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Donor−Acceptor 9-Uncapped Fluorenes and Fluorenones as Stable Blue Light Emitters[†,‡]

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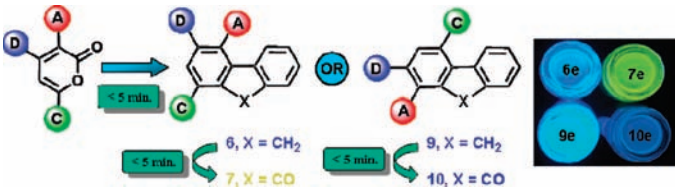
ABSTRACT



The "green emission defect" (GED) produced by fluorenones has significantly retarded the commercial scope of fluorene-based B-OLEDs. In this paper, for the first time, it is demonstrated that the "green light" emitting fluorenones 7 can be converted to "blue light" emitting fluorenones 10 by appropriate positioning of donor−acceptor and chromophoric groups onto the fluorene/fluorenone backbone. Additionally, we report an elegant highly rapid synthetic route for donor−acceptor fluorenes and fluorenones at room temperature with excellent yields.

Numerous tailor-made mono-, oligo-, or polyfluorenes[1−3] have proven their potential for preparing blue organic light emitting diodes (B-OLEDs) with high quantum efficiencies, but the scope of their commercialization suffers from the appearance of an additional undesirable low energy "green emission band" (so-called g-band) during device operation, covering a broad range from 500 to 600 nm, which not only reduces the emission efficiency but also destroys the blue color purity.[4,5] The mechanism of the origin of the "g-band" has been controversial,[6−9] and debates still continue.[6,7] There is compelling evidence based on the experiments[5,9] on fluorene-fluorenone systems that suggests that the oxidation[9–12] of fluorene to fluorenone is responsible for the emergence of this specific band. In order to avoid oxidation

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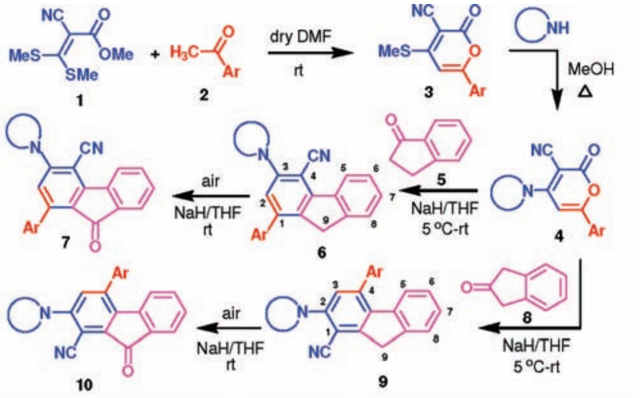
at position 9 of fluorenes, several 9,9-dialkylated fluorenes and spirofluorenes were prepared by blocking the reactive methylene moiety of fluorenes, but they are also found to be vulnerable to photo- or electrooxidative degradation leading to emission band broadening and/or with low electron−hole recombination efficiency.[13] Holmes et al.[14] recently demonstrated that it is possible to prepare oxidatively stable polyfluorenes by carefully prefixing the dialkyl substitution at position 9 of fluorenes. In this paper, we describe a novel strategy[15] which demonstrates that 9-unsubstituted small molecule fluorenes can be stable bright blue light emitters providing that fluorene/fluorenone systems are “appropriately functionalized” with donor−acceptor and chromophoric groups.

Based on important literature reports on the electrooptical properties of fluorenes,[16,17] we envisaged that an optimistic strategy is to equip the scaffold with donor−acceptor (D−A) and chromophoric π-groups for controlling emission characteristics, morphological stability, and/or electron−hole recombination efficiency. Despite a large number of synthetic efforts and studies on the fluorene system, to our surprise, only limited synthetic methodologies are available in the literature to architect the fluorene framework.[18,19] In most of the reports, commercially available fluorene has been used as a crucial precursor for preparing mono-, oligo-, or polyfluorenes, which offers very limited options for substituent variations.[20,21]

We recently developed a new methodology[22] for functionalized quateraryls and demonstrated that donor−acceptor quateraryls are potential candidates for developing small molecule blue organic light emitting diodes.[23] In order to understand the GED phenomenon, a methodology for the preparation of fluorenes with donor−acceptor groups was desirable. Our approach to prepare diversely functionalized fluorenes is depicted in Scheme 1. The key intermediates 6-aryl-2-oxo-4-methylsulfanyl-2*H*-pyran-3-carbonitriles **3a−d** were prepared from easily accessible precursors α-cyano-ketene-*S*,*S*-acetal **1**and various aryl methyl ketones **2a−d** as described earlier.[24] Our aim to prepare fluorenes with amine-donor and nitrile-acceptor groups was achieved by preparing 6-aryl-2-oxo-4-pyrrolidin/piperidin-1-yl-2*H*-pyran-3-carbonitriles (**4a−e**) from **3a−d** (see the Supporting Information) and reacting them separately with 1-indanone (**5**) and 2-indanone (**8**) in the presence of a base, which furnished 1-aryl-3-pyrrolidin/piperidin-1-yl-9*H*-fluorene-4-carbonitrile **6a−e** and 4-aryl-2-pyrrolidin/piperidin-1-yl-9*H*-fluorene-1-carbonitrile **9a−e**, respectively, in excellent yields (Scheme 1). All of the fluorenes (**6a−e**, **9a−e**) were efficiently converted to corresponding 9-fluorenones (**7a−e**, **10a−e**) by aerial oxidation in the presence of sodium hydride.[15] A plausible mechanism for the formation of fluorenes is shown in the Supporting Information.

Scheme 1. Synthesis of Fluorenes (**6a−e**, **9a−e**) and Fluorenones (**7a−e**, **10a−e**)[a]



entry	Ar	amine	yield[a] (%)			
			6	7	9	10
a	phenyl	pyrrolidine	85	92	90	75
b	phenyl	piperidine	89	94	89	79
c	1-naphthyl	piperidine	79	86	83	69
d	2-naphthyl	piperidine	81	84	87	81
e	1-pyrenyl	piperidine	88	89	90	76

[a] Yields are given with respect to their immediate precursors.

The photophysical properties of all of the synthesized compounds **6a−e**, **7a−e**, **9a−e**, and **10a−e** were examined by UV−vis and photoluminescence techniques (Table 1). All of the fluorenes (**6a−e**) substituted at position 1 with different chromophoric groups (π-groups) such as phenyl, naphthyl, or pyrenyl showed PL in the blue region (**6a−e**, λ_{PL} 442−462 nm), while their corresponding fluorenones (**7a−e**) showed PL in the yellowish green region (**7a−e**, λ_{PL} 526−529 nm). When we changed the positions of these donor−acceptor and chromophoric groups as shown in a series of fluorenes **9a−e**, all fluorenes exhibited PL in the blue region (**9a−e**, λ_{PL} 446−481 nm) but their corresponding fluorenones showed either blue PL (**10c**: λ_{PL} 460 nm, **10e**: λ_{PL} 473 nm) or no PL (**10a**,**b**,**d**) depending on the chro-

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Table 1. Photophysical Properties of Fluorene (**6a**−**e**, **9a**−**e**) and Fluorenones (**7a**−**e**, **10a**−**e**)

compd	$\lambda_{\max,\ \mathrm{abs}}$[a] (nm)	$\lambda_{\max,\ \mathrm{em}}$[b] (nm)	Stoke's shift[c] (cm^{-1})	E_{op}[d] (eV)	PL color[e]
6a	353	446	5900	3.30	B
6b	360	453	5700	3.18	B
6c	358	442	5310	3.19	B
6d	362	462	5980	3.20	B
6e	346	460	7170	3.18	B
7a	392	527	6540	2.55	YG
7b	392	529	6610	2.77	YG
7c	390	526	6630	2.75	YG
7d	392	527	6540	2.61	YG
7e	393	528	6510	2.70	YG
9a	382	446	3750	3.09	B
9b	358	449	5660	3.20	B
9c	358	451	5760	3.25	B
9d	362	465	6120	3.20	B
9e	344	481	8270	3.22	B
10a	358				NF
10b	348				NF
10c	344	460	7330	3.39	B
10d	346				NF
10e	344	473	7930	3.38	B

[a] Longest wavelength absorption maximum. [b] Fluorescence emission maximum. [c] Stokes shift = $(1/\lambda_{\mathrm{abs}} - 1/\lambda_{\mathrm{em}})$. [d] Energy band gap from the absorption edge. [e] Color of the emitted light: B (blue), YG (yellowish green), NF (no fluorescence).

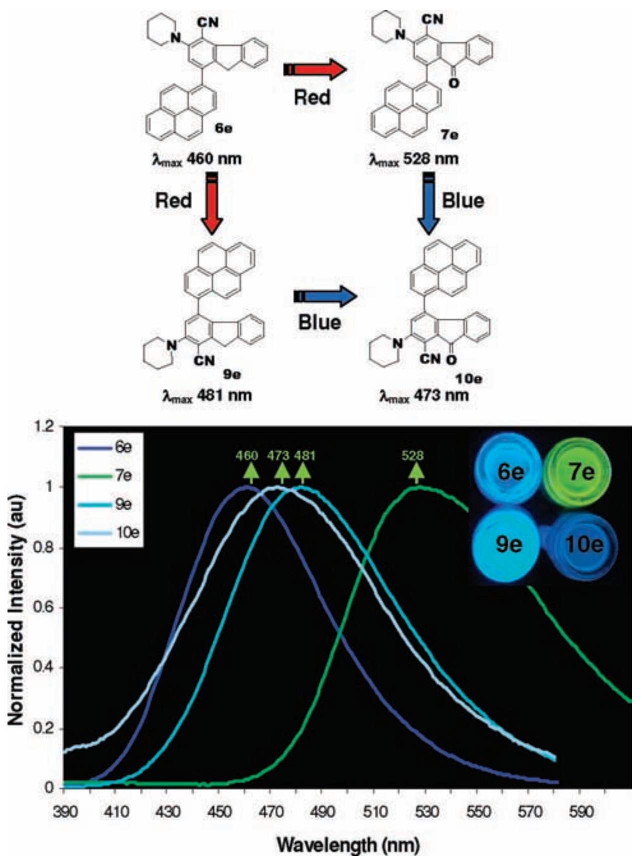

Figure 1. Normalized PL spectra of fluorene (**6e**, **9e**) and fluorenone (**7e**, **10e**) in THF. Inset: emission color variability produced by these compounds. Colored arrows indicate either a red shift or a blue shift in PL.

mophores attached at position 4 on the fluorenone scaffold. Our approach to demonstrate GED is shown in Figure 1 taking pyrenylfluorenes (**6e**, **9e**) and pyrenylfluorenones (**7e**, **10e**) as representative compounds. Figure 1 revealed that *yellowish green light emitting fluorenone* **7e** ($\lambda_{\max}$ 528 nm) can be converted to *blue light emitting fluorenone* **10e** ($\lambda_{\max}$ 473 nm) by rearranging the substitution pattern on the fluorenone scaffold.

Based on emission spectra of **6e**, **7e**, **9e**, and **10e**, it may be predicted that the device made up of **6e** may in principle show GED because its corresponding fluoreneone **7e** showed PL in the yellowish green region, while the device made up of **9e** as emissive layer should be free from GED because its corresponding fluorenone **10e** showed PL in the blue region. In other words, preparing OLED with a small molecule such as 4-pyrenyl-2-piperidin-1-yl-9*H*-fluorene-1-carbonitrile **9e**, where both fluorene (**9e**, $\lambda_{\max}$ 481 nm) and corresponding fluorenone (**10e**, $\lambda_{\max}$ 473 nm) showed PL in the blue region, should retain blue color purity in the OLED device (Figure 1).

In order to validate our novel approach for inhibiting the defect, fluorenes **6e** and **9e** were selected for detailed study and for fabrication of an OLED device to understand the GED phenomenon. The cyclic voltammogram of **9e** showed one fully reversible oxidation wave at +1.14V, corresponding to a one-electron acceptor process, providing scope as a good hole transporting material (see the Supporting Information). All of the representative pyrenylfluorenes (**6e**, **9e**) and pyrenylfluorenones (**7e**, **10e**) exhibited good thermal stability (see the Supporting Information). The fluorene **9e** and its corresponding fluorenone **10e** showed less than 10% decomposition at >300 °C under nitrogen. The fluorescent quantum yields of fluorene **6e**, **9e** and fluorenone **7e**, **10e** were Φ, 0.40, 0.35, 0.20, and 0.39, respectively, taking harmine as a standard (see the Supporting Information).

To validate our concept of swapping the donor−acceptor sites in the fluorene framework, we employed the compounds **6e** and **9e** separately as an emissive layer in a multilayer OLED. The following layer structure was prepared and tested: ITO/PEDOT:PSS/TPD (30nm)/**9e** or **6e** (60nm)/BCP (8nm)/ LiF(0.5nm)/Al (160 nm). The EL characteristics of both compounds are shown in Figure 2. EL of compound **9e** showed a sharp peak at 476 nm with a fwhm of 60 nm, and that of **6e** exhibited a peak at 489 nm with fwhm of 120 nm. The $\lambda_{\max}$ of PL (solution) of **9e** agrees well with the EL spectrum, while a red shift of 29 nm is observed in EL of **6e**. The broad and low intensity emission band in **6e** appears to be coming from the oxidation of fluorene **6e** to fluorenone **7e** during device operation, which is also in agreement with the photoluminescence studies performed by mixing fluorenes (**6e** or **9e**) and their corresponding fluorenones (**7e** or **10e**) in varying weight fractions (see the Supporting Information). To further evaluate the electrochemical stability of fluorenes **6e** and **9e**, the EL spectra of these fluorenes were

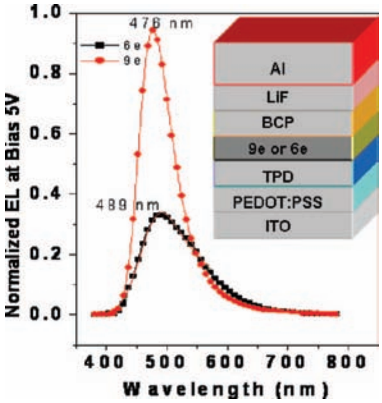

Figure 2. EL characteristics of the fluorenes **6e** and **9e**.

recorded with increase in applied voltage at an interval of 1V. The shift in wavelength of **6e** and **9e** is plotted in Figure 3. A remarkable red shift is observed in the device of **6e** with an increase in the applied voltage, while the device **9e** was found to be stable even under bias stress. This shows the effectiveness of the model **9e** in containing the emission of the blue region. The degradation of **6e** at applied voltage >9 V shows the formation of fluorenone responsible for green emission defect and a bathochromic shift.

The current density−voltage and luminance−voltage characteristics of device **6e** and **9e** are plotted in the inset of Figure 3. The current efficiency of both the molecules is shown in the Supporting Information (Figure S4). The device made of **9e** is more efficient than the device made of **6e** under similar processing conditions and device structure. Despite an overall device thickness of about ∼100 nm, the device for the **9e** compound shows substantially low (3.5 V) "ON" voltage with good luminescence efficiency (0.85 Cd/A) and good brightness as shown in the inset of Figure 3. At a luminescence density of 572.5 Cd/m^2, the efficiency is still 0.61 Cd/A (Figure S4, Supporting Information).

The (*x*,*y*) coordinates of emission color produced by **6e** and **9e** are (0.23, 0.37) and (0.16, 0.26), respectively, in the chromaticity graphs. The compound **9e** gives more saturated and bright color in comparison to **6e** and also remains comparatively stable during the device operation as evident from Figures 3 and S4 (Supporting Information). The stable blue color clearly confirms the role of appropriately swapped donor−acceptor moieties in the fluorene ring.

We described an elegant and highly rapid methodology for novel series of donor−acceptor fluorenes and fluorenones in excellent yields. We also demonstrated a novel strategy to improve blue color purity by shifting the fluorenone emission band from the "green region" to the "blue region" by appropriate positioning of donor−acceptor and chromophoric groups onto the fluorene/fluorenone backbone. The photoluminescent and electroluminescent studies of 4-pyrenyl-2-piperidin-1-yl-9*H*-fluorene-1-carbonitrile **9e** revealed stable blue emission with a low turn on voltage of 3.5V and a brightness of 573 Cd/m^2 with good chemical, thermal, and electrochemical stability. Our concept of swapping donor−acceptor and chromophores on the fluorene scaffold at appropriate positions would offer futuristic approaches toward both synthetic and device performance and more importantly to improve blue color purity of fluorene-based OLEDs for paving the way for commercialization.

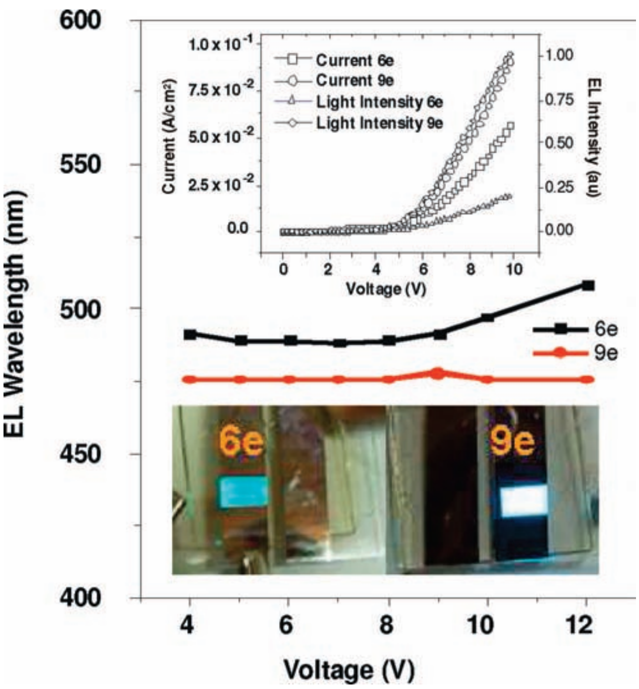

Figure 3. Plot of EL wavelength as a function of voltage for the device made with **6e** and **9e** compounds.

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Supporting Information Available: Complete experimental details and characterization data, UV−vis and fluorescence spectra, DSC, TGA, CV, and OLED device for compounds **1**, **3a**−**d**, **4a**−**e**, **6a**−**e**, **7a**−**e**, **9a**−**e**, and **10a**−**e**.This material is available free of charge via the Internet at http://pubs.acs.org.

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