

Optimized Synthesis of Tetrafluoroterephthalic Acid: A Versatile Linking Ligand for the Construction of New Coordination Polymers and Metal-Organic Frameworks

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Pure 2,3,5,6-tetrafluoroterephthalic acid (H₂tfBDC) is obtained in high yields (95%) by reacting 1,2,4,5-tetrafluorobenzene with a surplus (>2 equiv) of *n*-butyllithium in tetrahydrofuran (THF) and subsequent carbonation with CO₂ without any extensive purification procedure. A single crystal X-ray structure analysis of H₂tfBDC (**1**) confirms former data obtained for a deuterated sample (P1, Z = 1). Recrystallization from water/acetone leads to single crystals of H₂tfBDC · 2H₂O (**2**, P2₁/c, Z = 2), where an extensive hydrogen bonding network is found. By reacting H₂tfBDC with an aqueous ammonia solution, single crystals of (NH₄)₂tfBDC (**3**, C2/m, Z = 2) are obtained. **3** is thermally stable up to 250 °C and shows an enhanced solubility in water compared to H₂tfBDC. Monosubstituted 2,3,5,6-tetrafluorobenzoic acid (H₂tfBC, **4**) is obtained by reacting 1,2,4,5-tetrafluorobenzene with stoichiometric amounts (1 equiv) of *n*-butyllithium in THF. Its crystal structure (Fdd2, Z = 16) shows dimeric units as characteristic structural feature.

Introduction

Coordination polymers and especially their porous congeners, which are frequently termed MOFs (Metal-Organic Frameworks),¹ are in the focus of many research groups worldwide. The interest in this class of compounds is mainly based on their easy synthetic accessibility and potential applications.^{2–4} One of the most frequently used linker ligands is the dianion of terephthalic acid (H₂BDC), from which two of the most prominent members of this class of compounds, MOF-5¹ and MIL-53,⁵ are constructed. For its perfluorinated counterpart, that is 2,3,5,6-tetrafluoroterephthalic acid (H₂tfBDC), theoretical investigations predict superior H₂ adsorbing properties of MOFs built with this linker ligand.⁶ By contrast, a different computational study concludes that the interaction between H₂ and fluoroaromatic compounds may be even weaker compared with their non-fluorinated analogues.⁷

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The beneficial properties of fluorinated linkers are, however, supported by experimental results for a MOF based on a triazolate with CF₃ substituents, which shows excellent gas storage capacities for O₂ and H₂.⁸ To date only few coordination polymers or MOFs employing perfluorinated linking terephthalates (tfBDC²⁻) have been published.^{9–21} Most of them are non-porous.

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In 1964 a synthesis of H₂tfBDC was described starting from 1,2,4,5-tetrafluorobenzene, which was reacted with *n*-butyllithium and carbonated with CO₂.²² Although this route yielded 67% of pure product, it suffers from incomplete lithiation, and consequently the monosubstituted tetrafluorobenzene is always obtained as a byproduct. This disadvantage makes an extensive and time-consuming purification procedure necessary.

In the following we will present an optimized synthesis, which allows the preparation of gram quantities of pure H₂tfBDC by a comparatively simple procedure, also starting from 1,2,4,5-tetrafluorobenzene, which is available at a reasonable price. Crystal structures of H₂tfBDC (**1**), H₂tfBDC·2H₂O (**2**), and (NH₄)₂tfBDC (**3**) are presented, as well as the synthesis and crystal structure of the monosubstituted 2,3,5,6-tetrafluorobenzoic acid (**4**), which can be obtained as a byproduct using a slightly modified procedure.

Experimental Section

General Remarks. All sample handling was carried out in a dry argon atmosphere using Schlenk techniques. 1,2,4,5-Tetrafluorobenzene was obtained from Molekula and Fluorochem, *n*-butyllithium (1.6 M solution in hexane) and magnesium sulfate from Acros Organics. They were used as purchased. Tetrahydrofuran (THF) was dried using a MBRAUN MB SPS-800 solvent purification system. All other solvents were used as purchased.

Synthesis. 2,3,5,6-Tetrafluoroterephthalic Acid (1). Synthesis Protocol (a). In an argon atmosphere, 2.13 g of 1,2,4,5-tetrafluorobenzene (14.2 mmol, 1.0 equiv) were dissolved in 250 mL of dry THF and cooled to approximately -75 °C. During 30 min 25 mL of *n*-BuLi (40.0 mmol, 2.8 equiv) were added dropwise, while the reaction mixture was stirred. After 4 h of stirring, CO₂ obtained by sublimating dry ice was bubbled through the solution, upon which the mixture became a white sludge. The solvent was removed, and the white solid residue was hydrolyzed with 100 mL of aqueous HCl (7.5%) and 100 mL of Et₂O. The aqueous phase was additionally extracted two times with each 100 mL of Et₂O. The collected ether phases were dried over magnesium sulfate. After removing all volatiles the obtained white raw product was recrystallized from ethylacetate by adding cyclohexane. The total yield after recrystallization was 3.2 g (13.4 mmol, 95% based on C₆F₄H₂). Elemental analysis for C₈O₄H₂F₄ (238.096): calcd C, 40.35%, H, 0.85%; found C, 40.44, H, 0.85%. mp: 275 °C (dec.). The melting point is somewhat lower than that given in the literature (283–284 °C),²² but agrees well with the melting point of the raw material before recrystallization (261–276 °C)²² and the commercially available product (275–277 °C, Sigma-Aldrich). We assume that recrystallization from water²² leads to the dihydrate (**2**), which shows a slightly higher melting point. Actually, **1** does not melt, instead it decomposes. A proof based on DTA/TG investigations will be given below. ¹H NMR (acetone-d₆): [ppm] = 11.2 (s, 2H; COOH). ¹³C NMR (acetone-d₆) [ppm] = 160.1 (s; COOH); 145.9 (dm; ¹J_{CF} = 253.1 Hz, C_{2,3,5,6}), 116.4 (m, C_{1,4}). ¹⁹F-NMR (acetone-d₆) = -140.75 (s; F_{2,3,5,6}). The purity was checked by NMR and X-ray Powder Diffraction (XRPD). As no additional signals or reflections were visible in the NMR spectra (¹H, ¹³C, ¹⁹F) and XRPD patterns the purity can be estimated to be >98%.

Synthesis Protocol (b). A 5.00 g portion of 1,2,4,5-tetrafluorobenzene, (33.3 mmol, 1.0 equiv), dissolved in THF (200 mL), was cooled to approximately -75 °C, and 42.7 mL of *n*-BuLi (68.3 mmol, 2.05 equiv) were added over a period of 30 min. The suspension was allowed to stir for 30 min at this temperature never rising over -60 °C. Dried CO₂ (passed through a P₄O₁₀ column) was bubbled through the solution, 10 min at about -70 °C, and then

continued, while the mixture was allowed to reach ambient temperature (1 h). To the recooled (0 °C) solution, aqueous HCl (1M) was added and stirred overnight. The solvents were removed by distillation (the fraction boiling around 105° was collected, as it contains almost pure monocarboxylic acid, as described in literature²²). The residue of the distillation was washed with a small amount of pentane yielding a crude product mixture of **1** and **4** in a ratio of about 7:3. The above-described procedure, lithiation and subsequent carbonation, employing the product mixture of **1** and **4**, rather than tetrafluorobenzene was repeated two or three times giving highly pure **1** in a total yield of about 44% based on C₆F₄H₂ (3.53 g, 14.8 mmol). Purity (>97%) was determined by ¹⁹F-NMR spectroscopy.

2,3,5,6-Tetrafluoroterephthalic Acid Dihydrate (2). Single crystals of a dihydrate of **1** were obtained by recrystallization of **1** from a water/acetone mixture.

Diammonium-2,3,5,6-tetrafluoroterephthalate (3). A 250.0 mg portion of tetrafluoroterephthalic acid (**1**) (1.05 mmol) was suspended in 25 mL of deionized water. Gaseous ammonia was bubbled through the suspension, until it became clear. Water and excess ammonia were removed by distillation, and **3** was obtained as a white powder in a total yield of 98% (280.2 mg, 1.03 mmol). After recrystallization from water, colorless flaky crystals suitable for a single crystal structure determination were obtained after 3 weeks. Elemental analysis for C₈O₄H₈F₄N₂ (272.164): calcd N, 10.30%, C, 35.30%, H, 2.96%; found N, 10.24%, C, 35.87%, H, 2.94%. Purity was additionally checked by XRPD. No additional reflections were found.

2,3,5,6-Tetrafluorobenzoic acid (4). **4** was obtained as a byproduct of the synthesis of **1** using the synthesis protocol (b) as described above. The fraction boiling between 100–108 °C was collected and contains almost pure 2,3,5,6-tetrafluorobenzoic acid. Single crystals were obtained by recrystallization of the crude reaction mixture from acetone. An alternative synthesis of **4** was already described in ref 23. ¹H NMR (acetone-d₆): [ppm] = 11.7 (s, 1H; COOH) 7.74 (tt, ³J_{HF} 10.2 Hz, ⁴J_{HF} 7.4 Hz, C₄-H). ¹³C NMR (acetone-d₆) [ppm] = 160.5 (s; COOH); 146.96 (dm, ¹J_{CF} 243.5 Hz, C_{3,5}), 145.27 (dm, ¹J_{CF} 252.6 Hz, C_{2,6}), 114.76 (t, ³J_{CF} 18.7 Hz, C₁), 109.76 (t, ³J_{CF} 23.0 Hz, C₄). ¹⁹F-NMR (acetone-d₆) = -139.82 (m, -F_{2,6}), -142.03 (br.s., -F_{3,5}).

X-ray Single Crystal Structure Analysis. Single crystals of **1–5** were isolated as described above and mounted in sealed glass capillaries on a Stoe four-circle (STADI), Stoe IPDS II, or a Bruker APEX-II single crystal diffractometer (MoK α radiation). For data collection and reduction the Stoe program package was applied.²⁴ The structural models were solved using SIR-92 (**3**) or SHELXS (**1**, **2**, **4**, **5**) and completed using difference Fourier maps calculated with SHELXL-97, which was also used for final refinements.^{25,26} For the structure of **3** and **5** all programs were run under the WinGX system.²⁷ All non-hydrogen atoms were refined anisotropically. The treatment of hydrogen atoms is described in the following chapter for each compound. More details of the structural analysis are given in Table 1.²⁸ Selected interatomic distances and angles are listed in Table 2.

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(28) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-770475 (H₂tfBDC, **1**), CCDC-770476 (H₂tfBDC·2H₂O, **2**), CCDC-770477 ((NH₄)₂tfBDC, **3**), and CCDC-770478 (H₂tfBC, **4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax.: (internat.) + 44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

Table 1. Details of X-ray Single Crystal Structure Determination of Compounds 1–5

| | H ₂ tfBDC (1) | H ₂ tfBDC·2H ₂ O (2) | (NH ₄) ₂ tfBDC (3) | H ₂ tfBC (4) | H ₂ tfBC·NH ₄ HtfBC (5) |
|--|--|--|--|---|---|
| formula | C ₈ H ₂ F ₄ O ₄ | C ₈ H ₆ F ₄ O ₆ | C ₈ H ₈ F ₄ O ₄ N ₂ | C ₇ H ₂ F ₄ O ₂ | C ₁₄ H ₇ F ₈ O ₄ |
| formula weight | 238.10 | 274.13 | 272.16 | 194.09 | 405.21 |
| crystal description | block, colorless | block, colorless | platelet, colorless | block, colorless | needles, colorless |
| crystal size | 0.36 × 0.22 × 0.18 mm | 0.40 × 0.36 × 0.36 mm | 0.2 × 0.1 × 0.1 mm | 0.24 × 0.18 × 0.12 mm | 0.44 × 0.06 × 0.04 mm |
| space group; <i>Z</i> | <i>P</i> $\bar{1}$ (No. 2), 1 | <i>P</i> 2 ₁ / <i>c</i> (No. 14), 2 | <i>C</i> 2/ <i>m</i> (No. 12), 2 | <i>F</i> dd2 (No. 43), 16 Flack <i>x</i> = −0.5(10) | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19), 4 Flack <i>x</i> = 0.2 (7) |
| unit cell | | | | | |
| <i>a</i> , Å | 4.565(2) | 8.5206(15) | 6.632(2) | 10.1937(15) | 6.5616(3) |
| <i>b</i> , Å | 5.832(2) | 7.9910(8) | 19.771(6) | 12.890(3) | 7.2376(4) |
| <i>c</i> , Å | 7.452(2) | 7.2845(14) | 3.7145(11) | 20.425(4) | 30.442(2) |
| α , deg | 87.32(3) | 90 | 90 | 90 | 90 |
| β , deg | 78.41(3) | 99.739(15) | 92.38(3) | 90 | 90 |
| γ , deg | 74.11(3) | 90 | 90 | 90 | 90 |
| volume, Å ³ | 186.92(10) | 488.84(14) | 486.6(3) | 2683.8(9) | 1445.71(13) |
| calc. density, g·cm ^{−3} | 2.115 | 1.862 | 1.857 | 1.921 | 1.862 |
| absorption correction | none | none | numerical | none | none |
| diffractometer, radiation | Stoe four-circle (STADI), MoK α | Stoe four-circle (STADI), MoK α | Stoe IPDS II, MoK α | Stoe four-circle (STADI), MoK α | Bruker APEX-II CCD, MoK α |
| temperature, °C | −178(2) | −178(2) | 20(2) | −178(2) | −183(2) |
| 2 θ _{max} , deg | 60.00 | 60.00 | 59.00 | 52.00 | 52.00 |
| index ranges | −6 ≤ <i>h</i> ≤ 6 −8 ≤ <i>k</i> ≤ 8 −9 ≤ <i>l</i> ≤ 10 | −9 ≤ <i>h</i> ≤ 11 −11 ≤ <i>k</i> ≤ 11 −10 ≤ <i>l</i> ≤ 10 | −9 ≤ <i>h</i> ≤ 9 −27 ≤ <i>k</i> ≤ 27 −5 ≤ <i>l</i> ≤ 4 | 0 ≤ <i>h</i> ≤ 12 −1 ≤ <i>k</i> ≤ 15 −1 ≤ <i>l</i> ≤ 25 | −8 ≤ <i>h</i> ≤ 8 −8 ≤ <i>k</i> ≤ 7 −37 ≤ <i>l</i> ≤ 37 |
| reflections | 1376/1086 | 2758/1426 | 2857/701 | 898/683 | 25193/2825 |
| collected/independent | | | | | |
| significant reflections, with <i>I</i> > 2 σ (<i>I</i>) | 951 | 1314 | 479 | 652 | 2285 |
| <i>R</i> (int) | 0.030 | 0.026 | 0.054 | 0.016 | 0.048 |
| data/parameters/ restraints | 1086/76/0 | 1426/94/3 | 701/52/2 | 683/127/1 | 2825/257/4 |
| GoF = <i>S</i> _{all} | 1.08 | 1.07 | 1.00 | 1.07 | 1.04 |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] | 0.034 | 0.035 | 0.041 | 0.025 | 0.031 |
| <i>wR</i> (<i>F</i> ²) | 0.091 | 0.091 | 0.103 | 0.063 | 0.081 |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$, e·Å ^{−3} | 0.38/−0.24 | 0.38/−0.26 | 0.26/−0.20 | 0.18/−0.24 | 0.23/−0.21 |

XRPD. XRPD data were collected on a Huber G670 with a germanium monochromator and Cu K α ₁ radiation at room temperature, with exposure times of approximately 2 h. Samples were sealed in capillaries (Ø 0.3–0.5 mm). Within the WinXPow software suite²⁹ the recorded patterns were compared with theoretical patterns calculated from the obtained crystal structure data.

Thermoanalytical Investigations. A differential thermal analysis (DTA) and thermogravimetry (TG) investigation was performed on diammonium-2,3,5,6-tetrafluoroterephthalate (3) (sample mass: 19.1 mg) in the temperature range 24–400 °C using a Netzsch STA 409C housed in a glovebox (M. Braun, Garching/Germany), heating rate 10 °C/min.

NMR. NMR spectra have been recorded on a Bruker Avance 300 spectrometer (¹H, 300.13 MHz, ¹³C, 75.47 MHz, ¹⁹F, 282.35 MHz), with ¹H decoupling for ¹⁹F and ¹³C. Chemical shifts are specified relative to the residual solvent signal (¹H, ¹³C) and CCl₃F as internal standard (¹⁹F).

Results and Discussion

Pure 2,3,5,6-tetrafluoroterephthalic acid (H₂tfBDC, 1) is obtained in high yields (95%) by reacting 1,2,4,5-tetrafluorobenzene with a surplus (> 2 equiv) of *n*-BuLi in THF and subsequent carbonation with CO₂ without any extensive purification procedure. The underlying reactions are summarized in Scheme 1. It was found that a larger surplus (approximately 2.8 equiv) of *n*-BuLi is needed to avoid the formation of the monosubstituted product 2,3,5,6-tetrafluorobenzoic acid (4). A mixture of the mono- and disubstituted products makes an extensive purification procedure necessary, as was shown in the

literature²² and was confirmed by us (see protocol (b)). So the synthesis described in protocol (a), which exclusively leads to H₂tfBDC, presents a convenient route to gram quantities of pure 1.

Crystal Structure of 2,3,5,6-Tetrafluoroterephthalic Acid (1). Compound 1 crystallizes in the triclinic space group *P* $\bar{1}$ as colorless blocks from acetone. The unit cell constants are quite similar to those previously reported in X-ray and neutron diffraction studies of the deuterated derivative, which have been performed at room temperature.³⁰ The molecular structure of 1 (Figure 1) is almost identical to the reported structures from these studies, although slight deviations occur. For instance, the plane of the carboxylate group is twisted by 19.3(1)° around the bond C1–C7 out of the least-squares plane of the aryl ring, which is slightly smaller than reported for the structure of the perdeuterated acid (19.8(1)°). But in both structures a disordered proton H1 is found. This disorder is also reflected in similar C7–O1 and C7–O2 distances (Table 2).

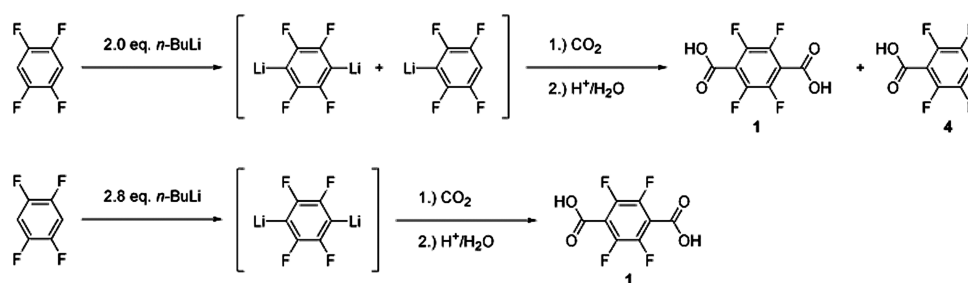
Compound 1 shows an infinite one-dimensional chain structure (Figure 2) connected by hydrogen bonds between neighboring carboxylate units. As mentioned the H atoms of the OH groups are disordered over two sites. They were refined with site occupation factors of 0.5, tetrahedral C–O–H angles, enabling rotation around the C–O bond, O–H distances of 0.84 Å, and with individual isotropic displacement parameters. Relevant distances and angles of the hydrogen bonds are given in Table 3.

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Table 2. Selected Interatomic Distances [Å] and Angles [deg] for Compounds 1–4

| H ₂ tfBDC (1) | | H ₂ tfBDC·2H ₂ O (2) | | (NH ₄) ₂ tfBDC (3) | | H ₂ tfBC (4) | |
|--------------------------|------------|--|------------|---|------------|-------------------------|------------|
| C1–C3 | 1.395(2) | C1–C2 | 1.391(2) | C1–C3 | 1.389(2) | C11–C12 | 1.399(3) |
| C1–C2 | 1.397(2) | C1–C3 | 1.394(2) | C3–C3 | 1.380(3) | C12–C13 | 1.376(4) |
| C2–C3 | 1.383(2) | C2–C3 | 1.384(2) | C1–C2 | 1.524(3) | C13–C14 | 1.379(3) |
| C1–C7 | 1.500(2) | C1–C4 | 1.502(2) | | | C11–C15 | 1.499(5) |
| | | | | | | C21–C22 | 1.392(3) |
| | | | | | | C22–C23 | 1.383(3) |
| | | | | | | C23–C24 | 1.375(3) |
| | | | | | | C21–C25 | 1.488(5) |
| C2–F2 | 1.3310(13) | C2–F2 | 1.3406(12) | F1–C3 | 1.343(2) | C12–F12 | 1.343(3) |
| C3–F3 | 1.3379(13) | C3–F3 | 1.3411(13) | | | C13–F13 | 1.347(3) |
| | | | | | | C22–F22 | 1.339(3) |
| | | | | | | C23–F23 | 1.343(3) |
| C7–O1 | 1.257(2) | C4–O1 | 1.2194(14) | C2–O1 | 1.244(2) | C15–O15 | 1.266(2) |
| C7–O2 | 1.2638(14) | C4–O2 | 1.3042(14) | | | C25–O25 | 1.270(2) |
| | | | | | | C14–H14 | 0.95 |
| | | | | | | C24–H24 | 0.95 |
| C3–C1–C2 | 115.81(10) | C2–C1–C3 | 116.72(10) | C3–C1–C3 | 115.9(2) | C12–C11–C12 | 116.5(3) |
| C3–C2–C1 | 121.85(10) | C3–C2–C1 | 122.01(10) | C3–C3–C1 | 122.05(9) | C13–C12–C11 | 121.3(3) |
| C2–C3–C1 | 122.34(10) | C2–C3–C1 | 121.26(10) | C3–C1–C2 | 122.05(9) | C12–C13–C14 | 121.7(3) |
| C3–C1–C7 | 121.94(10) | C2–C1–C4 | 120.43(10) | | | C13–C14–C13 | 117.5(3) |
| C2–C1–C7 | 122.23(10) | C3–C1–C4 | 122.82(10) | | | C12–C11–C15 | 121.73(14) |
| | | | | | | C22–C21–C22 | 117.5(3) |
| | | | | | | C23–C22–C21 | 121.0(2) |
| | | | | | | C24–C23–C22 | 120.8(2) |
| | | | | | | C23–C24–C23 | 118.9(3) |
| | | | | | | C22–C21–C25 | 121.3(2) |
| F2–C2–C3 | 116.65(10) | F2–C2–C3 | 117.77(10) | F1–C3–C3 | 117.93(7) | F12–C12–C13 | 117.8(2) |
| F2–C2–C1 | 121.49(10) | F2–C2–C1 | 120.17(10) | F1–C3–C1 | 120.00(13) | F12–C12–C11 | 120.9(2) |
| F3–C3–C2 | 116.46(10) | F3–C3–C2 | 118.01(10) | | | F13–C13–C12 | 118.3(2) |
| F3–C3–C1 | 121.18(10) | F3–C3–C1 | 120.70(10) | | | F13–C13–C14 | 120.0(2) |
| | | | | | | F22–C22–C23 | 118.2(2) |
| | | | | | | F22–C22–C21 | 120.6(2) |
| | | | | | | F23–C23–C24 | 120.8(2) |
| | | | | | | F23–C23–C22 | 118.5(2) |
| O1–C7–O2 | 125.42(11) | O1–C4–O2 | 125.21(10) | O1–C2–O1 | 125.7(2) | O15–C15–O15 | 124.5(3) |
| | | | | | | O25–C25–O25 | 124.2(3) |
| O1–C7–C1 | 117.69(10) | O1–C4–C1 | 121.13(10) | O1–C2–C1 | 117.13(10) | O15–C15–C11 | 117.7(2) |
| O2–C7–C1 | 116.89(10) | O2–C4–C1 | 113.66(10) | | | O25–C25–C21 | 117.9(2) |
| C7–O1–H1 | 109.5 | C4–O2–H2 | 109.8 | | | C15–O15–H15 | 109.5 |
| C7–O2–H2 | 109.5 | H31–O3–H32 | 104.6 | H1–N1–H2 | 109(2) | C25–O25–H25 | 109.5 |
| | | | | | | C13–C14–H14 | 121.2 |
| | | | | | | C23–C24–H24 | 120.5 |

Scheme 1. Reactions of 1,2,4,5-Tetrafluorobenzene with Different Amounts of *n*-BuLi and Subsequent Carbonation with CO₂

The packing of the structures of **1** and its deuterated congener reveal, however, significant differences.³⁰ In different layers the infinite chains are arranged in a way that the carboxylate groups are above and below the aryl rings of the neighboring layers for **1**, while in the deuterated variety the aryl rings are stacked above each other. In **1** the planes of the aryl rings of different layers are related by

translation along the crystallographic *a*-axis showing a distance C3–C3' of 3.294(2) Å, which is significantly shorter than in its perdeuterated analogue (3.377 Å). Concomitantly, the centroids of the aryl rings are closer in **1** (4.565(2) Å) than in the deuterated variety (4.617(2) Å). This arrangement results in a short intramolecular contact between the layers (O1–O2: 3.033(2) Å). Furthermore,

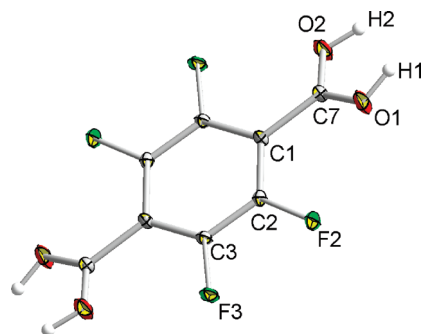


Figure 1. ORTEP diagram of H₂tfBDC (**1**) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Hydrogen atoms (H1, H2) are disordered over two sites with occupancy of 0.5.

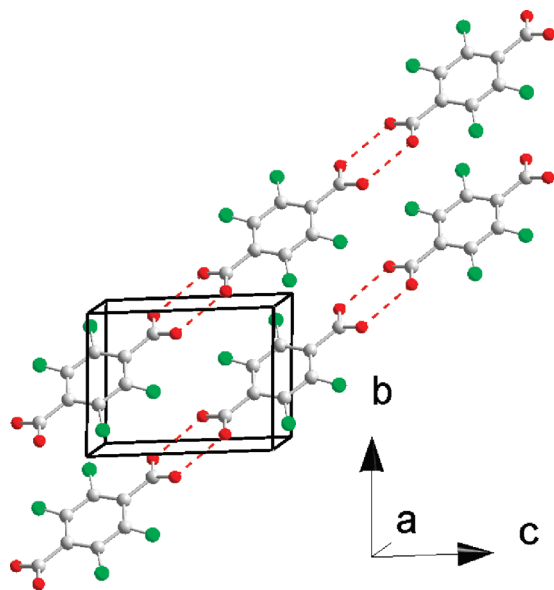
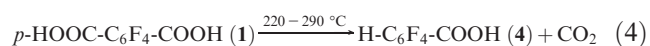


Figure 2. Packing diagram of H₂tfBDC (**1**) (C: white, O: red, F: green). Disordered hydrogen atoms have been omitted for clarity. Hydrogen bonds between oxygen atoms are drawn as red broken lines.

short F–C_{aryl} (2.979(2) Å–3.109(2) Å) contacts contribute to the packing of this structure.

According to a preliminary DTA/TG investigation a mass loss of **1** accompanied by an exothermal signal started at approximately 220 °C. This process is finished at approximately 290 °C with no mass remaining. To prove whether this effect is due to decomposition or sublimation of **1**, in an additional experiment performed in an argon atmosphere some of the gases evolved upon heating were condensed at the wall of a glass tube. XRPD data revealed that the colorless solid is solely 2,3,5,6-tetrafluorobenzoic acid (**4**). Thus, **1** decomposes to give **4** by releasing CO₂:



Crystal Structure of 2,3,5,6-Tetrafluoroterephthalic Acid Dihydrate (2). In the presence of water, **1** forms a 1:2 adduct with this solvent (Figure 3). Compound **2** crystallizes in the monoclinic space group *P*2₁/*c*. The hydrogen atoms were refined with individual isotropic displacement parameters. All O–H distances were fixed

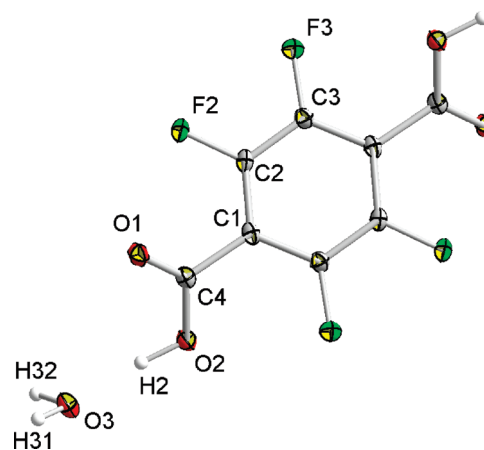


Figure 3. ORTEP diagram of H₂tfBDC·2H₂O (**2**) showing 50% probability thermal ellipsoids and the atom-numbering scheme.

Table 3. Hydrogen Bonds (Å, deg) in Compounds 1–5

| D–H···A | D–H | H···A | D···A | D–H···A |
|--|---------|---------|----------|---------|
| H ₂ tfBDC (1) | | | | |
| O1–H1···O2 | 0.84 | 1.84 | 2.655(2) | 162 |
| O2–H2···O1 | 0.84 | 1.83 | 2.655(2) | 168 |
| H ₂ tfBDC·2H ₂ O (2) | | | | |
| O2–H2···O3 | 0.95 | 1.59 | 2.540(1) | 174 |
| O3–H31···O1 | 0.95 | 1.95 | 2.859(1) | 160 |
| O3–H32···O1 | 0.95 | 1.89 | 2.817(1) | 164 |
| (NH ₄) ₂ tfBDC (3) | | | | |
| N1–H1···O1 | 0.97(2) | 1.93(2) | 2.821(2) | 151(2) |
| N1–H2···O1 | 0.98(2) | 1.98(2) | 2.908(2) | 158(2) |
| H ₂ tfBC (4) | | | | |
| O15–H15···O25 | 0.95 | 1.72 | 2.644(2) | 163 |
| O25–H25···O15 | 0.95 | 1.76 | 2.644(2) | 154 |
| H ₂ tfBC·NH ₄ HtfBC (5) | | | | |
| O1–H1B···O4 | 0.84 | 1.71 | 2.541(2) | 171 |
| N1–H3···O3 | 0.84(2) | 2.09(2) | 2.868(2) | 153(2) |

to a bond length of 0.95 Å, but no further constraints were applied to the hydrogen atoms. Structural parameters for the perfluoro aryl moiety are almost identical to the parameters of **1** (Table 2). The carboxylate group shows two distinctive CO distances of 1.219(1) Å and 1.304(1) Å, which is in the typical range for C=O and C–O bonds, respectively. The planes spanned by the aryl moiety and the carboxylate group enclose an angle of 39.9(1)°, which is significantly larger than in **1**. The acids are bridged by H₂O molecules (Figure 4). The O–H···O distances are 1.59(2) Å, 1.89(2) Å, and 1.95(2) Å (Table 3). Via these hydrogen bonds the acids are connected to a complex three-dimensional (3D) structure.

Crystal Structure of Diammonium-2,3,5,6-tetrafluoroterephthalate (3). Compound **3** crystallizes in the monoclinic spacegroup *C*2/*m* as colorless platelets. Hydrogen atoms were located in difference Fourier maps and refined with fixed N–H distances (1.00(2) Å) (Figure 5). The resulting N–H bond lengths and H–N–H bond angles (Tables 2 and 3) agree well with those expected for a perfect tetrahedral NH₄⁺ cation. Structural parameters

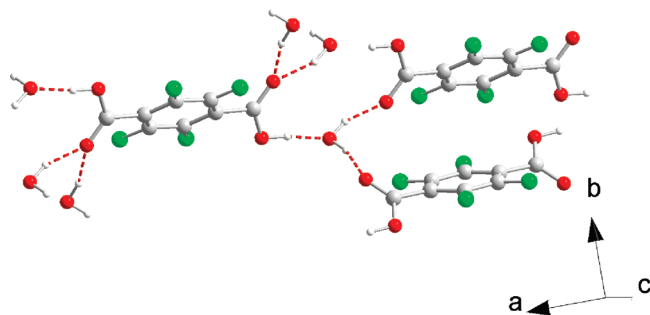


Figure 4. Packing diagram of $\text{H}_2\text{tfBDC}\cdot 2\text{H}_2\text{O}$ (**2**) (C, white; O, red; F, green; H, white, small spheres). Hydrogen bonds are drawn as red broken lines.

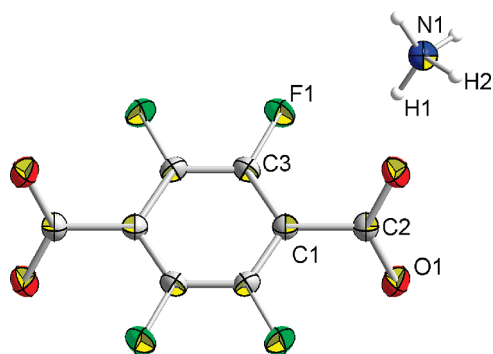


Figure 5. ORTEP diagram of $(\text{NH}_4)_2\text{tfBDC}$ (**3**) showing 50% probability thermal ellipsoids and the atom-numbering scheme.

for the perfluoro aryl moiety are almost identical to the parameters obtained for **1** and **2** (Table 2). The perfluoro aryl moieties are aligned parallel to each other along [010]. The carboxylate groups of one tfBDC anion are parallel to each other and enclose an angle of $44.5(2)^\circ$ with the plane of the aryl ring. This twist is much larger than in **1**, slightly larger than in **2** and also larger than in the non-fluorinated congener ($18(1)^\circ$ and $29(2)^\circ$).³¹ But as the latter was solved and refined from powder diffraction data the reliability of these angles is somewhat lower. Thus, a further comparison between the fluorinated and the non-fluorinated compound shall be omitted here. The tfBDC anions are bridged via oxygen atoms of the carboxylate groups and protons of the ammonium cations to form a 3D structure (Figure 6). As each oxygen atom is connected to two NH_4^+ cations the tfBDC anion acts as an 8-connector. Consistently, each NH_4^+ cation connects to four different tfBDC anions. The resulting $\text{H}\cdots\text{O}$ distances of these hydrogen bonds are 1.93(2) Å and 1.98(2) Å. We found that **3** shows an enhanced solubility in water compared to **1**. This makes **3** an attractive candidate for the synthesis of new coordination polymers with tfBDC²⁻ as bridging ligand in aqueous solutions.

To explore the thermal stability of **3** we performed basic thermoanalytical measurements. In Figure 7 results of the DTA/TG investigation on **3** are shown. Starting at approximately 225 °C a complete mass loss is observed, which is accompanied by a strong endothermic signal. This effect is finished at about 300 °C. For comparison decomposition of $(\text{NH}_4)_2\text{ADC}$ (ADC^{2-} = acetylenedicarboxylate) to NH_3 ,

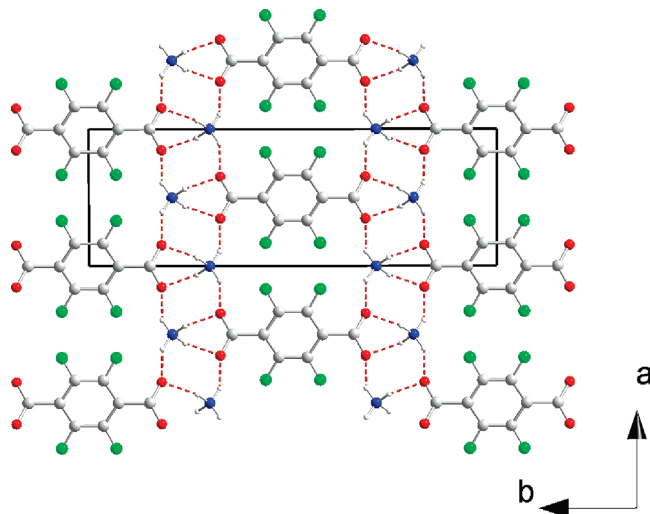


Figure 6. Packing diagram of $(\text{NH}_4)_2\text{tfBDC}$ (**3**) in a projection along [001] (C, white; O, red; F, green; N, blue; H, white, small spheres). Hydrogen bonds are drawn as red broken lines.

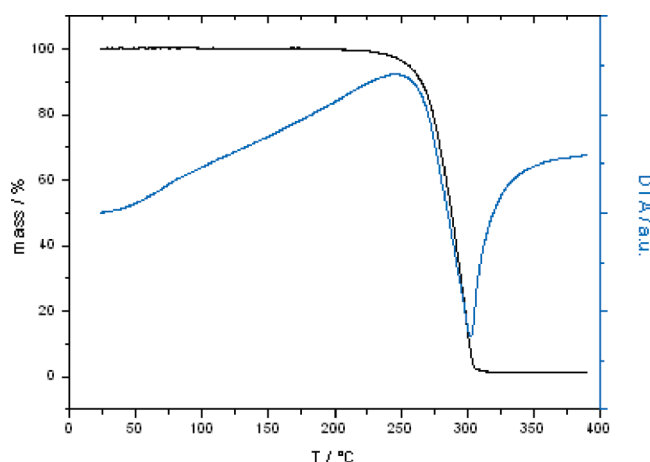


Figure 7. $(\text{NH}_4)_2\text{tfBDC}$ (**3**): DTA (blue) and TG (black) curves.

CO_2 , and C_2H_2 gives an exothermic signal.³² To check whether **3** decomposes or sublimates, some of the gases evolved upon heating were condensed at the wall of a glass tube in an argon atmosphere. XRPD data revealed that the collected colorless solid is neither **3** (sublimation) nor **1** or **4** (decomposition). By recrystallization from dry acetone single crystals have been obtained. According to the structure solution, the composition of this new compound (**5**) can be described as a 1:1 adduct of 2,3,5,6-tetrafluorobenzoic acid (**4**) with its ammonium salt (Figure 8). Elemental analysis of the white residue gave N, 5.98%, C, 40.90%, H, 2.28%. The calculated values for **5** are $\text{C}_{14}\text{O}_4\text{H}_7\text{F}_8\text{N}$ (405.201): N, 3.46%, C, 41.50%, H, 1.74%. The large deviation between these values proves that the collected white residue does not contain 2,3,5,6-tetrafluorobenzoic acid and ammonium 2,3,5,6-tetrafluorobenzoate in a 1:1 ratio. The high value for nitrogen indicates a higher fraction of ammonium 2,3,5,6-tetrafluorobenzoate.

Crystal Structure of Ammonium 2,3,5,6-Tetrafluorobenzoate 2,3,5,6-Tetrafluorobenzoic Acid Adduct (5). Compound **5** crystallizes in the orthorhombic chiral space group

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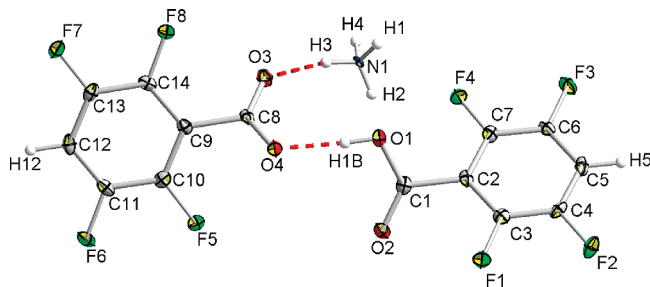


Figure 8. ORTEP diagram of $\text{H}_2\text{tfBC}\cdot(\text{NH}_4)\text{HtfBC}$ (**5**) showing 50% probability thermal ellipsoids and the atom-numbering scheme. The H atom of carboxylic acid was refined isotropically with tetrahedral C–O–H angles.

$P2_12_12_1$ as colorless needles (Table 1).³³ All non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms H5 and H12 were put at the external bisector of the C–C–C angle at a C–H distance of 0.95 Å, but the individual isotropic displacement parameters are free to refine. H atoms of the ammonium ion are located in the difference Fourier map and refined isotropically. The H atom of carboxylic acid was refined isotropically with a tetrahedral C–O–H angle. Owing to the lack of heavier atoms, determination of the absolute structure was not possible. In **5** tetrafluorobenzoic acid forms a quite strong hydrogen bond³⁴ to tetrafluorobenzoate via the carboxylic OH group (donor–acceptor [D/A] distance 2.541(2) Å), which is significantly shorter than in **1** and **4**. A second hydrogen bond between the ion pairs of the tetrafluorobenzoate and the ammonium ion (D/A distance 2.833(2) Å) is formed, resulting in a 2-dimensional network built up by the ammonium ion acting as a 4-connector. The carboxylic groups are twisted out of the least-squares planes of the aryl rings by 40.2(1)° and 50.1(1)° for the tetrafluorobenzoic acid and the tetrafluorobenzoate, respectively, which is for the latter even larger than in **3**. In essence, the composition of **5** proves that the thermal decomposition of **3** involves the release of both CO_2 and NH_3 .

Crystal Structure of 2,3,5,6-Tetrafluorobenzoic Acid (4). Compound **4** crystallizes in the acentric orthorhombic space group $Fdd2$ as colorless blocks. Non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms H14 and H24 were put at the external bisector of the C–C–C angle at a C–H distance of 0.95 Å, but the individual isotropic displacement parameters are free to refine. The disordered H atoms H15 and H25 of the COOH groups were refined with site occupation factors of 0.5, tetrahedral C–O–H angles, enabling rotation around the C–O bond, O–H distances of 0.95 Å, and with individual isotropic displacement parameters. The molecules are lying on 2-fold axes parallel to the c -axis forming dimers held together by two hydrogen bonds (Figure 9). Whereas the two carboxylate groups are almost coplanar (angle between the root mean square (rms) planes $\phi = 2.7(1)^\circ$), there are considerable torsions around the C–C single

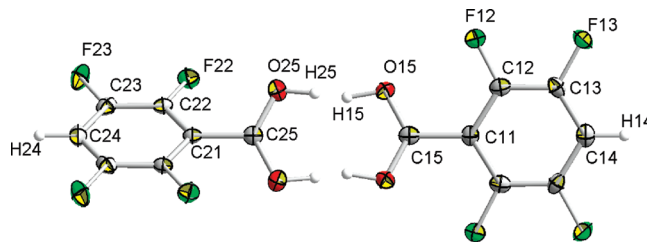


Figure 9. ORTEP diagram of H_2tfBC (**4**) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Hydrogen atoms (H15, H25) are disordered over two sites with occupancy of 0.5.

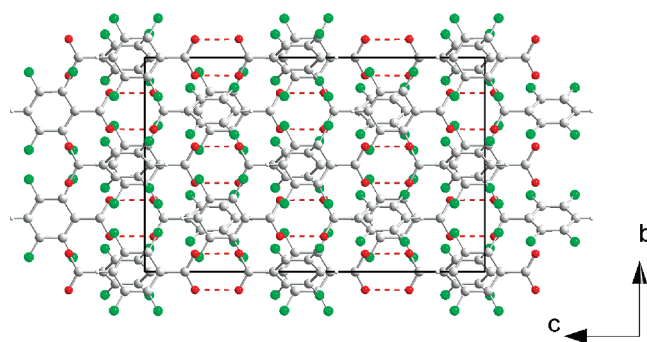


Figure 10. Packing diagram of H_2tfBC (**4**) (C, white, O, red, F, green, H, white, small spheres). Disordered hydrogen atoms (H15, H25) have been omitted for clarity. Hydrogen bonds between oxygen atoms are drawn as red broken lines.

bonds between the phenyl rings and the carboxylate groups ($\phi = 22.8(1)^\circ$ and $\phi = 40.9(1)^\circ$ for C11–C15 and C21–C25, respectively) resulting in a torsional angle between the two aryl groups of 60.9(1)°. Structural parameters of the phenyl ring and the carboxylic moiety in **4** are almost identical to its disubstituted congener **1** (Table 2). The $\text{F22}\cdots\text{H24}$ and $\text{F12}\cdots\text{H14}$ distances are 2.418(2) Å and 2.771(2) Å, which is for the former significantly shorter than the sum of their van der Waals radii (2.67 Å). The axis along the dimers is perpendicular to the (001) plane (Figure 10). This is in sharp contrast to crystal structures of benzoic acid, which also forms dimers in the solid state, but in the packing two distinctive orientations of the dimers are found.^{35,36}

Conclusion

By a simple modification of the synthesis known from the literature²² we developed a convenient synthesis for pure 2,3,5,6-tetrafluoroterephthalic acid (H_2tfBDC). Just by adding a surplus of $n\text{-BuLi}$ the formation of the byproduct 2,3,5,6-tetrafluorobenzoic acid is suppressed so that an extensive purification procedure no longer is necessary. This allows the synthesis of gram quantities of this acid with comparatively low efforts. As tfBDC^{2-} is expected to be an important ligand in the synthesis of coordination polymers and MOFs we think that this synthesis might boost the research with this ligand. Several compounds have already been synthesized with this ligand,^{9–21} but only few of them show permanent porosity. To the best of our knowledge an “all-F-MOF” is still unknown, although such a compound

(33) Crystallographic data (excluding structure factors) for the structure of **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-790323. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

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should show interesting hydrogen storage properties and would be a perfect model compound for the investigation of H₂ bonding sites in such a MOF, as no deuteration of the ligand for neutron diffraction experiments is necessary. But it was stated that “a second, non-fluorinated ligand is usually necessary to facilitate the incorporation of perfluorinated dicarboxylates into hybrid structures”.²¹ With gram quantities of H₂tfBDC at hand at comparatively low costs, it might be worthwhile to prove whether this assumption is correct.

Next to H₂tfBDC (**1**) the dihydrate H₂tfBDC·2H₂O (**2**), the ammonium salt (NH₄)₂tfBDC (**3**), and the monosubstituted acid H₂tfBC (**4**) were synthesized and characterized by an X-ray single crystal structure analysis. **1** and **4** exhibit hydrogen bonding via the carboxylate groups, which leads to a dimer in **4** (Figure 9) and a chain-like polymer in **1** (Figure 2). In both compounds the proton is disordered. In **2** additionally water molecules are included so that a complex 3D hydrogen bonding network is formed (Figure 4), where, with respect to the distances, the strongest hydrogen bond is found (O2–H2···O3; D···A 2.540(1) Å, Table 3), which are comparable to those found for **5** (O1–H1B···O4; D···A 2.541(2) Å, Table 3). In **3** the cations (NH₄⁺) and anions (tfBDC²⁻) are connected by hydrogen bonds again arranged in a 3D network (Figure 6).

For **1**, **3**, and **4** non-fluorinated congeners are known, but all of them exhibit crystal structures with distinct differences compared to the fluorinated counterparts, although the general structural arrangements of **1** (*P* $\bar{1}$, *Z* = 1) and its non-fluorinated congener (*P* $\bar{1}$, *Z* = 1)³⁷, both form infinite chains of H₂tfBDC and H₂BDC molecules linked by double hydrogen bonds, and **4** (*Fdd*2, *Z* = 16) and its non-fluorinated congener (*P*2₁/*c*, *Z* = 4)³⁶, both form dimers with disordered H atoms participating in the hydrogen bonds, are very similar.

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In contrast, for the fluorinated compounds the carboxylate groups are tilted with respect to the plane of the aryl rings (**1**: 19.35(7)°; **4**: 22.8(1)° and 40.9(1)°, respectively), whereas in the non-fluorinated compounds they are almost coplanar. The crystal structure of the non-fluorinated congener (*Pbc*2₁, *Z* = 4)³¹ of **3** (*C*2/*m*, *Z* = 2) was solved and refined from synchrotron powder diffraction data. Here angles between the planes of the carboxylate groups and the aryl ring of 29.0(8)° and 31(1)° are found, which are also significantly smaller than in **3** (44.54(7)°). Thus, the presence of the F atoms reduces the electron density in the aryl rings and therefore conjugation between the aryl π -system and the carboxyl group, which in turn allows stronger deviations from the coplanarity. Furthermore, deviation from coplanarity may be a consequence of electrostatic repulsion between O and the *o*-fluorine atoms.^{38,39} Both effects work synergistically and illustrate nicely that structural properties of non-fluorinated compounds cannot be transferred one to one to their fluorinated counterparts. This different structural behavior might be among the reasons why perfluorinated analogues of MIL-53 or MOF-5 are currently still unknown.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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