Table S1. Amounts of C_2H_2 and CH_4 sorption [$cm^3\ g^{-1}$ at stp] and sorption ratios of various materials

Material	C_2H_2	CH_4	Sorption ratio [mol mol^{-1}]	Condition	Ref.
Ic	3.3[a]	0.25[a]	13	198 K, 100 kPa	This work
SBA-15	1.5[b]	0.2[b]	7.5	303 K, 100 kPa	1
Sodium montmorillonite	0.19[b]	0.085[b]	2.2	298 K, 100 kPa	2
Acid montmorillonite	0.22[b]	0.086[b]	2.6	298 K, 100 kPa	2
$Cu_3(BTC)_2$ (HKUST-1)[c]	200	13	15	295 K, 100 kPa	3,4
M(OH)(BDC) (M = Cr^{3+}, Al^{3+})[d] (MIL-53)	72	11	6.5	295 K, 100 kPa[e]	3,5
Fe_2(dobdc) (Fe-MOF-74)[f]	2.1[a]	0.2[a]	11	318 K, 100 kPa	6
Cu(BDC-OH)(4,4'-bpy)[d,g]	34	5.0	6.8	296 K, 100 kPa	7
$Zn_4L(DMA)_4$[h]	97[i]	9.2[i]	6.5	296 K, 100 kPa	8
$[Cu_3(H_2L)(H_2O)_3]$[h]	160	30	5.3	296 K, 100 kPa	9
$Cu_6(PDC)_6$[j]	90	18	5.0	296 K, 100 kPa	10
$Zn_2(BBA)_2(CuPyen)$[k]	21	2.9	7.2	295 K, 100 kPa	11

[a]amount of sorption is mol mol^{-1}, [b]amount of sorption is mmol g^{-1}, [c]BTC = benzenetricarboxylate, [d]BDC = benzenedicarboxylate, [e]data for methane is measured at 304 K, [f]dodbc = 2,5-dioxido-1,4-benzenedicarboxylate, [g]4,4'-bpy = 4,4'-bipyridine, [h]H_8L = 1,2,4,5-tetra(5-isophthalic acid)benzene, DMA = *N*,*N*'-dimethylacetamide, [i]amount of sorption is mg g^{-1}, [j]PDC = 3,5-pyridine-dicarboxylate, [k]BBA = biphenyl-4,4'-dicarbozylate.

[1] B. L. Newalkar, N. V. Choudary, P. Kumar, S. Komarneni, T. S. G. Bhat, *Chem. Mater.*, 2002, **14**, 304. [2] C. Volzone, J. Ortiga, *Process Saf. Environ.*, 2004, **82**, 170. [3] S. Xiang, W. Zhou, J. M. Gallegos, Y. Liu, B. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 12415. [4] E. García-Pérez, J. Gascón, V. Morales-Flórez, J. M. Castillo, F. Kapteijn, S. Calero, *Langmuir*, 2009, **25**, 1725. [5] P. L. Llewellyn, S. Bourrelly, C. Serre, Y. Filinchuk, G. Férey, *Angew. Chem. Int. Ed.*, 2006, **45**, 7751. [6] E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Broan, J. R. Long, *Science*, 2012, **335**, 1606. [7] Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal, P. Li, D. Zhao, B. Chen, *Inorg. Chem.*, 2011, **50**, 3442. [8] Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna, B. Chen, *Chem. Eur. J.*, 2012, **18**, 613. [9] Y. He, Z. Zhang, S. Xiang, H. Wu, F. R. Fronczek, W. Zhou, R. Krishna, M. O'Keeffe, B. Chen, *Chem. Eur. J.*, 2012, **18**, 1901. [10] H. Xu, Y. He, Z. Zhang, S. Xiang, J. Cai, Y. Cui, Y. Yang, G. Qian, B. Chen, *J. Mater. Chem. A*, 2013, **1**, 77. [11] Z. Zhang, S. Xiang, K. Hong, M. C. Das, H. D. Arman, M. Garcia, J. U. Mondal, K. M. Thomas, B. Chen, *Inorg. Chem.*, 2012, **51**, 4947.

Table S2. Amounts of CO_2 and CH_4 sorption [$cm^3\ g^{-1}$ at stp] and sorption ratios of various materials

Material	CO_2	CH_4	Sorption Ratio [mol mol^{-1}]	Condition	Ref.
Ic	3.8[a]	0.25[a]	15	198 K, 100 kPa	This work
Ic	2.5[a]	0.23[a]	11	298 K, 1 MPa	This work
Zeolite 5A	21[b]	1.3[b]	5.9	298 K, 100 kPa	1
Zeolite 13X	4.0[c]	0.9[c]	4.4	295 K, 100 kPa	2
SBA-15	8.8[c]	2.4[c]	3.7	298 K, 4 MPa	3
Activated carbon	10[c]	5.0[c]	2.0	298 K, 1 MPa	4
γ-Al_2O_3	1.0[c]	0.7[c]	1.4	295 K, 100 kPa	2
Sodium montmorillonite	0.17[b]	0.085[b]	0.7	298 K, 100 kPa	5
Acid montmorillonite	0.21[b]	0.086[b]	0.9	298 K, 100 kPa	5
MOF-5	3.5[b]	0.2[b]	6.4	298 K, 100 kPa	1
M(OH)(BDC) (M = Cr^{3+}, Al^{3+})[d] (MIL-53)	8.0[c]	3.0[c]	2.7	304 K, 10 MPa	6
Al(OH)(BDC-NH_2)[d] (NH_2-MIL-53)	1.0[c]	negligible	> 10	283 K, 100 kPa	7
$Cu_3(BTC)_2$ (HKUST-1)[e]	284	98	2.9	298 K, 1.5 MPa	8
Zn(nbIm)(nIm) (ZIF-78)[f]	50	13	3.8	298 K, 100 kPa	9
$Zn_2(BBA)_2(CuPyen)$[g]	10	2.9	3.4	295 K, 100 kPa	10
$Mn(HCOO)_2$	100	10	10	195 K, 100 kPa	11
$[Zn_7O_2(BDC\text{-}NO_2)_5(DMF)]$[e,h]	8.8	4.4	2	195 K, 100 kPa	12
$[Zn_2(sdb)_2(bpy)_2]$[i]	28	negligible	> 10	195 K, 100 kPa	13
$[Zn_2(sdb)_2(dabco)_2]$[i,j]	65	35	1.9	195 K, 100 kPa	13
$(Me_2NH_2)In(NH_2BDC)_2$[d]	170	negligible	> 10	298 K, 3 MPa	14
Cu(BDC-OH)(4,4'-bpy)[d,i]	30	5.0	6.0	296 K, 100 kPa	15
$Cu_6(PDC)_6$[k]	65	18	3.6	296 K, 100 kPa	16
$[Cu(dpa)_2(SiF_6)]$[l]	238[m]	7.5[m]	12	298 K, 100 kPa	17
$[Zr_6O_4(BDC)_6]$ (UiO-66)[d]	5.6[c]	3.2[c]	1.8	306 K, 2.5 MPa	18
UiO-66-COOH	6.4[c]	2.7[c]	2.0	306 K, 2.5 MPa	18
$[Y_2(TPBTM)(H_2O)_2]$[n]	130	30	4.3	273 K, 100 kPa	19

[a]amount of sorption is mol mol^{-1}, [b]amount of sorption is wt%, [c]amount of sorption is mmol g^{-1}, [d]BDC = benzenedicarboxylate, [e]BTC = benzenetricarboxylate, [f]nIm= 2-nitroimidazolate, nbIm= 5-nitrobenzimidazole, [g]BBA = biphenyl-4,4'-dicarboxylate, [h]DMF = N,N-dimethylformamide, [i]sdb =

4,4'-sulfonyldibenzoate, bpy = 4,4'-bipyridine, [j]dabco = 1,4-diazabicyclo[2,2,2]octane, [k]PDC = 3,5-pyridine-dicarboxylate, [l]dpa = 4,4'dipyridylacetylene, [m]amount of sorption is mg g^{-1}, [n]TPBTM = N,N',N''-tris(isophthalyl)-1,3,5-benzenetricarboxamide.

[1] D. Saha, Z. Bao, F. Jia, S. Deng, *Environ. Sci. Technol.*, 2010, **44**, 1820. [2] S. U. Rege, R. T. Yang, M. A. Buzanowski, *Chem. Eng. Sci.*, 2000, **55**, 4827. [3] X. Liu, J. Li, L. Zhou, D. Huang, Y. Zhou, *Chem. Phys. Lett.*, 2005, **415**, 198. [4] C. A. Grande, R. Blom, A. Möller, J. Möllmer, *Chem. Eng. Sci.*, 2013, **89**, 10. [5] C. Volzone, J. Ortiga, *Process Saf. Environ.*, 2004, **82**, 170. [6] S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, *J. Am. Chem. Soc.*, 2005, **127**, 13519. [7] S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. Serra-Crespo. J. Juan-Alcañiz, A. M. Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron, J. F. M. Denayer, *Chem. Sus. Chem.* 2012, **5**, 740. [8] Z. Liang, M. Marshall, A. L. Chaffee, *Energy & Fuels*, **2009**, 23, 2785. [9] R. Banerjee, H, Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc*. **2009,** *131*, 3875. [10] Z. Zhang, S. Xiang, K. Hong, M. C. Das, H. D. Arman, M. Garcia, J. U. Mondal, K. M. Thomas, B. Chen, *Inorg. Chem.* 2012, **51**, 4947. [11] D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, *J. Am. Chem. Soc*. **2004,** *126*, 32. [12] S. S. Iremonger, R. Vaidhyanathan, R. K. Mah, G. K. H. Shimizu, Inorg. Chem. in press. [13] Y. Hijikata, S. Horike, M. Sugimoto, M. Inukai, T. Fukushima, S. Kitagawa, *Inorg. Chem.*, 2013, **52**, 3634. [14] S. Biswas, J. Zhang, Z. Li, Y. Y. Liu, M. Grzywa, L. Sun, D. Volkmer, P. Van Der Voort, *Dalton. Trans.* 2013, **42**, 4730. [15] Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal, P. Li, D. Zhao, B. Chen, *Inorg. Chem.*, 2011, **50**, 3442. [16] H. Xu, Y. He, Z. Zhang, S. Xiang, J. Cai, Y. Cui, Y. Yang, G. Qian, B. Chen, *J. Mater. Chem. A*, 2013, **1**, 77. [17] P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature*, 2013, **495**, 80. [18] M. Lin Foo, S. Horike, T. Fukushima, Y. Hijikata, Y. Kubota, M. Takata, S. Kitagawa, *Dalton. Trans.*, 2012, **41**, 13791. [19] K. Tang, R. Yun, Z. Lu, L. Du, M. Zhang, Q. Wang, H. Liu, *Cryst. Growth Des.* 2013, **13**, 1382.

Table S3. Amounts of C_2H_4 and C_2H_6 sorption [$cm^3\ g^{-1}$ at stp] and sorption ratios of various materials

Material	ethylene	ethane	Sorption Ratio [mol mol^{-1}]	Condition	Ref.
Ic	1.8[a]	0.36[a]	4.9	198 K, 100 kPa	This work
Ic	1.1[a]	0.37[a]	3.0	298 K, 1 MPa	This work
Ic	0.35[a]	0.069[a]	5.1	298 K, 100 kPa	This work
$[Cr_3O(OOCCH_2Cl)_6(H_2O)_3]_4$ -[α-$SiW_{12}O_{40}$]	0.57	0.16	3.6	298 K, 100 kPa	1
$[Cr_3O(OOCCH_2Br)_6(H_2O)_3]_4$ -[α-$SiW_{12}O_{40}$]	0.19	0.068	2.8	298 K, 100 kPa	1
Zeolite 5A	8[b]	8[b]	1.1	298 K, 100 torr	2
Zeolite 13X	3.0[c]	2.0[c]	1.5	295 K, 100 kPa	3
SBA-15	0.8[c]	0.5[c]	1.6	303 K, 100 kPa	4
γ-Al_2O_3	0.7[c]	0.2[c]	3.5	295 K, 100 kPa	3
$[Zn_2(sdb)_2(bpy)_2]$[d]	12	6	2	195 K, 100 kPa	5
$[Zn_2(sdb)_2(dabco)_2]$[d,e]	35	30	1.2	195 K, 100 kPa	5
$Zn_4L(DMA)_4$[f]	76[b]	83[b]	1.0	296 K, 100 kPa	6
$[Cu_3(H_2L)(H_2O)_3]$[f]	95	95	1.0	296 K, 100 kPa	7
Fe_2(dobdc) (Fe-MOF-74)[g]	1.8[a]	1.5[a]	1.2	318 K, 100 kPa	8
Zn(PhIM)$_2$ (ZIF-7)[h]	negligible	1.7[c]	> 0.1	298 K, 20 kPa	9
$Cu_3(BTC)_2$ (HKUST-1)[i]	5.5[c]	4.7[c]	1.2	295 K, 100 kPa	10

[a]amount of sorption is mol mol^{-1}, [b]amount of sorption is wt%, [c]amount of sorption is mmol g^{-1} [d]sdb = 4,4'-sulfonyldibenzoate, bpy = 4,4'-bipyridine, [e]dabco = 1,4-diazabicyclo[2,2,2]octane, [f]H_8L = 1,2,4,5-tetra(5-isophthalic acid)benzene, DMA = *N*,*N*'-dimethylacetamide, [g]dodbc = 2,5-dioxido-1,4-benzenedicarboxylate, [h]PhIM = phenylimidazole, [i]BTC = benzenetricarboxylate.

[1] S. Uchida, R. Eguchi, S. Nakamura, N. Kurosawa, N. Mizuno, *Chem. Mater.*, 2012, **24**, 325. [2] D. Caputo, P. Corbo, F. Iucolano, F. Migliardini, C. Colella, *Sep. Sci. Tech.*, 2004, **39**, 1547. [3] S. U. Rege, R. T. Yang, M. A. Buzanowski, *Chem. Eng. Sci.*, 2000, **55**, 4827. [4] B. L. Newalkar, N. V. Choudary, P. Kumar, S. Komarneni, T. S. G. Bhat, *Chem. Mater.*, 2002, **14**, 304. [5] Y. Hijikata, S. Horike, M. Sugimoto, M. Inukai, T. Fukushima, S. Kitagawa, *Inorg. Chem.*, 2013, **52**, 3634. [6] Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna, B. Chen, *Chem. Eur. J.*, 2012, **18**, 613. [7] Y. He, Z. Zhang, S. Xiang, H. Wu, F. R. Fronczek, W. Zhou, R. Krishna, M. O'Keeffe, B. Chen, *Chem. Eur. J.*, 2012, **18**, 1901. [8] E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Broan, J. R. Long, *Science*, 2012, **335**, 1606. [9] C. Gücüyener, J. van den Bergh, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.*, 2010, **132**, 17704. [10] Q. M. Wang, D. Shen, M. Bulow, M. L. Lau, S. Deng, F. R. Fitch, N. O. Lemcoff, J. Semanscin, *Microporous Mesoporous Mater.*, 2002, **55**, 217.

Table S4. Water sorption enthalpies of various materials

Material	Enthalpy [kJ mol^{-1}]	Reference
Ic	25-35	This work
H-ZSM-5 zeolite	61 ± 3[a]	1
H-mordenite zeolite	75 ± 3[a]	1
Na-X zeolite	75[b]	2
K-X zeolite	70[b]	2
Cs-X zeolite	63[b]	2
Ba-X zeolite	70-95[c]	3
Silicate	20-65	4
Aluminophosphate ($AlPO_4$-5)	40-50	5
TiO_2 (anatase)	55-69	6
γ-Al_2O_3	44[d]	7
Sodium montmorillonite	44-56	8
Activated carbon	20-45	9
$[Co_3(ndc)(HCO_2)_3(OH)(H_2O)]$[e]	45[f]	10
$Fe_3O(H_2O)_2F(BTC)_2$ (MIL-100)[g]	49[a]	11
$Cr_3O(H_2O)_2F(BTC)_3$ (MIL-101)[g]	45[a]	11
$Cu_3(BTC)_2$ (HKUST-1)[g]	39-52	12
Barium tetraethyl-1,3,6,8-pyrenetetraphosphonate	45	13

[a]average values calculated from adsorption branches, [b]amounts of water adsorption is 2 molecules per cavity, [c]amounts of water adsorption is 0-0.15 g g^{-1}, [d]amounts of water adsorption is > 10 molecules per nm^2, [e]H_2ndc = 5-(4-pyridyl)-isophthalic acid), [f]fractional filling of water is 1/e, [g]BTC = benzenetricarboxylate,.

[1] D. T. Chen, L. Zhang, C. Yi, J. A. Dusemic, *J. Catal.*, 1994, **146**, 257. [2] O. M. Dzhigit, A. V. Kiselev, K. N. Mikos, G. G. Muttik, T. A. Rahmanova, *Trans. Faraday Soc.*, 1971, **67**, 458. [3] J. C. Moïse, J. P. Bellat, A. Méthivier, *Microporous Mesoporous Mater*. 2001, **43**, 91. [4] C. C. Lee, R. J. Gorte, W. E. Farneth, *J. Phys. Chem. B*, 1997, **101**, 3811. [5] K. Tsutsumi, K. Mizoe, K. Chubachi, *Colloid Polym. Sci.*, 1999, **277**, 83. [6] M. Egashira, S. Kawasumi, S. Kagawa, T. Seiyama, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3144. [7] R. H. R. Castro, D. V. Quach, *J. Phys. Chem. C*, 2012, **116**, 24726. [8] R. W. Mooney, A. G. Keenan, L. A. Wood, *J. Am. Chem. Soc.*, 1952, **74**, 1367. [9] I. I. Salame, A. Bagreev, T. J. Bandosz, *J. Phys. Chem. B*, **1999**, 103, 3877. [10] H. Li, W. Shi, K. Zhao, Z. Niu, X. Chen, P. Cheng, *Chem. Eur. J.*, 2012, **18**, 5715. [11] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, *Microporous Mesoporous Mater*. 2009, **120**, 325. [12] J. M. Castillo, T. J. H. Vlugt, S. Calero, *J. Phys. Chem. C*, 2008, **112**, 15934. [13] J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2012, **134**, 14338.

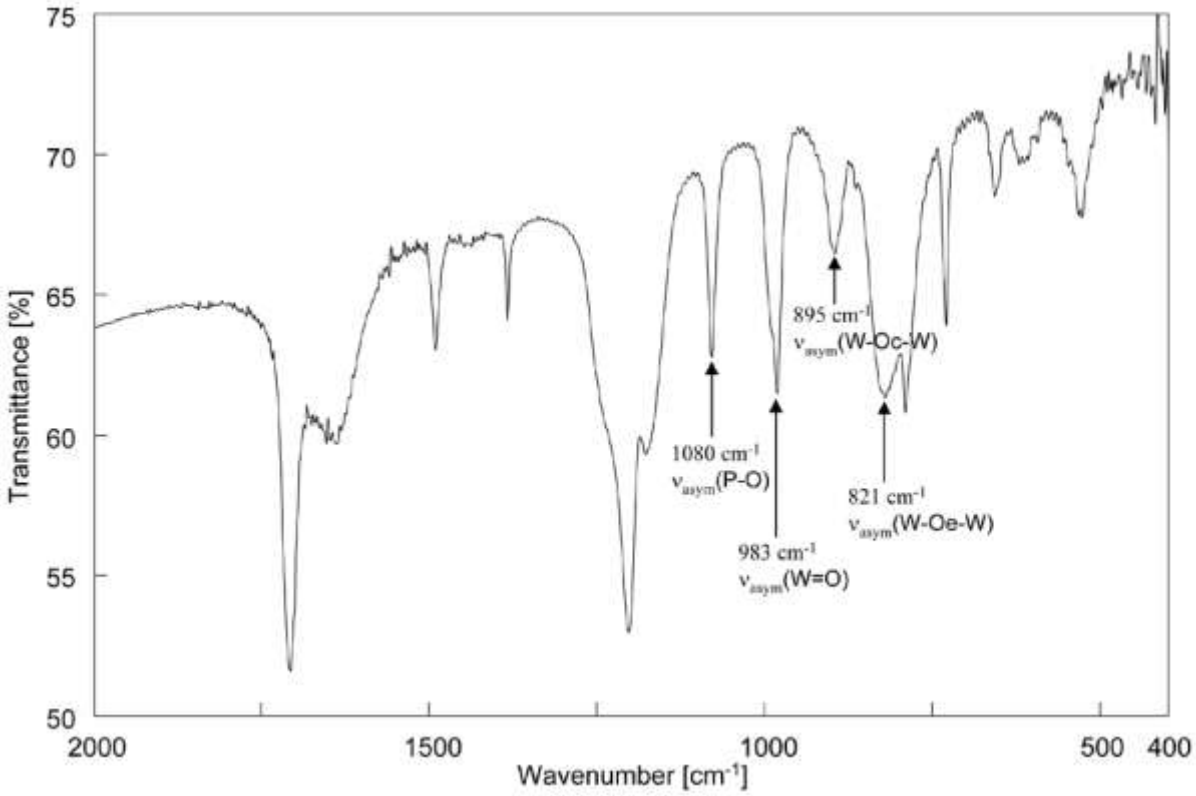

Figure S1. IR spectra of **Ib**. The bands assigned to $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ are indicated by the arrows.

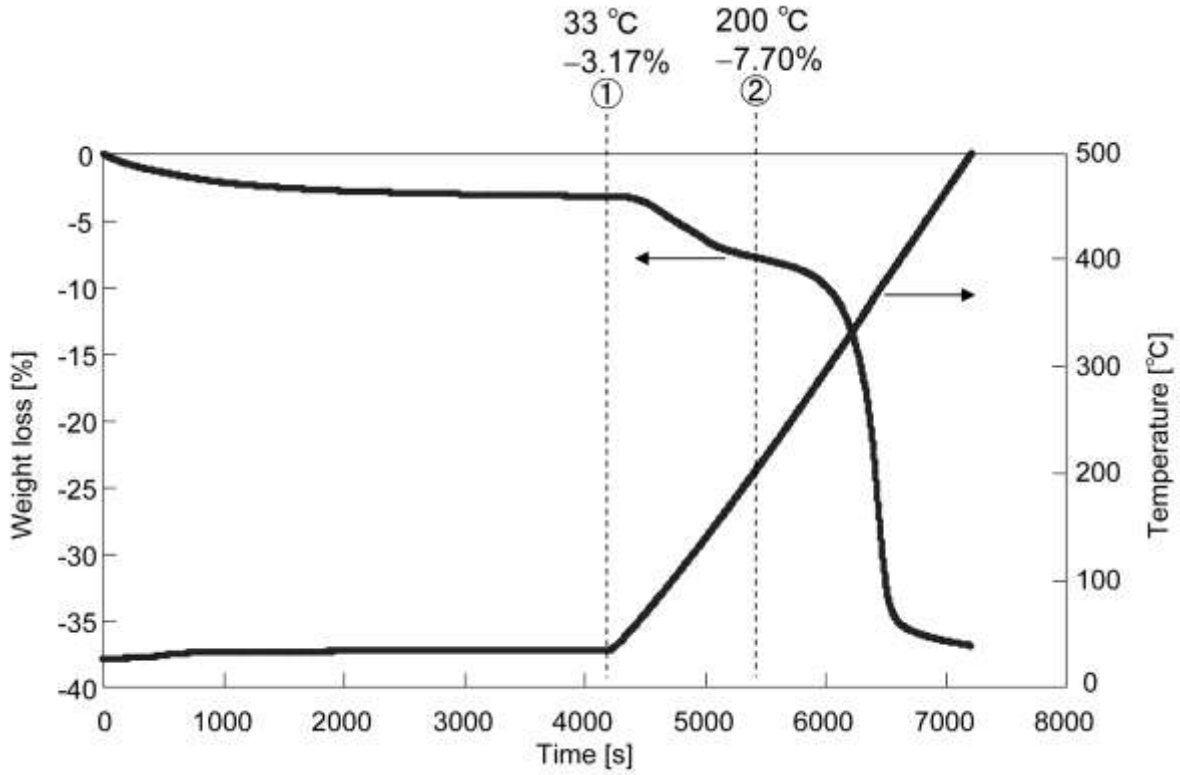

Figure S2. Thermogravimetric analysis of **Ib** (under dry N_2 flow). Compound **Ic** and anhydride (i.e., $[Cr_3O(OOCCF_3)_6(H_2O)_3]_3[\alpha\text{-}PW_{12}O_{40}]$) are formed at point ① and ②, respectively.

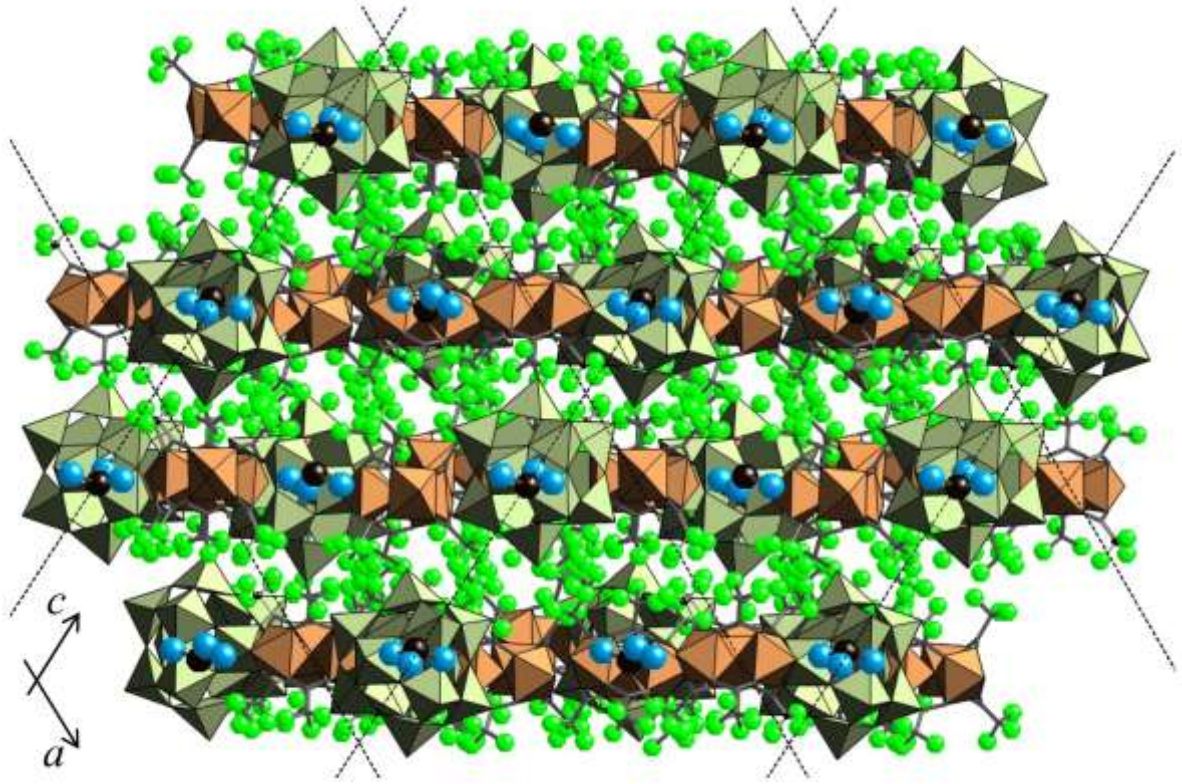

Figure S3. Schematic synthesis and crystal structure of **Ia** normal to the *ac*-plane. Green, purple, and orange polyhedra show the [WO_6], [SiO_4], and [CrO_6] units, respectively. Green spheres show the fluorine atoms. Blue and black spheres show the chlorine and carbon atoms, respectively, of the chloroform molecules.

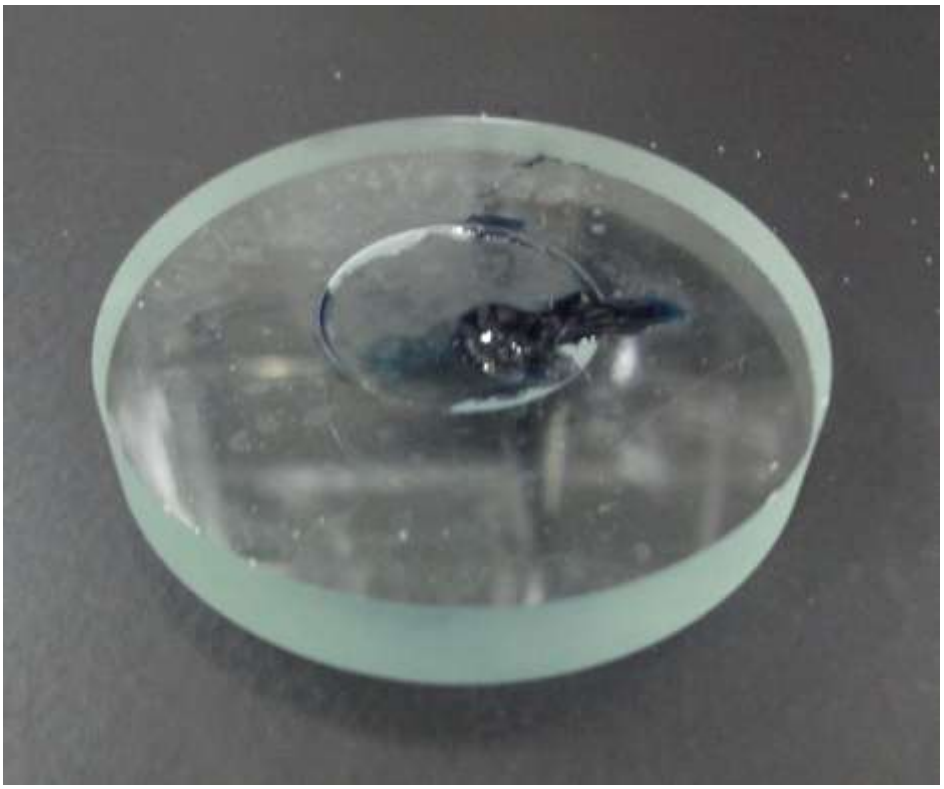

Figure S4. Photo image of the compound obtained by the complexation of $[Cr_3O(OOCCF_3)_6(H_2O)_3]^+$ with $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ in water. Initially, the obtained compound was powdery and could be placed on the glass cell for powder XRD measurement. However, the powder was extremely hygroscopic, sorbed water in the the atmosphere, and became a highly viscous liquid as shown in the photo image.

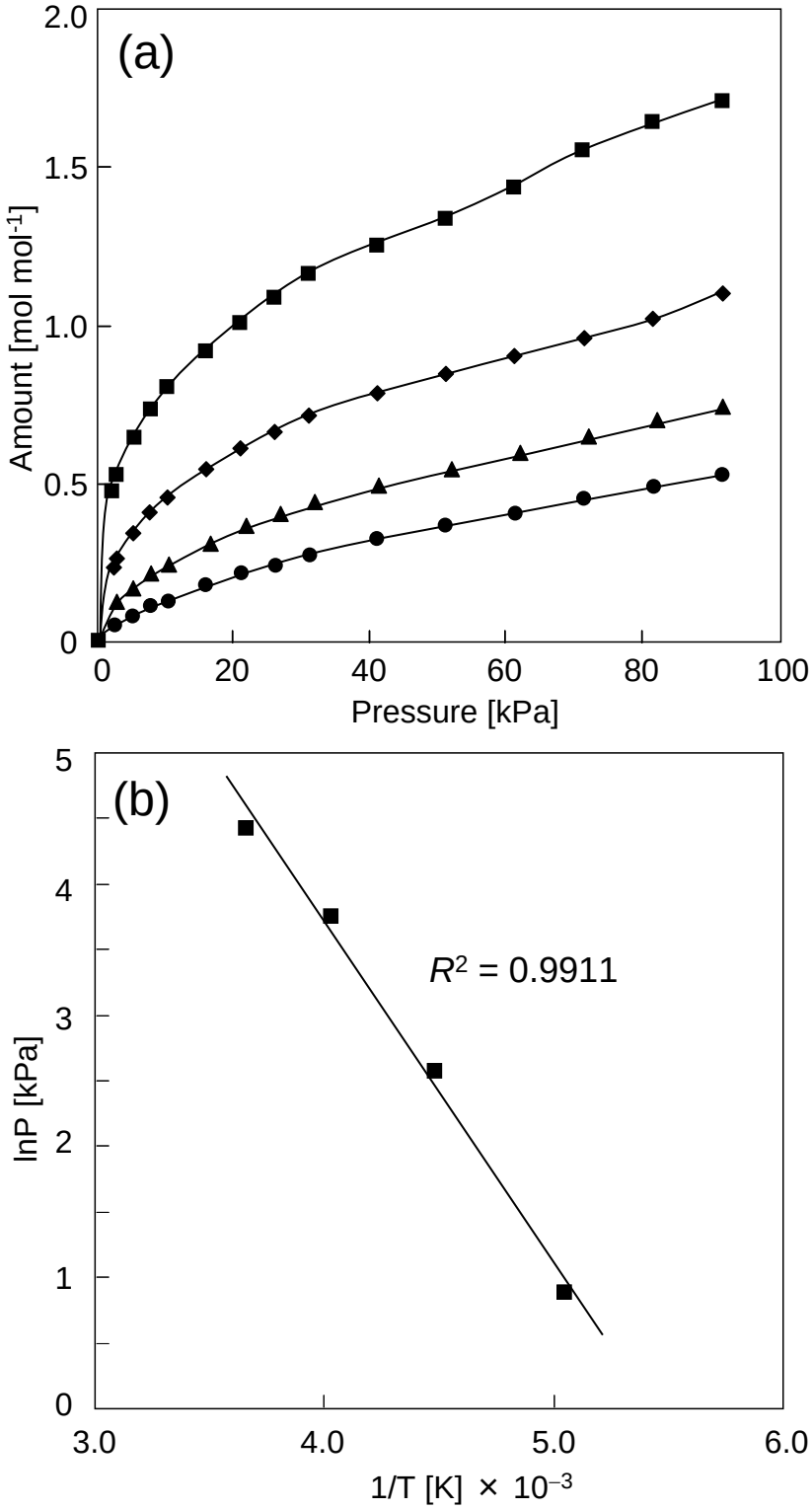

Figure S5. (a) Ethylene sorption isotherms of **Ic**. Square, diamond, triangle, circle symbols show the data at 198, 223, 248, and 273 K. (b) Clausius-Clapeyron plot (amount of sorption: 0.5 mol mol^{-1}).

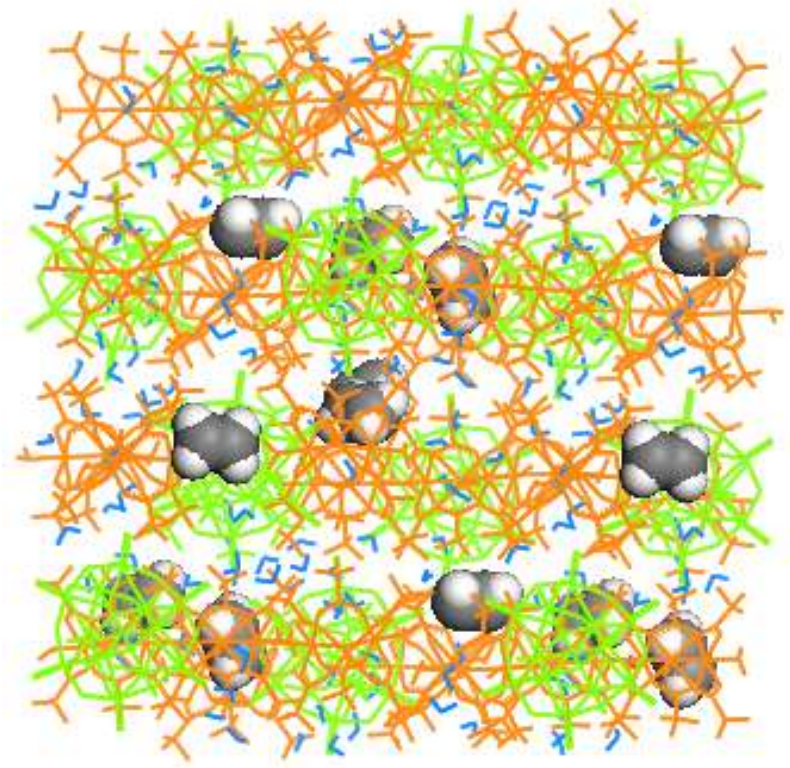

Figure S6. Typical optimized geometries of 1.5 mol mol^{-1} of ethylene in **Ic** (*ac*-plane). Green, orange, and blue molecules show the phosphododecatungstates, macrocations, and water, respectively. Gray and white atoms show the carbon and hydrogen atoms, respectively.

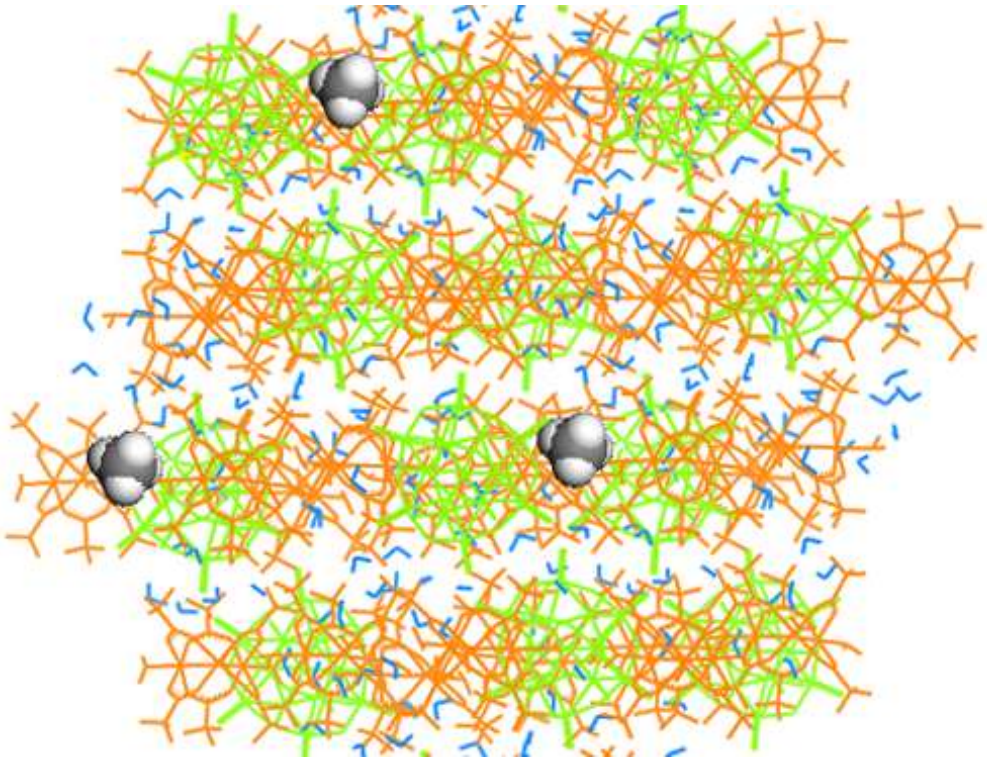

Figure S7. Typical optimized geometries of 0.25 mol mol^{-1} of methane in **Ic** (*ac*-plane). Green, orange, and blue molecules show the phosphododecatungstates, macrocations, and water, respectively. Gray and white atoms show the carbon and hydrogen atoms, respectively.