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Metal cation- and anion-induced assembly: structures and luminescent properties†

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Three complexes $HgLBr_2$ (**1**), $[HgLI_2]\cdot CH_3CN$ (**2**) and $HgL(SCN)_2$ (**3**) were synthesized by self-assembly of a multidentate ligand containing pyridyl and pyrazolyl groups, namely, 6-phenyl-4-(4-(1*H*-pyrazolyl)phenyl)-2,2′-bipyridine (abbreviated as L), with corresponding mercury(II) salts. While the ligand reacted with $Cd(NCS)_2$ and $Co(NCS)_2$, complexes $[CdL_2(NCS)_2]\cdot H_2O$ (**4**) and $[CoL_2(NCS)_2]\cdot CH_3OH$ (**5**) were obtained. The structures of these complexes were determined by X-ray crystallography. In **1** and **3**, the hydrogen bonding or C–H⋯π interactions based on the anions and the pyrazolyl nitrogen atom contribute to the 2-D and 3-D structures, respectively. Compared with **1** and **3**, no hydrogen bonding interaction based on the I^- anion can be found in **2**. As a result, only the C–H⋯N hydrogen bonding interactions based on the pyrazolyl nitrogen atom link the molecules to form a 1-D structure. In complexes **3–5**, the difference in their structures is attributed to the different metal center ions with diverse coordination modes. The results reveal that the anions and metal ions have great impact on the final structures of the supramolecular architectures. The relationships between the structures and luminescent properties were investigated in detail.

Introduction

Recently, the design and synthesis of organic–inorganic hybrid complexes based on strong coordinate bonds and multiple weak non-covalent forces have become a research field of rapid expansion in coordination chemistry and crystal engineering not only for their fascinating structural features but also for their interesting properties as new functional materials with tremendous potential applications in the areas of luminescence, catalysis, separation, adsorption, biological chemistry, and so on.[1–4] The hybrid materials combine the advantageous properties of inorganic solids with those of organic compounds. So far, a number of complexes with various topologies and special properties have been synthesized and many strategies have been studied and used by researchers.[5] However, rational control in the construction of supramolecular structures of complexes is still a great challenge and much more work is required to understand the assembly process.

The complex assembly process can be affected by many factors, among them, the metal ions, anions and ligands are based-control factors.[6] It is well known that different metal ions possess different properties and coordination modes, which play key roles in the formation of both molecular structures and packing structures of complexes. For example, Hg(II) ion may adopt different coordination modes, such as four-, five- or six-coordination modes according to the specific structures of the different ligands.[7] Cd(II) and Co(II) ions often show six-coordination when they react with organic ligands with N donors.[8] The introduction of different small anions can also have a significant effect on the structural construction of complexes and their properties. In coordination chemistry, halogen and thiocyanate ions have been widely used as anions for the construction of the metal coordination complexes because they can adjust the topologies of complexes through different coordinate bonds or non-covalent interactions.[9]

The organic ligands can control the topology of coordination complexes. The design and synthesis of new organic ligands is a key approach for construction of metal–organic complexes with desired structures and properties. In the past few decades, a lot of new organic ligands with different structures, properties and donor groups have been synthesized and used to construct the coordination complexes. At present, it is still a challenge to synthesize new organic ligands with

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† Electronic supplementary information (ESI) available: Crystal data and refinement, selected bond lengths and angles, *etc.* CCDC 854404 (for complex **1**), 857231 (for complex **2**), 854147 (for complex **3**), 850218 (for complex **4**) and 872923 (for complex **5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce26685k

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special functionality in supramolecular architectures because of the synthetic difficulties involved. In designing coordination complexes, pyridyl and pyrazolyl derivatives have been widely used as ligands due to their ability to coordinate to several metal centers in various modes.[10]

Taking the above into consideration, and in order to construct new coordination complexes with specific structures and properties, a multidentate ligand containing pyridyl and pyrazolyl groups, namely, 6-phenyl-4-(4-(1*H*-pyrazolyl)phenyl)-2,2′-bipyridine (L) has been designed and synthesized.[11] It is a potential multidentate ligand for the construction of novel complexes based on the following considerations. On the one hand, the ligand has different coordination modes with pyrazolyl and pyridyl groups, which may be completely or partially coordinated with metal ions to construct different structural complexes. On the other hand, all the groups of the ligand are linked through single bonds, and they can rotate freely around the single bonds to meet the different geometric requirements of the metal ions and the formation of weak interactions.

In order to evaluate the role of anions and metal ions with different geometric requirements in crystal engineering of organic–inorganic hybridized compounds, reactions of L with various metal salts were carried out. By self-assembly, a series of novel Ag(I), Hg(II) and other metal complexes were synthesized. The Ag(I) complexes with metallomacrocyclic structures have been previously reported.[11] Here, we present the syntheses, structures and luminescent properties of the following complexes $HgLBr_2$ (**1**), $[HgLI_2]\cdot CH_3CN$ (**2**), $HgL(SCN)_2$ (**3**), $[CdL_2(SCN)_2]\cdot H_2O$ (**4**) and $[CoL_2(SCN)_2]\cdot CH_3OH$ (**5**).

Experimental section

General procedure

All commercially available chemicals are of analytical grade and used without further purification. Elemental analyses were carried out on Perkin-Elmer 240 analyzer. IR spectra were recorded from KBr discs in the 4000–40 cm^{-1} range on a nicolet Nexus 870 spectrophotometer. The solid state luminescence spectra were measured on a F-4500 FL spectrophotometer. In the measurements of emission and excitation spectra, the pass width is 2.5 nm for L and complex **4**, and 5 nm for complexes **1**, **2**, **3** and **5**. For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA HuoroMax-4P). The decays were analyzed by least-squares. The quality of the exponential fits was evaluated by the goodness of fit (χ^2).

X-ray crystallography and structure solution

The X-ray diffraction measurements were performed on Bruker SMART CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) at 298 (2) K. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package.[12] Details of the crystal parameters, data collections and refinements are listed in Table S1 (in ESI†), and selected bond distances and angles are given in Table S2 (ESI†).

Synthesis of the complexes

$HgLBr_2$ (1). A methanol solution (25 mL) of $HgBr_2$ (0.360 g, 1 mmol) was added to a dichloromethane solution (15 mL) of L (0.374 g, 1 mmol). The clear mixture solution was allowed to evaporate slowly at room temperature for a few days, and pale yellow, needle-like crystals of **1** suitable for single crystal X-ray diffraction analysis were obtained. Yield: 0.51 g (70%). Anal. calc. for $C_{25}H_{18}HgBr_2N_4$: C, 40.86; H, 2.47; N, 7.62. Found: C, 40.51; H, 2.16; N, 7.90. IR ν(cm^{-1}): 521(m), 642(w), 703(m), 754(m), 773(m), 786(m), 835(s), 934(s), 1013(m), 1044(m), 1123(w), 1201(w), 1243(m), 1337(m), 1393(s), 1440(m), 1482(m), 1527(s), 1546(m), 1603(s).

$[HgLI_2]\cdot CH_3CN$ (2). An acetonitrile solution (15 mL) of HgI_2 (0.454 g, 1 mmol) was added to a dichloromethane solution (15 mL) of L (0.374 g, 1 mmol). The clear mixture solution was allowed to evaporate slowly at room temperature for a few days, and pale yellow, needle-like crystals of **2** suitable for single crystal X-ray diffraction analysis were obtained. Yield: 0.566 g (65%). Anal. calc. for $C_{27}H_{21}HgI_2N_5$: C, 37.28; H, 2.43; N, 8.05. Found: C, 37.51; H, 2.16; N, 8.41. IR ν(cm^{-1}): 520(m), 641(w), 702(m), 737(s), 771(w), 787(m), 834(s), 933(s), 1011(m), 1044(m), 1200(m), 1242(m), 1338(m), 1392(s), 1439(m), 1480(m), 1527(s), 1545(m), 1603(s), 2256(s).

$HgL(SCN)_2$ (3). The reaction was carried out using the same method used for **2**, and the colorless, needle-like crystals of **3** suitable for single crystal X-ray diffraction analysis were obtained. Yield: 0.51 g (70%). Anal. calc. for $C_{27}H_{18}HgN_6S_2$: C, 46.92; H, 2.62; N, 12.16. Found: C, 46.61; H, 2.33; N, 12.39. IR ν(cm^{-1}): 522(m), 641(w), 702(m), 739(m), 770(m), 791(m), 832(s), 894(m), 936(s), 1003(m), 1045(m), 1121(w), 1169(m), 1199(s), 1245(s), 1336(m), 1363(s), 1394(s), 1442(s), 1490(s), 1529(s), 1572(w), 1604(s), 2123(s).

$[CdL_2(NCS)_2]\cdot H_2O$ (4). A clear methanol solution (25 mL) of $Cd(SCN)_2$ (0.229 g, 1 mmol) was carefully layered onto a solution of L (0.748 g, 2 mmol) in dichloromethane (25 mL). Colorless, needle-like crystals suitable for single crystal X-ray diffraction were obtained by slow interlayer diffusion. Yield: 0.606 g (60%). Anal. calc. for $C_{53}H_{40}CdN_{10}OS_2$: C, 63.06; H, 3.99; N, 13.87. Found: C, 63.33; H, 3.62; N, 13.51. IR ν(cm^{-1}): 568(s), 678(s), 745(s), 703(m), 759(s), 801(s), 819(m), 885(w), 949(m), 1005(s), 1029(m), 1057(m), 1119(s), 1170(s), 1219(s), 1329(m), 1399(s), 1441(m), 1479(m), 1526(s), 1547(m), 1604(s), 1663(s), 2078(s), 3107(s).

$[CoL_2(NCS)_2]\cdot CH_3OH$ (5). The reaction was carried out using the same method used for **4**, and the red, block crystals of **5** suitable for single crystal X-ray diffraction analysis were obtained. Yield: 0.525 g (55%). Anal. calc. for $C_{53}H_{40}CoN_{10}OS_2$: C, 66.59; H, 4.22; N, 14.65. Found: C, 66.96; H, 4.58; N, 14.39. IR ν(cm^{-1}): 521(m), 645(w), 702(m), 733(m), 771(m), 791(m), 835(s), 896(m), 933(s), 1001(m), 1041(m), 1126(w), 1168(m), 1195(s), 1245(s), 1333(m), 1363(s),

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1398(s), 1440(s), 1494(s), 1523(s), 1571(w), 1603(s), 2065(s), 3455(s).

Results and discussion

Syntheses and characterization

In order to investigate the effect of different metal ions on the crystal structures, the metal salts with the different metal cations and the same anions, namely, $Hg(SCN)_2$, $Cd(NCS)_2$ and $Co(NCS)_2$ were used. $Hg(SCN)_2$, HgI_2 and $HgBr_2$ were employed in order to study the influence of different anions on the construction of structures. Complexes **1–5** were obtained in methanol or acetonitrile and dichloromethane mixed solvent system by self-assembly of L with different metal salts. In the five complexes, the pyrazolyl group is not directly involved in the coordination, which is different to that in previously reported Ag(I) complexes.[11] However, it can serve as the donor of hydrogen bonding and still play important roles in formation of higher-dimensional structures through C–H···N hydrogen bonding interactions. Furthermore, the mononuclear complexes **1–5** were always obtained when reaction conditions were changed, such as temperature, solvent and the ligand-to-metal ratio. All complexes are air stable and can retain their structural integrity at room temperature for a few months.

In the IR spectra of complexes **3–5**, the intense *v*(CN) stretching bands of NCS^- at 2123, 2078 and 2065 cm^{-1}, respectively, indicate that thiocyanate ions act as terminal N-bonded ligands in **4** and **5**, and intense absorption at 2123 cm^{-1} for **3** corresponds to the terminal S-bonded thiocyanate groups,[9] which agrees with the crystal structures analyses. The strong and broad absorption bands at 3107 and 3455 cm^{-1} in **4** and **5** are assigned to the characteristic peaks of *v*(O–H) stretching vibrations from water and methanol molecules, respectively.

Description of X-ray crystal structures

Structure of $HgLBr_2$ (1). Complex **1** crystallizes in the monoclinic system, space group $P2_1/c$. In the molecular structure, there are two crystallographically and conformationally independent molecules in the asymmetric unit cell, as shown in Fig. 1a. Each Hg(II) ion is coordinated with two terminal bromine ions and two N atoms of pyridyl groups to form distorted tetrahedral geometry. The bond angles around the Hg(1) and Hg(2) ions are in the range of 69.4(3)–134.78(6)

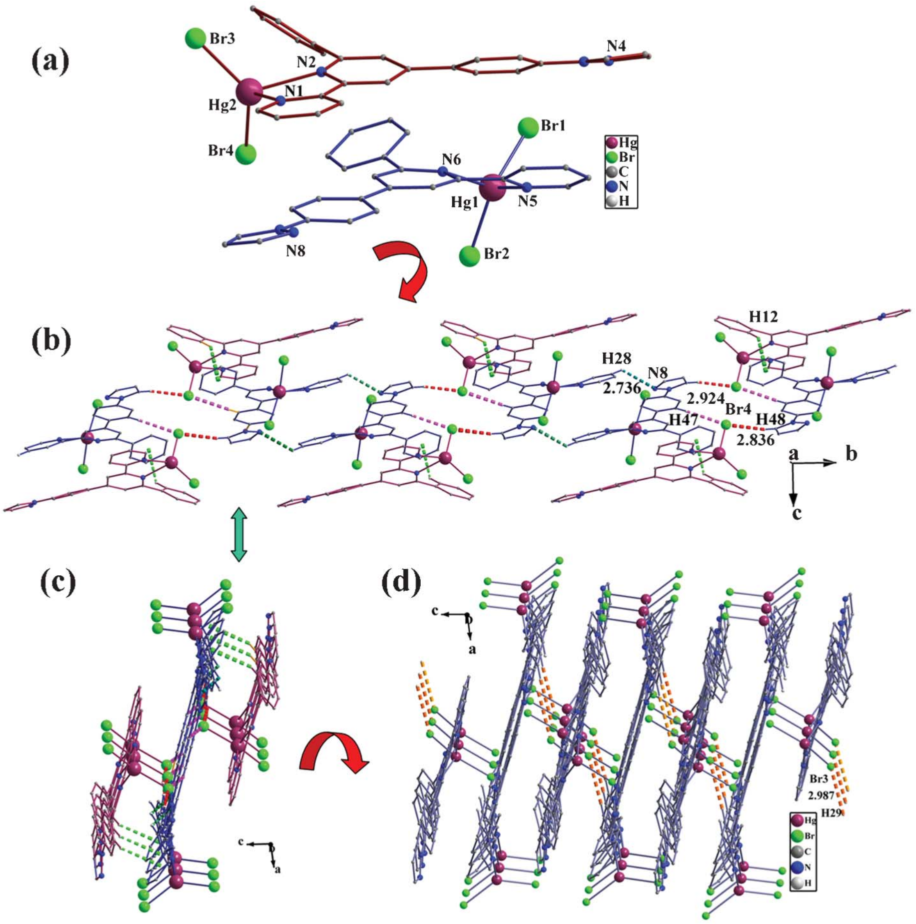

Fig. 1 (a) The structural unit of complex **1**. (b) The one-dimensional structure of complex **1** viewed along the *a*-axis. (c) The one-dimensional structure of complex **1** viewed along the *b*-axis. (d) The two-dimensional structure of complex **1**. Dotted lines represent the weak interactions. Hydrogen atoms are omitted for clarity.

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and 70.2(3)–130.38(5)°, respectively. The selected bond distances and angles are given in Table S2 (ESI†). C(47)–H(47)···Br(4) hydrogen bonding and C(12)–H(12)···π interactions occur between the two independent molecules. The H(47)···Br(4) and H(12)···centroid distances are 2.924 and 2.705 Å, respectively.

As shown in Fig. 1b, the pyrazolyl nitrogen atom of the ligand is not directly involved in coordination, but it plays an important role in the formation of the higher dimensional structures through C–H···N hydrogen bonding interactions. The independent units are linked through C(48)–H(48)···Br(4) and C(28)–H(28)···N(8) hydrogen bonding interactions to generate a chain along the *b*-axis. The H(48)···Br(4) and H(28)···N(8) distances are 2.836 and 2.736 Å, respectively. The C(29)–H(29)···Br(3) hydrogen bonding interactions link the one-dimensional structures to form a two-dimensional structure along the *bc* plane [*d*(H(29)···Br(3) = 2.987 Å], as illustrated in Fig. 1d. In addition, C(41)–H(41)···π and C(23)–H(23)···π interactions with H(41)···centroid and H(23)···centroid distances of 2.804 and 3.913 Å, respectively, provide further stability to the layer structure.

Structure of [$HgLI_2$]·CH_3CN (2). The single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the monoclinic system, space group $P2_1/c$ with one molecule of the complex in the unit cell together with a solvent acetonitrile molecule. Details of the crystal parameters, data collections and refinements are listed in Table S1 (ESI†), and selected bond distances and angles are given in Table S2 (ESI†). As depicted in Fig. 2a, the Hg(II) ion is located in a distorted tetrahedral geometry and coordinated by two terminal iodine ions and two pyridyl nitrogen atoms from the ligand (Hg–N(1) = 2.456(3) Å, Hg–N(2) = 2.364(3) Å, Hg–I(1) = 2.634(1) Å, Hg–I(2) = 2.671(1) Å). The bond angles for Hg are in the range of 68.98(11)–129.59(2)°.

As shown in Fig. 2b, similar to complex **1**, the pyrazolyl nitrogen atom of the ligand is not directly involved in coordination, but it plays an important role in the formation of higher structures through C–H···N hydrogen bonding interactions. The neighboring molecules are linked by intermolecular C(16)–H(16)···N(4) hydrogen bonding interactions into zigzag one-dimensional chains along the *c*-axis. The distances of H(16)···N(4) is 2.615 Å and the C(16)–H(16)···N(4) angle is 149.31°. Every molecule of the complex is connected to an acetonitrile molecule through C(18)–H(18)···N(5) hydrogen bonding interactions [*d*(H(18)···N(5) = 2.686 Å]. It is noted that no H···I hydrogen bonding interaction can be found in complex **2**.

Structure of [$HgL(SCN)_2$] (3). Complex **3** crystallizes in the monoclinic system, space group $P2_1/c$. As shown in Fig. 3a, the Hg(II) ion is coordinated with two S atoms of thiocyanate anions and two N atoms of pyridyl groups. The bond angles around the Hg(II) ion are in the range of 71.10(10)–123.38(9)°. Hg(II) ion, a soft acid, is preferentially coordinated by the soft base (S) terminus of the SCN^- ligand. The thiocyanate anion is coordinated in a bent fashion through the sulfur atom.

The uncoordinated pyrazolyl N atom and SCN^- play key roles in the formation of the higher-dimensional structures. As shown in Fig. 3b, the neighboring molecules are linked in a head-to-tail mode by intermolecular C(1)–H(1)···N(4) hydrogen bonding interactions (the distance of H···O is 2.576 Å, and the C–H···N angle is 163.78°) to form a one-dimensional structure along the *b* axis. In the *bc* plane, the molecules are also interconnected by C(18)–H(18)···N(5) and C(22)–H(22)···N(6) hydrogen bonding interactions (the distances of H(18)···N(5) and H(22)···N(6) are both 2.502 Å, and the C(18)–H(18)···N(5) and C(22)–H(22)···N(6) angles are 165.72 and 157.75°, respectively) to aggregate in a two-dimensional net (Fig. 3c), and the π···π interactions with centroid···centroid distances of 3.634 Å exist in the sheet. The two-dimensional nets further extend

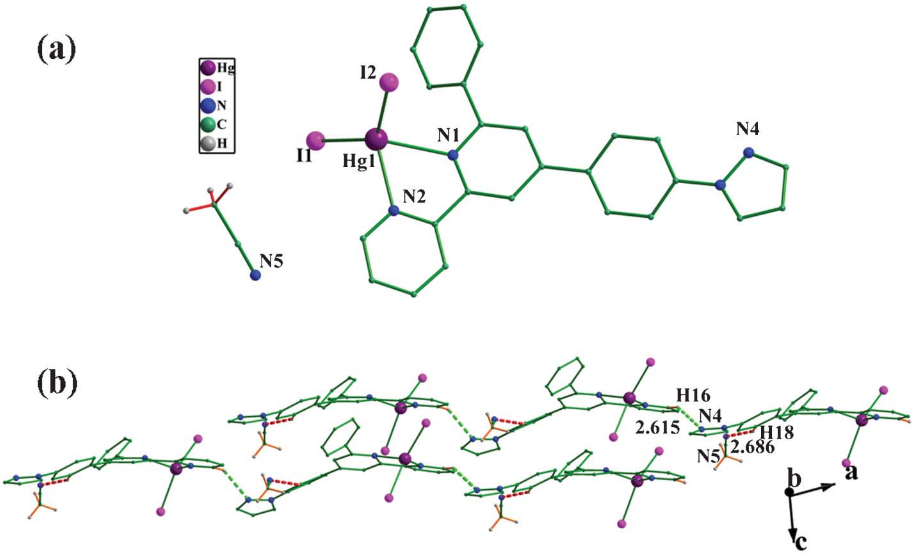

Fig. 2 (a) The structural unit of complex **2**. (b) The one-dimensional structure of complex **2**. Dotted lines represent the weak interactions. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

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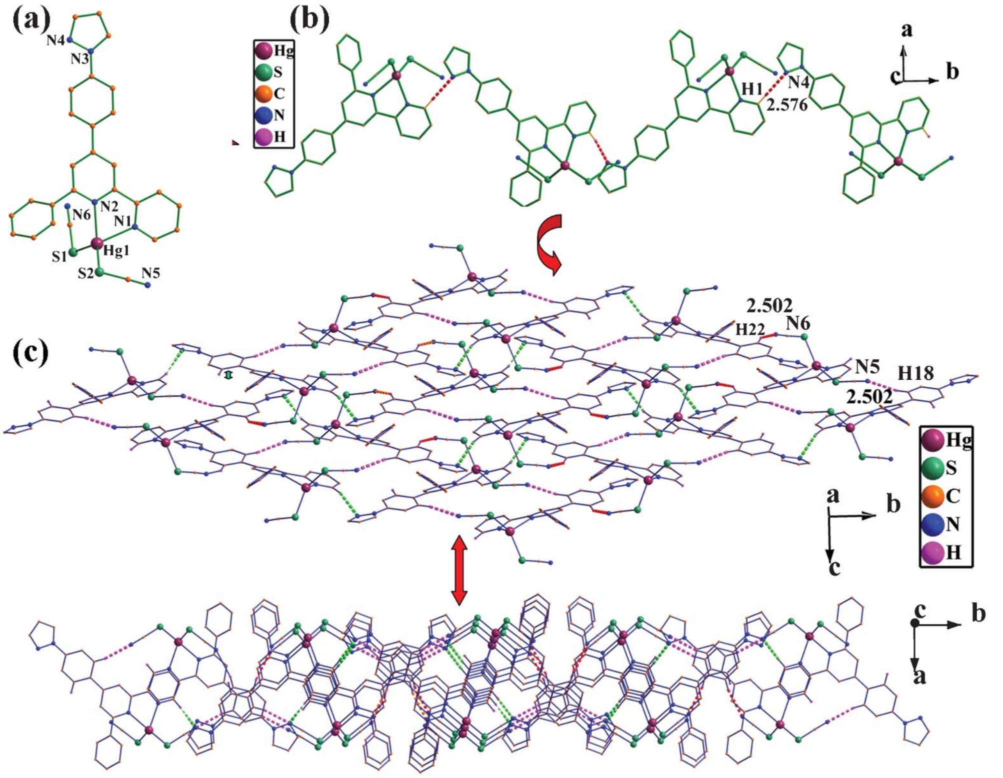

Fig. 3 (a) The structural unit of complex **3**. (b) The one-dimensional structure of complex **3**. (c) The two-dimensional structure of complex **3**. Dotted lines represent the weak interactions. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

into three-dimensional supramolecular structures through C(24)–H(24)···S(1) hydrogen bonding interactions in another direction (the distance of H···S is 2.866 Å, and the C–H···S angle is 163.68°), as shown in Fig. 4.

Structure of $[CdL_2(NCS)_2]\cdot H_2O$ (4). Single-crystal X-ray diffraction analysis reveals that complex **4** crystallizes in the orthorhombic system, space group *Fdd*2 with one molecule of the complex in the unit cell together with a disordered water molecule. As shown in Fig. 5a, the central metal Cd(II) ion is six coordinated by two N atoms from two thiocyanate anions and four pyridyl N atoms from two ligands, to form a distorted octahedral geometry. The bond angles around the Cd(II) ion are in the range of 69.26(9)–170.34(8)°. The selected bond distances and angles are shown in Table S2 (ESI†).

In the molecular packing structure of complex **4**, no C–H···N hydrogen bonding interaction based on the pyrazolyl N atom

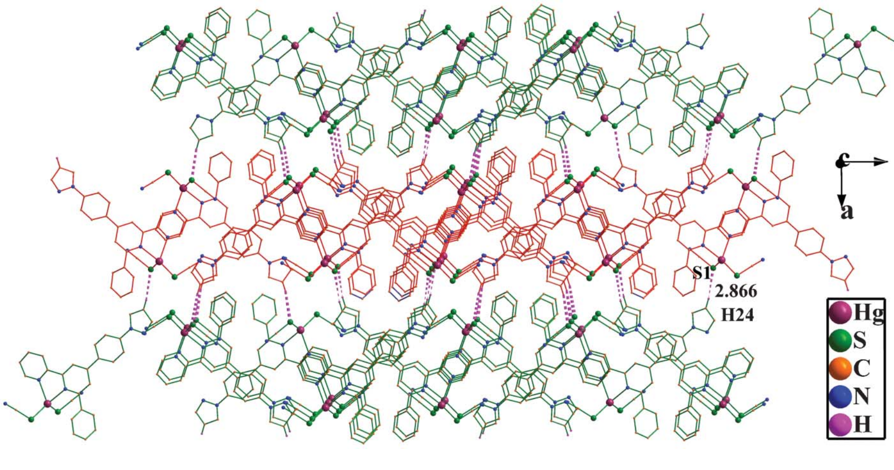

Fig. 4 The three-dimensional structure of complex **3**. Dotted lines represent the weak interactions. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

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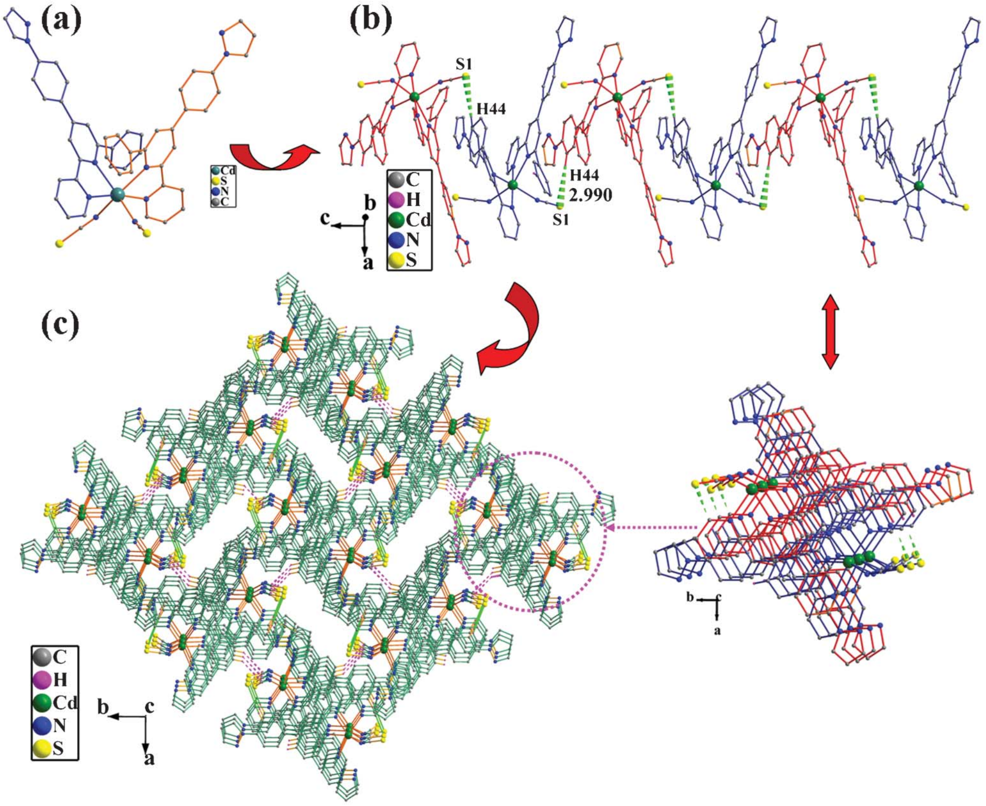

Fig. 5 (a) The structural unit of complex **4**. (b) The one-dimensional chain of complex **4** formed by C–H···S hydrogen bonding interactions. (c) The three-dimensional structure of complex **4**. Dotted lines represent the weak interactions. Hydrogen atoms not participating in hydrogen bonding and water molecules are omitted for clarity.

of the ligand is found, but thiocyanate anions play important roles in forming the higher dimensional structure. As shown in Fig. 5b, two adjacent molecules are linked by C(44)–H(44)···S(1) hydrogen bonding interactions to form a zigzag 1-D chain. The H(44)···S(1) distance is 2.990 Å. The C(13)–H(13)···π interaction based on the thiocyanate anion links the neighboring chains to form a 3-D supramolecular structure, as shown in Fig. 5c. The distance of H(13)···C(52) is 2.776 Å. Further more, the hydrogen bonding interactions based on disordered water molecules also contribute to the formation of the 3-D structure.

Structure of $[CoL_2(NCS)_2]\cdot CH_3OH$ (5). Single-crystal X-ray diffraction analysis reveals that complex **5** crystallizes in the triclinic system, space group $P\bar{1}$ with one molecule of the complex in the unit cell together with a solvent methanol molecule. As shown in Fig. 6a, the central metal Co(II) ion is six coordinated by two N atoms from two thiocyanate anions and four pyridyl N atoms from two ligands, to form a distorted octahedral geometry. The bond angles around the Co(II) ion are in the range of 74.02(7)–177.64(7)°. The selected bond distances and angles are shown in Table S2 (ESI†).

Similar to **4**, no C–H···N hydrogen bonding interaction based on the pyrazolyl N atom of the ligand is formed. However, the multiple C–H···π and π···π interactions play a significant role in the molecular packing of the crystal. As shown in Fig. 6b, two adjacent molecules are linked by the π···π and C(50)–H(50)···π interactions to form a 1-D chain. The centroid-to-centroid and H(50)···centroid distances are 3.703 and 2.836 Å, respectively. The neighboring chains are further linked by π···π interactions (the distance of centroid···centroid is 3.809 Å), giving rise to an extended layer structure, as shown in Fig. 6c. The adjacent layers are stacked through C(19)–H(19)···π and C(44)–H(44)···π interactions to form a 3D supramolecular structure (Fig. 7). The H(19)···centroid and H(44)···centroid distances are 3.840 and 3.614 Å, respectively. In addition, the hydrogen bonding interactions based on methanol molecules provide further stability to the 3D structure.

Structural comparison and effect of anion and metal cation

In complexes **1–3**, the pyrazolyl N atom of the ligand does not directly take part in coordination. However, it can serve as the donor of hydrogen bonding and still play an important role in the formation of higher-dimensional structures through C–H···N hydrogen bonding interactions. Making a comparison, in complexes **1–3**, which have the same four-coordinated metal center Hg(II), the different ions are clearly critical in determining the packing structures of them. It would be interesting and essential to compare the effect of the anions in the Hg(II) complexes. The difference in the coordinating ability, size, geometric shape, symmetry and hydrogen-bonding ability of anions is the underlying reason behind the

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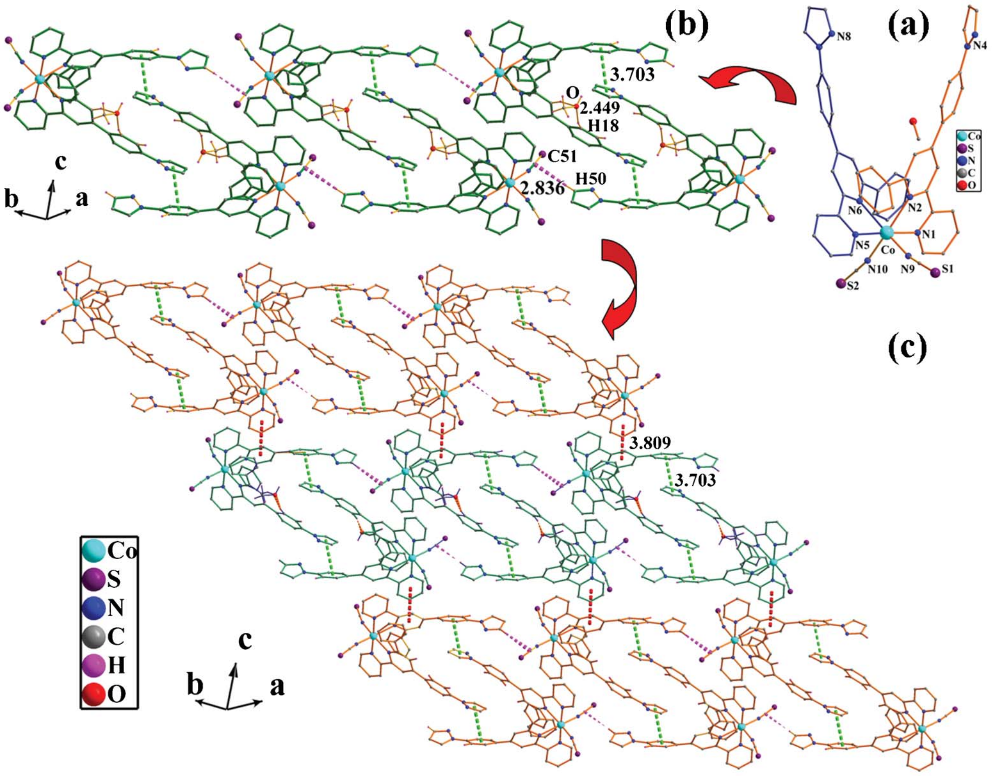

Fig. 6 (a) The structural unit of complex **5**. Hydrogen atoms are omitted. (b) The one-dimensional chain of complex **5**. (c) The two-dimensional structure of complex **5**. Dotted lines represent the weak interactions. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

differences in the structures of complexes.[13] In the present system, anions Br$^-$, I$^-$ and SCN$^-$ all coordinate to Hg(II) centers in a terminal fashion, due to the restriction of the coordination geometry of the mercury ion and the chelating coordination pattern of L as well as the nature of the anions. The absence or different hydrogen bonding interactions based on the anions lead to the formation of the supramolecular structures with different characters in the present series of mercury complexes. In **1** and **3**, the hydrogen bonding or C–H···π interactions based on the anions contribute to the 2-D and 3-D structures, respectively. Compared with **1** and **3**, no hydrogen bonding interactions based on the anion can be found in **2**, which may be attributed to the greater size and smaller electronegativity of the iodide anion.[14] As a result, only the C–H···N hydrogen bonding interactions based on the pyrazolyl nitrogen atom link the molecules to form a 1-D structure.

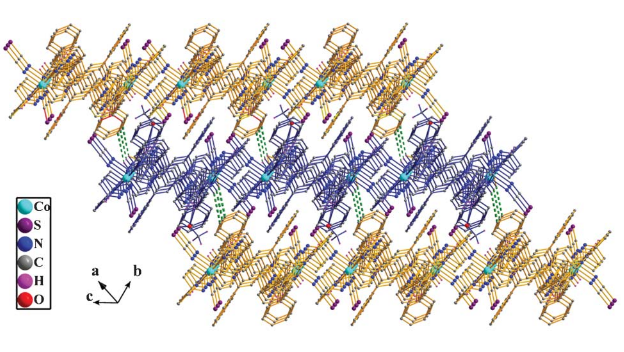

Fig. 7 The three-dimensional structure of complex **5**. Dotted lines represent the weak interactions. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

In complexes **3–5**, which possess the same thiocyanate anion, the different metal center ions determine the structures of the complexes due to the different coordination nature of them. For the Hg(II) complex, anion SCN$^-$ coordinates to the metal ion in terminal η^1-S mode. However, anion SCN$^-$ ligates to Cd(II) and Co(II) ions in terminal η^1-N fashion. The Cd(II) and Co(II) ions both adopt the distorted N$_6$-coordination geometry. It is notable that no C–H···N hydrogen bonding interactions based on the pyrazolyl N atom of the ligand are formed in complexes **4** and **5**. However, because two ligands are involved in coordination, there are more chances to form C–H···π and π···π interactions between the ligands, which play significant roles in constructing the three-dimensional structures. All in all, the different structures of complexes **1–3** reveal that the anions have an effect on the higher-dimensional architectures of the complexes, and the different structures of complexes **3–5** indicate that the central metal ions determine the molecular structure and the crystal packing of complexes.

Compared with the free L, the ligands in complex **1**, **2**, **3** and **5** have the larger twist angles between the pyrazolyl ring and the near-by benzene ring plane (Table S3, ESI†), which may be attributed to the larger number of weak interactions in the complexes. However, in complex **4**, one ligand has better

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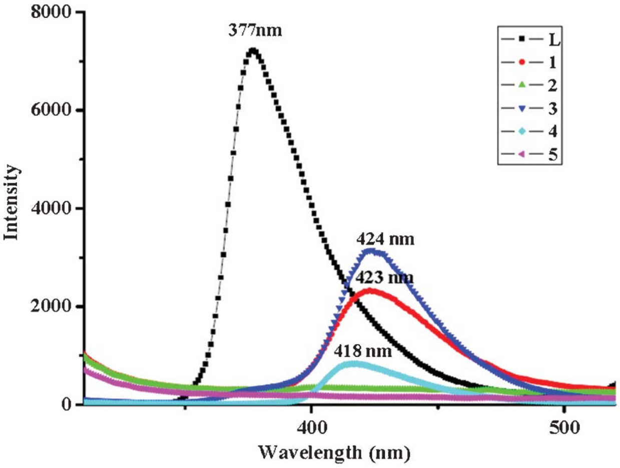

Fig. 8 Solid-state emission spectra of L and complexes **1–5** at room temperature. In the measurements of emission and excitation spectra, the pass width is 2.5 nm for L and complex **4**, and 5 nm for complexes **1**, **2**, **3** and **5**.

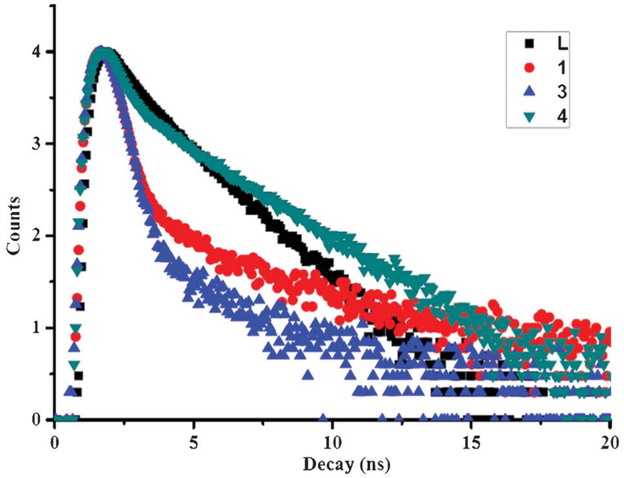

Fig. 9 Time-resolved fluorescence curves of L and complexes **1**, **3** and **4** in the solid state at room temperature.

planarity than the free ligand, which would have significant influences on the solid state emission properties of the crystal.

Luminescent properties

Coordination complexes with d^{10} metal atoms show fluorescence properties and are promising candidates for photoactive materials with potential applications.[15] For potential applications as luminescent materials, the luminescent properties of ligands and complexes have been investigated in the solid state at room temperature.

The compounds are excited at the excitation wavelength of 290 nm. In the measurements of emission and excitation spectra, the pass width is 2.5 nm for L and complex **4**, and 5 nm for complexes **1**, **2**, **3** and **5**. No clear photoluminescence was observed for complexes **2** and **5**. The luminescence emissions are probably quenched by the iodine and Co(II) ions, respectively.[15] Fig. 8 presents the comparison of the emission spectra of free ligand and complexes **1**, **3** and **4**. The free ligand exhibits an emission maximum at 376 nm, which is assigned to the π–π* transition. In contrast to the free ligand, complexes **1**, **3** and **4** exhibit broader fluorescent emission band maxima at 419, 424 and 418 nm, respectively, which may be assigned to the intraligand π–π* transitions because of the resemblance of the emission spectra in comparison with the free ligand. The red shifts may be attributed to the coordination of ligand to the metal centers.[16] Compared to free ligand, all these complexes exhibited relatively weaker emissions, which may be a result of the heavy-atom effect of the metal central ions. The emission intensity of complexes **4** is relatively stronger than those of **1** and **3**, and the possible explanation is the better planarity of L in complex **4** (Table S3, ESI†) and the heavy-atom effect of Hg(II) ion in **1** and **3**.

The fluorescence decay profiles of L and complexes **1**, **3** and **4** were measured at their optimal excitation wavelengths in the solid state at room temperature. The results are shown in Fig. 9. The fluorescence lifetimes of complexes **1** (0.10 ns) and **3** (0.13 ns) are shorter than that of L (0.16 ns), which may be a result of the heavy-atom effect of the Hg(II) ion.[17] The fluorescence lifetime of complex **4** is 0.33 ns, which was a remarkable increase compared with that of L, which may be derived from the better planarity of L in complex **4** and the supramolecular structures in the solid state complex.[13d,18]

Conclusions

A series of complexes have been synthesized by self-assembly. In **1–3**, the different anions result in different weak intermolecular interactions, which are responsible for the crystal packing of the different complexes. However, in **3–5**, the different weak non-covalent forces are generated because of the different coordination modes of Hg, Cd and Co ions. Complexes **1**, **3** and **4** all show fluorescence emissions which are likely to originate from the intraligand π–π* transitions with red shifts and decreased intensity compared to the free ligand. The results indicate that both anions and metal center ions have a marked influence on the final structures and fluorescence properties of the complexes. Obviously, the rational choice of the anions and the metal centers may be an effective way to construct novel coordination complexes with desired structures and properties.

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Notes and references

1 (*a*) L. Sun, G. Z. Li, M. H. Xu, X. J. Li, J. R. Li and H. Deng, *Eur. J. Inorg. Chem.*, 2012, 1764; (*b*) S. M. Humphrey and P. T. Wood, *J. Am. Chem. Soc.*, 2004, **126**, 13236; (*c*) A. Galet, A. B. Gaspar, G. Agusti, M. C. Munoz, G. Levchenko and J. A. Real, *Eur. J. Inorg. Chem.*, 2006, 3571; (*d*) P. D. Harvey and D. Fortin, *Coord. Chem. Rev.*, 1998, **171**, 351; (*e*) L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, *Coord. Chem. Rev.*, 2000, **205**, 59; (*f*) K. J. Franz, N. S. Bernhard, B. Spingler and S. J. Lippard, *Inorg. Chem.*, 2000, **39**, 4081; (*g*) P. S. Weiss, *J. Am. Chem. Soc.*, 2010, **132**, 10954.

2 (*a*) M. J. Vitorino, T. Devic, M. Tromp, G. Ferey and M. Visseaux, *Macromol. Chem. Phys.*, 2009, **210**, 1923; (*b*) S. Haneda, Z. B. Gan, K. Eda and M. Hayashi, *Organometallics*, 2007, **26**, 6551; (*c*) K. Yu, B. B. Zhou, Y. Yu, Z. H. Su and G. Y. Yang, *Inorg. Chem.*, 2011, **50**(5), 1862; (*d*) A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009; (*e*) Y. Y. Li, C. K. Lin, G. L. Zheng, Z. Y. Cheng, H. You, W. D. Wang and J. Lin, *Chem. Mater.*, 2006, **18**, 3463.

3 (*a*) Q. K. Liu, J. P. Ma and Y. B. Dong, *J. Am. Chem. Soc.*, 2010, **132**, 7005; (*b*) Q. K. Liu, J. P. Ma and Y. B. Dong, *Chem. Commun.*, 2011, **47**, 12343; (*c*) L. Duan, Z. H. Wu, J. P. Ma, X. W. Wu and Y. B. Dong, *Inorg. Chem.*, 2010, **49**, 11164; (*d*) C. M. Liu, D. Q. Zhang, X. Hao and D. B. Zhu, *Eur. J. Inorg. Chem.*, 2012, 4210.

4 (*a*) C. M. Aikens, S. Z. Li and G. C. Schatz, *J. Phys. Chem. C*, 2008, **112**, 11272; (*b*) R. Satapathy, Y. H. Wu and H. C. Lin, *Org. Lett.*, 2012, **14**, 2564; (*c*) P. J. Stang, *J. Am. Chem. Soc.*, 2012, **134**, 11829; (*d*) C. B. Tian, H. B. Zhang, Y. Peng, Y. E. Xie, P. Lin, Z. H. Li and S. W. Du, *Eur. J. Inorg. Chem.*, 2012, 4029.

5 (*a*) B. Li, S. Q. Zhang, C. Ji, H. W. Hou and T. C. W. Mak, *Cryst. Growth Des.*, 2012, **12**, 1443; (*b*) D. G. Ding, B. L. Wu, Y. T. Fan and H. W. Hou, *Cryst. Growth Des.*, 2009, **9**, 508; (*c*) Z. P. Deng, L. N. Zhu, S. Gao and L. H. Huo, *Cryst. Growth Des.*, 2008, **8**, 3277; (*d*) Z. P. Deng, L. H. Huo, M. S. Li, L. W. Zhang, Z. B. Zhu, H. Zhao and S. Gao, *Cryst. Growth Des.*, 2011, **11**, 3090; (*e*) H. P. Zhou, F. X. Zhou, P. Wu, Z. Zheng, Z. P. Yu, Y. X. Chen, Y. L. Tu, L. Kong, J. Y. Wu and Y. P. Tian, *Dyes Pigm.*, 2011, **91**, 237.

6 (*a*) I. Bassanetti, F. Mezzadri, A. Comotti, P. Sozzani, M. Gennari, G. Calestani and L. Marchiò, *J. Am. Chem. Soc.*, 2012, **134**, 9142; (*b*) L. S. Song, H. M. Wang, Y. Y. Niu, H. W. Hou and Y. Zhu, *CrystEngComm*, 2012, **14**, 4927; (*c*) J. L. Gulbransen and C. M. Fitchett, *CrystEngComm*, 2012, **14**, 5394; (*d*) X. H. Yan, Z. Z. Yan, Y. Zhang, W. S. Liu, Y. Tang and M. Y. Tan, *CrystEngComm*, 2012, **14**, 4989.

7 (*a*) H. P. Zhou, J. H. Yin, L. X. Zheng, P. Wang, F. Y. Hao, W. Q. Geng, X. P. Gan, G. Y. Xu, J. Y. Wu, Y. P. Tian, X. T. Tao, M. H. Jiang and Y. H. Kan, *Cryst. Growth Des.*, 2009, **9**, 3789; (*b*) H. P. Zhou, P. Wang, L. X. Zheng, W. Q. Geng, J. H. Yin, X. P. Gan, G. Y. Xu, J. Y. Wu, Y. P. Tian, X. T. Tao and M. H. Jiang, *J. Phys. Chem. A*, 2009, **113**, 2584; (*c*) H. P. Zhou, X. P. Gan, X. L. Li, Z. D. Liu, W. Q. Geng, F. X. Zhou, W. Z. Ke, P. Wang, L. Kong, F. Y. Hao, J. Y. Wu and Y. P. Tian, *Cryst. Growth Des.*, 2010, **10**, 1767.

8 (*a*) H. F. Zhu, W. Zhao, T. Okamura, J. Fan, W. Y. Sun and N. Ueyamab, *New J. Chem.*, 2004, **28**, 1010; (*b*) W. Y. Sun, L. Zhang and K. B. Yu, *J. Chem. Soc., Dalton Trans.*, 1999, 795; (*c*) X. M. Ouyang, B. L. Fei, T. Okamura, H. W. Bu, W. Y. Sun, W. X. Tang and N. Ueyama, *Eur. J. Inorg. Chem.*, 2003, 618.

9 (*a*) B. Machura, I. Nawrot and K. Michalik, *Polyhedron*, 2011, **30**, 2619; (*b*) X. M. Zhang, Z. M. Hao and H. S. Wu, *Inorg. Chem.*, 2005, **44**, 7301; (*c*) Q. Ma, M. L. Zhu, C. X. Yuan, S. S. Feng, L. P. Lu and Q. M. Wang, *Cryst. Growth Des.*, 2010, **10**, 1706; (*d*) M. Du, S. T. Chen and X. H. Bu, *Cryst. Growth Des.*, 2002, **2**, 625.

10 (*a*) K. Matsumoto, Y. Harada, N. Yamada, H. Kurata, T. Kawase and M. Oda, *Cryst. Growth Des.*, 2006, **6**, 1083; (*b*) Y. B. Xie, J. R. Li, C. Zhang and X. H. Bu, *Cryst. Growth Des.*, 2005, **5**, 1743; (*c*) D. L. Reger, R. P. Watson, J. R. Gardinier and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 6609.

11 F. Jin, X. F. Yang, S. L. Li, Z. Zheng, Z. P. Yu, L. Kong, F. Y. Hao, J. X. Yang, J. Y. Wu, Y. P. Tian and H. P. Zhou, *CrystEngComm*, 2012, **14**, 8409.

12 G. M. Sheldrick, *SHELXTL V5.1 Software Reference Manual*, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.

13 (*a*) C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim and H. C. Loye, *J. Am. Chem. Soc.*, 2003, **125**, 8595; (*b*) Z. G. Gu, Y. T. Liu, X. J. Hong, Q. G. Zhang, Z. P. Zheng, S. R. Zheng, W. S. Li, S. J. Hui and Y. P. Cai, *Cryst. Growth Des.*, 2012, **12**, 2178; (*c*) Y. P. Cai, C. Y. Su, H. X. Zhang, Z. Y. Zhou, L. X. Zhu, A. S. C. Chan, H. Q. Liu and B. S. Kang, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2321; (*d*) X. X. Zhou, H. H. Cai, Y. Y. Ge, Z. Y. Zhou, Z. G. Gu, X. Gong, G. Zhao, Q. G. Zhang, R. H. Zeng and Y. P. Cai, *Cryst. Growth Des.*, 2010, **10**, 4014; (*e*) S. Wang, L. R. Zhang, G. H. Li, Q. S. Hou and Y. L. Liu, *CrystEngComm*, 2008, **10**, 1662–1666; (*f*) J. B. Lin, J. P. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2010, **132**, 6654; (*g*) A. Bacchi, E. Bosetti, M. Carcelli, P. Pelagatti and D. Rogolino, *CrystEngComm*, 2004, **6**, 177; (*h*) R. Custelcean, *Chem. Soc. Rev.*, 2010, **39**, 3675.

14 Y. F. Hsu, W. Hsu, C. J. Wu, P. C. Cheng, C. W. Yeh, W. J. Chang, J. D. Chen and J. C. Wang, *CrystEngComm*, 2010, **12**, 702–710.

15 (*a*) J. E. McGarrah, Y. J. Kim, M. Hissler and R. Eisenberg, *Inorg. Chem.*, 2001, **40**, 4510; (*b*) G. D. Santis, L. Fabbrizzi, M. Licchelli, A. Poggi and A. Taglietti, *Angew. Chem., Int. Ed.*, 1996, **35**, 202; (*c*) J. J. Jiang, C. Yan, M. Pan, Z. Wang, H. Y. Deng, J. R. He, Q. Y. Yang, L. Fu, X. F. Xu and C. Y. Su, *Eur. J. Inorg. Chem.*, 2012, 1171.

16 G. B. Li, J. M. Liu, Y. P. Cai and C. Y. Su, *Cryst. Growth Des.*, 2011, **11**, 2763.

17 N. Kundu, A. Audhya, S. M. T. Abtab, S. Ghosh, E. R. T. Tiekink and M. Chaudhury, *Cryst. Growth Des.*, 2010, **10**, 1269.

18 (*a*) J. G. Xu and Z. B. Wang, *Analytical Methods*, Chinese Science Publishing Company, Beijing, 3rd edn, 2006, p. 58; (*b*) H. S. Cho, H. Rhee, J. K. Song, C. K. Min, M. Takase, N. Aratani, S. Cho, A. Osuka, T. Joo and D. Kim, *J. Am. Chem. Soc.*, 2003, **125**, 5849; (*c*) M. Royzen, A. Durandin, V. G. Young Jr., N. E. Geacintov and J. W. Canary, *J. Am. Chem. Soc.*, 2006, **128**, 3854; (*d*) H. C. Wu, P. Thanasekaran, C. H. Tsai, J. Y. Wu, S. M. Huang, Y. S. Wen and K. l. Lu, *Inorg. Chem.*, 2006, **45**, 295.