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Extended benzodifuran–furan derivatives as example of π-conjugated materials obtained from sustainable approach

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ABSTRACT

The synthesis of extended benzodifuran–furan systems are described as an example of π-conjugated materials prepared by following a green approach with only water being produced as waste and using furan derivatives from renewable sources. Investigation of their optical and electrochemical properties shows that the new compounds present electronic properties compatible for application in organic electronics.

1. Introduction

The development of π-conjugated materials is motivated by their potential technological applications as organic semiconducting materials for the fabrication of (opto)electronic devices, such as field-effect transistors (OFET), electroluminescent diodes (OLED) and photovoltaic cells.[1–4] The major goal in the development of organic-based electronic devices resides in the low cost process for their fabrication by using spin coating or inkjet printing.[5–8] On the other hand, the flexibility of the organic chemistry allows the access to various π-conjugated structures that can be tailored for the specific electronic or optical properties to optimize the performances of the devices.[9–12]

Although current organic photovoltaic cell technology represents a promising clean energy production, it still falls short to consider the green criteria for the conception of the organic semiconductors. Indeed, the synthetic procedures of the π-conjugated systems are essentially based on organometallic coupling reaction, such as Stille or Kumada couplings for the syntheses of oligo or polyheterocycles[13–18] or the use of Wittig or Wittig Horner reactions for building ethylenic bonds.[15,19–22] Such synthetic pathways involve stoichiometric amounts of by-products, which require high degree of purification of the semiconducting materials. Moreover, the resulting wastes are often toxic for the environment. Nevertheless, possible alternatives consist in developing conjugated structures via synthetic pathways, such as Knoevenagel condensation[19,23,24] or Schiff base reactions[25–27] leading only to water as waste. Hence, the formation of ethylenic or the isoelectronic azomethine bonds (–C=N–) to lengthen the conjugated systems by clean reactions between aldehydes and carbanions or amines contrast with the Wittig or Wittig Horner reactions, which produce phosphine oxide or phosphate derivatives as waste.

In this context, we have focused on the synthesis via green chemistry approach of π-donors **Ia–c** composed of a benzodifuran moiety connected to furan units by azomethine junctions (Fig. 1). The two steps of the synthetic pathway are based on condensation reactions giving only water as by-product. For these two steps, green solvents, such as ethanol or ethyl lactate were used and the purifications were done by precipitation and recrystallization.

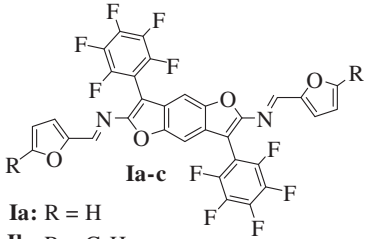

Fig. 1. Structure of the new conjugated derivatives **Ia–c**.

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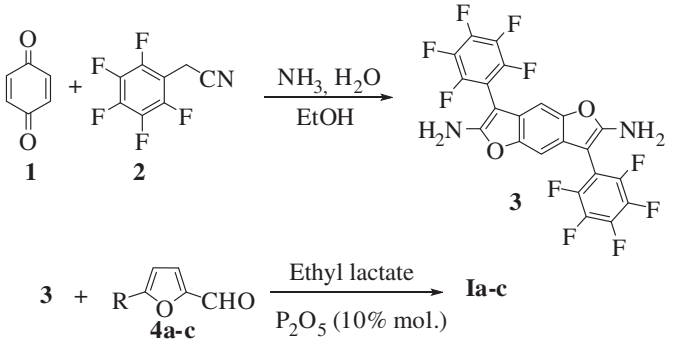
Benzodifuran derivatives have been reported as hole transporting materials in organic electroluminescent cells[28] or as electron-donor in organic solar cells[29,30] and several examples of conjugated materials based on azomethine have been described.[31–34] Moreover furaldehyde and furyl alcohol used as starting materials are well known as renewable materials that are obtained by the dehydration of glucose or by transformation of lignocellulosic biomass.[35–37] Organic semiconductors based on furan moieties have recently been evidenced in OFET and photovoltaic cells.[38–40]

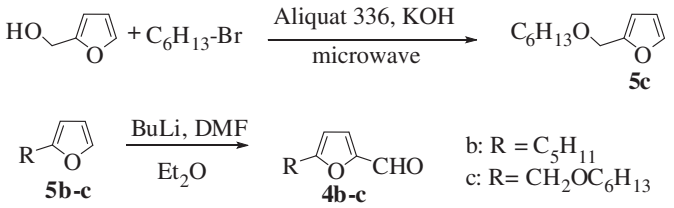
2. Synthesis

The synthetic pathway of compounds **Ia**–**c** is shown in Scheme 1. The first step involves a Michael addition between the carbanion of 2-perfluorophenylacetonitrile **1** and the benzoquinone **2** that affords after two intramolecular cyclisations the diaminobenzodifuran derivative **3** in 40% yield.[41–43] By using ethanol as solvent, the compound **3** rapidly precipitates in the mixture. It is easily isolated by filtration then washed with EtOH before using it for the next step with no more purification. The conjugated system has been extended by the condensation of the two amino groups of **3** with an excess of aldehyde derivatives **4a**–**c** (3 equiv). The condensation reactions are carried out in the presence of a little amount of P_2O_5 (10% mol) in ethyl lactate as solvent. Ethyl lactate can be considered as a green solvent miscible in water.[44,45] Addition of methanol–water (50/50 vol) mixture provokes the precipitation of compounds **Ia**–**c** that are obtained in 70–80% yields after filtration and washing with methanol. Excess aldehyde can be partially recovered from the solution.



Scheme 1. Synthetic pathway of **Ia**–**c**.

In order to increase the low solubility of the unsubstituted derivative **Ia**, pentyl or hexyloxymethyl chains have been introduced by using the aldehyde derivatives **4b**–**c**, obtained, respectively in 85 and 70% yields by the sequence BuLi/DMF from **5b**–**c** (Scheme 2). The furan derivative **5b** is available while **5c** has been prepared in 75% yield by reaction of furyl alcohol with bromohexane in Aliquat 336 in the presence of KOH under microwave irradiation (t=30 mn, T=80 °C, P=150 W).



Scheme 2. Syntheses of aldehydes **4b**–**c**.

3. X-ray structure of Ib

The crystallographic structure of single crystal of **Ib** obtained by slow evaporation of a chlorobenzene solution has been analyzed by X-ray diffraction. The compound **Ib** crystallizes in the monoclinic $P2_1/c$ space group. As shown in Fig. 2, the two azomethine bonds are coplanar with the central benzodifuran moiety and adopt an E configuration. The two lateral perfluorophenyl groups are not coplanar with the conjugated systems assuming a torsional angle of 55° with respect to the benzodifuran plane. The stacking of the molecules present an overlapping of the perfluorophenyl moieties with azomethine bonds and terminal furan units.[46] The distances between the planes of perfluorophenyl and furan cycles are close at 3.2 Å. On the other hand, molecules are also in contact through C–H···F interactions involving the hydrogen atoms of central benzene ring with d_{H-F} distances of 2.61 Å and the ones of terminal furans with d_{H-F} distances of 2.50 Å (Fig. S1 in Supplementary data).

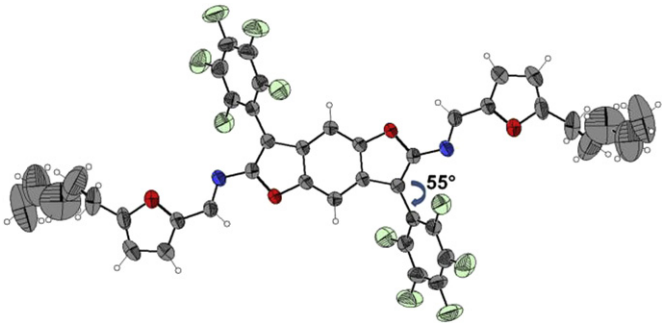


Fig. 2. X-ray structure of compounds **Ib**.

4. Theoretical calculations

In order to know the respective role of the pentafluorophenyl and imino–furan groups on the electronic properties of compounds **Ia**–**c**, theoretical calculations were performed at the ab initio density functional level with the Gaussian09 package by considering **Ia**–**c** in a phase gas. Becke's three parameters gradient-corrected functional (B3LYP) with a polarized 6-31G (d,p) was used for the geometrical optimization and for the HOMO and LUMO levels determination. In order to limit the computational calculation time, pentyl or hexyl lateral chains of **Ib** and **Ib** were replaced by methyl group. The theoretical data are gathered in Table 1 and the contours of the orbitals for the HOMO and LUMO levels of **Ib** are presented in Fig. 3. The optimized structures of **Ia**–**c** present a good planarity of the conjugated systems while the lateral pentafluorophenyls units present a torsional angle of 49° with benzodifuran moiety. The torsion angle between the benzodifuran moiety and the perfluorophenyl groups are in agreement with the X-ray structure of **Ib**. It can be noted that the use of the geometry obtained from the X-ray structure to calculate the HOMO and LUMO energy levels for **Ib** led to difference inferior at 5%. The HOMO and the LUMO of compounds **Ia**–**c** reside wholly at the conjugated backbones (Fig. 3). By comparison with compound **3**

Table 1
Calculated HOMO and LUMO levels and theoretical bandgap[a]

Compounds	HOMO (eV)	LUMO (eV)	ΔE_{Th} (eV)
3	−4.91	−0.91	4.0
Ia	−5.07	−2.36	2.71
Ib	−5.05	−2.38	2.67
Ic	−5.06	−2.37	2.68

[a] B3LYP/6-31G(d,p).

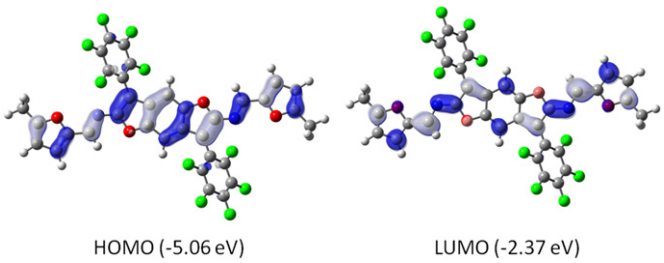


Fig. 3. Frontiers orbitals of compound **Ib**.

that presents a HOMO level at −4.91 eV, the replacement of the two amino groups by the electron withdrawing azomethine junctions leads to a slight stabilization of the HOMO for compounds **Ia**–**c** at −5.0 eV. By contrast the LUMO levels of **Ia**–**c** are strongly stabilized from −0.91 eV for **3** to −2.37 eV for **Ia**–**c**, thus leading to a reduction of the bandgap to reach ≈2.7 eV for **Ia**–**c**.

5. Electronic properties

The electronic properties of compounds **3** and **Ia**–**c** have been analyzed by cyclic voltammetry (CV) and by UV–vis spectroscopy. Electrochemical and optical data are gathered in Table 2.

Table 2
Electrochemical and optical data

Compounds	Eox[a] (V)	Ered[a] (V)	ΔE_{ele}[b] (eV)	λ_{max}[c] (nm)	ΔE_{op}[d] (eV)
3	0.68, 0.82	—	—	318	3.9
Ia	1.22	−1.51	2.5	452	2.6
Ib	1.18	−1.51	2.5	469	2.4
Ic	1.20	−1.51	2.6	461	2.5

[a] 10^{-4} M in 0.1 M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV s^{-1}.
[b] Electrochemical bandgap $\Delta E_{ele}=Eox_{onset}-Ered_{onset}$.
[c] 10^{-4} M in CH_2Cl_2.
[d] Optical bandgap calculated from the onset of the absorption band.

The CV of **3** presents two reversible mono-electronic oxidation waves at E_{ox1}=0.68 V and E_{ox2}=0.82 V corresponding to the successive formation of a cation radical and a dication. By contrast for compounds **Ia**–**c** only one oxidation process is observed at around 1.2 V. As shown in Fig. 4 for **Ib**, by increasing the scan rate in potential, the oxidation peak becomes reversible from a scan rate of 500 mV s^{-1}. For the reversible oxidation process at 500 mV s^{-1} the anodic–cathodic peak separation is slightly inferior to 90 mV thus suggesting a mono electronic process leading to the formation a cation radical. Although no reduction process is observed for **3**, compounds **Ia**–**c** present an irreversible reduction peak at Ered=−1.51 V. The more anodic oxidation for compounds **Ia**–**c** compared to **3** and the access to the reduction state agree with the theoretical calculation that indicated the stabilization both of the HOMO and LUMO levels for **Ia**–**c**. Using an offset of −4.99 eV for SCE versus the vacuum level and using the onset of the oxidation or reduction peaks leads to estimate HOMO and LUMO levels about −6.0 eV and −3.6 eV for compounds **Ia**–**c**.[47] The experimental data are lower than the computational data (Table 2) but it should be underlined that solvent effect was neglected in calculation. Nevertheless the gap between HOMO and LUMO levels calculated from computational or experimental data are very close with an electrochemical bandgap measured at ΔE_{elec}=2.5 eV.

Fig. 5 displays the UV–vis absorption spectra of compounds **3** and **Ib** in solution in CH_2Cl_2 and film of **Ib** on glass. Compound **3** presents two absorption bands at 292 and 318 nm while compounds **Ia**–**c** show a structured absorption band around 500 nm with the formation of three maxima. Vibronic fine structure in the absorption band is the indication of a high degree of rigidification of the conjugated chain due to the combination of the intrinsically rigid benzodifurane and the azomethine junctions. The lengthening of the conjugated systems leads to a strong batchromic shift corresponding

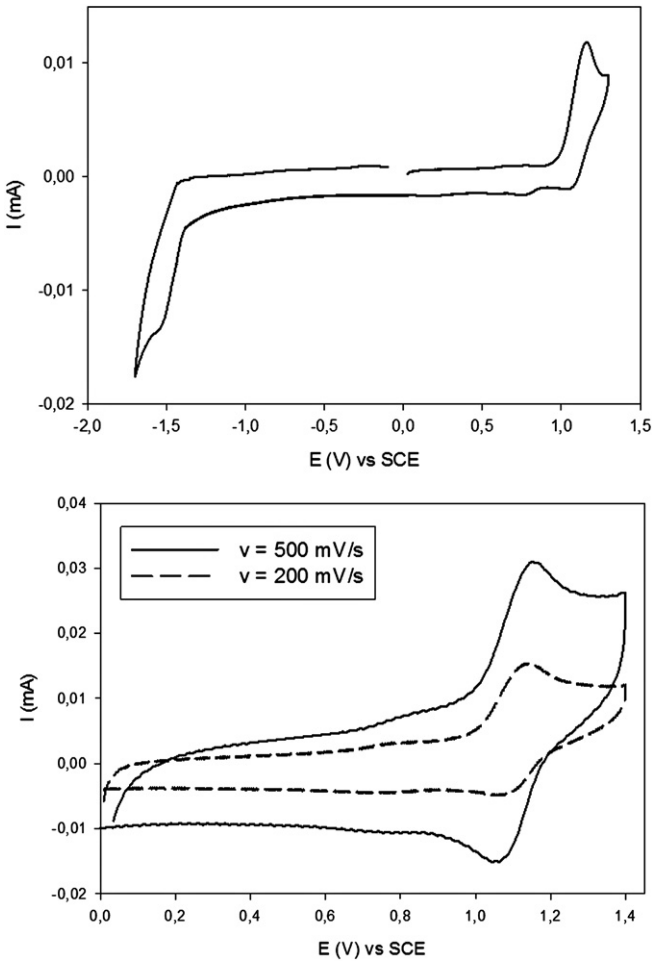


Fig. 4. CV trace of compound **Ib** $5\cdot10^{-4}$ mol L^{-1} in 0.1 Bu_4NPF_6/CH_2Cl_2, top v=100 mV s^{-1}; bottom v=200 mV s^{-1} and v=500 mV s^{-1}.

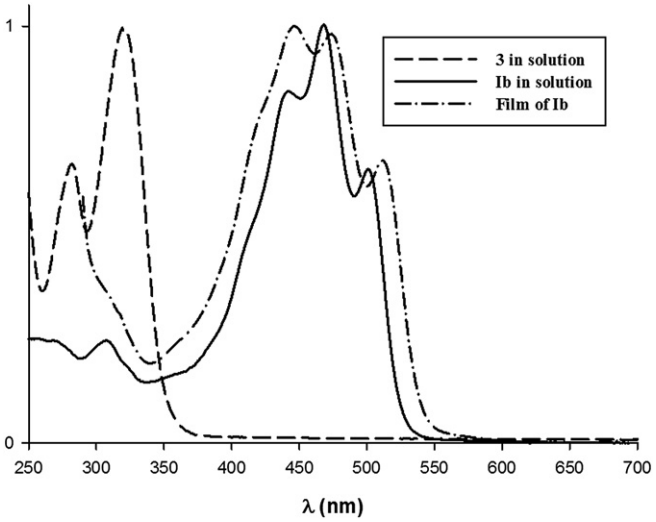


Fig. 5. Normalized absorption spectra of **3** and **Ib** in solution in CH_2Cl_2 and film of **Ib** deposited on glass.

to a decrease of the HOMO–LUMO gap from 3.9 eV for **3** to 2.5 eV for compounds **Ia–c**. Films of **Ib** have been deposited on glass by spin coating technique using chloroform as solvent. The UV–vis absorption spectrum of the film shows a broader and structured absorption band with the presence of three maxima at 512, 475 and 446 nm and a shoulder at 410 nm. The film has been annealed till 130 °C without any UV spectrum modification indicating a good stability of the film. For higher temperature, the intensity of the absorption decreases due to a degradation of the film.

6. Conclusion

In conclusion, we synthesized a new series of π-conjugated materials by following a green approach consisting in two subsequent condensation reactions, which give only water as by-products. The optical and electrochemical studies have shown that the combination of the benzodifuran and furan units via azomethine junction leads to extended systems presenting electronic properties adapted for applications in organic electronics. On the other hand, the solubility of these compounds in common solvent is beneficial for developing devices via solution processable techniques, thus suggesting the interest of these compounds as semiconductors materials. The preparation of photovoltaic cells with these materials, as well as analogues with longer conjugated chain, is now underway and will be reported in future publications.

7. Experimental section

7.1. General

NMR spectra were recorded on a Bruker Avance 300 (^{1}H and ^{19}F: 300.1 MHz, ^{13}C: 75.7 MHz, T=300 K). The spectra were referenced against the internal NMR-solvent standard. Chemical shifts were expressed in parts per million (ppm) and were reported as s (singlet), d (doublet), t (triplet), td (doublet triplet), m (multiplet) and coupling constants J were given in Hz. Mass spectra were recorded under EI mode on a VG-Autospec mass spectrometer or under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer. The main peaks are described according to m/z. The peak corresponding to molecular mass is expressed as (M+•). IR Spectra were performed on a Bruker VERETEX 70. UV-visible optical data were recorded with a Perkin–Elmer lambda 19 spectrophotometer. HPLC solvents were used for the measurements. Electrochemical experiments were performed with a Biologic SP150 potentiostat in a standard three electrodes cell using platinum electrodes and a saturated calomel reference electrode (SCE).

1,4-benzoquinone **1**, pentafluorophenylacetonitrile **2**, 2-furyl alcohol, 2-furaldehyde **4a** and 2-pentylfuran **4b** were purchased from Acros or Lancaster and used without further purification.

7.2. Preparation of precursors 3 and 5c

7.2.1. 3,7-Bis(perfluorophenyl)benzo[1,2-b:4,5-b′]difuran-2,6-diamine: ***3***. 2,3,4,5,6-Pentafluorophenylacetonitrile 2 (7.1 ml, 3 equiv, 55.5 mmol) was added to a solution of 1,4-benzoquinone 1 (2.0 g, 18.5 mmol) in ethanol (50 mL) at room temperature. Then addition of an excess of aqueous solution of ammoniac (7.0 mL) resulted in a fast exothermic reaction and precipitation of a white solid. After 1 h stirring the solid was recovered by filtration and was washed with ethanol (25 mL). Drying under vacuum afforded 3.8 g (40%) of **3** as a white powder, which was used in the next step without any further purification.

Mp: 260 °C. ^{1}H NMR (DMSO-d_6): 6.98 (s, 2H), 6.68 (s, 4H) ppm ^{19}F NMR (DMSO-d_6): −139.7 (dd, 4F, J=6.8 Hz, J=22.4 Hz), −162.3 (t, 2F, J=22.4 Hz), −165.8 (td, 4F, J=6.8 Hz, J=22.4 Hz) ppm ^{13}C NMR (DMF-d^7): 157.9, 146.9, 124.2, 108.7, 97.6, 75.5 ppm.

IR: 3110, 1481 cm^{-1}. Mass (MALDI-TOF):$C_{22}H_6F_{10}N_2O_2$, Calcd 520.03 (M+), Found 519.4.

Anal. Calcd for $C_{22}H_6F_{10}N_2O_2$: C, 50.70; H,1.15; N, 5.38. Found: C, 50.59; H, 1.40; N, 5.33.

7.2.2. 2-((Hexyloxy)methyl)furan: ***5c***. Furyl alcohol (0.156 mol, 13 mL), bromohexane (0.197 mol, 27.8 mL), KOH (0.23 mol, 12.9 g) and aliquat 336 (7 mL) were stirred in a flask adapted for microwave in open vessel. The mixture was irradiated under microwave till the temperature reached 80 °C and this temperature was maintained for 30 min. Water was added to the mixture and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$ and evaporated under vacuum. The crude mixture was purified by distillation with a Kugelroch apparatus under reduced pressure (P=35 mbar, T_{oven}=105 °C) to afford **5c** as a colourless oil in 75% yield.

^{1}H NMR ($CDCl_3$): 7.40 (dd, 1H, J=1.8 Hz and J=0.9 Hz), 6.32 (m, 2H), 4.34 (s, 2H), 3.45 (t, 2H, J=6.6 Hz), 1.58 (q, 2H, J=7.5 Hz), 1.33 (m, 6H), 0.85 (t, 3H, J=6.9 Hz) ppm ^{13}C NMR ($CDCl_3$): 152.1, 142.5, 110.1, 108.9, 70.3, 64.6, 31.7, 29.6, 25.8, 22.6, 13.9 ppm. MS (EI): m/z=182 (100%).

7.3. General procedure for the formation of aldehydes 4b and 4c

To a stirred solution of compounds **5b** or **5c** (0.04 mol) in dry ethyl ether (80 mL) at −10 °C, was added dropwise n-BuLi (1.2 equiv). The mixture was stirred for 30 min at −10 °C and quenched with DMF (2.2 equiv, 3.2 mL). The mixture was allowed to warm to ambient temperature and was stirred for 4 h. An ammonium chloride solution (20 mL, 1 M) was added. The aqueous phase was then extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtrated, concentrated in vacuum and purified by column chromatography.

7.3.1. 5-Pentylfuran-2-carbaldehyde ***4b***. Eluent for the chromatography: ethyl acetate–cyclohexane (2–8).

Pale yellow oil, 5.81 g, 85% yield.

^{1}H NMR ($CDCl_3$): 9.51 (s, 1H), 7.16 (d, 1H, J=3.3 Hz), 6.22 (d, 1H, J=3.3 Hz), 2.71 (t, 2H, J=7.5 Hz), 1.69 (m, 2H), 1.33 (m, 4H), 0.89 (t, 3H, J=6.9 Hz) ppm ^{13}C NMR ($CDCl_3$): 177.1, 164.3, 151.7, 123.9 (broad signal), 108.7, 31.3, 28.4, 27.2, 22.3, 13.9 ppm. MS (EI): m/z=166 (100%).

7.3.2. 5-((Hexyloxy)methyl)furan-2-carbaldehyde ***4c***. Eluent for the chromatography: ethyl acetate–cyclohexane (3–7).

Pale yellow oil, 6.3 g, 70% yield.

^{1}H NMR (CDCl3): 9.52 (s, 1H), 7.14 (d, 1H, J=3.3 Hz), 6.44 (d, 1H, J=3.3 Hz), 4.44 (s, 2H), 3.43 (t, 2H, J=6.6 Hz), 1.51 (q, 2H, J=7.8 Hz), 1.25 (m, 6H), 0.80 (t, 3H, J=6.9 Hz) ppm ^{13}C NMR ($CDCl_3$): 177.8, 158.9, 152.5, 122.2 (broad signal), 111.0, 71.4, 64.9, 31.6, 29.5, 25.7, 22.5, 14.0 ppm. MS(EI): m/z=210 (100%).

7.4. General procedure for the formation of Ia–c

Aldehyde **4a–c** (3 equiv, 0.57 mmol) and a catalytic amount of P_2O_5 were successively added to a solution of **3** (100 mg, 0.19 mmol) in ethyl lactate (3 mL) at room temperature. After one night stirring, the solution was poured in 10 ml of water–methanol. (50/50 vol) solution to give a precipitate. After filtration, the solid was recovered, washed with methanol (30 mL) and dried under vacuum.

7.4.1. 2,6-N-Di[(furan-2′-yl)carboxylimino]-benzo[1,2-b:4,5-b′]difuran-3,7 pentafluorophenyl: ***Ia***. Orange solid; yield 60%. The solubility is too low for allowing purification by chromatography or recrystallization.

^{1}H NMR ($CDCl_3$) saturation: 8.77 (s, 1H), 7.70 (d, 1H, J=3.3 Hz), 7.43 (s, 1H), 7.14 (d, 1H, J=3.3 Hz), 6.63 (m, 1H) ppm.

IR: 3115, 1487 cm^{-1}. Mass (MALDI-TOF): $C_{32}H_{10}F_{10}N_2O_4$, Calcd 677.0 (M^++H), Found 676.6.

7.4.2. 2,6-N-Di[(5′-pentylfuran-2′-yl)carboxylimino]-benzo[1,2-b:4,5-b′]difuran-3,7-pentafluoro-phenyl: ***Ib***. Recrystallisation from ethyl acetate solution, orange solid; yield 58%; Mp: 212 °C.

^{1}H NMR ($CDCl_3$): 8.64 (s, 2H), 7.35 (s, 2H), 7.03 (d, 2H, J=3.6 Hz), 6.22 (d, 2H, J=3.6 Hz), 2.73 (t, 4H, J=7.5 Hz), 1.70 (q, 4H, J=7.2 Hz), 1.36 (m, 8H), 0.91 (t, 6H, J=7.0 Hz) ppm ^{19}F NMR ($CDCl_3$): −139.46 (dd, 4F, J=6.8 Hz, J=22.4 Hz), −157.22 (t, 2F, J=22.4 Hz), −164.79 (td, 4F, J=6.8 Hz, J=22.4 Hz) ppm ^{13}C NMR ($CDCl_3$): 163.4, 155.4, 150.8, 149.0, 145.7, 134.8, 127.3, 121.1, 109.2, 101.2, 31.4, 28.5, 27.3, 22.4, 13.9 ppm.

IR: 3120, 1491 cm^{-1}. Mass (MALDI-TOF): $C_{42}H_{30}F_{10}N_2O_4$, Calcd 817.20 (M^++H), Found 816.8. Anal. Calcd for $C_{42}H_{30}F_{10}N_2O_4$: C, 61.77; H, 3.70; N, 3.43. Found: C, 61.81; H, 3.64; N, 3.75.

7.4.3. 2,6-N-Di[(5′(2-2-oxa-heptylfuran-2′-yl))carboxylimino]-benzo[1,2-b:4,5-b′]difuran-3,7-pentafluoro-phenyl: ***Ic***. Recrystallisation from ethyl acetate solution, orange solid; yield 65%; Mp: 210 °C.

^{1}H NMR ($CDCl_3$): 8.70 (s, 2H), 7.37 (s, 2H), 7.07 (d, 2H, J=3.3 Hz), 6.51 (d, 2H, J=3.6 Hz), 4.54 (s, 4H), 3.52 (t, 4H, J=6.6 Hz), 1.60 (m, 4H), 1.29 (m, 12H), 0.88 (t, 6H, J=6.9 Hz) ppm ^{19}F NMR ($CDCl_3$): −139.53 (dd, 4F, J=6.8 Hz, J=22.4 Hz), −158.82 (t, 2F, J=22.4 Hz), −164.55 (td, 4F, J=6.8 Hz, J=22.4 Hz) ppm ^{13}C NMR ($CDCl_3$): 158.0, 155.1, 152.1, 149.1, 146.0, 127.4, 111.7, 109.9, 101.4, 71.2, 65.1, 31.7, 29.6, 25.8, 22.6, 14.0 ppm. IR: 3121, 1492 cm^{-1}. Mass (MALDI-TOF): $C_{46}H_{38}F_{10}N_2O_6$, Calcd 905.3 (M^++H), Found 905.7. Anal. Calcd for $C_{46}H_{38}F_{10}N_2O_6$: C, 61.06; H, 4.23; N, 3.10. Found: C, 60.68; H, 4.21; N, 3.18.

7.5. X-ray structure of Ib

X-ray single-crystal diffraction data were collected at 293 K on a BRUKER KappaCCD diffractometer, equipped with a graphite monochromator utilizing MoKα radiation (λ=0.71073Å). The structure was solved by direct methods and refined on F^2 by full matrix least-squares techniques using SHELX97 package (G.M. Sheldrick, 1998). All non-hydrogen atoms were refined anisotropically and the H atoms were added by calculation and treated with a riding model. Absorption was corrected by SADABS program (Sheldrick, Bruker, 2008).

7.5.1. Crystal data for ***Ib***. Red plate (0.46×0.39×0.05 mm^3), $C_{42}H_{30}F_{10}N_2O_4$, Mr=816.78, monoclinic, space group $P2_1/c$, a=15.6792(8) Å, b=12.1688(7) Å, c=10.5804(6) Å, β=108.048(4)°, V=1918.4(2) $Å^3$, Z=2, ρ_{calcd}=1.413 gcm^{-3}, μ (MoKa)=0.124 mm^{-1}, F(000)=836, θ_{min}=4.05°, θ_{max}=27.54°, 36,101 reflections collected, 4364 unique (R_{int}=0.1247), restraints/parameters=0/263, $R1$=0.0675 and $wR2$=0.1334 using 2144 reflections with $I>2\sigma(I)$, $R1$=0.1656 and $wR2$=0.1730 using all data, GOF=1.037, $-0.335<\Delta\rho<0.383e$ $Å^{-3}$.

Crystallographic data excluding structure factors have been deposited with the Cambridge Crystallographic Data under reference CCDC: 858095.

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Supplementary data

Copies of ^{1}H and ^{13}C and ^{19}F NMR of compounds **3**, **4b**, **4c**, **5c**, **Ib** and **Ic**. Fig. S1 presenting the packing of **Ib** in the crystal. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tet.2012.07.079. These data include MOL files and InChiKeys of the most important compounds described in this article.

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