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Polyfluorenes without Monoalkylfluorene Defects

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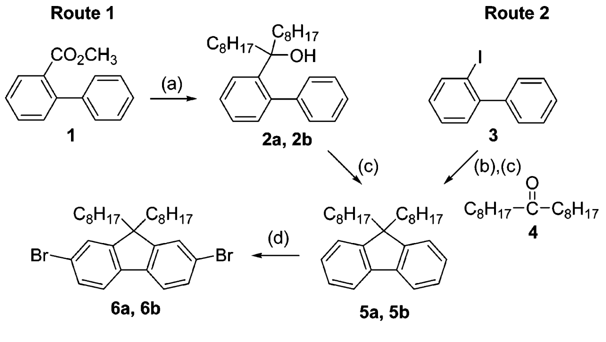
Polymer-based light-emitting diodes (PLEDs) are one of the most important emerging technologies in the field of organic electronics.[1] Poly(dialkylfluorene)s have played a leading part in the evolution of the commercial technology, although the presence of emissive fluorenone defects formed by oxidation of monoalkylfluorene impurities is a disadvantage.[2] In this paper, an alkylative cyclization[3] route to defect-free 9,9-dioctyl-9*H*-fluorene is described. Polyfluorenes prepared by Yamamoto and Suzuki polymerization of the defect-free monomers, when incorporated in light-emitting devices, exhibited minimal green emission attributable to fluorenone formation. By contrast, devices fabricated with polyfluorene arising from conventionally synthesized 9,9-dioctyl-9*H*-fluorene showed significant emission at 533 nm, even at the turn-on voltage. Incorporation of as little as 0.06 mol % of 9-octyl-9*H*-fluorene comonomer in polyfluorene led to evolution of green fluorescence in the photoluminescence (PL) and electroluminescence (EL) emission spectra.

In this work, two routes to the fluorene **5** were developed (Scheme 1). Both involved cyclization of the tertiary alcohol **2**, with Route 2 being preferred as it guarantees the incorporation of both octyl substituents before the alkylative cyclization step. The dibromofluorenes **6a** and **6b** (Scheme 1) and the bis(boronate) **7b** (Scheme 2) were prepared by standard methods.

The effect of complete dialkylation in the fluorene monomers **6a** and **6b** compared with conventionally prepared 9,9-dioctyl-9*H*-fluorene **6c** was evaluated by preparation and luminescence studies of the corresponding polymers. Poly(9,9-dialkyl-9*H*-fluorene)s **8a**−**c** were prepared from fluorene monomers **6a**−**c**, respectively, by Yamamoto coupling reactions with phenyl group end-capping using bromobenzene.[4] Polymer **8d** was prepared by Suzuki polycondensation of the dibromide **6b** and the bis(boronate) **7b** using $Pd(PPh_3)_4$ and 20% aqueous Et_4NOH in toluene as catalyst system and was also end-capped with phenyl substituents.[5] Polymers (M_w = 20 000−40 000) were obtained with polydispersities ranging from 1.7 to 3.5. The optical properties of polymer films **8a**−**d** are described in Figure S1 (see Supporting Information).

Polymers **8a**, **8b**, and **8d**, prepared from the fully dialkylated monomers, exhibited striking improvements over the conventional material **8c** in simple electroluminescent devices which were fabricated with the configuration ITO/PEDOT:PSS (75 nm)/polymer **8** (65 ± 5 nm)/LiF (0.2 nm)/Al (100 nm). Deposition of the polymer layers was deliberately carried out in air to accelerate the possible degradation of the devices and to emphasize the differences between the fully dialkylated and conventional material. Once annealed, the polymer-coated substrates were transferred to a glovebox for deposition of the cathode and testing. All devices were made and tested in parallel such that the only variable between devices was the synthetic origin of the emissive layer. In all devices, electroluminescence arose from polymer **8** aligned in the β-phase. All devices showed turn-on voltages of about 4 V and maximum brightnesses of between 80 and 140 cd/m^2. The EL spectra of **8a**, **8b**, and **8d** are very similar with all devices appearing blue (Figure 1a). The EL spectra of **8a**, **8b**, and **8d** were all stable up to a drive voltage of 10 V. By contrast, the conventionally synthesized

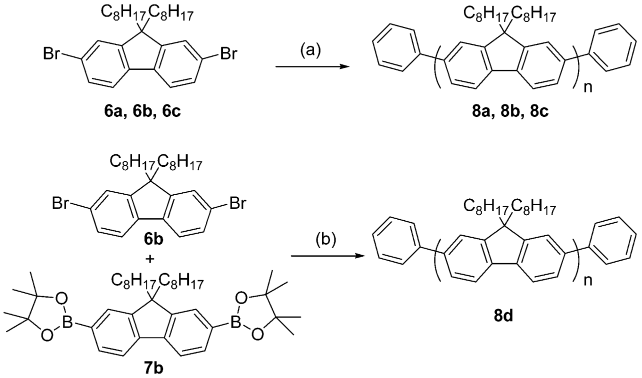
Scheme 1. Synthesis of Monomers **6a** and **6b**[a]



a: Prepared from **1** (Route 1, Scheme 1)
b: Prepared from **3** (Route 2, Scheme 1)

[a] Reagents and conditions: (a) $C_8H_{17}Br$, Mg, ether, 0−25 °C, 36%; (b) *n*-BuLi, THF, −78 °C, **4**, then 25 °C; (c) $BF_3 \cdot Et_2O$, CH_2Cl_2, 25 °C, 12 h, 97% (**5a**), 80% (**5b** over two steps); (d) Br_2, I_2, CH_2Cl_2, 0−25 °C, 3 h, 74% (see Supporting Information).

Scheme 2. Synthesis of Polyfluorenes **8a**−**d**[a]



[a] Reagents and conditions: (a) $Ni(COD)_2$, 2,2′-bipyridyl, COD, DMF, toluene, 75 °C, 24 h, bromobenzene, 12 h; (b) $Pd(PPh_3)_4$, toluene, 20% aq Et_4NOH, 90 °C, 24 h, bromobenzene, 12 h, phenylboronic acid, 12 h. **a**-series, prepared from **1** (Route 1, Scheme 1); **b**-series, prepared from **3** (Route 2, Scheme 1); **c**-series, prepared by conventional dioctylation of 2,7-dibromo-9*H*-fluorene.

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10.1021/ja074634i CCC: $37.00

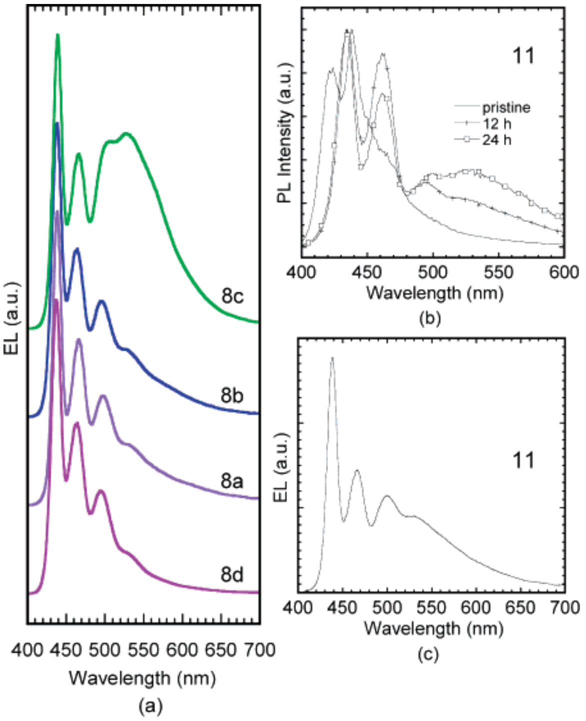


Figure 1. (a) Electroluminescence spectra of polymers **8a**, **8b**, **8c**, and **8d**. (b) Photoluminescence spectra of polymer **11**: pristine (−), 12 h at 110 °C (+), 24 h at 110 °C (□). (c) Electroluminescence spectrum of polymer **11**. Device configuration of ITO/PEDOT:PSS (70 nm)/polymer (65 nm)/LiF (0.2 nm)/Al (100 nm). EL spectra are at their turn-on voltage (4 V). For PL and EL data for **10**, see Figures S3 and S4.

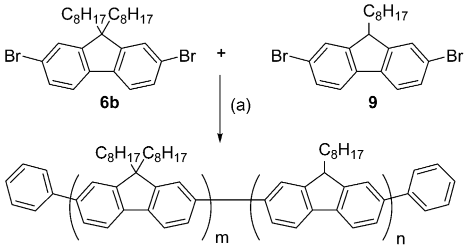
polymer **8c** exhibited significant emission from a low-energy band at 533 nm in a device, even at its turn-on voltage. This behavior, which became even more significant with time and at higher drive voltages, is fully consistent with the emergence of ketone defects attributed to incomplete alkylation at the 9-position in a fraction of fluorene units in the polymer chain[6] and is distinct from the underlying band in pristine polyfluorene at around 530 nm.[7] The photoluminescence emission spectra of the polymers **8a**−**c** when thermally annealed at 110 °C for 12 and 24 h (Figure S1) mirrored the observations reported in the electroluminescent devices. In other words, complete dialkylation in polyfluorenes drastically suppresses the green emission in both PL and EL.

In order to confirm unequivocally that the long wavelength green emission in polyfluorene-based devices correlated with the presence of monoalkylfluorene defects and to provide a qualitative assessment of the proportion sufficient to cause this effect, we prepared the statistical copolymers **10** and **11** containing, respectively, 0.06 and 0.6 mol % of monooctylfluorene (Scheme 3).

Monooctylfluorene monomer **9** was prepared in good yield by selective monoalkylation using octan-1-ol and base,[8] followed by bromination. The copolymers **10** (M_w = 71 000) and **11** (M_w = 64 600) were prepared by controlling the feed ratios of the monomers **6b** and **9** in Yamamoto polymerizations. The PL spectra of the pristine films indicated that the polymer changed from the amorphous phase to the β-phase after thermal treatment.

After the polymers had been thermally annealed at 110 °C in air for 12 and 24 h respectively (Figure 1b, **11**; Figure S3, **10**), they both showed clear evidence in the PL of the presence of the low-energy band at 533 nm. The long wavelength emission in EL devices fabricated with polymers **10** and **11** was not as prominent as that of **8c** but evolved over time and with increasing drive voltages (see Figure 1c and Figure S4). This evolution may be related to the electrochemically generated defects discussed by Montilla and Mallavia.[9]

Scheme 3. Synthesis of Statistical Copolymers **10** and **11**[a]



10 (m:n = 99.94:0.06)
11 (m:n = 99.4:0.6)

[a] Reagents and conditions: (a) Ni(COD)$_2$, 2,2′-bipyridyl, COD, DMF, toluene, 90 °C, 24 h, bromobenzene, 12 h.

In summary, fully dialkylated polyfluorenes suppress the emission attributed to ketone defects in PL and EL of polyfluorenes. The present work has shown that as little as 0.06 mol % of monoalkylated fluorene comonomer can lead eventually to the emergence of long wavelength emission, and there is no evidence of ketone formation from fully 9,9-dialkylated polyfluorenes. These findings support the previous report by the Eindhoven group that treatment with base and subsequent chromatography can remove monoalkylfluorene impurities from the dialkyl compound.[6] The latter is a pragmatic approach to removing putative monoalkyl impurities from dialkylfluorenes (as are conventional purification techniques) but can only be validated in the final polymeric product, whereas Grignard coupling of the iodobiphenyl **3** with the ketone **4** unambiguously guarantees the incorporation of two octyl groups in the 9-position of the fluorene **5b**.

Acknowledgment. We thank the Australian Research Council, CSIRO, and the Victorian Endowment for Science, Knowledge and Innovation (VESKI) for generous financial support. We thank the EPSRC National Mass Spectrometry Service (UK) for provision of some mass spectra. This Communication is dedicated to the memory of Dr. Carl R. Towns, Cambridge Display Technology Limited.

Supporting Information Available: General experimental methods for the preparation and characterization of **1**−**11** as well as UV−vis spectra and TGA data (**8a**−**d**, **10**, **11**) and PL and EL spectra for polymers **8a**−**d** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA074634I