An Unusual 3D Interdigitated Architecture Self-Assembled from Sidearm-Containing 2D Bilayer Motifs with a Cuboidal Framework

Xin-Long Wang,[a] Chao Qin,[a] En-Bo Wang,*[a] and Lin Xu[a]

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The new complex [Zn(H_2bptc)(bpy)]·0.5bpdo (**1**) [H_4bptc = 3,3′,4,4′-biphenyltetracarboxylic acid, bpy = 4,4′-bipyridine, and bpdo = 4,4′-bipyridine *N*,*N*′-dioxide] has been synthesized and characterized. It exhibits a novel (2D→3D) interdigitated architecture that is obtained for the first time from the self-assembly of sidearm-containing bilayer motifs with a cuboidal framework, in which each cuboidal box of one bilayer is interdigitated by two arms that belong to two adjacent bilayers. The luminescent properties of **1** are discussed.

Introduction

The interest in entangled systems is rapidly increasing not only for their potential applications as functional materials[1] but also their aesthetic and often complicated architectures and topologies.[2] Interpenetrating networks are the most popular among the entangled polymeric systems, and many appealing interpenetrated frameworks have been constructed, aided by the rapid growth of network-based crystal engineering, and have been well discussed in two comprehensive reviews by Robson and Batten.[3] More recently, a complete analysis of all 3D interpenetrated metal-organic framework structures contained in the CSD database has been proposed with a rationalization and classification of the topology of interpenetration.[4] A characteristic feature of interpenetration is that it is necessary to break internal connections in order to separate the individual nets. In contrast, other types of polymeric supramolecular architectures can, in principle, be disentangled without the need for breaking links (hereafter referred to as "extricable entanglement"), and their resulting overall architectures are more flexible than the usual networks entirely based on coordination bonds − a functional property that has potential applications ranging from drug-delivery vehicles to sensor devices.[5] Unfortunately, these species are much less known, as evidenced by a recent review by Ciani and co-workers.[6] At present, limited examples include infinite multiple helices,[7] cloth-like warp-and-weft sheet structures,[8] interdigitation,[9] and polypseudo-rotaxane structures.[10] Up to now, of the previously reported interdigitated examples, almost all are related to highly undulating *single* layers containing small and cramped windows,[9a,9b] including two exceptional cases in which interdigitation occurs between two different structural motifs (a 1D chain and a 2D puckered layer).[9c,9d] A molecular bilayer as a new structural motif was not reported until recently,[11] although since then several types of bilayer architectures have been fabricated by the assembly of T-shaped,[12] non-T-shaped,[13] or rectangular segments.[14] To the best of our knowledge, the only known interdigitated species containing *double* layer motifs is [Ag(bpe)($L_{0.5}$)]·H_2O [bpe = 1,2-bis(4-pyridyl)ethane; L = 4,4′-biphenyldicarboxylate,[9e] which is comprised of two sets of polycatenated T-shaped bilayers and where, quite surprisingly, the closest bilayers belonging to the different sets are interdigitated in pairs in a tongue-and-groove fashion.[15] An interesting question that arises from this is whether interdigitated structures can also be generated by the aggregation of other types of bilayers, and, if so, what would they be like.

Fortunately, by trial and error we have isolated such a complex, namely [Zn(H_2bptc)(bpy)]·0.5bpdo (**1**) [H_4bptc = 3,3′,4,4′-biphenyltetracarboxylic acid, bpy = 4,4′-bipyridine, and bpdo = 4,4′-bipyridine *N*,*N*′-dioxide], which, for the first time, defines a 3D interdigitated architecture assembled by sidearm-containing bilayer motifs with a cuboidal framework.

Results and Discussion

Single-crystal X-ray diffraction reveals that **1** (see Exp. Sect. for synthesis) is an extended 3D interdigitated network involving 2D bilayers with dangling arms. Each Zn^{II} atom is coordinated by three carboxylate oxygen atoms from three different bptc ligands and two nitrogen atoms from two bpy ligands to give a distorted trigonal-bipyrami-

[a] Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University,
Changchun, 130024, China
Fax: +86-431-509-8787
E-mail: wangenbo@public.cc.jl.cn

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dal geometry (Figure 1). Two crystallographically equivalent zinc atoms are bridged by a pair of bptc carboxylate ends into a dinuclear zinc unit with a Zn···Zn distance of 3.82(7) Å. The dizinc carboxylate moieties are linked by four *exo*-tridentate bptc ligands (two of the four carboxylate groups do not take part in coordination but are pendent) to two adjacent dinuclear zinc units, thus generating a 1D $[Zn_2(Hbptc)_2]_n$ double chain (Figure S1). The zinc ions have an affinity for a five-coordinate environment, as discussed above, three of which have been used in the construction of the double chain, therefore the remaining two provide additional binding sites, i.e. two bpy ligands coordinate *trans* to each metal center in an axial position, thereby further connecting adjacent double chains into a unique 2D bilayer containing cuboidal boxes of approximate dimensions 11.4×13.0×3.8 Å, as illustrated in Figure 2. The 2D bilayer framework can also be considered as being constructed by two (4,4) grid sheets of composition $[Zn(H_2bptc)(bpy)]$ linked by μ_2-carboxylato groups of bptc.

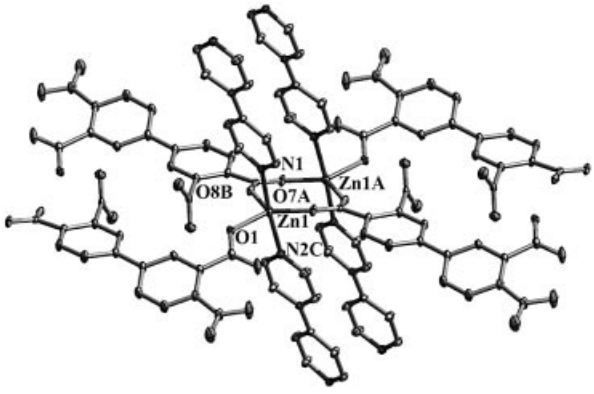

Figure 1. ORTEP view of the Zn^{II} coordination environments. Selected bond lengths [Å]: Zn(1)–O(1) 1.9935(15), Zn(1)–O(7A) 2.0007(14), Zn(1)–O(8B) 2.0189(14), Zn(1)–N(1) 2.1642(16), Zn(1)–N(2C) 2.1665(17). Symmetry codes: A: *x*, *y*, *z* + 1; B: –*x* + 1, –*y* + 1, –*z* + 1; C: *x*, *y* – 1, *z*.

It should be noted that, different from the previously reported bilayers assembled from rectangular building blocks, the unusual bilayer structure reported here has lateral arms pointing out from both sides of the bilayer (Figure 2, bottom). This remarkable feature is a necessary condition for the formation of interdigitation. To sum up, three factors can be envisaged to play roles in the generation of mutual interdigitation in **1**: (i) the presence within the 2D bilayer motifs of very large cuboidal boxes (with dimensions 11.4×13.0×3.8 Å) built up by four pairs of dizinc units, four bptc, and four bipy ligands, (ii) the existence of dangling bptc groups that are disposed in a mutual *anti* orientation with respect to the bilayer plane, and (iii) the fact that all the bilayers are stacked parallel at a distance of about 5.72 Å, while the effective length of each dangling arm is around 8.64 Å (from the baricenter of the dizinc unit to the uncoordinated carboxyl oxygen atom end), thus providing, obviously, the possibility for the ultimate realization of mutual interdigitation. Under these premises, the lateral arms of each bilayer point into the cuboidal voids of the adjacent

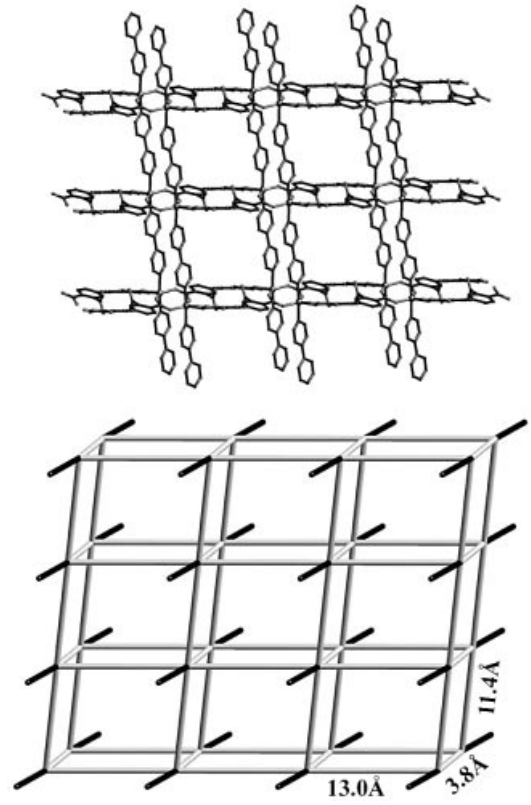

Figure 2. View of the 2D bilayer (top) and a schematic representation of the sidearm-containing 2D bilayer with large cuboidal boxes (bottom).

bilayers, in a mutual relationship. Each cuboidal box is therefore interdigitated by two arms that belong to two different bilayers, one entering from one side and the other from the opposite one, as shown in Figure 3. Finally, this unique fashion originated by the entanglement of three adjacent polymeric motifs at a time gives the novel (2D→3D) interdigitated array of compound **1** (see Figure 4). The aromatic rings of bptc pointing into the cuboidal box are parallel to those of edges bridged by bptc ligands, thus generating the π–π stacking interactions with a face-to-face separation of 3.61 Å that stabilize the whole entanglement. The schematic representation of the "mutual interdigitation" in this species shows that two adjacent bilayers are displaced by about one third of the polymer period along the direction of extension. The sequence of the bilayers in the 3D network is therefore of the ABCABC type (Figure 4).

A potential driving force for interdigitation is the need to fill the void space of a single network. However, in spite of this feature, the resulting 3D network still contains one-dimensional channels running along the *a*-axis and the effective free volume is 20.2%, as calculated by PLATON (Figure S2). Guest bpdo molecules reside in the channels and are hydrogen-bonded to the uncoordinated carbonyl oxygen atom of the bptc [O(6)···O(9) 2.577(3) Å]. Moreover, they form significant π–π stacking interactions with the arm moieties [interplanar distance of 3.55(6) Å], thereby stabilizing the whole 3D host-guest network.

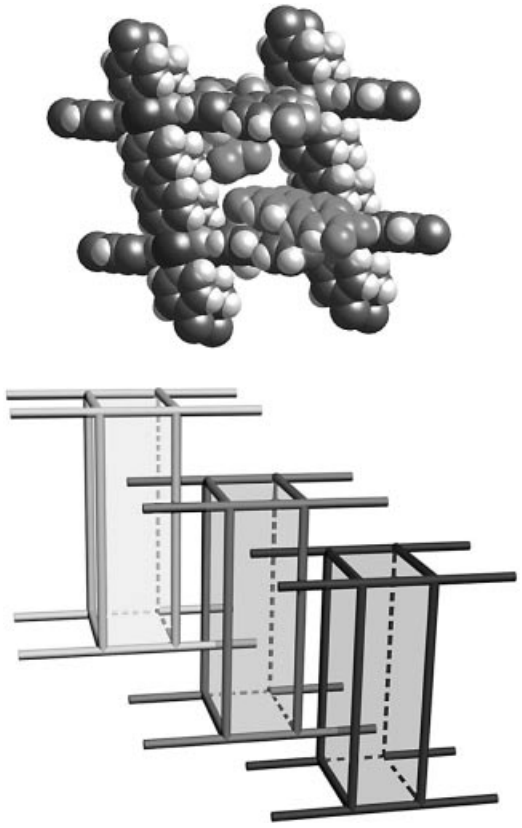

Figure 3. A space-filling model of a cuboidal box of the bilayer showing the two interdigitated arms (top), and a schematic illustration of the mutual interdigitation of three cuboidal boxes from three polymeric bilayers (bottom).

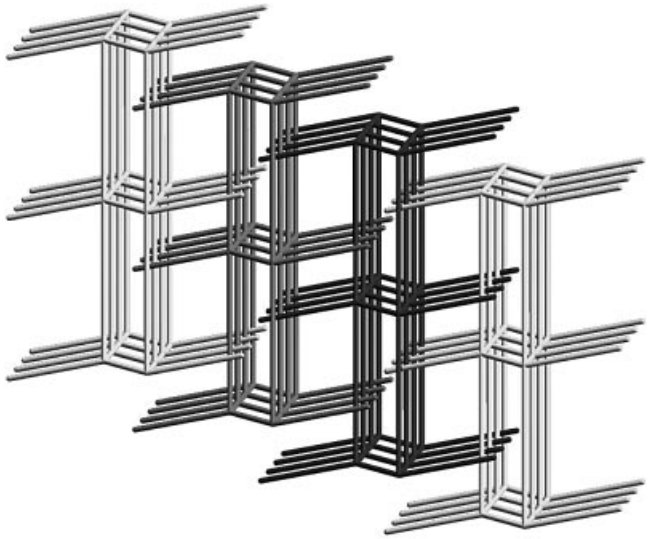

Figure 4. Schematic view of the (2D→3D) interdigitated array showing the relative displacement of the adjacent bilayers.

Compound **1** shows a strong photoluminescence in the solid state at room temperature, with a maximum emission band at 456 nm upon excitation at 338 nm (Figure 5). As there are no obvious emissions observed for the organic components under the same experimental conditions, the intense luminescence in compound **1** may be attributable to ligand-to-metal charge transfer.[16]

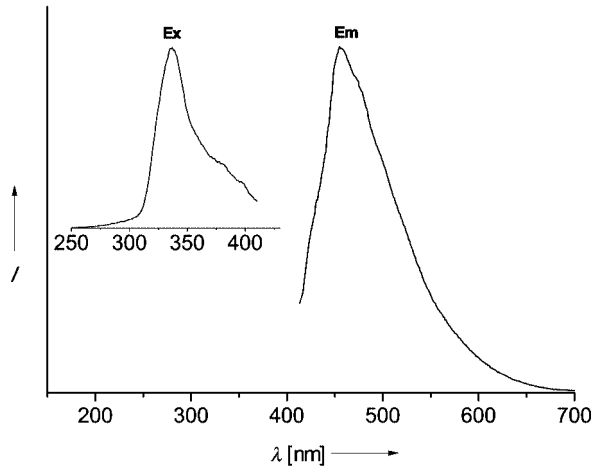

Figure 5. Photoluminescent spectra of **1** in the solid state at room temperature. Ex = excitation, Em = emission.

Conclusions

In summary, this work has, for the first time, demonstrated that an interdigitated structure can be produced by the assembly of bilayer motifs with a cuboidal framework. Compound **1**, besides adding a new member to the class of extricable entanglement, provides a remarkable new structural motif for the entangled system. Based on this new motif, one can envisage using it to construct another unknown entangled type − polythreading of bilayers − when the lateral arms are long enough to ensure complete threading through the cuboidal box. Further development and study of this interesting molecular module are in progress in our laboratories.

Experimental Section

Synthesis of 1: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (149 mg, 0.5 mmol), H_4bptc (165 mg, 0.5 mmol), bpy (78 mg, 0.5 mmol), bpdo (47 mg, 0.25 mmol), triethylamine (0.05 mL, 0.35 mmol), and water (10 mL) in a 23-mL Teflon-lined reactor were heated at 160 °C under autogenous pressure for 5 d and then cooled to room temperature at a rate of 10 °C h^{-1} to give colorless crystals of **1** (yield: 135 mg, 42% based on Zn). $C_{31}H_{20}N_3O_9Zn$ (643.87): calcd. C 58.72, H 3.13, N 6.53; found C 58.35, H 3.47, N, 6.46. FT-IR (KBr): $\tilde{\nu}$ = 1715 (s), 1604 (vs), 1519 (s), 1491 (s), 1410 (s), 1380 (vs), 1210 (m), 1170 (m), 1150 (m), 805 (m), 782 (m) cm^{-1}.

X-ray Crystallographic Study: The data were collected with a Rigaku R-AXIS RAPID IP diffractometer with Mo-K_α monochromated radiation (λ = 0.71073 Å) at 173(2) K. An empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package.[17] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms were included at idealized positions. Crystal data for **1**: $C_{31}H_{20}N_3O_9Zn$, M = 643.87, triclinic, space group $P\bar{1}$, a = 9.6477(19), b = 11.410(2), c = 12.980(3) Å, α =

98.34(3)°, β = 96.44(3)°, γ = 111.36(3)°, V = 1295.4(4) Å^3, Z = 2, μ = 1.016 mm^{-1}, 12679 reflections measured, 5776 unique (R_{int} = 0.0202), final R [$I > 2\sigma(I)$] R_1 = 0.0311, wR_2 = 0.0892. CCDC-271719 contains 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 Available (see footnote on the first page of this article): Additional figures (Figures S1 and S2) for **1**.

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[1] a) D. M. Proserpio, R. Hoffman, P. Preuss, *J. Am. Chem. Soc.* **1994**, *116*, 9634–9637; b) J. S. Miller, *Adv. Mater.* **2001**, *13*, 525–527; c) O. Ermer, *Adv. Matter.* **1991**, *3*, 608–611; d) J. P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611–619; e) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem. Int. Ed.* **2003**, *42*, 428–431.

[2] a) L. Carlucci, G. Ciani, M. Moret, D. M. Proserpio, S. Rizzato, *Angew. Chem. Int. Ed.* **2000**, *39*, 1506–1510; b) S. A. Bourne, J. Lu, B. Moulton, M. J. Zaworotko, *Chem. Commun.* **2001**, 861–862; c) Y. H. Li, C. Y. Su, A. M. Goforth, K. D. Shimizu, K. D. Gray, M. D. Smith, H. C. zur Loye, *Chem. Commun.* **2003**, 1630–1631.

[3] a) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; b) S. R. Batten, *CrystEngCommun.* **2001**, *3*, 67–73.

[4] V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngCommun.* **2004**, *6*, 377–395.

[5] a) J. P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611–619; b) K. Kim, *Chem. Soc. Rev.* **2002**, *31*, 96–107.

[6] L. Carlucci, G. Ciani, D. M. Proserpio, *Coord. Chem. Rev.* **2003**, *246*, 247–289.

[7] a) L. Carlucci, G. Ciani, D. W. V. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812–3813; b) S. Sailaja, M. V. Rajasekharan, *Inorg. Chem.* **2000**, *39*, 4586–4590; c) Y. Cui, S. J. Lee, W. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 6014–6015; d) X. C. Huang, J. P. Zhang, Y. Y. Lin, X. M. Chen, *Chem. Commun.* **2005**, 1–4.

[8] a) P. M. Van Calcar, M. M. Olmstead, A. L. Balch, *J. Chem. Soc., Chem. Commun.* **1995**, 1773–1774; b) L. Carlucci, G. Ciani, A. Gramaccioli, D. M. Proserpio, S. Rizzato, *CrystEngCommun.* **2000**, *2*, 154–163; c) Y. H. Li, C. Y. Su, A. M. Goforth, K. D. Shimizu, K. D. Gray, M. D. Smith, H. C. zur Loye, *Chem. Commun.* **2003**, 1630–1631.

[9] a) L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio, S. Rizzato, *Chem. Eur. J.* **1999**, *5*, 237–243; b) S. R. Batten, B. F. Hoskins, R. Robson, *Chem. Eur. J.* **2000**, *6*, 156–161; c) P. Ayyappa, O. R. Evans, W. Lin, *Inorg. Chem.* **2002**, *41*, 3328–3330; d) X. L. Wang, C. Qin, E. B. Wang, L. Xu, Z. M. Su, C. W. Hu, *Angew. Chem. Int. Ed.* **2004**, *43*, 5036–5040; e) Z. Y. Fu, X. T. Wu, J. C. Dai, S. M. Hu, W. X. Du, *New J. Chem.* **2002**, *26*, 978–980.

[10] a) C. V. K. Sharma, R. D. Rogers, *Chem. Commun.* **1999**, 83–84; b) M. B. Zaman, M. D. Smith, H. C. zur Loye, *Chem. Commun.* **2002**, 2256–2257; c) K. Biradha, M. Fujita, *Chem. Commun.* **2002**, 1866–1867; d) G. F. Liu, B. H. Ye, Y. H. Ling, X. M. Chen, *Chem. Commun.* **2002**, 1442–1443; e) L. Carlucci, G. Ciani, D. M. Proserpio, *Chem. Commun.* **1999**, 449–450; f) M. L. Tong, H. J. Chen, X. M. Chen, *Inorg. Chem.* **2000**, *39*, 2235–2238; g) C. Qin, X. L. Wang, L. Carlucci, M. L. Tong, E. B. Wang, C. W. Hu, L. Xu, *Chem. Commun.* **2004**, 1876–1877.

[11] a) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725–1727; b) T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 972–973.

[12] a) K. N. Power, T. L. Hennigar, M. J. Zaworotko, *New J. Chem.* **1998**, *22*, 177–181; b) J. C. Dai, X. T. Wu, Z. Y. Fu, C. P. Cui, S. M. Hu, W. X. Du, L. M. Wu, H. H. Zhang, R. Q. Sun, *Inorg. Chem.* **2002**, *41*, 1391–1396; c) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375–376; d) A. Rujiwatra, C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 2307–2308; e) S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739; f) M. J. Zaworotko, *Chem. Commun.* **2001**, 1–2; g) J. Zhang, Z. J. Li, J. K. Cheng, Y. Kang, Y. Y. Qin, Y. G. Yao, *New J. Chem.* **2005**, *29*, 421–423.

[13] J. C. Dai, S. M. Hu, X. T. Wu, Z. Y. Fu, W. X. Du, H. H. Zhang, R. Q. Sun, *New J. Chem.* **2003**, *27*, 914–918.

[14] a) S. M. F. Lo, S. S. Y. Chui, L. Y. Shek, Z. Y. Lin, X. X. Zhan, G. H. Wen, I. D. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 6293–6294; b) Z. Y. Fu, X. T. Wu, J. C. Dai, L. M. Wu, C. P. Cui, S. M. Hu, *Chem. Commun.* **2001**, 1856–1857; c) J. H. Luo, M. C. Hong, R. H. Wanf, R. Cao, L. Han, D. Q. Yuan, Z. Z. Lin, Y. F. Zhou, *Inorg. Chem.* **2003**, *42*, 4486–4488; d) X. L. Wang, C. Qin, E. B. Wang, Y. G. Li, C. W. Hu, L. Xu, *Chem. Commun.* **2004**, 378–379; e) R. J. Hill, D. L. Long, M. S. Turvey, A. J. Blake, N. R. Champness, P. Hubberstey, C. Wilson, M. Schröder, *Chem. Commun.* **2004**, 1792–1793.

[15] L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngCommun.* **2003**, *5*, 269–279.

[16] a) A. Meijerink, G. Blasse, M. Glasbeek, *J. Phys.: Condens. Matter* **1990**, *2*, 6303–6313; b) R. Bertoncello, M. Bettinelli, M. Cassrin, A. Gulino, E. Tondello, A. Vittadini, *Inorg. Chem.* **1992**, *31*, 1558–1565; c) J. Tao, J. X. Shi, M. L. Tong, X. X. Zhang, X. M. Chen, *Inorg. Chem.* **2001**, *40*, 6328–6330.

[17] a) G. M. Sheldrick, *SHELXS-97, A Program for the Solution of Crystal Structures from X-ray Data*, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXL-97, A Program for the Refinement of Crystal Structures from X-ray Data*, University of Göttingen, Germany, **1997**.

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