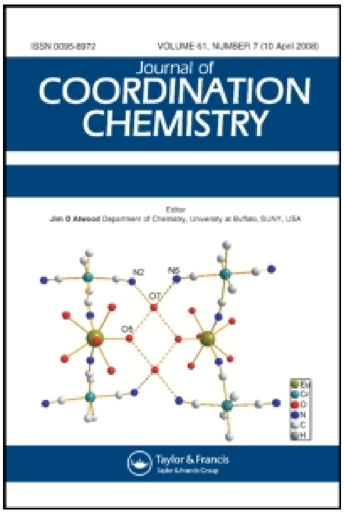

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A 2D Zn(II) metal-organic framework constructed from 4,4'-(perfluoropropane-2,2-diyl)dibenzoic acid, synthesis, structure and photoluminescence

Abulikemu Abudu Rexit[a]
[a] The College of Life Science and Chemistry, Xinjiang Normal University, Urumqi, China

To cite this Article Rexit, Abulikemu Abudu(2009) 'A 2D Zn(II) metal-organic framework constructed from 4,4'-(perfluoropropane-2,2-diyl)dibenzoic acid, synthesis, structure and photoluminescence', Journal of Coordination Chemistry, 62: 8, 1373 — 1378

To link to this Article: DOI: 10.1080/00958970802668844

URL: http://dx.doi.org/10.1080/00958970802668844

Journal of Coordination Chemistry
Vol. 62, No. 8, 20 April 2009, 1373–1378

Taylor & Francis
Taylor & Francis Group

A 2D Zn(II) metal-organic framework constructed from 4,4′-(perfluoropropane-2,2-diyl)dibenzoic acid, synthesis, structure and photoluminescence

ABULIKEMU ABUDU REXIT*

The College of Life Science and Chemistry, Xinjiang Normal University, Urumqi, China

(*Received 23 May 2008; in final form 8 August 2008*)

A Zn(II) metal-organic framework (MOF) $[Zn_2(FPDB)_2(pyridine)_2] \cdot 5H_2O$ (**1**) was synthesized solvothermally via reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ and 4,4′-(perfluoropropane-2,2-diyl)dibenzoic acid (H_2FPDB). The X-ray single crystal diffraction analysis reveals that **1** crystallizes in monoclinic $C2/c$ space group with $a = 23.279(5)$ Å, $b = 7.837(5)$ Å, $c = 26.776(5)$ Å, $\beta = 106.7(6)°$ and $Z = 4$. In **1**, two adjacent zinc ions are bridged to form a dinuclear paddle-wheel SBU, and four neighboring SBUs are linked by FPDB ligands to construct a chair-type grid. Distorted grids extended along *a* and *b* axes to complete a double-sheet 2D layer and these layers stack with van der Waal's interactions to build the final structure. Compound **1** shows strong luminescence at room temperature in the solid state, suggesting that **1** may be an excellent fluorescent material.

Keywords: Solvothermally; Metal-organic framework; Trifluoromethyl; Carboxylate; Paddle-wheel; SBU; Photoluminescence

1. Introduction

Metal-organic frameworks (MOFs) have potential applications in gas storage and adsorption [1], luminescence [2], magnetism [3], catalysis [4], and ion-exchange processes [5]. Organic ligands play an important role in construction of MOFs allowing changes in symmetry, geometry, and flexibility. Many polycarboxylate linkers are bridges in MOFs, but polycarboxylate ligands containing trifluoromethyl is a developing area [6]. We applied 4,4′-(perfluoropropane-2,2-diyl)dibenzoic acid (H_2FPDB) to build MOFs. Herein, we report the synthesis, crystal structure and luminescence property of a Zn(II) MOF $[Zn_2(FPDB)_2(pyridine)_2] \cdot 5H_2O$ (**1**), based on the H_2FPDB ligand.

2. Experimental

2.1. *Materials and measurements*

All reagents and solvents were used as received from commercial supplier without purification. Infrared samples were prepared as KBr pellets and spectra were obtained

---

*Email: aarexit@xjnu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802668844

from 400–4000 cm^{-1} using a Perkin-Elmer 2000 FTIR spectrometer. Thermal gravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10°C min^{-1} using a Shimadzu TGA-50H thermal gravimetric analyzer. Powder X-ray diffraction data were collected on a Philips X'Pert Pro Super diffractometer with Cu radiation (λ) 1.54187 Å (Supplemental Material). Elemental analyses were performed on a Vario EL-III elemental analyzer. All fluorescence measurements were carried out on a Jobin Yvon Fluorolog-3-TAU spectrofluorimeter at room temperature.

2.2. *Synthesis of [$Zn_2(FPDB)_2(pyridine)_2$]·$5H_2O$ (1)*

A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (36 mg, 0.1 mmol) and H_2FPDB (15 mg, 0.038 mmol) was added to isobutanol (0.2 mL), water (0.1 mL) and pyridine (0.2 mL) in a heavy-walled Pyrex tube at room temperature. After 2 min sonication dispersing, the tube was frozen under liquid nitrogen, sealed under vacuum and placed inside an oven at 100°C. After 12 h heating, colorless single crystals suitable for X-ray analysis were obtained. Yield: 17.7 mg (81%). The complex was stable in air and insoluble in water and solvents such as ethanol, methanol, dichloromethane, chloroform, DMF, and DMSO. Elemental Anal. Calcd for $C_{44}H_{30}F_{12}N_2O_{13}Zn_2$ (%): C, 45.82; H, 2.62; N, 2.43. Found: C, 45.91; H, 3.14; N, 2.67. FTIR (KBr pellets): $\upsilon = 3439$ (w), 1640 (s), 1612 (m), 1570 (m), 1453 (w), 1408 (vs), 1259 (s), 1210 (m), 1173 (m), 1046 (m), 960 (m), 843 (m), 781 (m), 724 (m), 696 (m).

2.3. *X-ray crystallographic study*

Diffraction intensities for **1** were collected on a Oxford Diffraction Gemini S Ultra CCD diffractometer equipped with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 293 K. The structure of **1** was solved by direct methods and refined by full-matrix least-squares with the SHELXL-97 program [7]. CCDC 688447 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/data_request/cif). Crystallographic data of **1** are summarized in table 1, and selected bond lengths and angles are listed in table 2.

3. Results and discussion

X-ray crystallography reveals that **1** is a 2D structure crystallizing in the monoclinic space group $C2/c$. As shown in figure 1, each zinc is five coordinate with four carboxyl oxygens (O1, O2, O3, and O4) from FPDB in basal positions and one pyridyl nitrogen (N1) at the apical position in distorted square-pyramidal geometry. The Zn(1)–O(N) distances vary from 2.031 Å to 2.066 Å, while the O–Zn(1)–O(N) angles are in the range 86.31–105.04°. Two adjacent zincs are bridged by four carboxylates from four FPDB ligands to generate a paddle-wheel dinuclear building unit (SBU), in which the Zn $\cdots$ Zn separation is 2.971 Å.

Every four neighboring paddle-wheels interlink with the help of FPDB ligands to form a distorted tetragonal grid [figure 2a, view down the *c*-axis]. When viewed slightly

Table 1. Crystallographic data of **1**.

Empirical formula	$Zn_2C_{44}H_{30}F_{12}N_2O_{13}$
Formula weight	1153.44
Crystal system	Monoclinic
Space group	$C2/c$
Units of dimensions (Å, °)	
a	23.279(5)
b	7.837(5)
c	26.776(5)
α	90
β	106.7(6)
γ	90
V (Å^3)	4677(3)
Z	4
T (K)	293
λ (Å)	0.71073
ρ_{Calcd} (g cm^{-3})	1.638
$F(000)$	2320
Data/parameters	4115/361
$R_1{}^a$ [$I > 2\sigma(I)$] (for all data)	0.0390(0.0607)
$wR_2{}^b$ (for all data)	0.0976(0.1025)
Goodness of fit (for all data)	0.951(0.951)
Largest difference peak and hole (e Å^3)	0.629, −0.510

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR_2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°).

Zn(1)–O(1)	2.034(2)	O(1)–Zn(1)–O(2)	158.4(3)	O(2)–Zn(1)–O(4)	89.3(6)
Zn(1)–O(2)	2.042(2)	O(3)–Zn(1)–O(4)	158.7(4)	N(1)–Zn(1)–O(1)	104.4(3)
Zn(1)–O(3)	2.066(2)	O(1)–Zn(1)–O(3)	88.5(9)	N(1)–Zn(1)–O(2)	96.9(6)
Zn(1)–O(4)	2.036(2)	O(1)–Zn(1)–O(4)	87.8(4)	N(1)–Zn(1)–O(3)	96.1(5)
Zn(1)–N(1)	2.031(3)	O(2)–Zn(1)–O(3)	86.3(1)	N(1)–Zn(1)–O(4)	105.0(4)

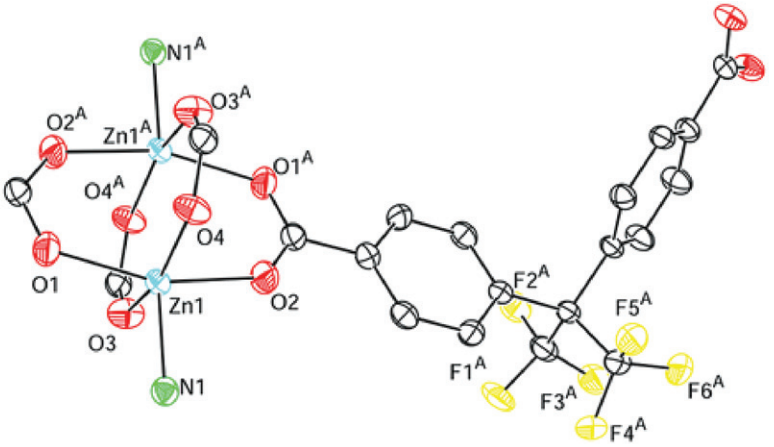

Figure 1. ORTEP drawing (at 30% probability) of the coordination environments of zinc in **1** (guest water molecule and hydrogen atoms are omitted for clarity).

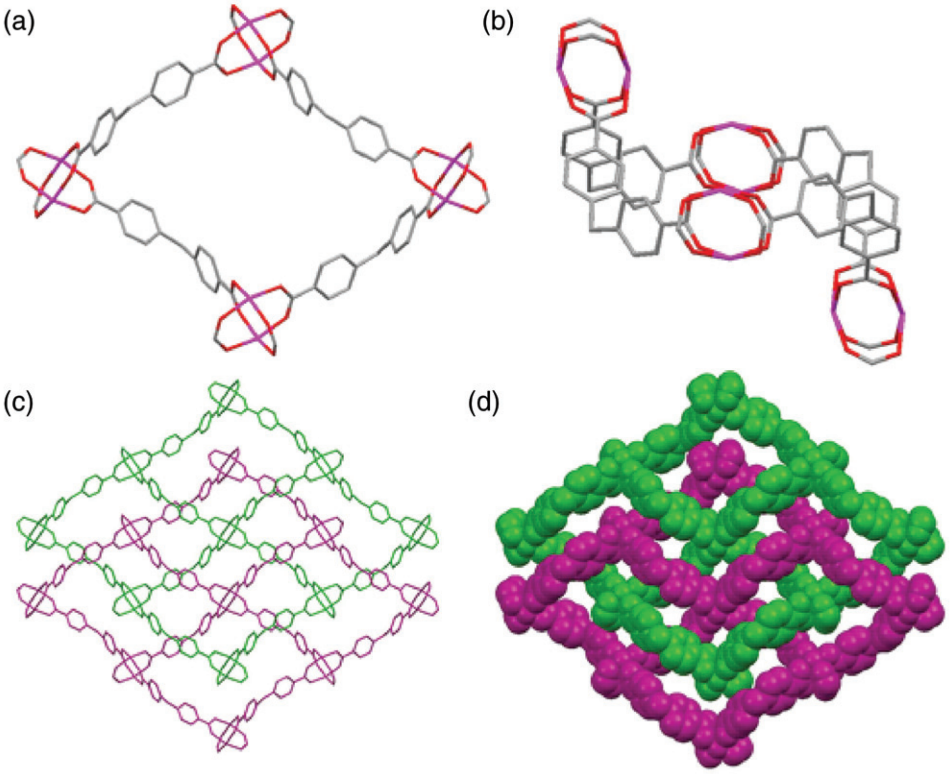

Figure 2. (a) Distorted grid built by four adjacent paddle-wheel SBUs as viewed down the *c*-axis. (b) The distorted grid shows chair-type configuration viewed slightly off the *a*-axis. (c) Two layers interweave to complete the double-sheet 2D layer as viewed down the *c*-axis. (d) Spacefill mode of the double-sheet layer (guest water molecule and hydrogen atoms are omitted for clarity).

off the *a*-axis, it is clear that the distorted grid is a chair-type configuration [figure 2b]. Chair-type grids extend along *a* and *b* axes, giving an infinitive 2D sheet [figure 2c, in green]. Furthermore, each chair-type grid captures a SBU inside, and these surrounded SBUs also interlink to construct the second sheet [figure 2c, in purple]. Generally, every paddle-wheel SBU is fixed inside one chair-type grid in the other sheet, and as a result, these two sheets interweave tightly to complete the double-sheet 2D layer as viewed down the *c*-axis [figure 2d]. Adjacent layers stack in an aligned fashion with van der Waal's interactions to build the final structure of **1**.

Similar structure based on Cu(II) and H_2FPDB ligand were reported by Li and co-workers [6(a) and (b)]. Our study provides another example of an H_2FPDB-based MOF; the ligand has strong tendency to form paddle-wheels.

3.1. *Photoluminescent properties*

The photoluminescence spectra of H_2FPDB and **1** were investigated in the solid state at room temperature. As shown in figure 3, H_2FPDB exhibits a single emission band at 320 nm when excited at 296 nm, attributed to the $\pi^* \rightarrow \pi$ transition. Compound **1** shows more complicated red-shifted emission bands, a main emission band at 471 nm and a

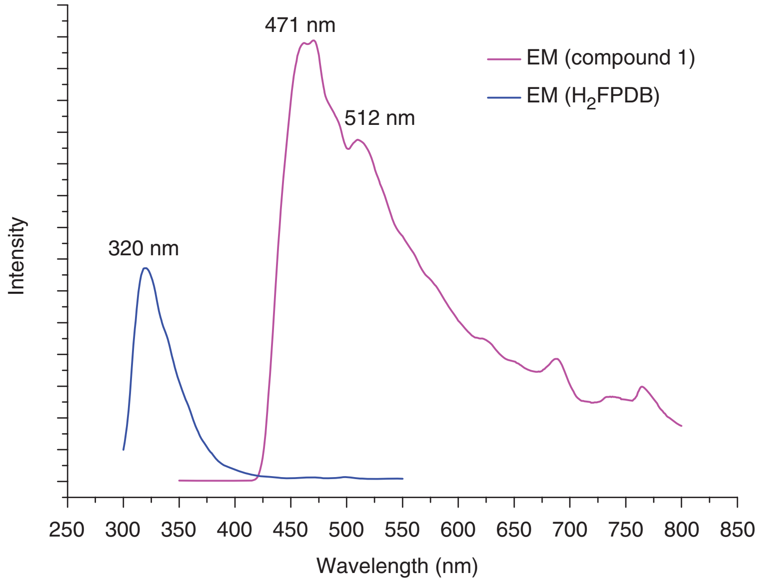

Figure 3. Solid-state excitation-emission spectra of free H_2FPDB ligand and **1**.

shoulder band at 512 nm upon excitation at 365 nm. The red-shifted emission of **1** compared to the free ligand may be attributed to metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT). Therefore, **1** may be a candidate as fluorescent materials.

4. Conclusion

We have synthesized a new Zn(II) 2D MOF (**1**) based on a polycarboxylate ligand containing trifluoromethyl groups. The strong luminescence of compound **1** at room temperature in the solid state suggests that **1** may be a candidate as fluorescent materials.

Acknowledgment

This work was supported by the Natural Science Foundation of Xinjiang Normal University.

References

[1] (a) S. Noro, S. Kitagawa, M. Kondo, K. Seki. *Angew. Chem., Int. Ed.*, **39**, 2081 (2000); (b) M.P. Suh, J.W. Ko, H.J. Choi. *J. Am. Chem. Soc.*, **124**, 10976 (2002); (c) N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi. *Science*, **300**, 1127 (2003); (d) G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guégan. *Chem. Commun.*, 2976 (2003); (e) D. Bradshaw, T.J. Prior, E.J. Cussen, J.B. Claridge, M.J. Rosseinsky. *J. Am. Chem. Soc.*, **126**, 6106 (2004); (f) B. Kesanli, Y. Cui, M.R. Smith, E.W. Bittner, B.C. Bockrath, W. Lin. *Angew. Chem., Int. Ed.*, **44**, 72 (2005); (g) J.L.C. Rowsell, O.M. Yaghi. *J. Am. Chem. Soc.*, **128**, 1304 (2006).

[2] (a) L.G. Beauvais, M.P. Shores, J.R. Long. *J. Am. Chem. Soc.*, **122**, 2763 (2000); (b) J. He, J. Yu, Y. Zhang, Q. Pan, R. Xu. *Inorg. Chem.*, **44**, 9279 (2005).

[3] (a) G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murray, J.D. Cashion. *Science*, **298**, 1762 (2002); (b) S. Xiang, X. Wu, J. Zhang, R. Fu, S. Hu, X. Zhang. *J. Am. Chem. Soc.*, **127**, 16352 (2005); (c) Y.Z. Zheng, M.L. Tong, W.X. Zhang, X.M. Chen. *Chem. Commun.*, 165 (2006).

[4] (a) M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994); (b) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim. *Nature*, **404**, 982 (2000); (c) L. Pan, H. Liu, X. Lei, X. Huang, D.H. Olson, N.J. Turro, J. Li. *Angew. Chem., Int. Ed.*, **42**, 542 (2003); (d) B. Kesanli, W. Lin. *Coord. Chem. Rev.*, **246**, 305 (2003); (e) C.D. Wu, A. Hu, L. Zhang, W. Lin. *J. Am. Chem. Soc.*, **127**, 8940 (2005); (f) D.N. Dybtsev, A.L. Nuzhdin, H. Chun, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, K. Kim. *Angew. Chem., Int. Ed.*, **45**, 916 (2006); (g) T. Uemura, R. Kitaura, Y. Ohta, M. Nagaoka, S. Kitagawa. *Angew. Chem., Int. Ed.*, **45**, 4112 (2006); (h) C.D. Wu, W. Lin. *Angew. Chem. Int. Ed.*, **46**, 1075 (2007).

[5] T.Y. Shvareva, S. Skanthakumar, L. Soderholm, A. Clearfield, T.E. Albrecht-Schmitt. *Chem. Mater.*, **19**, 132 (2007).

[6] (a) L. Pan, M.B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J.K. Johnson. *J. Am. Chem. Soc.*, **126**, 1308 (2004); (b) L. Pan, D.H. Olson, L.R. Ciemnolonski, R. Heddy, J. Li. *Angew. Chem., Int. Ed.*, **45**, 616 (2006); (c) R.Q. Zou, R.Q. Zhong, M. Du, T. Kiyobayashi, Q. Xu. *Chem. Commun.*, 2467 (2007); (d) R.Q. Zhong, R.Q. Zou, M. Du, T. Yamada, G. Maruta, S. Takeda, Q. Xu. *Dalton Trans.*, 2346 (2008); (e) C. Yang, X. Wang, M.A. Omary. *J. Am. Chem. Soc.*, **129**, 15454 (2007).

[7] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen University, Göttingen, Germany (1997).