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Supporting Information for

Functional Mesoporous Ionic Crystal based on Polyoxometalate

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Experimental details

Themogravimetry-differential thermal analysis (TG-DTA) was performed using a thermogravimetry/differential thermal analyzer Thermo Plus Evo (Rigaku) in a dry N_2 flow (100 mL min^{-1}) at 303−773 K. The temperature was held at 303 K for > 1 h prior to the temperature increase (10 K min^{-1}). Powder XRD pattern was measured at room temperature with a New advance D8 X-ray diffractometer (Bruker) by using Cu Kα radiation (λ = 1.54056 Å, 40 kV-40 mA) at 1.8 deg min^{-1}. IR spectra were measured with a JASCO FT/IR 4100 spectrometer (JASCO) equipped with a MCT detector at a resolution of 4 cm^{-1} and a typical average of 64 scans. Solid state ^{1}H MAS NMR spectrum was measured with a Bruker AVANCE III 400 WB spectrometer (Bruker) equipped with a 4 mm standard probe operating at 400.18 MHz.

Table S1. Pore sizes and volumes of porous ionic crystals

Compound	Pore size	[a]Pore volume [%]	Ref.
$Cr[Cr_3O(OOCCH_2CN)_6(H_2O)_3]_3[PW_{12}O_{40}]_2$	3.0 nm × 2.0 nm	44.2	This work
$[Al_{13}O_4(OH)_{24}(H_2O)_{24}][H_2W_{12}O_{40}](OH)$	7.4 Å × 12.8 Å	34.4	1
$[Al_{13}O_4(OH)_{24}(H_2O)_{24}][V_2W_4O_{19}]_3(OH)_2$	13.9 Å × 14.2 Å	52.8	[b]2
[Calix[4]arene-Na]$_3$$[PW_{12}O_{40}]$	6 Å × 9 Å	34.0	3
$K_3[Cr_3O(OOCH)_6(H_2O)_3][SiW_{12}O_{40}]$	5 Å × 8 Å	26.7	4
$[Cr_3O(OOCCHCH_2)_6(H_2O)_3]_3[PW_{12}O_{40}]$	3.5 Å × 3.5 Å	13.5	5
$TBA_8[\{Ni(OH_2)_2(OH)\}_2\{Zn(OH_2)\}_2\{HSiW_{10}O_{36}\}_2$	3.8 nm^3	42.0	6
$[Ni(bpp)(H_2O)_2]_3[P_2W_{18}O_{62}]$	13.3 $Å^2$, 16.3 $Å^2$	38.4	7
$Bi_2[VMo_{9.4}V_{2.6}O_{40}]$	7.7 $Å^2$, 3.4 $Å^2$	20.2	8
$(C_{15}H_{28}N_2)_4(C_9H_6O_6)[H_{15}Mo_{12}NaO_{62}P_8]$	9 Å × 19 Å	14.6	9
$[Co_8OQ_{12}](NO_3)_2$ (HQ = 8-hydroxyquinoline)	4.3 $Å^2$, 10 $Å^2$	25.7	10
$[Co(en)_3]Cl_3$ (en = ethylenediamine)	10.8 Å × 10.8 Å	19.6	11

[a]Pore volumes were calculated according to the cif files with a structure visualization program Mercury (CCDC). Crystallization solvents were removed and hydrogen atoms were added to the structure. A probe radius and a grid spacing of 1.2 Å and 0.7 Å were used, respectively. [b]Porous structure irreversibly collapses under ambient conditions.

(1) J. H. Son, Y. U. Kwon, *Inorg. Chem.* **2003**, *42*, 2702. (2) J. H. Son, Y. U. Kwon, *Inorg. Chem.* **2004**, *43*, 1929. (3) Y. Ishii, Y. Takenaka, K. Konishi, *Angew. Chem. Int. Ed.* **2004**, *43*, 2702. (4) S. Uchida, M. Hashimoto, N. Mizuno, *Angew. Chem. Int. Ed.* **2002**, *41*, 2814. (5) R. Kawahara, S. Uchida, N. Mizuno, *Inorg. Chem.* **2014**, *53*, 3655-3661. (6) K. Suzuki, Y. Kikukawa, S. Uchida, H. Tokoro, K. Imoto, S. Okoshi, N. Mizuno, *Angew. Chem. Int. Ed.* **2012**, *51*, 1597. (7) X. L. Wang, Y. G. Li, Y. Lu, H. Fu, Z. M. Su, E. B. Wang, *Cryst. Growth Des.* **2010**, *10*, 4227. (8) Z. Zhang, M. Sadakane, T. Murayama, S. Izumi, N. Yasuda, N. Sakaguchi, W. Ueda, *Inorg. Chem.* **2014**, *53*, 903. (9) C. Streb, D. L. Long, L. Cronin, *Chem. Commun.* **2007**, *43*, 471. (10) X. N. Cheng, W. Xue, J. B. Lin, X. M. Chen, *Chem. Commun.* **2010**, *46*, 246. (11) S. Takamizawa, T. Akatsuka, T. Ueda, *Angew. Chem. Int. Ed.* **2008**, *47*, 1689.

Table S2. Proton conductivities of POM-based compounds measured around rt.

Compound	Condition (Temp., RH)	Conductivity [S cm^{-1}]	Activation energy [eV]	Ref.
$Cr[Cr_3O(OOCCH_2CN)_6(H_2O)_3]_3[PW_{12}O_{40}]_2$	303 K, 95%	1.0×10^{-4}	0.34	This work
$H_3PW_{12}O_{40}\cdot29H_2O$	298 K, 80%	0.18	0.16	1
$H_3PMo_{12}O_{40}\cdot29H_2O$	298 K, 80%	0.17	0.12	1
$H_4SiW_{12}O_{40}\cdot28H_2O$	298 K, 80%	2×10^{-2}	0.39	2,3
$[Cu(phen)(H_2O)]_3[P_2Mo_5O_{23}]\cdot5H_2O$	301 K, 98%	2.2×10^{-5}	0.23	4
$[M(H_2O)_8][H(H_2O)_{2.5}](HINO)_4[PMo_{12}O_{40}]$	298 K, 98%	3.8×10^{-6}	0.80	5
$Na_5[H_7\{N(CH_2PO_3)_3\}Mo_6O_{16}(OH)(H_2O)_4]_4$	303 K, 98%	7.6×10^{-4}	0.65	6
$H[Cu(Hbpdc)(H_2O)_2]_2[PM_{12}O_{40}]$ M = Mo, W	298 K, 98%	10^{-7}-10^{-6}	1.02	7
$H[Cu(Hbpdc)(H_2O)_2]_2[PM_{12}O_{40}]$ M = Mo, W	373 K, 98%	10^{-4}-10^{-3}	1.02	7
$Li_3[Mo_8S_8O_8(OH)_8\{HWO_5(H_2O)\}]$	r.t., 70%	2.2×10^{-5}	0.47	8

(1) O. Nakamura, T. Kodama, I. Ogino, Y. Miyake, *Chem. Lett.* **1979**, 17. (2) J. W. Phair, S. P. S. Badwal, *Ionics* **2006**, *12*, 103. (3) K. D. Kreuer, *J. Mol. Struc.* **1988**, *177*, 265. (4) C. Dey, T. Kundu, R. Banerjee, *Chem. Commun.* **2012**, *48*, 266. (5) M. L. Wei, P. F. Zhuang, H. H. Li, Y. H. Yang, *Eur. J. Inorg. Chem.* **2011**, 1473. (6) L. Yang, P. Ma, Z. Zhou, J. Wang, J. Niu, *Inorg. Chem.* **2013**, *52*, 8285. (7) M. Wei, X. Wang, X. Duan, *Chem. Eur. J.* **2013**, 19, 1607. (8) C. du Peloux, A. Dolbecq, P. Barboux, G. Laurent, J. Marrot, F. Sécheresse, *Chem. Eur. J.* **2004**, *10*, 3026.

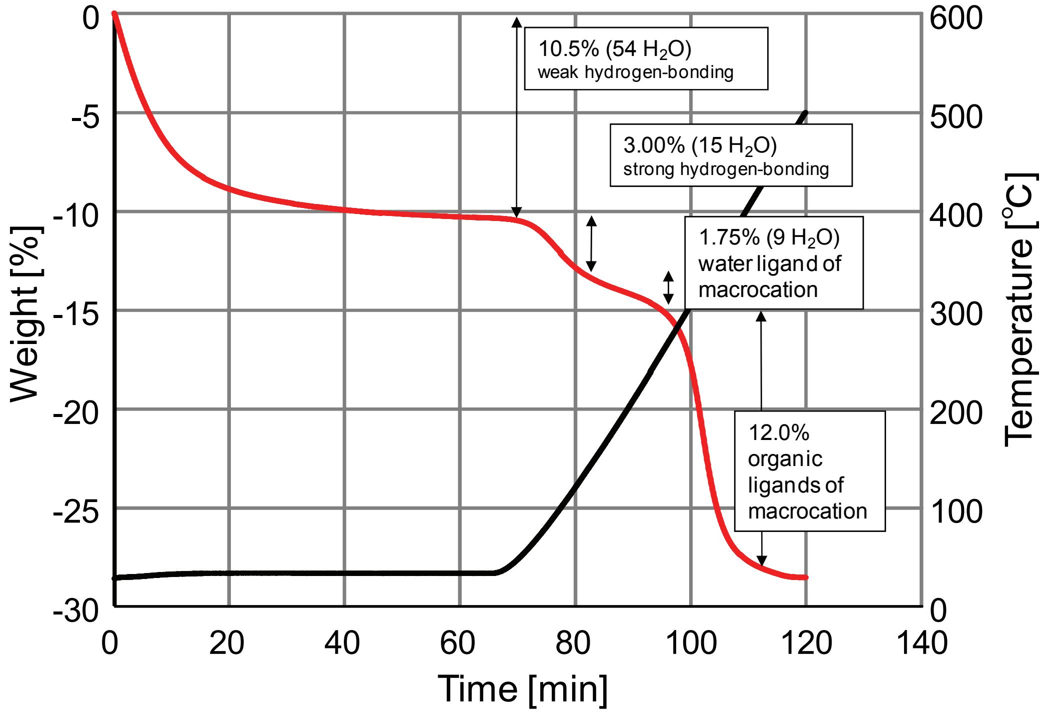

Figure S1. Thermogravimetry of **I**.

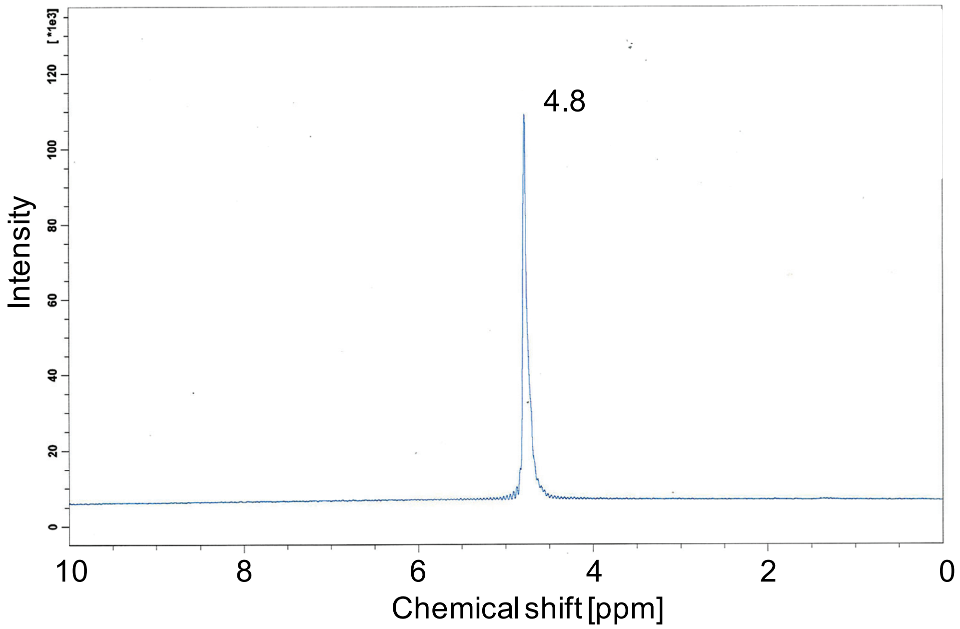

Figure S2. Solid state ^{1}H-MASNMR spectrum (MAS = 10 kHz) of **I**.

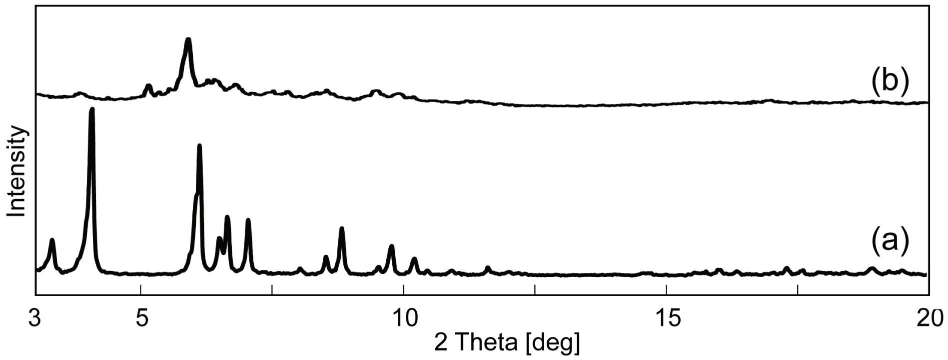

Figure S3. Powder XRD patterns of **I**. (a) As synthesized and (b) after evacuation at rt.

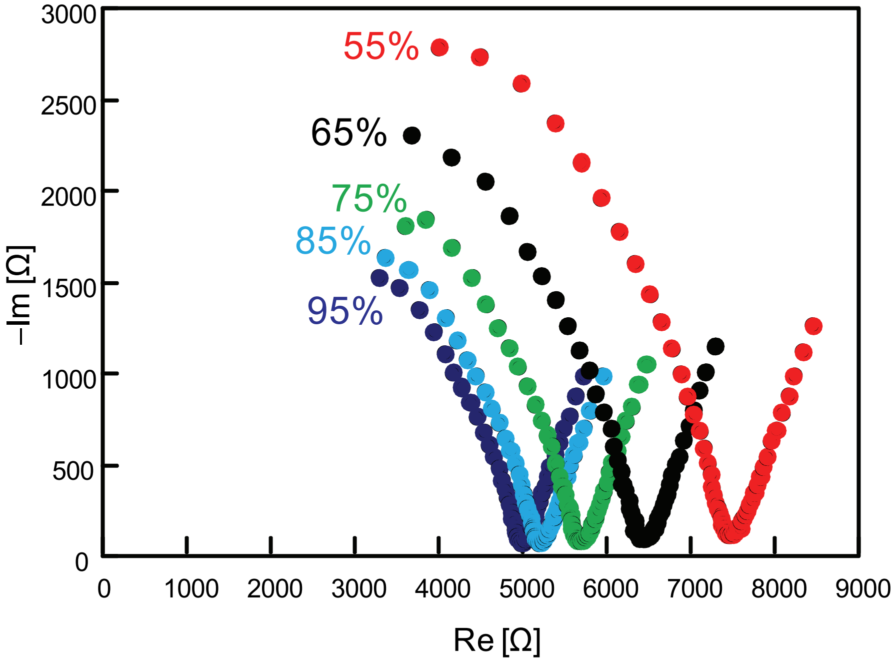

Figure S4. Nyquist plots of the impedance spectra of **I** at 303 K under 55−95% RH.

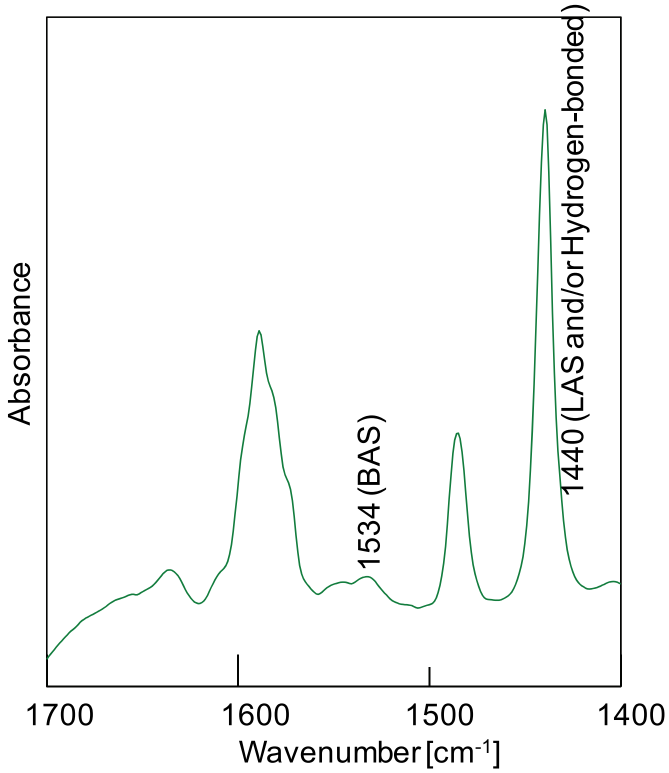

Figure S5. Difference IR spectrum of **I** treated with pyridine.