

Two Novel 3-D Zinc Compounds with Mixture Ligands of H₃BTB and 4,4'-Bipy: Crystal Structures, Blue Fluorescence and Single Point Energy Calculation

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Two 3-D zinc framework compounds, [Zn₆(BTB)₄(4,4'-bipy)₄(H₂O)₄]₉H₂O (**1**) and [Zn₃(BTB)₂(4,4'-bipy)₂(H₂O)₂]₅H₂O (**2**) (H₃BTB = 1,2,3-benzenetricarboxylic acid, 4,4'-bipy = 4,4'-bipyridine), are obtained from the diffusion method and hydrothermal reaction respectively. Though **1** and **2** has the same coordination geometries of zinc atoms and coordination mode of BTB³⁻, their 2-D layers are different: mirror symmetric layers in **1**; parallel ones in **2**, further connecting by 4,4'-bipy into 3-D frameworks. The hydrothermal reaction of **2** results in a more stable 3-D framework than the one in **1**, which is supported by the single point energy calculations. **1** and **2** show similar blue fluorescence at 417 nm, which can be assigned to LMCT.

Key Words: 1,2,3-Benzenetricarboxylic acid, Crystal structure, Fluorescence, Single point energy calculation

Introduction

A rapid improvement has been achieved in the field of constructing polycarboxylic metal-organic polymers for their intriguing structural features, and physicochemical properties.¹ One of the most fundamental strategies is to select suitable metal centers and organic linkers to assemble multidimensional frameworks.² Metal centers are not only a key factor in fabricating frameworks through the metal coordination preferences and the rational assembly process,³ but a source for imparting a particular physical property.⁴ By the selection of organic linkers, an asymmetric aromatic rigid polycarboxylic acid, 1,2,3-benzenetricarboxylic acid (H₃BTB) attracted our interest, which can bind up to nine metals with its three carboxylic groups as short bridges and a benzene ring as a long bridge. Compared to its extensively studied isomer 1,3,5-benzenetricarboxylic acid,⁵ the investigation on H₃BTB system is still in its youth.⁶ The strong steric hindrance of the three special-orientation carboxylic groups may result in different framework structures, which cannot be obtained through its isomers. In view of the coordination characterizations of H₃BTB, herein, we synthesized two 3-D zinc framework compounds, [Zn₆(BTB)₄(4,4'-bipy)₄(H₂O)₄]₉H₂O (**1**) and [Zn₃(BTB)₂(4,4'-bipy)₂(H₂O)₂]₅H₂O (**2**), using H₃BTB as asymmetric organic spacer and 4,4'-bipy as co-ligand, with their structures determined, blue fluorescence observed, and single point energies compared.

Experimental Section

Materials and physical measurements. Solvents and starting materials were purchased commercially and used without further purification. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet in the range of

4000 ~ 400 cm⁻¹. Elemental analyses of C, H and N were carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a FluoroMax-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s.

Synthesis of 1. Aqueous solution containing Zn(OAc)₂·2H₂O (110 mg, 0.5 mmol), H₃BTB (105 mg, 0.5 mmol), and NaOH (40 mg, 1.0 mmol) was stirred for 6 h. Then the 10 mL filtrate was covered with 10 mL ethanol solution of 4,4'-bipy (78 mg, 0.5 mmol). Over a period of approximated 10 d, the colorless prismatic crystals of **1** were obtained. Yield based on Zn: 64 mg, 37%. IR (cm⁻¹, KBr): 3434.12 (s), 2930.59 (w), 1613.03 (vs) 1492.18 (w), 1384.86 (s), 1351.33 (s), 1139.67 (w), 986.92 (w), 807.95 (w), 780.27 (w), 712.00 (w), 643.75 (w). Elemental analysis (%) calcd. for C₇₆H₇₀N₈O₃₉Zn₆: C 43.23, H 3.34, N 5.31; found: C 43.32, H 3.41, N 5.22.

Synthesis of 2. The reaction was carried out by heating the aqueous solution containing Zn(OAc)₂·2H₂O (440 mg, 2 mmol), NaOH (60 mg, 1.5 mmol), and H₃BTB (105 mg, 0.5 mmol) with 4,4'-bipy (78 mg, 0.5 mmol) in a Teflon-lined stainless steel autoclave at 170 °C for three days, then cooled with a step of 10 °C/d to obtain colorless prismatic crystals of **2**. Yield based on H₃BTB: 71 mg, 27%. IR (cm⁻¹, KBr): 3433.14 (vs), 2813.17 (w), 1618.72 (vs), 1415.09 (w) 1385.03 (s), 1351.22 (s), 1139.89 (w), 986.85 (w), 808.01 (w), 780.45 (w), 712.08 (w), 644.29 (w). Elemental analysis (%) calcd. for C₃₈H₃₆N₄O₁₉Zn₃: C 43.52, H 3.46, N 5.34; found: C 43.43, H 3.54, N 5.29.

Structure determinations and refinements of 1 and 2. Data collection for compounds **1** and **2** were performed on Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 20 °C, corrected for Lorentz and polarization

Table 1. Crystal data and refinement parameter of **1** and **2**

	1	2
Empirical formula	C ₇₆ H ₇₀ N ₈ O ₃₉ Zn ₆	C ₃₈ H ₃₆ N ₄ O ₁₉ Zn ₃
Color and Habit	Colorless Prism	Colorless Prism
Crystal Size (mm)	0.20 × 0.10 × 0.30	0.28 × 0.23 × 0.21
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P $\bar{1}$
<i>a</i> (Å)	20.954(7)	9.349(4)
<i>b</i> (Å)	9.472(3)	10.441(5)
<i>c</i> (Å)	23.124(7)	12.177(6)
α (°)	-	109.956(5)
β (°)	109.3430(10)	103.388(4)
γ (°)	-	90.275(4)
<i>V</i> (Å ³)	4331(2)	1082.4(9)
<i>Z</i>	2	1
<i>F</i> _w	2079.62	1048.82
<i>D</i> _c (mg/m ³)	1.595	1.609
μ (mm ⁻¹)	1.729	1.731
<i>F</i> (000)	2116	534
θ (°)	3.23 to 25.03	3.23 to 27.48
Reflections measured	13658	8137
Independent reflections	3765 (<i>R</i> _{int} = 0.0202)	4772 (<i>R</i> _{int} = 0.0177)
Observed Reflection (<i>I</i> > 2σ(<i>I</i>))	3211	4048
Final ^a <i>R</i> ₁ , ^b <i>wR</i> ₂	0.0408, 0.1163	0.0373, 0.1059
<i>R</i> ₁ , <i>wR</i> ₂ (all)	0.0471, 0.1216	0.0445, 0.1114
Goodness-of-fit on <i>F</i> ²	1.000	1.003
(Δ/σ) _{max/min}	0.009, 0.001	0.010, 0.001
(Δρ) _{max/min} (e/Å ³)	0.674, -0.423	0.737, -0.353

$$^a R_1 = (\sum |F_o| - |F_c|) / \sum |F_o|, \quad ^b wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w F_o^2)]^{1/2}$$

Table 2. Selected bond distances (Å) and bond angles (°) for **1** and **2**

	1		2
		Distance	
Zn1-O15#1	1.9378(10)	Zn(1)-O(16)#1	1.9317(15)
Zn1-O11	1.9615(10)	Zn(1)-O(11)	1.9497(14)
Zn1-O14#2	1.9831(10)	Zn(1)-O(14)#2	1.9849(14)
Zn1-N21	2.0217(10)	Zn(1)-N(21)	2.0087(16)
Zn2-O2W	2.0739(14)	Zn(2)-O(1W)	2.0969(15)
Zn2-O1W	2.1251(15)	Zn(2)-O(15)	2.1669(15)
Zn2-N22#3	2.1402(11)	Zn(2)-N(22)#4	2.1746(18)
Zn2-O16	2.1741(10)		
		Angle	
O15#1-Zn1-O11	130.39(5)	O(16)#1-Zn(1)-O(11)	122.18(7)
O15#1-Zn1-O14#2	94.53(3)	O(16)#1-Zn(1)-O(14)#2	94.22(5)
O11-Zn1-O14#2	98.44(4)	O(11)-Zn(1)-O(14)#2	97.42(6)
O15#1-Zn1-N21	113.78(4)	O(16)#1-Zn(1)-N(21)	120.43(6)
O11-Zn1-N21	104.02(4)	O(11)-Zn(1)-N(21)	103.65(6)
O14#2-Zn1-N21	113.89(4)	O(14)#2-Zn(1)-N(21)	116.86(6)
O2W-Zn2-O1W	180.0	O(1W)#3-Zn(2)-O(15)	83.49(5)
O2W-Zn2-N22#3	91.97(3)	O(1W)-Zn(2)-O(15)	96.51(5)
O1W-Zn2-N22#3	88.03(3)	O(1W)#3-Zn(2)-O(15)#3	96.51(5)
N22#3-Zn2-N22#4	176.05(6)	O(1W)-Zn(2)-O(15)#3	83.49(5)
O2W-Zn2-O16	90.36(2)	O(1W)#3-Zn(2)-N(22)#4	87.83(5)
O1W-Zn2-O16	89.64(2)	O(1W)-Zn(2)-N(22)#4	92.17(5)
N22#3-Zn2-O16	88.22(3)	O(15)-Zn(2)-N(22)#4	87.59(5)
N22#4-Zn2-O16	91.75(3)	O(15)#3-Zn(2)-N(22)#4	92.41(5)
O16#5-Zn2-O16	179.27(5)		

Symmetry codes. **1**: #1 = *x*, *y*+1, *z*; #2 = -*x*+0.5, *y*+0.5, -*z*+0.5; #3 = -*x*+1, -*y*+2, -*z*+1; #4 = *x*, -*y*+2, *z*-0.5; #5 = -*x*+1, *y*, -*z*+0.5; **2**: #1 = *x*-1, *y*, *z*; #2 = -*x*+2, -*y*+4, -*z*+3; #3 = -*x*+3, -*y*+3, -*z*+3; #4 = -*x*+2, -*y*+3, -*z*+2; #5 = *x*+1, *y*, *z*+1.

effects as well as for absorption by the ω scan technique, and reduced using CrystalClear program.⁷ The structures were resolved by direct method using SHELXTLTM package and refined by full-matrix least-squares technique on F^2 .⁸ All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions and refined with isotropic thermal parameters included in the final stage of the refinement on calculated positions bonded to their carrier atoms. Atoms O12, O6W in **1** and O2W in **2** are position disorder. Crystallographic data, and the selected bond distances and angles for compounds **1** and **2** are listed in Table 1 and 2 respectively.

Results and Discussion

Structural descriptions of compounds 1 and 2. Single crystal X-ray analysis of **1** reveals that there are two crystallographically independent zinc atoms (Figure 1). The Zn1 atom exhibits a pseudo-tetrahedral configuration coordinated by three carboxylic oxygen atoms from three separate BTB³⁻ moieties and one nitrogen atom from one 4,4'-bipy. Different from Zn1, the coordination environment of Zn2 atom is lighted by two carboxylic oxygen atoms from two BTB³⁻ moieties and two water molecules lying on the equatorial plane, two nitrogen atoms from 4,4'-bipy on the axial positions to complete an octahedral geometry. The coordinated oxygen atoms O1W and O2W have bond-valence sums of 0.33 and 0.28 respectively, suggesting that O1W and O2W are coordinated water molecules. Atoms O11, O14, O15, O16 have bond-valence sum of 1.93, 1.86, 1.87 and 1.76, respectively, showing that all the carboxylic groups have been deprotonated.⁹ These results are consistent with charge-balance considerations of compound **1**.

The μ_4 -BTB³⁻ ligand adopts monodentate and bis-didentate coordination mode as shown in Scheme 1. The most attention-

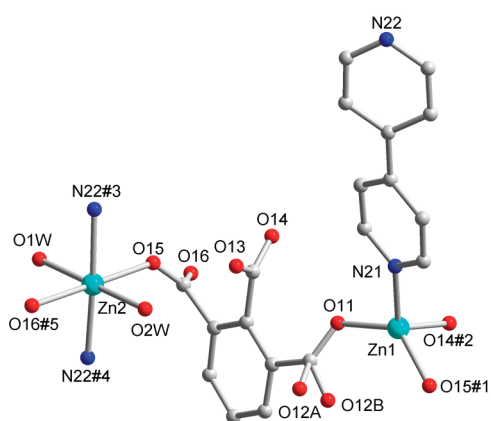
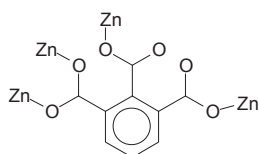


Figure 1. The coordination spheres of zinc(II) atoms in compound **1**.



Scheme 1. The coordination mode of H₃BTB in **1** and **2**

getting feature of **1** is that three carboxylic groups of BTB³⁻ *via* monodentate coordination mode link three symmetry-related Zn1 atoms into an infinite double-ribbon chain along the *b* direction. The neighboring ribbons are interlinked through O16-Zn2-O16 bonds to form a 2-D layer (Figure 2a). A mirror symmetry can be observed between the neighboring ribbons through the -Zn2-Zn2- plane with one of the ribbon being left-tropism and the other right-tropism. The subunits of [Zn₃(BTB)₃] and [Zn(H₂O)₂]²⁺ were dummied as S1 and S2 respectively thus to get the topological drawing of the 2-D framework (Figure 2b). 4,4'-bipy ligands act as pillars to link the adjacent 2-D layers into an extended 3-D coordination network containing 1-D hexagon channels along the *c* axis with the size of 13.99 × 11.50 Å², in which the lattice water molecules are

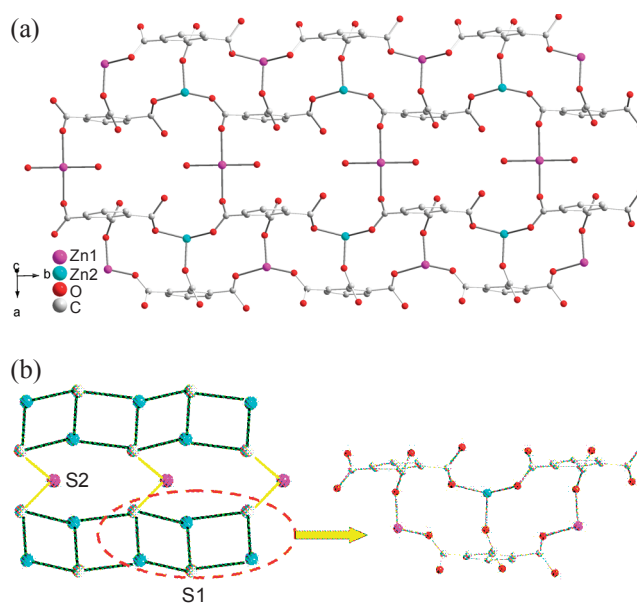


Figure 2. (a) The 2-D layer of **1** constructed from the interconnection of double-ribbon chains and the linkers of Zn2 atoms. (b) The topological drawing of the 2-D framework in **1**. The subunit of [Zn₃(BTB)₃] (right) is dummied as S1, [Zn(H₂O)₂]²⁺ as S2.

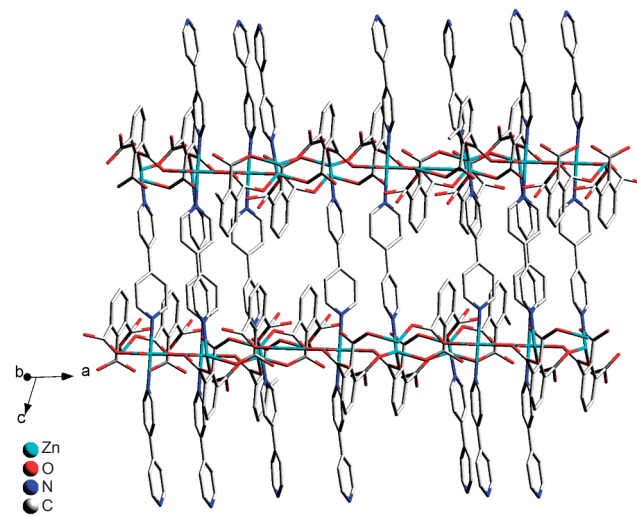


Figure 3. The 3-D network of **1** (hydrogen atoms are omitted for clarity).

located (Figure 3). Taking the van der Waals radii of C and H (1.7 and 1.2 Å, respectively) into account, the effective aperture of the channels is 3.25×4.51 Å. The total solvent-accessible volume of the channels in the unit is 930.3 Å³ accounting for 21.5% calculated by PLATON.¹⁰

As a polymorph of **1**, the skeleton structure of **2** is similar to **1**. The coordination spheres of the independent zinc atoms of Zn1 and Zn2 are the same to those in **1**. Similarly, the BTB³⁻ link Zn1 atoms into infinite double-ribbon chain along the *b* direction, and the double-ribbon are further connected through O15-Zn2-O15 bonds into a 2-D layer (Figure 4a). The interconnection of S1 and S2 results in the topological drawing of the

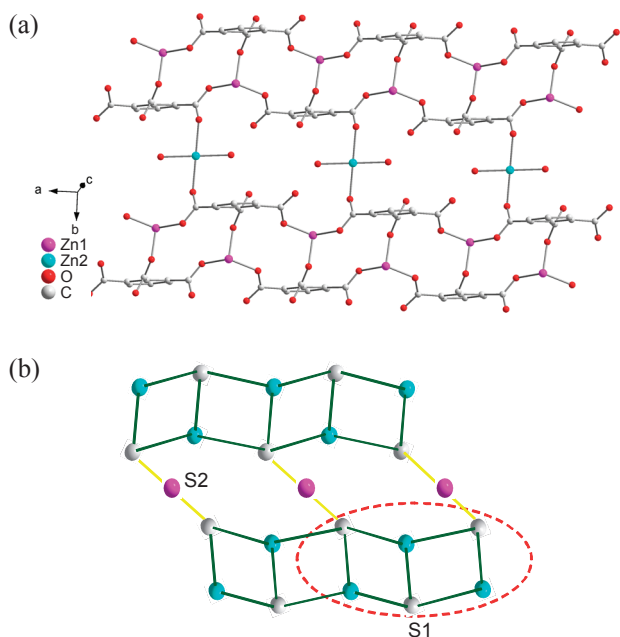


Figure 4. (a) The 2-D layer of **2** constructed from the interconnection of infinite double-ribbon chains and the linkers of Zn2 atoms. (b) The topological drawing of the 2-D framework in **2**. The subunit of $[\text{Zn}_3(\text{BTB})_3]$ is dummed as S1, $[\text{Zn}(\text{H}_2\text{O})_2]^{2+}$ as S2.

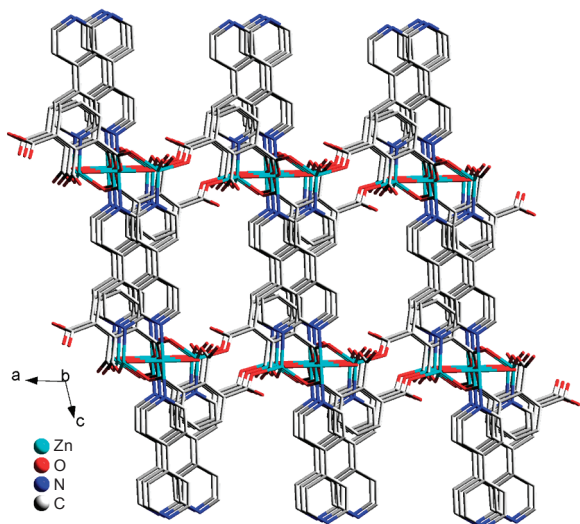


Figure 5. The 3-D network of **2** (hydrogen atoms are omitted for clarity).

2-D framework (Figure 4b). 4,4'-Bipy ligands also act as pillars to link the adjacent 2-D layers into a 3-D coordination network. The growth of 2-D layers on the 4,4'-bipy pillars produces a different 3-D network containing 1-D quadrangle channel with the size of 13.06×14.64 Å² viewing along the *c* direction (Figure 5). Minusing the van der Waals radii of C and H (1.7 and 1.2 Å, respectively), the effective aperture of the channels are 7.26×8.84 Å. The total solvent-accessible volume of the channels in the unit is 237.6 Å³ accounting for 22.0%. Except the reaction conditions, though with the same reagents, coordination modes of BTB³⁻, coordination sphere of metal centers and the construction of the 2-D layer, the 2-D layers in **2** in significantly different from those in **1**, in which the neighboring ribbons are parallel along the $-\text{Zn2}-\text{Zn2}-$ plane, not mirror symmetry.

Single point energy calculation. Considering the similar structures of **1** and **2**, we were interested in the energy distinction between the two complexes. The single point energy calculations of them were carried out at the Density Function Theory (DFT) level. Under the gradient-corrected approximation, the hybrid Becke3-Lee-Yang-Perdew exchange-correlation functional was employed. And at the same time, the effective core potential (ECP) basis sets were supplemented for metal atoms in view of the relativistic effects and electronic correlation effects. The choice of the basis sets was as following: for metals Zn, the Los Alamos ECP plus DZ basis set (Lanl2dz)¹¹ was used. For atoms C, N, O and H, the basis set 6-31G* was used. These calculations were completed using the Gaussian03 program.¹² The computational values were -1572.2134721 hartrees and -1572.2254998 hartrees separately for **1** and **2**. The single point energy calculations exhibited that the energy of **2** was a little lower approximately by 0.012 hartrees than that of **1**, indicating that **2** was slightly more stable than **1** in thermodynamics.

The result of more stability of **2** may come from the violent conditions in hydrothermal reaction, which results in the difference of the structures of **1** and **2**: a mirror symmetry can be found in the neighboring ribbons in **1**; While in **2**, the ribbons are parallel along the $-\text{Zn2}-\text{Zn2}-$ plane. The dihedral angle between the two Py rings of 4,4'-bipy in **1** twists to 30.56° , much larger than that of 12.39° in **2**. It exhibits that the stronger steric hindrance forces Py rings to twist and the parallel fashion in **2** should be easier for 4,4'-bipy to arrange with less steric hindrance, thus produces a more stable framework of **2**. But other factors, such as hydrogen bondings in the structure, cannot be excluded: there is a half more water molecule in **2**, indicating more possibilities of hydrogen bondings.

Fluorescence. The electronic emission spectra of **1**, **2** and free H₃BTB in the solid state at room temperature are shown in Figure 6. The fluorescent properties of **1** and **2** are very similar. The very strong pale blue fluorescence for the both compounds can be observed, where both maximum emission wavelengths at 417 nm by excited the solid sample under UV at $\lambda_{\text{ex}} = 349$ nm for **1** and 350 for **2**. Compared to the free neutral ligand (maximum emission wavelengths at 445 nm under UV at $\lambda_{\text{ex}} = 330$ nm), the blue fluorescence at 417 nm of compounds **1** and **2** with 28nm blue shift can be assigned to originate from LMCT,¹³ indicating a large disturbance of full filled d^{10} metal of Zn(II) to π orbital of phenyl rings.

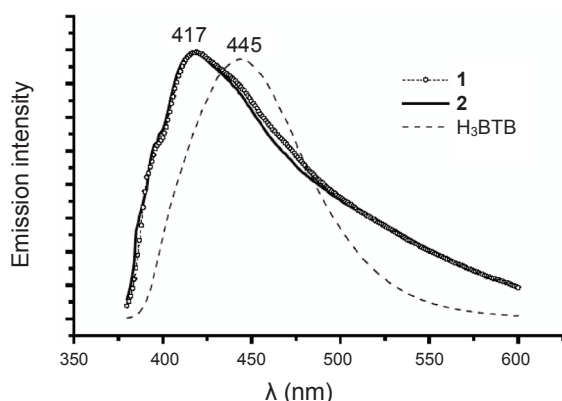


Figure 6. The solid state emission spectra of **1** ($\lambda_{em} = 417$ nm, $\lambda_{ex} = 349$ nm), **2** ($\lambda_{em} = 417$ nm, $\lambda_{ex} = 350$ nm) and H_3BTB ($\lambda_{em} = 445$ nm, $\lambda_{ex} = 330$ nm) recorded at room temperature.

Conclusion

In this study, we synthesized two similar 3-D zinc MOFs, $[Zn_6(BTB)_4(4,4'-bipy)_4(H_2O)_4] \cdot 9H_2O$ (**1**) and $[Zn_3(BTB)_2(4,4'-bipy)_2(H_2O)_2] \cdot 5H_2O$ (**2**), through the diffusion method and hydrothermal reaction respectively. The coordination geometries of zinc atoms and coordination modes of BTB^{3-} in **1** and **2** are same. However, because of the reaction conditions or possible hydrogen bondings, the resulting 2-D layers are different: the neighboring layers in **1** are mirror symmetric and those in **2** are parallel. By the linkage of 4,4'-bipy, final 3D MOFs are formed with water molecules locating in the cavities. The single point energy calculations exhibits that **2** is slightly more stable than **1** in thermodynamic. It accords with the analysis of steric hindrance corresponding to the dihedral angles of Py rings in 4,4'-bipy. With similar structures, **1** and **2** show very similar solid state fluorescent features that very strong pale blue fluorescence for the both compounds can be observed at 417 nm. Compared to that of the free H_3BTB , the Emissions at 417 nm can be assigned to LMCT.

Supplementary Material. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-285115 for **1** & 285114 for **2**). That data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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