Supplemental Information

Structural Diversity through Ligand Flexibility: Two Novel Metal-Organic Nets *via* Ligand-to-Ligand Cross-Linking of "Paddlewheels"

Wenge Qiu,[a,b] Jason A. Perman,[a] Łukasz Wojtas,[a] Mohamed Eddaoudi and Michael J. Zaworotko*[a]

Experimental Sections

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using APEX2 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01.[2] Absorption correction was performed by multi-scan method implemented in SADABS. [3] Space groups were determined using XPREP implemented in APEX2.[1] The structure was solved using SHELXS-97 and refined using SHELXL-97 contained in APEX2 [1] and WinGX v1.70.01[4,5,6] programs packages. Hydrogen atoms were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using riding model. The crystal **2** was a racemic twin (two crystals were checked). Crystal structure of **1** was refined by using restraints and with isotropic displacement parameters for sixteen atoms. Low angle diffraction only (Theta = 50.43 deg) and significant disorder of the ligand was observed in this case. For both structures the contribution of disordered solvent molecules was treated as a diffuse using Squeeze procedure implemented in Platon program.[7, 8]

All the reagents and solvents, unless described otherwise, were commercially available and used as received. ^{1}H-NMR data were collected on a Bruker DRX 250-MHz spectrometer. FT-IR data were recorded on a Nicolet AVATAR 320 FT-IR instrument. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer STA6000 instrument under nitrogen

atmosphere (20mL/min). The sample was heated at a constant rate of 10°C/min from 30°C to 800°C. Powder X-ray diffraction was performed on a Bruker D8 Advance, θ/2θ diffractometer using Cu-*K*α radiatipon (λ=1.54178Å) at room temperature. The experimental parameters included a scan speed of 3°/h and a step size of 0.05° with respect to 2θ. The data was collected over the range of 3-40° with respect to 2θ and was analyzed using the EVA software suite.

References

1 Bruker (2008). *APEX2* (Version 2008.1-0). Bruker AXS Inc., Madison, Wisconsin, USA.

2 Bruker (2001b). SAINT-V6.28A. Data Reduction Software.

3 G. M. Sheldrick, (1996). *SADABS. Program for Empirical Absorption Correction*. University of Gottingen, Germany.

4 L. J. Farrugia, *J. Appl. Cryst*., 1999, **32**, 837.

5 G.M. Sheldrick, (1997) SHELXL-97. Program for the Refinement of Crystal.

6 G.M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467.

7 T. L. Spek, *Acta Cryst*., 1990, **A46**, 194.

8 T. L. Spek, *Acta Cryst*., 1990, **A46**, c34.

Table S1. Crystal data and structure refinement for complex **1** and **2**.

	Complex **1**	Complex **2**
Empirical formula	$C_{62}H_{51}Cu_6NO_{35}$	$C_{57}H_{48}Cu_6O_{36}$
Formula weight	1751.28	1690.19
Temperature	100(2)K	100(2)K
Crystal System	Orthorhombic	Hexagonal
Space Group	Pnma	$P6_322$
Unit Cell Dimensions	a = 34.3624(13)Å b = 18.6807(7)Å c = 25.8757(9)Å α = β = γ = 90°	a = b = 18.5773(3)Å c = 22.6933(5) Å α = β = 90° γ = 120°
Volume	16610.0(11) $Å^3$	6782.6(2) $Å^3$
Z	4	2
Density	0.700 Mg/m^3	0.828Mg/m^3
Absorption coefficient	1.186 mm^{-1}	1.443 mm^{-1}
F(000)	3536	1704
Crystal Size	0.15 × 0.10 × 0.07mm	0.20 ×0.15 × 0.04 mm
Theta range for data collection	2.14 to 50.43 deg.	2.75 to 67.08 deg.
Reflections collected	31349	49779
Independent reflections	9036 [R(int) = 0.0728]	4033 [R(int) = 0.1095]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Max. and min. transmission	0.9216 and 0.8422	0.9446 and 0.7613
Data / restraints / parameters	9036 / 86 / 398	4033 / 0 / 150
GOF on F^2	1.090	0.985
Final R indices [I>2σ(I)]	R_1 = 0.0881, wR_2 = 0.2230	R_1=0.0328, wR_2=0.0775
R indices (all data)	R_1 = 0.1447, wR_2 = 0.2456	R_1=0.0398, wR_2=0.0798
Largest diff. peak and hole	0.546 /-0.550 eÅ3	0.186 /-0.310 e. $Å^{-3}$

Additional Figures

Figure S1. Experimental and calculated X-ray diffraction patterns for complex **1**, indicating the phase purity of the as-synthesized product.

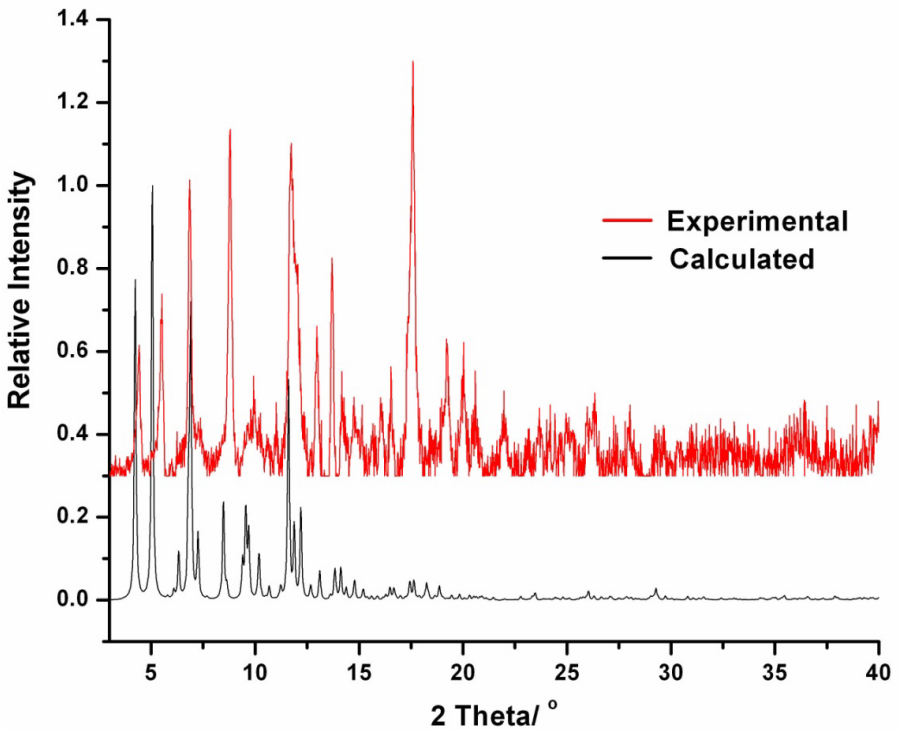

Figure S2. Two kinds of conformation of the ligand **L** in **1**: **La** (left) and **Lb** (right).

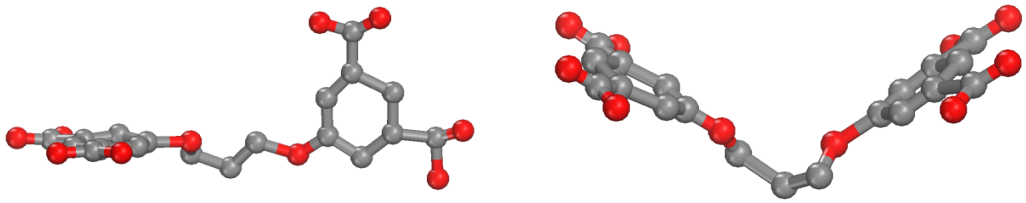

Figure S3. The cavities in **1** viewed along *a*-axis.

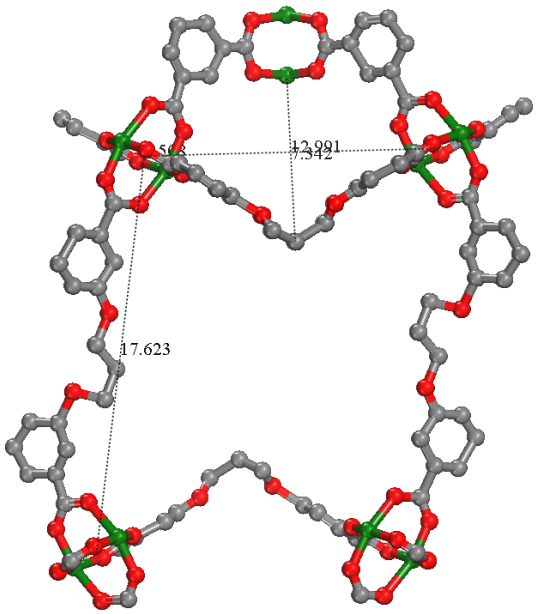

Figure S4. Framework structure of compound **1** viewed down the ***c*** axis, showing the Kagomé like layers. **L** ligands span the hexagonal windows.

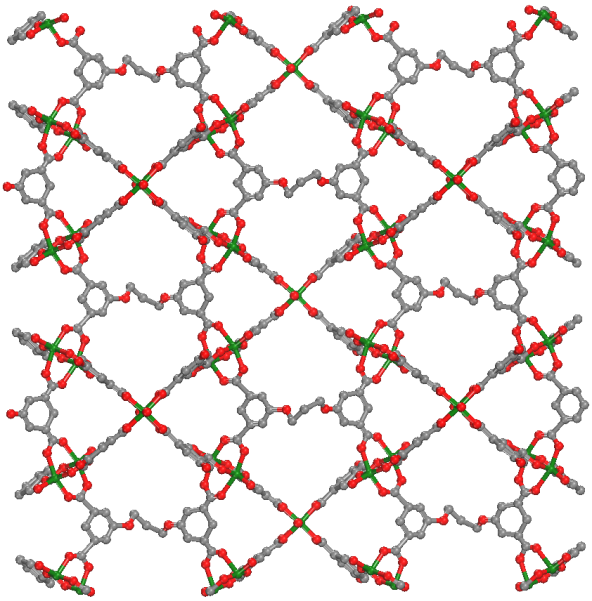

Figure S5. Framework structure of compound **1** viewed down the *b* axis.

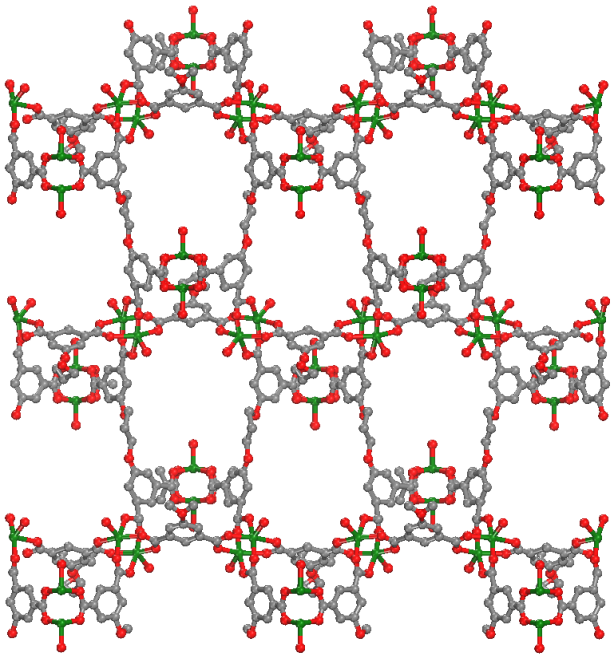

Figure S6 TGA data and analysis for complex **1**.

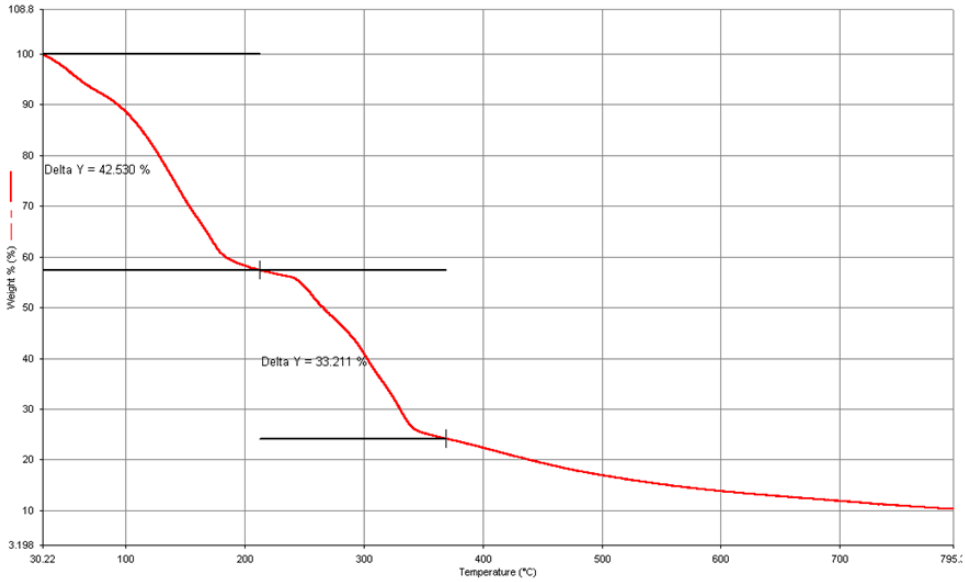

Fig. S7. Crystal shapes of **1** (left) and **2** (right).

Figure S8. Experimental and calculated X-ray diffraction patterns for compound **2**, indicating the phase purity of the as-synthesized product.

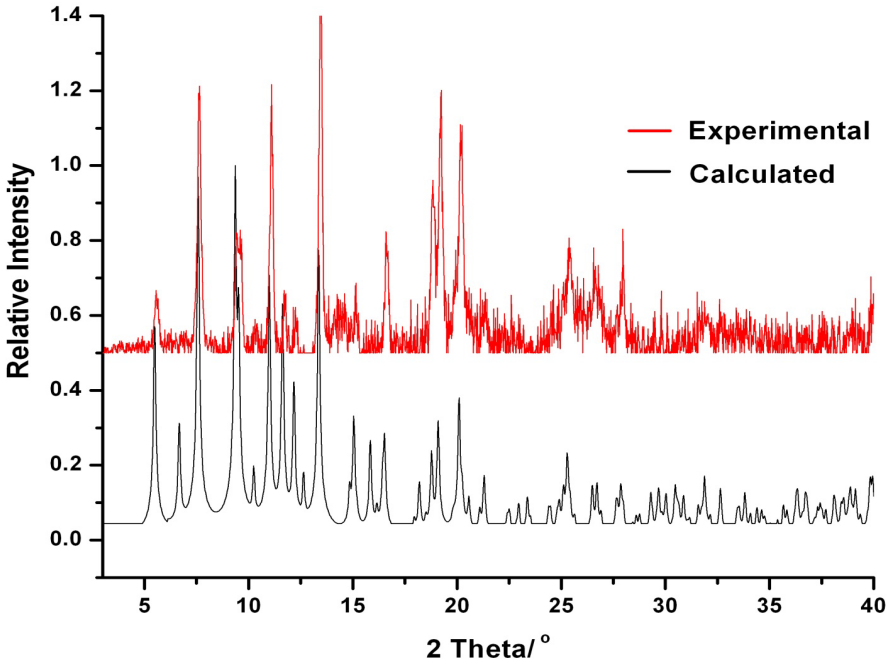

Figure S9. One trigonal prism connected with six trigonal prismatic units through its vertices to afford the *acs*-like topology.

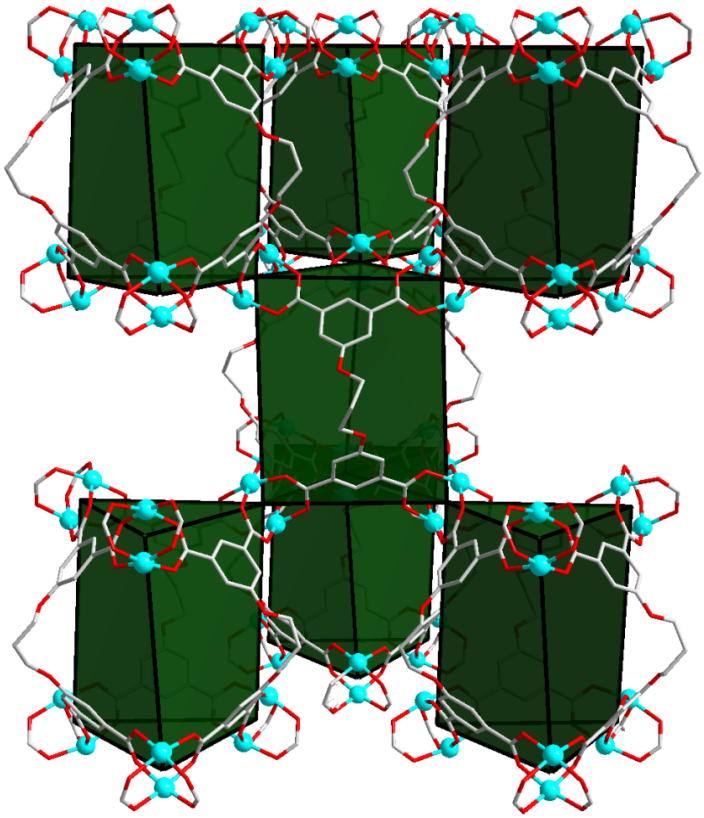

Figure S10. Space filling model of compound **2** viewed down the ***c*** axis.

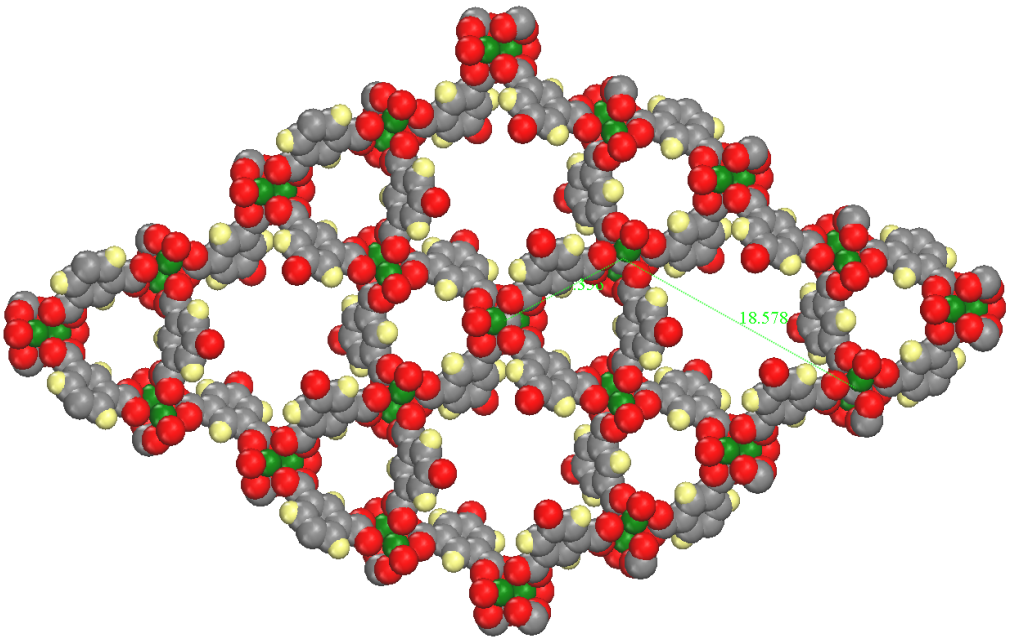

Figure S11. Framework structure of compound **2** viewed down the *b* axis.