Phenyl/Pentafluorophenyl Interactions and the Generation of Ordered Mixed Crystals: *sym*-Triphenethynylbenzene and *sym*-Tris(perfluorophenethynyl)benzene**

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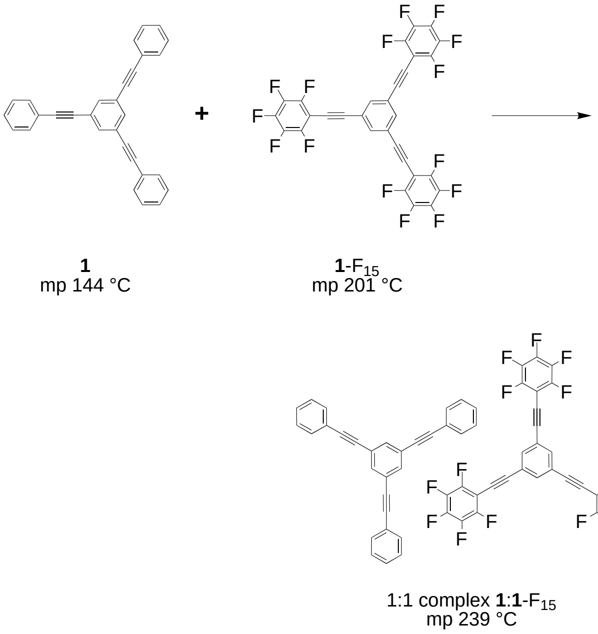
Although benzene and perfluorobenzene adopt crystal structures with "herringbone" (T-shaped) pairwise orientations,[1, 2] combination of the two liquids produces an intimate 1:1 solid complex in which the basic short range order is a face-to-face stack.[3, 4] The driving force for this specific mixing stems from the quadrupole moment and van der Waals surface of benzene and perfluorobenzene.[5–8] Recent dynamic studies have provided quantitative evidence for a general, polar-π phenyl/perfluorophenyl attraction.[9, 10] These studies of ours and related work have developed a design principle for ordered mixed-crystals of aromatic/perfluoroaromatic compounds.[9–14] Studies on tolan/perfluorotolan and related compounds support these ideas.[15–17] A powerful extension of the principle is to use the attractive phenyl/perfluorophenyl interactions to anchor other groups in a specific order within a crystal, that is, to accomplish crystal engineering.[18] We provide a striking demonstration of such control through the crystal structures and mixing behavior of *sym*-triphenethynylbenzene (**1**) and *sym*-tris(perfluorophenethynyl)benzene (**1**–F$_{15}$); the pure compounds pack in slipped stacks and the 1:1 complex displays face-to-face stacks alternating **1** and **1**–F$_{15}$.



1
mp 144 °C

1-F$_{15}$
mp 201 °C

1:1 complex **1**:**1**-F$_{15}$
mp 239 °C

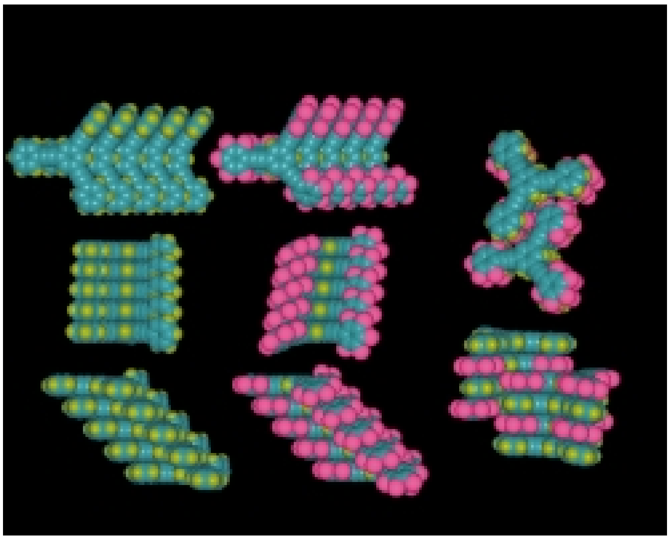


Figure 1. Three views of the stacked structures in (left to right) **1**, **1**–F$_{15}$, and **1**:**1**–F$_{15}$ (1:1 complex), with reaction scheme and melting points above. From upper to lower: a) top view, b) back view, c) side view.

Reaction of 1,3,5-tribromobenzene with phenylacetylene under Sonagoshira conditions (Pd^{IV} 5 %, dimethylformamide, base) resulted in the formation of **1** in 58 % yield. Under similar conditions 1,3,5-triethynylbenzene and pentafluoroiodobenzene were coupled to form **1**–F$_{15}$ in 30 % yield. Pure **1** was crystallized from hexanes/dichloromethane to produce needles that melted at 142–146 °C (visual inspection), 144 °C (differential scanning calorimetry (DSC)). Pure **1**–F$_{15}$ was recrystallized from hexanes/dichloromethane to produce needles that melted at 199–201 °C (visual inspection), 201 °C (DSC). Equimolar amounts of **1** and **1**–F$_{15}$ were ground in an agate mortar to produce a fine powder (Figure 1, top). Unlike most solid mixtures, the melting point of the 1:1 mixture was higher than either of the two pure compounds (235–239 °C, visual inspection; 239 °C, DSC). Recrystallization of this powder from hexanes/dichloromethane by evaporation of a clear solution produced crystals (**1**:**1**–F$_{15}$) with identical melting behavior to the original powder. The sharp and higher melting point of the mixture indicated that a solid compound had formed and it was inferred that the special phenyl/perfluorophenyl interaction was involved.

Crystallographic analysis of single crystals of **1**, **1**–F$_{15}$, and **1**:**1**–F$_{15}$ (1:1 complex) revealed two structural classes: slipped stacks and columnar stacks (Figure 1, bottom).[19–24] The monoclinic centered (*C*2/*c*) structure of **1** displays a twisted rotor form. The interplanar angles between the radial and central benzene rings are 0, 9, and 80°. The acetylenic bonds are bent slightly (175–180° with an average of 178°). The rings are not face-stacked with respect to one another in the crystal, but rather slipped such that one radial benzene ring sits atop the acetylene of its neighbor within the stack. The acute angle of the vector passing through the middle of the central benzene rings in each stack with the normal to the best

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plane of those rings can be defined as a slip angle. That angle would be 0° for a perfect columnar stacking and 90° for a single lamellar sheet. Assuming a 3.6 Å distance between layers and "normal" benzenoid bond lengths, an angle of 35° (sin of 0.81) would place the hydrogen of one ring over the center of its neighbors, the face-to-face/center-to-edge conformation (Figure 2). In the case of **1** the slip angle is approximately 48°, well beyond the face-to-face/center-to-edge conformation. Packing between the stacks seems to be dominated by shape selection, with each stack nestling into the other.

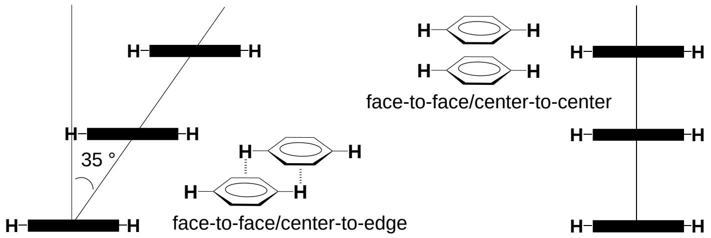

Figure 2. Relation of face-to-face/center-to-edge (left) and face-to-face/center-to-center (right) geometries to the packing slip angle.

A remarkably similar structure is observed for the monoclinic ($P2_1/c$) crystal structure of **1**–F_{15}. Again a twisted structure is adopted, however, with more severe interplanar torsion angles of 4, 28, and 90°. The acetylenic bonds are bent slightly more (171–177° with an average of 174°). The slip-angle of the stack is 46°, only 2° off from the 48° seen in **1**. Thus, again the radial ring in one molecule tends to pack over the acetylenic unit of its neighbors.

Things change markedly for the mixed crystal **1**:**1**–F_{15}. The triclinic ($P\bar{1}$) form displays an alternating motif of **1** and **1**–F_{15} in each stack. The stacks are nestled together by shape complementarity, but are shifted out of register with each other to juxtapose molecules of **1** as lateral neighbors to molecules of **1**–F_{15}. The proximity of hydrogen and fluorine atoms (2.4–2.7 Å) could be viewed as evidence for favorable C–H to F interactions, but it could also be due to the benefit of having commensurate layers (maximum packing density) or to lateral quadrupolar interactions.[25] More importantly, the molecules of **1** and **1**–F_{15} do not adopt twisted rotor conformations but are essentially planar and the slip-angle is only about 20°, significantly less than that predicted for the center-to-edge slipped stacking and approaching columnar stacking. Thus, it would seem that the anchoring principle of benzene-to-perfluorobenzene interactions applies in this case.

In conclusion, design principles and predictability in crystal engineering remain a frontier question in supramolecular chemistry.[26] Simple ideas like hydrogen-bond complementarity have made it possible to reduce the gamut of structures and to increase the chances that short-range supramolecular order will appear in the solid state.[27] The elucidation of other locally favored motifs, such as those induced by polar-π interactions, expands our control in the engineering of solids.[9, 15–17] Indeed, the use of phenyl/perfluorophenyl attractions is a useful and reliable way to control local order in crystal packing.[10] The underlying physics of this interaction is not limited to crystal packing; therefore, one could apply this principle to a number of constructions and exploit it in related short-range packing problems such as receptor–substrate interactions.

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[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132202, -132203, and -132204. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[21] In general, the quality of these room temperature analyses can be viewed as reasonable, R and R^2 factors are 5–8%, the data to parameter ratio exceeds 10, and residuals are small. The density of **1**:**1**–F_{15} falls within 2% of the average for **1** and **1**–F_{15}. The average bond lengths for any given bond type are normal; however, the ranges leave something to be desired. In addition, the average aromatic carbon–carbon bond length is unusually small in the radial benzene rings, but normal for the central benzene rings in all three structures. Some of these range and average anomalies can be explained if thermal motion is focused into librational motion of the outer rings. For our purposes, detailed analyses of the specific bond lengths is not necessary, and this caveat is in place for others who might want to

overinterpret the data. Despite the above mentioned concerns, we believe the supramolecular aspects of the crystal structures to be valid.

[22] Crystal data for **1**: crystal dimensions $0.50 \times 0.25 \times 0.10$ mm^3, monoclinic space group $C2/c$ (No. 15), $a = 35.645(11)$, $b = 4.851(3)$, $c = 24.804(9)$ Å, $\beta = 98.55(3)^\circ$, $V = 4241(3)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.185$ g cm^{-3}, $\mu = 0.067$ mm^{-1}, F(000) = 1584; 6107 reflections with $1.16 < \theta < 21.98^\circ$. Structure solution and refinement for 2591 independent reflections ($R_{\text{int}} = 0.192$) with $I > 2\sigma(I)$ and 272 parameters, $R = 0.0541$, $R_w = 0.0600$, max./min. residual electron density 0.139/ – 0.140 e Å^{-3}.

[23] Crystal data for **1**–F$_{15}$: crystal dimensions $0.80 \times 0.08 \times 0.08$ mm^3, monoclinic space group $P2_1/c$ (No. 14), $a = 18.308(7)$, $b = 4.887(4)$, $c = 27.145(14)$ Å, $\beta = 96.38(4)^\circ$, $V = 2414(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.784$ g cm^{-3}, $\mu = 0.186$ mm^{-1}, F(000) = 1272; 6965 reflections with $1.12 < \theta < 21.97^\circ$. Structure solution and refinement for 2943 independent reflections ($R_{\text{int}} = 0.088$) with $I > 2\sigma(I)$ and 406 parameters, $R = 0.0869$, $R_w = 0.0742$, max./min. residual electron density 0.250/ – 0.229 e Å^{-3}.

[24] Crystal data for **1**:**1**–F$_{15}$ (1:1 complex): crystal dimensions $0.30 \times 0.05 \times 0.05$ mm^3, triclinic space group $P\bar{1}$ (No. 2), $a = 7.4913(5)$, $b = 14.0798(9)$, $c = 22.2722(14)$ Å, $\alpha = 94.779(1)^\circ$, $\beta = 92.692(1)^\circ$, $\gamma = 91.580(1)^\circ$, $V = 2337.3(3)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.459$ g cm^{-3}, $\mu = 0.126$ mm^{-1}, F(000) = 1032; 23084 reflections with $0.92 < \theta < 28.66^\circ$. Structure solution and refinement for 10394 independent reflections ($R_{\text{int}} = 0.162$) with $I > 2\sigma(I)$ and 676 parameters, R = 0.0628, $R_w = 0.0582$, max./min. residual electron density 0.144/ – 0.172 e Å^{-3}.

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Inorganic – Organic Hybrid Materials Constructed from $[(VO_2)(HPO_4)]_\infty$ Helical Chains and $[M(4,4'\text{-bpy})_2]^{2+}$ (M = Co, Ni) Fragments[**]

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The design and synthesis of inorganic – organic hybrid materials have generated significant interest for their potential application in the fields of catalysis, biology, and optical and electromagnetic functional materials.[1] Huge structures have been reported for these materials over the past few years, in which various architectures with one- (1D), two- (2D), and three-dimensional (3D) connections between inorganic and organic species are displayed. Polyoxoanions associated with organic templates[2] or with metal coordination compounds[3, 4] have become a well-established class of inorganic – organic materials, among these the major interest has been shown in the few helical or chiral structures reported. For instance, a double helical chain has been described in $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7] \cdot 4\,H_2O$,[5] spirals of InO$_6$ octahedra in RbIn(OH)PO$_4$,[6] and a spiral-shaped chain in $[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]^{4-}$.[7] The rational synthesis of inorganic – organic compounds containing a helical array is a challenging goal.[8] Our aim was to synthesize such helical structures for the inorganic – organic compounds generated from a combination of vanadium phosphates[9] and metal coordination compounds. The diversity of polyhedra and valence states of vanadium together with the coupling characteristics of the components in the synthetic system provide the basis for constructing unusual structures.

Unlike the above examples, herein we report the synthesis and X-ray crystal structure analyses of the inorganic – organic hybrid materials **1** and **2**, which have not only an infinite helical chain $[(VO_2)(HPO_4)]_\infty$, but also both left-handed and right-handed helical chains in one compound.

$[M(4,4'\text{-bpy})_2(VO_2)_2(HPO_4)_4]$
(**1**: M = Co; **2**: M = Ni; bpy = bipyridine)

Compounds **1** and **2** were synthesized by the hydrothermal reaction of NaVO$_3$, NaH$_2$PO$_4$, Co(NO$_3$)$_2$ (for **1**) or Ni(NO$_3$)$_2$ (for **2**), 4,4'-bpy, and H$_2$O in a molar ratio 1:1:1:1:556 at 160 °C for five days. The crystalline product in each case was characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis/differential thermal analysis (TGA – DTA), and single-crystal X-ray diffraction analysis.[10]

Single-crystal X-ray diffraction analysis revealed that **1** and **2**, which are analogues, have a novel 3D structure constructed from two subunits, namely $[(VO_2)(HPO_4)]_\infty$ helical chains and $[M(4,4'\text{-bpy})_2]^{2+}$ fragments. These helical chains are composed of alternately corner-sharing HPO$_4$ tetrahedra and VO$_4$N trigonal bipyramids (Figure 1). The central axis of each helical chain is a twofold screw axis. Two oxygen atoms from adjacent VO$_4$N and HPO$_4$ units in the helical chain chelate an M atom of $[M(4,4'\text{-bpy})_2]$, generating a 3-ring {MVPO$_3$}. These 3-rings link the left-handed helical and right-handed helical $[(VO_2)(HPO_4)]_\infty$ chains to produce a layer motif {MV$_2$P$_2$O$_{20}$} in the (101) plane (Figure 1 a). Adjacent M/V/P/O layers are connected by 4,4'-bpy ligands, which generates a 3D structure (Figure 2).

Each vanadium atom resides in a distorted trigonal-bipyramidal environment, coordinated to four oxygen atoms and to a nitrogen atom from 4,4'-bpy. Three of the four oxygen atoms lie in an equatorial plane; one of these oxygen atoms is terminal, and two are bridging, one with P and one with M. The remaining oxygen atom, which bridges P and the N atom from 4,4'-bpy, is oriented axially, perpendicular to the equatorial plane. PO$_4$ tetrahedra link two V atoms, an M atom, and a proton. The M atoms reside in octahedral environments, coordinated to four oxygen atoms from VO$_4$N and HPO$_4$ in the equatorial plane and to two nitrogen atoms from 4,4'-bpy ligands occupying the axial positions.

When 4,4'-bpy functions as a rodlike ligand it usually coordinates with only central metals. In the case reported herein, it acts as a bifunctional organic ligand, directly linked to M (Co or Ni) and to V atoms in the P-V-O chains. To our knowledge, this coordination mode has not been observed in

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