Blue Solid-State Photoluminescence and Electroluminescence from Novel Poly(*para*-phenyleneethynylene) Copolymers

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We report the synthesis of a series of random copolymers composed of phenyleneethynylene and 3,7-di-*tert*-butylnaphthalene units by alkyne metathesis with simple catalyst systems, formed from $Mo(CO)_6$ and 4-chlorophenol in situ. These novel copolymers give rise to efficient ($\Phi = 0.16-0.76$) blue solid-state emission ($\lambda_{max} = 422-443$ nm) which can be fine-tuned according to their naphthalene content differing greatly from that of standard dialkyl-PPE (λ_{max} 500−520 nm). The effective and blue-shifted solid-state emission is a result of disrupting the solid-state alignment thereby diminishing π-π interactions of the copolymers in addition to the efficient interruption of planarization of the conjugated backbone. Electroluminescent multilayer devices showed low turn-on voltages (5.5 V) and a maximum brightness of 100 cd/m^2.

Introduction

We report synthesis, optical, phase, and electroluminescent properties of a series of novel PPE-based copolymers **5**, which display blue solid-state fluorescence and electroluminescence.

Electroluminescent devices from conjugated organic polymers[1−9] offer advantages such as improved processing, low operating voltages, and low manufacturing costs, as well as the ability to manipulate optical properties by choice of the emitter. Polymer based light-emitting diodes (PLEDs) are especially important for their amenability to large full-color displays. Full-color displays require the color blue, whose electroluminescence from inorganic phosphors is possible but not very effective due to their poor mechanical properties and size limitations. Polymeric blue-emitting phosphors, applicable to the fabrication of large area devices, have been explored only recently.[1e] Blue emission from PLEDs has been reported for the high band-gap polymer poly(*para*-phenylene) (PPP), the processing of which can be problematic.[1] Recently, highly efficient PLEDs were fabricated from poly(dialkylfluorene)s (PAF).[2] A conceptually different approach to blue EL has been reported from polymers in which the conjugated segments are interrupted with non- or weakly conjugated units.[3−6]

The synthesis of high molecular weight poly(*p*-phenyleneethynylene)s (PPEs) by alkyne metathesis using mixtures of $Mo(CO)_6$ and phenols in off-the-shelf solvents has been developed in our laboratory.[10] PPEs are highly emissive in solution ($\lambda_{max} = 425$ nm) with quantum yields approaching unity.[10] The observed red-

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shifted emission of PPEs ($\lambda_{max} = 500-520$ nm) in the solid state is probably the result of aggregation, planarization, and excimer formation.[10] It has been reported for polythiophenes[11] and polyphenylenes[12] that planarization leading to conformational locking of the arene units with respect to one another results in red-shifted absorption and emission, similarly observed for PPEs.[10b] Planarity of the main chain alone will effect an accountable decrease in the HOMO−LUMO gap (rotation of phenyleneethynylenes < 1 kcal/mol[13]), despite the accommodating electronic nature of the acetylene linker. Therefore *intrachain* effects may be involved in the red shift observed when going from solution into the solid state. Planarity of the polymer backbone in the solid state however likewise allows for phenyl rings of neighboring polymers to pack closely according to X-ray powder diffraction[10c] and, thus, enables *inter*chain interactions.

To achieve blue solid-state emission, we attempt to prohibit both interchain interactions and planarization, enforcing emission from individual polymer chains as is seen in solution spectra. To this end, PPE copolymers possessing sterically obtrusive aryl units (3,7-di-*tert*-butylnaphthalene) were of particular interest.[14−19] As the comonomer feed ratio (i.e. naphthalene content) increases, we expect aggregate formation and planarization to diminish, which would result in intense blue solid-state photoluminescence.

Experimental Section

Synthesis. All chemicals were used as purchased unless otherwise stated.

1,5-Diiodo-3,7-di-*tert*-butylnaphthalene (2). To a mixture of **1** (10.0 g, 40.3 mmol), I_2 (11.2 g, 44.3 mmol), and KIO_4 (2.27 g, 8.94 mmol) were added acetic acid, sulfuric acid, and $CHCl_3$ (25 mL; 4 mL; 7 mL). This solution was refluxed at 115 °C for 5 days. The progress of the reaction was determined by ^1H NMR spectroscopy. The cooled reaction mixture was poured into a solution of sodium sulfite in H_2O. After extraction with hexanes and several washes with H_2O, the product was dried over $MgSO_4$ and solvent was evaporated. Brown crystals were filtered over silica gel using hexanes as eluent and then recrystallized from EtOH. **2** (11.5 g, 60%) was obtained as colorless crystals, mp 203−206: ^1H NMR ($CDCl_3$) $\delta = 8.19$ (d, $J = 1.7$ Hz, 2H), 8.04 (d, $J = 1.8$ Hz, 2H), 1.45 (s, 18 H); ^{13}C NMR ($CDCl_3$) $\delta = 150.9$, 137.4, 132.2, 128.7, 100.2, 35.0, 31.2. Anal. Calcd for $C_{17}H_{19}I_2$: C, 42.79; H, 4.01. Found: C, 44.34; H, 4.34.

1,5-Dipropynyl-3,7-di-*tert*-butylnaphthalene (3). **2** (16.7 g, 35.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.300 g, 0.430 mmol), CuI (0.200 g, 1.05 mmol), and piperidine (40 mL) were added to a 500 mL Schlenk flask. After evacuation, propyne gas was added (appropriate amount of propyne gas was determined according to the volume of the selected Schlenk flask). The flask was placed on a Parr shaker for 14−16 h. The reaction mixture was extracted with CH_2Cl_2 and washed with NH_4OH and H_2O. After evaporation of solvent, **3** was filtered over silica using hexanes as eluent followed by crystallization from EtOH (colorless crystals, 8.53 g, 73%), mp 227−229: ^1H NMR ($CDCl_3$) $\delta = 8.17$ (d, $J = 2.0$, 2H), 7.71 (d, $J = 2.0$ Hz, 2H), 2.23 (s, 6H), 1.41 (s, 18 H); ^{13}C NMR ($CDCl_3$) $\delta = 147.8$, 131.3, 129.3, 121.3, 90.1, 78.3, 34.9, 31.3, 4.8. Anal. Calcd for $C_{25}H_{32}$: C, 90.30; H, 9.70. Found: C, 90.28; H, 9.69.

Copolymer 5a. **3** (0.047 g, 0.14 mmol), **4** (0.350 g, 0.713 mmol), $Mo(CO)_6$ (0.021 g, 0.09 mmol), 4-chlorophenol (0.110 g, 0.856 mmol), and 1,2-dichlorobenzene (20 mL) were held at 140 °C under a steady stream of N_2 for 25 h. The reaction mixture was cooled and extracted with CH_2Cl_2 (50 mL) and washed with H_2O (100 mL), 10% NaOH (100 mL), and 25% HCl (100 mL). The organic layer was precipitated into MeOH (400 mL), filtered out, and dried, furnishing the yellowish polymer **5a** (0.300 g, 86%): ^1H NMR ($CDCl_3$) $\delta = 8.40$ (bs), 7.90 (bs), 7.42−7.23 (m), 2.98−2.83 (m), 2.10 (s), 1.72−1.52 (m), 1.50−1.25 (m), 0.87−0.86 (m); ^{13}C NMR ($CDCl_3$) $\delta = 148.3$, 141.8, 132.5, 132.4, 131.2, 129.8, 122.7, 121.1, 93.1, 35.1, 34.3, 34.0, 32.1, 31.4, 30.9, 30.8, 29.9, 29.8, 29.5, 22.8, 14.3. Anal. Calcd: C, 88.10; H, 11.90. Found: C, 87.7; H, 12.26.

Copolymer 5b. **3** (0.220 g, 0.662 mmol), **4** (0.647 g, 1.32 mmol), $Mo(CO)_6$ (0.049 g, 0.20 mmol), 4-chlorophenol (0.255 g, 1.98 mmol), and 1,2-dichlorobenzene (20 mL) were held at 140 °C under a steady stream of N_2 for 18 h. Workup (vide supra) as described for **5a** furnished **5b** (0.490 g, 64%): ^1H NMR ($CDCl_3$) $\delta = 8.51-8.38$ (m), 8.03 (bs), 7.90 (bs), 7.57−7.21 (m), 2.98−2.67 (m), 2.24 (bs), 2.18−2.07 (m), 2.02 (s), 1.74−1.63 (m), 1.49−1.20 (m), 0.92−0.86 (m); ^{13}C NMR ($CDCl_3$) $\delta = 148.2$, 141.8, 141.6, 132.5, 132.3, 132.2, 131.2, 129.8, 123.3, 122.8, 121.9, 121.1, 93.2, 92.5, 92.1, 78.6, 35.1, 34.3, 34.0,32.0, 31.4, 31.3, 30.9, 30.8, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 14.2, 4.7. Anal. Calcd: C, 88.68; H, 11.32. Found: C, 88.13; H, 11.87.

Copolymer 5c. **3** (0.237 g, 0.713 mmol), **4** (0.350 g, 0.713 mmol), $Mo(CO)_6$ (0.034 g, 0.114 mmol), 4-chlorophenol (0.091 g, 0.71 mmol), and 1,2-dichlorobenzene (20 mL) were held at 140 °C under a steady stream of N_2 for 17 h. Workup furnished the greenish-yellow polymer **5c** (0.400 g, 79%): ^1H NMR ($CDCl_3$) $\delta = 8.58-8.54$ (m), 8.07 (bs), 7.94 (bs), 7.60−7.42 (m), 3.02−2.89 (m), 2.13 (bs), 2.12 (bs), 1.79−1.68 (m), 1.51−1.22 (m), 0.88−0.87 (bs); ^{13}C NMR ($CDCl_3$) $\delta = 148.4$, 141.9, 132.5, 131.3, 123.0, 122.8, 121.1, 92.7, 35.1, 34.4, 32.0, 31.4, 31.3, 30.8, 29.8, 29.5, 29.4, 22.8, 14.2 Anal. Calcd: C, 89.22; H, 10.78. Found: C, 88.16; H, 11.84.

Copolymer 5d. **3** (0.200 g, 0.601 mmol), **4** (0.147 g, 0.299 mmol), $Mo(CO)_6$ (0.022 g, 0.089 mmol), 4-chlorophenol (0.116 g, 0.902 mmol), and 1,2-dichlorobenzene (15 mL) were held at 140 °C under a steady stream of N_2 for 12 h. Workup furnished **5d** (0.230 g, 77%): ^1H NMR ($CDCl_3$) $\delta = 8.57-8.43$ (m), 8.06 (bs), 7.95−7.93 (m), 7.90 (m), 7.59−7.22 (m), 3.03 (m), 2.26 (bs), 2.25 (bs), 2.12 (s), 1.83−1.67 (m), 1.52−1.21 (m), 0.85 (m); ^{13}C NMR ($CDCl_3$) $\delta = 148.4$, 141.9, 132.8, 132.5, 132.3, 132.2, 131.3, 131.2, 130.0, 122.9, 122.2, 121.1, 93.2, 92.7, 35.2, 34.4, 34.0, 32.0, 31.4, 31.3, 30.7, 30.6, 29.8, 29.6, 29.5, 29.4, 22.8, 14.2, 2.5. Anal. Calcd: C, 89.76; H, 10.24. Found: C, 88.35; H, 11.65.

Characterization. Photoluminescent data and quantum yields were obtained using a Jasco FP-6500 spectrofluorometer equipped with an integrating sphere and a quantum counter.

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Solution quantum yields ($CHCl_3$) were measured relative to quinine sulfate in sulfuric acid, and thin film quantum yields (spin cast from toluene or chloroform (12 mg/mL)) were measured relative to 9,10-diphenylanthracene in a poly(methyl methacrylate) film.[20]

For electrochemical experiments, thin films of all polymers on indium tin oxide (ITO)-coated slides (Delta Technologies Ltd.) were prepared by spin coating chloroform solution (25 mg/mL) of the polymer onto ITO at a speed of 1500 rpm. The experimental instrumentation for electrochemistry consisted of an EG & G Parc model 263A potentiostat/galvanostat, controlled by Power CV electrochemistry software (Perkin-Elmer). Cyclic voltammetry (CV) of the thin films was performed in a standard 3-electrode cell using tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium tetrafluoroborate supporting electrolyte in dichloromethane (DCM) and acetonitrile (ACN). Polymer-coated ITO was the working electrode, and platinum wire was the counter electrode. Potentials were measured against a silver/silver nitrate reference electrode using ferrocene as an additional internal standard (with ferrocene's absolute energy level being 4.8 eV below the vacuum[21]). Experiments to determine reduction potentials were carried out in a glovebox under argon atmosphere.

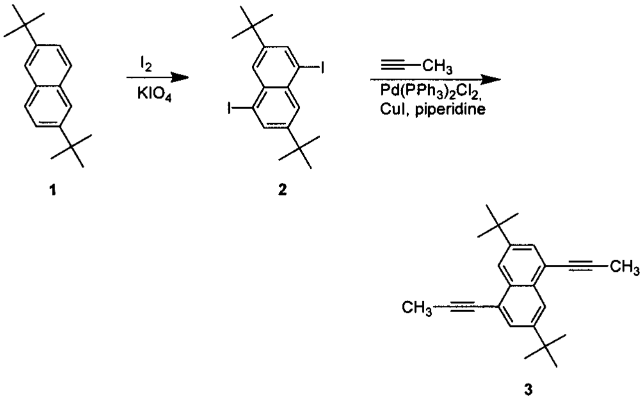
For the fabrication of the devices, glass substrates patterned with 100 nm ITO electrodes (Balzers) were cleaned subsequently in ultrasonic baths of acetone, ionic detergent water solution, ultrapure water (MilliQunit from Waters), and 2-propanol. After drying, a 20 nm layer of polyethylenedioxythiophene doped with poly(styrenesulfonate) (PEDOT:PSS) was coated on top. The films were dried in a vacuum for 6 h at room temperature. Then, the emitting copolymers **5** or PPE were spin-coated on top from a 10 g/L polymer in toluene/chloroform (1:1) solution to obtain films of a final thickness of ca. 80 nm. After drying of the sample overnight under vacuum at room temperature, a 1 nm thick LiF layer was deposited by thermal evaporation at a pressure of $\sim 3 \times 10^{-6}$ mbar at rate of 1 Å s^{-1}, followed by a 100 nm thick Al electrode evaporated at 5 Å s^{-1}. The overlap between the two electrodes resulted in a device area of 5×2 mm^2. The device characterization was carried out in an evacuated sample chamber.

Measurements were carried out with a computer-controlled Keithley 236 Source/Measure unit. Luminescence results were recorded by either a Newport model 818-UV photodiode, an E686 Princeton Applied Research model 1235 digital triple grating spectrograph, or a spot photometer (MINOLTA CS-100).

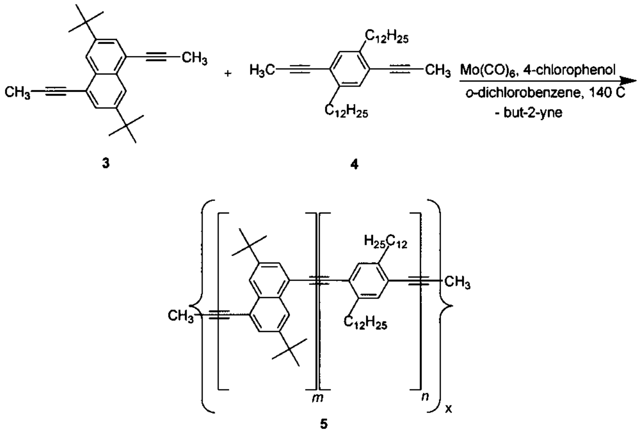
Results and Discussion

Synthesis and Characterization. The synthesis of monomer **3** begins with a Friedel–Crafts dialkylation of naphthalene,[15] followed by iodination of **1** to furnish the 1,5-diiodonaphthalene derivative **2** (Scheme 1). Sonogashira coupling of gaseous propyne to **2** affords monomer **3**. The ADIMET polymerization of **3** results in a nonfluorescent, highly insoluble, low molecular weight poly(naphthyleneethynylene).[16] The copolymerization of monomers **3** and **4** (for the synthesis of **4**[10]) results in a series of highly fluorescent copolymers of substantial molecular weights (Scheme 2, Table 1). The copolymers **5** were obtained by heating monomers **3** and **4**, molybdenum hexacarbonyl, and 4-chlorophenol to 140 °C in off-the-shelf *o*-dichlorobenzene for 16–24 h. Gel permeation chromatography based on polystyrene standards approximated the molecular weight of the copolymers to be between $P_n = 42$ for the polymer containing the largest naphthalene percentage (**5d**) to 96 in the case of **5a**. The reason for the lower molecular weights found in **5d** is a result of the poor solubility provided by the *tert*-butyl substituent. The bulky side chains are, however, beneficial in the prevention of solid-state aggregate formation.

Scheme 1. Synthesis of Naphthalene Monomer



Scheme 2. Copolymerization via Alkyne Metathesis



Optical Properties. To determine the optical and aggregation properties of the copolymers we investigated their solvatochromatic behavior. The UV–vis spectra of **5a–d** are nearly identical in chloroform and show a single broad absorbance centered between 388 and 395 nm, quite similar to that of dialkyl-PPEs (388 nm).[10] The minimal blue shift from **5a** to **5d** suggests a slight decrease in electron delocalization as the less conjugated butylnaphthalene monomer concentration increases. Upon the addition of methanol (nonsolvent) to a copolymer solution in chloroform, an "aggregate-induced" band forms in **5a** (Figure 1, 433 nm) and also in **5b** (434 nm), similar to that of the parent PPEs (439 nm).[10] Copolymers **5c,d**, however, show no apparent aggregation upon the addition of nonsolvent, suggesting that planarization/aggregation is suppressed. Thin film UV–vis spectra of **5a,b** show a second, red-shifted absorption at 420 nm as seen in the case of the dialkyl-PPEs (439 nm). This second band is not present in **5c,d** where the thin film and solution absorptions are identical, suggesting a lack of ordering of polymer chains in the solid state.

More interesting are the photoluminescent properties of these copolymers. In dilute chloroform solution **5a–d** all possess two well-resolved emission bands, the first

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Table 1. Characterization of 5a−d

entry	ratio **4**:**3**	yield (%)	GPC P_n[a]	GPC PDI	abs (nm) $CHCl_3$	abs (nm) thin film	emission (nm) $CHCl_3$ (Φ_{fl}[b])	thin film (toluene) (Φ_{fl})	thin film (chloroform) (Φ_{fl})
5a	5:1	86	96	2.9	395	395, 420	425, 446 (0.88)	443, 470 (0.55)	(0.76)
5b	2:1	64	49	2.9	390	390, 420	422, 443 (0.85)	442, 469 (0.34)	(0.27)
5c	1:1	79	56	4.7	391	391	421, 444 (0.81)	432 (0.50)	(0.16)
5d	1:2	77	42	2.3	388	388	419, 440 (0.72)	422 (0.28)	(0.23)
didodecyl-PPE	1:0	na	na	na	388	439	425, 450 sh (1.0)	na	520 (0.13)
dialkoxy-PPE[18]	na	na	na	na	453	483	478 (0.27)	496 (0.09)[c]	na

[a] Gel permeation chromatography results based on polystyrene standard. [b] Quantum yields given in parentheses are the average of 10 experiments and possess approximately 10% relative standard deviation. [c] See: Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605, Table 11.

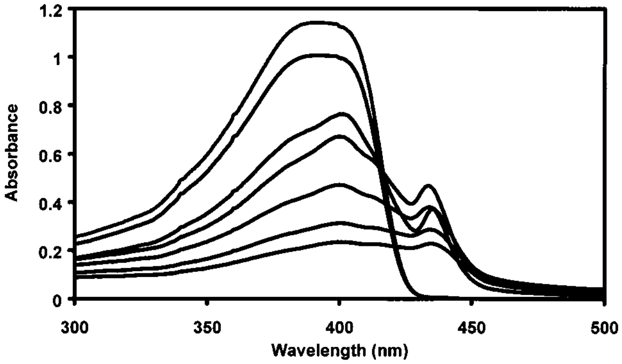

Figure 1. Absorption Spectra of **5a** ($CHCl_3$) upon the addition of MeOH (0, 17, 29, 38, 44, 55, and 62% top to bottom). The "aggregate band" is observed at 433 nm.

centered between 419 and 425 nm and a second transition between 440 and 446 nm, being least pronounced in **5d**. The spacing of 1082 cm^{-1} cannot be attributed to any *specific* molecular vibration. The narrow and well-defined emission spectra are evidence of localized and/or planarized excited states. As the naphthalene content increases, a slight hypsochromic shift is observed, suggesting perhaps a small electronic contribution as the conjugated segments are redefined by the less conjugated naphthalene units. In the case of the PPEs, upon the addition of methanol (62% MeOH), the major emission band is suppressed, leaving only the intensified second band and the excimer bands between 475 and 580 nm.[10] Figure 2 shows that with increasing naphthalene content (**5c,d**), the red-shifted bands are significantly decreased, suggesting the effective reduction of both planarization and interchain interactions. This results in polymers with *blue* solid-state photoluminescence, *where the spectra of thin films of* **5c−d** *are nearly identical to those in solution* (Figures 2 and 3), with the exception of a low-intensity emission at 550 nm and beyond.

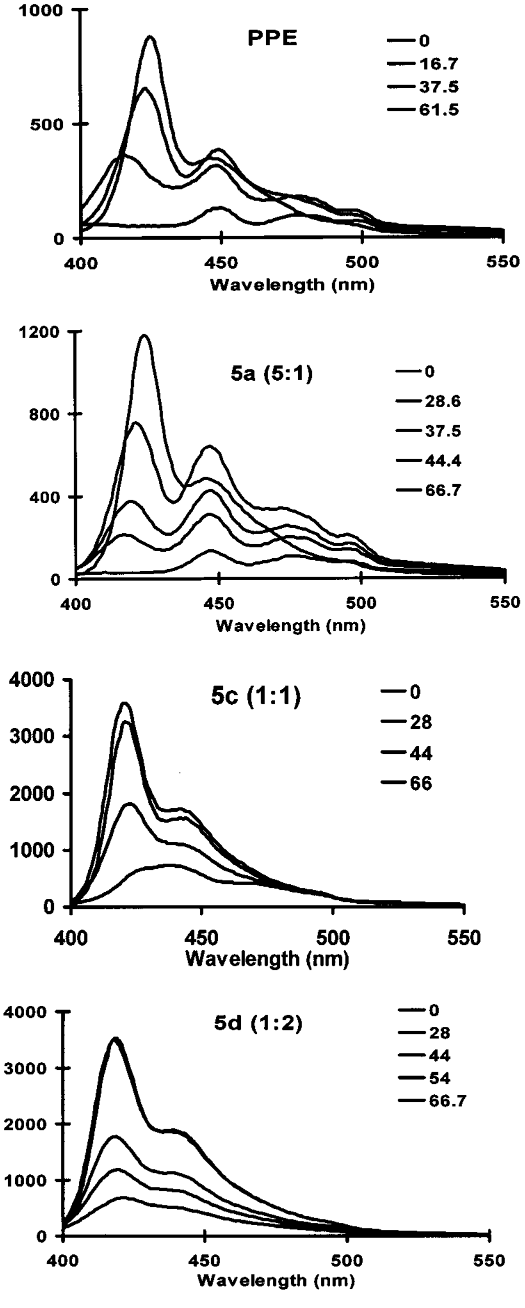

Figure 2. Emission spectra of didodecyl-PPE, **5a**, **5c**, and **5d** in $CHCl_3$ upon the addition of MeOH. (Percentages of MeOH top to bottom are in accordance to the same order in the spectra.)

Fluorescence quantum yields Φ (in $CHCl_3$) of the copolymers **5** range from 0.72 (**5d**) to 0.88 (**5a**), showing a steady increase as we approach the parent PPE ($\Phi = 1$). More important for optical device construction are of course solid-state quantum yields. As the polymers become somewhat more ordered as spin cast films, the quantum yields decrease as expected.[22] The solid-state quantum yields were however quite high (0.16−0.76) when compared to that of dialkyl-PPEs ($\Phi = 0.13$) and to dialkoxy-PPEs ($\Phi = 0.09$)[19] (Table 1) and even exceed that of Swager's ipticene-containing PPEs.[19] Interestingly, the solid-state quantum yields are—in an obscure

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[22] Bazan and Yu have showed this elegantly in the synthesis of highly emissive, amorphous conjugated oligomers: (a) Wang, S.; Oldham, W. J.; Hudack, R. A.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695. Oldham, W. J.; Lachiotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 2987. (b) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079. Maddux, T. M.; Li, W.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 844.

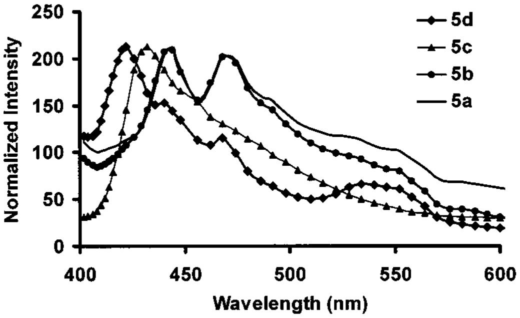

Figure 3. Photoluminescence spectra of **5a**−**d** as thin films.

Table 2. Cyclic Voltametry Data for 5a−d

copolym	E_{ox} (V vs Fc/Fc$^+$)	I_P (eV)	E_{red} (V vs Fc/Fc$^+$)	EA (eV)	electrochem band gap (eV)	opt band gap (eV)
5a	0.85	5.65	−2.35	2.45	3.2	2.74
5b	0.85	5.65	−2.35	2.45	3.2	2.76
5c	0.95	5.75	−2.5[a]	2.3	3.45	2.84
5d	0.95	5.75	−2.5[a]	2.3	3.45	2.89

[a] The reduction onset is determined by color change.

way—dependent upon the solvent from which the films are spun. Supramolecular ordering perhaps plays a major role in the determination of **5**'s emissive properties.[22]

Thermal Properties. The thermal behavior of the emissive polymers is important for device fabrication, and when they are liquid crystalline, entry into polarized emission may be possible. We have reported that dialkyl-PPEs are liquid crystalline.[14,17] The introduction of naphthalene units bearing bulky *tert*-butyl groups should disrupt/modify their LC behavior. Differential scanning calorimetry (DSC) was performed on all copolymers (range 50−250 °C). Polymers **5a**−**c** show side-chain melting of the dodecyl chains between 40 and 44 °C, **5c** shows a second melting transition near 60 °C, and in **5d** only the second transition (64 °C), attributed to a solid-state structure transition is observed. Copolymer **5a** features a reproducible LC−isotropic transition at 161 °C upon heating and a liquid crystalline transition upon cooling (126 °C, exothermic, 0.27 kcal mol^{-1} per repeating unit). Polarizing light microscopy (PLM) revealed a nematic phase evidenced by a Schlieren texture. **5b** shows only the LC−crystalline transition at 43 °C upon cooling, according to DSC; however, a nematic phase was evidenced upon cooling (129 °C) by PLM. Copolymers **5c,d**, which contain 50% and 66% naphthalene, show no isotropic transitions by DSC, but an LC−isotropic transition was evidenced by PLM at 170 °C for **5c**.

Electrochemistry. Optical properties of conjugated polymers are related to their band gap, the difference between the HOMO and LUMO energy levels. To determine the energy levels of the copolymers, electrochemical measurements were made on thin polymer films using cyclic voltammetry (CV). The ionization potential (I_p) was determined by the onset of oxidation in dichloromethane and was nearly identical for **5a**−**d**. The HOMO values (5.65−5.75 eV; see Table 2) of these copolymers are lower than the values reported by Weder et al.[18] for dialkoxy-PPEs (6.3 eV). However I_p values obtained in acetonitrile were found to be shifted anodically by 0.2 to 0.3 V, illustrating the effect of electrochemical environment on polymer redox behavior. The I_p found by us for hexyl-dodecyl PPE under similar conditions was 5.3 eV.[23]

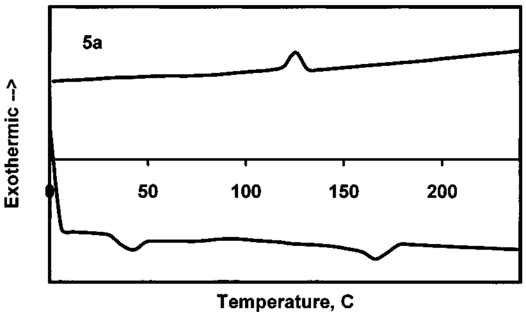

Figure 4. DSC of **5a** (heating, 40.2, 167.9 °C; cooling, 125.8 °C).

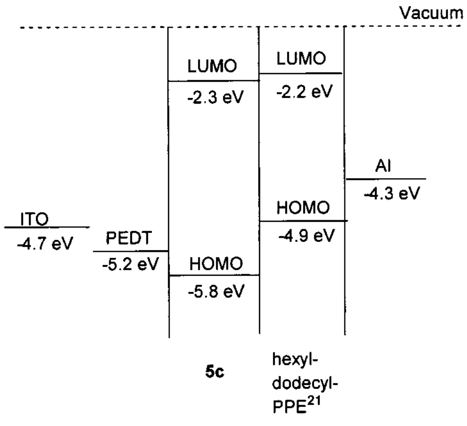

Figure 5. Schematic representation comparing energy levels of hexyl-dodecyl PPE[21] with copolymer **5c**.

The onset of reduction in acetonitrile was found to occur for **5a,b** at −2.35 V vs Fc/Fc$^+$ and was reversible. However for **5c,d** the cathodic currents were not significantly above the baseline to determine onset potentials, but at the edge of the potential window −2.6 V vs Fc/Fc$^+$ both polymers undergo a color change to dark green, indicating the onset of reduction. Band gaps obtained electrochemically were larger than those estimated from UV−vis data but follow the same trend, despite the fact that the UV−vis data do not account for exciton binding energy.[24] Increasing the naphthalene content lowers the HOMO energy as compared to dialkyl-PPEs, probably due to the breaking of conjugation (Figure 5).

Electroluminescence Properties. Electroluminescent devices[25] fabricated from PPEs and their derivatives are almost unknown, and only recently Weder[18] and Barton[26] reported LEDs based on dialkoxy-PPEs.[25] Both reported relatively disappointing results. There seem to be two reasons for the poor performance of PPEs in devices: (a) The relatively low-lying HOMO makes hole injection from ITO difficult, and (b) the highly

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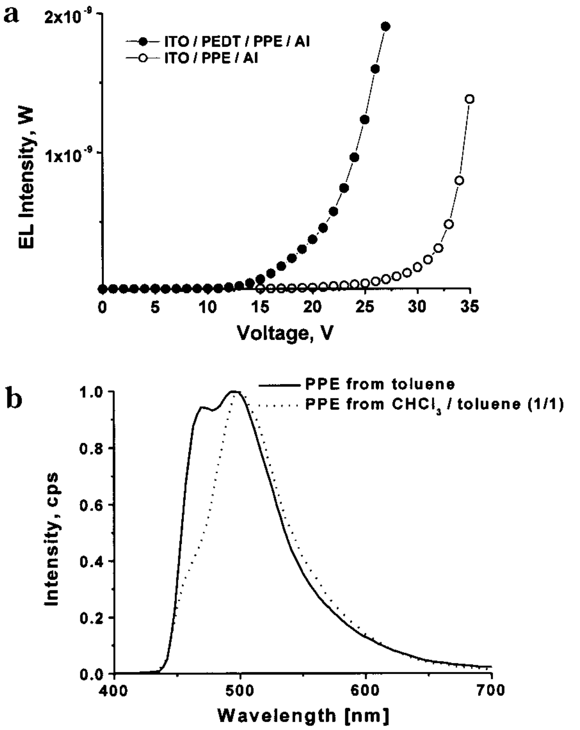

Figure 6. (a) Spectrally integrated EL emission intensity for a PPE-based OLED with (solid symbols) and without (open symbols) a PEDT hole injection layer. (b) Normalized electroluminescence spectra of hexyl-dodecyl-PPE where the emissive layer is spin-cast from toluene and from $CHCl_3$/toluene (1:1).

ordered PPEs have low solid-state fluorescence quantum yields, probably due to efficient interchain interactions leading to the formation of aggregates or excimers. Aggregate/excimer formation has been identified as a major source for the reduced performance of PPE devices.[10f] The latter problem has been solved efficiently here by the introduction of bulky di-*tert*-butylnaphthalene units while the former problem can be addressed by the incorporation of a hole-injection layer. As demonstrated in Figure 6a, where PPE is the emissive layer, incorporation of a PEDT layer significantly reduces the turn-on voltage. The emission spectrum is quite sensitive to the solvent used for spin-coating (Figure 6b) and the blue-emitting contribution is more pronounced when the layer is deposited from a chloroform/toluene (1:1) mixture. This behavior indicates that solid-state ordering and aggregation is less significant for films spun from that solvent. In a second generation LED we utilized polymer **5b,c** in a multilayer device structure that proved to be much more efficient. The device with **5b** as emitting layer has a low turn-on voltage (5.5 V) and a peak brightness of 100 cd/m^2 at 10 V, while emitting greenish-blue light ($\lambda_{max} = 472$ nm). Copolymer **5c** displayed blue luminescence ($\lambda_{max} = 428$ nm) with maximum brightness of 20 cd/m^2 at 16 V (see Figure 7). Most important, OLEDs from copolymer **5c** exhibit an electroluminescence spectrum similar to the photoluminescence spectrum of **5c** in toluene solution proving that aggregate formation in the solid state is largely suppressed. As expected, copolymer **5b**, which contains a lower fraction of *tert*-butylnaphthalene units, exhibits a more red-shifted electroluminescence. In some cases we have used Ca cathodes instead of Al; however, devices utilizing the less sensitive Al cathodes had larger efficiencies, in agreement with the findings by Weder et al. for the case of pure PPE emission layers.[18] Even though the overall efficiencies of the devices (ca. 0.1 Cd/A for the greenish-blue emitting polymer **5b** and 0.02 Cd/A for blue-emitting **5c**) are not very high, the external quantum efficiency is ca. 0.1−0.15% for diodes made from **5b,c**. These very encouraging results indicate that nonradiative decay channels caused by aggregates can be avoided by our copolymer approach, and we feel that there is room for improvement when fabricating polyaryleneethynylene-based LEDs.

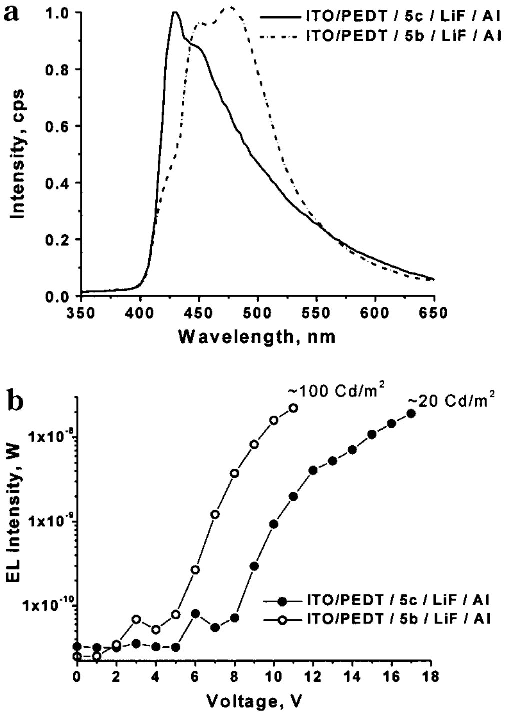

Figure 7. (a) Normalized electroluminescence spectra of devices with **5b,c** as emissive layers. (b) Spectrally integrated EL intensity vs voltage characteristics for devices with emissive layers made from **5b,c**.

Conclusion

We have demonstrated that (a) PPE-types displaying blue solid-state fluorescence can be synthesized by alkyne cometathesis of dipropynyldidodecylbenzene and 1,5-dipropynyl-2,6-di-*tert*-butylnaphthalene, (b) these copolymers display high solid-state fluorescence quantum efficiencies, and c) blue-emitting OLEDs were fabricated by utilizing these polymers. The OLEDs show low turn-on voltages and increased efficiency as compared to previously reported PPE devices. With this carefully engineered approach we show that even polymers, which were recently deemed to be of little interest as emissive layers OLEDs, can give attractive results.

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