

## Supplementary Information

(CrystEngComm, Dec. 2007)

Supramolecular frameworks assembled via intermolecular lone pair-aromatic interaction between carbonyl and pyridyl groups

Chong-Qing Wan,<sup>a</sup> Xu-Dong Chen,<sup>a,b</sup> and Thomas C. W. Mak<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, P. R. China.

Fax: +852-2603 5057. E-mail: [tcwmak@cuhk.edu.hk](mailto:tcwmak@cuhk.edu.hk)

<sup>b</sup> College of Chemistry and Life Science, Tianjin Normal University, Tianjin, P. R. China.

## Experimental

### General materials and Instruments

Diethyl ether was purchased from LAB-SCAN and further refluxed over sodium and benzophenone. All other chemicals were obtained commercially from Aldrich and

used without further purification. Synthesis of L ligand was performed under a nitrogen atmosphere using standard Schlenk techniques. Elemental analyses of C, H and N were performed by the MEDAC LTD Brunel Science Centre, United Kingdom. IR spectra were recorded with a Nicolet Impact 420 FT-IR spectrometer using KBr pellets. <sup>1</sup>H NMR spectra were taken at 300 Hz with a Bruker-300 spectrometer using CDCl<sub>3</sub> as solvent.

## Synthesis

**2,6-Pyridinediylbis(3-pyridinyl)methanone (L).** The preparation of ligand L followed the procedure previously developed for 2,6-pyridinediylbis(2-pyridinyl)methanone.<sup>1</sup> Under the protection of N<sub>2</sub>, 3-bromopyridine (7.9 g, 50mmol) in 25ml anhydrous diethyl ether was added slowly into 31.5 ml *n*-butyllithium (15% in hexane, 50ml) in 75 ml anhydrous diethyl ether at -50 °C. After addition was complete, the mixture was stirred at -50 °C for 30 minutes. Then, after cooling to -90 °C, dimethyl 2,6-pyridinedicarboxylate (4.875 g, 25mmol) in 50 ml anhydrous dichloromethane was added with vigorous stirring within 50 minutes. After stirring at -90 °C for another 30 minutes, the solution was allowed to slowly warm to room temperature over 5 hours and stand overnight, after which it was further quenched with 50 ml HCl solution in water and methanol (water/methanol/conc. HCl = 5:5:1) at -40 °C. The crude product was extracted with chloroform, and the combined organic extract was dried over anhydrous sodium sulfate and finally concentrated in vacuo to give a brown oil. Further purification by chromatography on silica gel using ether acetate/dichloromethane (1:6) as the eluent gave 2.96 g of light yellow powder of 2,6-pyridinediylbis(2-pyridinyl)methanone in 41% yield; m.p. 111-113 °C; <sup>1</sup>H NMR (300 M Hz, CDCl<sub>3</sub>): δ 9.27(s, 2H), 8.77 (d, J = 4.5 Hz

2H), 8.43 (d,  $J = 7.8$  Hz, 2H), 8.40 (td,  $J_1 = 1.8$  Hz,  $J_2 = 7.8$  Hz, 2H), 8.22 (t,  $J_2 = 7.8$  Hz, 1H), 7.36 (dd,  $J_1 = 4.8$  Hz,  $J_2 = 7.8$  Hz, 2H); IR (KBr):  $1666\text{ cm}^{-1}$  (C=O); Anal. Calcd (Found) for  $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2$ : C, 70.58 (70.37); H, 3.83 (3.65); N, 14.52 (14.66)%.

**Synthesis of  $\text{Cu}(\text{L})_2(\text{BF}_4)_2$  (1).** 2,6-Pyridinediylbis(2-pyridinyl)methanone (L) (14.5 mg, 0.05 mmol) and  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (35 mg, 0.1 mmol) were added to 5 ml of acetonitrile and stirred at room temperature for 5 hours. After filtration, slow evaporation of the filtrate yielded block-like blue crystals of **1** suitable for X-ray diffraction. Changing the ligand to metal salt molar ratio to 1:1 yielded the same result. Yield: 14.5 mg (71.1%). Anal. Calcd. (Found) for  $\text{C}_{34}\text{H}_{22}\text{N}_6\text{O}_4\text{B}_2\text{F}_8\text{Cu}$ : C, 50.06 (49.55); H, 2.72 (2.75); N, 10.30 (10.90) %. IR (KBr)  $\bar{\nu}/\text{cm}^{-1}$ : 3073(w), 1689(vs), 1595(w), 1427(m), 1326(s), 1259(w), 1199(w), 1085(vs), 970(m), 843(w), 755(w), 702(m), 641(w).

**Synthesis of  $\text{Cu}(\text{L})_2(\text{NO}_3)_2 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  (2).** L Ligand (58 mg, 0.2 mmol) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (48 mg, 0.2mmol) were mixed in 10 ml methanol solvent and stirred for 1 hour. A light blue precipitate was deposited, and then 5 ml acetonitrile was added. The solution subsequently turned clear. After filtration, slow evaporation of the filtrate yielded blue crystals of **2** suitable for X-ray diffraction. Yield: 51.9 mg (63.1%). Anal. Calcd. (Found) for  $\text{C}_{36}\text{H}_{27}\text{CuN}_9\text{O}_{11}$ : C, 50.42 (50.82); H, 3.30 (3.11); N, 15.29 (15.58) %. IR (KBr)  $\bar{\nu}/\text{cm}^{-1}$ : 3078(w), 2356(m), 1681(vs), 1681(w), 1604(w), 1410(vs), 1332(s), 1195(w), 987(w), 930(m), 835(w), 752(w), 701(m), 646(w).

### X-Ray Crystallographic Studies

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART 1000 CCD diffractometer operating at 50KV and 30mA using Mo- $K\alpha$  radiation

( $\lambda = 0.71073\text{\AA}$ ). Each selected crystal was mounted inside a Lindemann glass capillary, and intensity collection at 293 K and data reduction were performed using the SMART and SAINT software.<sup>2</sup> An empirical absorption correction was applied using the SADABS program.<sup>3</sup> Both crystal structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL program package.<sup>4</sup> All non-hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms of the lattice water molecules in complex **2** could not be located, and were not included in the refinement.

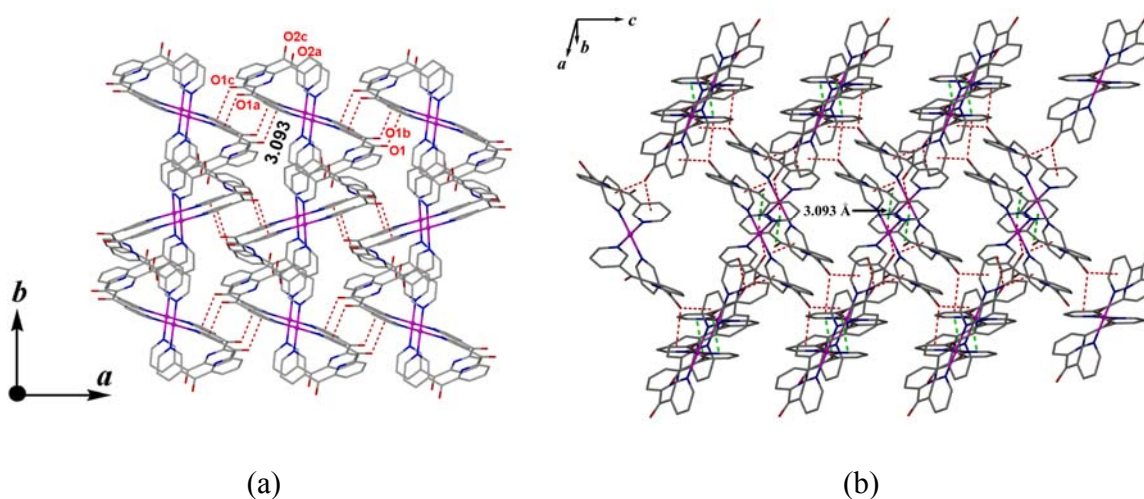
**Table 1.** Crystallographic data and refinement parameters for complex **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>34</sub> H <sub>22</sub> N <sub>6</sub> O <sub>4</sub> B <sub>2</sub> F <sub>8</sub> Cu	C <sub>36</sub> H <sub>27</sub> N <sub>9</sub> O <sub>11</sub> Cu
Formula weight	815.74	825.19
<i>T</i> /K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Crystal size/mm <sup>3</sup>	0.48×0.29×0.21	0.46×0.36×0.21
<i>a</i> /Å	10.284(1)	9.154(5)
<i>b</i> /Å	17.787(2)	21.374(1)
<i>c</i> /Å	9.391(1)	18.717(1)
$\alpha$ /°	90	90
$\beta$ /°	94.380(2)	90.286(1)
$\gamma$ /°	90	90
<i>V</i> /Å <sup>3</sup>	1712.7(3)	3662(3)
<i>Z</i>	2	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.583	1.493
$\theta$ /°	1.99-28.30	1.45-28.43
<i>F</i> (000)	822	1684
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.731	0.671
Reflections collected	11867	25386
Independed reflections( <i>R</i> <sub>int</sub> )	4263(0.0695)	9108(0.0373)
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2469	5394
Parameters	251	530
Goodness-of-fit ( <i>F</i> <sup>2</sup> )	1.001	1.034
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0560	0.0565
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1498	0.2226

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

**Table 2.** Selected bond lengths and angles of complex **1** and **2**.

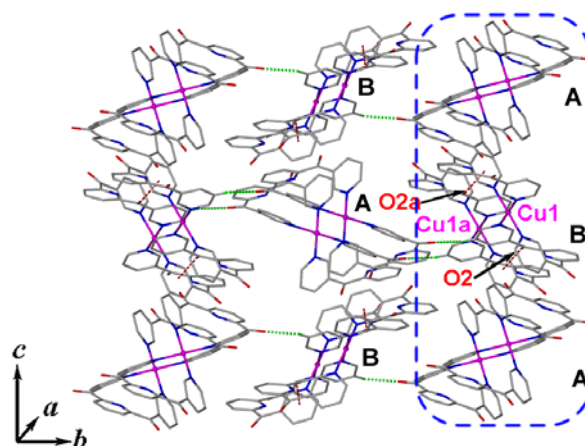
		<b>1</b>		<b>2</b>	
Bond length (Å)	Cu1-N1	2.040(3)	Cu1-N2	2.030(3)	
	Cu1-N3	2.027(3)	Cu1-N1	2.073(3)	
	C1-N1	1.350(4)	Cu2-N4	2.040(3)	
	C5-N1	1.341(4)	Cu2-N5	2.063(3)	
	C6-O1	1.215(4)	O1-C6	1.216(4)	
	Bond angle (°)	N3-Cu1-N3a	180.0	N2-Cu1-N1	90.99(1)
N3-Cu1-N1		91.41(1)	N2-Cu1-N1a	89.01(1)	
N3a-Cu1-N1		88.59(1)	N4-Cu2-N5	88.27(1)	
			N4-Cu2-N5b	91.73(1)	



**Figure S1** Crystal structure of  $\text{Cu}(\text{L})_2(\text{BF}_4)_2$  **1**. (a) The type **I**  $\text{C}=\text{O}\cdots\pi$  interactions in the  $ab$  plane are represented by red dashed lines. Symmetry code: a  $-x + 1, -y, -z + 1$ ; b  $x, y, z - 1$ ; c  $-x + 1, -y, -z$ . The type **II**  $\text{C}=\text{O}\cdots\pi$  interactions in the  $bc$  plane are omitted for clarity. (b) 3D cationic framework formed by the type **I**, **II** and **III**  $\text{C}=\text{O}\cdots\pi$  interactions in different directions. The type **I**  $\text{C}=\text{O}\cdots\pi$  interactions are shown in green for clarity, which shared one pyridyl ring with the type **II** (red

dashed lines) to compose the type **III**. All hydrogen atoms are omitted for clarity.

Color code: dark blue N, gray C, red O, purple Cu.



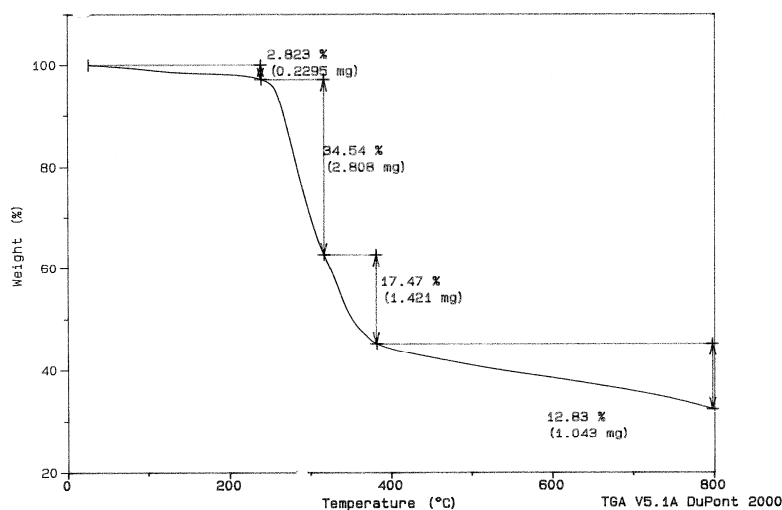
**Figure S2.** Three-dimensional molecular framework of **2** constructed by C-H...O(carbonyl) interactions (green dashed lines) along the *b* axis and C=O... $\pi$  interactions (type **I**, red dashed lines) along the *a* axis. All hydrogen atoms except those involved in hydrogen bonding, solvent molecules, nitrate ions, and the type **IV** C=O... $\pi$  interactions along the *c* axis are omitted for clarity.

Supplementary Material (ESI) for *CrystEngComm*  
This journal is © The Royal Society of Chemistry 2008

Sample: W22  
Size: 8.1300 mg  
Method: WAN

TGA

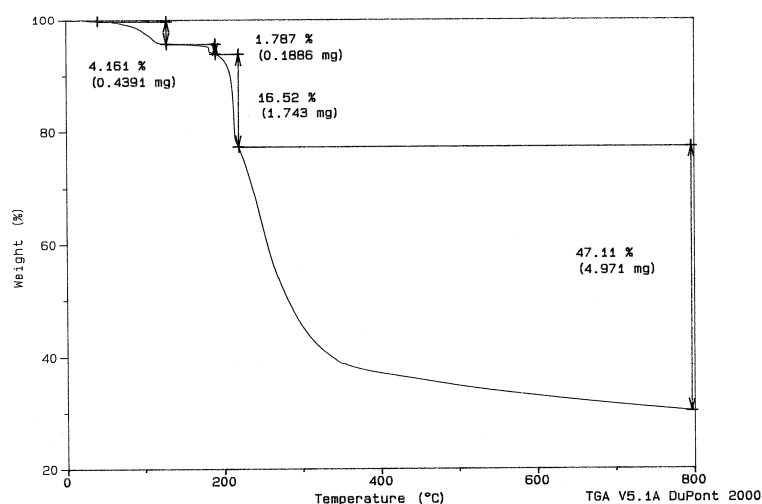
File: C:\07070901.001  
Operator: WAN  
Run Date: 8-Jul-07 21:14



Sample: W1  
Size: 10.5520 mg  
Method: WAN

TGA

File: C:\070509.002  
Operator: WAN  
Run Date: 8-May-07 21:13



**Figure S3** TGA analysis of complex **1** (top) and **2** (bottom). **2** shows a gradual weight loss of 4.161% in the 30~100 °C corresponding to the lattice actenitrile molecule liberation (calcd. 4.96%). The weight loss of 1.787% in the range 100~170°C is attributed to the removal of lattice water molecules (calcd. 2.18%).

## References

- 1 B. Abarca, R. Ballesteros and M. Elmasnaouy, *Tetrahedron* 1998, **54**, 15287.
- 2 Bruker, *SMART 5.0 and SAINT 4.0 for Windows NT, Area Detector Control and Integration Software*, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998.
- 3 G. M. Sheldrick, *SADABS: Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen: Göttingen, Germany, 1996.
- 4 G. M. Sheldrick, *SHELXTL 5.1 for Windows NT: Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.