Macromolecules **1997,** *30,* 3553−3559

Electroluminescence from New Polynorbornenes That Contain Blue-Light-Emitting and Charge-Transport Side Chains

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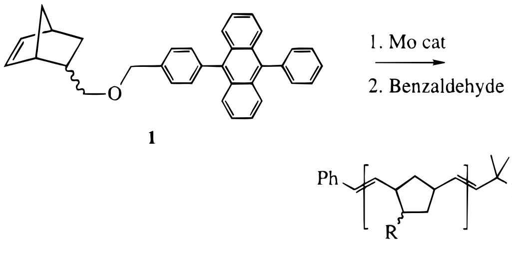
Received October 30, 1996; Revised Manuscript Received April 9, 1997[⊗]

ABSTRACT: A blue-light-emitting electroluminescent polymer was prepared by ring-opening metathesis polymerization (ROMP) of a norbornene monomer that contains a diphenylanthracene chromophore as a side chain ($\lambda_{\mathrm{max,em}} = 450$ nm). Norbornene monomers also were synthesized that contain an oxadiazole (for electron transport) or a tertiary arylamine (for hole transport). Oligomers (25mers or 50mers) of homo- and copolymers ($M_w/M_n = 1.02-1.08$) were prepared in toluene in 95−98% yield, employing $\mathrm{Mo(N\text{-}2,6\text{-}C_6H_3\text{-}}i\text{-}\mathrm{Pr_2)(CHMe_2Ph)(O\text{-}}t\text{-}\mathrm{Bu)_2}$ as the initiator. Electroluminescent devices made with a single layer of substituted polynorbornene, an ITO anode, and an Al cathode were prepared first. Two-layer devices were then constructed in which the substituted polynorbornene was spin cast onto a 25-bilayer poly(phenylenevinylene) (PPV) heterostructure. The two-layer device performed best in terms of efficiency, light output, and threshold voltage.

Introduction

Interest in polymer-based electroluminescent (EL) devices has increased substantially since stable, high-efficiency devices were constructed from a polymeric poly(phenylenevinylene) (PPV) precursor.[1] Polymer-based materials are more attractive than solid-state inorganic materials or organic small molecules in EL devices, especially devices with a large surface area, since polymers can be processed more easily. Therefore, a considerable body of work now has been published on EL of conjugated polymer systems, such as PPV, poly(*p*-phenylene) (PPP), and poly(thiophene).[2−9] Relatively rare blue-light-emitting polymers based on phenylenevinylene (PV) systems, with PV either as a side chain or part of the polymer backbone,[5,10−12] have been reported. Among these is a blue-light electroluminescent polynorbornene that contains a pendant PV trimer.[11] Polymers that contain pendant chromophores have not been studied nearly as widely in EL devices. The generally high threshold voltages (15−25 V) and low light emission levels in the few such systems that have been made so far have not made them attractive compared to materials prepared by more traditional approaches.[5,11,13]

In this paper we focus first on the incorporation of electrochemically stable diphenylanthracene (DPA), a blue-light-emitting molecule widely used in chemiluminescence,[14−16] into norbornene-based monomers, and polymerization of those monomers via ring-opening metathesis polymerization (ROMP) using a commercially available, well-defined initiator, $\mathrm{Mo(N\text{-}2,6\text{-}C_6H_3\text{-}}i\text{-}\mathrm{Pr_2)(CHMe_2Ph)(O\text{-}}t\text{-}\mathrm{Bu)_2}$ ([Mo]).[11,17,18] [Mo] reacts with a wide variety of functionalized, readily prepared norbornenes or norbornadienes to give polymers in a controlled (living) manner,[19−21] the polymerization being terminated in a Wittig-like reaction by adding benzaldehyde. Norbornene monomers that contain a variety of pendant groups[18,22] have been prepared from exo/endo-4-substituted-norbornene (e.g., exo/endo-4-(hydroxymethyl)norbornene). Polymers prepared by ROMP of exo/endo-4-substituted-norbornenes are amorphous since the polymer contains both exo and endo substituents, cis and trans double bonds, and head to tail, tail to tail, and head to head monomer relationships in the polymer backbone. Diphenylanthracene (DPA), either as a vacuum-deposited film or in a polymer matrix, has not been pursued as an emitter in EL devices, mainly due to DPA's poor film-forming qualities.[23] In amorphous films made by ROMP of **1** (eq 1), diphenylanthracene should not be able to migrate readily to form crystalline regimes.



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(1)

R = $\mathrm{CH_2OCH_2(DPA)}$

We also have prepared and polymerized related monomers that contain a hole-transporting group (a tertiary arylamine) or an electron-transporting group (*tert*-butylphenyl)-*p*-biphenylyloxadiazole or PBD). Copolymers incorporating both carrier transport and DPA structural units also have been prepared. Tertiary arylamines are used often for hole transport,[24−26] while PBD is widely used as an electron carrier or to "block" holes. The importance of carrier transport has been demonstrated many times in the literature. PBD crystallizes readily, making it unsuitable unless blended into a polymer matrix. However, PBD bound to polymerized norbornene should be unable to separate and crystallize.

Results

The blue-light-emitting monomer, **1**, was prepared in an overall yield of 21% following the route shown in Scheme 1. This approach should be a general method for attaching aromatic systems to a norbornene, and indeed, norbornenes that contain *p*-biphenyl and *p*-

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S0024-9297(96)01613-0 CCC: $14.00

Scheme 1

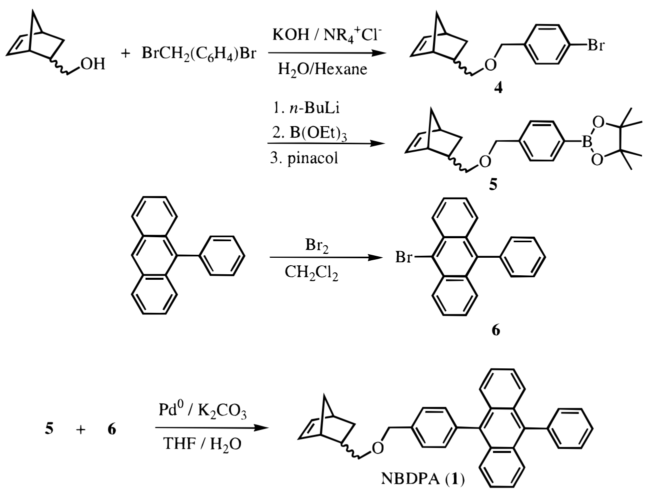


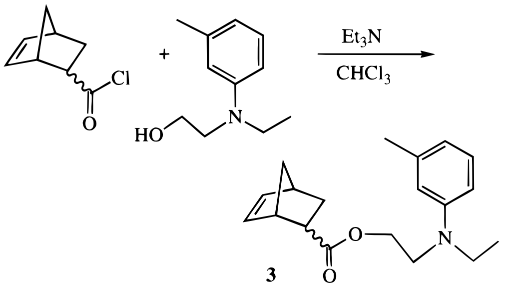
Table 1. Substituted Homopolymers and Copolymers

polymer	yield (%)	mol wt (calc)	M_n[a]	M_w/M_n
$\mathbf{1}_{25}$	95	12 800	19 400	1.04 ± 0.11
$\mathbf{2}_{50}$	97	24 700	53 800	1.05 ± 0.08
$\mathbf{(1/2)}_{50}$[b]	94	24 100	36 800	1.02 ± 0.06
$\mathbf{(1/3)}_{50}$[b]	98	19 300	23 800	1.08 ± 0.11

[a] All molecular weights were determined by GPC in CH_2Cl_2. [b] A mixture containing 25 equiv of each monomer was employed to prepare the copolymer.

terphenyl have also been synthesized in this manner.[27] The absorption and emission properties of **1** were similar to 9,10-diphenylanthracene itself:[28] $\lambda_{max,ab} = 398$ nm (DPA: $\lambda_{max,ab} = 388$ nm); $\lambda_{max,em} = 442$ nm $\{\lambda_{ex} = 360$ nm$\}$ (DPA: $\lambda_{max,em} = 422$ nm $\{\lambda_{ex} = 265$ nm$\}$). Polymerization of **1** by [Mo] in toluene, followed by quenching with benzaldehyde, gave a high yield of homopolymer $\mathbf{1}_{25}$ (Table 1). As expected, the polydispersity of $\mathbf{1}_{25}$ is low (Table 1), consistent with the living nature of this ROMP reaction. Unlike crystalline DPA, $\mathbf{1}_{25}$ forms transparent amorphous films. Polymers containing 25 or 50 equiv of monomer were chosen in this study since they can be precipitated readily in certain solvents yet dissolve readily in others to give solutions suitable for preparing films.

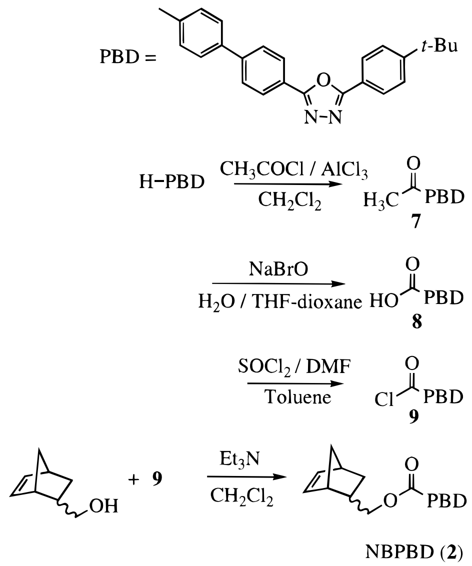
The electron-transport monomer, **2**, was synthesized in an overall yield of 65%, as outlined in Scheme 2. Absorption and emission wavelengths were shifted somewhat from (*tert*-butylphenyl)-*p*-biphenylyloxadiaxole itself:[28] $\lambda_{max,ab} = 325$ nm (PBD: $\lambda_{max,ab} = 302$ nm); $\lambda_{max,em} = 425$ nm $\{\lambda_{ex} = 360$ nm$\}$ (PBD: $\lambda_{max,em} = 360$ nm $\{\lambda_{ex} = 313$ nm$\}$). Homopolymer $\mathbf{2}_{50}$ also formed transparent amorphous films. The hole-transporting monomer, **3**, was prepared as shown in eq 2 in 69% yield.[26]



(2)

Two copolymers, one containing equimolar amounts of **1** and **2** and one containing equimolar amounts of **1**

Scheme 2



and **3**, were made by adding [Mo] to a 1:1 mixture of the two monomers. The presence of two different propagating alkylidene complexes and two different monomers ensures that four different propagation steps could take place. (The number of possibilities is actually twice that since two rotameric forms[29,30] of each propagating alkylidene could be present.) Although one might assume that **1**−**3** would react with a given alkylidene at approximiately the same rate, since structural differences and steric bulk occur well away from the norbornene double bond, we cannot assume that is the case and, therefore, cannot assume that the **1/2** and **1/3** copolymers are random. They could consist of essentially the homopolymers near the ends with varying degrees of "tapering" in between. The overall monomer ratio of 1:1 in each copolymer was verified by proton NMR peak integrations and the high yields (94% or greater based on total monomer feed).

Type A devices (Figure 1a) were made by spin-coating polymer (~600 Å thick) onto an indium tin oxide (ITO) anode and then evaporating aluminum onto the top to serve as the cathode. No other materials were blended into the polynorbornene layer. Table 2 lists the device characteristics. Blue light at $\lambda_{max} = 450$ nm was observed for devices $\mathbf{A\text{-}1}_{25}$, $\mathbf{A\text{-}(1/2)}_{50}$, and $\mathbf{A\text{-}(1/3)}_{50}$. There was no peak at $\lambda_{max} = 425$ nm (the photoluminescent emission of **2** alone) for $\mathbf{A\text{-}(1/2)}_{50}$. On the basis of the λ_{max} values, emission from $\mathbf{A\text{-}(1/2)}_{50}$ seems to occur solely from the DPA, indicating that energy transfer is possible between the DPA and PBD pendant groups. DPA has a smaller energy gap than the oxadiazole and therefore would be expected to be the sole emitter if energy transfer between PBD and DPA were efficient.

Type A device efficiency was improved by incorporation of hole- and electron-transport structural units into the polymer. The overall external device efficiencies (i.e. photons observed/electrons injected) were low, as was the maximum light output from these devices (light from $\mathbf{A\text{-}1}_{25}$ was just barely observable to dark-adjusted eyes). Low light intensity could be ascribed in part to poor charge balance. Also, at such high electrical fields (3.3 MV/cm at 20 V for a 600 Å film) and high currents (750−1000 mA/cm^2), the device may fail by polymer breakdown or by evaporation of the Al cathode.

A novel process for self-assembly of multilayered polymer structures containing light emitters has been

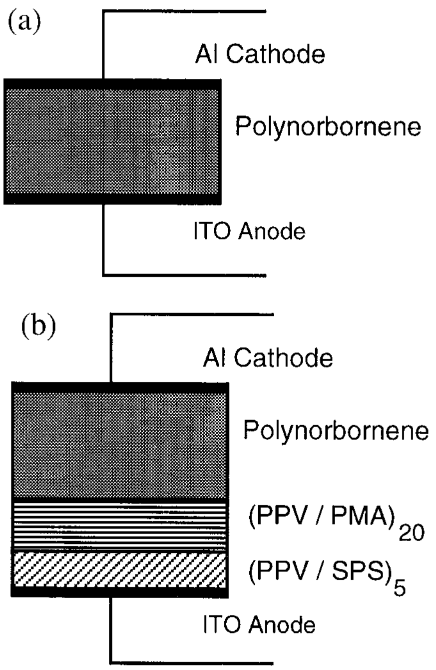


Figure 1. Configuration of polymer EL devices: (a) type A, ITO/polynorbornene/Al; (b) type B, ITO/PPV−SPS (5 bilayers)/PPV−PMA (20 bilayers)/polynorbornene/Al.

Table 2. Performance of Type A Devices

polymer	color	output (nW)	% efficiency[a] × 10^6	threshold (V)[b]
$\mathbf{1}_{25}$	blue[c]	0.5	0.34	22
$\mathbf{(1/2)}_{50}$	blue	31	19	21
$\mathbf{(1/3)}_{50}$	blue	26	48	13

[a] Photons/electron. [b] The threshold voltage is the voltage at which light output rises above 0.5 nW (well above baseline noise). [c] $\lambda_{\text{max,em}} = 450$ nm.

reported recently.[6,7] Alternating layers of polycation and polyanion are built up through a self-assembly technique, each held in place by ionic interaction with the preceding layer.[6] Typically, on top of the ITO anode were assembled 5 bilayers of a polycationic precursor to poly(*p*-phenylenevinylene) (PPV) and poly(styrene-4-sulfonate) (SPS). Next were added 20 bilayers of cationic PPV and polymethacrylate (PMA). This particular heterostructure has been shown to make stable electroluminescent devices with an emission wavelength of $\lambda_{\text{max,em}} = 530$ nm (green light from the PPV).[7] When such a structure was used as a hole injector in a device with a nonpolymeric ruthenium complex emitter, a significant increase in device efficiency was observed.[31] We have used a 25-bilayer PPV heterostructure of this type to serve as a "platform" in order to construct "type B" devices.

Norbornene polymers were spin-coated onto the PPV heterostructure platform, as shown in Figure 1b. Table 3 summarizes the characteristics of the type B devices. For **B-1**$_{25}$, **B-(1/2)**$_{50}$, and **B-(1/3)**$_{50}$ $\lambda_{\text{max,em}}$ is the same as for the type A devices, indicating that emission is occurring from DPA in the polynorbornene layer; no peak at $\lambda_{\text{max,em}} = 530$ nm from the PPV was observed. Since PPV has a smaller energy gap for emission, recombination of hole and electron carriers must be localized in the polynorbornene layer. It is likely that the polynorbornene acts as a partial barrier to electron movement through the device, while the PPV-containing heterostructure more easily transports holes. Figure 2a shows the electroluminescence and photoluminescence of **B-(1/2)**$_{50}$. The broad shoulder evident in the electroluminescent spectra is apparent in all devices (both type A and B) containing monomer **1**. We speculate that the shoulder arises from degradation of the DPA (see below) into lower energy emitting products. Since the shoulder is observed for devices that do not contain PPV, emission from the heterostructure is not implicated. However, the light emitted from the device is observed through the PPV and the ITO layers, so some light may be re-absorbed by the PPV. To what extent this occurs is unknown, although no PPV emission is observed.

Table 3. Performance of Type B Devices

polymer	color	output (nW)	% efficiency[a] × 10^6	threshold (V)[b]
$\mathbf{1}_{25}$	blue[c]	5.4	16	12
$\mathbf{2}_{50}$	green[d]	42	540	12
$\mathbf{(1/2)}_{50}$	blue	675	350	8
$\mathbf{(1/3)}_{50}$	blue	140	540	6

[a] Photons/electron. [b] The threshold voltage is the voltage at which light output rises above 0.5 nW (well above baseline noise). [c] $\lambda_{\text{max,em}} = 450$ nm. [d] $\lambda_{\text{max,em}} = 530$ nm.

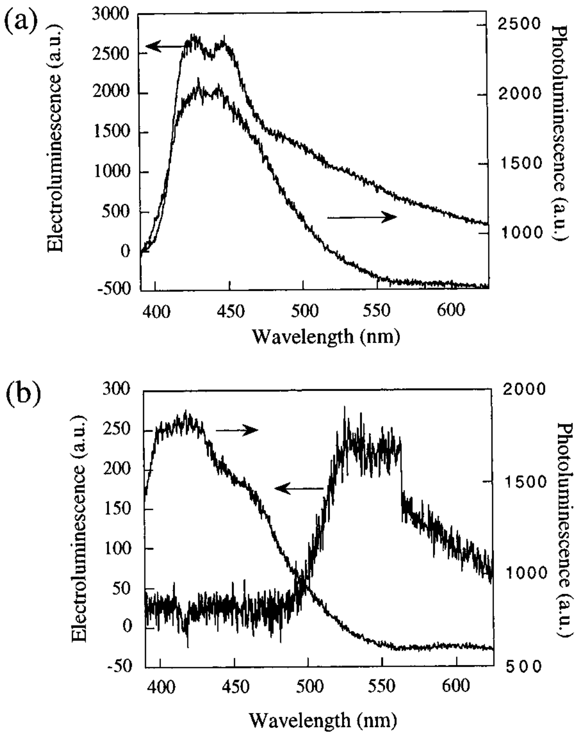


Figure 2. Optical spectra of polymers **2**$_{50}$ and **(1/2)**$_{50}$. (a) Device **B-(1/2)**$_{50}$: electroluminescence at 20 V and photoluminescence with excitation at 360 nm. (b) Device **B-2**$_{50}$: electroluminescence at 18 V and photoluminescence with excitation at 360 nm.

Device **B-2**$_{50}$ has $\lambda_{\text{max,em}} = 530$ nm (Figure 2b). This is not the same emission peak as observed in the photoluminescent spectra of **2**$_{50}$; it corresponds instead to the emission observed for the heterostructure alone, i.e., carriers recombine not in the polynorbornene layer, but in the PPV-containing layer. The ability of **2**$_{50}$ to block holes and to transport electrons through the polymer layer may help explain this effect.

Incorporation of the hole-transporting material, **3**, into the polynorbornene layer reduces the threshold voltage, as shown by data in Tables 2 and 3. The threshold voltage of **A-(1/3)**$_{50}$ is 9 V less than **A-1**$_{25}$, while that of **B-(1/3)**$_{50}$ is 6 V less than **B-1**$_{25}$. A device of type B is also clearly superior to a device of type A. Evidently, the PPV heterostructure facilitates hole

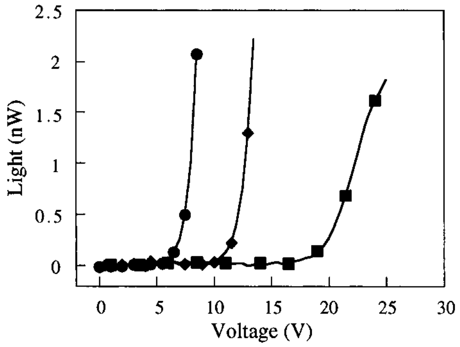


Figure 3. Variation in threshold voltage in devices **B-(1/3)$_{50}$** (circles), **B-(1/2)$_{50}$** (diamonds), and **A-(1/2)$_{50}$** (squares). **B-(1/3)$_{50}$** and **B-(1/2)$_{50}$** have a 900 Å total polymer thickness; **A-(1/2)$_{50}$** has a 600 Å polymer thickness. The *L*−*V* curves of **B-(1/3)$_{50}$** and **B-(1/2)$_{50}$** are cut off at 2 nW to facilitate comparison.

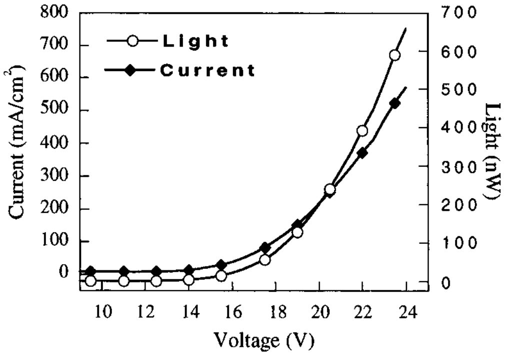


Figure 4. Performance of device **B-(1/2)$_{50}$**. Current−voltage (diamonds)and light−voltage (open circles) curves.

transport.[7] The light−voltage (*L*−*V*) curves are compared in Figure 3.

An increase in efficiency upon incorporation of an electron-transport material is seen in both device types, as expected.[2] The relative efficiency goes up dramatically from **A-1$_{25}$** to **A-(1/2)$_{50}$** and from **B-1$_{25}$** to **B-(1/2)$_{50}$**. The greater efficiency leads directly to greater emissive output from the devices. Figure 4 shows the current−voltage (*I*−*V*) and *L*−*V* curves for **B-(1/2)$_{50}$**. The highest output observed in this study was for device **B-(1/2)$_{50}$**; at 675 nW with an external quantum efficiency of EL (photons/electron), $\Phi_{EL,ext} = 3.50 \times 10^{-4}\%$.

B-2$_{50}$ and **B-(1/3)$_{50}$** have efficiencies that are comparable to that of **B-(1/2)$_{50}$**. In the case of **B-2$_{50}$** the device was unstable at high voltages. As noted above, on the basis of emission properties, electrons appear to pass completely through the 600 Å thick polynorbornene layer before recombination. Electron transport perhaps contributes to thermal degradation of the device. **B-(1/3)$_{50}$** also shows a higher efficiency than **B-1$_{25}$**.

Discussion

In general, type B devices operated with more consistency than type A devices (less prone to failure, more working “pixels”, etc.). The SPS/PPV/PMA heterostructure is a particularly uniform film,[7] which is likely to help alleviate problems resulting from small defects (such as pinholes) in the spin-cast polynorbornene layer. Devices based on monomer **1** had a short lifetime of operation (5−10 min), possibly as a consequence of decomposition of radical ions derived from DPA in the presence of traces of water or oxygen.[16,32,33] It should be possible to exclude water and oxygen more rigorously in the spin-casting step, both in the solvent and the atmosphere.

The observed degradation of the blue-light-emitting monomer, **1**, makes it a poor candidate for future applications. However, the approach used here to more optimally produce blue light can be applied to any norbornene-emitter system. In general the use of organic-based emitters such as DPA will be plagued by the instability of the radical species in the presence of trace contaminants. Electroluminescence from new monomers incorporating inorganic complexes, which are less reactive as radical ions, is currently being explored. In addition, since ROMP utilizing Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ as the initiator is living, block copolymers can be synthesized. Films should be preparable with specific morphologies (spheres, rods, layers) of the different side chains, separating the emitter from electron- or hole-transporting side chains. Further studies with these monomers will pursue this goal.

It may be possible to tune the color of emission by varying the percentage of monomer **2** in a copolymer. Some ratio of monomers **1** and **2** between 1:1 (such as **(1/2)$_{50}$**) and 0:1 (such as **2$_{50}$**) should show electroluminescence with a mixture of blue and green light in a type B device. Another method to control the emission may be to vary the thickness of the polynorbornene layer. A thicker layer would presumably help to confine the recombination within the polynorbornene layer, which is seen above in **B-1$_{25}$**, **B-(1/2)$_{50}$**, and **B-(1/3)$_{50}$**. Future work will investigate such possibilities.

Conclusion

A series of new blue-light-emitting polymers has been prepared. The incorporation of new hole- and electron-transport monomers as part of the polymer greatly improved the characteristics of the resulting electroluminescent devices. The use of a PPV heterostructure as a second layer improved the device characteristics even further. Devices with transport and emission structural units as well as the PPV layer provided the best performance: up to 675 nW of blue light was observed for **B-(1/2)$_{50}$**, and $\Phi_{EL,ext} = 5.40 \times 10^{-4}\%$ for both **B-2$_{50}$** and **B-(1/3)$_{50}$**.

Experimental Section

Characterization. HPLC grade CH$_2$Cl$_2$ was used in gel permeation chromatography (GPC) runs and was distilled over CaH$_2$ prior to use. GPC was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Visotek differential refractometer/viscometer H-500, and a Spectroflow 757 absorbance detector on samples 0.1−0.3% (w/v) in THF. Samples were first filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) that ranged from MW = 1260 to 2.75 × 10^6. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. NMR data were obtained at 300 MHz and listed in parts per million downfield from tetramethylsilane. Spectra were obtained at 25 °C unless otherwise noted. Film thicknesses were measured with a Sloan Dektak 8000 profilometer.

Measurements of current and luminescence as a function of applied field were made under forward bias. A silicon photodiode (Newport Instruments, Model 1830-C) was used to measure device light output, which is measured in nanowatts. Electroluminescence and photoluminescence spectra were taken using a spectrograph coupled to a Peltier-cooled CCD array (Oriel Instaspec IV). The system response was calibrated using a tungsten lamp. Excitation for the photoluminescence was from the multiline UV mode of an argon ion laser.

Preparation of Monomers. Unless otherwise stated, all experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or under an Ar atmosphere using standard Schlenck techniques. All chemicals were reagent grade and were purified by standard methods. Pd(PPh$_3$)$_4$ was purchased from Strem Chemicals. 2-(4′-Carboxybiphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (**8**) has been described elsewhere.[32] All other reagent grade chemicals were purchased from Aldrich Chemical Co. and used as received.

(5-Norbornenyl)methyl *p*-bromobenzyl Ether (4). To a solution of 5-norbornene-2-methanol (endo/exo mixture; 6.209 g, 50 mmol), 4-bromobenzyl bromide (12.497 g, 50 mmol), and a catalytic amount of tricaprylylmethylammonium chloride in 200 mL *n*-hexane was added 100 mL of a KOH (50 wt %) aqueous solution. The two-phase reaction mixture was vigorously stirred at room temperature for 1 week. The organic phase was washed three times with 200 mL of H_2O, then separated, and dried over $MgSO_4$. Solvent was removed in vacuo to afford 12.39 g (85% yield) of a slightly brownish oil. ^{1}H NMR (300 MHz, $CDCl_3$): (endo) δ 7.45 (d, 2H, Ar, $J = 8.3$ Hz), 7.20 (d, 2H, Ar, $J = 9.0$ Hz), 6.10 (m, 1H, olefin), 5.85 (m, 1H, olefin), 4.40 (dd, 2H, OCH_2Ar, $J = 20.0$ Hz), 3.17 (q, 1H, nor-CH_2O, $J = 6.2$ Hz and $J = 8.6$ Hz), 3.06 (t, 1H, nor-CH_2O, $J = 9.5$ Hz), 2.92 (broad s, 1H), 2.77 (broad s, 1H), 2.42−2.30 (m, 1H), 1.80 (m, 1H), 1.42 (d, 1H, $J = 7.4$ Hz), 1.31 (broad d, 1H, $J = 7.7$ Hz), 0.43 (m, 1H); (exo) δ 7.45 (d, 2H, Ar, $J = 8.3$ Hz), 7.20 (d, 2H, Ar, $J = 9.0$ Hz), 6.10 (m, 1H, olefin), 6.05 (m, 1H, olefin), 4.40 (dd, 2H, OCH_2Ar, $J = 20.0$ Hz), 3.50 (q, 1H, nor-CH_2O, $J = 6.2$ Hz and $J = 8.6$ Hz), 3.35 (t, 1H, nor-CH_2O, $J = 9.0$ Hz), 2.92 (broad s, 1H), 2.77 (broad s), 2.42−2.30 (m, 1H), 1.72 (m, 1H), 1.42 (d, 1H, $J = 7.4$ Hz), 1.31 (broad d, 1H, $J = 7.7$ Hz), 1.10 (m, 1H). TLC: $R_f = 0.73$ (SiO_2, CH_2Cl_2/*n*-hexane, 1/3).

***p*-(Pinacol borate)benzyl (5-Norbornenyl)methyl Ether (5).** A solution of **4** (2.000 g, 6.82 mmol) in 50 mL THF was cooled to −70 °C under argon, and 8 mL (20 mmol) of 2.5 M *n*-butyllithium in hexane was added. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The mixture was again cooled to −70 °C and triethyl borate (6.80 mL, 40 mmol) was added. The temperature was allowed to rise to 25 °C, pinacol (5.200 g, 44.0 mmol) was added, and the mixture was stirred overnight. CH_2Cl_2 (50 mL) was added. The organic phase was washed three times with 200 mL of H_2O, separated, and dried over $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography (triethylamine-deactivated SiO_2, CH_2Cl_2/Et_3N 98/2) affording 1.200 g (52% yield) of a slightly brownish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): (endo) δ 7.78 (d, 2H, Ar, $J = 7.7$ Hz), 7.32 (d, 2H, Ar, $J = 8.4$ Hz), 6.07 (m, 1H, olefin), 5.86 (m, 1H, olefin), 4.48 (dd, 2H, OCH_2Ar, $J = 21.4$ Hz), 3.16 (q, 1H, nor-CH_2O, $J = 6.2$ Hz and $J = 8.4$ Hz), 3.02 (t, 1H, nor-CH_2O, $J = 9.4$ Hz), 2.93 (broad s, 1H), 2.77 (broad s, 1H), 2.42−2.30 (m, 1H), 1.80 (m, 1H), 1.40 (broad d, 1H, $J = 7.4$ Hz), 1.33 (s, 12H, pinacol), 1.23 (m, 1H), 0.43 (m, 1H); (exo) δ 7.78 (d, 2H, Ar, $J = 7.7$ Hz), 7.32 (d, 2H, Ar, $J = 8.4$ Hz), 6.09 (m, 1H, olefin), 6.05 (m, 1H, olefin), 4.48 (dd, 2H, OCH_2Ar, $J = 21.4$ Hz), 3.48 (q, 1H, nor-CH_2O, $J = 6.2$ Hz and $J = 8.4$ Hz), 3.33 (t, 1H, nor-CH_2O, $J = 9.4$ Hz), 2.93 (broad s, 1H), 2.77 (broad s, 1H), 2.42−2.30 (m, 1H), 1.80 (m, 1H), 1.40 (broad d, 1H, $J = 7.4$ Hz), 1.33 (s, 12H, pinacol), 1.23 (m, 1H), 1.10 (m, 1H). TLC: $R_f = 0.70$ (SiO_2, CH_2Cl_2/Et_3N 98/2).

9-Bromo-10-phenylanthracene (6). In a modification of a published procedure,[33] bromine (112 mL, 2.16 mmol) was added to a solution of 9-phenylanthracene (500 mg, 1.97 mmol) in 10 mL of methylene chloride. The reaction mixture was stirred overnight, quenched with aqueous sodium sulfite, and washed with water. The organic phase was separated and dried over $MgSO_4$. Solvent was removed in vacuo to give a crude yellow solid. Chromatography (SiO_2, *n*-hexane) afforded 478 mg (73% yield) of **6**. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.61 (d, 2H, $J = 8.7$ Hz), 7.68−7.50 (m, 7H), 7.42−7.32 (m, 4H). TLC: $R_f = 0.50$ (SiO_2, *n*-hexane).

((9-Phenylanthracen-10-yl)phenyl)methyl (5-Norbornenyl)methyl Ether [NBDPA] (1). To a solution of **5** (1.100 g, 3.23 mmol) and **6** (1.077 g, 3.23 mmol) in 100 mL of THF was added 50 mL of a 1 M aqueous solution of K_2CO_3. The glassware was covered with aluminum foil. The reaction mixture was placed under argon and brought to reflux. A solution of Pd(PPh)$_4$ (75 mg, 0.06 mmol) in THF (5 mL), prepared in a N_2-filled drybox, was added with a syringe. After 12 h at reflux, *n*-hexane (200 mL) was added and the organic phase was washed three times with 200 mL of H_2O. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by column chromatography (SiO_2, toluene) to give 1.806 g (80%) of a white powder. ^{1}H-NMR (300 MHz, $CDCl_3$): (endo) δ 7.75−7.30 (m, 17H, Ar), 6.17 (m, 1H, olefin), 5.98 (m, 1H, olefin), 4.65 (dd, 2H, OCH_2Ar, $J = 21.1$ Hz), 3.38 (q, 1H, nor-CH_2O, $J = 6.2$ Hz and $J = 9.4$ Hz), 3.23 (t, 1H, nor-CH_2O, $J = 8.4$ Hz), 3.05 (broad s, 1H), 2.83 (broad s, 1H), 2.58−2.40 (m, 1H), 1.90 (m, 1H), 1.47 (broad d, 1H, $J = 7.4$ Hz), 1.30 (d, 1H, $J = 8.1$ Hz), 0.57 (m, 1H); (exo) δ 7.75−7.30 (m, 17H, Ar), 6.17 (m, 1H, olefin), 6.10 (m, 1H, olefin), 4.65 (dd, 2H, OCH_2Ar, $J = 21.1$ Hz), 3.70 (q, 1H, nor-CH_2O, $J = 6.2$ Hz and $J = 9.4$ Hz), 3.53 (t, 1H, nor-CH_2O, $J = 8.4$ Hz), 3.05 (broad s, 1H), 2.83 (broad s, 1H), 2.58−2.44 (m, 1H), 1.90 (m, 1H), 1.47 (broad d, 1H, $J = 7.4$ Hz), 1.30 (d, 1H, $J = 8.1$ Hz), 1.22 (m, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 139.51, 138.59, 137.45, 137.27, 132.80, 131.66, 131.62, 130.27, 128.66, 127.91, 127.72, 127.27, 127.24, 127.23, 74.85, 73.24, 49.78, 44.48, 42.62, 39.31, 29.64. TLC: $R_f = 0.70$ (SiO_2, CH_2Cl_2/*n*-hexane 1/3). Anal. Calcd for $C_{35}H_{30}O$: C, 90.09; H, 6.48. Found: C, 90.25; H, 6.47.

2-(4′-Acetylbiphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (7). To a suspension of anhydrous $AlCl_3$ (22.5 g, 169 mmol) in CH_2Cl_2 (50 mL) was added dropwise neat acetyl chloride (13.8 g, 176 mmol), then *t*-BuPBD (5.0 g, 14.1 mmol) in CH_2Cl_2 (50 mL) under Ar. The mixture was refluxed for 5 h once addition was complete. The solution was cooled and diluted with CH_2Cl_2 (500 mL) and then chilled to 0 °C. Water was added cautiously until the deep red solution turned yellow. The organic phase was separated, extracted with H_2O, $NaHCO_3$, and brine, dried over $MgSO_4$, and stripped. The product was recrystallized from hot acetone to yield 5.0 g of pale yellow **7** (89%), mp 194−195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, 2H, Ar, $J = 8.4$ Hz), 8.09 (dd, 4H, Ar, $J = 2.9$, 8.5 Hz), 7.81 (d, 2H, Ar, $J = 8.3$ Hz), 7.77 (d, 2H, Ar, $J = 8.2$ Hz), 7.58 (d, 2H, Ar, $J = 8.4$ Hz), 2.67 (s, 3H, COCH_3), 1.40 (s, 9H, *tert*-butyl). IR (Nujol): ν(CO) 1678, ν(C=C) 1603 cm^{-1}.

2-(4′-Carboxybiphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) (8). Into a freshly prepared, ice-cold solution of hypobromide (16 g of Br_2, 12 g of NaOH, 300 mL of H_2O) was slowly poured a solution of ketone **7** (8.5 g, 21.4 mmol) in THF−dioxane (3:2; total volume, 500 mL). The reaction mixture was stirred at 0 °C under Ar for 10 min and then warmed at 35 °C overnight. It was then treated with aqueous Na_2SO_3, chilled to 0 °C, and acidified with concentrated HCl to pH 1. The resulting precipitate was filtered off, washed with water, dried, and triturated with $CHCl_3$. Yield: 7.8 g (92%) of white **8**, mp >300 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 8.23 (d, 2H, Ar, $J = 8.4$ Hz), 8.07 (dd, 4H, Ar, $J = 1.8$, 9.3 Hz), 8.00 (d, 2H, Ar, $J = 7.8$ Hz), 7.90 (d, 2H, Ar, $J = 9.3$ Hz), 7.65 (d, 2H, Ar, $J = 9.3$ Hz), 1.34 (s, 9H, *t*-Bu). IR (Nujol): ν(CO) 1675, ν(C=C) 1608 cm^{-1}.

2-(4′-Chloroformylbiphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) (9). To a suspension of **8** (2.85 g, 7.15 mmol) in THF (250 mL) under Ar was added a solution of oxalyl chloride (9.0 mL (18 mmol, 2.5 equiv) of a 2 M solution in CH_2Cl_2). The suspension dissolved upon heating to yield a clear pale yellow solution, which was refluxed for 18 h, during which the disappearance of the carboxy ν(CO) band was monitored by IR. The solvent was stripped off under vacuum and the residue recrystallized from CH_2Cl_2 in the drybox to give white **9** (2.78 g, 93%), mp 235 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (t, 4H, Ar, $J = 8.4$ Hz), 8.10 (d, 2H, Ar, $J = 8.4$ Hz), 7.82 (d, 2H, Ar, $J = 8.4$ Hz), 7.81 (d, 2H, Ar, $J = 8.1$ Hz), 7.58 (d, 2H, Ar, $J = 8.4$ Hz), 1.40 (s, 9H, *t*-Bu). IR (Nujol): ν(CO) 1768, 1735 cm^{-1}; ν(C=C) 1602 cm^{-1}.

2-(4′-((5-Norbornenylmethoxy)carbonyl)biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole [NBPBD] (2). A solution of **9** (1.00 g, 2.40 mmol) and dry NEt_3 (0.36 g, 3.56 mmol) in CH_2Cl_2 (80 mL) was treated with a solution of NBE−CH_2OH (0.298 g, 2.40 mmol) in CH_2Cl_2 (0.5 mL). The reaction mixture was refluxed for 3 days, until the ν(CO) band of the acid chloride was no longer observable by IR. It was then extracted with H_2O, washed with $NaHCO_3$ and water, dried over $MgSO_4$, and stripped to a white solid. The crude product was purified by flash chromatography on neutral Al_2O_3 (9:1 CH_2Cl_2−EtOAC eluant) to afford 1.02 g (85%) of clean **2**, mp 228−229 °C. This material was passed through freshly activated Al_2O_3 in the drybox and recrystallized from a minimum of THF. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, 2H, Ar, $J = 8.0$ Hz), 8.17 (d, 2H, Ar, $J = 8.0$ Hz), 8.09 (d, 2H, Ar, $J = 8.2$ Hz), 7.79 (d, 2H, Ar, $J = 8.1$ Hz), 7.72 (d, 2H, Ar, $J = 8.2$ Hz), 7.56 (d, 2H, Ar, $J = 8.1$ Hz), 6.21 (m, 1H), 6.02 (m, 1H), 4.15 (q, 1H, nor-CH_2O, $J = 7.1$ Hz and $J = 10.8$ Hz), 3.92 (t, 1H, nor-CH_2O, $J = 10.9$ Hz), 2.99 (broad s, 1H), 2.86 (broad s, 1H), 2.63−2.50 (m, 1H), 1.92 (m, 1H, exo), 1.48 (d, 1H, $J = 7.9$ Hz), 1.37 (s, 9H, *tert*-butyl), 1.31 (d, 1H, $J = 9.6$ Hz), 0.67 (m, 1H, endo). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.43, 165.02, 164.28, 155.67, 144.34, 144.28, 143.32, 137.93, 137.24, 136.45, 132.42, 130.46, 130.33, 130.25, 128.09, 127.66, 127.30, 127.03, 126.30, 123.82, 121.25, 69.37, 68.71, 49.64, 45.25, 44.23, 43.97, 42.46, 41.86, 38.35, 38.15, 35.32, 31.33, 29.83, 29.20. IR (Nujol): ν(CO) 1712, ν(C═C) 1610 cm^{-1}. Anal. Calcd for $C_{33}H_{32}N_2O_3$: C, 78.55; H, 6.39; N, 5.55. Found: C, 78.89; H, 6.27; N, 5.53.

***N*-(((5-norbornenylcarbonyl)oxy)ethyl)-*N*-ethyl-3-methylaniline [NBHole] (3).** To a solution of 5-norbornenylcarbonyl chloride (1.88 g, 12.0 mmol) and triethylamine (1.66 mL, 12.0 mmol) in 50 mL of methylene chloride at 0 °C was added 2-(*N*-ethyl-*m*-toluidino)ethanol (1.97 g, 11.0 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 4 days. The organic phase was washed three times with 200 mL of water, then separated, and dried over $MgSO_4$. Solvent was removed in vacuo. Purification by chromatography (alumina, CH_2Cl_2) afforded 2.270 g (69%). ^{1}H-NMR (300 MHz, C_6D_6): (endo) δ 7.19−7.10 and 6.62−6.49 (m, 4H, Ar), 6.06−5.95 (m, 2H, olefin), 4.15−4.00 (m, 2H, OCH_2), 3.28−3.20 (t, 2H, CH_2N), 3.06 (q, 2H, NCH_2), 2.23 (s, 3H, CH_3), plus resonances in the 3.02−0.90 ppm similar to starting materials; (endo) 7.19−7.10 and 6.61−6.48 (m, 4H, Ar), 5.93−5.85 (m, 2H, olefin), 4.12 (t, 2H, OCH_2), 3.26 (t, 2H, CH_2N), 3.05 (q, 2H, NCH_2), 2.23 (s, 3H, CH_3), 0.90 (t, 3H, CH_3), plus resonances in the 3.02−0.90 ppm similar to starting materials. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 174.58, 138.94, 138.14, 137.79, 137.67, 135.86, 132.53, 129.26, 117.56, 113.34, 109.86, 62.08, 61.92, 60.06, 49.75, 49.18, 46.70, 46.54, 45.83, 45.33, 43.53, 43.33, 42.72, 41.80, 30.51, 29.46, 21.99, 14.39, 12.50. Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 75.93; H, 8.21; N, 4.36.

Preparation of Polymers. All handling of catalyst and polymerization was done in a nitrogen atmosphere drybox. Toluene for polymerization was distilled from sodium benzophenone ketyl and passed through alumina prior to use. Norbornene monomers were dissolved in dry CH_2Cl_2 or THF and passed through alumina in the drybox. **2** was subsequently recrystallized from THF. Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ was prepared as outlined in the literature.[20]

General Procedure. To a stirred solution of monomer (or monomers) (0.50 mmol total) in 10 mL of toluene was added the catalyst, Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ (11 mg, 0.020 mmol), in 3 mL of toluene all at once. The reaction mixture was stirred for 1 h, quenched with 1 mL of benzaldehyde and further stirred for 15 min. Precipitation in 300 mL of MeOH afforded a high yield (94−98%) of polymer. M_n and M_w are given in the text. ^{1}H-NMR data are given below.

(NBDPA)$_{25}$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70−7.10 (broad, 17H, Ar), 5.50−5.30 (broad, 2H, olefin), 4.65−4.40 (broad, 2H), 3.65−3.25 (broad, 2H), 2.80−1.10 (broad, 7H).

(NBPBD)$_{50}$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.20−7.90 (broad, 6H, Ar), 7.75−7.40 (broad, 6H, Ar), 5.50−5.25 (broad, 2H, olefin), 4.40−3.90 (broad, 2H), 2.80−1.60 (broad, 6H), 1.35 (s, 9H, *t*-butyl) 1.30−1.05 (broad, 1H).

(NBDPA)$_{25}$(NBPBD)$_{25}$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.20−7.95 (broad, 6H, Ar), 7.70−7.15 (broad, 23H, Ar), 5.50−5.25 (broad, 4H, olefin), 4.65−3.95 (broad, 4H), 3.65−3.25 (broad, 2H), 2.80−1.70 (broad, 8H), 1.34 (s, 9H, *t*-butyl), 1.40−1.10 (broad, 2H).

(NBDPA)$_{25}$(NBHole)$_{25}$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.80−7.00 (broad, 18H, Ar), 6.48 (broad s, 3H, Ar), 5.55−5.15 (broad, 4H, olefin), 4.70−4.40 (broad, 2H), 4.25−3.90 (broad, 2H), 3.60−3.20 (broad, 4H), 3.00-0.08 (broad, 22H).

Light-Emitting Device Fabrication. Devices of Type A. Commercially patterned indium tin oxide (2 mm wide strips, spaced 2 mm apart) on a 2 cm × 2 cm piece of glass was prepared by a previously described cleaning/sonication procedure.[7] Polynorbornene (600 Å) was spin-coated from chlorobenzene onto the cleaned ITO. Film thickness was controlled by both spin rate and solution concentration. Three 2000 Å thick aluminum strips, 2 mm wide and spaced 2 mm apart, were laid perpendicular to the ITO by thermal evaporation at 1×10^{-6} Torr. Connection to the electrodes was made with gold wire, generating 12 individually addressed "pixels" where the electrodes crossed.

Devices of Type B. A heterostructure of 5 bilayers of poly(*p*-phenylenevinylene)/poly(styrene-4-sulfonate) and 20 bilayers of poly(*p*-phenylenevinylene)/poly(methacrylic acid) (300 Å total thickness) was self-assembled from aqueous solution onto cleaned ITO using the procedure outlined in ref 7. Polynorbornene (600 Å) and the aluminum cathode were deposited as above.

Acknowledgment. This work was supported by the MRSEC program of the National Science Foundation under Award No. DMR-9400334. The authors thank Dr. Marysilvia Ferreira of MIT for her contribution to this work. Y.G. thanks the U.S. government for a Fullbright fellowship and the Belgian American Education Foundation for a Hoover fellowship.

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MA961613S