DOI: 10.1002/ejic.200701083

Two Photoluminescent Metal–Organic Frameworks Constructed from $Cd_3(\mu_3$-OH) Cluster or 1D $Zn_5(\mu_3\text{-OH})_2(\mu\text{-OH})_2$ Chain Units and In Situ Formed Bis(tetrazole)amine Ligands

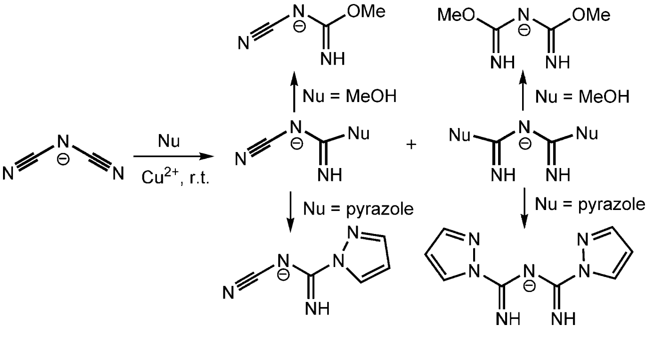
Ling-Ling Zheng,[a] Hao-Xiang Li,[a] Ji-Dong Leng,[a] Jing Wang,[a] and Ming-Liang Tong*[a]

Keywords: Cadmium / Zinc / Amines / Cluster compounds / MOFs / Photoluminescence

Hydrothermal reactions of $CdCl_2{\cdot}2.5H_2O$ or $ZnCl_2$, sodium dicyanamide, and sodium azide yield two interesting photoluminescent coordination polymers, namely, $[Cd\{Cd_3(\mu_3\text{-OH})(dcadtzH)_3(H_2O)_6\}_2]$ (**1**) and $[Zn_5(\mu_3\text{-OH})_2(\mu\text{-OH})_2(dcadtz)_2]{\cdot}2H_2O$ (**2**) [$dcadtzH_3$ = bis(5-tetrazolyl)amine], in which triangular $[Cd_3(\mu_3\text{-OH})]^{5+}$ cluster subunits in **1** and 1D $[Zn_5(\mu_3\text{-OH})_2(\mu\text{-OH})_2]_n^{6n+}$ chain subunits in **2** are linked by in situ generated bis(tetrazole)amine ligands to generate an interesting 2D coordination net and a 3D microporous metal–organic framework, respectively.

Introduction

Inorganic–organic hybrid polymers have attracted considerable attention in recent years because of their interesting molecular topologies and crystal packing motifs, alongside their potential applications in many areas including gas storage, separation, catalysis, magnetism, optics, as well as electrical conductivity.[1] Neutral as well ionic azides undergo cycloaddition with cyano groups to yield a huge variety of different tetrazole derivatives. The tetrazoles have found a wide range of applications in areas as diverse as coordination chemistry, medical chemistry, and materials science as high-density energy materials.[2] More recently, Sharpless et al. reported the preparation of a variety of 5-substituted 1*H*-tetrazoles in water and investigated the mechanism by which zinc(II) catalyzes the union of an azide ion with organic nitriles to form tetrazoles by means of density functional theory.[3] Although the role of Zn^{II} in the reaction is unclear, it allows us to explore the coordination chemistry of tetrazoles more extensively than in the past. We are interested in the construction of novel supramolecular motifs through in situ ligand reactions.[4] In our earlier work, we found interesting in situ nucleophilic addition reactions of sodium dicyanamide $\{Na[N(CN)_2]\}$[5] with some small molecules under mild conditions (Scheme 1), such as CH_3OH, pyrazole. As an extension of our continuing interest in such systems, we chose NaN_3 as the nucleophile. Herein, we report the synthesis and characterization of two photoluminescent coordination polymers, $[Cd\{Cd_3(\mu_3\text{-OH})(dcadtzH)_3(H_2O)_6\}_2]$ (**1**) and $[Zn_5(\mu_3\text{-OH})_2(\mu\text{-OH})_2(dcadtz)_2]{\cdot}2H_2O$ (**2**) [$dcadtzH_3$ = bis(5-tetrazolyl)amine].



Scheme 1. The known nucleophilic addition reactions of $Na[N(CN)_2]$ with some small molecules under mild conditions.

Results and Discussion

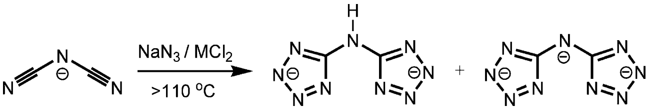
Compounds **1** and **2** were prepared by hydrothermal reactions of $CdCl_2{\cdot}2.5H_2O$ or $ZnCl_2$, $Na[N(CN)_2]$, and NaN_3 at 110 and 175 °C, respectively. The $dcadtz^{3-}$ ligand was generated in situ from the dicyanamide and azide ions in the presence of Zn^{2+} or Cd^{2+} ions (Scheme 2). The in situ formation of tetrazoles by a [2+3] cycloaddition reaction of azide and nitriles has been well established for the synthesis of different coordination complexes.[2,6] However, up to now, the use of dicyanamide as a source of CN was rarely

---

[a] MOE Key Laboratory of Bioinorganic and Synthetic Chemistry / State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University,
Guangzhou 510275, P. R. China
Fax: +86-20-8411-2245
E-mail: tongml@mail.sysu.edu.cn

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

documented.[7] Moreover, **2** cannot be obtained under the same hydrothermal reaction temperature as that used for the preparation of **1**.



Scheme 2. The in situ synthesis of $[dcadtzH]^{2-}$ and $[dcadtz]^{3-}$.

Single-crystal X-ray analysis showed that the structure of **1** is a 2D coordination polymer composed of $[Cd^{II}_3(\mu_3\text{-}OH)]^{5+}$ cluster units, $dcadtzH^{2-}$ ligands, and Cd^{II} ions (Figure 1). Each Cd1 ion displays a pseudooctahedral $[CdN_3O_3]$ coordination geometry, and it is ligated to three nitrogen atoms from two $dcadtzH^{2-}$ ligands [Cd1–N 2.304(1)–2.338(1) Å], two *trans* related aqua ligands [Cd1–O 2.316(1) and 2.353(1) Å], and one OH^- group [Cd1–O1 2.291(1) Å]. The hydroxy group lies on a threefold axis, and it acts as a μ_3 bridge linking three Cd1 ions, which leads to the formation of an equilateral triangle with Cd···Cd distances equal to 3.873(2) Å. The Cd–O1–Cd angle is 115.34(2)° and the OH^- group is out of the Cd_3 plane, which results in the formation of a noncoplanar $[Cd_3(\mu_3\text{-}OH)]^{5+}$ cluster unit. The $[Cd_3(\mu_3\text{-}OH)]^{5+}$ unit is surrounded by three $dcadtzH^{2-}$ ligands, each of which acts in the $\mu_3{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1$ chelating-bridging mode to link a pair of Cd1 atoms and one Cd2 atom. Each Cd2 lies on a crystallographic –3 position and adopts octahedral geometry with six symmetry-related N6 atoms from six $dcadtzH^{2-}$ ligands [Cd2–N 2.363(1) Å]. The $dcadtzH^{2-}$ ligand also links a Cd2 ion through the N6 atom, and hence, the tetrazolate group acts as a bridge between the $[Cd_3(\mu_3\text{-}OH)]^{5+}$ clusters and the Cd2 centers; the shortest Cd···Cd distance is 6.700(3) Å. Each Cd2 ion links six $[Cd_3(\mu_3\text{-}OH)]^{5+}$ cluster units, and each cluster connects three Cd2 ions, which results in a 2D layer parallel to the *ab* plane (Figure 1c).

The network topology can be simplified by considering only the 3-connected $[Cd_3(\mu_3\text{-}OH)]^{5+}$ cluster units and the 6-connected Cd2 centers as nodes; the $dcadtzH^{2-}$ ligands can be represented simply as links between the two types of nodes. The resulting net is shown in Figure 1d, which is a rare (3,6)-connected net.[8] The long topological vertex symbol is 4.4.4 for the $[Cd_3(\mu_3\text{-}OH)]^{5+}$ cluster node and 4.4.4.4.4.4.6.6.6.6.6.6.*.*.* for the Cd2 node, which gives the short vertex symbol $(4^3)_2(4^6.6^6.8^3)$. It should be noted that an artistic 3D metal–organic framework, $[Ag_3(ctc)(bsd)_3]\cdot1.5bsd\cdot3.5H_2O$ (H_3ctc = 1,3,5-cyclohexanetricarboxylic acid, bsd = 2,1,3-benzoselenadiazole),[9] constructed with ideal $Ag_3(ctc)$ honeycomb layers and the μ-bridging bsd ligands is a 3D (3,6)-connected topological net. It has the short vertex symbol $(4^3)_2(4^6.6^6.8^3)_3$, which is quite different from that in **1** mainly due to the octahedral geometry of the Cd2 ions; this results in a doubly decked layer structure that is similar to that in recently reported $[Mn\{Mn_3(\mu_3\text{-}F)(dcadtz)_3(H_2O)_6\}_2]$.[7b]

The coordinated water molecules play an important role as hydrogen donors for intra- and interlayer hydrogen bonding interactions. Within the layer, the hydrogen atom of the O1w water molecule forms a O–H···N [O1w···N3 2.757(1) Å] hydrogen bond with the N3 atom from the $dcadtzH^{2-}$ ligand. For the interlayer hydrogen bonding interactions, each O2w forms two interlayer O–H···N hydrogen bonds with two nitrogen atoms (N4 and N7) of the tetrazolate group [O2w···N4 2.780(1) Å, O2w···N7 2.767(1) Å]. These hydrogen bonds extend the 2D coordination layers into a 3D supramolecular network (Supporting Information, Figure S1). The nearest interlayer Cd···Cd distances are 5.688(3) and 7.793(4) Å.

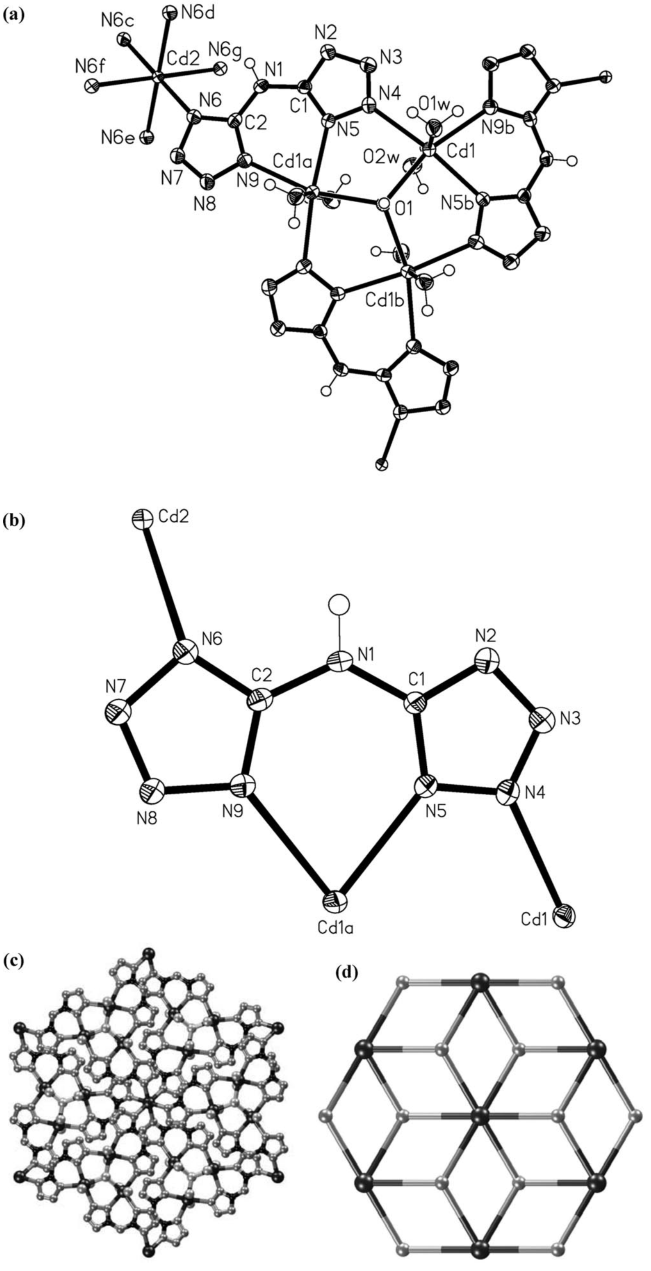


Figure 1. Perspective views of the coordination geometries of Cd^{II} ions (a), the bridging mode of the $[dcadtzH]^{2-}$ ligand (b), the 2D coordination layer (c), and the (3,6)-connected topological net of the coordination layer (d) in **1**.

The structure of **2** is a 3D coordination polymer composed by 1D unprecedented [Zn$_5$(μ_3-OH)$_2$(μ-OH)$_2$]$_n^{6n+}$ inorganic chains (Figure 3c) and fully-deprotonated dcadtz^{3-} ligands (Figure 2a,b). In **2**, the fully-deprotonated dcadtz^{3-} ligand acts as a μ_6 bridge, which is different from that found in **1**. The Zn^{2+} ions adopt three different coordination geometries. The Zn1 atom is in square-pyramid geometry [*cis* N/O$_{basal}$–Zn1–O/N$_{basal}$ 78.74(8)–96.69(7)°, *trans* N/O$_{basal}$–Zn1–O/N$_{basal}$ 145.42(8) and 165.30(8)°, N$_{apical}$–Zn1–O/N$_{basal}$ 93.89(8)–109.31(8)°] surrounded by two chelated nitrogen atoms [Zn1–N 2.046(2) and 2.175(2) Å] from a dcadtz^{3-} ligand, two hydroxide groups [Zn1–O 1.9835(19) 2.0960(17) Å] in the basal positions, and one nitrogen atom [Zn1–N1*a* 2.097(2) Å] from another dcadtz^{3-} ligand at the apical position. The Zn2 atom is coordinated in a distorted tetrahedral geometry to two nitrogen atoms [Zn2–N 2.016(2) and 2.018(2) Å] from two dcadtz^{3-} ligands and two hydroxide groups [Zn2–O 1.9152(18) and 2.0556(18) Å]. The O/N–Zn2–O/N bond angles range from 95.87(8) to 126.93(9)°. The Zn3 atom is in an octahedral geometry ligated by four nitrogen atoms [Zn3–N 2.156(2)–2.190(2) Å, *cis* N–Zn3–N 85.13(8)–96.36(11)°, *trans* N–Zn3–N = 176.17(8)°] from four dcadtz^{3-} ligands and two *trans* related hydroxide groups [Zn3–O 2.0654(17) and 2.0654(17) Å, O–Zn3–O 179.68(10), O–Zn3–N 86.61(7)–93.61(7)°]. There are two types of hydroxide groups adopting μ_2 and μ_3 bridging modes, respectively. Each μ_3 bridging hydroxide group (O1–H) connects three Zn ions (Zn1, Zn2, and Zn3), and the Zn···Zn distances are 3.614, 3.379, and 3.394 Å and the Zn–O1–Zn angles are 109.29(8)–121.04(8)°. A pair of [Zn$_3$(μ_3-OH)]$^{5+}$ units are further bridged by two μ_2 hydroxide groups [Zn1–O2–Zn2*b* 108.45(9)°] into an eight-membered Zn$_4$(OH)$_4$ circle. The circles are extended into 1D inorganic [Zn$_5$(μ_3-OH)$_2$(μ-OH)$_2$]$_n^{6n+}$ chains (Figure 2c) by Zn3–O1 coordination. Interestingly, the 1D inorganic chains are bridged by the μ_6 dcadpz^{3-} ligands into a 3D microporous metal–organic framework (Figure 2d). Analysis by using PLATON[10] suggested that the total void volume of **2** without water guests, V_{void}, occupy 17.3% of the crystal volume. The water guests are located at these channels and contact the MOF host through plentiful hydrogen-bonding interactions.

To examine the thermal stabilities of the networks of **1** and **2**, we carried out thermal gravimetric (TG) analyses and measured the XPRD patterns to confirm the purity of the two complexes (Figure 3). Samples of the complexes were heated to 650 °C in air. The TGA curve (Figure 4a) of **1** shows the first weight loss from 20 to 230 °C, and this is in accordance with the loss of all the coordinated water molecules; the dcadtzH^{2-} components were lost above 230 °C. Comparatively, the stability of **2** is higher than that of **1** for its 3D network connection. The TGA curve of **2** (Figure 4b) indicates the loss of lattice water molecules (calcd. 4.9%; found 4.7%) at about 230 °C, and the MOF began to decompose above 400 °C. The complex is finally decomposed to give the ZnO residue (calcd. 57.3%; found 55.7%) above 550 °C.

The fluorescent properties of the as-synthesized compounds were studied in the solid state at 66 K (Figure 5a, λ_{ex} = 311 nm). Both compounds exhibit weak fluorescence and therefore fluorescent spectra at lower temperature were recorded. Solid **1** displays blue emission with a maximum at ca. 390 nm (τ = 6.11 μs; Supporting Information, Figure S2). The emission of solid **2** is observed at about 402 nm

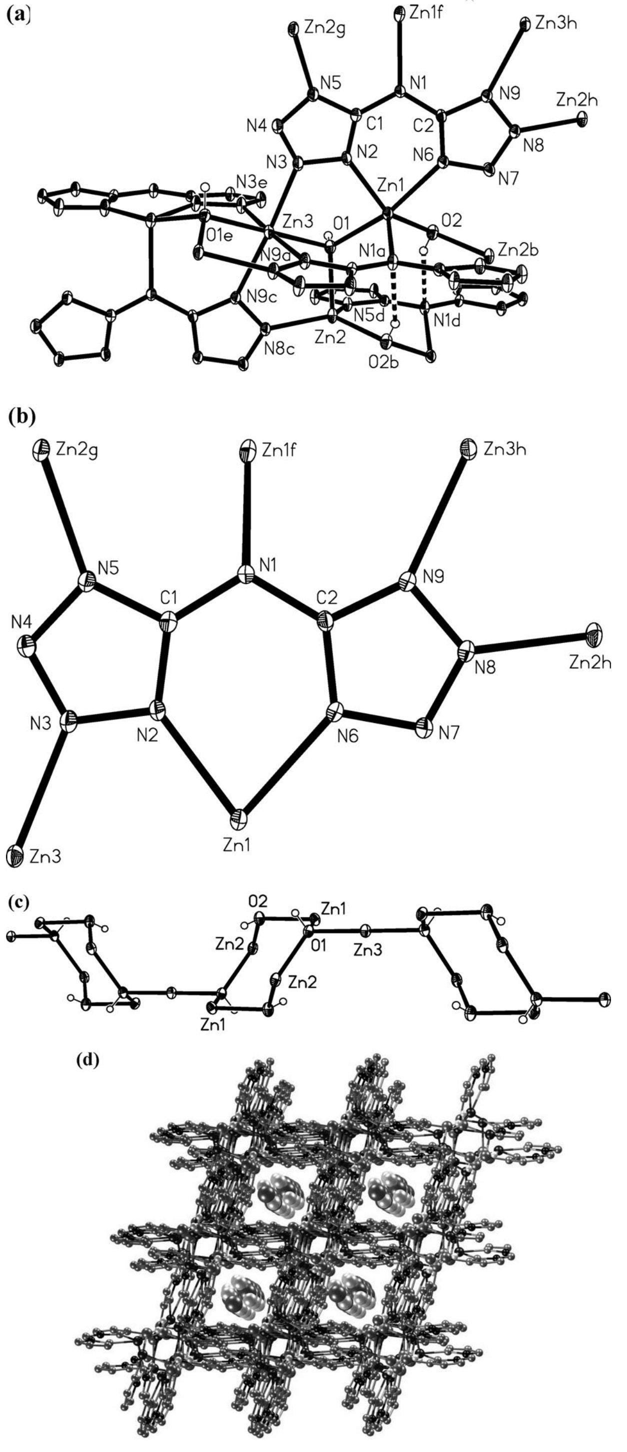


Figure 2. Perspective views of the coordination geometries of Zn^{II} ions (a), the bridging mode of the [dcadtz]$^{3-}$ ligand (b), the 1D [Zn$_5$(μ_3-OH)(μ-OH)]$_n^{8n+}$ chain (c), and the 3D microporous metal–organic framework (c) in **2**.

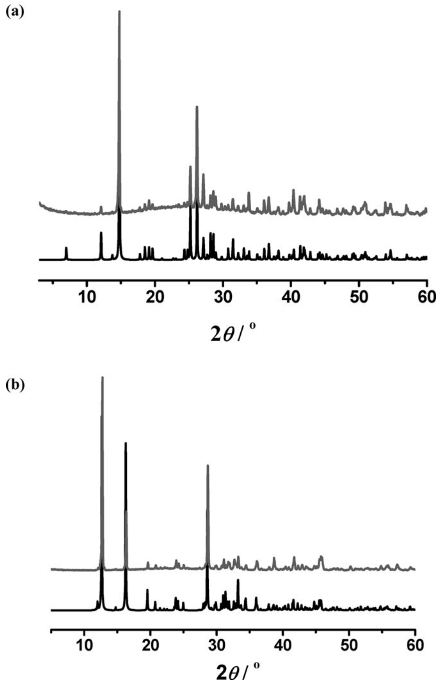


Figure 3. Observed (gray) and calculated (black) X-ray powder diffraction patterns for **1** (a) and **2** (b).

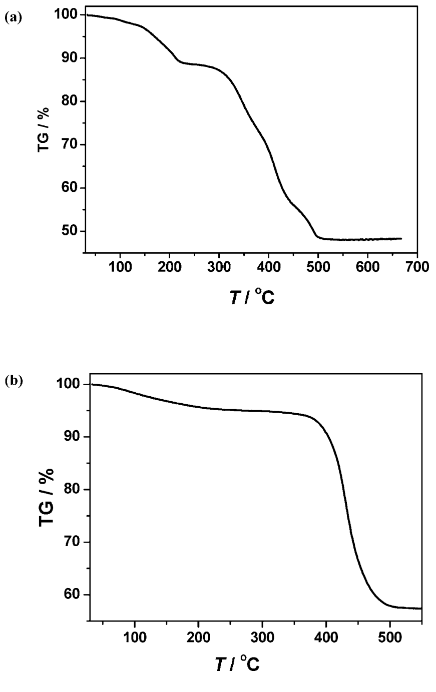


Figure 4. Thermogravimetric curves for **1** (a) and **2** (b).

(Figure 5b, λ_{ex} = 291 nm). The emission may be ascribed to the cooperative effects of intraligand emission and ligand-to-metal charge transfer (LMCT).[11] Moreover, the lifetime of **2** (τ = 28.48 ns) is also longer than that of **1**, which may be due to the stronger interactions of deprotonated dcadtz^{3-} ligands with zinc atoms in **2** (Figure 2b). The 3D connection and more rigid framework of **2** relative to that of **1** results in less vibrations of the skeleton and less radiationless decay of the energy.[12]

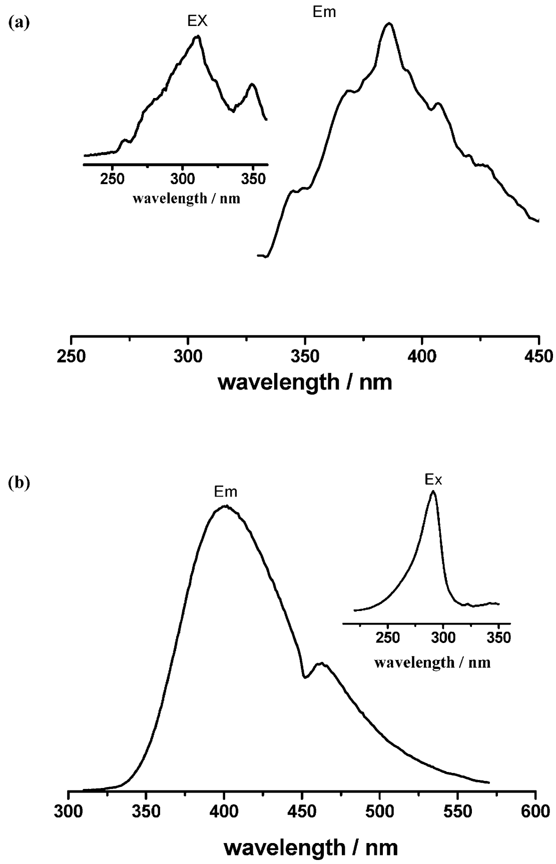


Figure 5. The solid-state emission spectra and excitation spectra (inset) of **1** (a) and **2** (b) at 66 K.

Conclusion

Hydrothermal reactions of $CdCl_2{\cdot}2.5H_2O$ or $ZnCl_2$, sodium dicyanamide, and sodium azide were performed at 110 or 175 °C and yielded an interesting 2D coordination net of $[Cd\{Cd_3(\mu_3\text{-}OH)(dcadtzH)_3(H_2O)_6\}_2]$ (**1**) or a 3D microporous metal–organic framework of $[Zn_5(\mu_3\text{-}OH)_2(\mu\text{-}OH)_2(dcadtz)_2]{\cdot}2H_2O$ (**2**). The deprotonated forms of the bis(5-tetrazolyl)amine ligand, dcadtzH^{2-} and dcadtz^{3-}, were generated in situ. We are expanding this reactivity to other transition-metal systems.

Experimental Section

Synthesis of 1 and 2: The single crystals of **1** and **2** were prepared by hydrothermal reaction of To a Teflon-lined stainless steel vessel was added $CdCl_2{\cdot}2.5H_2O$ (0.114 g, 0.5 mmol) [or $ZnCl_2$ (0.068 g, 0.5 mmol)], $Na[N(CN)_2]$ (0.045 g, 0.5 mmol), and NaN_3 (0.065 g, 1.0 mmol) in H_2O (5 mL). The vessel was sealed and heated for 4 d at 110 °C for **1** [or for 4 d at 175 °C for **2**]. After the mixture was slowly cooled to room temperature, colorless block crystals of **1** [or **2**] were obtained. Yield: 60% based on Cd for **1** [85% based on Zn for **2**]. **1**: $C_{12}H_{32}Cd_7N_{54}O_{14}$ (1943.72): calcd. C 7.42, H 1.66, N

38.92; found C 7.21, H 1.51, N 38.78. IR (KBr): $\tilde{\nu}$ = 3495 (s), 3159 (s), 3074 (s), 1624 (vs), 1539 (m), 1512 (vs), 1425 (m), 1314 (m), 1268 (s), 1180 (w), 1148 (w), 1125 (w), 1034 (w), 1014 (w), 861 (w), 798 (m), 723 (m), 651 (m) cm^{-1}. **2**: $C_4H_8N_{18}O_6Zn_5$ (731.13): calcd. C 6.57, H 1.10, N 34.48; found C 6.45, H 1.08, N 34.61. IR (KBr): $\tilde{\nu}$ = 3540 (s, br), 1618 (s), 1529 (vs), 1490 (vs), 1409 (s), 1350 (m), 1301 (m), 1281 (m), 1191 (w), 1159 (m), 1099 (w), 1047 (w), 873 (m), 787 (m), 763 (m), 506 (m), 469 (w) cm^{-1}.

X-ray Crystallographic Study: Diffraction intensities of **1** and **2** were collected with a Bruker Apex CCD area-detector diffractometer (Mo-K_a, λ = 0.71073 Å). The intensities were integrated with SAINT$^+$, which also applied corrections for Lorentz and polarization effects. Absorption corrections were applied by using multiscan program SADABS.[13] The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.[14] Compound **1**: $C_{12}H_{32}Cd_7N_{54}O_{14}$, M = 1943.72, trigonal, space group $P\bar{3}c1$ (No. 165), a = 14.6088(6) Å, c = 13.5875(11) Å, V = 2511.3(3) Å^3, Z = 2, T = 293(2) K, $F(000)$ = 1860, $D_{\text{calcd.}}$ = 2.570 g cm^{-3}, $\mu_{(\text{Mo-}K_a)}$ = 3.021 mm^{-1}; R_1 = 0.0310, wR_2 = 0.0784 and GOF = 1.119 for 154 parameters, 1572 reflections with $|F_o| \geq 4\sigma(F_o)$. Compound **2**: $C_4H_8N_{18}O_6Zn_5$, M = 731.13, monoclinic, space group $C2/c$ (No. 15), a = 16.139(2) Å, b = 8.4411(11) Å, c = 14.2879(18) Å, β = 111.498(2)°, V = 1811.1(4) Å^3, Z = 4, T = 293(2) K, $F(000)$ = 1424, $D_{\text{calcd.}}$ = 2.681 g cm^{-3}, $\mu_{(\text{Mo-}K_a)}$ = 6.604 mm^{-1}; R_1 = 0.0211, wR_2 = 0.0537 and GOF = 1.029 for 158 parameters, 1799 reflections with $|F_o| \geq 4\sigma(F_o)$.

CCDC-658316 (for **1**) and -658317 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): The 3D hydrogen-bonded supramolecular network in **1** and the luminescence decay for **1** and **2**.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20525102), the Research Fund for the Doctoral Program of Higher Education (20060558081) and the National Basic Research Program of China (2007CB815305).

---

[1] a) S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; b) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; c) C. Janiak, *Dalton Trans.* **2003**, 2781–2804; d) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273–282.

[2] a) S. J. Wittenberger, *Org. Prep. Proced. Int.* **1994**, *26*, 499–531; b) J. V. Dunica, M. E. Pierce, J. B. Santella, *J. Org. Chem.* **1991**, *56*, 2395–2400; c) S. J. Wittenberger, B. G. Donner, *J. Org. Chem.* **1993**, *58*, 4139–4141; d) D. P. Curran, S. Hadida, S.-Y. Kim, *Tetrahedron* **1999**, *55*, 8997–9006; e) H. Zhao, Z.-R. Qu, H.-Y. Ye, R.-G. Xiong, *Chem. Soc. Rev.*, DOI: 10.1039.b616738; f) S. Bhandari, C. G. Frost, C. E. Hague, M. F. Mahon, K. C. Molloy, *J. Chem. Soc. Dalton Trans.* **2000**, 663–669.

[3] a) Z. P. Demko, K. B. Sharpless, *J. Org. Chem.* **2001**, *66*, 7945–7950; b) Z. P. Demko, K. B. Sharpless, *Org. Lett.* **2001**, *3*, 4091–4094; c) F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, *J. Am. Chem. Soc.* **2002**, *124*, 12210–12216; d) Z. P. Demko, K. B. Sharpless, *Org. Lett.* **2002**, *4*, 2525–2527; e) Z. P. Demko, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2110–2113; f) Z. P. Demko, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2113–2116; g) F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, *J. Am. Chem. Soc.* **2003**, *125*, 9983–9987.

[4] a) X.-M. Chen, M.-L. Tong, *Acc. Chem. Res.* **2007**, *40*, 162–170; b) S. Hu, J.-C. Chen, M.-L. Tong, B. Wang, Y.-X. Yan, S. R. Batten, *Angew. Chem. Int. Ed.* **2005**, *44*, 5471–5475; c) J. Wang, S.-L. Zheng, S. Hu, Y.-H. Zhang, M.-L. Tong, *Inorg. Chem.* **2007**, *46*, 795–800.

[5] a) M.-L. Tong, Y.-M. Wu, Y.-X. Tong, X. M. Chen, H.-C. Chang, S. Kitagawa, *Eur. J. Inorg. Chem.* **2003**, 2385–2388; b) L.-L. Zheng, W.-X. Zhang, L.-J. Qian, J.-D. Leng, J.-X. Luo, M.-L. Tong, *Inorg. Chem.* **2007**, *46*, 9548–9557.

[6] a) T. Wu, B.-H. Yiand, D. Li, *Inorg. Chem.* **2005**, *44*, 4130–4132; b) L.-Z. Wang, Z.-R. Qu, H. Zhao, X.-S. Wang, R.-G. Xiong, Z.-L. Xue, *Inorg. Chem.* **2003**, *42*, 3969–3971; c) P. Lin, C. William, R. W. Harrington, R. A. Henderson, *Dalton Trans.* **2005**, 2388–2394; d) J.-R. Li, Y. Tao, Q. Y, X.-H. B, *Chem. Commun.* **2007**, 1527–1529.

[7] a) M. Friedrich, J. C. Gálvez-Ruiz, T. M. Klapo1tke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 8044–8052; b) E.-Q. Gao, N. Liu, A.-L. Cheng, S. Gao, *Chem. Commun.* **2007**, 2470–2472.

[8] a) L. Örhström, L. Larsson, *Molecule-Based Materials: The Structural Network Approach*, Elsevier, **2005**; b) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.

[9] C.-K. Tan, J. Wang, J.-D. Leng, L.-L. Zheng, M.-L. Tong, *Eur. J. Inorg. Chem.*, DOI: 10.1002/ejic.200700930.

[10] A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2001**.

[11] a) W. Chen, J.-Y. Wang, C. Chen, Q. Yue, H.-M. Yuan, J.-S. Chen, S.-N. Wang, *Inorg. Chem.* **2003**, *42*, 944–946; b) S.-L. Zheng, X.-M. Chen, *Aust. J. Chem.* **2004**, *57*, 703–712; c) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun, S. L. Qiu, *Inorg. Chem.* **2006**, *45*, 3582–3587; d) Q. R. Fang, G. S. Zhu, Z. Jin, M. Xue, X. Wei, D. J. Wang, S. L. Qiu, *Cryst. Growth Des.* **2007**, *7*, 1035–1037; e) J.-R. Li, Y. Tao, Q. Yu, X.-H. Bu, *Chem. Commun.* **2007**, 1527–1529; f) X. Shi, G. S. Zhu, Q. R. Fang, G. Wu, G. Tian, R. W. Wang, D. L. Zhang, M. Xue, S. L. Qiu, *Eur. J. Inorg. Chem.* **2004**, 185–191; g) X. L. Wang, C. Qin, E. B. Wang, Z. M. Su, L. Xu, S. R. Batten, *Chem. Commun.* **2005**, 4789–4791; h) Z. Y. Fu, X. T. Wu, J. C. Dai, S. M. Hu, W. X. Du, H. H. Zhang, R. Q. Sun, *Eur. J. Inorg. Chem.* **2002**, *41*, 2730–2735; i) L. L. Wen, D. B. Dang, C. Y. Duan, Y. Z. Li, Z. F. Tian, Q. J. Meng, *Inorg. Chem.* **2005**, *44*, 7161–7170; j) G. Blasse, K. C. Bleijenberg, R. C. Powell, *Structure and Bonding 42*: *Luminescence and Energy Transfer*, Spring, Berlin, **1980**; k) G. A. Crosby, R. G. Highland, K. A. Truesedell, *Coord. Chem. Rev.* **1985**, *64*, 41–53; l) C. Kutal, *Coord. Chem. Rev.* **1990**, *99*, 213–252.

[12] a) H. Yersin, A. Vogler, *Photochemistry and Photophysics of Coordination Compounds*, Springer, Berlin, **1987**; b) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2002**.

[13] G. M. Sheldrick, *SADABS 2.05*, University Göttingen.

[14] *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, **2000**.

Received: October 8, 2007
Published Online: December 3, 2007