Supporting Information

Insight into the Construction of (3,6)-connected rtl, ant and Chiral anh Nets Based on Structural Investigation of Several MOFs via Steric Tuning of Linkers

Hui-Yan Liu*, Kang Wang, Yi Sun, Rui Wang and Hai-Ying Wang*

School of Chemistry & Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China

EXPERIMENTAL SECTION

Synthesis of ligand (L-OCH$_3$). A mixture of 3,5-dibromo-4-methoxylbenzoate (2.0 g, 6.2 mmol), pyridin-4-ylboronic acid (2.5 g, 20.3 mmol), K_3PO_4 (15.0 g, 56.3 mmol), and $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol) was added to 1,4-dioxane (100 mL) and heated to 80 °C for 3 days under N_2 atmosphere. The resultant was taken up in CH_2Cl_2 and the CH_2Cl_2 solution was evaporated to dryness. The residue was washed briefly with ethanol to gain crude products, which were hydrolyzed by refluxing in 2 M aqueous NaOH and followed by acidification with 37% HCl to afford final products. Yield = 1.4 g (78.9 %). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 13.28 (s, COOH), 8.71 (d, 4H, J = 4.0 Hz, ArH), 8.01 (s, 2H, ArH), 7.65 (d, 4H, J = 8.0 Hz, ArH), 3.24 (s, 3H, CH_3). Anal. Calcd (Found) for $C_{18}H_{14}N_2O_3$: C, 70.58 (70.66); H, 4.61 (4.67); N, 9.15 (9.05) %. IR (KBr, cm^{-1}): 3040, 2994, 1698, 1606, 1547, 1463, 1431, 1399, 1333, 1250, 1234, 1220, 1125, 1073, 1017, 994, 834, 777, 696, 626, 608.

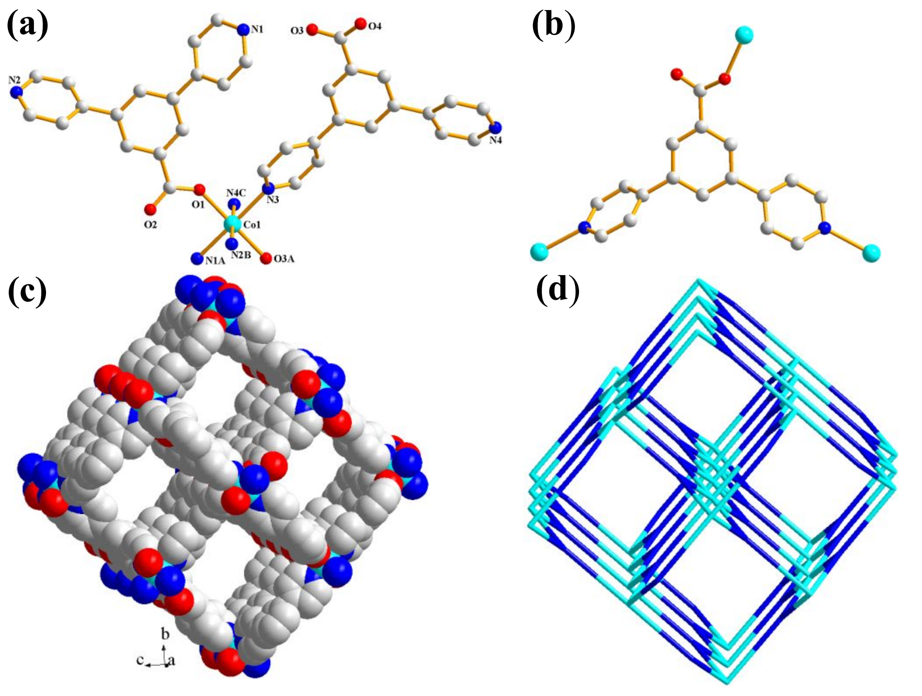


Figure S1. (a) Coordination environment of Co(II) ion **1**. (b) Coordination environment of L-H ligand. (c) The 3D framework of **1** viewed along *a* axis. (d) Schematic representations of (3,6)-connected ***rtl*** framework of **1** with $(4{\cdot}6^2)_2(4^2{\cdot}6^{10}{\cdot}8^3)$ topology.

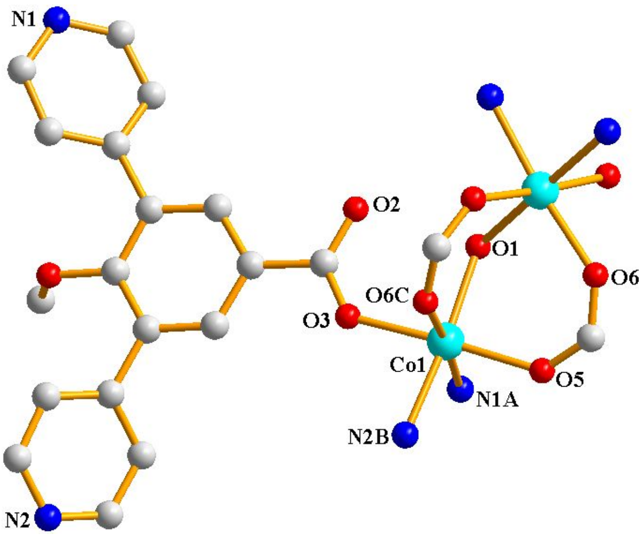


Figure S2. Coordination environment of Co(II) ion in **3**.

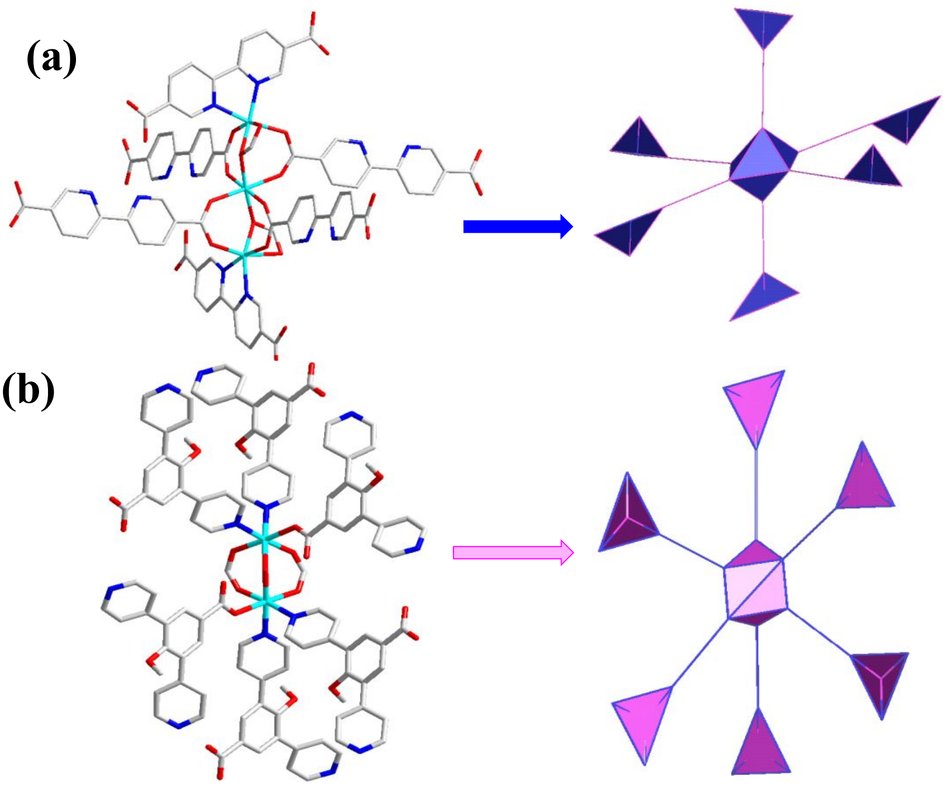


Figure S3. Structural comparison of two nodes of JIU-Liu3 (a) and **3** (b) with ***ant*** topology.

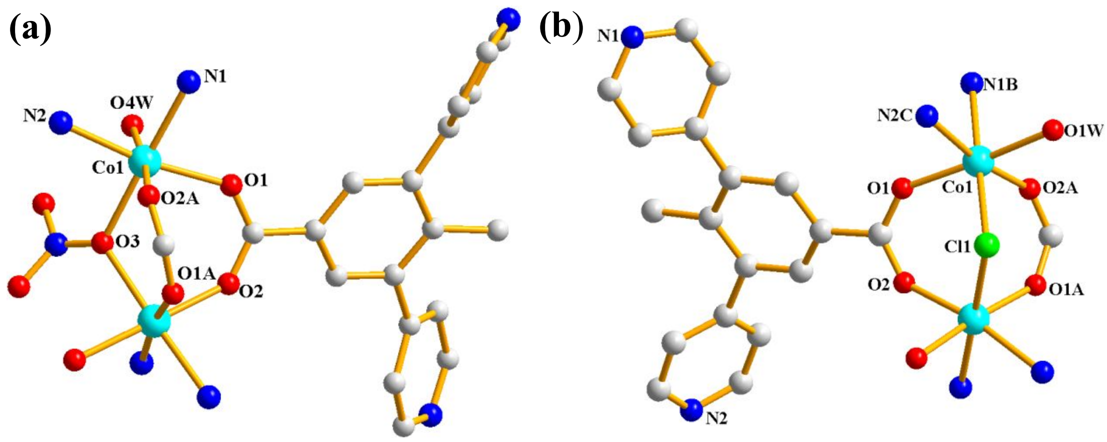


Figure S4. Coordination environment of Co(II) ion in **5** (a) and **6** (b).

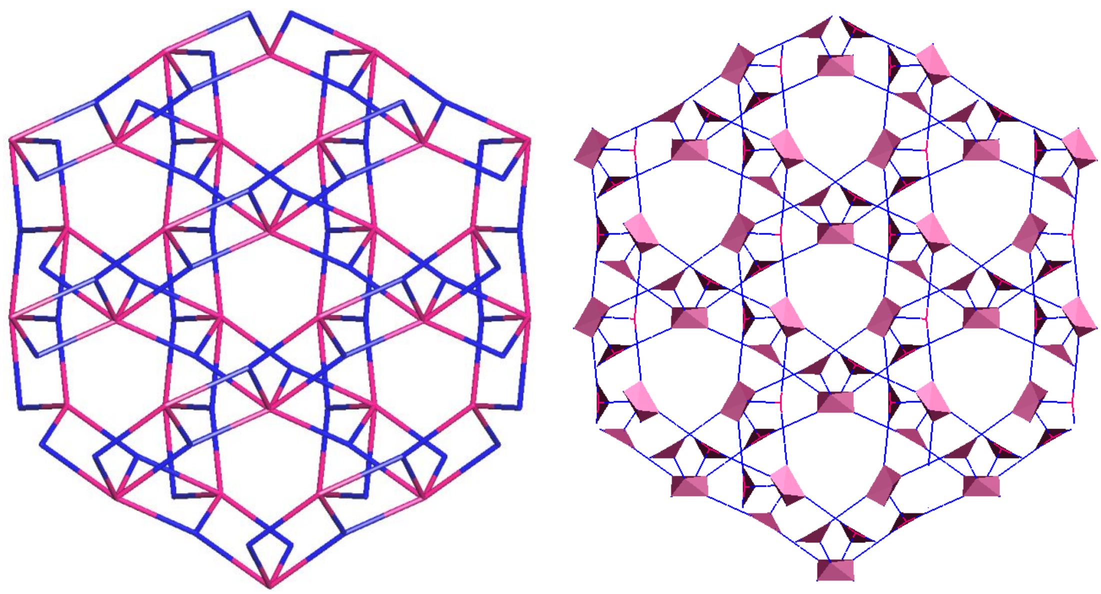


Figure S5. The (3,6)-connected 3D net of **5**/**6** with chiral ***anh*** topology shown as a stick diagram (left) and as a augmented form (right).

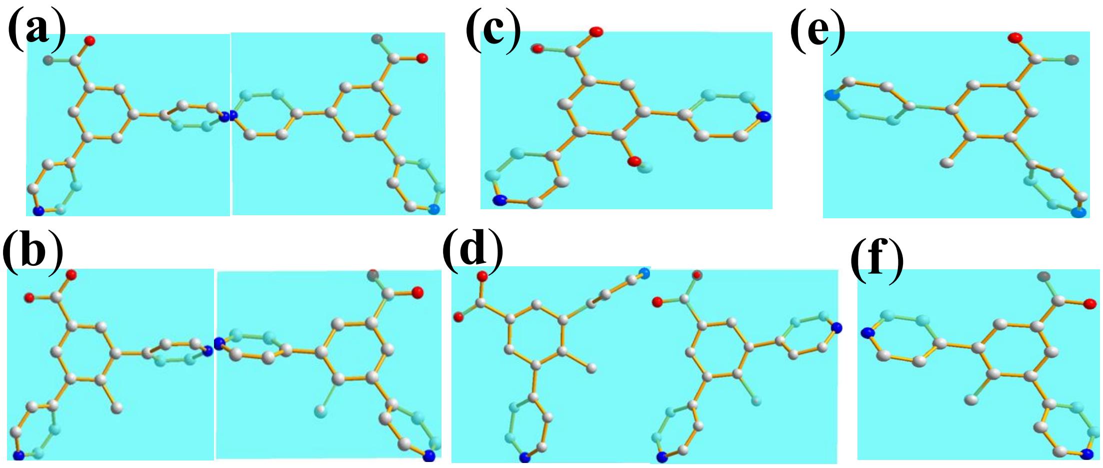


Figure S6. Conformation of the three tritopic pyridine-carboxylate linkers in **1-6**. (a, b) Conformation of L-H and L-CH_3 linkers in **1** and **2** (***rtl*** net). (c, d) Conformation of L-OCH_3 and L-CH_3 linkers in **3** and **4** (***ant*** net). (e, f) Conformation of L-CH_3 linker in **5** and **6** (chiral ***anh*** net).

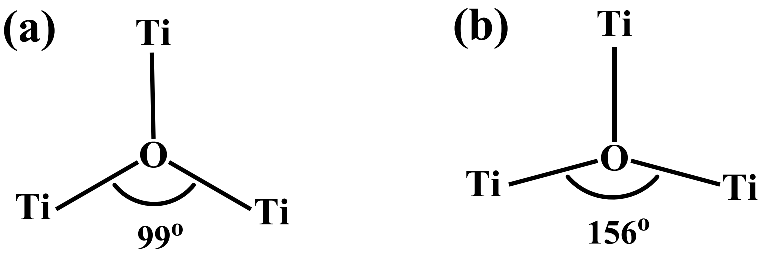


Figure S7. Coordination geometry of oxygen atoms in rutile (a) and anatase (b) with (Ti-O-Ti) angle is 99^0 and 156^0, respectively.

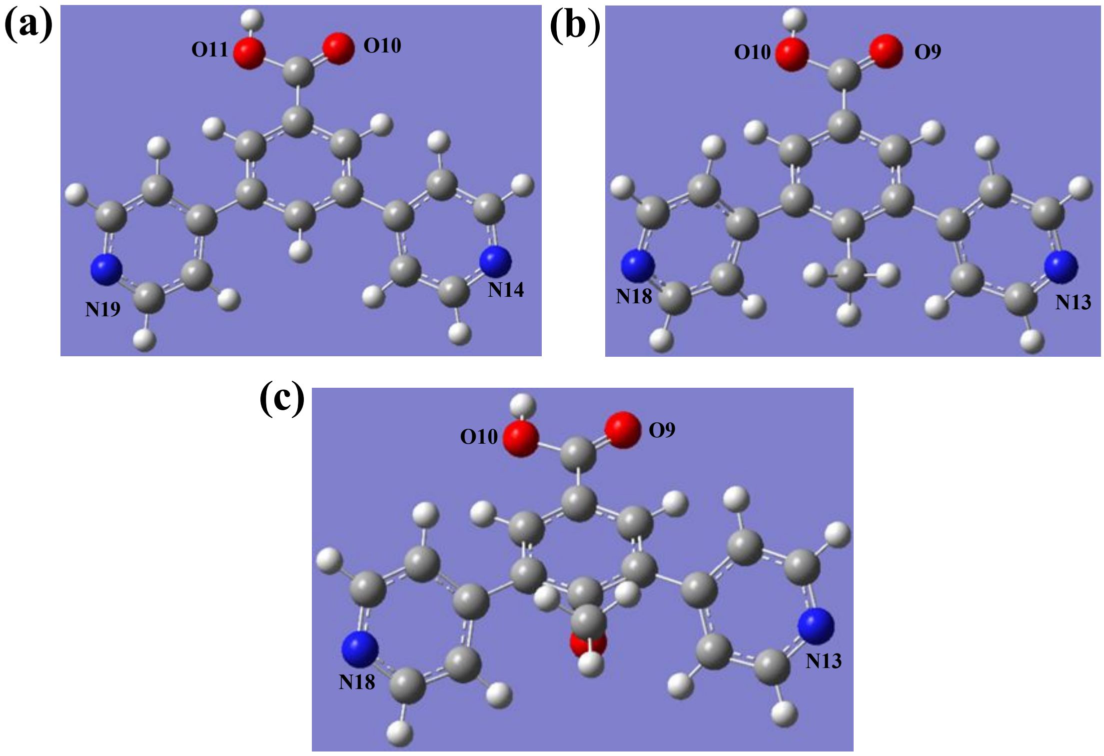


Figure S8. The optimized geometry and selected number of atom for tritopic pyridine-carboxylate linkers L-H (a), L-CH_3 (b) and L-OCH_3) (c). (The red, blue, gray and white spheres represent O, N, C and H atoms, respectively).

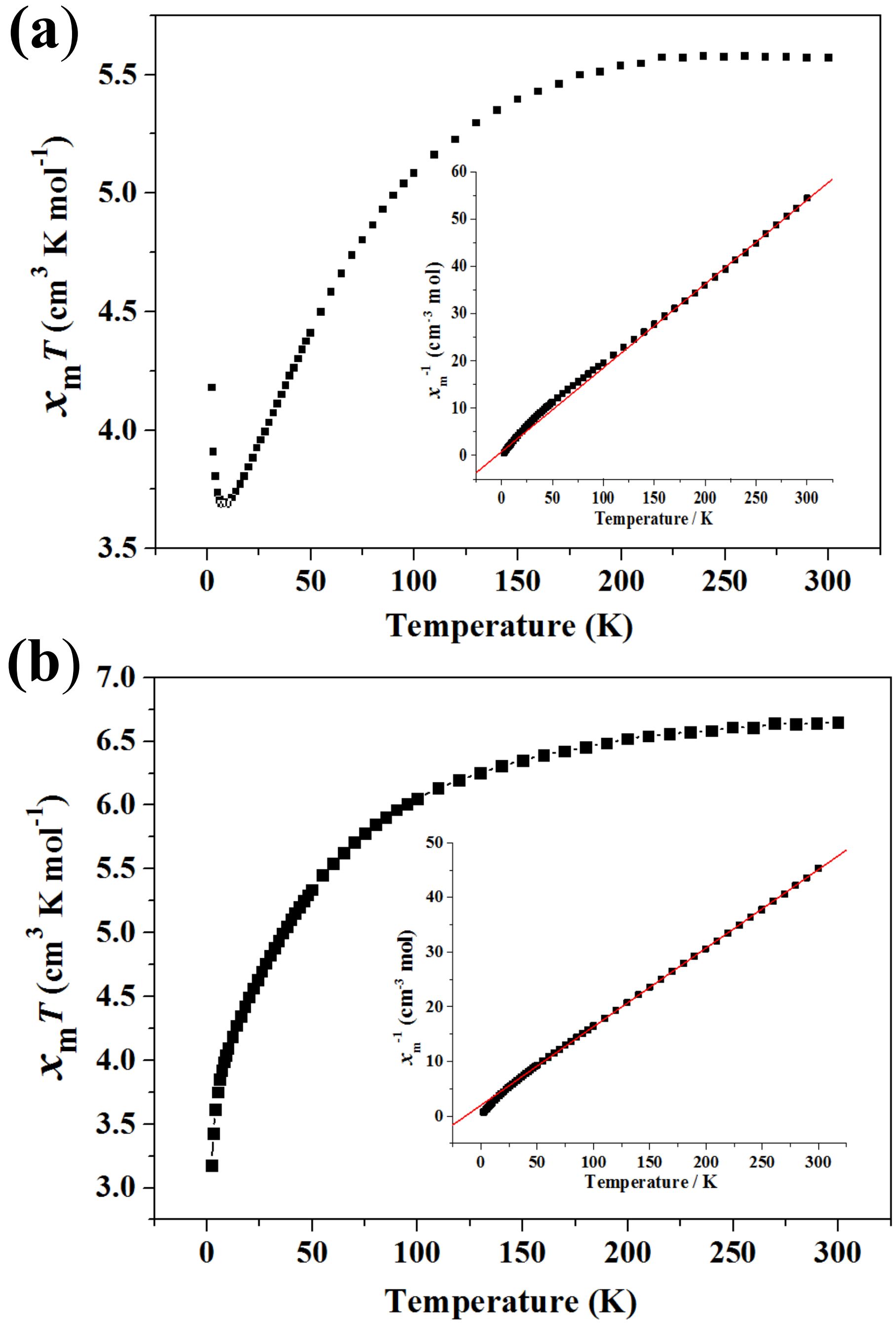


Figure S9. The $\chi_m T$ versus T curves for **4** (a) and **6** (b) at 1000 Oe. The inset is plots of χ_m^{-1} versus T for **4** and **6** and the red solid line shows the Curie−Weiss fitting.

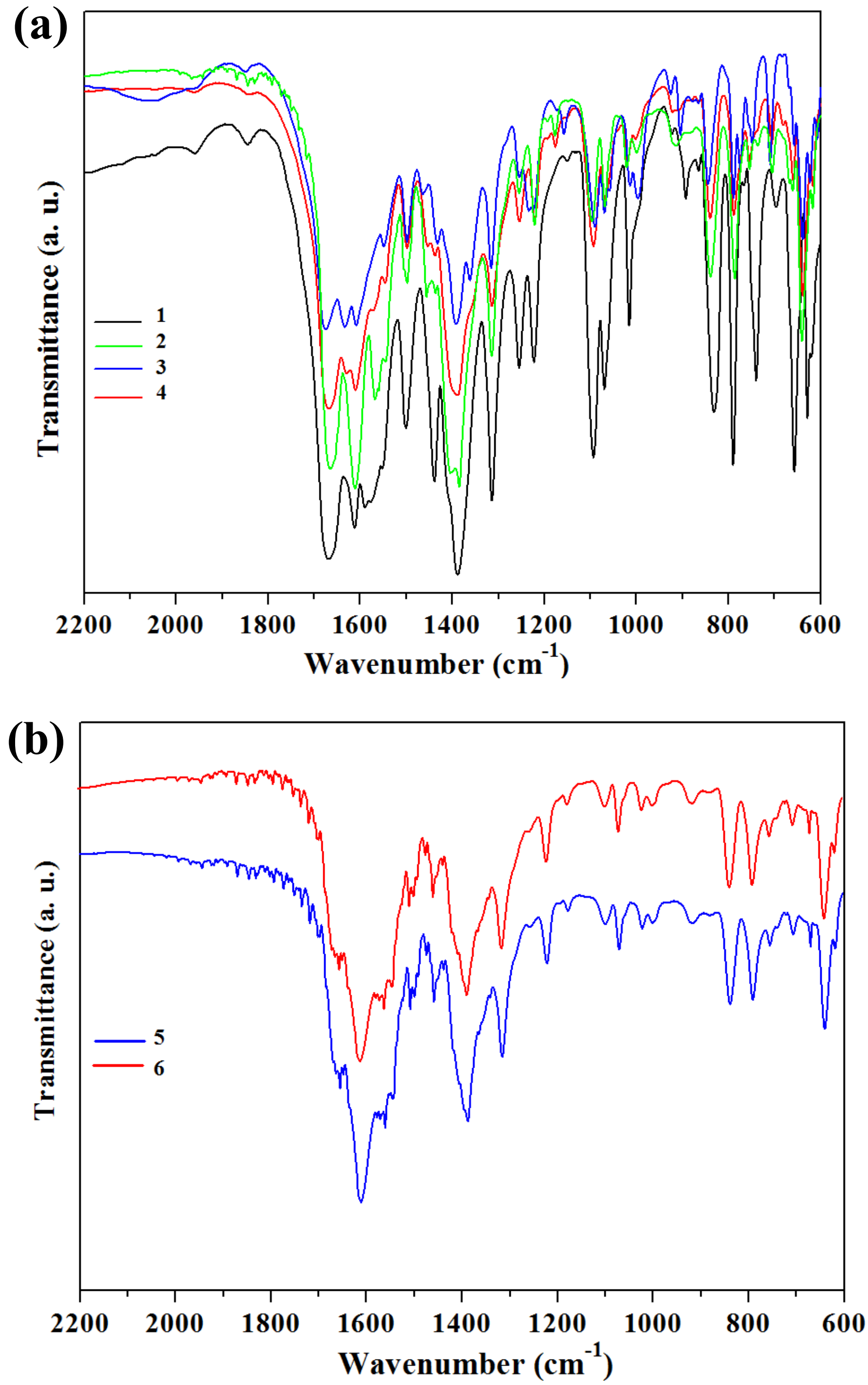


Figure S10. The infrared spectra for **1-6**.

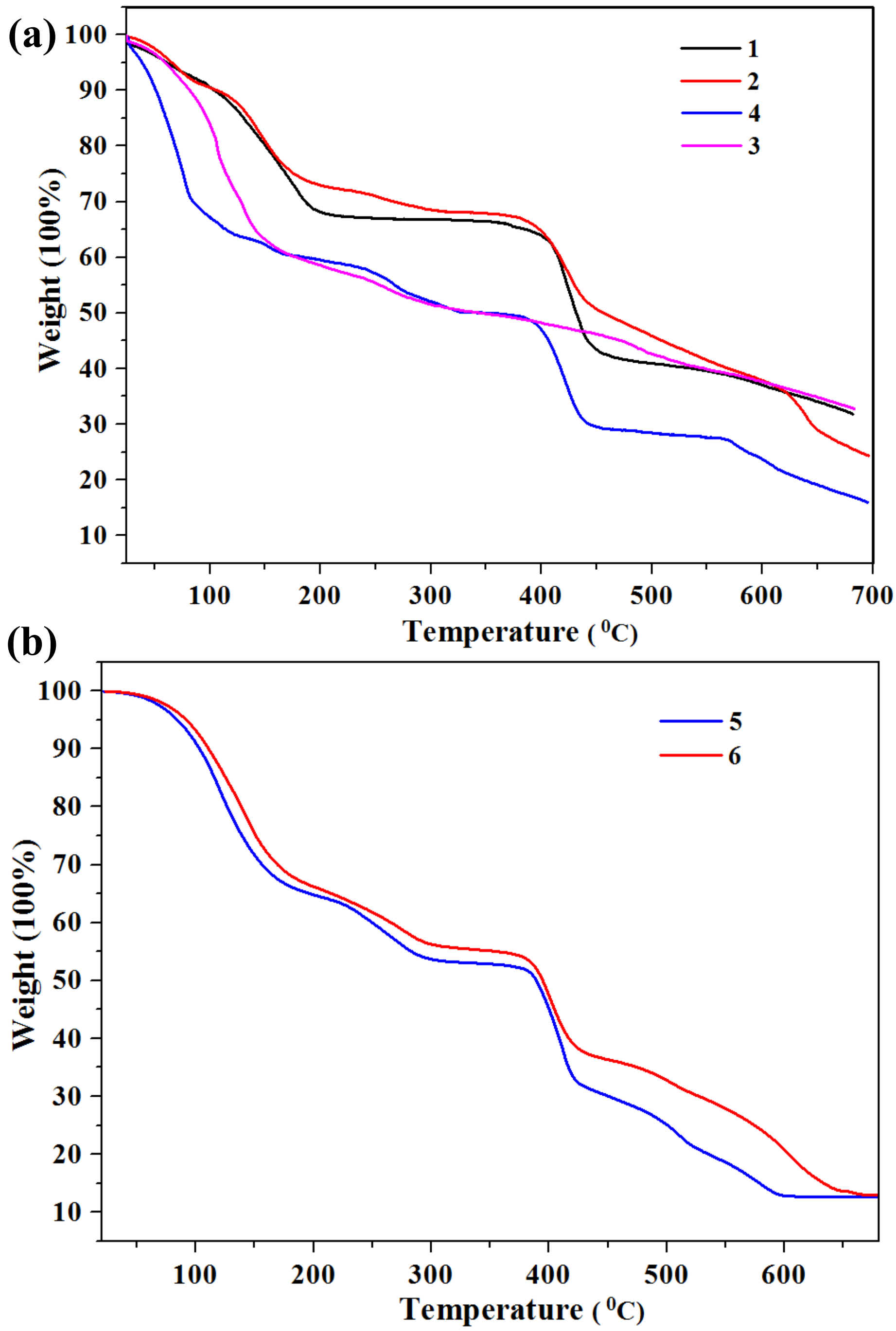


Figure S11. TGA data of as-synthesized **1-6**.

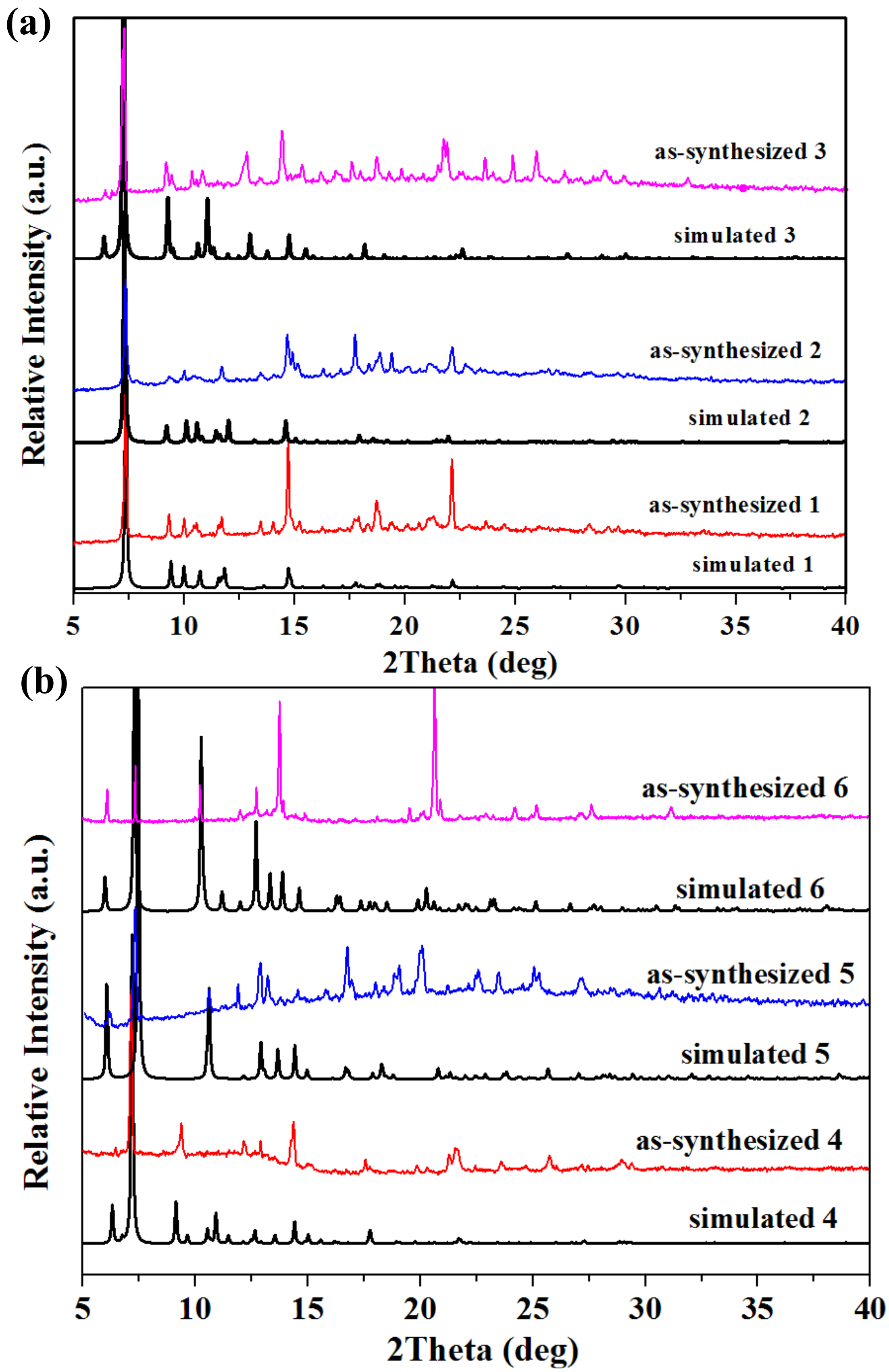
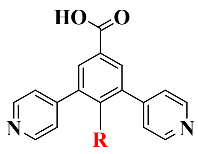
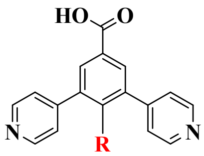
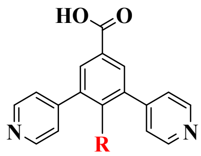
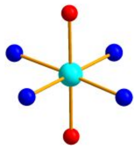
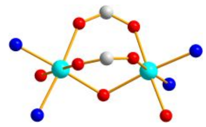
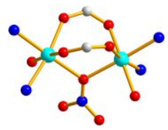
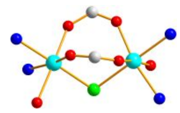
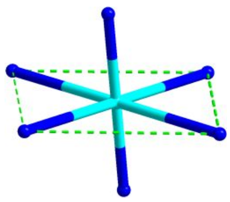
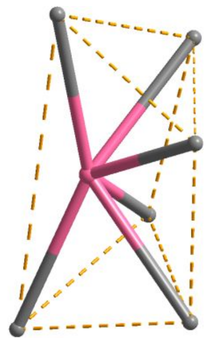
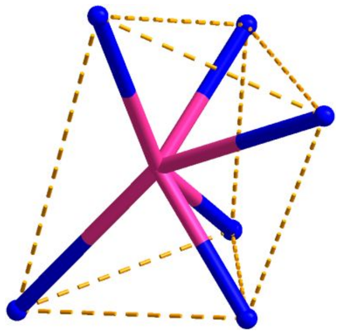
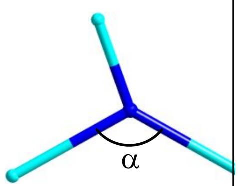
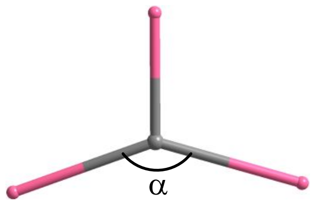
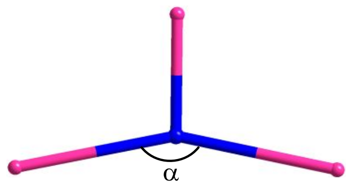
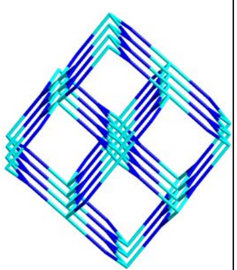
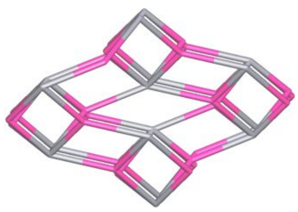
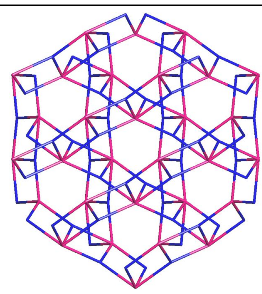


Figure S12. The PXRD patterns of **1-6**: a simulated PXRD pattern from the single-crystal structure and as-synthesized samples, respectively.

Table S1. Summary of Structural Information for **1-6**

MOFs	**1, 2**	**3, 4**	**5, 6**
linker	 R= -H(**1**); $-CH_3$ (**2**)	 R= $-OCH_3$ (**3**); $-CH_3$(**4**)	 R= $-CH_3$ (**5, 6**)
SBUs			 
geometry of 6-connected node	 octahedron	 distorted trigonal- prism	 significantly distorted trigonal- prism
shape of 3-connected node	 [a]α: 133-135° **Y**-type	 α: 140 -143° **T**-type	 α: 151-154° **T**-type
[b]Φ	**1**: 27.6°, 40.4°; 38.5°, 60.6 **2**: 45.0°, 48.5°; 48.6°, 72.6°	**3**: 34.2°, 42.4° **4**: 44.8°, 47.7°; 50.2°, 84.9°	**5**: 44.7°, 56.2° **6**: 45.8°, 52.4°
topology type	 ***rtl*** net	 ***ant*** net	 chiral ***anh*** net

[a]α: Three tritopic pyridine-carboxylate ligands can be simplified as tritopic nodes in **1-6** with different open angles (α).

[b]Φ: Dihedral angles (Φ) between the central benzene ring and terminal pyridyl rings.

Table S2. Summary of Geometrical Configuration of Nodes for **1-6** and Some (3,6)-connected ***rtl***, ***ant*** and Chiral ***anh*** Nets Reported

MOFs	**shape of tritopic node**	**geometry of 6-connected node**	**net**	**reference**
[Zn-(PNMI)]·2DMA	Y-shaped	octahedron	***rtl***	1
$[Cd_3(SO_4)_2L_2(H_2O)_4]_n$	Y-shaped	octahedron	***rtl***	2
$[Co_4(cpna)_4(H_2O)_8]$	Y-shaped	octahedron	***rtl***	3
$Mg(int)_2 \cdot H_2O$	Y-shaped	octahedron	***rtl***	4
$[Co(L\text{-}H)_2]\cdot 5H_2O\cdot 3DM$ (1)	Y-shaped	octahedron	***rtl***	this work
$[Co(L\text{-}CH_3)_2)]\cdot 4H_2O\cdot 3DMF$ (2)	Y-shaped	octahedron	***rtl***	this work
$\{[KCo_3(C_6H_4O_7)(C_6H_5O_7)(H_2O)_2]\cdot 8H_2O\}_n$	Y-shaped	octahedron	***ant***	5
Zn/BTB ant	Y-shaped	octahedron	***ant***	6
$[Cu_3(C_7H_2NO_5)_2]_n$	Y-shaped	octahedron	***ant***	7
[Cd(L)Cl]	Y-shaped	octahedron	***ant***	8
$[Co_3(bpydc)_2(HCOO)_2H_2O]\cdot 2DMF$ (JLU-Liu3)	T-shaped	octahedron	***ant***	9
$[Zn_3(bpydc)2(HCOO)_2]\cdot H_2O\cdot DMF$ (JLU-Liu4)	T-shaped	octahedron	***ant***	9
$Mg(nt)_2$	T-shaped	octahedron	***ant***	4
PPF-25	T-shaped	octahedron	***ant***	10
$[Co_2(\mu\text{-}H_2O)(\mu\text{-}HCOO)_2(L\text{-}OCH_3)_2]\cdot 5H_2O\cdot 7DMF$ (3)	T-shaped	triogal-prism	***ant***	this work
$[Co_2(\mu\text{-}H_2O)(\mu\text{-}HCOO)_2(L\text{-}CH_3)_2]\cdot 5H_2O\cdot 7DMF$ (4)	T-shaped	triogal-prism	***ant***	this work
$[Co_2(cpna)_2(H_2O)_3]\cdot DMF\cdot 9H_2O$	T-shaped	triogal-prism	***anh***	3
$[M_2(cpna)_2(H_2O)_3]\cdot 0.5H_2O\cdot DMF$	T-shaped	triogal-prism	***anh***	11
$[Co_2(\mu\text{-}NO_3)(L\text{-}CH_3)_2(H_2O)_2](NO_3)\cdot 3H_2O\cdot 8DMF$ (5)	T-shaped	triogal-prism	***anh***	this work
$[Co_2(\mu\text{-}Cl)(L\text{-}CH_3)_2(H_2O)_2](NO_3)\cdot 5H_2O$ 8DMF (6)	T-shaped	triogal-prism	***anh***	this work

1. Medishetty, R.; Jung, D.; Song, X.; Kim, D.; Lee, S. S.; Lah, M. S.; Vittal, J. J. Solvent-induced structural dynamics in noninterpenetrating porous coordination polymeric networks. *Inorg. Chem.* **2013,** *52*, 2951-2957.

2. Zhou, W. W.; Zhao, W.; Wang, F. W.; Fang, W. Y.; Liu, D. F.; Wei, Y. J.; Xu, M.; Zhao, X.; Liang, X. A 3D metal–organic framework with a rutile topology network, right- or left- handed helical chains and tunable UV-to-visible photoluminescence. *RSC Adv.* **2015,** *5*, 42616-42620.

3. Hou, L.; Liu, B.; Jia, L. N.; Wei, L.; Wang, Y. Y.; Shi, Q. Z. Two new (3,6)-connected frameworks based on an unsymmetrical tritopic pyridyldicarboxylate ligand and Co2 dimer: structures, magnetic, and sorption properties. *Crystal Growth Des.* **2012,** *13*, 701-707.

4. Liu, T.; Luo, D.; Xu, D.; Zeng, H.; Lin, Z. An open-framework rutile-type magnesium isonicotinate and its structural analogue with an anatase topology. *Dalton Trans.* **2013,** *42*, 368-371.

5. Xiang, S.; Wu, X.; Zhang, J.; Fu, R.; Hu, S.; Zhan, X. A 3D canted antiferromagnetic porous metal−organic framework with anatase topology through assembly of an analogue of polyoxometalate. *J. Am. Chem. Soc.* **2005,** *127*, 16352-16353.

6. Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. Phase selection and discovery among five assembly modes in a coordination polymerization. *Inorg. Chem.* **2008,** *47*, 7751-7756.

7. Zou, J. P.; Peng, Q.; Wen, Z.; Zeng, G. S.; Xing, Q. J.; Guo, G. C. Two novel metal−organic frameworks (MOFs) with (3,6)-connected net topologies: syntheses, crystal structures, third-order nonlinear optical and luminescent properties. *Crystal Growth Des.* **2010,** *10*, 2613-2619.

8. Ji, C.; Li, B.; Ma, M. L.; Zang, S. Q.; Hou, H. W.; Mak, T. C. W. A series of five divalent zinc and cadmium coordination polymers based on a new bifunctional ligand: syntheses, crystal structures, and properties. *CrystEngComm* **2012,** *14*, 3951-3958.

9. Wang, J.; Luo, J.; Zhao, J.; Li, D. S.; Li, G.; Huo, Q.; Liu, Y. L. Assembly of two flexible metal–organic frameworks with stepwise gas adsorption and highly selective

CO_2 adsorption. *Crystal Growth Des.* **2014,** *14*, 2375-2380.

10. Verduzco, J. M.; Chung, H.; Hu, C.; Choe, W. Metal-organic framework assembled from T-shaped and octahedral nodes: a mixed-linker strategy to create a rare anatase TiO_2 topology. *Inorg. Chem.* **2009,** *48*, 9060-9062.

11. Hou, J. J.; Zhang, R.; Qin, Y. L.; Zhang, X. M. From (3,6)-connected ***kgd***, chiral ***anh*** to (3,8)-connected tfz-d nets in low nuclear metal cluster-based networks with triangular pyridinedicarboxylate ligand. *Crystal Growth Des.* **2013,** *13*, 1618-1625.