

Luminescence of Molecular and Block Copolymeric 2,7-Bis(phenylethenyl)-fluorenones; Identifying Green-Band Emitter Sites in a Fluorene-Based Luminophore

Hemali P. Rathnayake,[†] Ali Cirpan,[‡] Frank E. Karasz,[‡] Michael Y. Odoi,[†]
Nathan I. Hammer,[†] Michael D. Barnes,[†] and Paul M. Lahti^{*,†}

Departments of Chemistry and Polymer Science & Engineering, University of Massachusetts,
Amherst, Massachusetts 01003

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2,7-Bis(3,4,5-trimethoxyphenylethenyl)fluorenone (OFOPV) and a segmented oligomer analogue linking OFOPV units with polymethylene flexible spacers—*alt*-poly(2,6-dimethoxyphenylene-4-vinylene-[9-fluorenone-2-yl-7-vinylene]3,5-dimethoxyphenylene-4-[1,6-hexanedioxy]) (pFOPV)—were synthesized and their luminescence properties studied. Solution-phase photoluminescence (PL) of OFOPV and pFOPV shows concentration-dependent relative intensities of a fine-structured higher energy band and a featureless lower energy band, consistent with solution excimer formation. Neat film PL and electroluminescence (EL) spectra using 100% OFOPV and pFOPV emitter layers show red emission bands ($\lambda_{\text{max}} \sim 610$ nm). Solid film PL spectra of OFOPV diluted in PMMA or Zeonex are significantly blue-shifted relative to the neat film spectra. PL and EL spectra of 2,7-bis(3,4,5-trimethoxyphenylethenyl)-9,9-diethylfluorene (OFPV) blended with <1% by weight of OFOPV gives significant green region (g-band) emission in addition to the normal blue emission of OFPV. Monomeric OFOPV produced by adventitious oxidation is therefore identified as giving g-band emission in thermally stressed OFPV-based OLEDs, due to intermolecular energy transfer from OFPV excitons to lower energy OFOPV. The red emission in neat solid-phase OFOPV and pFOPV appear to arise from fluorenone-type excimers that do not play a direct role in g-band emission in this case.

Introduction

Polyfluorene (PF)-based polymers and copolymers are promising blue-light-emitting materials for organic light-emitting diodes (OLEDs).¹ However, numerous fluorene and PF-based blue emitters exhibit undesired longer wavelength bands,² often termed g-bands³ (green emission). In spite of

much effort, various explanations are still put forward to explain g-band formation, including emission from monomeric fluorenone oxidative defects,⁴ from fluorenone excimers,^{3,5} or from intrachain electronic bands produced by fluorenone defects in a PF chain.⁶ The complexity of interpreting results from bulk state polymeric emitters adds to the difficulty of evaluating results to date. Studies of well-defined structures have an advantage by examining properties of one type of structure.

Some of us have previously reported the promising performance of the blue-light-emitting luminophore OFPV in OLEDs.⁷ But when OFPV is hot-recrystallized or its OLEDs are heated to 150 °C in air, a substantial solid-state luminescence g-band results. This raised the issue of

* To whom correspondence should be addressed. E-mail: lahti@chem.umass.edu.

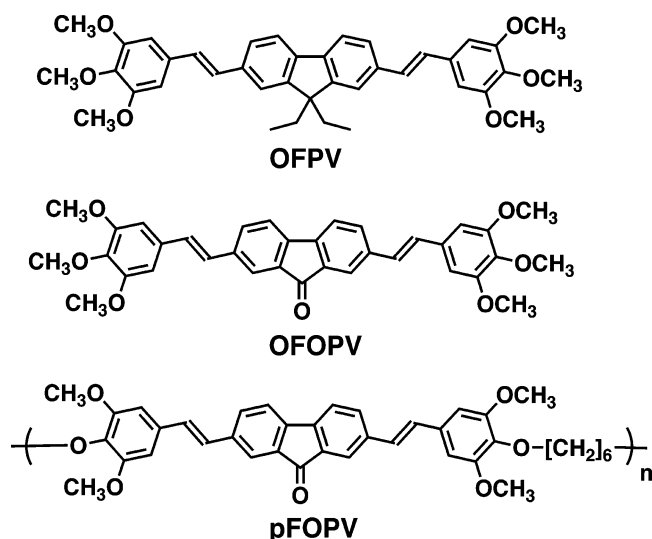
[†] Department of Chemistry.

[‡] Department of Polymer Science & Engineering.

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understanding the luminescence behavior of the fluorenone system OFOPV, a plausible product of 9-position oxidation of OFPV. In this article we report static photoluminescence studies of OFOPV and a copolymeric analogue with flexible polymethylene segments, pFOPV. The results show that monomeric fluorenones are the most likely cause of g-band emission by intermolecular energy transfer from blue-emitter OFPV, such that significant OLED g-band emission can be caused by <1% OFOPV in OFPV.



Experimental Section

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. Polymethylmethacrylate (MW = 15000) was obtained from Scientific Polymer Products. Zeonex was obtained from Zeon Chemicals LP.

2,7-Dibromofluorenone. To a mechanically stirred solution of 2,7-dibromofluorenone (1.0 g, 3.09 mmol) in 25 mL of acetic anhydride was added powdered CrO_3 (0.77 g, 7.72 mmol). The mixture was stirred for 5 h at room temperature and then poured into 2% aqueous HCl (40 mL). The resulted solid was collected by filtration and washed with cold water. The crude product was crystallized from 2-propanol to give 0.98 g of a yellow powder, yield 93%. mp 202–203 °C (lit.⁸ mp 201–203 °C). ^1H NMR (CDCl_3): δ 7.40 (d, 2 H, $J = 8.0$ Hz) 7.66 (dd, 2 H, $J = 1.6, 8.0$ Hz), 7.80 (d, 2 H, $J = 1.6$ Hz). IR (KBr, cm^{-1}): 1718 (C=O stretching).

2,7-Bis(3,4,5-trimethoxyphenylethenyl)fluorenone (OFOPV). To a three-necked round-bottom flask were added 660 mg (3.402 mmol) of 3,4,5-trimethoxystyrene,⁹ 500 mg (1.479 mmol) of 2,7-dibromofluorenone, tri-*o*-tolylphosphine (90 mg), and a catalytic amount of palladium acetate (11.0 mg). The flask was flushed with argon and 15 mL of dry *N,N*-dimethylformamide (DMF) was added. The solution was heated to 85 °C and stirred for 30 min. Triethylamine (8.98 g, 88.7 mmol) was added and heating continued at 85 °C for 3 days. The reaction was then cooled and poured into 10 mL of water, the mixture chilled with an ice bath, and 5 mL of 10% aqueous HCl added dropwise. The resultant yellow solid was vacuum-filtered, dissolved in chloroform, and filtered through Celite. The filtrate was concentrated in vacuo, precipitated by

addition to excess ethanol, collected with suction, and purified by crystallization from hot ethanol to yield 600 mg (72%) as a red-colored powder. mp 168–172 °C. UV-vis (chloroform) λ_{max} (nm)[$\log \epsilon$ ($\text{M}^{-1}\text{cm}^{-1}$)]: 314 (4.37), 375 (4.58), 475 (3.59). HR-MS (FAB) calcd for $\text{C}_{35}\text{H}_{32}\text{O}_7$ $m/z = 564.2148$, found $m/z = 564.2108$ (base peak). ^1H NMR (CDCl_3): δ 3.91 (s, 6 H), 3.96 (s, 12 H), 6.75 (s, 4 H), 7.04 (d, 2 H, $J = 16$ Hz), 7.12 (d, 2 H, $J = 16$ Hz), 7.50 (d, 2 H, $J = 8$ Hz), 7.57 (d, 2 H, $J = 8$ Hz), 7.86 (broadened s, 2 H). IR (KBr, cm^{-1}): 1718 (C=O stretching).

1,6-Bis[2,6-dimethoxy-4-formylphenoxy]hexane. This compound was made by a literature procedure¹⁰ from syringaldehyde and 1,6-dibromohexane in 62% yield. ^1H NMR (CDCl_3): δ 1.67–1.97 (m, 8 H), 3.98 (s, 12 H), 4.22 (m, 4 H), 7.40 (s, 4 H), 10.00 (s, 2 H).

1,6-Bis(2,6-dimethoxy-4-vinylphenoxy)hexane. This compound was made by a literature procedure¹⁰ from 1,6-bis(2,6-dimethoxy-4-formylphenoxy)hexane in 65% yield. ^1H NMR (CDCl_3): δ 1.50 (m, 4 H), 1.77 (m, 4 H), 3.85 (s, 12 H), 3.99 (t, 4 H, $J = 6.8$ Hz), 5.21 (d, 2 H, $J = 10.8$ Hz), 5.65 (d, 2 H, $J = 17.2$ Hz), 6.64 (overlapping s plus m, 6 H).

alt-Poly(2,6-dimethoxyphenylene-4-vinylene-[9-fluorenone-2-yl-7-vinylene]3,5-dimethoxyphenylene-4-[1,6-hexanedioxy]) (pFOPV). To a three-necked round-bottom flask were added 1,6-bis(2,6-dimethoxy-4-vinylphenoxy)hexane (150 mg, 0.339 mmol), 2,7-dibromofluorenone (172 mg, 0.508 mmol), tri-*o*-tolylphosphine (22.6 mg, 0.074 mmol), and a catalytic amount of palladium acetate (2.0 mg, 0.008 mmol) and flushed with argon, and 10 mL of dry DMF was added. The solution was heated to 100–120 °C and stirred for another 30 min. Triethylamine (200 mg, 1.976 mmol) was added, and then the reaction was heated at 100–120 °C for 2 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% aqueous HCl (10 mL). The resultant yellow solid was vacuum-filtered, dissolved in chloroform, and filtered through Celite to remove insoluble catalyst residues, and the filtrate was concentrated and reprecipitated into excess methanol. The solid was collected by filtration and dried under vacuum overnight to yield 2 as a red powder (100 mg, 58%). Elemental analysis showed no significant amount of Br in the product polymer. GPC of the material that is soluble in THF against polystyrene standards shows overlapping fractions with $\bar{M}_n \sim 3300$ (D.P. ~ 5) and $\bar{M}_n \sim 1000$; the latter is roughly a dyad. UV-vis (chloroform; λ (nm)[$\log \epsilon$ ($\text{cm}^{-1} \text{M}^{-1}$)]: 311 (4.68), 355 (4.71), 460 (3.55). ^1H NMR (CDCl_3): δ 1.57 (br m, 4 H), 1.82 (m, 4 H), 3.96 (s, 12 H), 4.01 (t, 4 H, 7 Hz), 6.72 (s, 4 H), 7.01 (d, 2 H, $J = 16$ Hz), 7.15 (d, 2 H, $J = 16$ Hz), 7.38 (d, 2 H, $J = 8$ Hz), 7.48 (d, 2 H, $J = 8$ Hz), 7.60 (m, 2 H), 7.85 (br s, 1 H). IR (KBr, cm^{-1}): 1722 (C=O stretching).

2,7-Bis(3,4,5-trimethoxyphenylethenyl)-9,9-diethylfluorenone (OFPV). This compound was made by a literature procedure^{7a} from 3,4,5-trimethoxystyrene and 2,7-dibromo-9,9-diethylfluorenone in 40% yield. mp 215–215.5 °C. UV-vis (chloroform; λ (nm)[$\log \epsilon$ ($\text{cm}^{-1} \text{M}^{-1}$)]: 384 (4.81). HR-MS (FAB) calculated for $\text{C}_{39}\text{H}_{42}\text{O}_6$, $m/z = 606.2981$, found $m/z = 606.2990$ (base peak). ^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).

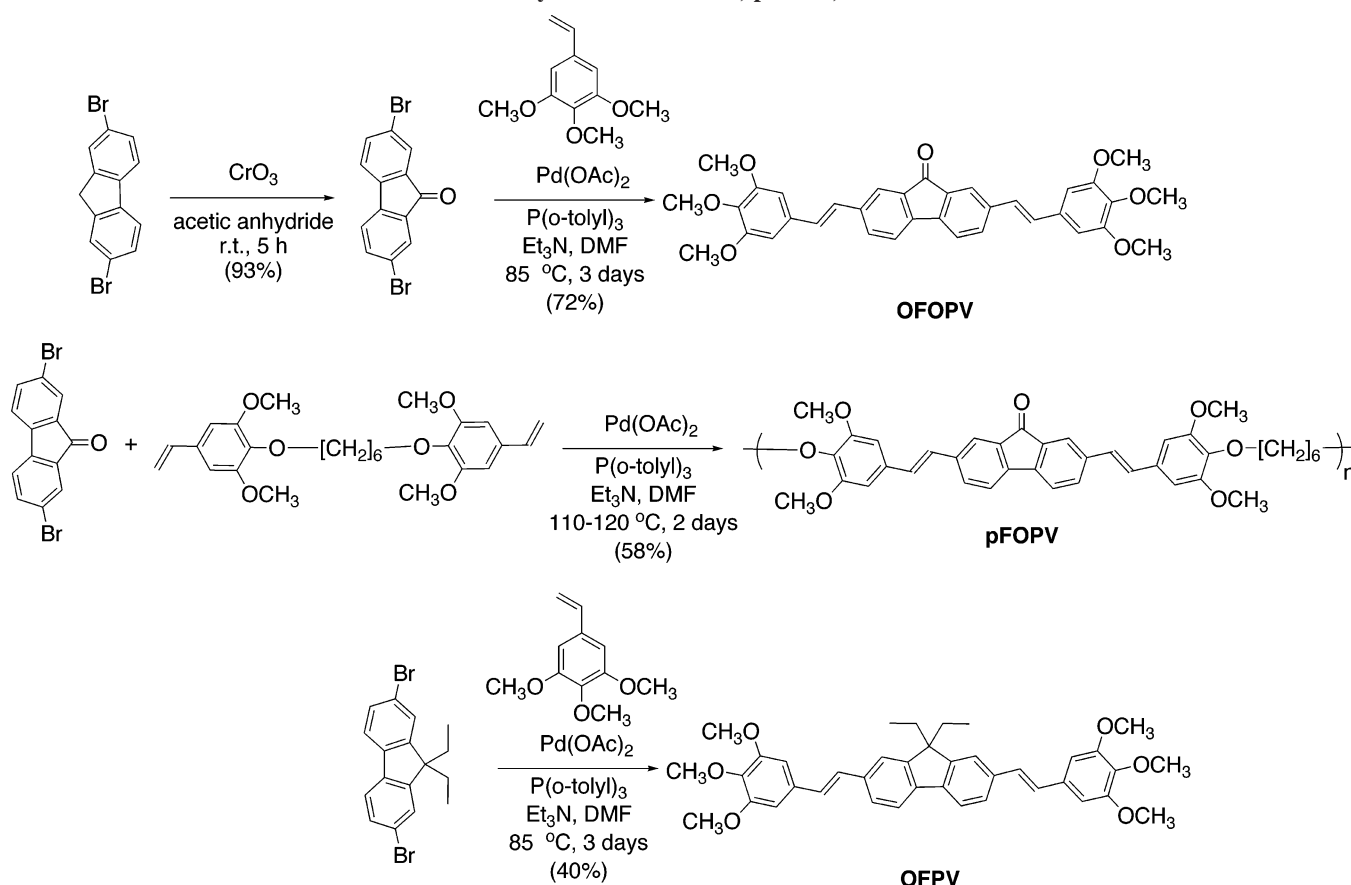
Single-Molecule Photoluminescence Spectroscopy. Single OFPV and OFOPV molecules were deposited from dilute dichloromethane solution (~ 0.1 nM) on clean glass coverslips. Photoexcitation sources were 457 nm radiation from a continuous wave Ar^+ laser, 405 nm from a diode laser, and 355 nm from the third

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Scheme 1. Synthesis of OFOPV, pFOPV, and OFPV



harmonic of a diode-pumped Nd⁺³ laser: typical powers were ~100 μ W and laser spot size of 15 μ m diameter. Fluorescence imaging and spectroscopic measurements were obtained using a Nikon TE300 inverted microscope with a 1.4 NA oil objective in a total internal reflectance (TIR) configuration. Fluorescence images were acquired with a Princeton Instruments PhotonMax CCD camera, with a typical exposure time of 1 s. Spectra were acquired by focusing the single-molecule emission from the side port of the microscope onto an Acton SP2150i dual-grating spectrograph and detected with a Roper Scientific Pixis 400B back-illuminated CCD. Further details are given elsewhere.¹¹

Results and Discussion

Synthesis and Characterization. OFOPV and pFOPV were synthesized by Pd(II)-catalyzed Heck coupling of 2,7-dibromofluorenone with 3,4,5-trimethoxystyrene and 1,6-bis-[2,6-dimethoxy-4-vinylphenoxy]hexane, respectively. OFPV was synthesized by the previously reported, analogous procedure of Rathnayake et al.^{7a} The methodology is summarized in Scheme 1. ¹H NMR and high-resolution mass spectrometry confirmed the structures of OFOPV and OFPV. The system ethenyl units are essentially all (*E,E*)-geometry, based on the lack of (*Z*)-stilbene type olefinic protons in the δ 6–7 range of the proton NMR spectrum, and the well-resolved *trans*-ethenyl =C–H doublets at δ 7.1–7.2 having J = 16 Hz.

¹H NMR also confirmed the structure of pFOPV, showing the fluorenone units and the α,ω -hexyldioxy flexibly units. The polymer is readily soluble in chloroform, from which film casting was straightforward; it is only partially soluble in tetrahydrofuran. During the Heck polymerization in dimethylformamide, the products remained in solution, though the reaction had to be run at significantly higher temperatures than the OFOPV reaction to give at least oligomeric material. Gel permeation chromatography (GPC) against polystyrene standards showed its degree of polymerization (D.P.) to be up to about five, consistent with its relatively narrow NMR peak line widths. The GPC also shows oligomers with D.P. ~2–3 in amounts that vary with the reaction conditions. The modest DP and polydispersity are not insupportable problems in these studies so long as the chromophores are essentially monodisperse, and the similarity of electronic spectra for pFOPV and OFOPV indicate that this condition is met.

Electronic Spectroscopy of Neat OFOPV and pFOPV.

Figure 1 shows solution UV–vis absorption spectra of OFOPV and pFOPV. The spectra are similar to one another, but the bands for the segmented oligomeric system are somewhat blue-shifted relative to the corresponding molecular spectra. The related segmented copolymer 3.5PV4PE also exhibits¹² a (smaller) absorption blue shift relative to the spectrum of its analogous molecular chromophore. The blue shifts in the segmented systems by comparison to the

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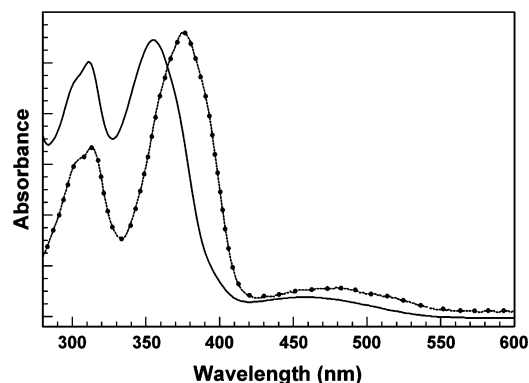


Figure 1. Absorption spectra in chloroform of OFOPV (broken line) and pFOPV (solid line).

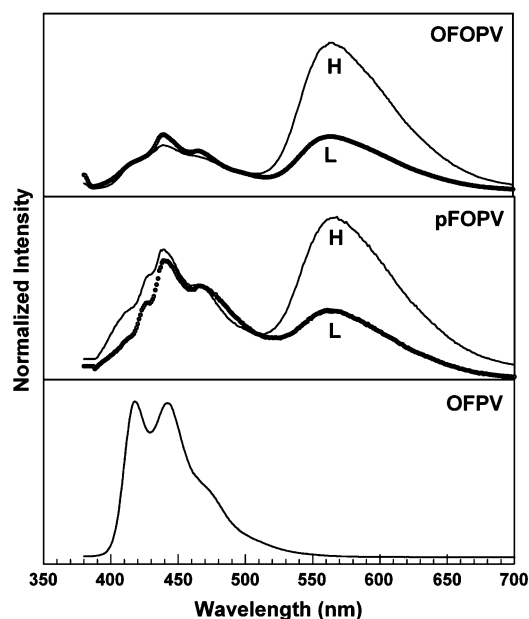


Figure 2. Photoluminescence spectra in chloroform of OFOPV, pFOPV, and OFPV (excitation at 360 nm). H = high concentration, L = low concentration, for OFOPV and pFOPV; these spectra are normalized on the high-energy band ordinate.

molecular systems may indicate π -system torsion due to the effect of the linker groups, but there is no other direct evidence for this at this time.

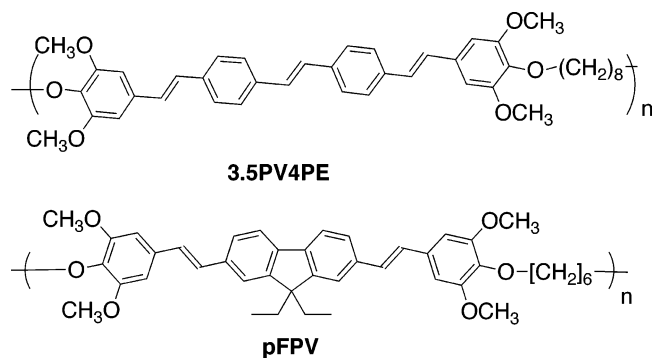


Figure 2 shows photoluminescence (PL) spectra for OFOPV and pFOPV compared to the spectrum⁷ of OFPV. The OFOPV and pFOPV PL spectra both show significant concentration dependence. In both, the featureless band at about 560–570 nm increases with increasing concentration at the expense of a shorter wavelength, fine-structured

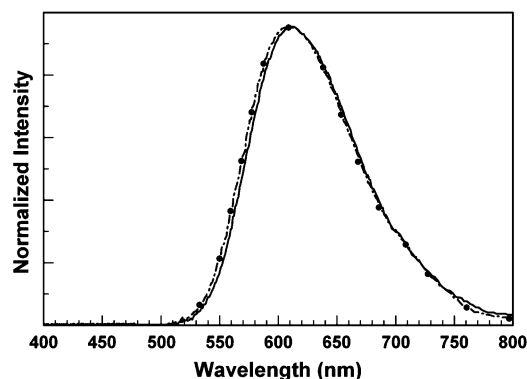


Figure 3. (a) EL spectra for OFOPV (dashed line) and pFOPV (dotted line) for OLED with configuration ITO/PEDOT:PSS/(emitter)/Ca(Al).

component at about 440 nm. By comparison, the fluorene OFPV and its segmented copolymeric analogue pFPV show no bands with excimeric behavior, but only a single monomeric (blue) emission band over 420–460 nm at various concentrations.^{7a} The OFOPV and pFOPV behaviors are consistent with excimer emission at higher concentrations. Simpler fluorenones exhibit monomeric PL in the 320–420 nm range, with excimer emission at wavelengths up to 600 nm.¹³

Figure 3 shows EL spectra and performance data for OLEDs made with a configuration ITO/PEDOT:PSS/(emitter)/Ca(Al) using neat OFOPV and pFOPV using a previously described⁷ fabrication procedure. Both spectra showed only a featureless maximum at about 610–620 nm, quite similar to the solid film PL spectra. The OLED turn-on voltages were 4 V for both; the maximum luminances were 0.019 and 0.059 cd/A, respectively.¹⁴ The CIE color coordinates¹⁵ for the OLEDs were red to red-orange (Table 1). Further details of the OLED electrical performance are given in the Supporting Information.

Electronic Spectroscopy of Bulk versus Diluted OFOPV and pFOPV. Figure 4 shows thin film PL spectra of neat OFOPV and pFOPV, as well as spectra of OFOPV diluted in PMMA. Both fluorenone systems show large peaks at ~610 nm, with only small peaks at ~460 nm. By comparison, fluorene OFPV shows only one emission envelope with a maximum at ~460 nm; segmented block copolymer pFPV has a similar spectrum red-shifted by ~20 nm and somewhat broadened.⁷

The PL band maxima of OFOPV and pFOPV as dilute films in PMMA are strongly blue-shifted by comparison to neat samples, exhibiting emission at ~540–570 nm; the maxima vary somewhat with concentration, as well as with means of making the film (spin casting versus drop casting). OFOPV samples blended into the polymer Zeonex also show

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Table 1. Summary of Photophysical Properties of OFOPV and pFOPV

	solution ^a UV-vis λ_{max} (nm)	solution ^a PL λ_{max} (nm)	film ^b PL λ_{max} (nm)	EL ^c λ_{max} (nm)	EL CIE coordinates ^d
OFOPV	314, 375, 475 (br, wk)	442*, 565*	430 (wk), 600*	610	0.501, 0.336
pFOPV	311, 355, 460 (br, wk)	443*, 570*	430 (wk), 600*	615	0.493, 0.334

^a Chloroform solution; br = broad, wk = weak, * = exhibits concentration-dependent relative intensities. ^b Neat film on quartz. ^c ITO/PEDOT:PSS/(emissive layer)/Ca–Al configuration. ^d Reference 15.

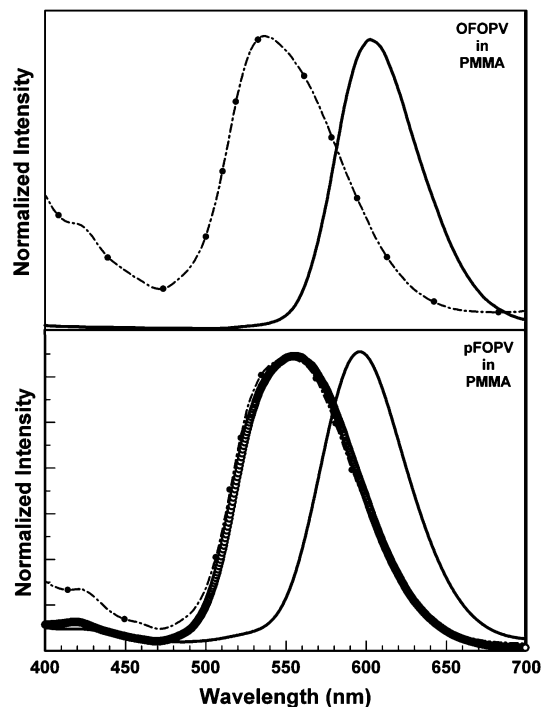


Figure 4. Photoluminescence spectra for solid film spectra of OFOPV (solid line is neat film, broken line is 25:75 (w/w) OFOPV/PMMA) and pFOPV (solid black line is neat film, broken line is 25:75 (w/w) OFOPV/PMMA, solid gray line is 15:85 (w/w) OFOPV/PMMA). Excitation at 360 nm.

strongly blue-shifted PL spectra relative to the neat film samples. These results show that aggregation has a significant effect on the emission. Films with >75% OFOPV show PL maxima nearing 600 nm, similar to the PL of the neat OFOPV films. Films with <25% OFOPV or pFOPV have PL maximum at about 540 nm, which we assign as the OFOPV monomer emission under these conditions. Also, single-molecule spectra of OFOPV deposited from high-dilution (subnanomolar) solutions onto glass using a literature microscopy procedure¹¹ show emission maxima at about the same position; example spectra from single-emitter sites under single-molecule conditions are shown in Figure 5. A histogram of the OFOPV single-molecule PL spectra has good overlap¹⁶ with the emission of OFOPV or pFOPV samples diluted in PMMA (see Supporting Information).

The red shift of the PMMA-diluted OFOPV and pFOPV solid film spectra, by comparison to the monomer bands in the dilute solution spectra of Figure 2, shows that the emission energies of these systems are sensitive to local environment (e.g., solution versus deposition on glass). This is reasonable, given the polar nature of fluorenone emitters.¹⁷ So the shorter wavelength solid-state emission bands at 540–

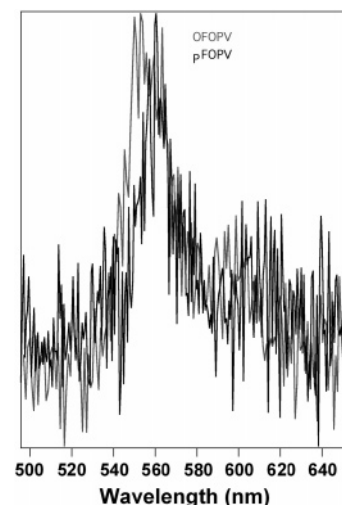


Figure 5. Single-molecule photoluminescence spectra for OFOPV (gray) and pFOPV (black).

570 nm seen in dilute OFOPV and pFOPV are attributable to monomer emission, which is supported by the single-molecule spectral results.

The longer wavelength, red emission in neat OFOPV and pFOPV systems is much lower in energy than the OFPV-derived g-type bands. The observation of solution-phase excimer emission in OFOPV and pFOPV suggests that this red band could also arise from excimers, with the emission position shifted relative to solution by solid-state local environmental differences. OFOPV and pFOPV solid-phase excimers are far more likely to form in neat films than in diluted films, which is consistent with the red emission being observed in neat solids. From this analysis, solid-phase fluorenone-type excimer emission occurs at too low an energy to be the source of 550–560 nm green-band emission in thermally stressed OFPV-based OLEDs.

However, the single-molecule PL emission and the diluted solid film emission of OFOPV and pFOPV are reasonable matches for the green band from OFPV. Since FTIR spectra showed no carbonyl band in intentionally heated OFPV-based OLEDs,^{7a} any OFOPV impurity generated from oxidation of OFPV must have been present in small amounts. With the presumed oxidative impurity molecule actually in hand, the amount of OFOPV needed to give observable g-band emission in OFPV could be directly tested by admixture.

Figure 6 shows thin film PL spectra for OFPV:OFOPV mixtures spin-cast from chloroform onto quartz, as well as

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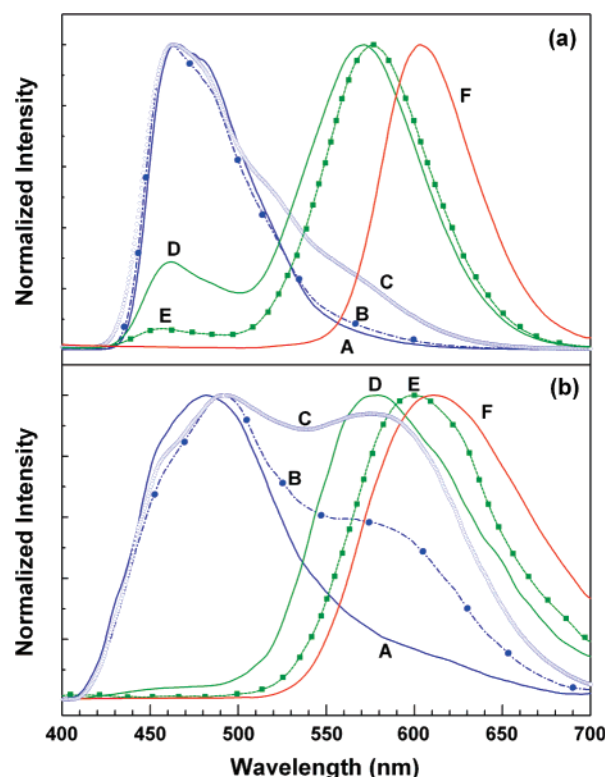


Figure 6. Thin film photoluminescence (a) and electroluminescence (b) spectra for OFPV:OFOPV blends (w/w %): A = 99.9:0.1, B = 99.5:0.5, C = 99:1, D = 90:10, E = 80:20, F = 0:100. PL excitation at 360 nm. EL spectra from ITO/PEDOT:PSS/blend/Ca(Al) OLED configuration.

the electroluminescence (EL) spectra for OLEDs made from the mixtures with the configuration ITO/PEDOT:PSS/OFPV:OFOPV/Ca(Al). For 100% OFPV, the expected blue emission band is produced at 480–490 nm in both PL and EL spectra. As OFOPV is added, a shoulder appears in the g-band region of the EL spectrum with only 0.5% (w/w), and in the PL spectrum with 1%. By a 10% addition of OFOPV, the longer wavelength band dominates both PL and EL spectra.

The OFOPV/OFPV blend PL and EL spectra give good matches to the luminescence of OFPV that has g-band impurities in it. Since diluted OFOPV in PMMA, OFOPV single-molecule PL sites, and dilute OFOPV in OFPV all show emission in the OFPV g-band region, *monomeric* fluorenone-containing species appear to be responsible for the OFPV g-bands. These emission bands are also similar to the green emission of a molecular fluorene–fluorenone–fluorene triad system reported^{4b} by Kulkarni et al. However, the present results are an extrapolation from various previous studies where fluorenone units are incorporated into a PF polymer chain to mimic oxidative defects. Although easy

energy transfer from OFPV excitons to lower energy OFOPV sites is important to give OFPV g-bands, *intramolecular* linkage is not required between fluorene and fluorenone units to give g-band region emission here. Rather, *intermolecular* energy transfer appears to happen quite readily, especially in the OFPV/OFOPV blends.

Conclusions

The present study establishes a quantitative limit on the amount of oxidative defect that is tolerable in an OFPV-based blue OLED, before g-band onset is readily visible: <0.5% (w/w). This level of sensitivity is comparable with results obtained by Zhou et al. for fluorenone units directly incorporated as part of well-defined PF oligomers.^{6a} Notably, our results show that fluorenones need not be covalently bonded to fluorene derivatives to give g-bands, but merely blended or cocrystallized with the fluorenes in small amounts.

While the findings of this study need not directly apply to all fluorene-related OLED g-bands, they show that green-emission bands in OFPV are attributable to monomeric oxidation product OFOPV since aggregate and bulk-phase emission from the same OFOPV is red and distinctly different. The quantitatively small amounts of OFOPV additive in bulk OFPV that give detectable green emission show the strong effect on luminescence of quite a low level of oxidized fluorenone sites in a fluorene-based blue emitter. This is consistent with mechanistic proposals¹⁸ that oxidation can produce fluorenones from quite small amounts of incompletely functionalized 9,9-dialkyl-substituted fluorenes. Given the small amount of fluorenone OFOPV needed to produce g-bands even in a case when it is not directly bonded to a fluorene or PF chain, caution should be exercised in ascribing any single cause or mechanism to the many cases of observed g-band emission.

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Supporting Information Available: Experimental general methods; performance data for OFOPV and pFOPV OLEDs; ¹H NMR spectra for OFOPV and pFOPV; comparison of thin film PL spectra of OFOPV under varying conditions; single-molecule spectral peak position histogram. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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