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Modulation of the Electronic Properties of 3π-2spiro Compounds Derived from Bridged Oligophenylenes: A Structure−Property Relationship

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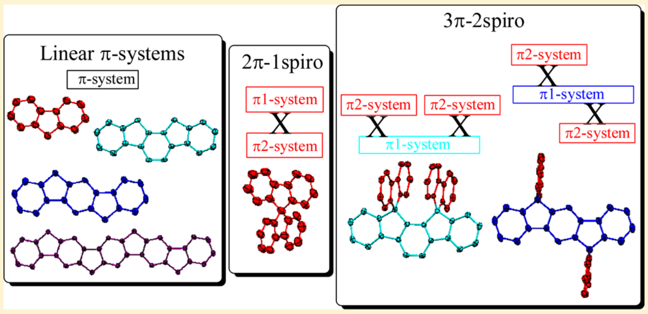
Supporting Information

ABSTRACT: 3π-2spiro compounds are constituted of three π-systems linked through two shared spiro carbons leading to a three-dimensional architecture. The modulation of the electronic properties of such molecular systems can be achieved through the modification and/or substitution of their different π-systems and by the modification of their geometry. The present work is focused on the tuning of the electrochemical properties of a wide range of 3π-2spiro compounds based on fluorenyl, xanthenyl, 2,7-disubstituted fluorenyl, 1,2-*b*- or 2,1-*a*-indenofluorenyl, and pentaphenylenyl fragments with a main emphasis on the localization of the successive electron transfers. A detailed structure−property relationship study of interest for the organic electronics scientific community is then drawn.



1. INTRODUCTION

The design and the synthesis of highly sophisticated π-conjugated molecules and polymers have driven the development of organic electronics.[1] One of the main challenges in organic electronics for the last two decades has been to design efficient and stable blue light emitters for organic light-emitting diodes (OLED) applications.[2−6] Thus, numbers of research groups such as those of Müllen,[7−10] Salbeck,[11,12] Holmes,[3] Bryce,[13,14] Ma,[15,16] Promarak,[17,18] and our[19−32] have developed novel π-conjugated molecules based on different molecular scaffolds with emission color varying from violet to deep blue. Bridged oligo- and polyphenylene derivatives are one class of materials that play a key role in blue-emitting materials. Of particular interest are the bridged biphenyl unit fluorene (**F**),[3,5,33−37] the bridged terphenyl unit indenofluorene (**IF**),[23−32,38,39] and the bridged tetra- and pentaphenyl units.[7,9,22,28,40,41] As the chain rigidity increases with an increasing number of bridged planar rings, a bathochromic shift of the emission wavelength signaling an extension of the π-conjugation is usually observed. That is, for example, 420/425 nm for polyfluorenes, 430 nm for polyindenofluorenes and 445 nm for ladder-type polypentaphenylenes.[9] However, it has been shown that, in the solid state, the emission is unstable due to the appearance of long-wavelength emission bands. This long wavelength emission, usually called green emission band (GEB), has been the subject of numerous studies in order to determine its origin.[6,22,42−47] Among the numerous solutions that have been proposed to suppress the GEB, the introduction of a rigid spiro linkage, such as spirobifluorene (**SBF**), into the polymer/oligomer backbone has been extensively developed, and this 2π-1spiro concept (Scheme 1, bottom right) has led to a strong enhancement of the OLED performances and stability.[36,48−52]

In this context, for the last 6 years, our group has designed new violet to blue emitters possessing a unique molecular architecture constituted of a central π1-system linked to two π2-systems through two shared spiro carbons (Scheme 1). This particular architecture introduced by our group has been named "3π-2spiro".[19−32]

An important point in the field of materials for organic electronics applications is linked to multifunctional compounds that display an easy tuning of their properties at the molecular level. The 3π-2spiro architecture is in this context a very appealing molecular scaffold as the modification and/or substitution of the different π-systems (π1-system, π2-systems or both) can lead to a modulation of the properties.

In this work, three distinct strategies have been investigated to tune the electronic properties of 3π-2spiro systems. The first consists of altering either the π2-systems (for example, switching from a fluorenyl unit in (1,2-*b*)-DSF-IF to a xanthenyl unit in (1,2-*b*)-DSX-IF), the π1-system (for example switching from an indenofluorenyl unit in (1,2-*b*)-DSF-IF to a penta-*p*-phenylenyl (**LPP**) unit in DSF-LPP), or both the π1- and π2-systems (for example switching from the indenofluorenyl/fluorenyl combination in (1,2-*b*)-DSF-IF to the penta-*p*-phenylenyl/xanthenyl combination in DSX-LPP).

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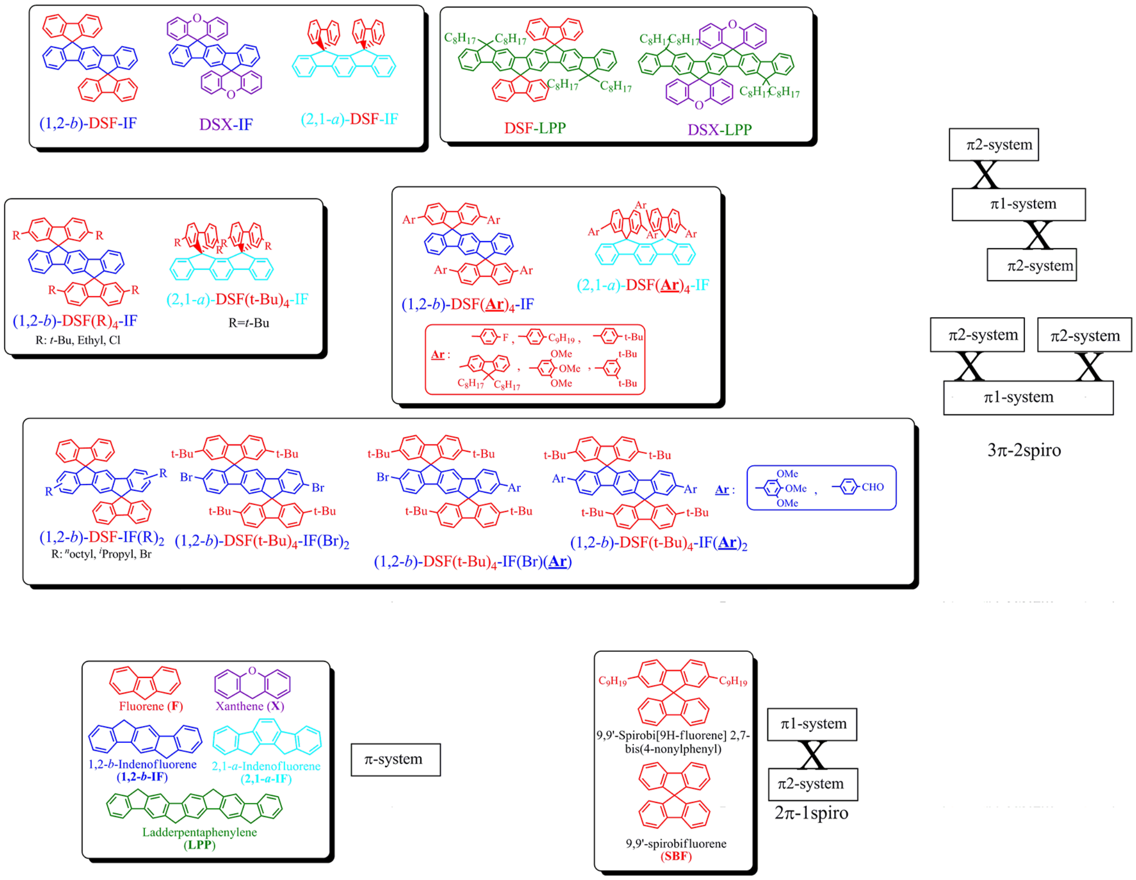
Scheme 1. 2π-1spiro and 3π-2spiro Compounds and Their Related Linear π-Systems Investigated in This Work



The second strategy consists of judiciously substituting the different π-systems: either the central indenofluorenyl (1,2-*b*)-DSF-IF(R)$_2$ or the fluorenyl cores (1,2-*b*)-DSF(R or Ar)$_4$-IF or both π-systems (1,2-*b*)-DSF(t-Bu)$_4$-IF(R or Ar)$_2$.

The third and most appealing strategy consists of altering the geometry of the molecular systems. Thus, the introduction of a (2,1-*a*)-indenofluorenyl core instead of a (1,2-*b*)-indenofluorenyl moiety as π1-system leads to molecules with their spiro-connected π2-systems in a face-to-face molecular arrangement (Scheme 1).

The synthesis and physicochemical properties of the 3π-2spiro compounds investigated in this work (Scheme 1, Table 1) have been previously reported by our group,[19−23,25,27−29,46] and some of these compounds have presented interesting behavior as blue light emitters in OLED.[20,25,28,29,32] The aim of the present work is to investigate in detail their *anodic* behavior in order to obtain a precise structure−property relationship of great interest to the organic electronics scientific community. Indeed, as the performances of optoelectronic devices are directly linked to the properties of the active organic layer, such study is of key importance to design, in the future, highly efficient and multifunctional materials. Thus, we report on the possibility of modulating (drastically or faintly) the electronic properties of 3π-2spiro compounds through the modification of (i) the π2-systems, (ii) the π1-system, and (iii) the geometry of the π1-system. The study of the successive electron transfers centered either on the π1- or π2-system will be particularly investigated.

2. RESULTS AND DISCUSSION

All compounds were studied using cyclic voltammetry (CV) both in oxidation and in reduction. For nearly all compounds, no "well-defined" reduction waves were observed in CH_2Cl_2 solution and only the onset reduction potential was detectable. When the reduction was studied in DMF or THF, either one irreversible reduction wave or two (the first one being reversible and the second one irreversible) reduction waves were observed. All reduction potentials are available in the Supporting Information (Table S1). Thus, in this work, only the anodic behavior of 3π-2spiro compounds in CH_2Cl_2 has been studied. Table 1 gathers the oxidation potentials and onset potentials of all compounds investigated in this work (entries 1−28 focus on 3π-2 spiro derivatives and entries 29−35 on their constituting building blocks).

1. Modulation of the Electronic Properties by Alteration of the π1-System: (1,2-b)-Indenofluorene, Disubstituted Indenofluorene, and Ladder Pentaphenylene.

1.a. (1,2-b)-DSF-IF, (1,2-b)-DSF-IF(^{n}Oct)$_2$, (1,2-b)-DSF-IF(^{i}Pr)$_2$, (1,2-b)-DSF-IF(Br)$_2$. The CV of the simplest analogue in the series, **(1,2-*b*)-DSF-IF** (Figure 1), is representative of the general behavior of dispirofluorene-indenofluorene derivatives substituted on the (1,2-*b*)-indenofluorenyl core with alkyl substituents **(1,2-*b*)-DSF-IF(R)$_2$** (R: isopropyl or ^{n}octyl). The oxidation occurs in two successive oxidation waves at E^1 (1.43 V, reversible) and E^2 (1.87 V, irreversible) (Figure 1, entry 1). Oxidation including E^2 leads to an electropolymerization process that will not be described here.[53]

As **(1,2-*b*)-DSF-IF** combines **SBF** and **(1,2-*b*)-IF**, the study of these constituting building blocks is highly informative to

Table 1. Oxidation Potentials and $E_{\text{onset}}^{\text{ox}}$[a]

entry	3π-2spiro compound	oxidation potential (V)	$E_{\text{onset}}^{\text{ox}}$ (V)
1	(1,2-*b*)-DSF-IF	1.43; 1.87	1.36
2	(1,2-*b*)-DSF-IF(^{n}Oct)$_2$	1.33; 1.87	1.22
3	(1,2-*b*)-DSF-IF(^{i}Pr)$_2$	1.33; 1.87	1.21
4	(1,2-*b*)-DSF-IF(Br)$_2$	1.44; 1.78; 1.97	1.30
5	(1,2-*b*)-DSX-IF	1.50; 1.86	1.39
6	DSF-LPP	1.09; 1.66; 1.95	0.96
7	DSX-LPP	~1.10; 1.92; 2.25	1.05
8	(1,2-*b*)-DSF(t-Bu)$_4$-IF	1.33; 1.61; 1.79; 2.03	1.36
9	(1,2-*b*)-DSF(Et)$_4$-IF	1.33; 1.57; 1.70; 1.80	1.21
10	(1,2-*b*)-DSF(Cl)$_4$-IF	1.52; 1.94	1.38
11	(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF	1.28; 1.53; 1.75; 1.96	1.09
12	(1,2-*b*)-DSF(4-FPh)$_4$-IF	1.45; 1.55; 1.66; 1.87; 1.96, 2.05	1.33
13	(1,2-*b*)-DSF(4-*t*-BuPh)$_4$-IF	1.42; 1.70	1.17
14	(1,2-*b*)-DSF(3,5-di-*t*-BuPh)$_4$-IF	1.42; 1.67; 1.79	1.15
15	(1,2-*b*)-DSF(4-nonylPh)$_4$-IF	1.30; 1.38; 1.68; 2.13	1.19
16	(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF	1.29; 1.47; 1.58; 2.01	1.06
17	(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$	1.16; 1.23; 1.43; 1.63; 1.93	1.03
18	(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(Br)$_2$	1.46; 1.65; (1.80); 2.09	1.32
19	(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)(Br)	1.38; 1.65; 1.93	1.23
20	(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)$_2$	1.33; 1.67; 1.90	1.13
21	(2,1-*a*)-DSF-IF	1.36; 1.69; 1.99	1.2
22	(2,1-*a*)-DSF(*t*-Bu)$_4$-IF	1.24; 1.55; 1.84; 1.96	1.12
23	(2,1-*a*)-DSF(3,4,5-triOMePh)$_4$-IF	1.07; 1.31; 1.51; 1.63; 1.93	0.93
24	(2,1-*a*)-DSF(4-FPh)$_4$-IF	1.20; 1.36; 1.58; 2.06	1.10
25	(2,1-*a*)-DSF(4-*t*-BuPh)$_4$-IF	1.13; 1.31; 1.57; 1.97	1.02
26	(2,1-*a*)-DSF(3,5-di-*t*-BuPh)$_4$-IF	1.10; 1.32; 1.73; 1.96	0.99
27	(2,1-*a*)-DSF(4-nonylPh)$_4$-IF	1.11; 1.25; 1.60; 1.87; 2.02	1.01
28	(2,1-*a*)-DSF(9,9-dioctylfluorene)$_4$-IF	1.12; 1.18; 1.64; 2.04	0.98
29	(1,2-*b*)-IF	1.31; 1.81	1.22
30	(2,1-*a*)-IF	1.31; 1.98	1.21
31	F	1.62	1.48
32	SBF	1.69; 1.86	1.54
33	2,7-di-*tert*-butylfluorene	1.44; 1.91	1.05
34	LPP	0.99; 1.36	0.87
35	9,9′-spirofluorene-(2,7-di-4-nonylphenylfluorene)	1.45; 1.72; 1.84; >1.90	1.14

[a] The data come from cyclic voltammetries recorded in Bu_4NPF_6 0.2 M in CH_2Cl_2 at a sweep rate of 100 mV/s on a platinum electrode (disk, ⌀: 1 mm). All potentials in volts refer to SCE.

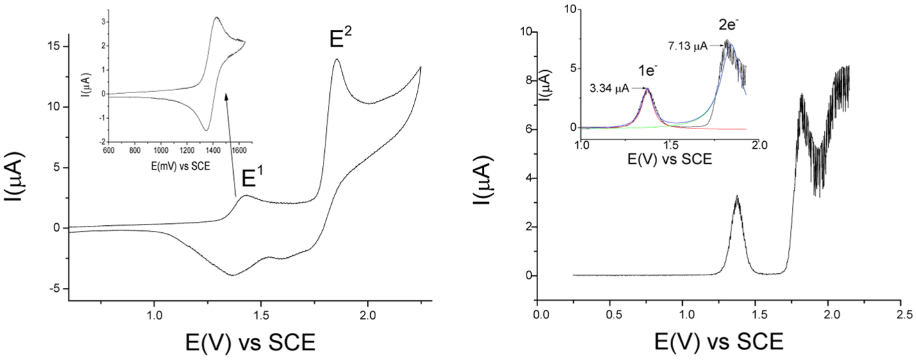


Figure 1. Cyclic voltammetry (left) and differential pulse voltammetry (right) of **(1,2-*b*)-DSF-IF** 2×10^{-3} M in CH_2Cl_2 + Bu_4NPF_6 0.2 M. Inset left: zoom on the first oxidation process. Inset right: multipeak fit in the 1.0–2.0 V potential range. Platinum disk (⌀: 1 mm) working electrode. Sweep-rate: 100 mV. s^{-1} for the CV. DPV setting: pulse height: 25 mV, scan rate 50 mV s^{-1}, scan increment 3 mV, and step time 60 ms.

assess the different electron transfers. Thus, **(1,2-*b*)-IF**[20,54] presents one reversible oxidation wave (1.31 V) and a second irreversible wave (1.81 V, entry 29). Oppositely, **SBF**[20,55] presents two irreversible oxidation waves (1.69/1.86 V, entry 32). As **(1,2-*b*)-DSF-IF** presents a first reversible oxidation wave at 1.43 V, this leads us to conclude that **(1,2-*b*)-DSF-IF** presents a first electron transfer centered on the (1,2-*b*)-indenofluorenyl π-system due to (i) its more extended π-conjugated core compared to the fluorenyl cores and to (ii) its similar first oxidation potential compared to **(1,2-*b*)-IF** (1.43 vs 1.31 V). The +0.12 V shift (1.43 vs 1.31 V) of the first oxidation of **(1,2-*b*)-DSF-IF** compared to that of **(1,2-*b*)-IF** is

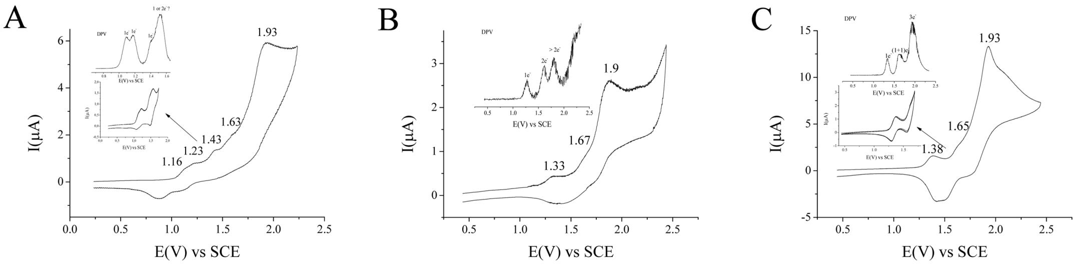


Figure 2. Cyclic voltammetry of (A) **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$**, (B) **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)$_2$**, and (C) **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)(Br)**; 2×10^{-3} M in CH_2Cl_2 + Bu_4NPF_6 0.2 M, sweep rate: 100 mV·s^{-1}. Platinum disk (⌀: 1 mm) working electrode. Inset: zoom on the reversible oxidation waves and/or DPV. DPV setting: pulse height 25 mV, scan rate 50 mV s^{-1}, scan increment 3 mV, and step time 60 ms.

due to the electron-withdrawing effect of the two fluorenyl units on the indenofluorenyl core. This first reversible oxidation leads to a stable indenofluorenyl radical. Differential pulse voltammetry (DPV) recorded in the same potential range (0.25−2.25 V) allows a more accurate analysis of the two distinct oxidation processes preceding the polymerization (figure 1, right). Indeed, a multiple peak fit of the two first oxidations of the DPV clearly shows a first monoelectronic oxidation followed by a second bielectronic oxidation. This feature is consistent with a first oxidation centered on the indenofluorenyl core followed by a second oxidation centered on the two fluorenyl units concomitant with the further electropolymerization process.[53]

Compared to **(1,2-*b*)-DSF-IF**, the first oxidation potential of structurally related **(1,2-*b*)-DSF-IF(^{n}Oct)$_2$** (entry 2, Figure S1, Supporting Information) and **(1,2-*b*)-DSF-IF(^{i}Pr)$_2$** (entry 3, Figure S2, Supporting Information) is slightly shifted (1.33 V vs 1.43 V) due to the introduction of electron-donating alkyl substituents (^{i}Pr or ^{n}Oct) on the C3 and C9 carbon atoms of the indenofluorenyl core.[56] The presence of these substituents renders the indenofluorenyl core more easily oxidizible than that of **(1,2-*b*)-DSF-IF**. However, this electron-donating effect does not totally neutralize the electron-withdrawing effect of the two fluorenyl units as the two compounds are less easily oxidizible than **(1,2-*b*)-IF** (E^1: 1.31 V).

On the other hand, **(1,2-*b*)-DSF-IF(Br)$_2$** possessing two bromine atoms on C2 and C8 carbon atoms of the indenofluorenyl core[56] is oxidized along three oxidation waves with maxima at 1.44, 1.78, and 1.97 V (entry 4, Figure S3A, Supporting Information). Compared to the oxidation of **(1,2-*b*)-DSF-IF**, the first oxidation is only slightly shifted (10 mV) to more anodic potential due to the withdrawing effect of the bromine atoms and consistent with the first electron transfer centered on the indenofluorenyl core. As polymerization is observed at the second electron transfer[53] and as DPV shows that the second oxidation involves more than one electron (see Figure S3B, Supporting Information), we believe this oxidation occurs on the fluorenyl units.

The comparison of the anodic behavior of the (1,2-*b*)-indenofluorenyl-substituted DSF-IFs with that of the model compounds **(1,2-*b*)-DSF-IF** and **(1,2-*b*)-IF** shows that a very fine-tuning of the first oxidation potential core can be achieved through (i) the substitution of the (1,2-*b*)-indenofluorenyl core with electron-donating/withdrawing groups and (ii) the electron-withdrawing effect of the spiroconjugated fluorenes.

1.b. (1,2-b)-DSF(t-Bu)$_4$-IF(3,4,5-triOMePh)$_2$, (1,2-b)-DSF(t-Bu)$_4$-IF(4-PhCHO)$_2$, and (1,2-b)-DSF(t-Bu)$_4$-IF(4-PhCHO)(Br): Extended (1,2-b)-Indenofluorenyl Central Core. The following section deals with the extension of the π-conjugation of the (1,2-*b*)-indenofluorenyl core with pendant differently substituted aryl units.

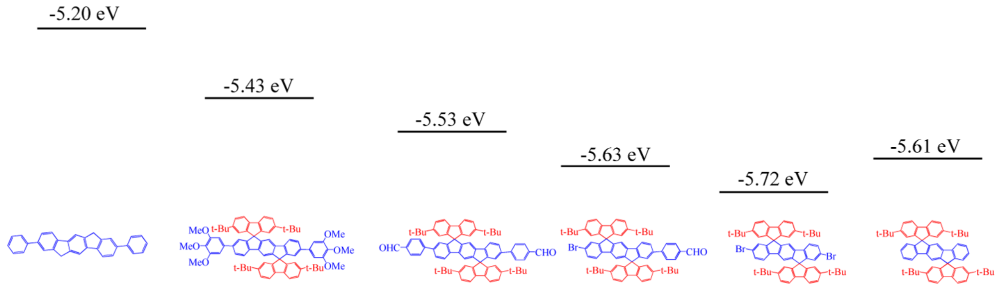
(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$, which possesses an extended indenofluorenyl central core substituted with two electron-donating 3,4,5-trimethoxyphenyl units at C2 and C8 carbon atoms,[56] is oxidized in five successive processes between 0.0 and 2.3 V (entry 17, Figure 2A). The first four waves are reversible with maxima at 1.16, 1.23, 1.43, and 1.63 V. The first oxidation (1.16 V) is cathodically shifted compared to that of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** (1.33 V) showing that it occurs on the central π1-system since the π-conjugation is extended on the whole diphenylindenofluorenyl unit.

The HOMO level of **(1,2-*b*)-DSF(t-Bu)$_4$-IF(3,4,5-triOMePh)$_2$** calculated from its onset oxidation potential[57] lies at −5.43 eV, whereas that of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** lies at −5.61 eV.[21] In addition, the literature reports for a structurally related diphenylindenofluorenyl derivative a HOMO level lying at −5.2 eV.[58] From these HOMO values, one can conclude that **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$** is less easily oxidized than its constituted building block 2,6-diphenylindenofluorene, showing that the withdrawing effect of the two spiro linked 2,7-di-*tert*-butylfluorenyl units prevails on the electron-donating effect of the six methoxy groups.

The second electron transfer (E^2: 1.23 V) also occurs on the diphenylindenofluorenyl central core leading to its dication. Indeed, it appears that the 2,7-di-*tert*-butylfluorenyl units are oxidized at higher potentials: at 1.44 V for 2,7-di-*tert*-butylfluorene (entry 33) and at 1.61 V for **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** (entry 8). The two further oxidations of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$** are very close together (1.43 V, 1.63 V, entry 17) and occur in a potential range close to that of the 2,7-di-*tert*-butylfluorene (1.44 V, entry 33) and may be assigned to the oxidation of the two 2,7-di-*tert*-butylfluorenyl units. Unfortunately, recording DPV for this molecule gives 1e$^-$/1e$^-$/1e$^-$/1e$^-$ or 1e$^-$/1e$^-$/1e$^-$/2e$^-$ successive signals depending on the setting of the DPV measurement and on the mathematical extrapolation used to determine the number of electrons in the successive electron transfer. In both cases, after the abstraction of the fourth electron, **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$** possesses *at least* a radical cation on each two π2-fluorenyl units and a dication on its π1-diphenylindenofluorenyl unit.

The structurally related **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)$_2$** (entry 20) possessing a similar aryl-indenofluorene-aryl core but, oppositely to the previous one, substituted with an electron-withdrawing aldehyde on the phenyl rings has also been investigated. Its CV presents three successive waves (Figure 2B). Because of the strong electron-withdrawing effect of the aldehyde, E^1 is anodically shifted by 170 mV in **(1,2-*b*)-**

Scheme 2. HOMO Levels of Various DSF(t-Bu)$_4$-IF Derivatives Compared to That of 2,8-Diphenylindenofluorene



DSF(*t*-Bu)$_4$-IF(4-PhCHO)$_2$ compared to **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$** (1.33 vs 1.16 V), leading to the stabilization of the HOMO level (−5.53 eV vs −5.43 eV). The second bielectronic oxidation (1.67 V) is assigned to an electron transfer on the 2,7-di-*tert*-butylfluorene units and leads therefore to a molecule with three π-systems under their radical cation form.

Finally, by reducing the central conjugation length to a simple indenofluorene−aryl system as exemplified by **(1,2-*b*)-DSF(t-Bu)$_4$-IF(4-PhCHO)(Br)** (Figure 2C), we noted a first oxidation potential at 1.38 V (HOMO level: −5.63 eV), (i) slightly increased compared to that of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)$_2$** (1.33 V) due to the less extended central π-system, IF-aryl vs aryl-IF-aryl and (ii) slightly decreased compared to that of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(Br)$_2$** (1.38 vs 1.46 V) (entry 18) due to a more extended π-system (IF-aryl vs IF) and the presence of only one bromine atom instead of two. The comparison of the HOMO levels of this series of structurally related DSF(*t*-Bu)$_4$-IF derivatives clearly shows (Scheme 2) that a fine-tuning of the electronic properties can be achieved by the extension of the indenofluorenyl core (π1-system) with pendant phenyl ring, which can be further substituted with various electron-donating/-withdrawing units.

1.c. DSF-LPP: Extended Ladder-p-Pentaphenylene Central Core. Various pentaphenylene derivatives with appealing properties for organic electronics have been widely studied for the last 10 years.[2,9,24,46,59] The oxidation of **DSF-LPP**[22] occurs along three processes with maxima at E^1, 1.09, E^2, 1.66, and E^3, 1.95 V (entry 6). The first oxidation E^1 is reversible and occurs at a potential similar to that of its constituting building block possessing methylene bridges instead of spirofluorene units, i.e., **LPP** (0.99 V, entry 34).[46] Thus, this first electronic process is assigned to the formation of a radical cation delocalized throughout the central pentaphenylenyl π-system. The 0.1 V shift of the first oxidation of **DSF-LPP** compared to that of **LPP** is due to the electron-withdrawing effect of the two spirofluorenyl units connected to the pentaphenylene core. A similar withdrawing effect has been highlighted between **(1,2-*b*)-DSF-IF** and **(1,2-*b*)-IF** (vide supra). The impressive 0.34 V potential difference between the first oxidation potential of **(1,2-*b*)-DSF-IF** (1.43 V) and that of **DSF-LPP** (1.09 V) clearly signals an extension of conjugation of the central π-system in **DSF-LPP**. Indeed, the four bridges allow keeping the five phenyl units in an almost flat configuration with a good delocalization of π-electrons. The oxidation of **DSF-LPP**$^{\bullet+}$ at E^2 (1.66 V) is multielectronic and occurs at a potential more anodic than that of **LPP**$^{\bullet+}$ (1.36 V) and close to that of **F** (1.62 V) or **SBF** (1.69 V). The **DSF-LPP** second multielectronic oxidation is therefore assigned to the oxidation of the two spiro linked fluorenyl cores concomitant with the second oxidation of the pentaphenylenyl unit.[60] In addition, there is an impressive 0.57 V shift between the first and the second oxidation of **DSF-LPP** showing that its radical cation is highly stable and strongly delocalized along the π1-pentaphenylenyl system.

In conclusion of this first section, the electronic properties of the 3π-2spiro compounds presented above can be tuned through the structural modification of the central π1 system. This can be achieved by the direct connection of electron-donating/-withdrawing groups and the extension of the π-conjugation of π1-system through either (i) the incorporation of pendant aryl units, which can be further substituted with electron-withdrawing/-donating groups or (ii) the incorporation of bridged phenyl units leading to a flat, rigid, and more extended pentaphenylenyl π1-system.

2. Modulation of the Electronic Properties by Alteration of the π2-Systems: Fluorene, Xanthene, Dialkyl-, or Diaryl-Substituted Fluorene. As mentioned above, the first oxidation potential of non-extended DSF-IF and DSF-LPP derivatives is centered on their π1-system. The aim of the following study is to define how the modifications of spirolinked π2-systems which are not directly conjugated to the π1-system can influence the first oxidation potential.

2.a. Xanthene Derivatives: (1,2-b)-DSX-IF, DSX-LPP. Xanthenyl derivatives are almost absent from the literature related to organic electronics, and this feature has driven all our interest for these compounds. Oxidation of **(1,2-*b*)-DSX-IF** possessing xanthenyl units as π2-systems instead of fluorenyl units (figure 3) appears to be very similar to that of **(1,2-*b*)-DSF-IF** (Figure 1) since both compounds present two successive oxidation waves E^1 and E^2 with only the first being reversible.

The peak potentials E^1 and E^2 are also almost identical for both molecules, that is 1.5/1.86 V for **(1,2-*b*)-DSX-IF** (entry 5) and 1.43/1.87 V for **(1,2-*b*)-DSF-IF** (entry 1). Hence, the first electron transfer in **(1,2-*b*)-DSX-IF** takes place on the (1,2-*b*)-

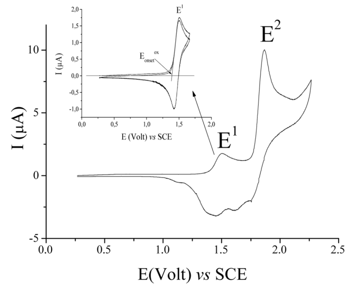


Figure 3. Cyclic voltammetry of **(1,2-*b*)-DSX-IF** 2×10^{-3} M recorded in CH_2Cl_2 + Bu_4NPF_6 0.2 M. Inset: zoom on the first oxidation process. Platinum disk (⌀: 1 mm) working electrode, sweep rate 100 mV· s^{-1}.

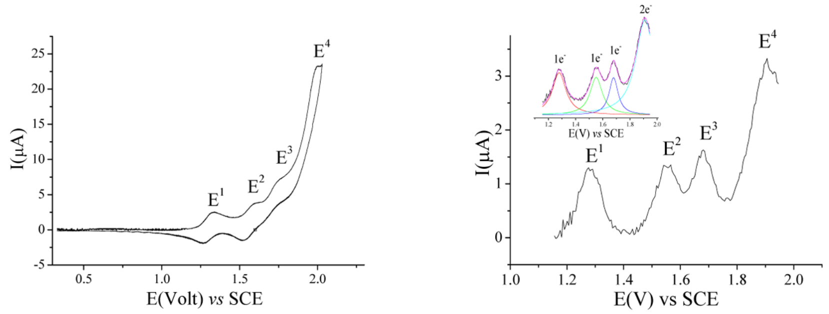


Figure 4. (Left) Cyclic voltammetry of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** 2 × 10^{-3} M in CH_2Cl_2 + Bu_4NPF_6 0.2 M, sweep rate 100 mV·s^{-1}. (Right) Differential pulse cyclic voltammetry in the same solution. Platinum disk (ø: 1 mm) working electrode. DPV setting: pulse height 25 mV, scan rate 2.5 mV s^{-1}, scan increment 3 mV and step time 2 s. Inset: multipeak fit in the 1.0−2.0 V potential range showing the three first monoelectronic processes.

indenofluorenyl core but is slightly shifted compared to **(1,2-*b*)-DSF-IF** due to the presence of xanthene units instead of fluorene.

DSX-LPP presents as observed for **DSF-LPP** one "quasi-reversible" oxidation wave around 1.10 V[61] followed by two more intense and irreversible waves (1.92 and 2.25 V, entry 7).[28] Due to the similarity with **DSF-LPP** (entry 6), it is rational to contend that **DSX-LPP** first oxidation occurs on the pentaphenylenyl core. The multielectronic oxidation (1.92 V) is assigned to the simultaneous second oxidation of the pentaphenylenyl radical-cation in dication together with the oxidation of the two xanthenyl units.

The influence of the xanthenyl units on the oxidation of the π1-systems is more clearly demonstrated by an anodic shift of the onset oxidation potentials of 30 mV for **(1,2-*b*)-DSX-IF** and 90 mV for **DSX-LPP** compared to their related fluorene analogues **(1,2-*b*)-DSF-IF** and **DSF-LPP**. This shows that the xanthenyl units have a slightly more intense withdrawing effect compared to that of fluorenyl units on the indenofluorenyl or pentaphenylenyl cores. As the difference between the electron withdrawing effects is weak, this allows a very fine-tuning of the onset oxidation potential and hence of the HOMO level.

2.b. (1,2-b)-DSF-IF with 2,7-Disubstituted Fluorenes: Incorporation of Electron-Withdrawing/-Donating Groups. The CV of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** (Figure 4) and **(1,2-*b*)-DSF(Et)$_4$-IF**, substituted on the fluorene units with *tert*-butyl and ethyl groups, respectively, are very similar. Indeed, both compounds present a first oxidation wave E^1 at 1.33 V (entries 8 and 9) cathodically shifted by 0.1 V compared to that of nonsubstituted **(1,2-*b*)-DSF-IF** (1.43 V, entry 1). This is in complete accordance with a first oxidation centered on the indenofluorenyl moiety, shifted by the electron-donating behavior of ethyl/*tert*-butyl groups leading hence to a lower withdrawing effect of the two 2,7-dialkylfluorenyl units compared to that of two nonsubstituted fluorenyl units. Thus, the 2,7-substitution of the spiro-connected fluorene units (despite not directly conjugated) with electron-donating groups slightly influences the electronic properties of the (1,2-*b*)-indenofluorenyl core, leading hence to a very appealing fine-tuning.

The (1,2-*b*)-indenofluorenyl oxidation (E^1) is followed by two monoelectronic oxidation waves 1.61 V (E^2)/1.79 V (E^3) for **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** and 1.57 V (E^2)/1.7 V (E^3) for **(1,2-*b*)-DSF(Et)$_4$-IF**). The existence of three successive monoelectronic processes for **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** and **(1,2-*b*)-DSF(Et)$_4$-IF** appears to be difficult to rationalize since the structure of the molecules should lead to the oxidation of the indenofluorenyl core (monoelectronic) followed by that of the two fluorenyl units (bielectronic) as stressed with nonsubstituted **(1,2-*b*)-DSF-IF**. Spectroelectrochemical studies along **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** oxidation and theoretical calculations have been carried out and seem to point to a rearrangement of the charges after the second electron exchange probably due to repulsion between positive charges in the bis-radical cation. (A similar charge rearrangement is also observed for the couple **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(Br)$_2$/(1,2-*b*)-DSF-IF(Br)$_2$**.) As this feature is not the main purpose of the present manuscript, it will not be presented here.[62]

In order to confirm the electronic influence of the π2-systems on the central π1-system, electron-withdrawing atoms (chlorine atoms) have been introduced on the DSF-IF scaffold. Thus, the oxidation of **(1,2-*b*)-DSF(Cl)$_4$-IF** (entry 10) leads to an anodic shift of the first oxidation potential compared to that of **(1,2-*b*)-DSF-IF** (1.52 V vs 1.43 V). This shift is clearly assigned to the presence of the two chlorine atoms on each fluorene units, leading to an intense electron-withdrawing effect on the indenofluorenyl core.

In summary, despite the partial interruption of the π-conjugation due to the spiro bridges, the substitution of the fluorenyl units with either electron-donating or electron-withdrawing groups leads to a slight shift of the first electron transfer nevertheless centered on the indenofluorenyl unit.

2.c. (1,2-b)-DSF-IF with 2,7-Diarylfluorenes. In 3π-2spiro compounds presented above, we have shown that the electronic properties are mainly governed by the π1-system but can be fine-tuned by the π2-systems. Increasing the π2-system's conjugation through the connection of pendant aryl groups appears hence as an interesting strategy to modify the electronic properties of these compounds.

Oxidations of aryl-substituted DSF-IFs occur either along two, **(1,2-*b*)-DSF(4-*t*-BuPh)$_4$-IF**, three, **(1,2-*b*)-DSF(3,5-di-*t*-BuPh)$_4$-IF**, four, **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** and **(1,2-*b*)-DSF(4-nonylPh)$_4$-IF** (Figure 5), or even more than six, **(1,2-*b*)-DSF(4-FPh)$_4$-IF** (Figure 5), successive oxidation processes with different relative intensities.[27] The first potential shifts from 1.28 V for **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** to 1.45 V for **(1,2-*b*)-DSF(4-FPh)$_4$-IF**.

All these differences might be, in a first instance, basically analyzed by the different electron-donating/electron-withdrawing effects of the substituents borne by the phenyl rings. Thus, **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** with three electron-donating methoxy groups on each phenyl ring presents the lowest oxidation potential of the series (1.28 V, entry 11). On the contrary, **(1,2-*b*)-DSF(4-FPh)$_4$-IF** with an electron-withdraw-

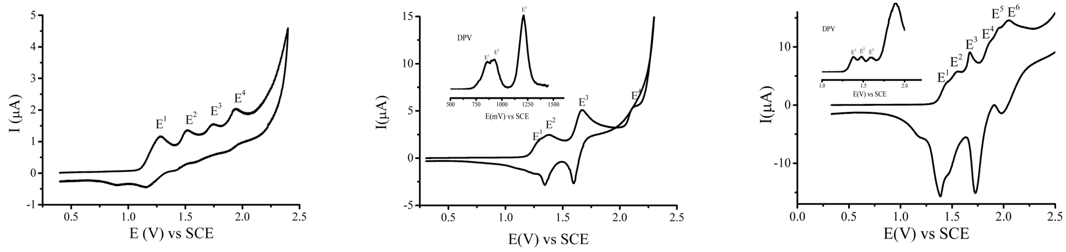


Figure 5. Cyclic voltammetries of (left) **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF**, (middle) **(1,2-*b*)-DSF(4-nonylPh)$_4$-IF**, and (right) **(1,2-*b*)-DSF(4-FPh)$_4$-IF** in CH_2Cl_2 + Bu_4NPF_6 0.2 M, concentration 2×10^{-3} M, sweep rate 100 mV·s^{-1}. Platinum disk (⌀: 1 mm) working electrode. Inset, middle and right: DPV. DPV setting: pulse height 25 mV, scan rate 5 mV s^{-1}, scan increment 5 mV, and step time 1 s.

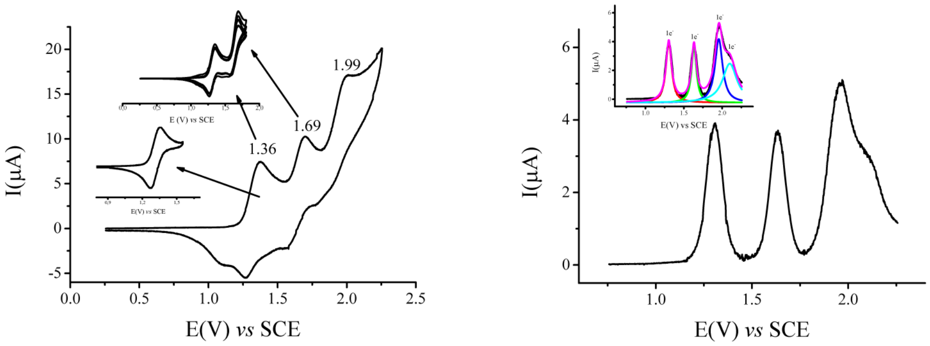


Figure 6. (Left) Cyclic voltammetry of **(2,1-*a*)-DSF-IF** 2×10^{-3} M in CH_2Cl_2 + Bu_4NPF_6 0.2 M, sweep rate 100 mV·s^{-1}. (Right) Differential pulse cyclic voltammetry in the same solution. DPV setting: pulse height 25 mV, scan rate 10 mV s^{-1}, scan increment 2 mV, and step time 200 ms. Platinum disk (⌀: 1 mm) working electrode. Inset left: zoom on the first and on the two first oxidation processes. Inset right: multipeak fit of the DPV in the 0.5−2.5 V potential range showing the three successive monoelectronic processes.

ing fluorine atom on each phenyl ring presents the highest oxidation value of the series (1.45 V, entry 12). The first oxidation potential of **(1,2-*b*)-DSF(phenyl substituted)$_4$-IF** may be hence tuned through the nature of the different substituents borne by the phenyl rings.

However, there is a drastic difference between alkyl (presented above) and aryl-substituted DSF-IFs. Indeed, in alkyl-substituted DSF-IFs, the first electron transfer was demonstrated to be centered on the indenofluorenyl core (*π*1-system), whereas in **(1,2-*b*)-DSF(phenyl substituted)$_4$-IF**, the assignment of the first electron transfer either on the indenofluorenyl core (*π*1-system) or on the diaryl-substituted fluorenyl units (*π*2-system) is far from obvious. Indeed, the first oxidation potential of "aryl-fluorene-aryl" moieties described in the literature is very close (~ 1.39 V)[12,63] to that of a (1,2-*b*)-indenofluorenyl moiety in **(1,2-*b*)-DSF-IF** (1.43 V) due to comparable conjugation length.

Key information to assign the first electron transfer has been obtained by the comparison of the electrochemical behaviors of **(1,2-*b*)-DSF(4-nonylPh)$_4$-IF** (entry 15 and Figure 6) and of a model compound (entry 35), namely 9,9′-spirobi[9*H*-fluorene]-2,7-bis(4-nonylphenyl) (see structure in Scheme 1, bottom-right). The first oxidation of the latter[27] occurs at 1.45 V and is assigned to the oxidation of the "aryl-fluorene-aryl" moieties as expected by the longer conjugated length of an "aryl-fluorene-aryl" core compared with the fluorene. The comparison of this oxidation potential (1.45 V) to that of **(1,2-*b*)-DSF(4-nonylPh)$_4$-IF** (1.30 V) is an argument to conclude that the first electron transfer in **(1,2-*b*)-DSF(4-nonylPh)$_4$-IF** leans more toward the (1,2-*b*)-indenofluorenyl core than to the "aryl-fluorene-aryl" moieties. DPV recorded for **(1,2-*b*)-DSF-(phenyl substituted)$_4$-IF** compounds confirm, except for **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** (detailed below), that the two first oxidations are monoelectronic. This feature is not fully unravelled, for instance, and will not be described here. By increasing the electron-donating strength of the substituents born by the "aryl-fluorene-aryl" fragment or by extending the *π*-conjugation of the *π*2-systems, it should be possible to (i) simultaneously oxidize the three *π* systems (the indenofluorenyl and the two "aryl-fluorene-aryl" units, 3e$^-$) or (ii) to fully reverse the order of the electron transfers: a first oxidation centered on the "aryl-fluorene-aryl" unit, 2e$^-$, followed by a second centered on the indenofluorenyl core, 1e$^-$. This feature has been evidenced by the two last examples of this series: **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** and **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF**. In the case of **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF**, the presence of the six electron-donating methoxy groups on the phenyl rings renders the two "aryl-fluorene-aryl" units more easily oxidizible, and hence, the first oxidation occurs as a trielectronic process, assigned to the concomitant oxidation of the indenofluorenyl backbone (1e$^-$) and to the two "triOMePh-fluorene-triOMePh" units (2e$^-$). In the case of **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF** possessing terfluorenyl units, we note four successive oxidation processes in a ratio of 2e$^-$, 2e$^-$, 1e$^-$, and 3e$^-$.[29] The two first oxidation potentials (1.29 V/1.47 V) are in accordance with those of other terfluorenyl derivatives.[35,64,65] It seems then consistent to assign the two first bielectronic oxidations of **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF** to the oxidation of the two terfluorenyl arms leading to terfluorenyl centered bis-dication. The third reversible oxidation (1.58 V) is then assigned to the oxidation of the (1,2-*b*)-indenofluorenyl core at a potential slightly more anodic than that recorded for **(1,2-*b*)-DSF-IF** (1.43 V, entry 1). This shift to more anodic values is probably due to the electron-withdrawing effect of the terfluorenyl arms that are under their dicationic states at this potential. It is interesting to stress that the three first oxidations, involving 5 electrons, are reversible leading to highly charged and stable organic species, very rarely observed in literature.[66−69]

In conclusion, the general rule for aryl-substituted DSF-IFs is that the first oxidation centered on the (1,2-*b*)-indenofluorenyl core (π1-system) is followed at higher potential by its second oxidation (in dication) concomitant with the oxidation of the fluorenyl cores (π2-system). By increasing the strength of the electron-donating substituents or by increasing the conjugation length, we managed to significantly change this general rule and hence the whole properties of the resulting molecules. Two remarkable examples have been pointed out: (i) **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** with the concomitant oxidation of the three π-systems (π1- and π2-systems) leading to a first trielectronic process and (ii) **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF** with the two first bielectronic oxidations centered on each terfluorenyl units (π2-systems) preceding the indenofluorenyl unit oxidation (π1-system).

3. Modulation of the Electronic Properties through the Modification of the Geometry of the Molecular Scaffold: 2,1-*a*-Indenofluorenyl Central Core. A simple way to tune the properties of a molecular system consists of modifying its geometry. The **(2,1-*a*)-IF** is a positional isomer of **(1,2-*b*)-IF** and possesses its two methylene bridges on the same side of the *p*-terphenyl backbone (Scheme 1, bottom left). The molecular structure of the 2,1-*a*-indenofluorenyl core leads to a face-to-face arrangement of the π-systems, strongly modifying the geometry of the resulting **(2,1-*a*)-DSF-IF** derivatives (bent suprafacial structure) compared to their **(1,2-*b*)**-isomers (linear antarafacial structure).[70]

3.a. (2,1-a)-DSF-IF and (2,1-a)-DSF(t-Bu)$_4$-IF. The anodic oxidation of the nonsubstituted **(2,1-*a*)-DSF-IF** model compound of the series (entry 21 and Figure 6) consists of three successive oxidations with maxima at 1.36, 1.69, and 1.99 V, followed by a polymerization process.[53] The first oxidation is reversible and monoelectronic whereas the second is monoelectronic but less reversible (insets of Figure 6 left and DPV Figure 6 right). Compared to its positional isomer **(1,2-*b*)-DSF-IF** (entry 1), two main differences are pointed out: (i) the first oxidation at 1.36 V is cathodically shifted (1.43 V for **(1,2-*b*)-DSF-IF**) and (ii) an additional oxidation process is surprisingly observed at 1.69 V. At this stage, it is crucial to mention that the two linear π-systems with methylene bridges, i.e., **(2,1-*a*)-IF** and **(1,2-*b*)-IF**, are oxidized at the same potential (1.31 V, entries 29/30).[19,20] Therefore, the shift observed between the first oxidation potentials of **(1,2-*b*)-DSF-IF** and **(2,1-*a*)-DSF-IF** cannot be ascribed to the different geometry of the two indenofluorenyl cores but to the specific structural arrangement of the two fluorene units (face-to-face in **(2,1-*a*)-DSF-IF** or not in **(1,2-*b*)-DSF-IF**).

The smaller potential difference observed for **(2,1-*a*)-DSF-IF**/**(2,1-*a*)-IF** (50 mV) compared to that observed for **(1,2-*b*)-DSF-IF**/**(1,2-*b*)-IF** (120 mV) may be explained by a less important withdrawing effect of the cofacial difluorenyl π-dimer in **(2,1-*a*)-DSF-IF** compared to that of two noninteracting fluorenyl units in **(1,2-*b*)-DSF-IF**. More surprising is the extra oxidation observed at 1.69 V for **(2,1-*a*)-DSF-IF**. It does not exist for either **(1,2-*b*)-DSF-IF** or **(2,1-*a*)-IF** and may be therefore ascribed to the oxidation of the cofacial fluorenyl dimer in **(2,1-*a*)-DSF-IF**. Indeed, it is known that cofacial interacting π-systems are more easily oxidized that non interacting π-systems.[71] Rathore has, for example, reported the shift of the fluorene oxidation potential from 1.74 V for an "isolated" fluorene to 1.42 V for two π-stacked fluorenes due to electronic coupling between the two stacked fluorene moieties.[72,73] Other cofacial systems based on paracyclophanes or tetrathiafulvalenes have also displayed similar potential shifts.[74,75] The extra oxidation of **(2,1-*a*)-DSF-IF** (1.69 V) was hence assigned to the oxidation of the cofacial fluorenyl dimer.

The oxidation of its homologue **(2,1-*a*)-DSF(*t*-Bu)$_4$-IF** (entry 22) occurs in four successive oxidation processes (1.24, 1.55, 1.84, and 1.96 V).[21] The three first reversible oxidations are monoelectronic, whereas the fourth irreversible wave is at least bielectronic and accompanied by a polymerization process. The first wave is assigned to the oxidation of the (2,1-*a*)-indenofluorenyl core slightly shifted to less positive potentials due to the electron-donating effect of the *tert*-butyl units (1.24 V vs 1.36 V in **(2,1-*a*)-DSF-IF**). The second oxidation of **(2,1-*a*)-DSF(*t*-Bu)$_4$-IF** is slightly shifted by 60 mV compared to the second oxidation of its isomer **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** (1.55 V vs 1.61 V) and by 140 mV compared to the second oxidation of **(2,1-*a*)-DSF-IF** (1.55 V vs 1.69 V). This second oxidation may then be ascribed to the oxidation of the 2,7-(*t*-Bu)$_2$-fluorenyl dimer occurring at a lower anodic potential compared to that of (i) "isolated" 2,7-(*t*-Bu)$_2$-fluorenyl units in **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF** and of (ii) cofacial interacting fluorenyl dimer, found in **(2,1-*a*)-DSF-IF**, which may be due to the electron-donating effect of the *tert*-butyl groups or to the different molecular arrangement of the two dimers (2,7-(*t*-Bu)$_2$-fluorenyl dimer vs fluorenyl dimer).

Finally, the third reversible monoelectronic oxidation at 1.84 V is assigned to the second oxidation of the 2,7-(*t*-Bu)$_2$-fluorenyl dimer. Indeed, the second oxidation of the 2,1-*a*-indenofluorenyl unit would lead to polymerization process which is not observed in the present case. After this third electron transfer, a triradical-cation species with one radical on each π-system is postulated.[21]

3.b. (2,1-a)-DSF-IF with 2,7-Diarylfluorene. The final approach to tune the electronic properties of these systems is based on molecules combining both approaches developed above: an extension of the π-conjugation of π2-fluorenyl units and the specific geometry of the 2,1-*a*-indenofluorenyl π1-core forcing the two diarylfluorene units to interact in a cofacial arrangement.

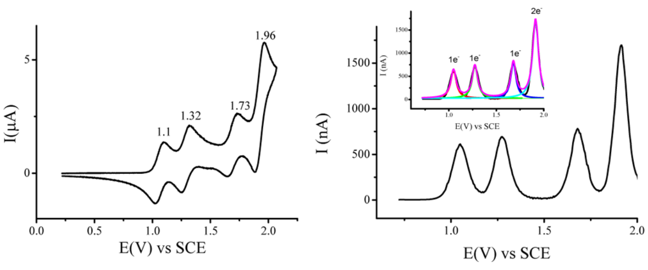


Figure 7. (Left) Cyclic voltammetry of **2,1-*a*-DSF(3,5-di-*t*-BuPh)$_4$-IF** 2×10^{-3} M in CH_2Cl_2 + Bu_4NPF_6 0.2 M, sweep rate 100 mV·s^{-1}. (Right) Differential pulse cyclic voltammetry in the same solution. Platinum disk (ø: 1 mm) working electrode. DPV setting: pulse height: 25 mV, scan rate 5 mV s^{-1}, scan increment 5 mV and step time 1 s. Inset: multipeak fit of the DPV in the 0.5−2.0 V potential range showing the three successive monoelectronic processes preceding the last two electron oxidation.

The anodic oxidation of the **2,1-*a*-DSF(2,7-substituted phenyl)$_4$-IF** series (entries 23–27) may be exemplified by the CVs recorded for **2,1-*a*-DSF(3,5-di-*t*-BuPh)$_4$-IF** (Figure 7). All of the compounds of this series are oxidized along at least four successive processes between 0.0 and 2.5 V.[27] For all compounds, the first oxidation wave appears around 1.1 V (from 1.07 V for **(2,1-*a*)-DSF(3,4,5-triOMePh)$_4$-IF** (entry 23) to 1.20 V for **(2,1-*a*)-DSF(4-FPh)$_4$-IF**) (entry 24), and the three first oxidation waves are always monoelectronic and reversible, except for **(2,1-*a*)-DSF(3,4,5-triOMePh)$_4$-IF**, which presents a first bielectronic oxidation process.[76]

As exposed above for their **(1,2-*b*)-DSF(2,7-phenyl-substituted)$_4$-IF** related isomers, the first oxidation potential of **(2,1-*a*)-DSF(2,7-phenyl-substituted)$_4$-IF** is slightly shifted depending on electron-donating/electron-withdrawing effects of the different substituents borne by the phenyl rings. However, all **(2,1-*a*)-DSF(2,7-phenyl-substituted)$_4$-IF** are oxidized at a significantly lower potential compared to their corresponding isomers **(1,2-*b*)-DSF(2,7-phenyl-substituted)$_4$-IF**.

As the first oxidation of the model compound of this series, **(2,1-*a*)-DSF-IF**, occurs at 1.36 V and is centered on the (2,1-*a*)-indenofluorenyl core,[26] the first oxidation of the **(2,1-*a*)-DSF(2,7-phenyl-substituted)$_4$-IF** (ca. 1.1 V) is definitively not centered on the (2,1-*a*)-indenofluorenyl core. However, this first reversible oxidation is not centered on the "aryl-fluorene-aryl" moieties, where oxidations are found at higher potentials for **(1,2-*b*)-DSF(2,7-phenyl-substituted)$_4$-IF** isomers (see above). The "aryl-fluorene-aryl" cofacial arrangement is hence at the origin of the present remarkable low first oxidation potential[71,72] assigned to an oxidation centered on the "aryl-fluorene-aryl" cofacial dimer.

For all the compounds of this series, and despite their different substitution, the second oxidation process is recorded around 1.3 V (from 1.25 V for **(2,1-*a*)-DSF(4-nonylPh)$_4$-IF** to 1.36 V for **(2,1-*a*)-DSF(4-FPh)$_4$-IF**). This value is close to the first oxidation potential of the **(2,1-*a*)-DSF-IF** (1.36 V) and may then be exclusively centered on the (2,1-a)-indenofluorenyl core. DPV of **(2,1-*a*)-DSF(2,7-phenyl-substituted)$_4$-IF** derivatives show that all compounds, except **(2,1-*a*)-DSF-(3,4,5-triOMePh)$_4$-IF**,[76] present a third monoelectronic oxidation around 1.6/1.7 V (from 1.57 V for **(2,1-*a*)-DSF(4-*t*-BuPh)$_4$-IF**) to 1.73 V for **(2,1-*a*)-DSF(3,5-di-*t*-Bu-Ph)$_4$-IF**)). This oxidation, occurring at a less anodic potential compared to the second oxidation of the (2,1-*a*)-indenofluorenyl core, 1.99 V for **(2,1-*a*)-DSF-IF** (entry 21), seems then to take place on the π-dimer radical cation leading to the π-dimer dication.

Compared to its isomer **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF** (1.29, 1.47, 1.58 V, entry 16), the two first oxidation potentials of **(2,1-*a*)-DSF(9,9-dioctylfluorene)$_4$-IF** (1.12, 1.18 V, entry 28) are shifted to less anodic values whereas the third one occurs at more anodic potentials (1.64 V).[29] DPV shows that the successive five-electron oxidations are in a ratio of 1/1/3 for **(2,1-*a*)-DSF(9,9-dioctylfluorene)$_4$-IF** as it was of 2/2/1 for **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF**.[29] Hence, the two first one-electron transfers of **(2,1-*a*)-DSF(9,9-dioctylfluorene)$_4$-IF** are centered on the "terfluorenyl dimer" leading to its dication. The third three-electron oxidation at 1.64 V leads then to a highly charged molecule with a dication centered on each terfluorenyl units and a radical cation on the (2,1-*a*)-indenofluorenyl core. This five-electron oxidation is reversible demonstrating a high stability of the molecule in its five-electron oxidation state.[29]

In conclusion, the specific geometry of **(2,1-*a*)-DSF(diaryl-substituted)-IF** molecules leads to a face-to-face arrangement of the two diarylsubstituted-fluorenyl units and shifts their first oxidation potential to lower potentials compared to that of their corresponding (1,2-*b*)-isomers. Successive oxidations of most of the **2,1-*a*-DSF(diaryl-substituted)-IF** lead to highly charged species that remain stable at the time-scale of the cyclic voltammetry. Such behavior appears to be very rare for organic species.[66−69]

3. CONCLUSION

In summary, the 3π-2spiro compounds investigated in this work present successive oxidation processes leading to differently charged species. Schemes 3 and 4 gather these molecules according to their charge at their highest accessible stable state (determined by the reversibility of the cyclic voltammetry).

First, for (1,2-*b*)-indenofluorenyl and pentaphenylenyl derivatives (Scheme 3), we pointed out five types of stable charged species (radical-cation, dication, tris-radical cation, $4^{\bullet+}$ and $5^{\bullet+}$) gathered below.

(i) **(1,2-*b*)-DSF-IF**, **(1,2-*b*)-DSF-IF(^{n}oct)$_2$**, **(1,2-*b*)-DSF-IF(^{i}Pr)$_2$**, **(1,2-*b*)-DSF-IF(Br)$_2$**, **(1,2-*b*)-DSF(4-*t*-Bu-Ph)$_4$-IF**, **(1,2-*b*)-DSF(3,5-di-*t*-Bu-Ph)$_4$-IF**, and **(1,2-*b*)-DSX-IF** only lead to a stable radical cation centered on the (1,2-*b*)-indenofluorenyl core.

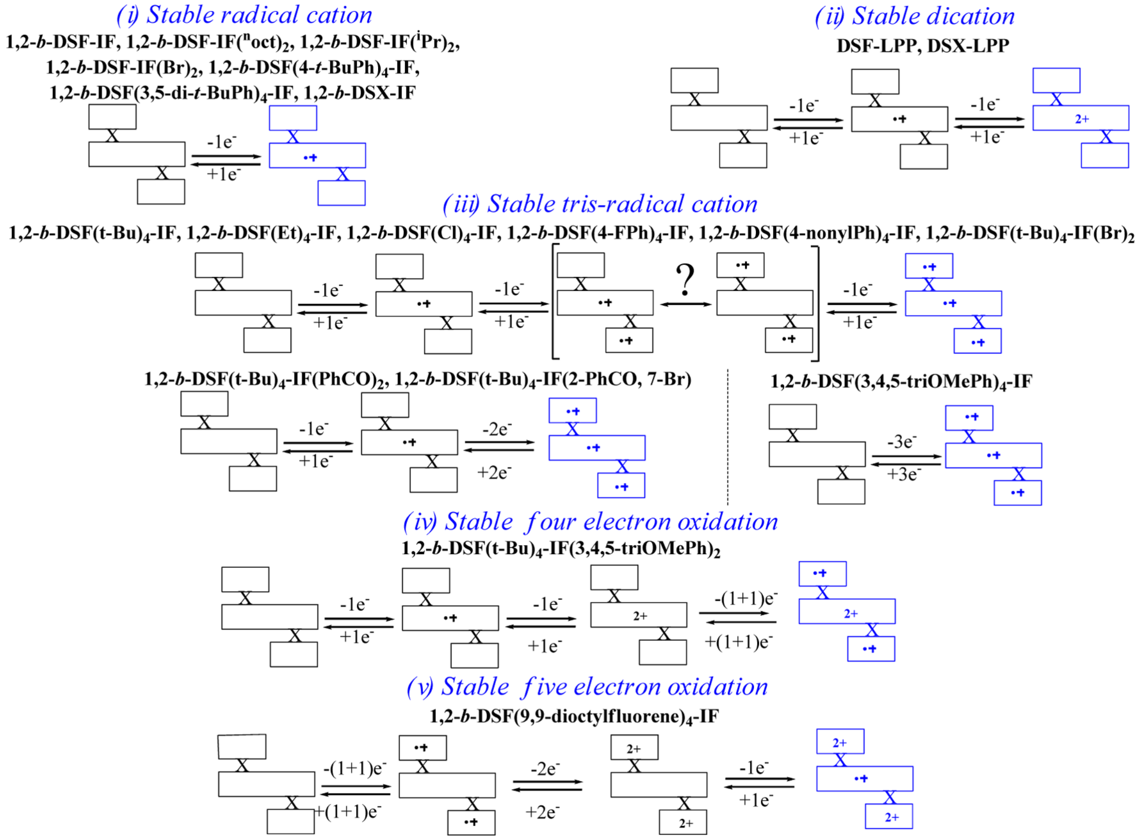
(ii) **DSF-LPP** and **DSX-LPP** lead to stable dicationic species after two successive one-electron oxidations centered on the pentaphenylenyl unit.

(iii) Stable tris-radical cations are obtained by successive oxidation of nine compounds. (a) For **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF**, **(1,2-*b*)-DSF(Et)$_4$-IF**, **(1,2-*b*)-DSF(Cl)$_4$-IF**, **(1,2-*b*)-DSF(4-FPh)$_4$-IF**, and **(1,2-*b*)-DSF(4-nonylPh)$_4$-IF**, the tris-radical cations are obtained along three successive reversible one-electron oxidations. The first oxidation leads to the (1,2-*b*)-indenofluorenyl radical cation. The second oxidation occurs on one fluorenyl arm, is probably accompanied by charge reorganization in the molecule leading to a stable bis radical-cation, each charge being centered on the π2-fluorenyl units. Finally, the third electron is abstracted on the indenofluorenyl core leading to the stable tris-radical cation. For **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(Br)$_2$** unambiguous three monoelectronic oxidations are pointed through DPV with only two first being reversible. (b) Oxidation of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)$_2$** and of **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PhCHO)(Br)** also occurs in a first monoelectronic oxidation of the π1-indenofluorenyl system leading to a stable radical-cation followed by the oxidation of the two π2-fluorenyl units leading to the stable tris-radical cation. (c) The tris-radical cation of the **(1,2-*b*)-DSF(3,4,5-triOMePh)$_4$-IF** is obtained in a single three-electron oxidation process.

(iv) A stable four-oxidation process is observed for **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$**. The first two oxidations are monoelectronic and successively lead to a stable radical cation and then to a dication centered on the π1-system. The two successive monoelectronic oxidations occur in a close potential range and lead to the oxidation of the π2-fluorenyl units giving a highly charged stable species with two radical-cations on each π2-systems and to a dication on the π1-system.

(v) Finally, for **(1,2-*b*)-DSF(9,9-dioctylfluorene)$_4$-IF**, a first two-electron oxidation leads to a bis-radical cation centered on

Scheme 3. Stable Charged Species Obtained from Oxidations of (1,2-*b*)-DSF-IF Derivatives and from (1,2-*b*)-DSX-IF, DSF-LPP, and DSX-LPP



the two π2-terfluorenyl units and is followed by a two-electron oxidation leading to a bis-dication also centered on the π2-terfluorenyl units. The central π1-indenofluorenyl core is then oxidized at higher potential leading to the highest charged stable species with a formal 5^+ oxidation state. Such a singular oxidation is allowed by the stability of the terfluorenyl units under their dicationic form[65] at potential less anodic than the oxidation potential of the (1,2-*b*)-indenofluorenyl unit.

Second, for 2,1-*a*-indenofluorenyl derivatives, we only pointed out three types of stable charged species (bis-radical-cation, tris-radical cation, and five-electron oxidation) gathered in Scheme 4.

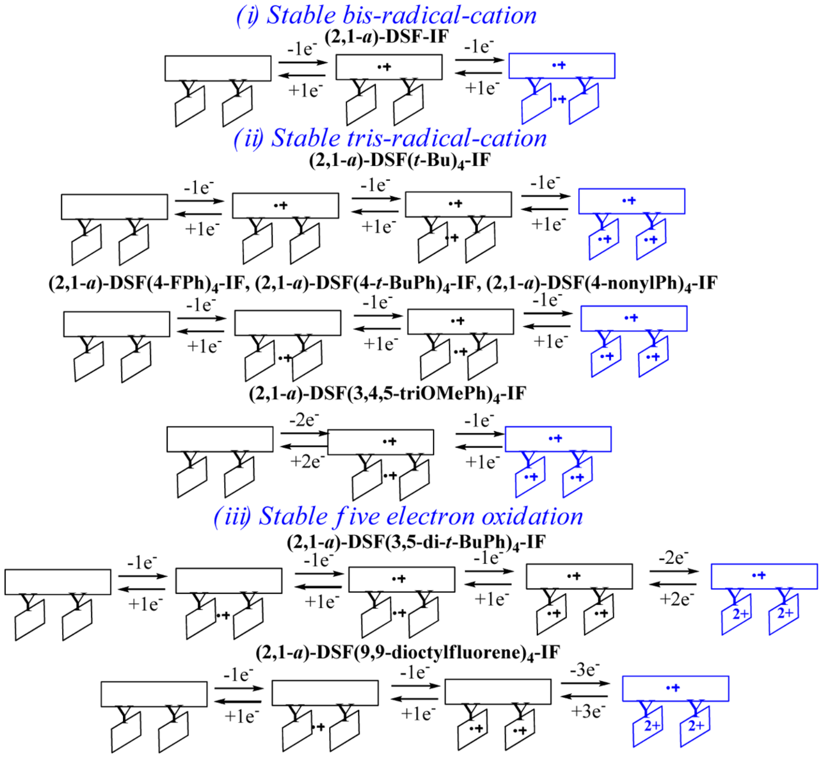
(i) The simplest compound of the series **(2,1-*a*)-DSF-IF** remains stable under its bis-radical-cation state formed along a first 1-electron oxidation centered on the 2,1-*a*-indenofluorenyl core followed by a second 1-electron transfer centered on the face-to-face fluorenyl dimer. This last oxidation is specific to the **(2,1-*a*)-DSF-IF** series and is due to the face-to-face arrangement of the two π2-systems.

(ii) Access to stable tris-radical cation is obtained along either three successive 1-electron processes or along a 2-electron oxidation followed by a second 1-electron oxidation. The three successive 1-electron processes may occur differently with either a first oxidation on the 2,1-*a*-indenofluorenyl core followed by two successive 1-electron oxidations on the face-to-face (2,7-*t*-Bu)$_4$-fluorenyl dimer for **(2,1-*a*)-DSF(*t*-Bu)$_4$-IF** or with a first 1-electron oxidation on the face-to-face aryl-fluorene-aryl dimer followed by a second 1-electron oxidation on the 2,1-*a*-indenofluorenyl core and followed by a third monoelectronic oxidation on the face-to-face fluorenyl dimer radical cation for **(2,1-a)-DSF(4-FPh)$_4$-IF**, **(2,1-a)-DSF(4-*t*-BuPh)$_4$-IF** and **(2,1-a)-DSF(4-nonylPh)$_4$-IF**. On the other hand, **(2,1-a)-DSF(3,4,5-triOMePh)$_4$-IF** oxidation occurs along a two-electron oxidation leading to a bis-radical cation centered on the 2,1-*a*-indenofluorenyl core and on the face-to-face aryl-fluorene-aryl dimer, followed by a second 1-electron oxidation of the aryl-fluorene-aryl dimer radical cation leading to one radical cation on each π-systems.

(iii) Finally, stable 3π-2spiro compounds bearing a dicationic charge on each π2-system and a radical cation on the indenofluorenyl π1-system may be obtained either through three successive 1-electron oxidations followed by a 2-electron oxidation as for the **(2,1-a)-DSF(3,5-di-*t*-BuPh)$_4$-IF** or through two successive 1-electron oxidations and a third 3-electron oxidation as for the **(2,1-*a*)-DSF(9,9-dioctylfluorene)$_4$-IF**. In each case, the first oxidation occurs on the face-to-face aryl-fluorene-aryl dimer.

This extensive study reveals that the electronic properties of 3π-2spiro derivatives can be drastically or very finely tuned by the nature and/or substitution of their different π-systems and also by their structural organization with the possibility of through-space π−π interactions. Such electronic modulation was previously pointed through the optical properties of the different molecules and particularly through the tuning of their emission wavelength. Such a structure−property relationship may allow research groups to comprehend the electronic properties of bridged oligophenylenes to further synthesize highly efficient materials with specific properties for organic electronic applications. In order to obtain other appealing 3π-2spiro materials with specific geometries, various indenofluorenyl building blocks are currently under development in our laboratory.[31]

Scheme 4. Stable Charged Species Obtained from Oxidations of (2,1-*a*)-DSF-IF Derivatives



■ EXPERIMENTAL SECTION

Electrochemical Experiments and Instrumentation. All compounds have been studied using cyclic and differential pulse voltammetry (CV and DPV). All electrochemical experiments were performed under an argon atmosphere, using a Pt disk electrode (⌀: 1 mm), the counter electrode was a vitreous carbon rod and the reference electrode was a silver wire in a 0.1 M $AgNO_3$ solution in CH_3CN. Ferrocene was added to the electrolytic solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc^+) couple served as the internal standard. All potentials are referred to the SCE electrode that was calibrated at −0.405 V vs Fc/Fc^+ system. Activated Al_2O_3 was added to the electrolytic solution to remove excess moisture.

Synthesis. The synthesis of the molecules investigated in the present work have been previously reported: **(1,2-*b*)-DSF-IF**, **(1,2-*b*), DSF-IF(^{i}Pr)$_2$** and **(1,2-*b*)-DSF-IF(^{n}Oct)$_2$**;[19,20] **(1,2-*b*)-** and **(2,1-*a*)-DSF(*t*-Bu)$_4$-IF**;[21] **(2,1-*a*)-DSF-IF**;[26] **(1,2-*b*)-DSX-IF**;[25] **DSF-LPP**;[22] **DSX-LPP**;[28] **(1,2-*b*)-DSF(Et)$_4$-IF**, **(1,2-*b*)-** and **(2,1-*a*)-DSF(3,4,5-triOMePh)$_4$-IF**, **(1,2-*b*)-** and **(2,1-*a*)-DSF(3,5-di-*t*-BuPh)$_4$-IF**;[24] **(1,2-*b*)-** and **(2,1-*a*)-DSF(4-FPh)$_4$-IF**, **(1,2-*b*)-** and **(2,1-*a*)-DSF(4-nonylPh)$_4$-IF**; **(1,2-*b*)-** and **(2,1-*a*)-DSF(4-*t*-BuPh)$_4$-IF**,[23,27] **(1,2-*b*)-** and **(2,1-*a*)-DSF(9,9-dioctyfluorene)$_4$-IF**;[29] **(1,2-*b*)-IF**,[20] **(2,1-*a*)-IF**,[26] **LPP**,[46] **9,9′-SBF**,[20,55] **9,9′-spirofluorene-(2,7-di-4-nonylphenyl-fluorene)**,[27] **2,7-fluorene(*t*-Bu)$_2$**;[21] **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(Br)$_2$** and **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(4-PHCHO)(Br)**;[30] **(1,2-*b*)-DSF(*t*-Bu)$_4$-IF(3,4,5-triOMePh)$_2$**.[32]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CVs and DPVs for **1,2-*b*-DSF-IF(^{n}octyl)$_2$**, **1,2-*b*-DSF-IF-(^{i}propyl)$_2$**, **1,2-*b*-DSF-IF(Br)$_2$**, and **1,2-*b*-DSF(*t*-Bu)$_4$-IF(Br)$_2$**, numbering of the carbon atoms in **1,2-*b*-DSF-IF** and oxidation and reduction potentials, $E_{onset}{}^{ox}$ and $E_{onset}{}^{red}$ for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(76) It should be mentioned that the number of electrons involved in the first electronic process in (2,1-*a*) DSF(3,4,5-triOMePh)4-IF and (1,2-*b*)-DSF(3,4,5-triOMePh)4-IF are surprisingly different than those observed for the other phenyl-substituted DSF-IFs. Indeed, it seems that the two "aryl-fluorene-aryl" arms (face to face or not) within these two molecules are simultaneously oxidized; in (1,2-*b*)-DSF(3,4,5-triOMePh)4-IF: 3e$^-$ at 1.16 V (1e$^-$ for the 1,2-*b*-indenofluorenyl unit and 2e$^-$ for "aryl-fluorene-aryl") and in (2,1-*a*)-DSF(3,4,5-triOMePh) 4-IF: 2e$^-$ at 1.07 V for "aryl-fluorene-aryl" units.