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Tuning the Optical Properties of Aryl-Substituted Dispirofluorene-Indenofluorene Isomers through Intramolecular Excimer Formation

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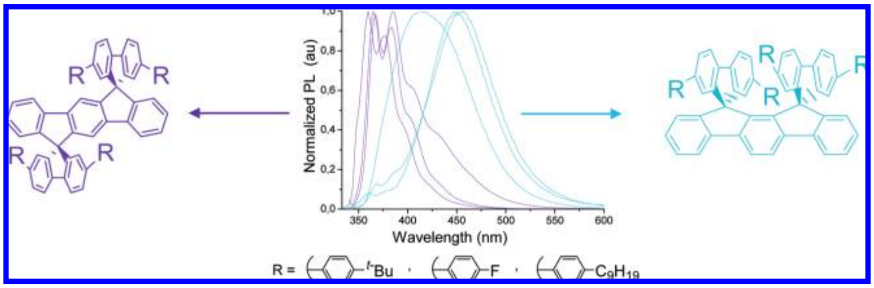
ABSTRACT



Two families of positional isomers of dispirofluorene-indenofluorene substituted by phenyl groups at the 2,7-positions of the fluorene moieties present drastically different optical properties. The emission wavelengths may be gradually and conveniently modulated for one of the two isomers by the phenyl group’s substituent whose bulkiness controls the extent of the excimeric interaction evidenced in this paper.

The synthesis of new materials with well-defined geometry and specific properties is strongly sought worldwide for applications in organic electronics.[1−5] As the molecular structure has a significant impact on the properties of organic materials, it seems of great interest to prepare, through a common intermediate, different molecules that possess different and tunable properties. Such an approach is illustrated by the synthesis, *via* a common intermediate, of aryl-substituted **(1,2-*b*)-DSF(R)$_4$-IF 1** and **(2,1-*a*)-DSF(R)$_4$-IF 2** (DSF, dispirofluorene; IF, indenofluorene), presenting distinct geometry profiles that translate into different physicochemical properties (Scheme 1). After consideration of structural features present within **2b**, one representative of **DSF-IFs 2**, we report the marked difference observed in the electrochemical and optical properties of the **DSF-IF 1** and the **DSF-IF 2** families. We then address the tuning of the emission band within the **DSF-IF 2** family, through the

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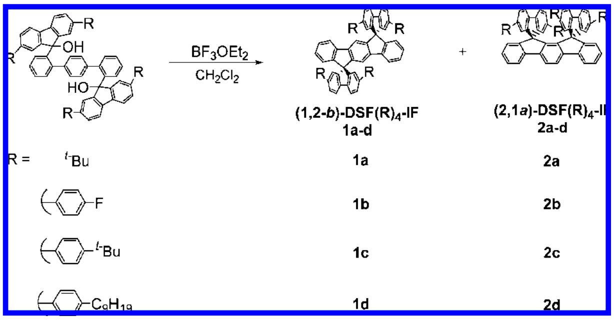
Scheme 1. DSF-IFs 1a−d and 2a−d



nature and size of the para-substituent of the phenyl groups borne by the fluorene moieties.

The intramolecular cyclization[6,7] of a difluorenol derivative in the presence of a Lewis acid (Scheme 1) leads to the formation of two positional isomers possessing distinct geometry: **(1,2-*b*)-DSF-IF 1** and **(2,1-*a*)-DSF-IF 2**, which were separated by column chromatography. We note that, with identical substituents, the **DSF-IFs 2** are always more soluble than their corresponding **DSF-IF 1** congeners.

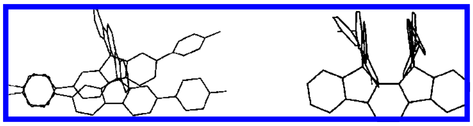


Figure 1. Two different views of **2b** from X-ray data.

The X-ray diffraction data of single crystals of **2b** reveal an asymmetric unit containing two independent molecules (Figure 1, only one of the two independent molecules is represented).[8] Due to the face-to-face arrangement of the fluorene units in **2b**, one of the spiro carbon points slightly above the indeno[2,1-*a*]fluorene plane (defined through the central phenyl ring) while the other spiro carbon points below this plane.[6] The dihedral angles between the fluorene moiety and its 4-fluorophenyl substituent span a wide range, i.e. from 26° to 41° (see Supporting Information (SI)). The two lowest dihedral angles (ca. 26.3° and 27.4°) correspond to two face-to-face phenyl rings (Figure 1, left) with a ring-centroid/ring-centroid distance estimated at ca. 3.76 Å. The corresponding vertical displacements between these two phenyl rings are 0.94 and 1.14 Å, and their corresponding ring slippage angles are very low, i.e. approximately 14° and 18° (see SI). As discussed by Janiak, such values of ring-centroid/ring-centroid distance, vertical displacements, and ring slippage angles may indicate strong π/π interactions in the solid state.[9,10]

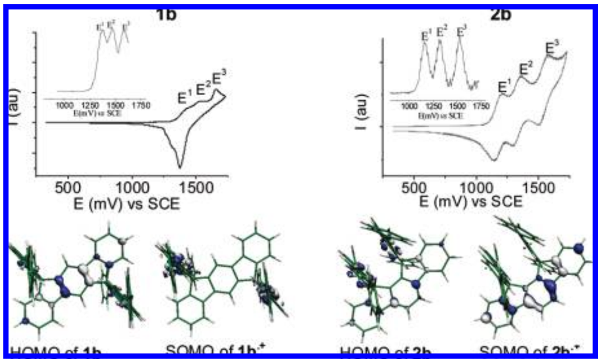


Figure 2. Cyclic voltammetry[13] (and DPVs as insets) recorded in CH_2Cl_2−$[NBu_4][PF_6]$ 0.2 M, using Pt anode; sweep rate: 100 mV•s^{-1}. Calculated nature of the highest occupied orbitals of **1b** and **2b** and their cation radicals.

The general electrochemical behaviors of **1b−d** and **2b−d** (see SI) are exemplified with **1b** and **2b** (Figure 2). Each compound is oxidized along three successive isoelectronic oxidation steps as more clearly depicted with the differential pulse voltamogram (DPV) (inset Figure 2). The first monoelectronic oxidation (E^1; peak potential obtained from CV) occurs at 1.45 V for **1b** and at a significantly lower potential (1.20 V) for **2b**. It is well-known that the oxidation of π-stacked systems is more facile than their nonstacked analogues.[11,12] The "phenyl-fluorene-phenyl" cofacial arrangement present in **2b** is thus likely at the origin of its observed low oxidation potential. Analogous observations, highlighting interactions between two stacked aryl moieties, were reported by Rathore and co-workers for bichromophoric dibenzobicyclo[4.4.1]undecane or oligofluorene derivatives.[11,12] Theoretical calculations indicate that the HOMOs of **1b** and **2b** have a mixed character with nevertheless major coefficients found on the indenofluorene core for **1b** and on the "phenyl-fluorene-phenyl" moieties for **2b** (Figure 2). Accordingly, the SOMOs of **1b**$^{\bullet+}$ and **2b**$^{\bullet+}$, involved in the second monoelectronic oxidation ($E^2 = 1.55$ V for **1b** and 1.36 V for **2b**), are centered on the "phenyl-fluorene-phenyl" moieties for **1b**$^{\bullet+}$ and on the indenofluorene core for **2b**$^{\bullet+}$.

The shape of the **1b−d** UV−vis spectra consists of a large absorption band comprising four maxima at ca. 314, 330,

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(8) Selected data for **2b**: $C_{141}H_{88}F_8$, $M = 1934.11$, triclinic, space group $P\bar{1}$, $a = 14.2342(8)$ Å, $b = 16.3982(11)$ Å, $c = 23.0578(15)$ Å, $\alpha = 106.176(2)°$, $\beta = 91.373(2)°$, $\gamma = 106.571(2)°$, $V = 4922.9(5)$ Å^3, $Z = 2$, $T = 100$ K, Mo Kα ($\lambda = 0.710\,73$ Å) $Dc = 1.305$ g•cm^{-3}, m(Mo) = 0.085 mm^{-1}, 57 009 reflections measured, of which 22 263 independent ($R_{int} = 0.0959$), $R_f = 0.0758$ [15 093 data, $I > 2\sigma(I)$], $wR(F^2) = 0.2013$, GOF = 1.082.

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(13) Comparison of the cyclic voltammograms shows the different solubility of **1b** and **2b** polycations. Indeed, an adsorption/desorption process is evident on the CV of **1b**, while the three redox waves of **2b** are all diffusion controlled. This observation is consistent with the fact that **DSF-IFs 2** are always more soluble than their corresponding **DSF-IF 1** congeners.

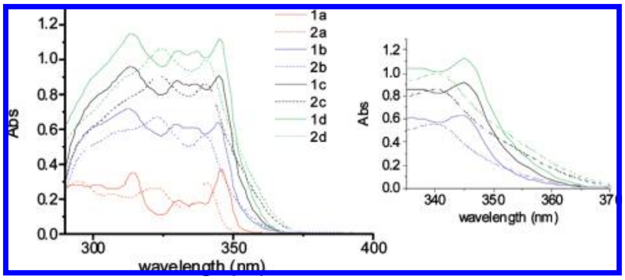

Figure 3. Absorption spectra of **1a**−**d** and **2a**−**d** (10^{-5} M in THF). Inset: focus on the 335/365 nm portion of the spectra.

336, and 345 nm (Figure 3, solid lines). Despite the broadness of these absorption bands, the four maxima fit well with both those of **1a**[6] and those of known chromophores containing the "phenyl-fluorene-phenyl" moieties.[14,15] The broader spectra of **1b**−**d**, compared with that of **1a**, are rationalized by the combined contributions of two chromophores (namely, the "phenyl-fluorene-phenyl" moieties and the indeno[1,2-*b*]fluorene core) and by the rotational freedom of the phenyl rings around the C−C bonds joining the fluorene and phenyl units.[16] Thus, despite the extension of conjugation of the fluorene units with the phenyl rings, the lowest energy transition is assigned to the indeno[1,2-*b*]fluorene core and is detected at 345 nm for all molecules, as previously observed for **1a**. For the phenyl-substituted **DSF-IFs 2b**−**d**, the UV−vis absorption spectra (Figure 3, dashed lines) also exhibit broad bands, with two maxima at ca. 323 and 340 nm. The lowest energy transition at 340 nm is found for all **DSF-IFs 2b**−**d** and fits well with that of **2a**. This transition is ascribed to the indeno[2,1-*a*]fluorene core, similarly to the above discussion on the **DSF-IF 1** molecules. In addition, the band in **2b**−**d** observed at ca. 320 nm is assigned to the "phenyl-fluorene-phenyl" moieties and is blue-shifted compared to the corresponding large split band (330/336 nm) of **1b**−**d**. Another significant feature is the absorption onset of **2b**−**d**, which is always found at higher intensity and wavelength than those of **1b**−**d**, respectively (see inset of Figure 3 focusing on the low energy part of the spectra). Similar features in the absorption spectra of other molecular systems containing two chromophores in a face-to-face arrangement have been previously reported in the literature and assigned to intramolecular excitonic interactions in the ground state.[17−20]

The fluorescence spectra of **1b**−**d** in THF (Figure 4a) display an intense contribution with well-resolved vibrational features at 360/368 and 377/385 nm and a relatively small Stokes shift[21] of 15/23 nm. The fact that the fluorescence spectra are better resolved than the absorption spectra suggests that, in the excited state, the bonds joining the fluorene and the phenyl rings acquire some double bond character, giving rise to a more rigid/planar structure.[16] Moreover, the emission maxima of **1b**−**d** are consistent with those reported in the literature for chromophores containing the "phenyl-fluorene-phenyl" moieties.[14,15] The emission band for **1b**−**d** is red-shifted with respect to **1a** due to the important contributions of the phenyl rings leading to a more conjugated excited state. This effect has been previously observed with indenofluorene derivatives.[22] The fluorescence spectra of **DSF-IFs 2** were also studied in solution (Figure 4b). **2a** presents two well-resolved emission bands at 346 and 365 nm.[6] The very small Stokes shift (6 nm) leads us to conclude that the **DSF-IF 2** core is highly rigid, restricting structural deformation upon photoexcitation. Interestingly, **DSF-IFs 2b**−**d** exhibit a significantly different behavior than **2a**. Indeed, for **2b**−**d**, a large, structureless, and red-shifted band (with respect to **1b**−**d**) is observed with maxima, respectively, at 450, 413, and 454 nm (Figure 4b). At this stage, this large band can be tentatively assigned to an intramolecular excimer formation, as previously observed for example by Scherf and co-workers for oligophenyl based cruciforms.[23] Moreover, and in contrast to **1b**−**d**, the Stokes shifts become extremely large, i.e. 110 nm (**2b**), 73 nm (**2c**), and 114 nm (**2d**), highlighting the dramatic effect of the face-

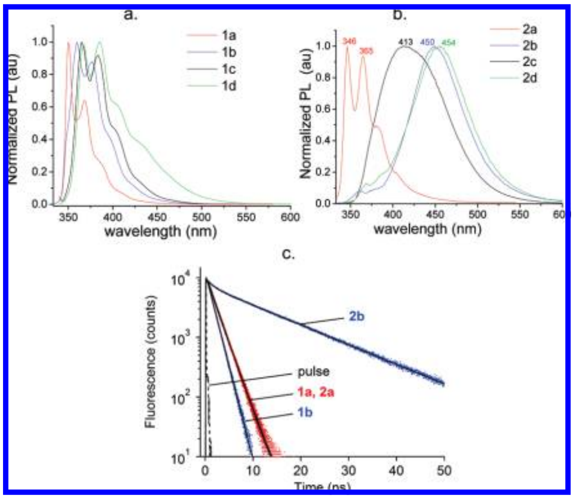

Figure 4. Emission spectra (10^{-6} M in THF) of (a) **1a**−**d** ($\lambda_{exc} = 345$ nm); (b) **2a**−**d** ($\lambda_{exc} = 340$ nm). (c) Fluorescence decay curves of **1a**−**b**/**2a**−**b** (THF). $\lambda_{exc} = 330$ nm, $\lambda_{em} = 375$ nm (**1a**−**b**, **2a**) or 450 nm (**2b**).

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Table 1. Optical Properties of **DSF-IFs 1** and **2**

	λ_{abs} (nm)[a]	λ_{em} (nm)[a]	$\lambda_{em} - \lambda_{abs}$ (nm)	Φ_{sol} (%)[b]
1b	313, 329, 336, 345	360, 377, 397[c]	15	77
2b	308,[c] 323, 340	450	110	30
1c	314, 331, 337, 345	365, 384, 403[c]	20	77
2c	310,[c] 323, 340	413	73	48
1d	314, 331, 337, 345	368, 385, 406,[c] 432[c]	23	77
2d	310,[c] 324, 340	454	114	30

[a] Measured in THF ($C = 10^{-6}$ M), [b] Quantum yields in solution (ϕ_{sol}) were calculated relative to quinine sulfate (see Supporting Information).[22] [c] Shoulder.

to-face "phenyl-fluorene-phenyl" arrangement in these molecules (Table 1).

The fluorescence decay curves also show a marked difference between **DSF-IFs 1** and **2**. Indeed, the decay curves of **1a−d** and **2a** were successfully fitted by single exponentials (Figure 4c), and their lifetimes were measured in the range 1.1 to 2.0 ns. On the other hand, **2b−d** showed a much more complex behavior. The emission decays were found to be multiexponential, and the mean time-constants were calculated to be much longer ($\langle\tau\rangle \approx 5-15$ ns). As typical examples, fluorescence decay curves of **1a−b** and **2a−b** are shown in Figure 4c. Despite their different geometries, **1a** and **2a** show almost identical lifetimes, respectively $\tau_F = 1.93 \pm 0.07$ ns and $\tau_F = 1.83 \pm 0.02$ ns. The lifetime of **1b** is slightly shorter ($\tau_F = 1.34 \pm 0.02$ ns). A totally different behavior is observed for **2b**. Hence, its fluorescence decay curve needed at least three time constants to reach a satisfactory fit ($\chi_R^2 < 1.2$) with a major contribution of a quite slow component (13.0 ± 0.1 ns). This marked difference in the fluorescence decay behaviors provides another eloquent illustration of the unique effect of the "phenyl-fluorene-phenyl" cofacial arrangement.[20]

DSF-IFs 1a and **2a** both possess a high quantum yield (*ca.* 70%).[6] The substitution of the fluorene rings with phenyl arms in **1b−d** does not affect the quantum yield that remains at ∼75% (Table 1). However in **2b−d**, the introduction of the phenyl rings leads to a strong decrease in the quantum yield, i.e. 30/48% (Table 1). Hence, compared to their congeners in the **DSF-IF 1** family, **DSF-IFs 2b−d** possess a broad and a red-shifted emission band[23] associated with long and multiexponential decay curves[20] and a lower quantum yield. Thus, it is reasonable to contend that the emission in **2b−d** arises from intramolecular excimers.[11,20,24,25] Finally, in **2b−d**, the emission wavelength can be easily tuned by the careful choice of the steric bulk of the substituents borne by the phenyl rings. Indeed, in the **2b−d** series, **2c** possesses the smallest Stokes shift (73 nm), the highest quantum yield (48%), and a dissymmetric blue-shifted emission band ($\lambda = 413$ nm) (Figure 4b). These differences found for **2c** have been ascribed to a larger steric hindrance between the face-to-face phenyl rings, induced by their *tert*-butyl substituents, leading to weaker $\pi-\pi$ interactions in the excited state. It can thus be concluded that the structural environment of the phenyl rings plays a crucial role in the tuning of the emission color of this unique new family of fluorophores.

In summary, we have discussed and rationalized the properties of two new families of aryl-substituted **DSF-IFs 1** and **2**, possessing different geometric profiles. The original geometry of the **DSF-IF 2b−d** family, with face-to-face "phenyl-fluorene-phenyl" moieties, leads to excimer emission through intramolecular interactions in the excited state. Moreover, these molecules possess not only large Stokes shifts but also remarkable tunable optical properties. Indeed, the emission colors can be easily modulated through the steric hindrance between the adjacent substituted phenyl rings.

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Supporting Information Available: Full characterization of **DSF-IF 1b−d** and **2b−d**, ^{1}H/^{13}C NMR spectra, electrochemical and crystallographic data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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