



Templated synthesis of a layered erbium-organic framework based on 4,6-dimethyl-5-nitroisophthalic acid (H₂dna)

Guoqing Zhang^{a,1}, Xiaoliang Zhao^{a,1}, Fangna Dai^a, Daofeng Sun^{a,b,*}

^a Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China

ARTICLE INFO

Article history:

Received 9 February 2011

Accepted 14 March 2011

Available online 22 March 2011

Keywords:

Lanthanide

Templated synthesis

Cavity

4,6-dimethyl-5-nitroisophthalic acid

ABSTRACT

A new 2D lanthanide-organic framework with 1D rod-shaped SBUs based on 4,6-dimethyl-5-nitroisophthalic acid has been solvothermally synthesized. The uncoordinated 4,4'-bipy ligands, which are trapped in the cavities by forming weak offset face-to-face pyridine-phenyl interaction with the wall of the cavities, play a template role in the formation of the 2D layer. To the best of our knowledge, this is the first 2D lanthanide-organic framework that synthesized by templated synthesis.

© 2011 Elsevier B.V. All rights reserved.

Crystal engineering of metal-organic frameworks (MOFs) provides a powerful tool for the design and synthesis of new crystalline materials with unique physical properties [1]. In the past decades, many functional metal-organic frameworks based on transition metal, lanthanide ion or their combination with catalysis, gas adsorption and separation properties have been synthesized and characterized through various synthetic methods [2–4]. In particular, the use of organic structure-directing agents as templates is an efficient strategy on the construction of desirable compounds. The templated organic molecules or hybrid metal ion can play different roles, including framework support and/or charge balance to the hosts, which has been widely used in the synthesis of zeolite, phosphates, and sulfates system [5], but are still rare in MOF system [6]. Recently, the 3D porous lanthanide-organic frameworks templated by organic molecules, such as 4,4'-bipyridine, have been reported by Cahill group [7]. Hong and coworkers have synthesized two 3D cavity lanthanide-organic frameworks with trapped or bonded transition-metal complexes [8]. However, the 2D layered lanthanide-organic frameworks with cavity that can trap organic molecules or templates are still rare. In this communication, we report a layered erbium-organic framework, Er₂(H₂O)(dmf)(dna)₃·(bipy)_{0.5}·2H₂O·dmf (**1**) (H₂dna = 4,6-dimethyl-5-nitroisophthalic acid, bipy = 4,4'-bipyridine), with 4,4'-bipyridine molecules as the template in the large cavity.

The solvothermal reaction of Er(NO₃)₃·6H₂O, H₂dna and 4,4'-bipyridine in dmf resulted in the formation of a large amount of pink crystals of **1** [9], which is structurally characterized by single crystal X-ray diffraction [10]. The formula of Er₂(H₂O)(dmf)(dna)₃·(bipy)_{0.5}·2H₂O·dmf was further confirmed by elemental analysis and thermal gravimetric analysis (TGA).

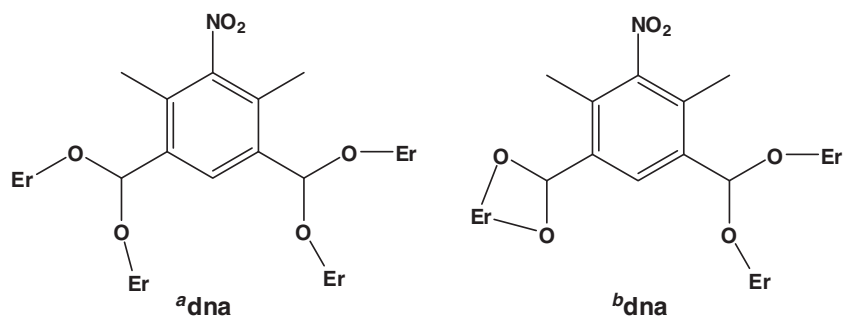
X-ray single crystal structure analysis reveals that complex **1** crystallizes in monoclinic *P*2₁/*n* space group. The asymmetric unit consists of two erbium ions, three dna ligands, one coordinated water molecule, one coordinated dmf molecule, half uncoordinated 4,4'-bipy molecule, two uncoordinated water molecules and one uncoordinated dmf molecule. There are two crystallographically independent erbium ions (Er1 and Er2): Er1 is coordinated by seven oxygen atoms from six dna ligands, while Er2 is coordinated by seven oxygen atoms from five dna ligands, one coordinated water molecule and one coordinated dmf molecule, with the average Er–O distance of 2.234 and 2.282 Å, respectively. There are two types of dna ligands with different coordination modes: a) each carboxylate group adopts bidentate bridging mode to link two erbium ions (^adna, Scheme 1a); b) one carboxylate group adopts bidentate bridging mode to link two erbium ions, whereas the other one adopts chelating mode to coordinate to one erbium ion (^bdna, Scheme 1b).

Thus, Er1 and Er2 ions were connected by ^adna ligands along *b* axis to generate a 1D double helical chain with infinite Er–O–C rods (Fig. 1). The 1D Er–O–C rods in **1** are slightly different from other reported results [11]. The nearest Er–Er distance in the double helical chain is 4.608 Å. The 1D double helical chains were further connected by ^bdna ligands to result in the formation of a 2D layer with large cavities, in which the uncoordinated 4,4'-bipy molecules reside (Fig. 2). The cavity consists of eight dna ligands and is hydrophobic. Hence, there are no hydrogen

* Corresponding author at: Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, China. Tel.: +86 531 88364218; fax: +86 531 88364464.

E-mail address: dfsun@sdu.edu.cn (D. Sun).

¹ These authors contributed equally to this work.



Scheme 1. The coordination modes of dna in **1**.

bonding interactions between the 4,4'-bipy molecules and the wall of the cavity. However, as shown in Fig. 3, the trapped 4,4'-bipy molecules interact with two ^adna ligands through weak offset face-to-face pyridine–phenyl interactions ($d_{\text{centroid}\cdots\text{centroid}} = 3.947 \text{ \AA}$), which is different from other results containing uncoordinated 4,4'-bipy molecules [12]. Thus, the uncoordinated 4,4'-bipy molecules may play the role of template in the formation of the 2D layer framework. In the 2D layer, all the coordinated dmf molecules and the nitril groups of dna

ligands point out of the layer, whereas the uncoordinated dmf and water molecules locate above the windows of the cavities. The separation of the 2D layers is 15.19 Å.

Thermogravimetric analysis has measured for complex **1**. A TGA study on an as-isolated crystalline sample of **1** shows a 10.2% weight loss from 99 to 160 °C, corresponding to the loss of one uncoordinated water molecule, one uncoordinated dmf molecule and two coordinated water molecules (calcd: 9.6%). The second gradual weight loss

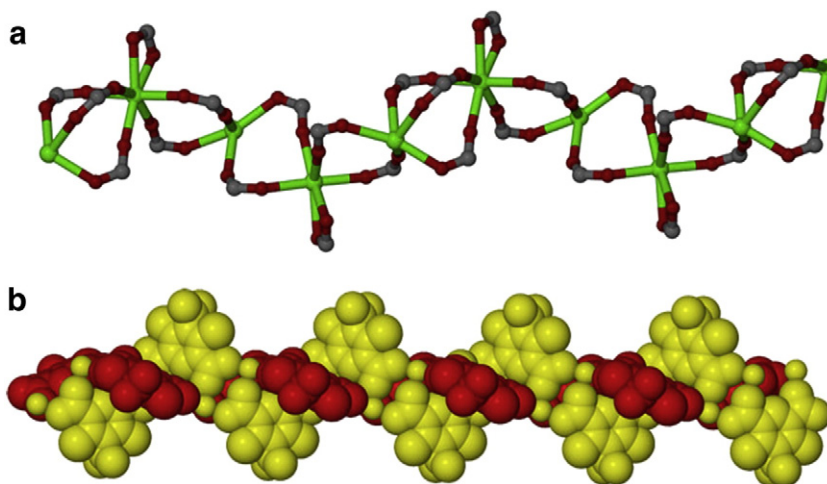


Fig. 1. a) the 1D rod-shaped SBU; b) the 1D double helical chain existed in **1**.

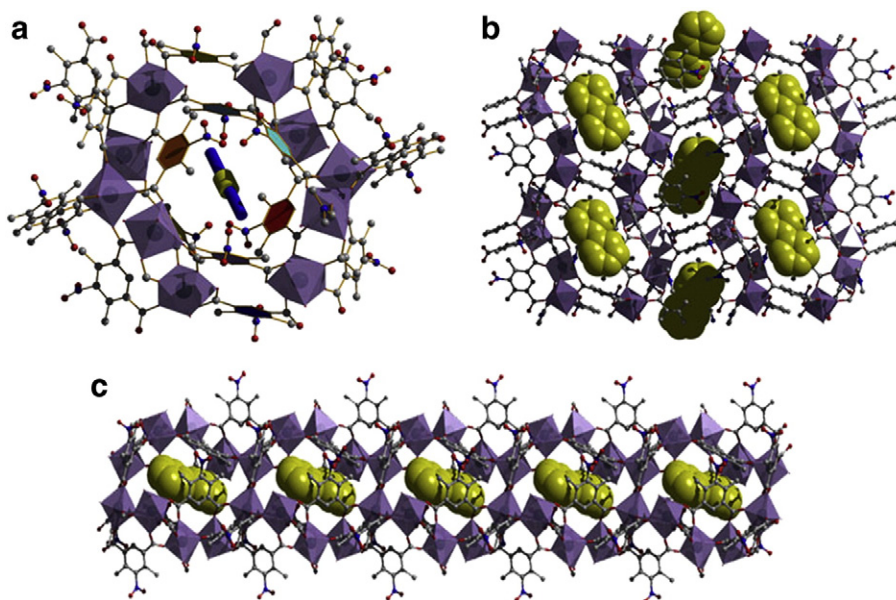


Fig. 2. a) The cavity with trapped 4,4'-bipy (blue rod); b) and c) the 2D layer viewed in different directions (the uncoordinated bipy molecules were shown in yellow color).

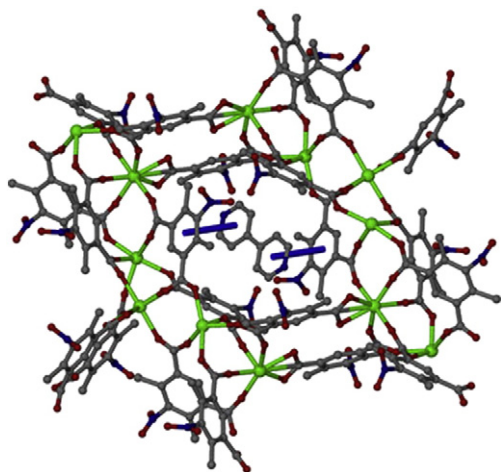


Fig. 3. View of the 4,4'-bipy molecule trapped in the cavity, showing the weak offset face-to-face pyridine–phenyl interactions between the pyridine groups and the dna ligands.

of 5.8% from 160 to 257 °C corresponds to the loss of one coordinated dmf molecule (calcd: 5.5%), and after 257 °C, the loss of uncoordinated 4,4'-bipy molecules starts, and following that is the decomposition of the framework.

In summary, a new 2D erbium-organic framework with uncoordinated 4,4'-bipy molecules as the template has been synthesized and characterized. The 4,4'-bipy molecules have weak offset face-to-face pyridine–phenyl interactions with the wall of the cavities. To the best of our knowledge, this is the first example that 4,4'-bipy acts as structure directing agent to template the formation of the layered erbium-organic framework with large cavities. Further study will focus on the assembly of other lanthanide-organic frameworks through templated synthesis.

Acknowledgements

We gratefully thank the financial support of the National Natural Science Foundation of China (Grant 90922014), the Shandong Natural Science Fund for Distinguished Young Scholars (2010JQE27021), the National Natural Science Foundation of Shandong Province (Y2008B01, BS2009CL007), and Independent Innovation Foundation of Shandong University (2010JQ011).

Appendix A. Supplementary material

CCDC 809482 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

- (a) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal-organic carboxylate frameworks, *Acc. Chem. Res.* 34 (2001) 319–330;
- (b) B.F. Abrahams, P.A. Jackson, R. Robson, A robust (10,3)-a network containing chiral micropores in the AgI coordination polymer of a bridging ligand that provides three bidentate metal-binding sites, *Angew. Chem. Int. Ed.* 37 (1998) 2656–2659;
- (c) M. Sarkar, K. Biradha, Crystal engineering of metal-organic frameworks containing amide functionalities: studies on network recognition, transformations, and exchange dynamics of guests and anions, *Cryst. Growth Des.* 7 (2007) 1318–1331.
- For recent reviews, see: (a) D.J. Collins, H.C. Zhou, Hydrogen storage in metal-organic frameworks, *J. Mater. Chem.* 17 (2007) 3154–3160; (b) L. Q. Ma, C. Abney, W. B. Lin, Enantioselective catalysis with homochiral metal-organic frameworks, *Chem. Soc. Rev.* 38 (2009) 1248–1256; (c) L. J. Murray, M. Dinca, J. R. Long,

- Hydrogen storage in metal-organic frameworks, *Chem. Soc. Rev.* 38 (2009) 1294–1314; (d) R. Q. Zou, A. I. Abdel-Fattah, H. W. Xu, Y. S. Zhao, D. D. Hickmott, Storage and separation applications of nanoporous metal-organic frameworks, *CrystEng-Comm.* 12 (2010) 1337–1353; (e) R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Q. Yuan, D. Zhao, W. J. Zhuang, H.C. Zhou, Potential applications of metal-organic frameworks, *Coord. Chem. Soc.* 253 (2009) 3042–3066; (f) A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks, *Acc. Chem. Res.* 43 (2010) 58–67.
- (a) C.Y. Su, A.M. Goforth, M.D. Smith, P.J. Pellechia, H.C. zur Loye, Exceptionally stable, hollow tubular metal-organic architectures: synthesis, characterization, and solid-state transformation study, *J. Am. Chem. Soc.* 126 (2004) 3576–3586;
 - (b) L.J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C.M. Brown, J.R. Long, Highly-selective and reversible O₂ binding in Cr₃(1,3,5-benzenetricarboxylate)₂, *J. Am. Chem. Soc.* 132 (2010) 7856–7857;
 - (c) F.J. Song, C. Wang, J. Falkowski, M. Joseph, L.Q. Ma, W.B. Lin, Isorecticular chiral metal-organic frameworks for asymmetric alkene epoxidation: tuning catalytic activity by controlling framework catenation and varying open channel sizes, *J. Am. Chem. Soc.* 132 (2010) 15390–15398;
 - (d) Z. Jin, H.Y. Zhao, X.J. Zhao, Q.R. Fang, J.R. Long, G.S. Zhu, A novel microporous MOF with the capability of selective adsorption of xylenes, *Chem. Commun.* 46 (2010) 8612–8614;
 - (e) C.M. Jin, C.F. Ye, B.S. Zabinski, W.M. Liu, J.M. Shreeve, Polyethylene glycol functionalized dicationic ionic liquids with alkyl or polyfluoroalkyl substituents as high temperature lubricants, *J. Mater. Chem.* 16 (2006) 1529–1535;
 - (f) D.F. Sun, S.Q. Ma, Y.X. Ke, D.J. Collins, H.-C. Zhou, An interweaving MOF with high hydrogen uptake, *J. Am. Chem. Soc.* 128 (2006) 3896–3897.
 - (a) T.F. Liu, J. Lue, X. Lin, R. Cao, Construction of a trigonal bipyramidal cage-based metal-organic framework with hydrophilic pore surface via flexible tetrapodal ligands, *Chem. Commun.* 46 (2010) 8439–8441;
 - (b) M.R. Kishan, J. Tian, P.K. Thallapally, C.A. Fernandez, S.J. Dalgarno, J.E. Warren, B.P. McGrail, J.L. Atwood, Flexible metal-organic supramolecular isomers for gas separation, *Chem. Commun.* 46 (2010) 538–540;
 - (c) H.J. Park, M.P. Suh, Stepwise and hysteretic sorption of N₂, O₂, CO₂, and H₂ gases in a porous metal-organic framework [Zn₂(BPnDC)₂(bpy)], *Chem. Commun.* 46 (2010) 610–612;
 - (d) S. Mohapatra, K.P.S.S. Hembram, U. Waghmare, T.K. Maji, Immobilization of alkali metal ions in a 3D lanthanide-organic framework: selective sorption and H₂ storage characteristics, *Chem. Mater.* 21 (2009) 5406–5412;
 - (e) H.L. Jiang, N. Tsumori, Q. Xu, A series of (6,6)-connected porous lanthanide-organic framework enantiomers with high thermostability and exposed metal sites: scalable syntheses, structures, and sorption properties, *Inorg. Chem.* 49 (2010) 10001–10006;
 - (f) C.M. Jin, L.Y. Wu, H. Lu, Two distinct supramolecular motifs from bis(2-methylimidazo-1-yl)methane: an infinite [n]catenane and a discrete M₆ metal-organic framework, *Cryst. Growth Des.* 8 (2008) 215–218.
 - (a) L. Gomez-Hortiguera, A.B. Pinar, J. Perez-Pariante, F. Cora, Structure-directing effect of (S)-(–)-N-benzylpyrrolidine-2-methanol and benzylpyrrolidine in the synthesis of STA-1: a new computational model for structure direction of nanoporous systems, *Chem. Mater.* 21 (2009) 3447–3457;
 - (c) S.I. Zones, A.W. Burton, G.S. Lee, M.M. Olmstead, A study of piperidinium structure-directing agents in the synthesis of silica molecular sieves under fluoride-based conditions, *J. Am. Chem. Soc.* 129 (2007) 9066–9079;
 - (d) J.H. Yu, R.R. Xu, Rational approaches toward the design and synthesis of zeolitic inorganic open-framework materials, *Acc. Chem. Res.* 43 (2010) 1195–1204.
 - (a) Q.R. Fang, G.S. Zhu, M. Xue, Z.P. Wang, J.Y. Sun, S.L. Qiu, Amine-templated assembly of metal-organic frameworks with attractive topologies, *Cryst. Growth Des.* 8 (2008) 319–329;
 - (b) Z.-G. Sun, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng, Guest controlled coordination framework: syntheses, crystal structures and thermal properties of two three-dimensional structures of [Ce₂(adipate)₃(OH₂)₄]·6H₂O and [Ce₂(adipate)₃(OH₂)₄]·4H₂O·(adipic acid), *Inorg. Chem. Commun.* 5 (2002) 629–632;
 - (c) Z. Shi, G. Li, L. Wang, L. Gao, X. Chen, J. Hua, S. Feng, Two three-dimensional metal-organic frameworks from secondary building units of Zn₈(OH)₄(O₂C–)₁₂ and Zn₂((OH)(O₂C–)₃: [Zn₂(OH)(btc)]₂(4,4'-bipy) and Zn₂(OH)(btc)(pipe), *Cryst. Growth Des.* 4 (2004) 25–27.
 - (d) D.T. de Lill, N.S. Gunning, C.L. Cahill, Toward templated metal-organic frameworks: synthesis, structures, thermal properties, and luminescence of three novel lanthanide-adipate frameworks, *Inorg. Chem.* 44 (2005) 258–266.
 - (f) Y.F. Zhou, F.L. Jiang, D.Q. Yuan, B.L. Wu, R.H. Wang, Z.Z. Lin, M.C. Hong, Copper complex cation templated gadolinium(III)-isophthalate frameworks, *Angew. Chem. Int. Ed.* 43 (2004) 5665–5668.
 - (g) H₂dna (2.4 mg, 0.01 mmol), ErCl₃·6H₂O (15.2 mg, 0.04 mmol) and 4,4'-bipy (1.9 mg, 0.01 mmol) were dissolved in DMF/EtOH/H₂O (1:1:1, v/v, 1 ml). The solution was sealed in a glass tube and heated to 75 °C for 50 hours. The pink crystals were obtained and washed with dmf. Yield: 57%. Elemental analysis calcd (%) for 1: C 37.27, H 3.20, N 6.36; found: C 38.34, H 3.25, N 6.78 %.
 - (h) Crystal data for 1: C₄₁H₄₃Er₂N₆O₂₂, Monoclinic, space group P2₁/n, M = 1306.33, a = 16.2217(8) Å, b = 14.4577(7) Å, c = 23.2526(11) Å, β = 109.3110(10)° V = 5146.6 (4) Å³, Z = 4, ρ = 1.686 g/cm³, GOF = 1.019. A total of 31856 reflections were collected and 13569 reflections are unique (Rint = 0.0567). R1/wR2 = 0.0442/0.1255 for 640 parameters and 13569 reflections I > 2σ(I). The intensity data was collected on a Bruker Smart APEXII CCD Diffractometer with graphite-monochromated Mo-Kα

- radiation ($\lambda = 0.71073 \text{ \AA}$). All absorption corrections were performed by using the SADABS program. The structure was solved by direct methods and refined by SHELXL-97 program. All non-hydrogen atoms were refined anisotropically.
- [11] (a) X.D. Guo, G.S. Zhu, F.X. Sun, Z.Y. Li, X.J. Zhao, X.T. Li, H.C. Wang, S.L. Qiu, Synthesis, structure, and luminescent properties of microporous lanthanide metal-organic frameworks with inorganic rod-shaped building units, *Inorg. Chem.* 45 (2006) 2581–2587;
- (b) T.M. Reineke, M. Eddaoudi, M.O. Keeffe, O.M. Yaghi, A microporous lanthanide-organic framework, *Angew. Chem. Int. Ed.* 38 (1999) 2590–2594;
- (c) C. Serre, F. Millange, J. Marrot, G. Ferey, Hydrothermal synthesis, structure determination, and thermal behavior of new three-dimensional europium terephthalates: MIL-51LT, HT and MIL-52 or $\text{Eu}_2\text{n}(\text{OH})_x(\text{H}_2\text{O})_y(\text{O}2\text{C-C}_6\text{H}_4 - \text{CO}_2)_z$ ($n = \text{III, III, II}$; $x = 4, 0, 0$; $y = 2, 0, 0$; $z = 1, 1, 2$), *Chem. Mater.* 14 (2002) 2409–2415;
- (d) L. Pan, M. Zheng, Y. Wu, S. Han, R. Yang, X. Huang, J. Li, Synthesis, characterization and structural transformation of a condensed rare earth metal coordination polymer, *Inorg. Chem.* 40 (2001) 828–830.
- [12] (a) H.Y. He, F.N. Dai, A.P. Xie, X. Tong, D.F. Sun, Three novel 3D metal-organic frameworks with a 1D ladder, tube or chain as assembly units, *CrystEngComm.* 10 (2008) 1429–1435;
- (b) C.M. Wang, C.H. Liao, H.M. Kao, K.H. Lii, Hydrothermal synthesis and characterization of $[(\text{UO}_2)_2\text{F}_8(\text{H}_2\text{O})_2\text{Zn}_2(4,4'\text{-bpy})_2] \cdot (4,4'\text{-bpy})$, a mixed-metal uranyl aquofluoride with a pillared layer structure, *Inorg. Chem.* 44 (2005) 6294–6298.