Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Polyoxovanadate-based Organic-Inorganic Hybrids: From $\{V_5O_9Cl\}$ Clusters to Nanosized Octahedral Cages

Yu-Teng Zhang, Xin-Long Wang,* En-Long Zhou, Xue-Song Wu, Bai-Qiao Song, Kui-Zhan Shao and Zhong-Min Su*

Institute of Functional Material Chemistry, Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China

*Corresponding author. E-mail address: zmsu@nenu.edu.cn.

1. Materials and Methods

All the reagents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) measurement was recorded ranging from 5 to 50º at room temperature on a Siemens D5005 diffractometer with Cu-*Kα* (λ = 1.5418 Å). The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 ºC under nitrogen at the heating rate of 10 °C·min^{-1}. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer.

2. Gas sorption experiments

The N_2 sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the samples were immersed in methanol for 72 h, and the samples were activated by drying under a dynamic vacuum at room temperature overnight. Before the measurement, the samples were dried again by using the "outgas" function of the surface area analyzer for 12 h at 90 °C.

3. Synthesis

(i) Preparation of **VMOP-1**:

Reaction of 1, 4-benzenedicarboxylate (H_2BDC) (0.032 g, 0.19 mmol) with VCl_3 (0.030 g, 0.19 mmol) in 2 mL DMF (N,N'-dimethylformamide) and 0.5 mL CH_3CH_2OH at 150 °C for 2 days. After slow cooling to room temperature, block crystals were obtained (washed with CH_3CH_2OH) with a yield of ~22 % based on H_2BDC. Elemental analysis (%) cacld: C, 32.24; H, 4.16; N, 6.38. Found: C, 31.98; H, 3.95; N, 6.26. IR (KBr, cm^{-1}): 3440 (br), 2969 (br), 2732 (br), 2472 (w), 1666 (s), 1562 (s), 1400 (vs), 990 (s), 887 (w), 827 (w), 744 (s), 640 (w), 574 (s).

(ii) Preparation of **VMOP-2**:

The synthetic procedure is similar to that of **VMOP-1** except that H_2BDC was replaced by 2-amino-1,4-benzenedicarboxylate (H_2BDC-NH_2). Reaction of H_2BDC-NH_2 (0.020 g, 0.11 mmol) with VCl_3 (0.030 g, 0.19 mmol) in 2 mL DMF and 0.5 mL CH_3CH_2OH at 150 °C for 2 days. After slow cooling to room temperature, block crystals of **VMOP-2** were obtained (washed with CH_3CH_2OH) with a yield of ~15 % based on H_2BDC-NH_2. Elemental analysis (%) cacld: C, 30.73; H, 4.04; N, 8.41. Found: C, 30.81; H, 3.95; N, 8.32. IR (KBr, cm^{-1}): 3446 (w), 2998 (br), 2763 (br), 2472 (w), 1621 (w), 1542 (s), 1421 (s), 1382 (s), 1253 (s), 979 (s), 836 (w), 761 (m), 600 (m).

(iii) Preparation of **VMOP-3**:

The synthetic procedure is similar to that of **VMOP-1** except that H_2BDC was replaced by 2-bromo-1,4-benzenedicarboxylate (H_2BDC-Br). Reaction of H_2BDC-Br (0.030 g, 0.123 mmol) with VCl_3 (0.030g, 0.19 mmol) in 2 mL DMF and 0.5 mL CH_3CH_2OH at 150 °C for 2 days. After slow cooling to room temperature, block crystals of **VMOP-3** were obtained (washed with CH_3CH_2OH) with a yield of ~25 % based on H_2BDC-Br. Elemental analysis (%) cacld: C, 25.97; H, 2.86; N, 4.21. Found: C, 25.88; H, 2.95; N, 4.16. IR (KBr, cm^{-1}): 3405 (br), 2962 (br), 2742 (br), 2480 (w), 1666 (m), 1565 (s), 1403 (vs), 1278 (w), 981 (s), 883 (w), 761 (m), 632 (w), 590 (s).

Table S1. Summary of some typical vanadium-based metal-organic materials (VMOMs) from 2002 to 2015.

V-MOMs	V source	organic linker	reaction condition	Ref
[a]**MIL-47**	VCl_3	1,4-benzenedicarboxylate	hydrothermal	**1**
NH_2-MIL-47	VCl_3	2-amino-1,4-benzenedicarboxylate	hydrothermal	**2**
MIL-59	VCl_3	1,3-benzenedicarboxylate	hydrothermal	**3**
MIL-60, -61	VCl_3	1,2,4,5-benzenetetracarboxylic acid	hydrothermal	**4**
$[V(O)(bdc)](H_2bdc)_{0.71}$	VO_2	1,4-benzenedicarboxylate	hydrothermal	**5**
MOF-48	VO_2	2,5-dimethyl-benzen-dicarboxylic acid	hydrothermal	**6**
MIL-68	$VOSO_4 \cdot 5H_2O$	1,4-benzenedicarboxylate	solvothermal	**7**
$\{(H_2PIP)_{0.5}[VO(CEP)]$ $3H_2O\}$	$VOSO_4$	2-carboxyethylphosphonic acid	hydrothermal	**8**
V-molecular capsules	$NaVO_3$	organoarsenic or organophosphonic acids	solvothermal	**9**
[b]**COMOC-2**	$VOSO_4 \cdot H_2O$	4,4′-biphenyldicarboxylic acid	solvothermal	**10**
V-MIL-101	VCl_3	1,4-benzenedicarboxylate 2-amino-1,4-benzenedicarboxylate	solvothermal	**11**
V-MOF-1~7	VCl_3	1,4-benzenedicarboxylate 2,6-naphthalenedicarboxylic acid 1,4-naphthalenedicarboxylic acid 2,5-dimethylterephthalic acid 2,5 dihydroxyterephthalic acid tetrabromoterephthalic acid tetrachloroterephthalic acid	microwave-assisted	**12**
MIL-88B(V)	VCl_3	1,4-benzenedicarboxylate	solvothermal	**13**
Hyball-3,-4 -5	VCl_3	1,3,5-benzentricarboxylate	solvothermal	**14**
Hydoughnut-1	VCl_3	1,3-benzenedicarboxylate	solvothermal	**15**

[a] MIL = Materials of Institut Lavoisier.

[b] COMOC = Center for Ordered Materials, Organometallics and Catalysis, Ghent University.

4. Crystallography details

Table S2. Crystallographic data for **VMOP-1**

Empirical formula	$C_{171}H_{263}Cl_6N_{29}O_{119}V_{30}$
Formula weight	6369.99
Crystal system	Cubic
Space group	*F* m -3 m
Temperature	296(2) K
Wavelength	0.71069 Å
Unit-cell dimensions	$a = b = c$ =33.453(5) Å $\alpha = \beta = \gamma$ = 90°
Volume	37437(10) Å^3
Z	4
Density (calculated)	0.819 g/cm^3
Absorption coefficient	0.796 mm^{-1}
F(000)	12944
Crystal size	0.24 x 0.22 x 0.21 mm^3
Limiting indices	-39<=h<=20, -39<=k<=39, -39<=l<=39
Theta range for data collection	1.05-24.98°
Reflections collected	54126
Independent reflections	1686 [*R*(int) = 0.0755]
Completeness to theta = 24.98°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1686 / 0 / 58
Goodness-of-fit on F^2	1.126
Final R indices [I > 2sigma(I)]	R_1 = 0.0527, wR_2 = 0.1601
R indices (all data)	*R*1 = 0.0718, *wR*2 = 0.1752
Largest diff. peak and hole	0.470 and -0.290 eA^{-3}

Table S3. Crystallographic data for **VMOP-2**

Empirical formula	$C_{162}H_{254}Cl_6N_{38}O_{116}V_{30}$
Formula weight	6330.92
Crystal system	Cubic
Space group	*F* m -3 m
Temperature	298(2) K
Wavelength	0.71069 Å
Unit-cell dimensions	$a = b = c$ =33.394(5) Å $\alpha = \beta = \gamma$ = 90°
Volume	37240(10) Å^3
Z	4
Density (calculated)	1.129 g/cm^3

Absorption coefficient	0.823 mm^{-1}
F(000)	12848
Crystal size	0.24 x 0.22 x 0.19 mm^3
Limiting indices	-39<=h<=28, -39<=k<=39, -39<=l<=38
Theta range for data collection	1.06-24.99°
Reflections collected	54252
Independent reflections	1675 [*R*(int) = 0.1386]
Completeness to theta = 24.99°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1675 / 18 / 76
Goodness-of-fit on F^2	1.133
Final R indices [I > 2sigma(I)]	*R*1 = 0.0762, *wR*2 = 0.2080
R indices (all data)	*R*1 = 0.1144, *wR*2 = 0.2372
Largest diff. peak and hole	0.405 and -0.578 eA^{-3}

Table S4. Crystallographic data for **VMOP-3**

Empirical formula	$C_{144}H_{188}Br_{12}Cl_6N_{20}O_{110}V_{30}$
Formula weight	6658.95
Crystal system	Cubic
Space group	F m -3 m
Temperature	293(2) K
Wavelength	0.71069 Å
Unit-cell dimensions	$a = b = c$ =33.331(5) Å $\alpha = \beta = \gamma = 90°$
Volume	37029(10) $Å^3$
Z	4
Density (calculated)	1.194 g/cm^3
Absorption coefficient	2.115 mm^{-1}
F(000)	13136
Crystal size	0.27 x 0.25 x 0.23 mm^3
Limiting indices	-39<=h<=39, -38<=k<=39, -32<=l<=39
Theta range for data collection	1.06-25.00°
Reflections collected	53582
Independent reflections	1672 [*R*(int) = 0.0857]
Completeness to theta = 25.00°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1672 / 69 /103
Goodness-of-fit on F^2	1.261
Final R indices [I > 2sigma(I)]	*R*1 = 0.0887, *wR*2 = 0.2902
R indices (all data)	*R*1 = 0.1127, *wR*2 = 0.3132
Largest diff. peak and hole	0.707 and -0.396 eA^{-3}

Table S5. BVS results for the vanadium ions in **VMOP-1**.

		Bond distance (Å)	BVS calc. for V(III)	BVS calc. for V(IV)	BVS calc. for V(V)
V1	O(4)	1.613	1.421	1.588	1.671
	O(3)	1.918	0.623	0.696	0.733
	O(3)#1	1.918	0.623	0.696	0.733
	O(3)#2	1.918	0.623	0.696	0.733
	O(3)#3	1.918	0.623	0.696	0.733
	Cl(1)	3.224	0.054	0.054	0.054
Charge			3.967	4.426	**4.657**
V2	O(2)	1.589	1.516	1.694	1.783
	O(1)	2.012	0.483	0.540	0.568
	O(1)#1	2.012	0.483	0.540	0.568
	O(3)	1.956	0.562	0.628	0.661
	O(3)#1	1.956	0.562	0.628	0.661
	Cl(1)	2.946	0.115	0.115	0.115
Charge			3.721	**4.145**	4.356

Table S6. BVS results for the vanadium ions in **VMOP-2**.

		Bond distance (Å)	BVS calc. for V(III)	BVS calc. for V(IV)	BVS calc. for V(V)
V1	O(2)	1.599	1.476	1.649	1.736
	O(1)	1.927	0.608	0.679	0.715
	O(1)#1	1.927	0.608	0.679	0.715
	O(1)#2	1.927	0.608	0.679	0.715
	O(1)#3	1.927	0.608	0.679	0.715
	Cl(1)	3.230	0.053	0.053	0.053
Charge			3.961	4.418	**4.649**
V2	O(1)	1.950	0.572	0.638	0.672
	O(1)#1	1.950	0.572	0.638	0.672
	O(4)	2.009	0.487	0.544	0.573
	O(4)#1	2.009	0.487	0.544	0.573
	O(3)	1.591	1.508	1.685	1.774
	Cl(1)	2.932	0.119	0.119	0.119
Charge			3.745	**4.168**	4.353

Table S7. BVS results for the vanadium ions in **VMOP-3**.

		Bond distance (Å)	BVS calc. for V(III)	BVS calc. for V(IV)	BVS calc. for V(V)
V1	O(5)	1.589	1.516	1.694	1.783
	O(2)	1.919	0.621	0.694	0.731
	O(2)#1	1.919	0.621	0.694	0.731
	O(2)#2	1.919	0.621	0.694	0.731
	O(2)#3	1.919	0.621	0.694	0.731
	Cl(1)	3.219	0.055	0.055	0.055
Charge			4.055	4.525	**4.762**
V2	O(1)	2.012	0.483	0.540	0.568
	O(1)#1	2.012	0.483	0.540	0.568
	O(2)	1.946	0.578	0.645	0.679
	O(2)#1	1.946	0.578	0.645	0.679
	O(3)	1.567	1.609	1.798	1.892
	Cl(1)	2.944	0.116	0.116	0.116
Charge			3.847	**4.284**	4.504

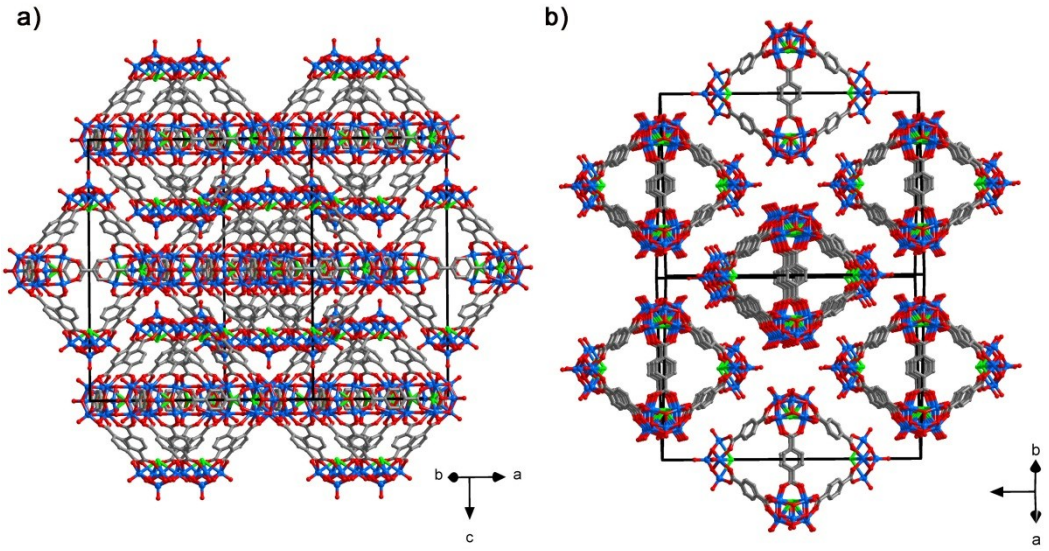

Figure S1. Packing arrangements in different directions of **VMOP-1**. Color codes: V, blue; Cl, green; O, red; C, gray; H atoms are omitted for clarity.

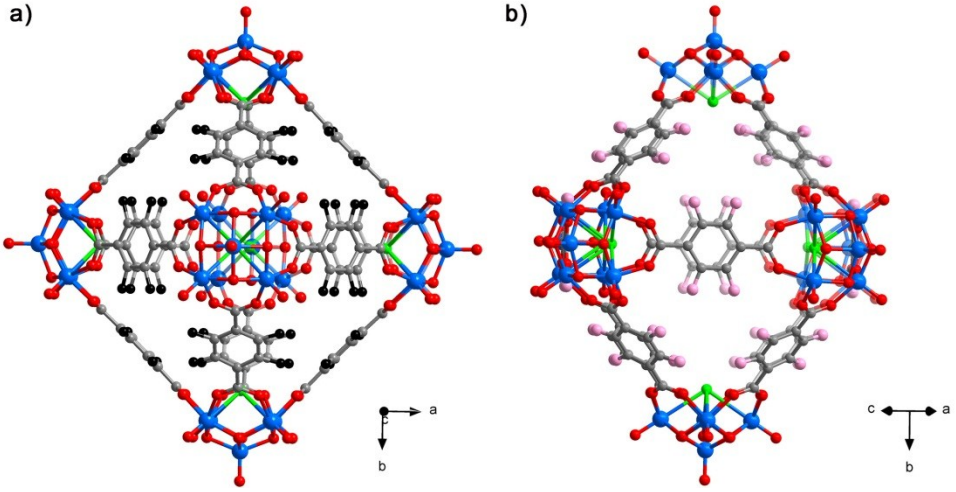

Figure S2. Ball-and-stick view (a and b) of **VMOP-2** and **VMOP-3**. Color codes: V, blue; Cl,

green; O, red; C, gray; N, black; Br, rose. N and Br atoms of ligands have low occupancy (0.25) due to disorder. (H atoms are omitted for clarity).

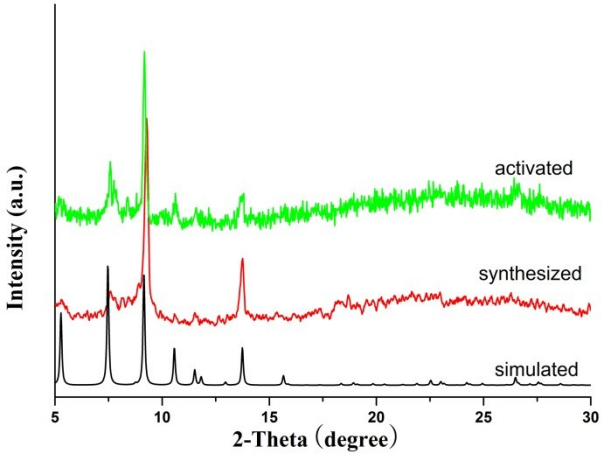

Figure S3. Experimental and simulated powder X-Ray diffraction patterns for **VMOP-1**.

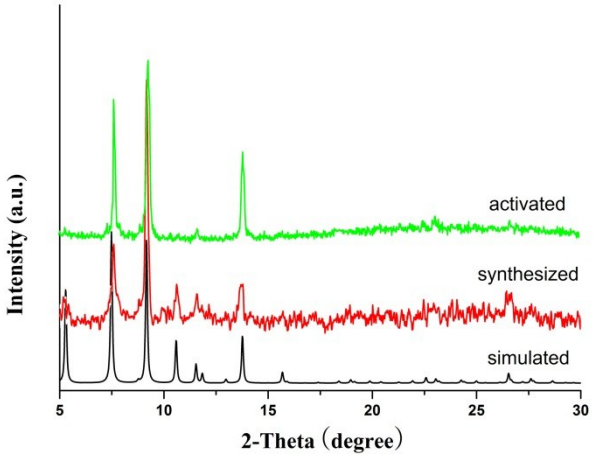

Figure S4. Experimental and simulated powder X-Ray diffraction patterns for **VMOP-2**.

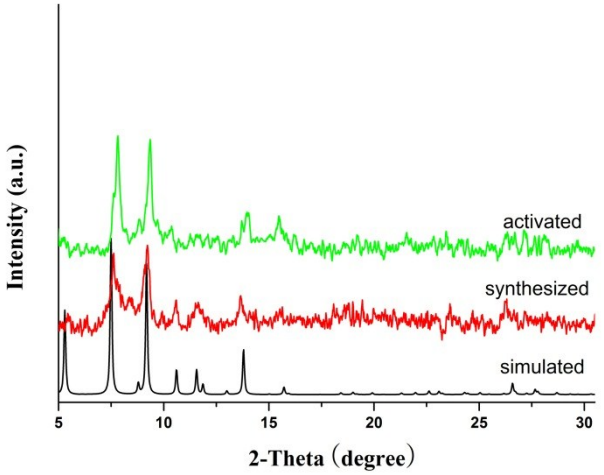

Figure S5. Experimental and simulated powder X-Ray diffraction patterns for **VMOP-3**.

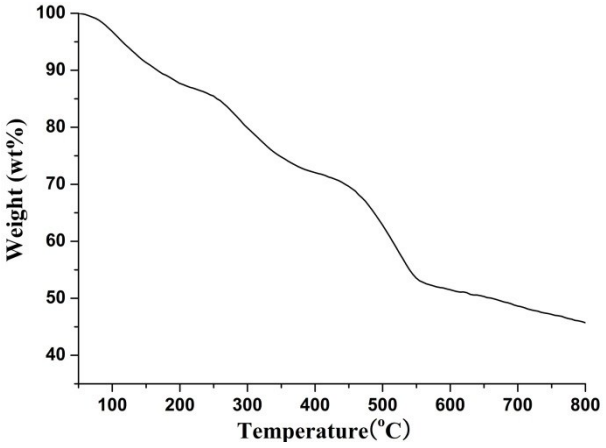

Figure S6. The TGA curve of **VMOP-1**.

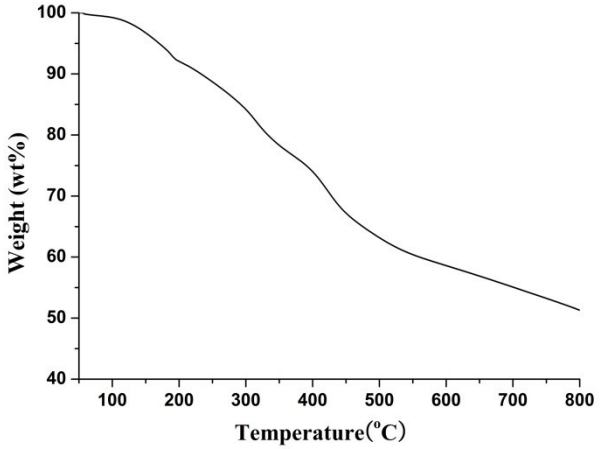

Figure S7. The TGA curve of **VMOP-2**.

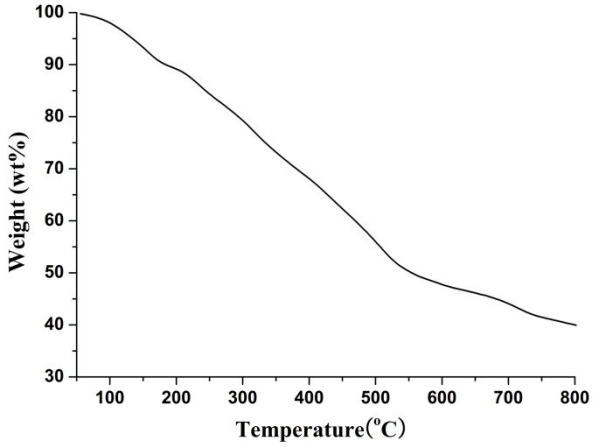

Figure S8. The TGA curve of **VMOP-3**.

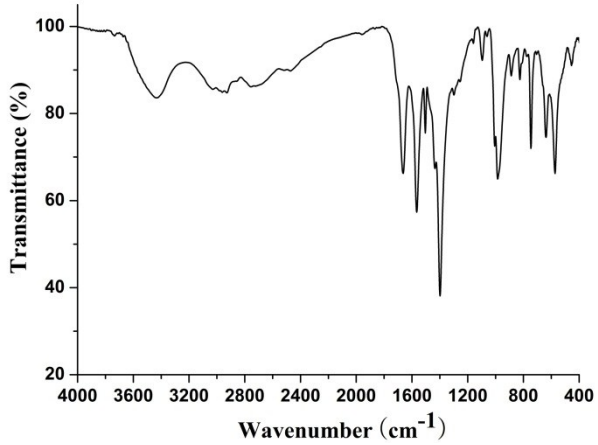

Figure S9. The IR spectrum of **VMOP-1**.

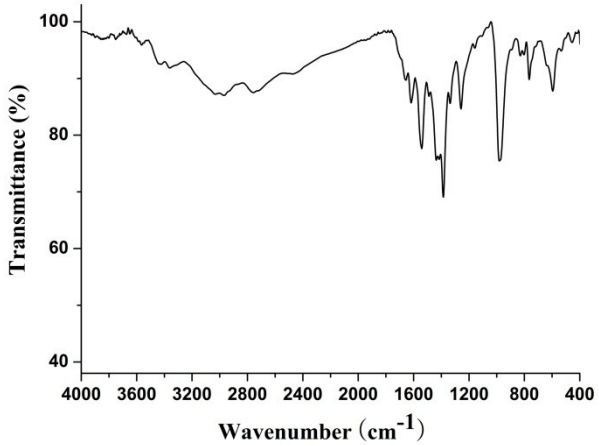

Figure S10. The IR spectrum of **VMOP-2**.

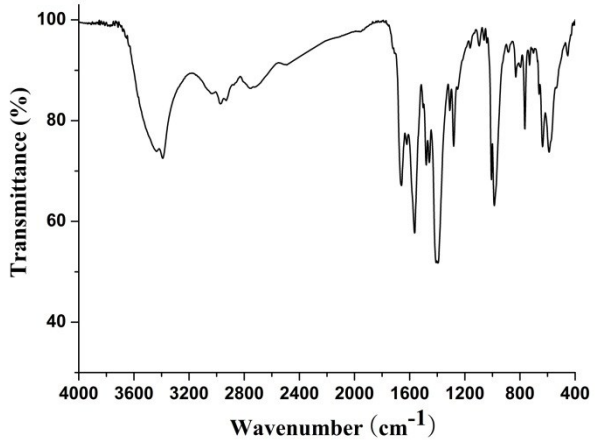

Figure S11. The IR spectrum of **VMOP-3**.

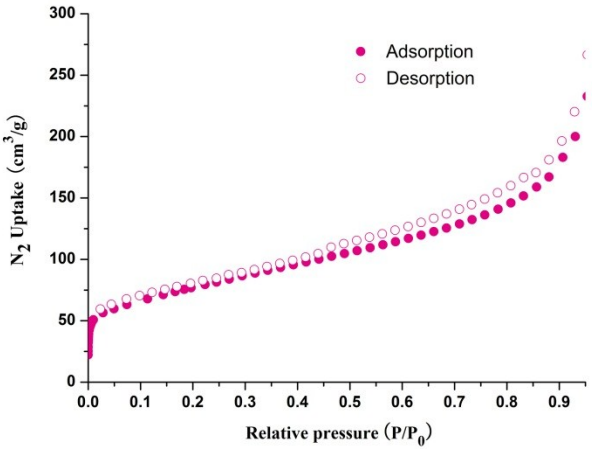

Figure S12. N_2 isotherm at 77 K for **VMOP-1.**

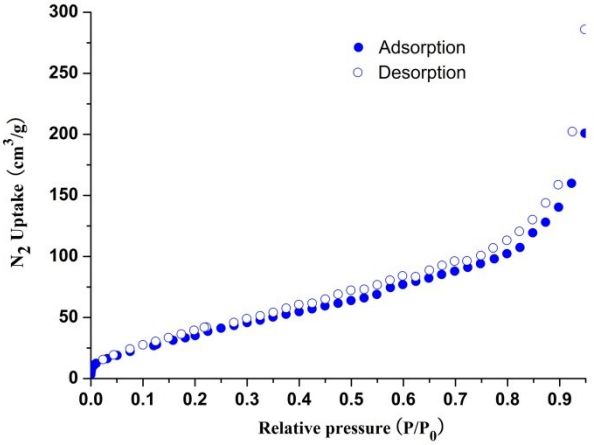

Figure S13. N_2 isotherm at 77 K for **VMOP-2.**

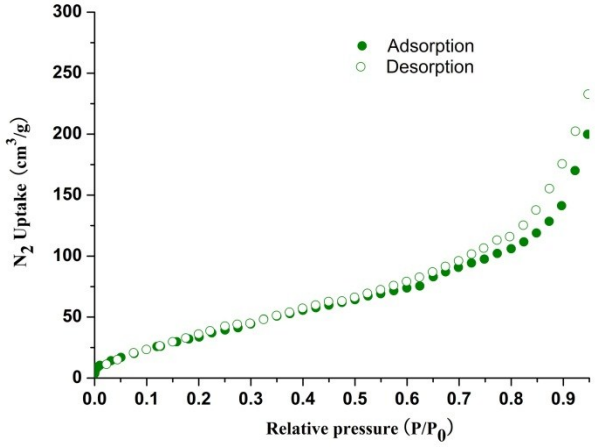

Figure S14. N_2 isotherm at 77 K for **VMOP-3.**

References

(1) K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem. Int. Ed*., 2002, **114**, 291–294.

(2) K. Leus, S. Couck, M. Vandichel, G. Vanhaelewyn, Y. Y Liu, G. B. Marin, I. Van Driessche, D. Depla, M. Waroquier, V. Van Speybroeck, J. F. M. Denayer and P. Van Der Voort, *Phys. Chem. Chem. Phys*., 2012, **14**, 15562–15570.

(3) K. Barthelet, D. Riou and G. Férey, *Chem. Commun*., 2002, 1492–1493.

(4) K. Barthelet, D. Riou, M. Nogues and G. Férey, *Inorg. Chem*., 2003, **42**, 1739−1743.

(5) X. Q. Wang, L. M. Liu and A. J. Jacobson, *Angew. Chem. Int. Ed., 2006*, **45**, 6499−6503.
(6) A. Phan, A. U. Czaja, F. G andara, C. B. Knobler and O. M. Yaghi, *Inorg. Chem*., 2011, **50**, 7388−7390.
(7) K. Barthelet, J. Marrot, G. Férey and D. Riou, *Chem. Commun*., 2004, 520−521.
(8) P. Kanoo, A. C. Ghosh and T. K. Maji, *Inorg. Chem*., 2011, **50**, 5145–5152.
(9) (a) J. M. Breen and W. Schmitt, *Angew. Chem. Int. Ed.,* 2008, 47, 6904-6908; (b) J. M. Breen, R. Clérac, L. Zhang, S. M. Cloonan, E. Kennedy, M. Feeney, T. McCabe, D. C. Williams and W. Schmitt, *Dalton Trans.,* 2012, **41**, 2918–2926; (c) M. B. Mahimaidoss, S. A. Krasnikov, L. Reck, C. I. Onet, J. M. Breen, N. Y. Zhu, B. Marzec, I. V. Shvets and W. Schmitt, *Chem. Commun*., 2014, **50**, 2265–2267.
(10) Y. Y. Liu, S. Couck, M. Vandichel, M. Grzywa, K. Leus, S. Biswas, D. Volkmer, J. Gascon, F. Kapteijn, J. F. M. Denayer, M. Waroquier, V. Van Speybroeck and P. Van Der Voort, *Inorg. Chem.,* 2013, **52**, 113−120.
(11) S. Biswas, S. Couck, M. Grzywa, J. F. M. Denayer, D. Volkmer and P. Van Der Voort, *Eur. J. Inorg. Chem.,* 2012, 2481–2486.
(12) A. Centrone, T. Harada, S. Speakman and T. A. Hatton, *Small*., 2010, **15**, 1598–1602.
(13) F. Carson, J. Su, A. E. Platero-Prats, W. Wan, Y. F. Yun, L. Samain and X. D. Zou, *Cryst. Growth.Des*., 2013, **13**, 5036−5044.
(14) Z. J. Zhang, L. Wojtas and M. J. Zaworotko, *Chem. Sci*., 2014, **5**, 927−931.
(15) Z. X. Zhang, W. Y. Gao, L. Wojtas, Z. J. Zhang, M. J. Zaworotko, *Chem. Commun.*, 2015, **51**, 9223−9226.