Angewandte
Zuschriften

Fluorocarbon Adsorption Hot Paper

Deutsche Ausgabe: DOI: 10.1002/ange.201505149
Internationale Ausgabe: DOI: 10.1002/anie.201505149

Mesoporous Fluorinated Metal–Organic Frameworks with Exceptional Adsorption of Fluorocarbons and CFCs

*Teng-Hao Chen, Ilya Popov, Watchareeya Kaveevivitchai, Yu-Chun Chuang, Yu-Sheng Chen, Allan J. Jacobson, and Ognjen Š. Miljanić**

Abstract: *Two mesoporous fluorinated metal–organic frameworks (MOFs) were synthesized from extensively fluorinated tritopic carboxylate- and tetrazolate-based ligands. The tetrazolate-based framework MOFF-5 has an accessible surface area of 2445 $m^2 g^{-1}$, the highest among fluorinated MOFs. Crystals of MOFF-5 adsorb hydrocarbons, fluorocarbons, and chlorofluorocarbons (CFCs)—the latter two being ozone-depleting substances and potent greenhouse species—with weight capacities of up to 225 %. The material exhibits an apparent preference for the adsorption of non-spherical molecules, binding unusually low amounts of both tetrafluoromethane and sulfur hexafluoride.*

Greenhouse gases have been receiving much attention because of their potential to dramatically affect Earth's climate. While CO_2 presents the biggest problem in absolute terms, other compounds have hundreds or even thousands of times higher global warming potentials (GWPs)[1] per unit of mass. Among these are chlorofluorocarbons (CFCs) and fluorocarbons: organic compounds in which one or more hydrogen atoms have been replaced with fluorine, that are being commonly used as refrigerants (R-134a, R-12, R-40, see Table 1 for structures), propellants (HFC-227ea, HCFC-225ca), blowing agents for foams (CFC-113), and in electronics industry (CF_4, SF_6, perfluorohexane).[2] As many CFCs cause ozone depletion in the upper atmosphere, their manufacture has been banned under the Montreal Protocol,[3] and they were replaced with alternatives, such as fluorocarbons. While these replacements are safer for the ozone layer, they remain potent greenhouse gases.[1,4] Thus, their capture and sequestration are of significant interest. Fluorocarbon capture and storage have been performed on fluorous microgel star polymers,[5] self-assembled coordination cages,[6] fluorinated porous molecular crystals,[7] and MOFs.[8] Fluorinated MOFs,[9] such as FMOF-1 pioneered by Omary and coworkers,[9e] are a particularly appealing platform for the adsorption of fluorocarbons and CFCs on account of their large pore sizes, fluorophilic character, and low affinity for moisture. However, exploration of high-surface-area fluorinated MOFs as adsorbents for fluorocarbons and CFCs has thus far not been possible because of the synthetic inaccessibility of the appropriately fluorinated ligands. Herein, we report the synthesis of two mesoporous, extensively fluorinated MOFs (MOFFs); one of these materials is the highest surface-area fluorinated MOF ever prepared. This high surface area translates into an exceptional capacity for fluorocarbon and CFC adsorption: in excess of 200 wt % for some guests.

Owing to their modular design, the applicability of MOFs in fluorocarbon adsorption has been systematically studied, but most studies focused on MOFs with open metal sites.[8] Fluorous MOFs with high capacities have been unexplored because of the paucity of readily available fluorinated organic linkers. We and others have previously reported a general strategy for the preparation of large, extensively fluorinated, rigid aromatic carboxylic acids and tetrazoles.[7,10,11] Using a variant of this approach (see Supporting Information for details), we prepared extensively fluorinated tritopic carboxylic acid **1** (Figure 1) and tetrazole **2** as ligands that could produce MOFFs with high porosities and high capacities for fluorocarbon/CFC storage.

Ligand **1** was combined with $Cu(NO_3)_2{\cdot}2.5\,H_2O$ in a mixture of *N,N*-dimethylformamide (DMF) and EtOH. After 4 days at 60 °C, greenish-blue crystals of MOFF-4 were isolated. Because of the large amounts of massively disordered solvent in the cavities, a synchrotron radiation source (ChemMatCARS, Advanced Photon Source, Argonne National Laboratory) was necessary to obtain data of sufficiently high quality for satisfactory crystal-structure refinement. Single-crystal synchrotron diffraction analysis[12] revealed a three-dimensional network with a large cubic unit cell $a = b = c = 47.326(5)$ Å, in which pairs of Cu atoms form paddlewheel-shaped $Cu_2(COO)_4$ clusters that are capped with one molecule of H_2O at each Cu center (Figure 2A). This structure permits formulating the obtained material as $Cu^{2+}_3(\mathbf{1}\text{-}3H^+)_2(H_2O)_3$. Six $Cu_2(COO)_4$ clusters are connected by four linkers **1** (Figure 2B) to form a small octahedral 23.7 Å-wide cage with four open 13.3 Å equilateral triangular faces (Figure 2C). Eight small cages build up a cubic unit cell containing a 33.5 Å-wide large cage with six open 13.3 Å-wide

---

[*] Dr. T.-H. Chen, Dr. I. Popov, Dr. W. Kaveevivitchai,
Prof. A. J. Jacobson, Prof. O. Š. Miljanić
Department of Chemistry
University of Houston
112 Fleming Building, Houston, TX 77204-5003 (USA)
E-mail: miljanic@uh.edu

Dr. Y.-C. Chuang
National Synchrotron Radiation Research Center
Hsinchu, 30076 (Taiwan)

Dr. Y.-S. Chen
Center for Advanced Radiation Source (ChemMatCARS)
The University of Chicago
c/o APS/ANL, 9700 South Cass Drive, Argonne, IL 60439 (USA)

Prof. A. J. Jacobson
Texas Center for Superconductivity
202 UH Science Center, Houston, TX 77204-5002 (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505149.

Table 1: Molecular weight and sorption capacities of guests adsorbed within the pores of MOFF-5.

Guest species	Molecular weight [g mol^{-1}]	100-year GWP (vs. CO_2)^1	Uptake (wt%) under 100% gas flow or vapor[a]	Uptake (moles per mole of Cu)[b] under 100% gas flow or vapor[c]	Uptake (wt%) under 10% gas flow[a]	Uptake (moles per mole of Cu)[b] under 10% gas flow[c]
Propylene	42.08	–	17.60 (17.18)	2.21	0.80 (0.83)	0.10
Propane	44.10	–	17.78 (17.83)	2.13	0.54 (0.52)	0.06
Chloromethane (R-40)	50.49	13	33.52 (34.48)	3.51	2.86 (2.65)	0.30
Isobutylene	56.11	–	73.72 (74.23)	6.94	11.28 (12.05)	1.06
Dichloromethane[d]	84.93	87	129.9 (129.0)	8.08	–	–
Hexane[d]	86.18	–	97.10 (97.40)	5.96	–	–
Tetrafluoromethane	88.00	1400	0.78 (0.67)	0.02	0.24 (0.15)	0.01
Toluene[d]	92.14	–	98.20 (98.22)	5.63	–	–
CF_3CH_2F (R-134a)	102.03	1430	55.22 (56.00)	2.86	14.64 (13.24)	0.76
Dichlorodifluoromethane (R-12)	120.91	10900	80.01 (79.24)	3.50	10.36 (9.57)	0.45
Sulfur hexafluoride	146.06	22800	25.40 (25.00)	0.91	1.28 (1.27)	0.05
CF_3CHFCF_3 (HFC-227ea)	170.03	3220	146.9 (147.0)	4.57	54.10 (53.08)	1.68
$Cl_2FC\text{-}CClF_2$ (CFC-113)[d]	187.38	6130	195.5 (188.9)	5.51	–	–
$CF_3CHFCHCl_2$ (HCFC-225ca)[d]	202.94	122	208.0 (207.6)	5.42	–	–
Perfluorohexane[d]	338.04	9300	224.8 (224.6)	3.51	–	–

[a] Values in parentheses indicate weight adsorption capacities observed in the second attempt. [b] Assuming $[Cu(H_2O)_6]_{1.5}[(Cu_4Cl)_3(\mathbf{2}\text{-}3H^+)_8(H_2O)_{12}]$ as the molecular formula of MOFF-5, each gram of this MOF contains 0.1211 g (1.892 mmol) of Cu, which was used as a basis for the calculation of molar ratios of guests to MOFF-5. [c] Molar values were calculated using weight adsorption data from the first attempt. [d] Liquid, only adsorption of vapor (100%) of the guest carried by N_2 was performed.

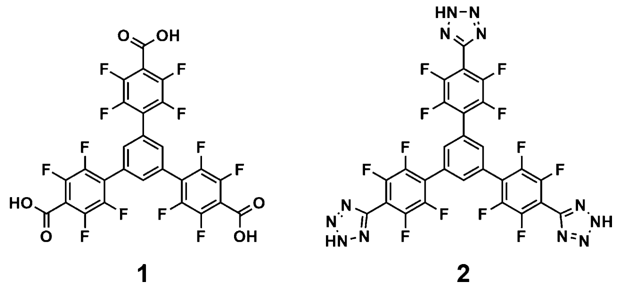

Figure 1. Extensively fluorinated tritopic MOF precursors **1** and **2**.

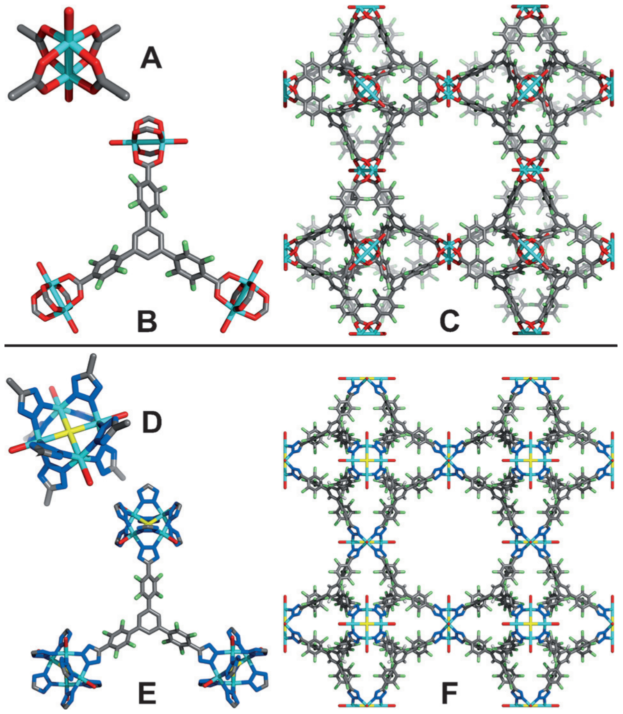

Figure 2. Synchrotron X-ray crystal structures of MOFF-4 (A–C) and MOFF-5 (D–F), formulated as $Cu^{2+}_3(\mathbf{1}\text{-}3H^+)_2(H_2O)_3$ and $[Cu(H_2O)_6]_{1.5}[(Cu_4Cl)_3(\mathbf{2}\text{-}3H^+)_8(H_2O)_{12}]$, respectively. Parts (A) and (D) highlight the metal clusters, (B/E) the structures of organic ligands, and (C/F) overall structures. Hydrogen atoms and disordered $[Cu(H_2O)_6]^{2+}$ ions in MOFF-5 are omitted for clarity. C gray, F lime green, N blue, O red, Cu cyan, Cl yellow.

square faces.[13] The void volume of the material calculated by PLATON is 80%,[14] which is comparable to its non-fluorinated analogue MOF-143.[15]

Tetrazole-based ligand **2** was combined with $CuCl_2{\cdot}2H_2O$ in a mixture of *N*,*N*-diethylformamide (DEF), MeOH, and H_2O. After 7 days at 40°C, green cubic crystals of MOFF-5 were isolated. Single crystal synchrotron diffraction analysis revealed a three-dimensional network (Figure 2F) similar to the non-fluorinated analogous framework reported by Long's group.[16] The structure of MOFF-5 was formulated as $[Cu(H_2O)_6]_{1.5}[(Cu_4Cl)_3(\mathbf{2}\text{-}3H^+)_8(H_2O)_{12}]$. In MOFF-5, a square-planar $[Cu_4Cl]^{7+}$ cluster (Figure 2D) is bridged by eight tetrazolates (Figure 2E) from eight discrete molecules of **2**, and each Cu is additionally coordinated by one H_2O molecule. Six $[Cu_4Cl]^{7+}$ units are connected by eight linkers **2** to form a small truncated octahedral 29.0 Å-wide cavity with ligand **2** on each face. Eight small cages build up a cubic unit containing a 34.1 Å-wide cave with six open 13.6 Å square faces. The anionic charge of the framework appears to be balanced by $[Cu(H_2O)_6]^{2+}$; because of the massive disorder of this ion in the pores, its presence was inferred only indirectly, by elemental composition and thermogravimetric analysis (TGA, see Supporting Information). The void volume of MOFF-5 calculated by PLATON is 75%.[14]

Thermal stabilities of MOFF-4 and MOFF-5 were evaluated using TGA under the stream of N_2 with 2°C min^{-1}

heating rate (Figure S11 and S12). TGA traces are relatively featureless, suggesting that the initial slow loss of coordinated and encapsulated solvent overlaps with the more rapid weight loss caused by framework decomposition occurring at around 220 °C. Overall, the decomposition temperatures for these two MOFFs are lower than those for similar non-fluorinated networks, possibly as a consequence of the weaker metal–ligand coordination owing to the decreased basicity of extensively fluorinated carboxylates and tetrazolates (relative to their non-fluorinated counterparts).

The gas adsorption measurements on mesoporous frameworks MOFF-4 and MOFF-5 were performed after the activation of materials by supercritical carbon dioxide (SCD) drying (as classical thermal activation methods led to decomposition). Despite extensive attempts to optimize activation methods, MOFF-4 lost its crystallinity and porosity under all conditions: its measured Brunauer–Emmett–Teller (BET) surface area was only 510 $m^2 g^{-1}$ (Figure S15) after activation, implying a structural collapse and hindering further studies. In contrast, MOFF-5 maintained its crystallinity (Figure S14), and the N_2 sorption isotherm (measured at 77 K, Figure 3) displays a stepwise adsorption profile attributed to the hierarchical pore sizes, with the total N_2 uptake reaching 884 $cm^3 g^{-1}$. The BET surface area of MOFF-5 was determined as 2445 $m^2 g^{-1}$, the highest among fluorinated porous materials reported to date. MOFF-5 proved stable to common organic solvents (EtOH, MeOH, DMF, toluene, EtOAc, acetone), but unstable to water and moist air.

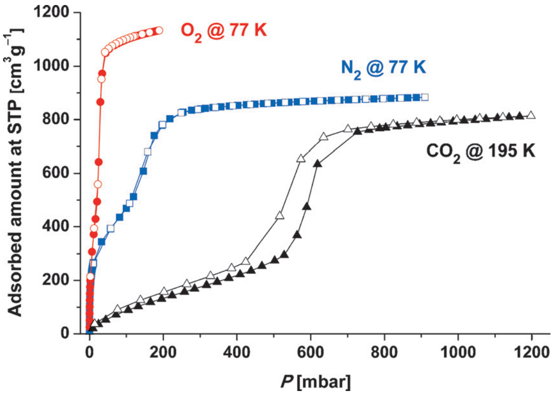

Figure 3. Gas sorption isotherms of MOFF-5. Adsorption: filled symbols; desorption: empty symbols.

The O_2 (77 K) sorption also shows a stepwise isotherm but higher uptake of 1133 $cm^3 g^{-1}$. The amounts of CO_2 adsorbed at 195 K and 297 K (Figure S19) under 1200 mbar were 814 and 27 $cm^3 g^{-1}$, respectively. It is noteworthy that both CO_2 sorption isotherms show a hysteresis; this phenomenon was also observed recently in fluorinated porous molecular crystals,[7] but is much more pronounced in MOFF-5. Hysteretic sorption of CO_2 is relatively rare in MOFs and mostly occurs within flexible networks;[17] the S-shaped CO_2 sorption isotherm—without hysteresis—is more common.[18] Enhancement of CO_2 adsorption in fluorinated MOFs at low P/P_0—caused by the polar C–F bonds—was previously predicted,[19] but has not been observed in MOFF-5. Total pore volume at P/P_0 was determined to be 1.37 $cm^3 g^{-1}$, resulting in the adsorption-based void volume of 65 %, which agrees reasonably well with the value of 75 % derived from the crystal structure data.

Adsorption of hydrocarbon, fluorocarbon, and chlorofluorocarbon (CFC) guests within the pores of MOFF-5 was monitored by TGA (see Figure S21 and S22 for schematic setup).[20] A typical result is illustrated in Figure 4 for perfluorohexane (C_6F_{14}). Crystals of MOFF-5 activated by the SCD drying method were placed into the thermogravimetric balance and the temperature was kept at 25 °C.[21] For gaseous species, the flow of pure N_2 was switched between 100 % or 10 % guests/N_2 (v/v) controlled by a flowmeter. For liquid species, the flow of carrier gas was switched from pure N_2 to N_2 that was allowed to pass over a reservoir containing the liquid guest of interest. Using this methodology, we were able to determine uptake capacities for several hydrocarbon and halogenated hydrocarbon guests shown in Table 1. At room temperature, all of the examined guests can be removed completely and within minutes from the pores of MOFF-5 if vacuum is applied; this removal occurs without loss of capacity. The halogenated guests in Table 1 are of particular interest because of their high GWPs, which are hundreds to thousands of times more severe than that of CO_2.[22] Taking perfluorohexane as an example (Figure 4), MOFF-5 adsorbs approximately 225 wt % of this analyte within seconds of being exposed to it.[23] From Table 1, MOFF-5 exhibits high sorption capacities for a number of other hydrocarbons, fluorocarbons, and CFCs. Two apparent preferences are of note: a) smaller guests (propane, propylene) are adsorbed at lower molar ratios than larger ones (hexane, isobutylene), and b) roughly spherical molecules (CF_4, SF_6) without a dipole moment are adsorbed at very low levels. The latter result indicates an opposite trend to the studies on fluorocarbon sorption in MOFs with exposed metal sites as adsorbents.[8,24] The fact that MOFF-5 “dislikes” hydrocarbons and spherical

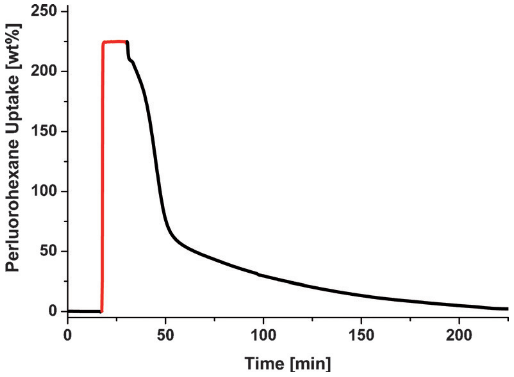

Figure 4. Uptake of perfluorohexane (C_6F_{14}) in crystals of MOFF-5, as a function of time. Crystals of MOFF-5 take up 225 % of their weight in the vapor of perfluorohexane at 25 °C. Black lines indicate the parts of the program when MOFF-5 was exposed only to N_2 stream, while red line describes the section of the program when N_2 carrying C_6F_{14} vapor was passed over MOFF-5.

fluorinated molecules could tentatively be rationalized by the low polarities of these guests, mismatched with the highly polarized environment inside fluorinated cavities; however, there is no overall correlation between dipole moments of guests and their adsorption capacities within MOFF-5. Even at 10% guest/N_2 flow, MOFF-5 is able to capture guest molecules.

In conclusion, we have synthesized two novel fluorinated aromatic tritopic linkers and demonstrated that they can be used to construct two mesoporous MOFs. Among these, MOFF-5—assembled from a trigonal tetrazolate ligand and Cu^{2+}—represents the most porous fluorinated MOF synthesized to date; this high porosity translates into exceptionally high uptake capacities for fluorocarbons and CFCs. This mesoporous material shows unique CO_2 sorption isotherms and preference for non-spherical guest molecules. With a synthetic pathway to highly porous fluorinated MOFs now open, we expect that exploration and understanding of their adsorption properties will increase. These promise to be distinctive, because of the highly polarized and fluorophilic pore surfaces and electron-deficient nature of aromatic nuclei.

Acknowledgements

We acknowledge the financial support from the University of Houston and its Grant to Advance and Enhance Research (to O.Š.M.), the National Science Foundation (award DMR-1507664 to O.Š.M.), and the Welch Foundation (awards E-0024 to A.J.J. and E-1768 to O.Š.M.). O.Š.M. is a Cottrell Scholar of the Research Corporation for Science Advancement. ChemMatCARS Sector 15 is principally supported by the National Science Foundation under grant number CHE-1346572. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Parts of this manuscript were written at New York University Abu Dhabi (NYUAD), where O.Š.M. was on a sabbatical stay.

Keywords: adsorption · C−H activation · chlorofluorocarbons · fluorocarbons · metal–organic frameworks

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13902–13906
Angew. Chem. **2015**, *127*, 14108–14112

---

[1] IPCC Fourth Assessment Report, Climate Change 2007: Net Global Radiative Forcing, Global Warming Potentials and Patterns of Forcing. http://www.ipcc.ch/publications_and_data/ar4/wg1/en/tssts-2-5.html.

[2] P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**.

[3] *United Nations Environment Programme Ozone Secretariat.* See: http://ozone.unep.org/new_site/en/montreal_protocol.php.

[4] J. C. Laube, M. J. Newland, C. Hogan, C. A. M. Brenninkmeijer, P. J. Fraser, P. Martinerie, D. E. Oram, C. E. Reeves, T. Röckmann, J. Schwander, E. Witrant, W. T. Sturges, *Nat. Geosci.* **2014**, *7*, 266–269.

[5] Y. Koda, T. Terashima, M. Sawamoto, *J. Am. Chem. Soc.* **2014**, *136*, 15742–15748.

[6] H. Takezawa, T. Murase, G. Resnati, P. Metrangolo, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 1786–1788.

[7] T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, O. Daugulis, A. J. Jacobson, O. Š. Miljanić, *Nat. Commun.* **2014**, *5*, 5131–5138.

[8] a) I. Senkovska, E. Barea, J. A. Rodríguez Navarro, S. Kaskel, *Microporous Mesoporous Mater.* **2012**, *156*, 115–120; b) R. K. Motkuri, H. V. R. Annapureddy, M. Vijaykumar, H. T. Schaef, P. F. Martin, B. P. McGrail, L. X. Dang, R. Krishna, P. K. Thallapally, *Nat. Commun.* **2014**, *5*, 4368–4373.

[9] For recent examples, see: a) 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*, 80–84; b) N. Nijem, P. Canepa, U. Kaipa, K. Tan, K. Roodenko, S. Tekarli, J. Halbert, I. W. H. Oswald, R. K. Arvapally, C. Yang, T. Thonhauser, M. A. Omary, Y. J. Chabal, *J. Am. Chem. Soc.* **2013**, *135*, 12615–12626; c) C. Yang, U. Kaipa, Q. Z. Mather, X. Wang, V. Nesterov, A. F. Venero, M. A. Omary, *J. Am. Chem. Soc.* **2011**, *133*, 18094–18097; d) C. Yang, X. Wang, M. A. Omary, *Angew. Chem. Int. Ed.* **2009**, *48*, 2500–2505; *Angew. Chem.* **2009**, *121*, 2538–2543; e) C. Yang, X. Wang, M. A. Omary, *J. Am. Chem. Soc.* **2007**, *129*, 15454–15455.

[10] a) H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2011**, *133*, 13577–13586; b) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074–1086; c) H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128–1129; d) H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 15185–15192.

[11] T.-H. Chen, I. Popov, O. Zenasni, O. Daugulis, O. Š. Miljanić, *Chem. Commun.* **2013**, *49*, 6846–6848.

[12] CCDC 1034688 (MOFF-4) and 1034689 (MOFF-5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[13] Dimensions of small (23.7 Å) and big (33.5 Å) cages were defined as the diagonal distances of two Cu atoms from two distinct paddlewheel clusters. The edge length of the virtually triangular windows (13.3 Å) is defined as the distance between two O atoms (from Cu-coordinated H_2O molecules) in two adjacent paddlewheel clusters. Similar analysis also applies to dimensions of MOFF-5 in this manuscript.

[14] PLATON (C) 1980–2011 A. L. Spek, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands.

[15] H. Furukawa, Y. B. Go, N. Ko, Y. K. Park, F. J. Uribe-Romo, J. Kim, M. O'Keeffe, O. M. Yaghi, *Inorg. Chem.* **2011**, *50*, 9147–9152.

[16] a) M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown, J. R. Long, *Angew. Chem. Int. Ed.* **2007**, *46*, 1419–1422; *Angew. Chem.* **2007**, *119*, 1441–1444; b) M. Dincă, A. Dailly, C. Tsay, J. R. Long, *Inorg. Chem.* **2008**, *47*, 11–13.

[17] a) S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake, M. Schröder, *Nat. Mater.* **2012**, *11*, 710–716; b) K. L. Mulfort, O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, J. T. Hupp, *Chem. Eur. J.* **2010**, *16*, 276–280; c) Y. Inubushi, S. Horike, T. Fukushima, G. Akiyama, R. Matsuda, S. Kitagawa, *Chem. Commun.* **2010**, *46*, 9229–9231; d) C. Li, W. Qiu, W. Shi, H. Song, G. Bai, H. He, J. Lia, M. J. Zaworotko, *CrystEngComm* **2012**, *14*, 1929–1932; e) J. Wang, J. Luo, J. Zhao, D.-S. Li, G. Li, Q. Huo, Y. Liu, *Cryst. Growth Des.* **2014**, *14*, 2375–2380; f) I. H. Hwang, J. M. Bae, Y.-K. Hwang, H.-Y. Kim, C. Kim, S. Huh, S.-J. Kim, Y. Kim, *Dalton Trans.* **2013**, *42*, 15645–15649; g) J. T. Culp, M. R. Smith, E. Bittner, B. Bockrath, *J. Am. Chem. Soc.* **2008**, *130*, 12427–12434; h) T.-H. Chen, I. Popov, Y.-C. Chuang, Y.-S. Chen, O. Š. Miljanić, *Chem. Commun.* **2015**, *51*, 6340–6342.

[18] a) K. S. Walton, A. R. Millward, D. Dubbeldam, H. Frost, J. J. Low, O. M. Yaghi, R. Q. Snurr, *J. Am. Chem. Soc.* **2008**, *130*,

406–407; b) A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998–17999.

[19] C. E. Wilmer, O. K. Farha, Y.-S. Bae, J. T. Hupp, R. Q. Snurr, *Energy Environ. Sci.* **2012**, *5*, 9849–9856.

[20] a) X. Wang, L. Liu, A. J. Jacobson, *Angew. Chem. Int. Ed.* **2006**, *45*, 6499–6503; *Angew. Chem.* **2006**, *118*, 6649–6653; b) L. Liu, X. Wang, A. J. Jacobson, *J. Mater. Res.* **2009**, *24*, 1901–1905.

[21] The crystals of MOFF-5 were activated at low temperature to focus on interactions between fluorinated ligands and guests, and to exclude the effects of exposed metal sites—which would have likely formed if high-temperature activation was used. Approximate size of crystals used was 0.1 × 0.1 × 0.05 mm.

[22] V. W. Bhatkar, V. M. Kriplani, G. K. AwariInt, *J. Environ. Sci. Technol.* **2013**, *10*, 871–880.

[23] This amount is approximately three-times greater than that adsorbed within the pores of an extensively fluorinated non-covalent framework reported in Ref. [7].

[24] K. C. Kim, C. Y. Lee, D. Fairen-Jimenez, S. T. Nguyen, J. T. Hupp, R. Q. Snurr, *J. Phys. Chem. C* **2014**, *118*, 9086–9092.

Received: June 5, 2015