DALTON
COMMUNICATION

A three-dimensional network coordination polymer, (terephthalato)(pyridine)cadmium, with blue fluorescent emission

Hoong-Kun Fun,*[a] S. Shnamuga Sundara Raj,[a] Ren-Gen Xiong,*[b] Jing-Lin Zuo,[b] Zhi Yu[b] and Xiao-Zeng You[b]

[a] *X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang. E-mail: hkfun@usm.my*

[b] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China. E-mail: xyz@netra.nju.edu.cn*

Received 16th March 1999, Accepted 30th April 1999

The first terephthalato (TPT) bis-tridentate bridging cadmium coordination polymer, [(TPT)(py)Cd] 1, with blue fluorescent emission, was synthesized by a hydrothermal reaction between $Cd(ClO_4)_2 \cdot 6H_2O$, 1,4-dicyanobenzene and pyridine (py).

The terephthalato (TPT) ligand has been extensively studied in the field of molecular magnetism on account of its promising application to areas of technology such as magnetic recording[1] due to TPT exhibiting a variety of chelating abilities as manifested by the formation of dinuclear,[2] tetranuclear,[3] one- and two-dimensional copper(II) systems,[4] as well as three-dimensional manganese(II) coordination polymers.[5] More recently, coordinatively unsaturated metal centers in the extended porous frameworks of $Zn_3(TPT)_3 \cdot 6MeOH$ and $Zn(TPT)(DMF)(H_2O)$ have been addressed and show a clear preference for the inclusion of alcohols and gas sorption properties.[6] However, it is noteworthy that in these compounds TPT adopts a μ_4-bridging mode of coordination with the metal atom and no μ_6-bridging TPT ligands have so far been found. To our surprise, we have successfully obtained a novel three-dimensional condensed polymer, $[Cd(TPT)(py)]_n$ **1**, with an unprecedented μ_6-TPT-bridging mode under hydrothermal synthesis conditions using 1,4-dicyanobenzene as starting material. Moreover, **1** also displays a very strong blue fluorescent emission in the solid state. Herein, we report the synthesis, structure and fluorescence properties of **1** which represents the first example of a metal coordination polymer with μ_6-TPT-coordination.

Polymer **1** was synthesized under hydrothermal reaction conditions from $Cd(ClO_4)_2 \cdot 6H_2O$ and 1,4-dicyanobenzene.† In this reaction, 1,4-dicyanobenzene was hydrolyzed to form TPT and is considered to be the precursor of TPT. The situation is quite similar to the reaction system of $Fe(ClO_4)_3$ and 4-pyridinecarbaldehyde in which 4-pyridinecarbaldehyde is the precursor of 4-pyridinecarboxylic acid.[7] The presence of a carboxylate group in **1** was confirmed by the very strong peaks at 1568, 1535 and 1386 cm^{-1}, in the IR spectrum. No peaks at about 2100 cm^{-1} were found, indicating that the cyano group no longer exists in **1**. It should be emphasized that with the replacement of 1,4-dicyanobenzene by 1,4-benzenedicarboxylic acid, we failed to get compound **1**, even if the same reaction conditions were used. This shows that the use of the precursor is crucial for the synthesis of the novel condensed metal coordination polymer.

The three-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction investigation.‡ The local coordination environment around the Cd(II) ion in **1** can best be described as approximately pentagonal bipyramidal with the two bidentate chelating carboxylates and one N atom of pyridine in the equatorial plane and with two monodentate carboxylates in the axial positions, as shown in Fig. 1. Each TPT in **1** adopts a μ_6-bridging mode to connect with 4 Cd(II) ions (see Fig. 2) to form a three-dimensional network structure. Though the TPT carboxylates in **1** can be considered as being in a common bridging mode (bis-tridentate),[8] to our knowledge, all of the carboxylate groups in the known compounds containing TPT take part in coordination to the metal ion with a *syn-syn* bridging mode. Furthermore, the seven-coordination of the Cd(II) ion is shown by the following. Firstly, two oxygen atoms of the two different TPT carboxylate anions coordinate with the Cd(II) ion almost equally in a bidentate chelating mode. The Cd–O distances (2.307–2.448 Å) are quite similar to normal Cd–OCO distances (2.251–2.879 Å).[9] Secondly, the Cd–O distance (2.497 Å) in the apical positions is slightly longer than those in the equatorial position, indicating that it shows some pendant oxygen characteristics. However, both of these carboxylates are bound asymmetrically with one Cd–O bond length somewhat longer than the other.[8] Thirdly, the Cd–N (2.281 Å) distance also has a typical bond length (2.32–2.39 Å).[10] It can be seen from a perspective view of **1** down the *b*-axis , as shown in Fig. 2 (pyridine omitted for clarity) that the TPT anion acts as bis-tridentate ligand to the two coplanar Cd(II) ions and of two Cd(II) ions in a different layer, thus resulting in the formation of a very regular three-dimensional network structure with channel dimensions of 11.23 × 11.23 Å. As a result, molecules such as 4- and 3-methylpyridine, imidazole *etc.* can be included in this channel. {The seventh coordinated ligand is labile, this situation is very similar to that of $[Cu_3(TMA)_2(H_2O)_3]_n$ (TMA = 1,3,5-benzenetricarboxylic acid) in which the lability of the aqua ligands allows their replacement by other groups.[11]} To study the thermal stability of compound **1**

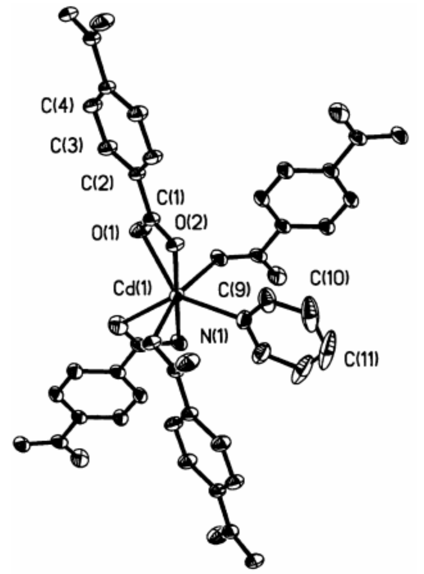

Fig. 1 An ORTEP[12] view of the coordination polymer [(TPT)(py)Cd] **1**. Hydrogen atoms are omitted for clarity.

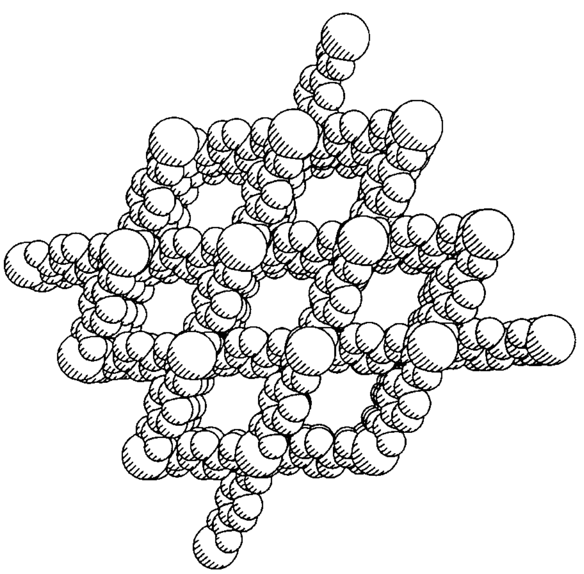

Fig. 2 A perspective view of **1** along the *b* axis (pyridine omitted for clarity).

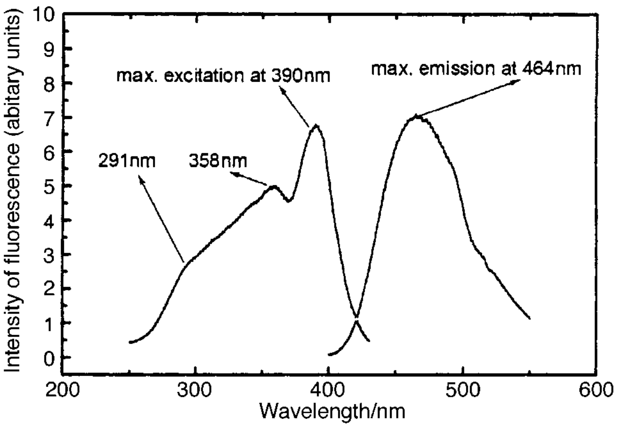

Fig. 3 Fluorescence emission spectrum of **1** in the solid state at room temperature.

thermogravimetric analysis (TGA) was performed on the polycrystalline sample, indicating that one strikingly clean weight loss step occurred at 220 °C (20.8% loss), corresponding to the removal of one pyridine molecule per formula unit (22.23% calculated). Most important is the fact that no weight loss was recorded between the temperatures 220 and 408 °C, probably suggesting the formation of a stable phase formulated as Cd(TPT) (see Fig. 2).

The most important feature of the structure of **1** is that its three-dimensionally condensed polymeric structure leads to significant enhancement of fluorescent intensity, almost 100 times larger than that of the free ligand, probably due to the symmetry decrease of TPT (seriously twisted) in **1** compared with the free ligand. The emission of **1**, $\lambda_{max} = 464$ nm (Fig. 3), is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can probably be assigned to the intraligand fluorescent emission since a very weakly similar emission (δ_{max} at 466 nm) is also observed for the TPT acid. On the other hand, the diffuse reflectance spectrum of **1** is dominated by an intraligand π–π* transition at 298 nm. Owing to the blue fluorescence emission of **1** it may be used as an advanced material for blue-light emitting diode devices. This condensed polymeric material may be an excellent candidate for highly thermally stable and solvent-resistant blue fluorescent material because **1** is almost insoluble in most common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene and water. In conclusion, we have synthesized an unprecedented and novel μ_6-TPT metal coordination polymer using the precursor of TPT, 1,4-dicyanobenzene, under hydrothermal hydrolysis conditions. This opens up a new synthetic route for novel metal coordination polymers with promising photo-electronic properties.

Acknowledgements

This work was supported by a grant for a key research project from the State Science and Technology Commission and the National Nature Science Foundation of China. The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R & D No. 190-9609-2801. SSSR thanks the Univerisiti Sains Malaysia for a Visiting Post-Doctoral Fellowship.

Notes and references

† Preparation of Cd (TPT)(py) **1**. Hydrothermal treatment of Cd-(ClO$_4$)$_2$·6H$_2$O (1.2 mmol), 1,4-cyanobenzene (1 mmol), pyridine (1 ml) and water (10 ml) for 1 day at 140 °C yielded a yellow prismatic crystalline product (only one pure phase). The yield of **1** was almost quantitative based on 1,4-cyanobenzene (Found: C, 43.65; H, 2.56; N, 4.01. (Calc.: C, 43.87; H, 2.53; N, 3.94%). IR(KBr, cm^{-1}): 1710vw, 1605vw, 1568vs, 1535vs, 1487m, 1449m, 1386vs, 1296vw, 1221m, 1143m, 1067m, 1038m, 1015m, 890m, 838s, 750s, 706s, 630m, 528m.

‡ Crystal data for **1**. C$_{13}$H$_9$NO$_4$Cd, monoclinic, *C*2/*c*, $a = 16.9875(4)$, $b = 9.9995(2)$, $c = 7.8476(1)$ Å, $\beta = 104.584(1)°$, $V = 1290.09(4)$ Å^3, $Z = 4$, $M = 355.6$, $D_c = 1.83$ Mg m^{-3}, $R_1 = 0.026$, $wR_2 = 0.059$ (2075 reflections), $T = 293$ K, $\mu = 1.70$ mm^{-1}. CCDC reference number 186/1446. See http://www.rsc org/suppdata/dt/1999/1915/ for crystallographic files in .cif format.

1 K. S. Burger, P. Chaudhuri, K. Wieghardt and B. Nuber, *Chem. Eur. J.*, 1995, **1**, 586.
2 C. E. Xanthopoulos, M. P. Sigalas, G. A. Katsoulos, C. A. Tsipis, A. Terzis , M. MenTzafos and A. Hountas, *Inorg. Chem.*, 1993, **32**, 5433.
3 E. G. Bakalbassis, A. P. Bozopoulos, J. Mrozinski, P. J. Kentzeperis and C. A. Tsipsi, *Inorg. Chem.*, 1988, **27**, 529.
4 E. Bakalbassis, P. Bergerat, O. Kahn, S. Jeannin, Y. Jeannin, Y. Dromzee and M. Guillot, *Inorg. Chem.*, 1992, **31**, 625.
5 C. S. Hong and Y. Do, *Inorg. Chem.*, 1997, **36**, 5684; C. S. Hong and Y. Do, *Inorg. Chem.*, 1998, **37**, 4470.
6 H. Li, C. E. Davis, T. L. Groy, D. G. Kelly and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 2186; H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571.
7 R.-G. Xiong, S. R. Wilson and W. Lin, *J. Chem. Soc., Dalton Trans.*, 1998, 4089.
8 R. L. Rardin, W. B. Tolman an S. J. Lippard, *New J. Chem.*, 1991, **15**, 417.
9 W. Clegg, J. T. Cressey, A. McCamley and B. P. Straughan, *Acta Crystallogr., Sect. C*, 1995, **51**, 234.
10 M. Fujita, Y. J. Kwon, M. Miyazawa and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1994, 1977; S. D. Huang and R.-G. Xiong, *Polyhedron*, 1997, **16**, 3929.
11 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
12 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Communication 9/02056J