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Maria Teresa Messina[a]; Pierangelo Metrangolo[a]; Giuseppe Resnati; Silvio Quici[b]; Amedea Manfredi[c]; Tullio Pilati[d]

[a] Dipartimento di Chimica, Politecnico di Milano, Milano, Italy [b] C.N.R. — Centro Studio Sintesi e Stereochimica Sistemi Speciali Organici, Università di Milano; 19, Milano, Italy [c] Dipartimento di Chimica Organica e Industriale, Università di Milano; 19, Milano, Italy [d] C.N.R. — Centro Studio Relazioni Struttura Reattività Chimica, Università di Milano; 19, Milano, Italy

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Herringbone Infinite Networks Formed by Terpyridine and Haloperfluoroarene Modules

MARIA TERESA MESSINA[a], PIERANGELO METRANGOLO[a], GIUSEPPE RESNATI[a]*, SILVIO QUICI[b], AMEDEA MANFREDI[c] and TULLIO PILATI[d]

[a]*Dipartimento di Chimica, Politecnico di Milano; 7, via Mancinelli; I-20131 Milano, Italy,* [b]*C.N.R. – Centro Studio Sintesi e Stereochimica Sistemi Speciali Organici,* [c]*Dipartimento di Chimica Organica e Industriale, and* [d]*C.N.R. – Centro Studio Relazioni Struttura Reattività Chimica, Università di Milano; 19, via Golgi; I-20133 Milano, Italy*

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4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine (**1**) self-assembles with dihaloperfluoroarenes (**2**). A chemo- and site-selective supramolecular synthesis occurs which preserves in the solid cocrystal the most stable *s-trans,s-trans* conformation of the pure terpyridine module. The single crystal X-ray structure of **3a**, prepared from **1** and 1,4-diiodotetrafluorobenzene (**2a**) (monoclinic, $a = 14.608(1)$, $b = 13.276(1)$, $c = 13.970(2)$ Å, $\beta = 109.808(8)°$, $U = 2549.4\ (4)$ Å^3, $T = 291\ (1)$ K, space group $C2/c$ $Z = 4$; μ(Mo-Kα) = 2.519 mm^{-1}; d_{calc}.: 1.890 g cm^{-3}; 5748 reflections measured, 3715 unique ($R_{int} = 0.024$) which were used in all calculations; the final R and wR (F^2) were 0.043 and 0.069, respectively) shows the presence of infinite ribbons where the two modules alternate in a zigzag arrangement.

Keywords: supramolecular chemistry, noncovalent interactions, molecular recognition, fluorine, pyridine

The terpyridine module (tpy is 2,2′:6′,2″-terpyridine) is extensively used to construct inorganic supramolecular architectures by reading the information it stores with transition metal cations.[2] In this process, tpy typically works as a tridentate electron donor; to the best of our knowledge only two cases have been described in which it acts as a monodentate ligand,[3] and in the limited examples in which it works as a bidentate donor, the 1,1′-nitrogen atoms bind the same metal ion.[4] Here we describe how the nitrogen atoms of 4′-(4-methylphenyl)-2,2′:6′-2″-terpyridine (**1**), and other pyridine derivatives work in solution as electron donors to the iodine and bromine atoms of 1,4-diiodotetrafluorobenzene (**2a**), its dibromo analogue **2b**, and 4,4′-dibromooctafluorobiphenyl (**2c**). In the solid state these non-covalent interactions drive the self-assembly of hydrocarbon (HC) and perfluorocarbon (PFC) modules, **1** and **2** respectively, into crystalline copolymers **3** where tpy **1** behaves as a bidentate donor to haloperfluoroarenes **2**. Single crystal X-ray analyses of the supramolecular architecture **3a**, prepared from **1**and **2a**, shows how the HC and PFC modules are ordered in a herringbone fashion by the "halogen bondings"[5] between the 1,1″-nitrogen atoms of one tpy unit and two iodine atoms of two distinct perfluoroarene units, resulting in infinite ribbons where tpy **1** and perfluoroarene **2a** alternate in a zigzag arrangement.

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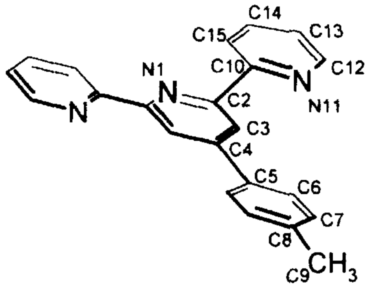
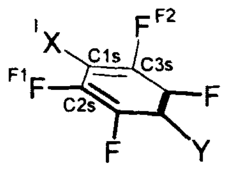
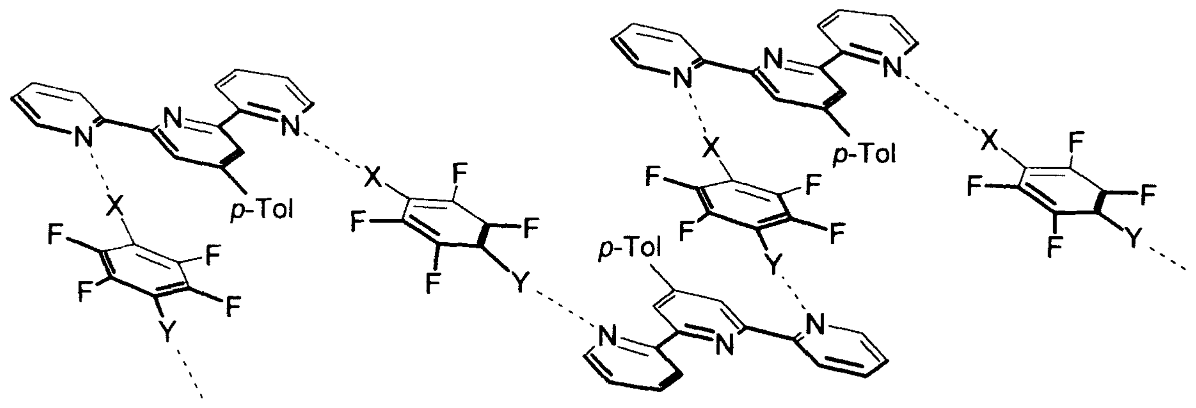
* Corresponding Author: E-mail: resnati@dept.chem.polimi.it



1



2a X = Y = I
2b X = Y = Br
2c X = Br, Y = 4-Br-C_6F_4



	X	Y
3a	I	I
3b	Br	Br
3c	Br	4-Br-C_6F_4

FORMULAE The numberings reported on **1** and on **2a** also apply to the same modules in **3a** (X-ray analyses)

We have already reported how pyridine and other heteroaromatic derivatives effectively act as electron donors to iodo and bromoperfluoroalkanes in solution[6]and in the solid state.[7] The general ability of the nitrogen atoms of pyridine derivatives to work as electron donors also to iodo and bromoperfluoroarenes is here revealed by the high field shift[6] shown, in ^{19}F NMR spectra, by chloroform solutions of co-crystals **3**, with respect to solutions containing pure precursors **2**. Observed signal shifts increased with nitrogen-donor: iodine-acceptor ratio.[8]No signal broadening has ever been observed, revealing that at room temperature the HC-PFC association process is rapid in the NMR time scale.

Slow evaporation of equimolar chloroform solutions of modules **1** and **2** affords non covalent copolymers **3** which are isolated as pale yel-

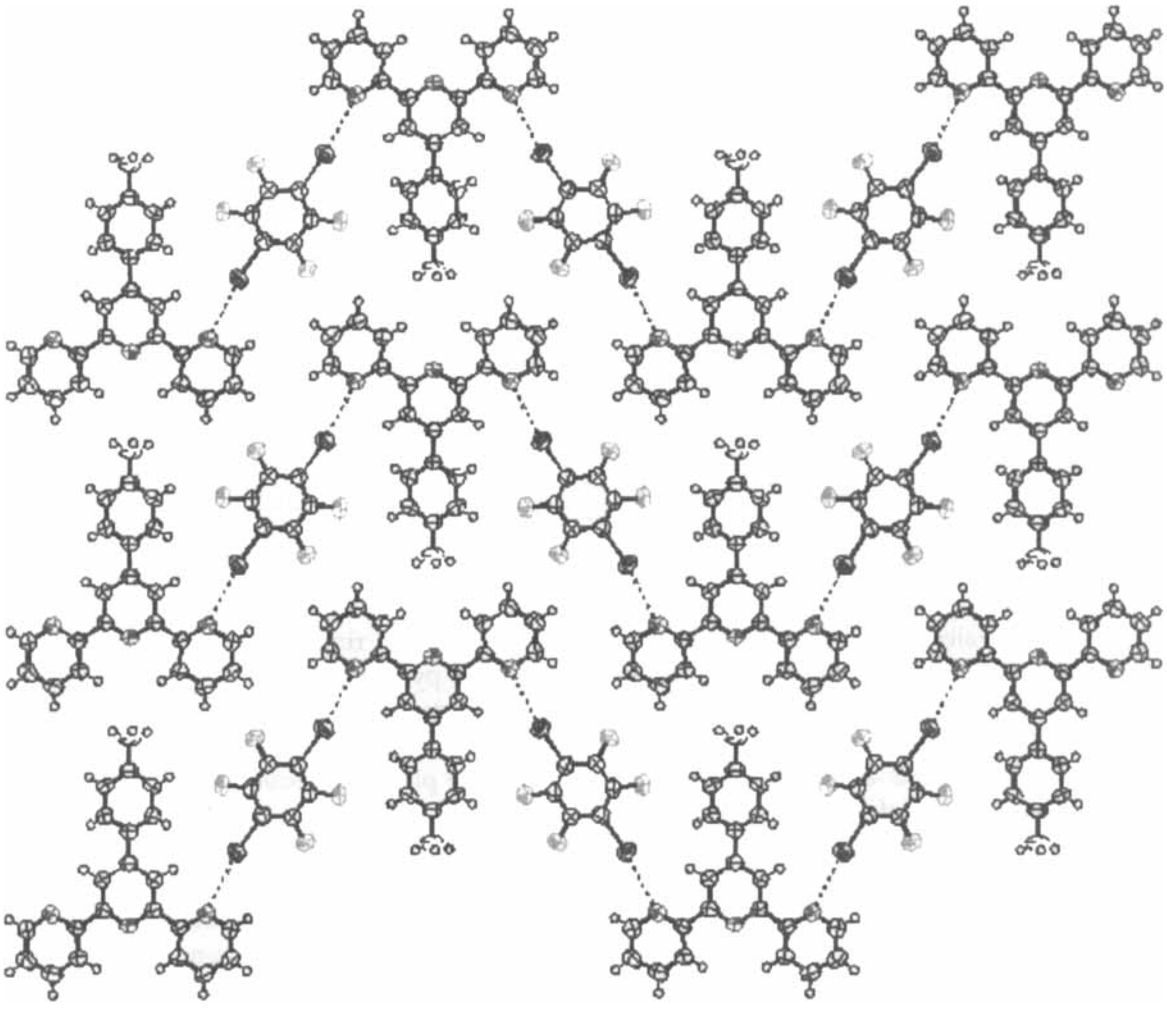


FIGURE Ortep view of the packing layer of **3a**. Colours are as follows: black, carbon; sky blue, fluorine; violet, nitrogen; red, iodine. Dashed lines represent the intermolecular N···I halogen bonds (see Color Plate at the back of this issue)

low and crystalline solids stable in air and light at room temperature. Differential scanning calorimetry of copolymers **3** shows how the sharp melting endotherms of pure HC and PFC precursors are not present in the corresponding copolymers which, in the case of **3a**, melts even higher than pure starting modules **1** and **2**.[9] This shows that the halogen bonding driven self-assembly of **1** and **2** results in the formation of well defined molecular aggregates rather than disordered mixtures. ^1H and ^{19}F NMR spectra of highly diluted solutions of infinite networks **3** are identical to those of single pure HC and PFC modules **1** and **2**, respectively, and unchanged starting copolymers **3** are obtained on evaporation of these diluted solutions. These observations prove the non-covalent nature of the N···halogen interaction in solids **3**. On copolymer **3** formation, some of the stretching modes of pure HC modules **1** (3100–3000 cm^{-1} region) and PFC modules **2** (ca. 1490, 980, and 750 cm^{-1}) shift, in IR spectra (KBr pellets), to higher and lower frequencies, respectively.[10] These spectral changes are similar to those given by diiodoperfluoroalkanes with amine[11] and pyridine[7] derivatives and are consistent with the HC and PFC modules being bound in **3** through an electron donation from nitrogen to iodine. Both in solution and in the solid, the physical and spectroscopic properties of halogen bonded adducts **3** reveal trends consistently implying that diiodotetrafluorobenzene **2a** is a better electron acceptor than its bromo analogues **2b, c**.[12] To confirm this relative strength of the N···I and N···Br bonds, a competitive experiment has been performed. When a clear chloroform solution of tpy **1** is added to a clear chloroform solution of **2a** and **2b**, a chemo-selective self-assembly of **1** with **2a** occurs and only **3a** precipitates in a pure form, as demonstrated by GC and TLC analyses.

Microanalyses (C, H, N, I), GC, and $^1H/^{19}F$ NMRs of non-covalent copolymers **3**, in the presence of $(CF_3CH_2)_2O$ as internal standard, prove the 1 : 1 ratio of the HC and PFC modules. Having two electron poor iodine, or bromine, atoms dihaloperfluoroarenes **2** are di-acceptor modules. The stoichiometry of supramolecular architectures **3** thus implies that here tpy **1** works as a bidentate donor, in contrast to its most frequent behaviour.[2]

Single crystal X-ray analysis of **3a** (Fig. 1) allowed the structural aspects of this architecture to be established in detail.[14] The intermolecular interaction largely responsible for the formation of the copolymers is the halogen bonding between tpy nitrogen atoms and tetrafluorobenzene iodine atoms. The N···I distance is 3.127(2) Å, definitively shorter than the sum of iodine and nitrogen van der Waals radii (1.98 and 1.55 Å, respectively),[15] but longer than the corresponding distance in copolymers where pyridine derivatives self-assemble with iodoperfluoroalkanes.[11] Consistent with a possible n → σ^* character of the nitrogen-iodine interaction,[16] the N···I non-covalent bonding develops approximately on the extension of the C-I bond (N···I-C angle 170.1(1)°). Quite similar geometries (170° < N···I-C angle < 180°) have been observed in several infinite chains formed by iodoperfluoroalkanes with trialkylamine[11] and pyridine[7] derivatives, in complexes where 1,4-diiodotetrafluorobenzene (**2a**) accepts electrons from iodide ions,[17] and in crystalline complexes that I_2 forms with nitrogen containing heteroaromatics.[18] The C10-N11···I angle in **3a** is 144.5(2)° and it is larger than what expected for an n → σ^* interaction between the nitrogen and iodine atoms, namely 120°, probably as this enlargement allows the *p*-tolyl and tetrafluorobenzene moieties to be accommodated in the coplanar arrangement of the packing.[19]

In the solid state and in solution,[20] the three pyridine rings of pure 2,2′:6′,2″-terpyridine[21] and of various derivatives[22] are nearly co-planar and adopt the most stable 2,2′-*s-trans*,6′,2″-*s-trans* conformation. A possible phenyl ring in position 4′ slightly tilts out of the pyridine plane.[23] The module **1** in the infinite network **3a** also adopts a *s-trans,s-trans* conformation where all the four aromatic rings are in the planes expected for the pure module (dihedral angle between two adjacent pyridines: 1.9(1)°; dihedral angle between the central pyridine ring and its *p*-tolyl appendage: 29.8(1)°). The formation of the infinite network **3a** through halogen bonding driven self-assembly of **1** with **2a** thus maintains the most stable conformation of pure **1**. In contrast, whenever tpy derivatives have self-assembled with a complementary module, they have to now adopted a partner induced conformation.[2]In most cases, complexation reshaped the whole conformation of tpys from the most stable II,2′-*s-trans*,6′,2″-*s-trans* to the less stable II,2′-*s-cis*,6′,2″-*s-cis* arrangement so that tpys can work as tridentate donors to a single cationic centre.[2] Exceptionally, only a partial reshaping of the tpy conformation to the 2,2′-*s-cis*,6′,2″-*s-trans*arrangement is induced leading tpy to work as bidentate donors by employing 1,1′-nitrogen atoms in the co-ordination of a single cationic centre.[4] In all cases, discrete adducts were formed, either dimeric, or trimeric, or oligomeric, the stechiometry depending on the possible presence of other ligands and on the co-ordination properties of the cation. In contrast, in the supramolecular architecture **3a**, the tpy module **1** works as a bidentate donor and forms one-dimensional infinite networks by using the 1,1″-nitrogen atoms in order to bind two iodine atoms of two different fluorocarbon modules **2a**. The self-assembly of **1** and **2a** is thus site-selective as only the nitrogen atoms of the terminal pyridine rings are involved in the infinite 1D network **3a** synthesis.

The iodine atoms of 1,4-diiodotetrafluorobenzene **2a** work as mono-acceptors in **3a** and in other infinite networks formed with nitrogen containing donors.[24] This monodentate behaviour may play a key-role in reading tpy **1** as a 1,1″-di-donor and in preserving its ground state *s-trans,s-trans*conformation in infinite networks **3**. The iodine atoms of 1,4-diiodobenzene behave as di-acceptors when interacting with some oxygen donors.[25] Iodine atoms of **2a** behaving as di-acceptors, mimic the binding ability of metal cations and on interacting with tpy **1** they could reshape it to a *s-cis,s-cis*, or *s-cis,s-trans*, conformation. Further studies are in progress by varying the substitution pattern on the tpy module and the degree of fluorination of the haloarene module in order to probe the general tendency of tpy modules to undergo chemo- and site-selective self-assembly processes when interacting with halofluoroarenes and to maintain their most stable *s-trans,s-trans* conformation in the formed network.

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8. ^{19}F NMR data; spectra were recorded in deuterochloroform solution: $\Delta\delta_F$(ppm) = $\delta_{\mathrm{pure}\,2} - \delta_{\mathrm{adduct}\,3}$: **3a** (0.1 M): $\Delta\delta_F = +\ 0.04$; **3b,c** (0.1 M): $\Delta\delta_F = +\ 0.01$. The observed shifts for **2a** and **2b** in pure pyridine as solvent (N: I molar ratio = 100) were $\Delta\delta_F = +\ 1.00$ and $\Delta\delta_F = +\ 0.32$, respectively. The observed shifts for **2a** and **2b** in a chloroform solution of 2,2′-bipyridine (N: I molar ratio = 50) were $\Delta\delta_F = +\ 0.42$ and $\Delta\delta_F = +\ 0.14$, respectively.
9. **1a** and **2a-c** melt at 173–175°C, 108–110°C, 78–80°C, and 113–115 °C, respectively, and halogen bonded co-crystals **3a-c** melt at 210 °C, 160 °C, and 105 °C, respectively.
10. IR data for **1**: ν_{max}(KBr)/cm^{-1}) 3049, 3015; **2a**: 1468, 944, 761; **2b**: 1497, 956, 789; **2c**: 1492, 995, 721; **3a**: 3053, 3015, 1464, 943, 760; **3b**: 3052, 3017, 1481, 955, 788; **3c**: 3050, 3015, 994, 721;.
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12. At the same molar concentrations, diiodotetrafluorobenzene **2a** gives larger shifts in ^{19}F NMR spectra than the bromo analogue **2b** on interacting with pyridine, 2,2′-bipyridine, and tpy **1**. Iodine containing copolymer **3a** immediately precipitates on mixing chloroform solutions of starting modules **1** and **2a**, while formation of **3b**, and even more **3c**, requires a slow solvent evaporation. Moreover, **3a** melts higher than its bromo analogues **3b** and **3c**. All these data are consistent with the rule that the tendency to form strong halogen bondings parallels the order of halogen polarizabilities (I > Br > Cl > [F]).[13].
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14. Crystal Data: monoclinic, a= 14.608(1), b = 13.276(1), c = 13.970(2) Å, β = 109.808(8) °, U = 2549.4 (4) Å^3, T = 291 (1) K, space group $C2/c$, Z = 4;

μ(Mo-Kα) = 2.519 mm^{-1}; d_{calc}: 1.890 g cm^{-3}; 5748 reflections measured, 3715 unique (R_{int} = 0.024) which were used in all calculations; the final R and wR (F^2) were 0.043 and 0.069, respectively. **1** lies on a C2 crystallographic axis, so the methyl group C9 is disordered, **2a** lies on a centre of symmetry.

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