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### (2,1-*a*)-Indenofluorene Derivatives: Syntheses, X-ray Structures, Optical and Electrochemical Properties

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**Abstract:** Two novel fluorophores based on the (2,1-*a*)-indenofluorenyl backbone, dispiro[fluorene-9,11'indeno[2,1-*a*]fluorene-12',9"-fluorene], (2,1-*a*)-DSF-IF and 11,12dihydroindeno[2,1-*a*]fluorene (2,1-*a*)-IF have been prepared through original and efficient synthetic approaches. After consideration of synthetic features, the structural, optical and electrochemical properties of these new

**Keywords:** blue/violet fluorescence • fluorescence • indenofluorene • intramolecular cyclization • spiro compounds • structure–properties relationship blue/violet emitters have been studied in detail by a combined experimental and theoretical approach. The properties of the (2,1-a)-DSF-IF and (2,1-a)-IF are also compared to those of their corresponding positional isomers based on the (1,2-b)-indenofluorenyl backbone and those of related dispirofluorene heteroacenes.

### Introduction

Recent developments in the design of efficient materials for organic electronics have shown that fused phenylene oligomers are highly promising building blocks for such applications.<sup>[1,2]</sup> For example, Müllen's<sup>[3-6]</sup> and Mark's<sup>[7-9]</sup> groups have developed highly efficient materials based on ladder oligo- or polyphenylenes for various applications including organic light emitting devices (OLED), organic field effect transistors (OFET) and photovoltaic cells. Notably, rigid and planar molecular structure of fluorene has turned this molecule as one of the most promising material for blue OLED applications.<sup>[1,2,10]</sup> The rigidity of the fluorene core arising from the methylene bridging unit at the 2,2'-position of the biphenyl core has led to the development of numerous other bridged oligophenylene materials.<sup>[1,2]</sup> Of particular interest was the structurally related (1,2-b)-indenofluorene (1,2-b)-IF (Scheme 1), which possess some unique properties due to the longer planar *p*-terphenyl backbone: for example, increase of the quantum yield. Thus, the pioneering works of Scherf's and Müllen's groups on (1,2-b)-IF<sup>[11-15]</sup> have

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paved the way to the development of such molecules in the field of organic electronics and the (1,2-b)-indenofluorenyl core is nowadays a useful and a widely studied building block not only for OLED applications<sup>[1,2,16–27]</sup> but also for two-photon absorption<sup>[28]</sup> or OFET applications.<sup>[7,29–32]</sup> On the contrary, the positional isomer of (1,2-b)-IF, namely (2,1-a)-indenofluorene (2,1-a)-IF, has been very seldom studied and has only been investigated for potential electronics applications very recently (Scheme 1).<sup>[33–36]</sup> An important feature of the two positional isomers is related to their distinct geometric profiles. The methylene bridges are



Scheme 1. (1,2-*b*)-DSF-IF, (2,1-*a*)-DSF-IF, DSF-DIT<sup>[37]</sup> and their building blocks (1,2-*b*)-IF, (2,1-*a*)-IF, DIT.<sup>[37]</sup> DIT: 10,11-dihydrodiindeno[1,2-*b*:2',1'-*d*]thiophene. DSF-DIT: dispiro[fluorene-9,10'-diindeno[1,2-*b*:2',1'-*d*]thiophene-11',9''-fluorene].

on opposite sides or on the same side of the terphenyl core in (1,2-b)-IF or (2,1-a)-IF, respectively. As a consequence, dispirofluorene derivatives (1,2-b)-DSF-IF or (2,1-a)-DSF-IF also possess their fluorene moieties on opposite side or on the same side, respectively, of the terphenyl backbone (Scheme 1). Similar face-to-face arrangement of the two fluorene moieties found in (2,1-a)-



Scheme 2. Synthesis of (2,1-a)-DSF(R<sub>4</sub>)-IF and (1,2-b)-DSF(R<sub>4</sub>)-IF.

DSF-IF has been recently reported by Ohe and co-workers with dispiro compounds, containing heterocycles such as thiophene (DSF-DIT, Scheme 1).<sup>[37]</sup>

As the synthesis of new materials with specific properties is strongly sought worldwide for electronics applications,<sup>[1,2,38-40]</sup> it remains highly important to develop efficient routes towards new fluorophores, such as (2,1-a)-indenofluorene derivatives, in order to fully explore their potential for organic electronic applications. This paper focuses on new approaches towards the synthesis of fluorophores based on the (2,1-a)-indenofluorenyl backbone namely dispiro[fluorene-9,11'-indeno[2,1-*a*]fluorene-12',9''-fluorene] (2,1-*a*)-DSF-IF and 11,12-dihydroindeno[2,1-a]fluorene (2,1-a)-IF. After consideration of synthetic details, the structural characterization, optical and electrochemical properties of these new blue/violet fluorophores are reported in detail by a combined experimental and theoretical approach. The properties of (2,1-a)-DSF-IF and (2,1-a)-IF are compared to those of their corresponding (1,2-b)-indenofluorenyl positional isomers and those of the diindenothiophene derivatives (DIT, DSF-DIT) recently reported by Ohe (Scheme 1).<sup>[37]</sup> Such structures-properties relationships are of great interest for the future design of efficient materials for organic electronics.

### **Results and Discussion**

#### Synthesis

Recently our group has developed an original synthetic approach towards spirofluorene–indenofluorene derivatives based on a double lithium–halogen exchange reaction between 2,2"-diiodo-[1,1';4',1"]-terphenyl and tailored 9-fluorenones (see Scheme 2).<sup>[35,41]</sup> This synthesis involves in the last step an intramolecular bicyclization reaction of a difluorenol. From a statistical point of view, this bicyclization may occur on either side of the terphenyl backbone, leading to the formation of two positional isomers possessing different geometry: (2,1-*a*)- and (1,2-*b*)-DSF(R<sub>4</sub>)-IF (Scheme 2). However, when R=H, the positional isomer with the face-to-face fluorene moieties (2,1-*a*)-DSF-IF is only obtained with a very low yield (<10%) and is difficult to separate by column chromatography from its isomer (1,2-*b*)-DSF-IF.

We thus started to investigate a new route towards (2,1-a)-DSF-IF, which presents the advantage of being also suitable for the synthesis of its parent hydrocarbon (2,1-a)-IF (Scheme 3). This new approach is based on a coupling reaction between the diketone **1** and a 2-halogenobiphenyl. The key feature in this approach is to build up the (2,1-a)-indenofluorenyl core prior to the final cyclization step in order to avoid isomers formation.

The different synthetic approaches investigated in this work for the synthesis of (2,1-a)-IF and (2,1-a)-DSF-IF are presented in Scheme 3. We first consider access to (2,1-a)-IF following the synthetic strategy reported by Covion Organic Semiconductors (Scheme 3, route 1).<sup>[33]</sup>

Route 1 started with a cycloaddition reaction between 1,4-diphenyl-1,3-butadiene and dimethyl-but-2-ynedioate to afford 2 with 85% yield. Dicarboxylate 2 was then dehydrogenated in the presence of Pd/C to build up the terphenyl backbone with the two methylcarboxylate groups in place. Dimethylcarboxylate 3 was then reduced in its corresponding diol 4 with diisobutyl aluminium hydride in dichloromethane. The final step towards (2,1-a)-IF was the electrophilic intramolecular cyclization reaction. Similar reactions have been described for related molecules, either in concentrated sulphuric acid at RT or 80°C,<sup>[26,42]</sup> in acetic acid/hydrochloric acid at  $100 \,^{\circ}C^{[40,43]}$  or in the presence of Lewis acids (TiCl<sub>4</sub> or BF<sub>3</sub>·OEt<sub>2</sub>).<sup>[44–47]</sup> However, acidic treatment of **4** in these different conditions failed to produce (2,1-a)-IF. In polyphosphoric acid at 180°C<sup>[33]</sup> we finally managed to isolate (2,1-a)-IF with a low yield (less than 8%). This low yield has been ascribed to intermolecular side oligomerization reactions. High dilution conditions and screening for solvent and acid types (Brønsted vs Lewis acids) did not significantly improve the yield of the reaction. After intensive scouting, the best cyclization procedure found was to slowly add a solution of diol 4 in 1,2-dichlorobenzene into polyphosphoric acid stirred at 140°C, giving (2,1-a)-IF with 27% yield. This route offers a rapid access to (2,1-a)-IF but the poor efficiency of the last cyclization step strongly hinders the overall yield of the whole approach (18%).

In the light of recent results for the synthesis of (1,2-b)-indenofluorenes,<sup>[22,31,46,48]</sup> ladder phenylenes,<sup>[3,42,46,49]</sup> isotruxenes<sup>[50–52]</sup> or for other fused aromatic molecules,<sup>[53,54]</sup> the synthetic approach has been modified. In this context diketone  $\mathbf{1}^{[36,55]}$  was the main target as this molecule would allow a

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Scheme 3. Synthesis of (2,1-a)-IF and (2,1-a)-DSF-IF. PPA = Polyphosphoric acid.

straightforward access not only to (2,1-a)-IF through a Wolf-Kishner reduction but also to (2,1-a)-DSF-IF through a coupling reaction with 2-bromobiphenyl (Scheme 3). Thus, the direct intramolecular cyclization of diester 3 was at-However, acidic treatment (concentrated tempted.  $H_2SO_4^{[26,48]}$  or various Lewis acids at RT) of diester 3 or of dicarboxylic acid 5 only led to traces of 1. Even the Lewis acid-promoted intramolecular Friedel-Crafts acylation (TiCl<sub>4</sub>) of the acid dichloride prepared from 5 (oxalyl chloride in DMF at RT) known to be highly efficient for such cyclization reaction,<sup>[46,53,56]</sup> did not give **1**. We note, however, that these different cyclization attempts at room temperature have led to the unexpected formation of the corresponding phthalic anhydride derivative, namely 4,7-diphenyl-2-benzofuran-1,3-dione, through an intramolecular side reaction (see Supporting Information). By increasing the temperature to 80 °C the intramolecular cyclization of 3 or 5 in concentrated  $H_2SO_4$  gave diketone 1 with a very low yield (ca. 8%). Yang et al. have recently reported new access to isotruxenone derivatives using similar intramolecular cyclization reaction and have highlighted the dramatic effect of the temperature on the yield of the reaction.<sup>[50]</sup> Following the Yang's conditions (5 min at 140 °C in concentrated  $H_2SO_4$ ) the cyclization of either **3** or **5** (Scheme 3, route 2) has finally led to the formation of the expected diketone 1 though with low to moderate yields (12 and 38%, respectively). It is important to note that under similar conditions, that is, 5 min at 140 °C in  $H_2SO_4$ , the phthalic anhydride has also led to the formation of 1 (yield:  $\approx 15-30\%$ , see Supporting Information). It should be noted that diketone 1 has also been obtained by the oxidation of the two methylene bridges of (2,1-a)-IF in the presence of chromium oxide in acetic anhydride with 75% yield (Scheme 3, route 1).

With key diketone 1 in hand, (2,1-a)-IF was finally obtained in basic media through a Wolf-Kishner reduction as

already described for similar fused phenylene derivatives.<sup>[26,49]</sup> The synthesis of (2,1-a)-DSF-IF was then carried out through a two-step procedure. The lithium-bromine exchange of 2-bromobiphenyl with n-butyllithium at low temperature, followed by addition of diketone 1 afforded diol 6 with 41% yield. It should be noted that several groups have also reported low to moderate yields for similar coupling reactions.<sup>[22,51,52]</sup> Diol 6 was then involved in an intramolecular cyclization reaction in the presence of boron trifluoride etherate to provide the expected (2,1-a)-DSF-IF with an overall yield of 38% over the two steps. Thus, the synthetic strategy followed in route 2 (Scheme 3) provides (2,1-a)-IF and (2,1-a)-DSF-IF with overall yields of 21 and 11%, respectively. Route 2 is efficient and straightforward but still suffers from the moderate yield of the intramolecular cyclization reaction leading to key diketone 1. It should be stressed that both (2,1-a)-IF and (2,1-a)-DSF-IF exhibit good solubility in common organic solvent such as CH<sub>2</sub>Cl<sub>2</sub> and THF, which is not the case for their corresponding (1,2b)-positional isomers (1,2-b)-IF and (1,2-b)-DSF-IF.<sup>[27]</sup> This is of great importance for further solution-processable electronic applications. Thus, the present findings suggest that diketone 1 has great potential as key structure to prepare various oligomers with the (2,1-a)-indenofluorenyl backbone.

The molecular structure of (2,1-a)-IF and (2,1-a)-DSF-IF were determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and by mass spectrometry. Moreover, the molecular arrangement of (2,1-a)-DSF-IF were also confirmed by HMBC NMR experiments (see Figure in Supporting Information). Indeed, we have recently shown that spiro carbons are convenient probes to detect neighboring hydrogen atoms through longrange shift correlations.<sup>[34]</sup>

#### **Physicochemical properties**

**Structural properties:** Single crystals of (2,1-a)-DSF-IF and (2,1-a)-IF were obtained by slow diffusion of hexane in CDCl<sub>3</sub> solution and analyzed by X-ray diffraction in order to elucidate their molecular structure (Figure 1).



Figure 1. Views of the molecular structure of (2,1-a)-DSF-IF (top) and (2,1-a)-IF (bottom) from single crystal X-Ray diffraction data (hydrogen atoms have been omitted for clarity).

(2,1-a)-DSF-IF is a dispiro molecule with a linear suprafacial geometry (Figure 1, top).<sup>[57]</sup> The (2,1-a)-indenofluorenyl core has a maximum length of 10.8, 0.3 Å shorter than the (1,2-b)-indenofluorenyl core.<sup>[27]</sup> Moreover, the (2,1-a)-indenofluorenyl core presents two distortions on both sides as previously observed for similar structures.<sup>[27,34,37]</sup> The dihedral angles between the plane of the central phenyl ring 2 and those of the side rings 1 and 3 have been measured to about 3.1 and 6.9°, respectively (see phenyl rings labelling in Figure 1). The distance between the two spiro carbons is 3.43 Å, very close to the distance measured for its congener (2,1-a)-DSF $(tBu)_4$ -IF  $(3.41 \text{ Å})^{[34]}$  but longer than that measured for (2,1-a)-IF (3.35 Å, Figure 1, bottom). This distance between the two spiro carbons is between that measured for  $\pi$ -stacked polyfluorenes (around 2.7 Å) described by Rathore and co-workers,<sup>[58]</sup> and those recently reported by Ohe and co-workers for similar dispirofluorene-heteroacenes derivatives with face-to-face fluorene moieties (>3.7 Å), as for example DSF-DIT<sup>[37]</sup> (see Scheme 1, bottom right; it should also be mentioned that an analogue to DSF-DIT incorporating a thiophene ring<sup>[59]</sup> has been recently reported). In these dispirofluorene-heteroacenes<sup>[37]</sup> the fluorene units display an eclipsed conformation. Oppositely, in the  $\pi$ -stacked polyfluorenes described by Rathore<sup>[58]</sup> and those described by Nakano<sup>[60]</sup> the fluorene units are not arranged in a perfect face-to-face manner but are slightly staggered. Within these polyfluorenes, through-space electronic interactions between the  $\pi$ -stacked fluorenes have been shown.<sup>[58,60]</sup> In (2,1-a)-DSF-IF, the fluorene units are also staggered since one of the spiro carbon points slightly above the (2,1-a)-indenofluorene plane (defined through the central phenyl ring 2) while the other spiro carbon points below this plane. This structural feature is not found in the crystal structure of

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(2,1-a)-IF (Figure 1, bottom) and has been ascribed to  $\pi$ stacking interactions in (2,1-a)-DSF-IF, induced by the faceto-face arrangement of the fluorene units. Indeed, in (2,1-a)-IF the methylene carbons are nearly within the (2,1-a)-indenofluorenyl plane (defined through the central phenyl ring 2). The distance between the (2,1-a)-indenofluorenyl plane (defined through the central phenyl ring 2) and the two methylene carbons have been evaluated around 0.03 Å. In addition, (2,1-a)-IF presents a flat structure, 10.8 Å long, with only two small distortions on both sides (dihedral angles between the plane of the central phenyl ring 2 and those of the side rings 1 and 3 are about 1.9 and 2.1°, respectively). All these observations lead us to conclude that in the crystal structure of (2,1-a)-DSF-IF  $\pi$ -stacking interactions occur between face-to-face fluorene units. The magnitude of the  $\pi$ -stacking interactions can be viewed as "medium to weak" if they exhibit rather long centroid-centroid distances (>4.0 Å) together with large slip angles  $(>30^{\circ})$  and vertical displacements (d>2.0 Å). In contrast, "strong"  $\pi$ -stackings show rather short centroid-centroid contacts (<3.8 Å), small slip angles ( $<25^{\circ}$ ) and vertical displacements (<1.5 Å), which translate into a sizable overlap of the aromatic planes.<sup>[61-63]</sup> In (2,1-a)-DSF-IF the ring-centroid/ring-centroid distances between two face-to-face phenyl rings were estimated at about 3.65 and 3.81 Å (see Supporting Information). The vertical displacements and ring slippages between two face-to-face phenyl rings span a narrow range of 1.27 to 1.7 Å for the vertical displacements and of 20.4 to 26.5° for the ring slippage angles (see Supporting Information). Such values of ring-centroid/ringcentroid distances, vertical displacements and ring slippage angles in (2,1-a)-DSF-IF may thus indicate "rather strong"  $\pi$ -stacking interactions in the solid state between the two face-to-face fluorene units.[61-63]

Optical properties: The absorption and emission spectra of (2,1-a)-IF and (2,1-a)-DSF-IF were measured in THF and compared to their respective isomers (1,2-b)-IF and (1,2-b)-DSF-IF, Table 1. The synthesis and the physico-chemical properties of (1,2-b)-IF and (1,2-b)-DSF-IF have been reported previously.<sup>[27]</sup> The absorption spectrum of (2,1-a)-IF presents well-defined bands with two maxima at 307 and 322 nm (Figure 2, left). The absorption maximum of (2,1-a)-IF is blueshifted by 12 nm compared to that of (1,2-b)-IF and hence the (2,1-a)-IF band gap (3.76 eV) determined from the edge of the UV/Vis absorption spectrum, is slightly larger than that determined for (1,2-b)-IF (3.61 eV). This band gap contraction suggests a better delocalization of  $\pi$ electrons in (1,2-b)-IF compared with (2,1-a)-IF. To the best of our knowledge, similar examples of band gap contractions between methylene-bridged *p*-terphenyl isomers are absent from the literature. Band gap contractions, however, have been previously reported in the literature between structurally related *p*-terphenyl derivatives bridged by two ethene linkers, that is, picene and dibenzo[1,2;5,6]anthracene.<sup>[64]</sup>

The absorption spectrum of the dispiro derivative (2,1-a)-DSF-IF, also presents well-defined bands with two maxima

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Table 1. Optical data for (1,2-*b*)-IF, (2,1-*a*)-IF, (1,2-*b*)-DSF-IF and (2,1-*a*)-DSF-IF.

	$\lambda_{abs}$ [nm]	$\lambda_{ex}$ [nm]	$\lambda_{em}$ [nm]	${\pmb{\varPhi}_{ ext{liq}}}^{[ ext{c}]}$	$\lambda_{\rm em} - \lambda_{\rm abs} \ [nm]$	$\Delta E^{\mathrm{opt}}  [\mathrm{eV}]^{\mathrm{[d]}}$	Ref.
(1,2-b)-IF <sup>[a]</sup>	289, 302, 319, 328, 334	334	339, 347, 356	61	5	3.61	[27]
(2,1-a)-IF <sup>[b]</sup>	307, 315, 322	308	326, 343, 360	60	4	3.76	this work
(1,2-b)-DSF-IF <sup>[b]</sup>	298, 310, 328, 336, 345	310	348, 355, 366, 388	62	3	3.51	this work
(2,1-a)-DSF-IF <sup>[b]</sup>	295, 311, 323, 339	311	345, 363, 380, 400	60	6	3.57	this work

[a] In decalin. [b] In THF. [c] The relative quantum yield was measured with reference to quinine sulphate in 1 N H<sub>2</sub>SO<sub>4</sub> ( $\Phi = 0.546$ ).<sup>[26]</sup> [d] Calculated from the edge of the absorption spectrum using  $\Delta E^{\text{opt}} = hc/\lambda$ .



Figure 2. Left: Absorption spectra of (2,1-a)-DSF-IF  $(10^{-6} \text{ M in THF}, \dots)$  and (2,1-a)-IF  $(10^{-6} \text{ M in THF}, \dots)$ . Right: Emission spectra of (2,1-a)-DSF-IF  $(10^{-6} \text{ M in THF}, \dots)$  and (2,1-a)-IF  $(10^{-6} \text{ M in THF}, \dots)$ .

at 323 and 339 nm, redshifted by 16-17 nm from those of (2,1-a)-IF (Figure 2, left). Thus, the incorporation of spirofluorenes within the (2,1-a)-indenofluorenyl framework leads to a bathochromic shift of the absorption maximum and hence to a contraction of the band gap from 3.76 eV for (2,1-a)-IF to 3.57 eV for (2,1-a)-DSF-IF. Ohe and co-workers have recently highlighted a similar red shift within a closely related series of DIT derivatives including some with face-to-face fluorene units (Scheme 1, right).<sup>[37]</sup> Indeed, the absorption spectrum of DSF-DIT presents a maximum wavelength ( $\lambda_{max} = 373$  nm) redshifted by 19 nm compared to that of its central constitutive building block, DIT ( $\lambda_{max}$ = 354 nm). On the contrary, the introduction of the two fluorene units through the spiro linkages within the (1,2-b)-indenofluorenyl core leads to a smaller red shift of the absorption bands ( $\approx$ 10–11 nm) and hence to a weaker contraction of the band gap (3.61 eV for (1,2-b)-IF vs 3.51 eV for (1,2b)-DSF-IF, see Table 1). The amplitude of the red shift measured in the (1,2-b)-series is comparable to the red shift measured between fluorene and 9,9'-spirobifluorene (8 nm).<sup>[27]</sup> Other similar red shift between spiro and nonspiro derivatives have been also reported in the literature and notably assigned to spiroconjugation.[49,65,66] Consequently, the larger red shift observed in the absorption spectra between (2,1-a)-IF and (2,1-a)-DSF-IF (16-17 nm), similar to that observed by Ohe and co-workers (19 nm), may be assigned to the specific face-to-face arrangement of the two spirofluorene units. Indeed, the electronic influence on the indenofluorene core of a cofacial fluorene  $\pi$ -dimer as found in (2,1-a)-DSF-IF, should be different than that of two non-directly interacting fluorene units as found in (1,2b)-DSF-IF.

The emission spectrum of (2,1-a)-IF presents two main bands at 326 and 343 nm and a shoulder at 360 nm (Figure 2, right), hypsochromically shifted by 13 nm compared to its positional isomer (1,2-b)-IF. This hypsochromic shift is similar to that recorded by UV/Vis spectroscopy (see above). Because of the rigid and planar structure of (2,1-a)-IF, the Stokes shift is very small (4 nm) highlighting very little rearrangements in the excited state. Moreover

(2,1-a)-IF is highly fluorescent with a quantum yield of about 60% (compared to quinine sulphate) that is similar to the quantum yield of (1,2-b)-IF.<sup>[26,27]</sup> The emission spectrum of (2,1-a)-DSF-IF also exhibits two main bands at 345 and 363 nm, a smaller one at 380 nm and a shoulder at 400 nm (Figure 2, right), blue shifted by around 19-20 nm compared to (2,1-a)-IF. A similar shift of 18 nm has also been highlighted in fluorescence spectroscopy by Ohe and co-workers between DSF-DIT and DIT.<sup>[37]</sup> As mentioned above this shift is larger than that observed between the emission maxima of (1,2-b)-IF and (1,2-b)-DSF-IF and may be attributed to the different electronic effect of the two cofacial fluorenes, found in (2,1-a)-DSF-IF, on the indenofluorenyl core compared to the two non-directly interacting fluorene moieties, found in (1,2-b)-DSF-IF. Finally, with a high quantum yield (60%) and a very small Stokes shift (6 nm), (2,1-a)-DSF-IF possess similar properties to those presented above for its central constituting core (2,1-a)-IF.

Despite the absence of a typical excimer emission on the fluorescence spectrum of (2,1-a)-DSF-IF (i.e., no large Stokes shift, a low quantum yield and a lack of fine vibronic structure)<sup>[35]</sup> the calculated optimized geometries in the ground state and the first excited singlet state show an interesting structural change (Figure 3). In the ground state (Figure 3, left), the optimized geometry of (2,1-a)-DSF-IF shows a typical up–down arrangement of the spiro carbon atoms yielding a staggered conformation of the face-to-face fluorene groups. Indeed, the calculated spiro–spiro torsion angle is 9.9° in the optimized geometry, a value consistent with that measured in the crystal structure (12.1°) and with other examples of this type of molecules.<sup>[34,35]</sup> On the other hand, the optimized geometry of (2,1-a)-DSF-IF in the first

Table 2. Electrochemical data and HOMO-LUMO levels for (1,2-b)-IF, (2,1-a)-	-IF, (1,2- <i>b</i> )-DSF-IF and (2,1- <i>a</i> )-DSF-IF.
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-	$E_{\rm ox}$ [V]/SCE <sup>[a]</sup>	$E_{\rm red}$ [V]/SCE <sup>[b]</sup>	HOMO [eV] <sup>[c]</sup>	LUMO [eV] <sup>[d]</sup>	LUMO [eV] <sup>[e]</sup>	Ref.
(1,2-b)-IF	1.31 (1e), 2.01 (>1e)	-2.55	-5.61	-1.99	-2.00	[67]
(2,1- <i>a</i> )-IF	1.31 (1e), 1.98 (>1e)	-2.6	-5.62	-1.94	-1.86	this work
(1,2-b)-DSF-IF	1.47 (1e), 1.95 (>1e)	-2.32	-5.76	-2.17	-2.25	[27]
(2,1-a)-DSF-IF	1.36 (1e), 1.69 (1e), 1.99 (>1e)	-2.48, -3.00	-5.64	-2.03	-2.07	this work

[a] Obtained from CVs recorded in  $CH_2Cl_2/[NBu_4][PF_6]$  0.2 M. [b] Obtained from CVs recorded in DMF/[NBu\_4][PF\_6] 0.1 M. [c] Calculated from the onset oxidation potential. [d] Calculated from the onset reduction potential. [e] Calculated from the HOMO energy level and the edge of optical band gap.

singlet excited state (Figure 3, right), shows that the indenofluorene core is now close to planarity with a calculated spiro–spiro torsion angle of 2.3°, and yield as a consequence, an eclipsed arrangement of the face-to-face fluorene groups. This significant structural change between the ground state and the first excited singlet state of (2,1-a)-DSF-IF is consistent with the larger Stokes shift observed for (2,1-a)-DSF-IF compared with that of (1,2-b)-DSF-IF (6 vs 3 nm, Table 1). Indeed, little structural change is found between the ground state and the first excited singlet state of the (1,2-b)-DSF-IF isomer (see Supporting Information). The geometry change in (2,1-a)-DSF-IF is likely to be at the origin of the spectacular excimer emission demonstrated previously for derived molecules bearing aryl groups at the 2,7-positions of the face-to-face fluorene moieties.<sup>[35,41]</sup>



Figure 3. Optimized geometry of (2,1-a)-DSF-IF in the ground state (left, spiro-spiro torsion angle 9.9°) and in the first singlet excited state (right, spiro-spiro torsion angle 2.3°) showing the change in the relative arrangement of the face-to-face fluorene groups.

*Electrochemical properties:* Electrochemistry of (2,1-*a*)-IF and (2,1-*a*)-DSF-IF were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV, see Supporting Information). Anodic and cathodic investigations were conducted in dichloromethane and dimethylformamide (DMF), respectively, and redox potentials were referenced to the saturated calomel electrode (SCE). Energy levels values have been calculated from the electrochemical measurements, Table 2.

The first oxidation of (2,1-a)-IF is reversible (see inset of Figure 4A) and occurs at a potential ( $E^1 = 1.31$  V) identical to that reported for (1,2-b)-IF.<sup>[67]</sup> This first oxidation is followed at higher potentials by an irreversible process, about twice in amplitude, with a maximum recorded at a potential ( $E^2 = 1.98$  V) almost identical to that reported for its positional isomer (1,2-b)-IF ( $E^2 = 2.01$  eV).<sup>[67]</sup> Reduction of (2,1-*a*)-IF (in DMF/[NBu<sub>4</sub>][PF<sub>6</sub>] 0.1 M) presents a quasi-reversible

redox wave with a maximum at -2.6 V (see CV in Supporting Information).



Figure 4. Cyclic voltammetry at 100 mVs<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 м. A)–B): (2,1-a)-IF 10<sup>-3</sup> м, 1 cycle between 0.2 and 2.2 V (A), 10 cycles between 0.2 and 2.05 V (B). Inset in A): 1 cycle between 0.2 and 1.4 V. C): Modified electrode (oxidation of (2,1-a)-IF 10<sup>-3</sup> м at 2.0 V for 180 s) investigated in a (2,1-a)-IF free solution, 3 cycles between 0.4 and 2.4 V.

For (2,1-a)-DSF-IF the first oxidation is also reversible and monoelectronic. It occurs at  $E^1 = 1.36$  V (inset Figure 5A, Table 2) and has been ascribed to the oxidation of the indenofluorenyl core, as in the case of (1,2-b)-DSF-IF  $(E^1 = 1.47 \text{ V})$ .<sup>[27]</sup> This assignment is consistent with the calculated indenofluorene character of the HOMO (Figure 6, bottom). This wave is anodically shifted by 70 mV compared to that of (2,1-a)-IF. This shift is smaller than that observed in the (1,2-b) series: 160 mV between (1,2-b)-DSF-IF and (1,2-b)-IF. Again, and as already highlighted in the optical properties section (see above), the structural arrangement of the fluorene units (face-to-face or not) has a crucial effect on the electronic properties of the indenofluorenyl core. One can thus assume that the electron-withdrawing effect of the cofacial fluorene  $\pi$ -dimer found in (2,1-a)-DSF-IF, is weaker than the non-cofacial fluorenes found in (1,2b)-DSF-IF. To the best of our knowledge similar examples appear to be very rare in the literature. House and co-workers have nevertheless reported diphenylanthracene deriva-

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Figure 5. Cyclic voltammetry at 100 mVs  $^{-1}$ in CH<sub>2</sub>Cl<sub>2</sub>/[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 м. A)–B): (2,1-*a*)-DSF-IF 2×10<sup>-3</sup> м, 1 cycle between 0.2 and 2.25 V (A), cycles 1, 5 and 10 between 0.2 and 2.25 V (B). Inset in A): cycles 1 and 3 between 0.25 and 1.55 V. C): Modified electrode (oxidation of (2,1-*a*)-DSF-IF at 2.05 V for 30 s) investigated in a (2,1-*a*)-DSF-IF free solution, 3 cycles between 0.25 and 2.0 V.

tives where the phenyl rings can either be in a close face-toface arrangement or not.<sup>[68]</sup> Thus, the oxidation potential of the anthracenyl core seemed to be influenced by the different electronic effects caused by the different arrangements of the phenyl rings. Indeed, when the phenyl rings are  $\pi$ stacked the oxidation potential of the anthracenyl core is lower (1.30 V/SCE) than when phenyl rings are not  $\pi$ stacked (1.34 V/SCE).<sup>[68]</sup>



Figure 6. Gas-phase DFT calculations (B3LYP/6-31G\*) for (1,2-b)-DSF-IF, (1,2-b)-IF, (2,1-a)-IF and (2,1-a)-DSF-IF (from left to right). The calculated frontier molecular orbitals (after geometry optimization with DFT) are shown with a cut-off of 0.04 [ebohr<sup>-3</sup>]<sup>1/2</sup>. The HOMO/LUMO energy levels have been estimated by electrochemistry and UV/Vis spectroscopy (see Table 2).

A second oxidation process (isoelectronic to the first) and a third oxidation process are observed for (2,1-a)-DSF-IF at 1.69 and 1.99 V (see DPV in Supporting Information). The second wave is partially reversible and is accompanied along recurrent sweeps by a weak polymerization process (see Supporting Information). Reduction of (2,1-a)-DSF-IF (in DMF-[NBu<sub>4</sub>][PF<sub>6</sub>] 0.1 M) presents two successive redox waves with maxima at -2.48 and -3.00 V, respectively, the first being twice in intensity compared to the second (see CV and DPV in Supporting Information).

From the redox and optical data (Tables 1 and 2), we could estimate the lowest unoccupied molecular orbital (LUMO) energy level and the highest occupied molecular orbital (HOMO) energy level.<sup>[69,70]</sup> The onset oxidation potentials of (2,1-a)-IF and (1,2-b)-IF (1.22 and 1.21 V, respectively) are almost identical and lead to HOMO level energy values around -5.6 eV for the two compounds (Table 2). The LUMO levels of (2,1-a)-IF and (1,2-b)-IF, calculated as follows:  $E_{\text{LUMO}}$  (eV) =  $\Delta E_{\text{opt}} + E_{\text{HOMO}}$  are thus lying at -1.86 and -2 eV, respectively. The LUMO energy levels of (2,1-a)-IF and (2,1-a)-DSF-IF have been also calculated (-1.94 and -2.03 eV, respectively) from the onset reduction potentials (-2.46 and -2.37 V, respectively, vs SCE) and are in accordance with the LUMO calculated from the optical band gap (Table 2). Such a trend in the LUMO energy levels has been previously observed in the dibenzo-[1,2;5,6]anthracene/picene series in which the LUMO level of picene is slightly higher than the LUMO level of dibenzoanthracene.[64]

Oppositely to (2,1-a)-IF and (1,2-b)-IF which possess identical HOMO level energy values (see above), (2,1-a)-DSF-IF presents a HOMO level lying at about -5.64 eV, slightly above that reported for its isomer (1,2-b)-DSF-IF (-5.76 eV, Table 2).<sup>[27]</sup> Theoretical calculations may shed light on this difference between the spiro and the non-spiro series. In the case of (1,2-b)-DSF-IF, theoretical calculations point to an indenofluorenyl-based primary oxidation as shown by the calculated nature of the HOMO level (Figure 6, bottom left).<sup>[27]</sup> However, the HOMO of (2,1-a)-DSF-IF presents a mixed character with major coefficients found on the (2,1-a)-indenofluorenyl core but with nevertheless a significant contribution of the fluorene units (Figure 6, bottom right). Such a difference in the character of the HOMO level in the di-spiro series has been assigned to the presence in (2,1-a)-DSF-IF of two face-to-face fluorene units. This feature may hence explain the different HOMO level energy values between (2,1-a)-DSF-IF and (1,2-b)-DSF-IF. Thus, the character of the HOMO of (2,1-a)-DSF-IF significantly extends into the spiro-linked fluorene units (oppositely to (1,2-b)-DSF-IF), leading to increased conjugation. The increased delocalization is hence consistent with the larger red shift observed in UV/Vis spectroscopy (see above) between the (2,1-a) series, (2,1-a)-IF vs (2,1-a)-DSF-IF, and the (1,2-b) series, (1,2-b)-IF vs (1,2-b)-DSF-IF.

The LUMO levels of (2,1-a)-DSF-IF and (1,2-b)-DSF-IF do not follow the trend observed for the HOMO levels. The LUMO energy level of (2,1-a)-DSF-IF is indeed lying at

-2.07 eV (above the LUMO of its positional isomer (1,2-*b*)-DSF-IF, -2.25 eV, Table 2). This trend in the LUMO energy values is consistent with that of (2,1-*a*)-IF and (1,2-*b*)-IF (LUMOs respectively lying at -1.86 and -2.00 eV, see above). Accordingly, we note that for both (2,1-*a*)-DSF-IF and (1,2-*b*)-DSF-IF theoretical calculations show a LUMO almost exclusively centred on the indenofluorene core (Figure 6) as opposed to the mixed character observed for the HOMO level of (2,1-*a*)-DSF-IF (Figure 6, bottom right). Similar differences between the electronic distributions of the HOMO and the LUMO levels have been also highlighted by Hintschich and co-workers<sup>[71]</sup> for a polyspirobifluorene derivative.

Regarding the subsequent oxidations, (1,2-b)-DSF-IF and (2,1-a)-DSF-IF display significantly different behaviors. Indeed, in (1,2-b)-DSF-IF the first oxidation (1.47 V, Table 2) is followed by a multiple electron process at 1.95 V, which may be assigned to the oxidation of the fluorenyl units (as pointed out by the calculated nature of the SOMO of [(1,2-b)-DSF-IF]<sup>++</sup> Figure 7, left) and also most certainly



Figure 7. Calculated frontier molecular orbital SOMO (after geometry optimization with DFT-B3LYP/6-31G\*), shown with a cut-off of 0.04 [ $e bohr^{-3}$ ]<sup>1/2</sup> of [(1,2-*b*)-DSF-IF]<sup>++</sup> (left) and [(2,1-*a*)-DSF-IF]<sup>++</sup> (right).

to the second oxidation of the indenofluorenyl core. Note that the second oxidation in (1,2-b)-IF occurs at 2.0 V,<sup>[67]</sup> whereas the second oxidation of 9,9'-spirobifluorene occurs at 1.86 V.<sup>[27]</sup> Oppositely to (1,2-b)-DSF-IF, (2,1-a)-DSF-IF is oxidized along three reversible one-electron processes at 1.36, 1.69 and 1.99 V. The second reversible and monoelectronic oxidation of (2,1-a)-DSF-IF (1.69 V) is not found either for (2,1-a)-IF or (1,2-b)-DSF-IF. The redox potential of the second reversible and monoelectronic oxidation of (2,1-a)-DSF-IF wave is lower than the redox potential of both the second oxidation of (2,1-a)-IF (1.98 V, Table 2) and of (1,2-b)-DSF-IF (1.95 V, Table 2).<sup>[27]</sup> Such a difference in the CVs of (1,2-b)-DSF-IF and (2,1-a)-DSF-IF may be rationalized by the nature of the SOMO involved in the second monoelectronic oxidation (1.69 V) of [(2,1-a)-DSF-IF]+. Indeed, theoretical calculations indicate that the SOMO of [(2,1-a)-DSF-IF]+ has mainly a fluorene character (Figure 7, right). As it is known that the oxidation of  $\pi$ stacked systems is more facile than their non-stacked analogues,<sup>[58,72,73]</sup> it is reasonable to assign the second oxidation of (2,1-a)-DSF-IF to the face-to-face fluorene dimer. Analogous observations highlighting interactions between two stacked aryl moieties, have been previously reported for dibenzobicyclo[4.4.1]undecane<sup>[72]</sup> and for different  $\pi$ -systems including among others naphthalene units bridged by biphenyl linkages,<sup>[73]</sup> various oligofluorene derivatives<sup>[58,60]</sup> or porphyrins dimers.<sup>[74]</sup> We also note that the oxidation of a fluorene  $\pi$ -dimer reported by Rathore and co-workers occurs at about 1.42 V/SCE.<sup>[58]</sup> The more anodic value found for (2,1-*a*)-DSF-IF (1.69 V/SCE) may be simply accounted for by the presence of a positive charge borne by the (2,1*a*)-indenofluorenyl core in [(2,1-*a*)-DSF-IF]<sup>++</sup>.

Anodic polymerization: Recurrent scans involving the (2,1a)-IF two oxidation waves lead to a regular electropolymerization process (Figure 4B). The polymerization is evidenced i) by the appearance and growth of new redox waves at potentials lower than  $E^1$  and between  $E^1$  and  $E^2$  (see arrows in Figure 4B), ii) by the gradual shift of the onset oxidation potential and iii) by the coverage of the electrode with an insoluble thin film of poly-(2,1-a)-IF. Such electrodeposition process has been previously observed for (1,2-b)-IF oxidation.<sup>[67]</sup> However, the yield of polymerization estimated by the measurement of the new waves intensity at each cycle (Figure 4B) appears largely lower for (2,1-a)-IF compared to (1,2-b)-IF.<sup>[67]</sup> Polymerization of (2,1-a)-IF is also observed along oxidation at fixed potential. For example, a deposit prepared by oxidation at 2 V for 180 s, removed from the electrolyte, rinsed in dichloromethane and studied in a new "monomer free" solution, presents the profile shown in Figure 4 C. The CV of poly-(2,1-a)-IF exhibits two reversible waves with maxima at 1.38 and 1.92 V and with an onset oxidation potential at 0.67 V. This onset oxidation potential is shifted by 550 mV towards less positive value compared to that of its corresponding monomer (2,1-a)-IF (1.22 V). It is important to note that the onset potential shift varies with the thickness of the deposit and with the method used for the electrodeposition process (recurrent sweeps along cyclic voltammetry or chronoamperometry). This onset potential difference between poly-(2,1-a)-IF and (2,1-a)-IF is consistent with an extended  $\pi$ -conjugation in poly-(2,1-a)-IF as previously observed for other electrogenerated  $\pi$ -conjugated polymers.<sup>[25,75]</sup> In addition, poly-(2,1-a)-IF appears stable in a wide potential range, that is, between 0.67 and 2.4 V. Poly-(2,1-a)-IF is hence highly more stable than structurally related electrogenerated polymer such as poly-(1,2-b)-indenofuorene, poly-(1,2-b)-IF<sup>[67]</sup> or poly-fluorene, poly(F).<sup>[76]</sup> Indeed, poly-(1,2-b)-IF and poly(F) present stable p-doping processes between 0.75 and 1.76 V and between 0.97 and 1.5 V, respectively. Poly-(2,1-a)-IF also possess interesting electrochromic properties, switching from yellow in its neutral state to green and blue in different oxidation states at higher potential values. These electrochromic properties clearly sign different *p*-doping levels of the polymer. Given the importance of electrochromic properties in material science, the present polymers might be of interest.<sup>[77]</sup>

(2,1-a)-DSF-IF may be also polymerized by anodic oxidation. Indeed, the electroplolymerization process is observed at the third oxidation wave recorded at 2 V (Figure 5B) whereas a very weak polymerization process is observed along recurrent sweeps involving only the two first oxidation processes (see Figure in Supporting Information). The (2,1a)-DSF-IF polymerization yield roughly evaluated by the measurement of the new waves intensity at each cycle appears higher than that of (2,1-a)-IF, indicating that the polymerization occurs both through the indenofluorenyl and the fluorenyl units. However the polymerization yield of (2,1-a)-DSF-IF is lower than that of (1,2-b)-DSF-IF<sup>[27]</sup> clearly indicating that the geometry of (2,1-a)-DSF-IF is less favourable to the carbon-carbon coupling of the monomer units. As exposed above the electrochemical behavior of poly-(2,1-a)-DSF-IF varies with the method used for the deposition and with the thickness of the deposit. For example, a poly-(2,1a)-DSF-IF deposit synthesized at fixed potential (2.05 V for 30 s) exhibits a reversible oxidation wave (Figure 5C) with a maximum at 1.44 V. The onset potential of poly-(2,1-a)-DSF-IF is recorded at 0.92 V, shifted by 280 mV towards less positive values compared to its monomer (2,1-a)-DSF-IF (1.2 V). Such a result is in accordance with extended  $\pi$ conjugation in the polymer. In addition, poly-(2,1-a)-DSF-IF is stable in a wide potential range, that is, between 0.92 and 2 V, although slightly less stable compared to poly-(2,1-a)-IF, which presents an electrochemical window of stability between 0.67 and 2.4 V (see above). Poly-(2,1-a)-DSF-IF also possesses electrochromic properties switching from transparent to green and blue when increasing its *p*-doping level. These electrochromic properties may be classically assigned to the *p*-doping level of the polymer but in part also to the high flexibility of the fluorene arrangement in the neutral, cation and dication states as suggested by theoretical calculations (Figure 8). Indeed, we note that geometry



Figure 8. Optimized geometries of (2,1-a)-DSF-IF in three incremental oxidation states  $(0/1^+/2^+)$  from left to right, spiro–spiro torsion angle respectively 9.9, 4.8 and 0°.

optimizations of (2,1-*a*)-DSF-IF in the neutral, cation and dication forms yield an interesting trend for the respective arrangement of its cofacial fluorene units. As (2,1-*a*)-DSF-IF gets oxidized, the fluorene moieties move towards an eclipsed conformation, while the concurrent decrease of the up-down tilt of the spiro carbon atoms brings the indeno-fluorene core to planarity in the dication, Figure 8. Given the importance of the fluorene arrangement for optical properties of phenyl substituted derivatives,<sup>[35,41]</sup> the present result may be significant in that it points to a large flexibility of the fluorene arrangement upon gradual oxidation, and, as

discussed before, in the first singlet excited state (see Figure 3).

#### Conclusion

In summary, we have developed new synthetic strategies toward original fluorophores based on the rarely studied (2,1-a)-indenofluorenyl core, namely (2,1-a)-DSF-IF and (2,1-a)-IF. These molecules have been prepared by expedient syntheses through a key diketone intermediate. We believe that this intermediate might be of great interest for the elaboration of other spiro or non-spiro derivatives based on the (2,1-a)-indenofluorenyl core. The structural, optical and electrochemical properties of (2,1-a)-DSF-IF and (2,1-a)-IF have been studied in detail by a combined experimental and theoretical approach. These properties have been compared to their corresponding positional isomers, namely (1,2-b)-DSF-IF and (1,2-b)-IF and also compared to structurally related diindenothiophene derivatives recently reported by Ohe and co-workers.<sup>[37]</sup> As the (2,1-a)-indenofluorenyl core is almost absent from the literature but seems to be promising for organic electronic applications, the present finding may pave the way to the development of this rarely studied class of molecules. The comparison of the di-spiro molecules, (2,1-a)-DSF-IF and (1,2-b)-DSF-IF, with their respective central cores, (2,1-a)-IF and (1,2-b)-IF, have stressed that the electronic properties of the present dispiro molecules are mainly governed by the central indenofluorene backbone but might be tuned by the structural arrangement of the two  $\pi$ -systems linked through the spirocarbons. Introduction of the (2,1-a)-indenofluorenyl core in organic electronic devices and elucidation of the excimer emission found with aryl substituted (2,1-a)-DSF-IFs<sup>[35]</sup> are currently underway in our laboratory.

#### **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). 1,2-Dichlorobenzene was distilled from  $\mathrm{CaCl}_2$  drying agent. 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. Reactions were stirred magnetically, unless otherwise indicated. Analytical thin layer chromatography was carried out using aluminium backed plates coated with Merck Kieselgel 60  $\mathrm{GF}_{254}$  and visualized under UV light (at 254 and/or 360 nm). Chromatography was carried out using silica 60A CC 40-63 µm (SDS). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker 300 MHz instruments (<sup>1</sup>H 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>; 7.26 ppm for the proton and 77.00 ppm for the carbon, CD<sub>2</sub>Cl<sub>2</sub>; 5.32 ppm for the proton and 53.80 ppm for the carbon,  $[D_6]DMSO$ ; 2.50 ppm for the proton and 39.52 ppm 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 Bruker MicrO-Tof-Q2 or on a Micromass MS/MS ZABspec Tof (EBE

Tof geometry) and reported as m/z. Elemental analyses were recorded at the Service de Microanalyse-CNRS (Gif sur Yvette). 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 Applied Chemistry and International Union of Biochemistry and Molecular Biology.

**Dimethyl 3,6-diphenylcyclohexa-1,4-diene-1,2-dicarboxylate (2)**: 1,4-Diphenyl-1,3-butadiene (12.5 g, 60.7 mmol) was dissolved in dry toluene (60 mL) under argon. Dimethyl but-2-ynedioate (8.2 mL, 66.7 mmol) was then added and the solution was stirred at reflux for 20 h. After evaporation to dryness, the crude yellow solid was washed with i) 2-propanol and ii) hexane. The title compound was obtained as a colorless solid (18.0 g, 85%). M.p. (hexane) 95 °C (lit. 98 °C);<sup>[78]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.40–7.26 (m, 10 H; ArH), 5.79 (s, 2 H; CH=), 4.48 (s, 2 H; CH), 3.56 ppm (s, 6H; Me); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =167.9 (COOMe), 141.2 (C), 135.6 (C), 128.7 (CH), 128.3 (CH), 127.1 (CH), 126.0 (CH), 52.0 (Me), 44.0 ppm (CH).

**Dimethyl 1,1':4',1"-terphenyl-2',3'-dicarboxylate (3)**: Compound **2** (10.0 g, 28.7 mmol) and palladium on carbon (5 % Pd, 3.0 g, 33.8 mmol) were dissolved in dry toluene (100 mL) under argon and the solution was stirred at reflux for 21 h. The hot mixture was filtered on Celite 545 and washed with hot toluene. After evaporation to dryness, the solid was washed with hexane. The title compound was obtained as a colorless solid (9.1 g, 91%). M.p. (hexane) 161°C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.54 (s, 2H; ArH), 7.46–7.35 (m, 10H; ArH), 3.60 ppm (s, 6H; Me); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 168.9 (COOMe), 140.2 (C), 140.1 (C), 132.4 (C), 132.1 (CH), 128.8 (CH), 128.6 (CH), 128.2 (CH), 52.7 ppm (Me); IR:  $\nu$  = 1741 (C=O), 1719 (C=O), 1437, 1311, 1231, 1157, 1070 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>, MeOH/CH<sub>2</sub>Cl<sub>2</sub> 99:1): *m*/*z*: calcd for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>K: 385.0842 [*M*+K]<sup>+</sup>; found: 385.0841.

**1,1':4',1"-Terphenyl-2',3'-diyldimethanol** (4): Compound **3** (3.9 g, 11.2 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) under argon. The solution was carefully added, in four portions, to a solution of diisobutylaluminium hydride (1 m in hexane) (56.0 mL, 56.0 mmol) over 40 min. The resulting mixture is stirred for 1.5 h, poured into a saturated solution of ammonium chloride (40 mL) and extracted with dichloromethane. The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent removed in vacuo. Recrystallization from hexane afforded **4** as a colorless solid (2.9 g, 88%). M.p. (hexane) 124°C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ = 7.49–7.38 (m, 10 H; ArH), 7.35 (s, 2 H; ArH), 4.73 (d, *J*=5.1 Hz, 4H; CH<sub>2</sub>), 3.23 ppm (t, 2 H; *J*=5.1 Hz, OH); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ = 142.9 (C), 141.5 (C), 138.3 (C), 130.2 (CH), 129.8 (CH), 128.5 (CH), 127.6 (CH), 60.8 ppm (CH<sub>2</sub>); R: *v*=3370 (OH), 3299 (OH), 1744, 1466, 1396, 1336, 1205 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>, MeOH/CH<sub>2</sub>Cl<sub>2</sub> 99:1): *m/z*: calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>Na: 313.1205 [*M*+Na]<sup>+</sup>; found: 313.1203.

**1,1':4',1"-Terphenyl-2',3'-dicarboxylic acid (5)**: Compound **3** (1.4 g, 4.0 mmol) was dissolved in a mixture of ethanol (200 mL) and water (15 mL). NaOH (6.5 g, 16.0 mmol) was added and the solution was stirred at 90 °C for 16 h. After cooling to room temperature, water (50 mL) was added, and concentrated HCl was added until pH 1. A colorless precipitate was obtained, filtered off and washed several times with water. The title compound was obtained as a colorless solid (1.22 g, 95 %). M.p. (hexane) > 300 °C; <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 13.14 (br, 2H; OH), 7.52 (s, 2H; ArH), 7.50–7.39 ppm (m, 10H; ArH); <sup>13</sup>C NMR (75 MHz, [D6]DMSO):  $\delta$  = 168.9 (COOH), 139.7 (C), 138.2 (C), 132.8 (C), 131.0 (CH), 128.5 (CH), 128.2 (CH), 127.7 ppm (CH); IR:  $\nu$  = 3371 (OH), 3231 (OH), 1743 (C=O), 1700 (C=O), 1452, 1418, 1214, 1186, 1157, 1068 cm<sup>-1</sup>; HRMS (ESI<sup>-</sup>, MeOH/H<sub>2</sub>O 95:5): *m/z*: calcd for C<sub>20</sub>H<sub>13</sub>O<sub>4</sub>: 317.0819 [*M*–H]<sup>-</sup>; found: 317.0815.

#### Indeno[2,1-a]fluorene-11,12-dione (1)

*Route 1:* (2,1-*a*)-IF (180 mg, 0.71 mmol) and chromium trioxide (495 mg, 4.95 mmol) were dissolved in acetic anhydride (60 mL) under argon. The solution was stirred for 20 h and poured into a solution of 10% HCl at 0°C and extracted with dichloromethane. The combined extracts were dried (MgSO<sub>4</sub>), the solvent removed in vacuo and the residue purified by column chromatography on silica eluting with light petroleum/ethyl acetate 7:3. Compound **1** was obtained as an orange solid (150 mg, 75%).

Route 2: Compound 3 (200 mg, 0.577 mmol) or 5 (200 mg, 0.628 mmol) was added to a solution of concentrated H2SO4 (30 mL) at 140 °C and stirred for 5 min. After cooling to room temperature the mixture was poured into water (300 mL) and extracted with i) ethyl acetate and ii) dichloromethane. The combined organic layers were dried (MgSO<sub>4</sub>), the solvent was removed in vacuo and the residue purified by column chromatography on silica eluting with light petroleum/ethyl acetate 7:3. Compound 1 was obtained as an orange solid (19.5 mg, 12% starting from 3 or 67.3 mg, 38% starting from 5). M.p. (hexane) 245 °C; <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 7.68 \text{ (s, 2H; ArH)}, 7.67 \text{ (d, } J = 7.2 \text{ Hz}, 2\text{ H}; \text{ArH}),$ 7.60–7.50 (m, 4H; ArH), 7.36 ppm (td, J=7.5, 0.9 Hz, 2H; ArH); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 190.8$  (CO), 145.6 (C), 144.0 (C), 135.2 (C), 134.0 (C), 132.6 (CH), 129.9 (CH), 125.4 (CH), 124.8 (CH), 120.6 ppm (CH); IR: v=1721 (C=O), 1604, 1469, 1425, 1267, 1187, 1084 cm<sup>-1</sup>; UV/Vis (THF):  $\lambda_{max}$ =389, 372, 290 nm; HRMS (ESI+, MeOH): m/z: calcd for C<sub>20</sub>H<sub>10</sub>O<sub>2</sub>Na: 305.0579 [*M*+Na]<sup>+</sup>; found: 305.0581

#### 11,12-Di(biphenyl-2-yl)-11,12-dihydroindeno[2,1-a]fluorene-11,12-diol

(6): 2-Bromobiphenyl (0.58 mL, 3.40 mmol) was dissolved in dry and degassed THF (20 mL) under argon. The mixture was cooled to -78 °C and stirred at this temperature for 10 min. A solution of nBuLi (1.6 M in hexane, 2.13 mL, 3.41 mmol) was added dropwise in 4 min. The resulting yellow solution was stirred for a further 50 min and ketone 1 (120 mg, 0.42 mmol), dissolved in dry and degassed THF (60 mL), was added dropwise in 4 min via a cannula. The reaction was allowed to stir overnight (from  $-78\,^{\circ}$ C to room temperature) and the resulting mixture was poured into a saturated solution of ammonium chloride (50 mL) and extracted with dichloromethane and ethyl acetate. The combined extracts were dried (MgSO<sub>4</sub>), the solvent removed in vacuo and the residue purified by column chromatography on silica eluting with light petroleum/ ethyl acetate 8:2. The resulting solid was washed with hexane to obtain 6 as a colorless solid (102 mg, 41%). M.p. (hexane) >300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.00$  (d, J = 7.5 Hz, 2H; ArH), 7.67 (t, J = 7.5 Hz, 2H; ArH), 7.43 (t, J=7.5 Hz, 2H; ArH), 7.25 (t, J=7.5 Hz, 2H; ArH),7.18–7.14 (m, 4H; ArH), 7.06 (d, J=7.5 Hz, 2H; ArH), 6.94 (d, J= 7.5 Hz, 2H; ArH), 6.85 (s, 2H; ArH), 6.80 (t, J=7.5 Hz, 2H; ArH), 6.60–6.48 (m, 4H; ArH), 6.37 (d, J=7.5 Hz, 2H; ArH), 5.66 (d, J=7.5 Hz, 2H; ArH), 1.88 ppm (s, 2H; OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ=149.2 (C), 144.9 (C), 141.4 (C), 140.7 (C), 140.5 (C), 140.3 (C), 139.4 (C), 132.2 (CH), 129.0 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 126.7 (CH), 126.5 (CH), 125.9 (CH), 125.2 (CH), 124.0 (CH), 120.3 (CH), 120.0 (CH), 82.5 ppm (COH); IR:  $\nu = 3527$ (OH), 1469, 1428, 1167, 1027 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>, MeOH/CH<sub>2</sub>Cl<sub>2</sub> 99:1): *m*/*z*: calcd for C<sub>44</sub>H<sub>30</sub>O<sub>2</sub>Na: 613.2144 [*M*+Na]<sup>+</sup>, found: 613.2139.

#### 11,12-Dihydroindeno[2,1-a]fluorene ((2,1-a)-IF)

*Route 1*: Polyphosphoric acid (6 g) was stirred at 140 °C for 5 min. Diol **6** (200 mg, 0.70 mmol) dissolved in 1,2-dichlorobenzene (30 mL) was then added to the polyphosphoric acid over 10 min and the solution was stirred for a further 5 min. After cooling to room temperature, the mixture was poured into a 10% aqueous NaOH solution (30 mL) and extracted with dichloromethane. The combined extracts were dried (MgSO<sub>4</sub>), the solvent removed in vacuo and the residue purified by column chromatography on silica eluting with light petroleum/dichloromethane (9:1). The resulting solid was washed with hexane to obtain (2,1-a)-IF as a colorless solid (47 mg, 27%).

*Route* 2: Compound 1 (30 mg, 0.11 mmol), hydrazine hydrate (200 µL, 3.30 mmol) and potassium hydroxide (150 mg, 2.67 mmol) were dissolved in diethylene glycol (10 mL) and the solution was stirred at 180 °C for 24 h. After cooling to room temperature, the mixture was poured into a solution of concentrated HCl at 0 °C. A colorless precipitate was obtained, filtered off and washed several times with water. (2,1-*a*)-IF was obtained as a colorless solid (21 mg, 75%). M.p. (hexane) 270 °C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =7.82 (s, 2H; ArH), 7.81 (d, *J*=7.2 Hz, 2H; ArH), 7.59 (d, *J*=7.2 Hz, 2H; ArH), 7.38 (t, *J*=7.2 Hz, 2H; ArH), 7.30 (t, *J*=7.2 Hz, 2H; ArH), 3.95 ppm (s, 4H; CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =143.6 (C), 142.3 (C), 141.1 (C), 139.9 (C), 127.2 (CH), 126.9 (CH), 125.5 (CH), 120.2 (CH), 119.0 (CH), 35.8 ppm (CH<sub>2</sub>); IR:  $\nu$ =1737, 1457, 1427, 1372, 1103 cm<sup>-1</sup>; UV/Vis (THF):  $\lambda_{max}$ =322, 315, 307 nm;

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HRMS (ESI<sup>+</sup>, MeOH/CH<sub>2</sub>Cl<sub>2</sub> 90:10): m/z: calcd for C<sub>20</sub>H<sub>14</sub>: 254.1096 [*M*]<sup>+</sup>, found: 254.1096. elemental analysis calcd (%) for C<sub>20</sub>H<sub>14</sub> C 94.45, H 5.55; found C 94.34, H 5.54.

Dispiro[fluorene-9,11'-indeno[2,1-*a*]fluorene-12',9"-fluorene] ((2,1-a)-DSF-IF): Difluorenol 6 (80 mg, 0.14 mmol) was dissolved in dichloromethane (60 mL) and stirred for 15 min at reflux. Boron trifluoride etherate (48% BF3) (100  $\mu L)$  was added and the resulting mixture was stirred 2 h at reflux. After evaporation to dryness, the crude mixture was purified by column chromatography on silica gel, eluting with light petroleum/ethyl acetate 8:2 and washed with hexane. The title compound was obtained as a colorless solid (72 mg, 93%). M.p. (cyclohexane) 234°C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): *δ*=8.08 (s, 2H; ArH), 7.79 (d, *J*=7.5 Hz, 2H; ArH), 7.25 (d, J=7.5 Hz, 4H; ArH), 7.20 (td, J=7.5 Hz, J=0.9 Hz, 2H; ArH), 7.01 (td, *J*=7.5 Hz, *J*=0.9 Hz, 4H; ArH), 6.83 (td, *J*=7.5 Hz, *J*=0.9 Hz, 2H; ArH), 6.59 (td, J=7.5 Hz, J=0.9 Hz, 4H; ArH), 6.15 (d, J=7.5 Hz, 4H; ArH), 5.97 ppm (d, J=7.5 Hz, 2H; ArH); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 151.2 (C), 146.1 (C), 143.9 (C), 143.7 (C), 141.1 (C), 140.2 (C), 127.8 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 123.3 (CH), 122.6 (CH), 120.5 (CH), 120.4 (CH), 119.9 (CH), 66.3 ppm ( $C_{spiro}$ ); IR:  $\nu =$ 1635, 1446, 1071, 942 cm<sup>-1</sup>; UV/Vis (THF):  $\lambda_{max} = 339$ , 323, 311, 295 nm; HRMS (ESI<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>): m/z: calcd for C<sub>44</sub>H<sub>26</sub>: 554.2035 [M]<sup>+</sup>, found: 554.2034.

**Spectroscopic studies**: UV-visible spectra were recorded in solution using a UV-Visible-NIR spectrophotometer CARY 5000-Varian or SHIMAD-ZU 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 [m]. With  $h = 6.6 \times 10^{-34} \text{ J s}^{-1}$  ( $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ ) and  $c = 3.0 \times 10^8 \text{ ms}^{-1}$ , this equation may be simplified as:  $\Delta E^{\text{opt}}$  [eV]= $1237.5/\lambda$  [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 ( $\phi_{sol}$ ) were calculated relative to quinine sulfate ( $\phi_{sol} = 0.546$  in H<sub>2</sub>SO<sub>4</sub> 1N) using standard procedures.<sup>[26]</sup>  $\phi_{sol}$  was determined according to the following Equation (1),

$$\phi_{\rm sol} = \phi_{\rm ref} \times 100 \times \frac{(T_{\rm s} \times A_{\rm r})}{(T_{\rm r} \times A_{\rm s})} \left(\frac{n_{\rm s}}{n_{\rm r}}\right)^2 \tag{1}$$

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. IR spectra were recorded on a VARIAN 640-IR using a PIKE Technologies MIRacle(TM) ATR (single Attenuated Total Reflectance) with a diamond crystal. Melting points were determined 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<sup>+</sup>) couple served as internal standard. 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 Al2O3 was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to the SCE electrode that was calibrated at -0.405 Vvs. Fc/Fc+ system. Following the work of Jenekhe,<sup>[69]</sup> we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionisation 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:  $\Delta E^{\rm el} = |\text{HOMO}-\text{LUMO}|$  (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>[79,80]</sup> and Time-Dependent Density Functional Theory (TD-DFT) calculations were performed with the hybrid Becke-3 parameter exchange<sup>[81–83]</sup> functional and the Lee–Yang–Parr non-local correlation functional<sup>[84]</sup> (B3LYP) implemented in the Gaussian 09 (Revision A.02) program suite<sup>[85]</sup> using the 6-31G\* basis set<sup>[86]</sup> and the default convergence criterion implemented in the program. The figures were generated with MOLEKEL 4.3.<sup>[87]</sup>

**X-ray determination**: Crystal was picked up with a cryoloop and then frozen at 100 K under a stream of dry N<sub>2</sub> on a APEX II Brucker AXS diffractometer for X-ray data collection ( $Mo_{K\alpha}$  radiation,  $\lambda = 0.71073$  Å). Structure was solved by direct methods (SIR97)<sup>[88]</sup> and refined (SHELXL-97)<sup>[89]</sup> by full-matrix least-squares methods as implemented in the WinGX software package.<sup>[90]</sup> An empirical absorption correction was applied. Hydrogen atoms were introduced at calculated positions (riding model) included in structure factor calculation but not refined.

CCDC 782136, 782137 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_ request/cif

(2,1-*a*)-IF:  $C_{20}H_{14}$ ; M = 254.31; colorless prism; crystal size  $0.33 \times 0.25 \times 0.12 \text{ mm}^3$ ; monoclinic; P21/c; a = 8.7210(3), b = 5.7602(2), c = 26.4151(9) Å;  $\beta = 91.6080(10)$ ; V = 1326.43(8) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.273 \text{Mgm}^{-3}$ ;  $Mo_{K\alpha}$  radiation ( $\lambda = 0.71073$  Å);  $\mu = 0.072 \text{ mm}^{-1}$ ; T = 100(2) K; 16703 data (3059 unique,  $R_{int} = 0.0263$ ,  $2.34 < \theta < 27.46^{\circ}$ );  $wR = {\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]}^{1/2} = 0.1404$ ; conventional R = 0.0441 for F values of reflections with  $F_o^2 > 2\sigma(F_o^2)$  (2539 observed reflections); S = 1.224 for 181 parameters. Residual electron density extremes were 0.259 and -0.235 e Å<sup>-3</sup>.

(2,1-*a*)-**DSF-IF**:  $C_{44}H_{26}$ ·CHCl<sub>3:</sub> M = 673.90; colorless prism; crystal size  $0.3 \times 0.2 \times 0.04$  mm; monoclinic; P21/n; a = 13.3572(4), b = 18.3088(5), c = 14.0511(4) Å;  $\beta = 109.1210(10)$ ; V = 3246.67(16) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.379Mgm^{-3}$ ;  $Mo_{K\alpha}$  radiation ( $\lambda = 0.71073$  Å);  $\mu = 0.316$  mm<sup>-1</sup>; T = 150(2) K; 38036 data (7426 unique,  $R_{int} = 0.0428$ ,  $2.70 < \theta < 27.41^{\circ}$ );  $wR = [\Sigma[w(F_o^{-2}F_c^{-2})^2]/\Sigma [w(F_o^{-2})^2]]^{1/2} = 0.1634$ ; conventional R = 0.0611 for F values of reflections with  $F_o^{-2} > 2\sigma(F_o^{-2})$  (6215 observed reflections); S = 1.048 for 473 parameters. Residual electron density extremes were 1.294 and -1.068 e Å<sup>-3</sup>.

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- [1] A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091.
- [2] A. C. Grimsdale, K. Müllen, Macromol. Rapid Commun. 2007, 28, 1676–1702.
- [3] M. Zhang, C. Yang, A. K. Mishra, W. Pisula, G. Zhou, B. Schmaltz, M. Baumgarten, K. Müllen, *Chem. Commun.* 2007, 1704–1706.
- [4] G. Zhou, N. Pschirer, J. C. Schöneboom, F. Eickemeyer, M. Baumgarten, K. Müllen, *Chem. Mater.* 2008, 20, 1808–1815.
- [5] A. K. Mishra, M. Graf, F. Grasse, J. Jacob, E. J. W. List, K. Müllen, *Chem. Mater.* 2006, 18, 2879–2885.
- [6] J. Jacob, S. Sax, M. Gaal, E. J. W. List, A. C. Grimsdale, K. Müllen, *Macromolecules* 2005, 38, 9933–9938.
- [7] H. Usta, A. Facchetti, T. J. Marks, Org. Lett. 2008, 10, 1385-1388.

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- [8] R. P. Ortiz, A. Facchetti, T. J. Marks, J. Casado, M. Z. Zgierski, M. Kosaki, V. Hernandez, J. T. L. Navarette, *Adv. Funct. Mater.* 2009, 19, 386–394.
- [9] M.-C. Chen, Y.-J. Chiang, C. Kim, Y.-J. Guo, S.-Y. Chen, J.-L. Liang, Y.-W. Huang, T.-S. Hu, G.-H. Lee, A. Facchetti, T. J. Marks, *Chem. Commun.* 2009, 1846–1848.
- [10] U. Scherf, E. J. W. List, Adv. Mater. 2002, 14, 477-487.
- [11] 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.
- [12] H. Reisch, U. Scherf, Synth. Met. 1999, 101, 128-129.
- [13] H. Reisch, U. Wiesler, U. Scherf, N. Tuytuylkov, *Macromolecules* 1996, 29, 8204–8210.
- [14] S. Setayesh, D. Marsitzky, K. Müllen, *Macromolecules* **2000**, *33*, 2016–2020.
- [15] C. Silva, D. M. Russel, M. A. Stevens, J. D. Mackensie, S. Setayesh, K. Müllen, R. H. Friend, *Chem. Phys. Lett.* **2000**, 319, 494–500.
- [16] T. Hadizad, J. Zhang, Z. Y. Wang, T. C. Gorjanc, C. Py, Org. Lett. 2005, 7, 795–797.
- [17] J. Jacob, J. Zhang, A. C. Grimsdale, K. Müllen, M. Gaal, E. J. W. List, *Macromolecules* 2003, *36*, 8240–8245.
- [18] D. Marsitzky, S. J. Campbell, J.-P. Chen, V. Y. Lee, R. D. Miller, S. Setayesh, K. Müllen, Adv. Mater. 2001, 13, 1096–1099.
- [19] S.-Y. Ku, L.-C. Chi, W.-Y. Hung, S.-W. Yang, T.-C. Tsai, K.-T. Wong, Y.-H. Chen, C.-I. Wu, J. Mater. Chem. 2009, 19, 773–780.
- [20] P. Sonar, J. Zhang, A. C. Grimsdale, K. Müllen, M. Surin, R. Lazzaroni, P. Leclère, S. Tierney, M. Heeney, I. McCulloch, *Macromolecules* **2004**, *37*, 709–715.
- [21] L.-C. Chi, W.-Y. Hung, H.-C. Chiu, K.-T. Wong, Chem. Commun. 2009, 3892–3894.
- [22] D. Vak, B. Lim, S.-H. Lee, D.-Y. Kim, Org. Lett. 2005, 7, 4229-4232.
- [23] T.-C. Tsai, W.-Y. Hung, L.-C. Chi, K.-T. Wong, C.-C. Hsieh, P.-T. Chou, Org. Electron. 2009, 10, 158–162.
- [24] D. Horhant, J.-J. Liang, M. Virboul, C. Poriel, G. Alcaraz, J. Rault-Berthelot, Org. Lett. 2006, 8, 257–260.
- [25] N. Cocherel, C. Poriel, L. Vignau, J.-F. Bergamini, J. Rault-Berthelot, Org. Lett. 2010, 12, 452–455.
- [26] S. Merlet, M. Birau, Z. Y. Wang, Org. Lett. 2002, 4, 2157-2159.
- [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] T.-C. Lin, C.-S. Hsu, C.-L. Hu, Y.-F. Chen, W.-J. Huang, *Tetrahedron Lett.* 2009, 50, 182–185.
- [29] W. Zhang, J. Smith, R. Hamilton, M. Heeney, J. Kirpatrick, K. Song, S. E. Watkins, T. Anthopoulos, I. McCulloch, J. Am. Chem. Soc. 2009, 131, 10814–10815.
- [30] H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Deliomeroglu, A. Zhukhovitskiy, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2009, 131, 5586–5608.
- [31] H. Usta, A. Facchetti, T.J. Marks, J. Am. Chem. Soc. 2008, 130, 8580–8581.
- [32] J. P. M. Serbena, I. A. Hümmelgen, T. Hadizad, Z. Y. Wang, Small 2006, 2, 372–374.
- [33] Covion Organic Semiconductors, Eur. Pat. Appl., EP 1491568, 2004.
- [34] C. Poriel, J. Rault-Berthelot, F. Barrière, A. M. Z. Slawin, Org. Lett. 2008, 10, 373–376.
- [35] D. Thirion, C. Poriel, F. Barrière, R. Métivier, J. Rault-Berthelot, Org. Lett. 2009, 11, 4794–4797.
- [36] W. Deuschel, Helv. Chim. Acta 1951, 34, 2403-2416.
- [37] T. Kowada, T. Kuwabara, K. Ohe, J. Org. Chem. 2010, 75, 906-913.
- [38] Thematic issue: Organic Electronics and Optoelectronics (Guest Eds.: S. R. Forrest, M. E. Thompson): *Chem. Rev.* 2007, 107, Issue 4.
- [39] R. Pudzich, T. Fuhrmann-Lieker, J. Salbeck, Adv. Polym. Sci. 2006, 199, 83-142.
- [40] T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker, J. Salbeck, *Chem. Rev.* 2007, 107, 1011–1065.
- [41] C. Poriel, F. Barrière, D. Thirion, J. Rault-Berthelot, *Chem. Eur. J.* 2009, 15, 13304–13307.

- [42] J. Jacob, S. Sax, T. Piok, E. J. W. List, A. C. Grimsdale, K. Müllen, J. Am. Chem. Soc. 2004, 126, 6987–6995.
- [43] Z. Jiang, H. Yao, Z. Liu, C. Yang, C. Zhong, J. Qin, G. Yu, Y. Liu, Org. Lett. 2009, 11, 4132–4135.
- [44] C. Xu, A. Wakamiya, S. Yamaguchi, J. Am. Chem. Soc. 2005, 127, 1638–1639.
- [45] Y. Wu, J. Zhang, Z. Bo, Org. Lett. 2007, 9, 4435-4438.
- [46] N. Cocherel, C. Poriel, J. Rault-Berthelot, F. Barrière, N. Audebrand, A. M. Z. Slawin, L. Vignau, *Chem. Eur. J.* 2008, 14, 11328– 11342.
- [47] C. Yang, J. Jacob, K. Müllen, Macromolecules 2006, 39, 5696-5704.
- [48] T. Nakagawa, D. Kumaki, J.-I. Nishida, S. Tokito, Y. Yamashita, *Chem. Mater.* 2008, 20, 2615–2617.
- [49] N. Cocherel, C. Poriel, O. Jeannin, A. Yassin, J. Rault-Berthelot, Dyes Pigm. 2009, 83, 339–347.
- [50] J.-S. Yang, H.-H. Huang, S.-H. Lin, J. Org. Chem. 2009, 74, 3974– 3977.
- [51] M. Kimura, S. Kuwano, Y. Sawaki, H. Fujikawa, K. Noda, Y. Taga, K. Takagi, J. Mater. Chem. 2005, 15, 2393–2398.
- [52] J. Luo, Y. Zhou, Z.-Q. Niu, Q.-F. Zhou, Y. Ma, J. Pei, J. Am. Chem. Soc. 2007, 129, 11314–11315.
- [53] C. Zhao, Y. Zhang, M.-K. Ng, J. Org. Chem. 2007, 72, 6364-6371.
- [54] S. Song, Y. Jin, S. H. Kim, J. Moon, K. Kim, K. Y. Kim, S. H. Park, K. Lee, H. Suh, *Macromolecules* **2008**, *41*, 7296–7305.
- [55] A. Behrendt, G. C. Screttas, D. Bethell, O. Schiemann, B. R. Steele, J. Chem. Soc. Perkin Trans. 2 1998, 2039–2045.
- [56] H. Koyama, T. Kamikawa, J. Chem. Soc. Perkin Trans. 1 1998, 203– 209.
- [57] L.-H. Xie, X.-Y. Hou, C. Tang, Y.-R. Hua, R.-J. Wang, R.-F. Chen, Q.-L. Fan, L.-H. Wang, W. Wei, B. Peng, W. Huang, *Org. Lett.* 2006, 8, 1363–1366.
- [58] R. Rathore, S. H. Abdelwahed, I. A. Guzei, J. Am. Chem. Soc. 2003, 125, 8712–8713.
- [59] 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, 4812–4814.
- [60] T. Nakano, T. Yade, J. Am. Chem. Soc. 2003, 125, 15474-15484.
- [61] C. Janiak, J. Chem. Soc. Dalton Trans. 2000, 3885-3896.
- [62] X.-J. Yang, F. Drepper, B. Wu, W.-H. Sun, W. Haehnel, C. Janiak, *Dalton Trans.* 2005, 256–267, and references therein.
- [63] T. Dorn, C. Janiak, Abu- K. Shandi, CrystEngComm 2005, 7, 633-641.
- [64] R. Vendrame, R. S. Braga, Y. Takahata, D. S. Galvão, J. Mol. Struct. (Theochem) 2001, 539, 253–265.
- [65] N. Johansson, G. A. Dos Santos, S. Guo, J. Cornil, M. Fahlman, J. Salbeck, H. Schenk, H. Arwin, J.-L. Bredas, W. R. Salaneck, J. Chem. Phys. 1997, 107, 2542–2549.
- [66] S. M. King, S. I. Hintschich, D. Dai, C. Rothe, A. P. Monkman, J. Phys. Chem. C 2007, 111, 18759–18764.
- [67] J. Rault-Berthelot, C. Poriel, F. Justaud, F. Barrière, New J. Chem. 2008, 32, 1259–1266.
- [68] H. O. House, D. Koepsell, W. Jaeger, J. Org. Chem. 1973, 38, 1167– 1173.
- [69] A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* 2004, 16, 4556–4573.
- [70] Y. Zhu, R. D. Champion, S. A. Jenekhe, *Macromolecules* 2006, 39, 8712–8719.
- [71] S. I. Hintschich, C. Rothe, S. M. King, S. J. Clark, A. P. Monkman, J. Phys. Chem. B 2008, 112, 16300–16306.
- [72] V. J. Chebny, R. Shukla, S. V. Linderman, R. Rathore, Org. Lett. 2009, 11, 1939–1942.
- [73] M. Iyoda, T. Kondo, K. Nakao, K. Hara, Y. Kuwatani, M. Yoshida, H. Matsuyama, Org. Lett. 2000, 2, 2081–2083.
- [74] A. Takai, C. P. Gros, J.-M. Barbe, R. Guilard, S. Kukuzumi, *Chem. Eur. J.* 2009, 15, 3110–3122.
- [75] G. Balaji, W. L. Shim, M. Parameswaran, S. Valiyaveettil, Org. Lett. 2009, 11, 4450–4453.
- [76] P. Hapiot, C. Lagrost, F. Le Floch, E. Raoult, J. Rault-Berthelot, *Chem. Mater.* 2005, 17, 2003–2012.

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### CHEMISTRY

- [77] P. M. Beaujuge, J. R. Reynolds, Chem. Rev. 2010, 110, 268-320.
- [78] L. F. Fieser, M. Haddadin, J. Am. Chem. Soc. 1964, 86, 2392-2395.
- [79] P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, B864-B871.
- [80] R. G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.
- [81] A. D. Becke, Phys. Rev. 1988, 38, 3098-3100.
- [82] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [83] A. D. Becke, J. Chem. Phys. 1993, 98, 1372-1377.
- [84] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
- [85] Gaussian 09, Revision A02, 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 Inc., Wallingford, CT, **2009**.

- [86] P. C. Hariharan, J. A. Pople, Chem. Phys. Lett. 1972, 16, 217-219.
- [87] MOLEKEL 4.3, H. P. Flükiger, S. Lüthi, S. Portmann, J. Weber, 2000, Swiss National Supercomputing Centre CSCS, Manno (Switzerland).
- [88] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 1994, 27, 435– 436.
- [89] SHELX97-Programs for Crystal Structure Analysis, Release 97-2, G. M. Sheldrick, 1998.
- [90] L. Farrugia, J. Appl. Crystallogr. 1999, 32, 837-838.

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