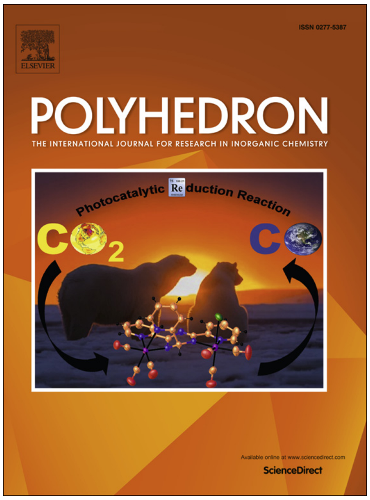

Construction of five dicyanamide based coordination polymers with diverse dimensionality: synthesis, characterization and photoluminescence study

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Construction of five dicyanamide based coordination polymers with diverse dimensionality: synthesis, characterization and photoluminescence study

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Abstract

A family of dicyanamido bridged compounds namely $\{[Co(dca)_4(2\text{-abim})_2]\}_n$(**1**),$\{[Ni(dca)_4(2\text{-abim})_2]\}_n$(**2**),$\{[Cd(dca)_4(2\text{-abim})_2]\}_n$(**3**), $\{[Zn(N(CN)_2)_2(4\text{-bpdb})]\}_n$(**4**) and $\{[Cd(N(CN)_2)_2(4\text{-bpdb})]\}_n$(**5**); [where dca = dicyanamide, 2-abim = 2 amino-benzimidazole and 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene] have been synthesized by stirring at room temperature. These compounds have been characterized by single crystal diffraction analysis, infrared spectroscopy (IR) and powder X-ray diffraction (PXRD). Complexes **1**-**3** are isostructural and exhibit two-dimensional (2D) metal-dca sheet with pendant 2-abim ligand. Compound **4** forms $[Zn(N(CN)_2)]_n$ chains with a pendent dca and a bridging dca linker, which are further connected by bridging 4-bpdb ligands extending into a 2D layer structure. In case of compound **5** each Cd(II) centers connect with four bridging dca linkers to form $[Cd(N(CN)_2)]_n$ double chains, which are further connected by bridging 4-bpdb ligands extending into a 2D layer structure. Here $[Cd_2(N(CN)_2)]$ and 4-bpdb spacer are interpenetrated to each other and resemble polyrotaxane-type structures. Photoluminescent properties of compounds **3**–**5** were also studied and they exhibit nice ligands based photoluminescence properties at room temperature.

Keywords: Coordination polymers, Single crystal X-ray structures, Network analysis Dicyanamide, Photoluminescence study.

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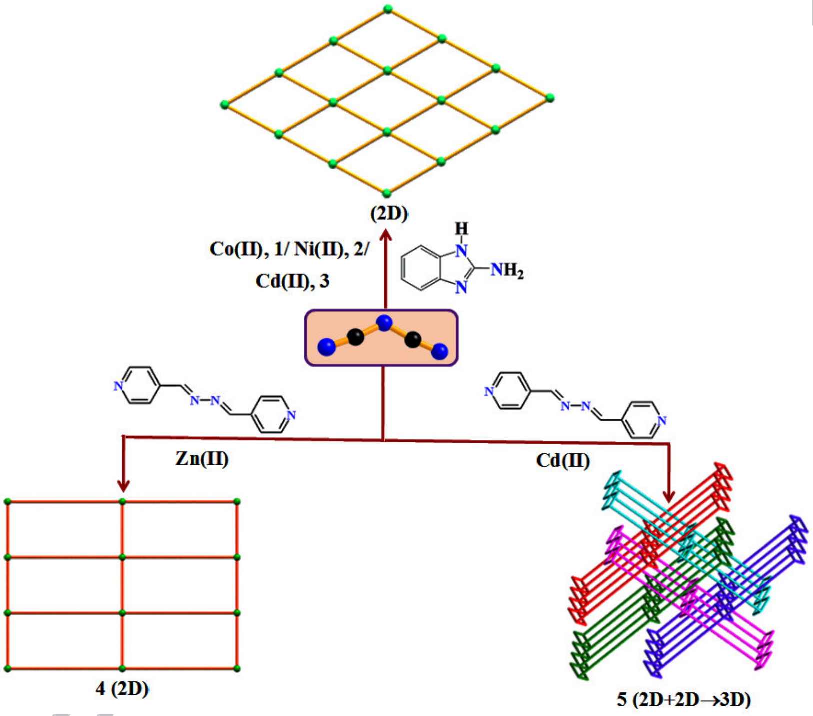
1. Introduction

Coordination polymer is one of the most pursed areas of synthetic inorganic chemistry because of their significant role for different functionality likes luminescence, magnetism, non linear optics, gas adsorption and catalysis [1-9]. Apart from the functionality these classes of compounds are intensely studied for their intriguing architectures and fascinating topologies [10-14]. One of the key operators to design the coordination polymers with an exciting structure is the thoughtful combination of mixed organic linkers and metal ion and in this way the use of pseudohalide ligands found pretty effective in combination with the other organic ligand. This variety of coordination polymers have long being studied for their interesting coordination, physical and magnetic properties [15-16]. Among the pseudohalides, comparatively larger sized and versatile dicyanamide (dca) ligand found very interesting bridging ligand with its three potential donor sites which allow the ligand to act as a monodentate up to a pentadentate donor [16]. Construction of diverse dimensionality like mononuclear, dinuclear, 1D chains, 2D (4,4) or (6,3) nets, and 3D network topologies could be possible with the use of dca by introducing auxiliary co-ligands or other bridging ligand [17-24]. Moreover, the dca can either act as terminal non-bridging ligands whose main function is to occupy certain portions of the metal-coordination sphere, or they may act as bridges with other metal ion. Beside their structural diversity, dca bridged coordination polymer display ferromagnetism, spin-canted antiferromagnetism and recently metal-organic nanotubes are also formed by [Mn_3(propandiolato)$_2$] building blocks and dca linkers [23].

On the other hand, N,N′-donor auxiliary neutral linkers have long been used as a bridging ligand to control structural assemblies in combination with dicraboxylate and divalent metal ions [25-28]. The conformational rigidness, configurations and substituent on N,N′-donor linkers have further impact on the overall network structures, dimensionality which also reflects in their property. In addition to that architecture of higher dimensionality can also be generated by polycatenation of the constituent structures of lower dimensionality [29-30]. Pyridyl based azine linkers namely-(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) have strong fluorescence properties due to a π conjugation effect and not been used for the construction of CPs in combination with dca ligand.

Taking into account the above-mentioned aspects, five compounds of general formula [M(dca)$_4$(2-abim)$_2$] [where M is the divalent transition metal cation: Co(**1**), Ni (**2**), Cd (**3**)] and

M(4-bpdb)(N(CN)$_2$)$_2$ M= Zn(**4**), Cd (**5**) have been synthesized and characterized structurally, spectroscopically (Scheme 1). Compounds **1**-**3** are isostructural and connected with four nitrile nitrogen atoms of dca ligand and formed a 2-D sheet structure. Compound **4** exhibits a 2D sheet with the help of 4-bpdb and bridging dca ligands containing the pendent dca ligand also. Finally, compound **5** exhibits a 2D→3D polycatenated framework due to the mutual interpenetration of 2D sheets constructed through the bridging of 4-bpdb ligand with [Cd$_2$(N(CN)$_2$)] chain. Moreover, the complexes **3-5** show ligand based photoluminescence in solid state.



Scheme 1

2. Experimental

2.1. Materials

High-purity 2 amino-benzimidazole (2-abim) and sodium dicyanamide were purchased from the Aldrich Chemical Co. Inc. and used without further purification. 1,4-bis-(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) were prepared according to literature procedure [31]. The starting material for the above synthesis such as, 4-pyridine carboxaldehyde and hydrazine hydrate were purchased from Sigma-Aldrich Chemical Co. Inc. and used as received. All other chemicals and solvents were AR grade and were used as received.

2.2. Physical Measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Heraeus CHNS analyzer. Infrared spectra (4000–400 cm^{-1}) were taken on KBr pellets, using a PerkinElmer Spectrum BX-II IR spectrometer. X-ray powder diffraction (PXRD) patterns of the bulk sample were recorded in Bruker D8 Discover instrument using Cu-Kα radiation. UV-vis spectra were recorded on a Perkin Elmer Lambda 35 UV-vis spectrophotometer. Emission spectra were recorded on a HORIBA Jobin Yvon (Fluoromax-3) fluorescence spectrophotometer.

2.3. Syntheses

2.3.1. $\{[Co(dca)_4(2\text{-}abim)_2]\}_n$ (1). An aqueous solution (5 mL) of $Co(NO_3)_2{\cdot}6H_2O$ (1 mmol, 0.291g) was mixed with an ethanolic solution (5 mL) of 2-abim (1 mmol, 0.133g) with constant stirring. Then an aqueous solution (5 mL) of sodium dicyanamide (2 mmol, 0.178g) was added to the mixture with continuous stirring. The pink colored solution was filtered and kept undisturbed in a $CaCl_2$ desiccator and after three days pink colored block shaped crystals suitable for X-ray diffraction were obtained from the filtrate. Yield 90%. Anal. Calc. for $C_{18}H_{14}CoN_{12}$: C, 47.26; H, 3.06; N, 36.74. Found: C, 47.96; H, 3.92; N, 36.10 %. IR spectra (in cm^{-1}): $\nu(N(CN)_2)^{-1}$ 2243, 2230, 2279; ν(N-H), 3104; and ν(C=C), 1530.

2.3.2. $\{$**$[Ni(dca)_4(2\text{-}abim)_2]\}_n$** (**2**). The similar procedure has been adopted as that of **1** using $Ni(NO_3){\cdot}6H_2O$ (1mmol, 0.290g) instead of $Co(NO_3)_2{\cdot}6H_2O$. Here the greenish block shaped crystals suitable for X-ray diffraction were obtained from the filtrate after three days. Yield 87%. Anal. calcd. for **2** $C_{18}H_{14}NiN_{12}$: C, 47.50; H, 2.63; N, 31.66. Found: C, 47.53; H, 2.65; N, 31.76 %. IR spectra (in cm^{-1}): $\nu(N(CN)_2)^{-1}$ 2250, 2283, 2177; ν(N-H), 3376; and ν(C=C), 1640.

2.3.3. $\{[Cd(dca)_4(2\text{-}abim)_2]\}_n$ (3). The similar procedure as that of **1** taking $Cd(NO_3)_2{\cdot}4H_2O$ (1 mmol, 0.308 g) in place of $Co(NO_3)_2{\cdot}6H_2O$ results the formation of yellowish block shaped crystals suitable for X-ray diffraction after three days. Yield 84%. Anal. calcd. for **3** $C_{18}H_{14}CdN_{12}$: C, 42.32; H, 2.74; N, 32.90. Found: C, 42.35; H, 2.79; N, 32.95%.IR spectra (in cm^{-1}) $\nu(N(CN)_2)^{-1}$ 2254, 2230, 2183; ν(N-H), 3376; and ν(C=C), 1640.

2.3.4. $\{[Zn(4\text{-}bpdb)(N(CN)_2)_2]\}_n$ (4) An aqueous solution (5 mL) of $Zn(NO_3){\cdot}6H_2O$ (1mmol, 0.297g) and sodium dicyanamide (2 mmol, 0.17g) was mixed with constant stirring. Then methanolic solution of 4-bpdb (1 mmol, 0.210 g) was added to the solution and stirred for about 30 mins at room temperature. After three days, yellowish block shaped crystals suitable for X-ray diffraction were obtained from the filtrate. Yield 85%. Anal. calcd. for **4** $C_{16}H_{10}N_{10}Zn$: C, 47.13; H, 2.45; N, 34.35. Found: C, 47.35; H, 2.59; N, 34.86%.IR spectra (in cm^{-1}) ν$(N(CN)_2)^{-1}$ 2298, 2235, 2159; ν(C=C), 1607; ν(C=N) 1423.

2.3.5. {[Cd(4-bpdb)($N(CN)_2)_2$]}$_n$ (5) This has been synthesized by following the similar procedure as stated in case of **4** but here $Cd(NO_3)_2{\cdot}6H_2O$ (1 mmol, 0.308 g) is used instead of $Zn(NO_3){\cdot}6H_2O$. After five days, yellowish block shaped crystals suitable for X-ray diffraction were obtained from the filtrate. Yield 82%. Anal. calcd. for **5** $C_{16}H_{10}CdN_{10}$: C, 42.25; H, 2.19; N, 30.80. Found: C, 42.35; H, 2.37; N, 31.95%. IR spectra (in cm^{-1}) ν$(N(CN)_2)^{-1}$ 2374, 2291, 2274; ν(C=C), 1606; ν(C=N) 1411.

2.4. Crystallographic Data Collection and Refinement

Suitable single crystals of compounds **1**-**5** were mounted on the tip of thin glass fibers with commercially available super glue. X-ray single crystal data collection of all five crystals were performed at room temperature using Bruker APEX II diffractometer, equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ= 0.71073Å). The data were integrated using SAINT [32] program and the absorption corrections were made with SADABS [33]. All the structures were solved by SHELXS 97 [34] using Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F^2 using SHELXL-97 [34] with anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were fixed geometrically by HFIX command and placed in ideal positions. All calculations were carried out using SHELXS 97, SHELXL 97, PLATON v1.15 [35], ORTEP-3v2 [36], and WinGX system Ver-1.80 [37] and TOPOS [38-39]. Data collection and structure refinement parameters and crystallographic data for all complexes are given in Table 1.

3. Results and discussion

3.1. IR spectra

The IR spectra of the complexes **1**-**5** exhibit strong absorption bands in the 2374-2159 cm^{-1} region attributed to the ν_{s+as} (C≡N), ν_{as} (C≡N), and ν_s (C≡N) vibrational modes of mono/di bridging dca ligand. The appearance of two new characteristic bands at ~ 434 cm^{-1} and ~ 560 cm^{-1} in the spectrum of the complexes, which are not generally observed in the spectra of the free dca ligand; can clearly indicates the presence of M-N bonding between the metal and the nitrogen atoms of the nitrile group of the dca ligand. This observation is confirmed by the X-ray structure of the complexes which show that metals are bonded to dca ligand through N-atoms.

3.2. X-ray structure description of the compounds

3.2.1. {**[M(dca)$_4$(2-abim)$_2$]}$_n$ [M=Co for 1, Ni for 2 and Cd for 3]**. Single-crystal X-ray structural analysis revealed that compounds **1**-**3** are isostructural and all of them are crystallizes in monoclinic *P2$_1$/n* space group with Z value of 2. All the compounds exhibit two-dimensional (2D) structure of M(II) [M= Co for **1**, Ni for **2** and Cd for **3**] ions linked by bridging dca ligand and the monodentate 2-abim ligand. The M(II) in all three structures shows distorted octahedral geometry with MN$_6$ coordination environment (Fig. 1a for **1**, S1a for **2** and S2a for **3**). Here, each metal center is connected to four nitrile nitrogen atoms (N4, N4^a N6^b, N6^c) from four different bridging dca ligands to create the equatorial plane of the octahedral coordination enviroment. Two epical sites are occupied by the two symmetry related nitrogen (N1 and N1^a) atoms from two monodented 2-abim ligand. In compounds **1**-**3**, the M(II)-N bond length varies from 2.1171(11)-2.1591(15) Å (Co-N for **1**), 2.096(2)-2.110(2) Å (Ni-N for **2**) and 2.3045(12)-2.3997(14) Å (Cd-N for **3**), respectively (Table S1-S3) which is commensurated with the covalent radii of the metal atoms used. Each M(II) ion (Fig. 1b for Co, S1b for Ni and S2b for Cd) links four neighboring metal ions via four $\mu_{1,5}$-dca ligands to form the 2D sheet structure in the crystallographic *ab* plane. The M-M distance through dca bridges are 8.186 A° for **1**, 8.134 A° for **2** and 8.052 A° for **3** respectively. The topological analysis using TOPOS [38-39] also reveals that all three structures can be represented as a 4-connected uninodal net with a point symbol $\{4^4.6^2\}$. The simplified diagram of the 4-connected net has been represented in Fig. 2c, Fig. S1c and Fig. S2c for the respective three structures.

3.2.2. {[Zn(4-bpdb)(N(CN)$_2$)$_2$]}$_n$ (4) Compound **4** also crystallizes in *P2$_1$/n* space group and the single-crystal X-ray structure analysis reveals the formation of a two dimensional (2D) sheet structure with Zn(II) metal ions bridged by both 4-bpdb and dca linkers. But unlike the previous three structures here one dca is acting as a bridging ligand whereas another dca acts as pendent monodentate ligand. Hence the asymmetric unit of **4** contains one Zn(II) ion, one bridging 4-bpdb ligand, one monodentate pendant dca linker and one bridging dca linker which makes the central metal ion Zn(II), penta-cordinated. Here each penta-coordinated Zn(II) ion shows distorted trigonal bipyramidal geometry with ZnN_5 coordination environment having 0.89 Addison parameter (tau) value [40]. The coordination environment is furnished by five nitrogen atoms from two distinct 4-bpdb ligands (N1 and $N4^a$), one pendant dca (N6) and two different bridging dca ligands (N5 and $N7^b$) (Fig. 2a). The Zn–N bond lengths are in the range of 1.979(2)–2.3020(17) Å and the angles around central atom (Zn1) lies in the range of 87.13(7)-177.80(7)° (Table 3). Here each Zn(II) centers connect with a bridging dca linker to form $[Zn(N(CN)_2)]_n$ chains, which are further connected by bridging 4-bpdb ligands extending into a 2D layer structure (Fig. 2b) in *bc* plane. The network analysis by TOPOS [38-39] also reveals that the structure can be represented as a 4-connected uninodal net (Fig. 2c) with point symbol $\{4^4.6^2\}$.

3.2.3. $\{[Cd(4\text{-bpdb})(N(CN)_2)_2]\}_n$ (5) To explore the effect of the metal ion on the overall structures of the CPs, Zn(II) of **4** has been replaced by Cd(II), to synthesize compound **5**. It crystallizes in the monoclinic system with slightly different space group $P2_1/c$ and the structure analysis revealed that a 2D network structure is formed by dca and 4-bpdb linkers. Here each Cd(II) centers are connected by two doubly bridged dca and bridging 4-bpdb linkers. In comparison to **4** the coordination number here increased from five to six; and with the effect of doubly bridged dca and larger sized Cd(II); is possibly responsible for the completely different structure of **5** in spite of its similar formula with **4**. Each asymmetric unit in **5** contains one Cd(II) ion located in a special position (0,0,0), half bridging 4-bpdb and one dca linker forming a distorted octahedral geometry with CdN_6 coordination environment (Fig. 3). Here each Cd(II) ions are ligated to six nitrogen atoms of two different 4-bpdb ligands (N1 and $N1^a$) and four nitrogen atoms of four different dca linkers (N3, $N3^a$, $N5^b$ and $N5^c$). The Cd–N bond lengths are in the range of 2.310(12)–2.363(9) Å and the angles around central atom (Cd1) lies in the range of 87.94-180° (Table 4). Here each Cd(II) centers connect with four bridging dca linkers to form $[Cd(N(CN)_2)]_n$ doubly bridged chains, which are further connected by bridging 4-bpdb ligands extending into a 2D layer structure (Fig. 3b). The network analysis by TOPOS [38-39] suggests that the structure of **5** can be represented as a 4-connected uninodal net and the corresponding Schläfli symbol is $\{4^4.6^2\}$ (Fig. 3c). The network structures are found interpenetrated to each other due to the organization of the network structure with two different spacer lengths. Here $[Cd_2(N(CN)_2)]$ square acts as a wheel whereas the long 4-bpdb spacer acts as an axle and these units are got interpenetrated with each other and resemble rotaxane-type structures (Fig. 4a), which are further connected to form the overall 2D network. These 2D networks are interpenetrated among each other to form a 2D→3D polycatenated framework (Fig. 4b) structure in the solid state.

3.3. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) analysis was carried out to confirm the phase purity of the bulk materials for all the compounds at room temperature. The experimental PXRD patterns of complexes **1–5** show good agreement with the simulated PXRD patterns from their corresponding single crystal X-ray structure (Figs. S8-S12). The matching of all major peaks in experimental as well as simulated pattern confirms the phase purity of the complexes.

3.4. Luminescent Properties

Luminescent properties of CPs with d^{10} metal centres have drawn an immense interest due to their potential applications in chemical sensors, photo-switching diodes, non linear optical (NLO) materials and electroluminescence display. The photo luminescent spectra of the complexes **3-5** and the free ligands (2-abim and 4-bpdb) in the solid state were recorded at room temperature, which are shown in Figure 5. All three complexes show ligand based emission spectra which are found commonly in case of coordination polymers or metal organic frameworks [41]. The solid-state fluorescence maximum of the 2-abim and N,N′-donor 4-bpdb ligands show the emission peak at 320 nm (λ_{ex} = 285 nm) and 394 nm (λ_{ex} = 250 nm) respectively. The emission peaks for both the ligands may be attributed to the π^*–n or π^*–π transition [41]. Compound **3** gives an emission maxima at 389 nm upon excitation at 385 nm which indicates a slight red shift as compared to the free ligand 2-abim in case of **3**. On the other hand, the photoluminescence spectra of both the complexes **4** and **5** exhibit slightly blue shifted emission maxima at around 400 nm (λ_{ex} = 394 nm) compared to free N,N′-donor 4-bpdb ligand which also be assigned to ligand-centered electronic transition. Generally, for the d^{10} complexes, no emission originates from metal-centered MLCT/LMCT excited states, since the d^{10} metal ions are difficult to be reduced or oxidized [42-43]. So, it can be confirmed that the emission spectra of complexes **3-5** has been originated due to the intra-ligand π^*–n or π^*–π electron transfer; in which the emission intensity can be tuned through the ligand coordination with the metal centers.

4. Conclusion

Five different coordination polymers (CPs) of transition metals have successfully synthesized and characterized based on dca linker along with two different ligands, 2-abim and 4-bpdb using stirring method at room temperature. A systematic study of structural diversities of compounds **1–5** reveals that dca act as an excellent bridging ligand and display versatile coordination abilities in combination with the monodentate 2-abim and bridging 4-bpdb ligand. Compounds **1-3** exhibit 2D sheet structure containing pendant 2-abim ligand whereas compound **4** displays a 2D layer structure with a pendent dca and a bridging dca linker and **5** results totally different polycatenated 2D→3D framework through the interpenetration of the nets constructed through both dca and 4-bpdb ligands. Though the synthetic procedure for compounds **4** and **5** are same but quite interestingly the difference in structural topology for both may be due to the different nature of metal ions as well as versatile binding mode of dca linkers.

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Appendix A. Supplementary data

CCDC 1471976-1471980 contain the supplementary crystallographic data for complexes **1-5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

The IR, PXRD patterns of complexes **1-5** along with different structural figures and tables related to the crystal structures reported in this paper are given as supplementary material. Supplementary data associated with this article and crystallographic data in CIF format can found online at http://dx.doi.org.

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Figures

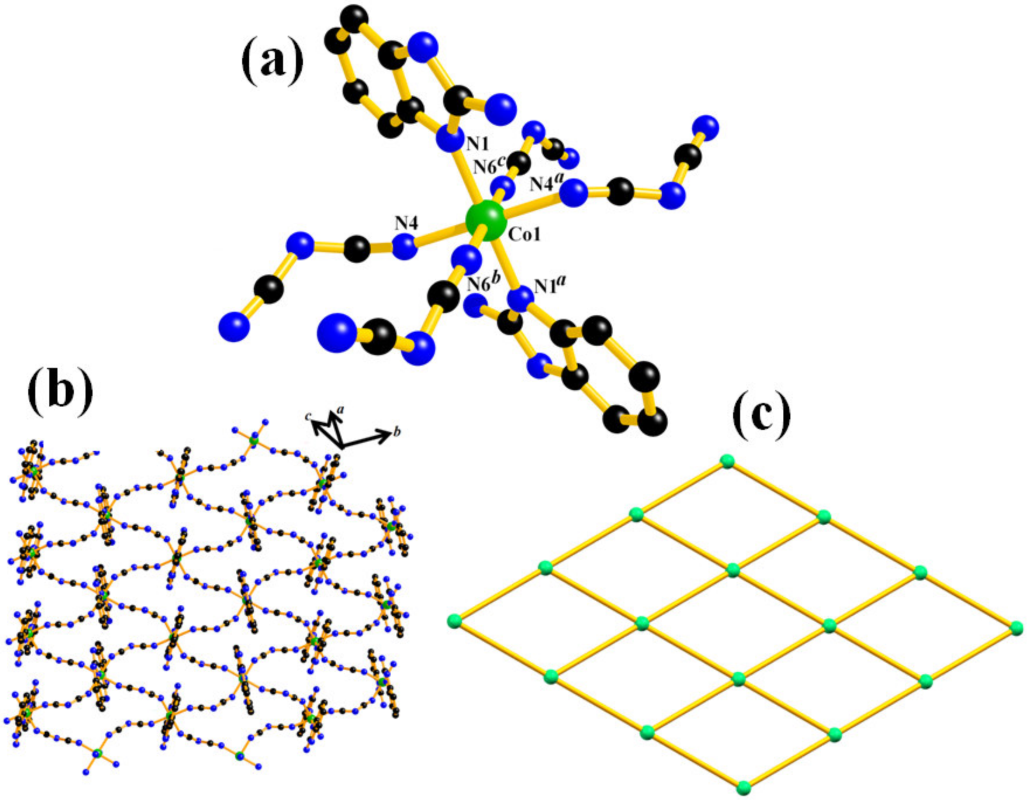


Fig. 1. (a) Coordination environment around the Co(II) ions in **1**; Co (green), N (blue), C (black). (b) 2D sheet in **1** constructed by $N(CN)_2^-$ linkers and 2-abim ligand. (c) Topological representation of 4-connected 2D sheet of **1**.

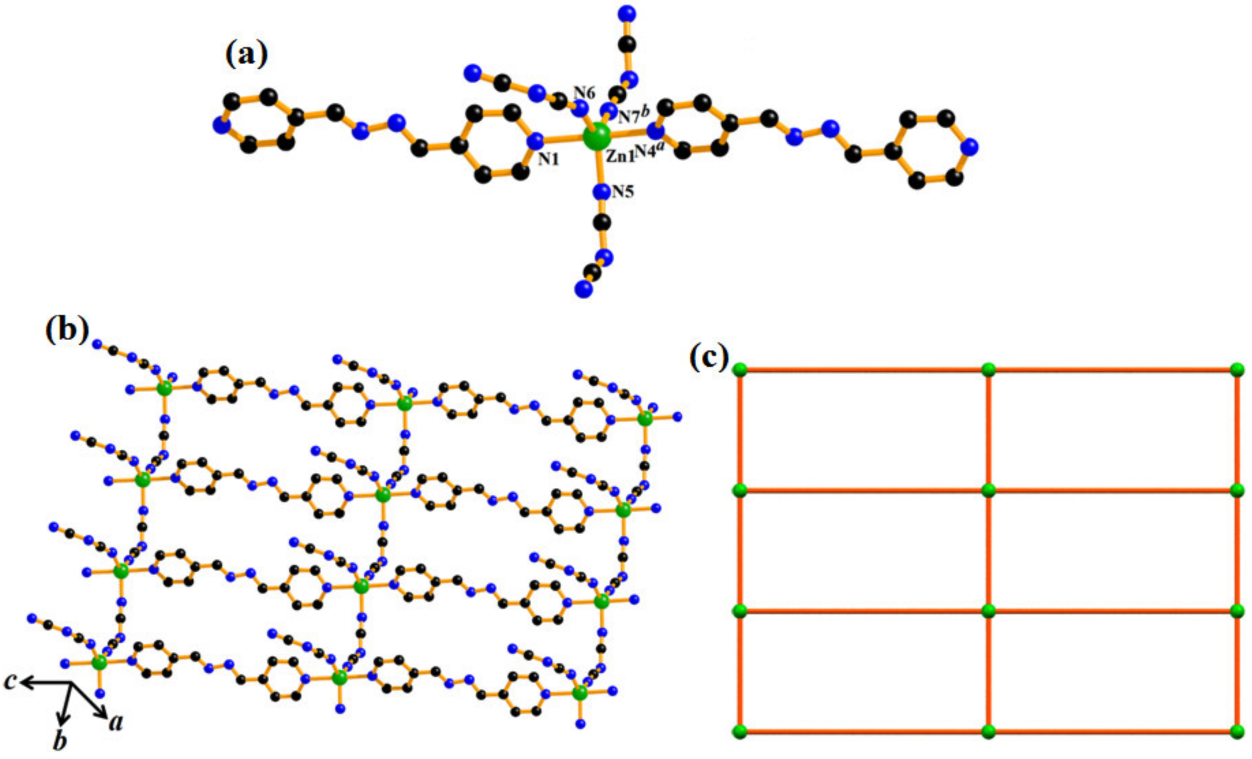


Fig. 2. (a) Coordination environment around the Zn(II) ions in **4**; Zn (green), N (blue), C (black). (b) 2D sheet in **4** constructed by both 4-bpdb and $N(CN)_2^-$ linkers. (c) Topological representation of 4-connected 2D sheet of **4**

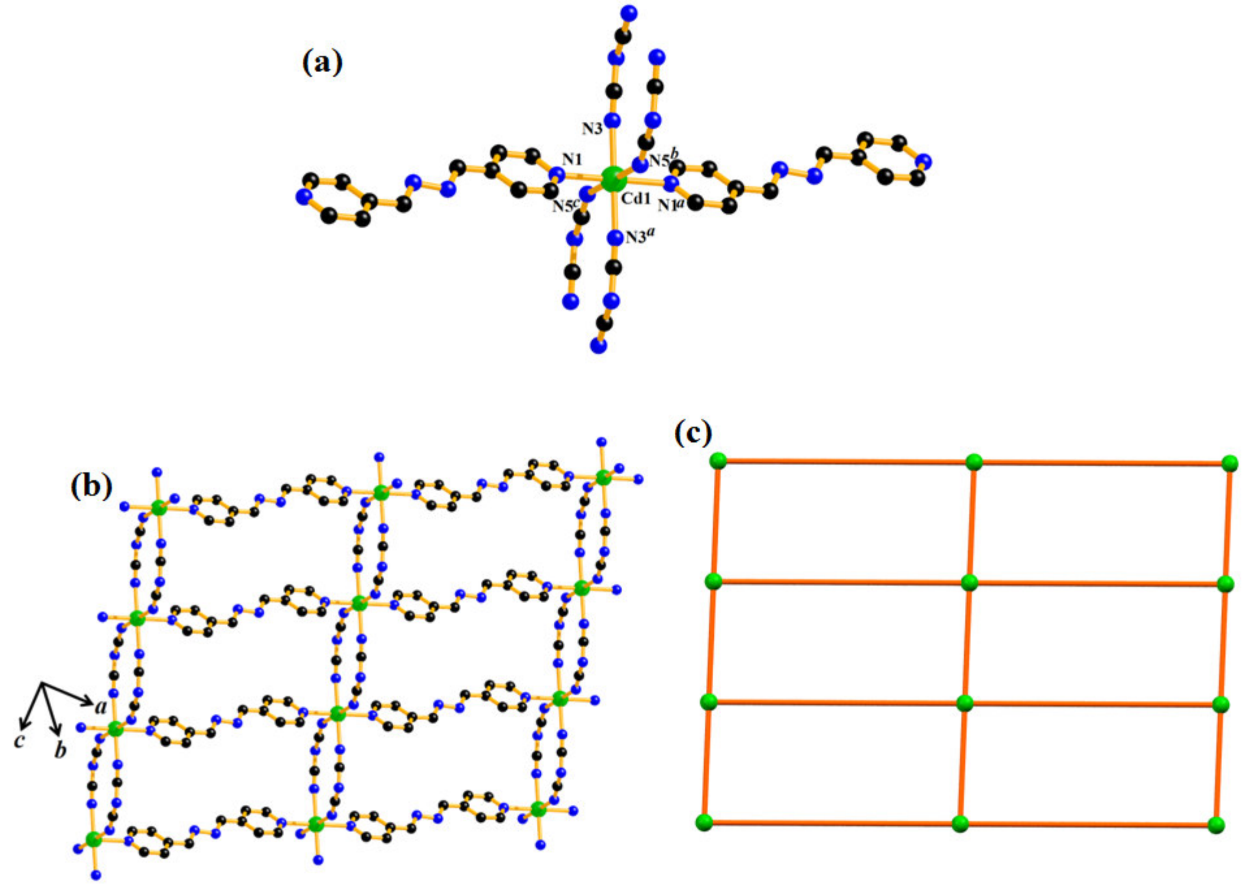


Fig. 3. (a) Coordination environment around the Cd(II) ions in **5**; Cd (green), N (blue), C (black). (b) 2D sheet in **5** constructed by both 4-bpdb and $N(CN)_2^-$ linkers. (c) Topological representation of 4-connected 2D sheet of **5**.

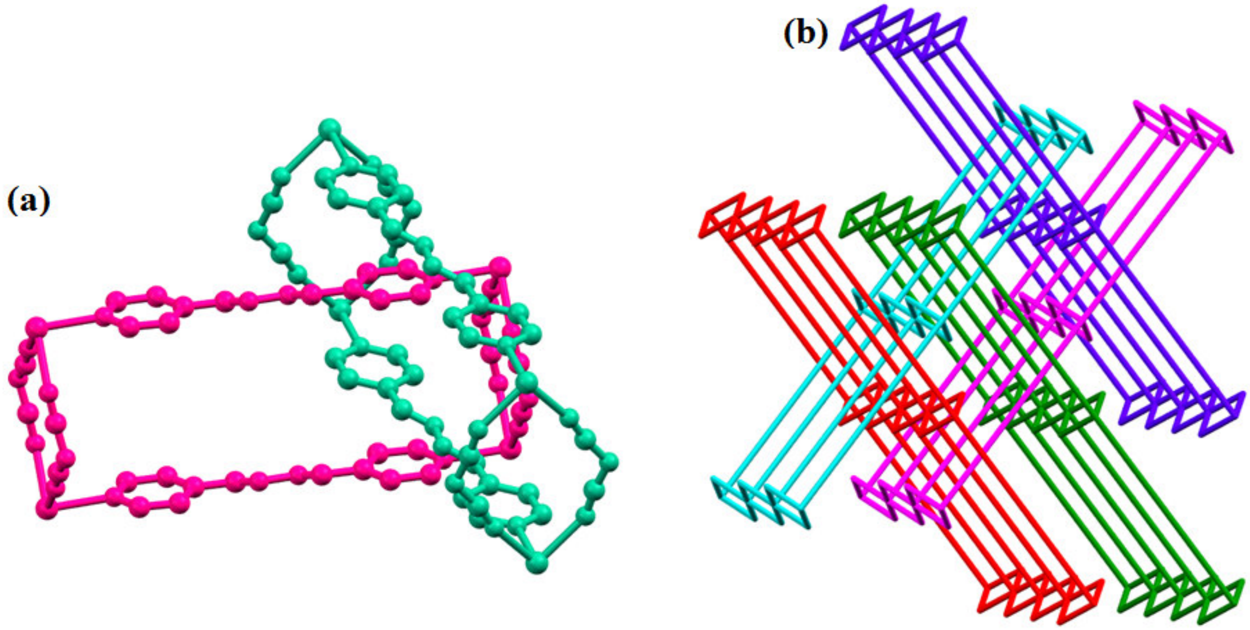


Fig. 4. (a) Representation of interpenetration in compound **5**. (b) Simplified 3D structural view of compound **5**, which is formed by 2D→3D polycatenation.

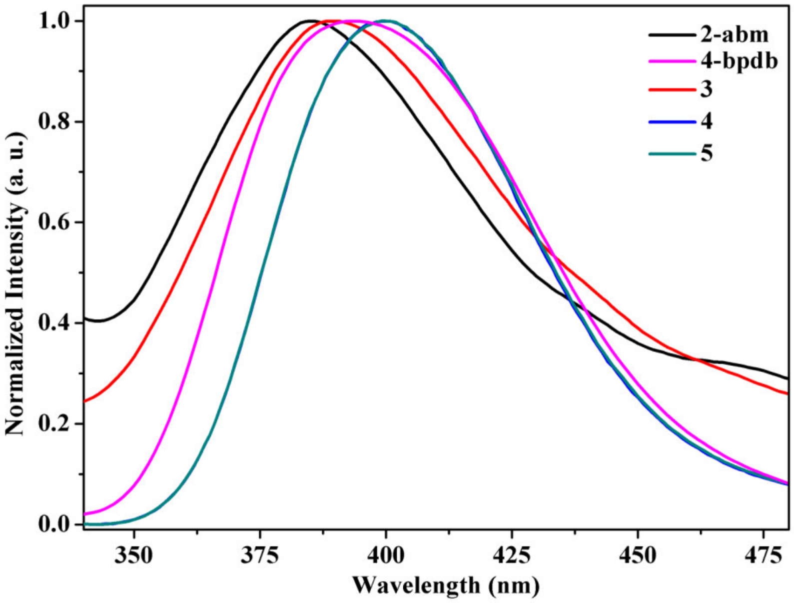


Fig. 5. Emission spectra of complex **3-5** with free 2-abim & 4-bpdb ligand.

Table 1. Crystallographic and structural refinement parameters of complexes **1-5.**

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$C_{18}H_{14}CoN_{12}$	$C_{18}H_{14}NiN_{12}$	$C_{18}H_{14}CdN_{12}$	$C_{16}H_{10}ZnN_{10}$	$C_{16}H_{10}CdN_{10}$
Formula Weight	457.34	455.09	510.82	407.73	454.75
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/ Å	9.2368(2)	9.1968(3)	9.3046(2)	15.0013(3)	9.2895(12)
b/Å	7.9054(1)	7.9084(3)	10.7334(2)	7.6847(2)	12.9991(16)
c/ Å	13.1246(2)	13.0855(4)	9.6007(2)	15.8275(4)	7.5531(10)
α/°	90	90	90	90	90
β/°	102.394(1)	102.891(2)	101.174(1)	108.305(1)	93.915(10)
γ/°	90	90	90	90	90
V/ Å^3	936.03(3)	927.75(5)	940.65(3)	1732.27(7)	910.0(2)
Z	2	2	2	4	2
D_c/ g cm^{-3}	1.623	1.629	1.804	1.563	1.660
μ /mm^{-1}	0.953	1.082	1.197	1.442	1.223
F(000)	466	464	508	824	448
θ range/°	2.5-27.5	3.0-27.5	2.8-27.6	1.6-27.5	2.7-28.0
Reflections collected	15339	14751	15802	27163	13138
Unique reflections	2146	2113	2165	3978	2098
Reflections $I > 2\sigma(I)$	1975	1584	1956	3131	1307
R_{int}	0.022	0.060	0.019	0.036	0.106
goodness-of-fit(F^2)	1.07	1.03	1.07	1.03	1.25
$R1$ ($I > 2\sigma(I)$)$^{[a]}$	0.0247	0.0421	0.0168	0.0313	0.1442
$wR2$($I > 2\sigma(I)$)$^{[a]}$	0.0679	0.1019	0.0472	0.0816	0.3595
Δρ min/max/e Å^3	-0.34, 0.28	-0.57, 0.33	-0.41, 0.27	-0.22, 0.29	-1.62, 8.38

$^{[a]}R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{½}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Co1-N1	2.1171(13)	Co1-N4	2.1591(15)
Co1-N6^c	2.1520(13)	Co1-N6^b	2.1520(13)
Co1-N1^a	2.1171(13)	Co1-N4^a	2.1591(15)
N1 -Co1-N4	88.50(5)	N4-Co1-N6^b	87.95(6)
N1-Co1-N4^a	91.47(5)	N1^a-Co1-N4	91.50(5)
N1-Co1-N6^b	92.36(5)	N1^a-Co1-N6^c	92.36(5)
N1-Co1-N6^c	87.64(5)	N4-Co1-N4^a	180.00
N4-Co1-N6^c	92.04(6)	N4^a-Co1-N6^b	92.05(6)
N1^a-Co1-N6^b	87.61(5)	N6^b-Co1-N6^c	180.00
N1^a -Co1-N4^a	88.50(5)	N4^a-Co1-N6^c	87.95(5)
N1-Co1-N1^a	180.00		

Symmetry code: a = 2-x,-y,-z, b= 3/2-x,-1/2+y,-1/2-z, c= 1/2+x, 1/2-y, 1/2+z

Table 3. Selected bond lengths (Å) and angles (°) for **4**

Zn1-N1	2.3020(17)	Zn1-N5	2.0002(17)
Zn1-N6	1.979(2)	Zn1-N4^{a}	2.2067(17)
Zn1-N7^{b}	1.9820(17)	N1-Zn1-N6	87.13(7)
N1-Zn1-N5	89.51(6)	N4^{a}-Zn1-N7^{b}	91.40(7)
N1-Zn1-N4^{a}	177.80(7)	N1-Zn1-N7^{b}	90.02(7)
N5-Zn1-N6	124.68(8)	N4^{a}-Zn1-N5	91.49(7)
N5-Zn1-N7^{b}	113.20(8)	N4^{a}-Zn1-N6	90.69(7)
N6-Zn1-N7^{b}	122.00(9)		

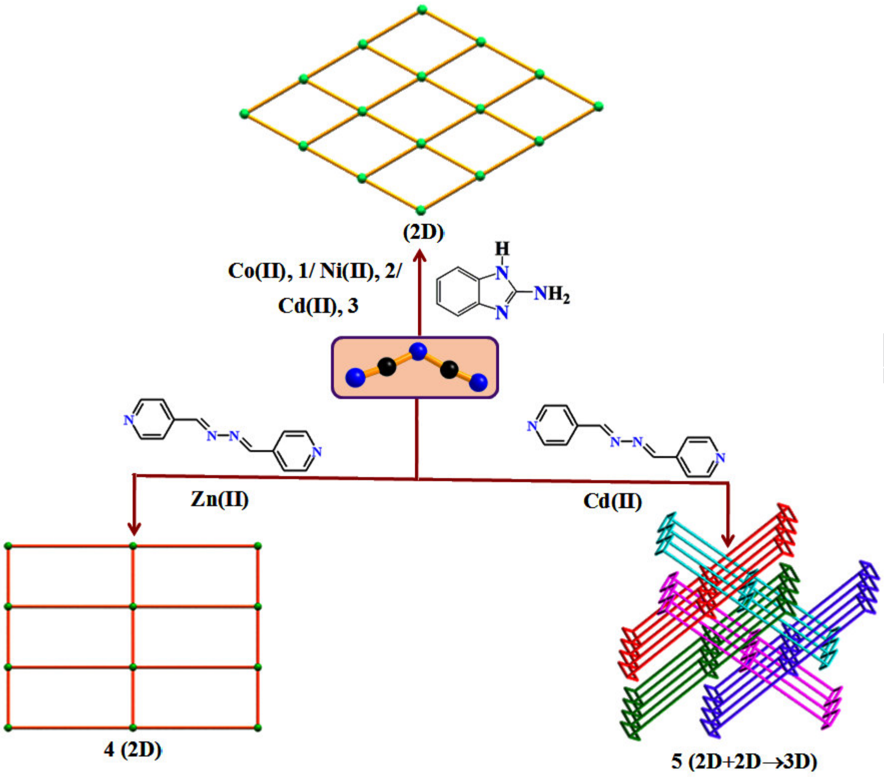
Symmetry code: *a* = x, y, -1+z; *b* = x, 1+y, z

Table 4. Selected bond lengths (Å) and angles (°) for **5**

Cd1-N1	2.363(9)	Cd1-N3	2.310(12)
Cd1-N5^{b}	2.339(14)	Cd1-N1^{a}	2.363(9)
Cd1-N3^{a}	2.310(12)	Cd1-N5^{c}	2.339(14)
N1-Cd1-N3	90.4(4)	N1-Cd1-N5^{b}	87.9(4)
N1-Cd1-N1^{a}	180.00	N1-Cd1-N3^{b}	89.6(4)
N1-Cd1-N5^{c}	92.1(4)	N3-Cd1-N5^{b}	90.0(5)
N1^{a}-Cd1-N3	89.6(4)	N3-Cd1-N3^{a}	180.00
N3-Cd1-N5^{c}	90.0(5)	N1^{a}-Cd1-N5^{b}	92.1(4)
N3^{a}-Cd1-N5^{b}	90.0(5)	N5^{b}-Cd1-N5^{c}	180.00
N1^{a}-Cd1-N3^{a}	90.4(4)	N1^{a}-Cd1-N5^{c}	87.9(4)

Symmetry code: *b* = x, y, -1+z; *a* = -x, -y, -z; *c* = -x, -y, 1-z.

Five dicyanamide based coordination polymers of diverse dimensionality have been synthesized and characterized by X-ray diffraction and photoluminescence study.


(2D)
Co(II), 1/ Ni(II), 2/
Cd(II), 3
H
N
NH₂
N
N
N–N
Zn(II)
Cd(II)
4 (2D)
5 (2D+2D→3D)