

Stabilization of Semiconducting Polymers with Silsesquioxane**

By Steven Xiao, My Nguyen, Xiong Gong, Yong Cao, Hongbin Wu, Daniel Moses, and Alan J. Heeger*

Polyhedral oligomeric silsesquioxanes (POSS) anchored to poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) (MEH-PPV-POSS), and to poly(9,9-dihexylfluorenyl-2,7-diyl) (PFO) (PFO-POSS) were synthesized. Compared with the corresponding parent polymers, MEH-PPV and PFO, MEH-PPV-POSS and PFO-POSS have better thermal stability. MEH-PPV-POSS and MEH-PPV have identical absorption and photoluminescent (PL) spectra, both in solution and as thin films. They also have identical electroluminescent (EL) spectra. Devices made from MEH-PPV-POSS exhibit higher brightness (1320 cd m^{-2} at 3.5 V) and higher external quantum efficiency ($\eta_{\text{ext}} = 2.2 \%$ photons per electron) compared to MEH-PPV (230 cd m^{-2} at 3.5 V and $\eta_{\text{ext}} = 1.5 \%$ photons per electron). Compared with PFO in the same device configuration, PFO-POSS has improved blue EL emission and higher η_{ext} .

1. Introduction

Semiconducting polymers have received much attention both in academic research and industrial development as materials with a unique combination of properties.^[1] They are promising materials for use in electroluminescent displays,^[2,3] solar cells,^[4] sensors,^[5,6] thin-film organic transistors,^[7] lasers^[8] and light-emitting electrochemical cells.^[9] However, the stability of these materials under operating conditions needs improvement if they are to be widely used in real products. Although there are many possible sources of material degradation (e.g., impurities and electrochemically induced side reactions), polymer interchain interactions and the associated formation of aggregates, excimers, and polaron pairs,^[10] are known sources of degradation of polymer-based devices.^[11]

Many approaches have been used in attempts to improve the stability of semiconducting polymers.^[12–16] Device performance can be improved by increasing the polymer molecular weight and narrowing the molecular weight dispersity (shorter polymer chains are thought less stable than longer chains).^[11] Introduction of structural asymmetry was introduced in order to limit the ability of chains to pack effectively in the solid state. For example, Son et al.^[17] engineered the distribution of *cis*

linkages in poly(phenylenevinylene) chains; the *cis* linkages interrupt conjugation and interfere with the packing order of the polymer chains. Pang et al.^[18] introduced a meta-linkage in the conjugated polymer chain. The meta-linkage simultaneously interrupts the conjugation of the π -conjugated polymer (reduces the conjugation length), and allows the polymer to bend and twist more effectively than the *para* linkage. Another approach to suppress long wavelength emission is to end-cap polyfluorenes with a bulky group,^[15,19] a crosslinkable moiety^[20] or a charge-transporting moiety.^[12] However, end-capping of conjugated polymers with inorganic groups has not been previously explored.

It is known that hybrid organic–inorganic polymers containing segments of polyhedral oligomeric silsesquioxanes (POSS) exhibit a number of potentially useful properties, including high thermal stability in air and good adhesion to a number of substrates.^[21] These materials are resistant to oxidation and degradation by ultraviolet light. They have been used as protective coatings for electronic devices and other substrates, and as precursors for ceramic coatings, foams, fibers, and other articles.

Semiconducting polymers must be as pure as possible for use in semiconductor device applications. Consequently, the introduction of a non-conjugated species into semiconducting polymers is not an obviously useful approach. Nevertheless, in this paper, we demonstrate semiconducting polymers with improved thermal stability, reduced chain mobility, and a decrease in the electroluminescent spectral features associated with excimer formation, by chemically incorporating bulky substitutes, such as polyhedral oligomeric silsesquioxanes (POSS), into the conjugated polymer chain. High external quantum efficiency and luminance were achieved from the light-emitting diodes made from this new class of semiconducting polymers. Two examples are explored in detail in order to demonstrate the potential advantages of this approach. They are POSS-anchored poly(2-methoxy-5-(ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) (MEH-PPV-POSS) and POSS-anchored poly(9,9-dihexylfluorenyl-2,7-diyl) (PFO) (see Scheme 1).

[*] Prof. A. J. Heeger, Dr. X. Gong, Dr. D. Moses
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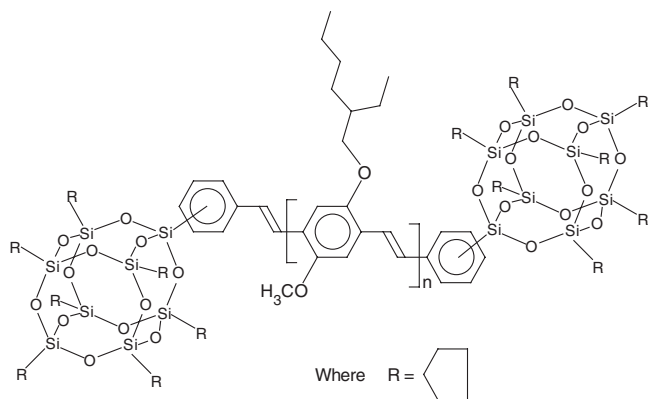
Institute for Polymers and Organic Solids
University of California at Santa Barbara
CA 93106 (USA)

E-mail: ajh@physics.ucsb.edu

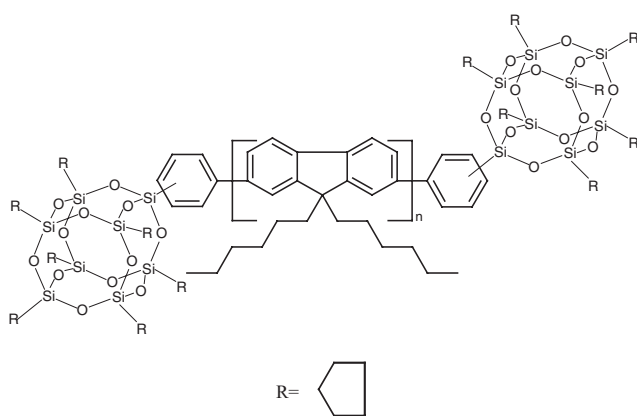
Dr. S. Xiao, Dr. M. Nguyen
American Dye Source Inc, Baie d'Urfe
Quebec, H9X 3T6 (Canada)

Dr. Y. Cao, H. Wu
College of Materials Science, South China University of Technology
Guangzhou, 510640 (China)

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(a) MEH-PPV-POSS



(b) PFO-POSS

Scheme 1. Molecular structures of a) MEH-PPV-POSS, and b) PFO-POSS.

2. Characterization of Polymers

Figure 1 shows the molecular weight and molecular-weight dispersion investigated by gel permeation chromatography (GPC). Similar molecular weight and molecular weight distri-

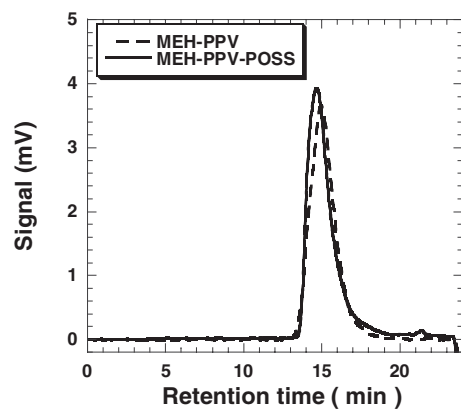


Fig. 1. Gel permeation chromatography (GPC) profile of MEH-PPV-POSS and MEH-PPV.

bution were observed for both MEH-PPV-POSS and MEH-PPV. Using polystyrenes as the standards, the MEH-PPV-POSS and MEH-PPV molecular weights are approximately, $M_w = 3.5 \times 10^5$ and $M_w = 1.2 \times 10^5$. Although the use of polystyrene as standard might cause the molecular weight of conjugated polymer to be overestimated,^[22,23] the GPC data indicate a molecular weight of approximately 10^5 .

The POSS unit contains eight Si atoms, each with one bond to an organic “antenna” group. Of these eight antennas, seven are cyclopentane, and one is functionalized with chlorophenyl and thus able to chemically bond to the conjugated MEH-PPV chain during polymerization. Since the POSS unit used in the synthesis has only one reactive functional group, POSS can only be incorporated into the polymer as an end-capper, as shown in Scheme 1a.

The silicon content in MEH-PPV-POSS was 0.09 % (w/w) as determined by atomic absorption. Assuming the structure shown in Scheme 1a, with a total of 16 Si atoms in the two POSS end groups, the implied molecular weight of the MEH-PPV chain is 5×10^5 . If the polymer chains had POSS units as end-caps on only one end, the implied molecular weight would be 2.5×10^5 . Thus, the Si content implies a molecular weight that is consistent with the molecular weight estimated from the GPC data, and with the proposed end-capped structure. Furthermore, the molecular structure of MEH-PPV and the MEH-PPV portion of MEH-PPV-POSS were confirmed by NMR and FTIR spectroscopy. Thus, the introduction of silsesquioxane segments as end-cappers during the polymerization has no significant effect on the polymerization mechanism. On average, there are approximately 2000 MEH-PPV repeat units in the MEH-PPV-POSS chain.

In the PFO-POSS synthesis, the POSS unit is functionalized with chlorophenyl, and thus able to chemically bond to the conjugated PFO chain during polymerization. Again, since the POSS unit used in the synthesis has only one reactive functional group, POSS can only be incorporated into the polymer as an end-capper, as shown in Scheme 1b. The silicon content in PFO-POSS was 0.27 % (w/w), as determined by atomic absorption. Assuming the structure shown in Scheme 1b, with a total of 16 Si atoms in the two POSS end groups, the implied molecular weight of the PFO chain is estimated to be 1.6×10^5 , consistent with the proposed end-capped structure. Thus, on average, there are approximately 500 PFO repeat units in the PFO-POSS chain. The molecular structure of PFO and the PFO portion of PFO-POSS were confirmed by NMR and FTIR.

Figure 2 presents the UV-vis absorption and photoluminescence (PL) spectra of MEH-PPV-POSS and MEH-PPV in solution and as thin films. Identical absorption and PL spectra are observed for both polymers, either in solution form or as solid thin films. Thus, the introduction of the silsesquioxane segment has no significant effect on the electronic structure of MEH-PPV.

Nevertheless, as shown in Figures 3a and b, significant improvement in thermal stability was observed from the polymers with silsesquioxane segments in the polymer (as end-caps) compared with the polymers which do not have the silsesquiox-

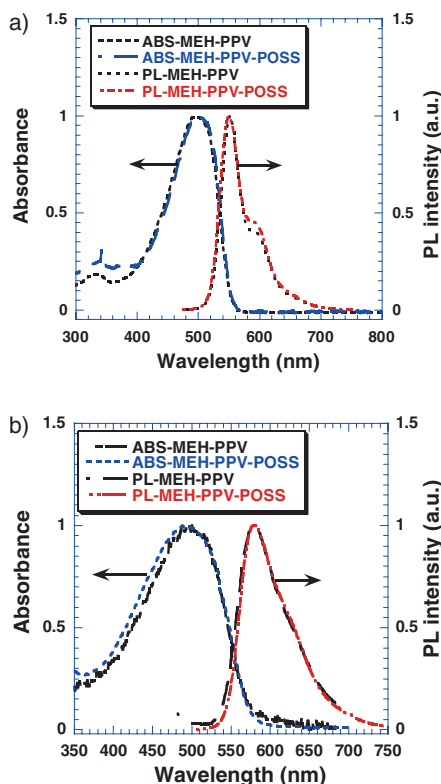


Fig. 2. a) The absorption and photoluminescence (PL) spectra of MEH-PPV-POSS and MEH-PPV in solution. b) The absorption and PL spectra of MEH-PPV-POSS and MEH-PPV thin films.

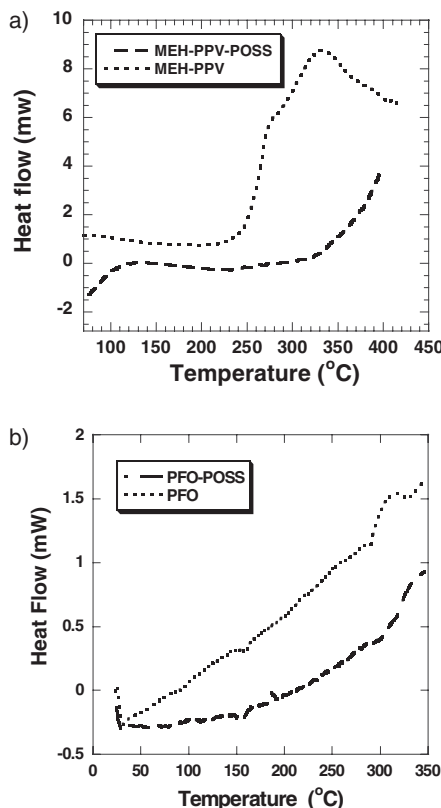


Fig. 3. Differential scanning calorimetry (DSC) profiles: a) MEH-PPV-POSS and MEH-PPV, and b) PFO-POSS and PFO.

ane end-caps. For MEH-PPV, decomposition starts at 200–250 °C, while MEH-PPV-POSS is stable at temperatures above 300 °C. Similarly for PFO, decomposition starts at 270 °C, while PFO-POSS is stable up to 320 °C.

In addition, it was observed that the polymers with silsesquioxane segments have higher solubility in common organic solvents. For example, clear solutions of MEH-PPV-POSS can be made with the solvent tetrahydrofuran (THF) at concentrations greater than 1 % (w/v), whereas MEH-PPV forms a gel even at concentrations less than 0.7 % (w/v).

3. Light-Emitting Diodes (LEDs) from POSS-Polymers

The electroluminescence (EL) spectra of LEDs made from MEH-PPV and MEH-PPV-POSS are shown in Figure 4. The two materials yield identical EL spectra.

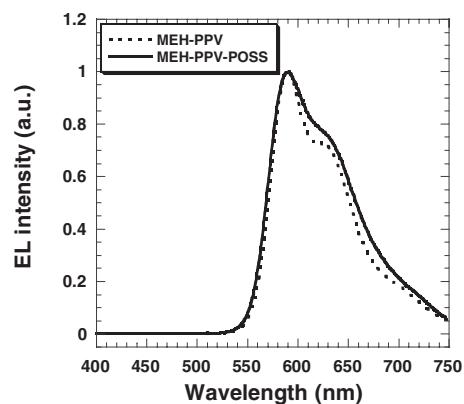


Fig. 4. Electroluminescence spectra of devices made from MEH-PPV-POSS and MEH-PPV with the following device configuration: ITO/PEDOT/polymers/Ca/Ag.

Figure 5 compares the current density vs. voltage, and luminance vs. voltage curves for devices made from MEH-PPV and MEH-PPV-POSS. Although both devices turn on at approximately 2 volts, the devices made from MEH-PPV-POSS exhibit much higher luminance. For example, at 100 mA cm⁻²,

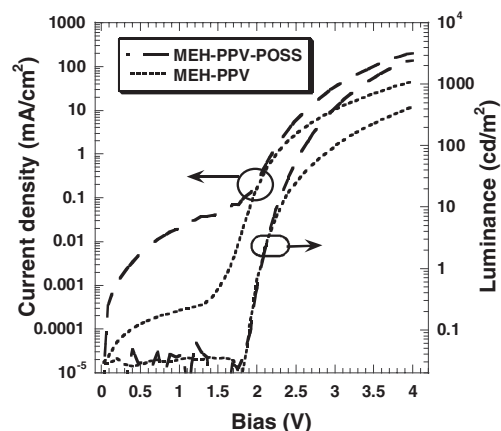


Fig. 5. Current density vs. voltage and luminance vs. voltage curves for the devices made from MEH-PPV-POSS and MEH-PPV.

the luminance is over 1320 cd m^{-2} , whereas at the same current density, the luminance of the MEH-PPV devices is only 230 cd m^{-2} . Note that for MEH-PPV-POSS, both current density and the luminance are higher than in MEH-PPV. Nevertheless, devices made from MEH-PPV-POSS have higher external quantum efficiency ($\eta_{\text{ext}} = 2.2 \% \text{ ph e}^{-1}$) than identical devices made from MEH-PPV ($\eta_{\text{ext}} = 1.5 \% \text{ ph e}^{-1}$).

Compared with devices made from MEH-PPV, the devices made from MEH-PPV-POSS have higher current density and luminance implying better injection and/or transport of charge carriers. This might be due (at least in part) to improved adhesion to the indium tin oxide (ITO)-glass substrate,^[21] which is an important requirement for electronic devices. Bao et al.,^[24] reported that silsesquioxane resins formed pinhole-free thin films; much better than those, for example, of poly(3-hexylthiophene) cast from a chloroform solution. The improved injection and/or transport is consistent with the higher film quality of the polymer-POSS films observed by visual inspection.

Identical absorption and PL spectra were also obtained from PFO-POSS and PFO, both in solution and as solid thin films. Figure 6 presents the EL spectra of the devices made from PFO-POSS and PFO with the same device configuration. As is

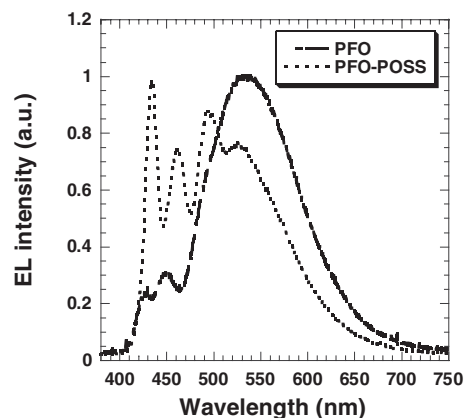


Fig. 6. Electroluminescence spectra of the devices made from PFO-POSS and PFO with the following device configuration: ITO/PEDOT/polymers/Ca/Ag.

typical of polyfluorene, the large peak centered at 525 nm in EL spectra gives the emission the undesired blue-green emission appearance.^[12,25,26] However, the contribution from the 525 nm peak is much reduced in PFO-POSS, with correspondingly improved blue EL compared to that of PFO. The reduced 525 nm peak in PFO-POSS might result from reduced formation of aggregates/excimers, or from a lower concentration of fluorenone defects.^[27-29] The current density-voltage and luminance-voltage characteristics of the devices made from both PFO and PFO-POSS are shown in Figure 7. Again, devices made from PFO-POSS exhibit significantly higher brightness compared with those made from PFO. Moreover, higher external efficiencies were obtained from the PFO-POSS devices. For example, at current density of 0.12 mA cm^{-2} , η_{ext} for the PFO-POSS device is $0.52 \% \text{ ph e}^{-1}$, while η_{ext} is $0.38 \% \text{ ph e}^{-1}$ for the device made from PFO.

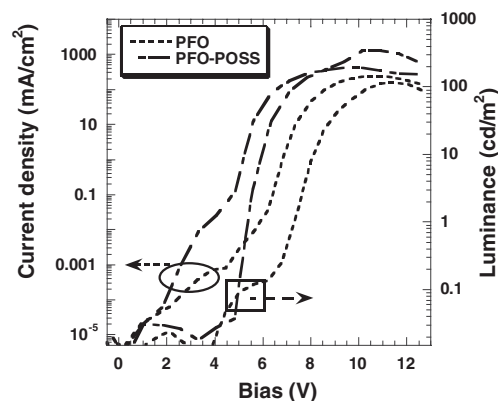


Fig. 7. Current density vs. voltage and luminance vs. voltage curves of the devices made from PFO-POSS and PFO.

4. Conclusions

We have synthesized the POSS-anchored semiconducting polymers, MEH-PPV-POSS and PFO-POSS. Compared with the corresponding parent polymers; MEH-PPV and PFO, MEH-PPV-POSS and PFO-POSS have higher thermal stability. MEH-PPV-POSS and MEH-PPV have identical absorption and photoluminescent (PL) spectra either in solution or as thin films. They also have identical electroluminescence (EL) spectra. Devices made from MEH-PPV-POSS exhibit higher brightness (1320 cd m^{-2} at 3.5 V) and higher external quantum efficiency ($\eta_{\text{ext}} = 2.2 \% \text{ ph e}^{-1}$) than MEH-PPV (230 cd m^{-2} at 3.5 V and $\eta_{\text{ext}} = 1.5 \% \text{ ph e}^{-1}$). Compared with PFO in the same device configuration, PFO-POSS has improved blue EL emission and higher η_{ext} . These results indicate that the class of POSS containing semiconductor polymers offer promise for improved performance in semiconductor device applications.

5. Experimental

Synthesis of Polymer MEH-PPV-POSS: 1.50 g of 1-[2-(chlorobenzyl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (4-chlorobenzyl-cyclopentyl-POSS) (Hybrid Plastics, California) and 4.5 g of 2-methoxy-5-(2'-ethylhexyloxy)-1,4-bis(chloromethyl)benzene (available from American Dye Source, Inc.) were dissolved in 400 mL of tetrahydrofuran, and then added quickly to a solution containing 750 mL of tetrahydrofuran and 15.0 g of potassium *tert*-butoxide in the three-neck reaction flask. The resulting orange-red viscous solution was stirred overnight, and then poured into 2000 mL of methanol. The precipitated red solid was collected by filtration, washed with methanol, and air dried to provide 2.07 g of soluble polymer. Spectroscopic analysis of the product was consistent with the resulting polymer having the structure shown in Scheme 1.

Synthesis of Polymer MEH-PPV: MEH-PPV was prepared in the same procedure as for preparation of MEH-PPV-POSS, but without adding 4-chlorobenzyl-cyclopentyl-POSS [30].

Synthesis of Polymer PFO-POSS: A dried three-neck round-bottom flask (500 mL) was flushed with nitrogen for 30 min. In this flask, 75 mL of anhydrous dimethylformamide (DMF), 5.0 g of 2,2'-dipyridyl (Aldrich Chemicals), 7.5 g of cyclooctadiene (Aldrich Chemicals) and 10 g of bis(1,5-cyclooctadiene)nickel(0) (Aldrich Chemicals) were quickly added. The mixture was heated to 80°C for 20 min, and a bright-purple solution was observed. 100 mL of

deoxygenated toluene containing 8.5 g of 9,9-dioctyl-2,7-dibromofluorene (American Dye Source, Inc.) was added quickly into this purple solution. After stirring 48 h at 80 °C, a 0.5 g of 1-[chlorophenyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (also called chlorophenyl-cyclopentyl-POSS, Hybrid Plastics, California) was added. The mixture was then stirred for 48 h at 80 °C. At room temperature, the reaction mixture was poured into 1000 mL of HCl, 1000 mL of acetone, and 1000 mL of methanol, and then stirred for 2 h. The solid was filtered out, redissolved in chloroform, and precipitated in methanol. The pale-yellow fiber-like product was dried in vacuum at 60 °C for 48 h, and yielded 4.8 g of the final product. Spectroscopic analysis demonstrated that the product has the structure in formula shown in Scheme 1.

Synthesis of Polymer PFO: PFO was prepared in the same procedure as for preparation of PFO-POSS, but replacing chlorophenyl-cyclopentyl-POSS with 9,9-dioctyl-2-bromofluorene [31].

Device Fabrication: The polymeric light-emitting diodes were fabricated as follows: a 40 nm-thick layer of poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) was spin-cast (at 4000 rpm) onto pre-cleaned ITO-glass substrates. The PEDOT:PSS was used to form a hole-injecting bilayer electrode (and to improve substrate smoothness). Next, the polymers (MEH-PPV, PFO, MEH-PPV-POSS and PFO-POSS) were spin-cast at room temperature under ambient conditions from solution to form thin films. Prior to spin-casting, each solution was filtered to remove aggregates and inhomogeneities. The solvent was thoroughly removed by subsequently baking the samples on a hot plate. The Ca cathode (50 nm thick) was then deposited through a shadow mask at a chamber base pressure of $<10^{-6}$ torr. Finally, a 100 nm-thick Ag capping layer was deposited onto the Ca layer. Layer thicknesses were determined using a crystal thickness monitor and a Dektak IIA profilometer for the evaporated and spin-cast films, respectively.

Characterization and Device Testing: The synthesized polymers were analyzed using an FTIR Spectrophotometer (Perkin-Elmer, Model 1760), and an NMR spectrometer (300 MHz, Perkin Elmer). The glass transition and melting temperature of the products were determined by differential scanning calorimetry (Instrument Specialist Incorporated, Model DSC 550). The average molecular weight was determined by gel permeation chromatography (Waters Breeze) using tetrahydrofuran as solvent and polystyrene standards.

Device fabrication and testing were carried out in a controlled atmosphere dry-box in N₂ atmosphere at room temperature. Current density–voltage–luminance (j–V–L) measurements were obtained using a Keithley 236 source measurement unit and a calibrated silicon photodiode (computer interfaced with LabView supplied by National Instruments). Electroluminescence (EL) spectra were recorded with a single-grating monochromator equipped with a photometric charge coupled device (CCD) camera as detector.

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