

Influence of Anions on the Self-assembly of Cd(II)-containing Coordination Polymers Based on the Flexible Ligand 2-((1*H*-1,2,4-Triazol-1-yl)methyl)-1*H*-benzimidazole

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Three Cd(II)-containing coordination polymers $[\text{CdCl}_2(\text{tmb})]_n$ (**1**) and two polymorphs of $\{[\text{CdI}_2(\text{tmb})]\cdot\text{DMF}\}_n$ (**2**, **3**) (tmb = 2-((1*H*-1,2,4-triazol-1-yl)methyl)-1*H*-benzimidazole) have been synthesized by the reactions of tmb with the cadmium salts. Polymer **1** exhibits an infinite $\cdots\text{Cd}(\text{ClI})_2\text{-Cd}(\text{ClI}_2)_2\text{-Cd}\cdots$ chain with $\mu_2\text{Cl}$ bridges, while polymers **2** and **3** are isomers, in which the Cd(II) ions are bridged by the bidentate tmb ligands leading to $\cdots\text{Cd-tmb-Cd}\cdots$ chains. The polymers form 3-D supramolecular frameworks through hydrogen bonds and $\pi\cdots\pi$ stacking interactions. The different structures of polymers **1–3** indicate that the anions and the flexibility of the tmb ligand can influence the structures of the coordination polymers. The infrared spectra and luminescent properties of the polymers have been investigated in the solid state at room temperature.

Key words: Crystal Structure, Anion Influence, Flexibility of Ligand, Luminescence

Introduction

In the past few years, investigation on the design, synthesis, structure, and properties of coordination polymers has been of great interest due to their intriguing variety of architectures, topologies, and the virtue of the design of materials with specific electronic, optical, magnetic and catalytic properties [1–5]. So far, the complexation of transition metal ions with *N*-donor ligands has been widely employed to construct coordination polymers with fascinating architectures and interesting properties. Among the *N*-donor ligands, flexible multidentate systems with 1,2,4-triazole and its derivatives have attracted more and more attention because of their various coordination modes and their prospective applications [6, 7]. In addition, organic spacers, such as alkyl linkers, play a role in the construction and structural tuning of the resulting polymers. The spatially extended directionality and the conformational preference provided by the ligands containing alkyl spacers can result in a remarkable class of polymers with diverse architectures and functions [8, 9]. Furthermore, anions also play an important role in the construction of coordination polymers as changing their size can control and adjust the structures of polymers.

In this paper, we use the unsymmetrical ligand 2-((1*H*-1,2,4-triazol-1-yl)methyl)-1*H*-benzimidazole (tmb) which has abundant *N*-donor sites and an alkyl spacer to self-assemble with Cd(II) salts, and have obtained three 1-D polymers, $[\text{CdCl}_2(\text{tmb})]_n$ (**1**) and two polymorphs of $\{[\text{CdI}_2(\text{tmb})]\cdot\text{DMF}\}_n$ (**2**, **3**). The structures of these coordination polymers, along with the influence of the coordination modes of the tmb ligands and the anions on the structures are presented and discussed. The solid-state IR spectra and fluorescence properties have also been investigated.

Experimental Section

The ligand 2-((1*H*-1,2,4-triazol-1-yl)methyl)-1*H*-benzimidazole (tmb) was synthesized according to a literature method [10]. All reagents and solvents employed were of AR Grade from commercial sources and used as received without further purification. IR data were recorded on a Bruker TENSOR 27 spectrophotometer with KBr pellets in the region 400–4000 cm^{-1} . Elemental analyses (C, H, and N) were carried out on a Flash EA 1112 elemental analyzer. Steady-state fluorescence measurements were performed on a Fluoro Max-P spectrofluorimeter at r. t. with solid powder on a round 1 cm quartz plate. The excitation slit was 5 nm, the emission slit was 5 nm, and the response time was 2 s.

	1	2	3
Empirical formula	C ₁₀ H ₉ CdCl ₂ N ₅	C ₁₃ H ₁₆ CdI ₂ N ₆ O	C ₁₃ H ₁₆ CdI ₂ N ₆ O
Formula weight	382.52	638.52	638.52
Temperature, K	293(2)	293(2)	293(2)
Crystal sizes, mm ³	0.21 × 0.19 × 0.18	0.19 × 0.18 × 0.15	0.19 × 0.16 × 0.14
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	P $\bar{1}$	P2 ₁ /c
<i>a</i> , Å	19.901(4)	8.5360(17)	7.7352(15)
<i>b</i> , Å	11.445(2)	10.367(2)	18.000(4)
<i>c</i> , Å	13.496(3)	11.278(2)	14.355(3)
α , deg	90	101.85(3)	90
β , deg	124.81(3)	92.35(3)	97.06(3)
γ , deg	90	102.60(3)	90
Volume, Å ³	2523.9(9)	949.4(3)	1983.6(7)
<i>Z</i>	8	2	4
Calculated density, g cm ⁻³	2.01	2.23	2.14
Absorption coefficient, mm ⁻¹	2.1	4.4	4.2
<i>F</i> (000), e	1488	596	1192
Reflections collected / unique	15089 / 3001	11697 / 4500	13687 / 3694
<i>R</i> _{int}	0.0212	0.0242	0.0336
Data / ref. parameters	3001 / 163	4500 / 208	4731 / 208
Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)] ^{a,b}			
<i>R</i> 1	0.0214	0.0300	0.0347
<i>wR</i> 2	0.0475	0.0636	0.0729
Final <i>R</i> indices (all data) ^{a,b}			
<i>R</i> 1	0.0230	0.0351	0.0397
<i>wR</i> 2	0.0485	0.0666	0.0757
Goodness-of-fit (<i>F</i> ²) ^c	1.099	1.071	1.121
Δρ _{fin} (max / min), e Å ⁻³	0.743 / -0.393	0.871 / -0.936	0.647 / -0.798

Table 1. Crystal data and structure refinement of polymers **1–3**.

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; ^b $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; ^c $\text{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Synthesis of [CdCl₂(tmb)]_n (**1**)

A mixture of CdCl₂ (0.05 mmol) and tmb (0.05 mmol) was stirred in CH₃OH-H₂O (8 mL, v/v, 1 : 1). The resultant solution was allowed to evaporate slowly at r.t. for about four weeks to give colorless crystals of **1**. Yield: 46 %. – C₁₀H₉CdCl₂N₅ (382.52): calcd. C 31.40, H 2.37, N 18.31; found C 31.31, H 2.46, N 18.22. – FT-IR (KBr, cm⁻¹): ν = 3448(m), 3116(m), 3077(s), 2927(m), 1805(m), 1618(m), 1511(m), 1453(m), 1415(m), 1331(m), 1286(s), 1223(m), 1147(s), 760(s), 673(s), 630(m), 439(w).

Synthesis of {[CdI₂(tmb)]·DMF}_n (**2**)

A mixture of CdI₂ (0.05 mmol) and tmb (0.05 mmol) was stirred in CH₃OH-H₂O (8 mL, v/v, 1 : 1). Then DMF (1 mL) was added to the mixture. The resultant colorless solution was allowed to stand in the dark at r.t. for about three weeks to give colorless crystals of **2**. Yield: 51 %. – C₁₃H₁₆CdI₂N₆O (638.52): calcd. C 24.45, H 2.53, N 13.16; found C 24.18, H 2.62, N 13.07. – FT-IR (KBr, cm⁻¹): ν = 3448(w), 3099(m), 2930(w), 2858(w), 2064(s), 1652(s), 1519(m), 1451(m), 1386(m), 1278(m), 1207(m), 1132(s), 1033(m), 981(m), 759(m), 744(s), 669(s), 429(w).

Synthesis of {[CdI₂(tmb)]·DMF}_n (**3**)

The synthesis of **3** was similar to that of **2**, but the pH value was adjusted to 8.0 by dropwise addition of

dilute NH₃·H₂O. Colorless crystals of **3** were obtained. Yield: 48 %. – C₁₃H₁₆CdI₂N₆O (638.52): calcd. C 24.45, H 2.53, N 13.16; found C 24.28, H 2.65, N 13.38. – Selected IR peaks (cm⁻¹): ν = 3104(m), 2965(m), 2876(m), 2064(w), 1652(s), 1590(m), 1490(m), 1447(m), 1387(s), 1278(s), 1132(s), 1107(s), 1040(s), 1020(m), 869(m), 853(m), 754(s), 667(s), 490(w).

Single-crystal structure determination

A suitable single crystal of each polymer was carefully selected and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Rigaku Saturn 724 CCD area detector diffractometer equipped with a graphite monochromator for the X-ray source (MoK α radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. The data were collected in an ω scan mode at 293(2) K, the crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by Direct Methods, completed by difference Fourier syntheses and refined by full-matrix least-squares based on *F*² (SHELXL/S-97 [11]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. All the hydrogen atoms were included in the final refinement. Crystallographic parameters and structural refinement for the coordination polymers are summarized in Table 1. Selected bond lengths and

Table 2. Selected bond lengths (Å) and angles (deg) for **1**, **2**, and **3** with estimated standard deviations in parentheses^a.

Polymer 1					
Cd1–N1	2.3354(17)	Cd1–N4	2.3998(17)	Cd1–Cl2	2.5771(7)
Cd1–Cl1	2.6164(7)	Cd1–Cl1 ^{#1}	2.6196(11)	Cd1–Cl2 ^{#2}	2.7032(12)
Cl1–Cd1 ^{#1}	2.6196(11)	Cl2–Cd1 ^{#2}	2.7032(12)	N1–Cd1–N4	78.16(6)
N1–Cd1–Cl2	94.89(4)	N4–Cd1–Cl2	168.98(4)	N1–Cd1–Cl1	164.76(4)
N4–Cd1–Cl1	87.10(4)	Cl2–Cd1–Cl1	100.253(18)	N1–Cd1–Cl1 ^{#1}	94.06(4)
N4–Cd1–Cl1 ^{#1}	90.92(5)	Cl2–Cd1–Cl1 ^{#1}	98.15(3)	Cl1–Cd1–Cl1 ^{#1}	82.240(17)
N1–Cd1–Cl2 ^{#2}	90.65(4)	N4–Cd1–Cl2 ^{#2}	85.79(5)	Cl2–Cd1–Cl2 ^{#2}	85.76(3)
Cl1–Cd1–Cl2 ^{#2}	92.088(17)	Cl1 ^{#1} –Cd1–Cl2 ^{#2}	173.586(16)	Cd1–Cl1–Cd1 ^{#1}	97.760(17)
Cd1–Cl2–Cd1 ^{#2}	93.22(3)				
Polymer 2					
Cd1–N1	2.242(3)	Cd1–N5 ^{#1}	2.345(3)	Cd1–I1	2.7283(12)
Cd1–I2	2.7445(8)	N1–Cd1–N5 ^{#1}	93.37(10)	N1–Cd1–I1	114.60(8)
N5 ^{#1} –Cd1–I1	97.54(8)	N1–Cd1–I2	116.08(8)	N5 ^{#1} –Cd1–I2	94.95(8)
I1–Cd1–I2	126.71(2)				
Polymer 3					
Cd1–N1	2.269(4)	Cd1–N5 ^{#1}	2.381(4)	Cd1–I2	2.715(7)
Cd1–I1	2.7231(7)	N1–Cd1–N5 ^{#1}	89.84(13)	N1–Cd1–I2	116.68(9)
N5 ^{#1} –Cd1–I2	98.28(10)	N1–Cd1–I1	113.71(9)	N5 ^{#1} –Cd1–I1	94.90(10)
I2–Cd1–I1	127.70(2)				

^a Symmetry transformations used to generate equivalent atoms: **1**: ^{#1} $-x+1, -y+1, -z+2$, ^{#2} $-x+1, y, -z+3/2$; **2**: ^{#1} $x+1, y, z$; **3**: ^{#1} $x, -y+3/2, z-1/2$.

D–H···A	<i>d</i> (D–H) (Å)	<i>d</i> (H···A) (Å)	<i>d</i> (D···A) (Å)	∠(D–H···A) (deg)
Polymer 1				
N2–H2B···N5 ^{#3}	0.86	2.18	3.025(3)	166.1
Polymer 2				
N2–H2B···O1 ^{#3}	0.86	1.88	2.725(4)	167.7
Polymer 3				
N2–H2B···O1 ^{#3}	0.86	1.87	2.685(5)	158.3

Table 3. Hydrogen bonds in crystals of **1–3**^a.

^a Symmetry transformations used to generate equivalent atoms: **1**: ^{#3} $-x+1/2, y+1/2, -z+3/2$; **2**: ^{#3} $-x+2, -y+1, -z+1$; **3**: ^{#3} $x+1, -y+1/2, z+1/2$.

bond angles are listed in Table 2. Hydrogen bond parameters are given in Table 3.

CCDC 840802–840804 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

IR spectroscopy of polymers **1**, **2** and **3**

The IR spectra of polymers **1**, **2** and **3** show absorption bands at 3116 for **1**, 3099 for **2** and 3104 cm^{−1} for **3** that can be attributed to the stretching vibrations of Ar–H. The absorption bands at 2927 for **1**, 2930 and 2858 for **2**, 2965 and 2876 cm^{−1} for **3** are associated with the stretching vibrations of CH₂. The sharp absorption bands at 1652 cm^{−1} in polymers **2** and **3** show the presence of solvate DMF molecules [12]. Bands at 1618, 1511, 1453 for **1**, 1519, 1451 for **2**, and 1590, 1490, 1447 cm^{−1} for **3** are associated with the stretching vibrations of C=C and C=N. Bands at 1286 for **1**, and at 1278 cm^{−1} for **2** and **3** are the results of C–N stretching vibrations, those at 760 for **1**, 759 for **2** and

754 cm^{−1} for **3** originate from characteristic stretching vibrations of phenylene groups. These data are consistent with the results of the X-ray diffraction study.

Structure of [CdCl₂(tmb)]_n (**1**)

Single crystals of **1** were obtained from aqueous methanol solutions. It crystallizes in the monoclinic space group *C2/c* with *Z* = 8. Fig. 1a depicts the coordination geometry of the Cd(II) ion, Table 2 summarizes important bond lengths and angles. Each Cd(II) ion is in a distorted octahedral environment with two nitrogen atoms from one tmb ligand and four bridging chlorine anions. The apical positions are occupied by N4 and Cl2 (Cd1–N4 2.3998(17), Cd1–Cl2 2.5771(7) Å). The equatorial plane is completed by N1, Cl1, Cl1A, and Cl2B with the mean deviations of 0.1261 Å from the plane (Cd1–N1 2.3354(17) Å, Cd1–Cl1 2.6164(7), Cd1–Cl1A 2.6196(11) and Cd1–Cl2B 2.7032(12) Å). The tmb ligand coordinates to the Cd(II) ion in a chelating fashion with two nitrogen atoms from the benzimidazole ring and the triazole ring. As depicted

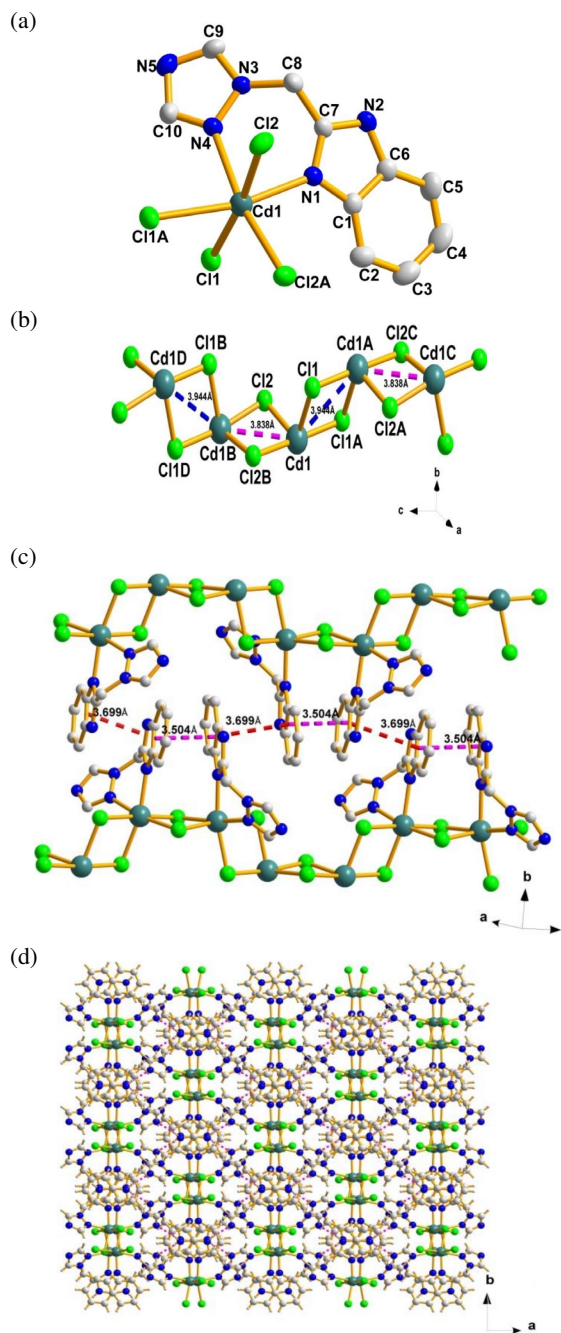


Fig. 1. (a) Coordination environment of the Cd(II) ion in polymer **1** with the atom numbering scheme. Hydrogen atoms are omitted for clarity. (b) View of the polymeric chain $\cdots\text{Cd}-(\text{Cl}1)_2-\text{Cd}-(\text{Cl}2)_2-\text{Cd}\cdots$ running parallel to the c direction. (c) View of $\pi\cdots\pi$ stacking interactions between benzimidazole rings. (d) View of the supramolecular network formed through hydrogen bonds and $\pi\cdots\pi$ stacking interaction.

in Fig. 1b, adjacent Cd(II) ions are interconnected by $\mu_2\text{Cl}$ to give an infinite $\cdots\text{Cd}-(\text{Cl}1)_2-\text{Cd}-(\text{Cl}2)_2-\text{Cd}\cdots$ chain running parallel to the c direction with Cd \cdots Cd separations of 3.838 and 3.944 Å. In addition, as shown in Figs. 1c and 1d, intrachain $\pi\cdots\pi$ stacking interactions between benzimidazole rings with centroid-to-centroid distances of 3.504 Å stabilize the configuration. Adjacent chains are further aggregated into a supramolecular network through further $\pi\cdots\pi$ stacking interactions with a centroid-to-centroid distance of 3.699 Å and hydrogen bonding ($\text{N}2-\text{H}2\text{B}\cdots\text{N}5^{\#3}$ 3.025(3) Å; Table 3).

Structure of $\{[\text{CdI}_2(\text{tmb})]\cdot\text{DMF}\}_n$ (**2**)

Single crystals of **2** were obtained from aqueous methanol solutions upon addition of DMF. Crystals are triclinic, space group $P\bar{1}$ with $Z = 2$. Table 2 contains important bond lengths and angles. The architecture of polymer **2** is different from that of **1**. Introduction of the iodide anion into the polymer not only influences the coordination modes of the tmb ligand, but also changes the coordination number of the metal ion. In polymeric **2**, the tmb acts as a bridging ligand, and the Cd(II) ion is tetracoordinated, while the Cd(II) ion is hexacoordinated in **1** probably because the radius of iodide is larger than that of chloride. Fig. 2a shows that the coordination geometry of each Cd(II) ion is a distorted trigonal pyramid. The bottom is comprised of Cd1, two terminal iodide anions and one nitrogen atom from the tmb ligand (Cd1–I1 2.7283(12), Cd1–I2 2.7445(8), Cd1–N1 2.242(3) Å). The mean deviation from the plane is 0.090 Å, the sum of the angles at Cd1 is 357.4°. The apical position is occupied by N5A (Cd1–N5A 2.345(3) Å). The angles at Cd1 involving N5A(apical) are close to 90° (N1–Cd1–N5A 93.37(10), N5A–Cd1–I1 97.54(8), N5A–Cd1–I2 94.95(8)°) (symmetry operation for N5A is $^{\#1}x+1, y, z$ in Table 2).

As shown in Fig. 2a, each tmb ligand coordinates to two Cd(II) ions with nitrogen atoms from the benzimidazole and triazole rings, and the Cd \cdots Cd separation is 8.536 Å. Furthermore, adjacent Cd(II) ions are interconnected by bridging tmb ligands to give an infinite $\cdots\text{Cd}-\text{tmb}-\text{Cd}\cdots$ chain running parallel to the a direction. There are hydrogen bonds between the tmb ligands and the DMF molecules ($\text{N}2-\text{H}2\text{B}\cdots\text{O}1^{\#3}$ 2.725(4) Å; Table 3). Adjacent chains are joined together through inter-chain $\pi\cdots\pi$ stacking interactions between the benzene rings of the tmb lig-

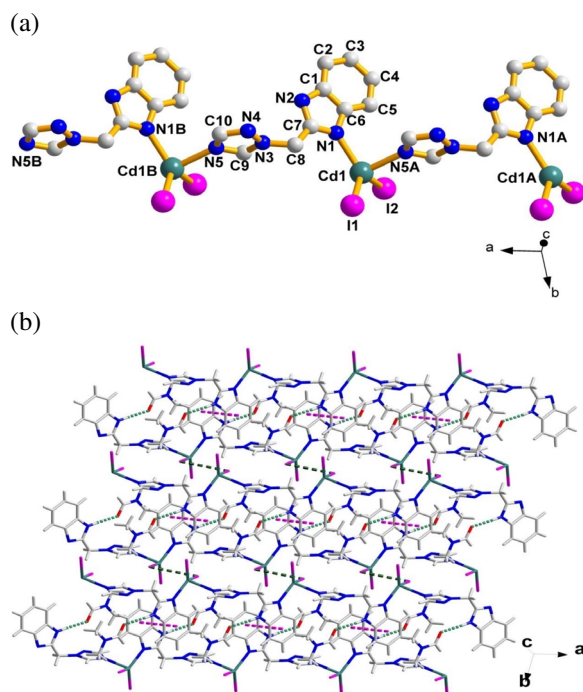


Fig. 2. (a) View of the polymeric chain formed by Cd(II) ions and tmb ligands running parallel to the *a* direction. Hydrogen atoms and DMF molecules are omitted for clarity. (b) View of inter-chain $\pi \cdots \pi$ stacking interactions between the benzene rings of tmb ligands and weak I \cdots I secondary halogen bonds in polymer 2.

ands with a centroid-to-centroid distance of 3.583 Å, and weak I \cdots I secondary halogen bonds to give a 3-D supramolecular architecture (Fig. 2b).

Structure of $\{[CdI_2(tmb)] \cdot DMF\}_n$ (**3**)

Single crystals of **3** were obtained from aqueous methanol after the addition of DMF but, in contrast to **2**, at higher pH values by addition of aqueous NH_3 . The crystallographic analysis reveals that polymer **3** is a polymorph of **2**, crystallizing in the monoclinic space group $P2_1/c$ with $Z = 4$. Table 2 contains bond lengths and angles. The coordination geometry of Cd1 again is in good approximation a trigonal pyramid, the tmb ligand acts as a bridging ligand as in **2**, and iodide anions are terminally coordinated. The configuration of the trigonal pyramids around Cd(II) is nearly identical to that in polymer **2** except for slight differences in the corresponding bond lengths and bond angles (Cd1–N1 2.269(3), Cd1–N5A 2.380(3), Cd1–I1 2.7234(7), Cd1–I(2) 2.7152(7) Å; angles at Cd1 involving the apical N atom N5A; N5A–Cd1–N1

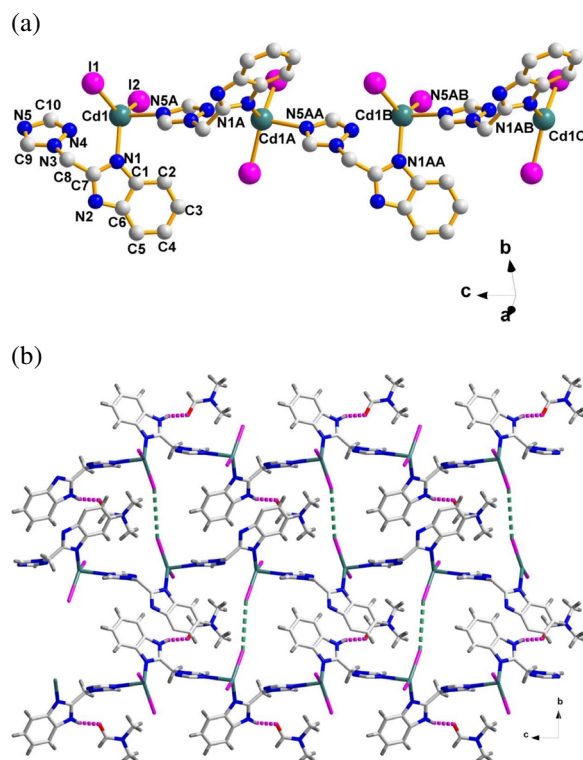


Fig. 3. (a) View of the polymeric chain formed by Cd(II) ions and tmb ligands running parallel to the *c* direction. Hydrogen atoms and DMF molecules are omitted for clarity. (b) View of the hydrogen bonding and weak I \cdots I secondary halogen bonds in polymer 3.

89.86(13)°, N5A–Cd1–I2 98.27(10)° and N5A–Cd10–I1 94.89(9)°; symmetry operation for N5A is $\#1$ $x, -y + 3/2, z - 1/2$, Table 2). Atoms Cd1, N1, I1, I2 occupy the bottom of the pyramid, the mean deviation from this plane being 0.0765 Å. The sum of the respective angles at Cd1 is 358.1°. In addition, there is a weak interaction between N4 and Cd1. The distance between these atoms is 2.705(3) Å which is longer than the bond lengths of Cd1–N1 and Cd1–N5A, but it may be additionally responsible for the peculiar trigonal-pyramidal coordination at Cd. Other factors may be, as in **2**, the space demand of the large iodine and the bridging nitrogen ligands. Each tmb ligand coordinates to two Cd(II) ions with nitrogen atoms from the benzimidazole and triazole rings, but the Cd \cdots Cd separation of 7.180 Å is shorter than that in **2**. The infinite \cdots Cd–tmb–Cd \cdots chain constructed from Cd(II) ions and bridging tmb ligands is running parallel to the crystallographic *c* direction. There are hydrogen bonds between the tmb ligands and the DMF molecules (N2–

$\text{H2B} \cdots \text{O1}^{\#3} = 2.685(5) \text{ \AA}$; Table 3). Adjacent chains are joined together through weak $\text{I} \cdots \text{I}$ secondary halogen bonds to give a 3-D supramolecular architecture (Fig. 3b).

It should be noted that there are striking differences not only in the crystal structures but also in the molecular structures of the polymer strands in **2** and **3** although they contain the same bridging ligands and counter anions. The differences can be clearly seen by comparing Figs. 2a and 3a. The tmb ligand in **2** adopts a TGT ($T = \text{trans}$ and $G = \text{gauche}$) conformation with the torsional angles of the fragments of N1-C7-C8-N3 , C7-C8-N3-C9 , C8-N3-C9-N5 of $-148.2(3)$, $76.6(5)$, and $175.3(3)^\circ$, respectively. As a result, the tmb ligands are on one side of the $\cdots\text{Cd-Cd}\cdots$ chain (shown in Fig. 2a). By contrast, in **3** tmb adopts a GTT conformation with the torsional angles of the fragments of N1-C7-C8-N3 , C7-C8-N3-C9 , C8-N3-C9-N5 of $73.1(5)$, $138.4(4)$, and $176.1(4)^\circ$. As a result, the tmb ligands are wrapped around the $\cdots\text{Cd-Cd}\cdots$ chain as shown in Fig. 3a. The conformational flexibility of the alkyl spacers as well as the rotational freedom of the benzimidazole and triazole rings of the tmb ligands are responsible for the variable relative orientation of the N -donor atoms, which leads to the different structures of **2** and **3**.

Fluorescence spectra

Polymers composed of d^{10} metal centers and organic ligands have been investigated with regard to their fluorescence properties because of their potential applications as luminescent materials, especially those involving Cd(II) ions as coordination centers [13–15]. For this reason, solid-state emission spectra of the free tmb ligand and of the polymers **1**, **2** and **3** were investigated at r. t. (Fig. 4). Upon excitation at 326 nm, the emission spectrum for the free tmb ligand shows a peak at 383 nm. For polymers **1** and **2**, the emission peaks occur at 350 and 374 nm, respectively (excitation at 298 nm for **1**, 317 nm for **2**). The emission peaks for the two polymers originate from the intraligand $\pi \rightarrow \pi^*$ transitions of tmb, as in the free ligand.

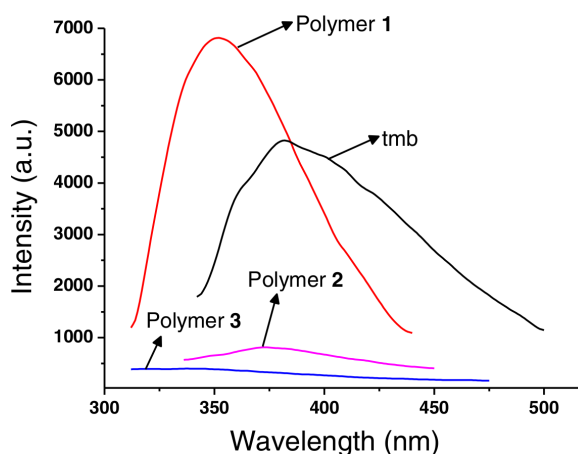


Fig. 4. Solid-state emission spectra of the tmb ligand, and of the polymers **1**, **2** and **3** at room temperature.

However, the fluorescence intensity of polymer **1** is much stronger than that of tmb because the rigidity of the ligand increases after coordination to the Cd(II) ions. The weaker fluorescent emission of polymers **2** and **3** could imply the fluorescence quenching effect of iodide anions [16]. That the emission of polymer **2** is stronger than that of **3** may be due to the existence of $\pi \cdots \pi$ interactions between the benzene rings of the tmb ligands in the crystal.

Conclusion

We have synthesized three Cd(II) polymers based on a flexible neutral ligand by varying the anions and the pH. The structural diversity of the final products shows that the change of anions can influence not only the coordination mode of the tmb ligand, but also the coordination number of the Cd(II) ion, and thus influence the architecture of the polymers. The results also demonstrate that the structure of the polymer strongly affects their luminescence properties.

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