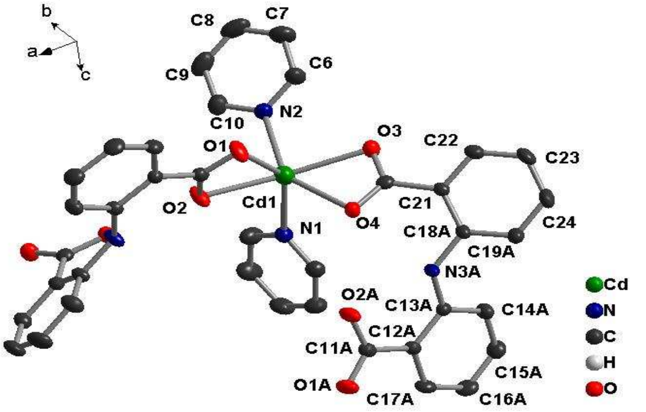


Figure 5 Coordination arrangements of the Cd(II) atoms of **2** (30% thermal ellipsoids)

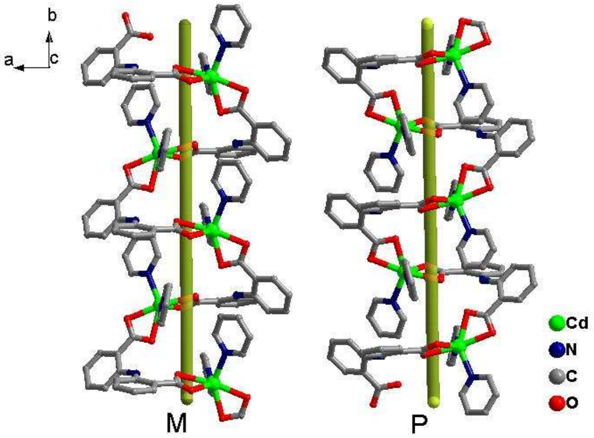


Figure 6 Left-handed helical chain (M) and right-handed chain (P) in **2**

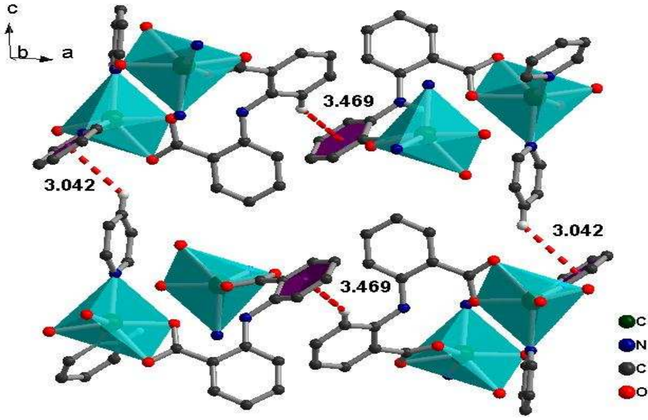


Figure 7 C–H$\cdots\pi$ interactions viewed along b-axis

[Zn$_2$(L)$_2$]$_n$ (3). The X-ray diffraction study for **3** reveals that it crystallized in space group $P2_1/c$, and each molecular unit consists of two L ligands and two zinc atoms. Zinc usually prefers tetrahedral coordination, however, **3** exhibits four-coordinated tetrahedral mode as well as five-coordinated rectangular-pyramidal mode with Zn-O bonds ranging from 1.900 to 2.245 Å.[16-18] Two carboxylate groups of different L connecting Zn1 and Zn2 atoms formed a dinucelar unit with eight-member ring Zn1-O1-C1-O2-Zn2-O8A-C14A-O7A (Figure 8). A 1D ribbon structure is formed along b-axis by connecting the zinc dinuclear units through joint atom O3B and two carboxylate groups in μ_2 chelating mode (Figure 9).

The ligands L adopt two kinds μ_4-coordination mode (μ_4-kO:kO,O′:kO″:kO‴; μ_4-kO:kO′:kO″:kO‴) to bridge four Zn(II) ions in O,O′-chelating, and monodentate fashions. The dihedral angle between two phenyl rings of the two L ligands is 41.4º and 39.3º respectively, and the dihedral angles between carboxylate groups and the corresponding phenyl rings are 19.6º and 28.2º for L of mode D, 22.5º and 23.9º for mode E (Figure 4). Finally, The weak C–H···π and π···π interactions and other noncovalent interaction-static attracting forces, like Columbic and vander Waals forces among the ribbon chains, link the chain structure into a 3D-dimensional network (Figure 10).[15,19-20]

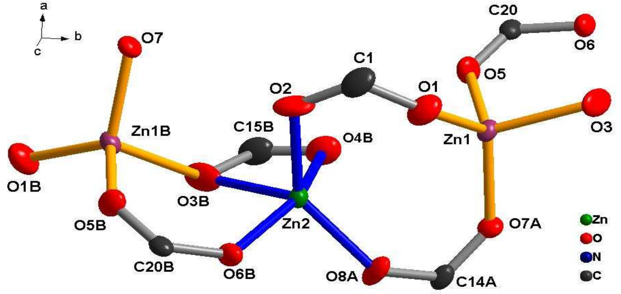


Figure 8 Coordination environment of Zn center, only the Zn, O and alpha-carbon atoms are shown for clarity (30% thermal ellipsoids)

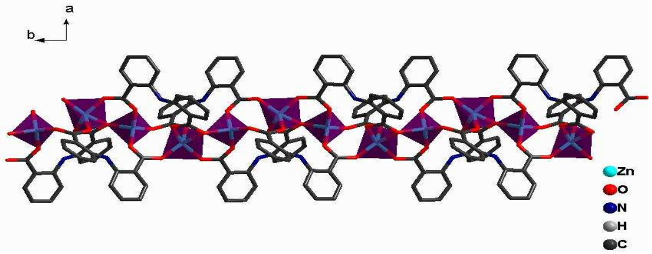


Figure 9 A view of 1D ribbon chain structure of **3** along c- axis.

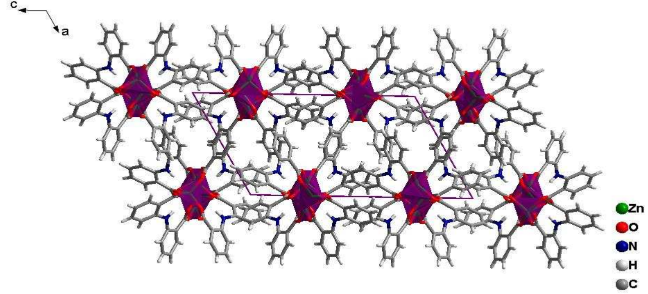


Figure 10 A view of the packing diagrams for **3** along b-axis, the 1D chain extending along b-axis and arraying in ac plane

3.2 Powder X-ray data

XRD was used to check the purity of **1-3**. The results show that all the peaks displayed in the measured patterns at room temperature closely match those in the simulated patterns generated from single-crystal diffraction data, indicating single phases of **1-3** were formed (Figure 11).

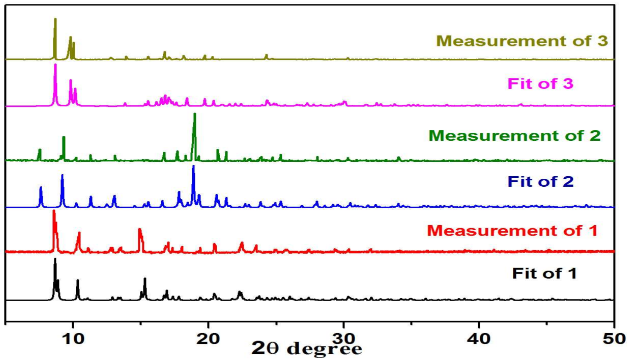


Figure 11 XRD powder patterns of complexes **1-3**.

3.3 Photophysical and Electrochemical Properties

Metal-organic coordination complexes constructed from d^{10} metal atoms (or d^{10} metal clusters) and conjugated organic ligands are promising candidates for hybrid photoactive materials with potential applications such as light-emitting diodes (LEDs).[21] The solid-state absorption spectra and luminescent emission spectra of **1**, **2**, **3** and free H_2L ligand were studied at room temperature (Figure 12 & Supporting Figure S1&S2). Both complexes and ligand exhibit absorption values in the 220nm-400nm region. It can be observed that one robust emission peak at 457 nm with the excitation at 350 nm was observed from free H_2L ligand, which is attributable to the π–π* transitions, similar emissions were also found from complex **1** and **2** (448 nm for **1** and 450 nm for **2**), the closeness in the emission wavelength among **1**, **2** and H_2L suggests that the emission of **1** and **2** are mainly ligand-centered electronic excitation.[22-23] However the emission peak of **3** posses a 28 nm red shifts from free ligand, we tentatively assign it to the intra ligand (π-π^*) fluorescence. The weaken luminescence emissions of the three complexes compared to free ligand may be attributed to flexibility of the H_2L free ligand to the metal cluster, which effectively increases the flexibility of the metal–organic framework and the loss of energy by radiationless decay.[24]

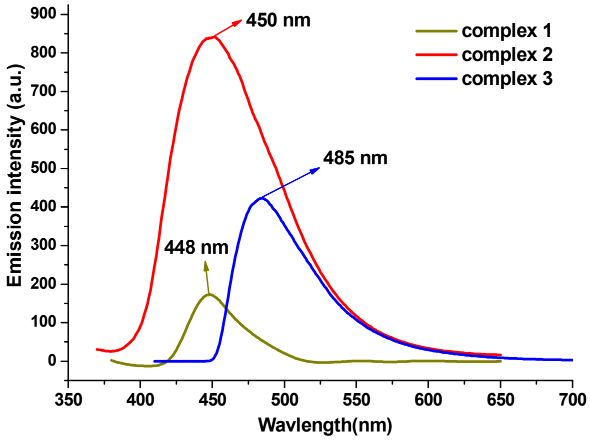


Figure 12 Fluorescent emission spectra of **1**, **2**, **3** in solid state at room temperature.

4. Conclusion

In conclusion, a versatile flexible semi-rigid V-shaped aza-bridged multicarboxylate ligand has been introduced to construct three new d^{10} metal complexes. Fine control over synthetic conditions such as the auxiliary ligand, solvent, and metal salt generated three complexes of metal 2,2'-azanediyldibenzoic acid which show structures ranging from one-dimensional to two dimensional framework. Five coordination modes of H_2L ranging from μ_2, μ_3 to μ_4 have been observed. The study reveals that the H_2L ligand coordinated with metal in chelate mode and monodentate fashions to link three different metal centers to result in two-dimensional structures in complex **1**, but the ligand coordinated in chelating fashions mode to link two different metal centers to generate one-dimensional structures in complex **2**, and coordinated with metal in chelate and monodentate mode to link four metal centers to offer one-dimensional structures in complex **3** (Figure 4). It reveals that that introduce of different ancillary ligands can mediate the coordination model of carboxylate groups and therefore afford structures with dimensional diversity. Moreover, complexes **1-3** exhibit solid-state fluorescence properties at room temperature.

Acknowledgements

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