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A Novel Metal−Organic Network with High Thermal Stability: Nonlinear Optical and Photoluminescent Properties

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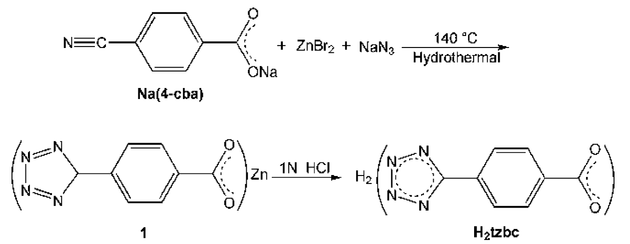
A novel zinc(II) 4-(5*H*-tetrazol)benzoic coordination polymer with an in situ generated tetrazole ligand exhibits the gsi (γ-silicon) topology and high thermal stability; this compound possesses second-order nonlinear optical and interesting heat-induced photoluminescent properties.

The current interest in crystal engineering of metal−organic coordination polymers (CPs) stems not only from their intriguing variety of architectures and topologies but also from their characteristic physical and/or chemical properties, including ferroelectricity, luminescence, magnetism, nonlinear optics, gas storage, etc.[1,2] Usually, at the level of the basic unit, one of these properties is used. The existence of two cooperative properties in the same crystal lattice might result in new physical phenomena and wide applications, and thus a new trend in this field is to add more than two physical properties to one metal−organic CP to achieve multifunctional materials, such as ferroelectromagnets, optoelectronics, magnetooptics, and magnetic conductors.[3] Here we report a hydrothermally synthesized three-dimensional (3D) metal−organic CP $[\mathrm{Zn(tzba)}]_n$ (**1**; H_2tzba = 4-(5*H*-tetrazol)benzoic acid] exhibiting the gsi (γ-silicon) topology. The obtained molecule-based compound with high thermal stability displays not only nonlinear optical effects but also interesting photoluminescence (PL), which can be modified from blue to white by means of a simple heat-treatment process.

Scheme 1



The reaction of NaN_3 and Na(4-cba) (4-Hcba = 4-cyanobenzoic acid) in the presence of $ZnBr_2$ under hydrothermal reaction conditions yielded **1** (Scheme 1), as evidenced by the absence of the cyano group peak in the 2244 cm^{-1} region and the presence of the tetrazole group peaks at 1586 and 1426 cm^{-1} in the IR spectrum of **1** (Figure S1 in the Supporting Information). The new tetrazole tzba was obtained by in situ ligand synthesis, which provides a new approach to the crystal engineering of metal−organic CPs.[4] Compound **1** can be treated with 1 N hydrochloric acid to produce H_2tzba,[5] but the reaction of H_2tzba with $ZnBr_2$ cannot directly yield **1**. Notably, there is no coordinated aqua or lattice water molecule found in **1**, although it was synthesized in a water solution. The experimental powder X-ray diffraction (PXRD) pattern of **1** agrees well with the simulated one based on the single-crystal X-ray data (Figure S2 in the Supporting Information), indicating that **1** is in a pure phase.

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(1) (a) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (b) Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490. (c) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770.

(2) (a) Gao, E. Q.; Bai, S. Q.; Wang, Z. M.; Yan, C. H. *J. Am. Chem. Soc.* **2003**, *125*, 4984. (b) Medina, M. E.; Iglesias, M.; Snejko, N.; Gutiérrez-Puebla, E.; Monge, M. A. *Chem. Mater.* **2004**, *16*, 594. (c) Pan, L.; Parker, B.; Huang, X.; Olson, D. H.; Lee, J. Y.; Li, J. *J. Am. Chem. Soc.* **2006**, *128*, 4180. (d) Li, X.-L.; Chen, K.; Liu, Y.; Wang, Z.-X.; Wang, T.-W.; Zuo, J.-L.; Li, Y.-Z.; Wang, Y.; Zhu, J.-S.; Liu, J.-M.; Song, Y.; You, X.-Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 6820.

(3) (a) Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcia, G. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (b) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443. (c) Ohkoshi, S.; Tokoro, H.; Hozumi, T.; Zhang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 270. (d) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 1419. (e) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607.

(4) (a) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1675. (b) Zhao, H.; Qu, Z.-R.; Ye, H.-Y.; Xiong, R.-G. *Chem. Soc. Rev.* **2008**, *37*, 84.

(5) Li, G.-Q.; Wu, A.-Q.; Li, Y.; Zheng, F.-K.; Guo, G.-C. *Acta Crystallogr.* **2008**, *E64*, o1368.

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Figure 1. Molecular structure of **1**. Symmetry codes: A, x, $1 - y$, $-0.5 + z$; B, $1 + x$, $1 - y$, $-0.5 + z$; C, x, $-y$, $-0.5 + z$. H atoms have been omitted for clarity.

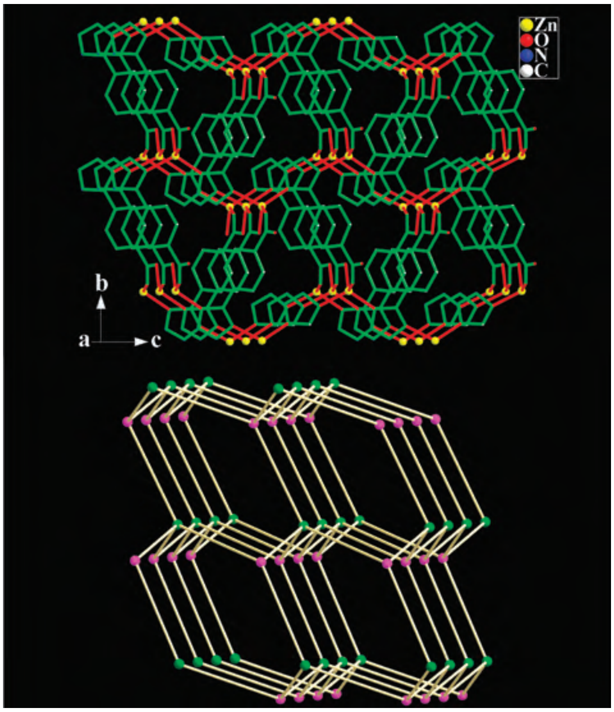

Figure 2. 3D coordination network of **1** (top) and its 3D gsi topological network (bottom).

A single-crystal X-ray analysis[6] reveals that the crystal structure of **1** consists of one crystallographically independent Zn^{II} atom and one crystallographically independent tzba ligand (Figure 1). The Zn^{II} atom is four-coordinated by two carboxylate O atoms in a syn−anti configuration and two tetrazole 1,4-N atoms from four symmetrically related tzba ligands to form a highly distorted tetrahedral coordination geometry, with the angles N/O−Zn−N/O varying from 103.43(12) to 135.5(2)°. The tzba ligand, exhibiting quadridentate coordination mode, is bound to four Zn^{II} atoms, and each Zn^{II} atom is bound to four tzba ligands to give a 3D coordination network (Figure 2). Recently, several metal−organic CPs with intriguing topological networks and potential applications have been constructed by carboxylate-introduced 5-substituted tetrazoles, isosteric with the dicarboxylate group.[7] When the structural feature of **1** are taken into account, the network can be best described as a gsi net 6^6 when the Zn^{II} centers and the tzba ligand units are treated as four-connected nodes, as depicted in Figure 2. Similar to the dia (diamondoid) net, the shortest ring involving each node in this net is 6-gon. The long topological (O'Keeffe) vertex symbol of this 6^6 net is $(6_2.6.6_2.6.6.6_2)$, which is similar to the 6^6 dia net $(6_2.6_2.6_2.6_2.6_2.6_2)$. To the best of our knowledge, the metal−organic CP with a gsi net has not been reported so far, though those with the dia nets have been well documented.[8]

Acentric materials are of special interest in materials chemistry because of their technologically important properties, such as ferroelectricity and second-order nonlinear optical behavior.[9] Because **1** crystallizes in the acentric space group *Pc* with the point group C_s belonging to one of the 10 polar point groups, its second-order nonlinear optical and ferroelectric effects were examined. Preliminary studies of a powder sample indicate that **1** is second harmonic generation (SHG)-active with a response 2.5 times that of KDP (KH_2PO_4), presumably as a result of the push−pull effect of the tzba ligand containing a donor−π-acceptor system (donor = tetrazole ring and acceptor = carboxylate group). The electric hysteresis loop measured on a pressed powder sample of **1** (Figure S3 in the Supporting Information) denotes that the remnant polarization mainly originates from the leakage and reveals the absence of ferroelectric effects or extremely weak ferroelectricity.

Thermogravimetric analysis (TGA) of **1** in an air atmosphere reveals one clean weight loss step occurring at 440 °C, which corresponds to decomposition of the tzba ligand (Figure S4 in the Supporting Information). The final inorganic residue ZnO was formed above 512 °C with a remnant weight of 32.33% (calcd 32.10%). It is well-known that one of the main concerns in metal−organic CP-based materials is thermal stability, which is usually in the range of 150−300 °C, and only a few metal−organic CPs may be thermally stable above 350 °C.[10] However, in order to exactly evaluate its practical application, high-temperature calcinations of **1**

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(6) $[Zn(tzba)]_n$, monoclinic, space group, *Pc*, $a = 4.8244(5)$ Å, $b = 8.2293(11)$ Å, $c = 10.5946(10)$ Å, $\beta = 96.162(8)°$, $V = 418.19(8)$ Å^3, $T = 293(2)$ K, $Z = 2$, $M_r = 253.52$, $D_c = 2.013$ g/cm^3, $F(000) = 252$, $\mu = 2.916$ mm^{-1}, $\lambda = 0.710\ 73$ Å, 1300 total reflections ($2.47 \leq \theta \leq 30.00°$), 1300 unique ($R_{int} = 0.000$). Structure solution and refinement based on 1272 observed reflections with $I > 2\sigma(I)$ and 136 parameters gave final $R = 0.0240$, w$R = 0.658$, and $S = 1.006$.

(7) (a) Qu, Z. R.; Zhao, H.; Wang, X. S.; Li, Y. H.; Song, Y. M.; Liu, Y. J.; Ye, Q.; Xiong, R. G.; Abrahams, B. F.; Xue, Z. L.; You, X. Z. *Inorg. Chem.* **2003**, *42*, 7710. (b) Chen, Q.-Y.; Li, Y.; Zheng, F.-K.; Zou, W.-Q.; Wu, M.-F.; Guo, G.-C.; Wu, A.-Q.; Huang, J.-S. *Inorg. Chem. Commun.* **2008**, *11*, 969. (c) Huang, X.-H.; Sheng, T.-L.; Xiang, S.-C.; Fu, R.-B.; Hu, S.-M.; Li, Y.-M.; Wu, X.-T. *Chinese J. Struct. Chem.* **2007**, *26*, 333. (d) Yu, Z. P.; Xie, Y.; Wang, S. J.; Yong, G. P.; Wang, Z. Y. *Inorg. Chem. Commun.* **2008**, *11*, 372.

(8) (a) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **1999**, *5*, 237. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **2002**, *8*, 1519.

(9) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10*, 2753.

(10) (a) Xiong, R. G.; Zuo, J. L.; You, X. Z.; Abrahams, B. F.; Bai, Z. P.; Che, C. M.; Fun, H. K. *Chem. Commun.* **2000**, 2061. (b) Yang, S. Y.; Long, L. S.; Jiang, Y. B.; Huang, R. B.; Zheng, L. S. *Chem. Mater.* **2002**, *14*, 3229. (c) Almeida Paz, F. A.; Klinowski, J. *Chem. Commun.* **2003**, 1484. (d) Perles, J.; Iglesias, M.; Martín-Luengo, M. Á.; Monge, M. Á.; Ruiz-Valero, C.; Snejko, N. *Chem. Mater.* **2005**, *17*, 5837. (e) Sun, D. F.; Ma, S. Q.; Ke, Y. X.; Petersen, T. M.; Zhou, H. C. *Chem. Commun.* **2005**, 2663. (f) de Lilla, D. T.; Cahill, C. L. *Chem. Commun.* **2006**, 4946. (g) Zou, R. Q.; Zhong, R. Q.; Du, M.; Kiyobayashia, T.; Xu, Q. *Chem. Commun.* **2007**, 2467.

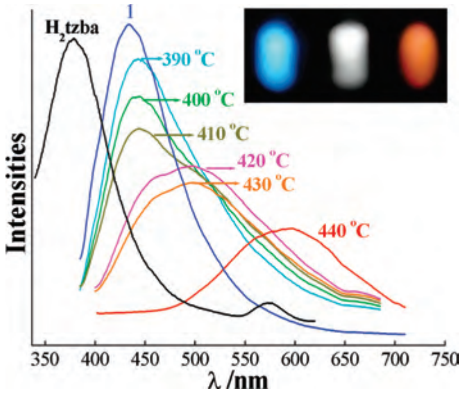

Figure 3. Solid-state PL spectra of H_2tzba, **1**, and the samples after calcination from 390 to 440 °C. Inset: PL images of **1** and the samples after calcination at 420−430 and 440 °C, respectively.

for 1 h proceeded from 390 °C every 10 °C. Compound **1** gradually turned to pale yellow from 390 to 410 °C, gray-yellow from 420 to 430 °C, and white at 440 °C. It is worth pointing out that the PXRD patterns of **1** after calcinations below 410 °C are in a good agreement with that of **1** at room temperature, while the PXRD patterns of **1** at 420 and 430 °C are more or less different from that of the original solid and the emergence of some small diffraction lines was observed, indicating alteration of the crystal structure topology and local distortion within the structure (Figure S5 in the Supporting Information). The sample became ZnO when the temperature was increased to 440 °C, evidenced by the PXRD results (Figure S6 in the Supporting Information) and PL spectra (Figure 3).[11] This phenomenon is not extremely consistent with the TGA result, possibly because of the hysteresis of the TGA measurement.

As shown in Figure 3, the PL of the H_2tzba ligand exhibits an emission maximum at 378 nm, while **1** displays a strong sharp blue PL at 432 nm upon photoexcitation at 365 nm. Interestingly, the PL of **1** can be adjusted from blue to white through calcinations from 390 to 430 °C, and an obvious 32-nm red shift and broadening of the PL were found. Samples after calcination from 390 to 410 °C display blue PL, and the red PL was observed after calcinations at 440 °C (Table 1). Unexpectedly, samples after heating to 420 and 430 °C display a broad visible PL spectrum that appears white to the naked eye (Figure 3, inset). This interesting heat-induced PL variation has been found in borate phosphors and porous glasses[12] but not found in metal−organic CPs before. It is worth noting that in spite of similarities in the PXRD patterns between **1** and samples after heating to 420 and 430 °C, their emission spectra are different from each other, which maybe originates from structural defects caused by heat treatment.[12] The luminescent analyses suggest that **1** is a good candidate for white phosphors.[13]

Table 1

calcination temperature	PL	PXRD pattern
below 410 °C	blue (λ_{ex} = 365 nm)	same as that of **1**
420 and 430 °C	white (λ_{ex} = 382 nm)	somewhat different from that of **1**
above 440 °C	red (λ_{ex} = 382 nm)	same as that of ZnO

In summary, we have prepared a novel 3D metal−organic CP [Zn(tzba)]$_n$ with the gsi net, which shows high thermal stability, second-order nonlinear optical effects, and interesting heat-induced PL. This compound may be a good candidate for SHG-active and efficient luminescent multifunctional materials.

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Supporting Information Available: Crystallographic data for **1** in CIF format, IR spectra of Na(4-cba), H_2tzba, and **1**, electric hysteresis loop at different voltages, frequencies, and temperatures, TGA curve of **1**, and PXRD diagrams of **1** and the calcined materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Li, L.; Qiu, X.; Li, G. *Appl. Phys. Lett.* **2005**, *87*, 124101.

(12) (a) Hayakawa, T.; Hiramitsu, A.; Nogami, M. *Appl. Phys. Lett.* **2003**, *82*, 2975. (b) Wang, M. S.; Guo, G. C.; Chen, W. T.; Xu, G.; Zhou, W. W.; Wu, K. J.; Huang, J. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 3909.

(13) Green, W. H.; Le, K. P.; Grey, J.; Au, T. T.; Sailor, M. J. *Science* **1997**, *276*, 1826.