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ARTICLE

Solvent modulated assembly of two Zn Metal-Organic Frameworks: syntheses, luminescent, and gas adsorption properties

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A 2D wave-like layered framework based on benzotriazole-5-carboxylic acid (H_2btca), 2,2'-bipy and zinc ions: $[Zn(btca)(2,2'-bipy)]_n$ (**1**) has been resoundingly designed and synthesized by solvothermal method. By changing DMF solvent to DMA, a 3D porous framework: $[Zn_2(btca)_2(bpy)(H_2O)]_n \cdot n(DMA)$ (**2**) was obtained. Complex **1** and **2** have been determined by single-crystal X-ray diffraction analysis and further characterized by powder X-ray diffraction (PXRD), elemental analysis, IR spectra, and thermogravimetric (TG) analysis. Complex **1** shows AA packing 2D layer structure and complex **2** displays 3D open honeycomb framework with a (3,4)-connected 2-nodal *fsc* topology. Moreover, gas adsorption of **2a** (the activated form of **2**) and luminescence properties of **1**, **2** and **2a** have also been investigated intensively.

Introduction

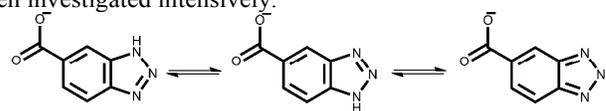
Rational design and assembly of porous metal-organic frameworks (MOFs) have attracted much interest in the past few decades owing to their versatile intriguing architectures and potential applications as multi-functional materials, such as gas adsorption and separation, sensing, catalysis, and drug delivery¹. Many functional MOFs of transition metal ions with interesting architectures and topologies have been well-established and synthesized successfully². A number of factors might affect the structures and properties of MOFs materials such as the choice of organic ligand, variety metal centers, solvents, pH value of the solution, the temperature, the counter ions, the template and metal-to-ligand stoichiometry, et.al³. As we all know that organic ligands play a key role in self-assembly and determining the structural and functional properties of the porous MOFs⁴.

Benzotriazole-5-carboxylic acid (H_2btca) is a good bridging ligand for constructing multi-dimensional polymers and has multiple coordinate sites,⁵ which involves three benzotriazole nitrogen atoms and two carboxylate oxygen atoms. The resonance structures of multi-dentate rigid $Hbtca^-$ ligand are shown in scheme 1. Consider of the structure of H_2btca , the introduction of nitrogen donor groups to the organic ligand will enhance the energetics and resultant gas adsorption amount in MOF materials, such as CO_2 ⁶. Furthermore, H_2btca bearing triazole functionality may improve the value of Q_{st} (~ 5 kJ mol^{-1}), which was exemplified by MTAf-3.⁷ Moreover, derivatives of benzotriazole are important ultraviolet absorbing compounds for industry. However, to the best of our knowledge,

3D porous MOFs on the basis of the H_2btca ligand have been rarely reported. Li's group reported a porous MOF, namely $[Zn_3(OH)_2(btca)_2] \cdot DMF \cdot 4H_2O$ with both significant breathing effect and photoluminescent response, during the gradual guest removal processes⁸. Chen's group reported 3D homometallic MOFs, whose magnetic transitions could be induced by desolvation⁹. Huang *et al.* presented 3D framework with 1D honeycomb channels constructed by the strip-shaped chains containing $[Cu_5(\mu_3-OH)_2(btca)_4]$ pentaclusters bridging to the adjacent $Cu_6(btca)_{12}^{6-}$ cages¹⁰. Han and Zeng described a Mn-based homometallic MOFs, which display high H_2 adsorption ability at lower pressure¹¹.

Meanwhile, solvent is another very significant factor in modulating the framework topology and the dimensionality by acting as a coordination ligand or a template for the assembly.¹² To some extent the kinetic and/or thermodynamical conformers could be controlled by changing the solvent. The coordination mode and configuration of ligand may be affected seriously by solvent, particularly for flexible carboxylic and imidazole ligand¹³

Herein, we report two new MOFs $[Zn(btca)(bpy)]_n$ (**1**) and $[Zn_2(btca)_2(bpy)(H_2O)]_n \cdot n(DMA)$ (**2**) modulated solely by different solvents based on H_2btca ligand and Zn ions, the luminescence properties and gas adsorption of **2a** have also been investigated intensively.



Scheme 1. Resonance structures of $Hbtca^-$ ligand.

Experimental section

Materials and methods All chemical reagents were used as commercially obtained without further purification. The IR spectra were operated on a Nicolet 330 FTIR Spectrometer in the range 4000-400 cm^{-1} . Thermogravimetric experiments (TGA) were performed using a Mettler-Toledo thermogravimetric Analyzer. Powder X-ray diffraction experiments were measured with a Bruker AXS D8 Advance instrument diffractometer working with Cu $K\alpha$ radiation, and the recording speed was 5°min^{-1} over the 2θ range of $5\text{--}50^\circ$ at room temperature. Photoluminescence spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 elemental analyzer. Gas sorption measurements were conducted using a Micromeritics ASAP 2020 system at various gas and temperatures. The fluorescence lifetimes were measured on a FLS920 with a time correlated single photon counting (TCSPC) method by excitation with a 375 nm picosecond laser (EPL 445). The data were deconvoluted with the instrument response function, recorded using dispersed light, and fitted to a multi-exponential function. The absolute fluorescence quantum yields were measured with an integrating sphere

Synthesis of Complex 1. H_2btca (5 mg, 0.03 mmol), 2,2'-bipy (9 mg, 0.05 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (22 mg, 0.07 mmol) were dissolved in a 1 mL mixture of N,N'-Dimethylformamide (DMF) and H_2O ($v/v = 1:1$), the clear solution was sealed in a glass tube and put into a programmed oven, slowly heated to 140°C from room temperature in 500 minutes, kept at 140°C for 5300 minutes, then slowly cooled to 30°C in 800 minutes, a large amount of colorless block crystals of **1** were separated in 84% yield based on H_2btca . Elemental analysis calcd (%) for **1**: $\text{C}_{17}\text{H}_{11}\text{N}_5\text{O}_2\text{Zn}$: C, 53.36; H, 2.90; N, 18.30. Found: C, 52.75; H, 2.73; N, 17.99. IR data (KBr cm^{-1}): 1662(w), 1587(s), 1551(s), 1470(w), 1407(s), 1158(w), 1019(w), 771(m), 709(w).

Synthesis of Complex 2. H_2btca (5 mg, 0.03 mmol), 2,2'-bipy (9 mg, 0.05 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (22 mg, 0.07 mmol) were dissolved in a 1 mL mixture of N,N'-Dimethylacetamide (DMA) and H_2O ($v/v = 1:1$), the clear solution was sealed in a glass tube and put into a programmed oven, slowly heated to 140°C from room temperature in 500 minutes, kept at 140°C for 5300 minutes, then slowly cooled to 30°C in 800 minutes, a large amount of colorless block crystals of **1** were separated in 70% yield based on H_2btca . Elemental analysis calcd (%) for **2**: $\text{C}_{28}\text{H}_{25}\text{N}_9\text{O}_6\text{Zn}_2$: C, 47.08; H, 3.53; N, 17.65. Found: C, 47.75; H, 4.01; N, 16.99. IR data (KBr cm^{-1}): 3440(s), 1640(s), 1602(m), 1564(w), 1404(m), 1280(w), 794(w), 755(w), 599(w), 455(w).

Single-crystal X-ray Structural Analysis. The data of single crystals were collected on a SuperNova diffractometer equipped with a Molybdenum micro-focus X-ray sources ($\lambda = 0.71073 \text{ \AA}$) and an Eos CCD detector under 293 K. The data were collected with a ω -scan technique and an arbitrary ϕ -angle. Data reduction were performed with the CrysAlisPro package,¹⁴ and an analytical adsorption correction was performed. The structure were solved by

direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package.¹⁵ The non-H atoms were treated anisotropically, whereas the aromatic and hydroxy-hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon or oxygen atoms. Structures were examined using the Addsym subroutine of PLATON¹⁶ to assure that no additional symmetry could be applied to the models. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center, CCDC 1062110 for **1** and 1062111 for **2**. These data can be obtained from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, U.K.

Table 1. Crystallographic data for complex 1 and 2

	1	2
empirical formula	$\text{C}_{17}\text{H}_{11}\text{N}_5\text{O}_2\text{Zn}$	$\text{C}_{28}\text{H}_{25}\text{N}_9\text{O}_6\text{Zn}_2$
formula weight	382.68	714.31
temperature (K)	293(2)	293(2)
crystal system	orthorhombic	orthorhombic
space group	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> (Å)	17.4695(3)	18.580(4)
<i>b</i> (Å)	8.64315(13)	9.962(2)
<i>c</i> (Å)	19.7657(4)	32.732(8)
α (deg)	90.00	90.00
β (deg)	90.00	90.00
γ (deg)	90.00	90.00
volume (Å ³)	2984.44(8)	6058(2)
<i>Z</i>	8	8
ρ_{calc} (g/cm ³)	1.703	1.566
μ (mm ⁻¹)	2.493	1.641
<i>F</i> (000)	1552.0	2912.0
data/restraints/parameters	2656/0/226	6995/30/410
Goodness-of-fit on F^2	1.053	1.114
final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0237$, $wR_2 = 0.0638$	$R_1 = 0.0342$, $wR_2 = 0.0853$
Final <i>R</i> indexes [all data]	$R_1 = 0.0260$, $wR_2 = 0.0653$	$R_1 = 0.0408$, $wR_2 = 0.0881$
$R_1 = \sum F_o - F_c / \sum F_o $. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{0.5}$.		

Results and discussion

Structure of complex 1 Crystals of **1** was obtained under solvothermal conditions by mixing H_2btca , 2,2'-bipy and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in a mixture of DMF/ H_2O (1:1) at 140°C for 3 days. Crystallographic studies revealed that compound **1** exhibits a 2D wave-like layered framework, crystallizes in an orthorhombic system with space group *Pbca*. The asymmetric unit contains one Zn^{2+} ion, one btca^{2-} ligand and one coordinated 2,2'-bipy ligand. As shown in Fig. 1a, the Zn^{2+} center adopts six-coordinated distorted ZnN_4O_2 octahedral environment, in which N1 and N2 comes from 2,2'-bipy ligand, N3 and N5 comes from two different btca^{2-} ligand, and the left coordinated sites were occupied by two oxygen atoms from one btca^{2-} ligand. The average Zn-N and Zn-O distances range from 2.14366 (45) and 2.2446 (64) Å. The btca^{2-} ligand in **1** adopts

tri-dentate coordination mode (Fig. 1b) to link three Zn centres via its two triazole nitrogen atoms (N3 and N5) and two oxygen atoms (O1 and O2), which results the 2D wave-like layer of complex **1**. Classic hydrogen bonds were not found in Complex **1**. Finally, the 2D layers are in contact to form a 3D supramolecular framework in an AA stack fashion because of C-H $\cdots\pi$ and intramolecular hydrogen bond weak interactions (Fig.1c). Complex **1** features C-H \cdots O intermolecular hydrogen bonding interactions between C8 as hydrogen atom donors and O1 (C8-H8 \cdots O1, H8 to O1 distance 2.58 Å, C8-H8 \cdots O1 angle 116°), Complex **1** also features intramolecular C-H \cdots N hydrogen bonding interactions between C17 as hydrogen atom donors and N4 (C17-H17 \cdots N4, H17 to N4 distance 2.38 Å, C17-H17 \cdots N4 angle 167 (3)°) [symmetry code: (a) -0.5+x, y, 0.5-z; (b) 1-x, -0.5+y, 0.5-z; (c) 0.5+x, y, 0.5-z; (d) 1-x, 0.5+y, 0.5-z].

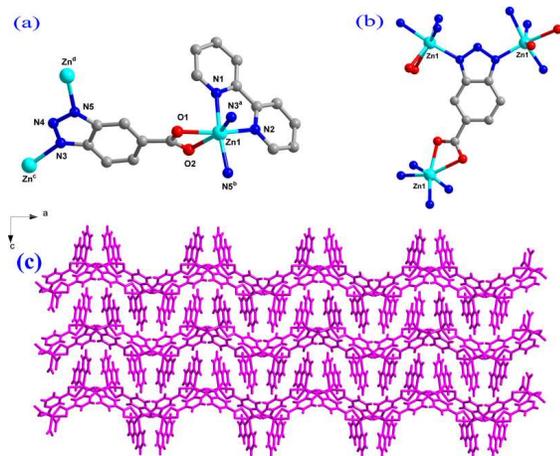


Figure 1. (a) The coordination environment of Zn(II) atoms in complex **1** (hydrogen atoms omitted for clarity). (b) The coordination mode of H₂btca ligand. (c) The AB packing mode structure of **1** view along *b* axis.

Structure of complex 2 Crystals of **2** were obtained under solvothermal conditions by mixing H₂btca, 2,2'-bipy and Zn(NO₃)₂·4H₂O in a mixture of DMA/H₂O (1:1) at 140 °C for 3 days. Crystallographic studies revealed that compound **2** crystallizes in an orthorhombic system with space group *Pbca*, and its asymmetric unit contains two Zn²⁺ ions, two btca²⁻ ligands, one 2,2'-bipyridine, and one lattice DMA molecule (Fig.2a). Zn1 is four-coordinated by one oxygen and three nitrogen atoms from four different btca²⁻ ligands forming tetrahedron geometry; The Zn2 ion in **2** adopts distorted trigonal bipyramidal geometry. Each Zn2 ion is five-coordinated by one carboxylate oxygen atom from one btca²⁻ molecule, one oxygen atom from coordinated water molecular and one nitrogen atom from one btca²⁻ molecule and two nitrogen atoms from one chelating 2,2'-bipy ligand. All the btca²⁻ ligands are in μ 3 bridging mode through two btca nitrogen atoms and μ 2: η 1: η 0-carboxylate group (Fig. 2b). One btca²⁻ ligand link three four-coordinated Zn1 centers and the other btca²⁻ ligand connect two five-coordinated Zn2 and one four-coordinated Zn1 centres, which give rise to the final 3D porous framework. DMA molecules are located into the pore of complex **2** by hydrogen bonds between O1W from coordinated water and O5 from DMA (O1Wa-H1Wa \cdots O5, H1Wa to O5 distance 1.83 Å, O1Wa-H1Wa \cdots O5 angle 157°)

[symmetry code: (a) -x, -y, -z; (b) 0.5-x, 0.5+y, z; (c) -0.5+x, y, 0.5-z; (d) 0.5-x, -0.5+y, z; (e) 0.5+x, y, 0.5-z].

From the topological point of view, the Zn1 atoms can be defined as 4-connected nodes, the organic ligands can be regarded as 3-connected nodes, and the [(Zn₂)₂(btca)₂] dimer unit can be simplified as linkers (Fig. 2c). Thus, the overall structure of **2** can be described as a 3D 2-nodal (3,4) connected *fsc* framework with a Schläfli symbol of {6³.8³} {6³} calculated with TOPOS¹⁷. The potential free volume of **2** is 65.1% as calculated by PLATON (1.8 Å probe radius) after removal of guest solvent molecules (Fig.3).

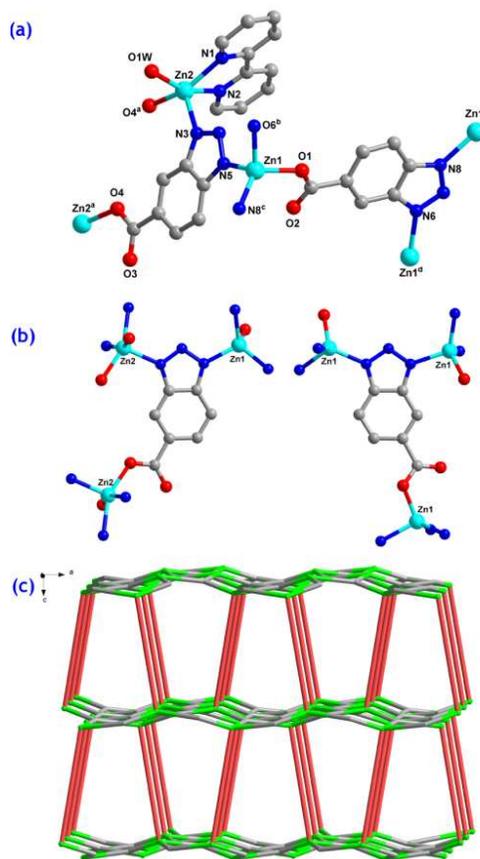


Figure 2. (a) The coordination environment of Zn(II) atoms in complex **2** (hydrogen atoms omitted for clarity). (b) The coordination mode of H₂btca ligand. (c) The 3D net structure of **2** along *b* axis.

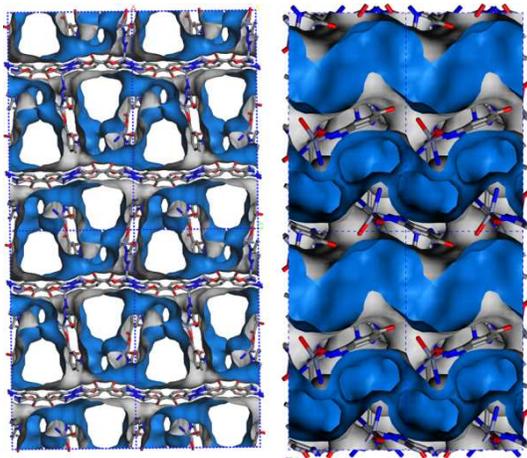


Figure 3. (left) and (right) Connolly surface representation along *b*- and *c*-axis respectively, showing that complex **2** is porous and comprises interconnected pores.

Powder X-ray diffraction (PXRD) measurements were performed to confirm phase purity, the experimental PXRD is consistent with the PXRD pattern calculated based on the crystal structure using the Mercury 3.3 (Fig. S1 and S2 Supporting Information). Thermogravimetric analysis (TGA) experiments performed on the as-synthesized **1**, **2** and **2a** reveal moderate thermal stabilities (Fig. S3, Supporting Information).

Gas Adsorption Measurements. The permanent porosity of complex **2a** prompts us to investigate the gas adsorption ability. The measurement of adsorption properties of complex **2a** was performed on a Micromeritics ASAP 2020 system. Complex **2** was sequentially exchanged with methanol and dichloromethane for three days, and the degassing process was performed at 60 °C for 5 hours. The gas sorption capabilities of complex **2a** were cubical investigated using several gases (N₂, H₂, CH₄, Ar and CO₂) at varying temperatures.

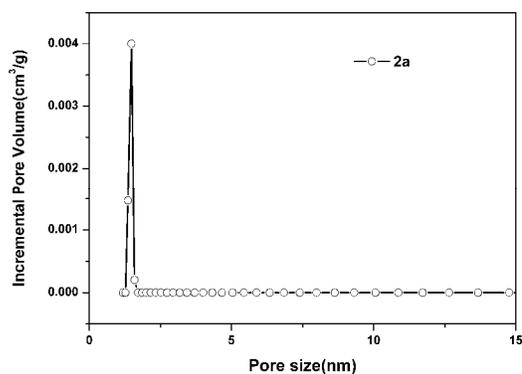
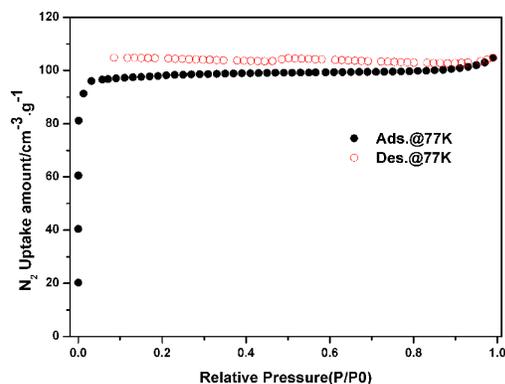


Figure 4. The nitrogen adsorption isotherms (Up) at 77K and corresponding pore size distribution curves (Down) for **2a**.

The permanent porosity of the activated sample **2a** was confirmed by the N₂ sorption experiment at 77 K. As shown in Fig. 4, the fully activated sample reveals a typical type-I behavior as expected for microporous materials, and the pore size is 1.48 nm, which is coincidental with the crystal structure. The adsorption isotherms of N₂ have an abrupt slope from 0.01 to 0.1 bar, which reveals that the pores are filled as the increasing of pressure from 0.01 to 0.1 bar. Then the uptake capacity of N₂ increases slightly and reaches a platform 98 cm³ g⁻¹ at 1 bar. Derived from N₂ adsorption, the Langmuir surface area of **2a** is 426 m² g⁻¹, the Brunauer-Emmett-Teller (BET) surface area and total pore volume are 384 m² g⁻¹ and 0.161 cm³ g⁻¹, respectively. The obtained pore volume is much smaller than that (0.638 cm³/g) calculated from X-ray data, which is due to the reduced volume of the activated phase of **2a** after the lattice solvents were eliminated. The desolvated **2a** also adsorbs Ar, and the maximum uptake amounts to 99.5 cm³/g at 1 atm and 77K (Fig. S4, Supporting Information). The Brunauer-Emmett-Teller (BET) surface area, Langmuir surface area and total pore volume obtained from Ar isotherm are 263 m² g⁻¹, 329 m² g⁻¹ and 0.412 cm³ g⁻¹, respectively.

The H₂ and CH₄ adsorption isotherms of activated **2a** are also measured. As depicted in Fig.5, the activated **2a** can adsorb 56.5 cm³ g⁻¹ (~0.5 wt%) of H₂ at 77 K and 1 bar and 14.5 cm³ g⁻¹ (~1.0 wt%) of CH₄ at 273 K and 1bar. The maximum H₂ uptake of **2a** at low pressures is relatively lower than the high capacity coordination framework reported to date, such as Cu₂(BPTC)¹⁸ and IRMOF-1¹⁹, which display high capacities of H₂ uptake (~2.47 wt% and 1.32 wt%) under similar conditions (77 K and 1 atm). The isosteric heat of H₂ adsorption (*Q_{st}*) value of complex **2a**, determined by applying the Clausius-Clayperon equation to the isotherms obtained at 77 and 87 K, is approximately 7.5 kJ·mol⁻¹ at low coverage, which is higher than those of non-N-containing MOFs, such as the NOTT series (5.68–6.70 kJ mol⁻¹),^{20a} Cu₆(BTTC)₄(H₂O)₆·xS₂(7.0 kJ mol⁻¹),^{20b} UMCM-150 (6.3 kJ mol⁻¹),^{20c} MIL-100 (6.3 kJ mol⁻¹)^{20d} and MIL-102 (6.0 kJ mol⁻¹)^{20e}. The isosteric heat values of CH₄ are 21.6 kJ·mol⁻¹, which were obtained at 273 and 295 K. Interestingly, the CO₂ adsorption isotherms of activated **2a** are also investigated, the CO₂ adsorption isotherm at 273 K indicated a clear terrace in the range of 155–330 mmHg. After this pressure, the uptake volume suddenly increased. This indicates that the structure could be

transformed into a new structure during this period of CO₂ adsorption and the maximum uptake of CO₂ is 40.0 cm³ g⁻¹. The desorption isotherm also displayed a sharp step at 407 mmHg. When the measurement temperature was increased to 295 K, the adsorption isotherm did not show the characteristic step, and the uptake volume dramatically decreased to 21.95 cm³ g⁻¹ as shown in Fig. S5. On the basis of the stepped CO₂ isotherms with a large hysteresis between adsorption and desorption branches at 273 K and significantly decreased adsorption amounts at higher temperatures, these results also imply **2a** is a dynamic framework.²¹

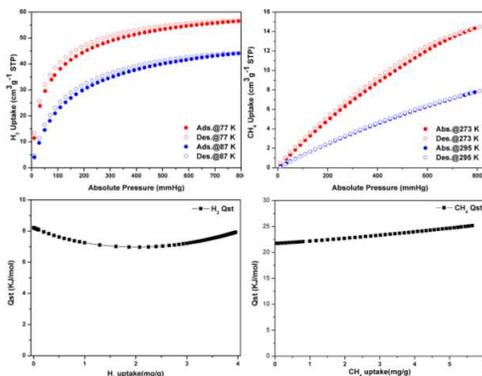


Figure 5. The H₂, CH₄, sorption isotherms for **2a** (left) and (right). H₂: red, 77 K; blue, 87 K. CH₄: red, 273 K; blue, 295 K. Isothermic heats of H₂ and CH₄ adsorption (Q_{st}) for complex **2a**

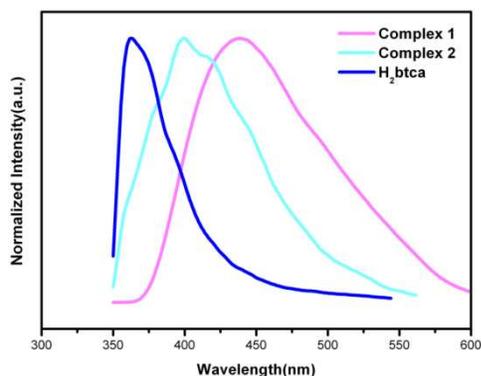


Figure 6. The luminescent spectra of H₂btca, complex **1** and **2**

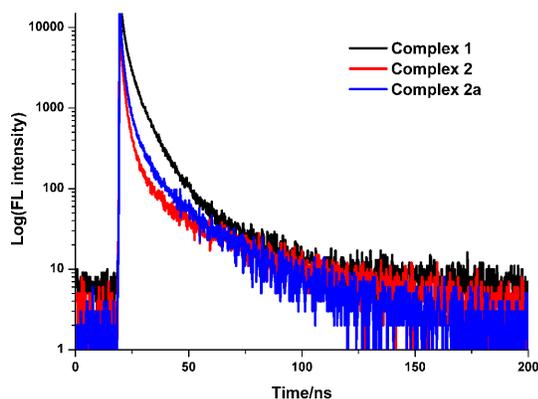


Figure 7. The solid state luminescent decay curve of complexes **1**, **2** and **2a**

Luminescent Properties of complex **1**, **2** and **2a**.

The luminescent properties of MOFs possess varied interesting ascribed to their application in chemical sensors, photochemistry and electroluminescent display, and so on.²² General d¹⁰ transition metal complexes are promising to exhibit the photoluminescence properties.²³ In addition, organic ligands, their coordination modes and different metals evidently affect the emission wavelength and luminescent theory.²⁴ In this work, the solid-state photoluminescent spectra of btca²⁻, complex **1** and **2** have been measured at room temperature (Fig. 6). The H₂btca ligand displays photoluminescence with emission maxima at 362 nm ($\lambda_{\text{ex}} = 300$ nm), which can be presumed to the $\pi \rightarrow \pi^*$ transitions.²⁵ Upon complexation of H₂btca and 2,2'-bipy ligands with Zn(II) ion, intense emissions are observed at 441 nm ($\lambda_{\text{ex}} = 330$ nm) for **1** and 400 nm ($\lambda_{\text{ex}} = 295$ nm) for **2**, respectively. Since Zn(II) ions are difficult to oxidize or reduce due to their d¹⁰ configurations, the emissions of complexes **1** and **2** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature. Thus, the emissions of **1** and **2** are probably attribute to the intraligand $\pi \rightarrow \pi^*$ transitions modified by metal coordination. In comparison with H₂btca, a red shift of 38 nm has been observed in **1** and 79 nm in **2**, which are probably attributable to the differences coordination mode of H₂btca ligands. It may affect the rigidity of the solid-state crystal packing and further influence their luminescence emission bands. Furthermore, a time-resolved luminescence study was performed on the complex **1**, **2** and **2a** by monitoring the most intense emission at ambient temperature. The decay curves can be fitted well as shown in Fig. 7, and detailed data are listed in Table S3 in the ESI. The τ values of complexes **1**, **2** and **2a** were fitted to tri-exponential decay curve. The lifetime (τ) is defined as the time in which the fluorescence intensity decays to 1/e of the initial intensity (I_0), where e is the natural log constant and is equal to 2.718. Quantum yield (Φ) of complexes **1**, **2** and **2a** were 2.72%, 2.85% and 4.35%, respectively.

Conclusions

In summary, two new MOFs based on H₂btca and zinc: [Zn(btca)(2,2'-bipy)]_n (**1**) and [Zn₂(btca)₂(bpy)(H₂O)]_n·n(DMA) (**2**) have been designed and synthesized by modulating solvent. Complex **1** displays 2D layer structure and complex **2** shows a (3,4)-connected 2-nodal *psc* topology. Gas sorption for **2a** gives a Langmuir surface area of 426 m² g⁻¹, 56.5 cm³ g⁻¹ (~0.5 wt %) of H₂ at 77 K and 1 bar and 14.5 cm³ g⁻¹ (~1.0 wt %) of CH₄ at 273 K and 1 bar. In addition, solid-state fluorescent exhibits a red shift 38 and 79 nm compared to H₂btca ligands.

Acknowledgements

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Notes and references

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†Electronic Supplementary Information (ESI) available: Selected bond length (Å) and angles (°) for complex **1** and **2**, PXRD patterns, TGA curves, IR spectra, Photophysical data, Excitation spectrum. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

- 1 (a) H. Furukawa, K. E. Cordova, M. O'Keefe, O. M. Yaghi, *Science*, 2013, **341**, 974; (b) M. O'Keefe, O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675; (c) J. P. Zhang, Y. B. Zhang, J. B. Lin, X. M. Chen, *Chem. Rev.*, 2012, **112**, 1001; (d) X. C. Shan, F. L. Jiang, D. Q. Yuan, H. B. Zhang, M. Y. Wu, L. Chen, J. Wei, S. Q. Zhang, J. Pan, M. C. Hong, *Chem. Sci.* 2013, **4**, 1484; (e) Y. W. Li, K. H. He, X. H. Bu, *J. Mater. Chem. A*, 2013, **1**, 4186; (f) J. R. Li, J. Sculley, H. C. Zhou, *Chem. Rev.*, 2011, **112**, 869; (g) Y. P. Li, H. R. Yang, Q. Zhao, W. C. Song, J. Han, X. H. Bu, *Inorg. Chem.*, 2012, **51**, 9642.
- (2) (a) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213; (b) J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science*, 2005, **309**, 1350; (c) T. R. Cook, Y. R. Zheng, P. J. Stang, *Chem. Rev.*, 2013, **113**, 734; (d) W. Zhang, R. G. Xiong, *Chem. Rev.*, 2012, **112**, 1163; (e) P. S. Nugent, V. L. Rhodus, T. Pham, K. Forrest, L. Wojtas, B. Space, M. J. Zaworotko, *J. Am. Chem. Soc.*; 2013, **135**, 10950; (f) Sun, H. L.; Wang, Z. M.; Gao, S. *Coord. Chem. Rev.*, 2010, 254, 1081.
- (3) (a) J. Ma, L. Chen, M. Y. Wu, S. Q. Zhang, K. C. Xiong, D. Han, F. L. Jiang, M. C. Hong, *CrystEngComm.*, 2013, **15**, 911; (b) M. Du, C. P. Li, C. S. Liu, S. M. Fang, *Coord. Chem. Rev.*; 2013, **257**, 1282; (c) Y. L. Gai, F. L. Jiang, K. C. Xiong, L. Chen, D. Q. Yuan, L. J. Zhang, K. Zhou, M. C. Hong, *Cryst. Growth Des.*, 2012, **12**, 2079; (d) L. N. Li, S. Y. Wang, T. L. Chen, Z. H. Sun, J. H. Luo, M. C. Hong, *Cryst. Growth Des.*; 2012, **12**, 4109.
- (4) (a) X. J. Li, F. L. Jiang, M. Y. Wu, S. Q. Zhang, Y. F. Zhou, M. C. Hong, *Inorg. Chem.*, 2012, **51**, 4116; (b) Y. Q. Chen, S. J. Liu, Y. W. Li, G. R. Li, K. H. He, Z. Chang, X. H. Bu, *CrystEngComm.*, 2013, **15**, 1613; (c) S. Bureekaew, H. Sato, R. Matsuda, Y. Kubota, R. Hirose, J. Kim, K. Kato, M. Takata, S. Kitagawa, *Angew. Chem., Int. Ed.*, 2010, **49**, 7660.
- (5) Z. H. Li, L. P. Xue, B. T. Zhao, J. Kan, W. P. Su, *CrystEngComm.*, 2012, **14**, 8485.
- (6) (a) Y. Liu, Z. U. Wang, H. C. Zhou, *Greenhouse Gases: Sci. Technol.* 2012, **2**, 239; (b) R. Sabouni, H. Kazemian, S. Rohani, *Environ. Sci. Pollut. Res.*, 2013, 1.
- (7) (a) W. Y. Gao, W. Yan, R. Cai, K. Williams, A. Salas, L. Wojtas, X. Shi, S. Ma, *Chem. Commun.*, 2012, **48**, 8898; (b) R. Luebke, L. J. Weselinski, Y. Belmabkhout, Z. J. Chen, L. Wojtas, M. Eddaoudi, *Cryst. Growth Des.*, 2014, **14**, 414.
- (8) J. Xiao, Y. Wu, M. Li, B. Y. Liu, X. C. Huang, D. Li, *Chem. Eur. J.*, 2013, **19**, 1891.
- (9) X. M. Zhang, Z. M. Hao, W. X. Zhang, X. M. Chen, *Angew. Chem., Int. Ed.*, 2007, **119**, 3526.
- (10) J. Xiao, B. Y. Liu, G. Wei, X. C. Huang, *Inorg. Chem.*, 2011, **50**, 11032.
- (11) Z. B. Han, R. Y. Lu, Y. F. Liang, Y. L. Zhou, Q. Chen, M. H. Zeng, *Inorg. Chem.*, 2012, **51**, 674.
- (12) (a) I. S. Lee, D. M. Shin, Y. K. Chung, *Chem. Eur. J.* 2004, **10**, 3158. (b) P. Pachfule, R. Das, P. Poddar, R. Banerjee, *Cryst. Growth Des.*, 2011, **11**, 1215.
- (13) (a) H. Y. He, D. Collins, F. N. Dai, X. L. Zhao, G. Q. Zhang, H. Q. Ma, D. F. Sun, *Cryst. Growth Des.*, 2010, **10**, 895; (b) J. Guo, L. L. Zhang, H. Q. Ma, Z. Chen, D. Sun, Y. H. Wei, D. F. Sun, *Inorg. Chem. Commun.*, 2013, **28**, 75; (c) J. P. Zhang, X. C. Huang, X. M. Chen, *Chem. Soc. Rev.*, 2009, **38**, 2385.
- (14) CrysAlisPro (Version 1.171.31.7), Agilent Technologies.
- (15) G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination, University of Gottingen, Germany, 1997;
- (16) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2002.
- (17) V. A. Blatov, IUCr CompComm Newsletter; 2006, 7, 4-38 (<http://www.topos.ssu.samara.ru>).
- (18) (a) M. Latroche, S. Surblé, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J. H. Lee, J. S. Chang, S. H. Jung, G. Férey, *Angew. Chem., Int. Ed.*, 2006, **45**, 8227; (b) H. Furukawa, M. A. Millerb, O. M. Yaghi, *J. Mater. Chem.*, 2007, **17**, 3197.
- (19) J. L. C. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.*; 2004, **73**, 3.
- (20) (a) X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness, M. Schröder, *J. Am. Chem. Soc.*; 2009, **131**, 2159; (b) Y. M. Huang, B. G. Zhang, J. G. Duan, W. L. Liu, X. F. Zheng, L. L. Wen, X. H. Ke, D. F. Li, *Cryst. Growth Des.*, 2014, **14**, 2866; (c) A. G. Wong-Foy, O. Lebel, A. J. Matzger, *J. Am. Chem. Soc.*, 2007, **129**, 15740; (d) M. Latroche, S. Suble, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J.-H. Lee, J.-S. Chang, S. H. Jung, G. Férey, *Angew. Chem., Int. Ed.*, 2006, **45**, 8227; (e) S. Surblé, F. Millange, C. Serre, T. Düren, M. Latroche, S. Bourrelly, P. L. Llewellyn, G. Férey, *J. Am. Chem. Soc.*, 2006, **128**, 14889.
- (21) (a) I. H. Hwang, J. M. Bae, Y. K. Hwang, H. Y. Kim, C. Kim, S. Huh, S. J. Kim, Y. Kim, *Dalton Trans*, 2013, **42**, 15645; (b) P. V. Dau, S. M. Cohen, *CrystEngComm.*, 2013, **15**, 9304.
- (22) S. Ma, D. F. Sun, J. M. Simmons, C. D. Collier, D. Yuan, H. C. Zhou, *J. Am. Chem. Soc.*, 2007, **130**, 1012.
- (23) (a) J. Guo, J. F. Ma, J. J. Li, J. Yang, S. X. Xing, *Cryst. Growth Des.*; 2012, **12**, 6074; (b) J. Guo, J. F. Ma, B. Liu, W. Q. Kan, J. Yang, *Cryst. Growth Des.*, 2011, **11**, 3609; (c) J. S. Hu, Y. J. Shang, X. Q. Yao, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng, Z. L. Xue, *Cryst. Growth Des.*, 2010, **10**, 2676; (d) J. Yang, Q. Yuo, G. D. Li, J. J. Cao, G. H. Li, J. S. Chen, *Inorg. Chem.*, 2006, **45**, 2857.
- (24) (a) H. C. Fang, J. Q. Zhu, L. J. Zhou, H. Y. Jia, S. S. Li, X. Gong, S. B. Li, Y. P. Cai, P. K. Thallapally, J. Liu, G. J. Exarhos, *Cryst. Growth Des.*, 2010, **10**, 3277; (b) X. T. Rao, T. Song, J. K. Gao, Y. J. Cui, Y. Yang, C. D. Wu, B. L. Chen, G. D. Qian, *J. Am. Chem. Soc.*, 2013, **135**, 15559. (c) H. L. Jiang, D. W. Feng, K. C. Wang, Z. Y.

- Gu, Z. W. Wei, Y. P. Chen, H. C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 13934; (d) S. Q. Zang, L. H. Cao, R. Liang, H. W. Hou, T. C. W. Mak, *Cryst. Growth Des.*, 2012, **12**, 1830; (e) X. Q. Liang, X. H. Zhou, C. Chen, H. P. Xiao, Y. Z. Li, J. L. Zuo, X. Z. You, *Cryst. Growth Des.*; 2009, **9**, 1041; (f) D. Niu, J. Yang, J. Guo, W. Q. Kan, S. Y. Song, P. Du, J. F. Ma, *Cryst. Growth Des.*, 2012, **12**, 2397.
- (25) E. Colacio, R. Kivekäs, F. Lloret, M. Sunberg, J. Suarez-Varela, M. Bardaji, A. Laguna, *Inorg. Chem.*, 2002, **41**, 5141.

TOC:

Two new MOFs based on H₂btca and zinc: [Zn(btca)(2,2'-bipy)]_n (**1**) and [Zn₂(btca)₂(bpy)(H₂O)•(DMA)]_n (**2**) have been designed and synthesized by modulating solvent.

