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PAPER

Competition between π – π or furan–perfluorophenyl stacking interactions in conjugated compounds prepared from azomethine connections†

Charlotte Mallet, Magali Allain, Philippe Leriche and Pierre Frère*

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Conjugated compounds associating phenyl or pentafluorophenyl units linked *via* azomethine bonds to a central furan or furylene–vinylene moiety have been synthesized. The crystal structures of compounds end capped with perfluorophenyl units are analyzed in terms of intermolecular interactions involving the C–H...F contacts, π – π interactions and furan–perfluorobenzene interactions. The compound with a furan moiety as spacer presents a stacking mode defined by C–H...F contacts and π – π interactions while the compound based on a furylene–vinylene unit shows a packing pattern exclusively due to strong furan–perfluorobenzene interactions.

Introduction

In the field of molecular materials, the control of the crystal structures which determines the physical properties of the materials requires intensive investigations in order to elucidate the relationships between molecular structures and supramolecular architectures. Weak intermolecular interactions such as hydrogen bonding, halogen bonding, π – π stacking and donor–acceptor interactions represent the main tools of crystal engineering.^{1–7} Thus arene–arene interactions between aromatic residues play a key role in the performance of conducting or semi-conducting materials.^{8,9} Since the discovery of the benzene–hexafluorobenzene co-crystallization by Patrick and Prosser,¹⁰ phenyl–perfluorophenyl interactions have been observed for many co-crystals or in crystalline structures of mixed derivatives built with both phenyl and perfluorophenyl groups.^{11–19} Such interactions, often resulting in eclipsed or staggered face to face π – π stacking, are the main driving forces for the self-organization of the molecules in those solids. Although the understanding of the role of the fluorine atoms is not yet clear, many theoretical and experimental works have shown that the arene–perfluoroarene interactions could be considered as an interesting supramolecular tool for crystal engineering.²⁰ By contrast with the great number of studies devoted to the arene–perfluoroarene interactions, the works to elucidate the interactions between perfluorophenyl and heterocycle units are surprisingly limited. In the field of organic semiconductor materials, a recent trend consists of associating perfluoroarene and thiophene units in order to enhance the electron affinity of corresponding

materials.^{21–27} X-Ray analyses of the described structures revealed the formation of mainly two kinds of supramolecular arrangements. In planar perfluoroarene–thiophene oligomers, the stacking of the molecules is promoted by close cofacial interactions between the electron-rich thiophene and the electron-poor perfluoroarene moieties.^{28,29} In contrast, when the perfluorophenyl and thiophene units are not coplanar, the organization shows a discrimination of systems and thiophenes stack together *via* π – π interactions and separately from perfluorophenyl units which also interact with each other.^{24,30} Although conjugated systems based on the furan moiety have emerged as a new alternative for the development of semi-conducting materials,^{31,32} conjugated systems associating perfluoroarene and furan have been scantily studied.^{33,34} Moreover, furan–perfluorophenyl interactions have not clearly been evidenced yet. There exists a study of furan–fluoroaromatic interactions concerning the intramolecular interactions in (heterocyclo)paracyclophane derivatives³⁵ and one example of an X-ray structure of a furan–perfluorophenyl conjugated compound recently published;³⁴ however, the stacking mode in the structure was not described.³⁶

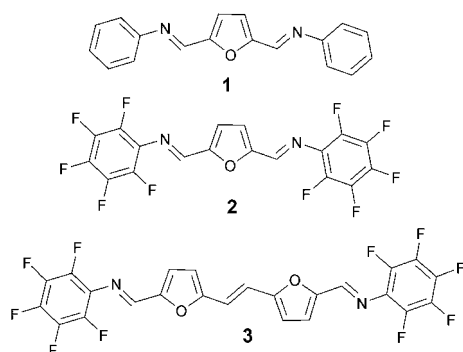
In the continuation of our current interest in conjugated systems based on furan units as electroactive materials from renewable biomass resources,^{37–39} we present here three conjugated compounds **1**, **2** and **3** associating furan moieties with phenyl or perfluorophenyl units *via* azomethine bonds (Scheme 1).

The use of furan cycles and azomethine bonds are part of a green chemistry approach. Thus azomethine bonds are formed by reaction between aldehydes and amines and produce only water as waste. Several examples of conjugated materials based on azomethine have been described.^{40–47}

Moreover, furaldehyde and 5-hydroxymethyl-furfural (HMF) used as starting materials are well known as renewable materials obtained by dehydration of glucose or by transformation of lignocellulosic biomass.^{48–50}

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Scheme 1 Structures of compounds 1–3.

In this contribution, we report on the electronic properties and on the solid state assemblies in crystals obtained from **1–3** and we show the key role of the furan–perfluorophenyl interactions on the supramolecular organizations of these later.

Results and discussion

Synthesis

Compounds **1–3** have been synthesized by condensation of the dialdehyde **4** or **5** with aniline or pentafluoroaniline (Scheme 2). Dialdehyde **4** was synthesized by oxidation of HMF⁵¹ while **5** was prepared in two steps from furaldehyde.³⁸ The easy protocol used for obtaining **1**, consisting of heating a mixture of **4** and aniline without solvent,⁵² could not be used with pentafluoroaniline, firstly because of the low reactivity of its nitrogen atom due to the electron withdrawing effect of the fluorine atoms and secondly because pentafluoroaniline is too volatile to allow long time of reaction or high temperature. The reactions of condensation were efficiently carried out by using a sealed vessel under microwave irradiation. Thus, a mixture of dialdehyde **4** or **5** and 2.2 equivalents of pentafluoroaniline in methylene chloride in the presence of a small amount of P₂O₅ (*T* = 80 °C,

P = 4.4 bar, power = 250 W) during 3 × 10 min led to target molecules **2** or **3** in 45% and 38% yield respectively.

Electronic properties

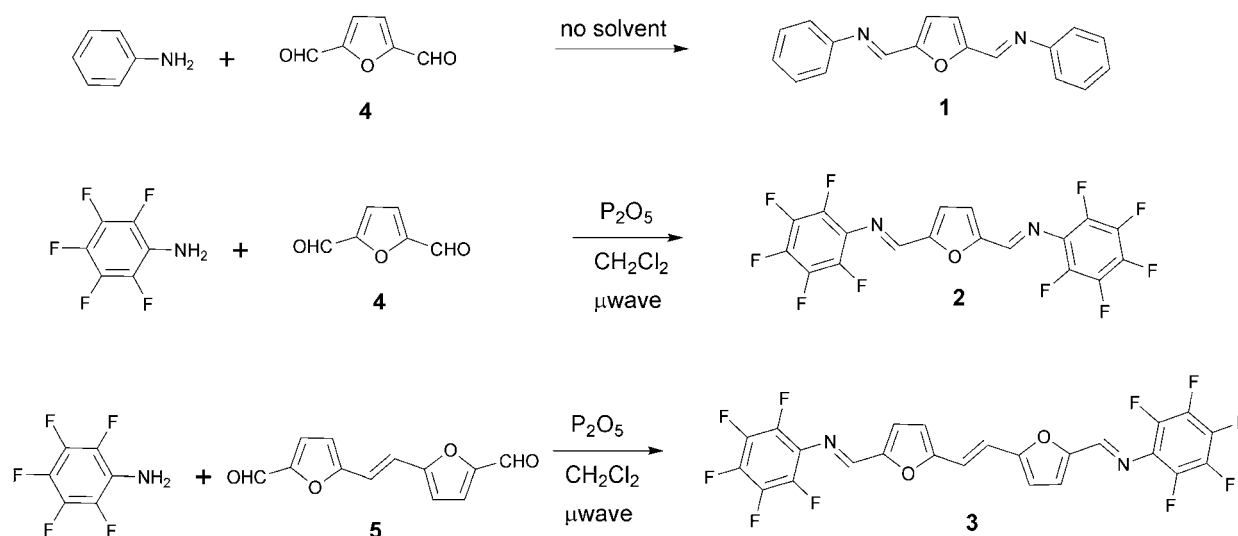
The electronic properties of compounds **1–3** have been analyzed by UV-vis spectroscopy and by cyclic voltammetry (CV). Optical and electrochemical properties are gathered in Table 1. The comparison of the UV-vis data of compounds **1** and **2** shows that the replacement of phenyl terminations by perfluorophenyl units leads to a slight blue shift of the absorption bands probably due to higher torsion of the azomethine bonds. The lengthening of the conjugated system in **3** leads to a bathochromic shift of the absorption band corresponding to a decrease of the HOMO–LUMO gap from 3.41 eV for **2** to 2.88 eV for **3**.

The electrochemical properties of compounds **1–3** have been analyzed both in oxidation and reduction. Compound **1** presents two irreversible oxidation processes respectively at 1.26 and 1.54 V corresponding to the formation of radical cation **1**^{•+} and dication **1**²⁺. The donating ability of compound **2** is strongly decreased due to the presence of the lateral perfluorophenyl groups. Thus this later only undergoes the non-reversible formation of a radical cation at the more anodic potential of 1.49 V. By contrast, the insertion of the furylene–vinylene (FV) unit as spacer in compound **3** enhances the electron donor character and thus allows an easier access to the oxidized states **3**^{•+} and **3**²⁺ as shown by the two oxidation peaks at 1.18 and 1.47 V.

Table 1 Electronic absorption^a and cyclic voltammetry^b data of compounds 1–3

Compound	λ_{\max}/nm	$\Delta E_{\text{opt}}/\text{eV}$	E_{ox1}/V	E_{ox2}/V	E_{red1}/V
1	371	3.34	1.26	1.54	−1.42
2	364	3.41	1.49	—	−1.31
3	430	2.88	1.18	1.47	−1.59

^a 10^{−5} M in CH₂Cl₂. ^b 10^{−3} M in 0.1 M Bu₄NPF₆/CH₂Cl₂, ν = 200 mV s^{−1}, reference AgCl/Ag.



Scheme 2 Synthesis of oligomers 1–3.

Compounds **1–3** present a reduction peak corresponding to the formation of radical anion. As expected, the replacement of the phenyl by perfluorophenyl groups allows a rise in the reduction potential from -1.42 V for **1** to -1.31 V for **2**. The lengthening of the spacer with the donor FV units for **3** enhances the reversibility of the reduction process but at a more cathodic potential of -1.59 V. These results show that the linkage of phenyl or perfluorophenyl groups to furan units by azomethine bonds leads to conjugated systems presenting both donor and acceptor properties. As expected the acceptor character is enhanced by the fluorine atoms, but their electron withdrawing effects are outweighed by the multiplication of the furan units.

Crystal structures

Slow evaporation of chloroform–ethanol solutions of compounds **1–3** gave single crystals suitable for X-ray diffraction analysis. The details of the data collections are gathered in Table 2.

Compound **1** crystallizes in the monoclinic space group $C2/c$. Its structure is defined from a half molecule which lies on a two-fold axis. As shown in Fig. 1a, the two azomethine bonds are coplanar with the central furan ring and adopt an *E* configuration and a δ -*cis* conformation (the nitrogen atoms are oriented in the direction pointing to the oxygen atom). The lateral phenyl rings are not coplanar with the central conjugated system assuming a torsional angle of 38° with respect to the furan ring.

Table 2 Details of the data collection and structural refinement of **1–3**

Crystal	1	2	3
Formula	$C_{18}H_{14}N_2O$	$C_{18}H_4F_{10}N_2O$	$C_{24}H_8F_{10}N_2O_2$
Molecular weight	274.31	454.23	546.32
Temperature/K	293	293	293
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P1$	$P2_1/c$
<i>a</i> /Å	31.930(8)	4.7787(2)	6.4323(9)
<i>b</i> /Å	6.041(2)	6.5029(4)	7.278(1)
<i>c</i> /Å	7.424(1)	13.9073(5)	22.578(4)
α /deg	90	78.371(3)	90
β /deg	97.04(1)	83.747(3)	93.06(1)
γ /deg	90	87.099(4)	90
$V/\text{\AA}^3$	1421.2(6)	420.60(3)	1055.5(3)
<i>Z</i>	4	1	2
Crystal colour	Colorless	Yellow	Orange
$D_c/g\text{ cm}^{-3}$	1.282	1.793	1.719
$F(000)$	576	224	544
μ/mm^{-1}	0.081	0.189	0.171
Transmission(min/max)	0.553/0.998	0.949/0.986	0.972/0.992
θ (min/max)/deg	3.43/28.05	3.01/27.96	3.61/29.00
Data collected	7548	13 816	19 128
Data unique	1644	3764	2630
Data observed [$I > 2\sigma(I)$]	971	2735	1397
$R(\text{int})$	0.077	0.084	0.099
Number of parameters	124	297	188
$R1$ [$I > 2\sigma(I)$]	0.0577	0.0568	0.0554
$wR2$ [$I > 2\sigma(I)$]	0.0943	0.1470	0.1056
$R1$ [all data]	0.1299	0.0872	0.1308
$wR2$ [all data]	0.1146	0.1655	0.1339
Absolute structure parameter	—	0.1(2)	—
GOF	1.108	1.049	1.061
Largest peak in final difference/ $e\text{\AA}^{-3}$	0.151/ −0.211	0.401/−0.323	0.212/−0.275

The molecules stack along the *c* axis in a head to tail overlap of the molecules which prevents π -interactions between the conjugated systems. The regular distances between the planes formed by the furan rings are about 3.3 Å. The molecular organization is mainly defined by C–H---Ph ($d = 2.63$ Å shown by dotted line in Fig. 1c)⁵³ interactions between the phenyl rings which present an edge to face arrangement as observed in crystalline structures of benzene or naphthalene.⁵⁴

The replacement of the phenyl terminations by perfluorophenyl groups leads both to a conformational change and to a strong modification of the interactions that determine the stacking of the molecules. Compound **2** crystallizes in the triclinic $P1$ space group. The molecule is unsymmetrical with an azomethine bond in a δ -*cis* conformation while the second adopts a δ -*trans* one (Fig. 2a). The δ -*trans* conformation presents a better planarity with a torsion angle of the perfluorophenyl of 11° whereas the torsion of the second perfluorinated cycle reaches 39° . This torsional angle is very close to the value observed in structure **1** for the two arms in the same δ -*cis* conformation.

The view of the structure shows that the molecules stack along the *a* axis. Between two adjacent columns, molecules are in contact through C–H---F contacts⁵⁵ with $d_{\text{H}\cdots\text{F}}$ distances ranging between 2.50(4) and 2.77(5) Å as indicated in Fig. 2b by red dotted lines. The stacking of the molecules presents an overlapping of quasi planar conjugated systems involving the δ -*trans* arm and the furan ring with a slight shift, so that a perfluorophenyl moiety is placed opposite of the azomethine bond of the δ -*trans* arm (Fig. 2c). The average distance between the conjugated systems is approximately of 3.4 Å which corresponds to classical distances observed for π - π interactions. The two shortest distances $d_1 = 3.382(4)$ Å and $d_2 = 3.385(6)$ Å involve the carbon atoms of the two azomethine links which are in contact with a carbon of furan ring and a carbon of a fluorinated aromatic ring.

At the other end of the molecule, the perfluorophenyl moieties of the δ -*cis* arms overlap with a shift leading to a superposition of the aromatic ring with the azomethine bond. The distances between the planes of the perfluorinated cycles are close to 3.3 Å and the shortest interatomic distance $d_3 = 3.286(5)$ Å is observed between the nitrogen atom of an imine linkage and carbon atom of an aromatic ring. A second short distance $d_4 = 3.330(5)$ Å involves fluorine and carbon atoms of two superposed perfluorophenyl rings. Thus the crystalline arrangement seems to be oriented by a subtle combination of π - π -interactions between conjugated systems and by electrostatic interactions between the electronegative fluorine and nitrogen atoms and the electropositive centre of perfluorinated rings.

The multiplication of the number of furan rings by the insertion of a FV unit as spacer between the two perfluorophenyl rings for **3** strongly modifies the packing mode in the crystal. Compound **3** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. The structure is defined from a half molecule and the molecule is located on a crystallographic inversion center. As shown in Fig. 3a, the central ethylenic bond is in an *E* configuration and the two azomethine bonds are in an *E* configuration and adopt a δ -*cis* conformation. The two azomethine links are co-planar with the FV unit while the two perfluorophenyl rings assume a torsional angle of 45° with the plane defined by the central conjugated system. Here the torsional

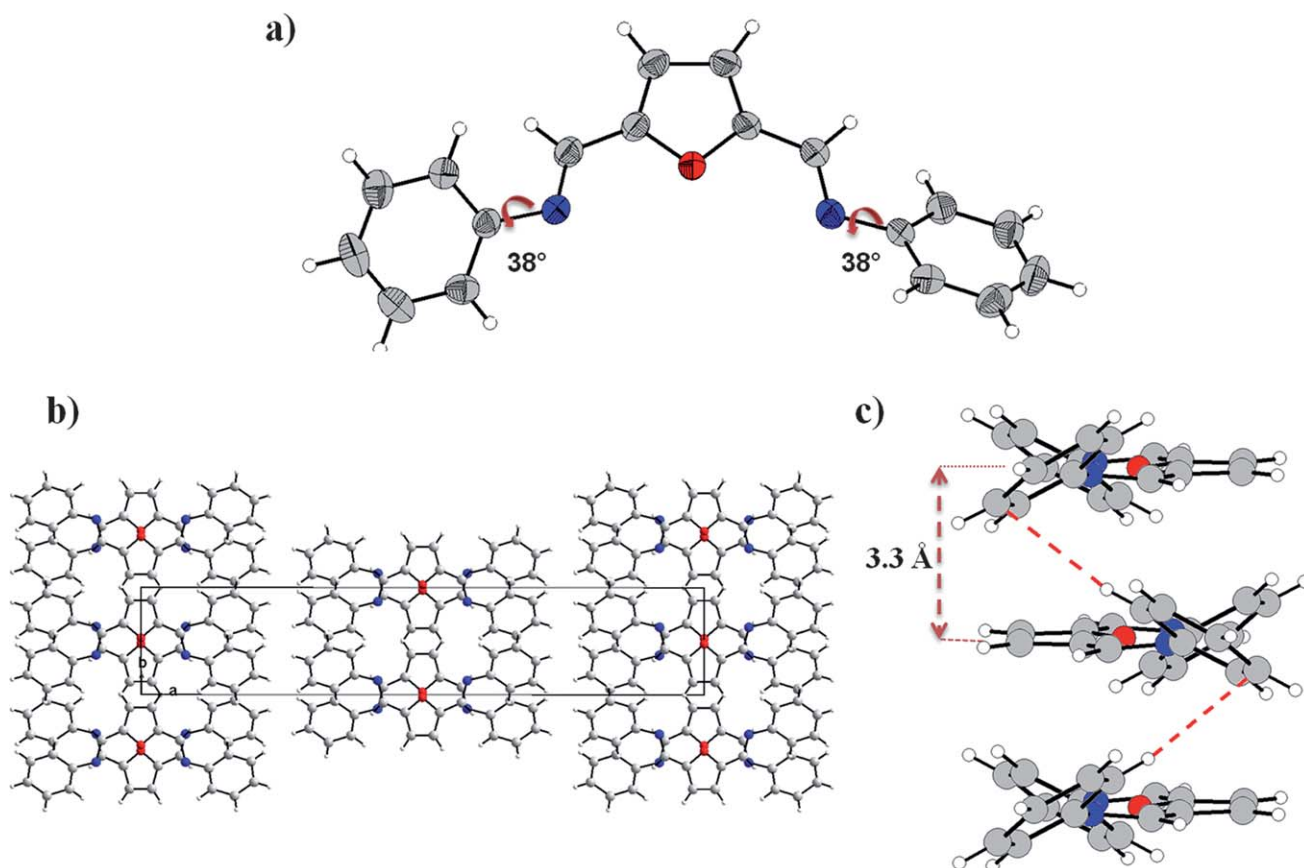


Fig. 1 X-Ray structure of **1**. (a) Molecular structure of **1** with anisotropic displacement ellipsoids drawn at the 50% probability level. (b) Crystal packing of **1** viewed along the cell *c* axis. (c) Stacking mode of molecules along the *c* axis, C–H...Ph interactions are shown in dotted lines.

angles are slightly larger than those obtained in structure **1** (38°) and **2** (39°) for the arm in the same δ -*cis* conformation. The structure shows ribbons of molecules oriented along the *c* axis which stack along the *b* axis. The ribbons are linked themselves by C–H...F contacts with $d_{\text{H}\cdots\text{F}}$ distances ranging between 2.38 (3) and 2.73(2) Å (Fig. 3b). The stacking along the *b* axis is done so that the furan cycles of a central FV unit of a molecule overlap two perfluorophenyl cycles of two other molecules. The distances between the two planes are about 3.4 Å with several inter-atomic distances ranging between 3.20 and 3.50 Å as shown by dotted lines in Fig. 3c. The centroid to centroid distance measured between perfluorophenyl and furan rings is of 3.748(2) Å. This typical face to face stacking, often observed in the structures of mixed fluoroarene–thiophene oligomers or in benzene–perfluorobenzene systems, results from non-covalent interactions between the electron-deficient perfluorophenyl rings and the electron-rich furan cycles. By contrast with the structure of **2**, such a disposition for **3** does not allow any π – π contact. Thus the lengthening of the conjugated system by insertion of a FV unit strongly favors the multiplication of furan–perfluorobenzene interactions to the detriment of the π – π interactions.

For a better understanding of the arrangements observed in the X-ray structures of **2** and **3** and to unravel the role of the fluorine atoms and azomethine bonds in the stacking of the molecules, we investigated the electrostatic potential (ESP) surface²³ of the two compounds **2** and **3** by considering the

conformations adopted in the structures (Fig. 4). For both compounds, the more negative potential regions (in red) are located on the nitrogen, oxygen atoms and on the fluorine atoms which point to the imine bonds. By contrast the internal part of the hexafluorobenzene and the external part of the central conjugated systems present positive potentials (blue).

As shown in Fig. 4 (right) in the case of **3**, the superposition of the perfluorobenzene and furan units in the crystal allows the optimization of the interactions between the positive and negative regions. Thus the furan–perfluorophenyl interactions are the main driving forces responsible for the molecular stacking.

For crystal **2**, the unsymmetrical conformation of the molecule leads to a slightly different repartition of the charges in the two perfluorinated cycles (Fig. 4 left). The fluorine atoms that are in line with the δ -*trans* azomethine bond show a less negative potential than the ones of the second perfluorobenzene unit. The slip-stacking of the two δ -*trans* arms thus mainly implicates π – π interactions strengthened by small electrostatic character.

In conclusion, we have synthesized new examples of conjugated systems associating furan and perfluorophenyl groups. The comparison of the crystal structures of three compounds varying by the lateral phenyl or perfluorophenyl rings or by the nature of the conjugated spacer evidences the key role of the perfluorophenyl groups in the stacking mode of the molecules. Although compound **1** built with phenyl groups does not present any π -stacking, the replacement of phenyl by perfluorophenyl

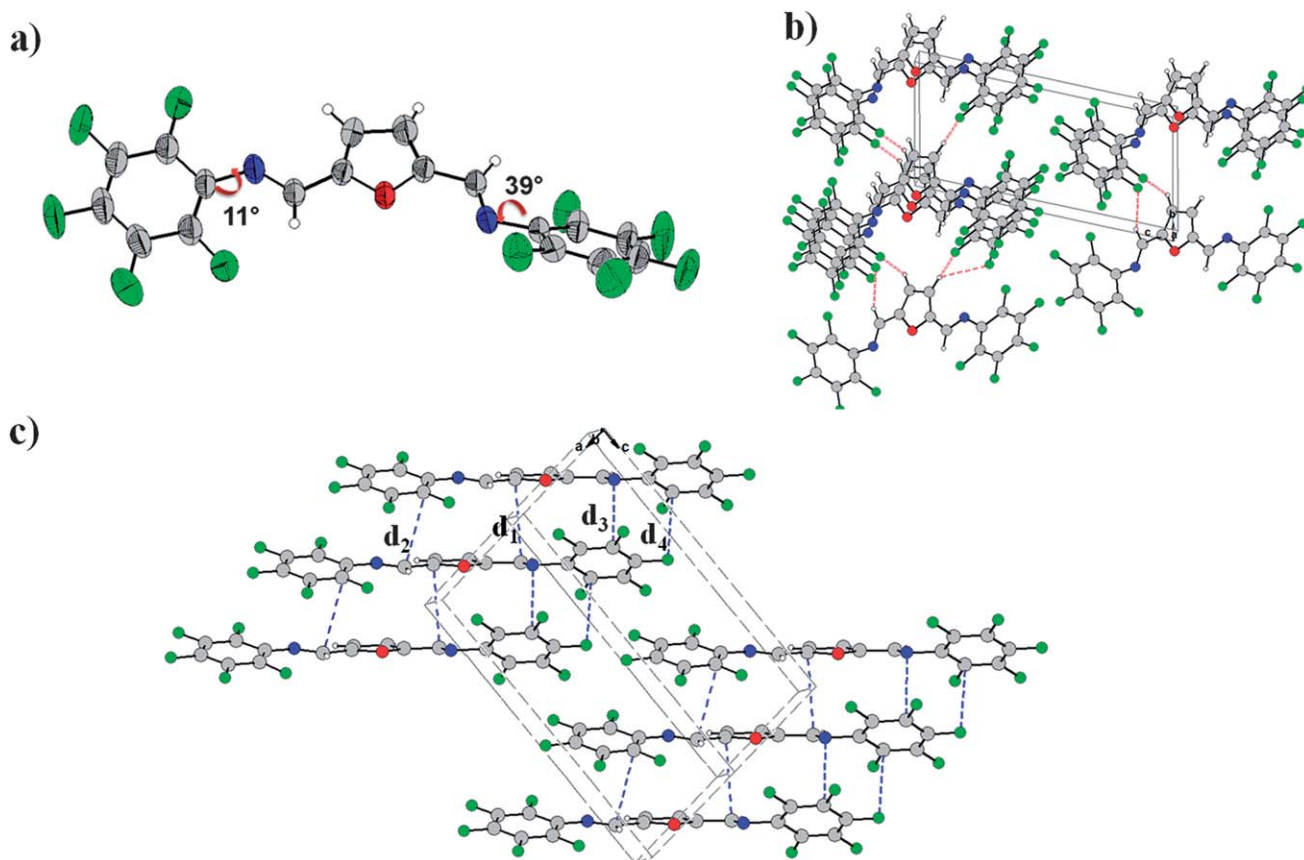


Fig. 2 X-Ray structure of **2**: (a) Molecular structure of **2** with anisotropic displacement ellipsoids drawn at the 50% probability level. (b) Crystal packing of **2** showing the intermolecular C–H...F contacts by red dotted lines. (c) Stacking mode in crystal **2**, the shortest interatomic distances between overlapping molecules are shown by blue dotted lines.

groups in **2** allows a π -stacking of the molecules due to subtle combination of π - π interactions and donor-acceptor interactions. The replacement of the furan by the FV unit as spacer in the conjugated systems leads to the formation of strong furan-perfluorophenyl interactions which can be considered as the main driving forces of the packing mode of **3** to the detriment of the π - π interactions.

Experimental

Syntheses

2,5-Bis(phenyliminomethyl)furan: 1⁵². A slight excess of aniline was added to a 25 mL Erlenmeyer flask containing 1 g of dialdehyde **4** (8 mmol) at rt. The temperature rapidly rose thus allowing the liberation of water vapor. After 10 min, the brown solid obtained was washed by adding 3 mL of methanol. The solid was recovered by filtration, recrystallized from methanol to give 2 g of compound **1** (91% yield).

Yellow pale solid, Mp = 156 °C.

¹H NMR (CD₃COCD₃): 8.53 (s, 2H), 7.43 (t, 4H, ³J = 4.8 Hz), 7.33 (d, 4H, ³J = 4.2 Hz), 7.28–7.25 (m 4H).

¹³C NMR (CD₃COCD₃): 154.6, 151.5, 147.9, 129.3 (2C), 126.6, 121.2 (2C), 117.1.

MS MALDI-TOF: calcd. for C₁₈H₁₄ON₂ 274.1; found 274.6 (M).

2,5-Bis(pentafluorophenyliminomethyl)furan: 2. A 10 mL tube equipped with a magnetic stirring bar was filled with 75 mg of dialdehyde **4** (0.6 mmol), 320 mg of perfluoroaniline (1.7 mmol) in 2 mL of CH₂Cl₂ and 50 mg of P₂O₅. The tube was sealed with a rubber cap and irradiated three times for 10 min at 80 °C and under a pressure of 4.4 bar with a power reactor of 200 W. The mixture was cooled to room temperature, poured on 20 mL of water, extracted twice with CH₂Cl₂ (2 × 20 mL) and the organic phase was dried on MgSO₄. After evaporation of the solvent the residue was purified by flash chromatography on silica gel in the presence of several drops of triethylamine (petroleum ether (40–60 °C)/CH₂Cl₂, 1/1) to give 125 mg (0.27 mmol) of compound **2** (45% yield).

Yellow solid, Mp = 98 °C.

¹H NMR (CD₃COCD₃): 8.59 (s, 2H), 7.34 (s, 2H).

¹³C NMR (CD₃COCD₃): 156.6, 154.2, 120.5.

¹⁹F NMR (CD₃COCD₃): –154.5 (dd, 4F, J = 21 Hz, J = 5 Hz), –162.4 (t, 2F, J = 21 Hz), –165.6 (dt, 4F, J = 21 Hz, J = 6 Hz).

MS MALDI-TOF: calcd. for C₁₈H₄ON₂F₁₀ 454.02; found 454.94 (M + H).

Elemental analysis for C₁₈H₄ON₂F₁₀: calcd. C 47.60, H 0.89, N 6.17; found C 47.28, H 1.01, N 5.99.

1,2-Bis(5-pentafluorophenyliminomethyl-furyl)-E-ethene: 3. A 10 mL tube equipped with a magnetic stirring bar was filled with 0.13 g of dialdehyde **5** (0.6 mmol), 320 mg of perfluoroaniline

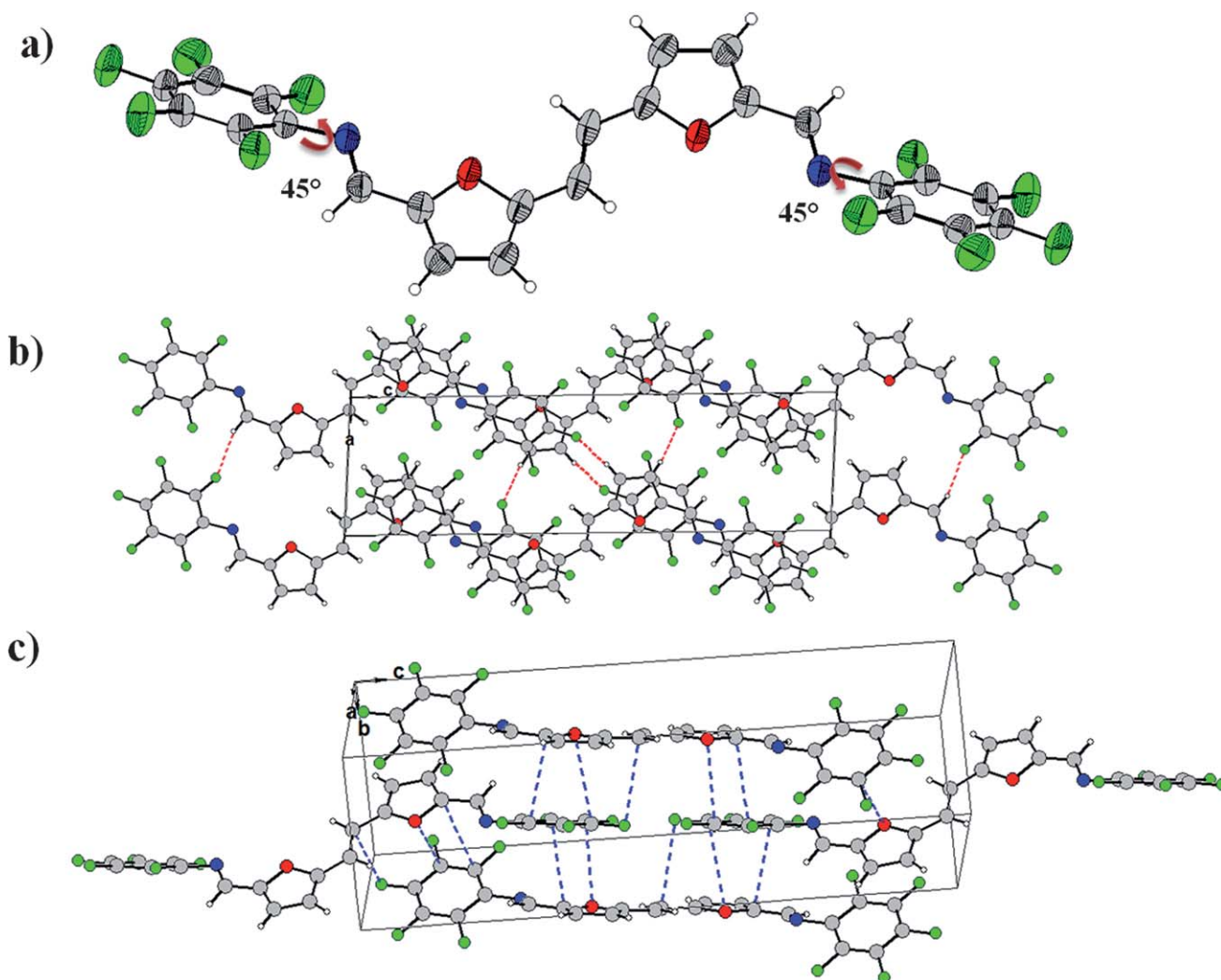


Fig. 3 X-Ray structure of **3**: (a) Molecular structure of **3** with anisotropic displacement ellipsoids drawn at the 50% probability level. (b) Crystal packing of **3** showing the intermolecular C–H...F contacts by red dotted lines. (c) Stacking mode in crystal **3**, the shortest interatomic distances between overlapping molecules are shown by blue dotted lines.

(1.7 mmol) in 2 mL of CH_2Cl_2 and 50 mg of P_2O_5 . The tube was sealed with a rubber cap and irradiated three times for 10 min at 80 °C and under a pressure of 4.4 bar with a power reactor of 200 W. The mixture was cooled to room temperature, poured on 20 mL of water, extracted twice with CH_2Cl_2 (2×20 mL) and

the organic phase was dried on MgSO_4 . After evaporation of the solvent the residue was purified by flash chromatography on silica gel in the presence of several drops of triethylamine (petroleum ether (40–60 °C)/ CH_2Cl_2 , 1/1) to give 125 mg of compound **3** (38% yield).

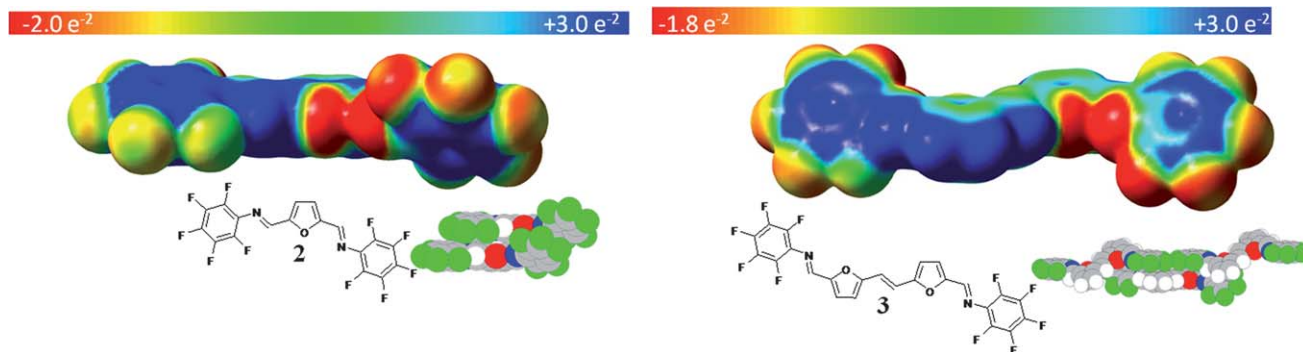


Fig. 4 Electrostatic potential surface of compounds **2** (left) and **3** (right), the values are in units of hartree. The overlapping of the molecules is represented in the inset.

Orange solid, Mp = 204 °C.

¹H NMR (CD₃COCD₃): 8.37 (s, 2H), 7.20 (s, 2H), 7.14 (d, 2H, ³J = 3.5 Hz), 6.65 (d, 2H, ³J = 3.5 Hz).

¹³C NMR (CD₃COCD₃): 156.7, 154.3, 150.9, 121.9, 117.5, 113.6.

¹⁹F NMR (CD₃COCD₃): -153.2 (dd, 4F, J = 21 Hz, J = 6 Hz), -160.3 (t, 2F, J = 21 Hz), -163.4 (td, 4F, J = 21 Hz, J = 6 Hz).

MS MALDI-TOF: calcd. for C₂₄H₈O₂N₂F₁₀ 546.06; found 546.95 (M + H).

Elemental analysis for C₂₄H₈O₂N₂F₁₀: calcd. C 52.76, H 1.48, N 5.13; found C 52.18, H 1.41, N 4.96.

Calculation of electrostatic potential surfaces

Electrostatic potential surfaces of compounds **2** and **3** were calculated with Gaussian 09 by using DFT method. From the geometry adopted in the X-ray structures, single-point energy calculations were performed by using the B3LYP/6-31g basis set. Electrostatic potential surfaces were created by using Gaussview for a density value of 0.002 electrons per au³.

X-Ray structures

X-Ray single-crystal diffraction data for the three compounds were collected at 293 K on a BRUKER KappaCCD diffractometer, equipped with a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SIR92 (Altomare *et al.*, 1993) and refined on F² by full matrix least-squares techniques using SHELXL97 (G.M. Sheldrick, 1998). All non-H atoms were refined anisotropically and the H atoms were found by Fourier difference synthesis. Absorption was corrected by the SADABS program (Sheldrick, Bruker, 2000) for compound **1** and by Gaussian technique for compounds **2** and **3**.

Acknowledgements

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