A New Type of Blue-Light-Emitting Electroluminescent Polymer

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ABSTRACT: A blue-light-emitting electroluminescent polymer was prepared by the ring-opening metathesis polymerization (ROMP) method from a norbornene monomer (NBTPV-C5) that contains a phenylenevinylene oligomer unit as a side chain. A 50mer of NBTPV-C5 (M_w/M_n = 1.10) was prepared in THF in 95% yield by employing Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ as the initiator. Electroluminescent devices were made with single layers of polyNBTPV-C5 with ITO as the anode and Ca as the cathode, both by itself and in blends containing the electron transport material, biphenyl–*tert*-butylphenyloxadiazole. Two layer devices using PPV as a hole transport layer also were prepared. Electroluminescent quantum yields of up to 0.55% have been obtained.

Introduction

Poly(*p*-phenylenevinylene) (PPV) has attracted much attention as an electroluminescent material.[1–11] PPV has several advantages as an emitting material in electroluminescence (EL) devices: a high-quality thin film can be prepared by spin-coating a soluble precursor polymer, and the emission wavelength can be tuned by either changing the substituents on the arene ring[12] or by partially converting the precursor polymer, i.e., by generating PPV that contains relatively short conjugated chains.[8,9,11] The object in either case usually has been to increase the band gap and thereby to generate a blue-shifted emission spectrum.[4] A blue EL device is particularly desirable for several reasons.[13–15] In general compounds that have shorter conjugation lengths have a higher PL (photoluminescence) quantum yield. For example, 1,6-diphenylhexatriene shows an 80% PL quantum yield in cyclohexane, but 1,8-diphenyloctatetraene shows only a 9% PL quantum yield in the same solvent.[16] 1,4-Bis[(4-isopropylphenyl)ethenyl]benzene, a short analog of PPV, has a 94% PL quantum yield in cyclohexane,[16] while the PPV PL quantum yield is reported to take values ranging from a few percent[17] to 25%.[18,19] Thus, polymers that have short conjugated segments in the polymer chain would be expected to have a higher PL quantum yield; they might have a higher EL quantum yield also. Recently, such an effect was observed in an alternating diblock copolymer.[20] An emitter that has a fixed conjugation length is most desirable, since a random distribution of conjugation lengths leads to broad emission bands. Pure blue-light emission therefore is relatively difficult to achieve under such circumstances.

In the past several years well-defined molybdenum-based initiators for living ring-opening metathesis polymerization (ROMP) have been developed.[21] Mo(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ is an especially mild ROMP initiator that reacts readily with norbornenes or norbornadienes to give polymers in a controlled (living) manner.[21–23] In some cases (e.g., 2,3-bis(trifluoromethyl)norbornadiene) an all trans polymer[24] that is highly tactic (probably syndiotactic[25]) is formed. In this paper, we discuss the synthesis of polymers made by ROMP (employing Mo(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ as the initiator) that contain a short conjugated emitter unit either in the main chain or as a side chain.

Results and Discussion

Short oligomers of PPV are highly insoluble.[26] Therefore the first approach we took to preparing "soluble" PPV oligomers is analogous to the method that we used previously to prepare "soluble" unsubstituted polyenes;[27,28] poly(methyltetracyclododecene) (polyMTD) was employed as a solubilizing chain in a block copolymer. As shown in Scheme 1, living polyMTD was treated with terephthaldehyde to yield aldehyde-capped polyMTD (**1**) that contained up to 100 equiv of monomer. The aldehyde-capped polyMTD was then treated with 0.5 equiv of the bis(phosphonate) compound[29–32] in order to generate triblock copolymers (**2**) that have a phenylene vinylene "trimer" in the middle of the polymer chain. These soluble polymers showed a λ_{max} in the absorption spectrum in THF at 384 nm and in the emission spectrum at 455 nm. A preliminary measurement of the PL quantum yield compared to an anthracene standard was relatively high (66%), but no EL was detected from a single layer ITO/polymer/Al device. We speculate that this is simply a consequence of the low concentration of the emitter. (The maximum concentration of the emitter is only 8% by weight.) In short, the majority of the polymer is an insulator in which holes and electrons cannot migrate, find one another, and generate an emissive excited state.

In order to increase the number of emitters in the polymer, we prepared monomers that contain one chromophore per monomer (Chart 1). The most successful (THF-soluble) of these was NBTPV-C5 (**3a**). (1,4-Bis-[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene has been reported to be relatively soluble in common solvents.[33]) The synthesis of **3a** shown in Scheme 2 proceeded with an overall yield of 17%. Monomers **3b**, **3c**, and **3d** were prepared by similar methods (see supplementary material) but were only slightly soluble in THF.

Attempted polymerization of **3b**, **3c**, or **3d** in THF employing Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ (Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$) was relatively unsuccessful, in part because the polymer precipitated out during the polymerization reaction. Consequently, yields were low and the resulting polymer had a broad molecular weight distribution. Evidently, the inherently high solubility of a polymer prepared from a 5-substituted norbornene is not great enough to outweigh the contribution of a relatively insoluble side chain. On the other hand NBTPV-C5 (**3a**)

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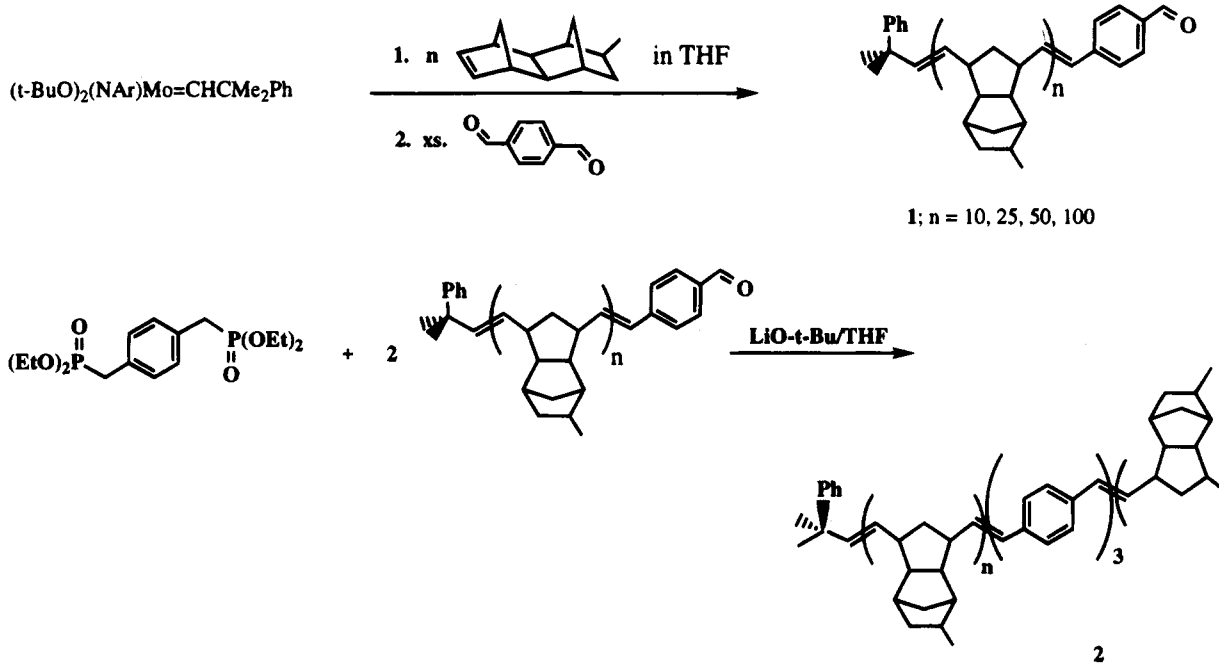
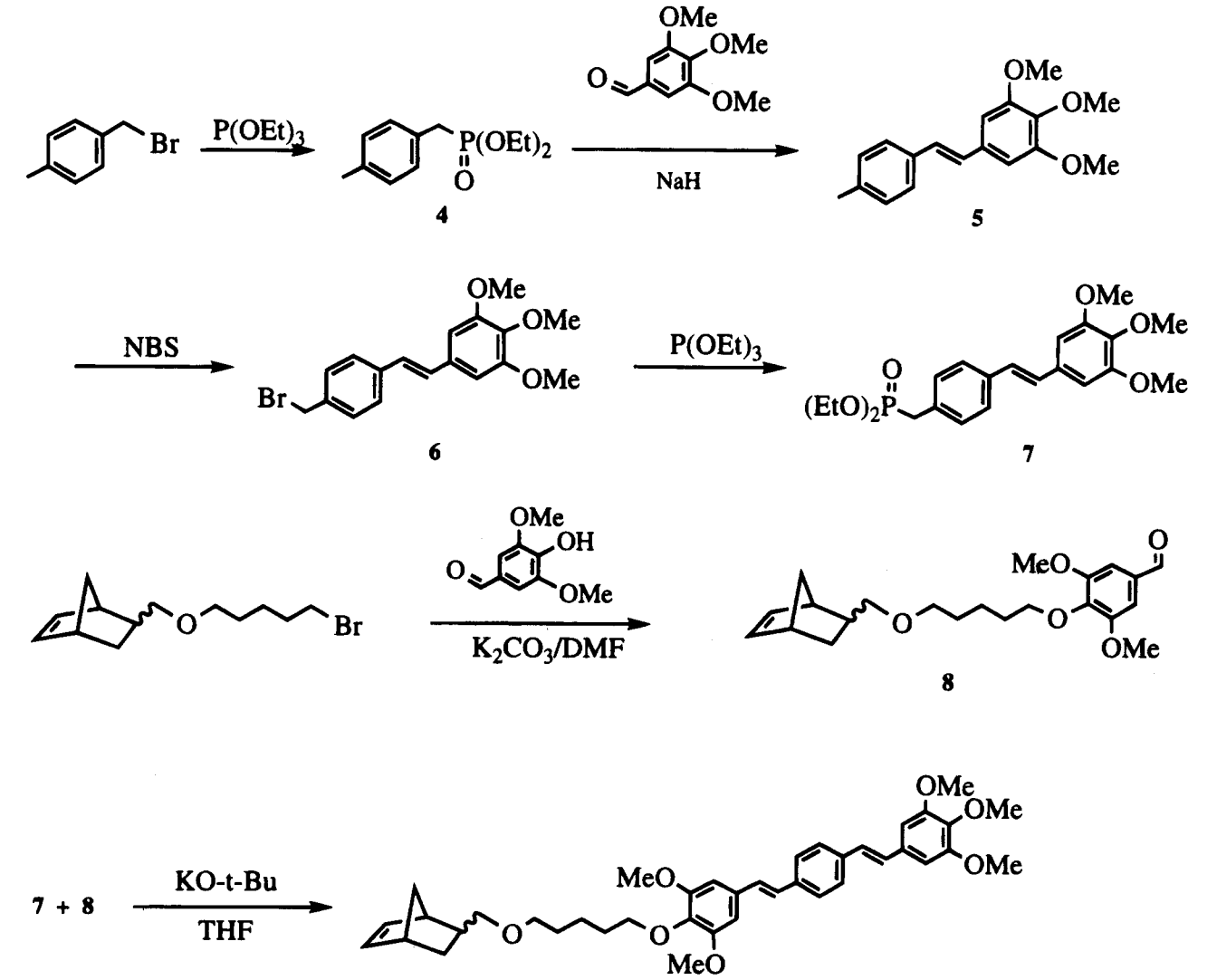
Scheme 1



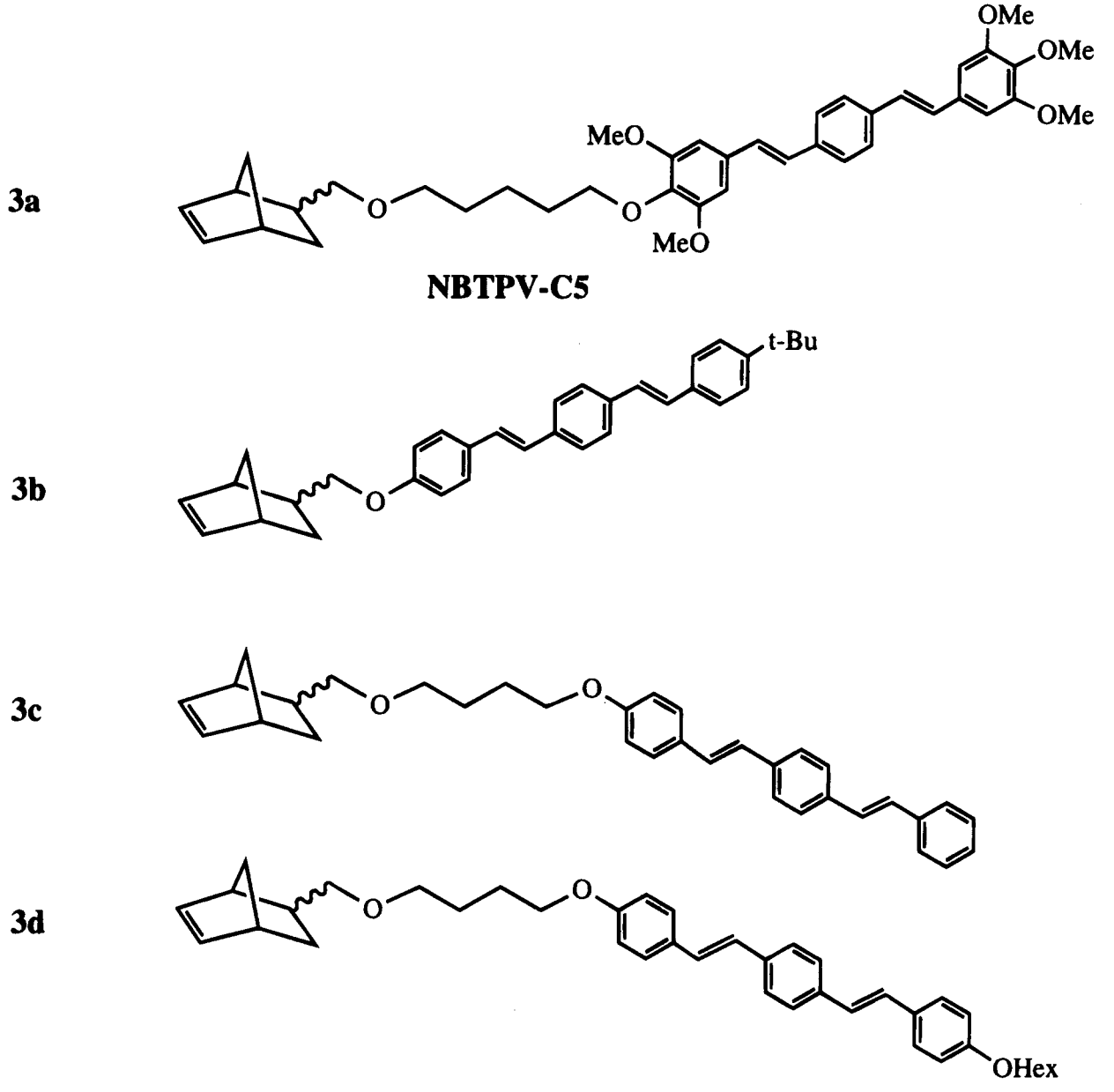
Scheme 2



NBTPV-C_5 (3a)

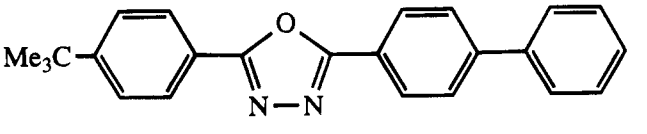
could be polymerized smoothly to give (after capping with benzaldehyde) a soluble low-polydispersity polymer in high yield (Scheme 3). This polymer has a λ_{max} = 368 nm in the absorption spectrum in THF solution.

Chart 1



Films of poly(**3a**) could be prepared by static casting from THF or chloroform. For the cast film λ_{max} = 362 nm for absorption and 475 nm for emission. Polymer films 150–200 nm thick could be prepared by spin-coating on a glass substrate covered with an ITO conducting layer (anode). The calcium electrode (cathode) was then evaporated onto it in vacuo. Since the EL and PL spectra for films prepared in this manner were similar (Figure 1), the origin of the emitting light in each spectrum is likely to be the same. This single layer device showed a turn-on voltage at ~12 V (Figure 2a) and an EL efficiency of 0.3%. The linear relationship between luminance and current (Figure 2b) is strong evidence that the light is generated by recombination of electrochemically generated holes and electrons.

A second single-layer device was prepared in which biphenyl–*tert*-butylphenyloxadiazole (*tert*-PBD), an electron transport material,[34,35] was dissolved in solution along with the polymer before spin-coating. It showed a higher EL efficiency (0.55%) with a turn-on voltage of 17 V. When a classically prepared film of PPV[1] was introduced as a hole transport material between the ITO and emitter layers, the turn-on voltage was about the same (15 V) but the EL efficiency was reduced to 0.21%. The low EL efficiency might be ascribed to reabsorption of emitted light by the PPV layer. The fact that the emitted light is green-blue instead of blue supports this proposal.



***tert*-PBD**

In all experiments a significant problem was the relatively short lifetime of the device (several minutes). A cyclic voltammogram of **3a** in acetonitrile showed an irreversible oxidation peak at 0.92 V vs SCE and a quasi-reversible reduction peak at −2.17 V, while poly(**3a**) in THF showed similar peaks at +0.82 and −2.18 V. After several scans from +1.5 V to −2.4 V the first oxidation peak disappeared in each case. An electrochemiluminescence (ECL) experiment of **3a** in acetoni-

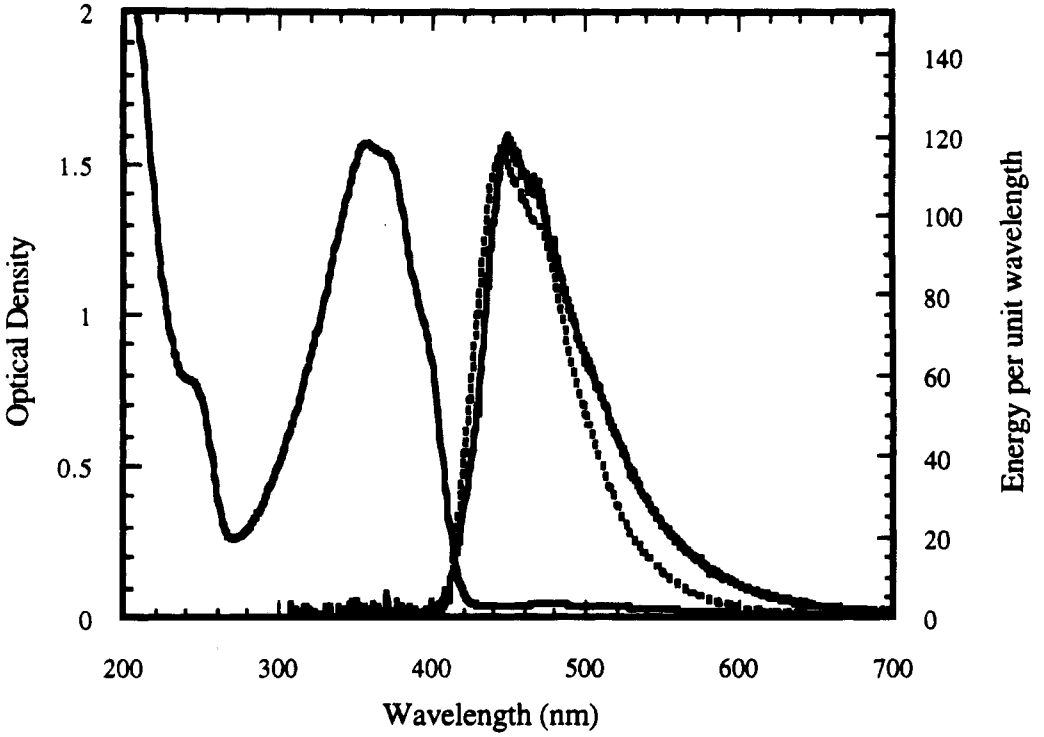
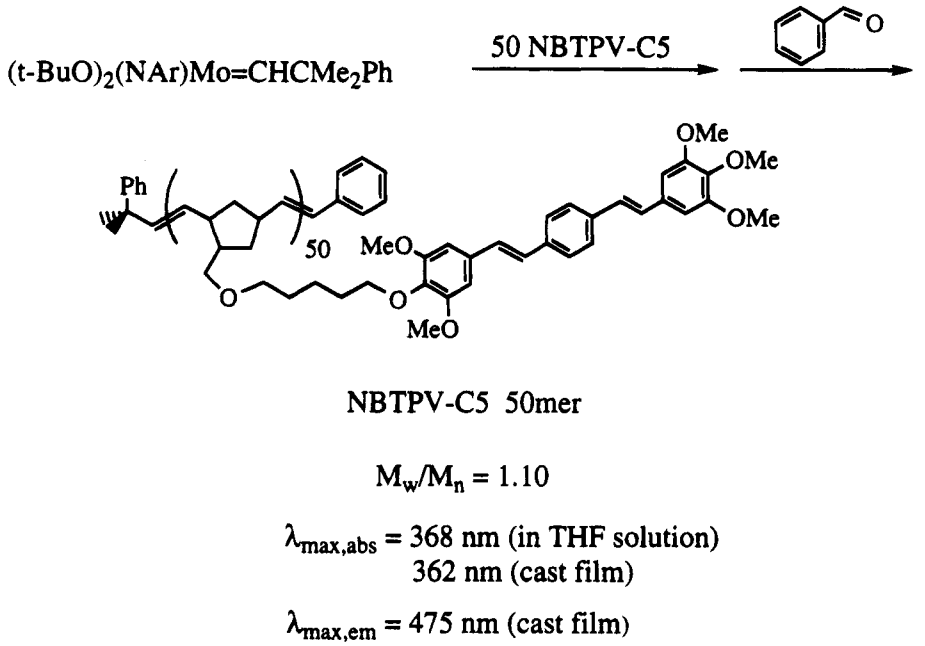


Figure 1. PL (broken line), EL, and absorption spectra of the NBTPV-C5 50mer.

Scheme 3



NBTPV-C5 50mer

$M_w/M_n = 1.10$

$\lambda_{max,abs}$ = 368 nm (in THF solution)
362 nm (cast film)

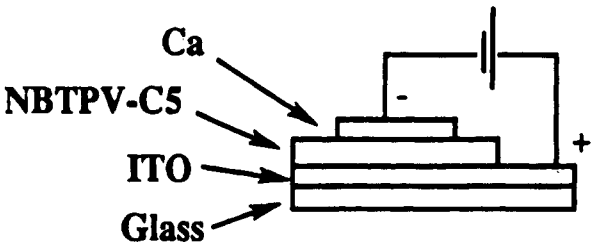
$\lambda_{max,em}$ = 475 nm (cast film)

trile with a ITO electrode showed a flash of blue light emitting from the solution near the electrode surface when the voltage was swept from +1.8 to −2.5 V at a speed of 5 cycles/s, but the ECL dimmed and stopped after ~10 s. At this point a yellowish material covered the surface of the ITO electrode. ECL could be observed again after the yellowish material was gently removed from the electrode surface with a tissue, but again ECL decayed rapidly. We conclude that the short lifetime of the EL device containing polyNBTPV-C5 most likely results from the electrochemical instability of the emitter. We hope to test this proposal in the future by preparing and testing similar polymers in which the emitter is more electrochemically stable.

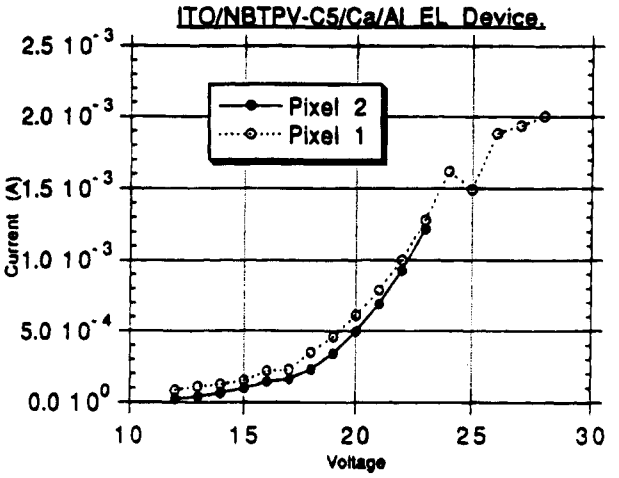
In summary we have shown that a new type of blue-light EL polymer can be prepared by the ring-opening metathesis polymerization (ROMP) method and that the EL device from this polymer showed up to a 0.55% EL efficiency. In theory a variety of emitter groups could be introduced as a side chain in the norbornene monomer system and a wide variety of EL materials could be prepared by the ROMP method. Since ROMP that employs Mo(NAr)($CHCMe_2Ph$)(O-*t*-Bu)$_2$ as the initiator is living, block copolymers can be prepared. Therefore films that contain emitters and hole- or electron-transporting side chains in specific morphologies (layers, rods, spheres) should be preparable. Further studies will be aimed in this direction.

Experimental Section

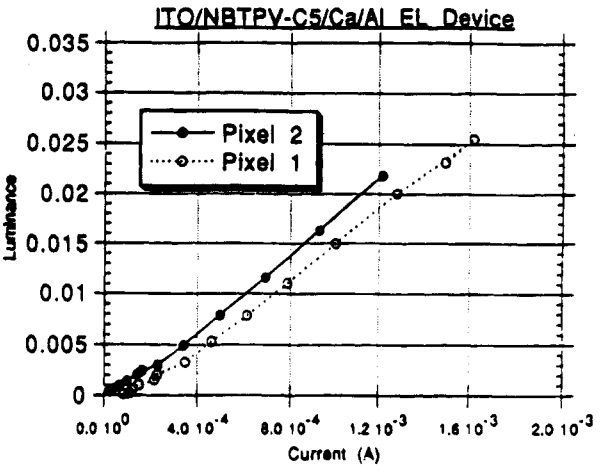
All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard



Turn-on voltage: 12V
ϕ_{EL} = 0.3%



(a)



(b)

Figure 2. Single-layer EL device (ITO/polyNBTPV-C5/Ca).

Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric acid/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade THF was vacuum transferred a second time from sodium benzophenone ketyl. Polymerization grade toluene was stored over sodium/potassium alloy and passed through alumina prior to use.

HPLC grade solvents were used in gel permeation chromatography (GPC) runs and were degassed prior to use. GPC was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Viscotek Differential Refractometer/Viscometer H-500, and a Spectroflow 757 absorbance detector on samples 0.1–0.3 % (w/v) in THF which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 to 2.75 × 10^6. Elemental analyses (C, H) 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.

All chemicals were reagent grade and were purified by standard methods. Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ was prepared as outlined in the literature.[22] Benzaldehyde was freshly distilled and stored at −35 °C. Silica gel (90–230 mesh, 60 Å) was used as received from Aldrich.

Measurements of current and luminance as a function of applied field were made under forward bias. A calibrated silicon photodiode was used to measure light output in the forward direction from the device. 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. The internal quantum efficiency of these devices was calibrated from measurements of the current and of the light output in the forward direction. Light emission within the polymer film was assumed to be isotropic, and refraction at the polymer interface was taken into account when calculating the internal quantum efficiency.[36] The refractive index of a NBTPV-C5 50mer film was measured using prism coupling of light into the optical waveguide modes and was found to be approximately 1.7.

PhMe$_2$CCH(MTD)$_{50}$C$_6$H$_4$CHO. Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ (20 mg, 42.9 μmol) was dissolved in 3 mL of toluene. MTD (373 mg, 2.14 mmol) was dissolved in 1 mL of toluene, and the solution was added all at once to a stirred solution containing the initiator. After 15 min, terephthaldehyde (58 mg, 429 μmol) was added and the solution was stirred for 1 h. The polymer was isolated by precipitation into methanol; yield 351 mg (92%). Other polymers (n = 10, 25, 100) were prepared similarly.

(EtO)$_2$(O)PC$_6$H$_4$P(O)(OEt)$_2$. P(OEt)$_3$ (6.71 g, 40 mmol) was mixed with α,α′-dibromo-*p*-xylene (5.44 g, 20 mmol), and the mixture was heated to 100 °C for 5 h. Above 80 °C, EtBr was generated and collected in a Dean-Stark trap. The reaction mixture was cooled to room temperature, and 8.2 g of crude solid product was obtained. Recrystallization from THF gave 6.13 g (81%) of the bis(phosphonate) compound: ^{1}H NMR (C$_6$D$_6$) δ 7.33 (s, 4, ring protons), 3.80 (m, 8, −OCH$_2$), 2.93 (d, 4, −CH$_2$P(O)−), 0.93 (t, 12, −CH$_3$).

Triblock Copolymers 2. The preparation of the polymer in which n = 10 (on average) is provided as an example. A solution containing the aldehyde-capped polyMTD (350 mg, 183 μmol), bis(phosphonate) (29 mg, 92 μmol), and LiO-*t*-Bu (29 mg, 366 μmol) in 30 mL of THF was refluxed for 24 h. The product was precipitated into MeOH and fractionated in THF/MeOH mixtures; yield 140 mg (40%) of pale-yellow polymer. The GPC of this polymer (in THF versus polystyrene standards) showed a unimodal peak with a polydispersity of 1.12.

MeC$_6$H$_4$CH$_2$P(O)(OEt)$_2$ (4). α-Bromoxylene (10 g, 54 mmol) was mixed with triethylphosphite (13.47 g, 81 mmol) and the mixture was heated to 100 °C for 12 h while EtBr was removed in a Dean-Stark trap. Residual EtBr and excess P(OEt)$_3$ were removed in vacuo. Vacuum distillation at 105–

106 °C (0.3 Torr) gave 12.66 g (97%) of pure **4**: ^{1}H NMR ($CDCl_3$) δ 7.10 (m, 4, ring proton), 3.95 (m, 4, OCH_2), 3.08 (2, CH_2P), 2.28 (d, 3, $PhCH_3$), 1.2 (t, 6, CH_3).

$MeC_6H_4CH=CHC_6H_2(OMe)_3$ (5). A mixture of (diethoxyphosphinyl)xylene (5 g, 21 mmol) and 3,4,5-trimethoxybenzaldehyde (4.33 g, 22 mmol) in 5 mL of THF was added to a suspension of NaH (0.73 g, 80%, 24.2 mmol) in 50 mL of THF/DMF (4/1). The mixture was refluxed for 11 h and worked up with ice-water. The product was extracted into ether and the extract was dried over $MgSO_4$. The ether was removed in vacuo to give 4.86 g (81%) of a pale-yellow solid. Pure product was obtained by recrystallization from $CHCl_3$: ^{1}H NMR ($CDCl_3$) δ 7.25 (dd, 4, ring proton), 6.97 (s, 2, vinyl proton), 6.70 (s, 2, ring proton), 3.90 (s, 6, OMe), 3.85 (s, 3, OMe), 2.35 (s, CH_3).

$BrCH_2C_6H_4CH=CHC_6H_2(OMe)_3$ (6). A mixture of MeC_6H_4-$CH=CHC_6H_2(OMe)_3$ (1.82 g, 6.4 mmol) and *N*-bromosuccinimide (1.25 g, 7.0 mmol) was refluxed for 13 h in the presence of a catalytic amount of AIBN (32 mg, 0.2 mmol). The reaction was worked up with water, and product was extracted into chloroform. The solvent was removed from the extract in vacuo to give viscous oily liquid. Trituration of the oil with ether gave 1.53 g (66%) of a pale-yellow solid product: ^{1}H NMR ($CDCl_3$) δ 7.42 (dd, 4, ring proton), 7.0 (m, 2, vinyl proton), 6.72 (s, 2, ring proton), 4.5 (s, 2, CH_2Br), 3.90 (s, 6, OMe), 3.85 (s, 3, OMe).

$(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_2(OMe)_3$ (7). $BrCH_2C_6H_4$-$CH=CHC_6H_2(OMe)_3$ (1.53 g, 4.2 mmol) and 1.40 g (8.4 mmol) of $P(OEt)_3$ were dissolved in 50 mL of toluene, and the mixture was refluxed for 15 h. (EtBr was removed in a Dean-Stark trap.) Residual EtBr and excess $P(OEt)_3$ were removed in vacuo. Pure product was obtained by recrystallizing the crude product from ether by adding pentane; yield 1.30 g (73%): ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 4, ring proton), 6.98 (m, 2, vinyl proton), 6.71 (s, 2, ring proton), 4.0 (m, 4, OCH_2), 3.9 (s, 6, OMe), 3.85 (s, 3, OMe), 3.25 (d, 2, CH_2P), 1.23 (t, 6, CH_3).

4-[5-(5-Norbornenylmethoxy)pentoxy]-3,5-dimethoxybenzaldehyde (8). A mixture of 5-(5-norbornenylmethoxy)-pentyl bromide (5.7 g, 21 mmol) and syringaldehyde (3.83 g, 21 mmol) was heated at 80 °C for 60 h in the presence of K_2CO_3 (4.28 g, 31 mmol). The mixture was worked up with water and the product was extracted into ether. The product (2.03 g, 26%) was separated by column chromatography (silica gel, 1/1 Et_2O/pentane): ^{1}H NMR ($CDCl_3$) δ 9.85 (s, 1, CHO), 7.10 (s, 2, ring proton), 3.78 (s, 6, OMe), plus resonances similar to those in the starting materials.

NBTPV-C5 (3a). $(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_2(OMe)_3$ (1.00 g, 2.4 mmol) in 20 mL of THF was added to a solution of KO-*t*-Bu (0.54 g, 4.8 mmol) in 10 mL of THF, and the mixture was stirred for 30 min. A solution of 4-[5-(5-norbornenylmethoxy)pentoxy]-3,5-dimethoxybenzaldehyde (900 mg, 2.4 mmol) in 3 mL of THF was added to this dark-red solution. The mixture was refluxed for 15 h and worked up with water. The product was extracted into ether and the extract was dried over $MgSO_4$. The solvent was removed from the extract in vacuo to give 0.67 g (44%) of product which was recrystallized from ether by addition of pentane: ^{1}H NMR ($CDCl_3$) δ 7.48 (s, 4, center ring proton), 7.10 (m, 4, vinyl proton), 6.73 (s, 2, side ring proton), 6.72 (s, 2, side ring proton), 3.97 (t, 2, $-CH_2O$), 3.91 (s, 6, OMe), 3.88 (s, 6, OMe), 3.86 (s, 3, OMe), plus resonances analogous to those in starting materials; λ_{max} = 372 nm (in THF). Anal. Calcd for $C_{40}H_{48}O_7$: C, 74.97; H, 7.55. Found: C, 74.56; H, 7.54.

Polymerization of NBTPV-C5 (3a). A solution of Mo(NAr)($CHCMe_2Ph$)(O-*t*-Bu)$_2$ (400 μL of a stock solution of 10 mg in 2.0 mL of THF; 3.64 μmol) was added quickly to a solution of NBTPV-C5 (117 mg, 182 μmol) in 5 mL of THF. After 3 h benzaldehyde (3.8 μL, 36 μmol) was added, and 1 h later the polymer was precipitated by pouring the polymerization reaction into pentane; yield 95%, PDI = 1.10 in THF versus polystyrene standard: $\lambda_{max,abs}$ = 368 nm (in THF), $\lambda_{max,abs}$ = 362 nm (cast film), $\lambda_{max,em}$ = 475 nm (cast film).

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Supplementary Material Available: Synthetic procedures and schemes for preparing **3b**, **3c**, and **3d** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered frm the American Chemical Society. See any current masthead page for ordering information.

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