Guest driven structural transformation studies of a luminescent metal–organic framework

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Abstract. A two-dimensional (2D) porous metal-organic framework (MOF) [$\{Zn_2(L)_4(OTf)_4\} \cdot 2(DCM) \cdot xG\}_n$ (**1**⊃**G**) (OTf = trifluoro methane sulfonate, DCM = Dichloromethane, L (1, 4-bis (4-pyridyl)-2, 3-diaza-1, 3-butadiene) synthesized at room temperature. Free guests DCM were encapsulated in the pores of the MOF. On air drying the MOF loses free DCM molecules and changed its structure in a crystal to crystal manner to produce compound **1** [$\{Zn(L)_2(OTf)_2\} \cdot XG\}_n$ (**1**). This guest-induced breathing of the framework was also supported from PXRD patterns. Solid state photoluminescence properties of the dynamic MOF were studied at room temperature.

Keywords. Metal-organic frameworks; coordination polymers; dynamic framework; crystal to crystal transformation; luminescence.

1. Introduction

Metal-Organic frameworks (MOFs) or porous coordination polymers have drawn immense attention not only due its aesthetic architectures but also due to its wide range of potential applications in the field of gas storage, chemical separation, drug delivery, catalysis, optics, sensing.^{1–6} In the recent past, flexibility in MOFs has been found to be of great interest due to its unique guest-responsive function and enhanced host-guest interactions over the rigid porous frameworks.⁷ Dynamic MOFs are very sensitive to external/chemical stimuli and they change their structure upon variation of guest molecules inside its frameworks.⁸ Such guest dependent dynamic structural property of the flexible PCPs makes them potential candidates for the smart sensors and gas separating materials.^{9,10} Dynamic behaviours of this kind of materials are often understood from their single crystal to single crystal (SCSC) transformation studies.¹¹ It is not always easy to get a single crystal after removal of a guest from the parent framework. Sometimes this guest removal process occurs so fast that a very weak crystalline phase or amorphous phase gets generated.

Combinations of flexible 4, 4'- N donor functionality of a ligand with metal salt in low boiling solvent system at room temperature often render MOFs which generally encapsulate low boiling solvents as free guests in the pores. These MOFs generally exhibit flexible character because they often lose those trapped guests upon air drying of the MOFs crystals and undergo structural variations, often termed as guest induced breathing phenomena.¹² Luminescence can be incorporated into the dynamic framework by making use of d¹⁰ metal ions with the complexation of a neutral flexible 4, 4' N donor ligand.¹³ Keeping all the above points in mind, a smart material with bimodal functionality (dynamic and luminescent) can be developed. Here we strategically choose flexible ligand L¹⁴ (1, 4-bis (4-pyridyl)-2, 3-diaza-1, 3-butadiene) and Zn (II) metal ion in low boiling solvent system to generate a dynamic luminescent MOF.

Herein, we present a 2D porous metal-organic framework [$\{Zn_2(L)_4(OTf)_4\} \cdot 2(DCM) \cdot x(G)\}_n$ (G are disordered guest molecules)(**1**) built from Zn(II) and ligand **L** synthesized at room temperature. The compound exhibits guest dependent structural dynamism. This guest dependent structural dynamism of the MOF has been well demonstrated by single crystal to single transformation (SCSC) and powder X-ray diffraction (PXRD) studies. Solid state photoluminescence of the air dried phase of the compound is measured at room temperature.

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2. Experimental

2.1 Materials

All the reagents were commercially available and used as supplied without further purification. Ligand **L** was synthesized according to the reported protocol.¹⁴ Zn(II) triflate was purchased from Aldrich Chemical. Co. All the other solvents used were purchased locally.

2.2 Synthesis of Compound $1\text{DG}[\{\text{Zn}_2(\text{L})_4(\text{OTf})_4\} \cdot 2(\text{DCM}) \cdot x(\text{G})_2]_n$ (**1DG**)

DCM solution of the ligand (21.023 mg, 1 mL) was taken into a glass tube, onto that 1-propanol (1 mL) was carefully layered and over the 1-propanol layer, solution of Zn(OTf)₂ (36.353 mg, 1 mL) in MeOH was very carefully layered. Block shaped yellow crystals suitable for X-ray studies were obtained after 15 days in 70% yield.

2.3 Synthesis of Compound $1[\{\text{Zn}(\text{L})_2(\text{OTf})_2\} \cdot x\text{G}]_n$ (**1**)

When the crystals of parent compound **1DG** were taken out from its mother liquor and kept for air drying

for about half an hour, it changed to yellow coloured compound **1**.

2.4 X-ray crystallography

Single-crystal X-ray data of **1DG** and **1** were collected at 100 K on a Bruker KAPPA APEX II CCD Duodiffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The data integration and reduction were processed with SAINT¹⁵ software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL¹⁶ and was refined on F² by full matrix least-squares technique using the SHELXL-97¹⁷ program package within the WINGX¹⁸ program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters. PLATON¹⁹ squeeze programme was used for the structures to remove diffuse electron density associated with badly disordered solvent molecules (tables 1 and 2).

Table 1. Crystal data and structure refinement for Compound **1DG**.

Identification code	Compound 1DG	
Empirical formula	C ₅₅ H ₄₅ Cl ₄ F ₁₂ N ₁₅ O ₁₂ S ₄ Zn ₂	
Formula weight	1736.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 19.8102(15) Å b = 24.4012(19) Å c = 18.1151(14) Å	
Volume	7704.3(10) Å ³	$\beta = 118.3790(10)^\circ$
Z	4	
Density (calculated)	1.497 Mg/m ³	
Absorption coefficient	0.962 mm ⁻¹	
F (000)	3504	
Crystal size	0.11 × 0.17 × 0.21 mm ³	
Theta range for data collection	1.51 to 25.00°	
Index ranges	−20 ≤ h ≤ 23, −28 ≤ k ≤ 28, −21 ≤ l ≤ 21	
Reflections collected	54434	
Independent reflections	10862 [R(int) = 0.0231]	
Completeness to theta = 25.00°	99.9%	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	10862/656/937	
Goodness-of-fit on F ²	2.931	
Final R indices [I > 2σ(I)]	R1 = 0.1383, wR2 = 0.3292	
R indices (all data)	R1 = 0.1446, wR2 = 0.3375	
Absolute structure parameter	0.28(2)	

Table 2. Crystal data and structure refinement for Compound 1.

Identification code	Compound 1	
Empirical formula	C ₂₆ H ₂₀ F ₆ N ₈ O ₆ S ₂ Zn	
Formula weight	783.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	I222	
Unit cell dimensions	a = 9.0511(11) Å	$\alpha = 90^\circ$
	b = 17.789(3) Å	$\beta = 90^\circ$
	c = 24.112(3) Å	$\gamma = 90^\circ$
Volume	3882.3(9) Å ³	
Z	4	
Density (calculated)	1.341 Mg/m ³	
Absorption coefficient	0.814 mm ⁻¹	
F(000)	1584	
Theta range for data collection	1.42 to 28.29°.	
Index ranges	−12 ≤ h ≤ 12, −23 ≤ k ≤ 23, −32 ≤ l ≤ 30	
Reflections collected	34931	
Independent reflections	4828 [R(int) = 0.0329]	
Completeness to theta = 28.29°	99.9%	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	4828/37/222	
Goodness-of-fit on F ²	2.739	
Final R indices [I > 2σ(I)]	R1 = 0.1047, wR2 = 0.3083	
R indices (all data)	R1 = 0.1077, wR2 = 0.3109	
Absolute structure parameter	0.49(4)	

2.5 Physical measurements

FT-IR spectra were measured on a Nicolet 6700 FT-IR spectrophotometer by making KBr pellets (400–4000 cm⁻¹). X-ray powder patterns were recorded on a BrukerD8 advanced X-ray diffractometer using Cu K α radiation (λ = 1.5406 Å) with scan rate 0.4 s/step and step size 0.01°, and thermogravimetric analyses were recorded with heating rate of 10°C/min under N₂ atmosphere on a Perkin-Elmer STA 6000 TGA analyzer. Solid state UV were recorded on Perkin Elmer Lamda 900 UV/ VIS Spectrometer. The solid-state fluorescence spectra were recorded on *Fluorolog 3*.

3. Results and Discussion

Combination of ligand L and Zn(II) triflate in a solvent system of DCM/1-propanol/ MeOH at room temperature yielded yellow coloured block-shaped crystals of [Zn₂(L)₄(OTf)₄].2(DCM).xG] (15G). The Single crystal X-ray analysis (SC-XRD) of compound 15G revealed that compound crystallized in monoclinic crystal system with space group Cc. An asymmetric unit of the compound contains two Zn(II),

four ligands (L), four CF₃SO₃⁻ (triflate) anions, two dichloromethane (DCM) molecules as guests and disordered guests. Coordination of four Nitrogens of different ligands and two oxygens of two different triflate anions makes each metal ion octahedral environment. Each ligand ligates to a metal centre through its nitrogen atom at the terminal position and at the same time another terminal nitrogen of the same ligand binds to another metal centre. Thus, extension of these co-ordinations formed 2D planar sheets along c axis. Careful analysis of the structure of 15G reveals that chlorine atom of DCM molecule and coordinated oxygen of CF₃SO₃⁻ undergo weak chemical interactions with central nitrogen of the long flexible ligand and 4 pyridyl nitrogen respectively. Overall 3D packing of 15G shows that the presence of 1D channels along c axis, which encapsulate free DCM molecules (figure 1). A noteworthy feature of the compound is its dynamic structural behaviour. When compound 15G was taken out from its mother liquor and kept outside for air drying for about half an hour, it showed a drastic structural change to a new phase (Compound 1) without losing its single crystalline nature. Single crystal analysis of compound 1 showed large differences in unit cell parameters with loss of free DCM molecules as

Figure 1. Guest induced dynamic structural transformation from compound **1D G** to **1** in a SCSC manner with the corresponding single crystal images.

guests as illustrated by **1** $[\{\text{Zn}(\text{L})_2(\text{OTf})_2 \cdot x\text{G}\}]_n$. Complete SCSC structural analysis revealed that the crystal system of compound **1** changed to orthorhombic with a change in space group from Cc to I222. The metal centre is in octahedral geometry and coordination environment remains almost unchanged. Bond lengths and bond angles around Zn(II) centre are very similar. The overall 3D packing of **1** also shows that formation of 1D channels along a axis (figure 1). Very close examination of both the structures revealed that the contraction of M-M-M angle of a single 2D net on departure of free guests.

During the structural transformation M-M-M angle of a single 2D net changed from 102.80° (**1D G**) to 100.77° (**1**) (figure 2) accompanied by a change in shape and size of 1D porous channels. This leads to the breathing of the framework from $8.772 \text{ \AA}$ (**1D G**) to $9.984 \text{ \AA}$ (**1**) considering M-M distances along the porous channels (figure 3).

Compound **1** is stable in its single crystalline form, but it changes its structure in powder form as evident

Figure 2. M-M-M angle (of a single 2D net) changes during the structural transformation.

from slight variation in powder X-ray diffraction (PXRD) patterns of compound **1** at different time intervals (figure 4). Hence we designate the bulk powder of compound **1** as **1'**.

The thermo gravimetric analysis (TGA) of compound **1'** in N_2 atmosphere revealed an approximate $\sim 6\%$ wt loss at temperature 133°C and the compound is further stable up to 240°C (figure 5).

FT-IR spectral analysis of the compound **1'** indicates the strong band observed at $\sim 1300 \text{ cm}^{-1}$ which corresponds to presence of CF_3SO_3^- in the framework (figure 6).

Solid state UV was measured for free ligand and compound **1'** in its air dried condition. The spectra showed minimum reflectance at wavelength $\sim 370 \text{ nm}$ for both free ligand and air dried compound (figure 7).

Solid state emission spectra were recorded for free ligand and compound **1'** at room temperature. Upon excitation at 370 nm , ligand **L** displays three emission bands at 407 nm , 428 nm and 563 nm respectively. Among the three bands, the band at 428 nm is the most intense one. Compound **1'** showed an intense band at 558 nm with a weak band at 431 nm and a shoulder at 409 nm .^{20,21} $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi$ intraligand transitions are mainly responsible for these emissions (figure 8).

Figure 3. Guest induced breathing of the framework during structural transformation.

Figure 4. Powder X-ray diffraction (PXRD) patterns of compound **1**.

Figure 6. FT-IR spectra of free ligand and Compound **1'**.

Figure 5. Thermogravimetric analysis of Compound **1'**.

Figure 7. Solid-state UV spectra of free ligand and compound **1'** at room temperature.

Figure 8. Solid state photoluminescence spectra of free ligand and compound **1'** at room temperature.

4. Conclusion

We have synthesized a 2D porous dynamic luminescent metal organic framework. The compound showed guest induced breathing of the framework. The guest dependent structural dynamism has been well demonstrated by SCSC experiments and PXRD patterns of the compounds. Solid state UV and photoluminescence were studied for the compound at room temperature. This structurally dynamic behaviour along with luminescence property of the compound might be very useful as a guest-responsive material for efficient separation purpose.

Supplementary Information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data Centre. CCDC 996229 (**15G**) and CCDC 996228 (**1**). Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK, Fax: (internet) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

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References

1. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O'Keeffe M and Yaghi O M 2002 *Science*. **295** 469
2. Li J-R, Kuppler R J and Zhou H-C 2009 *Chem. Soc. Rev.* **38** 1477
3. An J, Geib S J and Rosi N L 2009 *J. Am. Chem. Soc.* **131** 8376
4. Lee J Y, Farha O K, Roberts J, Scheidt K A, Nguyen S T and Hupp J T 2009 *Chem. Soc. Rev.* **38** 1450
5. Guo Z, Cao R, Wang X, Li H, Yuan W, Wang G, Wu H and Li J 2009 *J. Am. Chem. Soc.* **131** 6894
6. Chen B, Xiang S and Qian G 2010 *Acc. Chem. Res.* **43** 1115
7. Horike S, Shimomura S and Kitagawa S 2009 *Nat. Chem.* **1** 695
8. Ghosh S K, Bureekaew S and S Kitagawa 2008 *Angew. Chem. Int. Ed.* **47** 3403
9. Uemura K, Kitagawa S, Fukui K and Saito K 2004 *J. Am. Chem. Soc.* **126** 3817
10. Yanai N, Kitayama K, Hijikata Y, Sato H, Matsuda R, Kubota Y, Takata M, Mizuno M, Uemura T and Kitagawa S 2011 *Nat. Mater.* **10** 787
11. Manna B, Chaudhari A K, Joarder B, Karmakar A and Ghosh S K 2013 *Angew. Chem. Int. Ed.* **52** 998
12. Biradha K and Fujita M 2002 *Angew. Chem. Int. Ed.* **41** 3392
13. Chen Y-Q, Li G-R, Chang Z, Qu Y-K, Zhang Y-H and Bu X-H 2013 *Chem. Sci.* **4** 3678
14. Ciurtin D M, Dong Y-B, Smith M D, Barclay T, Loye H-C Z 2001 *Inorg. Chem.* **40** 2825.
15. SAINTPlus (Version 7.03); BrukerAXS Inc.: Madison, WI 2004
16. Sheldrick G MSHELXTL, Reference Manual, Version 5.1; BrukerAXS: Madison, WI, 1997
17. Sheldrick G M *Acta Crystallogr. Sect. A* 2008 112
18. Farrugia, L J WINGX version 1.80.05; University of Glasgow: Glasgow, 2009
19. Spek A L, PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2005
20. Zhang G, Yang G and Ma Jin Shi 2006 *Cryst. Growth. Des.* **6** 1897
21. Vyasamudri S Y and Maji T K 2009 *Chem. Phys. Lett.* **473** 312