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Reversible Phase Transformation and Luminescent Mechanochromism of Zn^{II}-Based Coordination Frameworks Containing a Dipyridylamide Ligand

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There has been a growing interest in utilizing crystal engineering for the construction of a wide range of infinite solid-state architectures and metal–organic frameworks (MOFs). Such structures have been designed and structurally characterized by X-ray diffraction studies.[1] Moreover, their functionalities in chemical sieving, sensing, catalysis, and gas sorption have been also examined, and some have shown exciting and valuable potential.[2] However, a challenge encountered in designing the assembly of such materials is the unpredictability of the polymeric networks and dimensionalities,[1,2] because they have been found to be structually dependent on the coordination geometry of the metal ions, metal/ligand ratios, flexibility of the ligand backbones, counterions, and solvents used in the reaction media.[3] Among the MOFs, there has been much attention directed to flexible and dynamic frameworks,[1g,4] the structures and properties of which could be reversibly changed by external stimuli. In this regard, the design and synthesis of a host framework with dynamic behavior that can interact with certain guest molecules in a switchable and reversible manner is of interest as a new generation of functional materials. Although the effects of water as a guest molecule on the destabilization of some MOFs are known, the mechanism by which it brings about framework destabilization has been unclear. Up to now, only a handful of examples demonstrating framework destabilization in the transformation process have been studied experimentally by powder (PXRD) and single-crystal X-ray diffraction studies,[5] and hence more experimental results are necessary for elucidating the details of such interesting phenomena.

Sauvage et al pioneered a new class of transition-metal-containing rotaxanes,[6] which were suggested to be the basic elements for constructing nanoscale machines and motors in the future. Later, interpenetrating polyrotaxane networks in which macrocycles such as cyclic polyethers and cyclodextrins threaded onto 1D polymer chains were described. As a representative example, Robson et al in 1997 first reported two coordination polymers,[7] $[Ag_2(bix)_3(NO_3)_2]_n$ and $[Zn(bix)_2(NO_3)_2]_n$ (bix = 1,4-bis(imidazol-1-ylmethyl)benzene), consisting of 1D polymeric chains knitted together to generate 2D and 1D polyrotaxane frameworks, respectively. It was not until 2001 that Chen et al reported an unprecedented polyrotaxane framework,[8] $[Cu_2(bpa)_2(phen)_2(H_2O)]_2$ (bpa = biphenyl-4,4′-dicarboxylate; phen = 1,10-phenanthroline), in which interlocking of the lateral phen ligands of the molecular $[Cu_2(bpa)_2(phen)_2(H_2O)]_2$ rhombi stacked into the cavities of the adjacent rhombi through intermolecular $\pi\cdots\pi$ interactions to give rise to another type of 2D polyrotaxanes in the solid state. Today, polyrotaxanes based on coordinative bonds or $\pi\cdots\pi$ interactions with various dimensionalities have been recognized as a new type of coordination architectures, which are anticipated to find useful applications as molecular switches.

In continuation of our previous efforts on investigating the self-assembly of MOFs based on pyridylamides,[9] dipyridylamide ligands that have the ability to form hydrogen bonds, as well as long and bent backbones, were recognized to be useful for the construction of complex and flexible supramolecular frameworks and thus drew our attention. Indeed, N,N′-bis(pyridylcarbonyl)-4,4′-diaminodiphenyl ether (papo) has been used to construct 1D double-zigzags based on Zn^{2+}, Cd^{2+}, and Co^{2+} ions,[10] but to the best of our knowledge no structural work that has used its related ligand, N,N′-bis(pyridylcarbonyl)-4,4′-diaminodiphenyl thioether (paps), has been done. Herein, we report 1D double-zigzag and 2D polyrotaxane frameworks containing the paps ligand, which have been obtained in the presence or absence of water in the reaction media, respectively. In addition, re-

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versible-phase transformation between these two frameworks and their luminescent mechanochromism have also been investigated.

The 1D double-zigzag framework, $\{[Zn(paps)_2(H_2O)_2](ClO_4)_2\}_n$ (**1**), was synthesized by the reaction of $Zn(ClO_4)_2$ with paps by a layer method. However, the same reaction, differing only in that dry solvents were used, led to the formation of a 2D polyrotaxane framework, $[Zn(paps)_2(ClO_4)_2]_n$ (**2**). The structural motif of **1** was revealed by single-crystal X-ray diffraction studies (see the Supporting Information), and the local coordination environment around Zn^{II} ions can be described as a distorted octahedron with four N atoms from four paps in the equatorial positions (Zn−N = 2.178(2) Å), and two water molecules in the axial positions with the $Zn-OH_2$ distance of 2.143(3) Å. In fact, because **1** is a 1D rhombohedral molecular square with a void dimension of 13.14 × 13.14 $Å^2$, it is isomorphous to $\{[Zn(papo)_2(H_2O)_2](ClO_4)_2\}_n$ (**3**)[10c] (void dimension 12.73 × 12.73 $Å^2$).[10c] The angle for C-S-C is 103.12(16)°, which is slightly smaller than the value of 115.9(3)° for C-O-C in **3**.[10c] The amide–amide hydrogen bond (N(2)···O(1) 2.802(2) Å) is also found in the crystal lattices of **1**, and thus it further increases the structural complexity to a 2D hydrogen-bonded framework. In addition, the shortest $Zn\cdots ClO_4$ distance is 4.55 Å, precluding any coordination to the Zn^{II} ion.

Whereas **1** has two water molecules coordinated to Zn^{II} in the axial positions, two ClO_4^- anions instead coordinate to the Zn^{II} ion in **2**. The local coordination environment around Zn^{II} ions in **2** can be also described as a distorted octahedron, with four N atoms from four paps ligands in the equatorial positions (Zn−N = 2.126(3) Å) and two ClO_4^- anions in the axial positions with a $Zn-ClO_4$ distance of 2.236(5) Å, as shown in Figure 1 (top). The double-zigzag component framework of **2** is also similar to those found in **1** and **3**,[10c] and the 1D rhombohedral molecular square shows a void dimension of 13.05 × 13.05 $Å^2$. The rhombohedral dimension and the angle of 102.5(2)° for C-S-C of **2** are also comparable to those of **1**. Surprisingly, the interlocking of the 1D rhombohedral molecular square through nonclassical hydrogen bonding (C(2)···O(4) 3.193(14) Å) into the void space of the adjacent rhombi generates a novel 2D polyrotaxane framework as shown in Figure 1 (middle and bottom). Although polyrotaxane frameworks are not uncommon,[7,11] examples of frameworks constructed from double-zigzags with coordinate bonds or other weak interactions are still limited.[8] Moreover, amide–amide hydrogen bonding (N(2)···O(1) 2.913(5) Å) is found in the crystal lattices, and thus it increases the structural complexity to a 3D hydrogen-bonded framework for **2**.

To ascertain the thermal stability of **1**, its TGA analysis was recorded (see the Supporting Information). A weight loss of 3.1 % (2 × H_2O: 3.0 %), indicative of the loss of two solvated water molecules, is observed upon heating the solid samples to 100 °C. When the temperature is heated to 220 °C, an additional loss of 3.1 % in weight due to the further loss of two coordinated water molecules (2 × H_2O: 3.0 %) can be observed. Above 285 °C, **1** starts to decompose until 550 °C. To examine the sample purity of **1** and **2**, PXRD studies were carried out (see the Supporting Information). Although the experimental PXRD pattern for the synthesized samples of **1** matches the simulated pattern for **1** well, the match was poor in the case of **2**, which had a pattern that also resembled the simulated pattern of **1**. In this regard, we set out to perform in situ PXRD studies for **2** in the mother liquor (i.e., $MeOH/CHCl_3/THF$), and the results show that the experimental and simulated patterns match well (see the Supporting Information). It appears that when the crystals of **2** left the mother liquor and were ground into powder form in the presence of moisture, phase transformation from **2** to **1** was already taking place. We reasoned that the key to the phase-transformation process should be due to water being present or absent in the coordination spheres. Indeed, upon heating solid samples of **1**, a phase transformation was observed from 180 to 270 °C in the TGA experiment, and the samples became amorphous above 420 °C as shown in the PXRD patterns in Figure 2. Notably, the PXRD pattern of **1** at 300 °C closely resembled that of **2**, and it strongly suggested that during the thermal treatment the double-zigzag framework of **1** not only lost two coordinated water molecules, but also underwent the phase-transformation process leading to the polyrotaxane framework of **2**. We surmise that when two coordinated water molecules are removed from the coordination spheres of Zn^{II} ions in **1**, the ClO_4^- anions near the Zn^{II} ions ($Zn\cdots ClO_4$ = 4.55 Å) in the crystal lattice approach and finally become coordinated

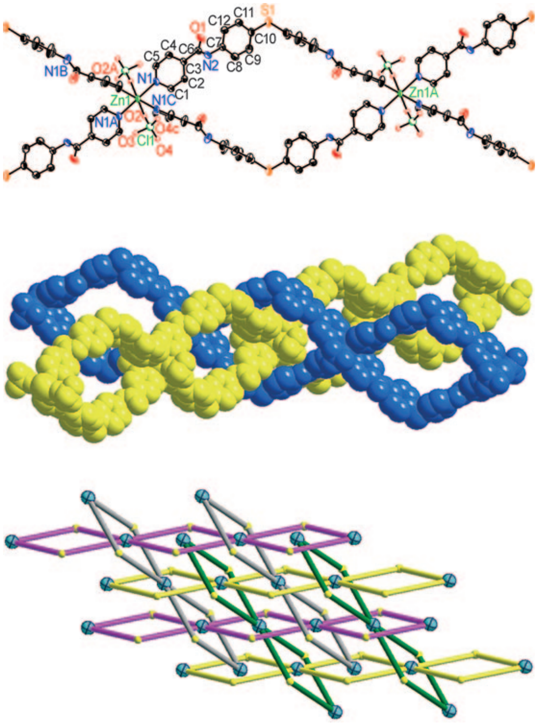

Figure 1. Top: A 1D double-zigzag component framework. Middle: A space-filling model diagram showing the interlocking for two 1D double-zigzags. Bottom: A schematic representation of polyrotaxanes of **2**.

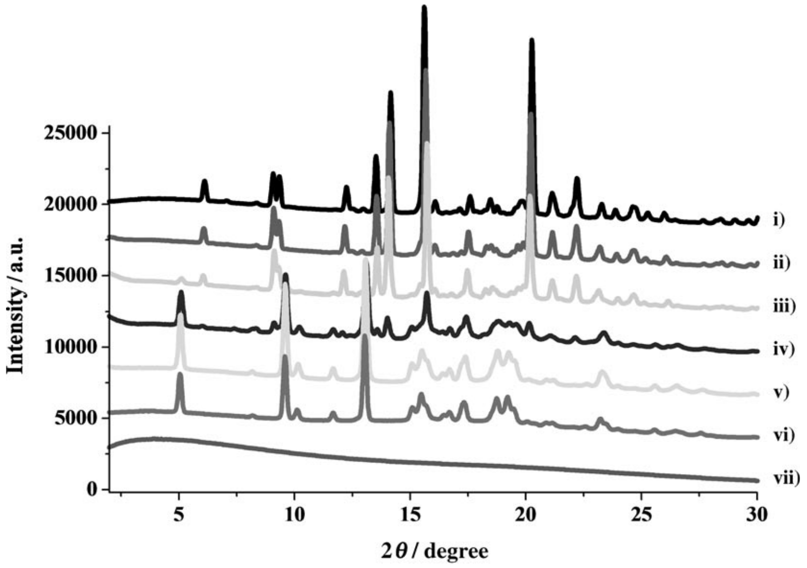

Figure 2. The variable-temperature PXRD patterns of **1** at i) room temperature, ii) 100, iii) 150, iv) 200, v) 250, vi) 300, and vii) 350 °C (with $\lambda = 1.33366$ Å).

to the Zn^{II} ions ($Zn{-}ClO_4 = 2.234(5)$ Å) in **2** and re-stabilize them. However, grinding the crystals of **2** in the presence of moisture permitted the addition and coordination of water molecules displacing the ClO_4^- anions, and therefore the double-zigzag framework of **1** was restored. Although the mechanism for the phase-transformation process still needs more detailed studies, it is clear that the loss of two coordinated water molecules concomitant with the movement of ClO_4^- toward Zn^{II} ions induces a phase transition, and the process of grinding in the presence of moisture facilitates phase transformation back to the original state. In the same temperature range, only an endothermic process with a heat absorbed of 12.9 kcal mol^{-1} can be calculated for the DSC experiment (see the Supporting Information). Thus, the data support that two coordinated water molecules were lost at approximately 150 °C simultaneously entailing phase transformation, in which the double-zigzag framework is anticipated to "open and close" in the crystal lattices for the formation of the polyrotaxane framework.

Complex **1** is strongly emissive with an emission maximum at approximately 495 nm at room temperature and 77 K, but complex **2** is poorly emissive in a similar spectral region as shown in Figure 3 (top). Given that there is a significant red shift from paps to **1** and **2**, in which paps poorly emits at room temperature and shows an emission maximum at 447 nm at 77 K, these emissions are mostly ascribed to an intraligand transition in combination with a charge-transfer transition. The poor emission of **2** may be due to intermolecular stacking interactions (i.e., π···π interactions). Significantly, an interesting luminescent mechanochromism can also be observed from **2** to **1** owing to the dark and bright emissions, respectively, described by their luminescence images in Figure 3 (bottom). When solid samples of **2** were put in a mortar and the dark emission was shown upon shining with a UV lamp, a bright-blue and then pale-yellow emission could be immediately observed while grinding the solid samples with the addition of one drop of water (manual grinding for 1 min and drying for 30 min), which is indicative of phase transformation from the polyrotaxane framework to the double-zigzag one. Therefore, this process is consistent with the PXRD results, and **1** and **2** could be reversibly interconverted by heating or grinding in the presence of moisture.

We have shown here a novel example of reversible phase transformation and luminescent mechanochromism of Zn^{II}-based coordination frameworks consisting of a dipyridylamide ligand, paps, which assembles

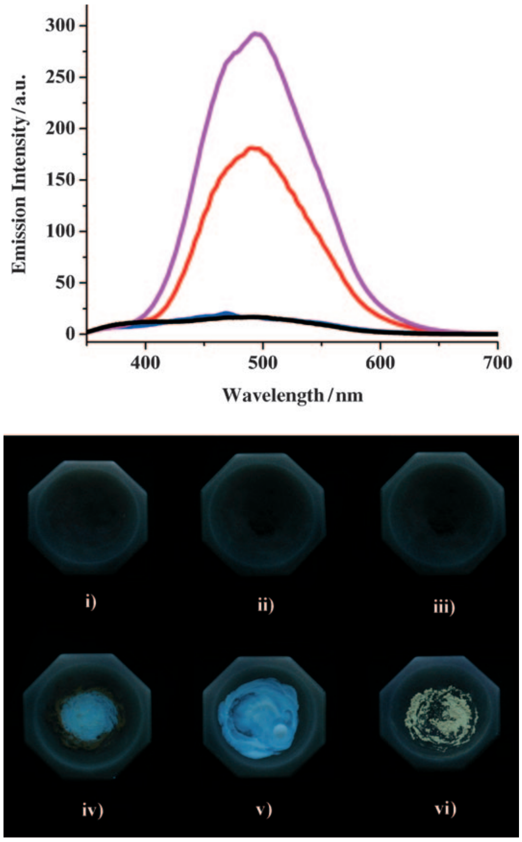

Figure 3. Top: The solid-state emission spectra of **1** at room temperature (red line) and at 77 K (pink line) and of **2** at room temperature (blue line) and at 77 K (black line). Excitation wavelengths are at 300–350 nm. Bottom: Luminescence images of **2** in the mortar : i) no solid samples, ii) with solid samples, iii) with solid samples ground, iv) with solid samples ground and addition of one drop of water, v) grinding solid samples in the presence of one drop of water, vi) the dry condition for v. A UV lamp at the excitation wavelength 365 nm was used.

into double-zigzag or polyrotaxane frameworks depending on the presence and absence of water. Heating or grinding in the presence of moisture induced the phase-transformation processes, which are reversible, and the structures have been experimentally proven by powder and single-crystal X-ray diffraction studies. The luminescent mechanochromic behavior of the double-zigzag and polyrotaxane frameworks has also been examined by their luminescence images. We anticipate that these MOFs with the ability to interconvert reversibly would find useful applications as sensing elements for nanoscale materials in the future.

Experimental Section

Synthesis of {[Zn(paps)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$}$_n$ 1: A solution of Zn(ClO$_4$)$_2$ (13 mg, 0.05 mmol) dissolved in MeOH (4 mL) was carefully layered onto a MeOH/CHCl$_3$ solution (1:1, 6 mL) of paps (20 mg, 0.05 mmol). Yellow crystals were obtained by ether diffusion in approximately 75% yield. FTIR (KBr): $\tilde{\nu}_{N-H}=3297$, $\tilde{\nu}_{C=O}=1650$, $\tilde{\nu}_{C=C}=1589$ and 1493 cm^{-1}, $\tilde{\nu}_{Cl-O}=1082$ cm^{-1}; elemental analysis calcd (%) for $C_{48}H_{40}Cl_2N_8O_{14}S_2Zn$: C 49.99, H 3.50, N 9.72; found: C 50.06, H 3.36, N 9.97.

Synthesis of [Zn(paps)$_2$(ClO$_4$)$_2$]$_n$ 2: The synthetic procedure is the same as that of **1** except that all the solvents used were dry. Yellow crystals were obtained by ether diffusion in ca. 60% yield under N$_2$ atmosphere. FTIR (KBr): $\tilde{\nu}_{N-H}=3297$, $\tilde{\nu}_{C=o}=1663$, $\tilde{\nu}_{C=C}=1590$ and 1492 cm^{-1}, $\tilde{\nu}_{Cl-O}=1121$ cm^{-1}; elemental analysis calcd (%) for $C_{48}H_{36}Cl_2N_8O_{12}S_2Zn$: C 51.60, H 3.25, N 10.03; found: C 51.86, H 3.46, N 10.25.

Crystal data for 1·2H$_2$O: $C_{48}H_{44}Cl_2N_8O_{16}S_2Zn$; $M_r=1189.34$; orthorhombic; space group *Ccca*; $T=294(2)$ K; $a=21.522(3)$, $b=25.392(3)$, $c=9.8663(12)$ Å; $V=5391.8(11)$ Å^3; $Z=4$; $\mu=0.707$ mm^{-1}; F(000) = 2448; 24880 reflections collected; 2475 independent; $R_{int}=0.0261$; final residuals $R1=0.0414$, $wR2=0.1208$ [$I>2\sigma(I)$].

Crystal data for 2: $C_{48}H_{36}Cl_2N_8O_{12}S_2Zn$; $M_r=1117.24$; orthorhombic; space group *Cmca*; $T=294(2)$ K; $a=29.740(3)$, $b=18.807(2)$, $c=9.1432(11)$ Å; $V=5114.0(10)$ Å^3; $Z=4$; $\mu=0.735$ mm^{-1}; F(000) = 2288; 13133 reflections collected; 2388 independent; $R_{int}=0.0289$; final residuals $R1=0.0561$, $wR2=0.1594$ [$I>2\sigma(I)$].

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Keywords: coordination frameworks · luminescence · mechanochromism · phase transformations · polyrotaxanes · rotaxanes

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[1] a) C. Janiak, *Dalton Trans.* **2003**, 2781; b) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474; c) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483; d) M. J. Zaworotko, *Angew. Chem.* **2000**, *112*, 3180; *Angew. Chem. Int. Ed.* **2000**, *39*, 3052; e) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460; f) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798; *Angew. Chem. Int. Ed.* **1999**, *38*, 2639; g) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[2] a) B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2076; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022; b) P. H. Dinolfom, J. T. Hupp, *Chem. Mater.* **2001**, *13*, 3113; c) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972; d) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369.

[3] a) O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1996**, *118*, 295; b) M. Kondo, T. Yoshitomi, K. Seki, K. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725; c) T. L. Hennigar, D. C. MacQuarie, P. Losier, R. D. Rogers, M. J. Zaworotko, *Angew. Chem.* **1997**, *109*, 1044; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 972; d) M. O. Awaleh, A. Badia, F. Brisse, *Cryst. Growth Des.* **2006**, *6*, 2674; e) P. A. Gale, M. E. Light, R. Quesada, *Chem. Commun.* **2005**, 5864; f) Z. Ni, J. J. Vittal, *Cryst. Growth Des.* **2001**, *1*, 195.

[4] a) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109; b) M. P. Suh, Y. E. Cheon, *Aust. J. Chem.* **2006**, *59*, 605.

[5] a) S. Supriya, S. K. Das, *J. Am. Chem. Soc.* **2007**, *129*, 3464; b) S. M. Mobin, A. K. Srivastava, P. Mathur, G. K. Lahiri, *Inorg. Chem.* **2009**, *48*, 4652; c) Z. X. Chen, S. S. Xiang, D. Y. Zhao, B. L. Chen, *Cryst. Growth Des.* **2009**, *9*, 5293.

[6] a) J. A. Faiz, V. Heitz, J. P. Sauvage, *Chem. Soc. Rev.* **2009**, *38*, 422; b) M. C. Jimenez-Molero, C. Dietrich-Buchecker, J. P. Sauvage, *Chem. Commun.* **2003**, 1613.

[7] a) B. F. Hoskins, R. Robson, D. A. Slizys, *J. Am. Chem. Soc.* **1997**, *119*, 2952; b) B. F. Hoskins, R. Robson, D. A. Slizys, *Angew. Chem.* **1997**, *109*, 2430; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2336.

[8] G.-F. Lin, B.-H. Ye, Y.-H. Lin, X.-M. Chen, *Chem. Commun.* **2002**, 1442.

[9] a) B.-C. Tzeng, H.-T. Yeh, Y.-L. Wu, J.-H. Kuo, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* **2006**, *45*, 591; b) B.-C. Tzeng, Y.-C. Huang, B.-S. Chen, W.-M. Wu, S.-Y. Lee, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* **2007**, *46*, 186; c) B.-C. Tzeng, T.-H. Chiu, B.-S. Chen, G.-H. Lee, *Chem. Eur. J.* **2008**, *14*, 5237; d) B.-C. Tzeng, T.-Y. Chang, *Cryst. Growth Des.* **2009**, *9*, 5343.

[10] a) Y.-X. Li, Y.-H. Li, X.-R. Zeng, R.-G. Xiong, X.-Z. You, H.-K. Fun, *Inorg. Chem. Commun.* **2003**, *6*, 1144; b) Y. W. Shin, T. H. Kim, K. Y. Lee, K. M. Park, S. S. Lee, J. Kim, *Inorg. Chem. Commun.* **2004**, *7*, 374; c) Y. W. Shin, T. H. Kim, K. Y. Lee, K. M. Park, S. W. Han, S. S. Lee, J. S. Kim, J. Kim, *Bull. Korean Chem. Soc.* **2005**, *26*, 473.

[11] a) L. Carlucci, G. Ciani, D. M. Proserpio, *Cryst. Growth Des.* **2005**, *5*, 37; b) M. T. Ng, T. C. Deivaraj, W. T. Klooster, G. J. McIntyre, J. J. Vittal, *Chem. Eur. J.* **2004**, *10*, 5853; c) C. S. A. Fraser, M. C. Jennings, R. J. Puddephatt, *Chem. Commun.* **2001**, 1310; d) C. Qin, X. L. Wang, E. B. Wang, Z. M. Su, *Inorg. Chem.* **2008**, *47*, 5555.

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