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Design and Synthesis of New Tectons for Halogen Bonding-driven Crystal Engineering

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The S_NAr between oxygen or nitrogen nucleophiles and iodopentafluorobenzene is a versatile modular approach for the synthesis of telechelic α,ω-di-(2,3,5,6-tetrafluoro-4-iodophenyl) derivatives 1. Despite the presence of a +M substituent in the *para* position to iodine, these derivatives are effective as halogen bond donors and form strong I···N interactions with telechelic α,ω-di-(4-pyridyl) derivatives 2. In the resulting 1D infinite chains 3 the starting tectons alternate in an almost collinear fashion. The detailed structures of 3a and 3c were established through X-ray analyses. The overall structural pattern of these co-crystals is largely independent of the size of the starting tectons. Simple variation of the length of the spacers connecting recognition sites into telechelic modules constitutes a sort of metric engineering.

Keywords: Crystal engineering; Halogen bonding; Perfluorocarbon compounds; Pyridine derivatives; Tectons

INTRODUCTION

The modular design of molecules and their directed assembly into more complex aggregates are important issues in crystal engineering. They have been addressed utilizing self-assembly techniques, host–guest chemistry or template syntheses [1,2]. Unfortunately, structural control of supramolecular architectures is often frustrated by the delicate nature of the intermolecular interactions that govern their formation. The control can be even more challenging when multi-component heteromeric supramolecular architectures are synthesized.

Another important issue in crystal engineering is to maintain structural control in the obtained architecture even following tailored changes in the assembling modules. Towards this target it is important to identify tectons [3,4] whose self-assembly is predictable and largely independent from their metrics. Fujita and co-workers have presented nice examples of this modular approach [5]. The supramolecular structural design of specifically tailored catenanes is obtained by modulating the cavity of the architecture formed through the *metal coordination driven* self-assembly of pyridine-based ligands of variable lengths. Recently, Ward and co-workers adopted a modular approach in the *hydrogen bonding driven* self-assembly of organo-disulfonate tectons having different sizes to give pillar-shaped supramolecular frameworks [6]. A guest-directed template synthesis affords libraries with defined metric parameters.

In this paper we show how tectons **1** and **2** undergo *halogen bonding driven* self-assembly to give one-dimensional (1D) infinite chains **3** and the important features of the process are independent from the nature and size of the bridging motifs X and Y (Scheme 1). The high strength, specificity and directionality of the halogen bonding allow the topology of the constructed network to be predicted with an accuracy that is unusual for crystal engineering. The palette of synthetic methodologies for introducing perfluorinated residues on hydrocarbon scaffolds is quite limited. In this paper it is also shown how the nucleophilic aromatic substitution of oxygen or nitrogen residues for

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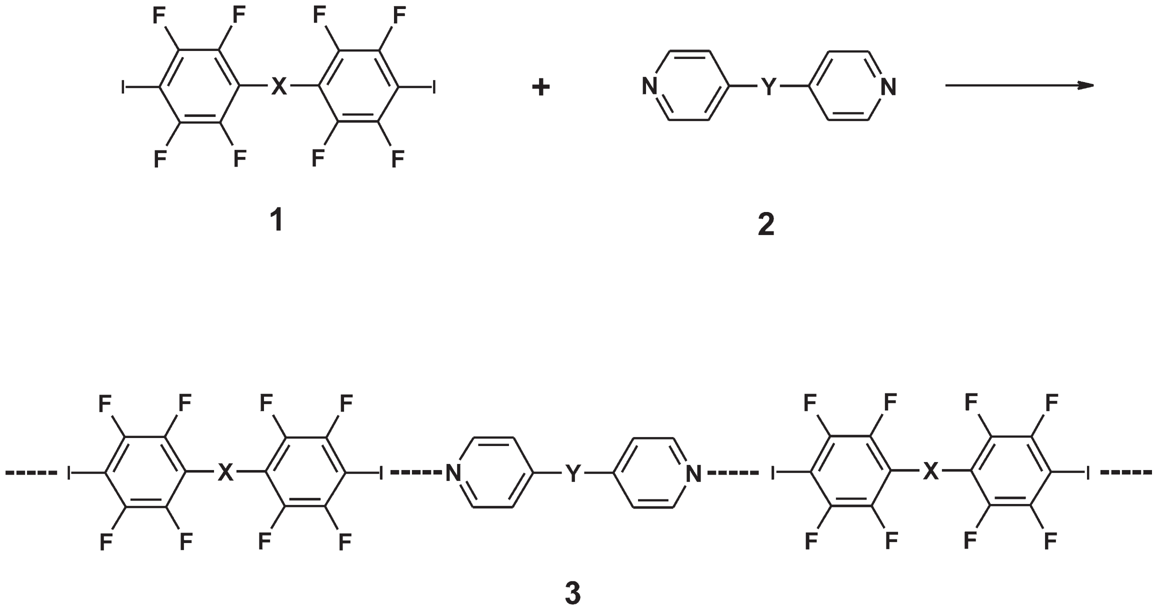


SCHEME 1

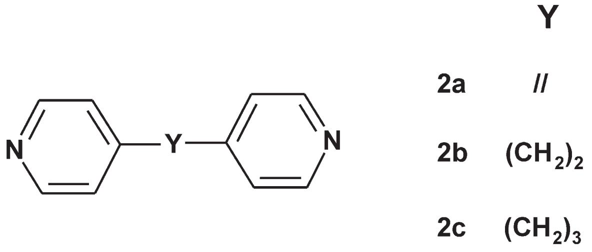
fluorine in pentafluoroiodobenzene (**4**) is a general approach to tectons **1** where the length of the bridging motif X can be easily varied.

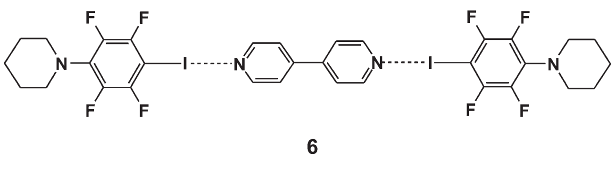
Halogen bonding, namely the attractive and non-covalent interaction between halogen atoms and lone-pair possessing heteroatoms [7–11], has been rationalized as a transfer of electron density from a donor atom's lone pair into an anti-bonding σ^* orbital of the acceptor atom [12]. Some similarities therefore exist with the much more famous hydrogen bonding [13]. When halogen bonds involve perfluorocarbon iodides as electron acceptor motifs and nitrogen atoms as donor motifs, the typical strength of the interaction has been calculated [14,15] and experimentally found [16] to be in the range 25–31 kJ mol^{-1}. Competitive experiments have shown that such halogen bonds can prevail over hydrogen bonds in controlling self-assembly processes, indicating the former interaction can be stronger than the latter. The average $\mathrm{N\cdots I{-}Ar_F}$ ($\mathrm{Ar_F}$ = perfluoroaryl residue) distance is 2.91 Å [17–23], a value that lies between the typical N···I covalent bond length (2.07 Å) [24], and the sum (3.53 Å) of the van der Waals radii for N (1.55 Å) and I (1.98 Å) [25,26]. Consistent with the $n \rightarrow \sigma^*$ character of the interaction, the C–I···N angle is in the range of 160–180°.

RESULTS AND DISCUSSION

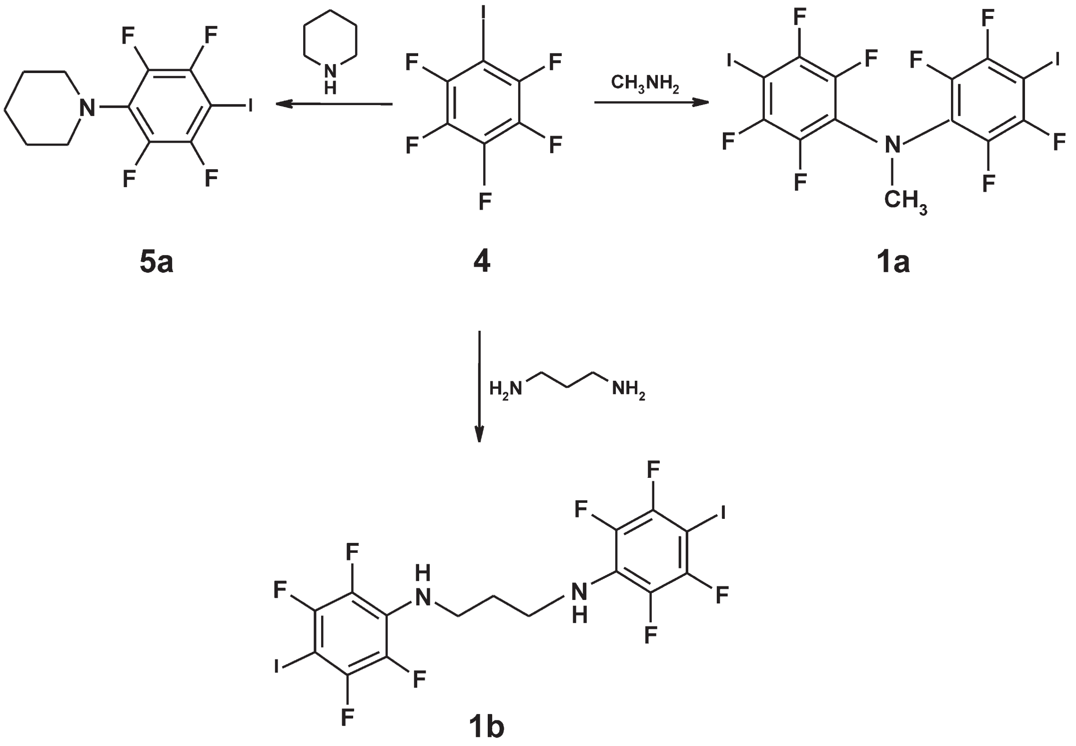
As a model system we tried the S_NAr reaction between piperidine and pentafluoroiodobenzene (**4**) [27–32]. When a 1:2 mixture of piperidine and **4** was refluxed for 1 h in the presence of one equivalent of triethylamine, 1-(2,3,5,6-tetrafluoro-4-iodophenyl) piperidine (**5a**) was isolated in 73% yield (Scheme 2). The *para* substitution on the tetrafluorobenzene ring was proven through ^{19}F NMR where two broad doublets were observed at −124.2 and −149.6 ppm, for $F_{2,5}$ and $F_{3,6}$, respectively.

The electron-withdrawing ability of fluorine markedly promotes the Lewis acidity of iodine in iodoperfluorocarbons [33], but the presence in **5a** of a nitrogen in the *para* position to iodine could reduce the Lewis acidity of this module. To test the ability of **5a** to act as halogen bonding donor (electron acceptor), the module was challenged with 4,4′-bipyridine (**2a**). After slow evaporation of the solvent, colorless co-crystal **6** was obtained. Elemental analysis and peak integration in the ^{1}H and ^{19}F NMR spectra of **6** with respect to $(CF_3CH_2)_2O$, used as internal standard, revealed that





6

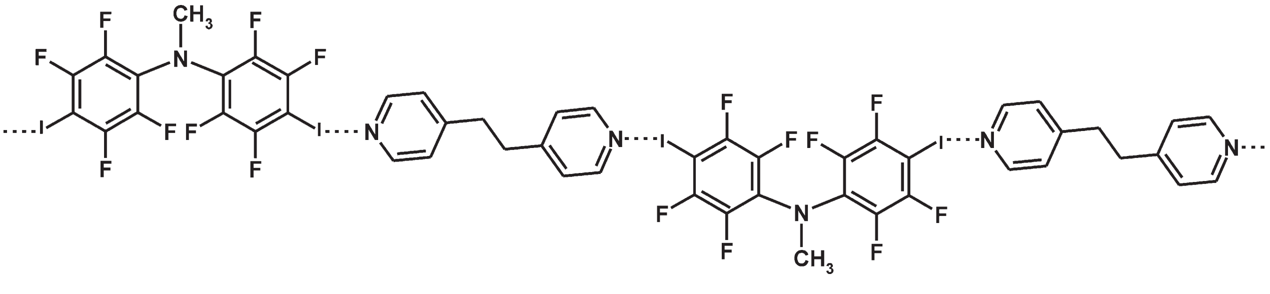


SCHEME 2

the **5a**/**2a** ratio is 2:1. In the IR spectrum of **6** the ν_{CH} absorptions of the pyridine ring ($3000-3050\,cm^{-1}$ region) appeared with a decreased intensity and at higher frequencies than in pure **2a**. These changes are diagnostic of the presence of halogen bonding [34] and it thus appears that in **6** the two molecules of **5a** are halogen bonded to one molecule of **2a** and a non-covalent trimer is formed. The presence of trimeric and well-defined structural units in the co-crystal formed by dinitrogen substituted hydrocarbons with monoiodoperfluorocarbons has already been observed and proven through X-ray analyses [35,36]. IR spectroscopy also showed that starting from the hydrated form of 4,4′-bipyridine (**2a**), no water is present in co-crystal **6**. Clearly **2a** prefers to act as a Lewis base towards **6** than towards water and the halogen bonding prevails over the hydrogen bonding in identifying the modules involved in the co-crystal formation. This is consistent with the ability of the iodine atom of **6** to work as an effective halogen bond donor, despite the *para* nitrogen substitution.

In the light of the results obtained and with the aim of forming 1D infinite chains through interaction with bidentate halogen bonding acceptors **2**, the bidentate halogen bonding donors *N*-methyl-*N*,*N*-bis(2,3,5,6-tetrafluoro-4-iodophenyl)amine (**1a**) and *N*,*N*″-bis(2,3,5,6-tetrafluoro-4-iodophenyl)propane-1,3-diamine (**1b**) were prepared (Scheme 2). These compounds were synthesized with complete regioselectivity by treatment of iodopentafluorobenzene **4** with methanamine and 3-aminopropylamine, respectively, according to procedures similar to that used for **5a**. The slow evaporation of an equimolar solution of **1a** and 4-(2-pyridin-4-ylethyl)pyridine (**2b**) afforded the colorless co-crystal **3a**.

$^1H/^{19}F$ NMR analyses in the presence of $(CF_3CH_2)_2O$ revealed that the hydrocarbon and fluorocarbon modules are present in a 1:1 ratio in **3a** and IR was consistent with the presence of N···I



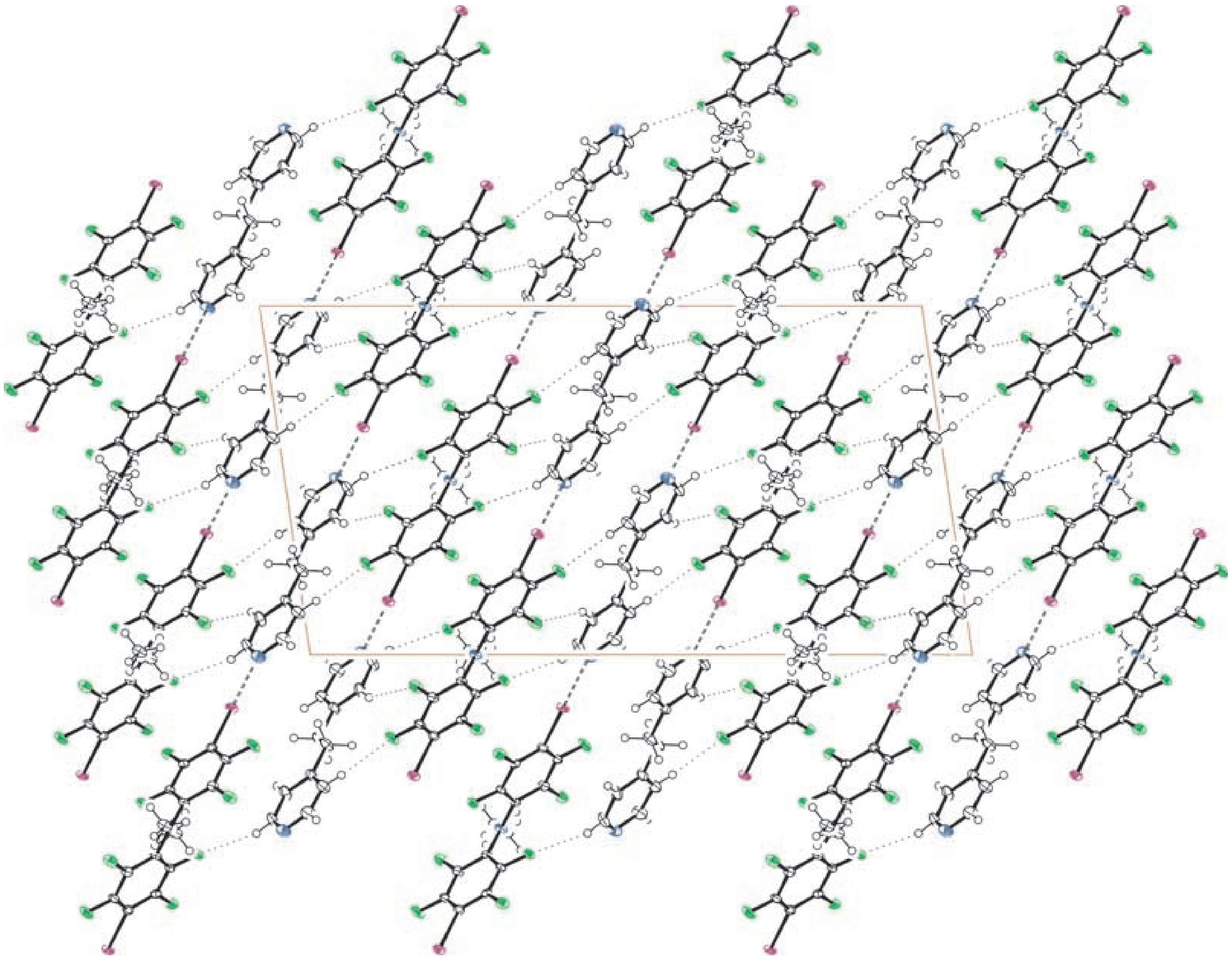


FIGURE 1 Crystal packing of the co-crystal **3a** viewed down the *b* axis. The strong N···I halogen bonds are dashed, the weak intermolecular H···F hydrogen bonds shorter than 2.5 Å are dotted. The fluorinated module **1a** lies on a *c2* crystallographic axis, the hydrocarbon module **2b** lies on a center of symmetry. Colors are as follows: black, carbon and hydrogen; purple, iodine; green, fluorine; blue, nitrogen.

TABLE I Details of data collection of single crystal X-ray structure analyses and of structure refinement for **3a** and **3c**

Compound	**3a**	**3c**
Chemical formula	$C_{13}H_3F_8I_2N{\cdot}C_{12}H_{12}N_2$	$C_{15}H_6F_8I_2O_2{\cdot}C_{13}H_{14}N_2$
Formula weight (M)	763.20	822.26
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	14.2349(6)	27.549(2)
b/Å	6.5825(3)	5.3024(5)
c/Å	26.7316(12)	21.325(2)
β/°	98.260(1)	111.94(2)
V/Å^3	2478.8(2)	2889.5(4)
T/K	90(2)	293(2)
Z	4	4
μ/mm^{-1}	2.619	2.258
$2\theta_{max}$/°	60	55
Refl. measured, ($R_{merging}$)	19574, 0.0234	73186, 0.0365
Indep. refl.,obs,[$I_o > 2\sigma(I_o)$]	3603, 3262	6643, 5897
Final R values, (obs.)	0.0288, (0.0244)	0.0596, (0.0495)
Final $wR(F^2)$, (obs.)	0.0592, (0.0578)	0.1028, (0.0974)

TABLE II Bond parameters in halogen bonded structures between tetrafluorodiiodobenzenes and pyridine derivatives

Entry	Halogen bonding donor	Halogen bonding acceptor	Structure reference code	N···I bond length/Å	C–I···N angle/°	T/K[a]
1	**1a**	**2b**		2.806(2)[b]	177.94(6)[b]	90
2	**1d**	**2c**		2.823(4), 2.921(4)[b]	176.6(2)b	293
3	3,6-TFDIB[c]	1,4-TMPDA[d]	MOFFUI	2.935(2)[e]	174.0n(7)[e]	291
4	3,6-TFDIB	DMAPM[f]	MOFGAP	2.954(2)[e]	172.3(1)[e]	291
5	3,6-TFDIB	BPMTtBC[4]A[g]	WOJMEN	2.904(5)[h]	169.4(2)[h]	291
6	3,6-TFDIB	1,2-b-4-PE[i]	MEKWOO	2.79(5)[j]	175.9(1)[j]	294
7	3,6-TFDIB	4′,4-MPTPY[k]	COLJIK	3.127(2)[l]	170.1(1)[l]	291
8	3,6-TFDIB	TPY[m]	CCDC 188260[n]	2.998(2)[o]	170.57(5)[o]	291
9	3,6-TFDIB	(*E*)-1,2-b-4-PE[p]	QIHCAL	2.810(5)[q]	179.3(5)[q]	294
10	5,6-TFDIB[r]	4,4′-bP[s]	MIYKOU	2.909(5), 2.964(5)[t]	172.1(2), 176.2(2)[t]	290

[a] Acquisition temperature of single crystal X-ray. [b] This paper. [c] 1,2,4,5-Tetrafluoro-3,6-diiodobenzene. [d] *N*,*N*,*N*′,*N*′-Tetramethyl-1,4-phenylenediamine. [e] Ref. [23]. [f] Bis[4-(*N*,*N*-dimethylaminophenyl)]methane. [g] 25,27-Dihydroxy-26,28-bis(2-pyridylmethyl)oxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene. [h] Ref. [21]. [i] 1,2-bis(4-pyridyl)ethane. [j] Ref. [16]. [k] 4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine. [l] Ref. [45]. [m] 2,2′:6′,2″-Terpyridine. [n] The reference code will be assigned after publication of the manuscript. [o] Ref. [46]. [p] (*E*)-1,2-bis(4-pyridyl)ethylene. [q] Ref. [15]. [r] 1,2,3,4-Tetrafluoro-5,6-diiodobenzene. [s] 4,4′-Bipyridine. [t] Ref. [47].

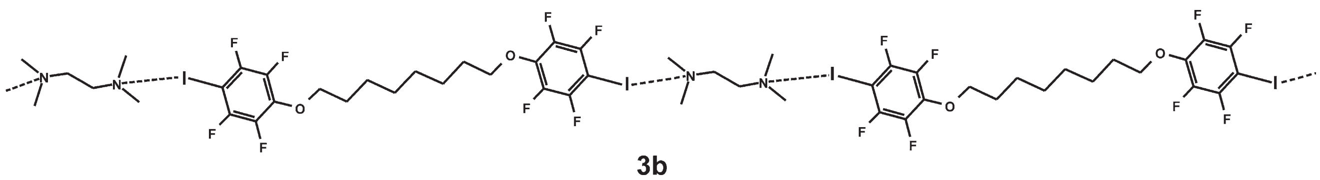
halogen bonds. Single crystal X-ray analysis of **3a** was performed at 90 K and showed that **1a** and **2b** alternate into infinite halogen bonded 1D chains (Fig. 1, Table I).

The N···I halogen bonds between the iodine atoms of **1a** and the nitrogen atoms of **2b** are largely responsible for the self-assembly process. Consistent with the $n \rightarrow \sigma^*$ character of the interaction, the C–I···N angle is nearly planar [177.94(6)°]. The N···I distance is 2.806(2) Å, i.e. quite close to those found in several other 1D infinite chains involving pyridine electron donors and iodoperfluoroarene acceptors (Table II).

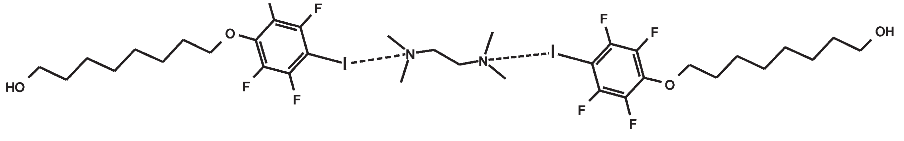
Furthermore, in view of the effect of the X-ray analysis temperature, the distance observed in **3a** is even shorter than those found in some other structures (e.g. Table II, entry 7). It is thus confirmed that the presence on the fluorophenyl ring of a +M substituent in the *para* position to iodine does not significantly affect the electron-accepting ability of that site. No substantial overlap seems to occur between the nitrogen lone pair and the fluorophenyl ring π electrons.

Probably thanks to the low temperature, all atoms are ordered, and only the methyl group shows some disorder. Consistent with an sp^3 hybridization at nitrogen (which disfavours electron donation from nitrogen to the fluorophenyl ring), different conformations at nitrogen have been assumed and the methyl has been split over two positions 0.49 Å apart from each other and corresponding to the umbrella inversion.

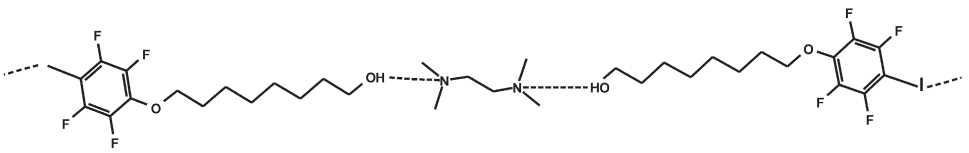
Some intermolecular hydrogen bonds are present in the structure of **3a**, as shown by the low



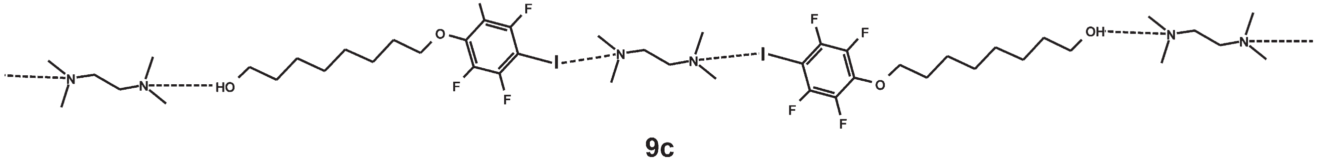
3b



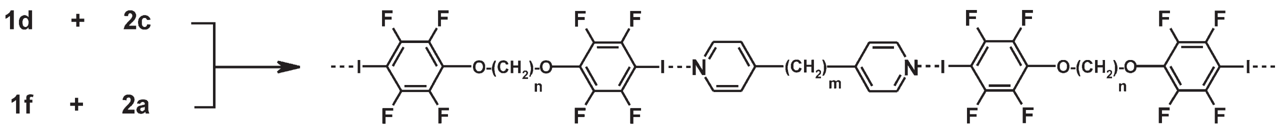
9a



9b



9c

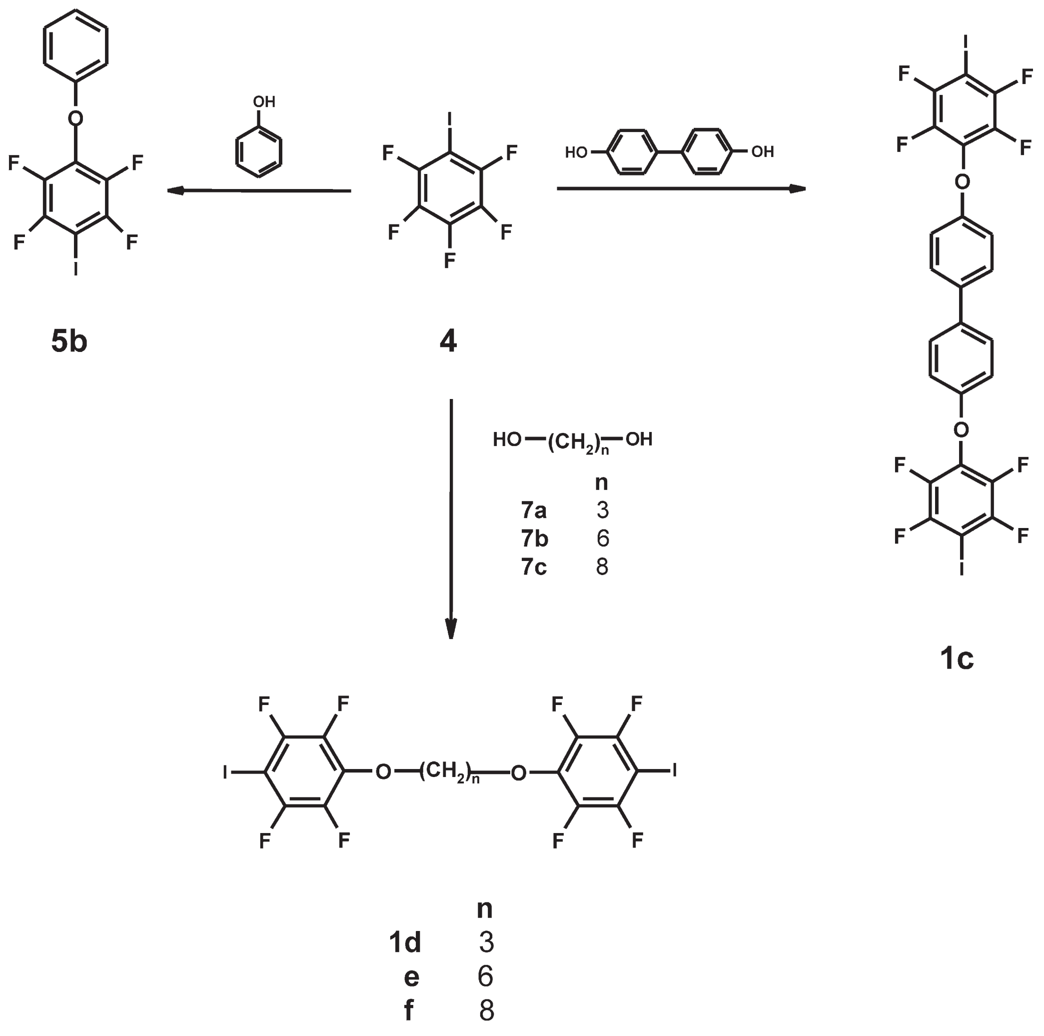


	n	m
3 c	3	3
d	8	--

temperature analysis [37]. The resulting network (substantially weaker than that of the halogen bond) [35] contributes to the overall crystal packing, which is mainly determined by the halogen bond.

In order to have a flexible access to new telechelic [38] Lewis acidic modules, we decided to verify if compounds with alcoholic or phenolic moieties could also be successfully used for the S_NAr reaction with iodopentafluorobenzene **4**. The reaction between phenol and **4** in the presence of cesium carbonate as base afforded the desired *para*-substitution product 2,3,5,6-tetrafluoro-4-iodophenyl phenyl ether **5b**. Under similar reaction conditions, 1,1′-biphenyl-4,4′-diol gave the telechelic halogen bonding donor 4,4′-bis(2,3,5,6-tetrafluoro-4-iodophenoxy)-1,1′-biphenyl **1c** in high yield (Scheme 3).

A survey of the literature revealed that alcoholic moieties could also be successfully involved in C–F bond cleavage through S_NAr reactions [39,40]. 1,*n*-Diols **7a–c** were refluxed in the presence of excess cesium carbonate and pentafluoroiodobenzene (**4**), which was used as solvent. This diol selection includes a chain length where different reactivity of nucleophilic sites was expected. Additionally, it



SCHEME 3

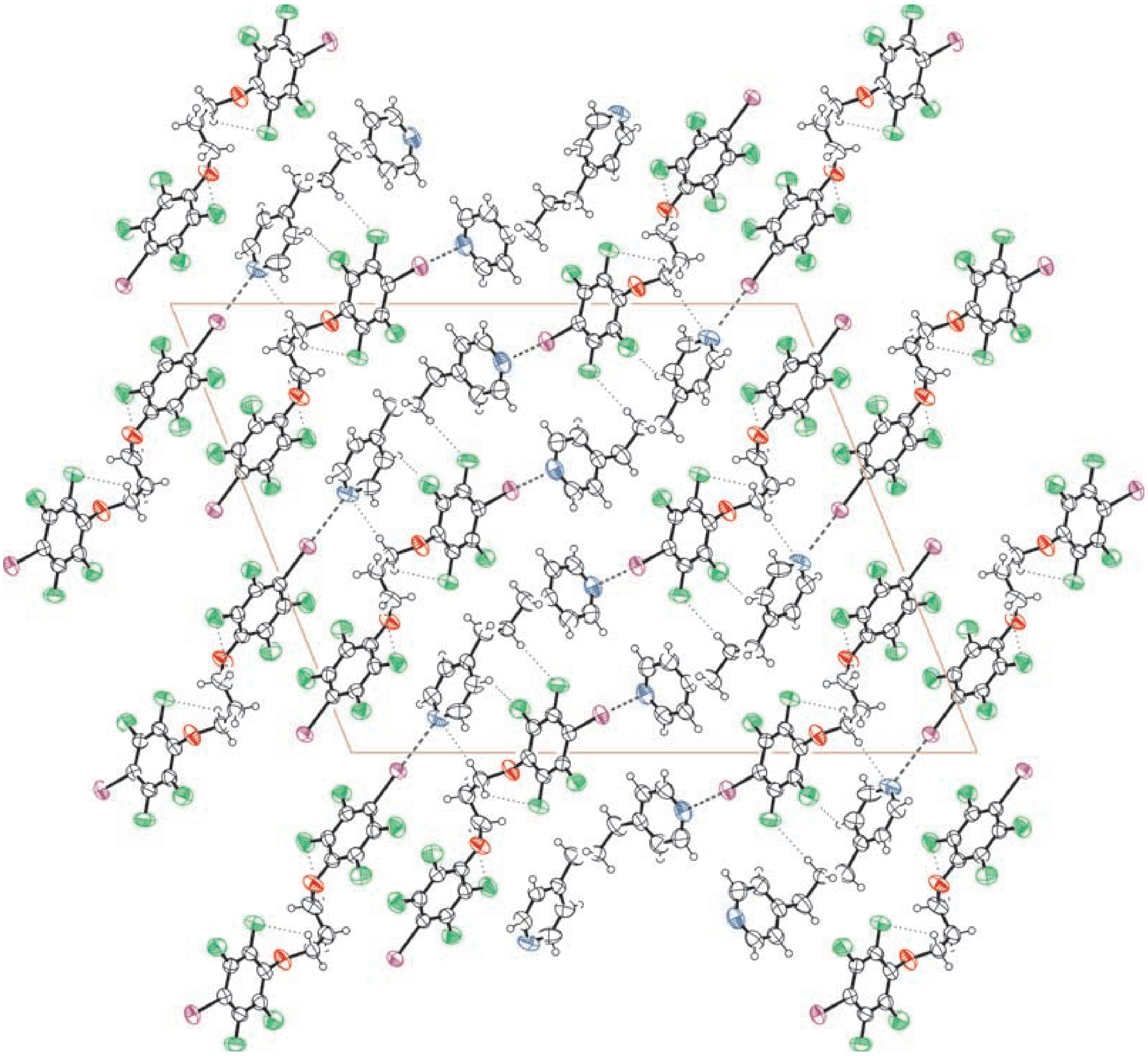


FIGURE 2 Crystal packing of the co-crystal **3c** viewed down the *b* axis. The strong N···I halogen bonds are dashed, the weak inter- and intramolecular H···F hydrogen bonds shorter than 265 pm are dotted. Colors are as follows: black, carbon and hydrogen; purple, iodine; green, fluorine; blue, nitrogen; red, oxygen.

exemplifies typical spacer sizes for the target co-crystals **3**. The desired substitution of the *para* positioned fluorine atom in **4** occurred and the small library of 1,*n*-bis(2,3,5,6-tetrafluoro-4-iodophenoxy)-alkanes **1d–f** was formed, $n = 3$,6 and 8 being the number of carbon atoms in the spacer.

In the crude reaction mixtures, variable amounts of intermediate hydroxy ethers **8**, where only one of the two hydroxy functions of starting diols **7** had reacted, were also present. The desired diethers **1d–f** were isolated in pure form either through flash chromatography or through co-crystal formation. For instance, the crude reaction mixture containing the diether **1f** and the intermediate hydroxy ether **8f** was co-crystallized with *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TMEDA). The diether **1f** is expected to give the halogen bonded 1D infinite chain **3b** while the hydroxy ether **8f** can afford either the halogen bonded trimer **9a**, if nitrogen acts as a base towards iodine, or the hydrogen bonded trimer **9b**, if nitrogen acts as a base towards the hydroxyl, or the mixed hydrogen/halogen bonded 1D infinite chain **9c** if both interactions occur.

Interestingly, precipitation of **3b** is by far the most favored process. The diether **1f** is obtained in pure form by dissolving in chloroform the co-crystal **3b** obtained after two successive co-crystallizations and removing the amine with acidic washings or through sublimation *in vacuo* at room temperature. The selective precipitation of **3b** once again emphasizes impressively the ability of halogen bonding to prevail over hydrogen bonding in driving competitive self-assembly processes in solution. To the best of our knowledge, this is the first successful application of halogen bonding-based technology to solve separation problems in organic synthesis.

Telechelic modules **1d,f** were co-crystallized with 1,3-di-(4-pyridyl)propane (**2c**) and 4,4′-bipiridine (**2a**) respectively. Co-crystals **3c,d** showed melting points higher than those of the starting modules, confirming that specific interactions, rather simple mechanical association, are occurring.

^{1}H and ^{19}F NMR spectra in the presence of $(CF_3CH_2)_2O$ as internal standard showed that the **1/2** ratios in co-crystals **3c,d** are 1:1. Both of the functionalities on the donor and the acceptor modules are thus involved in halogen bond formation. These results, along with the difunctional and telechelic character of the interacting partners, clearly allow the formation of infinite chain-like frameworks to be anticipated.

The vibrational spectra of co-crystals **3c,d** are highly diagnostic for the presence of strong halogen bonds. The pyridine ring absorption occurring at 991 cm^{-1} in pure **2a,c** characteristically shifts to higher frequencies on halogen bond formation [41]. In **3c,d** it appears over 1000 cm^{-1} as expected for strong halogen bonding. Furthermore, the absorptions in the fingerprint region are at higher frequencies [34] in **3c,d** than in pure **2a,c**. Moreover, some bands of the Lewis acid modules **1d,f** undergo a redshift on formation of the halogen-bonded co-crystal **3c,d.** These changes are consistent with $n \rightarrow \sigma^*$ electron donation from nitrogen to iodine which results in a higher positive charge on and a more acidic character of some hydrogen atoms in adducts **3c,d** than in pure modules **2a,c**.

Co-crystal **3c** was suitable for single crystal X-ray structure analysis (293 K). Alternating **1d** and **2c** modules into halogen bonded infinite 1D chains constitutes the crystal packing (Fig. 2, Table I).

As in the co-crystal **3a** and in several other 1D infinite chains formed by dinitrogen-substituted hydrocarbons and diiodoperfluorocarbons, in **3c** the starting tectons are arranged in an almost collinear fashion [17–23]. Both **1d** and **2c** give interactions at either molecular ends. Two independent I···N distances are present in the packing: $I2\cdots N1^{i}$ 2.921(4) Å [symmetry code: (i) $-x,\ 1-y,\ -z'$] and $I1\cdots N2^{ii}$ 2.823(4) Å [symmetry code: (ii) $1-x,\ -1-y,\ -z$] along with two distinct but nearly planar C–I···N angles: C13–I2···N1 173.1(2)° and C7–I1···N2 176.6(2)°. All these values indicate typical halogen bonding and indicate that, despite the possible +M effect of the *para*-positioned oxygen, the iodine atoms of **1d** work as halogen bond donors as strong as those of *o*- and *p*-diiodotetrafluorobenzenes and α,ω-diiodoperfluoroalkanes. The longer I2···N1 distance may be due to the reduced electron donor ability of N1, which is involved also in the formation of an intermolecular hydrogen bond [N1···H1A 2.74(4) Å]. Also some inter- and intramolecular H···F hydrogen bonds are present in the packing of **3c**, but they make a minor contribution in determining the overall structure [42].

CONCLUSIONS

Under basic conditions, 1,*n*-diols, bisphenols, and diamines easily undergo nucleophilic substitution of the *para*-positioned fluorine atom of iodopentafluorobenzene. This methodology provides a modular synthesis of structurally different telechelic tectons where a variable length spacer bears a *p*-iodotetrafluorobenzene moiety at either end. Despite the presence of an oxygen or nitrogen atom in the *para* position, the iodine atoms of these tectons effectively work as halogen bonding donors towards dinitrogen substituted hydrocarbon derivatives, which work as telechelic halogen bonding acceptors. As a result of the strength, selectivity and directionality of the halogen bond, 1D infinite chains are formed where the starting tectons alternate and are invariably arranged in an almost collinear fashion. The size of the spacers connecting the iodine and nitrogen atoms in the starting tectons, while influencing the length of the modules, does not affect the halogen bonding driven self-assembly process.

The modular approach to specifically designed tectons with variable length or size and their organization into predictable supramolecular architectures have been successfully introduced into the realm of halogen bonded supramolecular frameworks. More examples will emerge from our ongoing research activity.

EXPERIMENTAL

General Methods

Commercial HPLC grade solvents were used without further purification. Starting materials were purchased from Sigma-Aldrich Inc. and Apollo Scientific Ltd. DMF was dried over molecular sieves and stored under nitrogen. THF was freshly distilled from benzophenone ketyl. Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. NMR spectra were recorded with a Bruker Advance 500 instrument at 293 K. For ^{1}H-NMR (500 MHz) spectra $CDCl_3$ was used as solvent and TMS as internal standard, unless otherwise stated. ^{19}F-NMR (470 MHz) spectra were measured in $CDCl_3$ with $CFCl_3$ as internal standard, unless otherwise stated. 2,2,2-Trifluoroethyl ether was used as internal standard to determine the $^{19}F/^1H$-ratio in the co-crystals. If not specified differently, IR spectra were obtained from KBr pellets with a Perkin-Elmer 2000 FT-IR spectrometer.

Mass spectra were recorded with a Finnigan Mod TSQ-70 instrument in chemical ionization mode with isobutane. The X-ray crystal structure was determined using a Bruker Smart Apex diffractometer. Melting points were established with a Reichert instrument by observing the melting process through an optical microscope. Elemental analyses were performed by Redox Snc, Cologno Monzese, Milano, Italy.

Synthesis of Halogen Bonding Donor Modules 1a–f and 5a,b

1-(2,3,5,6-Tetrafluoro-4-iodophenyl)piperidine (5a)

A 1:2 mixture of piperidine (145 mg, 1.70 mmol) and 1,2,3,4,5-tetrafluoro-6-iodobenzene **4** (1.00 g, 3.40 mmol) was refluxed at 150°C under stirring for 1 h in the presence of one equivalent of triethylamine (172 mg, 1.70 mmol). The brown oil obtained after the removal of volatiles *in vacuo* was purified by flash chromatography on silica gel (AcOEt–petroleum ether 1:10). Product **5a** was isolated in 73% yield. Mp (AcOEt): 54–56°C; FT IR (ν/cm^{-1}, selected bands): 2937, 2845, 1629, 1476, 1103, 968, 907, 775; ^{1}H NMR (ppm) δ: 1.53–1.77 (m, 6H), 3.15–3.27 (m, 4H); ^{19}F NMR (ppm) δ: −149.2 (bd, 2F, $J = 15$ Hz), −124.1 (bd, 2F,$J = 15$ Hz); MS CI: 360 (MH^{+}); $C_{11}H_{10}F_4IN$ (359.1): calc. C 36.79, H 2.81, I 35.34, N 3.90; found C 36.93, H 2.82, I 35.20, N 3.88%.

N-Methyl-N,N-bis(2,3,5,6-tetrafluoro-4-iodophenyl)amine (1a)

Methanamine (530 mg, 17.0 mmol) was condensed in a steel bomb containing sodium hydride (816 mg, 34.0 mmol) and dimethylformamide (20 mL). A solution of iodopentafluorobenzene **4** (20.0 g, 68.0 mmol) in the same solvent (10 mL) was added and the mixture was heated at 130°C for 24 h. The crude reaction mixture was diluted with water (200 mL) and the organic products were extracted with ethyl acetate. The collected organic layers were dried with sodium sulphate and evaporated. Flash chromatography of the residue (*n*-hexane–AcOEt 1:4) afforded tecton **1a** in 56% yield. Mp (*n*-hexane): 120–126°C; FT IR (ν/cm^{-1}, selected bands): 2925, 2852, 1476, 1171, 1069, 962, 813, 661; ^{1}H NMR (ppm) δ:3.45 (s, 3H); ^{19}F NMR (ppm) δ: −147.6 (s, 4F), −121.2 (s, 4F); MS FAB: 579 (M^{+}); $C_{13}H_3F_8I_2N$ (579.2): calc. C 29.97, H 0.52, I 43.84, N 2.42; found C 30.09, H 0.51, I 43.66, N 2.41%.

N,N′-Bis(2,3,5,6-tetrafluoro-4-iodophenyl)propane-1,3-diamine (1b)

A 1:10 mixture of 2-aminopropylamine (1.26 g, 17.0 mmol) and **4** (50.00 g, 170.0 mmol) was refluxed for 3 h in the presence of potassium carbonate (22.16 g, 68.0 mmol). The crude reaction mixture was diluted with water and the organic products were extracted with chloroform. The collected organic layers were dried with sodium sulphate and evaporated. Flash chromatography of the residue on silica gel (*n*-hexane–AcOEt 1:1) afforded tecton **1b** in 84% yield. Mp (chloroform): 80–85°C; FT IR (ν/cm^{-1}, selected bands): 3423, 2918, 2850, 1644, 1489, 1295, 1266, 1149, 951, 809; ^{1}H NMR (ppm) δ: 1.9 (quintet, 4H,$J = 6$ Hz), 2.2 (s, 2H), 3.5 (t, 4H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −157.8 (bd, 4F,$J = 18$ Hz), −123.6 (bd, 4F,$J = 18$ Hz); $C_{14}H_6F_8I_2N_2$ (608.0): calc. C 27.66, H 0.99, I 41.74, N 4.61; found C 27.77, H 0.99, I 41.57, N 4.59%.

1,2,4,5-Tetrafluoro-4-iodophenyl Phenyl Ether (5b)

A mixture of phenol (0.15 g, 1.6 mmol), **4** (1.10 g, 3.7 mmol) and cesium carbonate (0.80 g, 2.4 mmol) was refluxed under stirring for 4.5 h. After removal of excess **4** under reduced pressure, the crude reaction mixture was diluted with water and organic products were extracted with ethyl acetate. The collected organic layers were dried with sodium sulphate and evaporated under reduced pressure. Flash chromatography of the residue on silica gel (*n*-hexane–chloroform 9:1) afforded *para*-substituted product **5b** (0.60 g, 88%). Mp (*n*-hexane): 70–74°C; FT IR (ν/cm^{-1}, selected bands): 3041, 2928, 1590, 1487, 1203, 1167, 1079, 975, 800, 763, 726, 690; ^{1}H NMR (ppm) δ: 6.98 (d, 2H,$J = 8$ Hz), 7.13 (t, 1H,$J = 7$ Hz), 7.33 (t, 2H); ^{19}F NMR (ppm)δ: −152.2 (bd, 2F,$J = 16$ Hz), −120.4 (bd, 2F,$J = 16$ Hz); MS FAB: 368 (M^{+}); $C_{12}H_5F_4IO$ (368.1): calc. C 39.16, H 1.37, I 34.48; found C 39.32, H 1.38, I 34.34%.

4,4′-Bis(2,3,5,6-tetrafluoro-4-iodophenoxy)-1,1′-biphenyl (1c)

To an ice-cooled suspension of sodium hydride (80 mg, 3.3 mmol) in anhydrous DMF (2 mL), a 0.48 M solution of 1,1′-biphenyl-4,4′-diol (89 mg, 0.48 mmol) in anhydrous DMF, and a 1.7 M solution of **4** in DMF (294 mg, 1.0 mmol), were added in order. The reaction mixture was heated at 80°C for 20 min., then poured on ice–water. The resulting solution was extracted with diethyl ether. The combined organic phases were dried over sodium sulphate, and the solvent was evaporated under reduced pressure. The obtained oil was purified by flash chromatography on silica gel (*n*-hexane–AcOEt 4:1) to afford the desired product **1c** (208 mg, 60%). Mp (*n*-hexane): 194–198°C; FT IR (ν/cm^{-1}, selected bands): 1492, 1209, 1079, 975, 821; ^{1}H NMR (ppm) δ: 7.04 (d, 4H,$J = 8$ Hz), 7.49 (d, 4H,$J = 8$ Hz); ^{19}F NMR (ppm) δ: −152.0 (bd, 2F,$J = 15$ Hz), −120.1 (bd, 2F,$J = 15$ Hz); MS CI: 734 (M^{+}); $C_{24}H_8F_8I_2O_2$

(734.1): calc. C 39.27, H 1.10, I 34.57; found C 39.43, H 1.11, I 34.43%.

1,3-Bis(2,3,5,6-tetrafluoro-4-iodophenoxy)propane (1d)

A mixture of **4** (7.00 g, 23.8 mmol), propane-1,3-diol (**7a**) (0.40 g, 5.26 mmol) and cesium carbonate (3.40 g, 10.44 mmol) was refluxed under stirring for 2.5 h. The resulting suspension was washed with water and extracted with diethyl ether. The combined organic phases were dried over sodium sulphate and the solvent removed under reduced pressure. The obtained oil was purified by flash chromatography on silica gel (*n*-hexane–AcOEt 2:1) to afford the mono-hydroxy ether 3-(2,3,5,6-tetrafluoro-4-iodophenoxy)propan-1-ol **8d** (497 mg, 27 %) and the diether **1d** (1.14 g, 35%). **8d**: Mp (chloroform): 50–52°C: ^{1}H NMR (ppm)δ: 1.63 (s, 1H), 2.05 (quintet, 2H,$J = 6$ Hz), 3.89 (t, 2H,$J = 6$ Hz), 4.40 (t, 2H,$J = 6$ Hz); ^{19}F NMR (ppm)δ: −154.9 (bd, 2F,$J = 15$ Hz), −121.7 (bd, 2F,$J = 15$ Hz); MS CI: 350 (M^+); $C_9H_7F_4IO_2$ (350.0): calc. C 30.86, H 2.00, I 36.29; found C 30.98, H 2.01, I 36.15%. Compound **1d**: Mp (chloroform): 60–62°C; FT IR (ν/cm^{-1}, selected bands): 2974, 2894, 1633, 1487, 1385, 1107, 1032, 974, 804; ^{1}H NMR (ppm)δ: 2.26 (q, 2H,$J = 6$ Hz), 4.46 (t, 4H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −152.5 (bd, 2F,$J = 18$ Hz), −121.6 (bd, 2F,$J = 18$ Hz); MS CI: 625 (MH^+); $C_{15}H_6F_8I_2O_2$ (624.0): calc. C 28.87, H 0.97, I 40.67; found C 28.99, H 0.98, I 40.51%.

1,6-Bis(2,3,5,6-tetrafluoro-4-iodophenoxy)hexane (1e)

A suspension of **4** (1.50 g, 5.10 mmol), hexane-1,6-diol (**7b**, 0.19 g, 1.60 mmol) and cesium carbonate (0.50 g, 1.53 mmol) was refluxed under stirring for 2.5 h. The resulting mixture was flash-chromatographed on silica gel (*n*-hexane–AcOEt 7:3) to yield mono-hydroxy ether 6-(2,3,5,6-tetrafluoro-4-iodophenoxy)hexan-1-ol **8e** (0.24 g, 38%) and the diether **1e** (0.59 g, 56%). Compound 8e: ^{1}H NMR (CD_3OD, ppm) δ: 1.34–1.70 (m, 6H), 1.81 (quintet, 2H,$J = 7$ Hz), 2.05 (s, 1H), 3.66 (t, 2H,$J = 7$ Hz), 4.24 (t, 2H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −154.9 (bd, 2F,$J = 14$ Hz), −122.0 (bd, 2F,$J = 14$ Hz); IR (ν/cm^{-1}, film): 3355, 2939, 2863, 1633, 1484, 1387, 1274, 1101, 976, 803; $C_{12}H_{13}F_4IO_2$ (392.0): calc. C 36.73, H 3.32, I 32.40; found C 36.88, H 3.33, I 32.27%. Compound **1e**: Mp (chloroform): 33–35°C; FT IR (ν/cm^{-1}, selected bands): 2945, 2863, 1633, 1485, 1387, 1101, 976, 803; ^{1}H NMR (ppm) δ: 1.58 (m, 4H), 1.82 (m, 4H), 4.25 (t, 4H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −155.0 (bd, 2F,$J = 15$ Hz), −122.0 (bd, 2F,$J = 15$ Hz); MS CI: 666 *m/e*; $C_{18}H_{12}F_8I_2O_2$ (624.0): calc. C 32.46, H 1.83, I 38.10; found C 32.59, H 0.98, I 37.95%.

1,8-Bis(2,3,5,6-tetrafluoro-4-iodophenoxy)octane (1f)

A suspension of **4** (1.50 g, 5.10 mmol), octane-1,8-diol (**7c**, 0.23 g, 1.60 mmol) and cesium carbonate (0.50 g, 1.53 mmol) was refluxed under stirring for 2.5 h. The resulting mixture was flash chromatographed on silica gel (*n*-hexane–AcOEt 75:25) to yield mono-hydroxy ether 8-(2,3,5,6-tetrafluoro-4-iodophenoxy)octan-1-ol **8f** (0.22 g, 33%) and the diether **1f** (0.65 g, 63%). Isolation and purification of **1f** from the reaction mixture was also achieved by co-crystallization with TMEDA as described in the text. **8f**: ^{1}H NMR (CD_3OD, ppm) δ: 1.21–1.90 (m, 12H), 2.18 (br, 1H), 3. 63 (bt, 2H,$J = 6$ Hz), 4.23 (t, 2H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −155.9 (bd, 2F,$J = 15$ Hz), −122.1 (bd, 2F,$J = 15$ Hz); $C_{14}H_{17}F_4IO_2$ (410.0): calc. C 40.98, H 4.15, I 30.98; found C 41.141, H 4.17, I 30.86%. Compound **1f**: FT IR (ν/cm^{-1}, selected bands): 3044, 2942, 1632, 1592, 1475, 1405, 1381, 1099, 985, 806, 613; ^{1}H NMR (ppm) δ: 1.55–1.34 (m, 8H), 1.78 (m, 4H), 4.23 (t, 4H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −122.1 (bd, 2F,$J = 15$ Hz), −155.0 (m, 2F,$J = 15$ Hz); $C_{20}H_{16}F_8I_2O_2$ (694.1): calc. C 34.61, H 2.32, I 35.56; found C 34.75, H 2.33, I 35.42%.

Supramolecular Synthesis of Infinite 1D Chains 3a,c,d and 6

Co-crystal 6

1-(2,3,5,6-Tetrafluoro-4-iodophenyl)piperidine (**5a**) and the bipyridine **2a** were dissolved in acetone in a 2:1 ratio. After slow evaporation of the solvent at room temperature, colorless crystals **6** were obtained. Mp (acetone) 86–90°C; FT IR (ν/cm^{-1}, selected bands): 3034, 2939, 2852, 1591, 1465, 1218, 1102, 960, 804, 613.

Co-crystal 3a

Equimolar amounts of **1a** and **2b** were dissolved in chloroform in a vial of clear borosilicate glass. The open vial was enclosed in a cylindrical wide-mouth bottle containing carbon tetrachloride. Solvent was allowed to diffuse at room temperature. After two days, colorless crystals of **3a** were isolated. Mp (chloroform) 192–196°C; FT IR (ν/cm^{-1}, selected bands): 3026, 2929, 1601, 1475, 1171, 1067, 964, 821, 658, 526; ^{1}H NMR (ppm) δ: 2.95 (s, 4H), 3.46 (s, 3H), 7.07 (d, 4H,$J = 6$ Hz), 8.50 (d, 4H,$J = 6$ Hz); ^{19}F NMR (ppm) δ: −148.1 (d, 4F,$J = 20$ Hz), −121.4 (d, 4F,$J = 20$ Hz).

Co-crystal 3c

Equimolar amounts of **1d** and **2c** were dissolved in acetone in a vial of clear borosilicate glass. The open vial was enclosed in a cylindrical wide-mouth bottle containing vaseline oil. Solvent was allowed to diffuse at room temperature. After two days, colorless crystals of **3c** were isolated. Mp (acetone) 90–95°C; FT IR (ν/cm^{-1}, selected bands): 3072, 3033, 2995, 2968, 1603, 1494, 1481, 1418, 1380, 1360, 1272, 1217, 1105, 1095, 1068, 1000, 969, 805, 795; ^{19}F NMR (ppm) δ: -153.1 (bd, 2F,$J = 18$ Hz), -121.8 (bd, 2F,$J = 18$ Hz).

Co-crystal 3d

A vial containing a 1:1 solution of **1f** and dipiridyl derivative **2a** in acetone was enclosed in a cylindrical wide-mouth bottle containing vaseline oil. Solvent was allowed to diffuse at room temperature. After two days, colorless crystals of **3d** were isolated. Mp (acetone) 108–112°C; FT IR (ν/cm^{-1}, selected bands): 3044, 2942, 2861, 1632, 1592, 1475, 1382, 1099, 967, 806, 613; ^{19}F NMR (ppm) δ: -156.2 (bd, 4F,$J = 16$ Hz), -122.5 (bd, 4F,$J = 16$ Hz).

X-ray Crystallographic Study of 3a and 3c

Single crystal data of **3a** and **3c** were collected on a Bruker APEX CCD diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reduction and absorption correction, based on multi-scan were performed by *SAINT* and *SADABS* programs [Bruker (1999), SADABS and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA]. The structures were solved by *SIR-92* [43], and refined on F^2 by *SHELX-97* [44]. Details of data collection and refinement are reported in Table II. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 188260 (**3a**) and CCDC 188261 (**3c**). 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 or e-mail: deposit@ccdc.cam.ac.uk]. In **3a** the aminomethyl residue is on a C_2 axis and the methyl is split over two equally populated locations corresponding to an umbrella inversion at nitrogen. Both methyls are involved in a net of weak hydrogen bonds.

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