### Blue Emitting 3π–2 Spiro Terfluorene–Indenofluorene Isomers: A Structure– Properties Relationship Study

### Cyril Poriel,\*<sup>[a]</sup> Joëlle Rault-Berthelot,\*<sup>[a]</sup> Damien Thirion,<sup>[a]</sup> Frédéric Barrière,<sup>[a]</sup> and Laurence Vignau<sup>[b]</sup>

**Abstract:** Two novel terfluorenyl derivatives, 2,2'',7,7''-tetrakis(9,9-dioctyl-9*H*fluoren-2-yl)dispiro[fluorene-9,11'indeno-(2,1-*a*)-fluorene-12',9''-fluorene] ((2,1-*a*)-DST-IF) and 2,2'',7,7''-tetrakis(9,9-dioctyl-9*H*-fluoren-2-yl)dispiro-[fluorene-9,6'-indeno-(1,2-*b*)-fluorene-12',9''-fluorene] ((1,2-*b*)-DST-IF) have been synthesized by two different synthetic approaches. These terfluorenyl derivatives possess a different central indenofluorene or (1,2-*b*)-indenofluorene, which imposes two distinct geometry profiles, and different structural environments for the terfluorenyl fluorophores that translates into drastically different optical and electrochemical properties for (2,1-a)-DST-IF and (1,2-b)-DST-IF. These properties have been carefully studied through a combined experimental and theoretical approach.

**Keywords:** blue-emitting materials • indenofluorene • OLEDs • semiconductors • spiro compounds • terfluorene The (2,1-*a*)-DST-IF isomer has been successfully used as emitting layer in a blue single-layer small-molecule organic light-emitting diode (SMOLED) and appears as the first example of a blue emission arising from intramolecular terfluorenyl excimers. Regarding the importance of terfluorenyl derivatives in organic electronics, the present structure–properties relationship study, may open new avenues in the design of efficient blue fluorophores.

### Introduction

Organic  $\pi$ -conjugated materials are of great interest for organic electronics such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells.<sup>[1,2]</sup> Among the organic  $\pi$ -conjugated materials, polyfluorenes and oligofluorenes are very promising candidates for blue OLED applications due to their high luminescent efficiency and good charge-carrier mobility.<sup>[3-9]</sup> In this context, terfluorene derivatives have emerged as an appealing class of materials, presenting, for example, intriguing ambipolar carrier-transport properties.[10] Various terfluorenyl derivatives have hence been investigated over the last ten years not only for blue OLEDs<sup>[11-14]</sup> but also for lightemitting OFETs (LE-OFETs).<sup>[15]</sup> As the molecular structure of the active layer is of key importance in LE-OFET and OLED devices, different molecular designs of the terfluorenvl backbone have thus been developed, including the incorporation of heterocycles,[16-18] hydroxyaminophenyl side

[a] Dr. C. Poriel, Dr. J. Rault-Berthelot, D. Thirion, Dr. F. Barrière Université de Rennes 1-CNRS UMR 6226
"Sciences Chimiques de Rennes"-MaCSE group, Bat. 10 C Campus de Beaulieu - 35042 Rennes Cedex (France) E-mail: cyril.poriel@univ-rennes1.fr joelle.rault-berthelot@univ-rennes1.fr
[b] Dr. L. Vignau

Université de Bordeaux - IMS/UMR CNRS 5218-site ENSCBP 16 Avenue Pey-Berland - 33607 Pessac cedex (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102212.

chains,<sup>[19]</sup> cyclopropane,<sup>[20]</sup> and spiro bridges.<sup>[10-12,15,16,21,22]</sup> The introduction of a spiro bridge into small molecules is indeed an efficient strategy to reduce the crystallization tendency of the materials, enhancing their solubility, thermal stability, and quantum yield.<sup>[23]</sup> For the last few years, our group has been involved in the synthesis of original blue fluorescent emitters based on a unique  $3\pi$ -2 spiro architecture, in which a central indenofluorene or ladderpentaphenylene is connected through two spiro carbons to two other  $\pi$ -conjugated systems such as xanthene,<sup>[24,25]</sup> fluorene,<sup>[26-30]</sup> 2,7-dialkyl fluorene,<sup>[31,32]</sup> or 2,7-diaryl fluorene<sup>[33,34]</sup> units. These materials, due to their specific three-dimensional architectures, possess appealing properties for blue OLED applications. In addition, we recently demonstrated that the fluorescent properties of 2,7-diaryl fluorenes with a  $3\pi$ -2 spiro architecture may be easily tuned not only by the nature of the different  $\pi$ -systems but also by their geometric profiles.<sup>[33,34]</sup> The present study describes the structure-properties relationships between two novel blue-emitting terfluorenyl materials with a  $3\pi$ -2 spiro architecture, namely (2,1-a)-DST-IF and (1,2-b)-DST-IF, which possess two terfluorenyl units connected to an indenofluorenyl backbone (see molecular structures in Scheme 1 and 2). These two regioisomers, which present distinct profiles due to the different geometry of their indenofluorenyl central cores, (2,1-a)-indenofluorene for (2,1-a)-DST-IF and (1,2-b)-indenofluorene for (1,2b)-DST-IF, respectively, possess cofacial terfluorenyl moieties or not. To the best of our knowledge, this molecular design, which involves the connection of terfluorenyl units to an indenofluorenyl framework, has never been reported



to date and appears to provide an appealing strategy to tune terfluorene properties. As the synthesis of new materials for electronics applications is strongly sought after worldwide, it remains highly important to develop efficient routes towards promising fluorophores, such as terfluorenyl derivatives, to fully explore their potential for organic electronics applications. Herein, we first report our rational synthetic investigations towards the synthesis of the two terfluorenyl derivatives (2,1-a)-DST-IF and (1,2-b)-DST-IF. Then, their electrochemical and optical properties, which appear to be drastically different due to their different geometry profiles, will be carefully studied through a combined experimental and theoretical approach. Finally, (2,1-a)-DST-IF, which surprisingly presents very different fluorescence properties in solution and in the solid state, has been successfully used in a single-layer blue small-molecule organic light-emitting diode (SMOLED) with an electroluminescence spectrum arising from terfluorenyl excimer emission. The (2,1-a)-DST-IF and (1,2-b)-DST-IF derivatives appear to be the first examples of dispirofluorene-indenofluorene derivatives with a HOMO-LUMO gap almost exclusively controlled by the terfluorenyl units and not by their indenofluorenyl unit.

### **Results and Discussion**

**Synthesis**: Recently, our group has developed several original synthetic approaches towards various blue fluorophores with the (2,1-a)-indenofluorenyl backbone.<sup>[28,32,33]</sup> One of these synthetic approaches involved an intramolecular bicyclization of a difluorenol in the last step (see Scheme 1, bottom).<sup>[32]</sup> This intramolecular bicyclization reaction usually leads to a mixture of regioisomers with the (2,1-a)-indenofluorenyl core found in (2,1-a)-DST-IF or the (1,2-b)-

indenofluorenyl core found in (1,2-b)-DST-IF. After mechanistic analyses of the reaction for aryl- and alkyl-substituted difluorenols, we were able to direct the synthesis preferentially towards one positional isomer over the other by altering medium and through steric effects.<sup>[31,32]</sup> Indeed, these mechanistic investigations have shown that the bulkiness of the substituents borne by the fluorenyl units of the difluorenol dictates the ratio of the regioisomers formed. Thus, the very bulky 9,9-dioctylfluorene attached to the fluorenyl units of the difluorenol 6 (Scheme 1) should, in principle, lead almost exclusively to the isomer (2,1-a)-DST-IF. However, as the nature of the solvent and the temperature of this intramolecular cyclization reaction allow also a fine tuning of the isomer ratio,<sup>[31,32]</sup> it should also be possible, in principle, to drive the reaction towards the formation of the positional isomer (1,2-b)-DST-IF. Thus, this synthetic strategy (route 1, Scheme 1) would theoretically allow access not only to the terfluorene derivative (2,1-a)-DST-IF but also to its positional isomer (1,2-b)-DST-IF. Route 1 starts with the dialkylation of the commercially available 2-bromofluorene in the presence of octyl bromide in basic medium, which leads to 2-bromo-9,9-dioctylfluorene (1) in 99% yield.<sup>[29]</sup> The lithium-bromine exchange of 1 with *n*-butyllithium at low temperature, followed by addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane easily afforded the 2-fluorene boronate 2.<sup>[29]</sup> Further reaction of 2 with 2,7-dibromofluoren-9-one (4) under Suzuki-Miyaura cross-coupling conditions with  $[Pd^{0}(PPh_{3})_{4}]$  as the catalyst and sodium carbonate as the base in a mixture of toluene and water (3/1) led to the terfluonenone 5 in 85% yield.<sup>[35]</sup>

With **5** in hand, the access to (2,1-a)-DST-IF and (1,2-b)-DST-IF required its coupling with diiodoterphenyl 2,2"-DITP **3** prepared according to a literature procedure.<sup>[27]</sup> Thus, the lithium–iodine exchange of 2,2"-DITP at -78 °C,



Scheme 1. Synthesis of terfluorenone 5 (top) and of (2,1-a)-DST-IF and (1,2-b)-DST-IF (route 1 bottom). TEBAC=triethyl benzyl ammonium chloride.

14032 \_\_\_\_\_

www.chemeurj.org

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 2. Synthesis of (2,1-*a*)-DST-IF and (1,2-*b*)-DST-IF (route 2).

followed by the addition of the terfluorenone 5 afforded the corresponding difluorenol 6 with the 9,9-dioctylfluorenyl units attached to the fluorenol cores in 25% yield. As mentioned above, our group has carried out detailed studies on the intramolecular aromatic electrophilic cyclization of difluorenol derivatives such as  $6^{[31,32]}$  Notably, we have recently shown that a polar solvent, combined with very bulky substituents attached to the fluorenyl units (here a 9,9-di <-< octylfluorene in 6), favors the synthesis of the isomer with the (2,1-a)-indenofluorenyl core. The opposite leads preferably to the isomer with the (1,2-b)-indenofluorenyl core. Thus, the intramolecular cyclization of difluorenol 6 in acetonitrile, a polar and donor solvent,<sup>[36]</sup> led to the formation of the expected two positional isomers (2,1-a)-DST-IF and (1,2-b)-DST-IF in a 9/1 ratio.<sup>1</sup> However, the separation of the two isomers by column chromatography turned out to be problematic due to the small difference in the retention factors between the isomers, which hinders isolation. Thus, following the route 1, only the isomer (2,1-a)-DST-IF was obtained as a pure product. Screening for solvents and temperatures in the light of our previous mechanistic studies<sup>[32]</sup> allowed us to slightly increase the amount of (1,2-b)-DST-IF over (2,1-a)-DST-IF. In dichloromethane, a low polarity, weak donor solvent,<sup>[36]</sup> the amount of (1,2-b)-DST-IF over (2,1-a)-DST-IF reaches almost 25%, but we still did not manage to isolate (2,1-a)-DST-IF as a pure product. In the light of these results, the synthetic approach has been modified keeping in mind that the size of the substituents borne by the fluorene units is paramount in controlling the (1,2-b)-DST-IF and (2,1-a)-DST-IF ratio. The key feature in the second approach (route 2, Scheme 2) is to favor the formation of the (1,2-b)-indenofluorenyl core, through the control of the size of the substituents borne by the fluorenyl units, prior to the elaboration of the terfluorenyl backbone. We then decided to focus on the synthesis of the difluorenol **7** with less bulky bromine substituents attached to the fluorenol units, which should, in principle, favor the formation of the (1,2-b)-indenofluorenyl core (Scheme 2).

Thus, the coupling of 2,2"-DITP 3 with 2,7-dibromofluorenone (4) (nBuLi/THF/-78°C) easily leads to the diol 7 with a particularly high yield (60%) for this type of coupling reaction. This high yield may be rationalized by the electronic effect of the two electron-withdrawing bromine atoms on the carbonyl group of the fluorenone 4. The intramolecular cyclization of the diol 7 under the same conditions as those mentioned above for the cyclization of 6, that is CH<sub>3</sub>CN/reflux, leads to the formation of the two tetrabrominated isomers 8 and 9 with an isomer distribution of 45/55. In addition, when the intramolecular cyclization is carried out in dichloromethane, a low polarity, weak donor solvent,<sup>[36]</sup> at room temperature, a significant excess of the isomer 9 with the (1,2-b)-indenofluorenyl core  $(8/9 \sim 3/7)$  is obtained. Compounds 8 and 9 are very insoluble in common organic solvents and no separation could be achieved. The mixture of isomers 8 and 9 nevertheless undergoes a Suzuki-Miyaura cross-coupling reaction in the presence of 2-fluorene boronate 2 leading to the mixture of (2,1-a)-DST-IF and (1,2-b)-DST-IF in a 3/7 ratio. The (1,2-b)-DST-IF derivative, now in large excess, was then further purified by column chromatography. Despite (2,1-a)-DST-IF and (1,2b)-DST-IF being closely related positional isomers, their <sup>1</sup>H NMR spectra differ significantly. An important feature is related to the differences observed between the chemical shifts of the hydrogen atoms of the indenofluorenyl cores of (2,1-a)-DST-IF and (1,2-b)-DST-IF. Thus, (2,1-a)-DST-IF

www.chemeurj.org

14033

<sup>&</sup>lt;sup>1</sup> Determined by the analysis of the crude mixture by <sup>1</sup>H NMR spectroscopy. For additional details see reference [32].



effect observed in (2,1-a)-DST-IF has been assigned to intramolecular  $\pi$ - $\pi$  interactions between face-to-face terfluorenyl moieties. Indeed, transannular  $\pi$ - $\pi$  interactions are usually accompanied by high-field shifts in <sup>1</sup>H NMR spectra and have been observed in different systems such as acridylnaphthalene,<sup>[37]</sup> paracyclophane,<sup>[38]</sup> polyfluorene,<sup>[39,40]</sup> or ethynyltriphenylene<sup>[41]</sup> or thiophene derivatives.<sup>[42]</sup> Thus,  $\pi - \pi$  interactions occur between the two cofacial terfluorenyl moieties of (2,1-a)-DST-IF and should lead to sigdifferent electronificantly chemical and optical properties compared to its isomer (1,2-b)-DST-IF, as discussed next.

Thermal properties: The thermal properties of (2,1-a)-DST-IF and (1,2-b)-DST-IF were investigated by using thermogravimetric analysis (TGA) (Figure 2). The (2,1-a)-DST-IF and (1,2-b)-DST-IF derivatives exhibit a high decomposition temperature  $T_d$ , corresponding to 5% weight loss<sup>[23]</sup> (315

Figure 1. Low-field portion of the  ${}^{1}HNMR$  spectra (CDCl<sub>3</sub>) of (2,1-*a*)-DST-IF (top) and (1,2-*b*)-DST-IF (bottom).

presents, for example, a low-field singlet at  $\delta = 8.13$  ppm, which is assigned to the hydrogen atom  $H_2$  of the central phenyl ring of the (2,1-a)-indenofluorenyl core (Figure 1, top), whereas (1,2-b)-DST-IF presents a singlet at  $\delta =$ 7.43 ppm, which is assigned to the hydrogen atom  $H_2$  of the central phenyl ring of the (1,2-b)-indenofluorenyl core (Figure 1, bottom).<sup>2</sup> Similarly, the hydrogen atom  $H_1$  of (2,1a)-DST-IF and (1,2-b)-DST-IF are found at  $\delta = 6.23$  and 6.81 ppm, respectively. The chemical shifts of the hydrogen atoms of the indenofluorenyl core in (2,1-a)-DST-IF are hence significantly different compared to those of (1,2-b)-DST-IF, whereas their two non-substituted parent indenofluorenes, that is (2,1-a)-indenofluorene and (1,2-b)-indenofluorene, present almost identical chemical shifts for all their hydrogen atoms.<sup>[34]</sup> This has been assigned to the different arrangement of the fluorene units (face-to-face or not), which differently affects the resonance of the hydrogen atoms of the indenofluorenyl cores. Indeed, all the signals of the hydrogen atoms of the terfluorenyl moieties of (2,1-a)-DST-IF such as H<sub>3</sub> (Figure 1) appear to be strongly deshielded compared to those of (1,2-b)-DST-IF. This shielding

and 320°C, respectively). Moreover, TGA shows the presence of two steps in the thermal decomposition processes. The first decomposition step involves around 43% of mass loss for both isomers (Figure 2). This first decomposition is ascribed to the loss of the eight octyl chains borne by the four external fluorene units of (2,1-a)-DST-IF and (1,2-b)-DST-IF.<sup>[43]</sup> After the first decomposition step, a plateau is recorded until around 550°C for (2,1-a)-DST-IF and around 620°C for (1,2-b)-DST-IF. The second decomposition step may be ascribed to the decomposition of the DST-IF backbones. Similar terfluorene derivatives bearing alkyl and/or aryl groups on the fluorene bridges have been previously reported in the literature for which the  $T_{d}$  values are strongly related to the substitution of their fluorene bridges (alkyl vs. aryl).<sup>[12,21]</sup> It is important to stress that a high  $T_d$  value is an asset for OLED applications, as Joule heating occurs under typical operating conditions.<sup>[44]</sup>

**Optical properties:** As (2,1-a)-DST-IF and (1,2-b)-DST-IF combine both dispirofluorene–indenofluorene (DSF-IF) and terfluorene frameworks, it was of interest to compare their optical properties with those of the two constituting building blocks: (2,1-a)-DSF-IF,<sup>[28]</sup> (1,2-b)-DSF-IF,<sup>[28]</sup> and 9,9-dioctyl-terfluorene  $(3-F)^{[35]}$  (Table 1). The absorption spectra of (2,1-a)-DST-IF and (1,2-b)-DST-IF are characterized by a large and poorly structured band between 300 and 400 nm.

<sup>&</sup>lt;sup>2</sup> The assignments of (2,1-*a*)-DST-IF and (1,2-*b*)-DST-IF have been performed by 2D NMR spectroscopy experiments: HMBC (heteronuclear multiple bond correlation), HMQC (heteronuclear multiple quantum coherence), and <sup>1</sup>H/<sup>1</sup>H COSY (correlation spectroscopy) (see portion of HMBC spectrum in Figure S1 and S2 in the Supporting Information).





(bottom) of (2,1-a)-DST-IF (dashed line) and (1,2-b)-DST-IF (solid line)

in THF ( $c = 10^{-6}$  M).

Figure 2. Thermogravimetric analysis of (2,1-a)-DST-IF (top) and (1,2-b)-DST-IF (bottom) (scan rate: 5 °C min<sup>-1</sup> under a nitrogen atmosphere).

Table 1. Optical properties.

Table 1. Optical properties.								
	$\lambda_{abs}^{[a]}$ lig. [nm]	$\lambda_{\rm em}^{[a]}$ liq. [nm]	$\Phi_{sol}^{[b]}$	Ref				
$(2.1 \circ)$ DST IE	226 (sh) 242 254	402,422,450 (ab)	<u>[</u> , ]	[c.d]				
(2,1-a)-DST-IF (1 2-b)-DST-IF	320 (81), 343, 334 314 (sh) 330 (sh) 347 355 (sh)	402, 422, 450 (sf) 395 417 441 (sh) 475 (sh)	80 83	[c,d]				
3-F	351	395, 416, 444 (sh), 479 (sh)	90	[35]				
(2,1-a)-DSF-IF	295, 311, 323, 339	345, 363, 380 (sh), 400 (sh)	60	[28]				
(1,2-b)-DSF-IF	298, 310, 328, 336, 345	348, 355, 366, 388 (sh), 405 (sh)	62	[28]				

[a] In THF. [b] The relative quantum yield was measured with reference to quinine sulfate in  $1 \times H_2SO_4$  ( $\Phi = 0.546$ ). The values are estimated  $\pm 10\%$ . [c] In CHCl<sub>3</sub>. [d] This work.

The absorption spectrum of (1,2-b)-DST-IF displays one maximum at 347 nm and shoulders at 314, 330, and 355 nm, whereas the absorption spectrum of (2,1-a)-DST-IF displays two maxima at 343 and 354 nm and a shoulder at 326 nm (Figure 3, top). The low-energy bands at 354–355 nm are similar to that of 3-F ( $\lambda_{max}$  351 nm)<sup>[35]</sup> and other terfluorenyl-based oligomers<sup>[12,21,45–47]</sup> and are hence attributed to  $\pi$ - $\pi^*$  electronic transitions involving the terfluorenyl units. The high-energy bands and shoulders at 343 nm for (2,1-*a*)-DST-IF and 347 nm for (1,2-*b*)-DST-IF, not observed with 3F, might be consequently attributed to the indenofluorenyl units. Indeed, the  $\pi$ - $\pi$ \* indenofluorene transition (334 nm in CH<sub>2</sub>Cl<sub>2</sub>)<sup>[27]</sup> is observed at 339 nm for (2,1-*a*)-DSF-IF and at 345 nm for (1,2-*b*)-DSF-IF (Table 1).<sup>[28]</sup>

The (2,1-a)-DST-IF and (1,2-b)-DST-IF derivatives present very similar optical gaps<sup>3</sup> of about 3.15 eV. This gap is close to the band gap recorded for

other terfluorenyl derivatives such as 9,9-dihexylterfluorene<sup>[47]</sup> or terfluorenyl spiro-bridged with either cyclopropane  $(3.25 \text{ eV})^{[20]}$  or indenothiophene (3.14 eV) units.<sup>[17]</sup> On the other hand, the (2,1-a)-DST-IF and (1,2-b)-DST-IF gaps are smaller than those recorded for (2,1-a)-DSF-IF (3.57 eV)and (1,2-b)-DSF-IF (3.51 eV) for which the gap is controlled by the central indenofluorenyl units.<sup>[28]</sup> Consequently, the

<sup>3</sup> Optical gap calculated from  $\Delta E^{\text{opt}}$  [eV]= $hc/\lambda$  [nm] ( $\Delta E^{\text{opt}}$  [eV]= 1237.5/ $\lambda$  [nm]).

gap contraction observed for (2,1-a)-DST-IF and (1,2-b)-DST-IF demonstrates that in the present case, the gaps are controlled by the terfluorenyl units and not by the indeno-fluorenyl cores. It should be stressed that DSF-IF molecules with two aryl groups on the fluorene units previously reported by our group present mixed properties with the gap controlled by both indenofluorenyl and diarylfluorenyl cores.<sup>[33,34]</sup> Thus, (2,1-a)-DST-IF and (1,2-b)-DST-IF appear to be the first examples of DSF-IFs derivatives with a HOMO–LUMO gap almost exclusively controlled by the external  $\pi$ -conjugated systems, namely the terfluorenyl units.

The (2,1-a)-DST-IF and (1,2-b)-DST-IF derivatives both exhibit deep blue fluorescence in solution (Figure 3, bottom) with however significant differences between the two fluorescent spectra. The fluorescence spectrum of (1,2b)-DST-IF is well defined with maxima recorded at 395 and 417 nm fitting well with those of 3-F (395, 416 nm, Table 1).<sup>[35]</sup> It is hence reasonable to infer that the main emission in (1,2-b)-DST-IF arises from the terfluorenyl arms. The important Stokes shift (46 nm) and the poor mirror images between absorption and fluorescence spectra indicate conformational changes between the ground state and the first excited state. They suggest that conformations are more rigid in the first excited state than in the ground state. Indeed, in the excited state, the bonds joining the fluorene units are shortened and the dihedral angles between the fluorene units are reduced leading hence to a more planar conformation.<sup>[48,49]</sup> Surprisingly, the (2,1-a)-DST-IF fluorescence spectrum is significantly different to that of its isomer as it appears red-shifted ( $\lambda_{em} = 402, 422 \text{ nm}$ ), larger, and less structured with a more intense shoulder around 450 nm and a long tail up to 600 nm (Figure 3, bottom). The emission bands of (2,1-a)-DST-IF found at 402 and 422 nm may be ascribed to the terfluorenyl units, nevertheless they are red-shifted by about 10 nm compared to those of 3-F (395, 416 nm) and those of (1,2-b)-DST-IF (395, 417 nm). The low-energy shoulder observed at 450 nm appears difficult to assign. Nevertheless, reports in the literature indicate that fluorene-excited dimer (fluorene excimer) displays an emission in solution centered at 400 nm.<sup>[40,50]</sup> whereas electrogenerated terfluorene excimers of the terspirobifluorene lead to an intense emission band in the 522-583 nm range.<sup>[51]</sup> The shoulder observed around 450 nm in the (2,1-a)-DST-IF fluorescence spectrum appears between the emission of the fluorene excimer and the emission of the terfluorene excimer. Assigning the emission at 450 nm is hence not trivial but should result either from 1) frustrated intramolecular terfluorene excimers, or 2) intermolecular indenofluorene or terfluorene excimers. Varying the DST-IF concentrations between  $10^{-7}$  and  $10^{-4}$  M should hence provide interesting information regarding this assignment (see Figures S3-S6 in the Supporting Information). For both compounds, no modification of the shape of the absorption nor of the emission spectra as a function of the concentration was observed, indicating that intermolecular interactions do not occur even at high concentration either for (2,1-a)-DST-IF or for (1,2-a)-DST-IF or

b)-DST-IF. This observation leads us to assign the emission shoulder at 450 nm in (2,1-a)-DST-IF to frustrated intramolecular interactions between two face-to-face terfluorene units. The emission of (2,1-a)-DST-IF in solution thus originates in part from the terfluorene units as for (1,2-b)-DST-IF and from frustrated intramolecular terfluorene excimers due to the specific face-to-face organization of the terfluorene units in this molecule. By using quinine sulfate in sulfuric acid as a standard,<sup>[52]</sup> the quantum yields in solution for (2,1-a)-DST-IF and (1,2-b)-DST-IF are estimated to be around 80 and 83%, respectively. These quantum yields are between those of (2,1-a)-DSF-IF (60%) and (1,2-b)-DSF-IF (62%), and those of 3-F (90%)<sup>[35]</sup> and ter-9,9-spirobifluorene (99%).<sup>[43]</sup> Thus, both (2,1-*a*)-DST-IF and (1,2-*b*)-DST-IF present very high quantum yields in the blue region and are promising for further OLED applications. The solid-state absorption spectra of (2,1-a)-DST-IF and (1,2-b)-DST-IF (Figure 4, top) appear less defined and slightly red-shifted compared to those in solution (Figure 3, bottom). Regarding the solid-state fluorescent properties (Figure 4, bottom), (1,2-b)-DST-IF presents two main maxima recorded at 399



Figure 4. Normalized thin-film absorption spectra (top) and fluorescence spectra (bottom) of (2,1-a)-DST-IF (dashed line) and (1,2-b)-DST-IF (solid line).

and 420 nm and shoulders at 444 and 480 nm, in accordance with those of 9,9-dihexylterfluorene,<sup>[47]</sup> highlighting hence that the terfluorenyl units are the main emitter in thin films. In addition, (1,2-b)-DST-IF presents a very well-defined spectrum almost identical to that in solution. Only a very small red shift of about 4 nm and a different relative intensity of the main emissive bands are observed. The fact that the fluorescent spectrum does not show significant change when going from solution to solid-state suggests that no specific intermolecular interactions involving the  $\pi$ -systems occur when the film is formed. The red shift between solution and thin-film fluorescence spectra of (1,2-b)-DST-IF is smaller than those reported in the literature for 9,9-dialkylterfluorene derivatives for which an important self-absorption of the highest energy emitted band is observed.<sup>[21]</sup> Similarly, the marked difference observed in the relative intensity of the emission bands between solution and thin-film fluorescence spectra of (1,2-b)-DST-IF (that at 399 nm is weakened, whereas that at 420 nm is strengthened) may be also explained by self-absorption phenomena due to the overlap of the 0-0 transition band and the absorption band.<sup>[21,53]</sup> In contrast, the solid-state fluorescent spectrum of (2,1-a)-DST-IF (Figure 4, bottom) appears to be significantly different both from that in solution and from that of its isomer (1,2-b)-DST-IF. Thus, the thin-film fluorescence spectrum of (2,1-a)-DST-IF is poorly resolved with a main emission band centered at 464 nm and with weak shoulders at 405 and 437 nm. The emission at 464 nm is close to the shoulder observed in solution (450 nm) and also to the thinfilm main emission of DSF-IF molecules with two aryl groups on the fluorene units. Indeed, these present in solution a poorly resolved emission band, which is assigned to intramolecular excimer emission arising from face-to-face aryl-fluorene-aryl units, ranging from 434-463 nm depending on the steric hindrance induced by the substituents borne by the aryl units.<sup>[33,34]</sup> Thus, with small substituents such as a methoxy group or a fluorine atom, the solid-state and solution spectra are almost identical (see Figures S7-S9 in the Supporting Information). In contrast, with bulky substituents such as tert-butyl groups, solid-state and solution spectra are drastically different due to the emission of nonstacked and stacked aryl-fluorene-aryl units in solution and almost exclusively of stacked aryl-fluorene-aryl units in the solid state (see Figures S10 and S11 in the Supporting Information). In the present case, the emission of (2,1-a)-DST-IF in solution is very different from that in a thin film. It is hence reasonable to contend that the emission principally arises in solution from non-stacked terfluorenyl units and to a lesser extent from stacked terfluorenyl units. However in the solid state, the main emission at 464 nm is attributed to intramolecular excimer formation arising from stacked faceto-face terfluorenyl units and the shoulders observed at lower wavelength may reflect the weak emission of nonstacked terfluorenyl units. Before any further SMOLED application, it is of great interest to study the behavior of the two terfluorenyl derivatives in the thin films and to study their stability upon heating. Indeed, it is known that an

## **FULL PAPER**

OLED device can reach a temperature of approximately 86 °C and the stability of the emitted color upon heating is of key importance.<sup>[44]</sup> Evolution of the fluorescent spectra of both (2,1-a)-DST-IF and (1,2-b)-DST-IF under thermal stress conditions was then investigated (Figure 5).



Figure 5. Evolution of normalized thin-film fluorescence spectra as a function of the temperature (1 h at each stage) of top: (1,2-*b*)-DST-IF (normalized at 422 nm) and bottom: (2,1-*a*)-DST-IF (normalized at 464 nm for T < 100 °C and at 424 nm for  $T \ge 100$  °C).

This study provides two main pieces of information. First, the fluorescence spectrum of (1,2-b)-DST-IF remains stable from room temperature to 150°C (Figure 5, top). However, at 200 °C, a green emission band (GEB,  $\lambda = 518$  nm) starts to grow and becomes very intense after one night at 200 °C. The origin of such a contribution at low energy has been extensively studied for the last decade as it remains an important problem in blue OLED technology.<sup>[6,54,55]</sup> While the GEB was initially explained by excimer emission (the formation of dimerized units in the excited state that emit at lower energies) due to  $\pi - \pi$  interchromophore interactions of the  $\pi$ -conjugated backbone,<sup>[56]</sup> it seems now that the GEB is linked to the presence of keto-defects appearing in the bridged  $\pi$ -conjugated backbone. Thus, Müllen and coworkers have notably demonstrated that alkylated poly(indenofluorene) and ladder-type poly(pentaphenylene) are less stable toward oxidation degradation than their aryl ana-

www.chemeurj.org

logues due to the dialkyl bridgeheads, which are sensitive to oxidation.<sup>[6,57,58]</sup> Similarly, Bredas and co-workers have also demonstrated the oxidative degradation process occurring in ladder-type poly-p-phenylene bearing either a hydrogen atom or a methyl group at the bridge.<sup>[59]</sup> However, the precise relaxation processes that follow excitation of the ketodefect sites are nevertheless still being debated.<sup>[54,60,61]</sup> To go deeper in the intimate understanding of this GEB, we decided to investigate the optical properties of the ketone 5 (see structure in Scheme 1) as a relevant oxidized model compound of (1,2-b)-DST-IF.<sup>[54]</sup> In diluted solution, 5 shows absorption bands with maxima at 308 and 349 nm that can be assigned to the  $\pi$ - $\pi$ \* transition of the terfluorene unit, and a less intense band around 455 nm believed to be due to the symmetry-forbidden carbonyl group  $n-\pi^*$  transition (see Figure S12 in the Supporting Information).<sup>[62,63]</sup> Increasing the concentration of 5 does not lead to any modification of its absorption spectrum. In addition, its thin-film absorption spectrum was also almost identical to its solution spectrum (see Figure S12 and S13 in the Supporting Information). In contrast, the fluorescence properties of terfluorenone 5 appear to be strongly dependent on the concentration and the environment (solution vs. thin film). Indeed, the fluorescence spectra of 5 only display one band ( $\lambda = 380$  nm) for diluted solutions but display two sets of emission bands at  $(\lambda = 380 \text{ nm and } 540/570 \text{ nm})$  when increasing the concentration (see Figure S14 in the Supporting Information). On the other hand, the thin-film emission spectrum of 5 only displays one large band at 580 nm (see Figure S15 in the Supporting Information) assigned, as recently proposed by Holmes and co-workers,<sup>[54]</sup> to intermolecular interactions in the solid state between the ketones units.<sup>4</sup> It is hence reasonable to similarly assign the large band (540/570 nm) observed in concentrated solutions of 5 (vide supra) to intermolecular interactions between the ketone units. In light of these results and since the fluorescence spectrum of a film of (1,2-b)-DST-IF, redissolved after thermal annealing at 200°C, is identical (with no trace of the GEB) to that of pristine compound in solution,<sup>[61]</sup> it is reasonable to contend that the GEB arises from intermolecular interactions between the keto-defects formed after thermal annealing (Figure 5, top). However, a red shift is observed between the GEB of 5 ( $\lambda$  = 580 nm) and the GEB of (1,2-b)-DST-IF  $(\lambda = 518 \text{ nm})$ . This can be explained by the position of the keto-defect in the terfluorene unit, since the appearance of keto-defects in (1,2-b)-DST-IF should lead to fluorenoneterminated terfluorene, whereas the model compound 5 is a fluorenone-centered terfluorene. Indeed, it has been reported that the main emission band of fluorenone-terminated terfluorene is recorded at about 528 nm, whereas that of fluorenone-centered terfluorene is red shifted to about 550 nm. This clearly indicates that the position of the ketone within the  $\pi$ -conjugated backbone significantly influences the wavelength of the emission band.<sup>[54]</sup>

<sup>4</sup> No evolution of the thin-film absorption and emission spectra was observed when increasing the temperature from room temperature to 200°C (see Figure S16 and S17 in the Supporting Information). Surprisingly, (2,1-a)-DST-IF displays drastically different behavior since the gradual heating of a spin-coated thin film in air from room temperature to 200 °C did not lead to the growth of a GEB. Consistently with the above discussion of (1,2-b)-DST-IF, we propose that some alkyl bridgeheads of (2,1-a)-DST-IF are also oxidized in ketones but it seems that these ketones do not interact, presumably due to the different arrangement in the thin film. Consequently, no trace of GEB in the thin-film fluorescence spectra of (2,1-a)-DST-IF was detected.<sup>5</sup>

The second key piece of information arises nevertheless from the modification of the fluorescence spectrum of (2,1a)-DST-IF as a function of temperature. The (2,1-a)-DST-IF fluorescence spectrum remains stable with a main emission centered at 464 nm, when the sample is heated from room temperature to 60°C. However, heating the sample at 100 °C is accompanied by a modification of the fluorescence spectrum of (2,1-a)-DST-IF, which now displays three maxima (402, 424, and 441 nm) and a shoulder (464 nm), surprisingly in accordance with those of its solution fluorescence spectra. Interestingly, a similar blue shift of the fluorescence maxima was also observed when heating a thin film of (2,1-a)-dispiro(3,4,5-trimethoxyphenylfluorene)-indenofluorene (see Figure S18 in the Supporting Information), which became nearly identical to its emission spectrum in solution (see Figure S9 in the Supporting Information). Similar changes in the solid-state fluorescence spectrum with temperature have been reported for butadiene derivatives<sup>[64-66]</sup> but in these examples, the monomer-like or excimer-like fluorescence come from specific "intermolecular packing", which may be modified with temperature. In a "herringbone" arrangement, minimal electronic coupling between molecules led to a monomer-like emission, whereas in a "brickstone" arrangement, molecular packing led to excimer-like fluorescence. In the case of (2,1-a)-DST-IF, heating of the films leads to a reorganization of the face-to-face terfluorene moieties in the solid, leading to a decrease in the amount of intramolecular emitting excimers. To our knowledge, variation of fluorescence with temperature due to "intramolecular packing reorganization" is almost absent from the literature<sup>[67]</sup> and appears to play a major role in deciding the solid-state fluorescence properties of (2,1-a)-DST-IF.

**Electrochemical properties**: The electrochemical behavior of (2,1-a)-DST-IF and (1,2-b)-DST-IF has been investigated by using cyclic and differential pulse voltammetry (CV and DPV, respectively). In the cathodic range (see Figure S18 in the Supporting Information), (1,2-b)-DST-IF presents an irreversible reduction wave with a poorly resolved maximum at -2.6 V and an onset reduction potential at -2.27 V. In contrast, (2,1-a)-DST-IF does not show any maximum of its reduction wave and presents an onset reduction potential at -2.35 V. From these onset potentials, the LUMO energy

<sup>5</sup> It should be noted that when a film of (2,1-*a*)-DST-IF was redissolved after thermal annealing at 200 °C, its fluorescence spectrum is identical to that of pristine compound in solution.

Table 2. Electrochemical data of (2,1-*a*)-DST-IF, (1,2-*b*)-DST-IF, (2,1-*a*)-DSF-IF, (1,2-*b*)-DSF-IF recorded in CH<sub>2</sub>Cl<sub>2</sub>-[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 м.

	E <sub>ox</sub> [V vs. SCE]	$E_{\text{onset}}^{\text{ox}}$ [V vs. SCE]	E <sub>onset</sub> red [V vs. SCE]	HOMO [eV] <sup>[a]</sup>	LUMO [eV] <sup>[b]</sup>	LUMO [eV] <sup>[d]</sup>	$\Delta E_{ m el}$ [eV] <sup>[c]</sup>	$\Delta E_{\rm opt}$ [eV] <sup>[e]</sup>	Ref.
(2,1- <i>a</i> )-DST-IF	$1.12 (1e^{-}), 1.18 (1e^{-}), 1.64 (3e^{-}), 2.04 (2e^{-})$	0.98	-2.35	-5.38	-2.05	-2.28	3.33	3.13	[f]
(1,2- <i>b</i> )-DST-IF	$1.04 (3c^{-}), 2.04 (2c^{-})$ $1.29 (2c^{-}), 1.47 (2c^{-}), 1.58 (1c^{-}), 2.01 (2c^{-}+1c^{-})$	1.06	-2.27	-5.46	-2.13	-2.36	3.33	3.16	[f]
(2,1- <i>a</i> )-DSF-IF	$1.36(1e^{-}), 2.61(2e^{-}+1e^{-})$ $1.36(1e^{-}), 1.69(1e^{-}),$ $1.99(> 1e^{-})$	1.20	-2.37	-5.64	-2.03	-2.07	3.61	3.57	[28]
(1,2-b)-DSF-IF	$1.47 (1e^{-}), 1.95 (>1e^{-})$	1.36	-2.23	-5.76	-2.17	-2.23	3.59	3.51	[28]

[a] Calculated from the onset oxidation potential. [b] Calculated from the onset reduction potential. [c]  $\Delta E_{elec} = |\text{HOMO-LUMO}|$  (in eV). [d] Calculated from the HOMO energy level and the edge of optical band gap. [e]  $\Delta E_{opt}$  is calculated from the edge of the absorption spectrum using  $\Delta E^{opt} = hc/\lambda$ . [f] This work.

levels of (2,1-a)-DST-IF and (1,2-b)-DST-IF were determined at -2.05 and -2.13 V respectively (Table 2).<sup>6</sup> In the anodic range, both compounds present successive oxidation processes between 0.2 and 2.5 V (Figure 6A). HOMO energy levels of (2,1-a)-DST-IF and (1,2-b)-DST-IF were determined from their onset oxidation potentials (0.98 V for (2,1-a)-DST-IF and 1.06 V for (1,2-b)-DST-IF) at -5.38 and -5.46 eV, respectively. The electrochemical gap calculated from the HOMO and LUMO level is 3.33 eV for both compounds. Interestingly, (2,1-a)-DST-IF and (1,2-b)-DST-IF also possess almost identical optical gap,  $\Delta E_{opt}$ , calculated from the edge of the solution absorption spectrum ( $\Delta E_{opt}$ = 3.16 eV for (1,2-b)-DST-IF and  $\Delta E_{opt} = 3.13$  eV for (2,1-a)-DST-IF). As theoretical calculations point to a terfluorenylbased primary oxidation and reduction in (2,1-a)-DST-IF and (1,2-b)-DST-IF, (see the calculated nature of their frontier molecular orbitals HOMO/LUMO in Figure 7 and 8), the HOMO/LUMO energy levels are mainly determined by their external terfluorenyl units and not by their central indenofluorenyl cores. This feature is considerably different from those recently reported for alkyl-substituted (1,2-b)-DSF-IF and (2,1-a)-DSF-IF, which possess HOMO/LUMO energy levels mainly centered on their indenofluorenyl cores<sup>[28,31]</sup> and for aryl-substituted (1,2-b)-DSF-IF and (2,1a)-DSF-IF, which possess HOMO/LUMO energy levels centered both on their indenofluorenyl cores and on their external aryl-fluorene-aryl units.[33,34]

The (2,1-a)-DST-IF and (1,2-b)-DST-IF derivatives present in CV successive mono or multiple electronic processes (Figure 6A) clearly pointed out by DPV (Figure 6B). The (1,2-b)-DST-IF derivative is first oxidized along two successive bielectronic oxidations at 1.29 and 1.47 V, followed by a reversible monoelectronic oxidation at 1.58 V and a three-electron oxidation at 2.01 V (in black, Figure 6A and B). The two first oxidations are reversible and are close to the two first reversible oxidations of terfluorene deriva-

<sup>&</sup>lt;sup>6</sup> The LUMO level was calculated from: LUMO (eV) =  $-[E_{onset}^{red}$  (vs. SCE) + 4.4] and the HOMO level from: HOMO [eV] =  $-[E_{onset}^{ox}$  (vs. SCE) + 4.4], based on an SCE energy level of 4.4 eV relative to the vacuum.<sup>[68]</sup> The electrochemical gap was calculated from :  $\Delta E^{el} = |\text{HO-MO-LUMO}|$  (in eV). The estimated errors in the determination of the onset potential values are  $\pm 20 \text{ mV}$  for  $E_{onset}^{ox}$  and  $\pm 50 \text{ mV}$  for  $E_{onset}^{red}$ .



Figure 6. CVs (A) and DPVs (B) in  $CH_2Cl_2-[NBu_4][PF_6]$  0.2 M in the presence of (2,1-*a*)-DST-IF (dashed line) and (1,2-*b*)-DST-IF (solid line), platinum working electrode. CVs (C) in  $CH_2Cl_2-[NBu_4][PF_6]$  0.2 M using a modified poly((2,1-*a*)-DST-IF) (dashed line) and poly((1,2-*b*)-DST-IF) (solid line) electrode previously modified by oxidation of their monomers at 2.0 V during 2 min.

Chem. Eur. J. 2011, 17, 14031-14046

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org



Figure 7. Sketch of frontier molecular orbitals for a simplified model of (1,2-*b*)-DST-IF (methyl instead of octyl groups) from Gaussian 03 B3LYP/6-31G\* calculations.<sup>[69-71]</sup>



Figure 8. Sketch of frontier molecular orbitals for a simplified model of (2,1-*a*)-DST-IF (methyl instead of octyl groups) from Gaussian 03 B3LYP/6-31G\* calculations.<sup>[69-71]</sup>

tives.<sup>[35,47,72]</sup> It seems then consistent to assign the two first oxidation processes of (1,2-b)-DST-IF to the oxidation of the two terfluorenyl arms successively leading to (1,2-b)-DST-IF bis-radical cations and (1,2-b)-DST-IF bis-dications. The assignment of these two first oxidation waves is clearly

systems is more facile than that of their non-stacked analogues,<sup>[39,73]</sup> and the cofacial arrangement of the two terfluorenyl units in (2,1-a)-DST-IF is hence at the origin of its observed low oxidation potential. Therefore, the first oxidation process of (2,1-a)-DST-IF may be assigned to the oxidation

confirmed by theoretical calculations since the HOMO and the SOMO levels of (1,2-b)-DST-IF presents a terfluorenyl character (see Figure 7 and 8 for the HOMO and Figure S23 and S24 in the Supporting Information for the SOMO molecular orbitals). The third reversible oxidation recorded at 1.58 V is assigned to the oxidation of the indenofluorenyl core at a potential slightly more anodic than that recorded for (1,2-b)-DSF-IF (1.47 V).<sup>[27]</sup> This shift to more anodic values is probably due to the electronwithdrawing effect of the terfluorenyl arms that are under their dicationic state at this potential. The electrochemical behavior of (2,1-a)-DST-IF (Figure 6A and B, dashed line) differs drastically to that of (1,2b)-DST-IF. Indeed, (2,1-*a*)-DST-IF is oxidized along two successive one-electron processes recorded at 1.12 and 1.18 V. These two first oxidation potentials are lower than those reported above for (1,2-b)-DST-IF and lead to a doubly charged species, stable up to 1.64 V at which a third three-electron oxidation process occurs.

The fourth oxidation of (2,1a)-DST-IF occurs at more than 2.0 V and appears as an irreversible two-electron oxidation process followed by a multielectronic process. The main difference between the oxidation of (2,1-*a*)-DST-IF and (1,2-*b*)-DST-IF is related to the different potentials of their first reversible electronic processes. Indeed, the first oxidation potential of (2,1-a)-DST-IF (1.12 V) is lower than the first oxidation potential of (1,2-b)-DST-IF (1.29 V). It is known that the oxidation of  $\pi$ -stacked

### of a "terfluorene dimer" that results from the specific faceto-face organization of the two terfluorenyl units in (2,1-a)-DST-IF. These $\pi-\pi$ interactions have also been evidenced in <sup>1</sup>H NMR spectra (vide supra). The second oxidation of (2,1-a)a)-DST-IF occurs at 1.18 V, which is also at a lower potential value than the oxidation of 3-F and (1,2-b)-DST-IF and may be assigned to the second oxidation of the intramolecular terfluorene dimer. This double radical cation is stabilized between the two terfluorenyl arms and appears thermody-

namically stable. Indeed, the further oxidation of the terfluorenyl arms occurs nearly 0.5 V higher, together with the oxidation of the indenofluorenyl unit. The different oxidation processes of (2,1-a)-DST-IF and (1,2-b)-DST-IF are summarized in Scheme 3. After these five-electron oxida-



Scheme 3. Step by step five-electron oxidation of (2,1-a)-DST-IF and (1,2-b)-DST-IF.

tions, (2,1-a)-DST-IF and (1,2-b)-DST-IF may be oxidized to higher oxidation states and these oxidations lead to polymerization processes. Indeed, recurrent scans for both compounds between 0 and 2.0 V lead to a regular polymerization process that is evidenced by the appearance and growth of new redox waves, by the gradual shift of the onset potential, and by the coverage of the electrode with an insoluble thin film (see Figure S19 in the Supporting Information). Polymerization is also observed by oxidation at fixed potential. For example, deposits prepared by oxidation at 2 V for 180 s, removed from the electrolyte, rinsed in dichloromethane, and studied in a new 'monomer free' solution, present the profile shown in Figure 6C. The oxidation of poly((2,1-a)-DST-IF) and of poly((1,2-b)-DST-IF) start at 0.8 V and 0.96 V, respectively, and both polymers are electrochemically stable up to 1.8 V, leading to an electroactivity window close to 1 V. The onset oxidation potential of the two polymers follows the same trend as that of their corresponding monomers. Thus, the oxidation of poly((2,1-a)-DST-IF) (onset oxidation potential: 0.8 V) starts at a 0.16 V less anodic potential than that of poly((1,2-b)-DST-IF)(onset oxidation potential: 0.96 V), Figure 6C. This shift of 0.16 V between the two polymers is nevertheless larger than that observed between their corresponding monomers (2,1a)-DST-IF and (1,2-b)-DST-IF, which possess onset oxidation potentials at 0.98 V and 1.06 V, respectively (Fig-

# FULL PAPER

ure 6 A). Similarly, the 0.16 V shift observed between poly-((2,1-*a*)-DST-IF) and poly((1,2-*b*)-DST-IF) is also larger than that observed between poly((2,1-*a*)-indenofluorene)<sup>[28]</sup> and poly((1,2-*b*)-indenofluorene)<sup>[74]</sup> (shift: 0.09 V) and also between poly((2,1-*a*)-DSF-IF)<sup>[28]</sup> and poly((1,2-*b*)-DSF-IF)<sup>[27,28]</sup> (shift: 0.02 V). In the light of these comparative results and since DSF-IF and DST-IF derivatives presents at least six sites of coupling (two on the two fluorenyl units and two on the indenofluorenyl unit), it is hence very difficult to precisely describe the polymerization processes.

Small-molecule organic light-emitting diodes (SMOLEDs) using (2,1-a)-DST-IF as the emitting layer: As discussed above, the gradual heating of a thin film of (2,1-a)-DST-IF from room temperature to 200°C did not lead, as observed for (1,2-b)-DST-IF, to the growth of a parasite GEB. Hence, the final OLED investigations were only carried out with (2,1-a)-DST-IF. To explore the potential applications of the new blue-emitting (2,1-a)-DST-IF, a basic spin-coated singlelayer SMOLED was fabricated and characterized. The structure of the devices was based on ITO as the anode, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT/PSS) as the hole injecting layer (HIL), (2,1-a)-DST-IF as the emitting layer (EML), and Ca as cathode. We decided to focus on a single-layer device to study the intrinsic properties of the (2,1-a)-DST-IF emitting layer. Indeed, through careful band engineering (addition of electron/hole transporting/blocking layers) it is always possible to improve the efficiencies of the device, whatever the emitting layer. Thus, the single-layer device using a spin-coated emissive layer of (2,1-a)-DST-IF gives a turn on voltage (at  $1 \text{ Cd m}^{-2}$ ) of 7 V, a maximum luminance of 100 Cd m<sup>-2</sup>, and a luminous efficiency of around  $0.05 \text{ Cd A}^{-1}$  (see Figure S20 and S21 in the Supporting Information). It is evident that the modest efficiencies of this device are attributed to the wide HOMO-LUMO gap of the blue-emitting material coupled to its very simple structure. Indeed, the electron-injection barrier from Ca (-2.9 eV) to (2,1-a)-DST-IF (-2.05 eV) is very large and hence the device efficiency could be easily improved by choosing suitable electrontransporting materials. It should be however stressed that the HOMO level of (2,1-a)-DST-IF fits well with the work function of the ITO/PEDOT anode, avoiding hence the use of a hole-transporting unit. The single-layer device using (2,1-a)-DST-IF as emitting layer presents comparable performances to those of other terfluorene single-layer devices previously reported in the literature. For example, Qin and co-workers have recently designed several poly(terfluorene) derivatives bearing electron-transporting units and have reported maximum luminances ranging from 102 to 235 Cdm<sup>-2</sup>.<sup>[13]</sup> The normalized electroluminescence spectrum recorded for the ITO/PEDOT/(2,1-a)-DST-IF/Ca device (Figure 9A) exhibits one emission peak in the blue region at 464 nm. The chromatic coordinates (Figure 9B) calculated from the electroluminescence spectrum in the CIE 1964 chromaticity diagram are (0.19; 0.23), corresponding to a blue color. It is worth noting that no parasite GEB

www.chemeurj.org

- 14041



Figure 9. A) Electroluminescence spectrum of ITO/(2,1-a)-DST-IF/Ca OLED; inset: picture of the device. B) Corresponding color placed on the CIE 1964 chromaticity diagram (0.19; 0.23).

emission was observed in the (2,1-a)-DST-IF-based OLEDs, which appear very stable. Hence, this behavior appears promising for the optimization of future OLEDs. Interestingly, both the maximum and the shape of the electroluminescence spectrum are almost identical to the thin-film fluorescence spectrum of (2,1-a)-DST-IF recorded at room temperature (Figure 5). Thus, this blue color clearly arises from electrogenerated intramolecular terfluorenyl excimer emission, which has not previously been described in the literature.

### Conclusion

To summarize, two new terfluorene derivatives (2,1-a)-DST-IF and (1,2-b)-DST-IF with different geometry profiles have been synthesized by a rational approach based on the intimate understanding of the distribution of positional isomers arising from the bicyclization of a difluorenol. Thus, with a very bulky substituent attached to the fluorene units (9,9-dioctylfluorene) and a polar solvent (CH<sub>3</sub>CN), we managed to drive the cyclization toward the isomer (2,1-*a*)-DST-IF. On the other hand, with a less bulky substituent attached to the fluorene units (bromine atom) and a low polarity solvent

 $(CH_2Cl_2)$ , the positional isomer (1,2-b)-DST-IF was obtained in a two-step sequence. The two blue-emitting molecules (1,2-b)-DST-IF and (2,1-a)-DST-IF possess a large HOMO-LUMO gap (about 3.15 eV), very high quantum yields, and are thermally stable. Despite the fact that the geometry profiles of (2,1-a)-DST-IF and (1,2-b)-DST-IF are imposed by their indenofluorenyl cores, the properties are mainly governed by the two terfluorenyl frameworks. For (1,2-b)-DST-IF, in solution and in the solid state, the fluorescence around 400/420 nm is attributed to the terfluorenyl units. However, the heating of (1,2-b)-DST-IF films up to 200°C, leads to a green emission band at 520 nm. Despite being a positional isomer, (2,1-a)-DST-IF with face-to-face terfluorenyl units, displays drastically different fluorescent behavior. The most striking feature is related to the different emitters (nonstacked and stacked terfluorenyl units) involved in solution and in the solid state, leading to different main emission wavelengths; that is 420 nm in solution and 464 nm in the solid state. In addition, the intriguing behavior of the (2,1a)-DST-IF fluorescence spectra as a function of the temperature was investigated, which clearly showed a blue shift of the main emission (from 464 nm to 420/440 nm). This intramolecular packing reorganization leads to a heated film with an emission comparable to the emission to that in solution for (2,1-a)-DST-IF. Finally, (2,1-a)-DST-IF was successfully used in a blue single-layer SMOLED (chromatic coordinates : 0.19; 0.23) presenting an electroluminescence spectrum in perfect accordance with its thin-film fluorescence spectrum. This stable blue emission arises from an electrogenerated intramolecular terfluorenyl excimer, which is to the best of our knowledge the first example, and may hence open new avenues in the design of efficient blue fluorophores for OLED applications.

#### **Experimental Section**

Synthesis: Commercially available reagents and solvents were used without further purification other than those detailed below. Dichloromethane was distilled from P2O5 drying agent Sicapent (Merck). THF was distilled from sodium/benzophenone, and toluene was distilled from sodium prior to use. Light petroleum refers to the fraction with b.p. 40-60°C. The reaction mixtures were stirred magnetically, unless otherwise indicated. Analytical thin-layer chromatography was carried out using aluminum-backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and/or 360 nm). Chromatography was carried out using silica 60A (0.06-0.2 mm). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by using Bruker 300 MHz instruments (1H frequency, corresponding <sup>13</sup>C frequency is 75 MHz); chemical shifts were recorded in ppm and J values in Hz. The residual signals for the NMR solvents are: CDCl<sub>3</sub>:  $\delta = 7.26$  ppm for the proton and  $\delta = 77.00$  ppm for the carbon; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta = 5.32$  ppm for the proton and  $\delta = 53.80$  ppm for the carbon;  $[D_8]$ THF:  $\delta = 3.58$  ppm for the proton and  $\delta = 67.57$  for the carbon. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet, m for multiplet and br for broad. High-resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (Rennes) on a Micromass MS/MS ZABspec Tof (EBE Tof geometry) and reported as m/z. Names of chemicals have been generated with the naming service of ACD-I lab, which determines the chemical name according to systematic application of the nomenclature rules agreed upon by the International Union of Pure and

14042 -

Applied Chemistry and International Union of Biochemistry and Molecular Biology. 9,9-Dioctylfluorene-2-boronate ester **2** was prepared according to literature procedures starting from commercially available 2-bromofluorene.<sup>[29]</sup> The compound 2,2"-DITP **3** was prepared according to literature procedures starting from commercially available 2-bromoaniline.<sup>[27]</sup>

9,9,9",9"-Tetraoctyl-9H,9'H,9"H-2,2':7',2"-terfluoren-9'-one (5): Sodium carbonate (1.100 g, 10.30 mmol) dissolved in water (6 mL) was added to a solution of 2,7-dibromofluorenone (0.088 g, 0.26 mmol), 2 (0.464 g, 0.77 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.015 g, 0.013 mmol) in toluene (30 mL). The schlenk tube was degassed and the mixture was allowed to stir vigorously at 100 °C for 24 h under an argon atmosphere. The reaction mixture was then quenched with water (30 mL) and extracted with dichloromethane (5×20 mL). The combined organic layers were washed with water (50 mL), dried (MgSO<sub>4</sub>), and evaporated in vacuo. Purification by column chromatography on silica gel, eluting with light petroleum and diethyl ether-light petroleum (1/15 to 1/9), afforded 5 as an orange solid (210 mg, 85%). M.p. 90°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ=8.04 (s, 2H; ArH), 7.85–7.73 (m, 6H; ArH), 7.66– 7.61 (m, 6H; ArH), 7.39–7.30 (m, 6H; ArH), 2.03 (t, J=7.0 Hz, 8H; ArH), 1.21–1.00 (m, 40 H; CH<sub>2</sub>), 0.79 (t, J=7.2 Hz, 12 H; Me), 0.72– 0.59 ppm (m, 8H; CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 194.1 (C=O), 151.6 (C), 151.0 (C), 142.9 (C), 142.6 (C), 141.1 (C), 140.5 (C), 138.5 (C), 135.2 (C), 133.3 (CH), 127.2 (CH), 126.8 (CH), 125.6 (CH), 123.0 (CH), 122.9 (CH), 121.0 (CH), 120.7 (CH), 120.1 (CH), 119.8 (CH), 55.2 (C), 40.4 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 29.2 (2×CH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 ppm (Me); HRMS (ESI+, MeOH/CH2Cl2 90/10): calcd for  $C_{71}H_{88}ONa: 979.67329 [M+Na]^+$ , found: 979.6739; IR (KBr):  $\tilde{\nu} = 3064$ (aryl CH), 2922 (CH2, CH3), 2852 (CH2, CH3), 1718 (C=O), 1603,  $1466 \text{ cm}^{-1}$ .

9',9"-(1,1':4',1"-Terphenyl-2,2"-diyl)bis(9,9,9",9"-tetraoctyl-9*H*,9'*H*,9"*H*-

2,2':7',2"-terfluoren-9'-ol) (6): In a schlenk tube under an argon atmosphere, 2,2"-DITP 3 (0.10 g, 0.21 mmol) was dissolved in dry THF (7 mL) and the solution was degassed. The mixture was cooled to -78°C and stirred at this temperature for 10 min. A solution of nBuLi (1.6 m in hexane, 0.52 mL, 0.83 mmol) was added dropwise in 3.5 min. The resulting yellow solution was stirred for a further 3.5 min and fluorenone 5 (0.44 g, 0.46 mmol), dissolved in dry and degassed THF, was added dropwise in 4 min by using a cannula. The reaction mixture was allowed to stir overnight (from -70°C to room temperature) and the resulting mixture was poured into a saturated solution of ammonium chloride (10 mL) and extracted with dichloromethane. The combined extracts were dried (MgSO<sub>4</sub>) and the solvent was removed in vacuo and purified by column chromatography on silica, eluting with dichloromethane-light petroleum (2/8 to 3/7), to afford as a colorless solid (0.11 g, 25%). M.p. > 300°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.59$  (d, J = 5.8 Hz, 2H; ArH), 7.65–7.25 (m, 40H; ArH), 7.23-7.19 (m, 4H; ArH), 6.99 (d, J=7.2 Hz, 2H; ArH), 5.52 (s, 4H; ArH), 2.43 (s, 2H; exch D<sub>2</sub>O, OH), 2.0-1.88 (m, 16H; ArH), 1.3-0.9 (m, 80H; CH<sub>2</sub>), 0.88–0.75 (m, 24H; Me), 0.72–0.55 ppm (m, 16H; CH<sub>2</sub>);  $^{13}$ C NMR (75 MHz; CDCl<sub>3</sub>):  $\delta$  = 151.5 (C), 151.3 (C), 151 (C), 142 (C), 141.3 (C), 140.7 (C), 140.4 (C), 140.1 (C), 139.9 (C), 138.8 (C), 137.2 (C), 131.2 (CH), 128.2 (CH), 127.3 (CH), 127.08 (CH), 127.01 (CH), 126.8 (CH), 126.58 (CH), 126.55 (CH), 126 (CH), 123.2 (CH), 123 (CH), 121.4 (CH), 120.1 (CH), 119.86 (CH), 119.83 (CH), 82.6 (C), 55.2 (C), 40.29 (CH<sub>2</sub>), 40.25 (CH<sub>2</sub>), 31.83 (CH<sub>2</sub>), 31.79 (CH<sub>2</sub>), 30.07 (CH<sub>2</sub>), 30.01 (CH<sub>2</sub>), 29.27 (CH<sub>2</sub>), 29.24 (CH<sub>2</sub>), 29.22 (CH<sub>2</sub>), 29.15 (CH<sub>2</sub>), 23.89 (CH<sub>2</sub>), 23.76 (CH<sub>2</sub>), 22.65 (CH<sub>2</sub>), 22.62 (CH<sub>2</sub>), 14.15 (Me), 14.10 ppm (Me); HRMS (LSIMS<sup>+</sup>, 3-nitrobenzenemethanol) calcd for  $C_{160}H_{190}O_2$  2143.4765 [M]<sup>+</sup>, found: 2143.4831.

2,2",7,7"-Tetrakis(9,9-dioctyl-9H-fluoren-2-yl)dispiro[fluorene-9,11'-

indeno[2,1-a]fluorene-12',9"-fluorene] (2,1-a)-DST-IF (general procedure): Difluorenol 6 (10 mg, 4.7 µmol) was dissolved in dichloromethane or acetonitrile and stirred for 15 min at room temperature or at reflux. Boron trifluoride etherate (48 % BF<sub>3</sub>) (5 µL) was added and the resulting mixture was stirred for one hour (until total conversion of the starting difluorenol) at the desired temperature. The crude mixture was evaporated to dryness, analyzed by <sup>1</sup>H NMR spectroscopy to determine the ratio of isomers (1,2-b)-DST-IF and (2,1-a)-DST-IF formed, and the isomer (2,1-

a)-DST-IF was purified by successive column chromatography on silica, eluting for each with dichloromethane-light petroleum (2/8) and by crystallization in a mixture of MeOH/CDCl<sub>3</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.13$  (s, 2H; ArH), 7.86 (d, J=7.5 Hz, 2H; ArH), 7.52-7.43 (m, 8H; ArH), 7.31-7.17 (m, 26H; ArH), 6.90 (t, J=7.5 Hz, 2H; ArH), 6.74 (s, J=8.5 Hz, 4H; ArH), 6.57 (s, 4H; ArH), 6.23 (d, J=7.5 Hz, 2H; ArH), 1.95-1.82 (m, 16H; ArH), 1.20-0.90 (m, 80H; CH<sub>2</sub>), 0.83-0.77 (m, 24H; Me), 0.70-0.50 ppm (m, 16H; CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 151.1$  (C), 151.0 (C), 150.9 (C), 147.4 (C), 143.8 (C), 143.4 (C), 140.7 (C), 140.4 (C), 140.2 (C), 140.0 (C), 139.67 (C), 139.66, (C), 127.8 (CH), 127.2 (CH), 126.7 (CH), 126.58 (CH), 126.52 (CH), 126.4 (CH), 122.9 (CH×2), 121.6 (CH), 121.0 (CH), 120.2 (CH×2), 119.7 (CH), 119.48 (CH), 119.41 (CH), 66.5 (C), 54.9 (C), 40.08 (CH<sub>2</sub>), 40.06 (CH<sub>2</sub>), 31.73 (CH<sub>2</sub>), 31.71 (CH<sub>2</sub>), 30.02 (CH<sub>2</sub>), 29.92 (CH<sub>2</sub>), 29.22 (CH<sub>2</sub>), 29.18 (CH<sub>2</sub>), 29.14 (CH<sub>2</sub>), 29.11 (CH<sub>2</sub>), 23.91 (CH<sub>2</sub>), 23.77 (CH<sub>2</sub>), 22.58 (CH<sub>2</sub>), 22.57 (CH<sub>2</sub>), 14.07 (Me), 14.05 ppm (Me); IR (KBr): v=3060 (aryl CH), 2923 (CH<sub>2</sub>, CH<sub>3</sub>), 2852 (CH<sub>2</sub>, CH<sub>3</sub>), 1440,1450, 1403, 1296, 1261 cm<sup>-1</sup>; UV/Vis (THF):  $\lambda_{max} = 343$ , 353 nm; HRMS (LSIMS+, o-nitrophenyloctyl ether/acetic acid/MeOH) calcd for C<sub>160</sub>H<sub>186</sub>: 2107.45546 [M]+, found: 2107.4606.

9,9'-(1,1':4',1"-Terphenyl-2,2"-diyl)bis(2,7-dibromo-9H-fluoren-9-ol) (7): In a schlenk tube under an argon atmosphere, 2,2"-DITP 3 (1.00 g, 2.1 mmol) was dissolved in dry THF (90 mL) and the solution was degassed. The mixture was cooled to -78 °C and stirred at this temperature for 10 min. A solution of nBuLi (1.6 M in hexane, 5.20 mL, 8.3 mmol) was added dropwise in 3.5 min. The resulting yellow solution was stirred for a further 3.5 min and 2,7-dibromofluorenone (1.54 g, 4.6 mmol), dissolved in dry and degassed THF, was added dropwise in 4 min by using a cannula. The resulting orange solution was allowed to stir overnight (from -70°C to room temperature) and the mixture was poured into a saturated solution of ammonium chloride (100 mL) and extracted with dichloromethane. The combined extracts were dried (MgSO<sub>4</sub>) and the solvent was removed in vacuo and purified by successive column chromatography on silica, eluting for each with ethyl acetate-light petroleum (0.5/9.5-3/7), dichloromethane-light petroleum (3/1-4/1), and dichloromethaneethyl acetate (2/1), to afford 7 as a colorless solid (1.12 g, 60%). M.p. >300 °C; <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta = 8.46$  (d, J = 7.8 Hz, 2H; ArH), 7.50 (t, J=7.1 Hz, 2H; ArH), 7.41 (t, J=7.1 Hz, 2H; ArH), 7.24 (d, J=8.0 Hz, 4H; ArH), 7.16 (s, 4H; ArH), 7.09 (d, J=8.0 Hz, 4H; ArH), 6.88 (d, J= 6.8 Hz, 2H; ArH), 5.43 (s, exch D<sub>2</sub>O, 2H; OH), 5.36 ppm (s, 4H; ArH);  $^{13}\text{C}\,\text{NMR}$  ([D<sub>8</sub>]THF):  $\delta$  =154.7 (2×C), 141.8 (C), 140.8 (C), 139.5 (C), 138.6 (C), 132.2 (CH), 131.9 (CH), 128.8 (CH), 128.03 (CH), 128.0 (CH) 127.9 (CH), 127.7 (CH), 122.3 (CH), 82.3 ppm (COH); HRMS (ESI+, MeOH/CH<sub>2</sub>Cl<sub>2</sub> 90/10): calcd for  $C_{44}H_{26}O_2^{79}Br_4Na$ : 924.85639 [*M*+Na]<sup>+</sup>; found: 924.8544; IR (KBr):  $\tilde{\nu} = 3574$  (OH), 3499 (OH), 3068 (arvl CH), 1574, 1590, 1480, 1448, 1413, 1317, 1241, 1163, 1118, 1059, 1005 cm<sup>-1</sup>.

 $2,2^{\prime\prime},7,7^{\prime\prime}\text{-}Tetrakis (9,9\text{-}dioctyl-9H\text{-}fluoren-2\text{-}yl) dispiro [fluorene-9,6^{\prime}\text{-}$ 

indeno[1,2-b]fluorene-12',9"-fluorene] (1,2-b)-DST-IF: Difluorenol 7 (150 mg, 0.16 mmol) was dissolved in dichloromethane and stirred at room temperature for 10 min. Boron trifluoride etherate (48% BF<sub>3</sub>) (150 µL) was added and the resulting mixture was stirred for one night (until total conversion of the starting difluorenol 7). The crude mixture was evaporated to dryness and analyzed by <sup>1</sup>H NMR spectroscopy to determine the ratio of isomers 8 and 9 formed. After washing with a THF/ MeOH mixture, the crude mixture of isomers 8 and 9 was involved in the next step without any further purification. Sodium carbonate (160 mg, 1.5 mmol) dissolved in water (120 mL) was added to the previous crude mixture of isomers 8 and 9 (130 mg, 0.15 mmol), 2 (464 mg, 0.90 mmol), and 1,1'-bis(diphenylphosphino)ferrocenepalladium(II) dichloride dichloromethane complex (12 mg,  $0.015 \; \text{mmol}). \; \text{DMF}$  (70 mL) was then added at room temperature, the schlenk tube degassed, and the mixture was allowed to stir at 130 °C for 12 h under an argon atmosphere. The reaction mixture was then quenched with a saturated ammonium chloride solution (100 mL) and extracted with dichloromethane (4×30 mL). The combined organic layers were washed with water (50 mL), dried (MgSO<sub>4</sub>), and evaporated in vacuo. Purification by column chromatography on silica gel eluting with dichloromethane/light petroleum (2/8) afforded (1,2-b)-DST-IF as a slightly yellow solid (55 mg, 17%); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 8.08$  (d, J = 7.5 Hz, 4H; ArH), 7.81 (d, J = 7.5 Hz, 4H; ArH), 7.67 (d, J=7.2 Hz, 2H; ArH), 7.58 (s, , 4H; ArH), 7.49 (t, J=

Chem. Eur. J. 2011, 17, 14031-14046

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 14043

7.5 Hz, 8H; ArH), 7.43 (s, 2H; ArH), 7.34–7.21 (m, 18H; ArH), 7.15 (s, 4H; ArH), 7.08 (t, J=7.5 Hz, 2H; ArH), 6.81 (d, J=7.5 Hz, 2H; ArH), 2.03–1.89 (m, 16H; ArH), 1.20–0.90 (m, 80H; CH<sub>2</sub>), 0.80–0.73 (t, J=7.5 Hz, 24 H; Me), 0.68–0.50 ppm (m, 16H; CH<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =151.8 (C), 151.4 (C), 150.5 (C), 149.5 (C), 149.4 (C), 142.6 (C), 142.1 (C), 141.7 (C), 141.1 (C), 141.0 (C), 140.9 (C), 139.9 (C), 128.2 (CH), 127.5 (CH), 127.4 (CH), 127.2 (2×CH), 126.1 (CH), 124.3 (CH), 123.3 (CH), 122.8 (CH), 121.7 (CH), 120.9 (CH), 120.7 (CH), 120.2 (2×CH), 116.4 (CH), 66.5 (C), 55.5 (C), 40.69 (CH<sub>2</sub>), 40.64 (CH<sub>2</sub>), 32.17 (CH<sub>2</sub>), 30.35 (CH<sub>2</sub>), 29.60 (CH<sub>2</sub>), 29.58 (CH<sub>2</sub>), 29.66 (CH<sub>2</sub>), 29.52 (CH<sub>2</sub>), 24.25 (CH<sub>2</sub>), 24.19 (CH<sub>2</sub>), 23.00 (CH<sub>2</sub>), 22.96 (CH<sub>2</sub>), 14.30 (Me), 14.28 ppm (Me); IR (KBr):  $\bar{\nu}$ =3060 (aryl CH), 2925 (CH<sub>2</sub>, CH<sub>3</sub>), 1440, 1451, 1403, 1260 cm<sup>-1</sup>; UV/Vis (THF):  $\lambda_{max}$ =347, 350 nm (br); HRMS (ESI<sup>+</sup>, MeOH/CHCl<sub>3</sub> 90/10): calcd for C<sub>160</sub>H<sub>186</sub>: 2107.45546 [M]<sup>+</sup>, found: 2107.4556.

**Spectroscopic studies**: UV/Vis spectra were recorded in solution using a UV-Visible-NIR spectrophotometer CARY 5000-Varian or SHIMADZU UV-1605 spectrophotometer. The optical band gap was calculated from the absorption edge of the UV/Vis absorption spectrum using the formula  $\Delta E^{\text{opt}}$  [eV]= $hc/\lambda$ ,  $\lambda$  being the absorption edge (in meter). With  $h = 6.6 \times 10^{-34}$ Js ( $1 \text{ eV} = 1.6 \times 10^{-19}$ J) and  $c = 3.0 \times 10^8 \text{ m s}^{-1}$ , this equation may be simplified as:  $\Delta E^{\text{opt}}$  [eV]= $1237.5/\lambda$  (in nm). Photoluminescence spectra were recorded with a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) using a Xenon lamp either in solution (THF). Quantum yields in solution ( $\varphi_{sol}$ ) were calculated relative to quinine sulfate ( $\varphi_{sol} = 0.546$  in H<sub>2</sub>SO<sub>4</sub> 1 N) using standard procedures.<sup>[52]</sup>  $\varphi_{sol}$  was determined according to Equation (1),

$$\phi_{sol} = \phi_{ref} \times 100 \times \frac{(T_s \times A_r)}{(T_r \times A_s)} \left[ \frac{n_s}{n_r} \right]^2 \tag{1}$$

where subscripts s and r refer to the sample and reference, respectively. The integrated area of the emission peak in arbitrary units is given as T, n is the refracting index of the solvent ( $n_s = 1.407$  for THF), and A is the absorbance (A < 0.1). IR spectra were recorded on a VARIAN 640-IR using a PIKE Technologies MIRacle(TM) ATR (single attenuated total reflectance) with a diamond crystal or on a BIORAD IRFTS175C (with KBR pellets).

**Thermal analysis:** Thermogravimetric analyses (TGA) were carried out with a Rigaku Thermoflex instrument under a nitrogen atmosphere between with a heating rate of 5°Cmin<sup>-1</sup>. Melting points were determined by using an electrothermal melting point apparatus.

Electrochemical studies: All electrochemical experiments were performed under argon, using a Pt disk working electrode (diameter 1 mm), the counter electrode was a vitreous carbon rod and the reference electrode was a silver wire in a 0.1 M AgNO3 solution in CH3CN. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc+) couple served as internal standard. For a further comparison of the electrochemical and optical properties, all potentials are referred to the SCE electrode that was calibrated at -0.405 V versus the Fc/Fc+ system. The three-electrode cell was connected to a PAR Model 273 potentiostat/galvanostat (PAR, EG&G, USA) monitored with the ECHEM Software. Dichloromethane with less than 100 ppm of water (ref. SDS 02910E21) was used without purification. Activated  $Al_2O_3$  was added to the electrolytic solution to remove excess moisture. Following the work of Jenekhe and co-workers,[68] we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from: LUMO  $[eV] = -[E_{onset}^{red}$  (vs. SCE) + 4.4] and the HOMO level from: HOMO  $[eV] = -[E_{onset}^{ox}$  (vs. SCE) + 4.4], based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from:  $\Delta E^{el} = |HOMO-LUMO|$  (in eV). The estimated errors in the determination of the onset potential values are  $\pm 20 \text{ mV}$  for  $E_{\text{onset}}^{\text{ox}}$  and  $\pm 50 \text{ mV}$  for  $E_{\text{onset}}^{\text{red}}$ 

**Computational details**: Full geometry optimization with density functional theory (DFT)<sup>[75,76]</sup> were performed with the hybrid Becke-3 parameter exchange<sup>[71,77,78]</sup> functional and the Lee–Yang–Parr non-local correlation functional<sup>[79]</sup> (B3LYP) implemented in the Gaussian 09 (Revision B.01) program suite<sup>[69]</sup> using the 6–31G\* basis set<sup>[80]</sup> and the default convergence criterion implemented in the program. The figures were generated with MOLEKEL 4.3.<sup>[70]</sup>

Fabrication and characterization of OLEDs: Organic light-emitting diodes were prepared according to the following procedure. The indium tin oxide (ITO) coated glass electrodes were partially etched and cleaned in successive ultrasonic baths using acetone, ethanol, and 2-propanol. UV-ozone treatment was applied to the substrates to increase the hydrophilic nature of the surface and to remove any residual contamination.<sup>[81]</sup> A water dispersion of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, Clevios) was spin-coated on top of the ITO sheets at 6000 rpm to form a 40 nm-thick layer. A thermal annealing under vacuum (10 mbar) at 80 °C for 30 min was subsequently applied to the PEDOT:PSS layer to remove any residual moisture. PEDOT:PSS possesses a HOMO level of -5.1 eV, which enables a better hole injection from the anode to the active layer. It also smoothes the ITO surface and therefore prevents any possible short circuits due to the ITO spikes.<sup>[82]</sup> The further device elaboration steps and characterizations were carried out under an inert atmosphere (N2) inside a glove box system. Then the emissive layer was spin-coated on top of the PEDOT-PSS layer at 1000 rpm from a xylene solution. Calcium cathodes were finally evaporated through a shadow mask under a secondary vacuum (ca.  $10^{-6}$  mbar). Current-voltage-luminance (I-V-L) curves were recorded by using a Keithley 4200 SCS instrument. Light emission was collected by using a calibrated photodiode coupled to a Hamamatsu Photosensor amplifier C9329. Electroluminescence spectra were measured with a CDD spectrometer (Ocean Optics HR 2000).

#### Acknowledgements

D.T. thanks Région Bretagne for a studentship. We thank Dr. Nathalie Audebrand (Université de Rennes 1) for TGA measurements, Dr Rémi Métivier (ENS Cachan) for helpful discussions, Vincent Quéméner for his contribution to the synthesis of terfluorenone 5, Stéphanie Fryars for IR data and technical assistance, the C.R.M.P.O (Centre Régional de Mesure Physique de l'Ouest, Rennes) for high-resolution mass measurements, and the CINES (Montpellier) for computing time.

- Chem. Rev. 2007, 107, 922–1386; thematic issue: Organic Electronics and Optoelectronics (Guest Eds.: S. R. Forrest, M. E. Thompson).
- [2] Chem. Mater. 2011, 23, 309-922; thematic issue: π-Functional Materials (Guest Eds.: J. L. Bredas, S. R. Marder, E. Reichmanis).
- [3] A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* 2009, 109, 897–1091.
- [4] U. Scherf, E. J. W. List, Adv. Mater. 2002, 14, 477-487.
- [5] D. Y. Kim, H. N. Cho, C. Y. Kim, Prog. Polym. Sci. 2000, 25, 1089– 1139.
- [6] A. C. Grimsdale, K. Müllen, Macromol. Rapid Commun. 2007, 28, 1676–1702.
- [7] S. Becker, C. Ego, A. C. Grimsdale, E. J. W. List, D. Marsitzky, A. Pogantsch, S. Setayesh, G. Leising, K. Müllen, *Synth. Met.* 2001, 125, 73–80.
- [8] L.-H. Xie, J. Liang, J. Song, C.-R. Yin, W. Huang, Curr. Org. Chem. 2010, 14, 2169–2195.
- [9] Z. Ma, P. Sonar, Z.-K. Chen, Curr. Org. Chem. 2010, 14, 2039-2069.
- [10] C.-C. Wu, T.-L. Liu, W.-Y. Hung, Y.-T. Lin, K.-T. Wong, R.-T. Chen, Y.-M. Chen, Y.-Y. Chien, J. Am. Chem. Soc. 2003, 125, 3710–3711.
- [11] C.-C. Wu, Y.-T. Lin, K.-T. Wong, R.-T. Chen, Y.-Y. Chien, Adv. Mater. 2004, 16, 61–65.
- [12] K.-T. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, S.-M. Peng, J. Am. Chem. Soc. 2002, 124, 11576–11577.
- [13] B. Huang, J. Li, L. Chen, J. Qin, C. A. Di, G. Yu, Y. Liu, J. Polym. Sci. Part A 2005, 43, 4517–4529.

14044 -

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 2011, 17, 14031-14046

- [14] F.-I. Wu, R. Dodda, D. S. Reddy, C.-F. Shu, J. Mater. Chem. 2002, 12, 2893–2897.
- [15] T. Oyamada, C.-H. Chang, T.-C. Chao, F.-C. Fang, C.-C. Wu, K.-T. Wong, H. Sasabe, C. Adachi, J. Phys. Chem. B 2007, 111, 108–115.
- [16] K.-T. Wong, R.-T. Chen, F.-C. Fang, C.-C. Wu, Y.-T. Lin, Org. Lett. 2005, 7, 1979–1982.
- [17] L.-H. Xie, T. Fu, X.-Y. Hou, C. Tang, Y.-R. Hua, R.-J. Wang, Q.-L. Fan, B. Peng, W. Wei, W. Huang, *Tetrahedron Lett.* **2006**, 47, 6421– 6424.
- [18] K.-T. Wong, T.-Y. Hwu, A. Balaiah, T.-C. Chao, F.-C. Fang, C.-T. Lee, Y.-C. Peng, Org. Lett. 2006, 8, 1415–1418.
- [19] L. Zhu, C. Yang, J. Qin, Chem. Commun. 2008, 6303-6305.
- [20] Z. Wang, H. Shao, J. Ye, L. Zhang, P. Lu, Adv. Funct. Mater. 2007, 17, 253–263.
- [21] S. Tang, M. Liu, P. Lu, G. Cheng, M. Zeng, Z. Xie, H. Xu, H. Wang, B. Yang, Y. Ma, D. Yan, Org. Electron. 2008, 9, 241–252.
- [22] D. Katsis, Y. H. Geng, J. J. Ou, S. W. Culligan, A. Trajkovska, S. H. Chen, L. J. Rothberg, *Chem. Mater.* 2002, 14, 1332–1339.
- [23] T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker, J. Salbeck, *Chem. Rev.* 2007, 107, 1011–1065.
- [24] N. Cocherel, C. Poriel, L. Vignau, J.-F. Bergamini, J. Rault-Berthelot, Org. Lett. 2010, 12, 452–455.
- [25] C. Poriel, N. Cocherel, J. Rault-Berthelot, L. Vignau, O. Jeannin, *Chem. Eur. J.* 2011, 17, 12631–12645.
- [26] D. Horhant, J.-J. Liang, M. Virboul, C. Poriel, G. Alcaraz, J. Rault-Berthelot, Org. Lett. 2006, 8, 257–260.
- [27] C. Poriel, J.-J. Liang, J. Rault-Berthelot, F. Barrière, N. Cocherel, A. M. Z. Slawin, D. Horhant, M. Virboul, G. Alcaraz, N. Audebrand, L. Vignau, N. Huby, L. Hirsch, G. Wantz, *Chem. Eur. J.* 2007, 13, 10055–10069.
- [28] D. Thirion, C. Poriel, J. Rault-Berthelot, F. Barrière, O. Jeannin, *Chem. Eur. J.* 2010, 16, 13646–13658.
- [29] N. Cocherel, C. Poriel, J. Rault-Berthelot, F. Barrière, N. Audebrand, A. M. Z. Slawin, L. Vignau, *Chem. Eur. J.* 2008, 14, 11328– 11342.
- [30] D. Thirion, J. Rault-Berthelot, L. Vignau, C. Poriel, Org. Lett. 2011, 13, 4418–4421.
- [31] C. Poriel, J. Rault-Berthelot, F. Barrière, A. M. Z. Slawin, Org. Lett. 2008, 10, 373–376.
- [32] C. Poriel, F. Barrière, D. Thirion, J. Rault-Berthelot, *Chem. Eur. J.* 2009, 15, 13304–13307.
- [33] D. Thirion, C. Poriel, F. Barrière, O. Jeannin, R. Métivier, J. Rault-Berthelot, Org. Lett. 2009, 11, 4794–4797.
- [34] D. Thirion, C. Poriel, R. Métivier, J. Rault-Berthelot, F. Barrière, O. Jeannin, *Chem. Eur. J.* 2011, 17, 10272–10287.
- [35] F. Jaramillo-Isaza, M. L. Turner, J. Mater. Chem. 2006, 16, 83-89.
- [36] W. Linert, Y. Fukuda, A. Camard, Coord. Chem. Rev. 2001, 218, 113–152.
- [37] X. Mei, C. Wolf, J. Org. Chem. 2005, 70, 2299-2305.
- [38] W.-L. Wang, J. Xu, Z. Sun, X. Zhang, Y. Lu, Y.-H. Lai, *Macromole-cules* 2006, 39, 7277–7285.
- [39] R. Rathore, S. H. Abdelwahed, I. A. Guzei, J. Am. Chem. Soc. 2003, 125, 8712–8713.
- [40] T. Nakano, T. Yade, J. Am. Chem. Soc. 2003, 125, 15474-15484.
- [41] R. Nandy, S. Sankararaman, Org. Biomol. Chem. 2010, 8, 2260– 2266.
- [42] D. Cornelis, E. Franz, I. Asselberghs, K. Clays, T. Verbiest, G. Koeckelberghs, J. Am. Chem. Soc. 2011, 133, 1317–1327.
- [43] S. Tang, M. Liu, P. Lu, H. Xia, M. Li, Z. Xie, F. Z. Shen, C. Gu, H. Wang, B. Yang, Y. Ma, Adv. Funct. Mater. 2007, 17, 2869–2877.
- [44] X. Zhou, J. He, L. S. Liao, M. Lu, X. M. Ding, X. Y. Hou, X. M. Zhang, X. Q. He, S.-T. Lee, *Adv. Mater.* 2000, *12*, 265–269.
- [45] G. Klaerner, R. D. Miller, Macromolecules 1998, 31, 2007-2009.
- [46] C.-C. Wu, T.-L. Liu, Y.-T. Lin, W.-Y. Hung, T.-H. Ke, K.-T. Wong, T.-C. Chao, Appl. Phys. Lett. 2004, 85, 1172–1174.
- [47] H. Li, A. S. Batsanov, K. C. Moss, H. L. Vaughan, F. B. Dias, K. T. Kamtekar, M. R. Bryce, A. P. Monkman, *Chem. Commun.* 2010, 46, 4812–4814.

- [48] M. Belletête, M. Ranger, S. Beaupré, M. Leclerc, G. Durocher, *Chem. Phys. Lett.* 2000, 316, 101–107.
- [49] J.-F. Wang, J.-K. Feng, A.-M. Ren, L. Yang, Chin. J. Chem. 2005, 23, 1618–1624.
- [50] D. Wenger, V. L. Malinovskii, R. Häner, Chem. Commun. 2011, 47, 3168–3170.
- [51] J.-P. Choi, K.-T. Wong, Y.-M. Chen, J.-K. Yu, P.-T. Chou, A. J. Bard, J. Phys. Chem. B 2003, 107, 14407–14413.
- [52] S. Merlet, M. Birau, Z. Y. Wang, Org. Lett. 2002, 4, 2157-2159.
- [53] A. Iida, S. Yamaguchi, Chem. Commun. 2009, 3002-3004.
- [54] K. L. Chan, M. Sims, S. I. Pascu, M. Ariu, A. B. Holmes, D. D. C. Bradley, *Adv. Funct. Mater.* **2009**, *19*, 2147–2154.
- [55] A. C. Grimsdale, Curr. Org. Chem. 2010, 14, 2196-2217.
- [56] M. Leclerc, J. Polym. Sci. Part A 2001, 39, 2867-2873.
- [57] J. Jacob, S. Sax, M. Gaal, E. J. W. List, A. C. Grimsdale, K. Müllen, *Macromolecules* 2005, *38*, 9933–9938.
- [58] A. K. Mishra, M. Graf, F. Grasse, J. Jacob, E. J. W. List, K. Müllen, *Chem. Mater.* 2006, 18, 2879–2885.
- [59] L. Romaner, G. Heimel, H. Wiesenhofer, P. Scanducci de Freitas, U. Scherf, J. L. Bredas, E. Zojer, E. J. W. List, *Chem. Mater.* 2004, 16, 4667–4674.
- [60] M. Sims, D. D. C. Bradley, M. Ariu, M. Koeberg, A. Asimakis, M. Grell, D. G. Lidzey, Adv. Funct. Mater. 2004, 14, 765–781.
- [61] R. Abbel, M. Wolffs, R. A. A. Bovee, J. L. J. van Dongen, X. Lou, O. Henze, W. J. Feast, E. W. Meijer, A. P. H. J. Schenning, *Adv. Mater.* 2009, 21, 597–602.
- [62] L. Oldridge, M. Kastler, K. Müllen, Chem. Commun. 2006, 885– 887.
- [63] F. Uckert, S. Setayesh, K. Müllen, Macromolecules 1999, 32, 4519– 4524.
- [64] N. S. S. Kumar, S. Varghese, N. Rath, P. S. Das, J. Phys. Chem. C 2008, 112, 8429–8437.
- [65] R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. Rath, P. N. Tamaoki, S. Das, J. Phys. Chem. C 2008, 112, 2137–2146.
- [66] S. Varghese, S. Das, J. Phys. Chem. Lett. 2011, 2, 863-873.
- [67] C.-H. Lu, C.-H. Tsai, F.-C. Chang, K.-U. Jeong, S.-W. Kuo, J. Colloid Interface Sci. 2011, 358, 93–101.
- [68] A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* 2004, 16, 4556–4573.
- [69] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, R. Scalmani, G. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brother, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, version A02, Gaussian, Inc., Wallingford, CT, **2009**.
- [70] H. P. Flükiger, S. Lüthi, S. Portmann, J. Weber, 2000, MOLEKEL 4.3, Swiss National Supercomputing Centre CSCS, Manno (Switzerland).
- [71] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [72] P. Hapiot, C. Lagrost, F. Le Floch, E. Raoult, J. Rault-Berthelot, *Chem. Mater.* 2005, 17, 2003–2012.
- [73] V. J. Chebny, R. Shukla, S. V. Lindeman, R. Rathore, Org. Lett. 2009, 11, 1939–1942.
- [74] J. Rault-Berthelot, C. Poriel, F. Justaud, F. Barrière, New J. Chem. 2008, 32, 1259–1266.
- [75] P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, B864-B871.
- [76] R. G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.
- [77] A. D. Becke, Phys. Rev. A 1988, 38, 3098-3100.
- [78] A. D. Becke, J. Chem. Phys. 1993, 98, 1372-1377.
- [79] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.

www.chemeurj.org

## **FULL PAPER**

- [80] P. C. Hariharan, J. A. Pople, Chem. Phys. Lett. 1972, 16, 217-219.
- [81] K. Sugiyama, H. Ishii, Y. Ouchi, K. Seki, J. Appl. Phys. 2000, 87, 295-298.
- [82] G. Wantz, L. Hirsch, N. Huby, L. Vignau, J. S. Silvain, A. S. Barrière, J. P. Parneix, *Thin Solid Films* 2005, 485, 247–251.

Received: July 19, 2011 Published online: November 14, 2011