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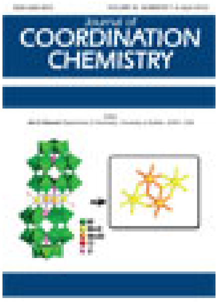

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Metallacycle-based complexes based on a flexible pyridyl–benzimidazole derivative

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Three new coordination complexes, $\{Cd(pbmb)(NO_3)_2\}_n$ (**1**), $\{Ag(pbmb)(NO_3)(C_3H_6O)\}_n$ (**2**), and $\{Hg_2(pbmb)_2Cl_4\}_n$ (**3**), have been synthesized under solvothermal or solution reactions based on a flexible N-heterocyclic ligand 1-((2-(pyridin-4-yl)-1H-benzoimidazol-1-yl)methyl)-1H-benzotriazole (pbmb) and structurally characterized by single-crystal X-ray diffraction, IR spectrum, and elemental analyses. Both **1** and **2** display a 1-D chain structure with metallacycle unit while **3** shows a binuclear cycle motif. The aromatic rings are directing groups for $\pi\cdots\pi$ stacking interactions. The $\pi\cdots\pi$ interactions and hydrogen bonds extend the simple chain structure and binuclear structure to 3-D supramolecular architectures. Complexes **1** and **3** exhibit strong luminescence in the solid state at room temperature whereas **2** shows fluorescence quenching.

Keywords: V-shaped ligand; Crystal structure; Luminescence property

1. Introduction

Metal–organic coordination architectures have attracted attention for intriguing structural motifs and extensive applications in catalysis, luminescence, ion exchange, gas adsorption, etc. [1]. The performance of the complexes depends on structure topologies and components, and thus much effort has been paid on synthetic strategies to such complexes [2, 3]. Multiple factors such as pH of the solution [4], the molar ratio of reagents [5], and geometrical and electronic properties of the metal ions and ligands [6] affect the final aggregates. Appropriate ligands and metal centers are two key factors with organic connectors that have alternative linking modes and orientation of donors tied closely to the architectures and applications of the materials. Accordingly, development of new ligand systems continues to be an important aspect for metal–organic architectures.

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By comparison with rigid synthons, flexible ligands that bear variable coordination can meet different coordination requirements of metal centers [7]. Numerous metal–organic structures based on flexible synthons, for example, $\{[Ni(cyclam)]_2[TCM]\} \cdot 2DMF \cdot 10H_2O$ [8], $\{[Ag_2(btpd)_2](CH_3OH)(H_2O)_{0.17}\}_n$ [9], $[Cu_2(3\text{-}BPFA)_4(H_2O)_2](ClO_4)_4 \cdot 34CH_3OH$ [10], and $[Pb_2(phda)_2(H_2O)]_n \cdot 2nH_2O$ [11], have been constructed with interesting topologies and properties, especially for metallamacrocycles or porous aggregates. The results indicating the existence of flexible groups endows synthons with coordination diversity. We have designed a V-shaped flexible ligand 1-((2-(pyridin-4-yl)-1H-benzoimidazol-1-yl)methyl)-1H-benzotriazole (pbmb), which comprises one pyridyl, one benzimidazole, and one benzotriazole. The $–CH_2–$ spacer bridging the benzimidazole and benzotriazole of pbmb orient the benzotriazole arm in divergent fashion to aggregate with transition-metal ions. Further, V-shaped multiple-dentate synthons are inclined to form macrocycle motifs. Three new coordination complexes, $\{Cd(pbmb)(NO_3)_2\}_n$ (**1**), $\{Ag(pbmb)(NO_3)(C_3H_6O)\}_n$ (**2**), and $\{Hg_2(pbmb)_2Cl_4\}_n$ (**3**), based on pbmb have been synthesized and structurally characterized. Photoluminescence properties show **1** and **3** to exhibit strong luminescence emission in the solid state at room temperature whereas **2** shows fluorescence quenching.

2. Experimental

2.1. *Materials and general methods*

Chemicals were purchased from commercial sources and used without purification. The 2-(4-pyridyl)-benzimidazole was synthesized according to the literature method [12]. 1-((2-(pyridin-4-yl)-1H-benzoimidazol-1-yl)methyl)-1H-benzotriazole (pbmb, scheme S1) was synthesized according to the literature [13]. Infrared (IR) spectra were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses (C, H, and N) were performed on a Flash EA 1112 elemental analyzer. Thermogravimetric experiments were performed using a TGA/SDTA instrument. Photoluminescence data were carried out using a Hitachi F-4600 spectrofluorimeter at ambient temperature in the solid state. The excitation and emission slit widths are both 2.5 nm, and the response time is 0.1 s.

2.2. *Synthesis of $\{Cd(pbmb)(NO_3)_2\}_n$ (1)*

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0062 g, 0.02 mmol), pbmb (0.0065 g, 0.02 mmol), ethanol (0.5 mL), chloroform (0.5 mL), and methanol (1 mL) was placed in a glass reactor (10 mL), which was heated at 85°C for 3 days and then gradually cooled to room temperature at a rate of 5°C h^{-1}. Colorless crystals of **1** were obtained. Yield: 65% (based on Cd). Elemental Anal. Calcd for $CdC_{19}H_{14}N_8O_6$ (%): C, 40.55; H, 2.51; N, 19.91; Found (%): C, 40.53; H, 2.52; N, 19.61. IR(KBr/pellet, cm^{-1}): 3449(s), 1621(w), 1456(s), 1384(s), 1308(s), 1220(w), 1193(w), 1068(w), 1035(w), 1009(w), 844(w), 768(m), 753(m), 597(w).

2.3. *Synthesis of* $\{Ag_2(pbmb)_2(NO_3)_2(C_3H_6O)\}_n$ *(2)*

An aqueous solution (3 mL) of $AgNO_3$ (0.0035 g, 0.02 mmol) was added slowly to a solution of pbmb (0.0065 g, 0.02 mmol) in acetone (3 mL). Then DMF (1 mL) was added with constant stirring to the reaction mixture. The resulting mixture was left to stand at room temperature for 3 weeks. Colorless block crystals were obtained. Yield: 67% (based on Ag). Elemental Anal. Calcd for $Ag_2C_{41}H_{34}N_{14}O_7$ (%): C, 46.88; H, 3.26; N, 18.67; Found (%): C, 46.46; H, 3.05; N, 18.91. IR(KBr/pellet, cm^{-1}): 3470(m), 3069(w), 1705(w), 1612(m), 1454(m), 1384(s), 1326(s), 1162(m), 1124(w), 1009(w), 840(m), 755(s), 599(m).

2.4. *Synthesis of* $\{Hg_2(pbmb)_2Cl_4\}_n$ *(3)*

A methanol solution (3 mL) of $HgCl_2$ (0.0054 g, 0.02 mmol) was added slowly to a solution of pbmb (0.0065 g, 0.02 mmol) in methanol (3 mL). Then DMF (2 mL) was added with constant stirring to the reaction mixture. The resulting mixture was left to stand at room temperature for 3 days. Yellow block crystals were obtained. Yield: 58% (based on Hg). Elemental Anal. Calcd for $Hg_2C_{38}H_{28}Cl_4N_{12}$ (%): C, 38.17; H, 2.36; N, 14.06; Found (%): C, 37.94; H, 2.26; N, 13.94. IR(KBr/pellet, cm^{-1}): 3449(s), 1613(m), 1450(m), 1419(m), 1350(w), 1302(w), 1267(w), 1180(m), 1080(w), 1005(w), 841(m), 759(s), 743(s), 689(w), 599(w).

2.5. *Crystal structure determination*

Single crystals suitable for X-ray determination were mounted on a glass fiber. The data for **1**–**3** were collected on a Rigaku Saturn 724 CCD with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were handled by direct methods and expanded with Fourier techniques. All calculations were solved with the SHELXL-97 crystallographic program [14–16]. All non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Crystallographic data and processing parameters of the three complexes are summarized in table 1. The selected bond lengths and angles are shown in table 2.

3. Results and discussion

3.1. *Crystal structure of 1*

X-ray crystallographic data show that **1** crystallizes in triclinic with space group $P\bar{1}$. As shown in figure 1, the building unit is one Cd(II), two NO_3^-, and one pbmb. The Cd(II) is seven-coordinate, binding four oxygen atoms (O2, O3, O4, and O5) from two NO_3^- groups, and three nitrogen atoms (N7, N8a, and N3b) from three pbmb molecules. The Cd–O distances range from 2.287 Å to 2. 679 Å and the Cd–N vary from 2.280 Å to 2.358 Å. Similar Cd–O and Cd–N bond lengths are found in other cadmium complexes [17]. The coordination environment of the cadmium center can be described as a distorted pentagonal bipyramid. N3b and O3 hold apical positions with the axial

Table 1. Crystal data and structure refinement for **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{19}H_{14}CdN_8O_6$	$C_{41}H_{34}Ag_2N_{14}O_7$	$C_{38}H_{28}Cl_4Hg_2N_{12}$
Formula weight	562.79	1050.56	1195.70
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Mo-Kα) (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	9.6726(19)	9.2599(19)	8.000(16)
b	9.753(2)	10.205(2)	8.9343(18)
c	11.203(2)	12.238(2)	13.683(3)
α	80.66(3)	89.41(3)	102.22(3)
β	88.69(3)	85.73(3)	94.06(3)
γ	88.99(3)	81.99(3)	90.20(3)
Volume (Å^3), Z	1042.5(3), 2	1142.0(4), 1	953.3(3), 1
$F(000)$	560	528	568
θ range for data collection (°)	1.84–27.92	2.23–26.00	2.33–25.99
Goodness-of-fit on F^2	1.112	1.104	1.141
Final R_1[a], wR_2[b]	0.0401, 0.0904	0.00612, 0.1633	0.0339, 0.0676

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680\,P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Cd(1)–N(7)#1	2.280(3)	Cd(1)–O(5)	2.288(3)
Cd(1)–N(3)	2.341(3)	Cd(1)–N(8)#2	2.358(3)
Cd(1)–O(3)	2.407(3)	Cd(1)–O(2)	2.483(3)
Cd(1)–O(4)	2.676(4)	O(2)–Cd(1)–O(4)	68.75(12)
O(3)–Cd(1)–O(4)	110.91(13)	N(7)#1–Cd(1)–N(3)	91.75(11)
O(5)–Cd(1)–N(3)	91.55(12)	O(5)–Cd(1)–O(3)	87.72(13)
N(3)–Cd(1)–O(3)	165.15(11)	N(8)#2–Cd(1)–O(4)	140.66(11)
N(3)–Cd(1)–O(2)	143.33(11)	O(5)–Cd(1)–O(2)	82.14(12)
O(3)–Cd(1)–O(2)	51.17(11)	N(7)#1–Cd(1)–O(4)	106.43(11)
O(5)–Cd(1)–O(4)	50.14(12)	N(3)–Cd(1)–O(4)	79.50(12)
2			
Ag(1)–N(1)	2.265(4)	Ag(1)–O(1)	2.566(5)
Ag(1)–N(3)#1	2.297(4)	Ag(1)–O(2)	2.590(6)
Ag(1)–N(6)#2	2.417(5)	N(1)–Ag(1)–N(6)#2	91.55(16)
N(1)–Ag(1)–O(1)	101.65(17)	N(3)#1–Ag(1)–O(1)	128.80(18)
N(6)#2–Ag(1)–O(1)	94.95(17)	N(1)–Ag(1)–O(2)	114.97(19)
N(3)#1–Ag(1)–O(2)	90.63(16)	N(6)#2–Ag(1)–O(2)	136.83(19)
O(1)–Ag(1)–O(2)	48.51(18)	N(1)–Ag(1)–N(3)#1	126.00(16)
3			
Hg(1)–Cl(1)	2.346(2)	Hg(1)–Cl(2)	2.3547(19)
Hg(1)–N(1)	2.457(5)	Hg(1)–N(6)#1	2.495(5)
Cl(1)–Hg(1)–Cl(2)	155.91(7)	Cl(1)–Hg(1)–N(1)	104.94(14)
Cl(2)–Hg(1)–N(1)	92.88(14)	Cl(1)–Hg(1)–N(6)#1	96.31(13)
Cl(2)–Hg(1)–N(6)#1	93.63(13)	N(1)–Hg(1)–N(6)#1	107.26(19)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y, -z + 1$; #2 $x - 1, y, z$ for **1**; #1 $-x, -y + 1, -z$; #2 $-x, -y, -z$ for **2**; #1 $-x + 2, -y + 1, -z + 2$ for **3**.

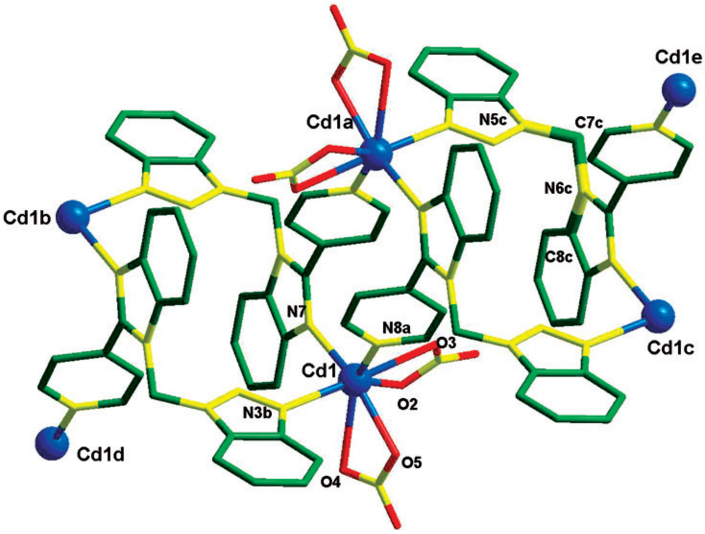

Figure 1. The coordination environment of Cd(II) (all hydrogen atoms are omitted for clarity).

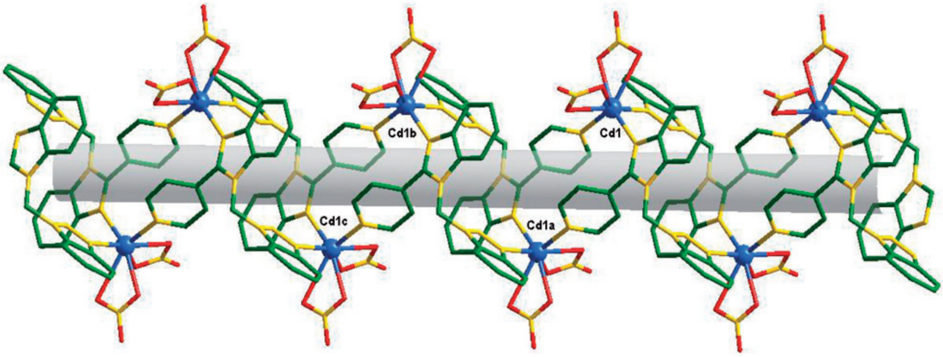

Figure 2. The 1-D chain of **1** (all hydrogen atoms are omitted for clarity).

bond angle (N3b–Cd–O3) 165.15°, with N7, N8a, O2, O4, N5 being almost coplanar with slight deviation from the plane. The Cd(II) centers are bridged by benzimidazole and benzotriazole moieties of the multifunctional pbmb to form a binuclear metallacycle with Cd $\cdots$ Cd (Cd1 $\cdots$ Cd1b) separations of 8.689 Å. Within the metallacycle unit, the flexible methylene group connects both benzimidazole and benzotriazole moieties oriented in divergent directions with appropriate angle to meet the coordination preference of Cd(II). These functional metallacycle units are further connected to give the 1-D chain structure **1** (figure 2).

There are $\pi \cdots \pi$ interactions between parallel adjacent pyridine groups in the chain with centroid distance of 3.688 Å and, thus, the chain structure is reinforced. The chains are also connected by weak hydrogen-bonding interactions (3.152 Å for C7 $\cdots$ O6′, 3.254 Å for C9 $\cdots$ O2′, 3.269 Å for C5 $\cdots$ O5′) [18, 19]. The $\pi \cdots \pi$ interactions and

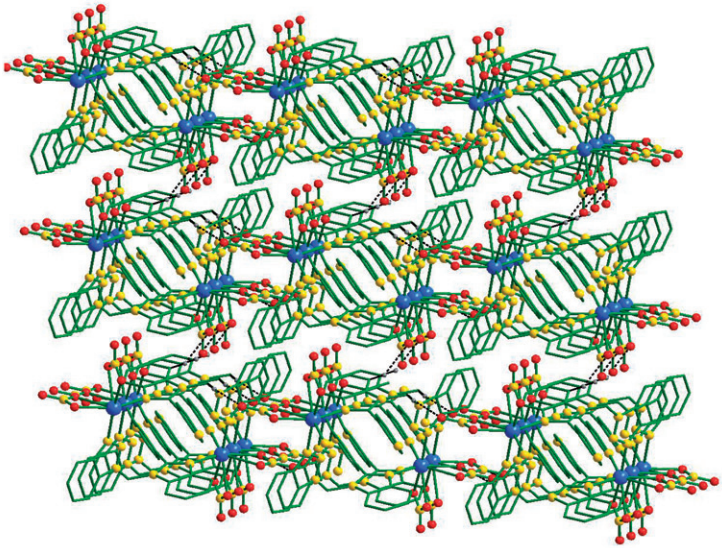

Figure 3. 3-D supramolecular structure of **1** stabilized by hydrogen bonds and $\pi \cdots \pi$ interactions (all hydrogen atoms are omitted for clarity).

hydrogen-bonds play crucial roles in constructing and stabilizing the 3-D supramolecule (figure 3).

The introduction of methylene moiety within the pbmb plays an important role to generate the architecture, which is greatly different from complexes based on a rigid synthon such as 2-(4-pyridyl)benzimidazole (PYBIM). There are four complexes $[Ag_2(4\text{-PyBIm})_2(H_2O)_2]SO_4H_2O$, $[(ZnCl_2)(4\text{-PyBIm})]$, $[Cu(4\text{-PyBim})_2(Cl)_2](H_2O)_2$, and $[Zn(4\text{-PyBim})_2(H_2O)_2(NO_3)_2]$ based on PYBIM, in which the first is a 1-D "zigzag" chain and the latter ones are binuclear structures [20–22]. By contrast, pbmb possesses rich coordination sites and versatile configurations owing to rotation of methylene. Based on such V-shaped flexible synthon, a binuclear metallacycle-based 1-D motif was achieved and the binuclear metallacycle units are bridged making **1** like "hollow bamboo."

3.2. *Crystal structure of 2*

Single-crystal structural determination reveals that **2** (figure 4) crystallizes in the triclinic space group $P\bar{1}$. Similar to **1**, the reaction of Ag(I) and pbmb yields a binuclear Ag(I) metallacycle-based 1-D chain **2** (figure 5). As shown in figure 4, the fundamental building unit contains one Ag(I), one NO_3^-, one pbmb, and one acetone. Ag(I) is five-coordinate with a distorted trigonal bipyramidal configuration defined by two oxygen atoms (O1, O2) from one NO_3^-, and three nitrogen atoms (N1, N3a, N6b) from the three pbmb molecules; O2 and N6b occupy apical positions with the angle (O2–Ag1–N6b) 136.831°. The remaining N1, N3a, and O1 are almost coplanar with slight deviation from the plane. The Ag–N distances range from 2.265 Å to 2.417 Å, and Ag–O bond lengths are 2.566 Å for Ag1–O1 and 2.590 Å for Ag1–O2. The Ag–O and Ag–N

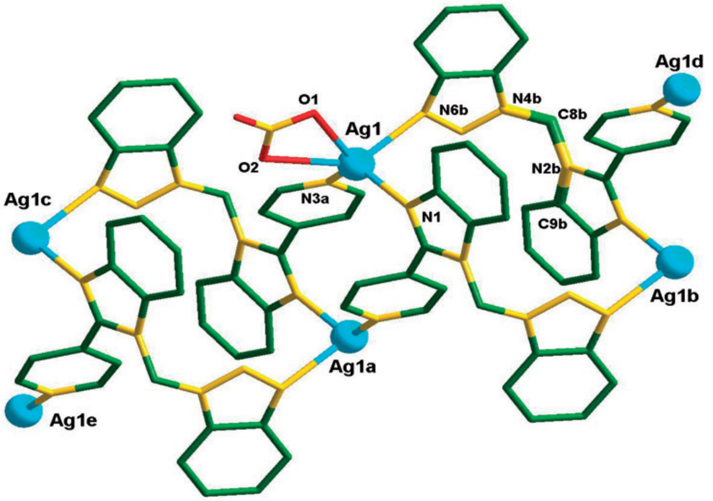

Figure 4. The coordination environment of Ag(I) in **2** (all hydrogen atoms and solvent molecules are omitted for clarity).

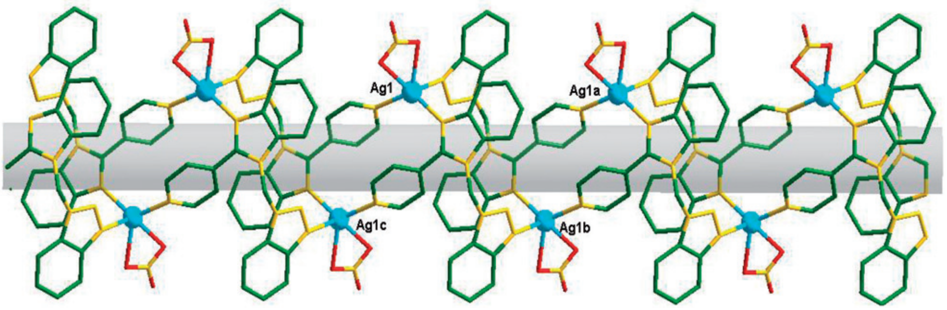

Figure 5. The 1-D chain of **2** (all hydrogen atoms and solvent molecules are omitted for clarity).

lengths are quite similar to reported complexes [23, 24]. All the Ag(I) centers are linked by pbmb with $\mathrm{Ag}\cdots\mathrm{Ag}$ separations of 6.852 Å–10.205 Å.

While pbmb exhibits tridentate coordination in **1** and **2**, the flexible "spacer" displays different angles (110.800° for N5c–C7c–N6c of **1**, 113.235° for N4b–C8b–N2b of **2**) and torsion angles (65.729° for C8c–N6c–C7c–N5c of **1**, 99.439° for C9b–N2b–C8b–N4b of **2**), which indicates that organic synthons meet coordination preferences of metal centers. In **2**, alternating phenyl rings of adjacent benzotriazoles display $\pi\cdots\pi$ interactions arranged along the *c*-axis with centroid–centroid distance of 3.767 Å and two adjacent phenyl rings parallel. There also exist weak hydrogen-bonding interactions (3.417 Å for $\mathrm{C4}\cdots\mathrm{O3'}$, 3.451 Å for $\mathrm{C10}\cdots\mathrm{O3'}$, 3.228 Å for $\mathrm{C8}\cdots\mathrm{O4'}$) [24]. Ultimately, the chains are further connected into a 3-D microporous supramolecular framework with tunnels by those hydrogen-bonding interactions as well as the $\pi\cdots\pi$ interactions (figure S1). Binuclear Ag(I) metallacycle-based structure indicates again that the V-shaped flexible ligand has great possibility to construct metallacycle structures.

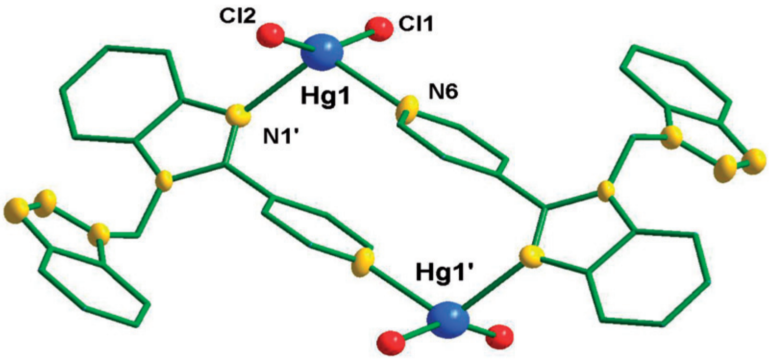

Figure 6. The coordination environment of Hg(II) (all hydrogen atoms are omitted for clarity).

3.3. *Crystal structure of 3*

The replacement of Ag(I) in **2** by Hg(II) gives an entirely different motif in **3**. Complex **3** also crystallizes in the triclinic space group *P*-1, yet with a binuclear motif. The Hg(II) is coordinated to two chlorides (Cl1, Cl2) and two nitrogen atoms (N1′, N6) from two pbmb molecules. Figure 6 shows the coordination environment of Hg(II) with a distorted tetrahedron in **3**. The Hg–Cl distances are 2.346 Å and 2.355 Å and the Cl–Hg–Cl angle is 155.91°, while the Hg1–N1′, Hg1–N6 bond lengths are 2.457 Å and 2.496 Å and the N–Hg–N bond angle is 107.258°. The Hg–Cl and Hg–N distances are very close to those recorded [25]. Coordination models of Hg(II) are simple and the benzotriazole does not participate in coordination. The behavior of pbmb implies that nitrogen atoms from benzimidazole and pyridine are more easily coordinated to mercury than those from benzotriazole. Hydrogen-bonding (3.346 Å for C4 $\cdots$ N4′, 3.674 Å for C8 $\cdots$ Cl2′, 3.666 Å for C8 $\cdots$ Cl2′) [22] and $\pi \cdots \pi$ interactions between parallel adjacent pyridine rings with the centroid distance of 3.565 Å and between parallel adjacent triazole rings with centroid distance of 3.830 Å also play a significant role in the structure. From hydrogen-bonding and weak $\pi \cdots \pi$ interactions that exist between triazole rings, the binuclear metallacycle becomes a 3-D supramolecular framework (figure 7).

3.4. *Thermogravimetric analysis of 2*

Complex **2** is air-stable and can retain crystal integrity at ambient temperature. Thermogravimetric analysis (TGA) of **2** was carried out by heating to 800°C. The TGA curve (figure S2) shows that weight loss takes place between 30°C and 210°C, and the total weight loss in this temperature range is 5.19% corresponding to uncoordinated acetone (Calcd 5.52%). The solid is then stable to 295°C. The DSC spectrum exhibits an endothermic peak near 90°C, which implies the loss of uncoordinated solvent, while an exothermic peak near 297°C may indicate **2** to decompose.

3.5. *Photoluminescence properties*

Metal–organic coordination polymers, especially for d^{10}-metal complexes, have attracted interest for applications in chemical sensors, photochemistry,

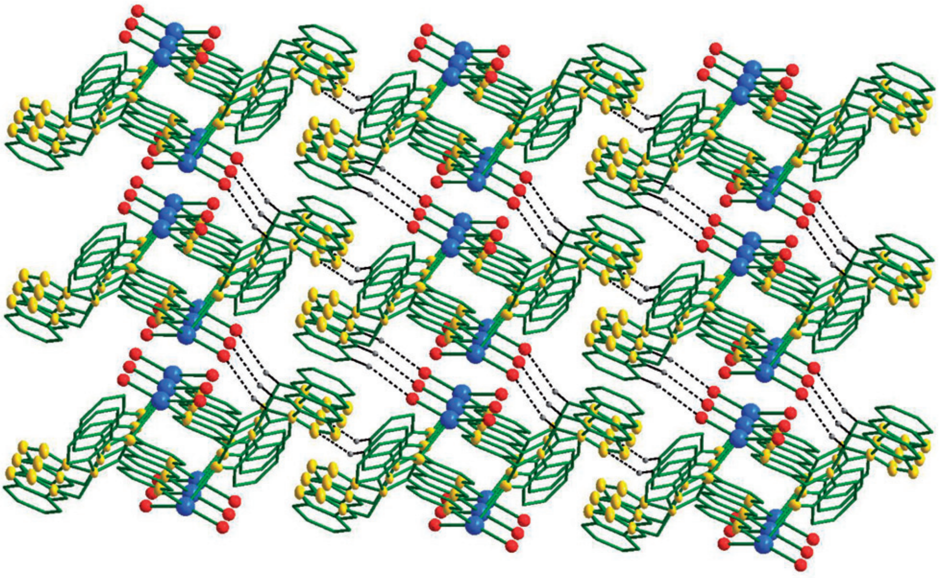

Figure 7. 3-D supramolecular structure of **3** stabilized by hydrogen bonds and $\pi \cdots \pi$ interactions (all hydrogen atoms are omitted for clarity).

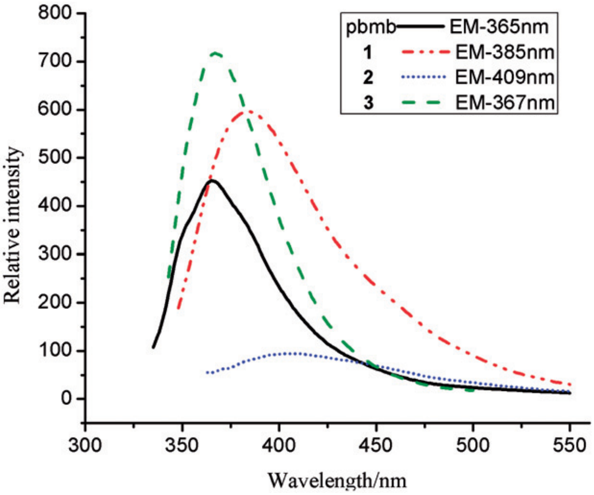

Figure 8. Solid-state photoluminescence spectra of **1**–**3** and pbmb at room temperature.

electroluminescent devices, and luminescent probes in biology [26]. Therefore, the luminescence properties of **1**–**3** and pbmb were measured in the solid state at room temperature (figure 8).

As shown in figure 8, the luminescence spectrum of pbmb shows emission maximum at 365 nm with excitation wavelength of 323 nm. Both **1** and **3** display strong emission at 385 nm ($\lambda_{ex} = 329$ nm) and 367 nm ($\lambda_{ex} = 323$ nm), respectively. Similar emissions of pbmb and **1** and **3** probably arise from π–π* intraligand fluorescence [27]. The enhancement of **1** and **3** may be attributed to pbmb coordination with metal centers increasing rigidity. The emissions of **1** and **3** reveal different Stokes shift (56 nm for **1**, 44 nm for **3**) from the excitation maximum to the low-energy emission maximum, which mainly originates from coordination of metal centers to pbmb, as well as different composition and architectures. Only weak emission of **2** was observed, which indicates that Ag(I) negatively impacts the fluorescence of **2**. Free acetone in the structure may be a non-radiative decay factor to quench the emission [28].

4. Conclusions

Three new complexes based on pbmb were synthesized under solvothermal or solution reactions. By altering the metal center with d^{10} electronic configuration from Cd(II) and Ag(I) to Hg(II), the architectures changed, which indicates the coordination preference of metal centers may act synergistically for formation of the final motifs. Both $\pi \cdots \pi$ interactions and hydrogen bonds play crucial roles in formation and stabilization of the coordination frameworks of **1**–**3**. The results imply that V-shaped flexible organic synthons combined with suitable metal centers have rich possibilities to form coordination polymers with metallacycle-based or porous structures. Complexes **1** and **3** exhibit strong luminescence emission in the solid state at room temperature whereas **2** shows fluorescence quenching.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 849585–849587. These data can be obtained free of charge *via* 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 336033).

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