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Highly Fluorinated Trianglimine Macrocycles: A Supramolecular Organic Framework

Α

Tom Kunde^{◊a} Tobias Pausch^{¢a} Guido J. Reiss^b Bernd M. Schmidt*^a

^a Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany bernd.schmidt@uni-duesseldorf.de

^b Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1. 40225 Düsseldorf, Germany

These authors contributed equally

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Abstract A novel highly fluorinated dialdehyde was prepared by a two-stage synthesis. This reactive building block for dynamic imine chemistry was used in a condensation reaction to generate the first extensively fluorinated trianglimine. An analysis of the material properties and, especially, the crystal structure of the [3+3] macrocycle revealed a supramolecular organic framework with tubular porous channels. The use of fluorinated ligands to generate hydrophobic electron-deficient channel-like pores is an important addition to the ever-expanding field of supramolecular networks and to trianglimine chemistry in general.

Key words supramolecular organic frameworks, trianglimines, porous materials, fluorinated ligands, crystal structure

The ever-growing need for porous materials as storage options for energy-relevant or climate-change-contributing gases, along with the use of such materials as storage units or cargo containers for small molecules, has led to a surge in the development of both covalent organic frameworks (COFs) and metal-organic frameworks (MOFs).^{1,2} Only in recent years have researchers shown a growing interest in the synthesis of supramolecular organic frameworks (SOFs) or porous organic crystals. Because porous SOFs often consist of sterically hindered or rigid small molecules that, through supramolecular interactions, crystallize in a highly regular fashion, they are superior to MOFs and COFs in terms of both cost and accessibility.^{3a-e} Although the pore sizes of COFs and MOFs are generally larger than those of SOFs, the smaller pores can be used, for example, as interactive surfaces for the detection of small molecules.^{3f} Porous crystals and SOFs have therefore been used to bind anesthetics,^{3e} to separate compound mixtures,^{3g} and to store CO₂ or H₂.^{3b} The porosity inside these materials is the result of single- or multidimensional channels that are created

during the crystallization of one or more of their components.^{3d} If macrocycles are used in the synthesis of SOFs, the resulting channels are mostly one-dimensional, permitting 'flow' through the tubular pores of the material.⁴

The trianglimines are one class of easily synthesized macrocycles. Consisting of three trans-1,2-diaminocyclohexane (DACH) and three meta- or para-substituted dialdehyde residues, trianglimines can be synthesized directly by imine condensation.^{5a} Because of their ease of preparation, trianglimines and their derivatives, the trianglamines (in which the imine bonds have been reduced to amine bonds), have found widespread use in the synthesis of functional materials.^{5,6} Nunes and co-workers were even able to generate a trianglamine-containing membrane capable of nanofiltration of several contaminants from a range of organic solvents.^{6f} The Khashab group demonstrated that trianglamines are well suited to the generation of SOFs with permanent porosity that can store CO₂ and CH₄, and that, after preloading with I₂, can even upgrade natural gas by separating those two components.^{6e} More recently, they also found that trianglimine macrocycles can form porous networks whose pore structure can be influenced by molecular guests.5g

To enhance the hydrophobicity of porous materials and to increase their uptake of CO₂ and H₂, fluorinated ligands can be used in their syntheses.⁷ Although Kuhnert and coworkers have done tremendous work on the accessibility of trianglimines and trianglamines, and have also investigated the cavity sizes obtained by using dialdehydes of different lengths,^{5a-d} to the best of our knowledge no work has been done on highly fluorinated trianglimine macrocycles. Given their ease of accessibility and their potential for the synthesis of porous materials, we wanted to investigate the synthesis and material properties of trianglimines containing perfluorinated aromatic aldehydes.



We therefore synthesized 2.2',3.3'.5.5'.6.6'-octafluorobiphenyl-4,4'-dicarbaldehyde (2) in two steps from cheap and readily available starting materials (Scheme 1). The intermediate dicarbonitrile 1 was obtained in 60% vield by following the procedure of Kaneko with 0.5 equivalents of tris(diethylamino)phosphine as a reagent.⁸ Because tris(diethylamino)phosphine can be synthesized at a low cost from diethylamine and phosphorus trichloride, it is suitable for bulk preparation. The reaction worked well up to a 5 g scale in our hands. Because of the structural similarity of bis(triethylamino)phosphine to the putative carcinogen hexamethylphosphoramide (HMPA), we also briefly investigated the use of the commercially available, potentially less cancerogenic, tris(1-pyrrolidinyl)phosphine, which we surmised would show similar reactivity. To compensate for the much higher price of this reagent, we examined the reaction by using catalytic amounts of the phosphine (10%), with regeneration of the active phosphorus(III) species from inactive phosphorus(V) fluoride⁹ with phenylsilane or diphenylsilane.¹⁰ Possibly due to the presence of more-active species in the mixture, the resultant reaction became difficult to control. Polycondensates formed by subsequent activation (in the ortho-position to the nitrile) of the expected product 1, leading to reaction with residual pentafluorobenzonitrile or with a second molecule of **1**. Due to the low polarity of all the compounds, their separation became increasingly difficult. Careful optimization led to yields of around 58%, identical to those obtained by using half an equivalent of tris(diethylamino)phosphine. Reduction of dinitrile **1** by using a slight excess of diisobutylaluminum hydride (DIBAL-H) gave the corresponding diimine, which underwent acid hydrolysis during workup to give dialdehyde **2** in a good yield (79%). Notably, both the homocoupling reaction and the nitrile reduction gave products of high purity that did not require further purification and crystallized after aqueous workup.

To investigate the use of the new building block **2**, we opted to synthesize a simple [3+3] trianglimine by condensation with three equivalents of diaminocyclohexane **DACH** to generate the first perfluorinated trianglimine macrocycle **RRF24** (Scheme 2), which we subsequently characterized by means of NMR, HRMS (ESI), Brunauer–Emmett–Teller (BET), and single-crystal X-ray diffraction (SXRD) analyses.

The resulting precipitate of **RRF24** was isolated by filtration and washed with MeCN to remove any remaining starting material or soluble low-mass oligomers and give a colorless solid.¹¹ After redissolving **RRF24** in CDCl₃, ¹H, ¹⁹F NMR, and DOSY experiments confirmed the formation of



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Figure 1 (a) Molecular structure of RRF24 as obtained from SXRD data, including an outline depicting the accessible surface area; (b) chiral tubular pores (green) in the crystal lattice; (c) view of the unit cell of RRF24 along the crystallographic *a* axis, including the pores (green); (d) gas-sorption isotherms for N₂ at 77 K, adsorption (blue, solid symbols) and desorption (red, hollow symbols) for a crystalline RRF24 sample activated by soaking in pentane; (e) corresponding BET plot.

the desired macrocycle with characteristic imine signals at δ = 8.40 ppm in the ¹H NMR, two sharp sets of signals in the ¹⁹F NMR. and a diffusion coefficient $D \approx 4.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. corresponding to a solvodynamic radius of 0.93 nm in solution at 298 K [see Supporting Information (SI)]. The molecular structure was ultimately established by SXRD (Figure 1). RRF24 crystallizes from MeCN in the monoclinic space group P2₁ with three crystallographically independent macromolecules and three MeCN molecules in the asymmetric unit. As a consequence, each tubular void is different, which also leads to three different orientations of the MeCN molecules seen in the voids. From a crystallographic point of view, this structure exhibits pseudosymmetry.¹² In this case, a description with a higher symmetry would result in one macromolecule in the asymmetric unit with the a axis divided by three, leading to serious disorder in many parts of the structure. Interestingly, the interactions between neighboring macromolecules in the stack are heavily influenced by the conformation of each of the twisted octafluorobiphenyl moieties, impacting the orientation of the next neighbor, possibly to maximize $F \cdots \pi$ interactions within the strands. Neighboring strands are slightly offset, permitting rather short intermolecular C-H…F contacts of around 2.6 Å.^{13b} To our delight, the one-dimensional tubular-like pores within the structure were found to be readily accessible. Supported by the chiral nature of the compound and the slightly different conformations of each of the three unique macromolecules, helical, one-dimensional channels are formed (Figure 1).

To investigate the porosity of **RRF24**, bulk crystalline samples were prepared by slow evaporation of a CH_2Cl_2 -MeCN (3:1) solution over the course of three to five days, followed by solvent exchange (see SI), before gas-sorption analysis. The specific surface area for the crystalline material was 88 m² g⁻¹, as determined from the BET isotherm and the N₂ gas uptake of 28.02 cm³ g⁻¹. As expected, the latter

value is slightly lower than that of the previously reported trianglamine-based **T-SOF-1** (prepared from terephthaldehyde and **DACH**);^{6e} this is presumably due to the ~50% reduction in the diameter of the inner tubes as a result of the introduction of the fluorine atoms onto the biphenyl moieties. This is also reflected in a smaller specific surface area for **RRF24**. **T-SOF-1**, however, only has properties suitable for materials applications after reduction to the corresponding trianglamine and it needs chloride counterions as directing agents, whereas **RRF24** is intrinsically porous. A recent investigation of guest uptake by the nonfluorinated trianglimine congener showed no N₂ uptake at 77 K, supposedly due to weaker interactions, thereby preventing the determination of its specific surface area.^{6g}

In conclusion, we have developed a synthesis of the novel dialdehyde building block **2**, paving the way to new materials with improved properties, such as better CO_2 -philicity, thermal stability, and crystallinity.¹³ Employment of our reactive ditopic aldehyde **2** and a diamine to synthesize the first highly fluorinated [3+3] trianglimine **RRF24** gave a porous material with helical chiral pores. Our study underscores the role of fluorine and organic synthesis in the rational design and development of new nanoporous materials for use in gas-storage and gas-separation materials.

Conflict of Interest

The authors declare no conflict of interest

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1470-6050.

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- (11) Supramolecular Organic Framework RRF24

A solution of DACH (91.4 mg, 800 µmol, 1.0 equiv) in MeCN (15 mL) was added dropwise to a stirred solution of dialdehyde 2 (283 mg, 800 µmol, 1.0 equiv) in MeCN (10 mL) over 1 h. The resulting solution was stirred overnight at r.t., and the precipitate that formed was collected by filtration and washed with MeCN ($2 \times 5 \text{ mL}$) to give a colorless powder; yield: 195 mg (150 µmol, 56%); mp 306.7 °C.

FTIR (ATR): 2933.7 (w), 2862.4 (w), 1643.4 (w), 1469.8 (s), 1384.9 (w)1278.8 (m), 1263.4 (w), 1089.8 (w), 1033.9 (w), 987.6 (m), 927.8 (m), 862.2 (w), 723.3 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.40 (s, 2 H, -CH_AN), 3.84-3.22 (m, 2 H, CH-N=), 2.12–1.72 (m, 6 H, $-C(H_B)_2$ – and C–H_C), 1.75–1.34 (m, 2 H, $C-H_c$). ¹³C{¹H} NMR (126 MHz, CDCl₃): $\delta = 149.7$ (Ar-CH₄O), 145.6 (dd, J = 257.3, 11.8 Hz, $C_{Ar}-F_A$), 143.7 (dd, J = 254.5, 15.5 Hz, C_{Ar} - F_B), 117.9 (t, J = 12.7 Hz, C_{Ar} - CH_AO), 108.1 (t, J = 16.2 Hz, Ar–C_{Ar}), 76.0 (–C–N=), 32.4 (–C–H_B), 24.3 (–C–H_B). $^{19}\mathrm{F}$ NMR (282 MHz, CDCl₃): δ -137.77 (dd, J = 16.8, 9.6 Hz, 4 F, Ar-F_A), -142.38 to -143.31 (m, 4 F, Ar- $F_{\rm B}$). HRMS (ESI): m/z [M + H]⁺ Calcd for $C_{60}H_{37}F_{24}N_6 = 1297.2691$; found: 1297.2688.

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