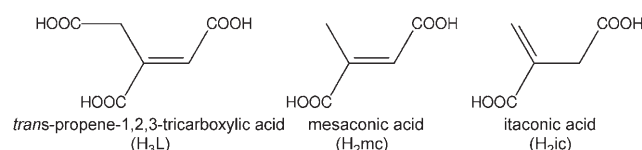


Photochromism of a 3D Cd^{II} Complex with Two Captured Ligand Isomers Generated In Situ from the Same Precursor**

Ming-Sheng Wang, Guo-Cong Guo,* Wen-Qiang Zou, Wei-Wei Zhou, Zhang-Jing Zhang, Gang Xu, and Jin-Shun Huang

Photochromic compounds have gained intense interest owing to their novel photochemical and photophysical reactions as well as their various potential applications such as in sunglasses and optical memories.^[1] An appreciable number of photochromic families have been reported to date;^[2] however, those based on an electron-transfer (redox) chemical process, especially for metal–organic compounds, are rare.^[3] We present herein a hydrothermally synthesized 3D complex $[\text{Cd}_2(\text{ic})(\text{mc})(4,4'\text{-bipy})_3]_n \cdot 4n \text{H}_2\text{O}$ (**1Y**; ic = itaconate, mc = mesaconate) which exhibits reversible radical-based redox photochromic behavior. This compound also merits attention for its unusual five-connected Archimedean-type topological structure and unexpected “capture” of isomeric ic and mc ligands that are generated in situ from *trans*-propene-1,2,3-tricarboxylic acid (H_3L , Scheme 1).



Scheme 1. Carboxylic acids relevant to this work.

Yellow prismatic crystals of **1Y** accompanied by a few colorless block crystals of $[\text{Cd}_3\text{L}_2(\text{H}_2\text{O})_6]_n$ (**2**; Figure S1 in the Supporting Information) were obtained by the hydrothermal reaction of CdCO_3 , 4,4'-bipy, H_3L , and deionized water in a molar ratio of 1:1:1:1111 at 120 °C for 12 h. Powder X-ray diffraction (PXRD) verified the purity of a mechanically separated sample of **1Y** (Figure S2 in the Supporting Information). Thermal analysis and PXRD data show that compound **1Y** still keeps its metal–organic framework at 200 °C after the elimination of lattice water molecules (Figure S2 and S3 in the Supporting Information).

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A single-crystal X-ray diffraction study of **1Y** revealed a 3D structure based on a network of seven-coordinated Cd^{II} centers linked by three kinds of bridging ligands. As shown in Figure 1, the central Cd1 atom is located in a pentagonal-

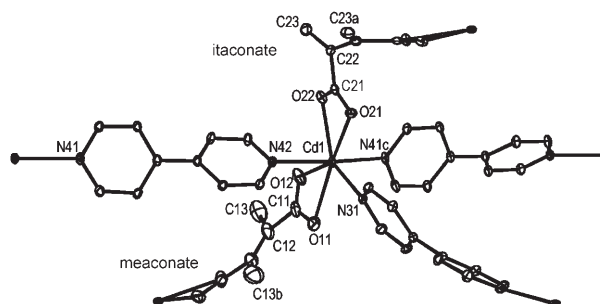


Figure 1. ORTEP drawing with 20% thermal ellipsoids of the coordination environment of the Cd center in **1Y**. Symmetry codes: a: $-x+3/4, -y+3/4, z$; b: $-x+1/4, -y+5/4, z$; c: $-x+1/2, y-1/4, z+1/4$. SOF (site of factor): C13, 0.5; C23, 0.5.

bipyramidal coordination environment with N41 and N42 atoms of crystallographically independent 4,4'-bipy ligands acting as the two pyramidal apexes. An important feature of **1Y** is the simultaneous “capture” of isomeric ic and mc ligands that originate from the in situ pyrolysis of H_3L .^[4] In situ ligand synthesis under hydro(solvo)thermal conditions has received intense interest in the past years.^[5] Like **1Y**, one compound capturing two in situ generated ligands from the same precursor was rarely reported in the literature.^[6] The vinyl bonds of the ic and mc ligands have lengths of 1.296(7) and 1.316(3) Å, respectively, which are comparable to those reported in the literature.^[7] The torsion angle of the two carboxylate groups in each ic ligand is 67.1(3)°, while that in each mc ligand is close to 180°.

Both ic and mc ligands in **1Y** serve as two-connecting ligands by linking Cd1 atoms to yield an arch-bridge-like 1D chain along the $[\bar{1}10]$ or $[110]$ direction (Figure 2a). The Cd···Cd separation between each ic ligand is about 1.942 Å shorter than that between each mc ligand. The 1D chains are connected by 4,4'-bipy ligands through the N31 atoms to form a bilayer of 8^210 topology (Figure 2b), which is similar to that of $[\text{Co}(4,4'\text{-bipy})_3(\text{NO}_3)_4]_n \cdot 4n \text{H}_2\text{O}$.^[8] Furthermore, these bilayers are cross-bridged by 4,4'-bipy ligands through the N41 and N42 atoms to generate a 3D Archimedean-type network with a 4^26^82 topology built upon five-connected Cd^{II} metal centers (Figure 2c,d). The long topological (O'Keeffe) vertex symbol of this 4^26^82 net is 4.4.6.6.6₃.6₃.6₃.6₃.8₄.8₅.^[9] To the best of our knowledge, this structural topology has not

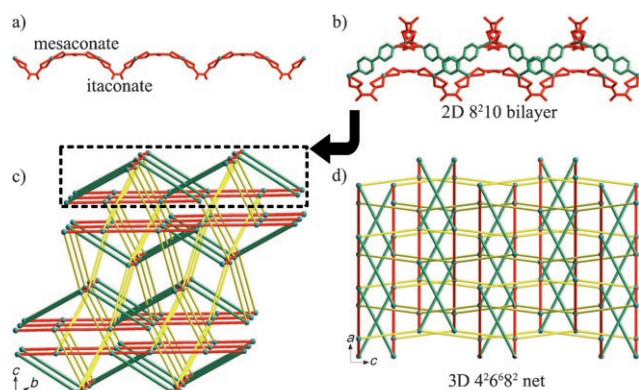


Figure 2. a) 1D arch-bridge-like chain in **1Y**. b) 2D bilayer in **1Y**. c, d) Schematic representations of the 3D $4^2 6^6 8^2$ net. Rods in (c) and (d): green: 4,4'-bipy ligands with N31 atoms; red: carboxylate ligands; yellow: 4,4'-bipy ligands with N41 atoms.

been reported in the literature.^[10] The known 3D five-connected $4^6 6^4$ and $4^4 6^6$ nets are characteristic of stacking 2D (6,3) nets in parallel, which do not occur in the $4^2 6^6 8^2$ net. The 3D metal–organic framework in **1Y** has a void space which accommodates lattice water molecules and corresponds to 13.7% of the unit cell volume (Figure S4 in the Supporting Information).

Compound **1Y** undergoes an interesting photochromic transformation from yellow to blue upon irradiation by light with $\lambda \leq 460$ nm (Figure 3). The blue sample **1B** is stable in air in a dark room for two weeks, after which it turns slowly to yellowish green and further reverts to **1Y**. The decoloration of **1B** can be achieved by heating at 80 °C for several hours. The infrared spectra of **1Y** and **1B** are unchanged (Figure S5 in the Supporting Information), but variation of the UV/Vis spectra

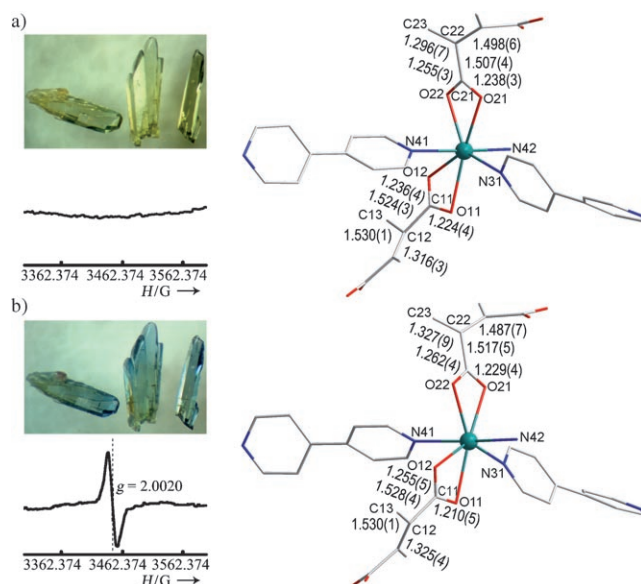


Figure 3. Photochromism and ESR spectral and structural variations between **1Y** (a) and **1B** (b). For clarity, only the bond lengths of the ic and mc ligands are shown (in Å). Other bond lengths are shown in Figure S7 in the Supporting Information.

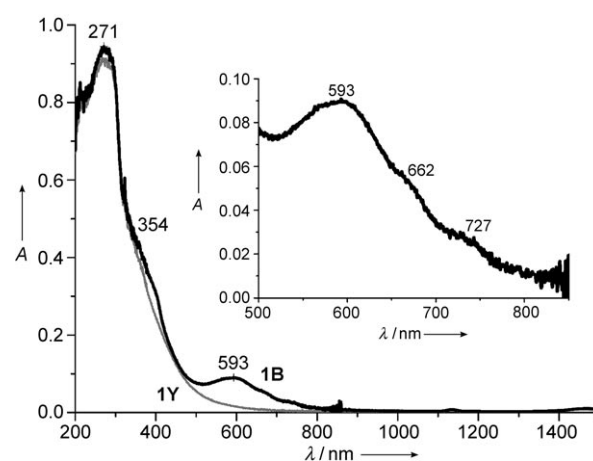


Figure 4. UV/Vis spectra of **1Y** and **1B**. The inset shows an enlargement of the signal for **1B**.

and ESR signals occurs. As shown in Figure 4, compound **1Y** exhibits a π – π^* absorption peak centered at 271 nm and a charge-transfer peak at 354 nm that is responsible for the yellowish appearance of **1Y**. After coloration, three new shoulder peaks (593, 662, and 727 nm) appear in the red-light range. In ESR studies sample **1Y** exhibits no signal, but a single-peak radical signal ($g = 2.0020$) emerges after irradiation (Figure 3). Thus, the three new peaks in the UV/Vis spectrum of **1B** should be ascribed to the radicals. Irradiation of **1Y** under strictly anaerobic conditions has no effect on the photochromism, which indicates that the photochromism is due to a solid-state transformation and that coloration–decoloration is not the result of a surface oxidation reaction.^[3g] The spin density of a powdered sample irradiated by UV light for 25 min, using 1,1-diphenyl-2-picrylhydrazyl (DPPH) as a reference, is about 1.59×10^{20} spins mol^{-1} .

The structures of the same single crystal before (**1Y**) and after (**1B**) irradiation were determined at room temperature to study the origin of the radical. As shown in Figure 3, an obvious structural variation occurs in the ic and mc ligands. The largest change is observed in the vinyl C–C bond (C22–C23) of the ic ligand, which is elongated by 0.031(8) Å. A theoretical calculation carried out at the B3LYP level (see the Supporting Information) shows that after irradiation the electronic transition mainly occurs in the ic and mc ligands and the transferred electron is located mainly on the ic ligand (Figure 5), which is in good agreement with the structural variation. Moreover, a population analysis of **1Y** shows that its HOMO is mostly dominated by the 2p and 3p orbitals of

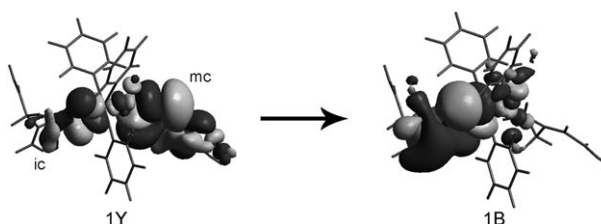


Figure 5. HOMOs for **1Y** and **1B**.

the O11, O12, O21, and O21 atoms. Hence, the radical originates from the lone pair of electrons on the O atoms in the carboxylate groups, and then results in the elongation of the vinyl C–C bond of the ic ligand owing to the increase in electronic density (Figure 5).

In summary, we have prepared a 3D Cd^{II} complex with two in situ generated isomers under hydrothermal conditions. This complex also exhibits the unusual five-connected 4²6⁶2 topology and reversible redox photochromism. Research on other photochromic compounds is ongoing in our group.

Experimental Section

Experimental details can be found in the Supporting Information.

Crystal data for **1Y**: C₄₀H₄₀Cd₂N₆O₁₂, *M_r* = 1021.58, orthorhombic, space group *Fddd* (no. 70), *a* = 15.433(3), *b* = 28.552(6), *c* = 36.861(8) Å, *V* = 16242(6) Å³, *Z* = 16, ρ_{calcd} = 1.671 g cm^{−3}, μ = 1.118 mm^{−1}, 6° ≤ 2 θ ≤ 51.00°, *T* = 293(2) K, *R*₁ = 0.0463 and *wR*₂ = 0.1110 for 3671 observed reflections (*I* > 2 σ (*I*)) of 3779 (*R*_{int} = 0.0316) unique reflections and 298 parameters. GOF = 1.158. Crystal data for **1B**: C₄₀H₄₀Cd₂N₆O₁₂, *M_r* = 1021.58, orthorhombic, space group *Fddd* (no. 70), *a* = 15.416(1), *b* = 28.641(2), *c* = 36.813(2) Å, *V* = 16254(2) Å³, *Z* = 16, ρ_{calcd} = 1.670 g cm^{−3}, μ = 1.117 mm^{−1}, 6° ≤ 2 θ ≤ 51.00°, *T* = 293(2) K, *R*₁ = 0.0583 and *wR*₂ = 0.1388 for 3705 observed reflections (*I* > 2 σ (*I*)) of 3785 (*R*_{int} = 0.0389) unique reflections and 298 parameters. GOF = 1.262. The methyl and ethylene groups of the mc and ic ligands in **1Y** and **1B** are twofold disordered. CCDC-604820 and CCDC-675753 contain the supplementary crystallographic data for **1Y** and **1B**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] H. Bouas-Laurent, H. Dürr, *Pure Appl. Chem.* **2001**, *73*, 639–665, and references therein.

- [2] a) E. Hadjoudis, I. M. Mavridis, *Chem. Soc. Rev.* **2004**, *33*, 579–588; b) K. Amimoto, T. Kawato, *J. Photochem. Photobiol. C* **2005**, *6*, 207–226; c) H. Nakai, M. Mizuno, T. Nishioka, N. Koga, K. Shiomi, Y. Miyano, M. Irie, B. K. Breedlove, I. Kinoshita, Y. Hayashi, Y. Ozawa, T. Yonezawa, K. Toriumi, K. Isobe, *Angew. Chem.* **2006**, *118*, 6623–6626; *Angew. Chem. Int. Ed.* **2006**, *45*, 6473–6476; d) T. He, J. Yao, *Prog. Mater. Sci.* **2006**, *51*, 810–879; e) S. Takami, L. Kuroki, M. Irie, *J. Am. Chem. Soc.* **2007**, *129*, 7319–7326.
- [3] a) J.-M. Aubry, C. Pierlot, J. Rigaudy, R. Schmidt, *Acc. Chem. Res.* **2003**, *36*, 668–675; b) C. Sporer, I. Ratera, D. Ruiz-Molina, Y. Zhao, J. Vidal-Gancedo, K. Wurst, P. Jaitner, K. Clays, A. Persoons, C. Rovira, J. Veciana, *Angew. Chem.* **2004**, *116*, 5378–5381; *Angew. Chem. Int. Ed.* **2004**, *43*, 5266–5268; c) J. M. Herrera, V. Marvaud, M. Verdager, J. Marrot, M. Kalisz, C. Mathonière, *Angew. Chem.* **2004**, *116*, 5584–5587; *Angew. Chem. Int. Ed.* **2004**, *43*, 5468–5471; d) J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcén, G. Chastanet, M. Marchivie, L. Goux-Capes, *Chem. Eur. J.* **2005**, *11*, 4582–4589; e) P. M. S. Monk, *The Viologens: Synthesis Physicochemical Properties and Applications of the Salts of 4,4'-Bipyridine*, Wiley, Chichester, **1998**; f) G. Xu, G.-C. Guo, M.-S. Wang, Z.-J. Zhang, W.-T. Chen, J.-S. Huang, *Angew. Chem.* **2007**, *119*, 3313–3315; *Angew. Chem. Int. Ed.* **2007**, *46*, 3249–3251; g) Y. Suenaga, H. Konaka, T. Sugimoto, T. Kuroda-Sowa, M. Maekawa, M. Munakata, *Inorg. Chem. Commun.* **2003**, *6*, 389–393.
- [4] M. Carlsson, C. Habenicht, L. C. Kam, M. J., Jr. Antal, N. Bian, R. J. Cunningham, M. Jones, Jr., *Ind. Eng. Chem. Res.* **1994**, *33*, 1989–1996.
- [5] a) X.-M. Zhang, *Coord. Chem. Rev.* **2005**, *249*, 1201–1219; b) X.-M. Chen, M.-L. Tong, *Acc. Chem. Res.* **2007**, *40*, 162–170.
- [6] Y.-T. Wang, H.-H. Fan, H.-Z. Wang, X.-M. Chen, *Inorg. Chem.* **2005**, *44*, 4148–4150.
- [7] a) J. E. Contreras, B. Ramirez, G. D. de Delgado, *J. Chem. Crystallogr.* **1991**, *27*, 391–395; b) E. Batchelor, J. Klinowski, W. Jones, *J. Mater. Chem.* **2000**, *10*, 839–848.
- [8] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844–1846; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725–1727.
- [9] M. O'Keeffe, *Z. Kristallogr.* **1991**, *196*, 21–37.
- [10] a) D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson, M. Schröder, *J. Am. Chem. Soc.* **2001**, *123*, 3401–3402; b) L. Pan, N. Ching, X. Huang, J. Li, *Chem. Commun.* **2001**, 1064–1065; c) M. R. Montney, S. M. Krishnan, N. M. Patel, R. M. Supkowski, R. L. LaDuca, *Cryst. Growth Des.* **2007**, *7*, 1145–1153.