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Dihydroindenofluorene positional isomers

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CONSPECTUS.

Bridged oligophenylenes are very important organic semiconductors (OSC) in Organic Electronics (OE). The fluorene unit, which is a bridged biphenyl, is the spearhead of this class of materials and has led in the last twenty years to fantastic breakthroughs in Organic Light-Emitting Diodes (OLEDs). The dihydroindenofluorenes belong to the family of bridged terphenyls and can be viewed as the fusion of a fluorene unit with an indene fragment. The dihydroindenofluorenes have also appeared as very promising building blocks for OE applications. In the dihydroindenofluorene family, there are five positional isomers, with three different phenyl linkages (*para/meta/ortho*) and two different ring bridges arrangements (*anti/syn*). We focused our attention on the concept of positional isomerism. Indeed, the structural differences of the dihydroindenofluorenyl cores lead to unusual electronic properties, which have been described by our group since 2006 thanks to the five DiSpiroFluorene-IndenoFluorene positional isomers (dihydroindenofluorenes substituted on the bridges by fluorenyl units, Figure 1).

6,12-dihydroindeno[1,2-*b*]fluorene (the *para anti* isomer) is constructed on a *para* terphenyl core and possesses an *anti* geometry. If this isomer has been widely investigated over the last twenty years, studies of the four others remain very scarce. Thus, 11,12-dihydroindeno[2,1-*a*]fluorene (the *para syn* isomer) is also built on a bridged *para* terphenyl but possesses a *syn* geometry. This particular geometry has been advantageously used by our group to drastically tune the electronic properties and this isomer has emerged as a promising scaffold to obtain a stable blue emission arising from conformationally-controlable intramolecular excimers. These preliminary studies have shown the crucial influence of the geometry on the electronic properties of the dihydroindenofluorenes.

The modification of the phenyl linkages from a *para* linkage to a *meta* linkage provides the '*meta* isomers', namely 7,12-dihydroindeno[1,2-*a*]fluorene (the *meta anti* isomer) and 5,7-dihydroindeno[2,1-*b*]fluorene (the *meta syn* isomer). With these two regioisomers, the strong impact of both the linkage and the geometry on the electronic properties were particularly highlighted over the years. The last positional isomer of the family is 5,8-dihydroindeno[2,1-*c*]fluorene, which possesses a central *ortho* terphenyl backbone and a *syn* geometry. This isomer offers a unique example due its *ortho* linkage which induces a particular helicoidal turn of the dihydroindenofluorenyl core.

Thanks to a structure-properties relationship approach, we describe in the present account the molecular diversity of the five DiSpiroFluorene-IndenoFluorene positional isomers, and its consequences both in terms of organic synthesis and of electronic properties. This account shows how positional isomerism can be a powerful tool to tune the electronic properties of OSCs.

PROJECT ORIGINS

Regioisomerism, also called positional isomerism, is a central concept in organic chemistry which can have remarkable consequences on the properties of molecules. A simple structural modification can drastically influence the electronic and physical properties of an OSC and hence the performance of the corresponding electronic device. With that in mind, our group has started in 2007 to investigate the impact of regioisomerism on the electronic properties of dihydroindenofluorene derivatives. This account focuses on this feature with the study of the five DiSpiroFluorene-IndenoFluorene regioisomers (DSF-IF, Figure 1).

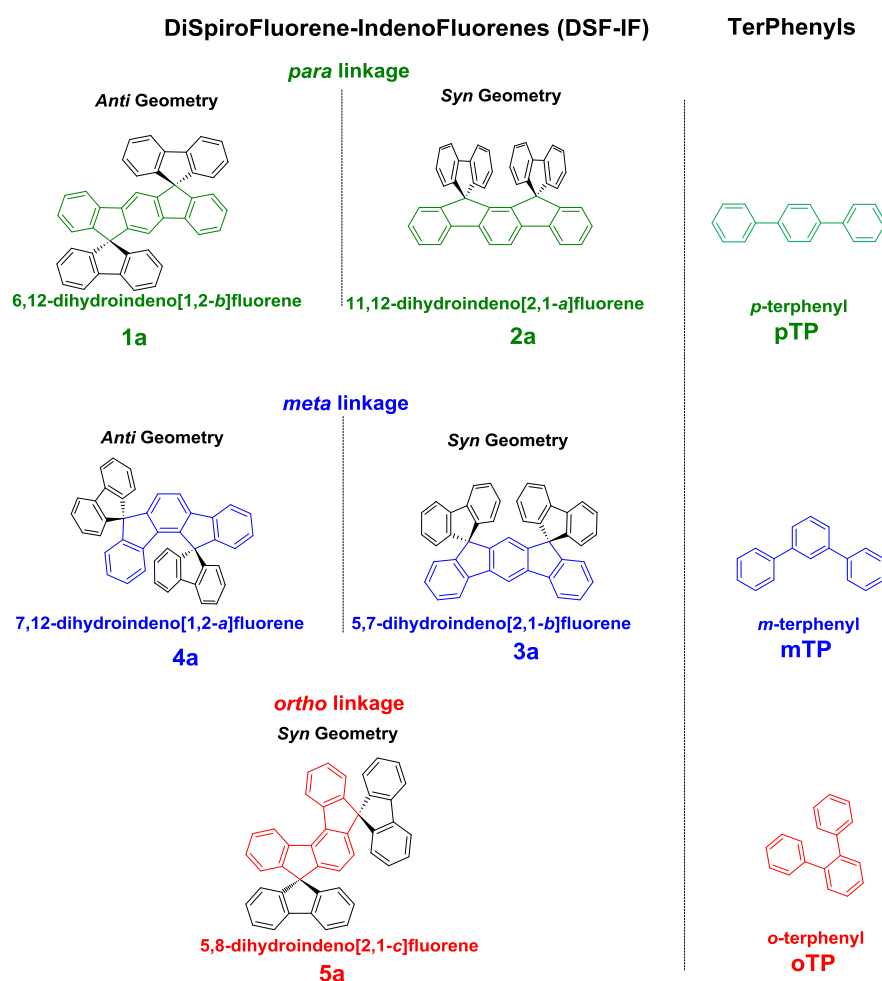


Figure 1. DiSpiroFluorene-IndenoFluorene and TerPhenyl regioisomers

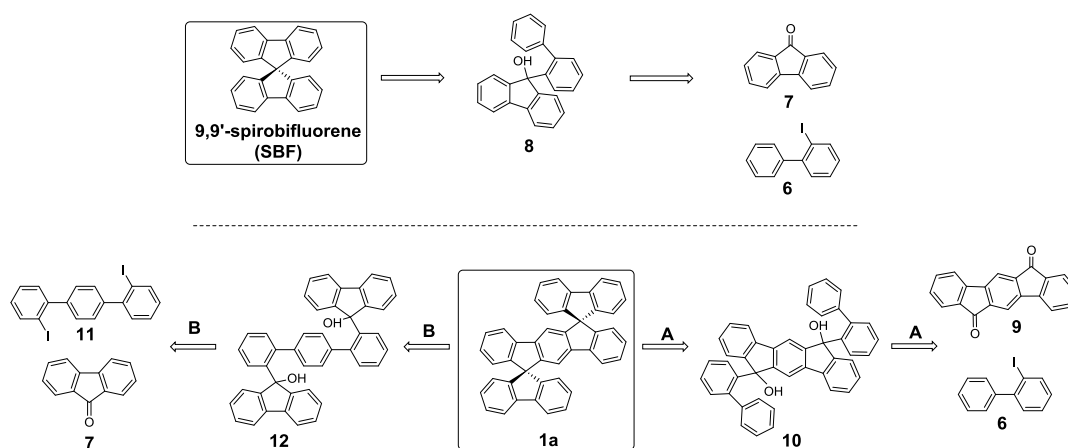
The dihydroindenofluorene family contains five regioisomers (Figure 1), with different phenyl linkages (*para/meta/ortho*) and different ring bridges arrangements (*anti/syn*). Although 6,12-dihydroindeno[1,2-*b*]fluorene (*para anti* isomer) has been described for the last twenty years, studies on the four other isomers remain very scarce. Thus, 11,12-dihydroindeno[2,1-*a*]fluorene is also constructed on a bridged *para* terphenyl but possesses a *syn* geometry. The modification of the phenyl linkages from a *para* to a *meta* linkage provides

7,12-dihydroindeno[1,2-*a*]fluorene and 5,7-dihydroindeno[2,1-*b*]fluorene with an *anti* and a *syn* geometry respectively. The last isomer is 5,8-dihydroindeno[2,1-*c*]fluorene, which possesses a central *ortho* terphenyl and a *syn* geometry. In the dihydroindenofluorene nomenclature, the letter is assigned to the edge of the indene/fluorene fusion. It should be mentioned that the antiaromatic counterparts, indenofluorenes, have also attracted remarkable attention notably from the Haley group.^{1,2} The present story begins in 2005 when our group started a new research field linked to materials for OE. Inspired by the work of Müllen³ and Scherf⁴ on dihydroindeno[1,2-*b*]fluorene and the work of Salbeck on spirobifluorene,⁵ the first example of a DiSpiroFluorene-IndenoFluorene, **1a**, constructed with the 6,12-dihydroindeno[1,2-*b*]fluorenyl backbone was reported in 2006.⁶

Synthetic approaches

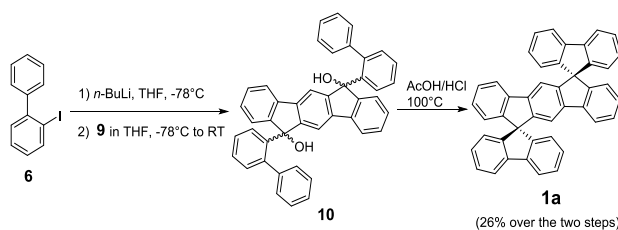
- a. Para isomers:** dispiro[fluorene-9,6'-indeno[1,2-*b*]fluorene-12',9''-fluorene] **1a** and dispiro[fluorene-9,11'-indeno[2,1-*a*]fluorene-12',9''-fluorene] **2a**

9,9'-spirobifluorene (SBF) is the association of two fluorenes through a shared spiro carbon and is obtained from the coupling of 2-iodobiphenyl **6** with fluorenone **7** followed by an intramolecular cyclisation of resulting fluorenol **8** (Scheme 1, Top).⁵ As **1a** can be considered as the fusion of two SBF, a similar strategy was imagined either from indeno[1,2-*b*]fluorene-6,12-dione **9** (Route A, Scheme 1, Bottom-Right) or from diiodoterphenyl **11** (Route B, Scheme 1, Bottom-Left). These two routes are drastically different in terms of regioselectivity. If route A is regioselective, exclusively leading to **1a**, route B is not and has led, in 2008, to the first example of a [2,1-*a*] regioisomer (**2b**, Figure 2).⁷ This notion of regioselectivity *vs* non-regioselectivity is an important concept in this account. Indeed, a regioselective approach appears in general more secure as it leads to a single regioisomer. Although more risky, a non-regioselective approach may lead to different regioisomers, which can be an appealing feature if their separation is possible.



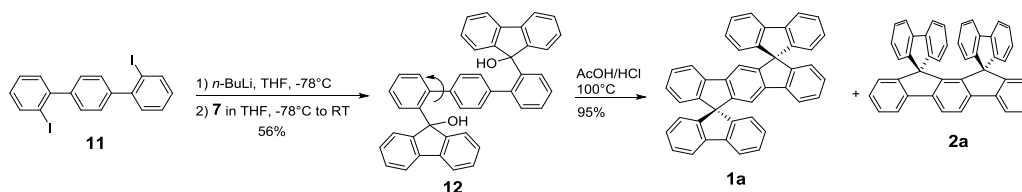
Scheme 1. Retrosynthetic analysis towards 9,9'-spirobifluorene (Top) and **1a** (Bottom)

Route A (Scheme 2) is based on the coupling reaction between **9**⁸⁻¹⁰ and **6**. This reaction provides diol **10** further involved in an intramolecular electrophilic cyclisation leading to **1a**.¹¹ This route is efficient and regioselective, exclusively providing **1a**. It should be noted that such types of intramolecular cyclisations are efficient and versatile tools to generate spiro carbons.



Scheme 2. Synthesis of **1a**-Route A

At first sight, the second strategy (Route B, Scheme 3)^{6,10} looked as straightforward as the first (Route A, Scheme 2). However, this route involves in its last step the intramolecular bicyclisation of the diol **12** providing as expected **1a** but also a second regioisomer **2a**. Unfortunately, we failed to detect in 2006⁶ the presence of **2a**, which was only revealed two years later.⁷ We did not expect, at that early stage, both the solvent and the temperature of the final cyclisation to be key parameters influencing the ratio of isomers formed.



Scheme 3. Synthesis of **1a** and **2a**-Route B

From a mechanistic point of view, the bicyclisation of **12** (Figure 2, Left) unfolds sequentially. The first cyclisation provides the 2-substituted spirobifluorene. The second cyclisation can occur either on the opposite side leading to the *anti* isomer **1a** or on the same side of the first cyclisation, leading to the *syn* isomer **2a**. In 2009, we observed that the ratio of the *anti/syn* isomers could be tuned as a function of three parameters: solvent, temperature and substituents borne by the fluorenes (Figure 2).¹² For example, the **1a/2a** ratio can be modified from 99/1 in CH₂Cl₂ at room temperature to 91/9 in CH₃CN at reflux. The effect on the **1b/2b** ratio is more pronounced shifting from 74/26 in CH₂Cl₂ at room temperature to 34/66 in CH₃CN at reflux. These effects are consistent with the stabilisation of the carbocation and to a less hampered interconversion between conformers.¹² In addition to these solvent and temperature effects on the selectivity, another important element that affects the isomers distribution is the nature of the R groups borne by the fluorenes. In fact, as R becomes more encumbering (from R=H in **1a/2a** to R=3,5-di-*tert*-butylphenyl in **1e/2e**), the distribution gradually shifts towards the formation of [2,1-*a*] isomers at the expense of [1,2-*b*] isomers. The reaction becomes even regioselective with R=3,5-di-*tert*-butylphenyl exclusively providing **2e**. This observation was at first confusing as **2a-2e** were less energetically stable compared to **1a-1e**.¹² The mechanistic investigations have shown that the increased selectivity towards [2,1-*a*] isomers as a function of the temperature, solvent and substituent, involved the relative locking of the encumbered rotamers in the more stable *pro-2* conformation due to a high energy barrier for the interconversion to the *pro-1* conformation. Thus, the synthesis can be directed towards the formation of [1,2-*b*] isomers with: (i) low polarity solvents, (ii) low temperature and (iii) small R groups. The opposite leads to the [2,1-*a*] isomers.

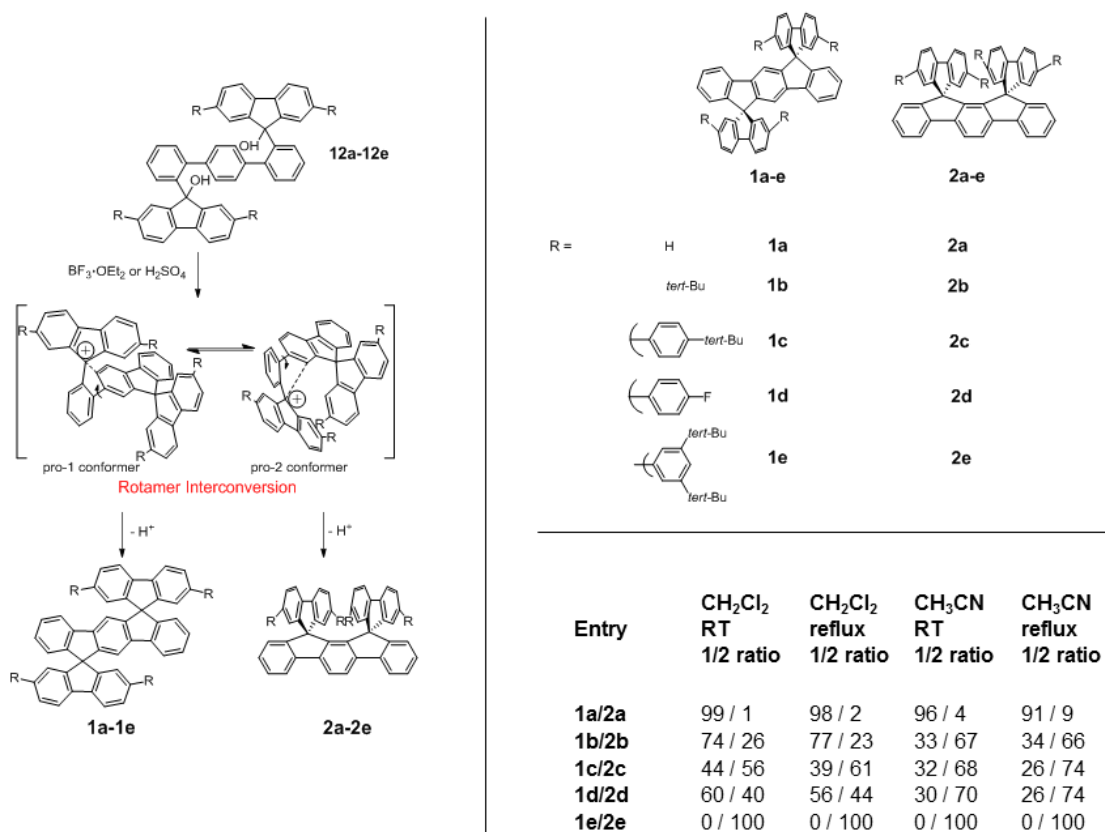
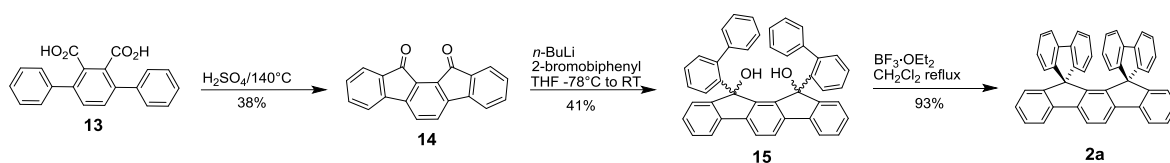


Figure 2. Proposed mechanism for the bicyclisation of difluorenols **12a-e** (Left). Molecules **1a-e/2a-e** (Top-Right). Ratio of regioisomers formed (Bottom-Right)

As above mentioned, when R=H, the maximum yield obtained for **2a** was low (9%) rendering very difficult its separation by column chromatography from its isomer **1a**. We thus started in 2010 to investigate a regioselective route towards **2a** involving the dione **14** (obtained from the intramolecular cyclisation of **13**,¹³ Scheme 4). The key feature of this approach is to build the dihydroindeno[2,1-*a*]fluorenyl core prior to the final cyclisation step of **15** in order to avoid the formation of the other isomer.

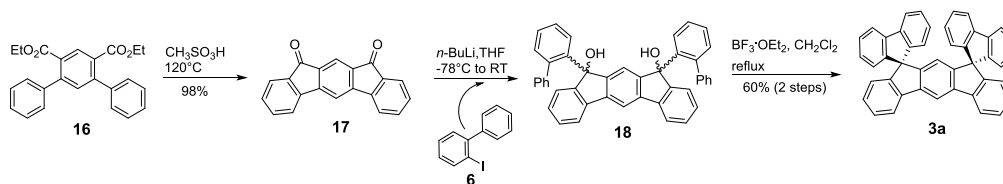


Scheme 4. Synthesis of **2a**-Route A

b. Meta isomers: dispiro[fluorene-9,10'-indeno[2,1-*b*]fluorene-12',9''-fluorene] **3a** and dispiro[fluorene-9,7'-indeno[1,2-*a*]fluorene-12',9''-fluorene] **4a**

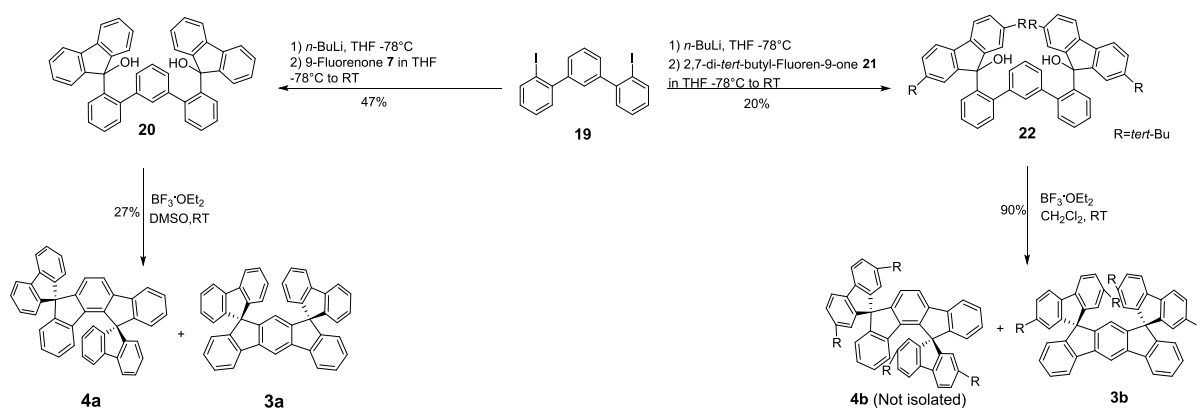
In 2013, the *meta* isomers **3a** (*syn* isomer) and **4a** (*anti* isomer) represented the second generation of DSF-IFs (Figure 1).¹⁴ Their respective dihydroindeno[fluorenyl] cores were nevertheless already described in 1955.¹⁵ Theoretically, these *meta* isomers **3a/4a** can be synthesized following similar approaches than those exposed above for *para* isomers, following either a regioselective route A (Scheme 5) or a non-regioselective route B (Scheme

6). Thus, **3a** was regioselectively synthesized from a short and efficient route involving the synthesis of dione **17** (obtained from *meta*-substituted terphenyl **16**), followed by the intramolecular cyclisation of indenofluorenol **18** (Scheme 5).^{16,17}



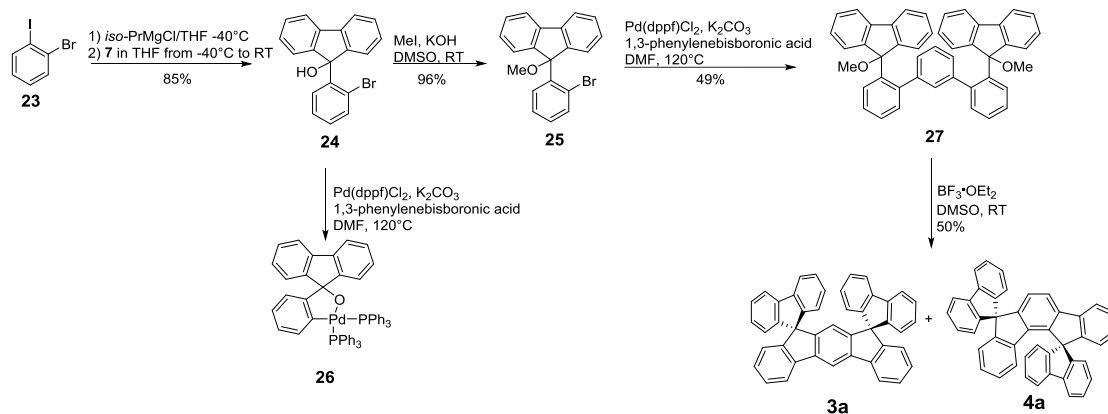
Scheme 5. Synthesis of **3a**-Route A

The same regioselective approach was unfortunately not successful for the synthesis of **4a**, which was instead synthesized from the non-regioselective Route B (Schemes 6 and 7). Two different synthetic strategies towards **3a/4a** were developed in this context. The first (Scheme 6) was directly adapted from that of **1a/2a** and involved diodoterphenyl **19** as precursor of **3a/4a** (ratio: 65/35).¹⁸ This route is versatile as many DSF-IF isomers substituted on the fluorenes can be synthesised by simply changing the fluorenone during the coupling with **19** (coupling with fluorenone **7** provides diol **20** and coupling with fluorenone **21** provides diol **22**). In 2011, we used this route to synthesise **3b/4b** substituted on the fluorenes with *tert*-butyl groups.¹⁹



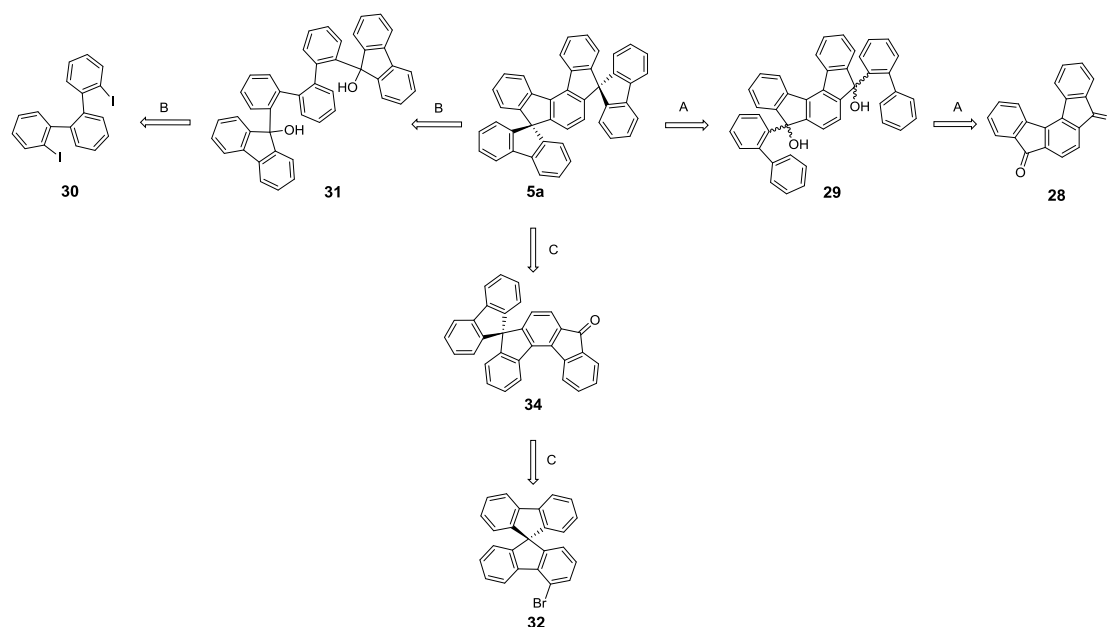
Scheme 6. Synthesis of **3a/4a** and **3b/4b**-Route B-Strategy 1

In all the non-regioselective synthetic routes based on an intramolecular bicyclisation, the diols were key compounds. Another route towards the methoxy protected diol **27** was therefore developed in 2013 (Scheme 7).¹⁴ The first step involved the synthesis of 9-(2-bromophenyl)-9*H*-fluoren-9-ol **24** from a Grignard reaction between **23** and **7**. Compound **24** was then protected with a methyl group (**25**) in order to avoid the formation of the palladacycle **26** during the cross-coupling which provided **27**. The intramolecular bicyclisation of **27** finally lead to the formation of the two isomers **3a/4a** (50/50).



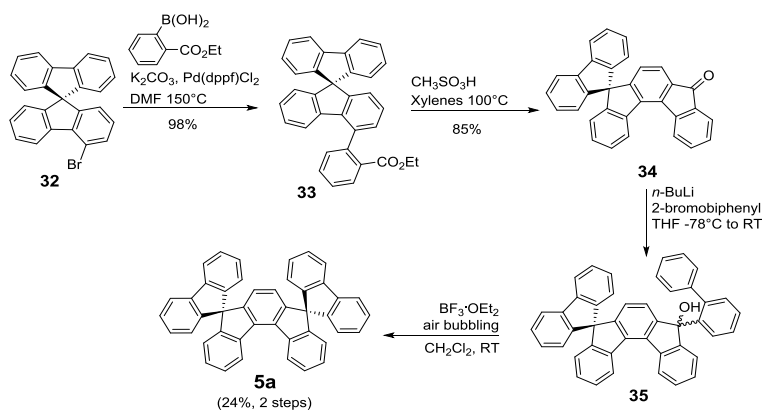
Scheme 7. Synthesis of **3a** and **4a**-Route B-Strategy 2

c. *Ortho* isomer: dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] **5a**



Scheme 8. Retrosynthetic analysis towards **5a**-Routes A, B and C

The last isomer **5a** derived from the *ortho*-terphenyl core may also theoretically be obtained through Route A (from **28/29**) or Route B (from **30/31**), Scheme 8. However, none of these two routes were used to prepare **5a** notably because both **28** and **30** appeared to be difficult to synthesize. Another synthetic approach towards **5a** (Scheme 8, Route C) involving an *ortho*-substituted spirobifluorene (**32**)²⁰ was therefore developed in 2015. This route is regioselective (Scheme 9).¹⁸ A phenyl carboxylate unit was first attached to C4 of the SBF backbone (**33**) before regioselectively constructing the dihydroindeno[2,1-*c*]fluorenyl core by an intramolecular cyclisation leading to the ketone **34**. Then, the anchoring of a biphenyl unit on **34** provided indenofluorene **35** further cyclised to provide **5a**.



Scheme 9. Synthesis of **5a**-Route C

We have shown in these studies that a non-regioselective synthesis can be a powerful tool to obtain two regioisomers in a single step. Although all these molecules were initially designed for electronics, the synthetic approach itself became, from an organic chemistry point of view, highly appealing to explore.

Physico-Chemical Properties: Influence of the linkages and of the ring bridges arrangements

Structural Properties

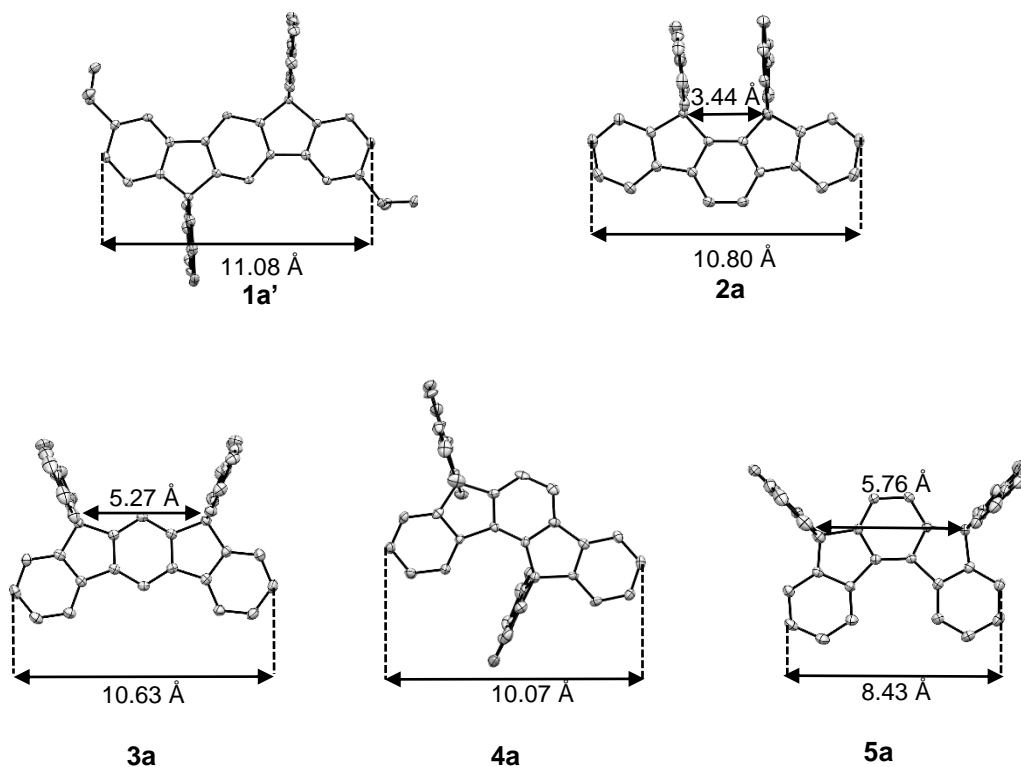


Figure 3. ORTEP drawing of **1a'** and of **2a-5a**

Due to the different linkages and bridges, the dihydroindenofluorenyl and fluorenyl fragments possess different structural characteristics (Figures 3 and 4) which have important consequences on the electronic properties described below. For example, the *meta* linkages in **3a/4a**¹⁴ and the *ortho* linkage in **5a**¹⁸ lead to a contraction of the dihydroindenofluorenyl core compared to **1a'**¹¹/**2a**¹³ (see dihydroindenofluorene length in Figure 3). It should be noted that the literature only reports the X-Ray structure of the diisopropyl analogue **1a'**¹¹ and not **1a** itself. The dihydroindenofluorene contraction is particularly visible in **3a** with its crescent moon shape and in **5a** with its particular helicoidal turn. However, the *meta* linkages of the dihydroindeno[1,2-*a*]/[2,1-*b*]-fluorenyl cores are only partially responsible for this contraction. In the case of **4a**, the contraction is accentuated by the *anti* geometry. A similar contraction effect caused by the ring bridging is also found for *para* isomers, the contraction being this time accentuated by the *syn* geometry (dihydroindenofluorenyl core of **2a** is shorter than that of **1a'**).

The ring bridging also has important consequences on the flatness and the deformations of the dihydroindenofluorenyl core. For example, in the *meta* isomers series the dihydroindeno[2,1-*b*]fluorenyl core of **3a** is almost flat whereas the dihydroindeno[1,2-*a*]fluorenyl core of **4a** presents more pronounced deformations due to the strong contraction imposed by the bridging.¹⁴

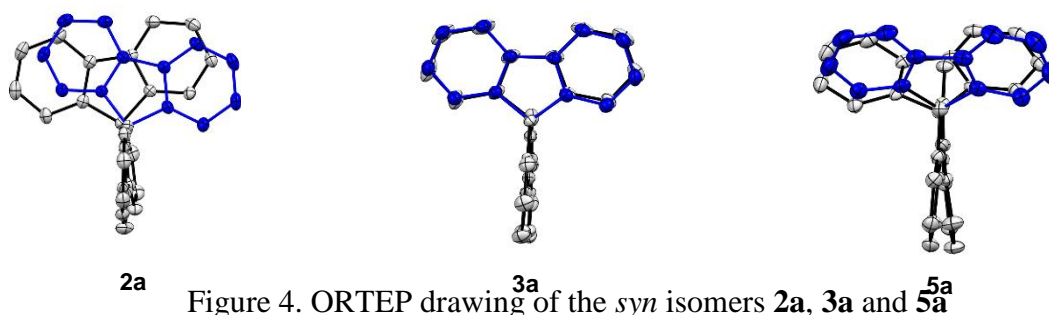


Figure 4. ORTEP drawing of the *syn* isomers **2a**, **3a** and **5a**

The spiro-connected fluorenes in the *syn* isomers **2a**, **3a** and **5a** are also strongly impacted by positional isomerism (Figure 4). As the distance between the spiro carbons is significantly shorter for **2a** (3.44 Å) compared to that of **3a** (5.27 Å), due to the different linkages (Figure 3), a different arrangement of the cofacial fluorenes is detected. The fluorene are staggered in **2a** and eclipsed in **3a** (Figure 4). Thus, in **2a**, there is an interaction between the two cofacial fluorenes (which will be used to tune the optical properties of aryl substituted [2,1-*a*] isomers, see below) and not in **3a**. The *ortho* linkage of the last *syn* isomer in the series, **5a**, leads to an even stronger elongation of the Cspiro-Cspiro distance (5.76 Å) and to a different arrangement of the fluorenes.

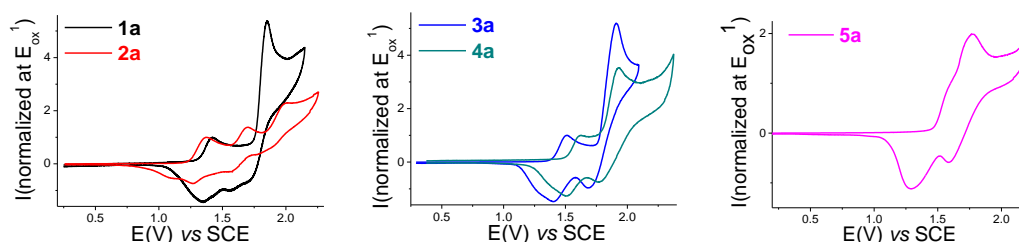
To conclude, the bridging and the linkages have strong repercussions on the structural properties of both dihydroindenofluorenes and fluorenes, which have themselves important consequences on the electronic characteristics described below. Table 1 provides a summary of the electronic properties of **1a-5a**.

Table 1. Selected electronic properties of **1a-5a**

	λ_{abs} (nm) ^a	λ_{em} (nm) ^a	$\Phi^{a,b}$	E_{T} (eV) ^c	E^{ox} (V) ^d	HOMO (eV)	E^{red} (V)	LUMO (eV)	τ (ns) ^a
1a	298, 310, 328, 336, 344	343, 358	0.62	2.52	1.47, 1.87	-5.76	-2.32 ^e	-2.17	2.08
2a	296, 311, 323, 339	345, 363, 381, 403	0.60	2.52	1.36, 1.69, 1.99	-5.64	-2.48, -3.0 ^e	-2.03	1.95
3a	298, 310, 326, 334, 342	346, 354, 363	0.54	2.76	1.53, 1.94	-5.80	-2.84 ^f	-1.75	3.95
4a	298, 308, 333, 342	341, 354	0.23	2.76	1.57, 1.88	-5.86	-2.86 ^f	-1.70	9.04, 2.73
5a	298, 309, 317, 338	344, 358	0.50	2.63	1.6 (sh), 1.77	-5.87	-2.59, -3.05 ^f	-2.00	7.32

a. in THF, b. quinine sulphate as reference, c. in methylcyclohexane/2-methylpentane, d. in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$, e. in $\text{DMF-Bu}_4\text{NPF}_6$, f. in $\text{THF-Bu}_4\text{NPF}_6$.

Electrochemical Properties

Figure 5. Cyclic voltammetry of **1a-5a** ($\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$, 0.2 M)

The five isomers display different electrochemical behaviour (Figure 5), which highlights the impact of isomerism on the electron transfers. **1a** presents two oxidation waves with maxima at 1.47 V and 1.87 V/SCE whereas **2a** possesses three waves at 1.36, 1.69 and 1.99 V (Figure 5, Left).¹³ The first monoelectronic oxidation wave has been assigned for **1a/2a** to the oxidation of the dihydroindenofluorenyl core. Compared to **1a**, two differences are pointed out for **2a**: (i) the first oxidation at 1.36 V is shifted towards less anodic potentials and (ii) an additional oxidation process is surprisingly observed at 1.69 V. The shift observed between the first oxidation potentials of **1a** and **2a** cannot be ascribed to the different geometry of the two dihydroindenofluorenyl cores but to the specific arrangement of the two fluorenyl units.¹³ In fact, in **2a**, the dihydroindenofluorenyl core is subjected to a less important withdrawing effect of the cofacial fluorene dimer compared to that of the two non-interacting fluorenyl units in **1a**. The additional oxidation observed at 1.69 V for **2a** was also at first sight

surprising and ascribed to the oxidation of this cofacial fluorene dimer. Thus, the different ring bridges arrangement of **1a** and **2a** and the resulting different geometry induce different electrochemical properties. As both molecules are constructed on an identical *para*-terphenyl core, this demonstrates that the linkage is not the only factor involved in the electronic properties.

Electrochemistry of the *meta* isomers **3a** and **4a** provides a different example (Figure 5, Middle). Both compounds possess two successive oxidation waves (**3a**: 1.53/1.94 V, **4a**: 1.57/1.88 V). The first monoelectronic oxidation has been assigned to the oxidation of the dihydroindenofluorenyl core and the second multielectronic wave to the concomitant oxidation of fluorenyl units and dihydroindenofluorenyl radical cation. Again, the effects of the phenyl linkages and of the ring bridging on the electrochemical properties need to be pointed out. The shift of the first oxidation potential to more positive values from **1a/2a**¹³ to **3a/4a**¹⁴ has been assigned to a linkage effect (*para* vs *meta* linkages) and translates a shorter π -conjugation pathway in *meta* isomers compared to *para* ones.

There is also a slight shift in the first oxidation potential between **3a** and **4a** despite their identical *meta* linkages. This small difference was assigned to the contraction and the deformation of the dihydroindeno[1,2-*a*]fluorenyl core of **4a** (vs the dihydroindeno[2,1-*b*]fluorenyl core of **3a**), which induce a poorer delocalisation of π -electrons and hence a more anodic oxidation potential.

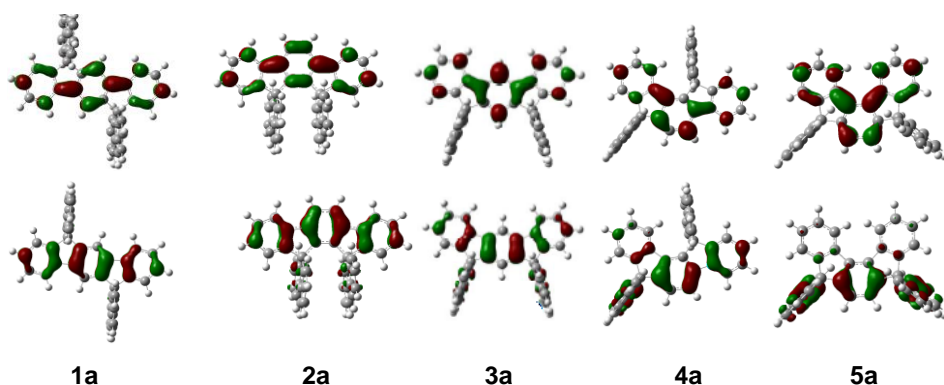


Figure 6. Calculated LUMO (Top) and HOMO (Bottom) of **1a-5a**

Isomer **5a** displays again a unique behaviour (Figure 5, Right). The first oxidation is only detected as a shoulder at 1.6 V, providing a HOMO level lying at -5.87 eV, almost identical to that of **4a** (-5.86 eV) but deeper than those of **1a-3a** (Table 1). However, the HOMO of **5a** (mainly located on the fluorenes) is noticeably different than those of all the other isomers (located on the dihydroindenofluorene), Figure 6. The *ortho* terphenyl linkage of **5a** causes the deformation of the dihydro[2,1-*c*]indenofluorenyl core leading to an inversion of the HOMO and HOMO-1 compared to the other isomers.¹⁸

These electrochemical investigations clearly show the diversity of these regioisomers.^{13,14,18,21-23} The linkage has important consequences on the π -electrons delocalization but is far from being the only parameter driving the electronic properties. The bridging is also important and has a double role: (i) it modifies the geometry (*syn* vs *anti*) and can force the two spiro-linked fluorenes to interact (such as in **2a**) and/or (ii) can increase the deformation of the dihydroindenofluorenyl core.

Optical Properties

The positional isomerism of the dihydroindenofluorenyl core also has strong repercussions on the optical properties. In THF, **1a-5a** present almost identical low-energy absorption maxima (Table 1) with nevertheless an impressive difference in the intensity of this band (Figure 7, Left). **1a** and **2a** possess similar and well resolved absorption spectra, which is a characteristic of highly rigid structures. With respect to **1a**, the UV-vis spectrum of **2a** exhibits a main absorption band slightly hypsochromically shifted. This blue shift has been assigned to a better delocalisation of π -electrons in **1a** compared to **2a**. Oppositely to the electrochemistry, **1a** and **2a** display a similar behaviour in absorption spectroscopy and the cofacial fluorenes of **2a** only have a limited influence on the electronic transitions. The spectrum of **3a** is also similar in shape but is red shifted compared to the *para syn* homologue **2a**. Therefore, *para* substituted derivatives do not always possess longer π -conjugated pathways compared to *meta* substituted derivatives and this feature shows that the linkages are not the only parameters involved in the optical properties and that the ring bridging is also of chief importance.²⁴ This is one of the most important findings we learned from these isomers. The different spectrum of **4a** displaying very weak bands at 333 and 342 nm confirms the key role played by the ring bridging on the transitions. Indeed, isomers **1a-3a** all possess intense low-energy absorption bands. Compared to **1a-3a** isomers, **4a** has no symmetry axis/plane, and its constrained structure leads to a deformation of the dihydroindeno[1,2-*a*]fluorenyl core, which has a strong influence on the partially allowed/forbidden character of its first π - π^* transition. Isomer **5a**, which also possesses a highly distorted dihydroindenofluorenyl backbone displays an identical characteristic with a weak band at 338 nm.¹⁸

Studying the corresponding non-bridged terphenyls (*para*-Terphenyl **pTP**, *meta*-Terphenyl **mTP** and *ortho*-Terphenyl **oTP**, Figure 1) has allowed a better understanding of the impact of the bridges on the electronic properties of dihydroindenofluorenes. There is indeed an impressive red shift between the absorption maxima of terphenyls (Figure 8) and those of their corresponding dihydroindenofluorene analogues. This feature has been attributed to the presence of the bridges in the latter. In fact, the bridges avoid any torsion between the constituted phenyl units in the dihydroindenofluorenes, feature responsible for the disruption of the π -conjugation in the terphenyls. In addition, the lowest energy band of each terphenyl corresponds to a HOMO/LUMO transition, which is not the case for **4a** and **5a**. Therefore, the presence of the bridges has changed the nature of the main transition in **4a** and **5a** compared to their terphenyl analogues **mTP** and **oTP** but not for the three other isomers **1a-3a**. This is an unexpected behaviour induced by the bridge effect in dihydroindenofluorenes.

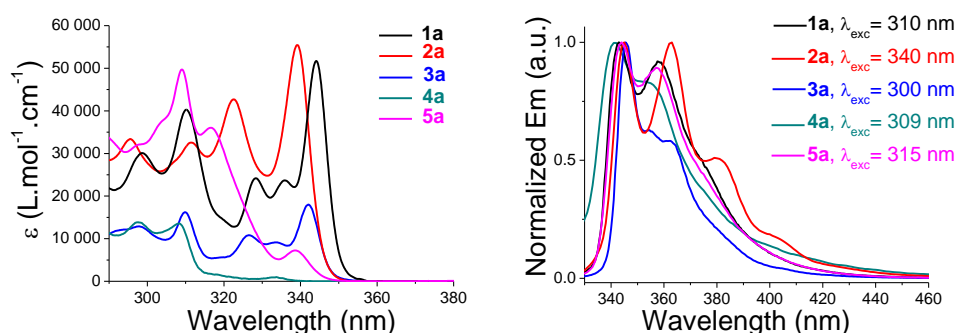


Figure 7. UV/Vis absorption (Left) and emission spectra (Right) of **1a-5a** (THF)

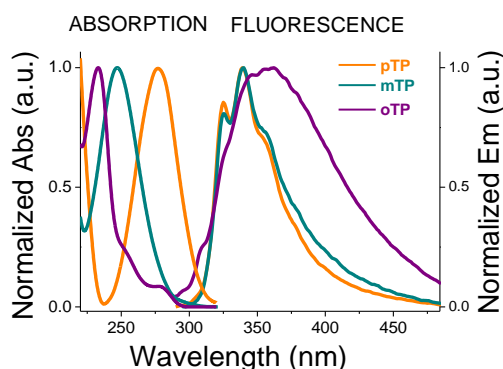


Figure 8. UV/Vis absorption and emission spectra of terphenyls **pTP**, **mTP** and **oTP** (cyclohexane)

Regarding the fluorescence properties, **1a-3a** possess well resolved spectra (Figure 7, Right) with a very small Stokes shift, both features being characteristic of highly rigid structures. **2a** possesses the largest Stokes shift which has been linked to structural changes by theoretical calculations.¹³ Indeed, at the ground state, **2a** shows a staggered conformation of the fluorenes whereas in the first singlet excited state a cofacial eclipsed arrangement is detected (Figure 9).¹³ Although this geometry change has no significant effect on the fluorescence spectrum of **2a**, it is at the origin of the spectacular excimer emission which will be discussed below for **2c-e**.

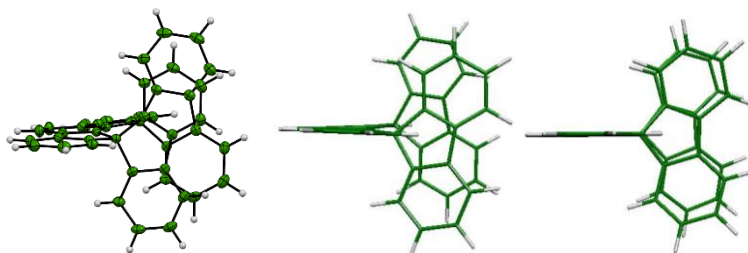


Figure 9. X-Ray structure (Left), optimised geometry in the ground state (Middle) and in the first singlet excited state (Right) of **2a**

Compared to all the other isomers, the quantum yield of **4a** was found to be significantly lower and its fluorescence decay more complex (two lifetimes *vs* one lifetime), Table 1. Such unusual emission properties are the signature of unconventional processes, such as the presence of several emissive states or partially decoupled excited states. These studies have revealed the unique photophysical properties of the dihydroindeno[1,2-*a*]fluorenyl backbone compared to the other isomers and the remarkable impact of the regioisomerism on the photophysics. Again, the fluorescence spectra of terphenyls have been precious tools in the understanding of the emission properties. There is indeed a strong similitude between the emission spectra of **1a/2a** and **3a/4a** and those of their corresponding terphenyls **pTP** and **mTP** whereas their absorptions were significantly different (Figures 7 and 8). Despite being built on a different linkage, these terphenyl isomers surprisingly display identical emission spectra. There is therefore a breakdown of the mirror image symmetry in their absorption/emission spectra assigned to the planarization of the terphenyl core in the excited state.²⁵ This planarization of **pTP** and **mTP** in the excited state leads to a geometry analogous to that of **1a/2a** and **3a/4a**, which are already planarized at the ground state. This important structural feature explains why the fluorescence spectra of dihydroindenofluorenes at room

temperature remain roughly similar and almost independent of the linkages. Emission spectra at low temperature (77 K) have led to different conclusions.

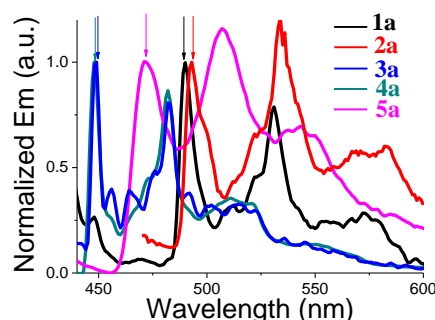
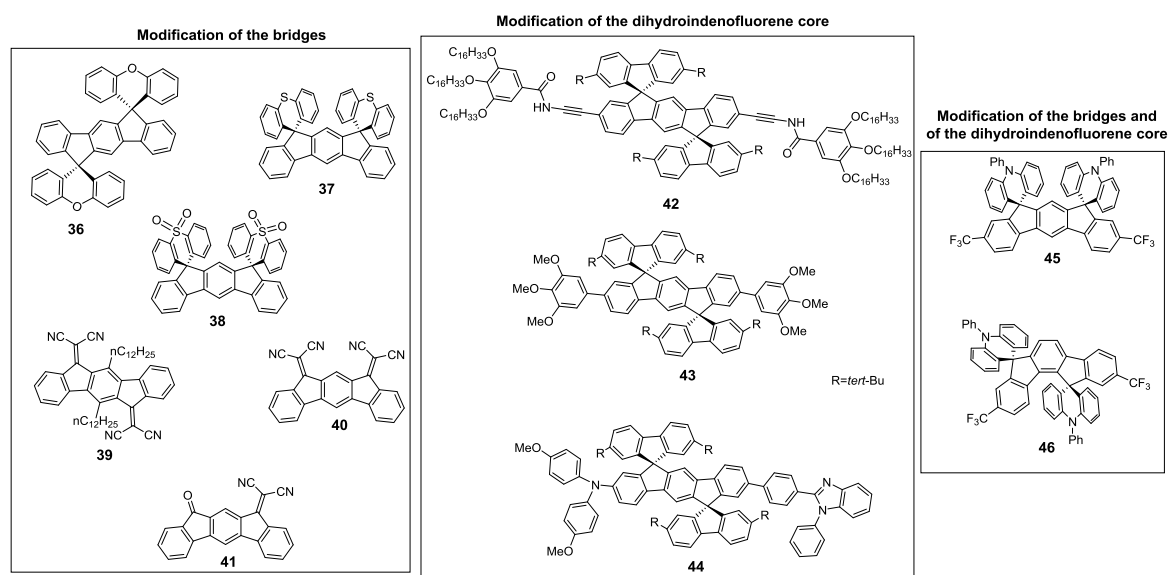


Figure 10. Emission spectra at 77K of **1a-5a** (methylcyclohexane/2-methylpentane)

Emission spectra at 77 K (Figure 10) allow to determine the triplet state energy (E_T), which is a key property for host phosphors in phosphorescent OLEDs (PhOLEDs).^{17,18} As the two *para* isomers **1a/2a** and the two *meta* isomers **3a/4a** present almost identical spectra, the phosphorescent contributions are fully driven by the linkages with a very weak influence of the bridging. The E_T is therefore identical for **1a/2a** (2.52 eV) and for **3a/4a** (2.76 eV). The E_T of the *ortho* isomer **5a** is reported at 2.63 eV. Interestingly, the corresponding terphenyls **pTP**, **mTP** and **oTP** (E_T = 2.55, 2.82 and 2.67 eV respectively) possess almost identical values than their corresponding dihydroindenofluorenes. Oppositely to the conclusions drawn above, this study of the terphenyls confirms that the nature of the linkage fully drives the E_T . This is an important feature that enables the tuning of the triplet energy without strongly modifying the singlet energy. This can be advantageously used for example in the field of Thermally Activated Delayed Fluorescence materials.²⁶

Properties modulation

The positional isomers offer many possibilities in terms of molecular design but only a few have been investigated yet. Basically, in such structures, one can modify (i) the bridges and/or (ii) the substituents attached to the dihydroindenofluorenyl core (Scheme 10).



Scheme 10. Examples of substituted dihydroindenofluorenes

In 2010, we reported the incorporation of xanthenyl units on the bridges of a dihydroindeno[1,2-*b*]fluorenyl core (**36**, Scheme 10-Left). This efficient emitter ($\Phi=0.63$) has been incorporated in non-doped blue-emitting OLEDs displaying high performance.²⁷ Following a similar design strategy, the bridges of the dihydroindeno[2,1-*b*]fluorenyl core were substituted by thioxanthene and dioxothioxanthene (**37-38**). The incorporation of the sulphur atom allows tuning the HOMO/LUMO levels, retaining nevertheless the high E_T of the dihydroindeno[2,1-*b*]fluorenyl core (2.76 eV), key feature for an application as host in blue PhOLEDs.¹⁷

Another appealing modification was presented by Marks *et al.*,²⁸ who have incorporated dicyanovinylene units on the bridges of a dihydroindeno[1,2-*b*]fluorene (**39**). As dicyanovinylene units are strong electron-withdrawing groups, the electronic properties of the dihydroindeno[1,2-*b*]fluorene was significantly modified. **39** is weakly fluorescent and displays a low LUMO level whereas its analogue **1a** is an efficient fluorophore with a high LUMO level (Table 1). In 2015, we reported a similar design with the incorporation of dicyanovinylene units on the bridges of a dihydroindeno[2,1-*b*]fluorene (**40**).¹⁶ This molecule possesses a low LUMO level (-3.81 eV vs -1.75 eV for **3a**) and was successfully used in n-channel OFETs with excellent electrical stability. This stability has allowed to incorporate these OFETs in “pseudo-complementary metal oxide semiconductor” inverters. During this work, compound **41** possessing differently substituted bridges was also reported.

Interestingly, **41** presents the electronic characteristics of the different functional groups borne by the bridges, *ie* dicyanovinylene and ketone. Such dihydroindenofluorenes possessing different bridge substitutions are almost absent from literature and could constitute an appealing future class of functional materials.

The second design strategy is related to the substitution of the dihydroindenofluorenyl core (Scheme 10, middle). Camerel *et al* reported the attachment of protomesogenic fragments on the dihydroindeno[1,2-*b*]fluorenyl core (**42**) to generate liquid crystalline phases.²⁹ Temperature-dependent solid-state luminescence measurements have notably revealed that this compound displays interesting thermochromic luminescence properties. Another symmetric dye (**43**) incorporating electron-donating trimethoxyphenyl units on the dihydroindeno[1,2-*b*]fluorenyl core was also reported.³⁰ Due to the π -conjugation extension, **43** is an efficient blue emitter (391/412 nm) displaying a very high quantum yield (0.9). These examples show how the electronic properties of the dihydroindenofluorenyl backbone can be easily tuned by molecular design to reach functional materials.

The first example of a non-symmetric DSF-IF (**44**) for OLEDs was reported in 2011.³¹ This molecule incorporates diarylamino (hole-transporting) and phenylbenzimidazolyl (electron-transporting) groups at each extremity of a dihydroindeno[1,2-*b*]fluorenyl core. This substitution gives to **44** very different properties than those of its unsubstituted analogue **2b**. For example, **44** is a blue emitter ($\lambda_{\text{max}}=435$ nm) whereas its constituting building block **2b** is a near-UV/violet emitter ($\lambda_{\text{max}}=348$ nm, Figure 11). As **44** possesses a high quantum yield (0.85) and bipolar properties, it has been successfully incorporated in single-layer OLEDs with performance impressively improved compared to **2b**.³¹

Finally, both the bridges and the dihydroindenofluorenyl core have been modified, although this strategy is difficult from a synthetic point of view. The first bipolar molecules based on dihydroindeno[2,1-*b*]/[1,2-*a*]fluorenes **45/46** (Scheme 10, Right) appeared in 2015 displaying very different electronic properties compared to those of **3a/4a**.³² When incorporated as host in blue PhOLEDs, **46** displays higher performance than **45** (External Quantum Efficiency of 7.9% and 2.6% respectively) which is attributed to a significant charge-carrier mobility difference (10^{-4} cm²/V.s and 10^{-6} cm²/V.s respectively). This highlights the crucial role played by the geometry profiles in the design of host materials for PhOLEDs.

We cannot report herein all the modifications made to the dihydroindenofluorenes. An exhaustive review is currently in preparation.

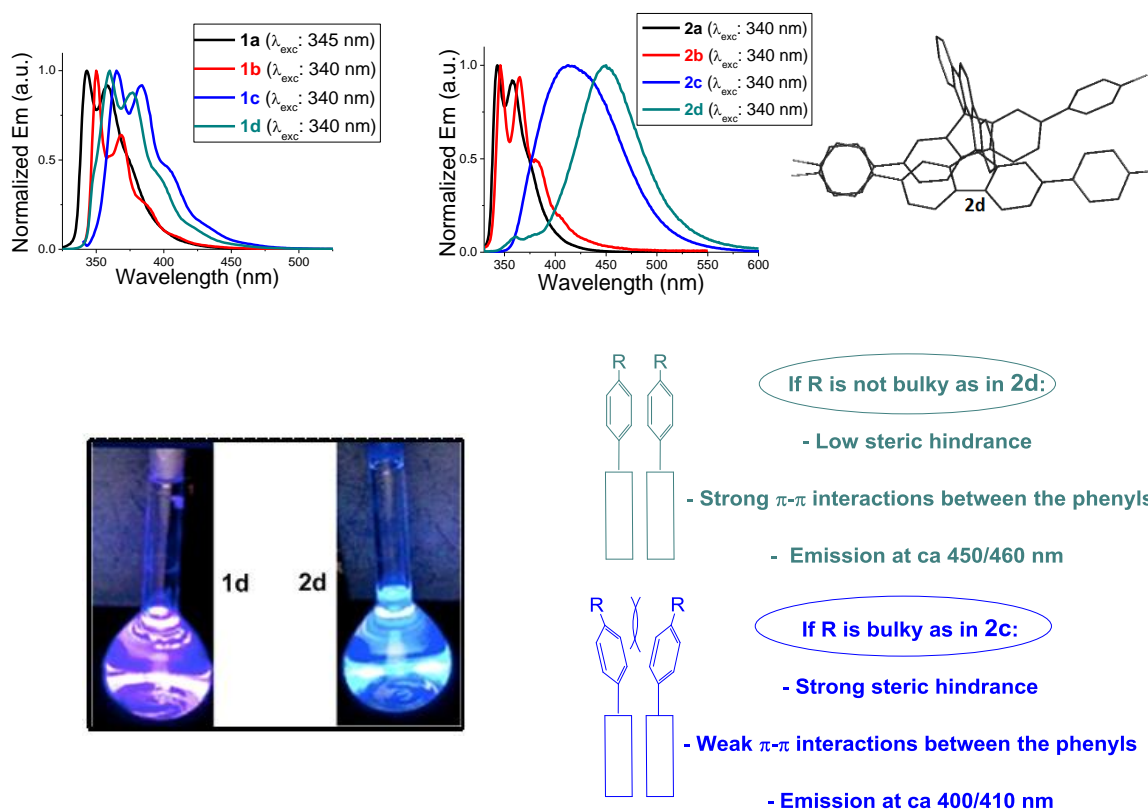


Figure 11. Top: Emission spectra in THF of **1a-d** (Left) and **2a-d** (Middle), X-Ray structure of **2d** (Right). Bottom: Photograph of the light emitted by **1d/2d**, $\lambda_{\text{exc}}=365$ nm (Left) and schematic representation of the phenyl substitution in [2,1-*a*] isomers (Right).

If all the previous design strategies are rather classic, the last with which we would like to conclude is much more original (Figure 11) and draws benefit from the particular *syn* geometry of **2a**.^{22,30,33} Thanks to this geometry, the dihydroindeno[2,1-*a*]fluorenyl core can hold two fluorescent units in a cofacial arrangement leading to an emission arising from intramolecular excimers. As above exposed, the couples **1a-2a/1b-2b** display very similar optical properties as the main emission is induced by the corresponding dihydroindenofluorenyl core (Figure 11). However, when the fluorenes are substituted by aryl units (**1c-d/2c-d**, see structures in Figure 2), drastically different emission properties are obtained. Indeed, if the aryl-substituted **1c-d** are violet emitters with classic emission properties, the **2c-d** isomers are blue emitters with emission arising from the interactions of the cofacial "aryl-fluorene-aryl" arms (Figure 11, Bottom-Left).²²

Finally, **2c-d** also possess remarkable tuneable optical properties since the emission wavelength can be modulated through the steric hindrance between the substituted phenyl rings leading to conformationally-controlable intramolecular excimer formation (Figure 11, Bottom-Right). When the substituent borne by the phenyl unit is bulky such as a *tert*-butyl group in **2c**, the two "aryl-fluorene-aryl" arms move away from each other reducing their mutual interactions, resulting in a blue shift of the emission compared to **2d**.²² These families of dyes can therefore cover a large wavelengths range from near-UV to sky-blue.

Conclusion

The concept of positional isomerism in the design of OSCs is more and more used and dihydroindeno[1,2-*b*]fluorene isomers have undergone a significant development in the last ten years. We show in this account how positional isomerism can be an efficient tool to tune the electronic properties of dihydroindeno[1,2-*b*]fluorenes. As the two main molecular parameters involved, *ie* bridges and linkages, can be combined in many different ways, they offer powerful design possibilities. However, except the dihydro[1,2-*b*]indeno[1,2-*b*]fluorene, the design of the other isomers for OE is poorly developed and provides an interesting future direction. Another appealing design strategy concerns the modification of the π -systems as recently exemplified with dihydroindacenodithiophene regioisomers.³⁴

Finally, if the use of dihydroindeno[1,2-*b*]fluorenes was mainly directed to electronics, it is clear that other applications will be developed in the future. The recent work on predicted ordered materials based on the dihydro[1,2-*b*]indeno[1,2-*b*]fluorene is an example of a new direction for these compounds.³⁵ It most likely won't be the only one.

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BIOGRAPHICAL INFORMATION

Cyril Poriel received his PhD in 2003 from the University of Rennes 1. After a postdoctoral stay at the University of Exeter (UK), he joined the CNRS (Rennes) in 2005, where he is currently senior researcher. His main research interest deals with the design of π -conjugated architectures for Organic Electronics: blue fluorophores for OLEDs, high-triplet hosts for PhOLEDs and electron deficient semiconductors for n-type OFETs. He is author/co-author of more than 80 publications, reviews and book chapters.

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