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 (Z, Z = 1). Recrystallization from water/acetone leads to single crystals of H₂tfBDC·2H₂O (P, Z = 2), where an extensive hydrogen bonding network is found. By reacting H₂tfBDC with an aqueous ammonia solution, single crystals of (NH₄)₂tfBDC (3, C/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 (Fdd, Z = 16) shows dimeric units as characteristic structural feature.

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 (tfBDC⁻) have been published. 9-21 Most of them are non-porous.

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-5 1 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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(1) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Nature 1999, 402, 276–279.
(2) Mueller, U.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastre, j. J. Mater. Chem. 2006, 16, 626–636.
(3) Frey, G. Chem. Soc. Rev. 2008, 37, 191–214.
(4) Czaia, A. U.; Trukan, N.; Mueller, U. Chem. Soc. Rev. 2009, 38, 1284–1293.
(5) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Butaille, T.; Frey, G. Chem. Eur. J. 2004, 10, 1373–1382.
(6) Zhang, L.; Wang, Q.; Liu, Y.-C. J. Phys. Chem. B 2007, 111, 4291–4295.
(7) Hubner, O.; Gloss, A.; Fichtner, M.; Klopper, W. J. Phys. Chem. A 2004, 108, 3019–3023.

(8) Yang, C.; Wang, X.; Omary, M. A. J. Am. Chem. Soc. 2007, 129(50), 15454–15455.
(9) Chisholm, M. H.; Wilson, P. J.; Woodward, P. M. Chem. Commun. 2002, 566–567.
(10) Kitaura, R.; Ihawahi, F.; Matsuda, R.; Kitagawa, S.; Kubota, Y.; Takata, M.; Kobayashi, T. C. Inorg. Chem. 2004, 43, 6522–6524.
(11) Liu, S. Q.; Konaka, H.; Kuroda-Sowa, T.; Maekawa, M.; Suenga, Y.; Ning, G. L.; Munakataa, M. Acta Crystallogr., Sect. E: Struct. Rep. Online 2004, 60, m1504–m1506.
(12) Ito, M.; Onaka, S. Inorg. Chem. Acta 2004, 357, 1039–1040.
(13) Chun, H.; Dybseev, D. N.; Kim, H.; Kim, K. Chem.− Eur. J. 2005, 11, 3521–3525.
(14) Chen, B.; Yang, Y.; Zapata, F.; Qian, G.; Luo, Y.; Zhang, J.; Lobkovsky, E. B. Inorg. Chem. 2006, 45, 8882–8886.
(15) Yoon, J. H.; Choi, S. B.; Oh, Y. J.; Seo, M. J.; Jhon, Y. H.; Lee, T.-B.; Kim, D.; Choi, S. H.; Kim, J. Catal. Today 2007, 120, 324–329.
(16) Zhu, E.-J.; Liu, Q.; He, M.-Y.; Chen, S.-C.; Huang, H.-X.; Yang, Q. Wuji Huaxue Xuebao (Chin. J. Inorg. Chem.) 2008, 24, 1428–1433.
(17) Zheng, C.-G.; Hong, J.-Q.; Zhang, J.; Wang, C. Acta Crystallogr., Sect. E: Struct. Rep. Online 2008, 64, m879.
(18) Zheng, C.-G.; Zhang, J.; Hong, J.-Q.; Li, S. Acta Crystallogr., Sect. E: Struct. Rep. Online 2008, 64, m965.
(19) Halvey, Z.; Falcao, E. H. L.; Eckert, J.; Cheetham, A. K. J. Mater. Chem. 2009, 19, 4307–4309.
(20) Halvey, Z.; Ayala, E.; Forman, J. D.; Forster, P. M.; Cheetham, A. K. J. Cryst. Growth Des. 2009, 9, 4759–4765.
(21) Halvey, Z.; Ayala, E.; Cheetham, A. K. Z. Anorg. Allg. Chem. 2009, 635, 1753–1757.
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Article

In 1964 a synthesis of H$_2$tfBDC was described starting from 1,2,4,5-tetrafluorobenzene, which was reacted with n-butyllithium and carbonated with CO$_2$\textsuperscript{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 H$_2$tfBDC by a comparatively simple procedure, also starting from 1,2,4,5-tetrafluorobenzene, which is available at a reasonable price. Crystal structures of H$_2$tfBDC (1), H$_2$tfBDC·2H$_2$O (2), and (NH$_4$)$_2$tfBDC (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. Tetrahydrofurane (THF) was dried using a MBRAUN MB SPS-800 solvent purification system. All other solvents were used as purchased.

Synthesis. 2,3,5,6-Tetrafluoroerophthalic Acid (1). Synthesis Protocol (a). In an argon atmosphere, 2.13 g of 1,2,4,5-tetrafluorobenzene (14.2 mmol, 1.0 equiv) was 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, CO$_2$ 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 Et$_2$O. The aqueous phase was additionally extracted two times with each 100 mL of Et$_2$O. The collected ether phases were dried over magnesium sulfate. The separated solution from acetone. An alternative synthesis of 1 was already described in ref\textsuperscript{23}. 1H NMR (acetone-d$_6$): [ppm] = 11.7 (s, 1H; COOH) 7.74 (tt, J$_{HF}$ 10.2 Hz, J$_{HF}$ 7.4 Hz, C$_4$–H4), 1.3 C NMR (acetone-d$_6$) [ppm] = 160.5 (s; COOH); 146.96 (dm, J$_{CF}$ 243.5 Hz, C$_3$, 145.27 (dm, J$_{CF}$ 252.6 Hz, C$_2$, 114.76 (t, J$_{CF}$ 18.7 Hz, C$_1$), 109.76 (t, J$_{CF}$ 23.0 Hz, C4). 19F-NMR (acetone-d$_6$) = −139.82 (m, −F2,6), −142.03 (br.s, −F3,5).

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 IPS II, or a Bruker APEX-II single crystal diffractometer (MoK\textsubscript{α} radiation). For data collection and reduction the Stoe program package was applied. The structural models were solved using SIR-92 (3) or SHELXS (1, 2, 26) and completed using difference Fourier maps calculated with SHELXL-97, which was also used for final refinements. For the structure of 3 and 5 all programs were run under the WinGX system. 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.

(23) Tamborski, C.; Soloski, E. J. J. Org. Chem. 1966, 31, 743–745.
(24) Stoe, IPS manual: X-Red 1.22, Stoe Data Reduction Program; Stoe & Cie GmbH: Darmstadt, Germany, 2001.
(25) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. Appl. Crystallogr. 1999, 32, 343–350.
(26) Sheldrick, G. M. SHELXL-97: A program for crystal structure refinement, release 97; University of Göttingen: Göttingen, Germany, 1997.
(27) WinGX, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data, Version 1.64,0; Department of Chemistry, University of Glasgow: Glasgow, U.K., 1997–2002; Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837–838.
(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 (H$_2$tfBDC, 1), CCDC-770476 (H$_2$tfBDC·2H$_2$O, 2), CCDC-770477 (NH$_4$)$_2$tfBDC, 3), and CCDC-770478 (H$_4$tfBDC·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 363/303; e-mail: deposit@ccdc.cam.ac.uk].
Table 1. Details of X-ray Single Crystal Structure Determination of Compounds 1–5

| Compound | H$_2$tBDC (1) | H$_2$tBDC·2H$_2$O (2) | (NH$_2$)$_2$tBDC (3) | H$_2$tcBC (4) | H$_2$tcBC·NH$_2$HtBC (5) |
|----------|---------------|----------------------|---------------------|---------------|-------------------------|
| formula  | C$_{10}$H$_8$F$_4$O$_4$ | C$_{10}$H$_8$F$_4$O$_4$ | C$_{10}$H$_8$F$_4$O$_4$N$_2$ | C$_{10}$H$_8$F$_4$O$_4$ | C$_{10}$H$_8$F$_4$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 | 0.40 × 0.36 | 0.2 × 0.1 | 0.24 × 0.18 | 0.44 × 0.06 |
| space group; Z | P$\overline{1}$ (No. 2), 1 | P$\overline{2}_1$/c (No. 14), 2 | C2/m (No. 12), 2 | Pd$\overline{2}$ (No. 43), 16 | Flack $x = -0.5(10)$ |
| unit cell | $a$, Å | 4.565(2) | 8.5206(15) | 6.632(2) | 10.193(15) |
| | $b$, Å | 5.832(2) | 7.9910(8) | 19.771(6) | 12.890(3) |
| | $c$, Å | 7.452(2) | 7.2845(14) | 3.7145(11) | 20.424(4) |
| | $\alpha$, deg | 87.32(3) | 90 | 90 | 90 |
| | $\beta$, deg | 78.41(3) | 99.739(15) | 92.38(3) | 90 |
| | $\gamma$, deg | 74.11(3) | 90 | 90 | 90 |
| volume, Å$^3$ | 186.92(10) | 488.84(14) | 486.63(3) | 2683.89(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$\alpha$ | Stoe four-circle (STADI), MoK$\alpha$ | Stoe IPDS II, MoK$\alpha$ | Stoe four-circle (STADI), MoK$\alpha$ | Bruker APEX-II CCD, MoK$\alpha$ |
| temperature, °C | −178(2) | −178(2) | 20(2) | −178(2) | −183(2) |
| 2$\theta_{\text{max}}$, deg | 60.00 | 60.00 | 59.00 | 52.00 | 52.00 |
| index ranges | $-6 \leq h \leq 6$ | $-6 \leq h \leq 6$ | $-6 \leq h \leq 6$ | $-6 \leq h \leq 6$ | $-6 \leq h \leq 6$ |
| reflections collected/ind. significant reflections, with $I > 2\sigma(I)$ | 1376/1086 | 2758/1426 | 2857/701 | 898/683 | 25193/2825 |
| R(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 = $S_{\text{ull}}$ | 1.08 | 1.07 | 1.00 | 1.07 | 1.04 |
| R($|F|^2 > 2\sigma(|F|^2)$ | 0.034 | 0.035 | 0.041 | 0.025 | 0.031 |
| wR($F^2$) | 0.091 | 0.091 | 0.103 | 0.063 | 0.081 |
| $\Delta$R$_{\text{free}}$/R$_{\text{free}}$ | 0.38/−0.24 | 0.38/−0.26 | 0.26/−0.20 | 0.18/−0.24 | 0.23/−0.21 |

XRDP. XRPD data were collected on a Huber G670 with a germanium monochromator and Cu K$\alpha$ 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 suite 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 CCl$_4$F as internal standard (19F).

Results and Discussion

Pure 2,3,5,6-tetrafluoroterephthalic acid (H$_2$tBDC, 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 CO$_2$ 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 literature and was confirmed by us (see protocol (b)). So the synthesis described in protocol (a), which exclusively leads to H$_2$tBDC, 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$\overline{1}$ 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. 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.

(29) Win XPOW; Version 1.04; Stoe & Cie GmbH: Darmstadt, Germany, 1999.

(30) Schajer, W.; Post, H.; Grosescu, R.; Haeberlen, U.; Blockus, G. J. Magn. Reson. 1983, 53, 213–228.
Reactions of 1,2,4,5-Tetrafluorobenzene with Different Amounts of n-BuLi and Subsequent Carbonation with CO₂

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 I and its deuterated congener reveal, however, significant differences. 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 I, while in the deuterated variety the aryl rings are stacked above each other. In I 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 I (3.377 Å) than in its perdeuterated analogue (3.417 Å). Furthermore,
According to a preliminary DTA/TG investigation a mass loss of 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:

\[
p\text{-HOOC-C}_6\text{F}_4\text{-COOH (1) } \xrightarrow{220–290 °C} \text{H-C}_6\text{F}_4\text{-COOH (4) + CO}_2 (4)
\]

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 \(P2_1/c\). The hydrogen atoms were refined with individual isotropic displacement parameters. All O–H distances were fixed 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 \(C2/m\) as colorless platelets. Hydrogen atoms were located in difference Fourier maps and refinement was performed 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 1.** ORTEP diagram of \(\text{H}_2\text{tfBDC (1)}\) 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 \(\text{H}_2\text{tfBDC (1)}\) (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.

**Figure 3.** ORTEP diagram of \(\text{H}_2\text{tfBDC·2H}_2\text{O (2)}\) showing 50% probability thermal ellipsoids and the atom-numbering scheme.

| D–H···A   | D–H | H···A | D···A  | D–H···A |
|-----------|-----|-------|-------|---------|
| O1–H1···O2 | 0.84| 1.84  | 2.655(2)| 162     |
| O2–H2···O1 | 0.84| 1.83  | 2.655(2)| 168     |
| 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     |
| O5–H51···O4| 0.97(2)| 1.93(2)| 2.821(2)| 151(2)  |
| O5–H52···O4| 0.98(2)| 1.98(2)| 2.908(2)| 158(2)  |
| O15–H15···O25| 0.95   | 1.72  | 2.644(2)| 163     |
| O25–H25···O15| 0.95   | 1.76  | 2.644(2)| 154     |
| O1–H1B···O4 | 0.84 | 1.71  | 2.541(2)| 171     |
| O1–H1B···O3 | 0.84(2)| 2.09(2)| 2.868(2)| 153(2)  |

\(\text{H}_2\text{tfBDC (1)}\)

\(\text{H}_2\text{tfBDC·2H}_2\text{O (2)}\)

\((\text{NH}_4)_2\text{tfBDC (3)}\)

\(\text{H}_2\text{BDC (4)}\)

\((\text{NH}_4)_2\text{tfBDC·NH}_4\text{HtfBC (5)}\)
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)/C176 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)/C176 and 29(2)/C176).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 NH4+ cations the tfBDC anion acts as an 8-connector. Consistently, each NH4+ cation connects to four different tfBDC anions. The resulting H⋯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 (NH4)2ADC (ADC2− = acetylenedicarboxylate) to NH3, CO2, and C2H2 gives an exothermic signal.32 To check whether 3 decomposes or sublimes, 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 C32H12F8N (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

\[ \text{C2221} \]
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 centrosymmetric orthorhombic space group $P2_12_12_1$ as colorless blocks. 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 angles 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 tetrahedral C–O–H angles.

The H$_2$tfBC (4) structure was determined and refined by the Siemens SMART program. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms H5 and H12 were refined isotropically with 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 bonds between the phenyl rings and the carboxylic 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)$^\circ$. Structural parameters of the phenyl ring and the carboxylic moiety in 4 are almost identical to its disubstituted congener 1 (Table 2). The F22⋯H24 and F12⋯H14 distances are 2.418(2) Å and 2.771(2) Å, respectively, 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.

**Conclusion**

By a simple modification of the synthesis known from the literature we developed a convenient synthesis for pure 2,3,5,6-tetrafluoroterephthalic acid (H$_2$tfBDC). Just by adding a surplus of n-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 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, 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

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(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].

(34) Steiner, T. Angew. Chem., Int. Ed. 2002, 41, 48–76.

(35) Bruno, G.; Randaceio, L. Acta Crystallogr., Sect. B: Struct. Sci. 1996, 52, 1711–1712.

(36) Wilson, C. C.; Shankland, N.; Florence, A. J. J. Chem. Soc., Faraday Trans. 1996, 92, 5051–5057.
should show interesting hydrogen storage properties and would be a perfect model compound for the investigation of H$_2$ 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”. With gram quantities of H$_2$tfBDC at hand at comparatively low costs, it might be worthwhile to prove whether this assumption is correct.

Next to H$_2$tfBDC (1) the dihydrate H$_2$tfBDC·2H$_2$O (2), the ammonium salt (NH$_4$)$_2$tfBDC (3), and the monosubstituted acid H$_2$tfBC (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 (NH$_4$$^+$) and anions (tfBDC$^{2-}$) 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 ($P\overline{1}$, $Z = 1$) and its non-fluorinated congener ($P\overline{1}$, $Z = 1$)$^{37}$, both form infinite chains of H$_2$tfBDC and H$_2$BDC molecules linked by double hydrogen bonds, and 4 ($Fdd2$, $Z = 16$) and its non-fluorinated congener ($P2_1/c$, $Z = 4$)$^{36}$, both form dimers with disordered H atoms participating in the hydrogen bonds, are very similar. In contrast, for the fluorinated compounds the carboxylate groups are tilted with respect to the plane of the aryl rings (1: 19.35(7)$^\circ$; 4: 22.8(1)$^\circ$ and 40.9(1)$^\circ$, respectively), whereas in the non-fluorinated compounds they are almost coplanar. The crystal structure of the non-fluorinated congener ($Pbc2_1$, $Z = 4$)$^{31}$ of 3 ($C2/m$, $Z = 2$) 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)$^\circ$ and 31(1)$^\circ$ are found, which are also significantly smaller than in 3 (44.54(7)$^\circ$). 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.

(37) Bailey, M.; Brown, C. J. Acta Crystallogr. 1967, 22, 387–391.
(38) Wang, Z.; Kravtsov, V. C.; Walsh, R. B.; Zaworotko, M. J. Cryst. Growth Des. 2007, 7, 1154–1162.
(39) Hulvey, Z.; Furman, J. D.; Turner, S. A.; Tang, M.; Cheetham, A. K. Cryst. Growth Des. 2010, 10, 2041–2043.