Novel Layered Organic–Inorganic Networks Assembled From PbI_2 and *N*,*N*′-bis(3-pyridylmethyl)-1,4-biphenylenedimethyleneimine

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Two novel metal-organic frameworks with different structures were obtained by reactions of PbI_2 with *N*,*N*′-bis(3-pyridylmethyl)-1,4-biphenylenedimethyleneimine (L) under different M/L ratios. When the M/L ratio is 1:1, L bridges $[PbI_2]_n$ chains to form a layered organic–inorganic hybrid compound with the empirical formula $[Pb(L)I_2]$ (**1**). When changing the M/L ratio to 2:1, L bridges the double chains $[Pb_2I_4]_n$ to form networks $[Pb_2(L)I_4]$ (**2**), which are further linked by C–H···I hydrogen bonds to give a 3D structure.

The rational design and construction of metal–organic frameworks (MOFs) with fascinating structure continues attracting interests in current supramolecular chemistry.[1–3] Furthermore, another motivation lies in the potential properties of the MOFs such as magnetism, spectroscopy, catalysis, and nonlinear optical activity.[4–6] Design of the ligands and selecting the metal centers are crucial in the construction of such MOFs. While the formation of the structure is also affected by other factors like the counter ions, the solvent system, and the ratio between metal salt and ligand.[7,8] So far, extensive studies have been carried out to give many novel one- (1D), two- (2D), and three-dimensional (3D) frameworks based on the assembly of metal salts with rigid *N*,*N*′-donor ligand, such as 4,4′-bipyridine and its derivatives like 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethylene, 1,3-bis(4-pyridyl)propane.[2,9] On the other hand, lead(II) complexes have been extensively studied due to their structural diversities and attractive optical properties such as photoluminescence and nonlinear optical effects.[6,10] Here we report two novel PbI_2-based organic–inorganic hybrid networks $[Pb(L)I_2]$ (**1**), $[Pb_2(L)I_4]$ (**2**) from the reactions of ligand *N*,*N*′-bis(3-pyridylmethyl)-1,4-biphenylenedimethyleneimine (L) with PbI_2 in DMF at different M/L ratios of 1:1 and 2:1, and we also studied their luminescent properties.

Ligand L was prepared by the similar method reported previously.[11] Complex $[Pb(L)I_2]$ (**1**) was prepared by slow diffusion of diethyl ether into a solution of L and PbI_2 in DMF. The single-crystal X-ray analyses revealed that the complex **1** crystallizes in space group $P\bar{1}$.[12] The coordination environment of Pb(II) is shown in Figure 1. Each Pb(II) is six-coordinated by four doubly bridged iodine atoms and two nitrogen atoms from two different ligands L in the *trans* fashion (N111–Pb–N111 = 180°), with the bond distances of Pb–I, 3.259(2)–3.263(2) Å and Pb–N, 2.672(6) Å, respectively. The lead atom has a slight distorted octahedral geometry with the coordination angles varying from 87.65(16) to 180°. It is noteworthy that each ligand serves as bridging one with its terminal pyridyl N atoms while its imine N atoms are free of coordination to the metal atoms. And the ligands L adopt a zigzag conformation. Thus the inorganic $[PbI_2]_n$ chains are linked by the ligands to form inorganic–organic layered structure (Figure 1), which is similar to the reported $[PbI_2(4,4'\text{-bipy})]$ (bipy = bipyridine).[13] When the crystal packing is viewed along the *a* axis, a zigzag layered structure was obtained. The centroid–centroid distance between the parallel benzene ring and pyridine ring of two adjacent layers is 4.77 Å, indicating no interlayer π–π interactions.

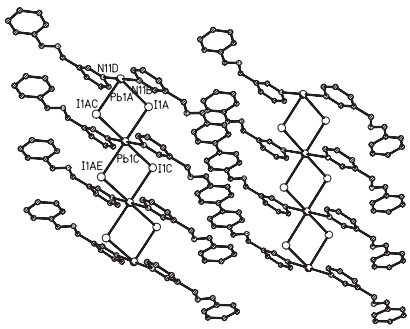
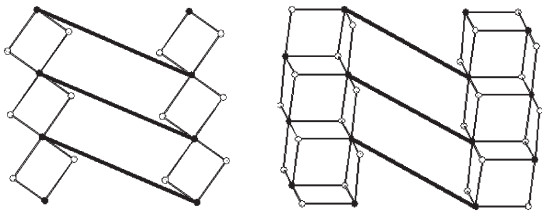


Figure 1. The layered structure of complex **1** viewed along the *b* axis, hydrogen atoms were omitted for clarity.

In order to investigate the effect of M/L ratio on the formation of the structure, a different coordination polymer $[Pb_2(L)I_4]$ (**2**) was prepared by changing the ratio of metal to ligand to 2:1 by the same method used for the preparation of **1**.[14] There are two types of iodine atoms in complex **2** defined by their connectivity to Pb: double and triple bridged (Figure 2a). From the simplified structure of complexes **1** and **2** (Scheme 1), it can be found that the bond Pb–I (triple bridged) makes the inorganic single chain $[PbI_2]_n$ to be unique double chains $[Pb_2I_4]$ that run along the *a* axis in the complex **2**. Similar chain structure was found in the complex $[C_6H_{10}N_2]Pb_2I_6 \cdot 3thf$.[15] To the best of our knowledge, such double chains structure is not well known. Structural analysis reveals that each Pb atom in complex **2** was also six-coordinated by one N atom from the ligand, two double bridged iodine atoms, and three triple bridged ones. The bond lengths of Pb–I (triple bridged) are 3.189(2), 3.375(2), 3.411(2) Å, and the distances of Pb–I (double bridged) are different also, with 3.125(2), 3.255(2) Å, which were slightly longer than that in complex $[C_6H_{10}N_2]Pb_2I_6 \cdot 3thf$[15] (3.178, 3.154 Å) and shorter than those in complex **1**. The Pb–N bond length is 2.572(7) Å, which is in the range of strong Pb–N bonds (2.40–2.60 Å) but shorter than that in complex **1** (2.672(6) Å) and in $[PbI_2(4,4'\text{-bipy})]_n$ (2.658 Å).[13] The coordination geometry of the Pb(II) center can be described as a little distorted octahedron with the I–Pb–I, I–Pb–N angles of diagonal were nearly linear (174.4–178.6°). And then the Pb–I–Pb angles are almost upright, ranging from 85.85(4) to 93.18(4)°, to result in stair-like layers

formed by $[Pb_2I_4N_2]_n$ double chains. The ligand L also serves as bidentate bridging ligand using its two terminal pyridyl N atoms and adopts the same conformations as that in complex **1**. The centroid–centroid distance between the parallel benzene rings and pyridine rings of two adjacent layers was 4.62 Å, which is similar to that in **1**. Interestingly, the networks of **2** were further linked by weak C–H···I interactions between methylene C(18)–H(7) from one layer and double bridged I(2) atom from adjacent layer to give a 3D framework (Figure 2b). It has been reported that any H···I contact less than 3.35 Å and C–H···I angle $>130^\circ$ may be considered significant.[16] In complex **2**, the distance of H···I is 3.12 Å and the C–H···I angle is 149°, which indicate the formation of C–H···I hydrogen bonds. The importance of such C–H···I interactions in supramolecular self-assembly has also been reported recently.[16,17]



Scheme 1. The simplified structure of complexes **1** and **2**. The Pb(II) centers and I atoms are represented by solid and open balls, respectively and the bold lines denote the ligands.

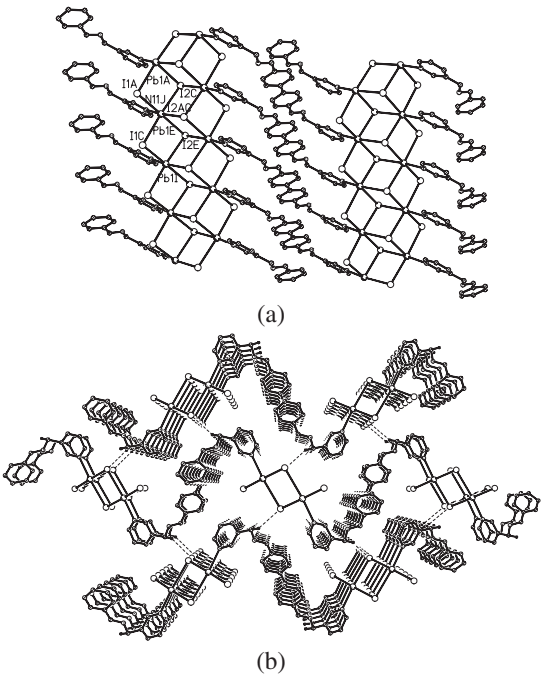


Figure 2. (a) The structure of complex **2** (hydrogen atoms were omitted for clarity); (b) Crystal packing of **2** along the *a* axis, with C–H···I hydrogen bonds shown in dashed lines.

The UV–vis spectra of complexes **1**, **2** in DMF solution show that there is only one absorption peak at 306 nm for **1** and 297 nm for **2**, which could be assigned to the π–π^* transitions of the ligand. It has been reported that PbX_2 (X = Cl, Br, I) complexes with 2,2′-bipyridine and 4,4′-bipyridine, 1,10-phenanthroline showed photoluminescence in the solid state.[13,18] We investigated the fluorescence of these two complexes in the solid state at room temperature. The complexes exhibit emissions at 534 nm for **1** and 537 nm for **2** when the powder samples were excited at 468 nm which were similar to the reported result 530 nm of $[PbI_2(4,4'\text{-bipyridine})]$. Compared with the free ligand L (emission maximum at 450 nm), **1** and **2** exhibit red-shifted emissions of 84 and 87 nm, respectively under the experimental conditions. Thus, the emissions of the complexes may be assigned to charge-transfer luminescence due to the existence of lone pair electrons of lead(II).[10,18]

In conclusion, two novel organic–inorganic hybrid networks were obtained from the assembly of flexible bidentate ligand L with PbI_2 in DMF at different M/L ratios of 1:1 and 2:1. The structural differences indicate that the M/L ratios exert a great impact on the self-assembly process.

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References and Notes

1 S. Kitagawa, R. Kitaura, and S. Noro, *Angew. Chem., Int. Ed.*, **43**, 2334 (2004).
2 C. Janiak, *J. Chem. Soc., Dalton Trans.*, **2003**, 2781.
3 S. L. James, *Chem. Soc. Rev.*, **32**, 276 (2003).
4 S. Takamizawa, E. Nakata, H. Yokoyama, K. Mochizuki, and K. Mori, *Angew. Chem., Int. Ed.*, **42**, 4331 (2003).
5 a) X. H. Bu, M. L. Tong, H. C. Chang, S. Kitagawa, and S. R. Batten, *Angew. Chem., Int. Ed.*, **43**, 192 (2004); b) M. Du, X. H. Bu, Y. M. Guo, and J. Ribas, *Chem.—Eur. J.*, **10**, 1345 (2004).
6 B. Sui, W. Zhao, G. H. Ma, T.-a. Okamura, J. Fan, Y. Z. Li, S. H. Tang, W. Y. Sun, and N. Ueyama, *J. Mater. Chem.*, **14**, 1631 (2004).
7 M. Kondo, Y. Irie, Y. Shimizu, M. Miyazawa, H. Kawaguchi, A. Nakamura, T. Naito, K. Maeda, and F. Uchida, *Inorg. Chem.*, **43**, 6139 (2004).
8 L. Carlucci, G. Ciani, D. W. v. Gudenberg, D. M. Proserpio, and A. Sironi, *Chem. Commun.*, **1997**, 631.
9 L. J. Twyman and A. S. H. King, *Chem. Commun.*, **2002**, 910.
10 S. K. Dutta and M. W. Perkovic, *Inorg. Chem.*, **41**, 6938 (2002).
11 H. F. Zhu, L. Li, T.-a. Okamura, W. Zhao, W. Y. Sun, and N. Ueyama, *Bull. Chem. Soc. Jpn.*, **76**, 761 (2003).
12 The data collection for **1** and **2** were carried on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å), T = 200 K. The structures were solved by direct methods with SIR92. All non-hydrogen atoms were refined anisotropically by the full-matrix least-square method. The hydrogen atoms were generated geometrically. Crystal data for **1**: $C_{26}H_{22}I_2N_4Pb$, Triclinic, $P\bar{1}$, $M = 851.47$, $a = 4.773(2)$, $b = 9.252(5)$, $c = 14.451(9)$ Å, $\alpha = 83.08(4)$, $\beta = 80.74(5)$, $\gamma = 89.47(6)^\circ$, $V = 625.2(6)$ Å^3, $Z = 1$, $D_{calcd} = 2.262$ g cm^{-3}, $\mu = 9.237$ mm^{-1}, Total 6302 reflections were collected of which 2853 are independent ($R_{int} = 0.0710$). The final $R_1 = 0.0350$ [$I > 2\sigma(I)$] CCDC 25389.
13 Y. J. Shi, Y. Xu, Y. Zhang, B. Huang, D. R. Zhu, C. M. Jin, H. G. Zhu, Z. Yu, X. T. Chen, and X. Z. You, *Chem. Lett.*, **2001**, 678.
14 Crystal data for **2**: $C_{26}H_{22}I_4N_4Pb_2$, Monoclinic, $P2_1n$, $M = 1312.46$, $a = 4.623(4)$, $b = 18.335(13)$, $c = 18.090(11)$ Å, $\beta = 80.74(5)^\circ$, $V = 1533.4(19)$ Å^3, $Z = 2$, $D_{calcd} = 2.842$ g cm^{-3}, $\mu = 15.014$ mm^{-1}, Total 14677 reflections were collected of which 3483 are independent ($R_{int} = 0.0725$). The final $R_1 = 0.0329$ [$I > 2\sigma(I)$] CCDC 252390.
15 V. Chakravarthy and A. Guloy, *Chem. Commun.*, **1997**, 697.
16 C. J. Horn, A. J. Blake, N. R. Champness, A. Garau, V. Lippolis, C. Wilson, and M. Schröder, *Chem. Commun.*, **2003**, 312.
17 G. Barberà, C. Viñas, F. Teixidor, G. M. Rosair, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, **2002**, 3647.
18 H. G. Zhu, Y. Xu, Q. J. Wu, H. K. Fun, and X. Z. You, *Polyhedron*, **18**, 3491 (1999).

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