

Dispirofluorene-indenofluorene (DSFIF): Synthesis, Electrochemical, and Optical Properties of a Promising New Family of Luminescent Materials

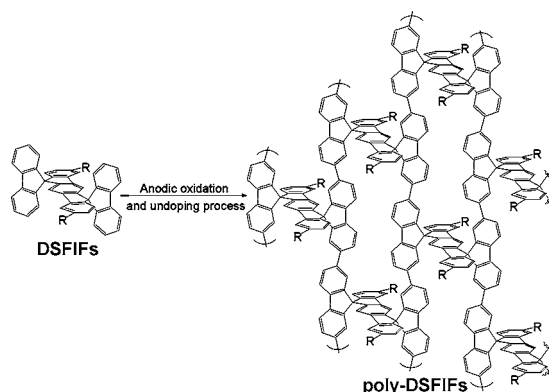
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ABSTRACT



A series of new dispiro[fluorene-9',6,9'',12-indeno[1,2b]fluorenes] (DSFIFs) that combine indenofluorene (IF) and spirobifluorene (SBF) architectural specificities have been prepared. Their anodic oxidations lead to the formation of nonsoluble transparent polymers. The photophysical and electrochemical properties of these new molecules have been evaluated for further blue OLED applications.

Poly-2,7-(9,9-dialkyl)fluorenes (PFs) and copolymers are among the most promising blue light emitting materials despite the problem of their long-term color stability.¹

The unsuitable low green-band emission generated during operation has been assigned to π -aggregation or excimer formation and on-chain defects.² To suppress it, many studies have been done by modifying the steric demand and

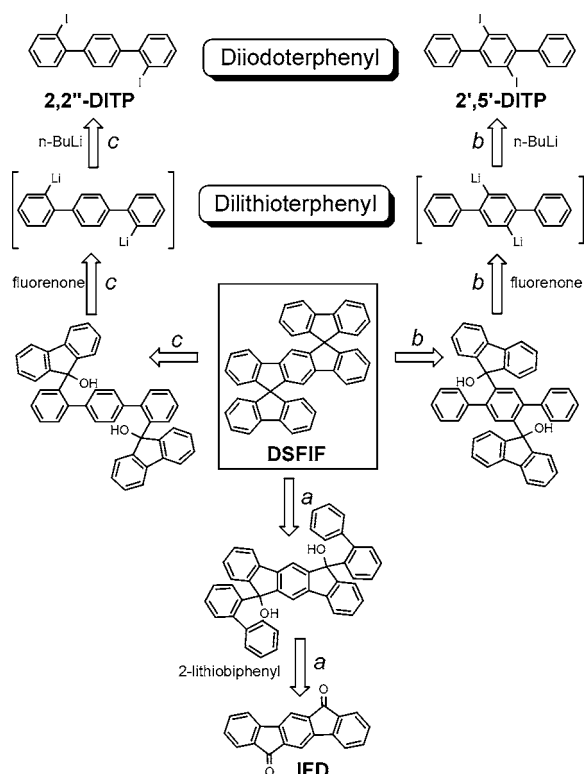
incorporating or building the conjugated polymers with requisite moieties of defined hindrance. In this aim, the spiro linkage has been used to minimize interchromophore packing. Indeed a better color stability has been obtained with spirobifluorene (SBF) units in more amorphous spirobifluorene-fluorene copolymers³ and more recently in polyspirobifluorenes.⁴ On the other hand, the introduction of the indenofluorene (IF) unit in various copolymers has also led

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Scheme 1



to a strong enhancement of the OLED properties.⁵ Interestingly, a new tendency consists of developing highly conjugated molecules of well-defined lengths displaying similar spectroscopic features at the single chromophore level.⁶ To obtain blue light emitting molecules or materials with long-term stability, we designed a new family of versatile electropolymerizable chromophores combining both IF and SBF architectural specificities.

In this communication we report a concrete, well-described route to dispiro[fluorene-9',6,9'',12-indeno[1,2*b*]fluorenes] (DSFIFs) as a new rigid ladder-type family of macromolecules. Their photophysical and electrochemical characteristics have been evaluated for further OLED applications.

The prototypical DSFIF (Scheme 1) can be considered as the joining of two SBF moieties through a shared phenyl ring. Since 9,9'-spirobifluorene can be easily obtained by Clarkson and Gomberg procedure,⁷ it seemed reasonable to adopt a similar strategy starting from either indeno[1,2-*b*]fluorene-6,12-dione (IFD)⁸ and 2-lithiodiphenyl (route a) or from dilithioterphenyl and fluorenone (routes b or c) (Scheme 1).

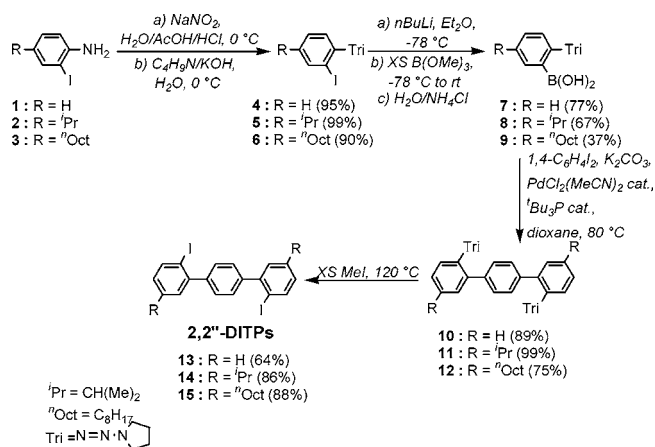
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Scheme 2

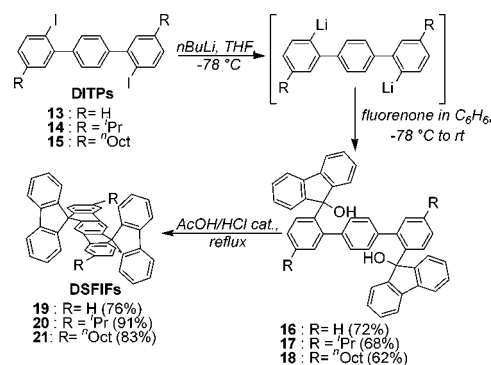


These later methods allow access to the diiodoterphenyl DITP patterns and in particular to the 2,2''-[1,1',4',1'']-diiodoterphenyl compound (2,2''-DITP) we were interested in for further synthetic purposes (route c).

To avoid long and sophisticated multistep syntheses, we developed an expedient method toward 2,2''-DITPs, which were the key molecules in our approach, involving original arylboronic acids bearing a triazene moiety in the *ortho* position readily convertible into iodide (Scheme 2). *o*-Triazenylboronic acids were obtained in a two-step sequence from the corresponding substituted diazotized *o*-iodoanilines **1–3** in situ quenched by pyrrolidine in basic medium. The resulting *o*-iodoaryltriazenes **4–6** were then converted into their corresponding boronic acids **7–9** by a standard lithiation/borylation sequence involving *n*-butyllithium and trimethylborate. Suzuki–Miyaura coupling⁹ of functionalized *o*-triazenylboronic acids with *p*-diiodobenzene afforded 2,2''-bis(triazenyl)terphenyl compounds **10–12**, which were converted into 2,2''-DITPs **13–15** in good isolated yields by a subsequent treatment with excess of methyl iodide.¹⁰

The lithium–iodine exchange of 2,2''-DITPs **13–15** with *n*-butyllithium in THF at low temperature followed by quenching with a solution of fluorenone in benzene afforded the corresponding diols **16–18**, which were finally heated to reflux with AcOH/HCl to lead to the corresponding

Scheme 3



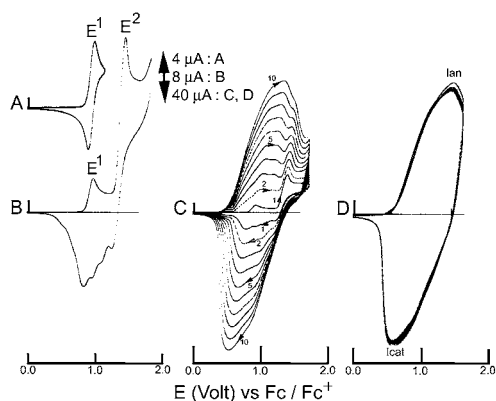


Figure 1. Cyclic voltammetry in CH_2Cl_2 ($n\text{Bu}_4\text{NPF}_6$ 0.2 M). (A–C) In the presence of **19** (3×10^{-3} M), 1 sweep between 0.0 and 1.2 V (A), 1 sweep between 0.0 and 1.9 V (B), and 10 cycles between 0.0 and 1.8 V (C). (D) In a **19** monomeric free solution. Working electrode: 1 mm diameter Pt disk (A–C); Pt modified during oxidation of **19** in C (D). Sweep rate $100 \text{ mV}\cdot\text{s}^{-1}$.

DSFIFs **19–21** that were isolated as white solids with 51–62% overall yield (Scheme 3).

The electrochemical behaviors of **19–21** have been investigated. Figure 1A–C present the cyclic voltammograms (CVs) recorded during the anodic oxidation of **19**.

The CV recorded between 0.0 and 1.2 V (Figure 1A) exhibits one reversible wave (E^1 , 1.03 V ref. Fc/Fc^+). Iterative cycles in this potential range do not show any modification of the CV nor of the electrode surface. This first reversible oxidation process leads to the oxidation of the indenofluorenyl part of DSFIF (**19**), which takes place at 1.25 V/ECS in the case of the IF.¹¹

This reversible wave is followed by a second irreversible one (Figure 1B) whose maximum occurs at 1.47 V (E^2), a slightly more positive value compared to the SBF second oxidation wave.¹² A similar behavior is observed during the oxidation of **20** and **21** ($E^1 = 0.96$ and 1.04 V; $E^2 = 1.48$ and 1.58 V, respectively). When scanning in a potential range

Table 1. Optical Properties of DSFIFs

	λ_{abs} (nm) ^c	λ_{em} (nm) ^c
19	231, 254, 300, 311, 330, 337, 345	367
20	231, 254, 300, 311, 333, 340, 348	372
21	228, 254, 301, 312, 334, 341, 349	373
F	227, 265, 290, 301	310
SBF	229, 252, 297, 309	325
poly- 19	300–450 ^a , 311 ^b , 345 ^b	

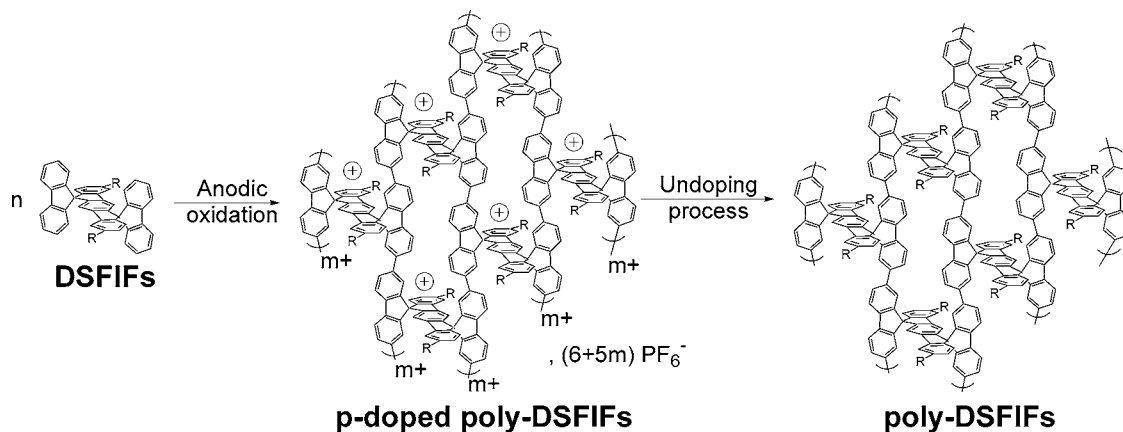
^a Large band between 300 and 450 nm ^b Fine band within the large band ^c Measured in CH_2Cl_2

including the two waves (Figure 1C), the CVs show the appearance and the regular growth of new reversible waves between 0.55 and 1.6 V due to the formation of a new electroactive species. When removed from the electrochemical solution after the 10th sweep, rinsed in dichloromethane, and then studied in a new electroactive species free solution, the electrode presents the profile shown in Figure 1D. This CV exhibits only one reversible wave with threshold and maximum potential (I_{an}) at 0.55 and 1.52 V, respectively. This feature clearly indicates the presence of a film at the electrode surface as a consequence of the **19** electropolymerization.

The electrochemical behavior of poly(**19–21**) is similar. The $I_{\text{an}}/I_{\text{cat}}$ wave corresponds to the reversible oxidation of the indenofluorene moieties together with the reversible p-doping/dedoping process. The comparison of the electrochemical properties of the film resulting, respectively, from DSFIFs and SBF electropolymerizations indicates that anodic oxidation of DSFIFs leads to carbon–carbon coupling involving the fluorene units at the classical 2 and 7 carbon atoms (Scheme 4). Indeed, the cation radical of the IF moieties is too stable in the CV time scale to allow their polymerization.

The UV–vis absorption of **19–21** was studied in solution and compared with the UV–vis absorption of F, SBF, and with the solid-state UV–vis absorption of poly-**19** (Table 1). F and SBF have similar absorption spectra, displaying a

Scheme 4



maximum around 300–310 nm. The electronic spectra of **19–21** present absorption bands around 230, 254, 300, and 310 nm as for F and SBF and three additional bands around 330–335, 335–340, and 345–350 nm. These bands are in accordance with the absorption band of IF.¹¹

Poly-**19** spectrum exhibits a large absorption band between 300 and 350 nm also present as the main absorption band in poly-SBF with two observable sharp bands at 311 and 345 nm due to the presence of IF patterns in the matrix.

The photoluminescence of soluble **19–21** was studied in CH₂Cl₂ and compared with F and SBF properties in order to evaluate the efficiency of these molecules as key structures for further OLED applications. The observed emission wavelength (Table 1) is bathochromically shifted from 310 nm for F and 325 nm for SBF to 367, 372, and 373 nm for **19**, **20**, and **21**, respectively. These emission wavelengths are close to those of IF reported in CHCl₃ solution (λ_{em} : 374 nm).¹³ Furthermore, in CH₂Cl₂ solution, **19** displays a fluorescence quantum efficiency of 1.5% magnified 150 and

7.5 times by comparison with F (0.01%) and SBF (0.20%) in the same conditions.

In summary, we have prepared, via a simple and original route, a series of new blue light emitters. These highly π -conjugated macromolecules combine IF and SBF architectural and optical properties. The preliminary results show that electrochemical oxidation enables the formation of polymer films at the electrode surface with high yield. Most interestingly, the examination of the DSFIF emission properties shows an important stimulation of the quantum fluorescence efficiency with respect to their constituting IF and SBF building blocks. Investigations in OLED's applications are currently underway.

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Supporting Information Available: Experimental procedure and spectroscopic characterization of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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