

Electronic Supplementary Information (ESI) for *CrystEngComm*

Two novel entangled metal-organic networks constructed from 4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl and dicarboxylates: From polycatenated 2D + 2D → 3D framework to polyrotaxane-like 2D + 2D → 2D layer

Di Sun,^{*a} Zhi-Hao Yan,^{ab} Yong-Kai Deng,^a Shuai Yuan,^a Lei Wang^{*,b} and Dao-Feng Sun,^a

^aKey Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, P. R. China. E-mail: dsun@sdu.edu.cn.

^bKey Laboratory of Eco-chemical Engineering, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: inorchemwl@126.com

(1) Experiment details.....	2
(2) X-ray Crystallography	3
(3) Synthesis of 1 and 2	4
(4) Table S1: The selected bond distances and angles for 1 and 2.....	5
(5) Table S2: Crystal data and structure refinement for 1 and 2	6
(6) Fig. S1: IR spectra of 1 and 2	7
(7) Fig. S2: XRD patterns of 1 and 2	8

(1) Experiment details

All the reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were recorded on a Nicolet AVATAT FT-IR330 spectrometer as KBr pellets in the frequency range 4000-400 cm^{-1} . The elemental analyses (C, H, N contents) were determined on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate. TG curves were measured from 30 to 600 °C on a SDT Q600 instrument at a heating rate 10 °C/min under the N₂ atmosphere (100 mL/min). X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-K α radiation.

(2) X-ray Crystallography

Single crystals of the complexes **1** and **2** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** and **2** were collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.5° scan in 5 s, followed by spot integration and least-squares refinement. Data were measured using ω scans of 0.5° per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.¹ Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.¹ In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97² and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.³ Atoms were located from iterative examination of difference F -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. For **2**, the ratio Observed / Unique Reflections is 49 Perc, which is a 'C' level alert caused by the following reason: The quality of the crystal was not optimal and it was weakly diffracting. Better crystals were very hard to be obtained and also we have no access to low-temperature device. All structures were examined using the Addsym subroutine of PLATON⁴ to assure that no additional symmetry could be applied to the models.

(1) Bruker. *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

(2) G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

(3) Sheldrick, G. M. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

(4) A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

(3) Synthesis of **1** and **2**

Synthesis of complex [Cd(bmimbp)(bdc)]_n (1).

A mixture of Cd(NO₃)₂·4H₂O (30.8 mg, 0.1 mmol), bmimbp (34.2 mg, 0.1 mmol) and H₂bdc (16.6 mg, 0.1 mmol), NaOH (12.0 mg, 0.3 mmol) were dissolved in 6 mL methanol-H₂O (v:v = 1:1) in a 25 mL Teflon-lined stainless steel vessel. The mixture was sealed and heated at 160 °C for 67 hours. After the mixture was cooled to room temperature at a rate of 9 °C/h. The resulting colorless block crystals were collected in 60% yield (based on Cd). Elemental analysis: Anal. Calc. for C₃₀H₂₆N₄O₄Cd: C 58.21, H 4.23, N 9.05%. Found: C 58.55, H 4.02, N 9.75 %. IR (KBr): $\nu(\text{cm}^{-1}) = 1638$ (s), 1588 (s), 1530 (m), 1502 (m), 1428 (s), 1385 (m), 1354 (s), 1273 (m), 1197 (w), 1159 (m), 1137 (w), 1110 (m), 1076 (w), 1024 (w), 989 (m), 884 (m), 847 (m), 831 (m), 737 (s), 664 (m), 478 (m).

Synthesis of complex [Zn(bmimbp)(tbtpa)]_n (2).

A mixture Zn(NO₃)₂·6H₂O (5.9 mg, 0.02 mmol), bmimbp (3.42 mg, 0.01 mmol) and H₂tbtpa (14.5 mg, 0.03 mmol), NaOH (0.8 mg, 0.02 mmol) were dissolved in 1 mL DMF-H₂O (v:v = 1:1) and heated in a sealed Perex tube at 120 °C for 83 hours. After the mixture was cooled to room temperature at a rate of 7 °C/h. Pale-yellow crystals of **2** were obtained in 65% yield (based on Zn). They were washed with a small volume of cold ethanol. Elemental analysis: Anal. Calc. for C₃₀H₂₂Br₄N₄O₄Zn: C 40.60, H 2.50, N 6.31 %. Found: C 40.25, H 2.02, N 6.05 %. IR (KBr): $\nu(\text{cm}^{-1}) = 1577$ (s), 1501 (m), 1470 (m), 1424 (s), 1273 (m), 1154 (w), 1138 (w), 1078 (w), 984 (w), 738 (s), 665 (s).

(4) Table S1: The selected bond distances and angles for 1 and 2

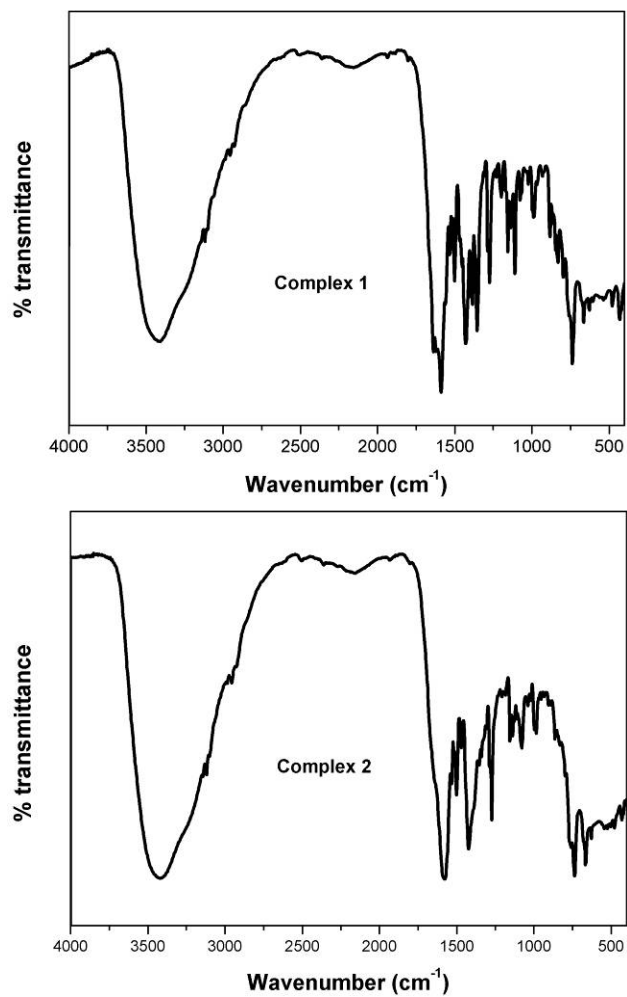
Complex 1			
Cd1—N3	2.244 (3)	Cd1—O4 ⁱ	2.308 (4)
Cd1—N1	2.244 (4)	Cd1—O3 ⁱ	2.479 (4)
Cd1—O1	2.293 (3)	Cd1—O2	2.584 (4)
N3—Cd1—N1	117.79 (13)	O1—Cd1—O3 ⁱ	136.28 (13)
N3—Cd1—O1	102.51 (13)	O4 ⁱ —Cd1—O3 ⁱ	53.59 (12)
N1—Cd1—O1	118.44 (13)	N3—Cd1—O2	83.24 (12)
N3—Cd1—O4 ⁱ	129.74 (13)	N1—Cd1—O2	86.90 (12)
N1—Cd1—O4 ⁱ	98.91 (14)	O1—Cd1—O2	52.43 (12)
O1—Cd1—O4 ⁱ	86.80 (12)	O4 ⁱ —Cd1—O2	134.73 (12)
N3—Cd1—O3 ⁱ	92.20 (13)	O3 ⁱ —Cd1—O2	171.16(12)
N1—Cd1—O3 ⁱ	88.56 (14)		
Symmetry code: (i) $x+1, y, z$.			
Complex 2			
Zn1—O1	1.947 (7)	Zn1—N1	2.004 (8)
Zn1—O3	1.967 (7)	Zn1—N4 ⁱ	2.030 (8)
O1—Zn1—O3	115.0 (3)	O1—Zn1—N4 ⁱ	113.2 (3)
O1—Zn1—N1	108.3 (3)	O3—Zn1—N4 ⁱ	96.6 (3)
O3—Zn1—N1	110.8 (3)	N1—Zn1—N4 ⁱ	112.7 (3)
Symmetry code: (i) $-x+1, -y-1, -z+2$.			

Electronic Supplementary Information (ESI) for *CrystEngComm*

(5) Table S2: Crystal data and structure refinement for 1 and 2

Complex	1	2
Empirical formula	C ₃₀ H ₂₆ CdN ₄ O ₄	C ₃₀ H ₂₂ Br ₄ N ₄ O ₄ Zn
Formula weight	618.95	887.53
Temperature/K	298(2)	298(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.995(2)	10.237(12)
b/Å	11.410(3)	11.827(14)
c/Å	11.572(3)	14.256(16)
α/°	87.877(4)	91.67(2)
β/°	88.749(4)	109.35(2)
γ/°	83.876(3)	103.26(2)
Volume/Å ³	1311.1(6)	1575(3)
Z	2	2
ρ _{calc} /mg/mm ³	1.568	1.872
μ/mm ⁻¹	0.877	5.897
F(000)	628.0	864.0
Crystal size/mm ³	0.10 × 0.10 × 0.07	0.12 × 0.10 × 0.10
2θ range for data collection	3.6 to 50°	3.56 to 50°
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 12, -13 ≤ l ≤ 6	-12 ≤ h ≤ 9, -10 ≤ k ≤ 14, -16 ≤ l ≤ 15
Reflections collected	6456	7596
Independent reflections	4534[R(int) = 0.0174]	5390[R(int) = 0.0501]
Data/restraints/parameters	4534/12/354	5390/0/390
Goodness-of-fit on F ²	1.032	0.887
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0382, wR ₂ = 0.0961	R ₁ = 0.0532, wR ₂ = 0.1195
Final R indexes [all data]	R ₁ = 0.0489, wR ₂ = 0.1043	R ₁ = 0.1194, wR ₂ = 0.1523
Largest diff. peak/hole / e Å ⁻³	0.52/-0.50	0.88/-1.06

(6) Fig. S1: IR spectra of 1 and 2



(7) Fig. S2: XRD patterns of 1 and 2

