# Luminescence of fluorenes 2,7-conjugatively extended with pyrenylvinylene and pyrenylvinylene-phenylenevinylene

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Received 6th March 2007, Accepted 26th April 2007 First published as an Advance Article on the web 18th May 2007 DOI: 10.1039/b703180g

2,7-Bis(1'-pyrenylvinylene)-9,9-diethylfluorene (1) and 2,7-bis(1'-pyrenylvinylene-4"phenylenevinylene)-9,9-diethylfluorene (2) were synthesized and their static luminescence behavior assessed. They show solution photoluminescence (PL) maxima in chloroform at 475 nm and 467 nm, with quantum efficiencies of 54% and 52%, respectively. Double-layer LED devices with configuration ITO/PEDOT-PSS/(1 or 2)/Ca–Al emitted blue-green light with turn-on voltages of 2.5 V and emission maxima at 500 nm (2.48 eV); their luminance efficiencies were 0.36 and 0.30 cd A<sup>-1</sup>, respectively. Blending of 1 at 20% (w/w) in PVK improved the luminance efficiency to 1.81 cd A<sup>-1</sup> for the same device configuration, with only a small increase in turn-on voltage to 3 V; the emission maximum was 497 nm (blue-green emission), the maximum luminance 7600 cd m<sup>-2</sup> with CIE color coefficients of (0.12, 0.45). For a 10% (w/w) blend of 2 in PVK using the same device configuration, the luminance efficiency was 1.47 cd A<sup>-1</sup>, turn-on voltage 3 V, maximum luminance 2600 cd m<sup>-2</sup> with CIE coefficients of (0.13, 0.45). Simple  $\pi$ -MO calculations show that structural extension of the nominal conjugation length in 2 does not significantly decrease the effective band gap relative to 1, consistent with the observed lack of red shift in 2.

# 1. Introduction

Fluorene-based polymers and copolymers have been extensively tested as prospective emitting layers for polymer light emitting diodes (PLEDs).<sup>1</sup> Some have high photoluminescence (PL) efficiencies both in solution and in solid film, with emission wavelengths tunable over much of the visible spectrum. However fluorene-incorporating LEDs frequently have unwanted longer wavelength green-emitting electroluminescent (EL) bands (g-bands) variously attributed to excimers derived from chromophoric  $\pi$ -stacking during device fabrication,<sup>2</sup> and/or from adventitious oxidation.<sup>3</sup> The variability of color purity and reproducibility in such systems can depend quite strongly on the nature and rate of energy transfer between different exciton sites in a light emitting material. The use of pyrene-containing units in various conjugated or polychromophoric systems<sup>4</sup> has been of particular interest to us.<sup>5</sup> For example, multifunctional EL materials incorporating pyrene plus triarylamines or carbazoles pared by various groups<sup>6</sup> can show good thermal stability, high brightness and high luminance efficiencies.

Recently we showed that small molecule phenylenevinylenefluorene-phenylenevinylene (OFPV) molecular chromophores give good blue to blue-green PL and EL color purity and OLED characteristics.<sup>7</sup> This article describes conjugative extension of the OFPV chromophore by attachment of pyrenylvinylene and pyrenylvinylene-phenylenevinylene to make 2,7-bis(1'-pyrenylvinylene)-9,9-diethylfluorene and 2,7bis(1'-pyrenylvinylene-4"-phenylenevinylene)-9,9-diethylfluorene, 1 and 2 respectively. We aimed to see whether conjugative extension of the OFPV unit would improve or degrade its OLED stability and color purity by comparison to the blue to blue-green emission of OFPV itself, especially in view of possible excimer formation in the solid state between pyrene units. In addition, we wished to investigate the effect on the emissive band gap of OFPV of these conjugation extensions. The static solution phase and solid film photoluminescence behaviors of the compounds are compared, as well as characteristics of organic light emitting diode (OLED) test devices made with both neat and PVK-blended 1 and 2 as emissive layers.

# 2. Results and discussion

# Synthesis and characterization of 1 and 2

Scheme 1 summarizes the syntheses of 1 and 2. 2,7-Dibromo-9,9-diethylfluorene (3)<sup>7,8</sup> was subjected to Heck coupling with 1-vinylpyrene 4, which itself was made by Wittig vinylation of pyrene-1-carboxaldehyde 5. Product 1 was obtained in high yield and purity having essentially all (*E*,*E*)-geometry, with no visible (*Z*)-stilbene type olefinic protons in the  $\delta$  6–7 range of the proton NMR spectrum, and the presence of well-resolved *trans*-ethenyl =C-H doublets at  $\delta$  7.13–7.17 having *J* = 16 Hz. Compound 4 was conjugation-extended by Heck coupling with 4-bromobenzaldehyde to make 6, vinylated to intermediate 7, and coupled to core precursor 3 to give product 2. The <sup>1</sup>H-NMR spectrum of 2 resembles that of 1 except for the

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Scheme 1 Syntheses of 1 and 2.

presence of *para*-phenylenevinylene resonances in the aromatic region. As with **1**, the <sup>1</sup>H-NMR spectrum of **2** shows no higher field (*Z*)-stilbenoid =CH resonances, so (*E,E*)-olefin formation exclusively predominates, or nearly so. The compounds are also resistant to thermal decomposition. Compound **1** shows virtually no mass loss by thermogravimetric analysis at temperatures up to 400 °C; it loses ~55% of mass over 400–500 °C.

Multiple attempts to obtain diffraction quality single crystals of **1,2** were unsuccessful, However, the compounds are reasonably soluble in organic solvents, and form films on glass that are quite adequate for use in fabricating test OLEDs.

#### Absorption and photoluminescence properties

The static photophysical behavior of 1,2 in dilute chloroform solution and in spin-cast thin films is summarized in Table 1. Absorption spectra in dilute chloroform (Fig. 1) and in the solid state (Fig. 2) are very similar. Compound 1 shows main absorption at 411 nm, with a weak set of absorptions that include vibronic fine structure in the 270–350 nm region. The latter region appears to be due to localized pyrene absorptions. Compound 2 has its main absorption at 411 nm with a small shoulder around 350 nm; the latter, again, appears to be a poorly resolved pyrene absorption. Based on the spectral onsets, the optical band gaps for 1 and 2 are nearly identical at 2.47–2.48 eV. The solid film absorption maxima and spectral shapes for 1,2 are quite similar to the solution spectra, indicating no major aggregation effects in the solid state.

The solution excitation spectra of 1 and 2 monitored at 525 nm essentially overlap their respective absorption spectra, indicating that the absorbing chromophores are the only significant emitters. Both compounds show very similar bluegreen solution photoluminescence (PL) bands in the 470-520 nm region (Fig. 1), with no localized pyrene emission peaks in the expected region of 360-425 nm. The fluorescence quantum yields in chloroform at room temperature relative to 9,10-diphenvlanthracence<sup>9</sup> were 0.54 and 0.52, respectively. The solid film PL spectra showed significant red shifts of about 0.15 and 0.22 eV, respectively, by comparison to the corresponding solution spectra (Table 1, Fig. 2). The shift of the solid compared to the solution PL spectrum is presumably due to different dielectric environment for emitting molecules in the neat solid by comparison to solution, and/or  $\pi$ -cloud interaction effects between proximal molecules in the solid state sample.

Pyrene derivatives can form excimers in solution.<sup>10</sup> The excimer appears as a longer wavelength, featureless PL band at

Table 1Optical properties of 1 and 2

Sample	$\lambda_{\max}(abs)^a/nm$	$\lambda_{\max}(abs)^b/nm$	Solution <sup><math>c</math></sup> $\Phi_{\rm PL}$	$\lambda_{\max}(PL)^a/nm$	$\lambda_{\max}(PL)^b/nm$
1	411	427	0.54	475 (503)	504
2	411	414	0.52	467 (495)	508
<sup>a</sup> Chloroforr	n solution DI speatre obtai	nad with 200 nm availation	wavelength <sup>b</sup> Neat film or	quartz <sup>c</sup> Polativo quantu	m viald commerced to

"Chloroform solution. PL spectra obtained with 390 nm excitation wavelength." Neat film on quartz. "Relative quantum yield compared to 9,10-diphenylanthracene standard (see ref. 9).



Fig. 1 Solution UV-vis (a) and PL (b) spectra for 1 and 2 in chloroform at room temperature. PL spectra at 1 millimolar concentrations with 390 nm excitation.



Fig. 2 Solid film absorption, PL and EL spectra for 1 and 2. PL spectra at 390 nm excitation.

longer wavelengths than the monomer emission at shorter wavelength; the monomer is seen readily in solution at lower concentrations, and the emission becomes weaker relative to the monomer emission at higher concentrations. For example, some PPV derivatives with pyrene segments incorporated into their main chains exhibit characteristic pyrene excimer emission at 510–530 nm.<sup>4c</sup> However neither **1** nor **2** show significant solution PL spectral shape changes over a 1–1000  $\mu$ M concentration range, so these appear to form no significant concentrations of excimers.

#### **Electroluminescent devices**

Double-layer OLEDs with the configuration ITO/PEDOT-PSS/(1 or 2)/Ca–Al were fabricated to investigate the electroluminescence spectra of 1,2 (Fig. 2), as well as their current–voltage and luminance–voltage characteristics (Fig. 3). The OLEDs emit blue-green light, with EL spectra that are virtually the same for both compounds. Both EL spectra show poorly resolved vibronic structure, while the corresponding solid film PL spectra are narrower and lack resolved fine structure. The different lineshapes may be due to the different exciton generation processes in PL and EL, and/or local thermochromic effects by comparison to room temperature PL spectra, which could occur because these simple OLEDs do not have heat sinks.<sup>11</sup> Table 2 summarizes OLED performances using neat **1,2**: compound **1** gave the best luminance efficiency of 0.36 cd A<sup>-1</sup> at a current density of 80 mA cm<sup>-2</sup>, with a maximum brightness of 2600 cd m<sup>-2</sup> at a current density of 740 mA cm<sup>-2</sup>.

The addition of PVK to the emissive layer to aid hole injection improves OLED performance significantly compared to neat 1 or 2. The PVK-diluted PL and EL spectra are quite similar as shown in Fig. 4, whereas the neat spectra show



Fig. 3 Current-voltage-luminance plots for ITO/PEDOT-PSS/(1 or 2)/Ca-Al LEDs.

	uni-on voltage/ v	Maximum luminance/cd m	Maximum luminance efficiency/cd A
00 2.5	5	2600	0.36
00 2.5	5	2000	0.30
0 3	,	7600	1.81
97 3	4	4800	2.10
97 3		2600	1.47
91 4		1200	0.60
38 5		1300	0.48
	$\begin{array}{ccccc} 0 & & 2. \\ 0 & & 2. \\ 0 & & 3 \\ 7 & & 3 \\ 7 & & 3 \\ 1 & & 4 \\ 8 & & 5 \end{array}$	0 2.5 0 2.5 0 3 7 3 7 3 1 4 8 5	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 2 EL characteristics of OLEDs made with neat 1 and 2 and with (1 or 2) : PVK blends

significantly narrower PL spectra with less fine structure than the corresponding EL spectra. The OLED performance results for the blend-based devices are shown in Fig. 5. The best luminance efficiency of 2.1 cd  $A^{-1}$  at 6 V was attained using a 10% (w/w) blend of 1 in PVK. The highest luminance of 7600 cd m<sup>-2</sup> was obtained using 20% (w/w) of 1 in PVK; this OLED also has a relatively low 2.5 V turn-on voltage. There was no noticeable difference in OLED performance stability between those using neat 1 or 2 and those using the PVK blends, over the timeframe of measurements made to characterize the devices.

The increase in turn-on voltages for the OLEDs made with more dilute blends reflects the greater difficulty of hole/ electron transport across greater distances between emitter sites. A small blue shift of 12 nm (60 meV) in the EL emission spectral maxima as the fluorophore concentration decreases to  $\leq 10\%$  (w/w) concentration is presumably due to decreasing aggregation of emitter sites. For the 10% (w/w) blend OLEDs with 1, the  $CIE^{12}$  color coordinates are (0.12, 0.45); for the 10% blend with 2, they are (0.13, 0.45). The OLEDs with neat 1 and 2 have CIE coefficients of (0.23, 0.42) and (0.23, 0.41), respectively. All these OLEDs emit light that is teal-colored, blue-green to the eye.

Some recent work offers comparisons to other small molecule systems incorporating conjugation between pyrene and fluorene. Recently Zhao *et al.* described<sup>13</sup> the synthesis and photoluminescent properties of **8**, which is similar to **1** save for having alkynyl instead of olefinic links between the fluorene and pyrene units. The solution absorption spectral maxima for **1** and **8** are nearly identical at 410–411 nm, but the solution PL spectrum for **8** was strongly blue-shifted relative to **1**, 431/457 nm *versus* 475/503 nm in solution (a difference of 0.27 eV). Diluted solid film PL spectra show a similar spectral trend, with the PL maximum of **8** in PMMA at 460 nm compared to 488 nm for **1** in PVK. The blue shift in the emission spectra of **8** relative to that of **1** is consistent with a



Fig. 4 PL of 10% blends of 1 or 2 with PVK, EL spectra for ITO/PEDOT-PSS/(10% 1 or 2 : PVK)/Ca-Al LEDs. PL spectra use 390 nm excitation.



Fig. 5 Current-voltage and luminance-voltage plots for ITO/PEDOT-PSS/1 : PVK/Ca-Al LEDs.

Published on 18 May 2007. Downloaded by Lomonosov Moscow State University on 22/08/2013 12:55:27.

typically smaller conjugation linkage effect for alkynes by comparison to alkenes. No EL experiments using **8** were reported. Tao *et al.*<sup>14</sup> described EL studies of pyrene-fluorene systems **9–11** with shorter nominal conjugation lengths than those in **1,2** and **8**. Tang *et al.*<sup>15</sup> described EL studies of similar species **12,13**. OLEDs made with these systems gave blue emission with good intensities in the 450–470 nm range. Tang's systems showed impressively strong blue emission in some multilayer OLEDs; these workers suggested that the nonplanarity of **9–11** contributes to their lack of longer wavelength emission bands. However, the present systems **1,2** are much more easily planarized than **9–11**, and **1,2** also show no long wavelength shoulders or excimer-like bands.



Structural elongation of the  $\pi$ -connectivity beyond that of 1 does not extend the effective spectral conjugation length. Torsional deconjugation of the pyrene units is likely in 9–13, but seems less likely in 1 and 2, especially in solution. A strongly twisted geometry for 1 or 2 should yield absorption spectra that more resemble a sum of pyrene plus fluorene components, with emission spectra resembling emission from fluorene, assuming energy transfer from twisted pyrene units to a nearly isolated, nonconjugated central fluorene. Small amounts of twisted conformations in 1 and 2 may be responsible for the small pyrene-like components in these absorption spectra, and for their lower solution fluorescence quantum yields (~50%) by comparison to those of 8 and 9–13 (68–78%).<sup>13–15</sup> However, the luminescence of 1,2 seems inconsistent with a deplanarized geometry.

Rather, the similarities of PL and EL wavelengths for 1 and 2 appear to be due to their inherent effective conjugation lengths. Simple Hückel  $\pi$ -MO computations that include all  $\pi$ -C centers give a HOMO–LUMO gap for 1 of 0.575  $\beta$ , while that for 2 is 0.554  $\beta$ . This small difference is consistent with the similarities in their absorption spectra. Addition of the extra phenylenevinylene units into 2 thus lengthens the structural conjugation relative to 1, but does not significantly affect the electronic conjugation.

# 3. Conclusions

Chromophores 1 and 2 exhibit solution phase bluish photoluminescence with moderate quantum yields. Double-layer OLEDs with PEDOT-PSS hole-injection layer and 1 or 2 as emitter layer give teal blue-green emission. OLEDs using simple PVK blends with 1 and 2 show significantly higher luminance than with neat 1 or 2, even for low weight percentages of emitter, with only modest increases in LED turn-on voltage and a small emission blue shift. Undesirable excimer or impurity emitter bands are not observed under any solution or solid state conditions used. The effective conjugation length for these systems is maximized in 1—an increase in nominal conjugation length by insertion of a phenylenevinylene unit in 2 does not decrease the band gap or emission energy. The simple fabrication methodology, high temperature stability, and good color purity for OLEDs made from 1 make it a good candidate for solid state luminescence applications.

# 4. Experimental

# General

All commercially available materials were used as received unless noted otherwise. Poly(3,4-ethylenedioxythiophene)/ poly(styrene sulfonate) (PEDOT-PSS) was obtained from Bayer Corporation. Tetrahydrofuran (THF) was distilled first from calcium hydride and then sodium/benzophenone under argon. Spectroscopic grade solvents (Aldrich) were used as received without further purification. Reported melting points are uncorrected.

Emission and excitation spectra were obtained using a Perkin-Elmer LS 50B spectrometer with a xenon lamp light source. Emission quantum yields in spectrograde chloroform were determined at an excitation wavelength of 380 nm using external standard 9,10-diphenylanthracene (0.1 mmol L<sup>-1</sup> in ethanol,  $\Phi_{PL} = 0.81$ ) by a literature<sup>9</sup> procedure. The maximum absorbance of sample solution was less than 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.

#### 2,5-Dibromo-9,9-diethylfluorene (3)

This compound was synthesized following previously published<sup>7,8</sup> procedures.

#### 1-Pyrenecarboxaldehyde (4)

To a suspension of 1-pyrenylmethanol (1.0 g, 4.30 mmol) in 30 mL of dichloromethane, powdered manganese dioxide (0.56 g, 6.45 mmol) was added and the mixture stirred at room temperature overnight. The mixture was filtered, then evaporated to give a yellow solid (0.85 g, 85%) that was used without further purification. Mp 120–123 °C (lit.<sup>16</sup> mp 125–127 °C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  8.03 (s, 3 H), 8.11 (m, 1 H), 8.20 (d, 1 H, J = 6 Hz), 8.31–8.28 (m, 2 H, J = 16 Hz), 9.37 (d, 2 H, J =9 Hz), 10.73 (s, 1 H).

## 1-Vinylpyrene (5)

To a suspension of triphenylphosphonium bromide (1.97 g, 5.53 mmol) in 25 mL of dry THF at 0 °C under argon was added dropwise 2.21 mL (5.53 mmol) of *n*-butyllithium

solution (2.5 M in hexanes). The resulting orange solution was allowed to warm to room temperature and stirred for an additional 10 min. Next, 4 (850 mg, 3.69 mmol) in 10 mL of THF was added to the reaction mixture dropwise over 30 min. The resulting yellow suspension was stirred at room temperature overnight. The reaction mixture was then filtered, and the filtrate was poured into 30 mL of water. The aqueous layer was back-extracted with 2  $\times$  15 ml of diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica using diethyl ether as the eluent to yield 530 mg (62%) of 5 as a vellow solid. For multiple determinations with samples obtained in this manner. Mp 120-123 °C (lit.17 mp 82-84 °C, lit.<sup>18</sup> mp 87–89 °C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  5.64 (d, 1 H, J = 11 Hz), 6.03 (d, 1 H, J = 17 Hz), 7.83 (dd, 1 H, J = 11,17 Hz), 8.03 (t, 1 H, J = 8 Hz), 8.09 (s, 2 H), 8.2 (m, 4 H), 8.35 (d, 1 H, J = 8 Hz), 8.52 (d, 1 H, J = 8 Hz).

#### 2,7-Bis(1'-pyrenylvinylene)-9,9-diethylfluorene (1)

To a three-necked round bottom flask were added 5 (280 mg, 1.22 mmol), 3 (236 mg, 0.613 mmol), tri-o-tolylphosphine (60 mg, 0.197 mmol) and a catalytic amount of palladium acetate (4.5 mg, 0.002 mmol). The flask was flushed with argon, 20 mL of DMF was added, and solution was heated to 90 °C and stirred for 30 min. Then triethylamine (1.14 g, 1.0 mL, 11.26 mmol) was added and heating continued at 90 °C for two days. The reaction was cooled and poured into 30 mL of water, the mixture chilled with an ice bath, and 5 mL of 10% aq. HCl added dropwise. The resultant yellow solid was vacuum-filtered, dissolved in chloroform, and filtered through Celite. The filtrate was concentrated in vacuo and purified by column chromatography on silica using hexane and chloroform (1:3) as eluent. The solid product was collected to yield 230 mg (55%) of 1 as a yellow powder. Mp 278–280 (decomp.) °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.52 (t, 6 H, J = 7 Hz), 2.25 (q, 4 H, J = 7 Hz), 7.51 (d, 2 H, J = 16 Hz), 7.71 (s, 2 H), 7.76, 7.82 (AA'BB' quartet, 4 H, J = 8 Hz), 8.05 (t, 2 H, J = 8 Hz), 8.11(s, 4 H), 8.2 (m, 8 H), 8.31 (d, 2 H, J = 16 Hz), 8.40 (d, 2 H, J = 8 Hz), 8.61 (d, 2 H, J = 8 Hz); HR-MS(FAB) calc. for C<sub>53</sub>H<sub>38</sub> m/z = 674.2974, found 674.3013.

# 4-(1'-Pyrenylvinylene)benzaldehye (6)

To a three-necked round bottom flask were added 4-bromobenzaldehyde (740 mg, 3.99 mmol), 1-vinylpyrene, **5** (820 mg, 3.59 mmol), tri-*o*-tolylphosphine (244 mg, 0.80 mmol) and a catalytic amount of palladium acetate (60 mg, 0.13 mmol). The flask was flushed with argon, 30 mL of dry DMF was added, the solution was heated to 85 °C and stirred for 30 min. Then triethylamine (0.7 ml, 7.99 mmol) was added and heating continued at 85 °C for two days. The reaction was then cooled and poured into 50 mL of water, the mixture chilled with an ice bath, and 15 mL of 10% aq. HCl added dropwise. The resultant yellow solid was vacuum-filtered, dissolved in chloroform, and filtered through Celite. The filtrate was concentrated *in vacuo* and purified by column chromatography on silica using diethyl ether as eluent. The solid product was collected to yield 800 mg (50%) of **6** as a yellow powder. Mp 96–99 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  7.41 (d, 1 H, *J* = 16 Hz), 7.85, 7.95 (AA'BB' quartet, 4 H, *J* = 7 Hz), 8.05 (t, 1 H, *J* = 7 Hz), 8.10 (s, 2 H), 8.2 (m, 4 H), 8.36 (s, 1 H), 8.38 (d, 1 H, *J* = 16 Hz), 8.52 (d, 1 H, *J* = 8 Hz), 10.06 (s, 1 H); MS(EI) calc. for C<sub>25</sub>H<sub>16</sub>O *m*/*z* = 332.1, found 332.1.

## 1-Vinyl-4-(1-pyrenylvinylene)benzene (7)

This compound was synthesized by following the same procedure used for **5**. Mp 136–137 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  5.31 (d, 1 H, *J* = 8 Hz), 5.82 (d, 1 H, *J* = 18 Hz), 6.97 (dd, 1 H, *J* = 8,18 Hz), 7.37 (d, 1 H, *J* = 16 Hz), 7.52, 7.67 (AA'BB' quartet, 4 H, *J* = 8 Hz), 8.03 (t, 1 H, *J* = 7 Hz), 8.08 (s, 2 H), 8.2 (m, 5 H), 8.34 (d, 1 H, *J* = 8 Hz), 8.52 (d, 1 H, *J* = 8 Hz); MS(EI) calc. for C<sub>26</sub>H<sub>18</sub> *m*/*z* = 330.1, found 330.1.

## 2,7-Bis(1'-pyrenylvinylene-4"-phenylenevinylene)-9,9diethylfluorene (2)

To a three-necked round bottom flask were added 7 (258 mg, 780 mmol), 3 (148 mg, 0.390 mmol), tri-o-tolylphosphine (23 mg, 0.075 mmol) and a catalytic amount of palladium acetate (2.0 mg, 0.008 mmol). The flask was flushed with argon, 20 mL of dry DMF was added, the solution was heated to 90 °C and stirred for 30 min. Then triethylamine (2.05 g, 1.8 mL, 20.27 mmol) was added and heating continued at 90 °C for two days. The reaction was then cooled and poured into 30 mL of water, the mixture chilled with an ice bath, and 5 mL of 10% aq. HCl added dropwise. The resultant yellow solid was vacuum-filtered, dissolved in chloroform, and filtered through Celite. The filtrate was concentrated in vacuum and purified by column chromatography on silica using hexane and chloroform (2:5) as eluent. The solid product was collected to yield 225 mg (65%) of **2** as a yellow powder. Mp 275–277  $^{\circ}$ C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  0.39 (broadened mult., 6 H, J = 7 Hz), 2.21 (broadened mult., 4 H), 7.41 (d, 2 H, J = 16 Hz), 7.57 (s, 4 H), 7.5–7.8 (overlapping m, 12 H), 8.04 (t, 2 H, J = 7 Hz), 8.11 (s, 4 H), 8.2–8.3 (overlapping m, 12 H), 8.42 (d, 2 H, J = 8 Hz), 8.65 (d, 2 H, J = 8 Hz); HR-MS(FAB) calc. for C<sub>69</sub>H<sub>50</sub> m/z = 878.3913, found 878.3972.

#### EL device fabrication

Double-layer light-emitting diode test devices (LEDs) were fabricated on indium/tin oxide (ITO) coated glass slides (OFC Corporation, 20 ohm sq<sup>-1</sup>) using the configuration ITO/ PEDOT-PSS/EM/Ca-Al. EM was the emissive material: 1 or 2 or blends of 1 with PVK. A hole injection layer of PEDOT-PSS was first spin-coated on top of the ITO, and then dried at 100 °C for 1 h under vacuum. Chloroform solutions of 1 or 2 or % (w/w) blends of them with PVK were then spin-coated onto the PEDOT-PSS layer under a nitrogen atmosphere. A Ca cathode about 400 nm thick was vapor-deposited, followed by a protective layer of aluminium. Typical device areas were 6 mm<sup>2</sup>. The devices were characterized using methods and instrumentation that have been previously described.<sup>19</sup>

# Acknowledgements

AC and FEK acknowledge support from the U.S. Air Force Office of Scientific Research. HR and PML acknowledge support from U.S. Department of Energy grant DE-FG02-05ER15695. Support from the U.S. National Science Foundation for the University of Massachusetts Amherst Mass Spectrometry Facility is acknowledged.

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