

Synthesis and Properties of a Blue Bipolar Indenofluorene Emitter Based on a D- π -A Design

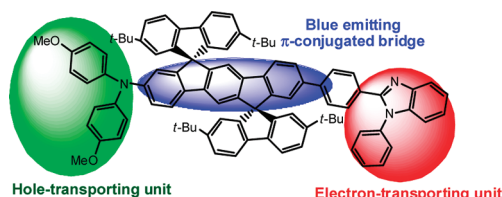
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ABSTRACT



Through a rational design, a novel Donor–Acceptor π -conjugated (D- π -A) blue fluorescent indenofluorene dye, DA-DSF-IF, has been synthesized for application in single-layer Small Molecule Organic Light Emitting Diodes (SMOLEDs). This new blue emitter possesses bipolar properties as well as good morphological and emission color stabilities and has been successfully used in a blue emitting single-layer SMOLED, with performances impressively magnified compared to a nonbipolar indenofluorene emitter.

For the past two decades of research in Organic Electronics, significant efforts have been devoted to the design and the synthesis of original π -conjugated molecules with specific properties.^{1–5} In this context designing efficient blue emitting fluorophores for Organic Light Emitting Diodes (OLEDs) is probably one of the most challenging tasks. Indeed, OLED technology is considered the most promising technology for the future generation of flat panel

display^{3,6–8} but still suffers from the shorter lifetime of blue emitting materials compared to the green and red materials. Despite the significant improvements in Small Molecule OLED (SMOLED) performances, the quest for a molecule with stable and efficient blue fluorescent emission continues to hold the attention of a number of research groups.⁹ Of particular interest for the future of this technology are the simple single-layer SMOLEDs, which do not require, theoretically, the use of additional hole/electron transporting layers, strongly simplifying the device structure.¹⁰

An appealing strategy to obtain efficient blue single-layer SMOLEDs involves the use of Donor–Acceptor π -

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(1) *Chem. Mater.* **2011**, 23, 309–922 (Thematic issue: π -Functional Materials. Special issue editors: Bredas, J. L.; Marder, S. R.; Reichmanis, E.).

(2) *Chem. Rev.* **2007**, 107, 922–1386 (Thematic issue: Organic Electronics and Optoelectronics. Guest editors: Forrest, S. R.; Thompson, M. E.).

(3) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, 109, 897–1091.

(4) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, 107, 1011–1065.

(5) Grimsdale, A. C.; Müllen, K. *Macromol. Rapid Commun.* **2007**, 28, 1676–1702.

(6) Müllen, K.; Scherf, U. *Organic Light-Emitting Devices: Synthesis, Properties and Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006.

(7) Geffroy, B.; Le Roy, P.; Prat, C. *Polym. Int.* **2006**, 55, 572–582.

(8) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Cong, Q.; Kido, J. *Adv. Mater.* **2011**, 23, 926–952.

(9) Ma, Z.; Sonar, P.; Chen, Z.-K. *Curr. Org. Chem.* **2010**, 18, 2039–2069.

(10) Jiang, H. *Macromol. Rapid Commun.* **2010**, 31, 2007–2034.

(11) Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y. *Adv. Mater.* **2011**, 23, 1137–1144.

(12) Fischer, A. L.; Linton, K. E.; Kamtekar, K. T.; Pearson, C.; Bryce, M. R.; Petty, M. C. *Chem. Mater.* **2011**, 23, 1640–1642.

(13) Che, C.-H.; Huang, W.-S.; Lai, M.-Y.; Tsao, W.-C.; Lin, J. T.; Wu, Y.-H.; Ke, T.-H.; Chen, L.-Y.; Wu, C.-C. *Adv. Funct. Mater.* **2009**, 19, 2661–2670.

(14) Liao, Y.-L.; Lin, C.-Y.; Wong, K.-T.; Hou, T.-H.; Hung, W.-Y. *Org. Lett.* **2007**, 9, 4511–4514.

(15) Huang, J.; Su, J.-H.; Li, X.; Lam, M.-K.; Fung, K.-M.; Fan, H.-H.; Cheah, K.-W.; Chen, C. H.; Tian, H. *J. Mater. Chem.* **2011**, 21, 2957–2964.

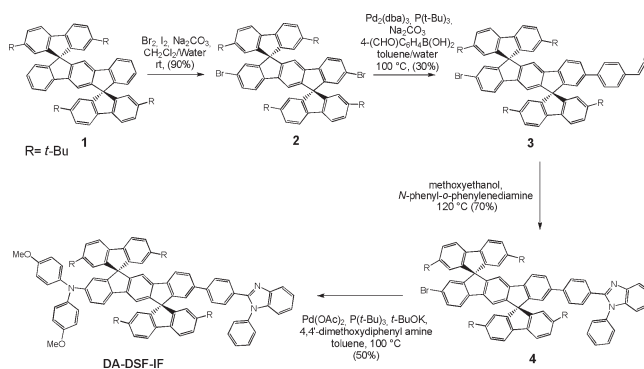
conjugated (D- π -A) fluorescent dyes with both electron-donating and -accepting groups linked by a π -conjugated bridge.^{10–15} Using this strategy, Bryce and co-workers have for example recently reported a very efficient blue single-layer SMOLED.¹² Alas, designing and synthesizing D- π -A blue fluorescent molecules which can be used in single-layer SMOLEDs is far from an easy task. Indeed, in designing a D- π -A blue fluorescent dye, one should notably avoid a strong charge transfer between the donor and the acceptor which causes the emission to shift to higher wavelengths while maintaining a high quantum yield. The nature of the donor, acceptor, and π -conjugated bridge is hence of key importance. In this context, the π -conjugated system (1,2-*b*)-indeno[1,2-*b*]fluorene, a very promising building block for blue OLED applications^{3,5,16–22} and for Organic Electronics in general,^{23–26} has not been used to date as a π -spacer in a D- π -A dye. Indeed, up to now, only symmetric indeno[1,2-*b*]fluorene derivatives have been reported for Organic Electronic applications, due to the synthetic complexity.

Herein, we report the design and the synthesis of a bipolar D- π -A blue emitter called **DA-DSF-IF** (Donor-Acceptor DiSpiroFluorene-IndenoFluorene) using an indeno[1,2-*b*]fluorenyl core as the π -conjugated bridge. Its electrochemical, optical, and morphological properties are disclosed as well as its first application as an emissive layer within a nondoped single-layer blue SMOLED. This work is, to the best of our knowledge, the first example of a D- π -A dye using the promising indeno[1,2-*b*]fluorenyl core.

The molecular design adopted in **DA-DSF-IF** is the following: a diarylamino and a phenylbenzimidazolyl group, two well-known hole and electron accepting units, have been integrated at each extremity of an indeno[1,2-*b*]fluorenyl moiety, known to possess a high quantum yield in the near-UV region.²¹ Because of its moderate electron affinity,¹³ the benzimidazolyl group has been chosen to avoid a strong charge transfer character in the molecule that will notably result in a red shift of the emission wavelength. In addition, two fluorene

units spirolinked to the central bridges of the indeno[1,2-*b*]fluorenyl core have also been introduced to give the molecule excellent morphological and thermal stabilities.⁴ Finally, the 2,7-positions of the fluorenyl units have been protected with *tert*-butyl groups to avoid intermolecular π – π interactions in the solid state and parasite anodic coupling processes.

Scheme 1. Synthesis of **DA-DSF-IF**



The synthesis of **DA-DSF-IF** (Scheme 1) starts with the synthesis of the key DiSpiroFluorene-IndenoFluorene scaffold (**DSF-IF(t-Bu)₄** **1**), constituted of an indeno[1,2-*b*]fluorenyl core spirolinked to two 2,7-*tert*-butyl fluorenyl moieties. **DSF-IF(t-Bu)₄** **1** has been prepared from 2,7-di-*tert*-butylfluorene-9-one and 2,2''-diiodoterphenyl²⁷ and will be used in this study as a relevant model to **DA-DSF-IF**. With **1** in hand, the next step was to introduce the bromine atoms on the indeno[1,2-*b*]fluorenyl core, prior to the selective Pd-catalyzed reaction. Since the 2,7-positions of the fluorenyl moieties have been protected, electrophilic bromination of **1** cleanly leads to the dibromination of the indeno[1,2-*b*]fluorenyl core with 90% yield. The key desymmetrization of **2** was then carried out through a careful Pd-catalyzed Suzuki–Miyaura cross-coupling reaction between **2** and 4-formylbenzeneboronic acid. After intensive scouting, the best conditions found to synthesize **3** (30% yield) include Pd₂(dba)₃/P(*t*-Bu)₃ as the catalytic system and sodium carbonate as the base in a mixture of toluene and water (6/1) at 100 °C. It should be noted that decreasing the temperature of the reaction or switching to other Pd catalysts (Pd(dppf)Cl₂, Pd(PPh₃)₄, or Pd(OAc)₂) only leads to lower yields, highlighting the very poor reactivity of the Bromine atoms. The benzimidazolyl group was then constructed through the condensation of **3** with *N*-phenyl-*o*-phenylenediamine in methoxyethanol leading to **4** in 70% yield. The Hartwig Pd-catalyzed C–N coupling reaction was finally adopted to introduce the dimethoxydiphenylamine unit providing the target molecule **DA-DSF-IF** with an overall yield of 10%. This synthetic strategy is straightforward and versatile and appears adaptable to synthesize other D- π -A indeno[1,2-*b*]fluorenyl dyes.

We investigated the bipolar character of **DA-DSF-IF** using cyclic voltammetry (CV) and differential pulse

(16) Jacob, J.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Gaal, M.; List, E. J. W. *Macromolecules* **2003**, *36*, 8240–8245.

(17) Marsitzky, D.; Scott, J. C.; Chen, J.-P.; Lee, V. Y.; Müller, R. D.; Setayesh, S.; Müllen, K. *Adv. Mater.* **2001**, *13*, 1096–1099.

(18) Ku, S.-Y.; Chi, L.-C.; Hung, W.-Y.; Yang, S.-W.; Tsai, T.-C.; Wong, K.-T.; Chen, Y.-H.; Wu, C.-I. *J. Mater. Chem.* **2009**, *19*, 773–780.

(19) Sonar, P.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Surin, M.; Lazzaroni, R.; Leclère, P.; Tierney, S.; Heeney, M.; McCulloch, I. *Macromolecules* **2004**, *37*, 709–715.

(20) Cocherel, N.; Poriel, C.; Vignau, L.; Bergamini, J.-F.; Rault-Berthelot, J. *Org. Lett.* **2010**, *12*, 452–455.

(21) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cocherel, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Hirsch, L.; Wantz, G. *Chem.—Eur. J.* **2007**, *13*, 10055–10069.

(22) Grimsdale, A. C.; Leclère, P.; Lazzaroni, R.; Mackenzie, J. D.; Murphy, C.; Setayesh, S.; Silva, C.; Friend, R. H.; Müllen, K. *Adv. Funct. Mat.* **2002**, *12*, 729–733.

(23) Zhang, W.; Smith, J.; Hamilton, R.; Heeney, M.; Kirkpatrick, J.; Song, K.; Watkins, S. E.; Anthopoulos, T.; McCulloch, I. *J. Am. Chem. Soc.* **2009**, *131*, 10814–10815.

(24) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Delimeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608.

(25) Kim, H.; Schulte, N.; Zhou, G.; Müllen, K.; Laquai, F. *Adv. Mater.* **2011**, *23*, 894–897.

(26) Kim, J.; Kim, S. H.; Jung, H. I.; Jeong, E.; Xia, Y.; Cho, S.; Hwang, I.-W.; Lee, K.; Suh, H.; Shim, H.-K.; Woo, H. Y. *J. Mater. Chem.* **2010**, *20*, 1577–1586.

(27) Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Slawin, A. M. Z. *Org. Lett.* **2008**, *10*, 373–376.

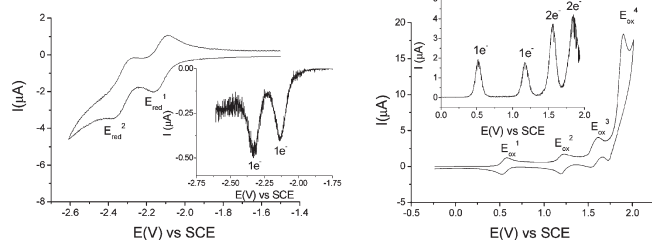


Figure 1. Cyclic voltammetry (and DPV inset) of **DA-DSF-IF** using Pt anode; sweep rate: $100 \text{ mV} \cdot \text{s}^{-1}$. Left: reduction in $\text{THF} \cdot [\text{NBu}_4][\text{PF}_6]$ 0.2 M. Right: oxidation in $\text{CH}_2\text{Cl}_2 \cdot [\text{NBu}_4][\text{PF}_6]$ 0.2 M.

voltammetry (DPV). **DA-DSF-IF** presents four successive oxidation processes (in CH_2Cl_2 , Figure 1, right), the first two being monoelectronic ($E_{\text{ox}}^1 = 0.575 \text{ V}$ and $E_{\text{ox}}^2 = 1.2 \text{ V}$), and the other bielectronic ($E_{\text{ox}}^3 = 1.61 \text{ V}$ and $E_{\text{ox}}^4 = 1.89 \text{ V}$), clearly pointed out by DPVs. In addition, **DA-DSF-IF** presents (in THF, Figure 1, left) two reversible monoelectronic reduction waves at -2.2 V (E_{red}^1) and -2.37 V (E_{red}^2). Compared to the model compound **DSF-IF(t-Bu)₄ 1**, which exhibits three reversible oxidations (1.33, 1.61, and 1.79 V, in CH_2Cl_2)²⁷ and one quasi reversible reduction (-2.6 V , in THF; see Supporting Information (SI)), **DA-DSF-IF** exhibits one additional oxidation ($E_{\text{ox}}^1 = 0.575 \text{ V}$) and one additional reduction ($E_{\text{red}}^1 = -2.2 \text{ V}$). These two reversible electronic processes have been respectively assigned to the oxidation of the diphenylamine unit²⁸ and to the reduction of the phenylbenzimidazolyl unit.¹³ The existence of stable radical cationic and radical anionic species for **DA-DSF-IF** clearly indicates that this molecule has a bipolar character and hence a great potential for efficient electron/hole transport in OLEDs. From electrochemical data,²⁹ the HOMO/LUMO levels of **DA-DSF-IF** have been respectively estimated to be around $-4.90/-2.3 \text{ eV}$ leading to an electrochemical HOMO/LUMO gap ΔE^{elec} of 2.6 eV . (HOMO and LUMO levels were determined either in CH_2Cl_2 or in THF with consistent results (see figures in SI).)

The UV-vis absorption spectrum of **DA-DSF-IF**, in cyclohexane, presents a maximum recorded at 410 nm , significantly red-shifted compared to that of its constituting building block **DSF-IF(t-Bu)₄ 1** ($\lambda_{\text{max}} = 345 \text{ nm}$),²⁷ clearly indicating that the π -conjugation was effectively extended once the D and A groups were connected into the D- π -A chromophore (Figure 2A). Thus, in cyclohexane, **DA-DSF-IF** presents an optical HOMO/LUMO gap ΔE^{opt} of 2.83 eV , strongly contracted compared to that of **DSF-IF(t-Bu)₄ 1** ($\Delta E^{\text{opt}} = 3.49 \text{ eV}$). The π -conjugation extension in **DA-DSF-IF** is also clearly observed in fluorescent spectroscopy (Figure 2A) as **DA-DSF-IF** presents a maximum at 435 nm (in cyclohexane) red-shifted by 87 nm compared to that of **DSF-IF(t-Bu)₄ 1** ($\lambda_{\text{max}} = 348 \text{ nm}$).²⁷ **DA-DSF-IF** possesses a

very well resolved fluorescence spectrum and a small Stokes shift (25 nm), consistent with a highly rigid molecular structure. (The Stokes shift is defined in this work as $\lambda_{\text{em}} - \lambda_{\text{abs}}$ (in nm).) In addition, we note that the fluorescence spectrum of **DA-DSF-IF** is better resolved than its absorption spectrum, suggesting that in the excited state the bond joining the indenofluorene and the aryl ring of the benzimidazolyl unit acquires some double bond character, hence a more rigid/planar structure.^{30,31}

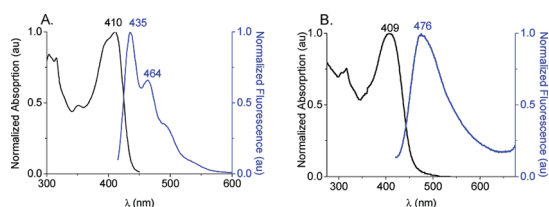


Figure 2. Absorption and emission spectra ($\lambda_{\text{exc}} = 404 \text{ nm}$) of **DA-DSF-IF**: in cyclohexane (A) and as vacuum evaporated thin film (B).

DA-DSF-IF also presents a very high quantum yield of ca. 85%, in the pure blue region, slightly increased compared to that of **DSF-IF(t-Bu)₄ 1** (70%) and ensuring hence its potential as an efficient D- π -A blue emitter. From a careful inspection of the dependence of the absorption behavior of **DA-DSF-IF** on solvent polarity, we note that the absorption maximum is almost insensitive to the dielectric constant of the environment (see SI). This indicates that the electronic and structural characteristics of the ground and Franck-Condon excited states do not differ much with a change in solvent polarity.³² Oppositely, the fluorescence spectra reveals a clear solvatochromic effect. Indeed, **DA-DSF-IF** is highly sensitive to the solvent polarity with fluorescence maxima ranging from 435 nm in cyclohexane to 537 nm in dichloromethane (Figure 3). This dependence of the emission wavelength on the solvent polarity is indicative of dipole-dipole interactions between **DA-DSF-IF** and polar solvent molecules and hence of a photoinduced intramolecular charge transfer.³³

A vacuum evaporated (at $T \sim 250^\circ \text{C}$) thin-film absorption spectrum of **DA-DSF-IF** appears to be slightly broader compared to its solution spectrum but nevertheless identical in shape and wavelength (Figure 2B). We can hence conclude that **DA-DSF-IF** does not aggregate in the solid state due to steric protection induced by the 2,7-di-*tert*-butylfluorene units. The fluorescence spectrum of **DA-DSF-IF** in thin-solid film presents a maximum in the blue region (476 nm), located between that in THF (504 nm) and that in

(28) Finlayson, C. E.; Kim, J.-S.; Liddell, M.; Friend, R. H.; Jung, S.-H.; Grimsdale, A. C.; Müllen, K. *J. Chem. Phys.* **2008**, *128*, 044703.

(29) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556–4573.

(30) Belletête, M.; Ranger, M.; Beaupré, S.; Leclerc, M.; Durocher, G. *Chem. Phys. Lett.* **2000**, *316*, 101–107.

(31) Wang, J.-F.; Feng, J.-K.; Ren, A.-M.; Yang, L. *Chin. J. Chem.* **2005**, *23*, 1618–1624.

(32) Ooyama, Y.; Ito, G.; Kushimoto, K.; Komaguchi, K.; Imae, I.; Harima, Y. *Org. Biomol. Chem.* **2010**, *8*, 2756–2770.

(33) Chi, C.-C.; Chiang, C.-L.; Liu, S.-W.; Yueh, H.; Chen, C.-T.; Chen, C.-T. *J. Mater. Chem.* **2009**, *19*, 5561–5571.

toluene (454 nm). The thin film of **DA-DSF-IF** was then gradually heated from rt to 200 °C (see SI). As no low energy emission bands beyond 500 nm were detected, the emission color of **DA-DSF-IF** appears to be stable and hence very promising for blue OLED applications.

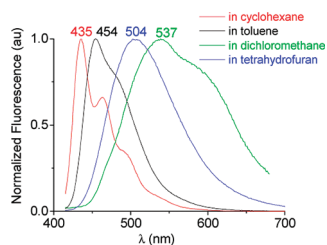


Figure 3. Emission spectra ($\lambda_{\text{exc}} = 404$ nm) of **DA-DSF-IF** in different solvents.

The morphology of **DA-DSF-IF** thin films has been studied by atomic force microscopy in acoustic mode (AC-AFM) to evaluate the effect of temperature on the thin-film structure (see SI), a key parameter before any OLED application. The surface has been hence exposed to air under thermal stress conditions from rt to 130 °C. The nonheated film surface presents a regular and smooth morphology. The surface roughness (R_a) of the film appears to be very low, around 0.2/0.3 nm, and is kept almost unchanged until 130 °C (see SI), highlighting the very good quality of the film surface and the high stability of **DA-DSF-IF** upon heating. **DA-DSF-IF** presents hence, due to its spiro linkages,⁴ a very good morphological stability in harsh conditions.

Several OLEDs have been finally investigated using two different emissive layers, namely **DA-DSF-IF** or its constituting building block **DSF-IF(*t*-Bu)₄ 1**. Indeed, to study the effect of the incorporation of electron and hole transporting units in **DA-DSF-IF**, we first decided to investigate for comparison several devices using the nonsubstituted indenofluorene emitter **DSF-IF(*t*-Bu)₄ 1** as an emissive layer. Thus, a nondoped device with a simple single-layer structure, ITO/PEDOT/**DSF-IF(*t*-Bu)₄ 1**/Ca, has been fabricated and characterized. The performance of this single-layer device using **1** as an emissive layer was nevertheless too low to be recorded (Luminance < 2 $\text{Cd}\cdot\text{m}^{-2}$) due to the large electron/hole injection barrier. A double layer device containing a hole-transporting layer (*N,N'*-di-(1-naphthyl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine-NPB) has then been investigated. The ITO/PEDOT/NPB/**1**/Ca device presents an electroluminescence (EL) spectrum in the blue region ($\lambda_{\text{max}} = 415/436$ nm) but possesses poor performance, with a maximum luminance of ca. 25 $\text{Cd}\cdot\text{m}^{-2}$, a luminous efficiency of 0.005 $\text{Cd}\cdot\text{A}^{-1}$, and a high turn on voltage (ca. 9 V); see SI.

A single-layer device, ITO/PEDOT/**DA-DSF-IF**/LiF/Al has been then fabricated using **DA-DSF-IF** as an emissive layer. Current density–voltage–luminance characteristics of the device are presented in Figure 4, left. The

turn on voltage of the device (for 1 $\text{Cd}\cdot\text{m}^{-2}$) is low (5.2 V), and the luminance reaches 320 $\text{Cd}\cdot\text{m}^{-2}$ with a luminous efficiency of 0.13 $\text{Cd}\cdot\text{A}^{-1}$ (see SI). The EL spectrum of the device reveals a main peak in the blue region ($\lambda_{\text{max}} = 470$ nm, Figure 4, right) in accordance with the thin-solid film fluorescence spectrum (Figure 2B) and shows no obvious sign of troublesome parasite emission. The single-layer nonoptimized SMOLED using **DA-DSF-IF** as an emissive layer presents hence a blue EL with a luminous efficiency magnified by ~25 compared to the double layer device using **DSF-IF(*t*-Bu)₄ 1** as an emissive layer. This effect is due to the incorporation of electron and hole transporting units in **DA-DSF-IF** and highlights the efficiency of the D- π -A strategy to design indenofluorene based materials for single-layer blue SMOLEDs. The blue EL of this single-layer SMOLED is one of the highest reported among those of indenofluorene based single-layer OLEDs.^{16,17,22,34}

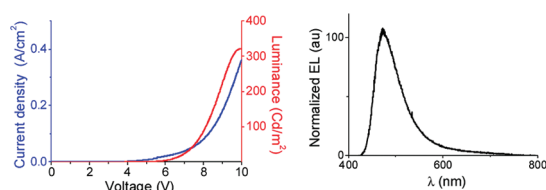


Figure 4. ITO/PEDOT/**DA-DSF-IF** (40 nm)/LiF/Al device. Left: I – V – L characteristics. Right: Normalized EL spectrum.

In summary, we have designed and synthesized, via an expedient route, a new efficient indenofluorenyl blue fluorophore **DA-DSF-IF** based on a D- π -A molecular design. This rational design allows **DA-DSF-IF** to present (i) a high quantum yield in the blue region, (ii) bipolar properties, and (iii) good morphological and emission color stabilities. The nonoptimized single-layer SMOLED using **DA-DSF-IF** as an emissive layer emits a blue color with performances impressively magnified compared to a classical indenofluorene emitter such as **DSF-IF(*t*-Bu)₄ 1**. This work represents the first example of a blue fluorescent D- π -A dye using the promising indenofluorenyl core as π -conjugated bridge. Regarding the importance of indenofluorene derivatives for the future of Organic Electronics, this work may pave the way to the development of this class of molecules.

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Supporting Information Available. Synthetic procedures, complete characterizations, and devices fabrication. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(34) Jacob, J.; Oldridge, L.; Zhang, J.; Gaal, M.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *Curr. Appl. Phys.* **2004**, *4*, 339–342.