Inorg. Chem. **2006**, *45*, 5254–5256

Inorganic Chemistry
Communication

Rational Design of New Bright Luminescent Zinc Diphosphonates with 12-Member Ring Channels

Ruibiao Fu, Xihe Huang, Shengmin Hu, Shengchang Xiang, and Xintao Wu*

State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Science, Fuzhou, Fujian, 350002 P. R. China

Received April 10, 2006

Three new zinc diphosphonates possessing bright purple fluorescence, high thermal stability, and an intriguing 3D pillared open framework with 1D 12-member ring channels encapsulating luminescent guest have been rationally designed and synthesized by introducing a luminescent guest as a structure-directing agent.

The design and synthesis of metal−organic frameworks has been received much research interest in the past decades due to their structural diversities, as well as many potential or practical applications in the area of gas adsorption, enantioselective separation, catalysis, electrical conductivity, nonlinear optics, and so on.[1] Particularly, metal phosphonates as a new class of organic−inorganic hybrid materials have been explored extensively during the past three decades, for example, pillared open frameworks, homochiral porous solids, and molecular sieves with extra-large cages.[2] However, most metal phosphonates were structurally characterized on the basis of powder X-ray diffraction (XRD) data because it is difficult to grow single crystals of suitable size and quality due to their low solubility. Therefore, it is still challenging to design, rationally synthesize, and characterize specify metal phosphonates by single-crystal XRD.

Recently, a sodium zinc 1,4-butylenediphosphonate with a polar pillarlike open framework has been obtained which captures Na^+ cations within the 8MR (8-member ring) in the Zn−O−P layer.[3] Inspired by this result, we propose a rational method to design and synthesize 3D pillared open frameworks with intriguing properties and novel structures through replacement of Na^+ cations with luminescent guests. Herein, we wish to report three new bright luminescent zinc diphosphonates with 1D 12MR channels encapsulating 2-methylpiperazines: $[(C_5H_{14}N_2)Zn_2(O_3P(CH_2)_3PO_3H)_2]$ (**1**), $[(C_5H_{14}N_2)Zn_4(HO_3P(CH_2)_4PO_3H)(O_3P(CH_2)_4PO_3)_2]$ (**2**), and $[(C_5H_{14}N_2)Zn_4(HO_3P(CH_2)_2PO_3H)(O_3P(CH_2)_2PO_3)_2]$ (**3**).

Single crystals of **1**−**3** were rationally obtained in 64−78% yield by using *R*-(−)-2-methylpiperazine as a structure-directing agent (SDA) under $H_2O/CH_3CH_2CH_2COOH$ (1:1, v/v) mixed solvothermal condition at 180 °C. Elemental analyses were in accord with the respective formulae. The purities of the products were all verified by powder XRD (PXRD). The IR spectrum of **1**−**3** displays the strong stretching vibrations of P═O and P−O in the range of 1003−1205 cm^{-1}.

Suitable single-crystal XRD reveals that solids **1**−**3** crystallize in central space group *P*2(1)/*c* with 3D pillared open frameworks (Figure 1).[4] **2** is isomorphous with **3**. All Zn(II) ions are in $[ZnO_4]$ distorted tetrahedral coordination geometries which are surrounded by four oxygen atoms from four different diphosphonate groups. The bond lengths (Zn−O) and angles (O−Zn−O) are in the ranges of 1.911(3)−1.972(3) Å and 98.2(2)−117.4(2)°, respectively. On the other hand, each $O_3P(CH_2)_3PO_3H$ group in **1** bonds four different Zn(II) atoms. Thus, $[ZnO_4]$ and $[PCO_3]$ tetrahedrons share corners to form a single organic−inorganic hybrid layer

---

* To whom correspondence should be addressed. E-mail: wxt@fjirsm.ac.cn.

(1) (a) Janiak, C. *Dalton Trans.* **2003**, 2781−2804. (b) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504−1518. (c) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703−706. (d) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 72−75. (e) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982−986. (f) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem.* Soc. **1994**, *116*, 1151−1152. (g) Zheng, S. L.; Zhang, J. P.; Wong, W. T.; Chen, X. M. *J. Am. Chem. Soc.* **2003**, *125*, 6882−6883.

(2) (a) Poojary, D. M.; Zhang, B.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 12550−12559. (b) Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801−2810. (c) Alberti, G.; Marmottini, F.; Murcia, S.; Vivani, R. *Angew. Chem., Int. Ed.* **1993**, *33*, 1594−1597. (d) Serre, C.; Férey, G. *Inorg. Chem.* **1999**, *38*, 5370−5373. (e) Evans, O. R.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2001**, *123*, 10395−10396. (f) Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 14298−14299. (g) Hu, A.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 11490−11491. (h) Hu, A.; Ngo, H. L.; Lin, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 6000−6003. (i) Evans, O. R.; Manke, D. R.; Lin, W. *Chem. Mater*. **2002**, *14*, 3866−3874. (j) Shi, X.; Zhu, G. S.; Qiu, S. L.; Huang, K. L.; Yu, J. H.; Xu, R. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6482−6485. (k) Cheng, C. Y.; Fu, S. J.; Yang, C. J.; Chen, W. H.; Lin, K. J.; Lee, G. H.; Wang, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 1937−1940. (l) Ouellette, W.; Yu, M. H.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **2006**, *45*, 3224−3239.

(3) Fu, R. B.; Hu, S. M.; Zhang, H. S.; Wang, L. S.; Wu, X. T. *Inorg. Chem. Commun.* **2005**, *8*, 912−915.

10.1021/ic060608u CCC: $33.50

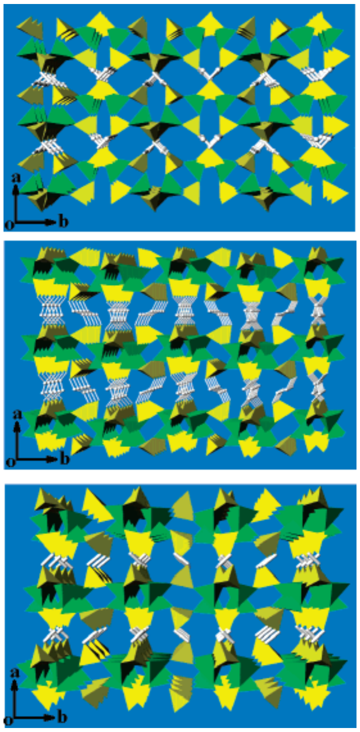

Figure 1. Polyhedral views of the pillared open frameworks for solid **1** (top), **2** (middle), and **3** (bottom). [ZnO_4] and [CPO_3] are indicated by green and yellow tetrahedrons, respectively. Unrelated atoms are omitted for clarity.

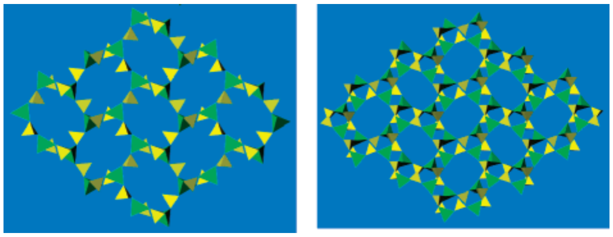

Figure 2. Polyhedral views of the hybrid layers of **1** (left) and **2** (right). [ZnO_4] and [CPO_3] are indicated by green and yellow tetrahedrons, respectively.

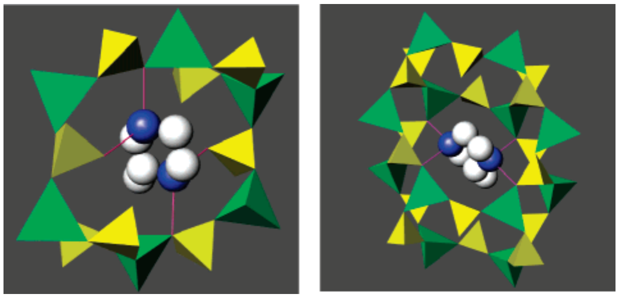

Figure 3. Views of the 12MR encapsulating 2-methylpiperazine cations of **1** (left) and **2** (right). [ZnO_4] and [CPO_3] are indicated by green and yellow tetrahedrons, respectively. C and N atoms are represented with white and blue balls, reactively. Unrelated atoms are omitted for clarity.

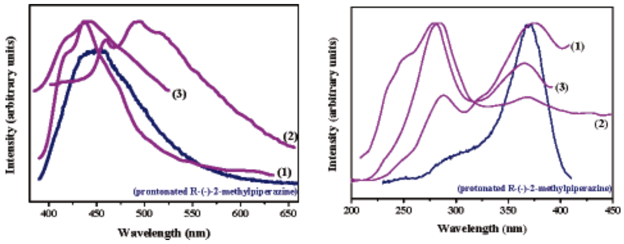

Figure 4. Solid-state fluorescent emission (left) and excitation (right) spectra of 0.6 M *R*-(−)-2-methylpiperazine dihydrochloride (pH = 1.17) and solids **1**−**3**.

(Figure 2), which consists of 12MRs with dimensions of about 7.1 Å × 6.7 Å (calculated from the distances of opposite oxygen atoms), while in **2** and **3**, $HO_3P(CH_2)_nPO_3H$ ($n = 2,4$) and $O_3P(CH_2)_nPO_3$ ($n = 2,4$) groups links four and six different Zn(II) atoms, respectively. [ZnO_4] and [PCO_3] tetrahedrons in **2** and **3** are corner-sharing in a double organic−inorganic hybrid layer, which also consists of 12-MRs with dimensions of about 8.8 Å × 7.0 Å (calculated from the distances of opposite oxygen atoms). Due to the high crystallizing temperature, the *R*-(−)-2-methylpiperazines are racemized during the reaction. Either in the single or double hybrid layers of **1**−**3**, all the 2-methylpiperazines with chair conformations are encapsulated into the 12MR through strong hydrogen bonds between the protonated nitrogen atoms and oxygen atoms (Figure 3). Intriguingly, 2-methylpiperazine cations in **1** can be ion-exchanged entirely by Li^+ cations in ethanol solution under ambient temperature with the retention of the open framework. The Li^+ ion-exchange of **1** is denoted as **1-Li**.

Thermogravimetric analysis (TGA) reveals that there are little weight loss up to 350 and 430 °C for **1** and **3**, respectively. For **2**, below 350 °C only 1.6% weight loss appears between 100 and 200 °C. Furthermore, after polycrystalline solids of **1** and **2** are heated at 250 °C for 2 h under ambient atmosphere and cooled to room temperature, PXRD patterns are all essentially similar to those of simulated from X-ray single-crystal data, which unambiguously indicates little change of the open framework of **1** and **2**, respectively.

Beside their attractive structures, as anticipated, **1**−**3** possess intriguing fluorescent properties. **1**−**3** could emit purple luminescence in the solid state with a maximum band at 438 (excited at 370 nm), 495 (excited at 284 nm), and 443 nm (excited at 275 nm), respectively (Figure 4). Since **1-Li** does not display any fluorescence, the luminescent emissions of **1**−**3** can probably be assigned to the intraligand fluorescent emission of protonated 2-methylpiperazine. It is interesting to note that fluorescent peak bands of solid **2** exhibit an ∼46 nm bathochromic shift compared to that of protonated *R*-(−)-2-methylpiperazine (λ_{max} = 449 nm,

---

(4) Crystal data for **1**: $C_{11}H_{28}N_2O_{12}P_4Zn_2$, monoclinic, space group *P2(1)/c* (No. 14), $a = 8.854(4)$ Å, $b = 13.474(5)$ Å, $c = 9.815(4)$ Å, $\beta = 98.523(8)°$, $V = 1158.1(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.821$ g cm^{-3}, $\mu = 2.406$ mm^{-1}, $6.04° \leq 2\theta \leq 55.00°$, $T = 130.15$ K, R1 = 0.0244 and wR2 = 0.0580 for 2478 ($I > 2\sigma(I)$) of 2658 [$R_{int} = 0.0197$] unique reflections and 145 parameters. GOF = 1.121. Crystal data for **2**: $C_{17}H_{40}N_2O_{18}P_6Zn_4$, monoclinic, space group *P2(1)/c* (No. 14), $a = 10.8658(17)$ Å, $b = 16.605(2)$ Å, $c = 10.3926(16)$ Å, $\beta = 103.965(2)$ °, $V = 1819.7(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.839$ g cm^{-3}, $\mu = 2.939$ mm^{-1}, $6.24° \leq 2\theta \leq 54.94°$, $T = 293(2)$ K, R1 = 0.0805 and wR2 = 0.1577 for 3226 ($I > 2\sigma(I)$) of 4147 [$R_{int} = 0.0670$] unique reflections and 217 parameters. GOF = 1.180. Crystal data for **3**: $C_{11}H_{28}N_2O_{18}P_6Zn_4$, monoclinic, space group *P2(1)/c* (No. 14), $a = 8.5989(17)$ Å, $b = 17.044(2)$ Å, $c = 10.165(2)$ Å, $\beta = 108.434(9)°$, $V = 1413.2(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.171$ g cm^{-3}, $\mu = 3.774$ mm^{-1}, $T = 130.15$ K, R1 = 0.0507 and wR2 = 0.1035 for 2793 ($I > 2\sigma(I)$) of 3232 [$R_{int} = 0.0461$] unique reflections and 190 parameters. GOF = 1.188. CCDC-299885, 299886, and 299887 for compounds **1**, **2**, and **3**, respectively.

excited at 365 nm). In addition, the luminescent lifetimes of protonated *R*-(−)-2-methylpiperazine and solids **1**−**3** are about 1.16, 14.7, 29.4, and 45.4 ns, respectively. The above results provide a new way to synthesize fluorescent solids by the incorporation of luminescent molecules into the organic−inorganic hybrid channel, which would enhance thermal stability and tune the luminescent lifetime.

TGA of **1-Li** reveals the release of the adsorbed water from room temperature to 170 °C and then no obvious weight loss stage between 170 and 520 °C. Furthermore, after **1-Li** was heated at 250 °C for 2 h under air atmosphere, PXRD patterns agree well with those of the pristine solid, which unambiguously indicates the retention of the open framework of **1-Li**. The N_2 sorption at 78 K for **1-Li** revealed Type II isotherm. Using the BET model, the apparent surface areas of **1-Li** were calculated to be 10.7 m^2/g. When **1-Li** solid is exposed to ambient atmosphere, it adsorbs water immediately with the mass increasing quickly up to about 40% in 8 h, which is in accord with the strongly hydrated tendency of Li^+ ion. After re-dehydration, the **1-Li** solid behavior was the same. This result shows that the **1-Li** solid could reversibly adsorb−desorb water. As shown in Figure 5, below 90 °C, the conductivity of **1-Li** increases exponentially with decreasing temperature. At room temperature, the conductivity reaches 2.5×10^{-4} S cm^{-1}. These results give **1-Li** potential applications as a water absorbent, a dryer, and a humidity sensor.

In summary, three new 3D pillared zinc diphosphonates with bright purple luminescence have been successfully designed, rationally synthesized, and characterized. The intriguing open frameworks possess 1D 12MR channels encapsulating 2-methylpiperazines. The properties of the Li^+ ion-exchanges of **1** have also been studied. Future efforts are focused on adjusting the porosity of these materials via the changes of metal centers, organoamines, and diphosphonic acids and investigating their properties.

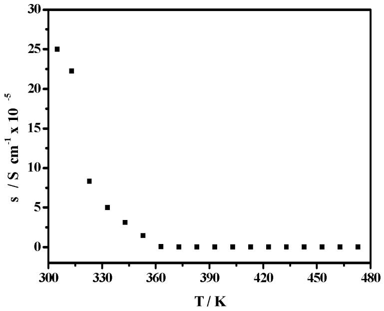

Figure 5. Conductivity versus temperature of **1-Li** under ambient atmosphere from 32 to 200 °C.

Acknowledgment. This work was supported by grants from the State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), the National Ministry of Science and Technology of China (001CB1089), the National Science Foundation of China (20333070, 90206040, and 90406024), and the Science Foundation of CAS and Fujian Province (2005HZ01-1, 2004HZ01-1, 2004J041, and Z0513022).

Supporting Information Available: Experimental procedures and 16 figures (PDF); crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC060608U