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14. ABSTRACT

This report results from a contract tasking Polytechnic of Milan as follows: When halogen bonding drives the self-assembly of new materials, the involved modules can be grouped into three main classes: XB donors, XB acceptors, XB self-complementary modules. The design of new XB donors was pursued in this project. Polydentate modules were pursued with the aim of having a better control on the self-assembled architectures they will form with XB acceptors. The high stereoselectivity of solid state reactions under the control of XB was further explored in other materials already prepared.

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17 July 2007

POLYDENTATE HALOGEN BONDING DONORS FOR THE SELF-ASSEMBLY OF NEW MATERIALS

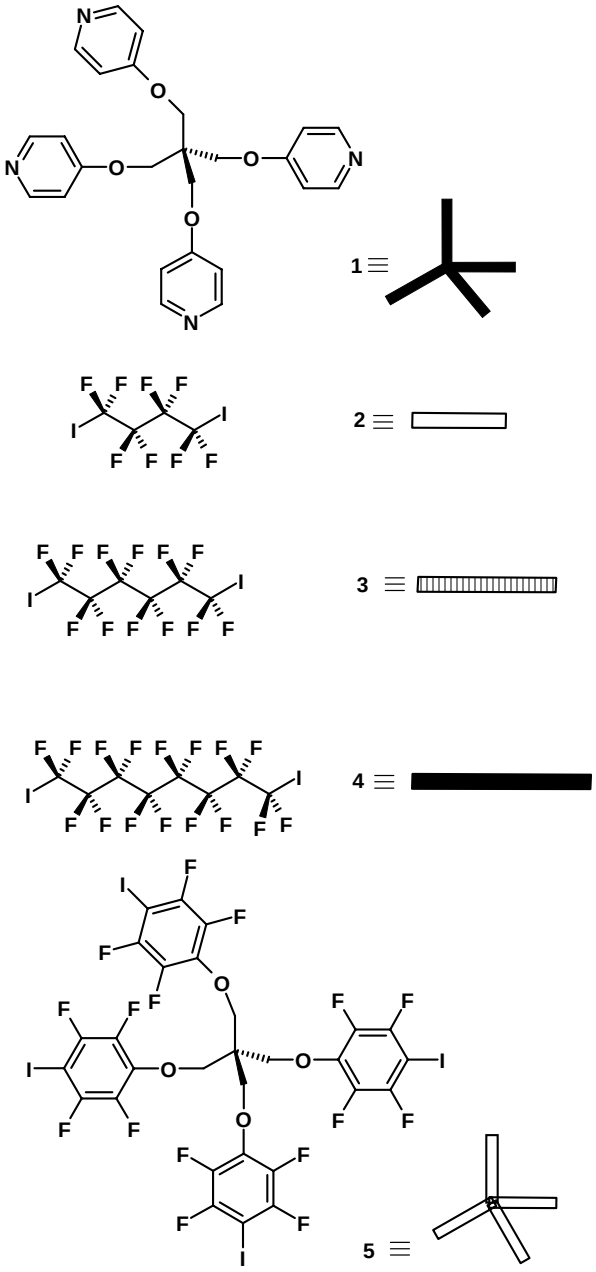
Grant/Cooperative Agreement No.: FA8655-06-1-3040
Performance Final Comprehensive Report 15 May 2006 – 14 May 2007

Part A: Tetra- and hexadentate halogen bonding donors.

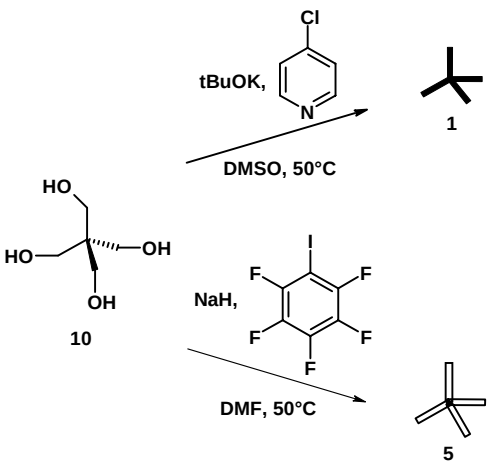
In the first three months of activity of this cooperative agreement, we have studied the self-assembly of the tetratopic halogen bonding donor **5** with the structurally related tetratopic halogen bonding acceptor **1** (Scheme 1). This latter module was also self-assembled with the α,ω-diiodoperfluoroalkanes **2-4** presenting alkyl chains of different lengths.

The tetratopic acceptor **1** was prepared through a synthetic sequence similar to that optimized for the synthesis of **5** (reaction of pentaerythritol with 4-chloropyridine, Scheme 2). The rational underlying the self-assembly of **1** and **5** was that both modules can adopt a tetrahedral conformation; thanks to a reciprocal self-induced fitting, this conformation was expected to be preferred over the other possible conformations in both modules and the construction of a diamondoid network was expected (Scheme 3). Indeed this was the case! The pairing of the complementary binding sites in **1** and **5** leads to the formation of a diamondoid net which presents a remarkable interpenetration in order to avoid the presence of huge voids. Specifically, two different sets of five diamondoid networks interpenetrate and form two separate 5-fold interpenetrated networks (Figure 1). Two such 5-fold interpenetrated networks further interpenetrate to give the overall crystal packing which thus present a 10-fold interpenetration (Figure 2). This is a record for interpenetration in halogen bonded architectures.

Scheme 1



Scheme 2



Scheme 3

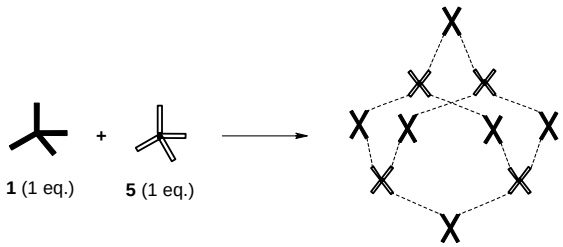


Figure 1

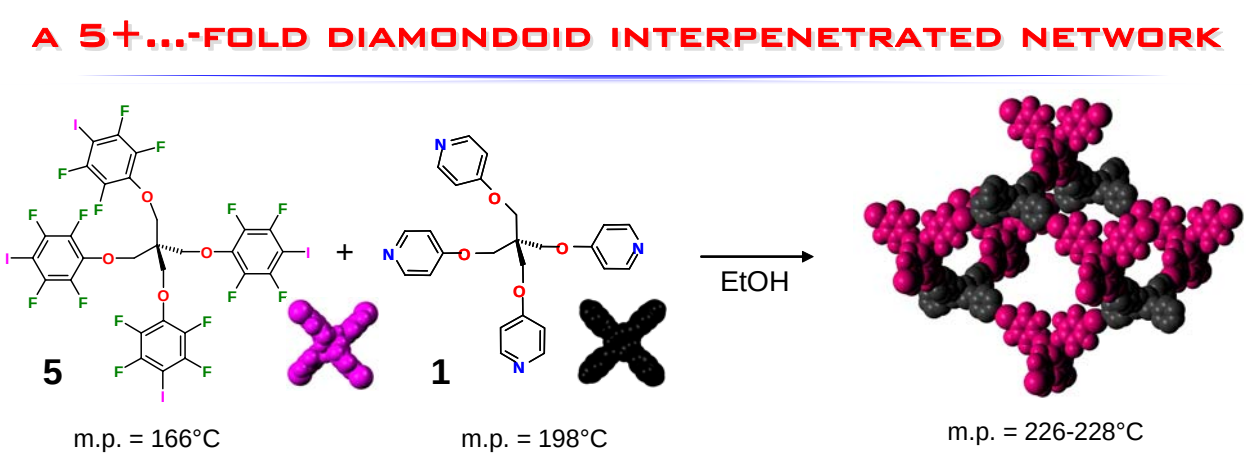
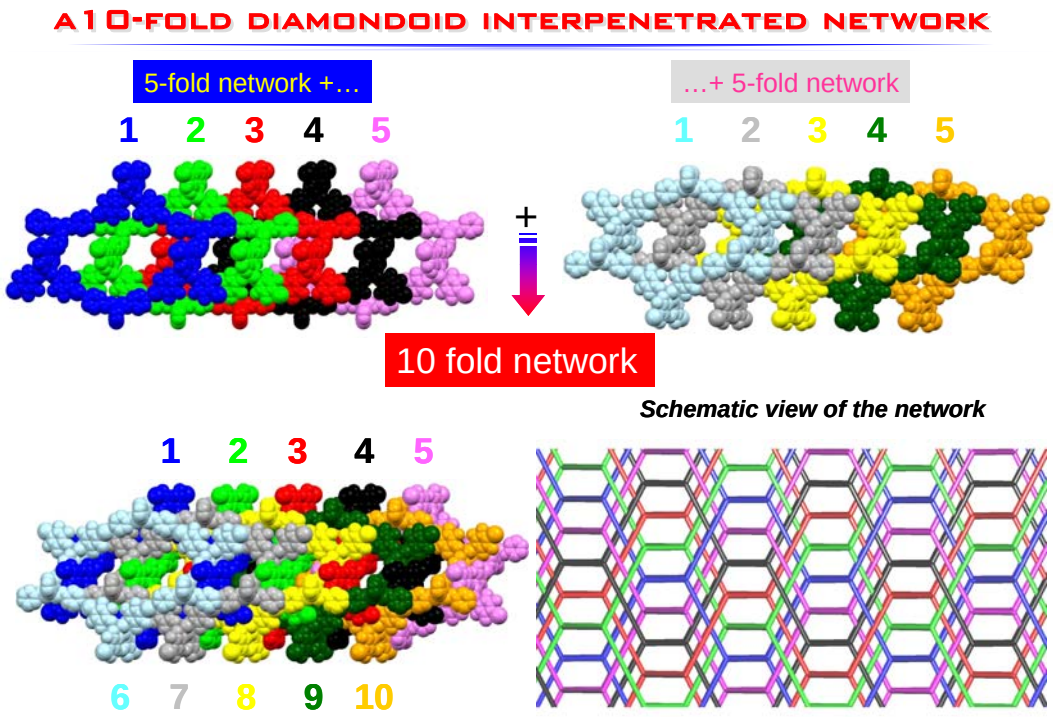


Figure 2



When the tetratopic module **1** was challenged with the ditopic modules **2-4**, the formed networks show a 1:2 ratio between the halogen bonding acceptor and donor modules and present complex interpenetrate assembly of different topologies. A rare diamondoid 8-fold network of class Ia[i] is formed when starting from 1,4-diiodotoctafluorobutane **2** (Scheme 4, Figure 3), while 2D square 4^4 layers with 4-fold and 5-fold interpenetration are obtained when starting from 1,6-diiodoperfluorohexane **3** and from 1,8-diiodoperfluorooctane **4**, respectively (Scheme 4, Figure 4). .

Scheme 4

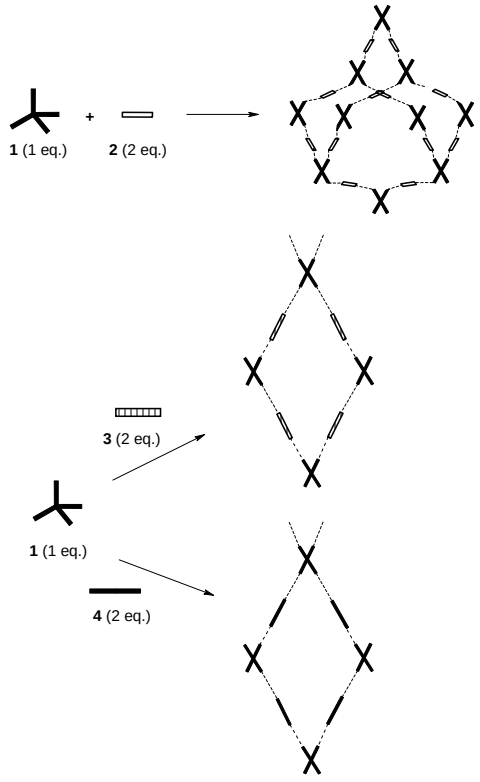


Figure 3

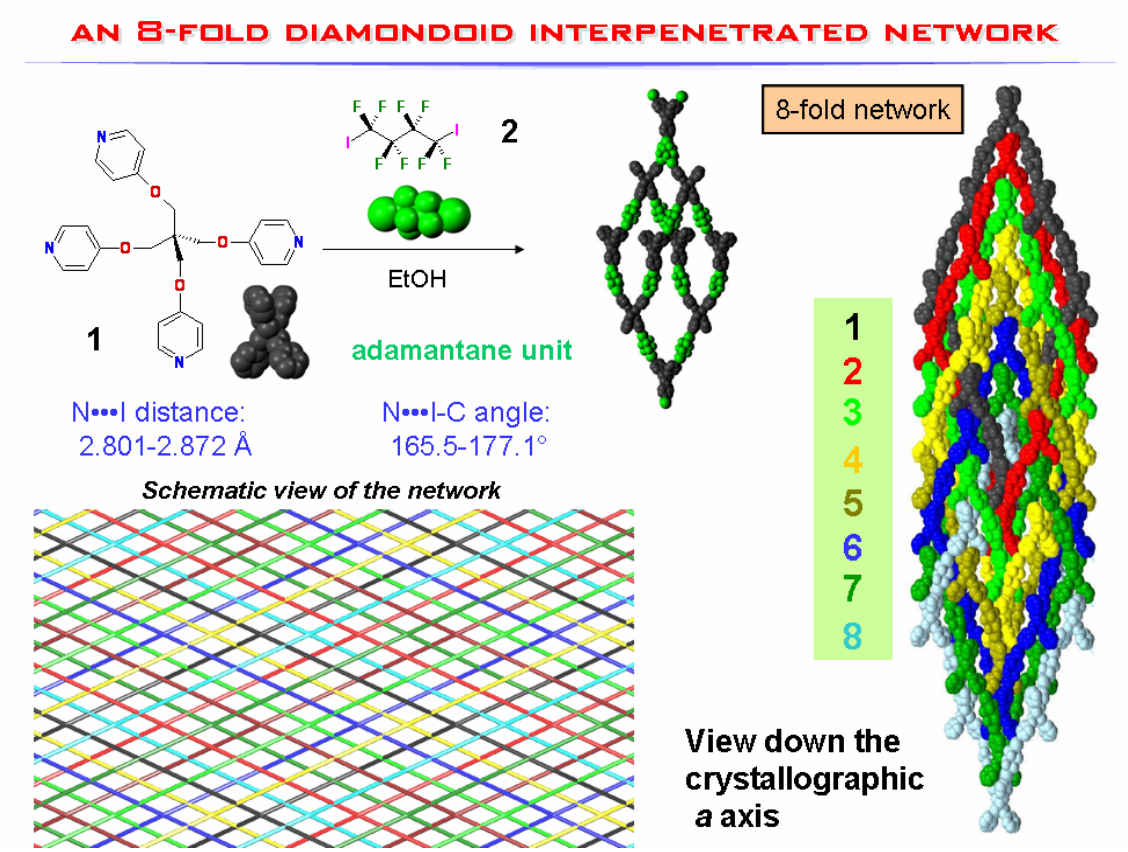
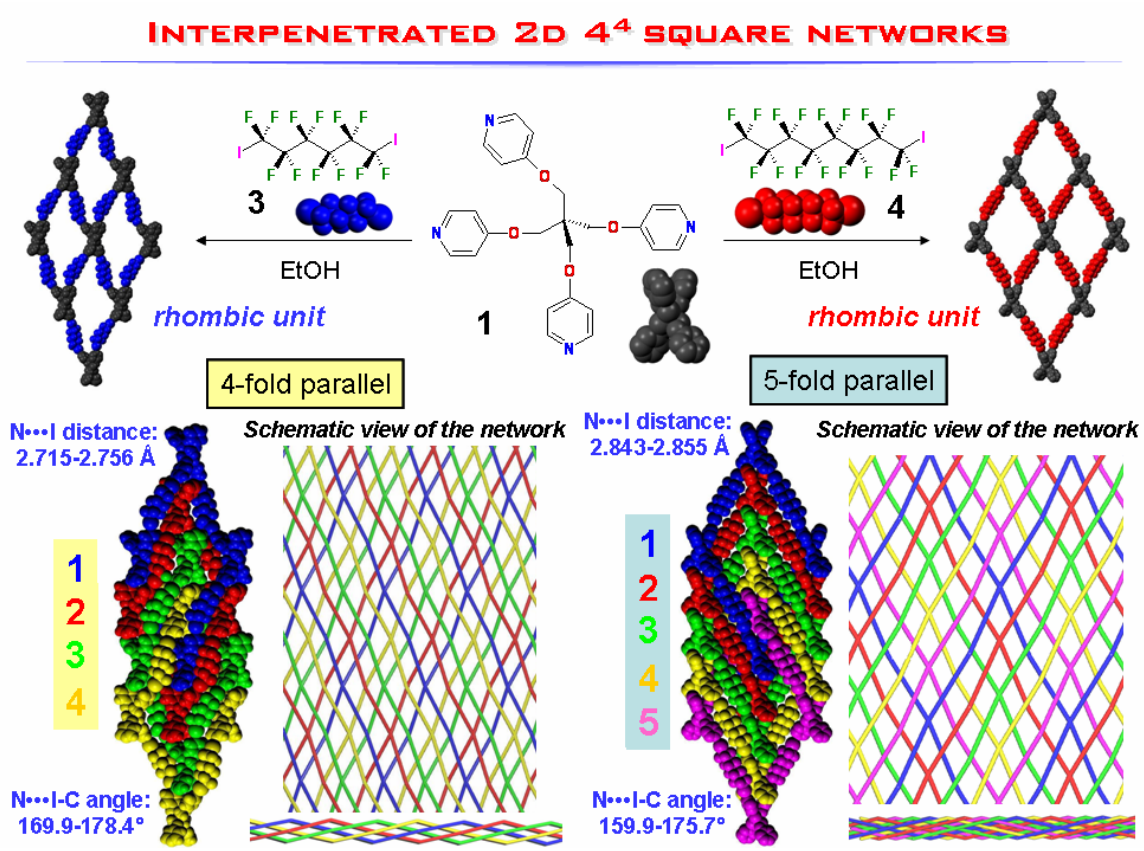


Figure 4



Besides studying bidentate and tetradentate halogen bonding donors (**2-4** and **5**, respectively), we also turned our attention to hexakis[4-(2,3,5,6-tetrafluoro-4-iodophenoxymethyl) phenoxy]cyclotriphosphazene **6** which is the first hexadentate halogen bonding donor ever studied. The compound was prepared by reacting 4-hydroxy benzaldeyde with hexachlorocyclotriphosphazene in the presence of a base, reducing the carbonyls of the hexasubstituted product by using $LiBH_4$ at room temperature, and finally forming regiosectively the hexakis[4-(2,3,5,6-tetrafluoro-4-iodophenoxy) derivative by reaction with iodopentafluorobenzene under basic conditions.

On evaporation of a solution containing 4,4'-dipyridylethylene, the phosphazene derivative **6** behaves as a nanopillar that self-assembles by halogen bonding with the telechelic partner and forms infinite supramolecular architectures (Scheme 5, Figure 5). Dipyridyl behaves in a strictly similar way (Figute 6). No interpenetration occurs as layered architectures are formed in both cases.

Scheme 5

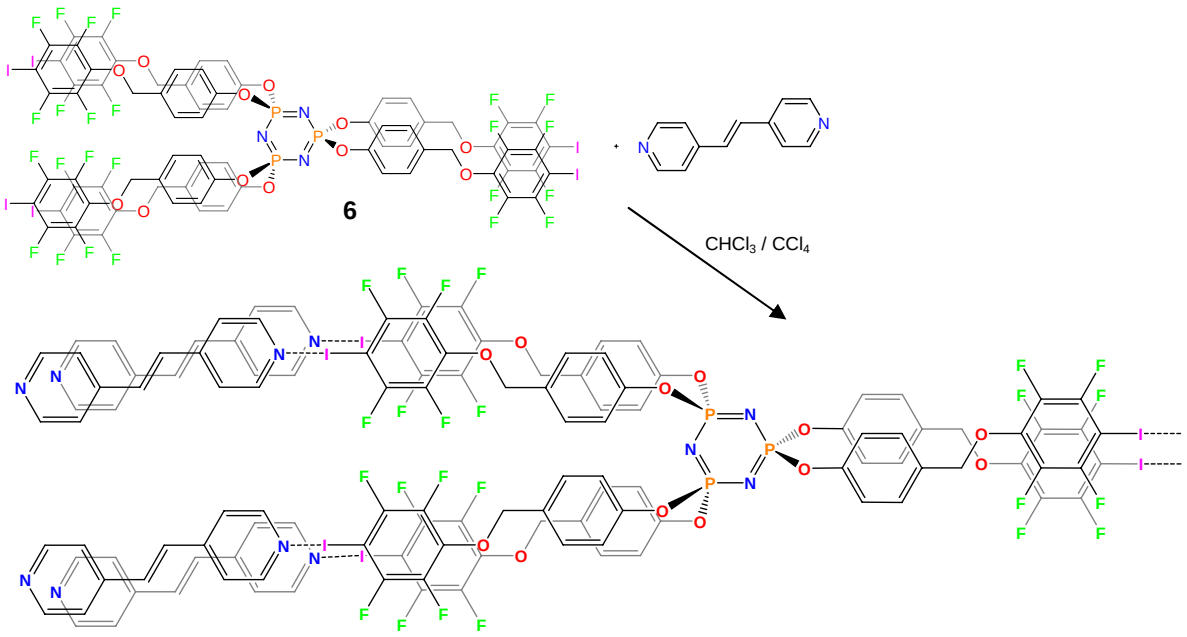


Figure 5

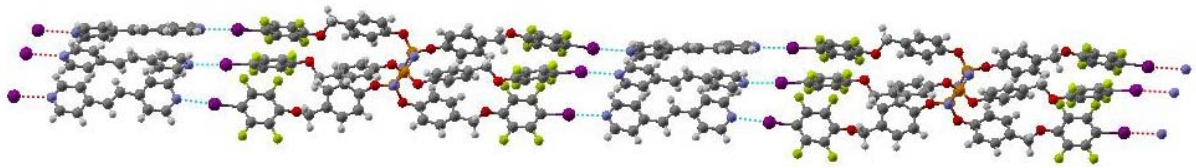
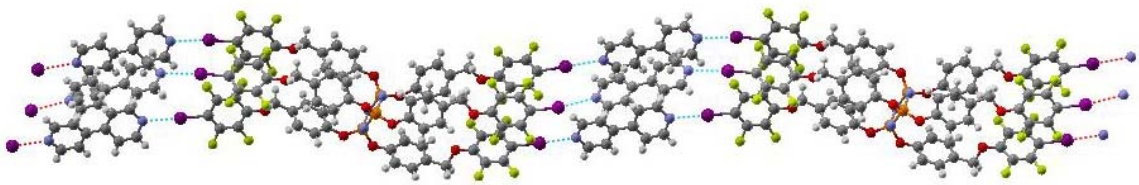


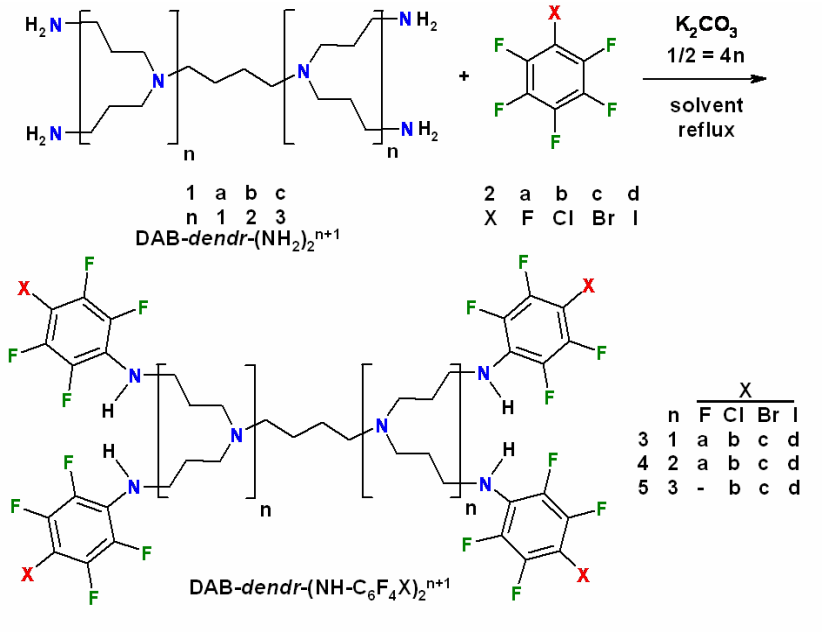
Figure 6



Part B: Halogen bonding donors with eight or more binding sites

We have also investigated the synthesis of fluorinated poly(propylene imine) dendrimers (DAB-Am) dendrimers of the first, second, and third generation in order to prepare a new type of halogen bond donors.

The functionalisation of poly(propylene imine) dendrimers (DAB-Am) with perfluorinated groups was carried out by nucleophilic attack of the nitrogen at the periphery on different halopentafluorobenzenes and hexafluorobenzene (Scheme 5).



Scheme 5. Synthesis of dendrimeric tectons **3a-d**, **4a-d**, and **5b-d**.

The S_NAr attack of DAB-*dendr*-$(NH_2)_2^{n+1}$ (**1a-c**) on the fluorobenzenes **2a-d** afforded three different generations of DAB-*dendr*-$(NHC_6F_4X)_2^{n+1}$ [with n = 1 (**3**), n = 2 (**4**), n = 3 (**5**) and X = F (**a**), Cl (**b**), Br (**c**), I (**d**)] (Scheme 1). The first generation derivatives **3a-d** (n = 1,) have been obtained in 52 to 92% isolated yields after chromatographic purification (dichloromethane/methanol as eluent); the second (n = 2, **4a-d**) and the third generations (n = 3, **5b-d**), in 45 to 86% isolated yields. ^{19}F NMR indicates that reactions invariably occur with high regioselectivity on the fluorine atom *para* to the heavy halogen of **2b-d**. Regioselectivity is largely unaffected by dendrimer size while it increases with the size of the heavy halogen (I > Br > Cl; the *ortho* by-product is 4% and 21% in **3d** and **3b**, respectively).

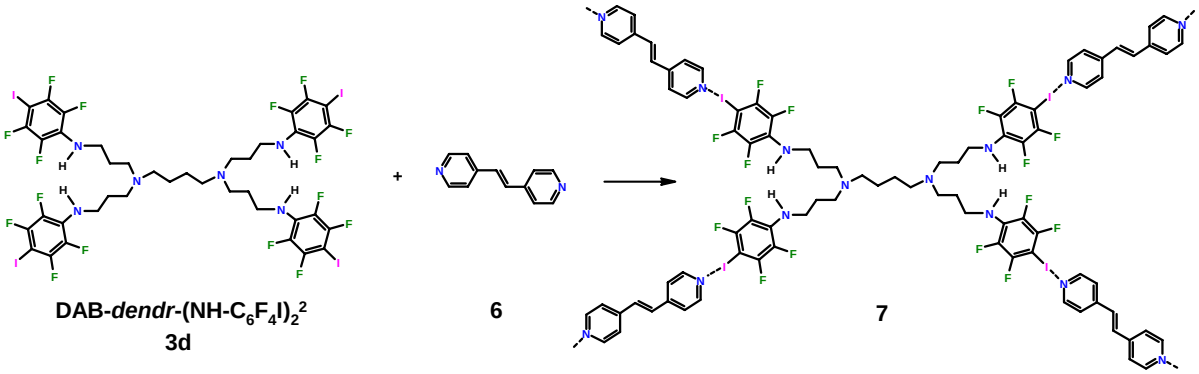
Clearly, the S_NAr reactions with **2c,d** transformed dendrimers **1**, which expose amine groups at their outer shells, into **3c,d-5c,d**, which expose C_6F_4-X groups, which are known to be strong XB-donor sites. The general ability of halotetrafluorophenyl substituted dendrimers to work as XB-based tectons was proven, in solution, by monitoring the high-field shift of the C*F*=CX signal in ^{19}F NMR spectra on pyridine addition (see Table 1). This shift is diagnostic of the occurrence of XB and, as expected, the larger the amount of added pyridine, the greater the upfield shift is. Similar changes of chemical shifts and similar trends in the changes were also shown by second and third generation dendrimers **4d** and **5d**. The bromotetrafluorophenyl substituted dendrimers of first, second, and third generation **3c**, **4c**, and **5c**, respectively, also showed a similar behaviour. The only difference was that, for a given XB-donor/XB-acceptor ratio, shift changes were invariably smaller, consistent with the fact that bromopefluoroarenes are weaker XB-donors than iodoperfluoroarenes.

Table 1. C*F*=CX signal shifts in ^{19}F NMR spectra of 3c,d-5c,d on pyridine addition.
Different amounts of excess pyridine were added to a 0.005 M solution of dendrimers **3c,d**, **4c,d**, and **5c,d** in $CDCl_3$ ($CFCl_3$ as internal standard). The upfield shift changes ($\Delta\delta$ (ppm) = δ(pure dendrimer) - δ(dendrimer in the presence of pyridine)) for the C*F*=CX signals are reported in Table 2, while the C*F*-CF=CX shift changes, if any, were negligible. The amount of added pyridine changed with the generation (*e.g.* 50 equivalents for generation 1, 100 equivalents for generation 2, 200 equivalents for generation 3) so that the ratio between iodine atoms number and pyridine nitrogen atoms number (namely the ratio between XB-donor and XB-acceptor sites) was either 2/25 or 2/10 in all the experiments.

Dendrimer	I/N ratio	$\Delta\delta$ (ppm)
3c	2/25	0.03
4c	2/25	0.04
5c	2/25	0.05
3d	2/25	0.05
3d	2/10	0.02
4d	2/25	0.06
4d	2/10	0.03
5d	2/25	0.09
5d	2/10	0.04

In solution, ^{19}F NMR proves the involvement of iodine atoms of the DAB-*dendr*-$(NHC_6F_4I)_2^2$ **3d** in the formation of strong XB. In the solid, the four chains of **3d** look adjusted for an *exo* recognition process driven by XB. These observations prompted us to study the self-assembly of the DAB-*dendr*-$(NH\text{-}C_6F_4I)_2^2$ **3d** with a telechelic nitrogen module, namely (*E*)-1,2-bis-(4-pyridil)-ethylene (**6**) (1:2 ratio, chloroform solution) (Scheme 6). Upon slow evaporation of the solvent, good quality crystals of **7** were deposited. ^{1}H NMR proved that the **3d**/**6** ratio in **7** is 1:2.

Scheme 6.



Few single X-ray structures of substituted DAB dendrimers are reported in the literature. For instance, it has been shown that chains of the DAB-*dendr*-(NH-Gly-*t*-BOC)$_4$ were backfolded due to the presence of hydrogen bonds between the CO and NH groups. After cristallisation in isopropylic ether, the structure of the DAB-*dendr*-$(NH\text{-}C_6F_4I)_4$ **2a** has been determined through a single crystal X-ray diffraction (Figure 7). The analysis revealed that two opposite chains are fully extended in a trans-trans (*tt*) conformation despite the presence of two H···F hydrogen bonds. On the other hand, the other two chains are in a gauche-gauche conformation (gg), due to two N···H···F hydrogen bonds.

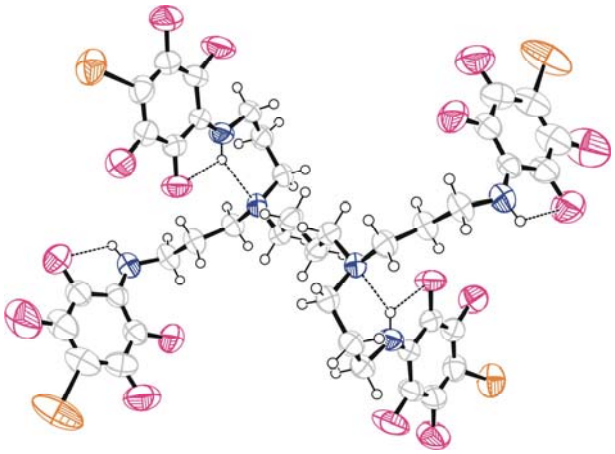


Figure 7: X-ray structure of DAB-*dendr*-$(NHC_6F_4I)_4$ **2a**.

In solution, ^{19}F NMR proves the involvement of iodine atoms of the DAB-*dendr*-$(NHC_6F_4I)_2^2$ **3d** in the formation of strong XB. In the solid, the four chains of **3d** look adjusted for an *exo* recognition process driven by XB. These observations prompted us to study the self-assembly of the DAB-*dendr*-$(NH\text{-}C_6F_4I)_2^2$ **3d** with a telechelic nitrogen module, namely (*E*)-1,2-bis-(4-pyridil)-ethylene (**6**) (1:2 ratio, chloroform solution) (see Scheme 2, Supporting Information). Upon slow evaporation of the solvent, good quality crystals of **7** were deposited. ^1H NMR proved that the **3d**/**6** ratio in **7** is 1:2. Single crystal X-ray diffraction analysis showed that all of the DAB

Single crystal X-ray diffraction analysis showed that all of the DAB units function as tetratopic electron acceptors and the bipyridine derivatives act, in turn, as ditopic donors. XB is the key feature in the structure of **7** (Figure 8). The I1···N35[*x*,1+*y*,*z*] and I2···N29[1/2-*x*,-3/2+*y*,1/2-*z*] distances are 2.838 and 2.943 Å, around 0.8 times the sum of van der Waals radii for N and I.[12] Consistent with the strong n→σ* character of the electron donation from nitrogen to iodine, the C-I···N angles that are almost linear (172.7 and 177.6°).

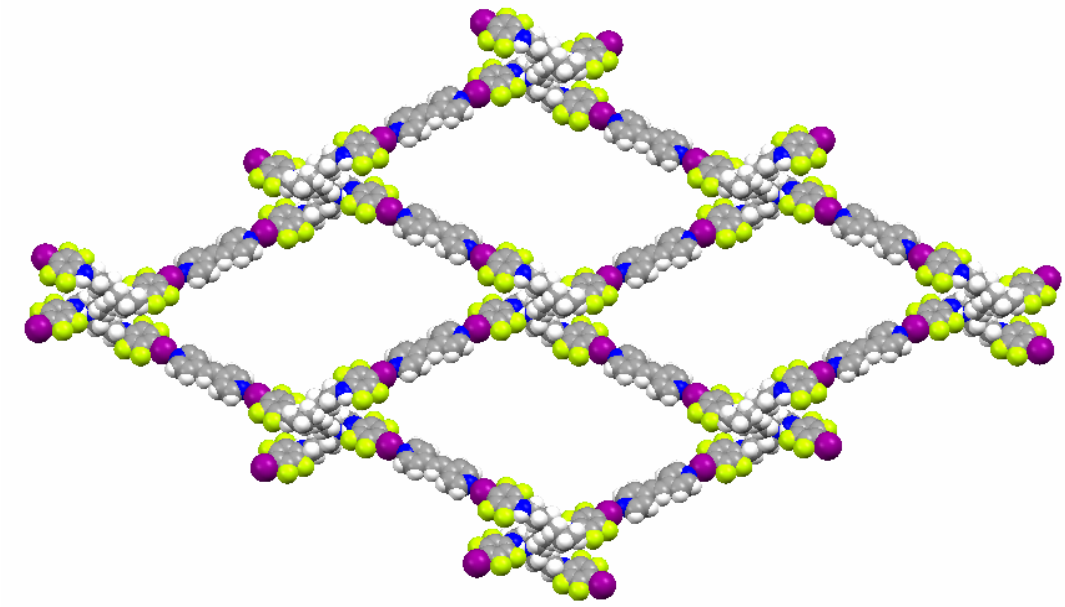


Figure 8. Single crystal X-ray structure of the supramolecular complex 7; 2D square layers with a 4^4 topology are formed.

Typical procedure for the reaction of DAB-*dendr*-$(NH_2)_4$ 1a with the perfluoroarene 2d.
A mixture of 100 mg (0.31 mmol) of DAB-*dendr*-$(NH_2)_4$, 0.33 mL (2.52 mmol) of pentafluoroiodobenzene and 196 mg (1.42 mmol) of K_2CO_3 is stirred in 1 mL of refluxing CH_3CN for 24 h. Then the reaction is cooled to room temperature and the solid is filtered. After evaporation of the solvent, the crude material is chromatographed on silica gel with CH_2Cl_2 then CH_2Cl_2 / MeOH 93/7 as eluent.

DAB-*dendr*-$(NH\text{-}C_6F_4I)_4$ ($C_{40}H_{36}N_6F_{16}I_4$) 3d
White solid, mp = 100-103°C; 68% yield; IR ν_{max} = 3424, 3165, 2953, 2823, 1640, 1524, 1488, 1149, 947, 796 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 5.03 (4H, l, NH), 3.47 (8H, m, NH-C*H*$_2$), 2.53 (8H, t, *J* = 6.4 Hz, C*H*$_2$-N), 2.42 (4H, m, C*H*$_2$-N), 1.75 (8H, qt, *J* = 6.4 Hz, C*H*$_2$-CH_2-NH), 1.45 (4H, m, N-CH_2-C*H*$_2$); ^{19}F NMR (235 MHz, $CDCl_3$): δ -158.2 (8F, d, *J* = 18 Hz, CF-CN), -124.5 (8F, d, *J* = 18 Hz, CF-CI); Ortho-substitution δ -168.3 (4F, m, C*F*-CF-CN), -156.6 (4F, m, CF-CN), -155.6 (4F, m, C*F*-CF-CI), -115.3 (4F, m, CF-CI) ; MS (ESI) m/z 1413 ($M+H^+$).

DAB-*dendr*-$(NH\text{-}C_6F_4Br)_4$ ($C_{40}H_{36}N_6F_{16}Br_4$) 3c
White solid, mp = 85-87°C; 74% yield; IR ν_{max} = 3423, 3220, 2954, 2822, 1640, 1518, 1494, 1154, 956, 821 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 4.89 (4H, l, NH), 3.45 (8H, m, NH-C*H*$_2$), 2.55 (8H, m, C*H*$_2$-N), 2.44 (4H, m, C*H*$_2$-N), 1.76 (8H, qt, *J* = 6.3 Hz, C*H*$_2$-CH_2-NH), 1.46 (4H, m, N-CH_2-C*H*$_2$); ^{19}F NMR (235 MHz, $CDCl_3$): δ -158.2 (8F, d, *J* = 18 Hz, CF-CN), -137 (8F, d, *J* = 18 Hz, CF-CBr) ; Ortho-substitution δ -170.2 (4F, m, C*F*-CF-CN), -158.2 (4F, m, CF-CN), -157.4 (4F, m, C*F*-CF-CBr), -130.9 (4F, m, CF-CBr) ; MS (ESI) m/z 1225 ($M+H^+$) most abundant peak of the isotope cluster of title compound.

DAB-*dendr*-$(NH\text{-}C_6F_4Cl)_4$ ($C_{40}H_{36}N_6F_{16}Cl_4$) 3b
White solid, mp = 73-75°C; 92% yield; IR ν_{max} = 3434, 3212, 2951, 2812, 1645, 1520, 1496, 1149, 953, 871, 856 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 4.93 (4H, l, NH), 3.45 (8H, m, NH-C*H*$_2$), 2.53 (8H, t, *J* = 6.1 Hz, C*H*$_2$-N), 2.42 (4H, m, C*H*$_2$-N), 1.75 (8H, qt, *J* = 6.1 Hz, C*H*$_2$-CH_2-NH), 1.45 (4H, m, N-CH_2-C*H*$_2$); ^{19}F NMR (235 MHz, $CDCl_3$): δ -159.9 (8F, d, *J* = 16.8 Hz, CF-CN), -144.7 (8F, d, *J* = 16.8 Hz, CF-CCl) ; Ortho-substitution δ -171.3 (4F, m, C*F*-CF-CN), -159.1 (4F, m, CF-CN), -158.8 (4F, m, C*F*-CF-CCl), -140.3 (4F, m, CF-CCl) ; MS (ESI) m/z 1047 ($M+H^+$) most abundant peak of the isotope cluster of title compound.

DAB-*dendr*-$(NH\text{-}C_6F_5)_4$ ($C_{40}H_{36}N_6F_{20}$) 3a
White solid, mp = 73-75°C; 52% yield; IR ν_{max} = 3440, 3210, 2963, 2823, 1662, 1520, 1483, 1018, 1000, 952, 800 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 4.60 (4H, l, NH), 3.38 (8H, m, NH-C*H*$_2$), 2.53 (8H, t, *J* = 6.5 Hz, C*H*$_2$-N), 2.43 (4H, m, C*H*$_2$-N), 1.74 (8H, qt, *J* = 6.5 Hz, C*H*$_2$-CH_2-NH), 1.45 (4H, m, N-CH_2-C*H*$_2$); ^{19}F NMR (235 MHz, $CDCl_3$): δ -160.6 (8F, d, *J* = 22.0 Hz, CF-CN), -165.2 (8F, t, *J* = 21.4 Hz, CF), -173.0 (4F, t, *J* = 21.4 Hz, CF) ; MS (ESI) m/z 981($M+H^+$).

Typical procedure for the reaction of DAB-*dendr*-$(NH_2)_8$ 1b with the perfluoroarene 2d.
A mixture of 100 mg (0.13 mmol) of DAB-*dendr*-$(NH_2)_8$, 0.30 mL (2.08 mmol) of pentafluoroiodobenzene and 161 mg (1.17 mmol) of K_2CO_3 were stirred in 0.5 mL of refluxing THF during 48h. Then, the solution is filtered and the solvent is evaporated.

The crude material was chromatographed on silica gel eluent CH_2Cl_2 then CH_2Cl_2 / MeOH 8/2. (Syntheses were carried out in refluxing acetonitrile for **4a,b** and refluxing THF for **4c,d**).

DAB-*dendr*-(NH-$C_6F_4I)_8$ ($C_{88}H_{88}N_{14}F_{32}I_8$) 4d
Yellow oil; 65% yield; IR ν_{max} = 3428, 2948, 2816, 1637, 1513, 1486, 1147, 947, 906, 800, 730 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 5.07 (8H, l, NH), 3.47 (16H, m, NH-CH_2), 2.53 (20H, m, N-CH_2-CH_2-CH_2-NH, N-CH_2-CH_2-CH_2-N), 2.41 (16H, m, N-CH_2-CH_2-CH_2-N, CH_2-CH_2-N), 1.75 (16H, qt, *J* = 5.9 Hz, CH_2-CH_2-NH), 1.61 (8H, m, N-CH_2-CH_2-CH_2-N), 1.34 (4H, m, N-CH_2-CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ -158.0 (2F, d, *J* = 19.9 Hz, CF-CN), -124.3 (2F, d, *J* = 19.9 Hz, CF-CI) ; Ortho-substitution δ -168.4 (8F, m, C*F*-CF-CN), -156.7 (8F, m, CF-CN), -155.6 (8F, m, C*F*-CF-CI), -115.3 (8F, m, CF-CI) ; MS (ESI) m/z 2965-2966 ($M+H^+$) isotope cluster.

DAB-*dendr*-(NH-$C_6F_4Br)_8$ ($C_{88}H_{88}N_{14}F_{32}Br_8$) 4c
Brown oil; 74% yield; IR ν_{max} = 3423, 3220, 2950, 2817, 1640, 1492, 1151, 951, 823 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 4.90 (8H, l, NH), 3.46 (16H, m, NH-CH_2), 2.54 (20H, m, N-CH_2-CH_2-CH_2-NH, N-CH_2-CH_2-CH_2-N), 2.43 (16H, m, N-CH_2-CH_2-CH_2-N, CH_2-CH_2-N), 1.76 (16H, qt, *J* = 5.9 Hz, CH_2-CH_2-NH), 1.61 (8H, m, N-CH_2-CH_2-CH_2-N), 1.35 (4H, m, N-CH_2-CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ -159.1 (16F, d, *J* = 18.9 Hz, CF-CN), -137.0 (16F, d, *J* = 18.9 Hz, CF-CBr) ; Ortho-substitution δ -170.0 (8F, m, C*F*-CF-CN), -158.1 (8F, m, CF-CN), -157.4 (8F, m, C*F*-CF-CBr), -130.8 (8F, m, CF-CBr); MS (ESI) m/z 2589 ($M+H^+$) most abundant peak of the isotope cluster of title compound.

DAB-*dendr*-(NH-$C_6F_4Cl)_8$ ($C_{88}H_{88}N_{14}F_{32}Cl_8$) 4b
Colourless oil; 86% yield; IR ν_{max} = 3421, 3222, 2949, 2815, 1644, 1497, 1156, 957, 869, 739 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 4.94 (8H, l, NH), 3.45 (16H, m, NH-CH_2), 2.54 (20H, m, N-CH_2-CH_2-CH_2-NH, N-CH_2-CH_2-CH_2-N), 2.42 (16H, m, N-CH_2-CH_2-CH_2-N, CH_2-CH_2-N), 1.76 (16H, qt, *J* = 5.9 Hz, CH_2-CH_2-NH), 1.62 (8H, m, N-CH_2-CH_2-CH_2-N), 1.35 (4H, m, N-CH_2-CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ -159.9 (16F, m, CF-CN), -144.6 (16F, d, *J* = 17.7 Hz, CF-CCl) ; Ortho-substitution δ -171.2 (8F, m, C*F*-CF-CN), -159.2 (8F, m, CF-CN), -158.8 (8F, m, C*F*-CF-CCl), -140.2 (8F, m, CF-CCl) ; MS (ESI) m/z 2233 ($M+H^+$) most abundant peak of the isotope cluster of title compound.

DAB-*dendr*-(NH-$C_6F_5)_8$ ($C_{88}H_{88}N_{14}F_{40}$) 4a
Colourless oil; 55% yield; IR ν_{max} = 3423, 3242, 2949, 2814, 1640, 1517, 1482, 1018, 992, 962 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 4.62 (8H, l, NH), 3.38 (16H, m, NH-CH_2), 2.52 (20H, t, *J* = 6.3 Hz, N-CH_2-CH_2-CH_2-NH, N-CH_2-CH_2-CH_2-N), 2.39 (16H, m, N-CH_2-CH_2-CH_2-N, CH_2-CH_2-N), 1.74 (16H, qt, *J* = 6.3 Hz, CH_2-CH_2-NH), 1.58 (8H, m, N-CH_2-CH_2-CH_2-N), 1.33 (4H, m, N-CH_2-CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ -160.6 (16F, d, *J* = 22.0 Hz, CF-CN), -165.2 (16F, t, *J* = 22.0 Hz, CF), -173.2 (5F, d, *J* = 18.4 Hz, CF), -173.3 (3F, d, *J* = 16.9 Hz, CF) ; MS (ESI) m/z 2101-2102 ($M+H^+$) isotope cluster.

Typical procedure for the reaction of DAB-*dendr*-$(NH_2)_{16}$ 1c with the perfluoroarene 2d.
A mixture of 100 mg (0.06 mmol) of DAB-*dendr*-$(NH_2)_{16}$, 0.25 mL (1.90 mmol) of pentafluoroiodobenzene and 141 mg (1.02 mmol) of K_2CO_3 were stirred in 0.5 mL of

refluxing THF during 48h. Then, the solution is filtered and the solvent is evaporated. The crude material was chromatographed on silica gel eluent CH_2Cl_2 then CH_2Cl_2 / MeOH 7/3.

DAB-*dendr*-(NH-$C_6F_4I)_{16}$ ($C_{184}H_{192}N_{30}F_{64}I_{16}$) 5d

Yellow oil; 50% yield; ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.10 (16H, l, NH), 3.46 (32H, m, NH-C*H*$_2$), 2.52 (56H, m, N-C*H*$_2$-CH_2-CH_2-NH, N-CH_2-CH_2-C*H*$_2$-N), 2.40 (28H, m, N-C*H*$_2$-CH_2-CH_2-N, CH_2-C*H*$_2$-N), 1.75 (32H, qt, *J* = 5.9 Hz, C*H*$_2$-CH_2-NH), 1.58 (24H, m, N-CH_2-C*H*$_2$-CH_2-N), 1.25 (4H, m, N-CH_2-C*H*$_2$) ; ^{19}F NMR (235 MHz, $CDCl_3$): δ -157.9 (2F, d, *J* = 19.0 Hz, CF-CN), -124.3 (2F, d, *J* = 19.0 Hz, CF-CI) ; Ortho-substitution δ -168.4 (8F, m, C*F*-CF-CN), -156.7 (8F, m, CF-CN), -155.6 (8F, m, C*F*-CF-CI), -115.3 (8F, m, CF-CI); MS (ESI) m/z 2024 $(M+3H)^{3+}$ isotope cluster not resolved.

DAB-*dendr*-(NH-$C_6F_4Br)_{16}$ ($C_{184}H_{192}N_{30}F_{64}Br_{16}$) 5c

Brown oil; 45% yield; ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.03 (16H, l, NH), 3.44 (32H, m, NH-C*H*$_2$), 2.54 (56H, m, N-C*H*$_2$-CH_2-CH_2-NH, N-CH_2-CH_2-C*H*$_2$-N), 2.44 (28H, m, N-C*H*$_2$-CH_2-CH_2-N, CH_2-C*H*$_2$-N), 1.93-1.42 (56H, m, C*H*$_2$-CH_2-N), 1.30 (4H, m, N-CH_2-C*H*$_2$) ; ^{19}F NMR (235 MHz, $CDCl_3$): δ -159.1 (32F, d, *J* = 18.3 Hz, CF-CN), -137.1 (32F, d, *J* = 18.3 Hz, CF-CBr) ; Ortho-substitution δ -170.2 (16F, m, C*F*-CF-CN), -158.2 (16F, m, CF-CN), -157.4 (16F, m, C*F*-CF-CBr), -130.9 (16F, m, CF-CBr); MS (ESI) m/z 2660 $(M+2H)^{2+}$ isotope cluster not resolved.

DAB-*dendr*-(NH-$C_6F_4Cl)_{16}$ ($C_{184}H_{192}N_{30}F_{64}Cl_{16}$) 5b

Colourless oil; 51% yield; ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.99 (16H, l, NH), 3.44 (32H, m, NH-C*H*$_2$), 2.52 (56H, m, N-C*H*$_2$-CH_2-CH_2-NH, N-CH_2-CH_2-C*H*$_2$-N), 2.37 (28H, m, N-C*H*$_2$-CH_2-CH_2-N, CH_2-C*H*$_2$-N), 1.75 (32H, m, C*H*$_2$-CH_2-NH), 1.59 (24H, m, N-CH_2-C*H*$_2$-CH_2-N), 1.32 (4H, m, N-CH_2-C*H*$_2$) ; ^{19}F NMR (235 MHz, $CDCl_3$): δ -159.9 (32F, d, *J* = 18.3 Hz, CF-CN), -144.7 (32F, m, CF-CCl) ; Ortho-substitution δ -171.3 (16F, m, C*F*-CF-CN), -159.2 (16F, m, CF-CN), -158.8 (16F, m, C*F*-CF-CCl), -140.3 (16F, m, CF-CCl) ; MS (ESI) m/z 2304 $(M+2H)^{2+}$ isotope cluster not resolved.

Characterization of supramolecular complex 7:

White solid, mp = 162-165°C; IR ν_{max} (cm^{-1}) = 3414, 3186, 2950, 2873, 2816, 1639, 1598, 1488, 1290, 1140, 944, 782 cm^{-1}.

The principal investigator
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