# Superhydrophobic perfluorinated metal-organic frameworks

Teng-Hao Chen, Ilya Popov,* Oussama Zenasni, Olafs Daugulis and Ognjen Š. Miljanić*
University of Houston ▪ Department of Chemistry
136 Fleming Building ▪ Houston, TX 77204-5003 ▪ USA
email: ilja.popovs@gmail.com; miljanic@uh.edu ▪ phone: 832.842.8827

## Supporting Information

### Table of Contents

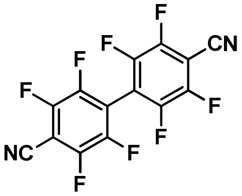
## Section S1. General Considerations and Materials

**General Considerations.** Schlenk flasks or vials with PTFE/Liner caps were used as reaction vessels for the synthesis of precursors, while standard scintillation vials were used as vessels for the synthesis of MOFFs. Solvents THF, $Et_2O$ and pentane were dried over activated alumina in an mBraun solvent purification system. Flash chromatography was performed on 60 Å silica gel (Sorbent Technologies). GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m×0.25 mm I.D.). The $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on JEOL ECA-500 or ECX-400P spectrometers using the peaks of TMS or residual solvent as standards. Trifluorotoluene ($PhCF_3$, $\delta = -63.72$ ppm) was used as the internal standard in $^{19}F$ NMR spectra. Melting points were measured in a Barnstead International Mel-TEMP® apparatus and are uncorrected. Analytical thin layer chromatography was performed on Fluka silica gel/TLC plates with a fluorescent indicator that emitted when irradiated at 254 nm. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer using Pike MIRacle Micrometer pressure clamp. Microanalyses were conducted by Intertek USA, Inc. Thermogravimetric analyses (TGA) were carried out on a TA Instruments TGA 2050 thermogravimetric analyzer at a temperature ramping rate of 2 °C/min under the flow of $N_2$ gas. Powder X-ray diffraction (PXRD) data were collected at 25 °C on a Phillips X'pert Pro diffractometer. Simulated PXRD patterns were calculated with the Material Studio software package[1] employing the structure model from the obtained single crystal data.

**Materials**. The following starting materials and solvents were obtained from the respective commercial sources and used without further purification: $ZnCl_2$ (Alfa Aesar); dioxane, $K_3PO_4$, CuI and phenanthroline (Acros); 2,3,5,6-tetrafluorobenzonitrile and $NaN_3$ (TCI America); triflic acid (SynQuest Labs); *n*-hexadecane, cis–perfluorodecalin and $CuCl_2$ (Aldrich); $Cu(NO_3)_2 \cdot 2.5H_2O$ and $CuCl_2 \cdot 2H_2O$ (JT Baker); water (Milli-Q, deionized). Compound 2,3,5,6-tetrafluoro-4-iodo-benzonitrile[2] was prepared from 2,3,5,6-tetrafluorobenzonitrile by reaction with *t*-BuOLi and iodine.[3] All the solvents for synthesizing MOFFs were obtained from commercial sources and used without further purification. Polished Silicon (100) wafers were purchased from Silicon Inc. and rinsed with absolute EtOH (Aaper Alcohol and Chemical Co) before use.

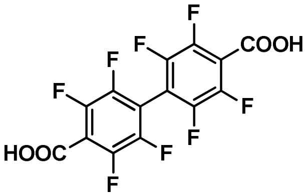
*Experiments are presented in the order following the discussion of the manuscript. Compound numbers are identical to those in the main text of the manuscript.*

## Section S2. Synthesis of the Starting Materials



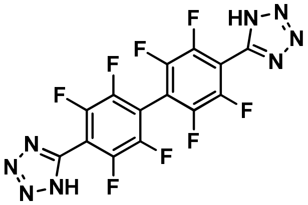
2,2',3,3',5,5',6,6'-Octafluorobiphenyl-4,4'-dicarbonitrile (**2**)

A 40 mL scintillation vial was equipped with a magnetic stirbar and charged with 2,3,5,6-tetrafluorobenzonitrile (2.27 g, 13.0 mmol) and 2,3,5,6-tetrafluoro-4-iodo-benzonitrile (3.01 g, 10.0 mmol). Vial was purged with $N_2$ and placed inside a nitrogen-filled glovebox. Phenanthroline (0.90 g, 5.00 mmol) and CuI (0.95 g, 5.00 mmol) were added, followed by $K_3PO_4$ (6.40 g, 30.0 mmol) and dioxane (12 mL). Vial was capped and taken out of the glovebox. Reaction mixture was stirred for 2 min at 25 °C and then placed inside an aluminum reaction block preheated to 125 °C, where it was stirred vigorously for 12 h. Reaction mixture was cooled to 25 °C, diluted with $CH_2Cl_2$ (50 mL) and filtered through the plug of Celite to remove the inorganic salts. Filter cake was washed with additional $CH_2Cl_2$ (3×25 mL). Resulting organic phases were combined and dry-absorbed on silica gel. After purification by column chromatography on silica gel using $CH_2Cl_2$ / hexanes (gradient 10 % to 50% of $CH_2Cl_2$) as eluent and evaporation of the fractions containing the product, title compound was obtained as a white crystalline solid (2.30 g, 66 %). $R_f = 0.27$ ($SiO_2$, hexanes/EtOAc 19/1), mp 124–127 °C (hexanes/$CH_2Cl_2$). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 148.5–148.2 and 146.4–146.1 (m, 4C), 145.0–144.8 and 143.1–142.8 (m, 4C), 111.9–111.5 (m, 2C), 106.6–106.4 (m, 2C), 97.3–97.1 (m, 2C) ppm. $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ –134.4 to –134.7 (m, 4F), –138.0 to –138.2 (m, 4F) ppm. FT-IR (neat): $\tilde{\nu}$ 2249, 1729, 1484, 1289, 1267, 1005, 991, 975 $cm^{-1}$. ESI MS m/z: 348 (100 %), 279 (24 %), 349 (16 %), 174 (15 %), 248 (7 %).



2,2',3,3',5,5',6,6'-Octafluorobiphenyl-4,4'-dicarboxylic acid (**3**)

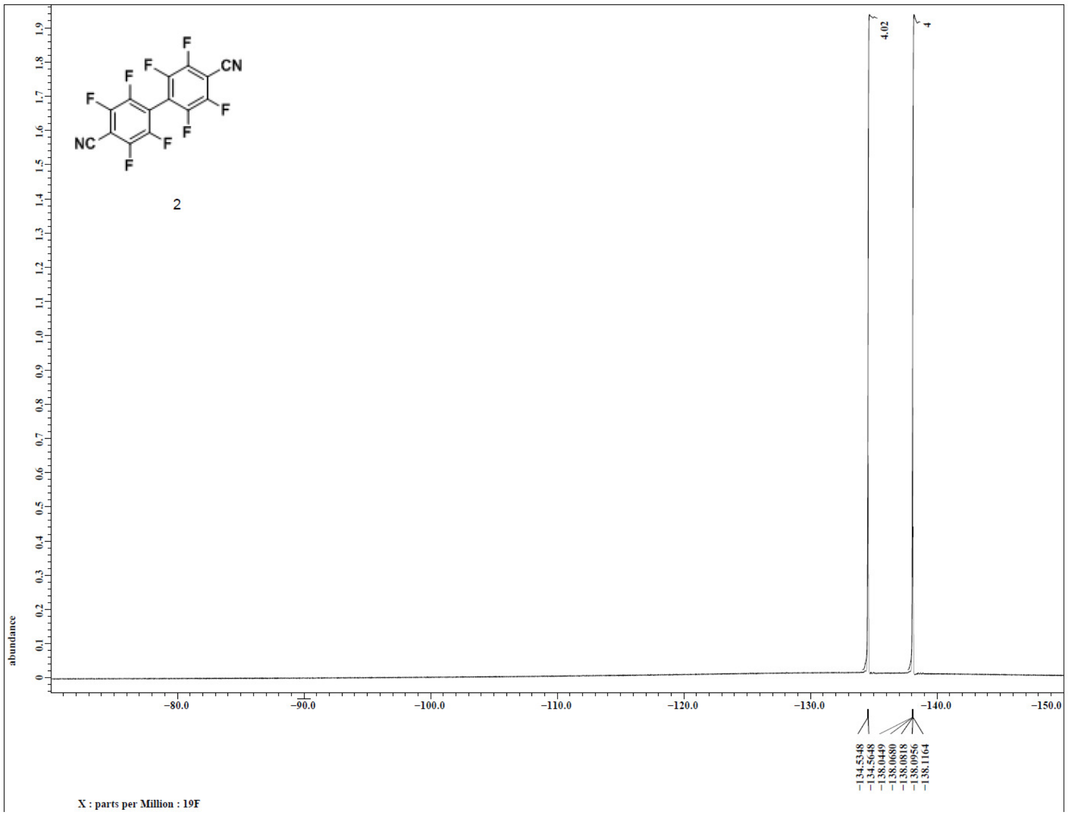
A 120 mL glass pressure vessel was equipped with a magnetic stirbar and charged with dinitrile **2** (3.56 g, 10.0 mmol) followed by trifluoroacetic acid (15 mL) and triflic acid (13.2 g, 88.0 mmol). Reaction mixture was stirred until all solids completely dissolved. Deionized $H_2O$ (7 mL) was carefully added, causing a **highly exothermic reaction (CAUTION!)**. This glass vessel was capped and placed inside an oil bath preheated to 130 °C, and the reaction mixture was vigorously stirred at this temperature for 48 h. After completion, reaction mixture was cooled to 25 °C and diluted with 1M HCl (100 mL) causing the precipitation of the reaction product. White solid was filtered off and washed with additional 1M HCl (2×50 mL) followed by $H_2O$ (20 mL). Solid was dried under high vacuum for 24 h over $P_2O_5$ affording the title compound (3.70 g, 96 %) as a white solid, mp 310–312 °C (dec). $^1H$ NMR (500 MHz, DMSO-$d_6$) $\delta$ 14.5 (br s, 2H) ppm. $^{19}F$ NMR (470 MHz, DMSO-$d_6$) $\delta$ −136.7 to −137.9 (m, 4F), −140.4 to −140.6 (m, 4F) ppm. FT-IR (neat): $\tilde{\nu}$ 1719, 1477, 1418, 1307 1262, 1231, 1004, 981 $cm^{-1}$.

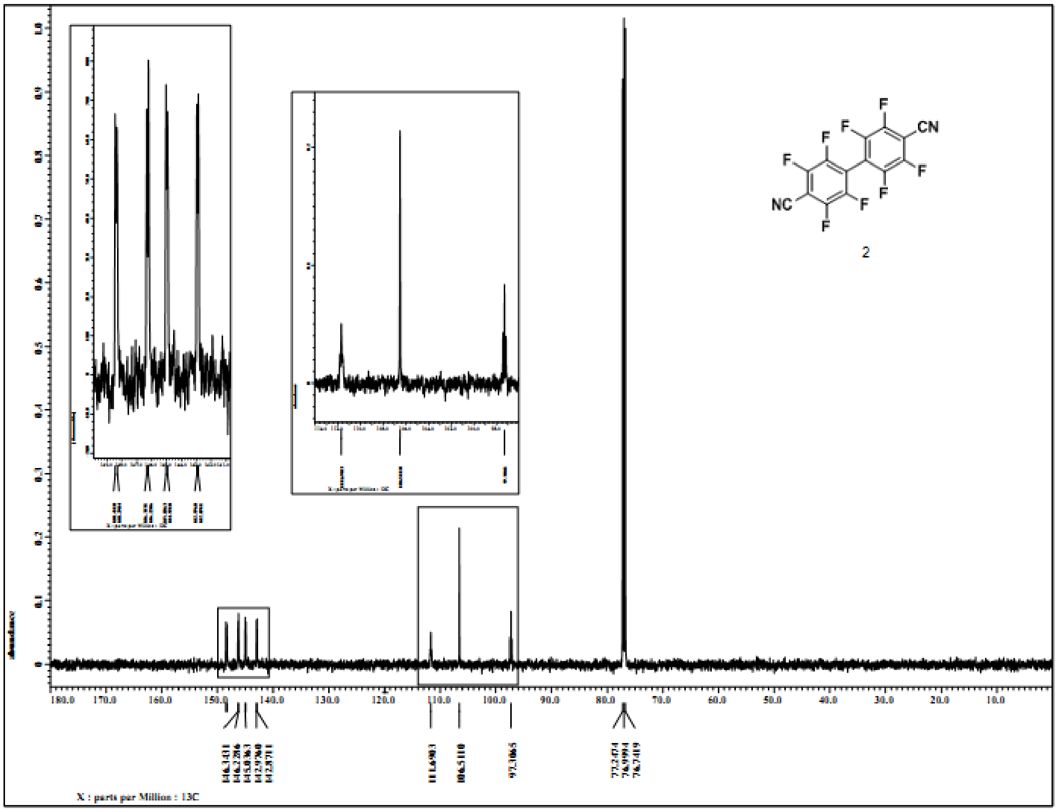


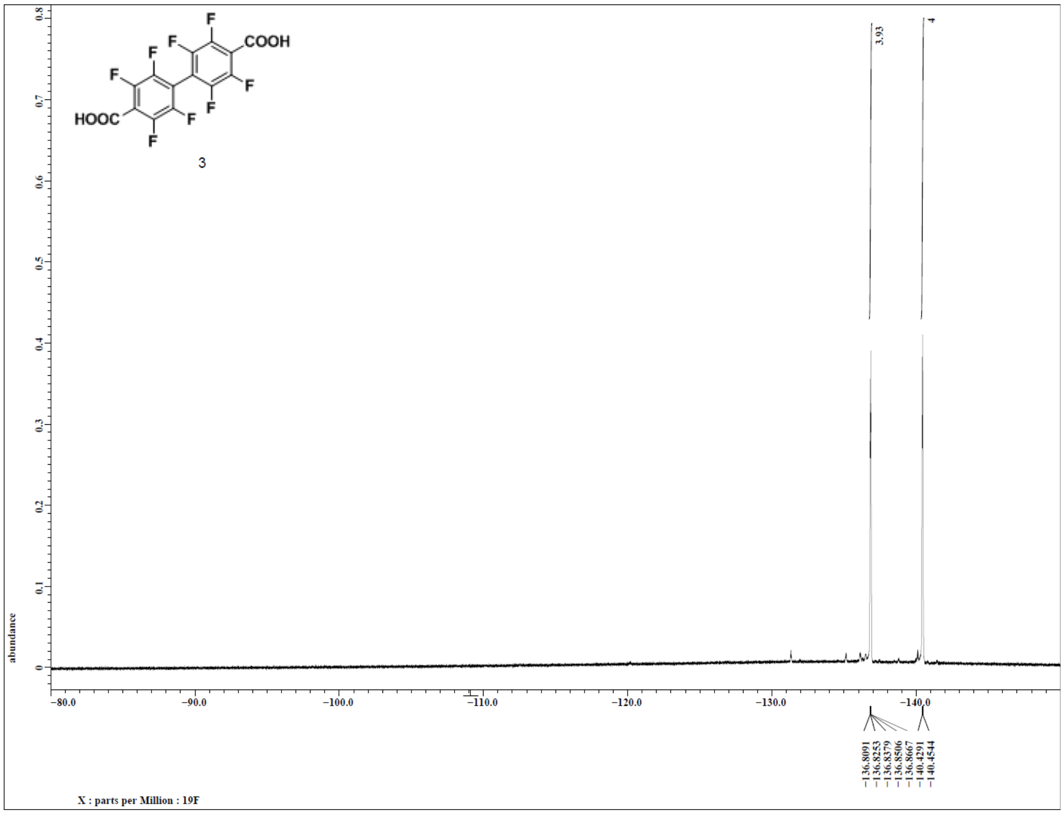
5,5'-(Perfluorobiphenyl-4,4'-diyl)bis(1*H*-tetrazole) (**4**)

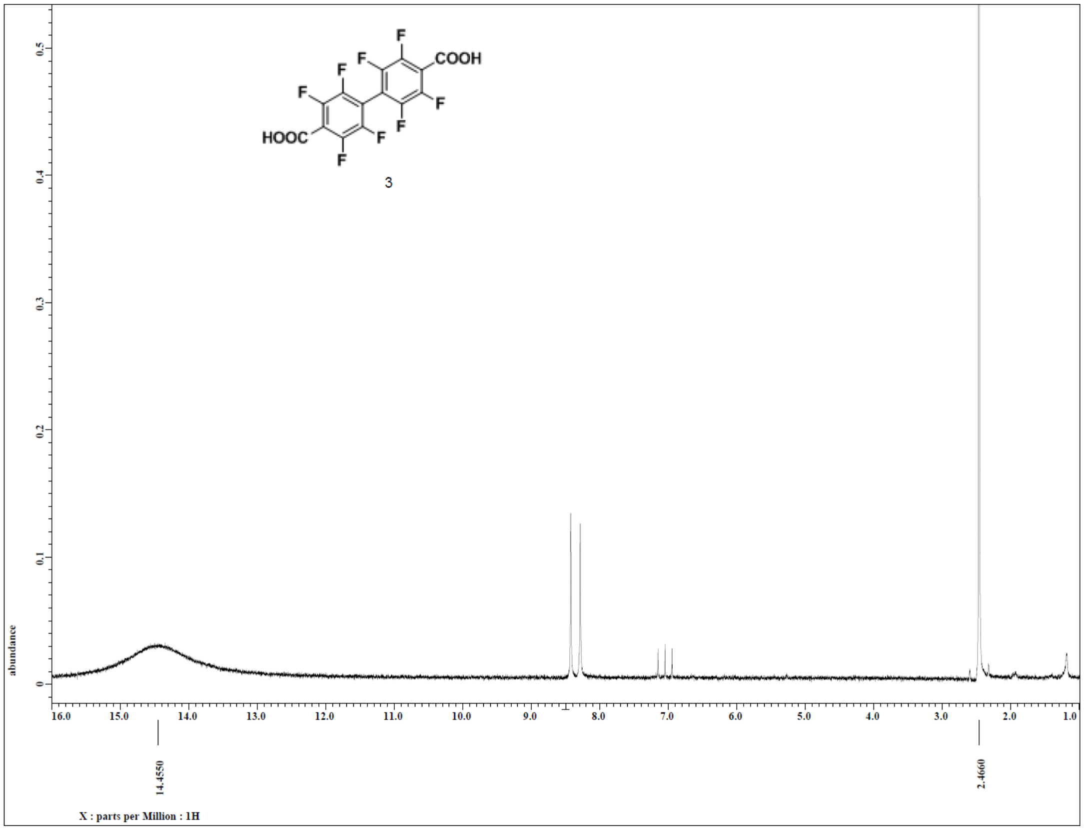
A 120 mL glass pressure vessel was equipped with a magnetic stirbar and charged with $ZnCl_2$ (6.00 g, 44 mmol) and $NaN_3$ followed by deionized $H_2O$ (7 mL). Mixture was stirred until all inorganic salts dissolved. Glacial acetic acid (35 mL) was added, followed by dinitrile **2** (1.40 g, 4.00 mmol) and additional acetic acid (7 mL). Pressure vessel was capped and placed in an oil bath preheated to 105 °C. Reaction mixture was vigorously stirred at that temperature for 24 h. After completion, reaction mixture was cooled to 25 °C and poured into a 1M aqueous solution of HCl (200 mL), causing the precipitation of the product. White solid was filtered and washed with additional 1M HCl (2×50 mL), followed by $H_2O$ (20 mL). Solid was dried under high vacuum for 24 h over $P_2O_5$, affording the title compound (1.74 g, 94 %) as a white solid, mp 260–263 °C (dec). $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 147.8 (s, 2C), 145.3–144.7 (m, 4C), 143.3–142.8 (m, 4C), 109.4–109.0 (m, 2C), 108.2–107.6 (m, 2C) ppm. $^{19}$F NMR (470 MHz, DMSO-$d_6$) $\delta$ −137.1 to −137.3 (m, 4F), −137.3 to −137.4 (m, 4F) ppm. FT-IR (neat): $\tilde{\nu}$ 3459, 1571, 1500, 1475, 1372, 1303, 1242, 1122, 1053, 999, 973 cm$^{-1}$.

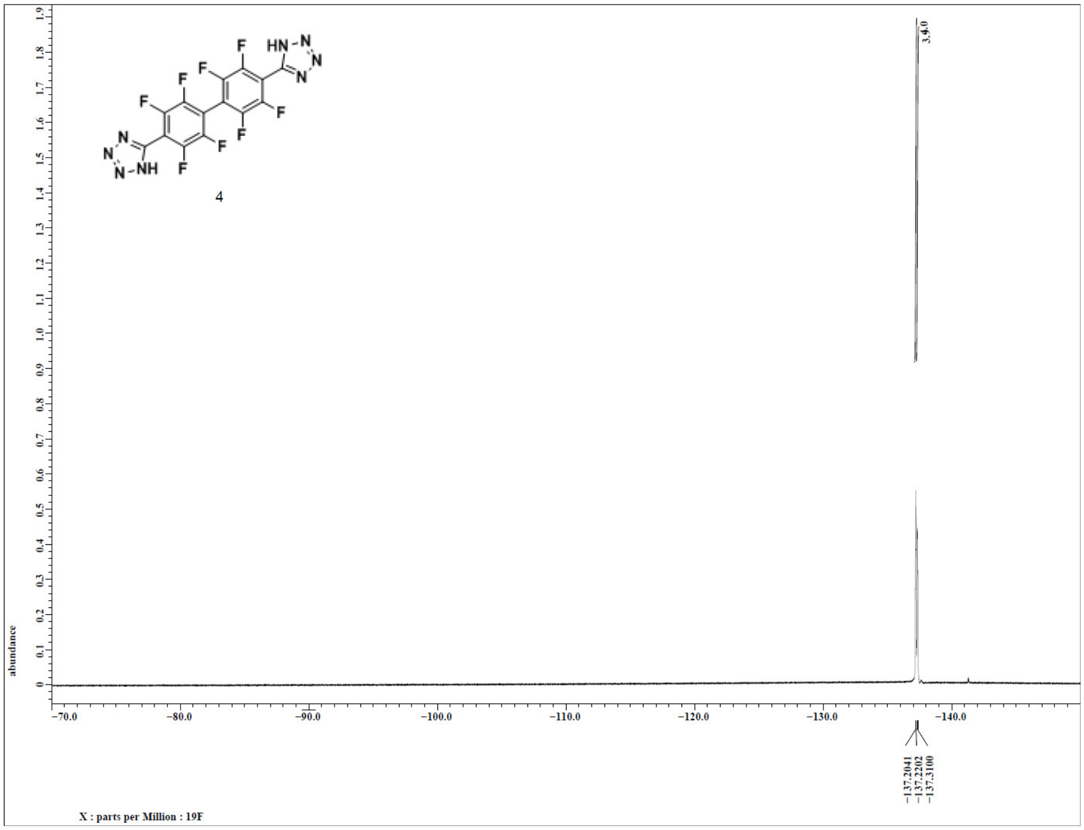
## Section S3. $^{19}$F, $^{1}$H and $^{13}$C NMR Spectra of Starting Materials.

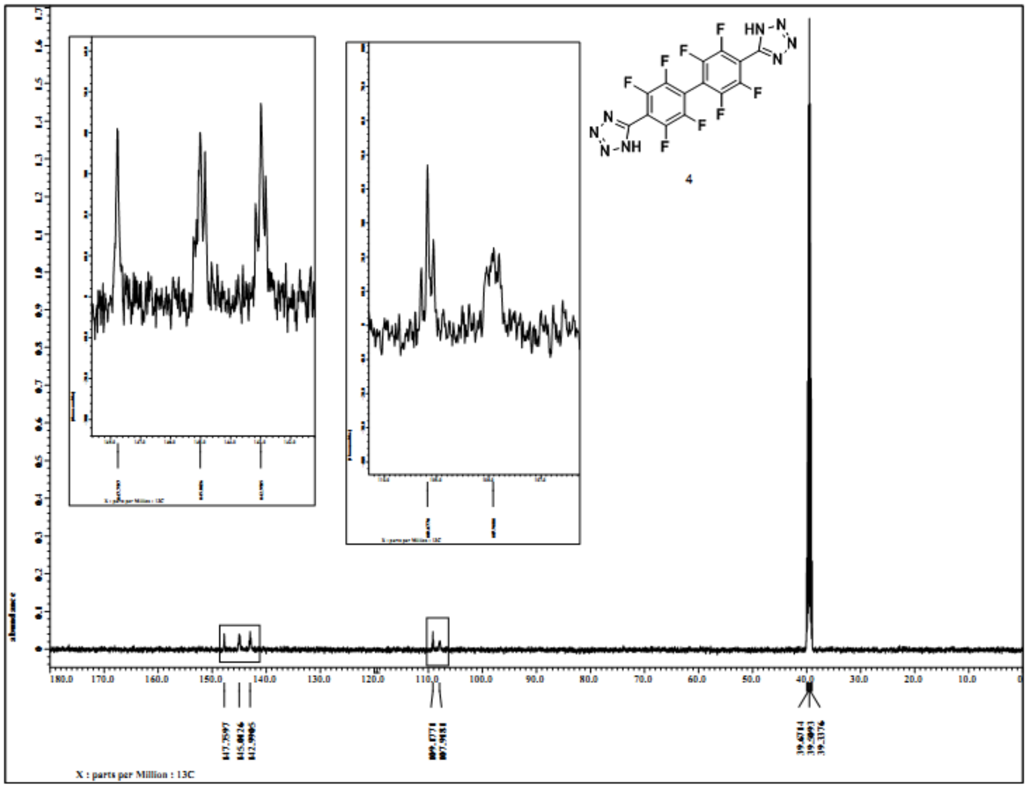





F
F
COOH
F
F
HOOC
F
F
F
3
3.93
4
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
−80.0
−90.0
−100.0
−110.0
−120.0
−130.0
−140.0
−136.8091
−136.8253
−136.8379
−136.8506
−136.8667
−140.4291
−140.4544
X : parts per Million : 19F


F
F
COOH
F
F
HOOC
F
F
F
3
abundance
0
0.1
0.2
0.3
0.4
0.5
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
14.4550
2.4660
X : parts per Million : 1H


4
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
3.4.0
−70.0
−80.0
−90.0
−100.0
−110.0
−120.0
−130.0
−140.0
−137.2041
−137.2202
−137.3100
X : parts per Million : 19F


4
abundance
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
147.7597
145.0126
142.9905
109.1771
107.9851
39.6714
39.5093
39.3376
X : parts per Million : 13C

## Section S4. Synthesis of MOFFs

### Synthesis of **MOFF-1**, $CuC_{15}O_5F_8H_4$

Ligand **3** (30.0 mg, 0.077 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (18.0 mg, 0.077 mmol) were added to a 20 mL glass scintillation vial. Solvents DMF (0.3 mL), MeOH (5.4 mL) and $H_2O$ (0.3 mL) were added to the solids, and the mixture was sonicated until dissolved. The vial was capped and placed into an oven at 40 °C for 4 d. The resulting greenish crystals were washed with MeOH and dried under reduced pressure. Yield calculated from the evacuated sample was 80 % based on Cu. FT-IR (neat): $\tilde{\nu}$ = 1605 (s), 1460 (s), 1384 (s), 1269 (w), 1005 (m), 978 (s), 811 (m), 774 (m), 720 (s) $cm^{-1}$. Anal. calcd (%) for $C_{28}F_{16}O_8Cu_2$: C 37.54; Found: C 37.06.

Crystals of **MOFF-1** are stable in THF, MeOH, $CH_2Cl_2$, DMF, toluene, DMSO, acetone and ether. They are rapidly decomposed in $H_2O$, 2M HCl, 10% $H_2SO_4$, 2M NaOH, and 10% KOH, as well as in EtOH.

### Synthesis of **MOFF-2**, $CuC_{17}O_4NF_8H_6$

Ligand **3** (75.0 mg, 0.19 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO, 11.0 mg, 0.098 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (45.0 mg, 0.19 mmol) were added to a 20 mL glass scintillation vial. Solvents DMF (1 mL), MeOH (6 mL) and $H_2O$ (0.3 mL) were added to the solids, and the mixture was sonicated until dissolved. The vial was capped and placed into an oven at 60 °C for 2 d. The resulting green crystals were washed with MeOH and dried under reduced pressure. Yield calculated from evacuated sample was 77 % based on Cu. FT-IR (neat): $\tilde{\nu}$ = 1663 (s), 1630 (m), 1472 (s), 1408 (s), 999 (m), 980 (s), 802 (w), 774 (s), 720 (s) $cm^{-1}$. Anal. calcd (%) for $C_{34}H_{12}N_2F_{16}O_8Cu_2$: C 40.51, H 1.20, N 2.78; Found: C 40.56, H 0.98, N 2.85.

Crystals of **MOFF-2** are stable in THF, MeOH, EtOH, $CH_2Cl_2$, DMF, toluene, DMSO, acetone and ether. They are rapidly decomposed in $H_2O$, 2M HCl, 10% $H_2SO_4$, 2M NaOH, and 10% KOH.

### Synthesis of **MOFF-3**, $CuC_{14}ON_8F_8H_2$

Ligand **4** (50.0 mg, 0.12 mmol) and $CuCl_2 \cdot 2H_2O$ (20.0 mg, 0.12 mmol) were added to a 20 mL glass scintillation vial. Solvent DMF (5 ml) was added to the solids, and the mixture was sonicated until dissolved. The vial was capped and placed into an oven at 70 °C for 4 d. The resulting blue crystals were washed with DMF. The activated crystals were obtained by heating them in a 120 °C oven for 1 d under reduced pressure. Yield calculated from evacuated sample was 26 % based on Cu. FT-IR (neat): $\tilde{\nu}$ = 1642 (s), 1493 (m), 1469 (s), 1420 (w), 1387 (w), 1266 (w), 1108 (s), 999 (s), 971 (s), 874 (s), 725 (s) $cm^{-1}$. Anal. calcd (%) for $C_{14}N_8F_8Cu$: C 33.88, N 22.60; Found: C 34.80, N 21.75.

Crystals of **MOFF-3** are stable in $H_2O$, as well as in THF, MeOH, EtOH, $CH_2Cl_2$, DMF, toluene, DMSO, acetone and ether. They are rapidly decomposed in 2M HCl, 10% $H_2SO_4$, 2M NaOH, and 10% KOH.

## Section S5. X-ray Crystallographic Analysis of MOFFs

### Crystal Data for **MOFF-1**

A blue plate 0.10×0.10×0.04 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 40 mm and exposure time was 10 s per frame using a scan width of 0.5 °. Data collection was 99.8% complete to 25.00 ° in $\theta$. A total of 27288 reflections were collected covering the indices, $-20<=h<=20$, $-18<=k<=18$, $-18<=l<=19$. 6865 reflections were found to be symmetry independent, with an $R_{\text{int}}$ of 0.0272. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2/c$ (No. 13). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2011) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Crystallographic twofold symmetry was imposed on the structure during the refinement.

| | | |
|---|---|---|
| Empirical formula | $C_{32}H_{16}Cu_2F_{16}O_{12}$ | |
| Formula weight | 1023.53 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2/c$ | |
| Unit cell dimensions | $a = 16.7149(9)$ Å | $\alpha = 90$ ° |
| | $b = 15.1584(8)$ Å | $\beta = 112.098(2)$ ° |
| | $c = 15.9373(8)$ Å | $\gamma = 90$ ° |
| Volume | 3741.4(3) $Å^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.817 $Mg/m^3$ | |
| Absorption coefficient | 1.278 $mm^{-1}$ | |

| | |
|---|---|
| $F(000)$ | 2024 |
| Crystal size | 0.10×0.10×0.04 $\text{mm}^3$ |
| $\theta$ range for data collection | 1.31 ° to 25.39 ° |
| Index ranges | $-20 \leq h \leq 20$, $-18 \leq k \leq 18$, $-18 \leq l \leq 19$ |
| Reflections collected | 27288 |
| Independent reflections | 6865 [$R(\text{int}) = 0.0272$] |
| Completeness to $\theta = 25.00$ ° | 99.8 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9507 and 0.8829 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6865 / 0 / 573 |
| Goodness-of-fit on $F^2$ | 1.091 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0394$, $wR_2 = 0.1050$ |
| $R$ indices (all data) | $R_1 = 0.0488$, $wR_2 = 0.1110$ |
| Largest diff. peak and hole | 0.846 and −0.808 $\text{e/Å}^{-3}$ |

Crystal Data for **MOFF-2**

A green prism 0.30×0.25×0.25 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected at 298(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 40 s per frame using a scan width of 0.3 °. Data collection was 99.8 % complete to 25.00 ° in $\theta$. A total of 13682 reflections were collected covering the indices, $-25<=h<=25$, $0<=k<=21$, $0<=l<=10$. 3310 reflections were found to be symmetry independent, with an $R_{\text{int}}$ of 0.0631. Indexing and unit cell refinement indicated a C-centered, monoclinic lattice. The space group was found to be *C*2/c (No. 15). All measurements were made with a Siemens SMART platform diffractometer equipped with a 4K CCD APEX II detector. A hemisphere of data (1271 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30\% in omega and an exposure time of 40 s/frame. The data were integrated using the Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 2215 reflections having *I*>10\s(I), and these, along with other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was shown to be either *C*c or *C*2/c. The data crystal was found to be twinned, consisting of two major domains. A twinned integration was performed on the two separate domains to correct for overlap. Final least squares was done using the independent structure factors measured from each domain, with a normalizing scale factor between them. The asymmetric unit consists of one Cu atom, one fluorinated dicarboxylate ligand, and one-half DABCO molecule situated about a two-fold axis. The dicarboxylate was found to be disordered over two slightly different orientations, and this was treated by use of ideal rigid body refinement. The DABCO was found to be seriously disordered over three different orientations, and this was treated using distance constraints based on literature values. The dicarboxylate ligand was refined anisotropically using restraints to make the U(ij) components approximate isotropic behavior. DABCO was refined isotropically. The final difference density map showed one very large peak of about 4.5 $e^{-}/Å^{3}$ located on the two-fold axis between equivalent Cu atoms, and another smaller but significant peak of about 1.5 $e^{-}/Å^{3}$ between Cu and DABCO. The distance between these peaks is 2.7A, virtually identical to the distance between the refined Cu atom and its two-fold relative. This larger density was included in the final refinement as atom C25X in order to improve the least squares model, however since it does not make chemical sense to belong to the structure it was omitted from all other calcuations. Because the distance between the "ghost peaks" coicides with the observed [Cu···Cu'] separation, they are presumed to be the locations of Cu atoms in very minor third and fourth orientations of the unit cell which could not be identified during twin analysis due to very weak scattering.

| | | |
|---|---|---|
| Empirical formula | $C_{34}H_{12}Cu_2F_{16}N_2O_8$ | |
| Formula weight | 1007.54 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | *C*2/c | |
| Unit cell dimensions | $a$ = 23.065(5) Å | $\alpha$ = 90 ° |
| | $b$ = 19.498(4) Å | $\beta$ = 94.91(3) ° |
| | $c$ = 9.529(2) Å | $\gamma$ = 90 ° |
| Volume | 4269.7(16) $Å^3$ | |
| *Z* | 8 | |
| Density (calculated) | 1.567 $Mg/m^3$ | |
| Absorption coefficient | 1.113 $mm^{-1}$ | |
| *F*(000) | 1984 | |
| Crystal size | 0.30×0.25×0.25 $mm^3$ | |
| $\theta$ range for data collection | 1.37 ° to 23.60 ° | |
| Index ranges | $-25 \le h \le 25$, $0 \le k \le 21$, $0 \le l \le 10$ | |

| | |
|---|---|
| Reflections collected | 13682 |
| Independent reflections | 3310 [$R$(int) = 0.0631] |
| Completeness to $\theta = 25.00$ ° | 99.8 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.7449 and 0.5664 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1752 / 261 / 345 |
| Goodness-of-fit on $F^2$ | 1.030 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0551$, w$R_2 = 0.1586$ |
| $R$ indices (all data) | $R_1 = 0.1031$, w$R_2 = 0.1972$ |
| Largest diff. peak and hole | 0.577 and −0.621 e/Å$^{-3}$ |

Crystal Data for **MOFF-3**

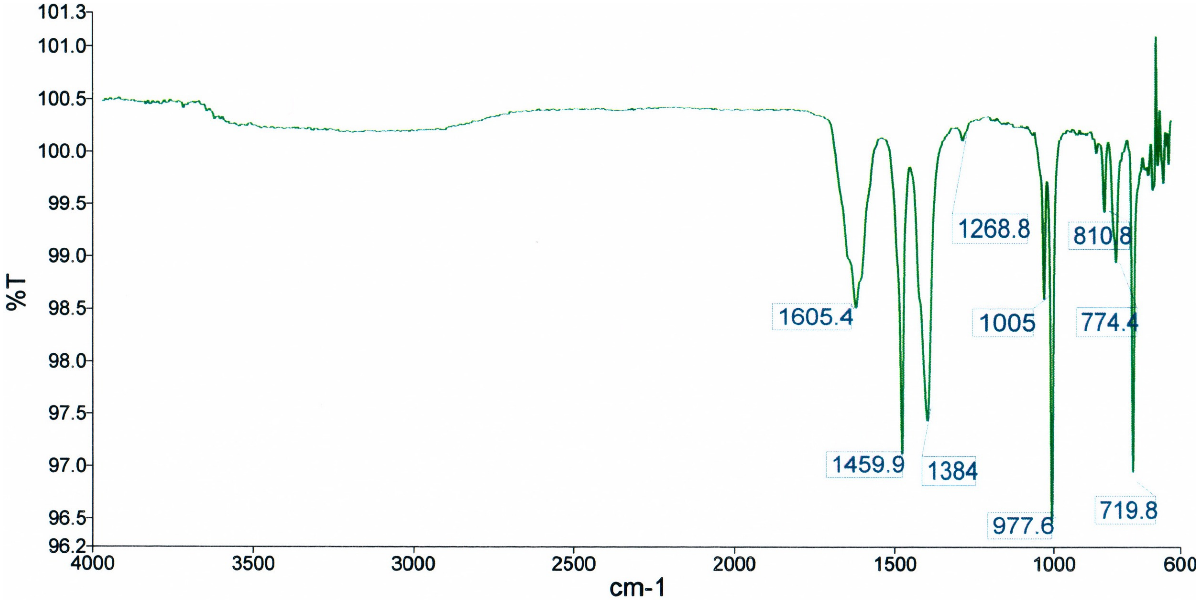
A blue block 0.12×0.06×0.04 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 40 mm and exposure time was 20 s per frame using a scan width of 1.0 °. Data collection was 99.8% complete to 25.00 ° in $\theta$. A total of 37915 reflections were collected covering the indices, $-19<=h<=17$, $-37<=k<=36$, $-15<=l<=16$. 5907 reflections were found to be symmetry independent, with an $R_{\text{int}}$ of 0.0693. Indexing and unit cell refinement indicated a C-centered, monoclinic lattice. The space group was found to be *C*2/m (No. 12). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-97) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. SQUEEZE was used to treat the diffuse solvent contribution in the crystal. Its use has been noted in the CIF file. Crystallographic symmetry was imposed upon this complex during the refinement; for example, Cu1 and Cu3 atoms are at sites with 2/m symmetry, while Cu2 and water oxygens O1 and O2 lie on a mirror plane.

| | |
|---|---|
| Empirical formula | $C_{14}H_2CuF_8N_8O$ |
| Formula weight | 513.78 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | *C*2/m |

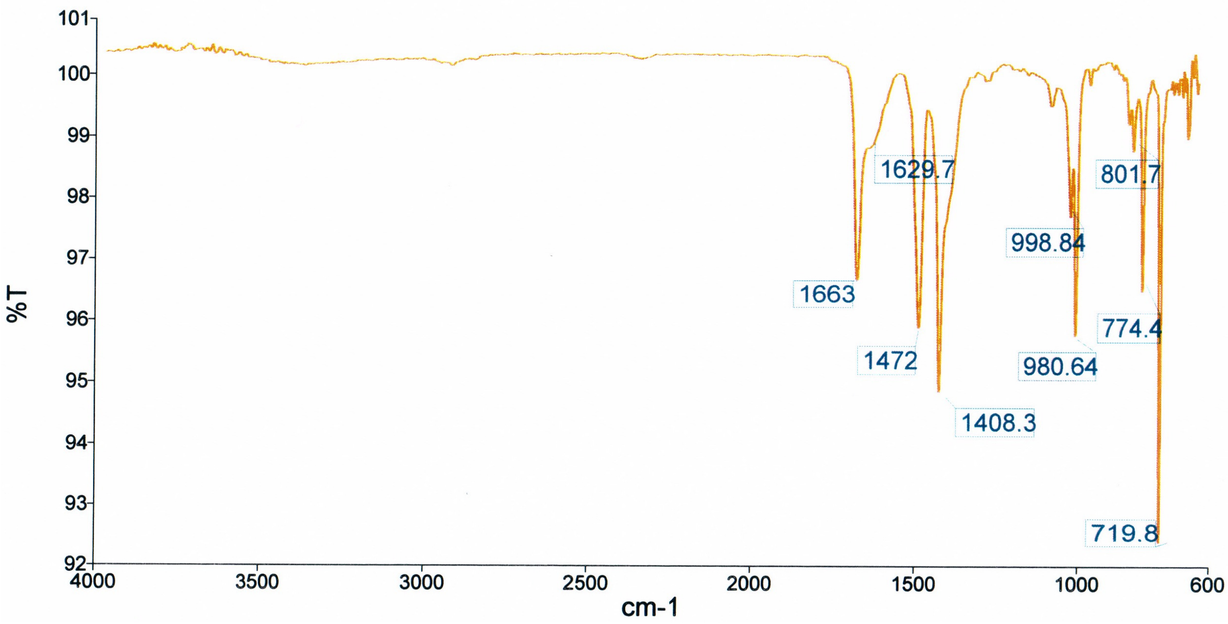
| | | |
|---|---|---|
| Unit cell dimensions | $a$ = 15.8991(10) Å | α = 90 ° |
| | $b$ = 31.5712(18) Å | β = 115.357(3) ° |
| | $c$ = 13.8721(8) Å | γ = 90 ° |
| Volume | 6292.3(6) Å$^3$ | |
| $Z$ | 8 | |
| Density (calculated) | 1.085 Mg/m$^3$ | |
| Absorption coefficient | 0.756 mm$^{-1}$ | |
| F(000) | 2008 | |
| Crystal size | 0.12×0.06×0.04 mm$^3$ | |
| $\theta$ range for data collection | 1.56 ° to 25.43 ° | |
| Index ranges | $-19 \le h \le 17$, $-37 \le k \le 36$, $-15 \le l \le 16$ | |
| Reflections collected | 37915 | |
| Independent reflections | 5907 [$R$(int) = 0.0693] | |
| Completeness to θ = 25.00 ° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9704 and 0.9148 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5907 / 4 / 303 | |
| Goodness-of-fit on $F^2$ | 1.119 | |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0753, w$R_2$ = 0.2272 | |
| $R$ indices (all data) | $R_1$ = 0.0896, w$R_2$ = 0.2346 | |
| Largest diff. peak and hole | 1.809 and −0.897 e/Å$^{-3}$ | |

## Section S6. Fourier Transform Infrared Spectra of MOFFs

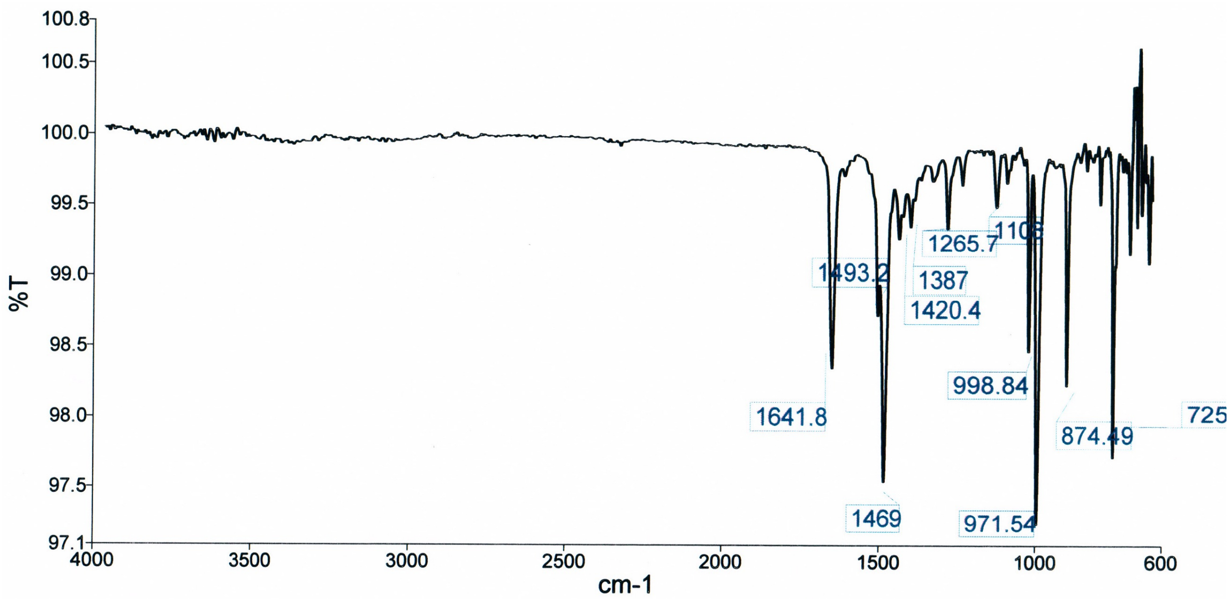
### Fourier-Transform Infrared Spectrum of **MOFF-1**



Fourier-Transform Infrared Spectrum of **MOFF-2**

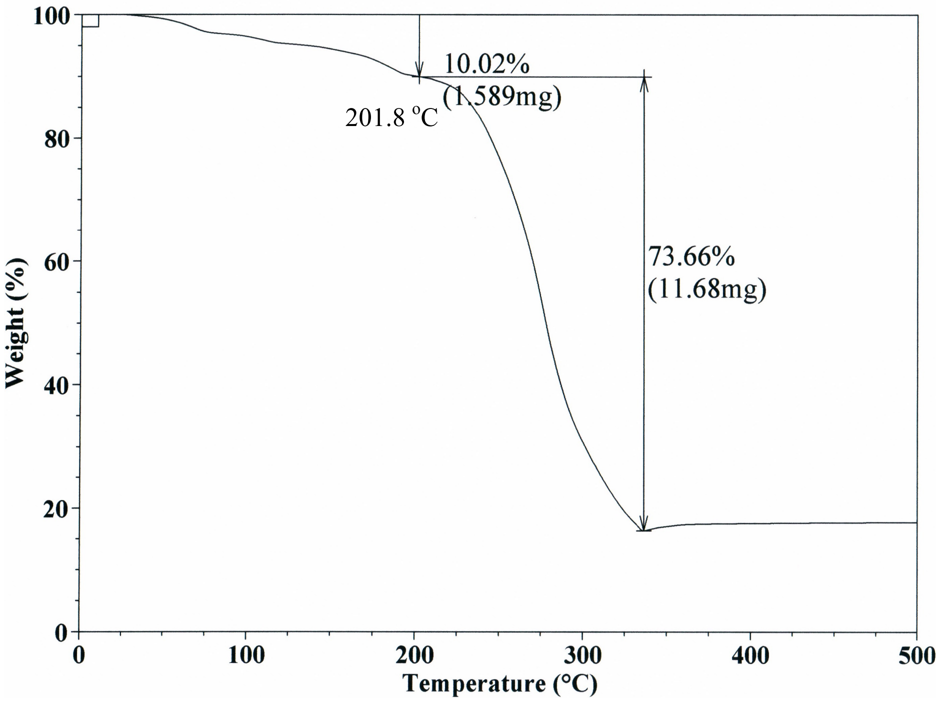


Fourier-Transform Infrared Spectrum of **MOFF-3**

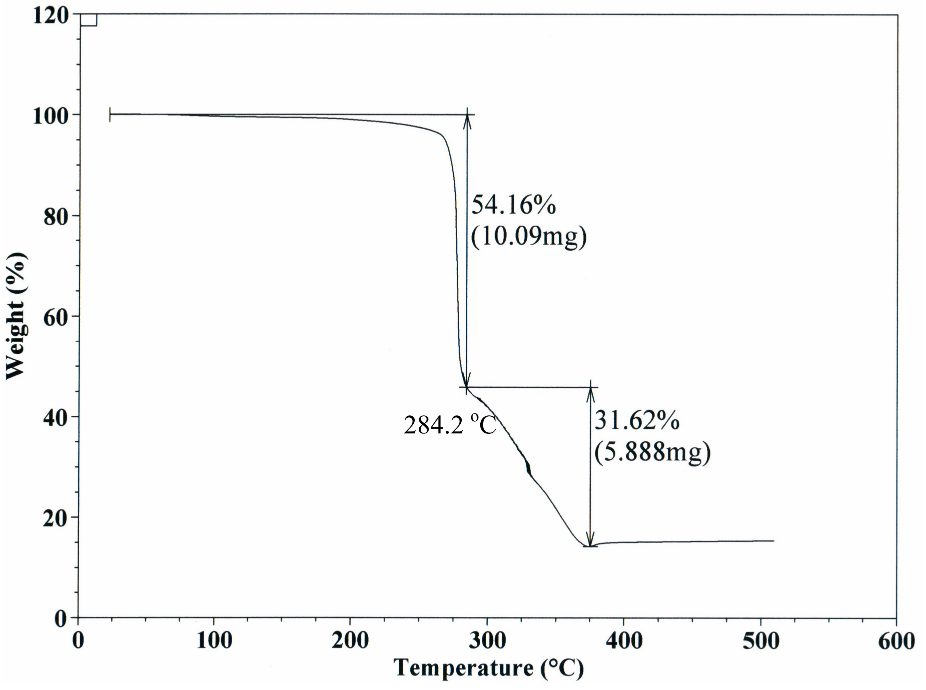


## Section S7. Thermogravimetric Analyses Traces of MOFFs

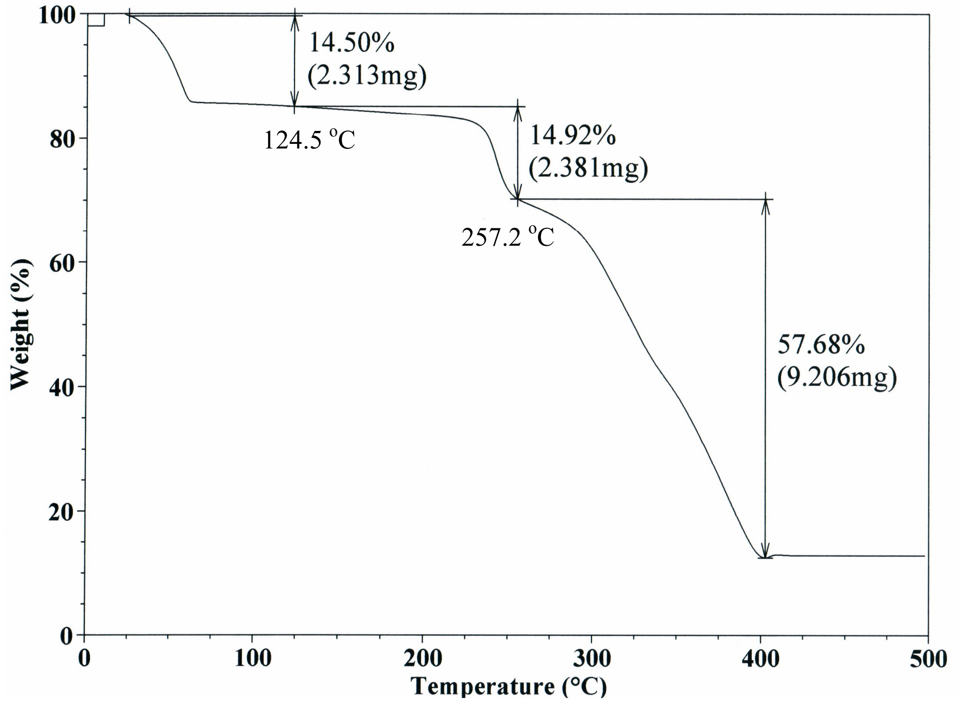
### Thermogravimetric Analysis Trace of **MOFF-1**



### Thermogravimetric Analysis Trace of **MOFF-2**



Thermogravimetric Analysis Trace of **MOFF-3**

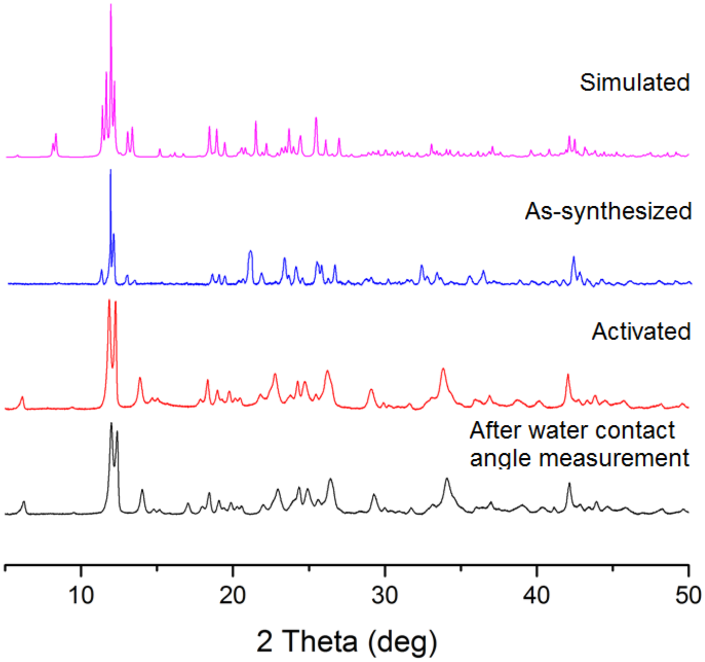


## Section S8. Powder X-Ray Diffraction Patterns of MOFFs

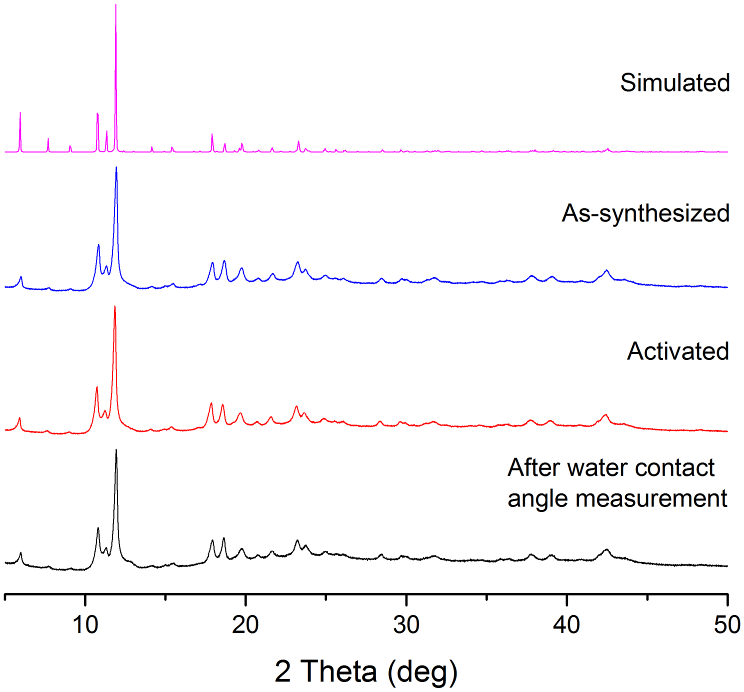
### Sample Activation

All MOFFs were dried in a 120 ºC vacuum oven for 24 h. For **MOFF-3**, in order to retain the $H_2O$ terminal groups in the channels, supercritical $CO_2$ drying (SCD) was also performed, using Tousimis™ Samdri® PVT-30 critical point dryer.[4]

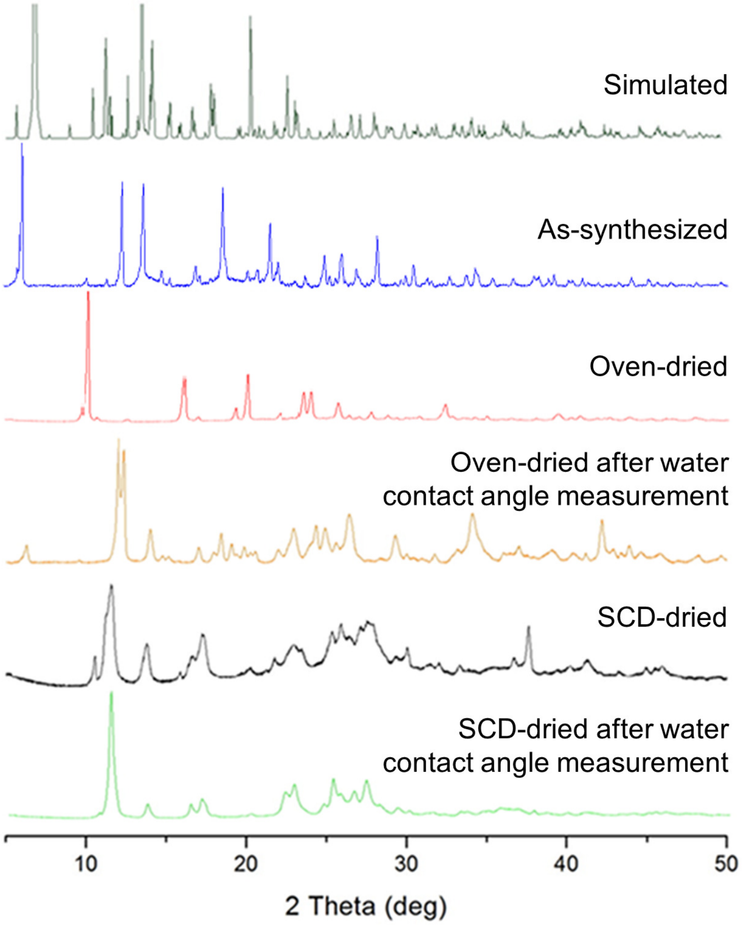
### Powder X-Ray Diffraction Patterns of **MOFF-1**



### Powder X-Ray Diffraction Patterns of **MOFF-2**



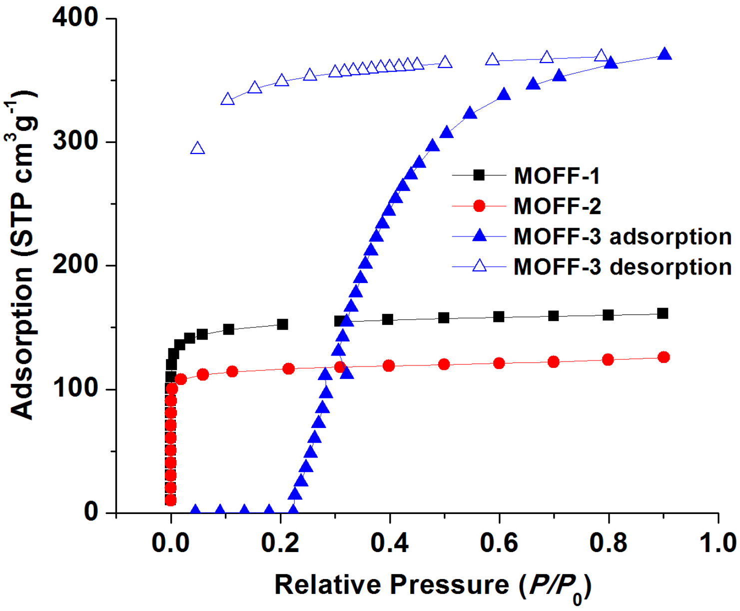
Powder X-Ray Diffraction Patterns of **MOFF-3**



## Section S9. Nitrogen Adsorption Isotherms

**Gas sorption measurements.** A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure nitrogen adsorption isotherms. Oven-dried sample tubes equipped with TranSeals™ (Micrometrics) were evacuated and tared. Samples (100–500 mg) were transferred to the sample tube, which was then capped by a TranSeal™. Samples were heated to 150 ˚C under high vacuum ($10^{-3}$–$10^{-4}$ Torr) and held until the outgas rate was less than 2 mTorr/minute. The evacuated sample tubes were weighed again, and the sample mass was determined by subtracting the mass of the previously tared tubes. Nitrogen isotherms were measured using a liquid nitrogen bath (77 K). Ultra high purity grade (99.999% purity) $N_2$ and He, oil-free valves and gas regulators were used for all free space corrections and measurements. Relative pressure ($P/P_0$) range for BET analysis was taken from $5\times10^{-5}$ to 0.1.

Nitrogen Adsorption Isotherms



**MOFF-1**: BET surface area is 580 $m^2g^{-1}$

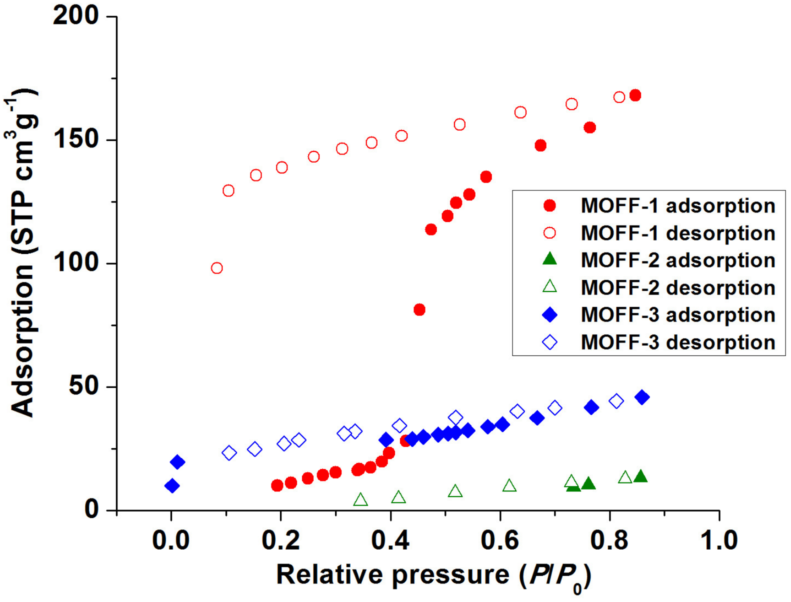
**MOFF-2**: BET surface area is 444 $m^2g^{-1}$

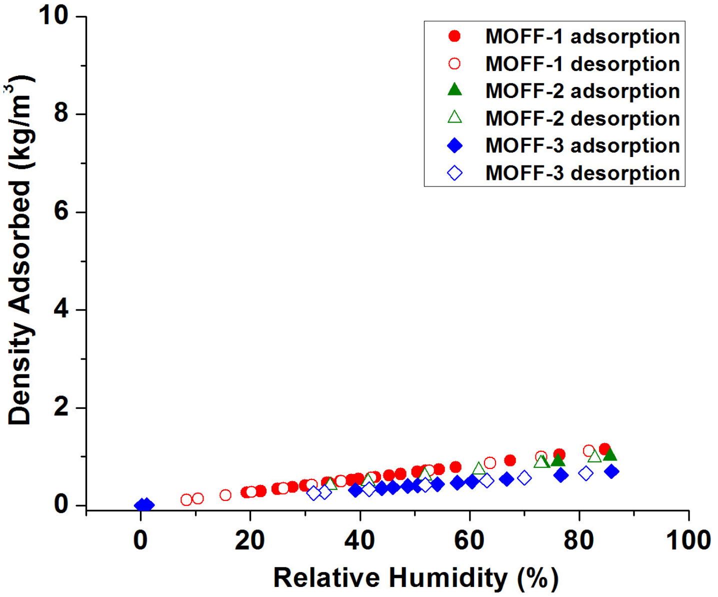
**MOFF-3**: BET surface area is not available from $N_2$ adsorption isotherm

## Section S10. Water Vapor Adsorption Isotherms

**Gas sorption measurements.** A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure $H_2O$ adsorption isotherms. Oven-dried sample tubes equipped with TranSeals™ (Micrometrics) were evacuated and tared. Samples (100–500 mg) were transferred to the sample tube, which was then capped by a TranSeal™. Samples were heated to 150 °C under high vacuum ($10^{-3}$–$10^{-4}$ Torr) and held until the outgas rate was less than 2 mTorr/minute. The evacuated sample tubes were weighed again, and the sample mass was determined by subtracting the mass of the previously tared tubes. $H_2O$ isotherms were measured at 293 K with temperature control provided by Neslab LT-50DD refrigerated circulating bath. Ultra high purity grade (99.999% purity) $N_2$ and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

Water Vapor Adsorption Isotherms





## Section S11. Dynamic Contact Angle Measurements

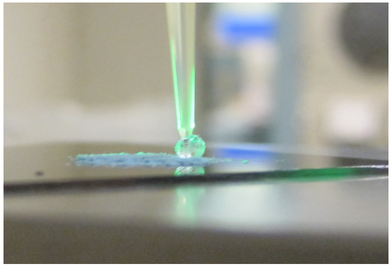
Before the measurements, all MOFFs were dried in a 120 ºC vacuum oven for 24 h. In addition, **MOFF-1** was air-dried, and **MOFF-3** was SCD-dried in order to retain their terminal MeOH and $H_2O$ groups, respectively. The finely ground MOFFs crystals were pressed between two Silicon (100) slides that had been previously rinsed with absolute EtOH and dried with a stream of nitrogen gas. After removing the upper slide, the exposed crystal surface was used for conducting contact angle measurements. A ramé-hart model 100 contact angle goniometer was employed to measure the contact angle of $H_2O$, *n*-hexadecane and cis–perfluorodecalin on the MOFFs**.** The contacting liquids were dispensed on the surface of the MOFFs using a Matrix Technologies micro-Electrapette 25 at the slowest speed of 1 μL/s. The measurements were performed at 293 K, with the pipet tip remaining in contact with the drop. The reported data for each sample were the average of three measurements obtained from three different slides for each MOFF with advancing contact angles ($\theta_a$) recorded for both edges of the drop.

Dynamic Contact Angle of MOFFs

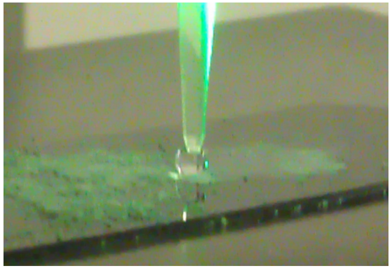
| **MOF** | contact angle with: | | |
|---|---|---|---|
| | **water** | ***n*-hexadecane** | ***cis*-perfluorodecalin** |
| MOFF-1, air-dried | ~0º | ~0º | ~0º |
| MOFF-1, oven-dried | 108 ± 2º | ~0º | ~0º |
| MOFF-2, oven-dried | 151 ± 1º | ~0º | ~0º |
| MOFF-3, oven-dried | 134 ± 1º | ~0º | ~0º |
| MOFF-3, SCD-dried | 135 ± 2º | ~0º | ~0º |

Pictures of oven-dried MOFF samples, after a drop of water was placed onto them

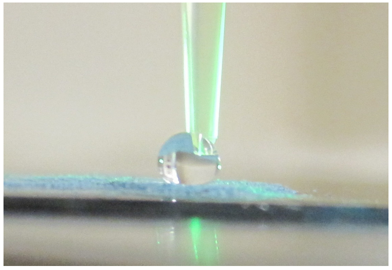
**MOFF-1**



**MOFF-2**



**MOFF-3**



## Section S12. References

[1] *Materials Studio program*, version 5.5; Accelrys, San Diego, CA, 2011.

[2] J. M. Birchall, R. N. Haszeldine and M. E. Jones, *J. Chem. Soc. C*, 1971, 1343–1348.

[3] I. Popov, H.-Q. Do and O. Daugulis, *J. Org. Chem.,* 2009, **74**, 8309–8313.

[4] A. P. Nelson, O. K. Farha, K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.,* 2009, **131**, 458–460.

[5] C. Yang, U. Kaipa, Q. Z. Mather, X. Wang, V. Nesterov, A. F. Venero and M. A. Omary, *J. Am. Chem. Soc.,* 2011, **133**, 18094–18097.