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Optimizing LED Properties of 2,7-Bis(phenylethenyl)fluorenes

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(*E,E*)-2,7-Bis(3,4,5-trimethoxyphenylethenyl)fluorene, **1**, and a segmented copolymer **2** composed of the same chromophore alternated with nonconjugated 1,6-hexanediyl (*alt*-oligo(2,6-dimethoxyphenylene-4-vinylene-[9,9-diethylfluorene-2-yl-7-vinylene]-3,5-dimethoxy-phenylene-4-[1,6-hexanedioxy])) were synthesized. They have solution photoluminescence emission maxima at 420–460 nm, with quantum efficiencies of 0.93 and 0.68, respectively, in chloroform. Electroluminescent spectra in an LED configuration ITO/PEDOT-PSS/(**1** or **2**)/Ca–Al both showed maxima at 470–480 nm, although the spectrum from **2** was significantly broader. The luminance of LEDs with **1** was over 10-fold higher than those with copolymer **2**, 0.515 versus 0.040 cd/A, with turn-on voltages of 3 and 5 V, respectively. The crystallography of **1** showed no chromophore π -stacking; this absence should limit tendencies for emission wavelength shifts due to solid state interchromophore interactions. When **1** was heated in air before incorporation into an LED emissive layer, a 540 nm emission component was produced, which did not occur if **1** was not heated before use. Emissive layers of **1** with PMMA gave stronger luminance than either neat **1** or **2**, with only a modest increase in turn-on voltage. A 10% (w/w) **1**:PMMA based LED emission showed a maximum at 444 nm (blue emission with CIE color coefficients of (0.153,0.312)), with a luminance efficiency of 4.5 cd/A and a turn on voltage of 4.5 V.

Introduction

Small modifications of the emitting chromophores of π -conjugated molecules can dramatically change their optical, electronic, and/or solid state packing behaviors. Therefore, extensive knowledge of structure–property relationships is essential for reasonably rational design of emissive organic materials. Fully conjugated fluorenes, polyfluorenes, and related systems have shown promise as blue light emitting materials with high photoluminescence quantum yields,¹ particularly because of the tunability of electronic, photonic, and morphological properties by structural modification of the fluorene 9-position. But, fluorene-incorporating polymers that have been used as electroluminescent (EL) emission layers have some disadvantages. A number of systems have shown unexpected long-wavelength EL emission bands that have variously been attributed to excimers derived^{1a,lj,2} from

chromophoric π -stacking during device fabrication and more recently from adventitious oxidation reactions.³

Our group has carried out numerous studies of electroluminescent properties of well-defined oligo-phenylenevinylene chromophores incorporated into segmented copolymers by linkage with nonconjugated polymethylene chains.⁴ Such systems combine chromophore monodispersity with processibility because of their flexible polymethylene chains. The present study compares the emissive properties of systems that incorporate fluorenes by comparison to the homo-PPV analogues, to see how they compare with fully conjugated fluorene-based polymers. One important goal was to limit formation of undesirable long-wavelength solid state emis-

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sion bands formed in some 9,9-dialkylfluorene-based emitters.³

The syntheses of *E,E*-(2,7-bis(3,4,5-trimethoxyphenylethenyl)-9,9-diethylfluorene) and a 1,6-hexanediy-linked segmented copolymer analogue *alt*-oligo(2,6-dimethoxyphenylene-4-vinylene-[9,9-diethylfluorene-2-yl-7-vinylene]-3,5-dimethoxyphenylene-4-[1,6-hexanedioyl]), **1** and **2**, respectively, are reported in this study. The static solution phase and solid film photoluminescence behaviors of these two compounds are compared as well as the characteristics of EL test devices made with both neat and poly(methyl methacrylate)-blended **1–2** as emissive layers.

Experimental Section

General Description. All commercially available materials were used as received unless noted otherwise. Compounds **3–6** were made by literature methods (see Supporting Information). Poly-(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS) was obtained from Bayer Corporation. Poly(methyl methacrylate) (PMMA) was obtained from Scientific Polymer Products (molecular weight = 15 000). Tetrahydrofuran (THF) was distilled first from calcium hydride and then from sodium/benzophenone under argon. Spectroscopic grade solvents (Aldrich) were used as received without further purification. Reported melting points are uncorrected.

Gel permeation chromatography (GPC) was carried out using a Waters GPC system having a Model 590 solvent delivery module equipped with a U6K injector and a Model 410 differential refractometer. Output trace data were collected using LabView software (National Instruments) and analyzed using the “GPC for Windows” software package (Mat Ballard, Melbourne, Australia). GPC runs were conducted using spectrophotometric grade THF at 30 °C. Molecular weights were calculated relative to monodisperse polystyrene standards.

NMR spectra were obtained using a Bruker DPX400 NMR spectrometer at 400 MHz proton. Mass spectral analyses were carried out at the University of Massachusetts Amherst Mass Spectrometry Center by Dr. Stephen Eyles. Crystallographic analysis was carried out at the University of Massachusetts Amherst X-ray Structural Characterization Facility (NSF CHE-9974648) by Dr. A. Chandrasekaran. FTIR spectra were recorded on a Midac M2000 spectrometer. Absorption spectra were measured using an IBM 9420 spectrometer or a Shimadzu UV 2600PC spectrometer. Emission and excitation spectra were obtained using a Perkin-Elmer LS 50B spectrometer with xenon lamp light source. Emission quantum yields were determined⁶ in spectrograde chloroform at an excitation wavelength of 380 nm against external standard 9,10-diphenylanthracene (0.1 mmol/L in ethanol, $\Phi_{\text{PL}} = 0.81$). The maximum absorbance of polymer solution was maintained at $A < 0.1$ in order to minimize errors due to internal filter effects. Solvent refractive index and instrumental spectral response corrections were made for quantum yield determination. The reported quantum yields are averages of three independent measurements.

2,7-Bis(3,4,5-trimethoxyphenylethenyl)-9,9-diethyl-9H-fluorene (1). To a three-necked round-bottom flask were added **3** (160 mg, 0.46 mmol), **4** (162.5 mg, 0.838 mmol), tri-*o*-tolylphosphine (32 mg), and a catalytic amount of palladium acetate (3.1 mg). The flask was flushed with argon, 10 mL of DMF was added, and

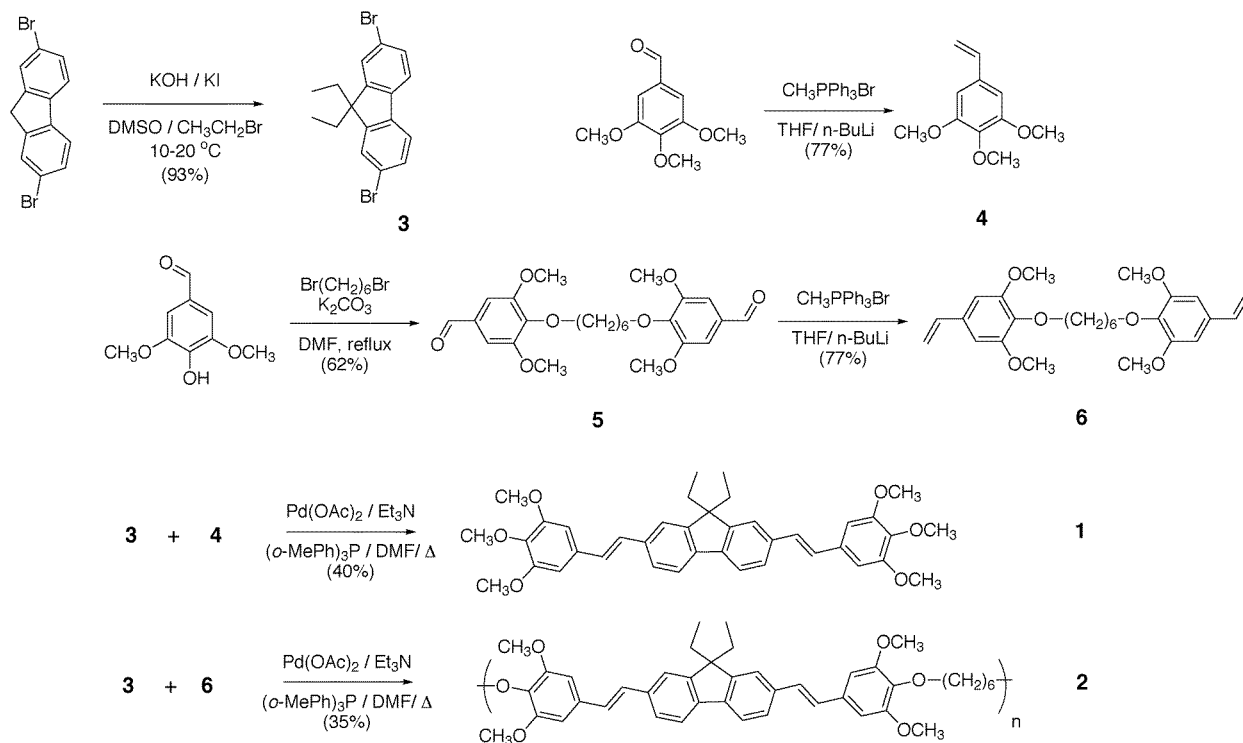
the solution was heated to 85 °C and stirred 30 min. Then triethylamine (600 mg, 27.2 mmol) was added, and heating continued at 85 °C for 3 days. The reaction mixture was then cooled and poured into 10 mL of water, the resulting mixture was chilled with an ice bath, and 5 mL of 10% aq HCl was added dropwise. The resultant yellow solid was vacuum-filtered, dissolved in chloroform, and filtered through Celite. The filtrate was concentrated in vacuo and precipitated into excess ethanol. The solid product was collected to yield 80 mg (40%) of **1** as a yellow powder that could be recrystallized from ethanol/THF at room temperature or below to give mp 215–215.5 °C. Analysis calculated for $\text{C}_{39}\text{H}_{42}\text{O}_6$: C 77.20, H 6.98, O 15.82. Found: C 76.97, H 6.92. UV–vis (CHCl_3 ; λ (nm) [$\log \epsilon$ ($\text{cm}^{-1} \text{M}^{-1}$)]): 384 (4.81). PL (CHCl_3 , λ_{max} (nm), excitation wavelength 375 nm): 440, 465. HR-MS(FAB) calculated for $\text{C}_{39}\text{H}_{42}\text{O}_6$: $m/z = 606.2981$. Found: $m/z = 606.2990$. ^1H NMR (CDCl_3): δ 0.42 (t, 6 H, $J = 8$ Hz), 2.10 (q, 4 H, $J = 8$ Hz), 3.91 (s, 6 H), 3.96 (s, 12 H), 6.80 (s, 4 H), 7.13 (s, 4 H), 7.50 (br s, 2 H), 7.53 (d, 2 H, $J = 8$ Hz), 7.69 (d, 2 H, $J = 8$ Hz).

X-ray Crystallography of 1. Single crystals of **1** were obtained by slow crystallization from ethanol/THF in air at room temperature or below with protection from direct light. X-ray diffraction analysis was carried out on a Nonius (Bruker) KappaCCD P4 instrument at ambient temperature with graphite monochromated Mo K α radiation, $\lambda = 0.71073$ Å, using a colorless needle, $0.50 \times 0.05 \times 0.05$ mm with μ (Mo K α) = 0.081 mm^{-1} . Unit cell analysis showed an orthorhombic space group, *Pnma* with $a = 7.3474$ Å, $b = 28.7742$ Å, $c = 15.6631$ Å, $\alpha = \beta = \gamma = 90.00^\circ$, $Z = 4$, density (calcd) = 1.217 g/cm^3 , $F(000) = 1296$, $V = 3311.4$ Å³. A total of 2800 reflections were collected (1547 unique, $R(\text{int}) = 0.0485$), of which 1135 had $I > 2\sigma$. The data were analyzed using SHELXTL97⁵ with 209 parameters and no restraints, giving a goodness of fit for $F^2 = 1.094$, $R_I(I > 2\sigma) = 0.0713$, $wR_2(I > 2\sigma) = 0.1595$, $R_I(\text{all}) = 0.1025$, $wR_2(\text{all}) = 0.1754$. The largest difference peak and hole were 0.357 and -0.215 e/Å^3 . One of the ethyl groups has significant disorder. Details have been deposited in CIF format with the Cambridge Crystallographic Databank Centre, CCDC Deposition #264678.

alt-Oligo(2,6-dimethoxyphenylene-4-vinylene-[9,9-diethyl-9H-fluorene-2-yl-7-vinylene]-3,5-dimethoxyphenylene-4-[1,6-hexanedioyl]) (2). To a three-necked round-bottom flask were added **6** (840 mg, 1.89 mmol), **3** (725 mg, 1.89 mmol), tri-*o*-tolylphosphine (500 mg), and a catalytic amount of palladium acetate (66 mg). The flask was flushed with argon, and 20 mL of dry DMF was added. The solution was heated to 100–120 °C and stirred for 30 min. Triethylamine (5.40 mL) was added, and then the reaction mixture was heated and held at 100–120 °C for 4 days, cooled, and poured into 20 mL of water. The reaction mixture was cooled with an ice bath and acidified by dropwise addition of 10 mL of 10% aq HCl (10 mL). The resultant yellow solid was vacuum-filtered and dissolved in chloroform, the mixture was filtered through Celite to remove insoluble catalyst residues, and the filtrate was concentrated and reprecipitated into excess methanol. The precipitate was isolated by filtration and dried under vacuum overnight to yield 426 mg (35%) of **3** as a dark yellow, fibrous solid. Analysis calculated for $\text{C}_{44}\text{H}_{50}\text{O}_6$: C 78.31, H 7.47, O 14.22. Found: C 75.18, H 7.04. UV–vis (chloroform; λ_{max} (nm) [$\log \epsilon$ ($\text{cm}^{-1} \text{M}^{-1}$)]): 380 [4.94]. PL (chloroform, λ_{max} (nm), excitation wavelength 375 nm): 420, 440. ^1H NMR (CDCl_3): δ 0.39 (t, 6 H, $J = 7$ Hz), 1.20–1.98 (m, 8 H), 2.11 (br q, 4 H, $J \sim 7$ Hz), 3.93 (s, 12 H), 4.00 (br t, 4 H, $J \sim 7$ Hz), 6.79 (br s, 4 H), 7.12 (overlapping br s, 4 H), 7.5 (overlapping br s, 2 H; br d, 2 H, $J \sim 7$ Hz), 7.69 (br d, 2 H, $J \sim 7$ Hz). UV–vis (CHCl_3 ; λ (nm) [$\log \epsilon$ ($\text{cm}^{-1} \text{M}^{-1}$)]): 357 [4.94]. PL (CHCl_3 , λ_{max} (nm), excitation

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Scheme 1. Syntheses of **1** and **2**

wavelength 375 nm): 420, 440. Very minor vinyl end group protons were observed at δ 5.6. GPC (THF, polystyrene std): M_n 4700, M_w 11900.

Electronic Spectroscopy. All spectra were obtained in spectrograde chloroform that was degassed with argon. For all fluorescence experiments, solution concentrations in the micromolar concentration range were used ($A \approx 0.05$ in the UV-vis spectrum). Relative quantum yields (ϕ_{PL}) were measured using 9,10-diphenyl anthracene ($\phi = 0.81$ at 0.1 mmol/L) as the standard at 380 nm excitation, using a literature procedure.⁶ Chloroform solutions (10 mg/mL) of **1** or **2** were passed through 0.2 μm Millex-FGS filters and spin-cast onto glass slides and then dried under vacuum at room temperature for 1 h to give photoluminescence thin films.

EL Device Fabrication. Double-layer light-emitting diode test devices (LEDs) were fabricated on indium/tin oxide (ITO) coated glass slides (OFC Corporation, 20 Ω/sq) using the configuration ITO/PEDOT-PSS/EM/Ca-Al. EM was the emissive material, **1** or **2** or blends of **1** with PMMA. Compound **1** was purified by column chromatography shortly before use (silica gel, 5:2 dichloromethane: hexane) avoiding hot recrystallizations. A hole injection layer of PEDOT-PSS was first spin-coated on top of the ITO (10 mg/mL, 1500 rpm) and then dried at 100 $^\circ\text{C}$ for 1 h under vacuum. Chloroform solutions of **1** or **2** or w/w-% blends of them with PMMA were then spin-coated (10 mg/mL, 2000 rpm) onto the PEDOT-PSS layer under nitrogen atmosphere. A Ca cathode of about 400 nm thickness was vapor-deposited, followed by a protective layer of aluminum. Typical device areas were 6 mm². The devices were characterized using methods and systems that were previously described.^{4a}

Results and Discussion

Synthesis and Characterization of **1 and **2**.** Scheme 1 summarizes the syntheses of **1** and **2**. Palladium catalyzed Heck coupling of 2,7-dibromo-9,9-diethyl-9H-fluorene **3** with 3,4,5-trimethoxystyrene **4** gave **1** in high yield and purity with essentially all (*E,E*)-geometry, as judged by a lack of

(*Z*)-stilbene type olefinic protons in the δ 6–7 range of the proton NMR spectrum, plus well-resolved *trans*-ethenyl = C–H doublets at δ 7.1–7.2 having $J = 16$ Hz.

The segmented copolymer **2** was made by a similar approach. A nonconjugated linker unit was synthesized by bis-etherification reaction between syringaldehyde and 1,6-dibromohexane to yield **5**, which was then subjected to Wittig methylenation to make **6**. Heck coupling of **6** with **3** gave **2** as units of chromophore **1** linked by flexible hexamethylene units. The ¹H NMR spectrum of **2** resembles that of **1** except for alkyl group resonances at δ 1–2 and O–CH₂ resonances at about δ 4.2, both from the linker group. As with **1**, the ¹H NMR spectrum of **2** indicates only (*E,E*)-olefinic bonds. GPC analyses against polystyrene standards show a monomodal distribution, $M_n = 4700$, $M_w = 11\,900$, degree of polymerization DP ~ 7 , polydispersity index = 2.5. The polymer forms good films when cast from organic solvents.

Crystallography of **1.** π -Stacking, aggregation, and other solid state intermolecular reordering of emitting chromophores during device production have been implicated in LED quenching mechanisms and variable emission wavelengths.^{2,7} In the Cambridge Structure Databank (version 5.26, November 2004), numerous 9,9-dialkylfluorenes stack either in a parallel or antiparallel manner, with various degrees of side-slipping, even when the 9-alkyl groups are fairly long.⁸ Compound **1** is designed to be a structurally simple, phenylene-vinylene-fluorene-vinylene-phenylene model system (an oligo fluorene phenylenevinylene, OFPV), an elongated version of a fluorene with various points for potential synthetic elaboration.

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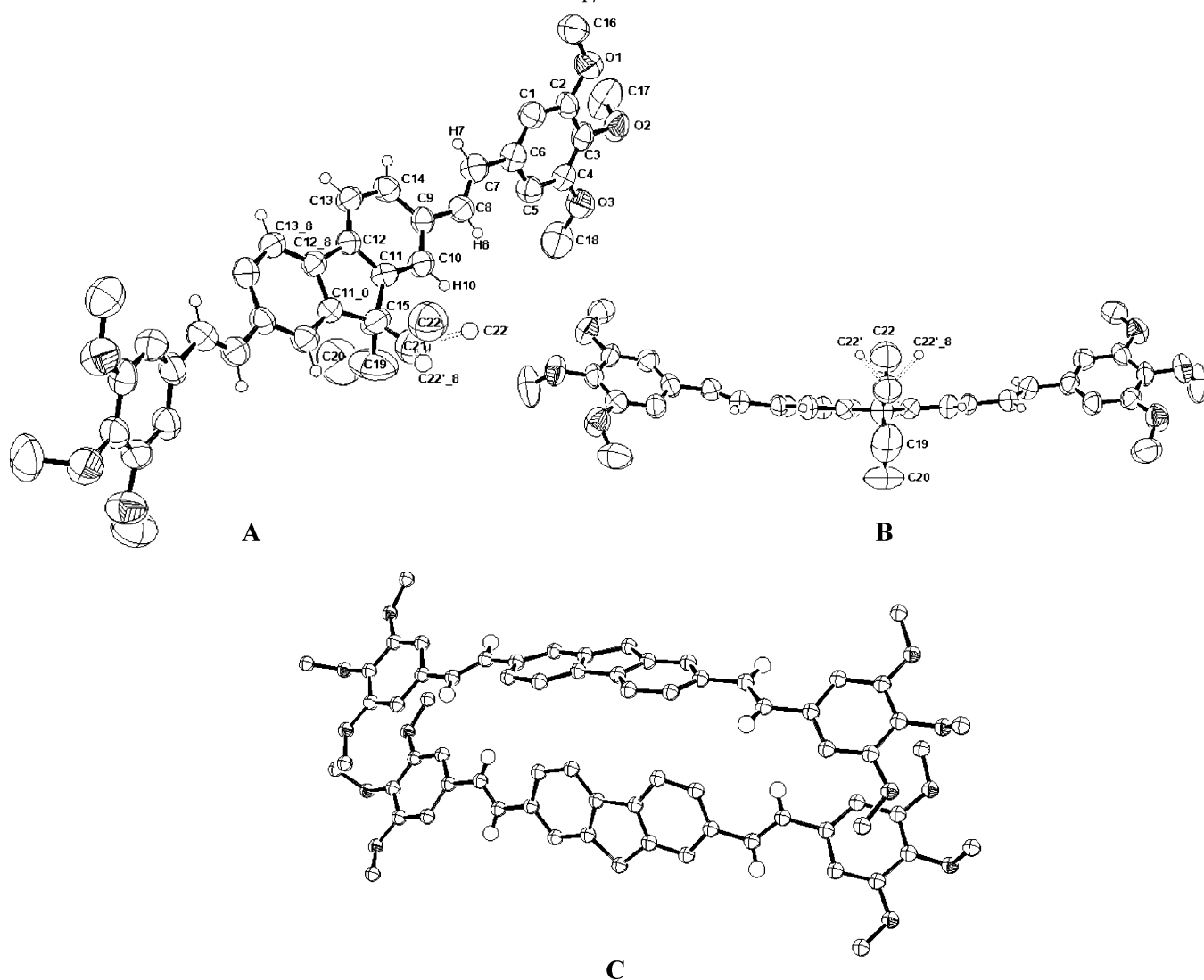


Figure 1. ORTEP representations of **1** at 50% probability ellipsoids (views A and B), with all hydrogen atoms omitted (except those on the vinylene units) for ease of viewing. The dotted atoms C22' and C22'_8 are alternate occupancy positions for a disordered ethyl group. View C shows a dyad with the fluorene herringbone motif between two molecules of **1** in the crystal lattice, with omission of all hydrogen atoms (except those on the vinylene units) and the ethyl groups for ease of viewing.

Figure 1 shows ORTEP-3⁹ representations of **1**, and a simplified representation of its major intermolecular close-contact approach. The structure shows some torsion of both terminal trimethoxyphenyl rings relative to the central ring. Torsion $-\text{C}(1)-\text{C}(6)-\text{C}(7)-\text{C}(8) = 23.7^\circ$ across the phenyl- $(\text{CH}=\text{CH})$ linkage, $-\text{C}(10)-\text{C}(9)-\text{C}(7)-\text{C}(8) = 21.6^\circ$ across the fluorine- $(\text{CH}=\text{CH})$ bonds, as shown in view A of the figure. The overall structure is slightly bowed and deplanarized as shown in view B, and it appears to disfavor π -stacking of the fluorene units. The only close contact between molecules is a herringbone "T"-type interaction (view C), with no fluorene π -stacking at all. This results from the OFPV design, since various other

fluorenes and oligofluorenes π -stack in a parallel or anti-parallel fashion.^{8a-c} 9,9-Disubstituted fluorenes that do not incorporate phenylenevinylene units seem not to crystallize with herringbone contacts similar to **1**, although the few reported crystal structures for 9,9-spirocycloalkyl fluorenes are an exception.¹⁰ Because **1** does not exhibit chromophore π -stacking, it was anticipated that **1** and **2** would show better color purity (narrower emission lines) and reproducibility in EL luminescence due to suppressed tendency for π -stacking.

Static Photophysical Studies. Table 1 summarizes photophysical properties obtained for **1** and **2**, including EL measurements described in the following section. Absorption spectra obtained in dilute chloroform (Figure 2) are nearly the same, showing that linkage of the chromophores in **2** does not lead to their aggregation. The absorption maxima

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Table 1. Photophysical Properties of 1 and 2

sample	solution ^a UV-vis λ_{max} (nm)	solution ^a PL λ_{max} (nm)	film ^b PL λ_{max} (nm)	solution ϕ_{PL}^c	EL ^d λ_{max} (nm)
1	380	416, 440	460	0.93	470–480
2	380	420, 446	480	0.68	470–480

^a Chloroform solution. ^b Neat film on quartz. ^c Solution results relative to 9,10-diphenylanthracene standard (ref 6). ^d ITO/PEDOT-PSS/EM/Ca–Al configuration.

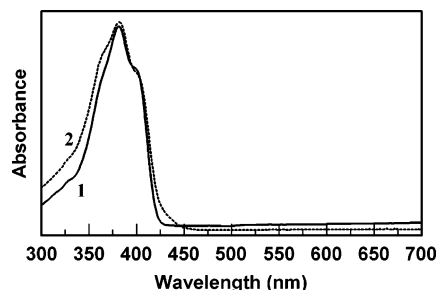
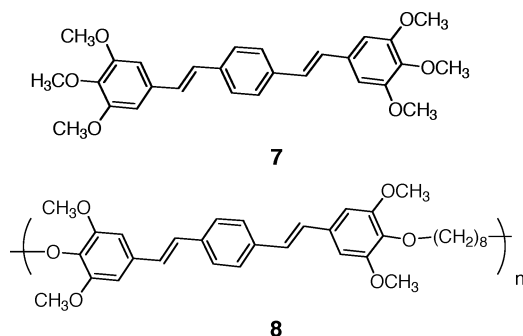


Figure 2. UV-vis spectra for **1** (—) and **2** (---) in chloroform at room temperature; spectra are normalized for comparison.

of **1** and **2** are similar to those observed¹¹ for the PPV 2.5-mer **7** and related copolymer **8**, which have a central phenylene unit instead of the fluorene unit.



Photoluminescence (PL) spectra of **1** and **2** are shown in Figure 3. Their excitation action spectra essentially overlap their absorption spectra, indicating that the absorbing chromophores are the only significant emitters with high purity. Both show strong blue fluorescence in solution, with broadened fine structure that may be associated with a coupled C=C vibronic stretching mode, as suggested by Ranger and Leclerc.¹² The CIE coefficients¹³ for the solution PL spectra of **1** and **2** are (0.148,0.256) and (0.133,0.362), respectively. The fluorescence quantum yields in chloroform at room temperature were 0.93 and 0.68, respectively, relative to 9,10-diphenylanthracene as standard.⁶ The lower quantum yield in **2** is probably due to chromophore self-quenching, because the polymethylene linker holds the chromophores together within a maximum center-to-center distance of 31–32 Å, assuming an extended, all-anti polymethylene conformation. Otherwise, the solution PL spectra of **1** and **2** are quite similar, save that the relative intensities of the vibronic

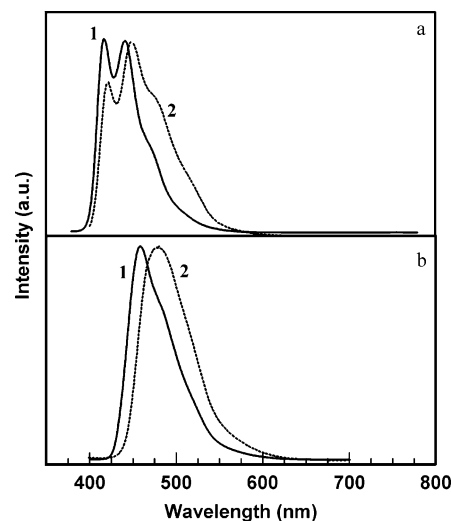


Figure 3. Photoluminescence spectra for **1** (—) and **2** (---) in chloroform (a) and as solid films cast on quartz plates (b). The spectra are normalized for comparison.

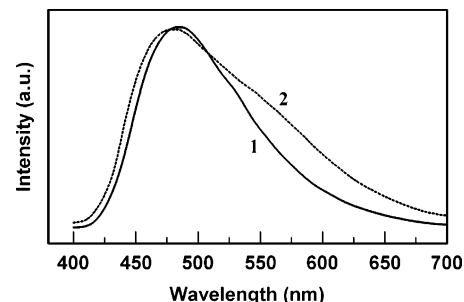


Figure 4. Electroluminescence spectra for **1** (—) and **2** (---). Device configurations are described in the text. Spectra are normalized for comparison.

bands are different in **2** by comparison to **1**. No significant changes in the fluorescence spectra of either **1** or **2** are seen to indicate excimer emission over 1–100 μM concentrations.

Electroluminescence with Neat Emissive Layers of 1 and 2. Double-layer LEDs with the configuration ITO/PEDOT-PSS/EM/Ca–Al give EL spectra for **1** (Figure 4, Table 1) that are slightly red shifted and broadened relative to its solid PL spectrum. The solid PL spectrum does not vary with film thickness, and the EL spectral maximum for a number of test LEDs is $\lambda_{\text{max}} = 470\text{--}480$ nm. The spectral similarities are consistent with the generation of EL and PL from radiative decay of excitons of the same or very similar nature. The EL spectrum of polymer **2** has the same maximum as its solid PL spectrum, but is broader, probably due to the variety of somewhat different emitter environments induced by the flexible linker units in **2**. The CIE color coordinates for the EL spectra of **1** and **2** are (0.186,0.404) and (0.229,0.388), respectively, making both species blue to blue-green emitters. At lower drive voltages, the emission looks blue to the eye, while at higher drive voltages the emission looks blue-white.

Current density–voltage–luminance characteristics of the LEDs using **1** and **2** (Figure 5) showed turn-on voltages of 3 and 5 V, respectively. The maximum luminance efficiency values were 0.515 and 0.040 cd/A, respectively. The values for **1** are quite respectable for nonoptimized LEDs, with brightness up about 450 cd/m² at 7 V, and good device

- (11) Gurge, R. M.; Hickl, M.; Krause, G.; Lahti, P. M.; Hu, B.; Yang, Z.; Karasz, F. E. *Polym. Adv. Technol.* **1998**, *9*, 504.
 (12) Ranger, M.; Leclerc, M. *Macromolecules* **1999**, *32*, 3306.
 (13) CIE color coordinates were based on the functions described in the Commission Internationale de l'Éclairage Proceedings (1964) Vienna Session, 1963, Vol. B, pp 209–220 (Committee Report E-1.4.1), Bureau Central de la CIE, Paris, France.

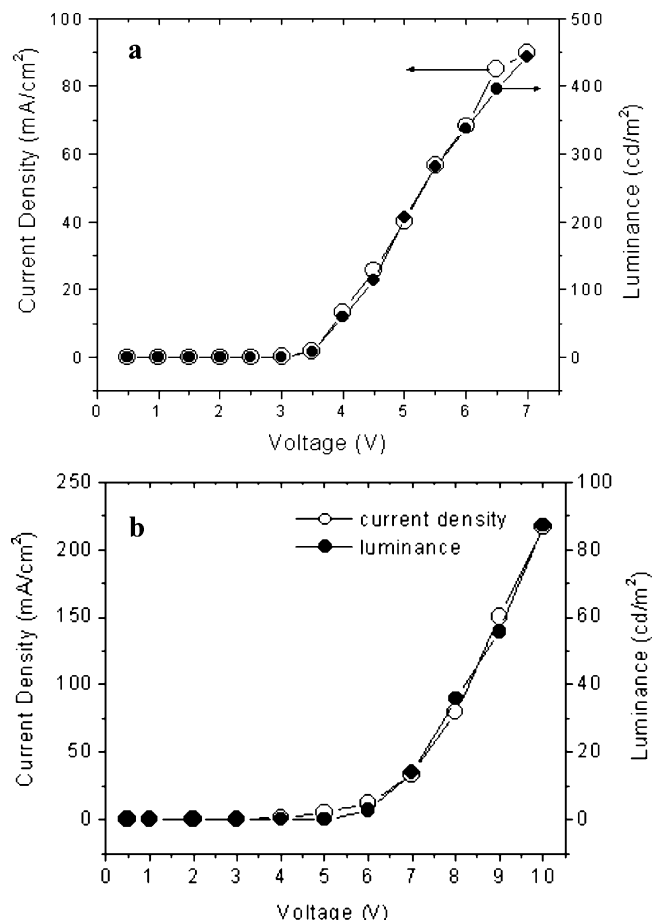


Figure 5. Current–voltage–luminance plots for ITO/PEDOT-PSS/EM/Ca–Al LEDs using **1** (a) and **2** (b).

stability when stored under argon. Test LEDs with **1** lit reliably with little loss of intensity after months in a glovebox.

Column chromatography of **1** at room temperature in subdued light allowed the elimination of variable amounts of a longer wavelength emission shoulder at 540 nm and longer that was seen in the EL spectrum of some test LEDs. This EL shoulder is significantly increased if **1** is purified by recrystallization from hot solvent before device fabrication. Similar long wavelength EL emission sites in fluorenes-based polymers have been attributed to fluorene oxidation, based on experiments exposing LEDs to photoirradiation^{3d} or heat^{3d,3g} in the presence of air; it has also been suggested that such oxidation occurs during^{3d} device fabrication. Solid films of **1** heated at 150 °C in air for 30 min or more gave a similar PL shoulder to that observed in the EL spectrum, which increased to give a new maximum at ~540 nm upon prolonged heating at higher temperatures (Figure 6). When heated under vacuum, the films show no PL shoulder formation until 200 °C, nearly the melting point of **1**. Although it is important to avoid heating **1** in air before incorporation into LEDs, no particular precautions to avoid air seemed necessary for a few days of storing **1** after chromatography but before LED fabrication; the effects of prolonged storage of **1** in air at room temperature were not evaluated.

LEDs heated at 100 °C for 30 min in air show spectral broadening on the long wavelength side (higher temperatures

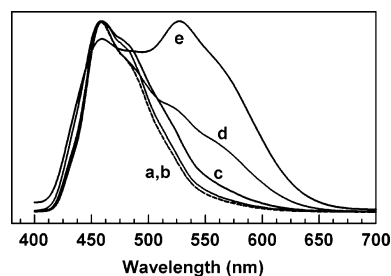


Figure 6. Solid film photoluminescence spectra of **1** on quartz: (a) at room temperature before annealing (---), (b) at 75 °C, (c) at 100 °C, (d) at 150 °C, (e) at 200 °C. Spectra are normalized for comparison.

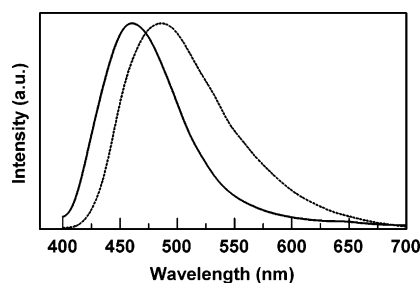
resulted in LED failure). Significant production of a 550–560 nm component was also seen (Figure 6) if **1** was heated in air at 150 °C or above for about 30 min before incorporation into an LED. The overall LED emissive strength also decreased significantly in heated samples. Although these experiments show oxidation to be a cause of the long wavelength emissive component, the FTIR spectrum of **1** was essentially unchanged after heating samples at 150 °C in air for 30 min (see Supporting Information). By comparison, heating of 9,9-dioctylfluorene-based polymers in air was reported to produce both carbonyl peaks in the FTIR and a long wavelength EL emission band.^{3g} Differential scanning calorimetric measurements for **1** showed no evidence of phase changes below its melting point, so the long wavelength component does not seem to be associated with a crystal annealing process. Thermogravimetric analysis showed no loss of mass up to about 300 °C in air, showing that **1** is highly stable. Any putative oxidation impurity that might give the long wavelength emission apparently is in low concentration.

Electroluminescence with PMMA-Blended Emissive Layers of 1 and 2. As its crystallography shows, OFPV **1** does not readily π -stack, thereby limiting aggregation related variations in the emission behavior of its LEDs. Flexibility and disorder among the OFPV chromophores in segmented **2** should also limit π -stacking and aggregation. However the chromophores in **2** can separate only up to the limits imposed by the length of the nonconjugated hexanediyl segment. Depending upon the amount of folding in **2** during film casting, undesired quenching could occur in regions having close intrachain or interchain chromophore contacts. In an alternative strategy to limit aggregation of the OFPV chromophore **1**, LED emissive layers were made using blends of **1** with PMMA. The intent was to find a blend regime to give good color purity through limiting the number of different environments for the chromophore that can occur in neat samples, to limit quenching mechanisms by separating the chromophores, and to retain sufficient emitting chromophore sites for low turn-on voltages with reasonably strong emission intensity.

Table 2 summarizes EL characteristics of LEDs made with varying PMMA blends of **1**, by comparison to results using neat **1**. Figure 7 compares the EL spectra for an LED made with neat **1** to one made with 10% (w/w) of **1** in PMMA. The blend EL spectrum is blue shifted by up to ~0.14 eV (~30 nm) relative to EL from pure **1**, is bluer (CIE = (0.155,0.375)), and is somewhat narrower at peak half-height

Table 2. EL Characteristics of LEDs Made with **1** and Its Blends with PMMA^a

%w/w 1	luminance efficiency (cd/A)	turn-on voltage (V)	current density at 7 V (mA/cm ²)
10	4.50	4.5	0.8
25	3.36	4.0	6.6
50	1.87	3.5	48.3
75	0.87	3.5	101.6
100	0.51	3.0	90.0

^a All LEDs made with ITO/PEDOT-PSS/EM/Ca–Al configuration.**Figure 7.** Electroluminescence spectra for LEDs made with neat **1** (---) and 10% (w/w) **1** in PMMA (—) as emissive layers. Device configurations are described in the text. Spectra are normalized for comparison.

(0.46 versus 0.51 eV). As the concentration of **1** in the blend decreases, the turn-on voltage increases somewhat, the luminance efficiency increases dramatically, and current density drops. A device brightness of 1000 cd/m² at 8 V was obtained for an LED with the 50% blend, about twice the maximum for the LEDs using neat **1** as an emitting layer. Overall, the LED characteristics of PMMA-blended **1** are improved over either neat **1** or **2**, since the spectral width is narrower with no significant long wavelength emission and only a modest increase in turn-on voltage. The blending with

PMMA reduces aggregation of **1** that contributes to luminescence self-quenching and peak broadening.

Conclusions. Model chromophore **1** and segmented copolymer analogue **2** both exhibit solution phase blue photoluminescence with high quantum yields. Neat emissive layers in test LEDs yield blue to blue-green emission. The molecular species, **1**, can be purified to eliminate a higher wavelength EL emission component that becomes substantial if the compound is heated in air before use in an LED. Copolymer **2** gives a somewhat broadened EL spectrum relative to **1** with decreased intensity and, generally, is an inferior LED emissive layer material to **1**. PMMA blends of **1** give significantly higher luminance than neat **1**, with only modest increases in LED turn-on voltage and a small emission blue shift.

Chromophore **1** has good prospects for use as an LED blue emitter material, if not heated in air before use. Blends with PMMA are as good or better than the neat materials as an emissive layer, in terms of color purity and emissive strength. Hopefully, these studies will be useful to achieve better control of electronic properties in organic LEDs that use fluorene-incorporating emissive layers.

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Supporting Information Available: Crystallographic data for **1** (CIF), EL luminance plots for various blends of **1** with PMMA (PDF), FTIR spectra of **1** before and after heating (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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