

Supporting Information-*New Journal of Chemistry*

One-pot self-assembly synthesis of $H_{3+x}PMo_{12-x}V_xO_{40}@[Cu_6O(TZI)_3(H_2O)_9(NO_3)_n]\cdot(H_2O)_{15}$ for enhanced proton conduction materials

Yuxiang Xin¹, Yijia Zhou¹, Longzhang Dong², Pengpeng Wei¹, Xiaoyan Zou^{1,*}, Fengming Zhang³ and Guangming Li^{1,*}

1. Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China

2. Jiangsu Collaborative Innovation Centre of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, P. R. China.

3. School of Material Science and Chemical Engineering, Harbin University of Science and Technology, No.4, Linyuan Road, Harbin 150040, P. R. China.

E-mail: gml_i_2000@163.com

E-mail: 2006151@hlju.edu.cn

Table S1. Crystallographic data for complexes **3** and **4**.

Parameters	3	4
Empirical formula	C ₁₀₈ H ₃₆ Cu ₂₄ N ₄₈ O ₁₂₇ PMo ₇ V ₅	C ₁₀₈ H ₃₆ Cu ₂₄ N ₄₈ O ₁₁₆ PMo ₄ V ₈
CCDC Nos.	2126950	2093327
Formula weight	6536.28	6401.28
Crystal system	cubic	cubic
Space group	<i>Fmm</i>	<i>Fmm</i>
Unit cell	$a=b=c=44.5096$ (2) Å	$a=b=c=44.4496$ (2) Å
Volume	$\alpha=\beta=\gamma=90^\circ$ 88178.2(12) Å ³	$\alpha=\beta=\gamma=90^\circ$ 87822.1(12) Å ³
<i>Z</i>	8	8
Density (calcd)	0.985 g·cm ⁻³	0.968 g·cm ⁻³
Temperature	293.00 (2) K	100.00 (2) K
Wavelength	1.54184 Å	1.54184 Å
Reflections collected	50415	24270
μ	1.480 mm ⁻¹	3.978 mm ⁻¹
<i>F</i> (000)	25311.0	24856.0
Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0652, 0.2000	0.0922, 0.2757
Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0697, 0.2040	0.0978, 0.2861
GOF on <i>F</i> ²	1.107	1.054

Table S2. A comparison of POMs@MOFs proton-conduction.

POMs@MOFs	Conditions	Conductivity/S cm ⁻¹	Ref
NENU-3	363K 70% RH	4.76×10 ⁻⁵	1
HPW@MIL-101	353K 100% RH	2.17×10 ⁻⁵	2
PMoV ₂ @MIL-101	353K 98% RH	6.31×10 ⁻³	3
PMoV@MIL-101	303K 98% RH	4.14×10 ⁻⁴	3
[Zn ₁₂ (trz) ₂₀][SiW ₁₂ O ₄₀] 11H ₂ O	368K 95% RH	1.2×10 ⁻⁴	4
NENU-530	348K 98% RH	1.5×10 ⁻³	5
NENU-531	348K 98% RH	1.7×10 ⁻⁴	5

Notes and References

1. Y. Liu, X. Yang, J. Miao, Q. Tang, S. Liu, Z. Shi and S. Liu, *Chem. Commun.*, 2014, **50**, 10023-10026.
2. X. Y. Lai, Y. W. Liu, G. C. Yang, S. M. Liu, Z. Shi, Y. Lu, F. Luo, and S. X. Liu, *J. Mater. Chem. A*, 2017, **5**, 9611-9617.
3. F. Wang, C. Liang, J. Tang, F. Zhang and F. Qu, *New J. Chem.* 2020, **44**, 1912-1920.
4. E. L. Zhou, C. Qin, X. L. Wang, K. Z. Shao and Z. M. Su, *Chem. Eur. J.*, 2015, **21**, 13058-13064.
5. J. Li, X. L. Cao, Y. Y. Wang, S. R. Zhang, D. Y. Du, J. S. Qin, S. L. Li, Z. M. Su and Y. Q. Lan, *Chem. Eur. J.*, 2016, **22**, 9299-9304.