Two Unprecedented Three–Dimensional PbII Polymorphs and Structural Diversities Built on a Kinked Flexible Dicarboxylate Building Block

6 **AUTHORS**, INCLUDING:

Stuart R. Batten

Monash University (Australia)

311 PUBLICATIONS **14,514** CITATIONS

Two Unprecedented Three-Dimensional Pb^{II} Polymorphs and Structural Diversities Built on a Kinked Flexible Dicarboxylate Building Block

Guo-Ping Yang,[†] Lei Hou,[†] Yao-Yu Wang,*,[†] Ya-Nan Zhang,[†] Qi-Zhen Shi,[†] and Stuart R. Batten*,[‡]

[†]Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education,
 Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University,
 Xi'an 710069, Shaanxi, P. R. China
[‡]School of Chemistry, Monash University, Victoria, 3800, Australia

S *Supporting Information*

ABSTRACT: Two unprecedented three-dimensional (3D) true coordination polymorphs, namely, $[Pb_2(phda)_2(H_2O)]_n \cdot 2nH_2O$ (**1a**, and **1b**) (H_2phda = 1,4-phenylenediacetate acid), which show distinct novel topological networks, have been successfully prepared by utilizing a kinked flexible H_2phda. This work shows the first example of two different isomers reported for a flexible ligand acting as a bridge.
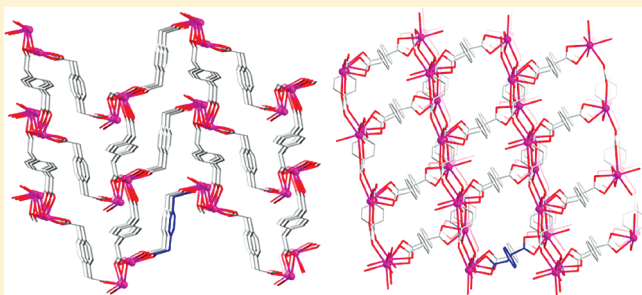
The current attention in metal−organic frameworks (MOFs) is rapidly expanding because of their potential applications as materials,[1] as well as their variety of intriguing architectural features and fascinating topologies.[2] A topological approach represents an important achievement in crystal chemistry and is an effective means to design and analyze crystal structures and materials. Thus far, network topology has become an extremely active subject of several related studies.[3] Now, a variety of topological types have been realized in three-dimensional (3D) MOFs, such as *pcu, dia, srs, cds, rtl*, etc.[4] However, there is an unfavorable lack of research about the higher-dimensional networks with the mixed nodes,[3c,d] for instance, (3,6)-, (4,6)-, and (4,8)-connected frameworks,[5] which are considered to be much more difficult to isolate. Therefore, the construction of new or unusual topological networks involving these nodes is of great interest and worth further exploration at the current stage.

Supramolecular isomerism, as first proposed by Zaworotko,[6] is another interesting focused field in supramolecular chemistry and crystal engineering in recent years, the study of which is not only essential to producing new materials with structural diversities and interesting properties but also may be helpful for finding the influencing factors on crystal growth.[6a] However, the rational design and controlled synthesis of supramolecular isomers is still a major challenge for synthetic chemists in crystal engineering of molecular solids to date.[7] Many reported complexes have been claimed as supramolecular isomers, but, in fact, a large number of them are based on the coexistence of different guest molecules.[6a,8] Thus, it would be more suitable to categorize

these coordination polymers as pseudopolymorphs rather than true isomers (i.e., polymorphs).

More recently, we have focused our attention on utilizing flexible multicarboxylate ligands to build novel MOFs, and we have found that a minor change of synthesis conditions may be applied to realize good structural control of the resulting polymers.[9] Meanwhile, we have also noticed that the *p*-block metal ion, Pb^{II} ion, with a lone-pair electron and large ionic radius, can adopt various coordination environments and stereochemical activities, which might provide a nice opportunity for the construction of unusual coordination polymers with suitable organic linkers. For example, recently Li et al. reported a self-penetrating coordination framework, namely, $[Pb_6(\mu_4\text{-}O)_2(L)_4]_n$ $[H_2L = 4,4'\text{-}(hexafluoroisopropylidene)bis(benzoic acid)]$, with $(4^{24}.6^4)$ network constructed from cage-shaped $[Pb_6(\mu_4\text{-}O)_2\text{-}(O_2C)_8]$ clusters and V-shaped dicarboxylate. In this complex, three distinct Pb^{II} hemidirected geometries exist which suggests that the electron lone-pairs of Pb^{II} ions are stereochemically active.[10] So these results promote us to purposely choose another flexible dicarboxylate as the starting building block materials (BBMs), namely, 1,4-phenylenediacetate acid (H_2phda) that has been proven an extremely good candidate for preparing new coordination polymers based on recent notable research reports,[11] with Pb^{II} ions to further explore some new MOFs with unique properties and novel topologies. Fortunately, the foregoing effort
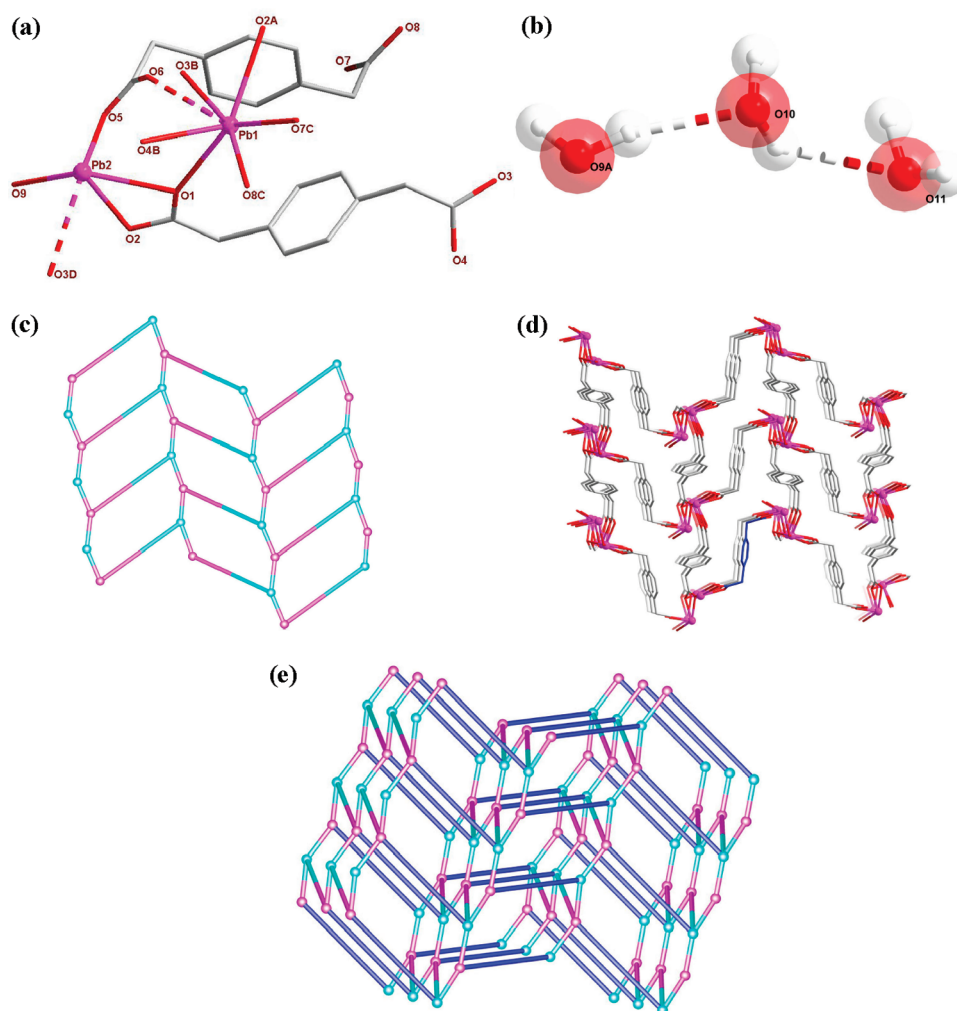
Figure 1. (a) The coordination environment of Pb^{II} ions in **1a**. Hydrogen atoms and guest water molecules have been omitted for clarity. Symmetry codes: A, $1 + x, y, z$; B, $x, y, 1 + z$; C, $1 - x, -0.5 + y, 1 - z$; (b) the discrete water cluster notated as $D3$; (c) the 3-connected 2D **hcb** network with the short Schläfli vertex symbol of 6^3 in **1a**; (d) the 3D framework of **1a**; (e) the 4-connected 3D **lon** topology of **1a**.

has led to the isolation of two true polymorphs, $[Pb_2(phda)_2 (H_2O)]_n \cdot 2nH_2O$ (**1a**, and **1b**), with entirely distinct topological networks by the assembly of Pb^{II} acetate with H_2phda ligand at different reaction temperatures.

Herein, two colorless block polymorphs were obtained by the hydrothermal reactions of $Pb(OAc)_2 \cdot 3H_2O$ with H_2phda ligand in water at 120 °C (for **1a**)/160 °C (for **1b**) for three days, which have been characterized by elemental analysis and IR spectra, and the phase purities of bulk products have also been identified by comparison of their powder X-ray diffraction (PXRD) patterns with those calculated from the single X-ray crystal data, showing the two products with high qualities (Figure S1, Supporting Information).

X-ray crystallography reveals that the conformational freedom of phda ligand (due to the free bending and rotation of methylene groups $-CH_2-$) manifests itself by sustaining two isomeric 3D network polymers. Two coordination polymers have the same molecular formula but distinct differences in morphology, monoclinic system with $P2_1$ space group for **1a** and triclinic system with $P\bar{1}$ space group for **1b**, respectively. In **1a**, there exists two types of Pb^{II} ion centers, two types of phda ligands, one aqua ligand, and two guest water molecules in the asymmetric unit

(Figure 1a), and the phda ligands adopt two entirely different coordination modes to link Pb^{II} ions. Interestingly, the careful inspection of **1a** found that a right helical chain $[Pb_1O_2Pb_2O_1]_n$ is formed by the bridging μ_2-O (O1, O2) atoms and Pb^{II} ion centers with a pitch of 6.972 Å (Figure S2, Supporting Information). Furthermore, a discrete water cluster is fused by two free water molecules (O10, O11) and one clathrated water molecule (O9) by H-bonded interlocks notated as $D3$ fashion[12] (Figure 1b). It is very clear that a two-dimensional (2D) subnet is formed by the 4-connected phda ligands and Pb^{II} ions; from the topological view, this 2D layer can be regarded as a uninodal 3-connected **hcb** network with the short Schläfli vertex symbol of 6^3 based on the Pb1 ions as the nodes (Figure 1c, because Pb2 ions are 2-connected nodes in the layer which are all ignored in the result). And then the bidentate phda ligands further support these adjacent 2D layers to give a 3D motif which shows a uninodal 4-connected **lon** topology with the short Schläfli vertex symbol of 6^6 and the long topological symbol of $[6(2).6(2). 6(2).6(2).6(2).6(2)]$ (Figure 1d,e). The topology of **1a** is completely different from the familiar 4-connected **dia** framework, although they have the same short Schläfli vertex symbols: in the **lon** network, the nodes are linked into boat- and chairlike 6-rings
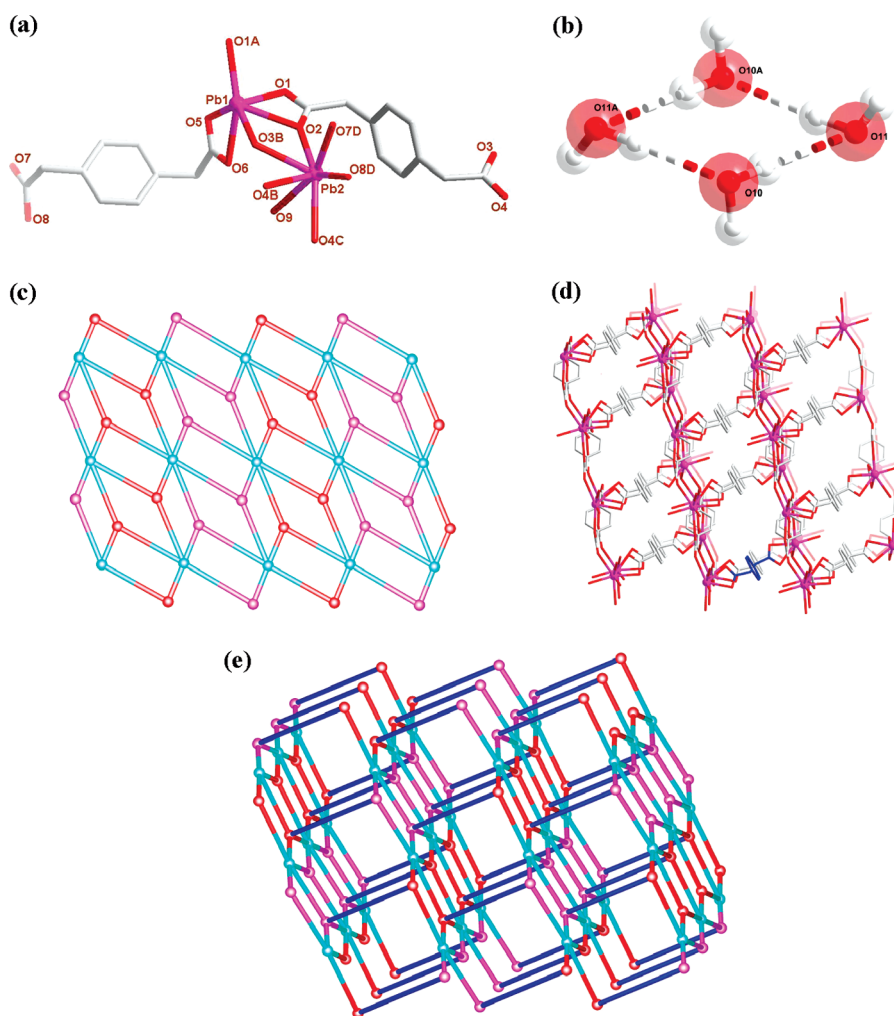
Figure 2. The coordination environment of Pb^{II} ions in **1b**. Hydrogen atoms and guest water molecules have been omitted for clarity. Symmetry codes: A, $1 - x, 1 - y, 2 - z$; B, $-1 + x, y, z$; C, $2 - x, -y, 1 - z$; D, $1 + x, -1 + y, z$; (b) The cyclic water tetramer $(H_2O)_4$; (c) the binodal (3,6)-connected *kgd* topology; (d) the 3D network of **1b**; (e) the binodal (4,6)-connected *fsh* topology of **1b**.

which form an enclosed 6^5 cage; however, the 6-rings all adopt the chair conformation in the **dia** framework. The **lon** network was first announced by O'Keeffe et al. in 1992 and is presented here for the first time based on a single flexible ligand.[2e]

For **1b**, there are the same components as that of **1a** in the fundamental unit (Figure 2a); however, the phda ligands take two different coordination fashions with Pb^{II} ions, which are distinguished from those of **1a**. Herein, different from that of **1a**, first, the structural feature of **1b** is that an unusual Pb–O cluster is fused by the bridging μ_2-O (O1, O2, O3, and O4) atoms and two types of Pb^{II} metal centers, imposing three different Pb···Pb separations (4.274 Å, 4.346 Å, and 4.397 Å), as shown in Figure S3 (Supporting Information). Moreover, the four guest lattice water molecules (O10, O11, and its symmetry related water molecules) self-assembled them into a cyclic water tetramer $(H_2O)_4$ via H-bonded interlocks notated as the $R_4^4(8)$ type[12] (Figure 2b), showing the unique *uudd* formation but not the *udud* conformation.[13] Furthermore, different from that of **1a**, a 2D subnet is formed by 6-connected phda dianions and Pb^{II} ions, and this layer can be simplified as a binodal (3,6)-connected *kgd* (kagome dual) topology (Figure 2c); then, like that in **1a**, the bidentate phda ligands link these adjacent 2D subnets to form a

3D framework which exhibits a binodal (4,6)-connected *fsh* topological network with the short Schläfli vertex symbol of $(4^3.6^3)_2(4^6.6^6.8^3)$ and the long topological vertex symbol of $[4.4.4.4.4.4.6(2).6(2).6(2).6(2).6(2).6(2).*.*.*][4.6(2).4.6(2).4.6-(2)]$ (Figure 2d,e). Thus far, although there are some mixed connected networks with two types of vertexes which have been identified and categorized by O'Keeffe et al., such as **btv**, **thp-a**, **asv**, **bab** and **bbm** topologies, as we know, the *fsh* topology has not been observed in the 3D MOFs solids but just only predicted in theory.[4]

Because there are some free guest water molecules in the crystal lattices of the two complexes, the transform experiments were taken in solution. It is very unfortunate that the attempt to transform complex **1a** to complex **1b** failed at some reaction temperatures that are higher than 120 °C and vice versa, which demonstrates the resultant coordination polymers were very sensitive to the reaction temperature, and the role of temperature in controlling syntheses could be rationalized as the higher temperature might be expected to afford more thermodynamically stable,[15] more complicated crystal forms which have been proven from the above-mentioned structural analysis. Moreover, the two true polymorphs herein should be classified as structural
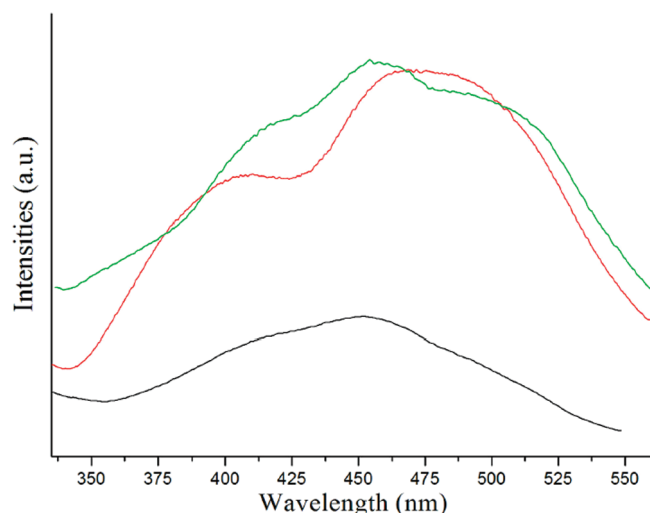
Figure 3. The solid-state fluorescent spectra of the two polymorphs and H_2phda ligand at the ambient temperature. H_2phda ligand (black): λ_{em} = 450 nm; **1a** (green); **1b** (red); λ_{ex} = 300 nm.

isomers,[14] where the inorganic and organic connectivities change from one isomer to the other (Figure S4, Supporting Information), and, to our knowledge, there is no case reported about the polymorphs constructed from a single flexible kinked dicarboxylate as the building block materials.

The two complexes are all stable in the air. At the same time, due to the presence of the free guest water molecules, thermogravimetric analysis (TGA) was also performed on the samples (Figure S5, Supporting Information). At first glance, the TGA curves show that the two complexes seem to possess similar thermal stabilities: the first weight loss of 5.23% for **1a** and 5.75% for **1b** (calcd: 6.34%) correspond to the loss of all water molecules, respectively. Then the framework of **1a** can remain stable to ~313 °C (~327 °C for complex **1b**). Beyond this temperature, the organic components begin to decompose and the frameworks collapsed. However, further study of the DSC curves for two polymers shows the different stable behaviors: in **1a**, the DSC curve shows a broad endothermic peak from ~57 to 209 °C which indicates that the water molecules were lost step by step; in fact, we could also find this information carefully from the TGA curve; in **1b**, the DSC curve shows a sharp peak from ~57 to 196 °C, the major reason of which is that one water molecule (O11) has a weak interaction with Pb1 ions with the distance of 2.791(86) Å; therefore, the three water molecules might be lost together.

Furthermore, the solid-state fluorescent properties of the two complexes and free H_2phda ligand were also investigated at room temperature. And their emission spectra are also very similar, as shown in Figure 3. Complex **1a** shows an intense fluorescent emission maximum at λ_{em} = 453 nm with a shoulder peak at 412 nm (λ_{em} = 473 nm with a shoulder peak at 408 nm for **1b**, λ_{ex} = 300 nm) compared with the H_2phda ligand (λ_{em} = 450, assigned to ligand-centered $\pi-\pi^*$ electronic transitions). And the low-energy fluorescent emissions are commonly observed for other s^2-metal complexes, which can be assigned to a metal-centered transition involving the s and p metal orbital.[16] The different emission bands of the two complexes may be assigned to the coordination diversities of the Pb^{II} ion centers and the rigid differences of these Pb^{II} coordination frameworks.

In summary, we have successfully isolated two unique 3D Pb^{II} true polymorphs at different reaction temperatures, which displays the first example of two different isomers reported for a flexible ligand acting as a bridge. And the resultant true polymorphs show distinct novel unreported topological networks. This work may provide a useful approach for the design and construction of other structural isomeric crystalline materials. Further research is underway in our group and will be reported as a full paper.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Detailed experimental procedures, some additional figures, coordination modes of phda, FT-IR spectroscopic data, elemental analysis (EA), TGA, PXRD, selected bonds of the complexes and crystal data; X-ray crystallographic data in CIF format for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: wyaoyu@nwu.edu.cn (Y.-Y.W.); stuart.batten@sci.monash.edu.au. (S.R.B).

■ ACKNOWLEDGMENT

■ REFERENCES

(1) (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (d) Li, J. R.; Kuppler, R. J.; Zhou, H. C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (e) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. *Chem Commun.* **2006**, 4780.

(2) (a) Tong, M. L.; Chen, X. L.; Batten, S. R. *J. Am. Chem. Soc.* **2003**, *125*, 16170. (b) Wang, X. L.; Qin, C.; Wang, E. B.; Li, Y. G.; Su, Z. M. *Chem. Commun.* **2005**, 5450. (c) Liu, C. S.; Wang, J. J.; Yan, L. F.; Chang, Z.; Bu, X. H.; Sanuso, E. C.; Ribas, J. *Inorg. Chem.* **2007**, *46*, 6299. (d) Wang, S. N.; Bai, J. F.; Li, Y. Z.; Pan, Y.; Scheer, M.; You, X. Z. *CrystEngComm* **2007**, *9*, 1084. (e) Ma, L. F.; Wang, L. Y.; Du, M.; Batten, S. R. *Inorg. Chem.* **2010**, *49*, 365. (f) Wang, S. N.; Xing, H.; Li, Y. Z.; Pan, Y.; Bai, J. F.; Scheer, M.; You, X. Z. *Eur. J. Inorg. Chem.* **2006**, 3041. (g) Yang, G. P.; Wang, Y. Y.; Zhang, W. H.; Fu, A. Y.; Liu, R. T.; Lermontova, E. K.; Shi, Q. Z. *CrystEngComm* **2010**, *12*, 1509. (h) Liu, D. S.; Huang, G. S.; Huang, C. G.; Huang, X. H.; Chen, J. Z.; You, X. Z. *Cryst. Growth Des.* **2009**, *9*, 5117.

(3) (a) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977; (b) O'Keeffe, M.; Hyde, S. T. *Zeolites* **1997**, *19*, 370. (c) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3. (d) Ockwig, N. W.; Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.

(4) Refer to RCSR: http://rcsr.anu.edu.au/.

(5) (a) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 971. (b) Natarajan, R.; Savitha, G.; Dominiak, P.; Wozniak, K.; Moorthy, J. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 2115. (c) Du, M.; Zhang, Z. H.; Zhao, X. J.; Xu, Q. *Inorg. Chem.* **2006**, *45*, 5785. (d) Du, M.; Zhang, Z. H.; Tang, L. F.; Wang, X. G.; Zhao, X. J.; Batten, S. R. *Chem.—Eur. J.* **2007**, *13*, 2578.

(6) (a) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 972. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (c) Abourahma, H.; Moulton, B.; Kravtsov, V.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 9990. (d) Moulton, B.; Abourahma, H.; Bradner, M. W.; Lu, J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2003**, 1342.

(7) (a) Sun, D. F.; Ke, Y. X.; Mattox, T. M.; Ooro, B. A.; Zhou, H. C. *Chem. Commun.* **2005**, 5447. (b) Zhang, J. P.; Chen, X. M. *Chem. Commun.* **2006**, 1689. (c) Han, L.; Zhao, W. N.; Zhou, Y.; Li, X.; Pan, J. G. *Cryst. Growth Des.* **2008**, *8*, 3504.

(8) (a) Soldatov, D. V.; Ripmeester, J. A.; Shergina, S. I.; Sokolov, I. E.; Zanina, A. S.; Gromilov, S. A.; Dyadin, Y. A. *J. Am. Chem. Soc.* **1999**, *121*, 4197. (b) Kumar, V. S. S.; Pigge, F. C.; Rath, N. P. *Cryst. Growth Des.* **2004**, *4*, 651.

(9) (a) Wang, H.; Wang, Y. Y.; Yang, G. P.; Wang, C. J.; Wen, G. L.; Shi, Q. Z.; Batten, S. R. *CrystEngComm* **2008**, *10*, 1583. (b) Yang, G. P.; Wang, Y. Y.; Liu, P.; Fu, A. Y.; Zhang, Y. N.; Jin, J. C.; Shi, Q. Z. *Cryst. Growth Des.* **2010**, *10*, 1443.

(10) Li, D. S.; Wu, Y. P.; Zhang, P.; Du, M.; Zhao, J.; Li, C. P.; Wang, Y. Y. *Cryst. Growth Des.* **2010**, *10*, 2037.

(11) (a) Li, X. J.; Weng, X. L.; Tang, R. J.; Lin, Y. M.; Ke, Z. L.; Zhou, W. B.; Cao, R. *Cryst. Growth Des.* **2010**, *10*, 3228. (b) Liu, T. F.; Lv, J.; Shi, L. X.; Guo, Z. G.; Cao, R. *CrystEngComm* **2009**, *11*, 583. (c) Li, D. S.; Zhang, M. L.; Zhao, J.; Wang, D. J.; Zhang, P.; Wang, N.; Wang, Y. Y. *Inorg. Chem. Commun.* **2009**, *12*, 1027. (d) Blake, K. M.; Farnum, G. A.; Johnston, L. L.; LaDuca, R. L. *Inorg. Chim. Acta* **2010**, *363*, 88.

(12) Infantes, L.; Chisholm, J.; Motherwell, S. *CrystEngComm* **2003**, *5*, 480.

(13) (a) Long, L. S.; Wu, Y. R.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2003**, *43*, 3798. (b) Li, Z. G.; Xu, J. W.; Jia, H. Q.; Hu, N. H. *Inorg. Chem. Commun.* **2006**, *9*, 969.

(14) Masaoka, S.; Tanaka, D.; Nakanishi, Y.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2530.

(15) Zhang, J. J.; Wojtas, L.; Larsen, R. W.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 17040.

(16) (a) Vogler, A.; Ford, P. C. *Acc. Chem. Res.* **1993**, *26*, 220. (b) Ding, B.; Liu, Y. Y.; Wu, X. X.; Zhao, X. J.; Du, G. X.; Yang, E. C.; Wang, X. G. *Cryst. Growth Des.* **2009**, *9*, 4176.

(17) Crystal data for **1a**: $C_{20}H_{22}O_{11}Pb_2$, $M_r = 852.76$, monoclinic, $P2_1$, $a = 6.9718(5)$ Å, $b = 18.1744(13)$ Å, $c = 8.9804(7)$ Å, $\beta = 96.357(1)°$, $V = 1130.89(14)$ Å^3, $Z = 2$, Flack value = 0.015(14), $D_c = 2.504$ g·cm^{-3}, $S = 1.006$, $R = 0.0349$ and $wR = 0.0767$ $[I > 2\sigma(I)]$, and $R = 0.0374$ and $wR = 0.0776$ (all data). CCDC number: 769815. **1b**: $C_{20}H_{22}O_{11}Pb_2$, $M_r = 852.76$, triclinic, $P\bar{1}$, $a = 9.1296(8)$ Å, $b = 10.2260(9)$ Å, $c = 13.0963(11)$ Å, $\alpha = 103.408(1)°$, $\beta = 90.242(1)°$, $\gamma = 99.456(1)°$, $V = 1172.03(18)$ Å^3, $Z = 2$, $D_c = 2.416$ g·cm^{-3}, $S = 1.011$, $R = 0.0318$ and $wR = 0.0753$ $[I > 2\sigma(I)]$, and $R = 0.0452$ and $wR = 0.0784$ (all data). CCDC number: 769816.

940

dx.doi.org/10.1021/cg101663a |*Cryst. Growth Des.* 2011, 11, 936–940