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# Novel dispirobifluorenes and indeno-spirobifluorenes: syntheses and properties

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ABSTRACT

Novel indeno-spirobifluorene and dispirobifluorene derivatives were synthesized and characterized. Their two positional isomers were unambiguously determined by X-ray crystallography. Preliminary investigations indicated that these indeno-spirobifluorene and dispirobifluorenes showed blue fluorescence with good quantum yields ($\Phi$>60%) and excellent thermal stabilities.



## 1. Introduction

The fabrication of the first efficient molecule-based organic light-emitting diodes (OLEDs), reported by Tang and van Slyke, led many efforts to bring OLEDs into commercial applications.[1]

In order to produce high-efficiency OLEDs with saturated color, low driving voltages as well as high quantum yield, many factors have to be considered. Conjugated aromatic compounds have been widely considered as organic semiconductors in fields of organic thin-film transistors (OTFTs) and organic light-emitting diodes (OLEDs).[2]Among all the known organic semiconductors and OLED applications, the fluorene-based compounds attracted most attention, owing to their unique properties, availability and processability.[3] Nowadays, only the red and green ones have shown sufficient efficiencies and lifetimes to be of commercial values from materials based either oligomers or polymers, while that of blue-emitting materials still remains as a big challenge.[4]

Research into blue-emitting materials has centered on conjugated fluorenes, such as polyfluorenes(PFs), Poly(indeno-fluorenes) (PIFs).[3a,5] Substituted fluorenes are known to have relatively high band gaps and low HOMO levels. As reported by Müllen and Leising, the block of interchain interaction and the enhancement of the thermal stability could be approached by introducing bulky groups at $C_9$ position of polyfluorene.[2,4c,6]

Particularly ladder-type materials are of great interest as promising units for organic electronic devices due to their high coplanarity, carrier mobility, and excellent luminescence.[7] Since the first report on ladder-type poly(*p*-phenylene)s in 1991,[8] many efforts have been done to clarify their structure–property relationships, 6,12-dihydroindeno[1,2-*b*]fluorene (called (1,2-*b*)-IF) is one of the simplest and ladder-type oligomer widely used as a building block leading to a strong enhancement of the OLED properties.[9]

Attention has also been paid to the ladder-type compounds with rigid spiro-linked structures. Recent elegant studies on novel families of dispiro derivatives, such as dispiro fluorene-9,6-indeno [1,2-*b*]fluorene-12,9-fluorene (called (1,2-*b*)-DSF-IF), which appeared to be highly promising for blue OLED applications, have been reported.[10] Compared with dispirobifluorenes, the indeno [1,2-*b*]spirobifluorenes, which could be used as host materials for electro-phosphorescent organic light-emitting devices (PhOLED) with unique properties, have been paid less attention.[10c] However, to the best of our knowledge, the (2,1-*a*)-IF positional isomers have been reported in few instances,[11] only (2,1-*a*)-DSF-($^t$Bu)$_4$-IF and (2,1-*a*)-DSF-(aryl)$_4$-IF have been reported so far.[10d–h] Additionally heterocycle-fused dispirofluorenes have called a lot of attention in very recently.[10i–k]

The reports on indeno[1,2-*a*]- or [2,1-*c*]spirobifluorene and dispirobifluorene are still rare, it is not until 1999 that a few indeno [1,2-*a*]fluorenes and its spiro-derivatives were reported.[12] The above mentioned studies have prompted us to explore novel indeno-spirobifluorenes and dispirobifluorenes with cores other than (1,2-*b*-IF). In this paper, we report the latest progress on rigid ladder-type molecules of indeno-spiro and dispiro bifluorenes:(1,2-*a*)-IF-SF (**8a**), (2,1-*c*)-IF-SF (**8b**), (1,2-*a*)-DSF-($^t$Bu)$_4$-IF (**10a**) and (2,1-*c*)-DSF-($^t$Bu)$_4$-IF (**10b**).

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## 2. Result and discussion

### 2.1. Synthesis

The synthetic routes to novel indeno-spirobifluorene and dispirobifluorene are presented in Scheme 1. Initially the reaction of ethynylmagnesium chloride with fluorenones afforded 9-ethynyl-9-fluorenols (**1a**,**b**) (yields: 63 and 73%); Then the Dields–Alder reaction of **1a** or **1b** with indanocyclone (**2**) at 240 °C led to the formation of **3a**,**b** and **4a**,**b**, which could easily be separated by column chromatography (yields: 61% and 71%) (Table 1). The fluorenols **3a**,**b** and **4a**,**b** were subsequently converted into indeno-spirobiflorenes **5a,b** and **6a,b** in excellent yields (90–96%) via Friedel–Crafts alkylation with HOAc/HCl. Compounds **5a** and **5b** are barely soluble in polar solvents, such as THF and $Et_2O$, which prevented further transfer into dispirobifluorene derivatives. In contrast, **6a**,**b** show higher solubility, and could be converted into the *tert*-butyl substituted fluoren-9-ols (**9a**,**b**)(yield: 93%). Then the acid promoted Friedel–Crafts reactions were employed to form dispirobifluorenes (**10a**,**b**) in the presence of HOAc/HCl with isolated yield ca. 85%. Compounds **9a**,**b** and **10a**,**b** appear to be the first examples of a spiro-type compounds with [1,2-*a*]-IF-and [2,1-*c*]-IF cores.

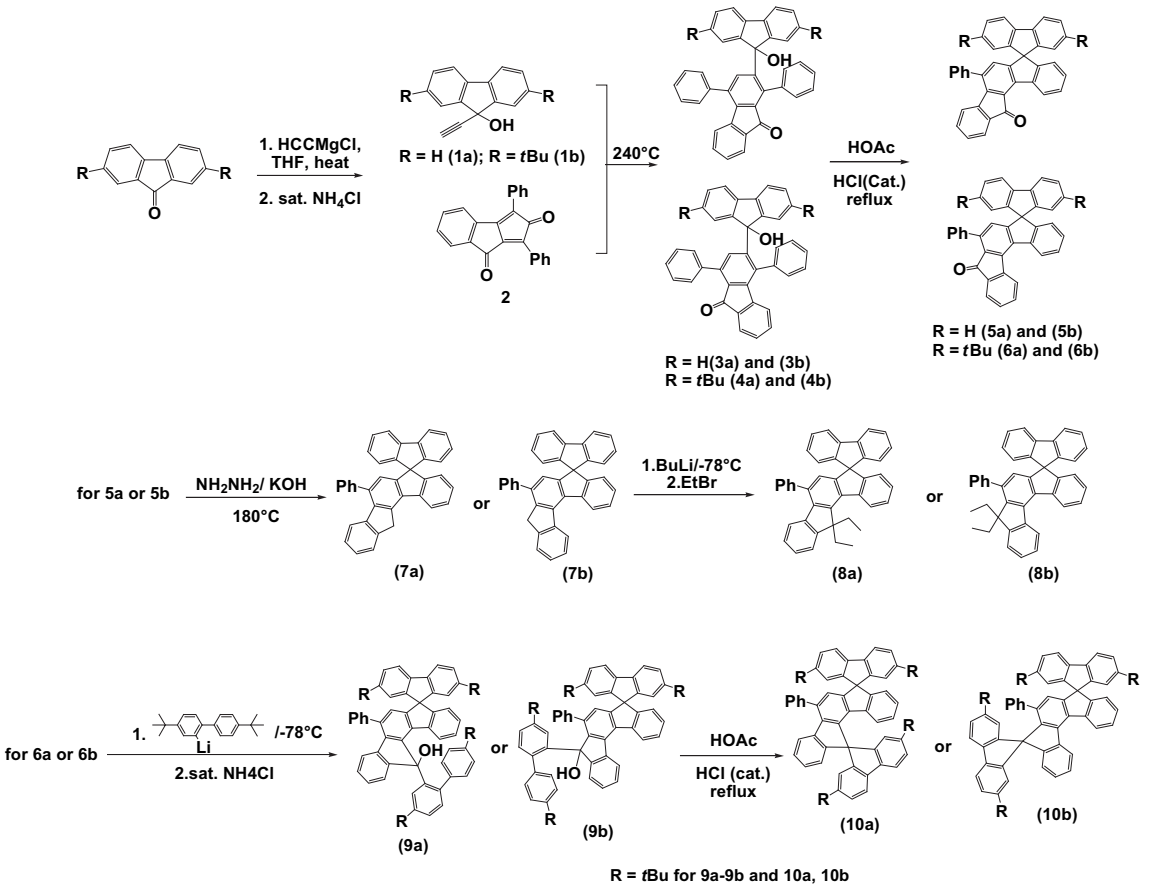
As **5a**,**b** have poor solubilities in common organic solvents, therefore Wolff–Kishner reaction was performed to obtain **7a**,**b** (yields: 62% and 78%), which were easily converted into diethyl-indenonspirobifluorenes (**8a**,**b**) via lithiation and halogen-exchange (yields 85% and 90%). The solubility of **8a**,**b** was improved dramatically compared to that of their precursors **7a**,**b**.

All new intermediates and final products were confirmed by NMR. In $^1$H NMR, due to the shielding effect of the carbonyl, the proton shift of **5a** and **6a** peaks both appear at ca. 9.5 ppm, which is larger than those of **5b** and **6b** (ca. 8.5 ppm) (Fig. 1). This phenomenon provides an useful solution to infer the absolute configuration of positional isomers for different indenofluorene skeletons.

It is noteworthy that synthetic routes described here are easy to handle with good overall yield, and under transition-metal catalysts free condition, the later has often been involved in cross-coupling reactions to obtain precursors for other indenofluorenes or dispirobifluorenes.

### 2.2. X-ray single crystal determination

Due to their good solubility in the common organic solvents, the suitable crystals of **8a**,**b** and **10a**,**b** for X-ray structure determination




**Scheme 1.**

**Table 1**
The Diels–Alder reaction yield of **3a**,**b** and **4a**,**b**

| | $R_f$ Data (PE/DCM=1:1) | Yield (%) | Total yield (%) |
|---|---|---|---|
| **3a** | 0.78 | 21 | 71 |
| **3b** | 0.64 | 50 | |
| **4a** | 0.75 | 21 | |
| **4b** | 0.56 | 40 | 61 |

were obtained. Fine crystals of compounds **8a**,**b** were obtained from $CHCl_3$/EtOH; while those of **10a** and **10b** were grown from EtOAc/EtOH, Toluene/EtOH, respectively. The X-ray structure determinations confirmed their structures in accordance with their NMR (Fig. 2). The crystallizations of **10a**,**b** were more difficult than those of **8a**,**b**.

It is interesting to find, there are two strong C–H···π effect, which impacts on the conjugate plane of the molecule in **8b** (the distance between H on aromatics to the centers of coplanar

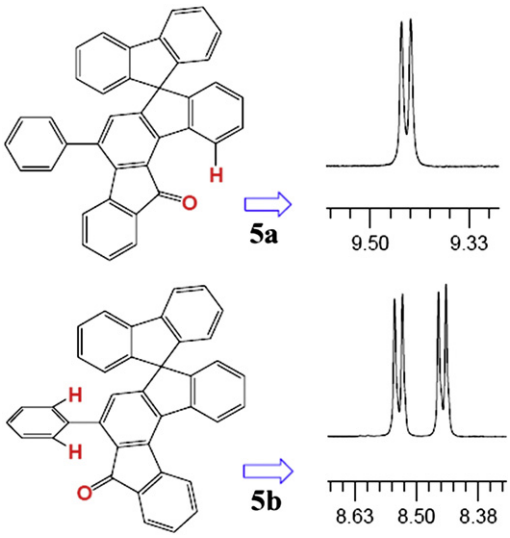



**Fig. 1.** Comparison of **5a**,**b**'s $^{1}$H NMR.

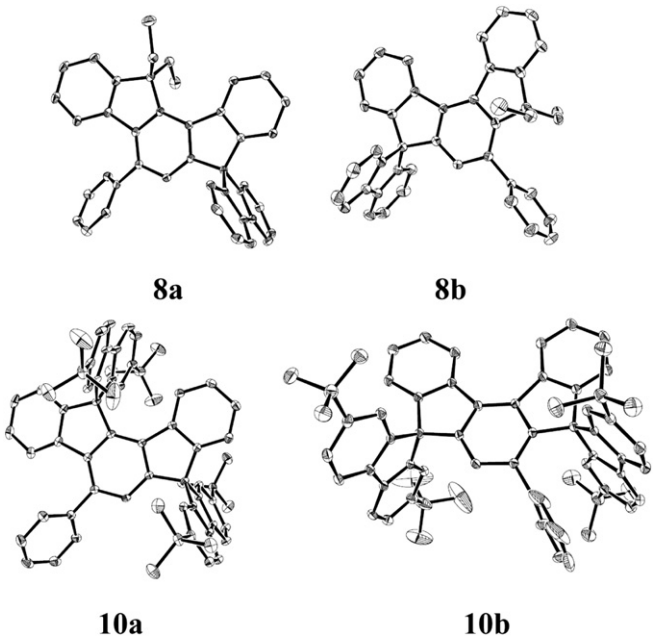



**Fig. 2.** Crystal structures of compound **8a**,**b** and **10a**,**b**.

phenyl-rings of dimeric spirobifluorene ranges from 3.024 to 3.085 Å) (Fig. 3). These results proved that the double spiro-skeletons would prevent crystallization and avoid interactions between molecules.

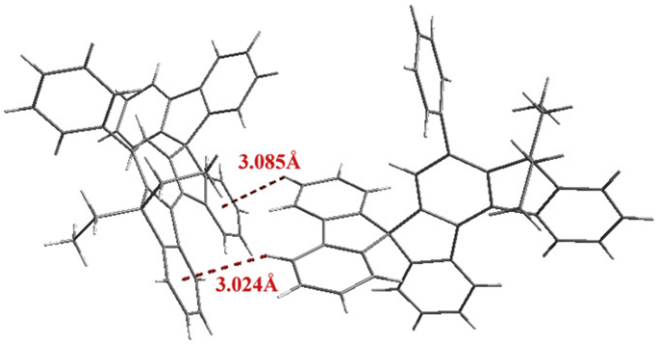



**Fig. 3.** The C–H···π affection of **8b**.

## 2.3. Optical studies

Table 2 shows the **8a**,**b** and **10a**,**b**'s Optical data and thermo-analysis data.

**Table 2**
The optical data and thermo-analysis data of **8a**,**b** and **10a**,**b**

| | $\lambda_{Abs}$ (nm)[a] | $\lambda_{em,solution}$ (nm)[b] | $\lambda_{em,solid}$ (nm)[c] | Φ (%)[d] | $T_m$ (°C)[e] | $T_d$ (°C)[f] |
|---|---|---|---|---|---|---|
| **8a** | 278,299 | 400 | 398 | 62 | 223 | 333 |
| **8b** | 261,310 | 370 | 395 | 83 | 264 | 337 |
| **10a** | 273,303,315 | 395 | 394 | 60 | 327 | 373 |
| **10b** | 272,316 | 372 | 370 | 70 | 362 | 375 |

[a] In dichloromethane($1.0\times10^{-6}$ M).
[b] In dichloromethane($1.0\times10^{-6}$ M).
[c] The solid emission spectrum was measured with solid powder.
[d] The relative quantum yield $\Phi$ was measured using standard procedures with reference to 9,10-diphenyl anthracene ($1.0\times10^{-6}$ M in *cyclo*-hexane, $\Phi$=90%).
[e] Read from DSC.
[f] Decomposition temperature $T_d$ is defined as the temperature at which 5% loss occurs during heating.

Due to the structural similarities, there are no significant difference in the UV–vis spectra (Fig. 4a) of compounds **8a**,**b** and **10a**,**b**, their absorption wavelengths peak between 250 and 340 nm are assigned to the $\pi\rightarrow\pi^*$ transitions.

The emission spectra (Fig. 4b) of the (1,2-*a*)-DSF-($^t$Bu)$_4$-IF (**10a**) and (1,2-*a*)-IF-SF (**8a**) in solution are shown at 395 nm and 400 nm, respectively, both at visible light area, while those of (2,1-*c*)-DSF-($^t$Bu)$_4$-IF **10b** and (2,1-*c*)-IF-SF **8b** are around 370 nm, which are compared to those of their isomers reported in literatures (ca. 360 nm).[10d–h]

Both dispirobifluorenes and indeno-spirobifluorenes show high quantum yields (60–83%) related to 9,10-diphenyl anthracene as reference. It is also quite interesting to find that the quantum yields of (1,2-*a*)-IF compounds (60–62%) are lower than their (2,1-*c*)-IF analogue (70–83%), and the Stokes shift of (1,2-*a*)-IF compounds is higher compared to the (2,1-*c*)-IF analogue.

The broaden peak appears on **8b** with red-shift to visible area, while the solid photoluminescent intensity decreased (Fig. 4c). The difference of emission spectra in **8b**'s solution and solid state is ca. 25 nm, this phenomenon might be due to the effect of C–H···π in solid state, which may enhance the energy transfer and non-radiative transition between the molecules. However, the solid emissions of dispirobifluorenes **10a**,**b** and **8a** are similar to those in solutions with wavelength shift 1–2 nm only. The comparison of the solution and solid emission spectra shows that the steric congestions and rigid spiro-skeletons could prevent the formation of dimmer in solid state, and therefore lead emissions more stable.

## 2.4. HOMO and LUMO studies

Cyclic voltammetry (CV) and calculations by the Gaussian-03 at B3LYP/6-31G*[13] level are useful tools for studying the front orbital energy. CV shows compounds **8a**,**b** and **10a**,**b** have a good electrochemical stability both in the reduction and the oxidation process (Fig. 5). The reversible monoelectric oxidation for **8a**,**b** and **10a**,**b** occurs at 1.80 to 1.91V, and reversible monoelectric reduction for them occurs at −1.94V to −2.00V. It is reasonable to assign the first oxidation and reduction process of **8a**,**b** and **10a**,**b** to the indenofluorene centered electron transfer as described previously. Thus the HOMO and LUMO energy levels were estimated at −5.75 eV to −5.88 eV, −1.97 eV to −2.01 eV, respectively. These values are closed to the HOMO of (1,2-*b*)-IF(−5.62 eV) and (2,1-*a*)-DSF-($^t$Bu)$_4$-IF(−5.48 eV) to those of (1,2-*b*)-DSF-IF(−5.76 eV), and (1,2-*b*)-DSF-($^t$Bu)$_4$-IF(−5.61eV).[10] So, the results indicate there is little difference of orbital energy between the (1,2-*a*)-IF and (2,1-*c*)-IF isomers, and almost all indenofluorene compounds have a low HOMO energy level and high LUMO energy level.

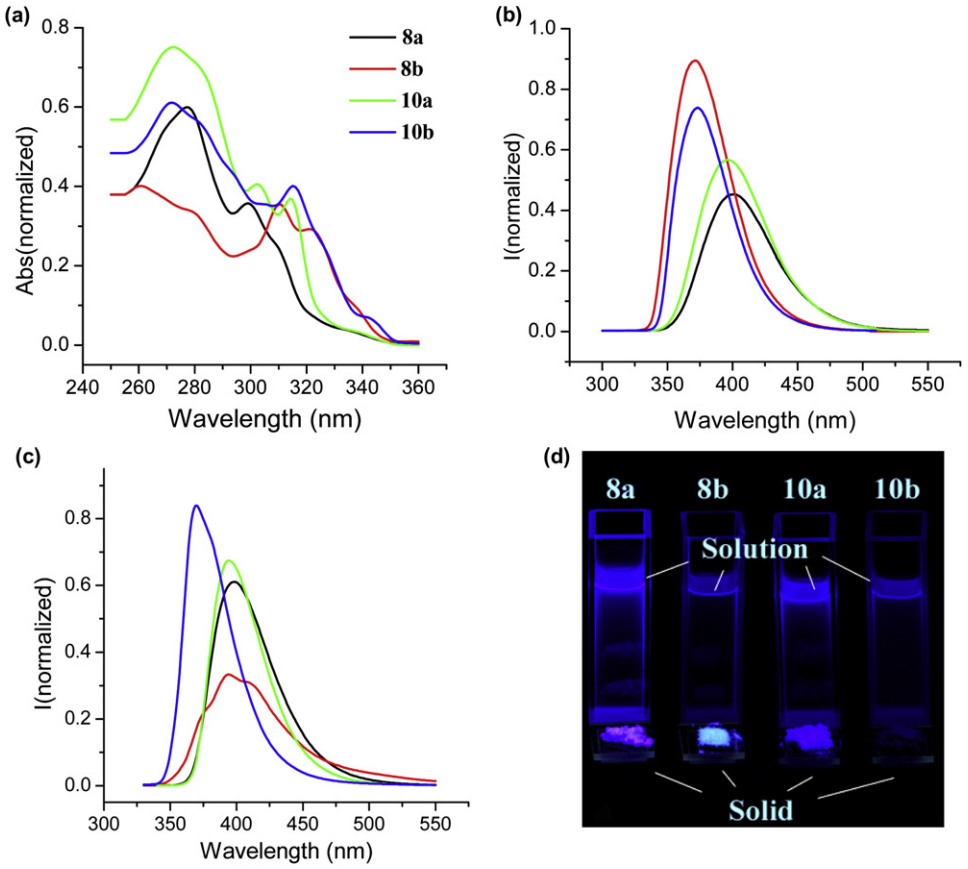



**Fig. 4.** (a). UV–vis spectra of **8a**,**b** and **10a**,**b**. (b) Liquid photoluminescence spectra of **8a**,**b** and **10a**,**b** (in $CH_2Cl_2$, $1.0\times10^{-6}$ M). (c) Solid photoluminescence spectra of **8a**, **b** and **10a**,**b**; (d) The photoluminescence photos of **8a**,**b** and **10a**,**b** (under 365 nm).

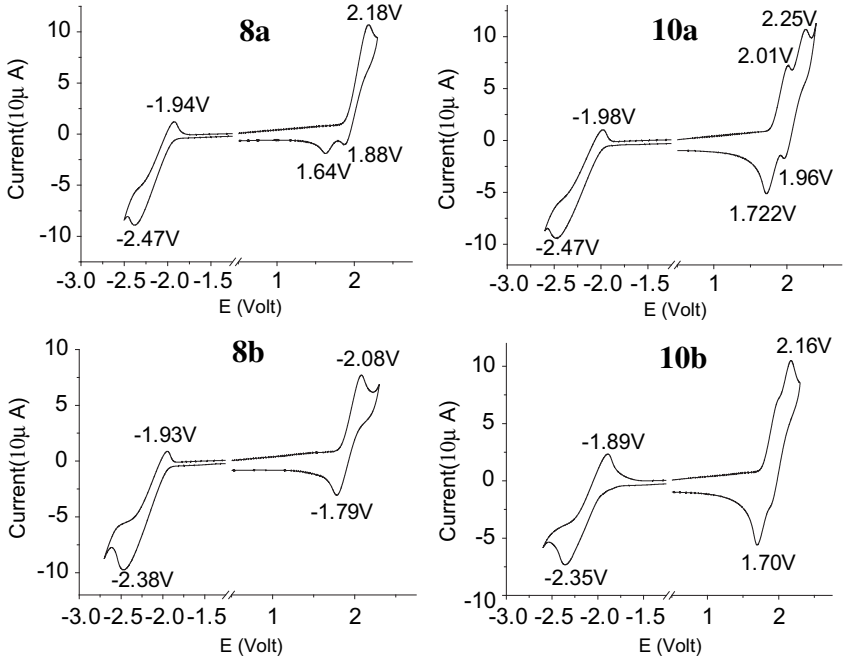



**Fig. 5.** Cylcicvoltammograms of **8a**,**b**; **10a**,**b**. Anodic oxidation of a $2\times10^{-3}$ M solution in $CH_2Cl_2$+$Bu_4NPF_6$ 0.1 M, 100 mV/s; Cathode reduction of a $2\times10^{-3}$ M solution in THF+$Bu_4NPF_6$ 0.1 M, 100 mV/s.

Calculations models of **8a**,**b** and **10a**,**b** based on the CIF data from their X-ray structures. Compared to (1,2-*b*)-DSF($^t$Bu)$_4$-IF and (2,1-*a*)-DSF($^t$Bu)$_4$-IF, the HOMO levels of **8a**,**b**, **10a**,**b** are lower while LUMO levels seem to be slight higher, while they both hold bigger band gaps. The HOMO and LUMO levels of compounds **10a**,**b** shows at −5.78 V and −5.75 V; −1.97 and −2.02 eV, while those of compounds **8a**,**b** lie at −5.88 V, −5.82 V, −2.01 and −2.01 eV, respectively. The similar electrochemical band gaps of

**Table 3**
Electrochemical properties and HOMO/LUMO levels of **8a**,**b**; **10a**,**b**

| | Electrochemical data | | | | | Calculation data | | |
|---|---|---|---|---|---|---|---|---|
| | $E_{Ox}$ (V)[a] | $E_{Red}$ (V)[b] | HOMO (eV)[c] | LUMO (eV)[d] | $\Delta E^{el}$ (eV, nm)[e] | HOMO$^{cal}$ (eV)[f] | LUMO$^{cal}$ (eV)[f] | $\Delta E^{cal}$ (eV)[f] |
| **8a** | 1.91 | −1.96 | −5.88 | −2.01 | 3.87, 320 | −5.31 | −1.05 | 4.26 |
| **8b** | 1.84 | −1.96 | −5.82 | −2.01 | 3.81, 325 | −5.52 | −0.96 | 4.56 |
| **10a** | 1.80 | −2.00 | −5.78 | −1.97 | 3.81, 325 | −5.21 | −0.98 | 4.23 |
| **10b** | 1.78 | −1.94 | −5.75 | −2.02 | 3.73, 332 | −5.25 | −1.00 | 4.25 |

[a] In $CH_2Cl_2$.
[b] In THF.
[c] From the onset oxidation potential.
[d] From the reduction potential.
[e] $\Delta E^{el}$= | HOMO−LUMO | ; $\lambda=h\nu/(\Delta E^{el},eV)=1237.5/\Delta E^{el}$(nm)from redox data.
[f] Using Gaussian 03 B3LYP/6-31G* calculation on models of the CIF documents; $\Delta E^{cal}$= | HOMO−LUMO |.

compounds **10a**,**b** and **8a**,**b** range 3.73−3.87 eV(310−320 nm), which are accordance with their UV−vis spectra. Both of the electrochemical band gaps and theoretical calculation values (4.23−4.56 eV) and are also close to the energy band gaps of other blue-emitting materials.

The calculation band gaps of (1,2-*a*)-IF products (**8a** and **10a**) are smaller than those of (2,1-*c*)-IF congeners (**8b** and **10b**), but the calculation HOMO levels of **8a** and **10a** are slight higher than **8b** and **10b** which might be explained by the different type of indeno-fused structures. However, The band gaps of **10a,b** are smaller than those of **8a,b** might be due to combination of the spiro-effect and the increase of molecular weights (Table 3).

We should emphasize that the large variation between the experimental and calculated LUMO data was due to the different calculation methods and conditions. The LUMO data from the CV was calculated from experiential equation and the DFT calculation was based on the Koopmans' theory, which ignored the electron gain and loss affect on other electrons. On the other hand, the effect between the molecules has not been considered in DFT calculation.

Fig. 6 shows the visual frontier molecular orbitals of the four products. Their π system established typical conjugated systems of indenofluorenes with (1,2-*a*)-IF and (2,1-*c*)-IF skeletons. Compared to **8b** and **10b**, the phenyl group of **8a** and **10a** partly conjugated with the indenofluorenyl moiety, this may be the reason for **8a** and **10a** with longer emission wavelengths than those of **10a** and **10b**. However, the partial conjugation of phenyl group has little impact on their frontier orbitals.

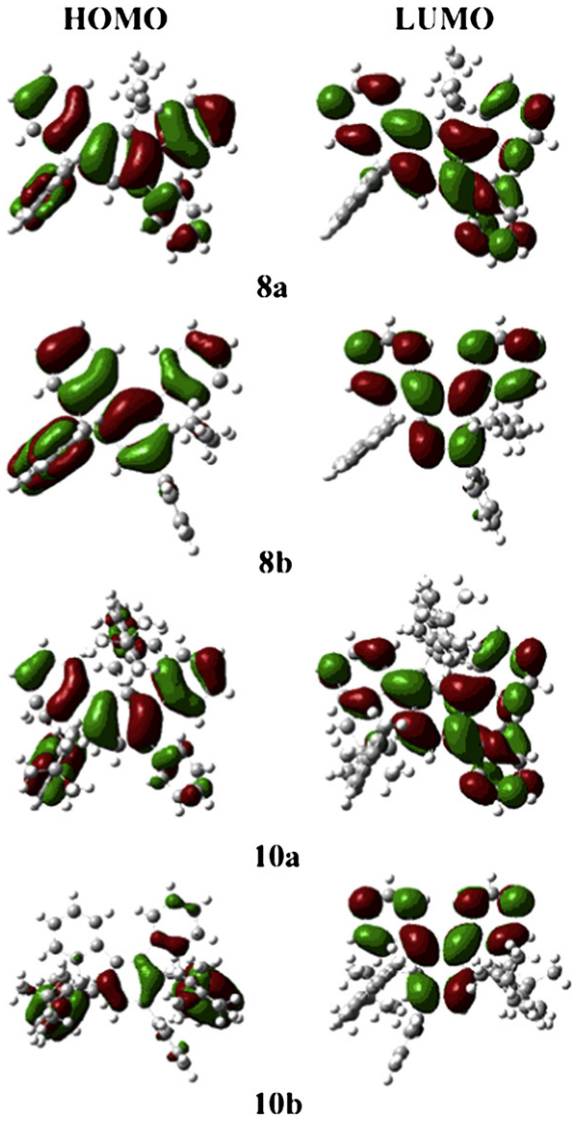



**Fig. 6.** Visual frontier molecular orbital of compounds **8a**,**b** and **10a**,**b**.

### 2.5. Thermo analysis

Thermo-gravimetric analysis confirmed the good thermal stability of **10a**,**b** and **8a**,**b** ($T_d$ of 373 and 375, 333, 337 °C, respectively) (Table 2) as expected by the presence of the rigid, spiro-fused orthogonal linkages and indeno-fused spirobiflurenes. Such behavior is very important to extend the lifetime of blue OLEDs. However, the ways of aromatic ring fused have strong influence on their molten temperatures ($T_m$); the values of (1,2-*a*)-IF compounds are always lower (ca. 40 °C) that those of (2,1-*c*)-IF analogue.[4b,14]

## 3. Conclusion

In summary, we developed well-defined synthetic routes to two families of aryl-substituted dispirobifluorene and indeno-spirobifluorene luminophores. These molecules are large band gap compounds with a high photoluminescence quantum yield both in solution and solid and are thermally stable. This method appears to be promising for preparing compounds with (1,2-*a*)-IF and (2,1-*c*)-IF skeletons. And the above results provided efficient routes to introduce indeno and indeno-spiroflurene fused at 1,2 or 3,4-positions of spirobifluorenes. The products appeared to be promising blue emission materials with excellent thermal stability and good quantum yields. Moreover, the indeno and indeno-spiroflurene units fused at 1,2 or 3,4-positions of spirobifluorene might also be considered to improve hole injection and transport properties, and might be potentially used as PhOLED materials as shown by (1,2-*b*)-IF congeners. The thermal and photo-physical properties of DSF-IFs and IF-SBFs indicated that they could be considered as promising for OLED applications. Further investigations will be focused on the application of different dispiro and indeno-spiro compounds ascribed here for OLED and PhOLED devices. This research is current underway in our laboratory.

## 4. Experimental

### 4.1. General information

Commercially available reagents, solvents, and other materials were used without further purification other than stated below. THF was distilled from Na/benzophenone prior to use. Pet. ether refers to the fraction with bp 60−90 °C fractions. All of operations were performed by standard Schlenk techniques unless otherwise stated. TLC was carried out by using silica gel 60 $GF_{254}$ and visualized under

UV lights (254 and 365 nm). Melting point was measured on X-4 micrographic measuring apparatus. $^1$H NMR and $^{13}$C NMR spectra were measured on a Bruker DR×500 spectrometer ($^1$H NMR 500 MHz, $^{13}$C NMR 125 Hz). Element analyses were measured on Vario EL element analysis instrument. IR spectra were recorded on an Infrared Spectrophotometer (Nicolet Nexus 670). High resolution mass spectra were recorded on the GCT Premier TM. All chemical are obtained from commercial sources and used as received.

The crystal data were collected by Bruker SMART CCD area detector with Mo Kα radiation ($\lambda$=0.71073 Å). The structure solution and refinement were solved on the computer by the Bruker *SHELXTL*. The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ values of all data. (*SHELXTL*, version 6.1, G. M. Sheldrick, Bruker AXS, Madison, WI, 2001).

UV–vis spectra were recorded using a UV–vis spectrophotometer (Carey-100). Photo-luminescence spectra were recorded at room temperature with a spectrofluorimeter (HITACHI F-4500) using a xenon lamp. Quantum yields ($\Phi_{sol}$) were calculated relative to 9,10-diphenyl anthracene ($1\times10^{-6}$ M in cyclohexane, $\Phi_{sol}$=90%) as standard procedures. $\Phi_{sol}$ was determined according to the following equation:[15]

$$\Phi_{sol} = \Phi_{ref} \times 100 \times \frac{(Fs \times Ar)}{(Fr \times As)} \times \left(\frac{n_s}{n_r}\right)^2$$

where, subscripts '*s*' and '*r*' refer, respectively to the sample and reference. The integrated area of the emission peak in arbitrary units is given as '*F*', '*n*' is the refracting index of the solvent ($n_s$=1.4244 for DCM; $n_r$=1.4264 for cyclohexane) and *A* is the absorbance. The emission spectra were recorded in solution in cyclohexane. The solid emission spectrum was measured by their solid powders.

All electrochemical experiments were performed using a Pt disk electrode (diameter 1 mm), the counter electrode was a vitreous carbon electrode (diameter 3 mm) and the reference electrode was AgI/Ag. The redox cyclic voltammograms were measured with electrochemical workstation (CH Instruments, CHI-840C), scan rate is 100 mV/s. All solvents must be dried. The experiment should be preceded by passing dry nitrogen gas for 5 min to remove oxygen in the system. With $^n$Bu$_4$NtPF$_6$ (0.1 M) as supporting electrolyte, the oxidation process was measured in $CH_2Cl_2$ and reduction process was measured in THF. All samples were prepared into a solution of $2\times10^{-3}$ M. The ferrocene/ferrocenium ($Fc^+/Fc$) couple served as internal standard and all reported potentials are referenced to its reversible formal potential.

The HOMO and LUMO can be calculated according to the following equation:[16]

$$\text{HOMO} = [-(E_{Ox} - \Psi) - 4.8]\text{eV}$$
$$\text{LUMO} = [-(E_{Red} - \Psi) - 4.8]\text{eV}$$
$$\Delta E^{el} = |\text{HOMO} - \text{LUMO}|$$

In the equation, $\Psi$ is the onset potential of ferrocene ($Fc^+/Fc$) versus AgI/Ag, the value of $\Psi$ is 0.6761 V. $E_{Ox}$ is the onset potential of oxidation process; $E_{Red}$ is the onset potential of reduction process. The constant 4.8 is the vacuum energy level of ferrocene.

Density functional theory (DFT) calculations were performed with the hybrid Becke-3 parameter exchange functional and the Lee–Yang–Parr non-local correlation functional (B3LYP)[13] implemented in the Gaussian 03 (Revision B.01) using the 6-31G* basis set.

Thermo-gravimetric analyses (TGA) have been performed with a Thermal analyzer (Mettler Toledo TGA851e/SF/1100) under a nitrogen atmosphere. TGA measurements were carried out between 20 and 800 °C with a heating rate of 10 °C/min$^{-1}$. The differential scanning calorimetry (DSC) thermogram was collected from the heat process.

### 4.2. Crystal data for 8a,b and 10a,b

Crystal data for **8a**: $C_{42}H_{32}$, *M*=536.68, colorless diamond, 0.52×0.47×0.25 mm, Monoclinic, space group: P2(1)/c, *a*=11.1520 (3) Å, *b*=10.7208(3) Å, *c*=24.2998(7) Å, α=90.00°, β=97.0770(10)°, γ=90.00°, *V*=2883.11(14) Å; *Z*=4; $D_c$=1.236 Mg/mm$^{-3}$; *T*=173(2) K; Final *R* ($I>2\sigma(I)$): *R*1=0.0391, *wR*2=0.0957; *R* indices (all data): *R*1=0.0456, *wR*2=0.1017. Crystal data for **8b**: $C_{43}H_{33}$ $Cl_3$, *M*=656.04, colorless diamond, 0.56×0.31×0.15 mm, Orthorhombic, space group: P2(1), *a*=22.9225(7) Å, *b*=13.3503(4) Å, *c*=11.1714(4) Å, α=90.00°, β=90.00°, γ=90.00°, *V*=3418.70(19) Å; *Z*=4; $D_c$=1.275 Mg/mm$^{-3}$; *T*=296(2) K; Final *R* ($I>2\sigma(I)$): *R*1=0.0530,*wR*2=0.1486; *R* indices (all data): *R*1=0.0610, *wR*2=0.1583. Crystal data for **10a**: $C_{132}H_{124}$, *M*=1710.31, colorless diamond 0.55×0.12×0.07 mm, Triclinic, space group: P-1, *a*=10.8743(5) Å, *b*=21.2176(9) Å, *c*=22.4523(10) Å, α=79.8000(10)°, β=86.8900(10)°, γ=86.8020(10)°, *V*=5085.3(4) Å; *Z*=2; $D_c$=1.117 Mg/mm$^{-3}$; *T*=173(2) K; Final *R* ($I>2\sigma(I)$): *R*1=0.0640, *wR*2=0.1696; *R* indices (all data): *R*1=0.1021, *wR*2=0.1964. Crystal data for **10b**: $C_{73}H_{70}$, *M*=947.29, colorless diamond 0.52×0.48×0.42 mm, Monoclinic, space group: P2(1)/c, *a*=13.3610(5) Å, *b*=15.3118(5) Å, *c*=15.8483(5) Å, α=111.4840(10)°, β=98.9620(10)°, γ=111.4840(10)°, *V*=2912.20(17) Å; *Z*=2; $D_c$=1.080 Mg/mm$^{-3}$; *T*=296(2) K; *R*1=0.0668, *wR*2=0.1860, *wR*2=0.0957; *R* indices (all data): *R*1=0.0859, *wR*2=0.2117.

### 4.3. General procedure for synthesis of 1a,b[17]

To the solution of fluorenone (100 mmol) in dry THF (50 mL) was added dropwise a solution of acetylene magnesium chloride in dry THF (250 mL, 0.6 M in THF, 150 mmol), the reaction mixture was heated to reflux for 12 h. After cooling to room temperature, the reaction was quenched by carefull addition of saturated ammonium chloride solution (200 mL). The mixture was extracted by dichlormethane (3×100 mL), then the combined organic phase was dried over anhydrous $Na_2SO_4$. The filtrate was evaporated to dryness, and the residue was chromatographed to give the fluoren-9-ols as white powders.

*4.3.1. 9-Ethynyl-9-fluorenol (**1a**).* Fluorenone (18 g, 100 mmol) was employed; product: 15 g (73%) elueted with $CH_2Cl_2$/PE=1:1. mp 102–104 °C (Ref.17:108–109 °C); $^1$H NMR (CDCl3, 500 MHz, ppm) δ 7.72 (dd, *J*=7.6, 1.4 Hz, 2H), 7.63 (dd, *J*=7.6, 1.4 Hz, 2H), 7.42 (td, *J*=7.6, 1.8 Hz, 2H),7.35 (td, *J*=7.6, 1.8 Hz, 2H), 2.53 (s, 1H), 2.48 (s, 1H); $^{13}$C NMR (CDCl3, 125 MHz, ppm): 146.52, 193.05. 129.83, 128.60, 124.24, 120.22, 83.78, 74.52, 71.37.

*4.3.2. 2,7-Di-tert-butyl-9-ethynyl-9-fluorenol (**1b**).* 2,7-Di-*tert*-butylfluorenone (29.2 g, 100 mmol) was employed; product: 20 g (63%) elueted with $CH_2Cl_2$/PE=1:2, mp170–172 °C (Ref.17: 158–159 °C); $^1$H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.77 (d, *J*=1.4 Hz, 2H), 7.53 (dd, *J*=8.0, 1.8 Hz, 2H), 7.46 (dd, *J*=7.6, 1.8 Hz, 2H), 2.53 (s, 1H), 2.48 (s, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 155.61, 146.65, 136.40, 126.84, 121.07, 119.48, 84.24, 74.73, 71.33, 35.02, 31.44.

### 4.4. General procedure for synthesis of 3a,b and 4a,b

The mixture of 9-ethynyl-fluoren-9-ol (**1a**) or 2,7-di-*tert*-butyl-9-ethynylfluoren-9-ol (**1b**)[9b] and indanocyclone **2** was heated up to 240 °C for 10 min. After cooling, the brown residue was eluented with PE/DCM (v/v=1:1) to afford compounds above, which were crystallized from different solvents to give analytical pure samples. For 9-(1,4-diphenylfluorenon-2-yl)fluoren-9-ol (**3a**) and 9-(1,4-diphenylfluorenon-3-yl)fluoren-9-ol (**3b**); 9-ethynylfluoren-9-ol (**1a**) (2.1 g, 10 mmol) and indanocyclone (**2**) (3.3 g, 10 mmol) were employed. For 2,7-di-*tert*-butyl-9-(1,4-diphenylfluorenon-2-yl)fluoren-9-ol (**4a**) and 2,7-di-*tert*-butyl-9-(1,4-diphenylfluorenon-3-yl)fluoren-9-ol

(**4b**): 2,7-di-*tert*-butyl-9-ethynylfluoren-9-ol (**1b**) (3.2 g, 10 mmol) and indanocyclone (**2**) (3.3 g, 10 mmol) were employed.

*4.4.1. 9-(1,4-Diphenylfluorenon-2-yl)fluoren-9-ol (**3a**).* $R_f$=0.75, recrystallized from $CH_2Cl_2$/hexanes; 1.1 g (21%) mp 235–237 °C; HRMS (ESI): $C_{38}H_{24}O_2$+Na requires 535.1674; Found [M+$Na^+$], 535.1669; IR (KBr)/$cm^{-1}$: $\nu$=3571 (OH), 3060, 2925, 2854, 1712, 1604, 1445, 1049; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.53(s, 1H), 7.68 (d, *J*=6.8 Hz, 2H), 7.60–7.53 (m, 3H), 7.36 (d, *J*=7.0 Hz, 2H), 7.29–7.28 (m, *J*=7.6 Hz, 2H), 7.22–7.29 (m, *J*=7.6 Hz, 4H), 7.72 (m, 3H), 7.12 (t, *J*=8.27 Hz, 1H), 6.88 (t, *J*=7.4 Hz, 1H), 6.82 (d, *J*=7.6 Hz, 1H), 6.65(t, *J*=7.8 Hz, 2H), 5.96 (d, *J*=7.4 Hz, 2H), 2.26 (s, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 192.43, 149.67, 143.10, 140.37, 140.16, 136.89, 134.75, 134.43, 134.38, 133.89, 129.07, 128.83, 128.68, 128.48, 128.27, 128.06, 127.90, 126.20, 125.38, 124.03, 123.67, 122.82, 120.18, 82.22.

*4.4.2. 9-(1,4-Diphenylfluorenon-3-yl)fluoren-9-ol (**3b**).* $R_f$=0.56, recrystallized from $CH_2Cl_2$/hexanes; 2 g (40%); mp 269–270 °C; HRMS (ESI): $C_{38}H_{24}O_2$+H requires 513.1855; Found [M+H]$^+$, 513.1849; IR (KBr)/$cm^{-1}$: $\nu$=3548 (OH), 3054, 2920,1710, 1693, 1603, 1450, 1037; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.46(s, 1H), 7.76 (d, *J*=7.4 Hz, 2H), 7.54 (t, *J*=8.0 Hz, 2H), 7.48 (t, *J*=7.6 Hz, 2H), 7.32 (d, *J*=7.4 Hz, 1.8 Hz, 2H), 7.22–7.26 (m, 4H), 7.15 (d, *J*=7.9 Hz, 2H), 7.02 (t, *J*=7.4 Hz, 1H), 6.99 (t, *J*=7.5 Hz, 2H), 6.85 (t, *J*=7.4 Hz, 1H), 6.72 (t, *J*=7.5 Hz, 2H), 6.04 (d, *J*=8.0 Hz, 2H), 5.20 (d, *J*=7.9 Hz, 1H), 2.32 (s, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 192.75, 149.58, 147.21, 144.12, 140.72, 140.23, 137.90, 135.64, 134.89, 133.82, 130.01, 129.41, 129.22, 128.91, 128.14, 128.10, 128.00, 127.80, 127.23, 126.01, 124.21, 123.39, 123.10, 120.20, 82.46.

*4.4.3. 2,7-Di-tert-butyl-9-(1,4-diphenylfluorenon-3-yl)fluoren-9-ol (**4a**).* $R_f$=0.78, recrystallized from $CH_2Cl_2$/MeOH; 1.3 g (21%); mp: 183–184 °C; HRMS (ESI): $C_{46}H_{40}O_2$+Na requires 647.2926; Found [M+$Na^+$], 647.2921; IR (KBr)/$cm^{-1}$: $\nu$=3533 (OH), 2962, 2902, 2867, 1712, 1605, 1478, 1363, 1252, 1183; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.74 (d, *J*=7.2 Hz, 2H), 7.59 (t, *J*=7.3 Hz, 2H), 7.54 (d, *J*=7.4 Hz, 1H), 7.36 (d, *J*=6.9 Hz, 1H), 7.25–7.22 (m, 4H), 7.15 (td, *J*=7.5, 1.0 Hz, 1H), 7.10 (t, *J*=7.3 Hz, 1H), 7.02 (d, *J*=7.8 Hz, 2H), 6.85 (t, *J*=7.4 Hz, 2H), 6.62 (t, *J*=7.3 Hz, 2H), 5.89 (d, *J*=6.4 Hz, 2H), 2.24 (s, 1H), 1,31(s, 18H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 192.65, 151.01, 149.72, 143.28, 142.27, 140.29, 139.39, 137.55, 136.86, 134.51, 133.89, 132.45, 129.18, 128.66, 128.44, 128.32, 128.05, 126.07, 125.74, 125.30, 123.68, 120.80, 119.54, 82.43, 34.86, 31.45.

*4.4.4. 2,7-Di-tert-butyl-9-(1,4-diphenylfluorenon-3-yl)fluoren-9-ol (**4b**).* $R_f$=0.64; recrystallized from $CH_2Cl_2$/MeOH; 3.1 g (50%); mp 299–300 °C; HRMS (ESI): $C_{46}H_{40}O_2$+Na requires 647.2926; Found: [M+$Na^+$], 647.2921; IR (KBr)/$cm^{-1}$: $\nu$=3599 (OH), 2960, 2867, 1710, 1601, 1552, 1478, 1251, 1183; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.51 (s, 1H), δ7.84 (d, *J*=7.5 Hz, 2H), 7.60 (t, *J*=7.4, 2H), 7.52 (t, *J*=6.4 Hz, 2H), 7.32–7.28 (m, 4H), 7.06 (t, *J*=6.5 Hz, 3H), 6.98 (t, *J*=7.3 Hz, 1H), 6.88 (t, *J*=7.6 Hz, 1H), 6.72 (t, *J*=7.5 Hz, 2H), 6.00 (d, *J*=7.4 Hz, 2H), 5.25 (d, *J*=7.7 Hz, 1H), 2.32 (s, 1H), 1.36 (s, 18H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 192.84, 151.20, 149.62, 144.05, 143.77, 140.66, 137.95, 137.61, 135.70, 135.37, 135.02, 133.76, 130.06, 129.51, 129.25, 128.13, 127.80, 127.09, 125.90, 125.85, 123.42, 123.06, 120.93, 119.55, 82.68, 34.88, 31.46.

### 4.5. General procedure for synthesis of 5a,b and 6a,b

9-(1,4-Diphenylfluorenonyl)fluoren-9-ol (**3a** or **3b**) or 2,7-di-*tert*-butyl-9-(1,4-diphenylfluorenonyl)fluoren-9-ol (**4a** or **4b**) (5 mmol) was dissolved in glacial acetic acid (100 mL) and the solution was heated at reflux, then 2 mL of hydrochloric acid was added dropwise, the yellow solid was formed spontaneously. After addition, the suspension was heated to reflux for another hour, then cooling to room temperature, the yellow crystals were filtered and washed with cold methanol for several times and dried under vacuum to afford desired products.

*4.5.1. 5′-Phenyl-indeno[1,2-a]spiro[fluorene-9,7′] fluorene (**5a**).* 9-(1,4-Diphenylfluorenon-2-yl) fluoren-9-ol (2.6 g, 5 mmol) was employed to afford 2.2 g product (90%); mp: 269–270 °C; IR (KBr)/$cm^{-1}$: $\nu$=3064, 2924, 2854, 1704, 1604, 1431; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 9.44 (d, *J*=7.8 Hz, 1H), 7.84 (d, *J*=7.5 Hz, 2H), 7.78 (d, *J*=7.2 Hz, 1H), 7.53 (t, *J*=7.6 Hz, 1H), 7.42–7.38 (m, 5H), 7.34–7.32 (m, 2H), 7.29–7.26 (m, 2H), 7.18 (m, 3H), δ6.86 (d, *J*=7.6 Hz, 2H), 6.77 (d, *J*=7.5 Hz, 2H), 6.66 (d, *J*=7.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 194.37, 150.93, 148.36, 144.27, 141.57, 139.9, 139.47, 137.25, 134.43, 134.08, 131.26, 129.71, 128.87, 128.49, 128.45, 128.14, 127.95, 127.90, 126.87, 124.07, 123.93, 123.51, 122.92, 120.05, 65.67.

*4.5.2. 6′-Phenyl-dihydroindeno[2,1-c]spiro [fluorene-9,8′]fluorene (**5b**).* 9-(1,4-Diphenylfluorenon-3-yl) fluoren-9-ol (2.6 g, 5 mmol) to afford 2.3 g product (93%); mp: 193–195 °C; IR (KBr)/$cm^{-1}$: $\nu$=3062, 2920, 2854, 1710, 1601, 1446; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.53 (d, *J*=7.9 Hz, 1H), 8.44 (d, *J*=7.6 Hz, 1H), 7.88 (d, *J*=7.6 Hz, 2H), 7.69 (td, *J*=7.6, 1.2 Hz, 1H), 7.54 (t, *J*=6.9 Hz, 1H), 7.45–7.41 (m, 3H), 7.39–7.34 (m, 5H), 7.27 (t, *J*=7.6 Hz, 1H), 7.19 (td, *J*=8.0, 1.0 Hz, 1H), 6.89 (d, *J*=7.6 Hz, 2H), 6.85 (d, *J*=7.4 Hz, 1H), 6.54 (s, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 192.53, 157.05, 149.64, 148.29, 143.90, 141.70, 141.64, 139.93, 137.56, 135.19, 134.38, 129.09, 129.03, 127.70, 128.07, 127.95, 127.87, 127.58, 126.72, 124.58, 124.42, 124.07, 123.77, 123.57, 120.17, 66.03.

*4.5.3. 5′-Phenyl-2,7-di-tert-butylindeno[1,2-a]spiro[fluorene-9,7′] fluorene (**6a**).* 2,7-Di-*tert*-butyl-9-(1,4-diphenylfluorenon-2-yl)fluoren-9-ol (3.1 g, 5 mmol) was employed to afford 2.9 g product (96%); mp: 282–284 °C; IR (KBr)/$cm^{-1}$: $\nu$=3060, 2962, 2904, 2868, 1708, 1604, 1469, 1252; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 9.42 (d, *J*=7.8 Hz, 1H), 7.75 (d, *J*=7.2 Hz, 1H), 7.68 (d, *J*=8.0 Hz, 2H), 7.50 (t, *J*=7.4 Hz, 1H), 7.39–7.37 (m,5H), 7.29–7.22 (m, 4H), 7.15 (t, *J*=7.4 Hz, 1H), 6.74 (d, *J*=7.4 Hz, 3H), 6.64 (d, *J*=4.6 Hz, 2H), 1.17 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): 194.56, 151.88, 150.97, 150.71, 148.59, 144.43, 141.17, 139.87, 139.72, 139.09, 137.19, 134.02, 131.41, 129.67, 128.90, 128.50, 128.36, 127.92, 127.89, 126.62, 124.95, 123.90, 123.77, 122.88, 120.65, 119.13, 66.01, 34.84, 31.41.

*4.5.4. 6′-Phenyl-2,7-di-tert-butyl-indeno[2,1-c]spiro[fluorene-9,8′] fluorene (**6b**).* 2,7-Di-*tert*-butyl-9-(1,4-diphenylfluorenon-3-yl)fluoren-9-ol (3.1 g, 5 mmol) was employed to afford 2.9 g (96%); mp: 275–276 °C; IR (KBr)/$cm^{-1}$: $\nu$=3065, 2962, 2902, 1711, 1604, 1466, 1363, 1252; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.53 (d, *J*=7.6 Hz, 1H), 8.47 (d, *J*=7.6 Hz, 1H), 7.73(t, *J*=7.4 Hz, 3H),7.68 (t, *J*=7.6 Hz, 1H), 7.51 (t, *J*=7.4 Hz, 1H), 7.43–7.40 (m, 3H), 7.32–7.26 (m, 5H), 7.23 (t, *J*=7.4 Hz, 1H), 6.82 (d, *J*=7.6 Hz, 1H), 6.79 (s, 1H), 6.52(s, 1H), 1.19(s, 18H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 192.62, 157.94, 151.10, 150.46, 148.58, 144.13, 141.64, 139.90, 139.16, 137.81, 135.38, 134.27, 129.06, 128.98, 128.63, 127.90, 127.63, 127.59, 126.94, 125.16, 124,84, 124.35, 123.93, 123.45, 120.61, 119.27, 66.38. 34.87, 31.42.

### 4.6. General procedure for the synthesis of 7a,b

To a suspension of indeno-spirobifluorene (0.49 g, 1 mmol) in diethylene glycol (50 mL) was added dropwise hydrazine hydrate (85%, 0.9 mL, 15.8 mmol); the resulting mixture was heated at 180 °C for 2 h. After cooling, solid potassium hydroxide1.69 g (30mmol) was added, then the mixture was heated at 180 °C with azeotropic distillation of water for 2 h. Then the solution was cooled and poured into water (100 mL) and the solution was neutralized to pH 7–8 with 1 N HCl and extracted with dichloromethane (3×20 mL). The combined organic extract was washed with water

and dried over anhydrous MgSO4. After workup, the residue was chromatographed with DCM/PE (1:1;v/v).

*4.6.1. 6′-Phenyl-dihydroindeno[1,2-a]spiro [fluorene-9,8′]fluorene (**7a**).* Yield 0.30 g (6 2%); mp:>300 °C; IR (KBr)/cm$^{-1}$: $\nu$=3062, 2920, 2854, 1604, 1431, 1100, 1016; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.74 (d, $J$=7.8 Hz, 1H), 8.67 (d, $J$=7.9 Hz, 1H), 7.87 (d, $J$=7.6 Hz, 2H), 7.62 (d, $J$=7.4 Hz, 1H), 7.58 (t, $J$=7.6 Hz, 1H), 7.51 (t, $J$=7.6 Hz, 1H), 7.45–7.37 (m, 7H), 7.33–7.31 (m, 1H), 7.16 (t, $J$=7.48 Hz, 2H), 6.87 (d, $J$=7.6 Hz, 2H), 6.83 (d, $J$=7.5 Hz, 1H), 6.67 (s, 1H), 4.05 (s, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 149.97, 149.82, 149.45, 144.66, 142.33, 142.13, 142.01, 141.96, 141.14, 138.39, 137.52, 136.25, 128.85, 128.50, 128.13, 127.91, 127.75, 127.38, 127.01, 126.82, 125.26, 124.52, 124.40, 123.80, 123.06, 120.21, 66.35, 37.78.

*4.6.2. 5′-Phenyl-dihydroindeno[2,1-c]spiro [fluorene-9,7′]fluorene (**7b**).* Yield 0.38 g (77.6%); mp 294–295 °C; IR (KBr)/cm$^{-1}$: $\nu$=3064, 2924, 2854, 1604, 1433, 1088, 1016; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.07 (d, $J$=7.6 Hz, 1H), 7.88 (d, $J$=7.6 Hz, 2H), 7.72 (d, $J$=7.4 Hz, 1H), 7.52 (t, $J$=7.5 Hz, 1H), 7.42–7.40 (m, 7H), 7.31 (t, $J$=7.7 Hz, 1H), 7.21 (t, $J$=7.5 Hz, 1H), 7.18–7.11 (m, 3H), 7.03 (d, $J$=7.8 Hz, 1H), 6.87–6.84 (m, 3H), 6.67 (s, 1H), 4.43(s, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 149.67, 148.98, 147.21, 143.66, 141.71, 141.69, 141.25, 137.36, 136.94, 136.92, 129.22, 128.25, 127.84, 127.70, 127.58, 127.36, 126.36, 124.90, 124.58, 124.20, 124.11, 122.82, 122.10, 119.98, 66.12, 36.21.

### 4.7. General procedure for synthesis of 8a,b

To a dihydroindeno-spirobifluorene (0.2 g, 0.4 mmol) in dry THF (10 mL) was added slowly with BuLi (2.5 M, 0.24 mL, 0.6 mmol) at −78 °C, the reaction mixture was kept at that temperature with stirring for half an hour, then ethyl bromide (0.45 mL, 0.6 mmol) was added slowly and stirring was continued for another hour. Then again the above operation was repeated once. The final mixture was stirred for further 6 h, then the reaction was quenched with saturated ammonium chloride and extracted with dichloromethane (2×10 mL); the combined organic phase was washed with water and solvents were evaporated. The residue was chromatgraphed with PE/DCM (1:1,v/v) to afford white crystalline solid.

*4.7.1. 12′, 12′-Diethyl-5′-phenyl-dihydroindeno [1,2-a]spiro[fluorene-9,7′]fluorene (**8a**).* Yield 0.2 g (90%); Found: C, 93.73; H, 6.27; $C_{42}H_{32}$ requires C, 93.99; H, 6.01%; HRMS (ESI): $C_{42}H_{32}$+Na requires 559.2402; Found: [M+Na$^+$], 559.2396; IR (KBr)/cm$^{-1}$: $\nu$=3056, 2962, 2929, 2872, 1599, 1446, 1380; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.38 (d, $J$=7.9 Hz, 1H), 7.83(d, $J$=7.6 Hz, 1H), 7.43(m, 2H), 7.37–7.30(m, 7H), 7.25(d, $J$=7.8 Hz, 1H), 7.13(t, $J$=7.5 Hz, 3H), 6.98(t, $J$=7.5 Hz, 1H), 6.79(d, $J$=7.5 Hz, 2H), 6.76–6.73(m, 2H), 6.53(s, 1H), 2 99(m, 2H), 2.30(m, 1H), 0.45(t, $J$=7.3 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 150.98, 149.42, 148.04, 141.70, 141.37, 141.25, 141.03, 137.27, 129.26, 128.20, 127.87, 127.63, 127.46, 127.27, 127.19, 126.71, 126.14, 124.95, 124.93, 124.30, 124.10, 122.37, 122.04, 119.96, 65.83, 57.21, 29.98, 9.02.

*4.7.2. 5,5′-Diethyl-6′-phenyl-dihydroindeno[2,1-c]spiro[fluorene-9,8′]fluorene (**8b**).* Yield 0.19 g (85%); $C_{42}H_{32}$ requires C, 93.99; H, 6.01%; Found: C, 93.84; H, 6.16%; HRMS (ESI): $C_{42}H_{32}$+Na requires 559.2402; Found: [M+Na$^+$], 559.2396; IR (KBr)/cm$^{-1}$: $\nu$=3062, 2961, 2930, 2872, 1600, 1447, 1374; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.64(t, $J$=7.0 Hz, 2H), 7.78(d, $J$=7.5 Hz, 2H), 7.49–7.42(m, 2H), 7.39 (t, $J$=7.5 Hz, 1H), 7.34(t, $J$=7.2 Hz, 3H), 7.25–7.23(m, 3H), 7.12(m, 5H), 6.84(d, $J$=8 Hz, 2H), 6.74(d, $J$=7.5 Hz, 1H), 6.37(s, 1H), 1.75(m, 4H), 0.28(t, $J$=7.2 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 151.58, 149.85, 149.31, 142.02, 141.67, 141.46, 141.38, 138.81, 128.81, 127.79, 127.53, 127.29, 127.23, 127.11, 126.95, 126.35, 124.72, 124.15, 124.13, 123.53, 122.89, 122.12, 119.86, 65.90, 57.72, 32.36, 8.32.

### 4.8. General procedure for synthesis of 9a,b

To a solution of 4,4′-di-*tert*-butyl-2-bromobiphenyl (0.7 g, 2 mmol) in THF (20 mL), was added BuLi (0.8 mL, 2.5 M; 2.0 mmol) at −78 °C the mixture was stirred for half an hour at the same temperature, then the solution of indeno-spirobifluorene (0.6 g, 1 mmol) in THF (15 mL) was added dropwise with stirring; the reaction was continued for another half an hour and slowly warmed up to room temperature and kept for 2 h, then quenched with saturated aqueous ammonium chloride. The mixture was extracted with DCM (3×15 mL), the combined organic phase was washed with water and dried over $Na_2SO_4$. After workup, the residue was mixed with methanol (30 mL) and heated to reflux for several minutes followed by filtration to obtain white crystalline product.

*4.8.1. 5′-Phenyl-12′-hydroxy-12′-(2″,7″-di-tert-butylfluoren-9-yl)-2,7-di-tert-butylindeno[1,2-a]spiro[fluorene-9,7′]fluorene (**9a**).* Yield 0.8 g (93%), mp:>300 °C; IR (KBr)/cm$^{-1}$: $\nu$=3556 (OH), 3062, 2962, 2903, 2867, 1479, 1362, 1253; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.99(d, $J$=7.8 Hz, 1H), 7.74(d, $J$=8.1 Hz, 1H), 7.69(d, $J$=8.0 Hz, 1H), 7.46(dd, $J$=8.1, 1.7 Hz, 1H), 7.37(td, $J$=8.0, 1.9 Hz, 2H), 7.30–7.28(m, 4H), 7.17–7.11(m, 3H), 7.04(td, $J$=7.33, 0.8Hz, 2H), 6.90 (m, 2H), 6.85(d, $J$=7.8 Hz, 1H), 6.75(d, $J$=7.5 Hz, 2H), 6.69(d, $J$=7.4 Hz, 1H), 6.33(d, $J$=1.4 Hz, 1H), 6.47(d, $J$=7.8 Hz, 1H), 6.43(s, 2H), 5.87(s, 1H), 2.74(s, 1H), 1.67(s, 9H), 1.29(s,9H), 1.15(s, 9H), 1.13(s, 9H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 150.76, 149.93, 149.59, 140.42, 138.93, 132.01, 129.01, 128.03, 127.55, 127.44, 127.28, 127.17, 126.69, 125.19, 125.06, 124.61, 124.45, 123.95, 123.32, 122.67, 120.55, 120.25, 119.19, 118.92, 82.75, 66.29, 35.03, 34.86, 34.80, 34.16, 31.65, 31.61, 31.42, 31.21.

*4.8.2. 5′-Hydroxy-5′-((2″,7″-di-tert-butylfluoren-9-yl))-6′-phenyl-2,7-di-tert-butyl-indeno[2,1-c] spiro[fluorene-9,8′]fluorene (**9b**).* Yield 0.8 g (93%), mp:>300 °C; IR (KBr)/cm$^{-1}$: $\nu$=3060, 2962, 2904, 2868, 1708, 1604, 1469, 1252; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.27(d, $J$=7.8 Hz, 1H), 8.08 (d, $J$=7.4 Hz, 1H), 7.71 (d, $J$=8.0 Hz, 1H), 7.67 (d, $J$=8.05 Hz, 1H), 7.57(s, 1H), 7.44–7.33 (m, 4H), 7.27 (t, $J$=7.4 Hz, 1H), 7.21(d, $J$=7.2 Hz, 1H), 7.17–7.11(m, 3H), 7.05(t, $J$=7.5 Hz, 3H), 6.85(d, $J$=7.0 Hz, 2H), 6.78(m, 4H), 6.65(d, $J$=1.2 Hz, 1H), 6.36(s, 1H), 6.15(br s, 1H), 6.03(d, $J$=7.9 Hz, 1H), 2.58(s, 1H), 1.31(s, 9H), 1.24 (s, 9H), 1.16 (s, 9H), 1.08(s, 9H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 151.75, 151.38, 150.82, 150.73, 149.29, 148.82, 139.88, 130.94, 129.21, 128.17, 127.82, 127.52, 127.25, 127.21, 126.89, 125.95, 124.67, 124.44, 124.36, 123.93, 123.69, 123.40, 121.02, 120.47, 119.03, 82.86, 66.01, 34.96, 34.83, 34.57, 31.66, 31.45, 31.14.

### 4.9. General procedure for the synthesis of 10a,b

General procedure for acid-catalyzed Friedel–Crafts intramolecular alkylation of *tert*-fluoren-9-ols to form dispirobifluorenes: 4,4′-di-*tert*-butyl-2-bromobiphenyl to indeno-spirobifluorenes: *tert*-fluoren-9-ols (0.5 g, 0.6 mmol) was suspended in glacial acetic acid (50 mL) and heated to reflux, hydrochloric acid (1 mL) was added stepwise and continued to reflux for 8 h, after cooling, the resulting solid was filtered and mixed with ethanol (30 mL) and heated to reflux for half an hour. The mixture was filtered while hot to afford white crystals.

*4.9.1. 2,2″,7,7″-tetra-tert-butyl-5′-phenyldispiro [fluorene-9,7′-indeno[1,2-a]fluorene-12′,9″-fluorene (**10a**).* Yield 0.4 g (85%); $C_{66}H_{62}$ requires C, 92.69; H, 7.31%; Found: C, 92.44%; H, 7.56; HRMS (ESI): $C_{66}H_{62}$+Na requires 877.4749; Found: [M+Na$^+$], 877.4744; IR (KBr)/cm$^{-1}$: $\nu$=3062, 2960, 2903, 2867, 1469, 1362, 1201; $^1$H NMR ($CDCl_3$,

500 MHz, ppm) δ 7.99(d, *J*=7.8 Hz, 1H), 7.66(d, *J*=8.0 Hz, 2H), 7.50(d, *J*=7.4 Hz, 2H), 7.44–7.40(m, 5H), 7.34(dd, *J*=7.9, 1.6 Hz, 2H), 6.96(d, *J*=1.2 Hz, 2H), 6.93–6.90(m, 3H), 6.76(t, *J*=7.5 Hz, 1H), 6.66(t, *J*=7.6 Hz, 1H), 6.64–6.60(m, 2H), 6.55(d, *J*=1.8 Hz, 2H), 6.47(d, *J*=7.3 Hz, 1H), 6.25(d, *J*=7.9 Hz, 1H), 1.14(s, 18H), 1.12 (s, 18H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 151.30, 151.21, 150.84, 149.84, 149.73, 148.28, 141.96, 141.59, 140.31, 140.26, 139.84, 139.43, 138.16, 137.11, 129.80, 128.59, 127.71, 127.37, 126.98, 126.88, 126.28, 124.92, 124.15, 123.58, 123.43, 122.87, 120.88, 120.69, 119.88, 119.31, 66.74, 66.34, 35.07, 34.96, 31.64, 31.59.

*4.9.2. 2,2″,7,7″-tetra-tert-butyl-6′-phenyldispirofluorene-9,8′-indeno-[2,1-c]fluorene-5′,9″-fluorene (**10b**).* Yeild 0.4 g (85%); $C_{66}H_{62}$ requires C, 92.69; H, 7.31%; Found: C, 92.48; H, 7.52%; HRMS (ESI): $C_{66}H_{62}$+H requires 855.4930; Found: $[M+H]^+$, 855.4958; IR (KBr)/$cm^{-1}$: *ν*=3060, 2960, 2903, 2868, 1468, 1368, 1252; $^1$H NMR ($CDCl_3$, 500 MHz, ppm): *δ* 8.83(d, *J*=7.8 Hz, 2H), 7.63 (d, *J*=8.0 Hz, 2H), 7.56 (t, *J*=7.5 Hz, 1H), 7.51(t, *J*=7.9 Hz, 1H), 7.32(d, *J*=7.9 Hz, 2H), 7.25–7.12(m, 6H), 6.86–6.78(m, 5H), 6.72–6.69(m, 2H), 6.44(t, *J*=7.6 Hz, 2H), 6.26(s, 1H), 5.80(d, *J*=7.1 Hz, 2H), 1.16(s, 36H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): 150.68, 150.10, 149.38, 148.86, 139.50, 139.22, 128.44, 127.52, 127.47, 127.28, 126.96, 125.91, 125.17, 125.02, 124.64, 124.54, 124.33, 123.95, 123.64, 123.48, 120.88, 120.47, 118.99, 66.32, 66.05, 34.83, 34.73, 31.49, 31.46.

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## Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.11.092. These data include MOL files and InChIKeys of the most important compounds described in this article.

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