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# Electronic Supplementary Information

## Unusual parallel and inclined interlocking modes in polyrotaxane-like metal-organic frameworks

**Jin Yang,[a] Jian-Fang Ma,*[a] Stuart R. Batten*[b] and Zhong-Min Su[a]**

[a] Key Lab for Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China; [b] School of Chemistry, Monash University, Victoria, 3800, Australia

*,[a] Correspondence author: Prof. Jian-Fang Ma

E-mail: jfma@yahoo.com.cn

Fax: +86-431-8509-8620

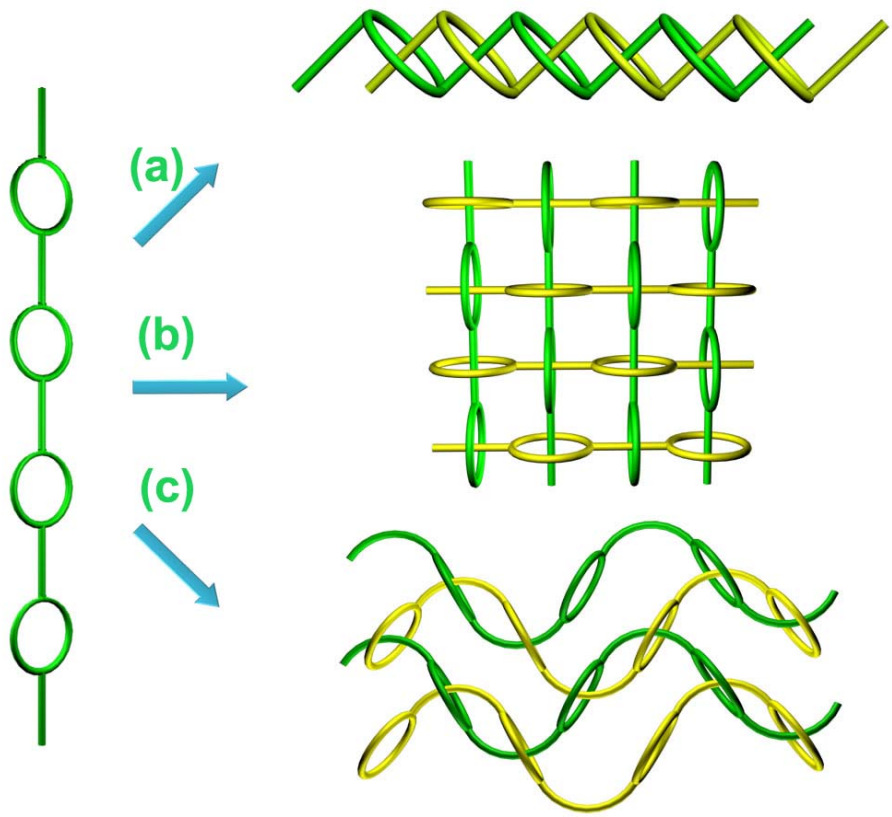
*,[b] Correspondence author: Dr. Stuart R. Batten

E-mail: stuart.batten@sci.monash.edu.au

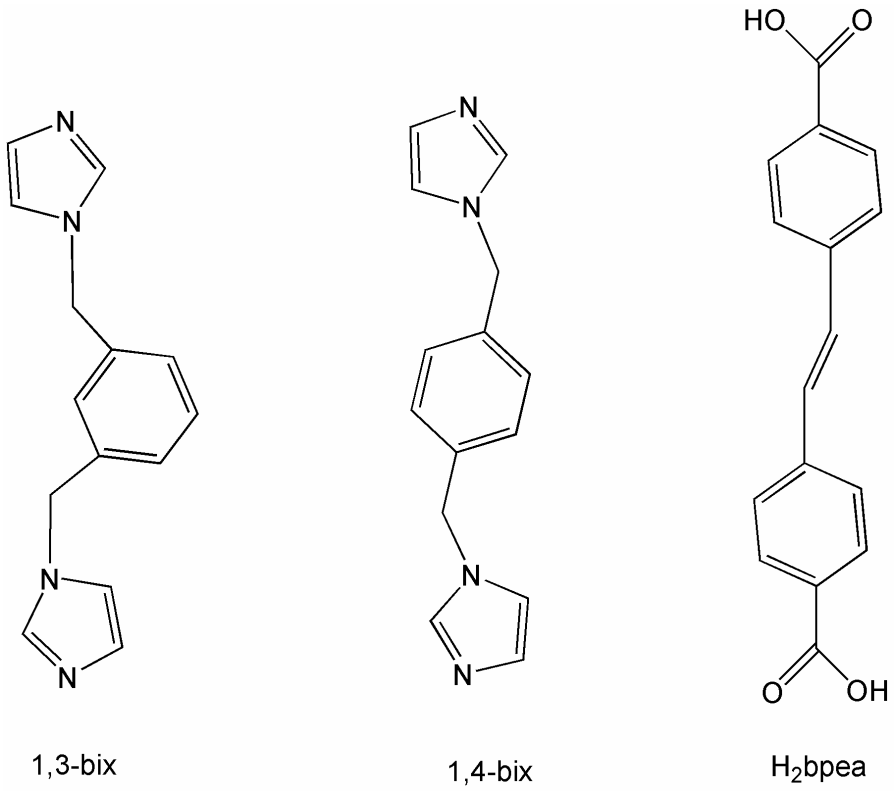
Fax: +61-3-9905-4597

**Materials.** All reagents and solvents for syntheses were purchased from commercial sources and used as received. The 1,4-bix and 1,3-bix were synthesized by following the procedures described previously.[1]

**General Characterization and Physical Measurements.** The C, H, and N elemental analyses were conducted on a Perkin–Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 $cm^{-1}$ on a Mattson Alpha-Centauri spectrometer. The photoluminescent properties of the 1,4-bix and compound **2** were measured on a Perkin-Elmer LS55 spectrometer.




**Scheme S1.** Schematic representations of the known (a) 1D→1D, (b) inclined 1D→2D, and (c) parallel 1D→2D polyrotaxane-like networks.




**Scheme S2.** The organic ligands used in the construction of coordination polymers **1** and **2**.

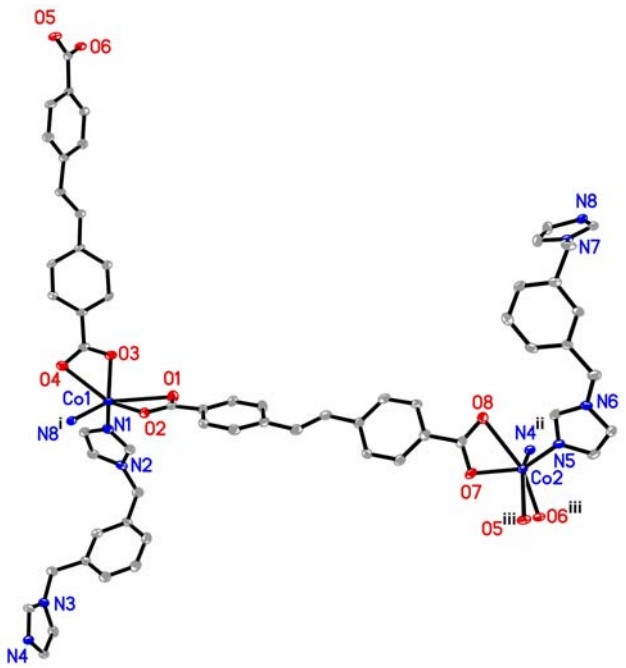



**Fig. S1.** The ORTEP figure of **1** (Displacement ellipsoids drawn at the 30% probability level). [Symmetry codes: (i) 2+x, y, z; (ii) x-2, y, z; (iii) x-1, y-1, z+1.]

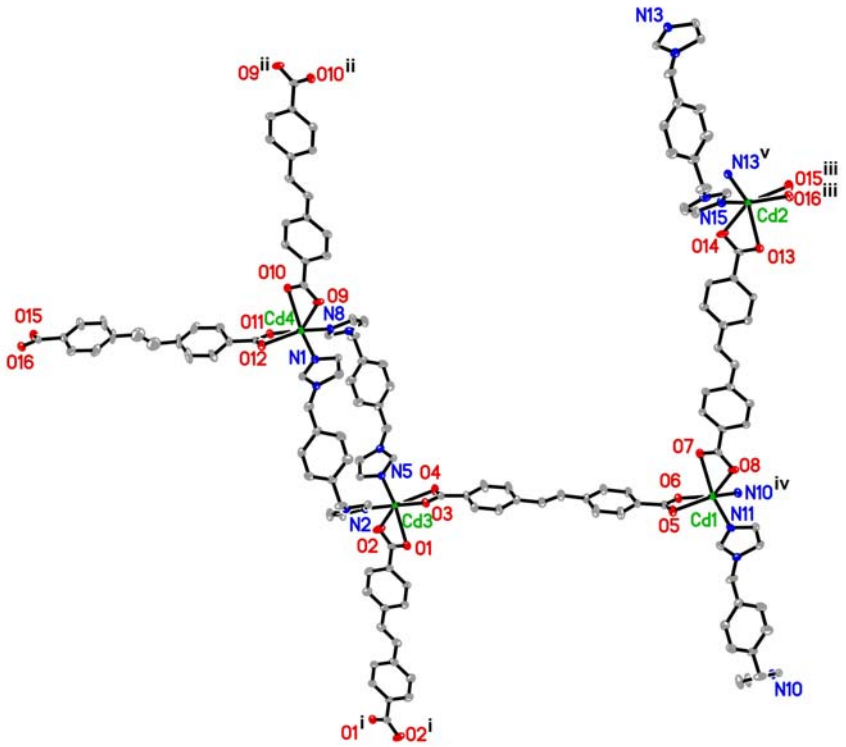



**Fig. S2.** The ORTEP figure of **2** (Displacement ellipsoids drawn at the 30% probability level). [Symmetry codes: (i) 1-x, -y, 2-z; (ii) 1-x, 1-y, -z; (iii) 1+x, 1+y, 1+z; (iv) 2-x, 1-y, 3-z; (v) 2-x, 2-y, 1-z.]

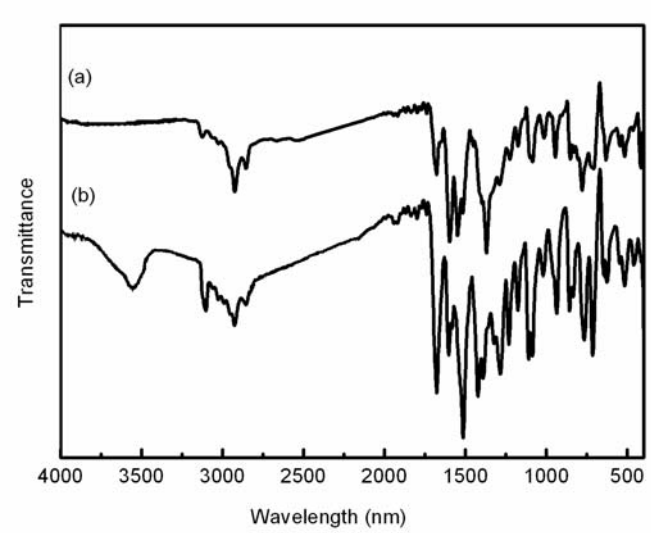
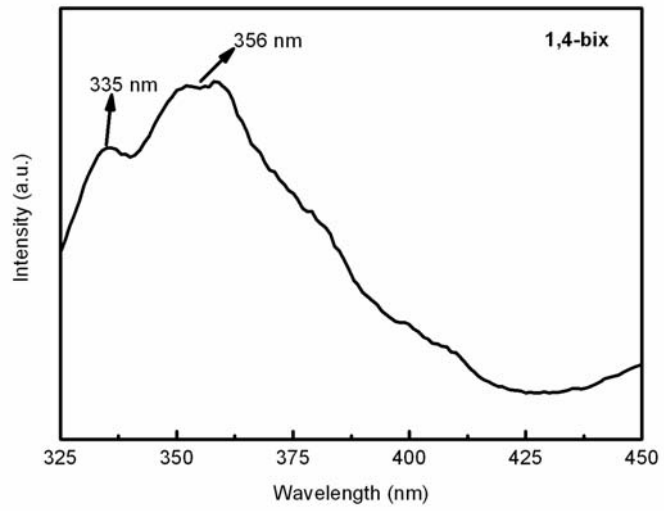



**Fig. S3.** IR spectra of (a) **1** and (b) **2**.



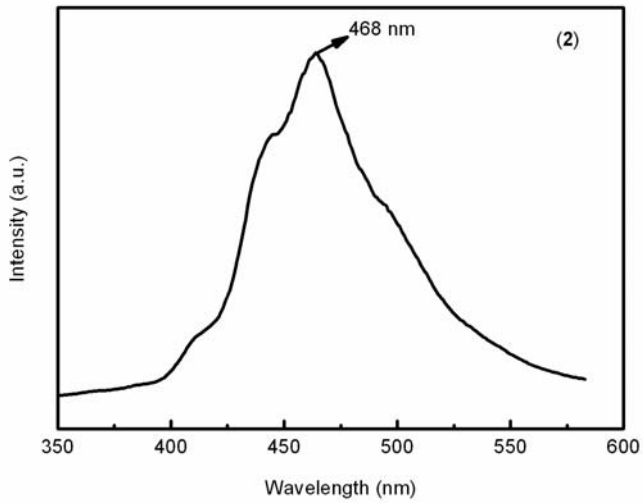



**Fig. S4.** Emission spectra of free 1,4-bix and **2** at room temperature.

**Luminescent Properties.**

Taking the luminescent properties of $d^{10}$ metal complexes into account, the luminescence of **2** was investigated. Two weak emissions at 335 and 356 nm were observed for free 1,4-bix ligands with the excitation peak at 300 nm. The emission peak of free $H_2$bpea ligand has been observed at about 460 nm.[2] Intense fluorescent emission occurs at 468 nm ($\lambda_{ex}$=386 nm) for **2**. Therefore, the emission of **2** may be assigned to the intraligand fluorescent emission. The enhancement of luminescence may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.

**References**

(1) B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.,* 1997, **119**, 2952.

(2) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su and C.-W. Hu, *Angew. Chem., Int. Ed.,* 2004, **43**, 5036.