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Azulene based metal–organic frameworks for strong adsorption of H_2†‡

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Two Zn MOFs, MOF-645 and MOF-646, comprised of polarized 1,3-azulenedicarboxylate were synthesized. The guest free MOF-646 showed strong MOF-H_2 interactions (7.8–6.8 kJ mol^{-1}), which revealed the significant impact of internally polarized azulene backbone to stabilized H_2 molecules in the framework.

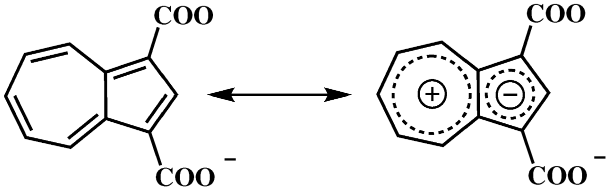
Due to the high fugacity coefficient of hydrogen, a dense storage form in a fuel cell vehicle has become important in the effort to achieve the DOE (US) targets.[1] In addition to the large storage space, implementation of the large adsorption enthalpy of H_2 (*ca.* 15 kJ mol^{-1}) is a key issue in building practical storage systems.[2] Because of the discovery of high surface area metal–organic frameworks (MOFs), it is possible to store more than 10 wt% of H_2 at 77 K,[3] but due to the very weak interactions between H_2 and the MOF framework, their storage capacity is not significant at 298 K.[1] Towards this end, creation of coordinatively unsaturated metal centers[4] and doping of MOFs with alkali metals[5] have been proposed. However, once these metal sites are blocked by H_2 molecules, the adsorption enthalpy should decrease drastically, which leads to another problem; *i.e.*, that the delivery amount of H_2 may not be large. Therefore, we believe that creation of MOFs with high charge density is another way to realize a high adsorption enthalpy with a wide loading amount of H_2.[6]

Azulenes constitute dipolar aromatic systems (Scheme 1) and we anticipated that azulenes contained in a MOF could contribute to the build up of coulombic fields required for the polarization and polarized binding of H_2.

The polarized binding state of H_2 provides considerable stabilization depending on the size of the electrical field.[7] It was calculated that the H_2 molecules over an azulene ring system would have higher interaction energy in comparison to simple benzene and isomeric naphthalene systems owing to its internal charge separation.[8] We believe that in MOFs the electrical field gradients of an appropriately arranged azulene unit should be cooperative and thus lead to an enhancement of polarized binding of H_2. Herein we report an alternate approach towards enhancing polarizability of the frameworks using internally polarized angular 1,3-azulenedicarboxylic acid (C_{2v} symmetry).[9] Specifically, we report the synthesis and characterization of two new MOFs,§ MOF-645 $[Zn_5(OH)_2(\mathbf{L})_4]$ (**L** = 1,3-azulenedicarboxylate) and MOF-646 $[Zn_4O(\mathbf{L})_3]$, and describe the H_2 uptake behaviors for guest free MOF-646.

Single crystals of MOF-645 were obtained by heating $H_2\mathbf{L}$ and zinc nitrate in a mixture of DMF/ EtOH/ H_2O (1.0 : 0.25 : 0.25 mL) at 90 °C (DMF = *N*,*N*-dimethylformamide).[10] The single crystal X-ray diffraction (SXRD) analysis¶ reveals that the structure of MOF-645 has a three-dimensional (3D) framework, which is constructed from unique pentanuclear zinc(II) clusters: $Zn_5(\mu_3\text{-}OH)_2(O_2C)_8(DMF)(H_2O)$ (Fig. 1a and b). Two Zn triangles, each with a central μ_3-OH group, share a central Zn corner. The central Zn atom is bridged to each of the other Zn atoms by a carboxylate.[11] The edges opposite the central Zn atom are each bridged by a carboxylate. Half of the edge Zn atoms have single chelating bidentate carboxylate,[11] respectively, while the other Zn atoms are coordinated to either DMF or a water molecule. In the overall crystal structure, these SBUs are linked to produce a **bcu** net (Fig. 1c).[12,13] If occluded and coordinated guests are removed, accessible void space is estimated to be 41%. However, in our attempt, the guest free form of MOF-645 did not take up N_2 at 77 K presumably due to structural decomposition as evidenced by the X-ray powder diffraction (PXRD) pattern.[13] Therefore, we strove to prepare another MOF with the same ligand **L**.

Synthesis of MOF-646 has been achieved by carrying out a solvothermal reaction between $H_2\mathbf{L}$ and zinc acetate in DMF.[10] From SXRD analysis (Fig. 1e), each Zn_4O unit is connected by ligand **L**. The Zn_4O unit is a slightly distorted tetrahedron and two DMF molecules are coordinated to one of the four Zn ions in the unit (Fig. 1d).[13,14] Although the chemical formula is the same as for other IRMOFs $[Zn_4O(\text{link})_3]$, the overall connectivity (**lcy**, Fig. 1f) is different from them (**pcu**) because of the bent ligand. The variation in the underlying topology from **pcu** to **lcy** could result in a



Scheme 1 Resonance form of 1,3-azulenedicarboxylate emphasizing its polar nature.

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‡ Electronic supplementary information (ESI) available: Full synthetic procedures and characterization data including TGA, IR, PXRD. N_2 isotherms and single crystal X-ray diffraction data. CCDC 771570–771571. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc02589e

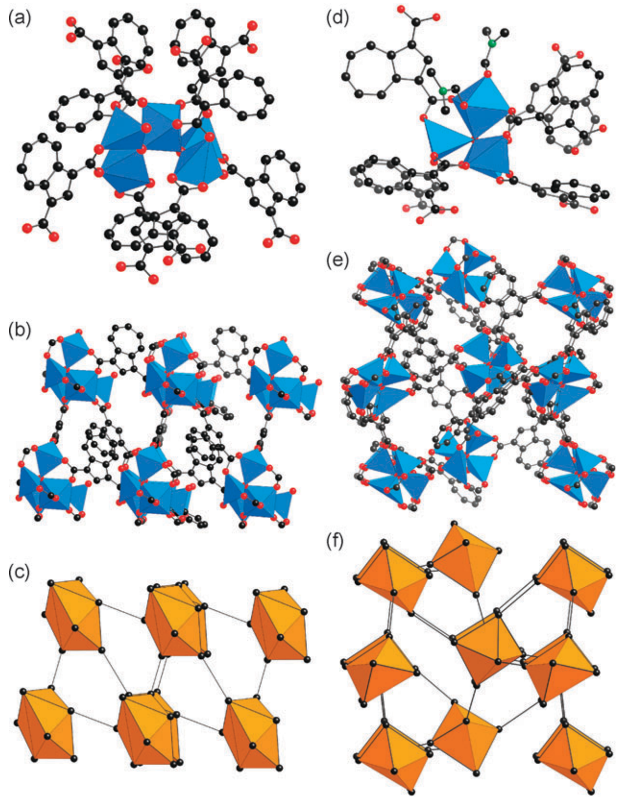

Fig. 1 $Zn_5(\mu_3\text{-}OH)_2(\mathbf{L})_8$ SBU with Zn shown as polyhedra (a) and view of crystalline framework of MOF-645 (b) in a **bcu** net (c). $Zn_4(\mu_4\text{-}O)(\mathbf{L})_6(DMF)_2$ SBU with Zn shown as polyhedra (d) and view of the single X-ray crystal structure of MOF-646 (e) in an **lcy** net (f). Atom colors: Zn, blue tetrahedra; O, red; C, black; N, green; all hydrogen atoms and terminal ligands on the SBUs except (d) are omitted for clarity.

smaller pore size distribution (<7 Å) which should allow an extensive overlap of attractive potential of the pore wall and could mitigate the entropic gain at a higher temperature.[15]

Solvent guests in the as-synthesized form of MOF-646 were removed by first immersing the crystals in chloroform and then evacuating at 45 °C for 24 h.[13] The PXRD pattern of activated MOF-646 confirmed that it retained crystallinity.[13] Elemental microanalysis of the activated sample is consistent with the guest free material of $[Zn_4O(\mathbf{L})_3]$. The removal of coordinated DMF may affirm the nature of the open metal site in the Zn_4O unit.

The permanent porosity of the activated MOF-646 was demonstrated by measuring the Ar gas adsorption at 87 K (Fig. 2a). MOF-646 takes up Ar in the low pressure region which is indicative of the presence of microporosity. A small step at $P/P_0 = 0.02$ is probably due to either the pore blocking effect or reorientation of adsorbed Ar molecules. The Langmuir and BET surface areas of activated MOF-646 are estimated to be 1130 $m^2\ g^{-1}$ and 925 $m^2\ g^{-1}$, respectively.[16] To evaluate the pore size distribution of MOF-646, the Ar isotherm was analyzed using nonlocal density functional theory (NLDFT) based on a zeolite/silica model containing cylindrical pores.[17] The distribution calculated by fitting the MOF-646 adsorption data (<6 Å) revealed the pore width is within the realm of an ultramicropore.

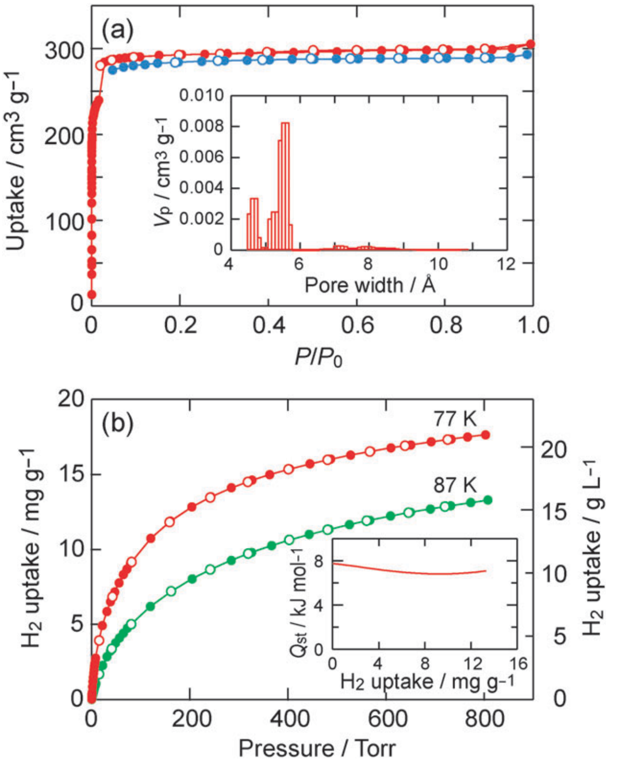

Fig. 2 (a) Ar isotherm for activated MOF-646 measured at 87 K. Inset: pore size distribution (histogram) for activated MOF-646, calculated from a NLDFT fit to the Ar adsorption data at 87 K.[13] (b) H_2 isotherms for activated MOF-646 measured at 77 (red) and 87 K (olive). Inset: the coverage dependencies of adsorption enthalpies of H_2 for activated MOF-646. Filled and open symbols for (a) and (b) represent adsorption and desorption branches respectively.

In conjunction with the polarized pore wall and the small pore size distribution of MOF-646, we recorded the H_2 adsorption isotherms on the activated material. In spite of relatively high crystal density (1.19 g cm^{-3}), activated MOF-646 shows considerable H_2 uptake up to 17.5 mg g^{-1} at 77 K and 1 bar (Fig. 2b). This gravimetric uptake outperforms MOFs with Zn_4O SBUs except for IRMOF-11 whose nets are interwoven.[18] More importantly, the H_2 uptake in the volumetric unit (20.9 g L^{-1}) is approaching that of high performance MOFs having Cu open metal sites (22–24 g L^{-1} for HKUST-1, PCN-14, and SNU-5)[4c,h,j] measured under similar conditions.

To investigate the reason for the excellent H_2 uptake on activated MOF-646, coverage dependencies of the isosteric heat of adsorption (Q_{st}) were calculated from fits of its 77 and 87 K isotherms. As shown in Fig. 2b (inset), the Q_{st} curve is nearly flat throughout the loading range examined, which is in sharp contrast to many MOFs, especially those possessing open metal sites.[4a,d,h,j] The estimated Q_{st} (7.8–6.8 kJ mol^{-1}) is higher than representative MOFs, such as MOF-5, MOF-177 and HKUST-1,[3c,4c] although this is lower than MIL-101, $M_3[(M_4Cl)_3(BTT)_8]_2$ (M = Mn, Fe, Co, BTT^{3-} = 1,3,5-benzenetristetrazolate) analogues and other MOF materials.[19,4a,d–f,h,j] It is worth noting that, to our best knowledge, 7.1 kJ mol^{-1} of Q_{st} at 13 mg g^{-1} of adsorbed H_2 is one of the highest values among physisorption media.[20]

From the Q_{st} curve it is not possible to speculate the adsorption sites of H_2; however, if each Zn_4O unit confines 4 H_2 molecules as suggested by neutron diffraction studies,[21] the H_2 uptake corresponds to 8.5 mg g^{-1}. Considering that the Q_{st} value does not drop off after the occupation of the relatively strong binding sites, it is presumed that the internally polarized azulene backbone is advantageous to stabilize H_2 molecules in the framework, because smaller pore size distribution should not be effective to enhance the Q_{st} (but can improve Henry's constant).

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Notes and references

§ Synthesis of MOF-645: A mixture of *N*,*N*-dimethylformamide (DMF)/ethanol/H_2O (1.00/0.25/0.25 mL) containing 1,3-azulenedicarboxylic acid (0.005 g, 2.3 × 10^{-5} mol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.014 g, 4.62 × 10^{-5} mol) was sealed in a 20-mL glass vial. The vial was heated at a constant rate 0.5 °C min^{-1} to 90 °C for 48 h and then cooled at a constant rate 0.1 °C min^{-1} to room temperature. The dark red crystals were washed with a DMF/ ethanol mixture (3 × 3 mL) to give 0.007 g (Yield: 88% based on 1,3-azulenedicarboxylic acid).

MOF-646: 1,3-Azulenedicarboxylic acid (0.010 g, 4.6 × 10^{-5} mol) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.010 g, 4.62 × 10^{-5} mol) were combined with 2 mL of DMF and sealed in a 20-mL glass vial and sonicated for several minutes. The vial was heated at a constant rate 2.0 °C min^{-1} to 120 °C for 20 h in a programmable oven. The vial was taken out from the oven while hot and the hexagonal plate-shaped crystals were washed with DMF (3 × 2 mL) to give 0.015 g (Yield: 80% based on 1,3-azulenedicarboxylic acid).

¶ Crystal data for MOF-645: $C_{51}H_{35}NO_{20}Zn_5{\cdot}C_3H_7NO$, M_r = 1381.85, monoclinic, space group *C*2, a = 15.7939(2), b = 16.3435(1), c = 12.2880(2) Å, β = 123.813(2)°, V = 2683.19(9) Å^3, Z = 2, d_{calcd} = 1.710 Mg m^{-3}, crystal size 0.33 × 0.21 × 0.06 mm^3, T = 153(2) K, λ = 0.71073 Å, R_1 = 0.0285 [$I > 2\sigma(I)$], wR_2 = 0.0770 (all data, 39 666 reflections), R_{int} = 0.0259, GOF = 1.022. Crystal data for MOF-646: $2(C_{84}H_{64}N_4O_{30}Zn_8){\cdot}5(C_3H_7NO){\cdot}4(H_2O)$, M_r = 4702.25, monoclinic, space group $P2_1$, a = 17.2344(6), b = 17.2237(6), c = 17.2923(7) Å, β = 90.548(4)°, V = 5132.8(3) Å^3, Z = 1, d_{calcd} = 1.521 Mg m^{-3}, crystal size 0.13 × 0.09 × 0.05 mm^3, T = 153(2) K, λ = 0.71073 Å, R_1 = 0.0468 [$I > 2\sigma(I)$], wR_2 = 0.0996 (all data, 30 148 reflections), R_{int} = 0.0520, GOF = 0.843.

1 (*a*) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (*b*) S. Ma and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 44.
2 S. K. Bhatia and A. L. Myers, *Langmuir*, 2006, **22**, 1688.
3 (*a*) S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176; (*b*) Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey and M. Schröder, *Chem. Commun.*, 2009, 1025; (*c*) H. Furukawa, M. A. Miller and O. M. Yaghi, *J. Mater. Chem.*, 2007, **17**, 3197; (*d*) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.
4 (*a*) M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 9376; (*b*) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4745; (*c*) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304; (*d*) M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876; (*e*) M. Latroche, S. Surblé, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J.-H. Lee, J.-S. Chang, S. H. Jhung and G. Férey, *Angew. Chem., Int. Ed.*, 2006, **45**, 8227; (*f*) M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown and J. R. Long, *Angew. Chem., Int. Ed.*, 2007, **46**, 1419; (*g*) X.-S. Wang, S. Ma, P. M. Forster, D. Yuan, J. Eckert, J. J. López, B. J. Murphy, J. B. Parise and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2008, **47**, 7263; (*h*) Y.-G. Lee, H. R. Moon and P. Suh, *Angew. Chem., Int. Ed.*, 2008, **47**, 7741; (*i*) W. Zhou, H. Wu and T. Yildirim, *J. Am. Chem. Soc.*, 2008, **130**, 15268; (*j*) S. Ma, J. M. Simmons, D. Sun, D. Yuan and H.-C. Zhou, *Inorg. Chem.*, 2009, **48**, 5263; (*k*) X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159.
5 (*a*) S. S. Han and W. A. Goddard, *J. Am. Chem. Soc.*, 2007, **129**, 8422; (*b*) K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2007, **129**, 9604; (*c*) D. Himsl, D. Wallacher and M. Hartmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 4639; (*d*) S. Yang, X. Lin, A. J. Blake, K. M. Thomas, P. Hubberstey, N. R. Champness and M. Schröder, *Chem. Commun.*, 2008, 6108.
6 (*a*) Y. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. C. Kravtsov, R. Luebke and M. Eddaoudi, *Angew. Chem., Int. Ed.*, 2007, **46**, 3278; (*b*) D. F. Sava, V. C. Kravtsov, F. Nouar, L. Wojtas, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 3768.
7 J.-Y. Hasegawa, M. Higuchi, Y. Hijikata and S. Kitagawa, *Chem. Mater.*, 2009, **21**, 1829.
8 (*a*) O. Hübner, A. Glöss, M. Fichtner and W. Klopper, *J. Phys. Chem. A*, 2004, **108**, 3019; (*b*) M. Wong, B. E. V. Kuiken, C. Buda and B. D. Dunietz, *J. Phys. Chem. C*, 2009, **113**, 12571.
9 L. J. Mathias and C. G. Overberger, *J. Org. Chem.*, 1980, **45**, 1701.
10 Microanalysis for MOF-645, $[Zn_5(\mu_3\text{-}OH)_2(\mathbf{L})_4(DMF)(H_2O)]{\cdot}(DMF)$, calcd: C, 46.94; H, 3.06; N, 2.03%. Found: C, 46.1; H, 3.13; N, 2.02%. For MOF-646, $[Zn_4(\mu_4\text{-}O)(\mathbf{L})_3(DMF)_2]{\cdot}(DMF)_{1.25}{\cdot}(H_2O)$, calcd: C, 46.74; H, 3.67; N, 3.87%. Found: C, 46.54; H, 3.61; N, 4.26%.
11 Three oxygen atoms (O2, O3 and O5) of carboxylate linkers are disordered over two positions with fixed site occupancy factors of 0.5 : 0.5. Constraints on their displacement parameters were applied using EADP. See Fig. S1 in ESI for details.
12 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.
13 See ESI for details.
14 (*a*) H. Chun and H. Jung, *Inorg. Chem.*, 2009, **48**, 417; (*b*) Y. Takashima, C. Bonneau, S. Furukawa, M. Kondo, R. Matsuda and S. Kitagawa, *Chem. Commun.*, 2010, **46**, 4142.
15 M. Rzepka, P. Lamp and M. A. de la Casa-Lillo, *J. Phys. Chem. B*, 1998, **102**, 10894.
16 The pore volume from the Ar isotherm is smaller than that from the N_2 isotherms. This indicates that the packing density of Ar in the pore should be lower than that of N_2. Indeed, estimated surface area based on the crystal structure (54% void space, 1260 m^2 g^{-1}) is almost the same as the Langmuir surface area from the N_2 isotherm (1250 m^2 g^{-1}).
17 P. I. Ravikovitch, D. Wei, W. T. Chueh, G. L. Haller and A. V. Neimark, *J. Phys. Chem. B*, 1997, **101**, 3671.
18 J. L. C. Rowsell, A. R. Millward, K. S. Park and O. M. Yaghi, *J. Am. Chem. Soc.*, 2004, **126**, 5666.
19 (*a*) M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172; (*b*) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 1833; (*c*) S. Ma and H.-C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 11734; (*d*) B. Chen, X. Zhao, A. Putkham, K. Hong, E. B. Lobkovsky, E. J. Hurtado, A. J. Fletcher and K. M. Thomas, *J. Am. Chem. Soc.*, 2008, **130**, 6411.
20 O. K. Farha, K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2008, **47**, 10223.
21 E. C. Spencer, J. A. K. Howard, G. J. McIntyre, J. L. C. Rowsell and O. M. Yaghi, *Chem. Commun.*, 2006, 278.