ORGANIC LETTERS

2010
Vol. 12, No. 3
452−455

DiSpiroXanthene-IndenoFluorene: A New Blue Emitter for Nondoped Organic Light Emitting Diode Applications

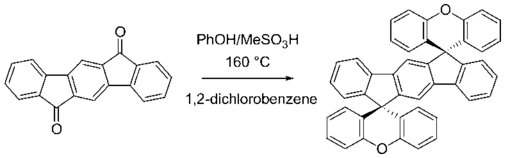
Nicolas Cocherel,[†] Cyril Poriel,*[,†] Laurence Vignau,[‡] Jean-François Bergamini,[†] and Joëlle Rault-Berthelot*[,†]

Université de Rennes 1 - UMR CNRS 6226 "Sciences Chimiques de Rennes"-MaCSE group, Bat 10C, Campus de Beaulieu - 35042 Rennes cedex, France, and Université de Bordeaux - IMS/UMR CNRS 5218-site ENSCBP, 16 Avenue Pey-Berland - 33607 Pessac cedex, France

cyril.poriel@univ-rennes1.fr; joelle.rault-berthelot@univ-rennes1.fr

Received November 9, 2009

ABSTRACT



Through an expedient synthesis, a novel blue emitter, DiSpiroXanthene-IndenoFluorene (DSX-IF) has been designed and synthesized. DSX-IF possesses good morphological and color stability upon heating, has a high quantum yield, and may be easily polymerized through anodic oxidation. Small molecule organic light emitting diodes (SMOLEDs), using this promising new dixanthene derivative as a blue emissive layer, exhibit a maximum luminance of ca. 3800 Cd.m^{-2} with a luminous efficiency of 1 Cd.A^{-1}.

During the last two decades, organic light emitting diodes (OLEDs) have attracted considerable interest owing to their promising display applications.[1,2] However, the shorter lifetime of blue emitting materials compared to the green and red materials has been one of the main drawbacks of OLED technology.[3] Despite the remarkable improvements in OLED performances, the quest for a material, e.g., polymer[1,4−10] or a small molecule,[11−24] with stable blue emission continues to hold the attention of a number of research groups. Alas, it is not a simple task to design a small molecule that possesses not only a very large band gap but also a high quantum yield in the solid state and that is thermally stable. In this context, the spiro concept in organic electronics,[25] introduced by Salbeck's group, has strongly enhanced the performances of blue emitting materi-

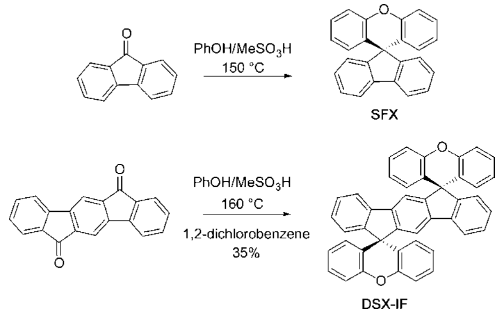
---

[†] Université de Rennes 1.
[‡] Université de Bordeaux.
(1) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091.
(2) Müllen, K.; Scherf, U. *Organic Light-Emitting Devices: Synthesis, Properties and Applications*; Wiley-VCH Verlag GMbH & Co. KGaA: Weinheim, 2006.
(3) Geffroy, B.; Le Roy, P.; Prat, C. *Polym. Int.* **2006**, *55*, 572–582.
(4) Song, S.; Jin, Y.; Kim, S. H.; Moon, J.; Kim, K.; Kim, K. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2008**, *41*, 7296–7305.
(5) Liu, J.; Zou, J.; Yang, W.; Wu, H.; Li, C.; Zhang, B.; Peng, J.; Cao, Y. *Chem. Mater.* **2008**, *20*, 4499–4506.
(6) Gather, M.; Heeney, M.; Zhang, W.; Whitehead, K. S.; Bradley, D. D. C.; Mc Culloch, I.; Campbell, A. J. *Chem. Commun.* **2008**, 1079–1081.
(7) Liu, J.; Cao, J.; Shao, S.; Xie, Z.; Cheng, Y.; Geng, Y. H.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2008**, *18*, 1659–1666.
(8) Song, S.; Jin, Y.; Kim, J.; Park, S.-H.; Lee, K.; Suh, H. *Polymer* **2008**, *49*, 5643–5649.
(9) Zhu, Y.; Gibbons, K. M.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2007**, *40*, 804–813.
(10) Mo, Y.; Jiang, X.; Cao, D. *Org. Lett.* **2007**, *9*, 4371–4373.
(11) Kim, S.-K.; Yang, B.; Ma, Y.; Lee, J.-H.; Park, J.-W. *J. Mater. Chem.* **2008**, *18*, 3376–3384.
(12) Liu, S.; He, F.; Wang, H.; Xu, H.; Wang, C.; Li, F.; Ma, Y. *J. Mater. Chem.* **2008**, *18*, 4802–4807.
(13) Qin, T.; Zhou, G.; Scheiber, H.; Bauer, R. E.; Baumgarten, M.; Anson, C. E.; List, E. J. W.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **2008**, *47*, 8292–8296.
(14) Moorthy, J. N.; Venkatakrishnan, P.; Natarajan, P.; Huang, D.-F.; Chow, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 17320–17333.
(15) Ionkin, A. S.; Marshall, W. J.; Fish, B. M.; Bryman, L. M.; Wang, Y. *Chem. Commun.* **2008**, 2319–2321.

10.1021/ol9025952

als. Indeed, this concept, in which a common sp^3-hybridized carbon atom links two perpendicular π-conjugated arms, possesses several advantages such as suppressing excimer formation in the solid state, improving the thermal and morphological stabilities, and increasing the solubility.[25] Since the first example of blue electroluminescence based on a spiro derivative,[26] various spiro moieties have been designed and incorporated into different polymer matrices such as polyspirobifluorene,[27−29] polyspirosilabifluorene,[30,31] polyspiroanthracenefluorene,[32] polyspiroindenofluoreneanthracene,[33] polyspirofluoreneindenofluorene,[34] and more recently polyspirofluorenexanthene.[35−37] The xanthene-based materials for organic electronics are however still very rare in the literature[23,35−39] mainly due to the lack of efficient synthetic approaches. To expand the scope of applications of spiro derivatives for electronics, it is of great interest to develop convenient and efficient synthetic methodologies toward SpiroFluoreneXanthene (**SFX**) derivatives. Thus, in 2006, Huang and co-workers reported an elegant one-pot synthesis of **SFX** (Scheme 1) involving a thermodynamically controlled cyclization reaction as the key step.[40] Recently, the same group has also reported a spin-coated OLED fabricated by using a spiro [dibenzoxanthene-7,9-fluorene] derivative:poly(*N*-vinylcarbazole) blend, as the emissive layer.[23] In our search for efficient small molecular weight organic materials for blue OLED applications,[34,41] we report herein a promising new blue emitter, dispiro-[xanthene-9,6′-indeno[1,2-*b*]fluorene-12′,9″-xanthene] (**DSX-IF**). **DSX-IF** possesses a 3π-2-spiro architecture (3π-systems/2 spiro bridges),[41] in which two xanthenyl cores are spirolinked to an indenofluorenyl backbone. Its electrochemical, optical, and morphological properties are disclosed as well as its first application as a blue emissive layer within a SMOLED. This work is, to the best of our knowledge, the first example of a blue emitting nondoped SMOLED based on a xanthene derivative.

Scheme 1. One-Pot Approach for the Synthesis of **SFX**[40] and **DSX-IF**



DSX-IF has been prepared according to the **SFX** one-pot synthetic approach (Scheme 1).[40] Starting from indeno-[1,2-*b*]fluorenone-6,12-dione, obtained in a three-step synthesis,[34,42] **DSX-IF** was obtained with 35% yield, after 3 days at 160 °C, in a mixture of MeSO$_3$H/phenol/1,2-dichlorobenzene. A plausible mechanism of this ring-closure reaction has been proposed by Huang and co-workers.[40] Despite the moderate yield of this reaction, probably due to the very low solubility of the starting diketone, this route offers a simple and highly adaptable access to dixanthene-based fluorophores.

The electrochemical properties of **DSX-IF** have been investigated by cyclic voltammetry (CV) and compared with the "all carbon" congener DiSpiroFluorene-IndenoFluorene (**DSF-IF**) and also with its molecular constituting building block, Indenofluorene (**IF**).[34,43] **DSX-IF** oxidation occurs along two processes with maxima recorded at $E^1 = 1.50$ V and $E^2 = 1.86$ V (Figure 1A), almost identical to those reported for **DSF-IF** (1.47 and 1.95 V).[34] Hence, the first oxidation of **DSX-IF**, as already observed for **DSF-IF**, is reversible and involves the indenofluorenyl core in a one-

---

(16) Park, Y.-I.; Son, J.-H.; Kang, J.-S.; Kim, S.-K.; Lee, J.-H.; Park, J.-W. *Chem. Commun.* **2008**, 2143–2145.

(17) Lai, M.-Y.; Chen, C.-H.; Huang, W.-S.; Lin, J. T.; Ke, T.-H.; Chen, L.-Y.; Tsai, M.-H.; Wu, C.-C. *Angew. Chem., Int. Ed. Engl.* **2008**, *47*, 581–585.

(18) Goel, A.; Chaurasia, S.; Dixit, M.; Kumar, V.; Prakash, S.; Jena, B.; Verma, J. K.; Jain, M.; Anand, R. S.; Manoharan, S. S. *Org. Lett.* **2009**, *11*, 1289–1292.

(19) Tsai, T.-C.; Hung, W.-Y.; Chi, L.-C.; Wong, K.-T.; Hsieh, C.-C.; Chou, P.-T. *Org. Electron.* **2009**, *10*, 158–162.

(20) Tong, Q.-X.; Lai, S.-L.; Chan, M.-Y.; Zhou, Y.-C.; Kwong, H.-L.; Lee, S.-T.; Lee, T.-W.; Noh, T.; Kwon, O. *J. Phys. Chem. C* **2009**, *113*, 6227–6230.

(21) Wu, C.-H.; Chien, C.-H.; Hsu, F.-M.; Shih, P.-I.; Shu, C.-F. *J. Mater. Chem.* **2009**, *19*, 1464–1470.

(22) Jiang, Z.; Yao, H.; Liu, Z.; Yang, C.; Zhong, C.; Qin, J.; Yu, G.; Liu, Y. *Org. Lett.* **2009**, *11*, 4132–4135.

(23) Liu, F.; Xie, L.-H.; Tang, C.; Liang, J.-J.; Chen, Q.-Q.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. *Org. Lett.* **2009**, *11*, 3850–3853.

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

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

(26) Salbeck, J.; Weissörtel, F.; Bauer, J. *Macromol. Symp.* **1997**, *125*, 121–132.

(27) Yan, J.-C.; Cheng, X.; Zhou, Q.-L.; Pei, J. *Macromolecules* **2007**, *40*, 832–839.

(28) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828–831.

(29) Marsitzky, D.; Murray, J.; Campbell Scott, J.; Carter, K. R. *Chem. Mater.* **2001**, *13*, 4285–4289.

(30) Wang, E.; Li, C.; Zhuang, W.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2008**, *18*, 797–801.

(31) Xiao, H.; Leng, B.; Tian, H. *Polymer* **2005**, *46*, 5707–5713.

(32) Vak, D.; CHun, C.; Lee, C. L.; Kim, J.-J.; Kim, D.-Y. *J. Mater. Chem.* **2004**, *14*, 1342–1346.

(33) Vak, D.; Lim, B.; Lee, S.-H.; Kim, D.-Y. *Org. Lett.* **2005**, *7*, 4229–4232.

(34) 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.

(35) Vak, D.; Shin, S. J.; Yum, J.-H.; Kim, S.-S.; Kim, D.-Y. *J. Lumin.* **2005**, *115*, 109–116.

(36) Tseng, Y.-H.; Shih, P.-I.; Chien, C.-H.; Dixit, A. K.; Shu, C.-F.; Liu, Y.-H.; Lee, G.-H. *Macromolecules* **2005**, *38*, 10055–10060.

(37) Mc Farlane, S. L.; Coumont, L. S.; Piercey, D. G.; Mc Donald, R.; Veinot, J. G. C. *Macromolecules* **2008**, *41*, 7780–7782.

(38) Yang, Y.; Lowry, M.; Schowalter, C. M.; Fakayode, S. O.; Escobedo, J. O.; Xu, X.; Zhang, H.; Jensen, T. J.; Fronczek, F. R.; Warner, I. M.; Strongin, R. M. *J. Am. Chem. Soc.* **2006**, *128*, 14081–14092.

(39) Morisaki, Y.; Imoto, H.; Miyake, J.; Chujo, Y. *Macromol. Rapid Commun.* **2009**, *30*, 1094–1100.

(40) Xie, L.-H.; Liu, F.; Tang, C.; Hou, X.-Y.; Hua, Y.-R.; Fan, Q.-L.; Huang, W. *Org. Lett.* **2006**, *8*, 2787–2790.

(41) Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Audebrand, N.; Slawin, A. M. Z.; Vignau, L. *Chem.—Eur. J.* **2008**, *14*, 11328–11342.

(42) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157–2159.

(43) Rault-Berthelot, J.; Poriel, C.; Justaud, F.; Barrière, F. *New J. Chem.* **2008**, *32*, 1259–1266.

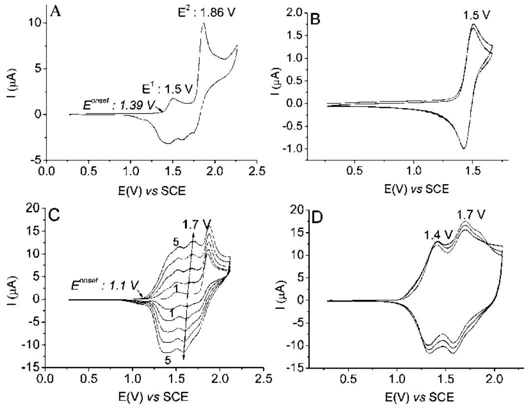


Figure 1. CV of **DSX-IF** (2×10^{-3} M) in $CH_2Cl_2-[NBu_4][PF_6]$, 0.2 M. Working electrode: Pt disk. Sweep-rate: 100 $mV.s^{-1}$. (A) One scan between 0.25 and 2.25 V. (B) Three scans between 0.25 and 1.65 V. (C) Five scans between 0.25 and 2.1 V. (D) CV (in the absence of **DSX-IF**) of the working electrode modified in C.

electron process, whereas the second oxidation occurs both on the xanthenyl units and on the indenofluorenyl core. The first oxidation peak of **DSX-IF** ($E^1 = 1.50$ V) is however shifted compared to **IF** ($E^1 = 1.31$ V)[43] resulting from the electron-withdrawing behavior of the spirolinked xanthenes. Iterative cycles in the E^1 potential range of **DSX-IF** do not show any modification of the CV nor of the electrode surface (Figure 1B). When scanning in a potential range including the two waves (Figure 1C), the CVs show a shift of the onset potential from 1.39 to 1.11 V and the regular growth of a new reversible wave at 1.70 V, clearly signing the formation of a polymer, poly(**DSX-IF**), at the electrode surface. Poly(**DSX-IF**) exhibits two reversible waves at 1.40 and 1.70 V (Figure 1D), and its p-doping process is stable in a wide range (0.8−2.1 V). Additionally, the similar behavior of poly(**DSX-IF**) and poly(**DSF-IF**)[34] in terms of polymerization yield (evaluated by the comparison of the increase of the polymers oxidation waves) indicates that polymerization process occurs both through the indenofluorenyl and the xanthenyl units, leading to attractive 3D networks.

The HOMO−LUMO levels of **DSX-IF** have been estimated from the redox data, using the SCE energy level of 4.4 eV relative to vacuum.[44] The HOMO and LUMO levels of **DSX-IF** were, respectively, recorded around −5.79 and −2.15 eV leading to a wide electrochemical band gap of 3.64 eV, in accordance with the optical band gap ($\Delta E^{opt} = 3.53$ eV) calculated from the UV−vis absorption spectrum (in cyclohexane, see Supporting Information, SI). The UV−vis absorption spectrum of the poly(**DSX-IF**) thin-film showed a broad absorption peak, characteristic of a polymeric system (see SI), with $\Delta E^{opt} = 2.98$ eV, which is less than that of the monomer **DSX-IF**. The HOMO level of poly(**DSX-IF**) is lying at −5.5 eV, whereas the LUMO level is lying at −2.52 eV ($E_{LUMO} = \Delta E^{opt} + E_{HOMO}$). Thus, the increase of the HOMO level of the polymer compared to the monomer, coupled to a smaller band gap, is consistent with extended π-conjugation in the polymer.

DSX-IF presents a fluorescence spectrum (Figure 2, left) with three main emissions at 347, 355, and 365 nm almost identical (±1 nm) to its congener **DSF-IF**.[34] The Stokes shift (defined in this work as $\lambda_{em} - \lambda_{abs}$ (in nm)) is very small (3 nm) and consistent with a highly rigid molecular structure. **DSX-IF** also appears to be highly fluorescent with a quantum yield of ca. 63% relative to quinine sulfate dihydrate.[42] A comparison of solution and thin-film fluorescence spectra of **DSX-IF** reveals a 25 nm red-shift between the two first emission peaks and a broader spectrum (Figure 2, right). We also noted a marked difference between solution and thin-film fluorescence spectra of **DSX-IF** in the relative intensity of the emission bands. This may be explained by self-absorption phenomena due to the overlap of the 0−0 transition emission band and the absorption band.[32,45] The spin-coated film of **DSX-IF** on quartz substrate was exposed to air under thermal stress conditions in an accelerated lifetime test (Figure 2, right). Under these conditions, the gradual heating of the film from room temperature to 200 °C (1 h for each stage and 1 day at 200 °C) did not lead to the appearance of low-energy emission bands beyond 500 nm assigned to ketonic defect formations and/or aggregates. Thus, thin-films of **DSX-IF** present a high color stability even after annealing for 1 day at 200 °C.

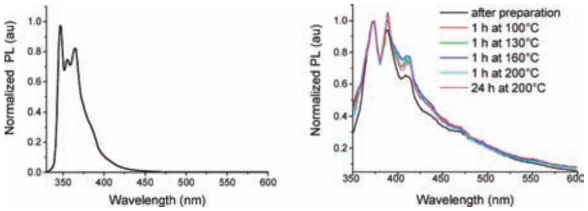


Figure 2. Left: Normalized (347 nm) emission spectrum of **DSX-IF** in cyclohexane (8×10^{-7} M, $\lambda_{exc} = 320$ nm). Right: Normalized (373 nm) thin-film emission spectra of **DSX-IF** after annealing, in air, at different temperatures ($\lambda_{exc} = 275$ nm).

The morphology of vacuum deposited thin-films of **DSX-IF** (30 nm) on sapphire wafers has been studied by atomic force microscopy in acoustic mode (AC-AFM) to evaluate the effect of temperature on the thin-film structure (Figure 3). The surface has been exposed to air under thermal stress conditions from room temperature to 130 °C. The nonheated film surface presents a regular and smooth morphology (Figure 3A). The surface roughness (Ra) of the **DSX-IF** film is in the range of 2.5/3 nm and is kept almost unchanged until 100 °C (Figure 3B), highlighting the stability of **DSX-IF** upon heating. However, at 130 °C, the morphology of the heated film became rough with Ra estimated around 14 nm, likely caused by crystallization (Figure 3C).[12,21,46] This morphological stability up to 100 °C is a key point for OLED

---

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

(45) Iida, A.; Yamaguchi, S. *Chem. Commun.* **2009**, 3002–3004.

(46) Kim, S.-K.; Park, Y.-I.; Kang, I.-N.; Park, J.-W. *J. Mater. Chem.* **2007**, *17*, 4670–4678.

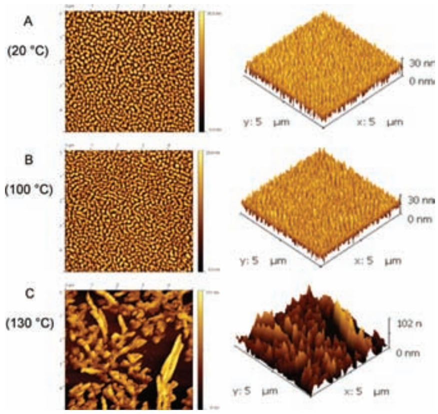


Figure 3. AC-AFM images of a thin-film of **DSX-IF** (left, 2D; right, 3D; 5 × 5 μm): (A) nonheated film, (B) film heated in air, at 100 °C, for 1 h, (C) film heated in air, at 130 °C, for 1 h.

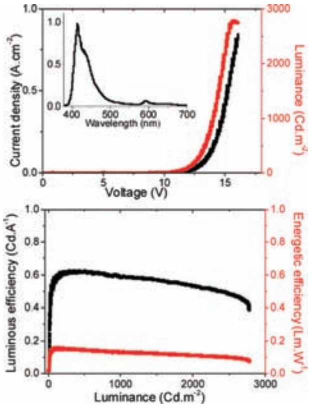


Figure 4. ITO/PEDOT/NPB (30 nm)/**DSX-IF** (40 nm)/Ca device. Top: I−V−L characteristics. Inset: Normalized electroluminescence spectrum. Bottom: luminous and energetic efficiencies.

applications as Joule heating occurs under typical operating conditions.[47] It was indeed reported that the device temperature can increase up to 86 °C on a glass substrate.[48,49] The decomposition temperature T_d, at which 5% of mass loss occurs,[25] has also been examined using thermogravimetric analysis, and it appears that **DSX-IF** is highly stable, i.e., $T_d = 380$ °C, due to the presence of the two rigid orthogonal “fluorene-xanthene” linkages (see SI).[25]

To investigate the potential applications of this new blue-emitting xanthene, a nondoped device with a simple two-layer structure, ITO/PEDOT/NPB/**DSX-IF**/Ca has been fabricated. In this device, ITO/PEDOT is the anode, in which PEDOT (poly(3,4-ethylene dioxythiophene)) doped with PSS (poly(styrene sulfonate)) is the hole injecting layer, NPB (*N*,*N*′-di(1-naphtyl)-*N*,*N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine) is the hole-transporting layer, and calcium is the cathode. As the LUMO level of **DSX-IF** is very low (−2.15 eV), a low work function cathode such as calcium (−2.90 eV) needs to be used to enable the electron injection into the **DSX-IF** layer. Current density−voltage−luminance characteristics of the ITO/PEDOT/NPB/**DSX-IF**/Ca device are presented in Figure 4. The turn on voltage appears around 10 V, which results from the high energetic barrier for electron injection (0.75 eV) and from the total thickness of the organic layers (70 nm). The luminance of the device reaches ca. 2800 Cd.m^{-2} with maximum luminous and energetic efficiencies of 0.6 Cd.A^{-1} and 0.16 Lm.W^{-1}, respectively. The normalized electroluminescence spectrum of the device reveals a main peak at 414 nm with a shoulder at 435 nm (Figure 4, inset). The chromatic coordinates calculated from the electroluminescence spectrum in the CIE 1964 chromaticity diagram are (0.19, 0.08). These coordinates correspond to a blue color and are suitable for display applications. To improve the performances of the device, a hole blocking layer of bathocuproin (BCP) has been evaporated between the emissive layer and the cathode. The low HOMO level of BCP (−6.4 eV)[24,50,51] is intended to prevent holes from crossing the device and reaching the cathode without recombination. The ITO/PEDOT/NPB/**DSX-IF**/BCP/Ca device shows enhanced properties with a high luminance of ca. 3800 Cd.m^{-2} at 12.5 V and maximum efficiencies of 1 Cd.A^{-1} and 0.3 Lm.W^{-1} (see SI).

In summary, we have designed and synthesized, via an expedient route, a new blue fluorophore **DSX-IF**, possessing an indenofluorenyl core spirolinked to two xanthenyl units. The nonoptimized three-layer SMOLED reaches a high brightness of ca. 3800 Cd.m^{-2} with a maximum luminous efficiency of 1 Cd.A^{-1}, which is promising for a blue fluorescent SMOLED and which can be further improved by adjusting the nature and the thicknesses of the different layers. This work, which appears to be the first report of a nondoped blue SMOLED based on a xanthene derivative, may pave the way to the development of this weakly studied class of materials.

Acknowledgment. The authors would like to thank Dr. J. Sperry (Auckland), the CRMPO, Dr. N. Audebrand (Rennes) for the TGA and the MENRT (N.C.).

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

OL9025952

---

[47] Chien, C.-H.; Chen, C.-K.; Hsu, F.-M.; Shu, C.-F.; Chou, P.-T.; Lai, C.-H. *Adv. Funct. Mater.* **2009**, *19*, 560–566.

[48] Zhou, X.; He, J.; Liao, L. S.; Lu, M.-C.; Ding, X. M.; Hou, X. Y.; Zhang, X. M.; He, X. Q.; Lee, S.-T. *Adv. Mater.* **2000**, *12*, 265–269.

[49] Chung, S.; Lee, J.-H.; Jeong, J.; Kim, J.-J.; Hong, Y. *App. Phys. Lett.* **2009**, *94*, 253302.

[50] Baldo, M. A.; Holmes, R. J.; Forrest, S. R. *Phys. Rev. B* **2002**, *66*, 035321.

[51] Kang, J.-W.; Lee, D.-S.; Park, H.-D.; Park, Y.-S.; Kim, J. W.; Jeong, W.-I.; Yoo, K.-M.; Go, K.; Kim, S.-H.; Kim, J.-J. *J. Mater. Chem.* **2007**, *17*, 3714–3719.