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Architectures Varying from Discrete Molecular Units to 2-Dimensional Coordination Polymers and Photoluminescent Behavior of Zinc and Cadmium Comprising of Anionic Zwitter ion of Rigid 4,5-Dicarboxy-1,3-dimethyl-1H-imidazolium iodide

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Abstract

A rigid imidazolium dicarboxylate ligand 4,5-dicarboxy-1,3-dimethyl-1H-imidazolium iodide (H_2DDII) was synthesized and employed in the construction of metal complexes or coordination polymer (CPs) comprising of anionic zwitter ion (DDI^-), $[Zn(Cl)(H_2O)_2(DDI)]\cdot(H_2O)$ (**2**), $\{[Zn_2(DDI)_3(H_2O)_2]\cdot I\}_n$ (**3**), $[Zn_2(DDI)_2I]\cdot 2H_2O$ (**4**), $[Zn(DDI)_2(H_2O)_3]\cdot(H_2O)_2$ (**5**) and $[Cd(DDI)_2]_n$ (**6**). In addition, the ligand upon crystallization forms a zwitter ion, [HDDI, (**1**)] by losing HI and shows both intra- and inter-molecular H-bonding and an interesting intermolecular C=O···C short contact. The carboxylate unit of the ligand exhibits terminal monodentate and bidentate chelate modes of coordination. The stoichiometric ratio of metal and ligand, nature of base, type of metal salt and solvent conditions affected the architectures and dimensionality of **2-6** from zero dimensional monomer and dimer to 2D coordination polymer (CP). Complex **2** forms a discrete molecular unit extended by supramolecular interactions to form 2D rectangular sheets. In **3**, a crown shaped macrocycle results into a 2D herringbone CP and extends to 3D supramolecular architecture on account of coordination network containing trapped iodide as counter anions. Complex **4** forms a dimer with coordinated iodide ions and forms an infinite 1D ladder shaped supramolecular architecture. Complex **5** forms another discrete molecular unit different from **2**, and extends in 3D through supramolecular interactions. Complex **6** forms a 2D CP with Cd(II) forming an interesting "*fish scale pattern*" and lacks any counter anion or solvent molecules. Additionally, thermal stability of complexes **2-6** was analyzed by thermo gravimetric analysis. In addition, solid state photoluminescence property of H_2DDII and compounds **2-6** was investigated at room temperature.

Introduction

The coordination polymers (CPs) or Metal Organic Frameworks (MOFs) constructed by ligands consisting of carboxylate donor groups are one of the main research areas since last two decades.[1] CPs comprising of carboxylate donor atoms has been employed in a wide area of applications including gas storage, separation, magnetism, luminescence and catalysis.[2-3] Multidentate carboxylate donor ligands on account of their diverse coordination modes adopt variable conformations and hence have proven to be excellent candidates for the construction of CPs or MOFs with diverse architectures. This study was extended to the design and synthesis of CPs having *N*-heterocyclic carboxylate ligands of pyridine, pyrazole and imidazole because of the available mixed multidentate coordination sites including nitrogen and oxygen centers as donor atoms to the metal ions. The presence of *N*-heterocyclic unit as well as multiple carboxylate units, with various deprotonated forms, allows for the various coordination modes resulting into different topologies.[4-6] In this context, imidazole-4,5-dicarboxylic acid (H_3IDC) and its different analogue ligands as linkers have been majorly used for the synthesis of novel CPs.[7-10]

Functionalized CPs having primary and secondary functional groups have been used as supports and employed in catalysis, wherein the primary functional group coordinates to the metal centre to form an extended network, while the secondary functional group acts as the catalytic site.[11] For past two decades, the imidazolium based ligands are potentially used as precursors for the preparation of *N*-heterocyclic carbene (NHC) metal complexes in catalysis.[12] In addition imidazolium containing systems are known as receptors for anion recognition.[13] Recently, few examples with N-carboxy-functionalized imidazolium salts have been employed in the synthesis of CPs.[14] Very recently we have reported the synthesis of backbone thiofunctionalized imidazolium salts and their metal complexes as well as the catalytic applications of palladium complex in catalysis.[15]

Keeping these facts in mind we have designed the rigid ligand 4,5-dicarboxy-1,3-dimethyl-1H-imidazolium iodide (H_2DDII), containing backbone functionalized imidazolium salt. The main interest behind the design of this ligand was to use it for the synthesis of metal carboxylate complexes/CPs and further use them as supports to incorporate catalytically active metal centers as well as to study the possible anion trapping inside the cavity. In this regard we have carried out the reaction of H_2DDII with the $(n\text{-}Bu_3Sn)_2O$ based on the versatile reactivity of organocarboxylic acids with the tin(IV) precursors and isolated a hexameric hexagonal organotin 42-membered macrocycle $[(n\text{-}Bu_3Sn)_6(\mu\text{-}L)_6(I^-)_2(MeOH)_6]$ (L=H_2DDII) with trapped iodide ions showing an interesting iodide-iodide short contact.[16] However if the reactions are carried out with zinc(II) or cadmium(II) precursors, mono or dinuclear zinc complexes or CPs of zinc and cadmium were obtained which were highly influenced by the nature of metal ion precursors, stoichiometry of the ligand and metal, type of base and the solvent conditions. Herein, we report the syntheses and structural characterizations of five metal complexes and/or CPS, namely $[Zn(Cl)(H_2O)_2(DDI)]\cdot H_2O$ (**2**), $\{[Zn_2(DDI)_3(H_2O)_2]\cdot I\}_n$ (**3**), $[Zn_2(DDI)_2I]\cdot 2H_2O$ (**4**), $[Zn(DDI)_2(H_2O)_3]\cdot 2H_2O$ (**5**) and $[Cd(DDI)_2]_n$ (**6**) whose structures are ranging from discrete molecular units (monomer and dimer) to 2D CPs and are composed of an anionic zwitter ion (DDI^-). Besides, we also discuss the structural characterization of the zwitter ion [HDDI (**1**)], obtained upon crystallization of H_2DDII, showing an intra- as well as an inter-molecular H-bonding in addition to the intermolecular C=O···C short contact and results in a supramolecular helical 2D network structure. The structural properties of compounds **1**-**6** have been discussed along with infrared spectra (IR), powder X-Ray diffraction (PXRD) and thermo gravimetric analysis (TGA). In addition the solid state fluorescence properties of H_2DDII and compounds **2-6** have been investigated.

Experimental section

General details

Anhyd. $ZnCl_2$ and $Zn(NO_3)_2{\cdot}6H_2O$ were obtained from Alfa Aesar, while $Cd(NO_3)_2{\cdot}4H_2O$ was obtained from SD Fine, India. 4,5-Imidazoledicarboxylic acid was obtained from Sigma-Aldrich. All other chemicals were used without further purification. Solvents were first dried and then used after distillation. 4,5-bis(ethoxycarbonyl)-1,3-dimethyl imidazolium iodide was prepared according to the reported literature procedure.[17] Microanalyses for all the compounds were recorded using Perkin Elmer Series-II CHNS/O model 2400 Analyzer. IR spectra were recorded on a Bruker model vertex 70 and Perkin–Elmer model 1320 spectrometer using KBr pellets between the region 4000-400 cm^{-1}. Thermogravimetric analyses were carried out under N_2 atmosphere with a heating rate of 10 °C/min on Mettler Toledo Star System. NMR spectra were recorded on JEOL ECX-500. Powder X-ray Diffraction (PXRD) data were collected on a PANalytical X'Pert Pro X-ray diffractometer with radiation Cu Kα radiation (λ = 1.540598 Å) at room temperature with a scan step size of 0.02 in 2θ. Solid state emission spectra were recorded using a ZSX primus series, Rigaku corporation spectrometer, at room temperature. DIAMOND (version 3.0) and Mercury (version 3) were used to view and draw the structures.

4,5-Dicarboxy-1,3-dimethyl-1H-imidazolium iodide (H_2DDII). H_2DDII was prepared by the acid hydrolysis of 4,5-bis(ethoxycarbonyl)-1,3-dimethyl imidazolium iodide, under reflux condition for 12 h, using 6N HCl. A clear yellow solution was obtained which was removed and the resulting compound was washed with acetone followed by diethyl ether to obtain H_2DDII as a light grey colored compound. Yield: 40% (based on 4,5-Imidazoledicarboxylic acid). Anal.

calcd. for $C_7H_9N_2O_4I$ (312.06 g): C, 26.94; H, 2.91; N, 8.98. Found: C, 26.80; H, 2.90; N, 8.92. IR (KBr, cm^{-1}): 3422 (w), 3145 (m), 3086 (m), 3010 (w), 2979 (w), 2709 (w), 1723 (vs), 1566 (vs), 1473 (vs), 1416 (s), 1370 (m), 1348 (s), 1352 (w), 1300 (s), 1245 (s), 1220 (s), 1144 (vs), 1091 (m), 894 (m), 869 (m), 826 (s), 762 (m), 692 (s), 629 (m), 602 (m), 482 (m). ^{1}H NMR (500 MHz, δ-DMSO-d_6): 9.27 (*s*, 1H, NC*H*N) and 3.96 (*s*, 6H, 2 *N*CH_3). ^{13}C-NMR (500 MHz, δ-DMSO-d_6) δ 159.1(2C, C=O), 141.1 (N*C*HN), 129 (2C, C=C), 37.7 (2C, N*C*H_3). ESI-MS (+ve) 185 [$(M+H)^+$, 100%] and ESI-MS (-ve) 126.90 (I^-).

HDDI(1). H_2DDII was dissolved in DMSO and layered with MeOH. Yellow colored crystals were obtained after one week. Yield: 63% (based on H_2DDII). Anal. calcd. for $C_7H_8N_2O_4$ (184.15 g): C, 45.66; H, 4.38; N, 15.21. Found: C, 45.65; H, 4.30; N, 15.14. IR (KBr, cm^{-1}): 3419 (w), 3139 (w), 3060 (m), 1728 (m), 1573 (vs), 1470 (vs), 1432 (s), 1397 (s), 1371 (s), 1303 (s), 1178 (m), 1024 (m), 907 (w), 869 (w), 833 (w), 770 (m), 657 (br), 629 (m), 600 (w), 498 (w). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.23 (*s*, 1H, NC*H*N) and 3.97 (*s*, 6H, 2 NCH_3). ^{13}C-NMR (500 MHz, δ-DMSO-d_6) 159.1(2C, C=O), 141.1 (N*C*HN), 129.1 (2C, C=C), 37.6 (2C, N*C*H_3). ESI-MS (+ve) 185 [$(M+H)^+$, 100%].

[Zn(Cl)(H_2O)$_2$(DDI)]·H_2O (2). To a solution of H_2DDII (46.6 mg, 0.15 mmol) in CH_3OH (10 mL) was added aq. NH_3 (0.1 mL) followed by the addition of anhyd. $ZnCl_2$ (20.4 mg, 0.15 mmol) and stirred the solution for 30 min. The solution was allowed to evaporate at room temperature very slowly to afford pale yellow crystals after one day. Yield: 90.2 mg (60% based on anhyd. $ZnCl_2$). Anal. calcd. for $C_7H_{13}N_2O_7ClZn$ (338.03 g): C, 24.87; H, 3.88; N, 8.29. Found: C, 24.83; H, 3.84; N, 8.26. IR (KBr, cm^{-1}): 3425 (s), 3335 (vs), 3128 (m), 3059 (s), 1640 (vs), 1559 (vs), 1474 (s), 1450 (m), 1407 (vs), 1373 (s), 1348 (s), 1321 (vs), 1271 (vs), 1220 (s), 1168 (vs), 899 (s), 880 (w), 826 (s), 802 (m), 723 (m), 698 (m), 632 (s), 617 (s), 474 (s).

Synthesis of {[$Zn_2(DDI)_3(H_2O)_2$]·I}$_n$ (3). To a solution of H_2DDII (93.2 mg, 0.3 mmol) in CH_3OH (20 mL) was added aq. NH_3 (0.2 mL) followed by the addition of $ZnCl_2$ (20.4 mg, 0.15 mmol) as solid. The solution was refluxed for 2 h and allowed to cool to room temperature. Colorless crystals of **3** were obtained after two days by the slow evaporation of the solution at room temperature. Yield: 57 mg (91 % based on $ZnCl_2$). Anal. calcd. for $C_{21}H_{25}N_6O_{14}IZn_2$ (843.15 g): C, 29.91; H, 2.99; N, 9.97. Found: C, 29.90; H, 2.96; N, 9.95. IR (KBr, cm^{-1}): 3325 (m), 3149 (m), 3073 (m), 1644 (vs), 1566 (vs), 1485 (m), 1411 (vs), 1383 (vs), 1348 (vs), 1327 (vs), 1174 (vs), 903 (m), 834 (m), 790 (m), 748 (m), 666 (m), 634 (m), 589 (w), 501 (w), 459 (w).

[$Zn_2(DDI)_2I$]·$2H_2O$ (4). To a solution of H_2DDII (93.2 mg, 0.3 mmol) in CH_3OH (10 mL) was added aq. NH_3 (0.2 mL) followed by the addition of $Zn(NO_3)_2·6H_2O$ (37.1 mg, 0.125 mmol). The solution was refluxed for 2 h and allowed to cool at room temperature. Colorless crystals of **4** were obtained after two days by the slow evaporation of the solution at room temperature. Yield: 35.1 mg (85 % based on $Zn(NO_3)_2·6H_2O$). Anal. calcd. for $C_{14}H_{18}N_4O_{10}IZn_2$ (659.96 g): C, 32.27; H, 3.63; N, 13.72. Found: C, 32.24; H, 3.60; N, 13.69. IR (KBr, cm^{-1}): 3436 (b), 3138 (m), 3064 (s), 2969 (br), 2925 (br), 1733 (m), 1565 (vs), 1470 (vs), 1432 (s), 1414 (m), 1396 (s), 1370 (s), 1300 (vs), 1176 (s), 1090 (s), 910 (w), 869 (m), 838 (m), 770 (s), 680 (w), 629 (s), 605 (w), 497 (m).

Synthesis of [$Zn(DDI)_2(H_2O)_3$]·$2H_2O$ (5). To a solution of H_2DDII (62.2 mg, 0.2 mmol) in CH_3CN/H_2O (6:8 mL) was added triethylamine (0.2 mL) followed by the addition of $Zn(NO_3)_2·6H_2O$ (59.4 mg, 0.2 mmol) as solid. The solution was refluxed for 15 h and allowed to cool at room temperature. The solution was allowed to evaporate at room temperature very slowly to afford colorless crystals of **5** after twenty-five days. Yield: 50 mg (25% based on

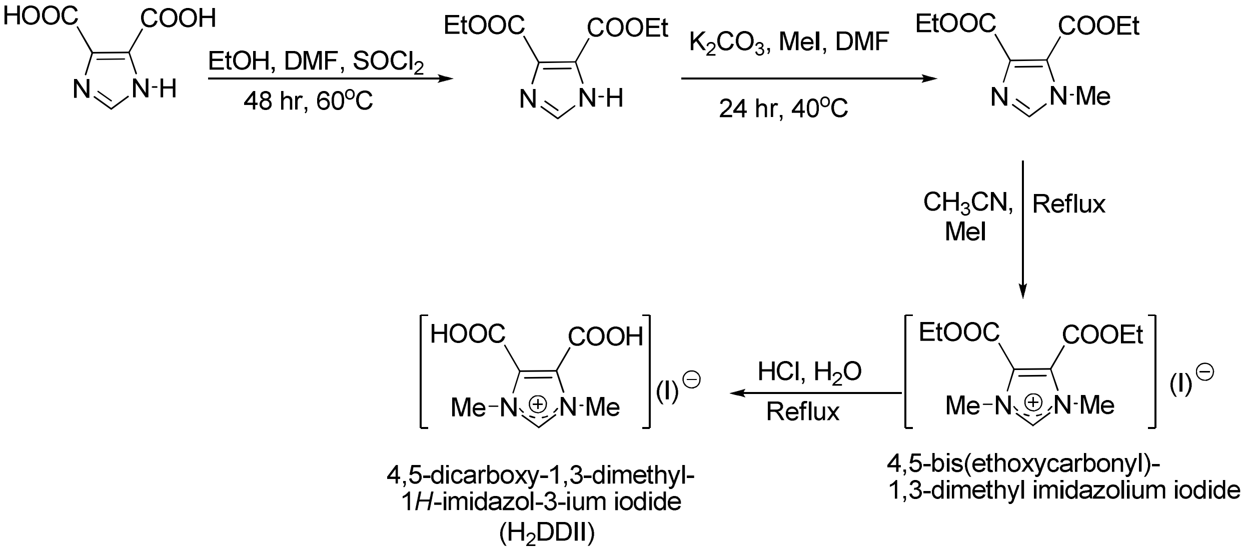
$Zn(NO_3)_2.6H_2O$). Anal. calcd. for $C_{14}H_{24}N_4O_{13}Zn$ (521.76 g): C, 32.23; H, 4.64; N, 10.74. Found: C, 32.22; H, 4.64; N, 10.71. IR (KBr, cm^{-1}): 3414 (m), 3149 (w), 3048 (m), 1630 (vs), 1611 (vs), 1570 (vs), 1474 (s), 1404 (s), 1375 (vs), 1313 (s), 1230 (w), 1175 (s), 1090 (w), 1034 (w), 894 (w), 827 (m), 789 (w), 765 (m), 745 (w), 626 (m), 599 (m), 487 (w), 435 (br), 405 (br).

Synthesis of $[Cd(DDI)_2]_n$ (6). A similar synthetic procedure as that of **5** except that $Cd(NO_3)_2{\cdot}4H_2O$ (61.6 mg, 0.2 mmol) was used in place of $Zn(NO_3)_2{\cdot}6H_2O$. Colorless crystals of **6** were formed after thirty days. Yield: 10 mg (17% based on $Cd(NO_3)_2{\cdot}4H_2O$). Anal. calcd. for $C_{14}H_{14}N_4O_8Cd$ (478.69 g): C, 35.13; H, 2.95; N, 11.70. Found: C, 35.11; H, 2.92; N, 11.65. IR (KBr, cm^{-1}): IR (KBr, cm^{-1}): 3411 (w), 3149 (w), 3085 (m), 1626 (vs), 1607 (vs), 1567 (vs), 1476 (s), 1406 (vs), 1383 (vs), 1357 (s), 1328 (s), 1220 (w), 1175 (s), 1091 (w), 903 (m), 874 (w), 839 (m), 796 (m), 764 (w), 741 (m), 617 (m), 575 (w), 477 (w).

X-ray Crystallography. Single crystal X-ray data for **1-6** were collected at 100 K (**1-4**) and 293 K (**5-6**) on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). The single crystal X-ray data were collected on Bruker Smart Apex diffractometer using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). All the structures were solved using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97.[18] All hydrogen atoms were included in idealized positions using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Topological analysis of CPs **3** and **6** was performed using the ADS program of the TOPOS 4.0 Professional structure-topological program package.[19]

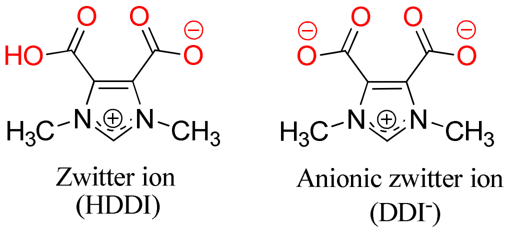
Results and discussion

4,5-Dicarboxy-1,3-dimethyl-1H-imidazolium iodide (H_2DDII). H_2DDII was prepared through step wise procedure. Firstly, 4,5-bis(ethoxycarbonyl)-1,3-dimethyl imidazolium iodide was synthesized according to literature procedure, through multi-step synthesis (Scheme 1). It was followed by the hydrolysis of 4,5-bis(ethoxycarbonyl)-1,3-dimethyl imidazolium iodide using 6N HCl, resulting into the ligand H_2DDII which was obtained as a grey colored compound with moderate yield. The formation of H_2DDII was confirmed by spectroscopic and spectrometric techniques and was found to be soluble in DMSO, DMF and MeOH. The complete hydrolysis of 4,5-bis(ethoxycarbonyl)-1,3-dimethyl imidazolium iodide to H_2DDII was confirmed through ^{1}H-NMR as indicated by the absence of COOCH_2CH_3 protons and also by the shielding effect observed for NC*H*N [9.41 (*s*, 1H)] and slight deshielding effect observed for NCH_3 [3.90 (*s*, 6H)] (Figure S1-S2).



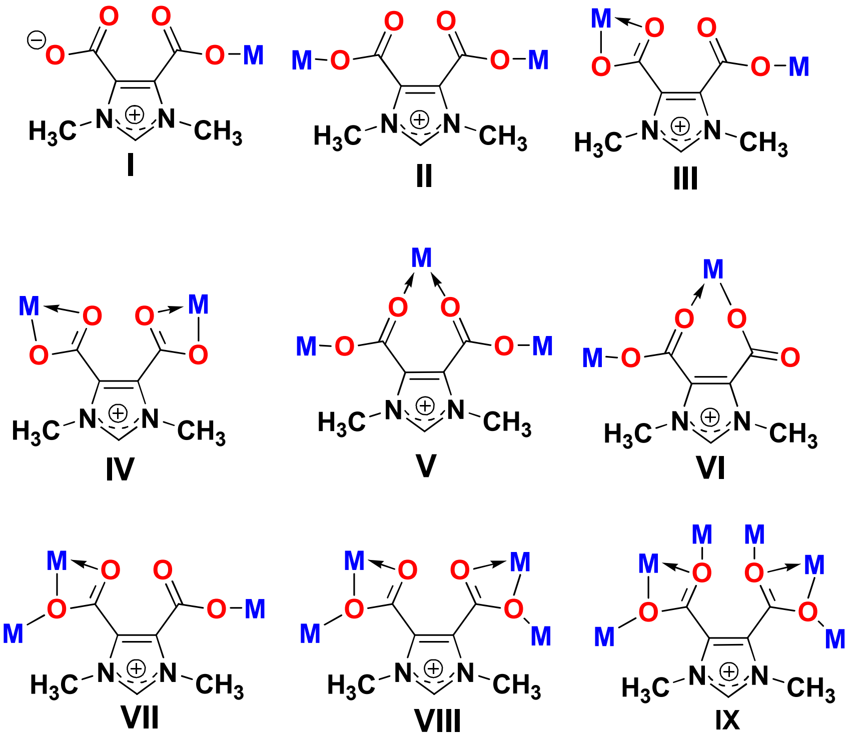
Scheme 1. Synthesis of H_2DDII

As it was observed in N-carboxy functionalized imidazolium salts, H_2DDII is expected to form zwitter ion [HDDI (**1**)] or anionic zwitter ion (DDI$^-$) (Scheme 2) in solution. HDDI could possibly coordinate to the metal through one or two oxygen atoms of deprotonated carboxylate moiety. Whereas DDI$^-$ has four carboxylate O-donor atoms which can possibly coordinate to the



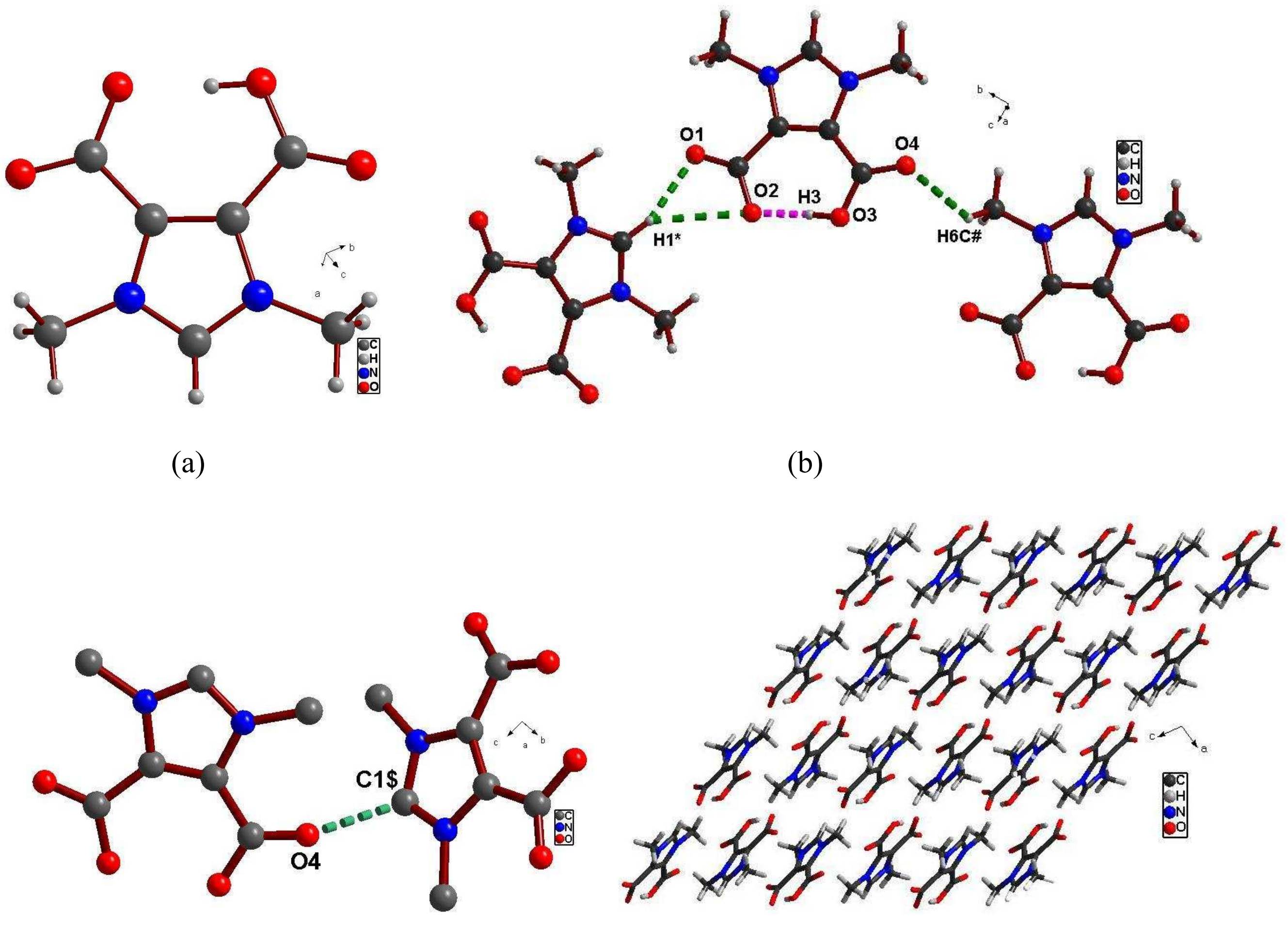
Scheme 2. Deprotonated forms of H_2DDI

metal centers in various fashions such as monodentate terminal/bridging, bidentate chelate/bridging or chelate-bridging[20] (Scheme 3), and result into structures having anionic zwitter ion with different topologies.



Scheme 3. Possible Coordination Modes of anionic zwitter ion (DDI⁻)

Interestingly, H_2DDII upon crystallization in DMSO and methanol led to the formation of HDDI (**1**) and was characterized by IR, NMR, ESI-MS and single crystal X-ray diffraction methods (Figure S3-S4). **1** crystallizes in monoclinic system with $P2_1/n$ space group (Table 1) and was found to be a zwitter ionic structure with the loss of HI (Figure 1a) in solution. In **1,** an intramolecular H-bond exists between O2···H3-O3, arising from the carboxylate units, of a distance of 1.587(2) Å (Figure 1b).[21] In addition, intermolecular O···H-C interactions[22] exists between O1···H1*-C1, O2···H1-C1 with adjacent HDDI units, while O4···H6C#-C6 interaction was present between the stacked up HDDI units one over the other layers (Figure 1b, Table 3). Besides, there also exists an interesting intermolecular C=O···C short contact between C5=O4···C1$ having a distance of 2.895(3) Å and connects two adjacent HDDI units (Figure 1c, Table 3).[23] These interactions collectively tend to form perpendicular adjacent layers of HDDI and also stacking up of one HDDI unit over the other, leading to an extended supramolecular helical 2D network structure (Figure 1d).



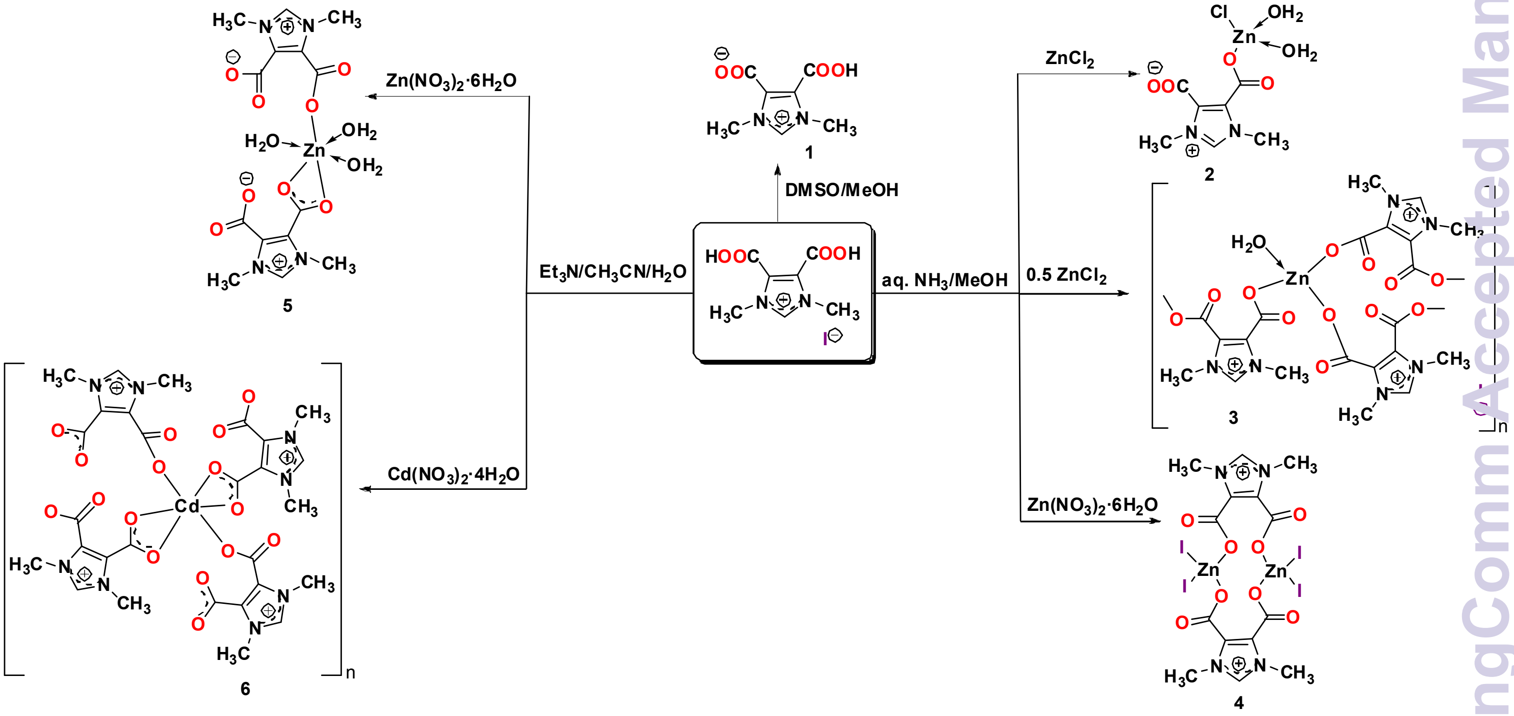
(a) (b)

(c) (d)

Figure 1. (a) The zwitter ionic structure of **1**. (b) Inter-(green color) and Intramolecular (pink color) H-bonding interactions in **1**. (c) Intermolecular C=O···C short contact in **1**. (d) Extended supramolecular architecture of **1**. [H1* is at -1/2 + x, 1/2 - y, -1/2 + z; H6C# is at x, 1 + y, z; C1$ is at 1/2 - x, 1/2 + y, 1/2 + z].

Syntheses of 2-6

The coordination ability of H_2DDII with the metal ions was evaluated by the synthesis of complexes of Zn(II) and Cd(II) using simple evaporation technique. The removal of carboxylic acid proton from H_2DDII was facilitated by the use of aq. NH_3 and Et_3N as base. In these reactions, the pH of the solution was maintained always between 8 and 9. The syntheses of complexes **2-4** were accomplished by using $ZnCl_2$ (**2** and **3**) and $Zn(NO_3)_2·6H_2O$ (**4**) as metal precursors and aq. NH_3 as base in methanol solvent (Scheme 4). The stoichiometry of metal and ligand plays an important role in determining the structure of the resulting products. The

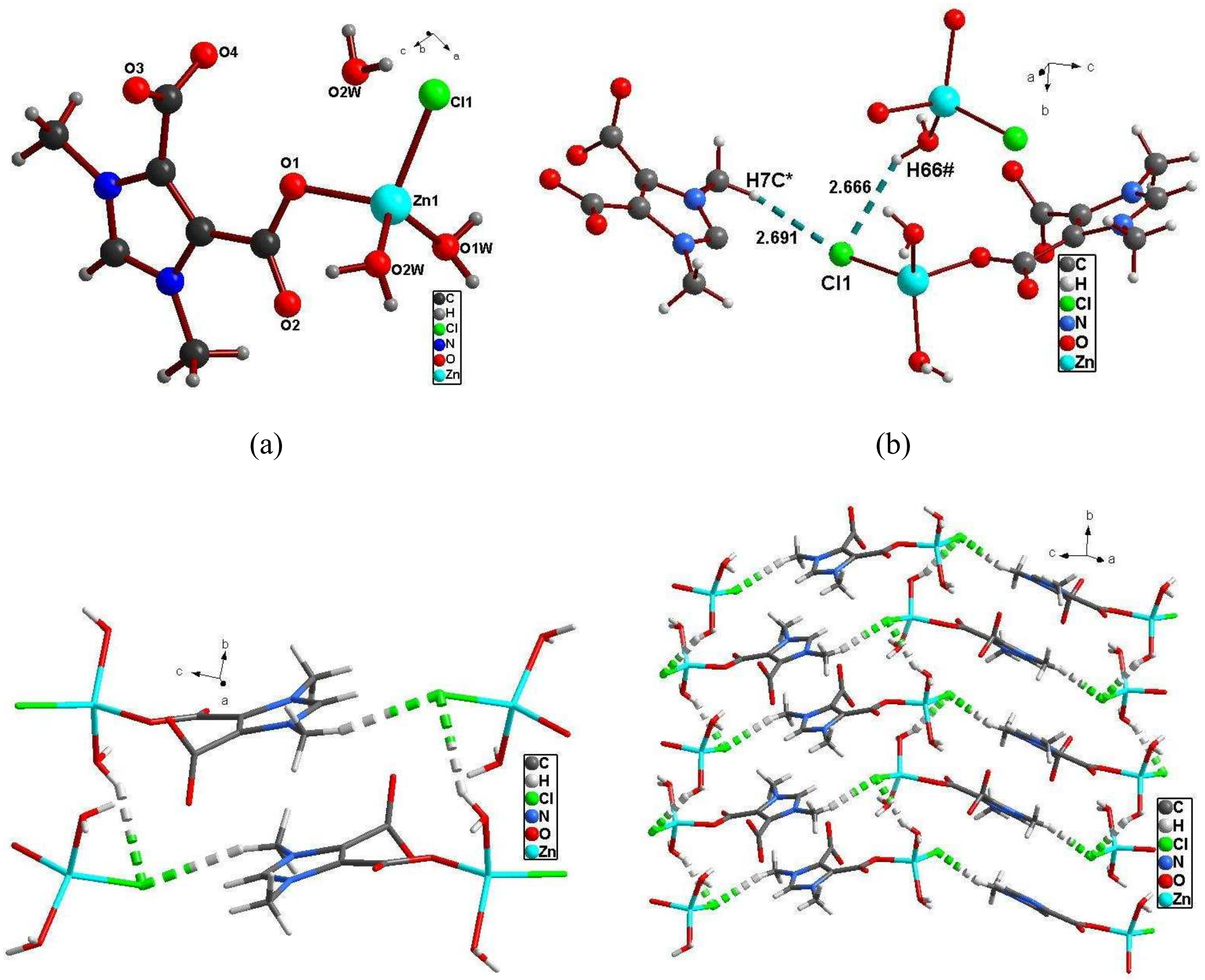


Scheme 4. Synthetic scheme and structure of **1-6**

stoichiometry of $ZnCl_2$ to H_2DDII in 1:1 and 1:2 yields **2** and **3** respectively. The same synthetic conditions as for **2** and **3** was followed for the preparation of **4**, except that $Zn(NO_3)_2{\cdot}6H_2O$ was used in the reaction. Whereas, the syntheses of **5** and **6** was carried out using strong base and $M(NO_3)_2{\cdot}xH_2O$ (M=Zn (**5**), x=6; M=Cd (**6**), x=4) in CH_3CN/H_2O medium (Scheme 4). All the products **2-6** were insoluble in common organic solvents. The IR spectra of **2-6** showed stretching frequencies for ν_{as} (COO^-) and for ν_s (COO^-) around 1600 cm^{-1} and 1400-1300 cm^{-1} respectively, which support the binding of carboxylate to the metal ion. Further, absence of strong IR bands around 1700 cm^{-1} in **2-6** and the presence of multiple stretching frequency peaks in the region of metal carboxylates suggest variable binding modes of carboxylate units to the metal ions. To understand better the product formation and the details of final structures of products **2-6**, a single crystal X-ray diffraction study was carried out.

Solid state structures of 2-6

$[Zn(Cl)(H_2O)_2(DDI)]{\cdot}H_2O$ (2). Single crystal X-ray diffraction studies shows that **2** crystallizes in monoclinic space group $P2_1/n$ (Table 1). It consists of Zn(II) ion, one DDI^- unit, one Cl^- ion and two coordinated H_2O molecules along with one H_2O molecule as water of crystallization. Zn(II) ion lies in a tetrahedral environment and is coordinated by one donor oxygen atom provided by DDI^- unit and one chloride ion, while remaining two sites are occupied by two H_2O molecules (Figure 2a). In **2**, both the hydrogen atoms from carboxylates along with iodide ion are being eliminated. The O-atom from the carboxylate unit of DDI^- coordinates to Zn(II) in a monodentate terminal mode (I; Scheme 3), while the second carboxylate unit has free oxygen-donor site. Hence, the charge is balanced since one of the carboxylate groups remains uncoordinated. Thus, **2** can be described as the anionic zwitter ion zinc complex as it was also observed in *N*-carboxy imidazolium metal dicarboxylates.[14]



(a) (b)

(c) (d)

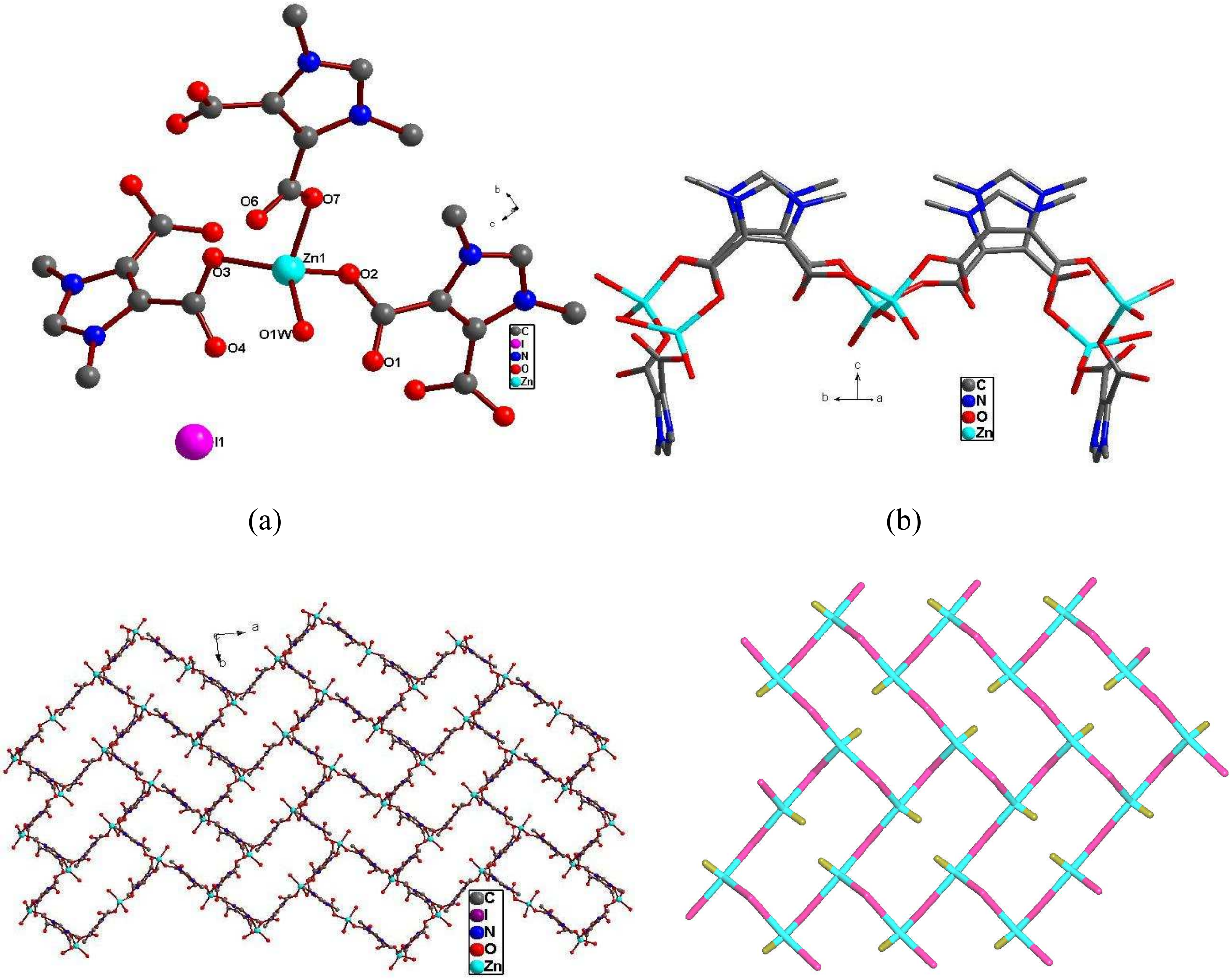
Figure 2. (a) The coordination environment around Zn(II) ions in **2**. (b) H-bonding interactions in **2**. [H7C* is at -1/2 + x, 3/2 - y, 1/2 + z; H66# is at 3/2 - x, -1/2 + y, 1/2 - z]. (c) Single unit of rectangular sheet in **2**. (d) 2D rectangular sheet in **2**.

The Zn-O bond distance for carboxylate oxygen to zinc in **2** is found to be 2.009(4) Å (Zn-O1), comparable to the bond lengths reported with such ligand system[9h], whereas the coordinated water molecules to the Zn(II) ion are nearly the same [av. 2.001(3) Å], while the bond distance for Zn-Cl is 2.274(11) Å (Table 2). The asymmetric unit in **2** extends further through H-bonding existing between the chloride ion and H7C* (from N-CH_3) and H66# (from

H_2O) (Figure 2b, Table 3) to form a 2D rectangular sheet (Figure 2c and d). Each such rectangular sheet comprises of four monomeric units of **2** in which the two DDI$^-$ units are involved in facilitating the extended structure formation. The orientation of the DDI$^-$ (along a-axis) within the rectangular sheet and in the 2D layers is anti-parallel to each other. The chloride ions are oriented in opposite directions between two layers, but are in the same direction to the ones adjacent to it. The orientations of DDI$^-$ and Cl ions play a significant role in extending the monomer through H-bonding. The distance between Zn(II) ions in such rectangular sheet was found to be 4.410(9) Å and 11.481(3) Å for the stacked up and adjacent one respectively (Figure S5). The 2D rectangular sheets are further connected via the lattice water molecules which tend to act as a bridge through CH···O interaction, (Table 3, Figure S6) leading to a 3D supramolecular architecture (Figure S7).

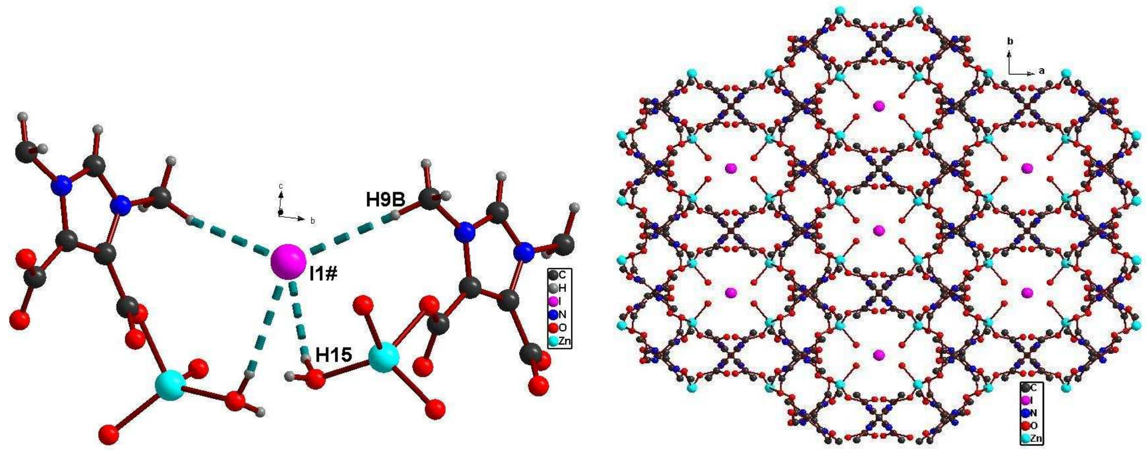
$\{[Zn_2(DDI)_3(H_2O)_2]\cdot I\}_n$ (3). Single crystal X-ray diffraction studies shows that **3** crystallize in orthorhombic space group *Pccn* (Table 1). The analysis of the crystal structure reveals that **3** is an anionic zwitter ion 2D CP with a basic unit composed of two zinc, three DDI$^-$ units, two water molecules and an iodide as counter anion, with a 2-fold imposed symmetry where C10-H10 bond and I1 lie on different 2-fold axes. Each Zn(II) ion lie in a tetrahedral environment and is coordinated by three donor oxygen-atoms provided by three individual DDI$^-$ units and one H_2O molecule occupies the fourth coordination site (Figure 3a). All the three oxygen atoms of DDI$^-$ coordinate to Zn(II) ion in a monodentate terminal mode (II; Scheme 3). The Zn-O bond distance in **3** of carboxylate oxygen atoms to zinc falls in the range of 1.985(3) Å to 2.041(5) Å and these are consistent with the already reported values in the literature.[9h] While the bond angles around zinc vary from 95.76(14)^o to 123.10(17)^o and hence the geometry of the zinc can be described as distorted tetrahedron (Table 2). In **3,** the oxygen atoms from second carboxylate unit of DDI$^-$

binds to the other zinc atoms to form a hexameric 42-membered crown-shaped macrocycle ring (Figure 3b). The macrocycle consists of six Zn(II) atoms which are connected through six DDI$^-$



(a) (b)

(c) (d)

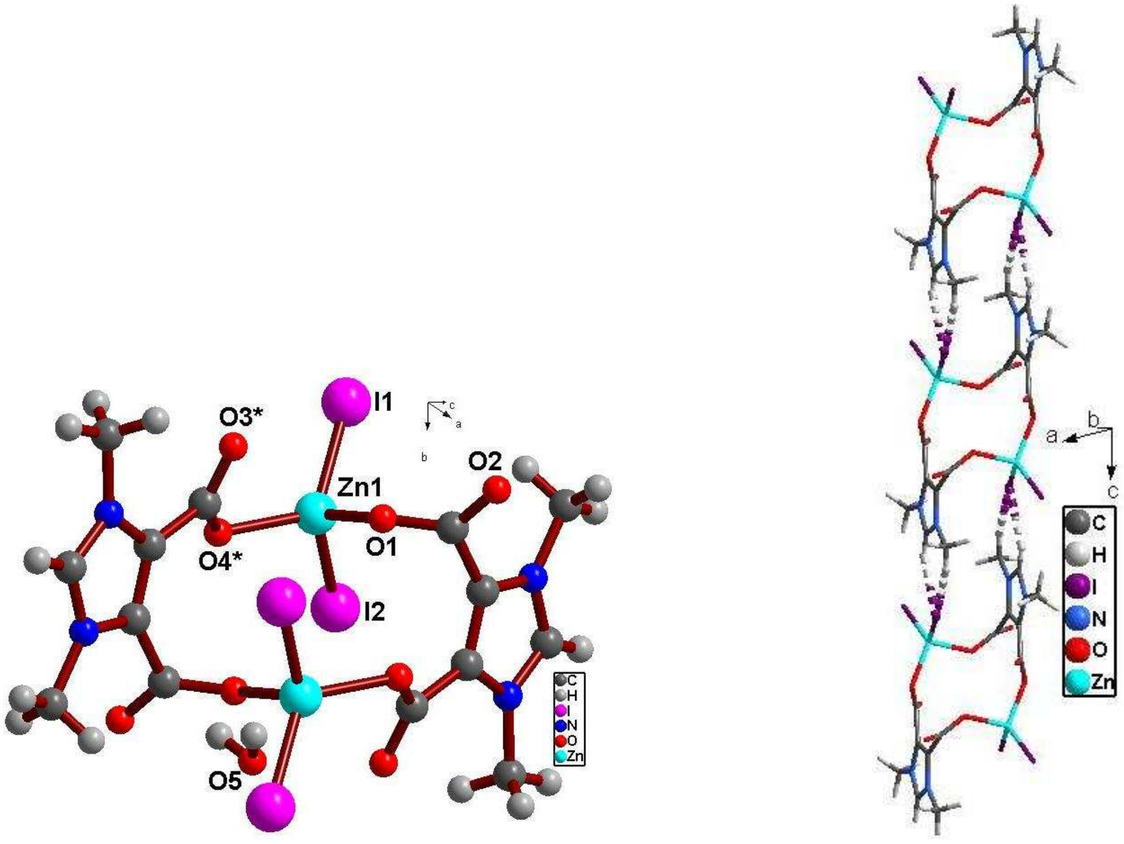


(e) (f)

Figure 3. (a) The coordination environment around Zn(II) ions in **3** (hydrogen atoms omitted for clarity). (b) Hexameric 42-membered crown-shaped macrocycle ring in **3**. (c) 2D herringbone pattern in **3**. (d) Topological representation of 3-connected nodes in **3**. (e) H-bonding interactions in **3**[I1# is at 1/2 - x, -1 + y, -1/2 + z]. (f) 3D supramolecular network of **3** with iodide ions.

same direction while the other two (breadthwise) are in the opposite and hence form the crown-shape of the macrocycle. Further, the O-atoms of the other carboxylate group of DDI$^-$ units from the hexamer coordinates to another Zn(II) ions, which extends to form a 2D anionic zwitter ion zinc CP with herringbone network (Figure 3c). Through topological analysis, **3** can be represented as 6^3 hcb topology with Zn centre as 3-connected uninodal net (Figure 3d). The iodide ions in **3** are trapped inside the *quasi* hydrophilic channels of the CP and are involved in the H-bonding between I1#···H9B (from N-CH_3) and I1#···H15 (from H_2O) (Figure 3e, Table 3). The 2D CP is further connected through an interlayer CH···O interaction between CH_3 and CH of imidazolium units resulting in the formation of a 3D supramolecular network (Figure 3f).

[Zn$_2$(DDI)$_2$I]·2H$_2$O (4). Single crystal X-ray analysis shows that the **4** crystallizes in triclinic space group *P*-1 (Table 1), and forms an anionic zwitter ion zinc dimer consisting of two Zn(II) ions, two DDI⁻ units, four iodide ions (one-fourth occupancy) and two lattice water molecules. Both Zn(II) ions lie in a distorted tetrahedral environment (bond angle vary from 101.94^o to 122.35^o), connected by two individual DDI$^-$ units. Each DDI$^-$ units provide two donor oxygen atoms to form a 14-membered macrocyclic ring, while the remaining four sites are occupied by four iodide ions (Figure 4a). Unlike **3**, in complex **4**, the iodide ions are coordinated to zinc ion terminally and forms a dimer, hence thwarts formation of extended CP. The oxygen atoms of DDI$^-$ unit are coordinated to zinc in monodentate terminal fashion (II; Scheme 3), with a bond distances of 1.992(4) Å and 1.966(4) Å for Zn-O1 and Zn-O4* respectively.[9h] Whereas the bond distances of Zn-I are 2.273(14) Å and 2.256(13) Å for Zn-I1 and Zn-I2 respectively.[24] Within the

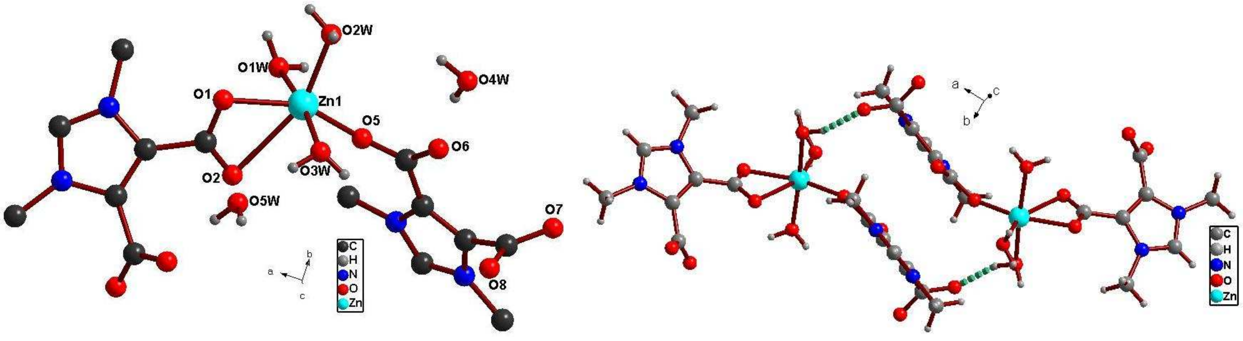


(a) (b)

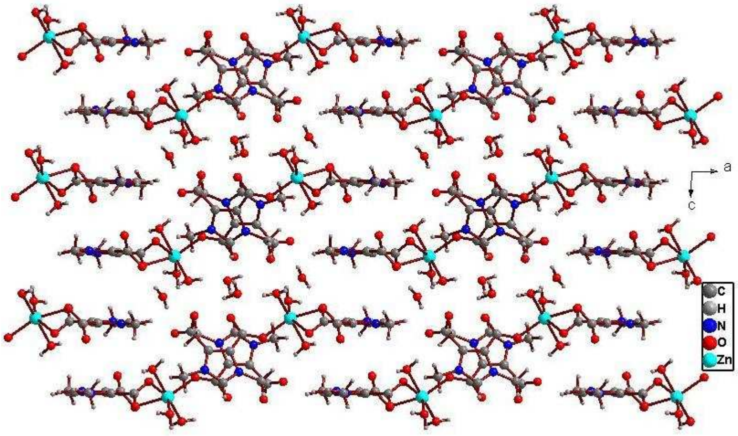
Figure 4. (a) The coordination environment around Zn(II) ions in **4**. [O3* and O4* are at equivalent position 1 - x, 2 - y, 1 - z]. (b) Infinite ladder-shaped 1D supramolecular network of **4**.

macrocycle, the orientations of the two DDI- units are anti-parallel to each other, while the iodide ions are perpendicular to the macrocycle. The orientation of DDI$^-$ units and iodide ions facilitates in the H-bonding interactions between two neighboring dimer units [I2···H1-C1 (Imidazolium) and I2···H6C (N-methyl) (Figure S9; Table 3)]. These supramolecular interactions between adjacent dimer unit lead to an infinite ladder-shaped 1D supramolecular network, (Figure 4b). The Zn(II) ions form the connections of the ladder and the distance between Zn···Zn in a ladder is 4.840(1) Å along the rung and 8.489(2) Å along the rail (Figure S10).

[Zn(DDI)$_2$(H$_2$O)$_3$]·2H$_2$O (5). It was observed that using aq. NH$_3$ doesn't always facilitate the complete removal of HX (Cl or I) and hence the expected CPs probably were not observed. Keeping this in mind Et$_3$N which is a stronger base as compared to aqueous NH$_3$ was used in the reaction medium. Thus, complex **5** was obtained by using a stoichiometric ratio of 1:1 of the ligand and Zn(NO$_3$)$_2$·6H$_2$O, using Et$_3$N as base in CH$_3$CN/H$_2$O mixture at room temperature.



(a) (b)



(c)

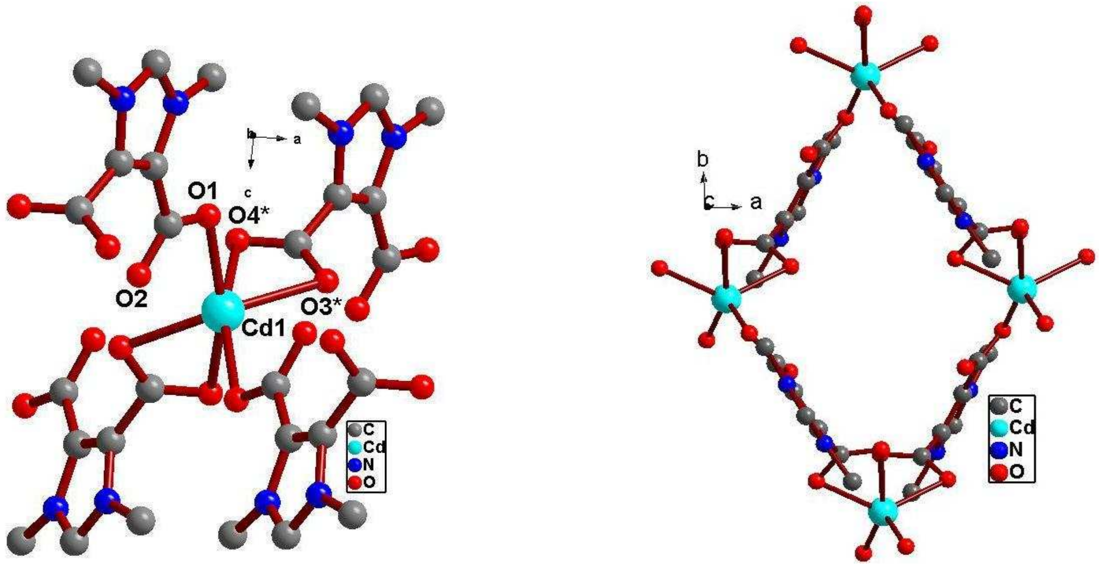
Figure 5. (a) The coordination environment around Zn(II) ions in **5**. (b) 20-membered macrocycle of **5**. (c) 2D supramolecular network of **5** (H-bonds omitted for clarity).

The same reaction procedure by using $ZnCl_2$ was not successful. Single crystal X-ray diffraction shows that the **5** crystallizes in monoclinic space group $P2_1/c$ (Table 1), and consists of one Zn(II) ion, two DDI^- units, three coordinated H_2O molecules and two lattice H_2O molecules. Zn(II) lies in an octahedral environment and three of the coordination sites are occupied by three O-atoms from two DDI^- units. Interestingly, in this case two coordination modes were observed by DDI^- *viz.* monodentate terminal and bidentate chelate. One of the DDI^- units coordinates to Zn(II) in monodentate terminal fashion, while the second unit of DDI^- shows bidentate chelate mode (III; Scheme 3). The remaining three sites are occupied by three H_2O molecules (Figure 5a). Like **1** and **2**, a loss of HI is observed in **5**, however the final product obtained here is once again anionic zwitter ion zinc complex formed by DDI^-.

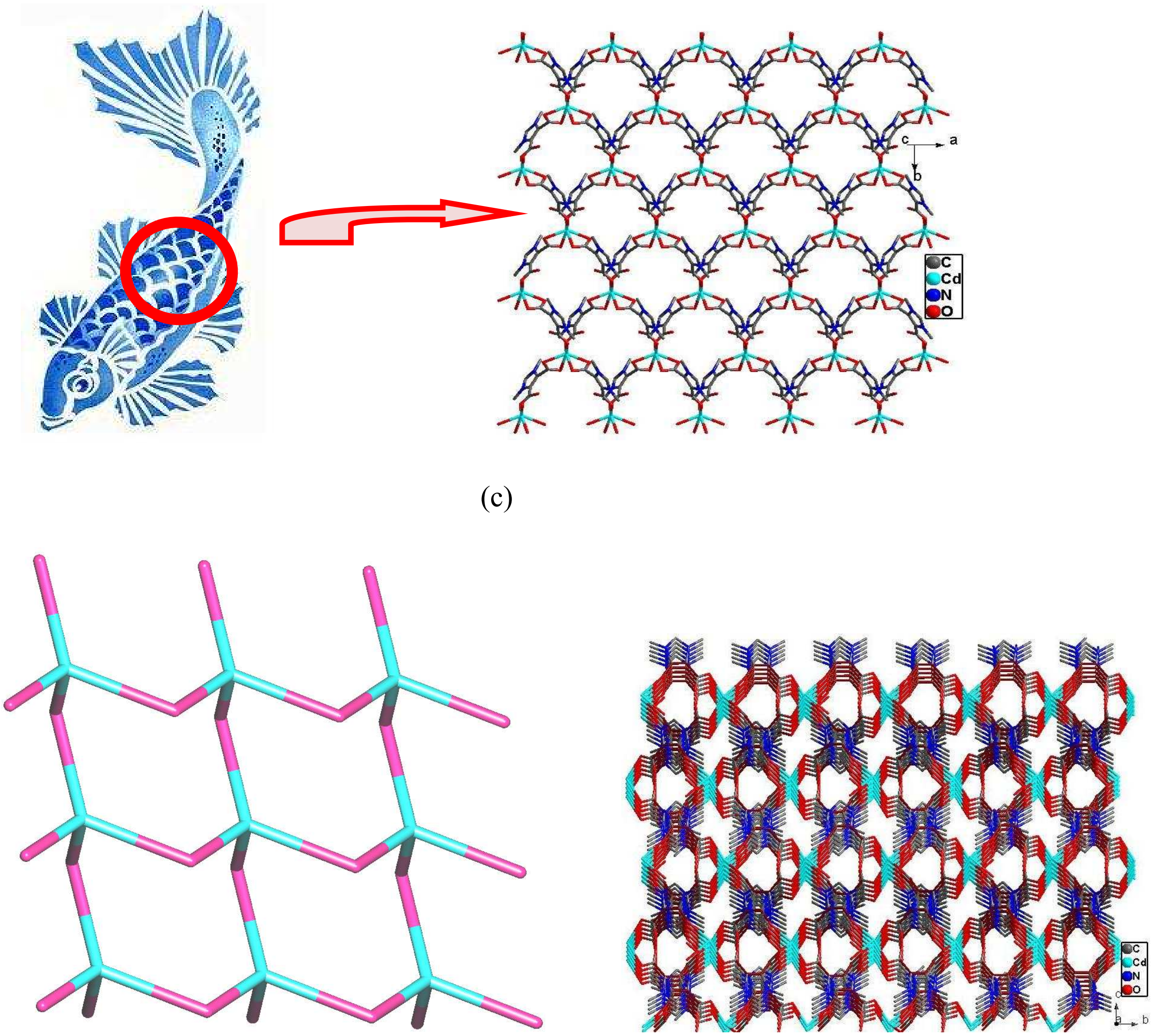
The Zn-O bond length in **5** is found to be in the range of 2.007(3) Å to 2.086 (3) Å which is comparable to the literature values.[9h] The bond angles in **5** vary from 86.41(12)° to 170.70(13)° (Table 2). Two of the monomer units are connected to each other by H-bonding and form an 18-

membered macrocycle (Figure 5b). Each of these macrocycles consists of two DDI$^-$ units, coordinated in monodentate terminal mode, from two adjacent monomers while the remaining two DDI$^-$ units, coordinated in bidentate chelate mode, lack any such supramolecular interactions. These monomer units along with the coordinated and lattice H_2O molecules further extend the macrocycle through CH···O interactions and H-bonds (Table 3, Figure 5c) and results into a 2D supramolecular network.

[Cd(DDI)$_2$]$_n$ (6). In order to evaluate the metal ion effect, the reaction was carried out using cadmium nitrate using NEt_3 under similar condition as that of **5**. The same synthetic procedure as for **2**-**4** was not fruitful in this case and performing same reaction by using $CdCl_2$ was not successful. Single crystal X-ray diffraction shows that **6** crystallize in monoclinic space group *C*2/*c* (Table 1). In **6**, each Cd (II) ion lie in a twofold axis and is in a distorted octahedron environment coordinated by six donor O-atom provided by four anionic DDI$^-$ unit (Figure 6a). Similar to **5**, in **6** two coordination modes of DDI$^-$, i.e. monodentate terminal and bidentate chelate was observed. Two of the DDI$^-$ units are coordinated to Cd (II) ion in a bidentate chelate



(a) (b)



(c)

(d) (e)

Figure 6. (a) The coordination environment around Cd(II) ions in **6** (hydrogen atoms omitted for clarity). [O3* and O4* are at equivalent position 3/2 - x, 1/2 + y, 1/2 - z]. (b) Tetrameric 28-membered macrocyclic ring of **6**. (c) Fish scale pattern of 2D CP **6**. (d) Topological representation of 4-connected nodes in **6**. (e) 3D supramolecular structure of **6**.

mode, while rest of the two DDI- units are coordinated in a monodentate terminal mode (III; Scheme 3). The Cd-O bond distance in **6** falls in the range of 2.417(3) Å to 2.248(3) Å all of which are comparable to those reported for other imidazole-based dicarboxyate Cd(II) complexes (Table 2).[9h,i] The DDI$^-$ units which are coordinated to one Cd(II) ion in a bidentate chelate mode, are further coordinated to another Cd(II) ion in a monodentate terminal mode and vice-versa. Thus, there exists a tetrameric 28-membered macrocyclic ring (Figure 6b). Each macrocycle consists of four Cd(II) ions which are coordinated to four DDI$^-$ units and the distance between two Cd(II) centers was found to be 8.025(6) Å. The four DDI$^-$ units are oriented perpendicular to each other. Further, each of these tetramer units in **6** extends through remaining carboxylate oxygen atoms forming another tetramer and result into a 2D anionic zwitter ion cadmium CP showing an interesting "*fish scale pattern*" (Figure 6c). Through topological analysis, **6** can be represented as $4^4 6^2$ sql topology with Cd centre as 4-connected uninodal net (Figure 6d). The 2D CP is further connected through intermolecular CH···O interaction existing between carboxylate oxygen with different H-donor carbon atoms, to form a 3D supramolecular network (Figure 6e). The 3D supramolecular network shows packing in ABAB fashion with the adjacent layer (Table 3, Figure S11 and Figure S12).

Thermogravimetric and Powder X-ray diffraction analyses.

The thermal stability of **2-6**, was studied using the thermogravimetric analysis (TGA) (Figure 7). The TGA curve of **2** shows an initial weight loss of 26.2% (calculated 26.46%) upto 211°C, corresponding to the loss of one chloride ion, two coordinated water molecules and one lattice water molecule. At 255 °C, **2** shows a gradual decrease in weight due to continuous loss of the ligand (residue 28.4%). The TGA curve of **3** shows initial weight loss of 3.3% (calculated 2.13%) at 96.68 °C corresponds to one coordinated water molecule. The second weight loss of 27% (calculated 22%) at 149 °C corresponds to loss of one of the coordinated ligand. The third weight loss of 42% (calculated 43.9%) at 262 °C, show the loss of remaining two coordinated ligands (residue 27.7%). The TGA curve of **4** shows that it is stable upto 180 °C and shows an initial weight loss of 32.7% (calculated 33.49%) at 185 °C, corresponding to one ligand and two lattice water molecules. At 250 °C 4 shows a gradual weight loss due to one ligand unit and iodide ions (residue 20.7%). The TGA curve of **5** shows that it is stable up to 193 °C and shows a sudden weight loss of 90% at 250 °C, corresponding to the coordinated ligands and water molecules (residue 10%). The TGA curve of **6** shows that it is stable up to 200 °C and shows a gradual weight loss of 62.91% (calculated 64.68%) corresponding to the loss of four ligand units which are coordinated to Cd(II) (residue 37.09%).

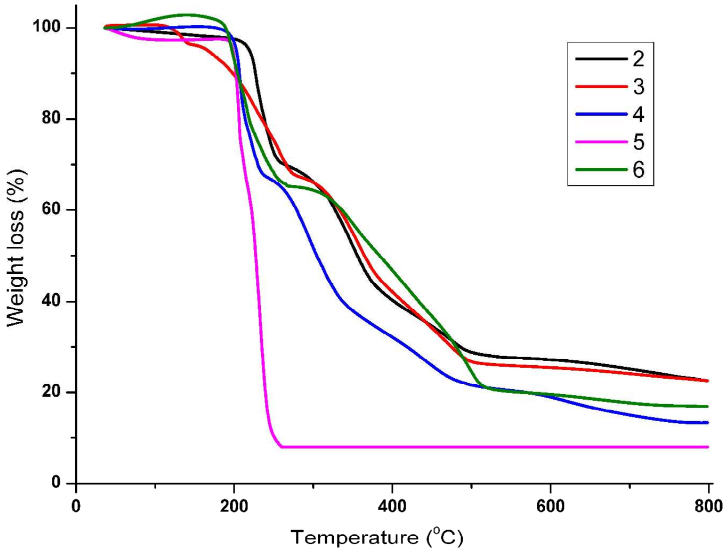


Figure 7. TGA curves of compounds **2-6**

To confirm the sample purity powder X-ray diffraction was performed for compounds **1**–**6** and it was observed that the simulated spectra correlates with the experimental spectra which confirms the phase purity of these compounds at room temperature (Figure S13). To confirm the stability of the complexes **2-6** at high temperature, variable temperature PXRD was also performed and it was observed that all the complexes are stable up to 100 °C. Complex **3** was found to be stable even after heating at 160 °C, while complexes **4**-**6** were found to be stable even at 200 °C. To check the reversibility of water removal in CP **3**, it was first heated at 100 °C and then reimmersed in water and it was found that the PXRD of the reimmersed compound does not match with that of CP **3** confirming the irreversible nature of water removal (Figure S14).

Photoluminescence

CPs consisting of transition metals with d^{10} electronic configuration such as Zn and Cd and suitable organic chromophores are found to exhibit excellent photoluminescent properties.[25] Therefore the complexes synthesized by using these metal ions can be employed as new luminescent materials. Consequently, the photoluminescent properties of complexes **2**-**6** were investigated at room temperature (Figure 8). In the solid state, unlike imidazole-4,5-dicarboxylic acid (H_3IDC) and its different analogous ligands which show moderate to weak luminescence, the free H_2DDII shows intense luminescence with emission maxima at 348 nm (λ_{ex} 315 nm) due to the π^*-π transition as well as XLCT (halide to ligand charge transfer) due to iodide ions.[8] Compounds **2**-**4** are red shifted from the ligand and exhibit intense luminescence emission at 397 nm (λ_{ex} 250 nm), 396 nm (λ_{ex} 250 nm) and 395 nm (λ_{ex} 265 nm) respectively. A similar red shift in the luminescence emission as well as fluorescence quenching, due to decrease in intensity, was observed in compounds **5** and **6** at 398 nm (λ_{ex} 255 nm) and 422 nm (λ_{ex} 365 nm) respectively as compared to the ligand. The cause of red shift for compounds **2**-**6** can be attributed to ligand to metal charge transfer (LMCT) transition.[8(c),25(c)] The difference in the emissive properties of complexes **2**-**4** as compared to **5**-**6** having same ligand could be due to the presence of anions, Cl^- (**2**) and I^- (**3** and **4**), and difference in the coordination environment around metal ion and variable architectures.[25(c), 26] The anion plays an important role in the fluorescence property of these complexes by enhancing the intensity by XLCT transition consequently reducing the probability of fluorescence quenching. On removal of the anion in **5**, in spite of same metal ion Zn(II) and ligand as that of **2**-**4**, a large decrease in the fluorescence intensity was observed due to absence of XLCT transition. The quenching in **6** can be explained by the absence of XLCT as well as taking into consideration the presence of heavy atom perturbation effect due to Cd which decreases the luminescence intensity due to non-radiative energy dissipation.[27]

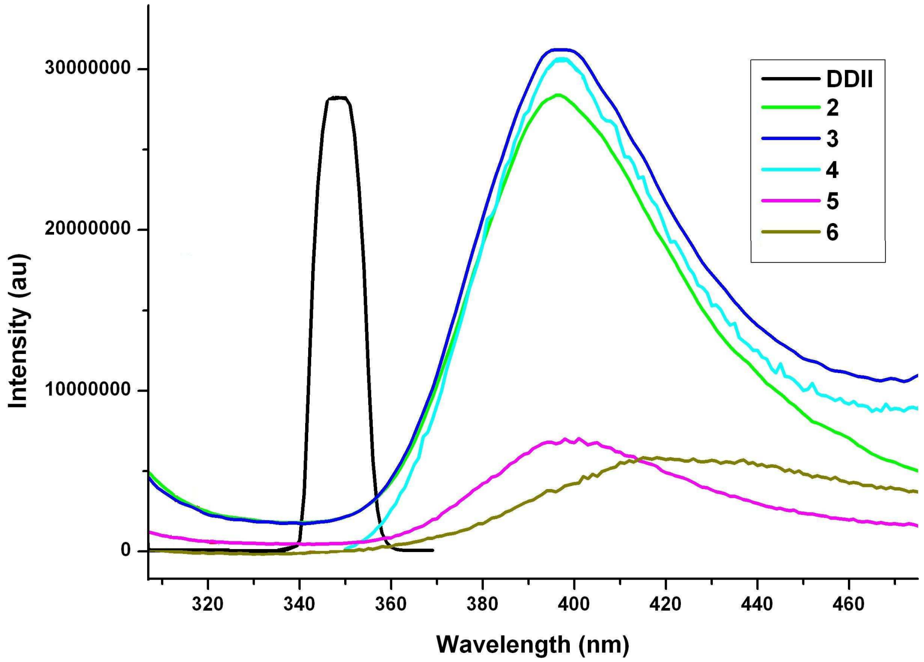


Figure 8. Solid state photoluminescence spectra of compounds **2-6**

Conclusions

In summary, we have designed a rigid imidazolium dicarboxylate ligand, H_2DDII which upon crystallization forms a zwitter ionic structure HDDI (**1**). Five anionic zwitter ion metal complexes and/or CPs were synthesized $[Zn(Cl)(H_2O)_2(DDI)]\cdot H_2O$ (**2**), $\{[Zn_2(DDI)_3(H_2O)_2]\cdot I\}_n$ (**3**), $[Zn_2(DDI)_2I]\cdot 2H_2O$ (**4**), $[Zn(DDI)_2(H_2O)_3]\cdot 2H_2O$ (**5**) and $[Cd(DDI)_2]_n$ (**6**), exhibiting different architectures ranging from discrete molecular units to 2D CPs. Complexes **2** and **5** were monomeric units, while **4** was a dimer which formed an infinite 1D ladder through supramolecular interactions. CP **3** and CP **6** resulted into 2D CP with herringbone and *fish scale* patterns respectively. The stoichiometric ratio of the metal and ligand, nature of metal salt, solvent conditions and nature of base influenced the structure of the resulting complexes. The iodide ion is present either as a coordinating anion to the metal centre or captured inside the CP as a counter anion. Further, solid state photoluminescence properties of H_2DDII and compounds **2-6** were also investigated. Compared to the imidazole or substituted imidazole dicarboxylic acids a strong emission was exhibited by the H_2DDII and compounds **2-6**. Employing these complexes/CPs as support systems is under progress.

Associated Content

Electronic Supplementary Information (ESI)

Additional figures, TGA, powder X-ray diffraction patterns. X-ray crystallographic data in CIF format have been deposited with the Cambridge Structural Database. CCDC: 1027616-1027621 contains the supplementary crystallographic data for this paper.

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Table 1. Crystallographic data and structural refinements for **1-6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_7H_8N_2O_4$	$C_7H_{13}N_2O_7ClZn$	$C_{21}H_{25}IN_6O_{14}Zn_2$	$C_{14}H_{18}IN_4O_{10}Zn_2$	$C_{14}H_{24}N_4O_{13}Zn$	$C_{14}H_{14}CdN_4O_8$
Fw	184.15	338.01	843.11	659.96	521.74	478.69
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$P\ 2_1/n$	*Pccn*	*P*-1	$P\ 2_1$/c	*C*2/c
a (Å)	7.052(2)	8.4910(17)	22.552(5)	7.9324(13)	15.075(2)	8.8373(8)
b (Å)	8.324(3)	8.0410(16)	10.123(2)	8.4897(14)	8.3079(12)	13.3995(8)
c (Å)	13.410(4)	18.847(4)	13.594(3)	10.8444(18)	16.676(3)	13.4110(10)
α (deg)	90	90	90	80.027(3)	90	90
β (deg)	102.299(6)	101.16(3)	90	72.510(3)	92.800(3)	91.947(2)
γ (deg)	90	90	90	64.679(2)	90	90
V (Å$^{3)}$	769.1(4)	1262.5(4)	3103.4(1)	628.8(2)	2086.1(5)	1587.2(2)
Z	4	4	4	1	4	4
ρ_{calc} (g cm^{-3})	1.590	1.778	1.804	1.743	1.661	2.003
μ/mm^{-1}	0.132	2.184	2.614	3.185	1.253	1.434
F(000)	384	688	1672	323	1080	952
T (K)	100(2)	100(2)	100(2)	100(2)	293(2)	293(2)
$\theta_{min/max}$ range (°)	2.90-26.00	2.20-25.99	1.81-26.00	2.66-26	1.35-26.00	2.76-26.00
Reflections collected/unique	4130/1504	6839/2461	16258/3049	3533/2413	11326/4082	4288/1532
Data/ restraints /parameter	1504/0/121	2461/9/183	3049/3/ 208	2413/3/164	4082/15/324	1532/6/125
GOF on F^2	1.165	1.071	1.035	1.091	1.143	1.252
R_{int}	0.0368	0.0460	0.0590	0.0189	0.0464	0.0311
$R1$; $wR2[I > 2\sigma(I)]$	0.0486; 0.1357	0.0397;0.1079	0.0527; 0.1418	0.0534; 0.1627	0.0516; 0.1324	0.0316; 0.0752
$R1$; $wR2$ (all data)	0.0602; 0.1669	0.0455; 0.1135	0.0683; 0.1576	0.0595; 0.1792	0.0713; 0.1726	0.0366; 0.1078

Table 2. Selected bond distances (Å) and angles (deg) for compounds **2-6**

[Zn(Cl)(H$_2$O)$_2$(DDI)]·H$_2$O (2)	**{[Zn$_2$(DDI)$_3$(H$_2$O)$_2$]·I}$_n$ (3)**	**[Zn$_2$(DDI)$_2$I]·2H$_2$O (4)**
Zn(1)-Cl1 2.2743(11)	Zn(1)#2-O2 2.034(4)	Zn(1)-I(1) 2.2733(14)
Zn(1)-O(1) 2.009(2)	Zn(1)-O3 1.985(3)	Zn(1)-I(2) 2.2564(13)
Zn(1)-O(1W) 2.002(3)	Zn(1)-(O1W) 2.041(5)	Zn(1)-O(1) 1.992(4)
Zn(1)-O(2W) 1.999(3)	Zn(1)-O7 1.999(3)	Zn(1)#1-O(4) 1.966(4)
O(2W)-Zn(1)-O(1W) 117.29(11)	O(3)-Zn(1)-O(7) 104.95(14)	Zn(1) -O(4)#1 1.967(4)
O(2W)-Zn(1)-O(1) 105.94(10)	O(3)-Zn(1)-O(2)#3 107.77(15)	O(4)#1-Zn(1)-O(1) 101.94(15)
O(1W)-Zn(1)-O(1) 105.59(10)	O(7)-Zn(1)-O(2)#3 95.76	O(4)#1-Zn(1)-I(2) 105.84(11)
O(2W)-Zn(1)-Cl(1) 113.46(8)	O(3)-Zn(1)-O(1W) 123.10(17)	O(1)-Zn(1)-I(2) 112.69(11)
O(1W)-Zn(1)-Cl(1) 109.15(8)	O(7)-Zn(1)-O(1W) 113.66(18)	O(4)#1-Zn(1)-I(1) 122.35(11)
O(1)-Zn(1)-Cl(1) 104.20(7)	O(2)#3-Zn(1)-O(1W) 108.08(17)	O(1)-Zn(1)-I(1) 103.03(12)
		I(2)-Zn(1)-I(1) 110.74(5)

[Zn(DDI)$_2$(H$_2$O)$_3$]·2H$_2$O (5)		**[Cd(DDI)$_2$]$_n$ (6)**	
Zn(1)-O(1)	2.073(3)	Cd(1)-O(1)	2.248(3)
Zn(1)-O(5)	2.007(3)	Cd(1)-O(3)	2.417(3)
Zn(1)-O(1W)	2.086(3)	Cd(1)-O(4)	2.438(3)
Zn(1)-O(2W)	2.023(3)	O(1)-Cd(1)-O(3)	94.65(12)
Zn(1)-O(3W)	2.055(3)	O(1)-Cd(1)-O(4)	82.13(12)
O(5)-Zn(1)-O(2W)	108.26(14)	O(3)-Cd(1)-O(4)	54.28(11)
O(5)-Zn(1)-O(3W)	92.23(13)	O(1)-Cd(1)-O(1)#3	117.04(18)
O(2W)-Zn(1)-O(3W)	97.06(13)	O(1)#3-Cd(1)-O(3)	109.58(13)
O(5)-Zn(1)-O(1)	150.98(14)	O(3)-Cd(1)-O(3)#3	133.04(16)
O(2W)-Zn(1)-O(1)	100.08(13)	O(1)#3-Cd(1)-O(4)	157.57(13)
O(3W)-Zn(1)-O(1)	90.36(13)	O(3)#3-Cd(1)-O(4)	89.03(11)
O(5)-Zn(1)-O(1W)	86.43(13)		
O(2W)-Zn(1)-O(1W)	92.09(13)		
O(3W)-Zn(1)-O(1W)	170.70(13)		
O(1)-Zn(1)-O(1W)	86.41(12)		

Symmetry codes for **3** #1 -x+1/2,-y+1/2,z #2 -x,y+1/2,-z+1/2 #3 -x,y-1/2,-z+1/2 ; **4** #1 -x+1,-y+2,-z+1 ; **6** #1 x-1/2,y-1/2,z #2 x+1/2,y+1/2,z #3 -x+2,y,-z+1/2

Table 3: Hydrogen bonding interaction parameters in **1-6**

(D-H···A)	*d* (H···A) (Å)	*d* (D···A) (Å)	< (A···H-D)(°)
1			
C1-H1*···O1	2.22	3.13(4)	161
C1-H1*···O2	2.69	3.52(1)	146
C6-H6C#···O4	2.57	3.33(2)	134
O3-H3···O2	1.58	2.42(6)	177
C5=O4···C1$	2.89(5)		133
2			
O2W-H66#···Cl1	2.66	3.46(5)	151
C7-H7C*···Cl1	2.69	3.61(9)	163
O3W-H78···O4	2.10	2.92(1)	171
C1-H1···O3W	2.28	3.12(7)	150
C6- H6A···O3W	2.58	3.44(5)	150
3			
O5-H15···I1#	3.01	3.84(1)	162
C9-H9B···I1#	3.12	4.00(4)	153
4			
C1-H1···I2	2.55	3.40(3)	150
C6- H6C···I2	2.79	3.68(9)	152
5			
O4W-H120···O6	1.88	2.67(7)	166
O5W-H131···O7	2.06	2.88(1)	176
C14- H14A···O7	2.69	3.56(2)	151
O1W-H9···O7	1.98	2.75(1)	158
O2W-H100···O8	1.96	2.70(9)	152
6			
C1-H4···O2	2.20	2.97(4)	140
C7-H5C···O3	2.41	3.28(9)	152

1. H1* is at -1/2 + x, 1/2 - y, -1/2 + z; H6C# is at x, 1 + y, z; C1$ is at 1/2 - x, 1/2 + y, 1/2 + z

2. H7C* is at -1/2 + x, 3/2 - y, 1/2 + z; H66# is at 3/2 - x, -1/2 + y, 1/2 - z]

3. I1# is at 1/2 - x, -1 + y, -1/2 + z

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Table of Contents Use Only

Architectures Varying from Discrete Molecular Units to 2-Dimensional Coordination Polymers and Photoluminescent Behavior of Zinc and Cadmium Comprising of Anionic Zwitter ion of Rigid 4,5-Dicarboxy-1,3-dimethyl-1H-imidazolium iodide

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A rigid ligand 4,5-dicarboxy-1,3-dimethyl-1H-imidazolium iodide (H_2DDII) was synthesized which crystallized as a zwitter ion (**1**) and was employed in the synthesis of anionic zwitter ion complexes and/or coordination polymers (CPs) **2-6** with variable dimensionality ranging from zero to two dimensional CPs and architectures with ladder, herringbone and *fish scale* patterns Solid state photoluminescence behavior of H_2DDII and compounds **2-6** has been investigated.