1280 *Inorg. Chem.* **2010**, *49*, 1280–1282
DOI: 10.1021/ic901504q

Inorganic Chemistry
Communication

# Structural and Catalytic Performance of a Polyoxometalate-Based Metal−Organic Framework Having a Lanthanide Nanocage as a Secondary Building Block

**Dongbin Dang,[†,‡] Yan Bai,[‡] Cheng He,[†] Jian Wang,[†] Chunying Duan,*[,†] and Jingyang Niu[‡]**

[†]*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China, and*
[‡]*Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China*

Received July 28, 2009

A polyoxometalate-based lanthanide−organic framework was achieved using the $\{[Ho_4(dpdo)_8(H_2O)_{16}BW_{12}O_{40}]\ (H_2O)_2\}^{7+}$ nanocage as a secondary building block for the heterogeneous catalysis of phosphodiester cleavage in an aqueous solution.

Recently, the chemistry of hybrid solid metal−organic frameworks (MOFs) constructed from organic linkers and metal nodes has received much attention, owing to the fine-desired properties by judicious choice of the building blocks. While the ability of these MOFs to incorporate functional groups makes them excellent candidates as heterogeneous catalysts, it remains a great challenge to engineer a strong Lewis acid in MOFs to find applications in many of the processes that are currently catalyzed by zeolites.[1,2] Polyoxometalates (POMs) represent a large class of inorganic oxo clusters that contain early transition metals. Because of the versatile chemical, structural, and electronic properties, they have attracted considerable interest in the fields of solid acid catalytic, electronic, and magnetic materials.[3−6] Also, because of the large number of potential coordination sites and the relatively weak coordination ability of POMs, embedding them into the nanocage or framework of the Werner-type solids might be an efficient approach to creating POM-based coordination polymers with novel structures and interesting properties, especially with homogeneous or heterogeneous catalytic functions.[7−9]

On the other hand, the development of rational approaches to the design of catalysts for hydrolysis of phosphate diesters is a subject continually attracting interest in bioorganic chemistry.[10] Complexes of lanthanide ions have proven to be among the most effective synthetic hydrolases reported to date besides those employing alkaline-earth metal ions such as $Ca^{2+}$ and $Mg^{2+}$. The Lewis acidity of the tri- and tetravalent lanthanide ions, together with their high coordination numbers, fast ligand-exchange rates, and absence of accessible redox chemistry, provides an opportunity to mimic the activity of hydrolases to bind and activate phosphate

---

*To whom correspondence should be addressed. E-mail: cyduan@dlut.edu.cn.

(1) (a) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248–1256. (b) Bee, J.; Farha, O.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459. (c) Czaja, A. U.; Trukhan, N.; Müller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284–1293.

(2) (a) Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 6312–6313. (b) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607–2614. (c) Doonan, C. J.; Morris, W.; Furukawa, H.; Yaghi, M. *J. Am. Chem. Soc.* **2009**, *131*, 9492–9493. (d) Horike, S.; Dinc, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 5854–5855.

(3) (a) Pope, M. T. *Heteropoly- and Isopolyoxometalates*; Springer-Verlag: New York, 1983. (b) Pope, M. T. Polyoxo anions: Synthesis and Structure. *Comprehensive Coordination Chemistry II*; Wedd, A. G., Ed.; Elsevier Science: New York, 2004; Vol. *4*, pp 635−678. (c) Pope, M. T., Müller, A., Eds. *Polyoxometalate Chemistry: From Topology Via Self-Assembly to Applications*; Kluwer: Dordrecht, The Netherlands, 2001. (d) Hill, C. L. Polyoxometalates: Reactivity. *Comprehensive Coordination Chemistry II*; Wedd, A. G., Ed.; Elsevier Science: New York, 2004; Vol. *4*, pp 679−759.

(4) (a) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed.* **1991**, *30*, 34–38. (b) Coronado, E.; Gomez-Garcia, C. J. *Chem. Rev.* **1998**, *98*, 273–296.

(5) (a) Rajkumar, T.; Rao, G. R. *J. Chem. Sci.* **2008**, *120*, 587–594. (b) Rao, G. R.; Rajkumar, T. *Catal. Lett.* **2008**, *120*, 261–273.

(6) (a) Cartuyvels, E.; Absillis, G.; Parac-Vogt, T. N. *Chem. Commun.* **2008**, 85–87. (b) Absillis, G.; Cartuyvels, E.; Deun, R. V.; Parac-Vogt, T. N. *J. Am. Chem. Soc.* **2008**, *130*, 17400–17408.

(7) (a) Kawamoto, R.; Uchida, S.; Mizuno, N. *J. Am. Chem. Soc.* **2005**, *127*, 10560–10567. (b) Jiang, C.; Lesbani, A.; Kawamoto, R.; Uchida, S.; Mizuno, N. *J. Am. Chem. Soc.* **2006**, *128*, 14240–14241. (c) An, H. Y.; Wang, E. B.; Xiao, D. R.; Li, Y. G.; Su, Z. M.; Xu, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 904–908. (d) Zheng, P. Q.; Ren, Y. P.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2005**, *44*, 1190–1192.

(8) (a) Lu, J.; Shen, E. H.; Li, Y. G.; Xiao, D. R.; Wang, E. B.; Xu, L. *Cryst. Growth Des.* **2005**, *5*, 65–67. (b) Ren, Y. P.; Kong, X. J.; Hu, X. Y.; Sun, M.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2006**, *45*, 4016–4023. (c) Kong, X. J.; Ren, Y. P.; Zheng, P. Q.; Long, Y. X.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2006**, *45*, 10702–10711.

(9) For recent examples, see:(a) Knaust, J. M.; Inman, C.; Keller, S. W. *Chem. Commun.* **2004**, 492–493. (b) Lisnard, L.; Dolbecq, A.; Mialane, P.; Marrot, J.; Codjovi, E.; Sécheresse, F. *Dalton Trans.* **2005**, 3913–3920. (c) Shi, Z. Y.; Gu, X. J.; Peng, J.; Yu, X.; Wang, E. B. *Eur. J. Inorg. Chem.* **2006**, 385–388. (d) Li, G. Z.; Salim, C.; Hinode, H. *Solid State Sci.* **2008**, *10*, 121–128. (e) Uehara, K.; Kasai, K.; Mizuno, N. *Inorg. Chem.* **2007**, *46*, 2563–2570.

(10) (a) Lu, Z. L.; Liu, C. T.; Neverov, A. A.; Brown, R. S. *J. Am. Chem. Soc.* **2007**, *129*, 11642–11652. (b) Bunn, S. E.; Liu, C. T.; Lu, Z.; Neverov, A. A.; Brown, R. S. *J. Am. Chem. Soc.* **2007**, *129*, 16238–16248. (c) Humphry, T.; Iyer, S.; Iranzo, O.; Morrow, J. R.; Richard, J. P.; Paneth, P.; Hengge, A. C. *J. Am. Chem. Soc.* **2008**, *130*, 17858–17866. (d) Cacciapaglia, R.; Casnati, A.; Mandolini, L.; Peracchi, A.; Reinhoudt, D. N.; Salvio, R.; Sartori, A.; Ungaro, R. *J. Am. Chem. Soc.* **2007**, *129*, 12512–12520. (e) Liu, C. T.; Neverov, A. A.; Brown, R. S. *J. Am. Chem. Soc.* **2008**, *130*, 16711–16720.

esters for cleavage.[11] However, there are only a few examples of heterogeneous catalysts for hydrolysis of phosphate diesters in an aqueous solution,[12] and no lanthanide-based MOF catalysts have been reported for phosphodiester cleavage in a heterogeneous fashion, to the best of knowledge. Despite that, heterogeneous catalysis exhibits significant potential advantages such as ease of separation, efficient recycling, and minimization of metal traces in the product.[13]

To seek efficient catalysts for hydrolysis of phosphate diesters, herein we report a POM-based MOF having a lanthanide-based nanocage as a secondary building block. It is anticipated that the weak conjugate bases $BW_{12}O_{40}^{5-}$ as counteranions could enhance the Lewis acidity of the lanthanide compound, which is one of the key factors in accelerating the rate of phosphate ester hydrolysis for the metal complexes. 4,4′-Bipyridine-*N*,*N*′-dioxide was selected to act as the longer spacer ligand not only because of the excellent hard acid/hard base complementarity of the lanthanide cations and the *N*-oxide donor but also because of the small steric size of this ligand, which avoids crowding at the metal centers and encourages high connectivity and a large volume of voids.[14]

Compound $\{[Ho_4(dpdo)_8(H_2O)_{16}BW_{12}O_{40}]\cdot 2H_2O\}(BW_{12}O_{40})_2\cdot(H_{1.5}pz)_2\cdot(H_2O)_{11}$ (**1**; Figures 1 and 2) was assembled through a hydrothermal synthesis method using $HoCl_3\cdot 6H_2O$, 4,4′-bipyridine-*N*,*N*′-dioxide hydrate (dpdo), $HoH_2BW_{12}O_{40}\cdot nH_2O$, and hexahydropyrazine (pz) as the reaction origins.[15] It crystallizes in a triclinic space group $P\bar{1}$.[16] Four $Ho^{III}$ ions connected by four bridged dpdo ligands, alternatively, consolidate the main skeleton of the nanocage $\{[Ho_4(dpdo)_8(H_2O)_{16}](H_2O)_2\}^{12+}$. The Ho···Ho separation in the equatorial plane is 13.3 Å. Two terminal dpdo ligands are toward one side of the rhombus, with the symmetry-related pair positioned on the other side. Each pair of terminal dpdo ligands positioned on one side forms hydrogen bonds with one water molecule to further complete the cagelike molecular cavity. The O···O separations of the hydrogen-bonding interaction are 2.67(1) and 2.58(1) Å for O(17W)···O(66) and O(17W)···O(68A), respectively.

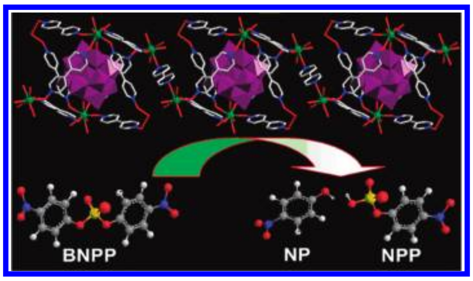

**Figure 1.** One-dimensional ribbon structural pattern of compound **1** composed of the $\{[Ho_4(dpdo)_8(H_2O)_{16}BW_{12}O_{40}](H_2O)_2\}^{7+}$ nanocages for catalysis of phosphodiester bond cleavage in an aqueous solution. The holmium ions, oxygen atoms, nitrogen atoms, phosphorus atoms, and carbon atoms are drawn in green, red, blue, yellow, and gray, respectively.

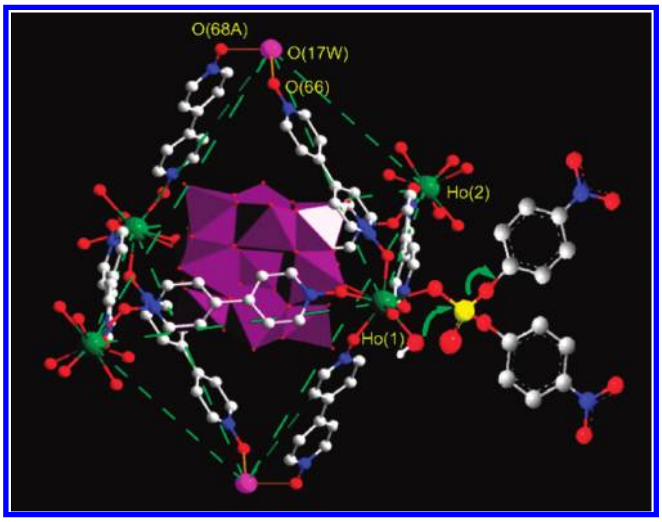

**Figure 2.** Molecular structure of the $\{[Ho_4(dpdo)_8(H_2O)_{16}BW_{12}O_{40}](H_2O)_2\}^{7+}$ nanocage showing the proposed rationale for the disparate reactivity of compound **1** toward BNPP. Selected bond distances (Å): Ho(1)−O(dpdo) 2.31(1), Ho(1)−O($H_2O$) 2.40(1), Ho(2)−O(dpdo) 2.29(2), and Ho(2)−O($H_2O$) 2.36(2) on average (symmetry code: A, 1 − *x*, 1 − *y*, 1 − *z*).

There are two crystallographic independent $Ho^{III}$ centers in a crystal of compound **1**. Ho(1) and Ho(2) are coordinated in distorted trigondodecahedra with three and five water molecules, respectively. The coordination geometry of the lanthanide ions is well consistent with that of the DNA-Foot printing active cyclen-based lanthanide(III) complexes. The water molecules occupy several coordination sites and have the potential to act as removable labile ligands, allowing for substrate binding and the simultaneous provision of a metal-bound nucleophile.[10a] One $BW_{12}O_{40}^{5-}$ anion bridging Ho(1) and Ho(1A) centers is found to fill the three-dimensional body with metal−ligand interactions between Ho(1) and the terminal oxygen atoms of the anion. The Lewis acidity of lanthanide ion Ho(1) is enhanced directly; thus, compound **1** has the potential to exhibit excellent catalytic properties of hydrolysis for modes of natural phosphate esters. Adjacent cages are linked together through coordination bonds between oxygen atoms of the bridging dpdo ligands and

---

(11) (a) Belousoff, M. J.; Ung, P.; Forsyth, C. M.; Tor, Y.; Spiccia, L.; Graham, B. *J. Am. Chem. Soc.* **2009**, *131*, 1106–1114. (b) Tsang, J. S. W.; Neverov, A. A.; Brown, R. S. *J. Am. Chem. Soc.* **2003**, *125*, 1559–1566. (c) Nwe, K.; Andolina, C. M.; Morrow, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 14861–14871. (d) Farquhar, E. R.; Richard, J. P.; Morrow, J. R. *Inorg. Chem.* **2007**, *46*, 7169–7177. (e) Camargo, M. A.; Neves, A.; Bortoluzzi, A. J.; Szpoganicz, B.; Martendal, A.; Murgu, M.; Fischer, F. L.; Terenzi, H.; Severino, P. C. *Inorg. Chem.* **2008**, *47*, 2919–2921.

(12) (a) Bodsgard, B. R.; Burstyn, J. N. *Chem. Commun.* **2001**, 647–648. (b) Zaupa, G.; Prins, L. J.; Scrimin, P. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3816–3820.

(13) Heitbaum, M.; Glorius, F.; Escher, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4732–4762.

(14) (a) Hill, R. J.; Long, D. L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 337–350. (b) Wei, M. L.; He, C.; Hua, W. J.; Duan, C. Y.; Li, S. H.; Meng, Q. J. *J. Am. Chem. Soc.* **2006**, *128*, 13318–13319.

(15) Compound **1** was prepared from a hydrothermal reaction by putting $\alpha$-$HoH_2BW_{12}O_{40}\cdot nH_2O$, $HoCl_3\cdot 6H_2O$, 4,4′-bipyridine-*N*,*N*′-dioxide hydrate, hexahydropyrazine, and water with a molar ratio of 1:3:3:7:1600 into a Teflon-lined stainless steel autoclave and keeping the resulting mixture under autogenous pressure at 120 °C for 3 days. Yellow crystals suitable for single-crystal X-ray structure analysis were isolated and washed with distilled water (about 70% yield based on $HoH_2BW_{12}O_{40}\cdot nH_2O$). Anal. Calcd for $C_{128}H_{175}B_3Ho_4N_{28}O_{172}W_{36}$: C, 12.63; H, 1.45; N, 3.22; B, 0.27; W, 54.39; Ho, 5.42. Found: C, 12.55; H, 1.50; N, 3.20; B, 0.25; W, 54.19; Ho, 5.52. IR (KBr, $cm^{-1}$): three characteristic asymmetric vibrations from heteropolyanions, $\nu(W{-}O_c)$ 809, $\nu(B{-}O_a)$ 905, $\nu(B{-}O_d)$ 955; four characteristic vibrations from dpdo molecules, $\nu$(N−O) 1227, $\nu$(ring) 1473, $\nu$(C−H, in-plane) 1180, $\nu$(N−O) 839.

(16) Crystal data of **1** for $C_{128}H_{175}B_3Ho_4N_{28}O_{172}W_{36}$, $M_r$ = 12 168.71, triclinic, space group $P\bar{1}$ with $a$ = 18.922(1) Å, $b$ = 20.038(1) Å, $c$ = 20.789(1) Å, $V$ = 6160.4(3) Å$^3$; $Z$ = 1; $\rho_{calcd}$ = 3.280 g cm$^{-3}$; $T$ = 293(2) K. The final refinement gave R1 = 0.0598, wR2 = 0.1270, and GOF = 1.03 for 11 697 observed reflections with $I > 2\sigma(I)$.

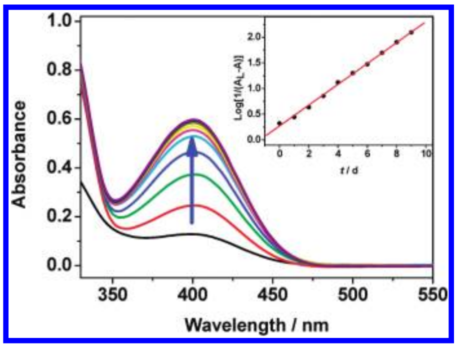

**Figure 3.** Family of UV−visible absorbance spectra of a 4-nitrophenoxide anion formed from the cleavage of BNPP in $H_2O$ at 50 °C. Inset: Kinetic plot of hydrolysis of BNPP using compound **1** as the catalyst. $A$ is the observed absorbance, and $A_L$ is the final absorbance at the end of the reaction.

two Ho(2) atoms from different cages, generating a one-dimensional ribbon composed of the nanocages. Adjacent ribbons are linked together through intermolecular hydrogen bonds and $\pi\cdots\pi$-stacking interactions in the crystal. Free $BW_{12}O_{40}{}^{5-}$ anions and solvent water molecules are found to fill the pores of the crystals.

The heterogeneous catalysis of compound **1** for phosphodiester bond cleavage is evidenced. An aqueous solution of Bis(4-nitrophenyl) phosphate (BNPP, 10 mM, pH 4.0) was stirred at 50 °C, with a polycrystalline sample of **1** (15 mol %) being suspended as the heterogeneous catalyst. Cleavage of BNPP was followed by monitoring of the increase in absorbance at 400 nm due to formation of an 4-nitrophenoxide anion, generally, and no obvious pH change was observed during the catalytic processes. As can be seen in Figure 3, a plot of the reaction progress $\log[1/(A_L - A)]$ against time fits well with the pseudo-first-order rate equation, giving a rate constant $k_{obs}$ of $2.35\ (\pm 0.04) \times 10^{-6}\ s^{-1}$ and a half-life time of $2.95 \times 10^5$ s, respectively.[17] Because the free $BW_{12}O_{40}{}^{5-}$ anions (in sodium salt) do not exhibit any significant catalytic activity for hydrolytic cleavage of the phosphodiester, the possible catalytic activity of compound **1** should be attributed to the lanthanide MOF. Furthermore, the conversion of BNPP is higher with a certain number of moles of the heterogeneous catalyst than it is in prior studies using a similar number of moles of a homogeneous catalyst,[18] indicative of a rapid acceleration of the cleavage of BNPP.

BNPP cleavage progress was also monitored by $^{31}P$ NMR. During the course of the reaction, there are three $^{31}P$ NMR signals corresponding to inorganic phosphate ($\delta$ 0.04), *p*-nitrophenyl phosphate ($\delta$ −4.81), and BNPP ($\delta$ −11.21). At the end of the reaction, only the signal due to inorganic phosphate remains. Interestingly, crystals of compound **1** were easily isolated from the reaction suspension by filtration alone and reused three times, displaying only a slight decrease in activity. The exact index of the X-ray diffraction (XRD) patterns of compound **1** after the catalytic reaction supports that the crystallographic data characteristic of compound **1** are maintained directly. The effect of the pH on the cleavage reaction was also investigated.[19] In a comparison under optimum conditions, $k_{obs}$ is only slightly decreased with a decrease or increase of the pH of the solution, and the fastest cleavage is observed at pH 4.0 (Table S4 in the Supporting Information).

From a structural point of view, the large size and high coordination number of $Ho^{3+}$, the small steric size of the dpdo ligand, and the steric constraints of the formation of cagelike molecular structures avoid crowding at the metal centers and encourage high connectivity. The presence of water molecules as the labile ligands allows for substrate binding and the simultaneous provision of a metal-bound nucleophile. The directed coordination of the $BW_{12}O_{40}{}^{5-}$ anion to the lanthanide ions results in a significant feature of the nanosize compound with the activity of the acid surface (Figure 1), benefitting facilitation of the transesterification step by virtue of its additional labile ligand sites, conceivable through the provision of a hydroxide ligand.[10a] In the meantime, the surface properties of the nanocages also meet a number of criteria of artificial phosphoesterases such as an overall positive charge, the presence of coordinated water, and the presence of functional groups for acid catalysis.[17,20]

In conclusion, a POM-based lanthanide MOF exhibiting a heterogeneous catalytic performance for phosphodiester bond cleavage in an aqueous solution was achieved using the nanocage $\{[Ho_4(dpdo)_8(H_2O)_{16}BW_{12}O_{40}](H_2O)_2\}^{7+}$ as a secondary building block. Phosphodiester bond cleavage promoted by the compound under heterogeneous conditions suggests a pseudo-first-order hydrolytic cleavage reaction. Studies involving other types of lanthanide polymers containing POMs as artificial phosphoesterases are currently underway.

**Acknowledgment.** We gratefully acknowledge financial support from the National Natural Science Foundation of China, the Key Project of Chinese Ministry of Education (Grant 207068), and the China Postdoctoral Science Foundation (Grant 20080431135).

**Supporting Information Available:** Physical measurements, crystallographic data in CIF format, IR, TGA, and XRD patterns of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[17] Hydrolysis of BNPP in the absence of a metal complex was almost negligible, compared to that of the catalytic reaction; however, the final value of $k_{obs}$ was also adjusted for the background cleavage.

[18] Takasaki, B. K.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 9337–9338.

[19] The pH of the solutions was adjusted with hydrochloric acid and NaOH and measured before and after the hydrolysis reaction.

[20] Williams, N. H.; Takasaki, B.; Wall, M.; Chin, J. *Acc. Chem. Res.* **1999**, *32*, 485–493.