Supporting Information for B618296H

A novel three-dimensional heterometallic compound: templated assembly of the unprecedented planar "Na⊂[Cu4]" metalloporphyrin-like subunits

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1. Preparation of 1 in different routes of 1 and 2

Route 1: Hydrothermal treatment of $Cu(NO_3)_2{\cdot}6H_2O$ (0.4 mmol), but-2-ynedioic acid (1 mmol)，NaN_3 (2.0 mmol), and water (9.0 mL) for 4 days at 150 °C yielded deep-blue rhombic crystals. The yield was about 35% based on but-2-ynedioic acid. The final pH value of the reaction mixture was about 7. Elemental analysis (%) calcd. for $C_{16}H_{14}N_{12}O_{23}Cu_4Na_4$: C 17.66, H 1.30, N 15.44; found C 17.78, H 1.53, N 15.72. IR data ($\tilde{v}$, cm^{-1}): 3619(m), 3510(m), 3400(m), 3304(m), 1688(s), 1650(vs), 1390(s), 1346(m), 1326(m), 1199(w), 1140(m), 863(w), 788(m).

Route 2: Hydrothermal treatment of $Cu(NO_3)_2{\cdot}6H_2O$ (0.4 mmol), 1,2,3-triazole-4,5-dicarboxylic acid (0.2 mmol), NaOH (1.0 mmol), and water (5.0 mL) for 4 days at 150 °C yielded deep-blue powder samples. Elemental analysis (%) calcd. for $C_{16}H_{14}N_{12}O_{23}Cu_4Na_4$: C 17.66, H 1.30, N 15.44; found C 17.63, H 1.82, N 15.99. IR data ($\tilde{v}$, cm^{-1}): 3619(m), 3513(m), 3405(m), 3302(m), 1685(s), 1650(vs), 1390(s), 1346(m), 1326(m), 1199(w), 1140(m), 863(w), 787(m) cm^{-1}.

2. Simulated and experimental powder XRD patterns for the product of Route 2

The following figure gives the powder XRD patterns for **1** of **Route 2**. The patterns measured for the bulk samples are in good agreement with those calculated from the single crystal data.

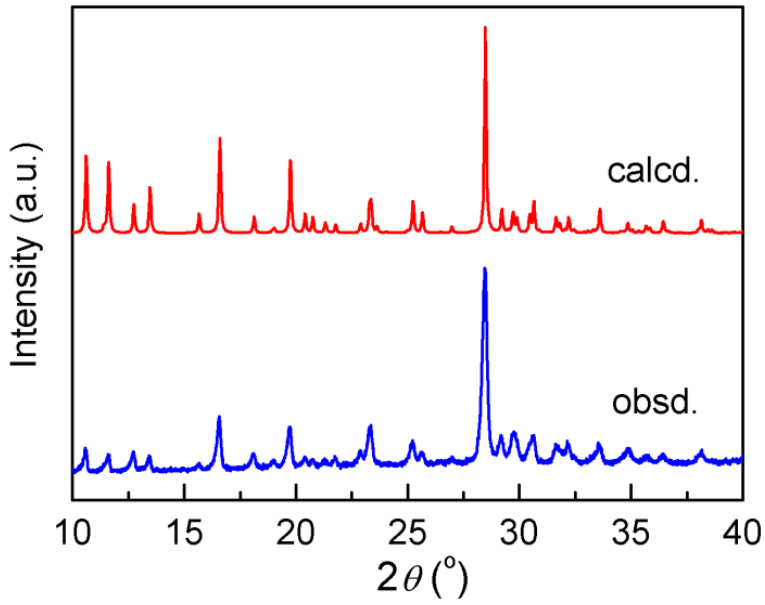

Figure S1. Simulated and experimental powder XRD patterns for the product of **Route 2**.

3. Calculation details

All the calculations are carried out with the Gaussian 03 program package[1]. An all-electron triple-ζ basis set is used for copper atom while double-ζ basis sets are used for all the other atoms. The d and f type functions are added to account the polarization and diffusion effect

References

1 Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J.

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