

Open Metal Sites within Isostructural Metal–Organic Frameworks for Differential Recognition of Acetylene and Extraordinarily High Acetylene Storage Capacity at Room Temperature**

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Open metal sites have played very important roles in synthetic assemblies and biological systems because of their specific recognition of small molecules and thus for their highly selective molecular transformations, transport, and storage.^[1–4] Understanding the molecular recognition between the open metal sites and the substrate molecules at the molecular level will not only facilitate the discoveries of new catalysts, sensing, and storage materials, but will also provide a deep insight in the functions of the open metal sites in the biological systems and thus stimulate studies of modeling compounds to mimic biological functions. However, the highly reactive nature of such open metal sites has mainly limited our capacities to elucidate the metal–substrate recognition processes fundamentally and systematically within molecular assemblies. This situation changed recently with the emergence of porous metal–organic frameworks (MOFs) with sustained open metal sites, which provided the promise of elucidating the bonding nature of the open metal sites with small gas molecules at the molecular level.^[5–7]

We realized that open Cu^{2+} sites within a porous HKUST-1 material have strong interactions with acetylene molecules (the adsorption enthalpy is 30.4 kJ mol^{-1} at a coverage of 1 mmol g^{-1}) and thus contribute significantly to the high acetylene storage with a volumetric storage capacity of $177 \text{ cm}^3 \text{ cm}^{-3}$ at 295 K and 1 atm.^[8] Because acetylene is a very important raw material for various industrial chemicals, fundamental studies on the metal site–acetylene interactions and their bonding nature will promote the discovery of new chemical transformations for the efficient usage of acetylene and new porous materials for high acetylene storage capacity.^[9] The highly explosive nature of acetylene has limited the possible storage materials to fulfill high acetylene storage capacities at room temperature and at pressures of under 0.2 MPa (the compression limit for the safe storage of acetylene). It is thus particularly important to target systems having very strong interactions with acetylene to secure high acetylene storage capacities.^[10–21] Herein, we report the differential interactions of the open metal sites with acetylene molecules within the isostructural CPO-27M or MOF-74 analogues $[\text{M}_2(\text{DHTP})]$ ($\text{M} = \text{Co}^{2+}$, Mn^{2+} , Mg^{2+} , and Zn^{2+} ; DHTP = 2,5-dihydroxyterephthalate), which have been exclusively established by the coordinated temperature-dependent adsorption isotherms, neutron diffraction studies, and first-principles calculation, featuring open Co^{2+} sites as the strongest sites for their interactions with acetylene molecules (adsorption enthalpy of 50.1 kJ mol^{-1} at the low coverage) and $[\text{Co}_2(\text{DHTP})]$ as the highest volumetric acetylene storage material ever reported with the capacity of $230 \text{ cm}^3 \text{ cm}^{-3}$ (standard temperature and pressure (STP): 295 K and 1 atm).

The temperature-dependent acetylene adsorption isotherms of these isostructural MOFs were examined to evaluate their adsorption enthalpies and thus their different interactions with acetylene molecules. The examined MOFs show repeatable adsorption isotherms.^[22] The coverage-dependent adsorption enthalpies of the MOFs to acetylene were calculated based on a virial method, a well established and reliable methodology from fits of their adsorption isotherms at 273 and 295 K.^[23] As shown in Figure 1, $[\text{Co}_2(\text{DHTP})]$ exhibits much higher adsorption enthalpy of C_2H_2 ($50.1 \pm 0.9 \text{ kJ mol}^{-1}$) than does $[\text{Mn}_2(\text{DHTP})]$ ($39.0 \pm 0.8 \text{ kJ mol}^{-1}$), $[\text{Mg}_2(\text{DHTP})]$ ($34.0 \pm 0.8 \text{ kJ mol}^{-1}$), or $[\text{Zn}_2(\text{DHTP})]$ ($24.0 \pm 0.7 \text{ kJ mol}^{-1}$) at low coverage. Such high adsorption enthalpies in $[\text{Co}_2(\text{DHTP})]$ might enforce its full loading of one acetylene molecule per open Co^{2+} site even at room temperature and 1 atm, conditions in which $[\text{Co}_2(\text{DHTP})]$ exhibits the highest volumetric acetylene storage capacity ever

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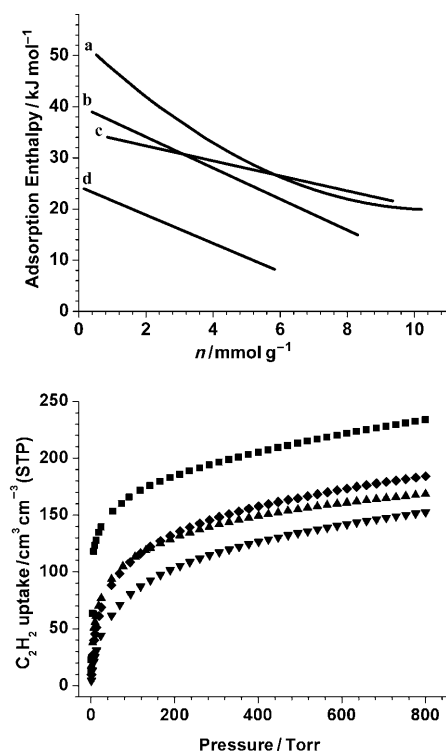


Figure 1. Top: Coverage dependencies of the adsorption enthalpies for C₂H₂ in MOFs calculated from fits of their 273 and 295 K isotherms a) [Co₂(DHTP)]; b) [Mn₂(DHTP)]; c) [Mg₂(DHTP)]; d) [Zn₂(DHTP)]. Bottom: Acetylene adsorption isotherms of microporous MOFs at 295 K: [Co₂(DHTP)] (■); [Mn₂(DHTP)] (◆); [Mg₂(DHTP)] (▲); [Zn₂(DHTP)] (▼).

reported with a capacity of 230 cm³ cm⁻³ (STP) at 295 K and 1 atm, which is significantly higher than the previously reported highest value of 177 cm³ cm⁻³ (STP) in HKUST-1. Apparently, the stronger the interactions of open metal sites with acetylene, the higher acetylene uptake the MOF will have within this series of isostructural MOFs; accordingly, the acetylene storage capacities decrease in the order [Co₂(DHTP)] > [Mn₂(DHTP)] > [Mg₂(DHTP)] > [Zn₂(DHTP)]. A detailed comparison of several high acetylene storage capacity materials is given in Table 1.

The very strong interactions of open Co²⁺ sites with acetylene molecules certainly play very important roles for

the extraordinarily high acetylene storage capacity of [Co₂(DHTP)]. Another crucial factor for [Co₂(DHTP)] to have very high acetylene storage capacity is the high open cobalt site density of 7.49 mmol Co²⁺ cm⁻³ in [Co₂(DHTP)], which is more than one and a half times higher than that of HKUST-1 (4.36 mmol Cu²⁺ cm⁻³). Assuming that each open Co²⁺ site can bind one acetylene molecule, the open Co²⁺ sites can contribute to 168 cm³ cm⁻³ (STP) of total 230 cm³ cm⁻³ (STP) volumetric acetylene storage capacity because of the high open Co²⁺ sites density (7.49 mmol Co²⁺ cm⁻³) in [Co₂(DHTP)] at 295 K and 1 atm. The remaining uptake of 62 cm³ cm⁻³ (STP) might be attributed from the pore space channel of 13.6 Å within [Co₂(DHTP)], which accounts for only 27 % of the total volumetric acetylene storage capacity, highlighting the crucial role of the high open Co²⁺ site density for the extraordinarily high volumetric acetylene storage capacity in [Co₂(DHTP)]. The potential contribution from the pore space within HKUST-1 for the volumetric acetylene storage capacity is expected to be more than 79 cm³ cm⁻³ (STP) (calculated from the total volumetric acetylene storage capacity (177 cm³ cm⁻³ (STP)) minus the volumetric acetylene storage capacity attributed from open Cu²⁺ sites (98 cm³ cm⁻³ (STP))), which is significantly higher than that in [Co₂(DHTP)] (62 cm³ cm⁻³ (STP)). The significant contribution from the high density open Co²⁺ sites for acetylene storage capacity of up to 168 cm³ cm⁻³ (STP) has featured the [Co₂(DHTP)] as the best volumetric acetylene storage material (230 cm³ cm⁻³ (STP)) with the highest safe acetylene storage density of adsorbed acetylene in bulk material (0.27 g cm⁻³ at 295 K and 1 atm, which is equivalent to the acetylene density at 25.1 MPa) ever reported.

The amount of acetylene gas adsorbed at room temperature reaches to 230 cm³ cm⁻³ (STP) at 295 K and 1 atm in [Co₂(DHTP)], which corresponds to 1.40 C₂H₂ molecules per Co²⁺ site. To verify the preferential adsorption sites experimentally and thus confirm our speculation that the high open Co²⁺ site density in [Co₂(DHTP)] is the determining role for the extraordinarily high acetylene storage capacity, we measured the 0.54 C₂D₂ per Co loaded [Co₂(DHTP)] with the high-resolution neutron powder diffractometer BT1 at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The data were analyzed using the program EXPGUI with Rietveld refinement.

From the Rietveld refinement results ($\chi^2 = 0.9280$), acetylene is only adsorbed at one site at 0.54 C₂D₂ per Co loading, that is, all acetylene gas molecules are adsorbed at open Co²⁺ sites. The experimental pattern and the calculated curves using the Rietveld method are shown in Figure S2a. The refinement results indicate that 0.54 C₂D₂ molecules per Co site are loaded inside the sample, which is in good agreement with the amount of gas loaded into the material. The distance between a C₂D₂ molecule and the closest Co atom is about 2.65 Å, which is comparable to that observed between a C₂D₂ molecule and the closest Cu atom in HKUST-1. Figure S2b shows the Fourier difference map of acetylene adsorbed in [Co₂(DHTP)]. The pink blobs are the locations indicating additional new neutron scattering length density after introduction of acetylene molecules into the sample. High-resolution neutron powder diffraction studies on the

Table 1: Acetylene uptake in the examined metal–organic frameworks at 295 K and 1 atm.

MOF	C ₂ H ₂ uptake		Density of adsorbed C ₂ H ₂ ^[a] [g cm ⁻³]	$P^{[b]}$ [MPa]
	[cm ³ cm ⁻³ (STP)]	wt%		
[Co ₂ (DHTP)]	230	22.9	0.27	25.1
[Mn ₂ (DHTP)]	182	19.5	0.21	19.8
[Mg ₂ (DHTP)]	167	21.4	0.19	18.2
[Zn ₂ (DHTP)]	150	14.2	0.17	16.4
HKUST-1	177	23.4	0.21	19.3

[a] Calculated density of adsorbed acetylene in bulk material. [b] Pressure of acetylene at 295 K corresponding to the calculated density of adsorbed acetylene in bulk material.

0.54 C₂D₂ per Co loaded [Co₂(DHTP)] sample exclusively confirm that the open Co²⁺ sites are the first preferential acetylene storage sites that make the major contribution to the high volumetric acetylene storage capacity.

Unlike the well-separated adsorbed C₂D₂ molecules in C₂D₂-loaded HKUST-1, the C₂D₂ molecules aligned along the *c* axis as pseudo-one-dimensional arrays with intermolecular C₂D₂ distance of about 4 Å in C₂D₂-loaded [Co₂(DHTP)] (Figure 2). The high density of adsorbed acetylene molecules is also clearly shown in that each 1D pore channel of 13.6 Å in diameter can encapsulate six such pseudo-1D C₂D₂ arrays (one C₂D₂ molecule per open Co²⁺ site).

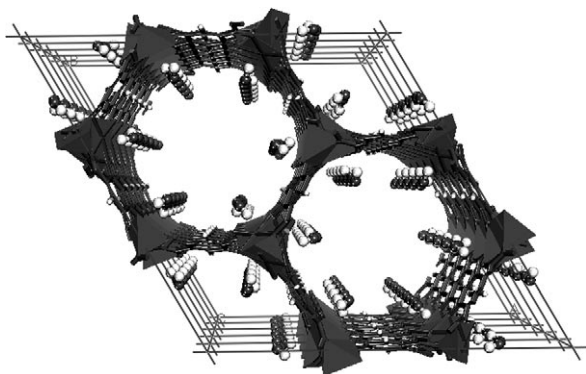


Figure 2. Crystal structure of [Co₂(DHTP)] with loading of 0.54 C₂D₂ per Co viewed along the *c* axis, exhibiting the high density of adsorbed acetylene molecules in pseudo-one-dimensional arrays.

To understand the interaction of C₂H₂ with different open metal sites within the four [M₂(DHTP)] frameworks (M = Co²⁺, Mn²⁺, Mg²⁺, and Zn²⁺), we performed first-principles total-energy calculations. The static binding energies derived from density-functional theory calculations are summarized in Table 2, along with the C≡C bond lengths and C≡C–H bond angles of the adsorbed C₂H₂ molecules. As expected, the local-density approximation (LDA) overestimates the binding strength, whereas the generalized gradient approximation (GGA) underestimates it. Nevertheless, the relative binding strengths of various metals derived from the two approaches

are consistent. Among the various metals investigated, Co²⁺ stands out for its highest affinity to C₂H₂.

The calculated static C₂H₂ binding energies on Co²⁺ are 71.4 kJ mol^{−1} and 18.5 kJ mol^{−1} (corresponding to LDA and GGA results, respectively), which are significantly larger than those found for the Mn, Mg, and Zn analogues. The overall trends of the calculated binding energies agree well with the experimentally derived adsorption enthalpies. The calculated C≡C–H bond angle is approximately 167° (in contrast to the value of 177–179.8° for adsorbed C₂H₂ on other open metals), suggesting a significant polarization of the adsorbed C₂H₂ molecule by the open Co²⁺ site. The C≡C bond lengths also suggest a high degree of bond activation by the Co ion. As we have shown before, the major contribution to the overall binding between C₂H₂ and the open metal ion is the Coulombic interaction between the adsorbed C₂H₂ dipole moment and the open metal charge density.^[8] It is thus the strong ability of open Co²⁺ to polarize and distort C₂H₂ molecule that leads to high affinity of C₂H₂ on Co²⁺.

In summary, a series of isostructural [M₂(DHTP)] MOFs (M = Co²⁺, Mn²⁺, Mg²⁺, and Zn²⁺) with open metal sites were examined for their differential recognition of acetylene molecules and realized as high acetylene storage materials. The open metal sites within this series of isostructural MOFs exhibit differential interactions with acetylene molecules in which Co²⁺ has the strongest interactions with acetylene and a very high adsorption enthalpy of 50.1 kJ mol^{−1} at the low coverage. Such a strong interaction makes [Co₂(DHTP)] the highest volumetric acetylene storage material reported so far, with a capacity of up to 230 cm³ cm^{−3} (STP) at 295 K and 1 atm. This high capacity maximizes the safe acetylene storage density of adsorbed acetylene in bulk material (up to 0.27 g cm^{−3}). The strong interaction of open Co²⁺ sites with acetylene was further confirmed by high-resolution neutron powder diffraction studies on acetylene-loaded [Co₂(DHTP)] and by first-principles calculations. The exceptionally high volumetric acetylene storage capacities make such microporous MOFs as very practical acetylene storage media. As acetylene is a very important raw material for various industrial chemicals, consumer products, and oxyacetylene cutting in metal fabrication, the realization of such safe and high-density acetylene storage media will facilitate the safe transportation and wider usage of acetylene in the future.^[24,25]

Table 2: Data derived from our calculations, including the static binding energies of C₂H₂ on the open metal sites in the MOFs, the C≡C bond lengths, and C≡C–H bond angles of the adsorbed C₂H₂ molecules.

	<i>E</i> _B , LDA/GGA [kJ mol ^{−1}]	C≡C–H bond angle, LDA/GGA [°]	C≡C bond length LDA/GGA [Å]
free C ₂ H ₂	/	180.0/180.0	1.200/1.208
C ₂ H ₂ on open Co ²⁺ ([Co ₂ (DHTP)])	71.4/18.5	167.5/166.7	1.228/1.232
C ₂ H ₂ on open Mn ²⁺ ([Mn ₂ (DHTP)])	55.0/17.3	177.2/176.9	1.208/1.213
C ₂ H ₂ on open Mg ²⁺ ([Mg ₂ (DHTP)])	53.0/16.9	179.2/178.8	1.204/1.210
C ₂ H ₂ on open Zn ²⁺ ([Zn ₂ (DHTP)])	51.5/16.5	179.3/179.0	1.206/1.211

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- [1] R. L. Koder, J. L. R. Anderson, L. A. Solomon, K. S. Reddy, C. C. Moser, P. L. Dutton, *Nature* **2009**, 458, 305.
- [2] L. L. Welbes, A. S. Borovik, *Acc. Chem. Res.* **2005**, 38, 765.
- [3] R. E. Morris, P. S. Wheatley, *Angew. Chem.* **2008**, 120, 5044; *Angew. Chem. Int. Ed.* **2008**, 47, 4966.
- [4] J. M. Thomas, *Top. Catal.* **2008**, 50, 98.

- [5] For examples, see: a) 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, M. Schröder, *J. Am. Chem. Soc.* **2009**, *131*, 2159; b) J. Zhang, T. Wu, S.-M. Chen, P. Feng, X. Bu, *Angew. Chem.* **2009**, *121*, 3538; *Angew. Chem. Int. Ed.* **2009**, *48*, 3486; c) Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem.* **2008**, *120*, 4212; *Angew. Chem. Int. Ed.* **2008**, *47*, 4144; d) W. Lin, J. W. Rieter, K. M. L. Taylor, *Angew. Chem.* **2009**, *121*, 660; *Angew. Chem. Int. Ed.* **2009**, *48*, 650; e) B. Chen, X. Zhao, A. Putkham, K. Hong, E. B. Lobkovsky, E. J. Hurtado, A. J. Fletcher, K. M. Thomas, *J. Am. Chem. Soc.* **2008**, *130*, 6411; f) B. Chen, Y. Yang, F. Zapata, G. Lin, G.-D. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693; g) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4745; h) M. Dinca, J. R. Long, *Angew. Chem.* **2008**, *120*, 6870; *Angew. Chem. Int. Ed.* **2008**, *47*, 6766; i) X.-S. Wang, S. Ma, P. M. Forster, D. Yuan, J. Eckert, J. J. Lopez, B. J. Murphy, J. B. Parise, H.-C. Zhou, *Angew. Chem.* **2008**, *120*, 7373; *Angew. Chem. Int. Ed.* **2008**, *47*, 7263; j) Y.-B. Zhang, W.-X. Zhang, F.-Y. Feng, J.-P. Zhang, X.-M. Chen, *Angew. Chem.* **2009**, *121*, 5391; *Angew. Chem. Int. Ed.* **2009**, *48*, 5287; k) S. Chen, J. Zhang, T. Wu, P. Feng, X. Bu, *J. Am. Chem. Soc.* **2009**, *131*, 16027; l) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, K. Kim, *Angew. Chem.* **2006**, *118*, 930; *Angew. Chem. Int. Ed.* **2006**, *45*, 916; m) Y.-G. Lee, H. R. Moon, Y. E. Cheon, M. P. Suh, *Angew. Chem.* **2008**, *120*, 7855; *Angew. Chem. Int. Ed.* **2008**, *47*, 7741; n) H.-S. Choi, M. P. Suh, *Angew. Chem.* **2009**, *121*, 6997; *Angew. Chem. Int. Ed.* **2009**, *48*, 6865; o) Q. Fang, G. Zhu, M. Xue, J. Sun, Y. Wei, S. Qiu, R. Xu, *Angew. Chem.* **2005**, *117*, 3913; *Angew. Chem. Int. Ed.* **2005**, *44*, 3845; p) L. Ma, W. Lin, *Angew. Chem.* **2009**, *121*, 3691; *Angew. Chem. Int. Ed.* **2009**, *48*, 3637; q) D. Britt, H. Furukawa, B. Wang, T. G. Glover, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20637.
- [6] a) P. D. C. Dietzel, Y. Morita, R. Blom, H. Fjellvag, *Angew. Chem.* **2005**, *117*, 6512; *Angew. Chem. Int. Ed.* **2005**, *44*, 6354; b) N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504; c) P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom, H. Fjellvag, *Chem. Commun.* **2006**, 959; d) P. D. C. Dietzel, R. E. Johnsen, R. Blom, H. Fjellvag, *Chem. Eur. J.* **2008**, *14*, 2389; e) J. G. Vitillo, L. Regli, S. Chavan, G. Ricchiardi, G. Spoto, P. D. C. Dietzel, S. Bordiga, A. Zecchina, *J. Am. Chem. Soc.* **2008**, *130*, 8386; f) P. D. C. Dietzel, R. E. Johnsen, H. Fjellvag, S. Bordiga, E. Groppo, S. Chavan, R. Blom, *Chem. Commun.* **2008**, 5125.
- [7] a) A. C. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megson, R. E. Morris, *J. Am. Chem. Soc.* **2008**, *130*, 10440; b) T. Yildirim, M. R. Hartman, *Phys. Rev. Lett.* **2005**, *95*, 215504; c) W. Zhou, T. Yildirim, *J. Phys. Chem. C* **2008**, *112*, 8132; d) W. Zhou, H. Wu, T. Yildirim, *J. Am. Chem. Soc.* **2008**, *130*, 15268; e) H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc.* **2009**, *131*, 4995; f) Y. Liu, H. Kabbour, C. M. Brown, D. A. Neumann, C. C. Ahn, *Langmuir* **2008**, *24*, 4772.
- [8] S.-C. Xiang, W. Zhou, J. M. Gallegos, Y. Liu, B. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 12415.
- [9] S. Budavari, *The Merck Index*, 12th ed., Merck Research Laboratories, New Jersey, **1996**, p. 16.
- [10] C. R. Reid, K. M. Thomas, *Langmuir* **1999**, *15*, 3206.
- [11] C. R. Reid, K. M. Thomas, *J. Phys. Chem. B* **2001**, *105*, 10619.
- [12] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238.
- [13] D. G. Samsonenko, H. Kim, Y. Sun, G.-H. Kim, H.-S. Lee, K. Kim, *Chem. Asian J.* **2007**, *2*, 484.
- [14] P. K. Thallapally, L. Dobranska, T. R. Gingrich, T. B. Wirsig, L. J. Barbour, J. L. Atwood, *Angew. Chem.* **2006**, *118*, 6656; *Angew. Chem. Int. Ed.* **2006**, *45*, 6506.
- [15] P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, J. L. Atwood, *J. Am. Chem. Soc.* **2008**, *130*, 16842.
- [16] D. Tanaka, M. Higuchi, S. Horike, R. Matsuda, Y. Kinoshita, N. Yanai, S. Kitagawa, *Chem. Asian J.* **2008**, *3*, 1343.
- [17] J.-P. Zhang, S. Kitagawa, *J. Am. Chem. Soc.* **2008**, *130*, 907.
- [18] D. G. Samsonenko, H. Kim, Y. Sun, G.-H. Kim, H.-S. Lee, K. Kim, *Angew. Chem.* **2008**, *120*, 3400; *Angew. Chem. Int. Ed.* **2008**, *47*, 3352.
- [19] M. Schubert, U. Mueller, J. Pastre, K. Schierle-Arndt, M. Triller, PCT Int. Appl. WO2008000694, **2008**.
- [20] J.-P. Zhang, X.-M. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 5516.
- [21] Y.-X. Hu, S.-C. Xiang, W.-W. Zhang, Z.-X. Zhang, L. Wang, J.-F. Bai, B. Chen, *Chem. Commun.* **2009**, 7551.
- [22] [Ni₂(DHTP)] exhibits significantly decayed adsorption possibly because of the polymerization of acetylene. We are now studying the mechanism for such decayed adsorption.
- [23] J. Roswell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304.
- [24] P. J. Stang, F. Diederich, *Modern Acetylene Chemistry*, VCH, New York, **1995**.
- [25] J. C. W. Chien, *Polyacetylene: Chemistry, Physics, and Material Science*, Academic Press, New York, **1984**.