Light-Emitting Polyacetylenes: Synthesis and Electrooptical Properties of Poly(1-phenyl-1-alkyne)s Bearing Naphthyl Pendants

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ABSTRACT: Disubstituted polyacetylenes bearing naphthalene pendants with varying spacer lengths $\{-[(C_6H_5)C=C(CH_2)_mONap]_n-$; P**1**(*m*) (*m* = 3, 4, 9), Nap = 1-naphthyl$\}$ are synthesized, and the effects of structural variations on the optical properties of the polymers are studied. The monomers are prepared by simple etherification and coupling reactions of ω-chloro-1-alkynes. Polymerizations of the monomers are effected by $NbCl_5-$ and WCl_6-Ph$_4$Sn catalysts, with the latter affording high molecular weight polymers in high yields (M_w up to 1.3×10^5 and isolation yield up to 91%). The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, UV, PL, and EL analyses. All the polymers enjoy high thermal stability. While they start to lose weights at temperatures of ∼430 °C under nitrogen, almost no decrease in molecular weight is observed when they are annealed in air for 2 h at 200 °C. Photoexcitation of their solutions induces strong blue light emissions at 460 nm, whose quantum efficiencies are comparable to that of poly(1-phenyl-1-octyne), a well-known highly emissive disubstituted polyacetylene. No significant shifts in the emission maxima are observed when the polymers are fabricated into thin films, suggesting that aggregate formation exerts little effect on the photophysical processes of the polymers. Multilayer electroluminescence devices with a configuration of ITO/P**1**(*m*):PVK/BCP/Alq$_3$/LiF/Al are fabricated, which emit a blue light of 464 nm with a maximum luminance of 1019 cd/m^2. The device performance varies with the spacer length, with P**1**(4) giving the highest value of external quantum efficiency of 0.61%.

Introduction

Much research effort has been devoted to the design and synthesis of polymers with extended π-conjugation due to their potential applications in optics and electronics.[1,2] Photoluminescence (PL) and electroluminescence (EL) of conjugated macromolecules have drawn special attention because of their crucial roles in the fabrication of all-plastic light-emitting diodes (LEDs).[3] Many research groups have worked on the development of light-emitting conjugated polymers.[4] As a result, red and green LEDs with high luminance and efficiency have been achieved. In contrast, strong blue emitters are still rare. Polyacetylene is the best-known conjugated polymer and exhibits a metallic conductivity upon doping.[5] The polymer, however, does not emit in the visible spectral region. Replacement of its hydrogen atoms can significantly perturb its electronic properties, and intense blue and green PLs have been observed in some disubstituted polyacetylenes such as poly(diphenylacetylene)s, poly(1-phenyl-1-alkyne)s (PPAs), poly(1-chloro-2-arylacetylene)s, and poly(1-methyl-2-naphthylacetylene)s,[6−8] offering the polymers the potential of being utilized in the construction of EL devices. Multilayer color-variable LEDs have been developed,[9] and a green photopumped-pulsed laser has been observed in cylindrical microcavities,[10] in both of which the active layers are thin films of disubstituted polyacetylenes. Although disubstituted polyacetylenes are EL-active, their performances are rather quite poor. The best results for blue and green emissions have been obtained from poly(1-phenyl-1-octyne) (PPO) and

poly[1-(*p*-butylphenyl)-2-phenylacetylene],[6e,f] with a maximum luminance of barely 0.5 and 30 cd/m^2 and an efficiency of 0.01 and 0.04%, respectively. Substituted polyacetylenes are thus generally referred to as weak EL luminophors and hence unpromising candidates for light-emitting materials.

Performance of an EL device can be improved by two approaches. One is the optimization of the device configuration with the aim of balancing the charge injections and improving the mobilities of the electrons and holes injected from the cathode and anode, respectively. This can be accomplished by the fabrication of multilayer devices. The second approach involves the structural design of light-emitting materials by molecular engineering endeavors, which can furnish conjugated polymers with HOMO and LUMO energy levels that well match the electrodes.

A wide variety of substituted acetylene monomers can be readily derived by simple chemical reactions, and our recent success in the development of functionality-tolerant catalysis systems has offered a large avenue in the design and synthesis of substituted polyacetylenes with polar functional groups.[7,11] In this paper, we report the preparation and electrooptical properties of a group of PPAs containing chromophoric naphthyl pendants with varying lengths of methylene spacer [P**1**(*m*); Scheme 1]. We show here that by proper design of polymer structure and modification of device configuration, disubstituted polyacetylenes can exhibit strong blue EL in high external quantum efficiency.

Results and Discussion

Monomer Synthesis. We designed 1-phenyl-1-alkyne monomers containing naphthyl units [**1**(*m*)] and elaborated a two-step reaction route for their synthesis (cf. Scheme 1). We first
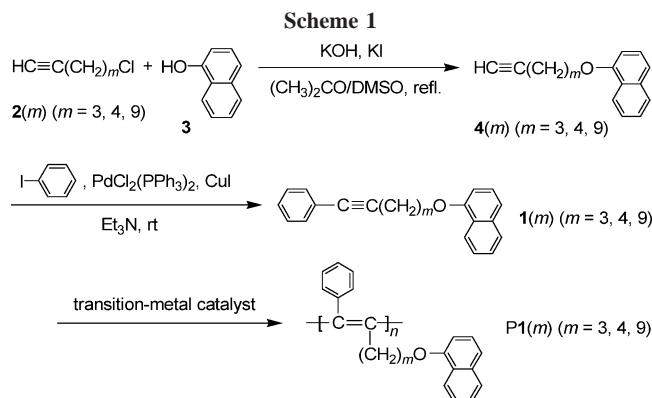
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Scheme 1

Table 1. Polymerization of 5-(1-Naphthoxy)-1-phenyl-1-pentyne [1(3)][a]

no.	catalyst	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]
1	NbCl$_5$–Ph$_4$Sn	60	31.8	56 000	4.1
2	TaCl$_5$–Ph$_4$Sn	60	0		
3	WCl$_6$–Ph$_4$Sn	rt	78.1	133 200	2.7
4	WCl$_6$–Ph$_4$Sn	60	91.2	112 700	2.4
5	MoCl$_5$–Ph$_4$Sn	60	0		

[a] Carried out under nitrogen in toluene for 24 h; [M]$_0$ = 0.2 M, [cat.] = [cocat.] = 10 mM. [b] Determined by GPC in THF on the basis of a polystyrene calibration.

Table 2. Polymerization of Naphthalene-Containing 1-Phenyl-1-alkynes[a]

no.	catalyst	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]
	6-(1-Naphthoxy)–1-phenyl-1-hexyne [1(4)]				
1	NbCl$_5$–Ph$_4$Sn	60	44.6	84 500	5.1
2	TaCl$_5$–Ph$_4$Sn	60	trace		
3	WCl$_6$–Ph$_4$Sn	rt	trace		
4	WCl$_6$–Ph$_4$Sn	60	90.2	58 500	2.4
5	MoCl$_5$–Ph$_4$Sn	60	0		
	11-(1-Naphthoxy)–1-phenyl-1-undecyne [1(9)]				
6	NbCl$_5$–Ph$_4$Sn	60	14.6	132 500	7.4
7	TaCl$_5$–Ph$_4$Sn	60	0		
8	MoCl$_5$–Ph$_4$Sn	60	0		
9	WCl$_6$–Ph$_4$Sn	rt	27.9	16 800	3.2
10	WCl$_6$–Ph$_4$Sn	60	76.8	216 200	3.3

[a] Carried out under nitrogen in toluene for 24 h; [M]$_0$ = 0.2 M, [cat.] = [cocat.] = 10 mM. [b] Determined by GPC in THF on the basis of a polystyrene calibration.

reacted ω-chloro-1-alkynes [**2**(m)] with 1-naphthol (**3**), which gave ω-(1-naphthoxy)-1-alkynes [**4**(m)] in ∼56−88% yields after column purification. Compounds **4**(m) were then transformed to the desired monomers **1**(m) by coupling reactions with iodobenzene, using PdCl$_2$(PPh$_3$)$_2$ as catalyst under basic conditions. All the reactions proceeded smoothly, and the final products were isolated in high yields (72−82%). The purified monomers were characterized by standard spectroscopic methods with satisfactory analysis data obtained (see Experimental Section for details).

Polymerization by Transition-Metal Catalysts. We first tried to polymerize the monomers by NbCl$_5$– and TaCl$_5$–Ph$_4$-Sn, which are effective catalysts for the polymerizations of 1-phenyl-1-alkynes.[12] Stirring a toluene solution of **1**(3) in the presence of NbCl$_5$–Ph$_4$Sn under nitrogen for 24 h produces a pale yellow powdery solid in a moderate yield (Table 1, no. 1). Analysis by GPC gives an M_w of 5.6 × 10^4 and a polydispersity (M_w/M_n) of 4.1, confirming the polymeric nature of the product. TaCl$_5$–Ph$_4$Sn, on the other hand, is ineffective in polymerizing the monomer. We also tested the catalytic activity of WCl$_6$– and MoCl$_5$–Ph$_4$Sn. While the polymerization catalyzed by WCl$_6$–Ph$_4$Sn at room temperature furnishes a high molecular
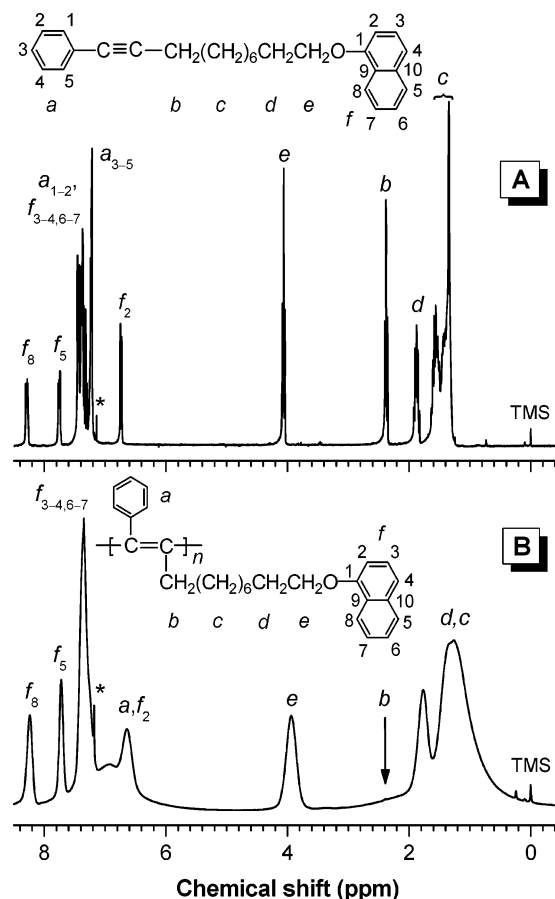
Figure 1. ^{1}H NMR spectra of chloroform-*d* solutions of (A) **1**(9) and (B) its polymer P**1**(9) (sample from Table 2, no. 10). The solvent peaks are marked with asterisks.

weight polymer in nearly 80% yield, the yield is further boosted to ∼90% when the temperature is raised to 60 °C. No polymer, however, is obtained when MoCl$_5$–Ph$_4$Sn is used.

The polymerization behaviors of **1**(4) are similar to those of **1**(3). While NbCl$_5$–Ph$_4$Sn affords a high molecular weight polymer in a satisfactory yield (Table 2, no. 1), the attempt to polymerize the monomer by TaCl$_5$–Ph$_4$Sn failed. Unlike **1**(3), the polymerization of **1**(4) catalyzed by WCl$_6$–Ph$_4$Sn at room temperature yields only a trace amount of polymeric product. Increasing the polymerization temperature to 60 °C dramatically activates the catalyst, giving a high molecular weight polymer in 90% yield. Again, MoCl$_5$–Ph$_4$Sn does not work as a catalyst for the polymerization.

The lower part of Table 2 shows the polymerization results of **1**(9). While a small amount of polymer is obtained from NbCl$_5$–Ph$_4$Sn, TaCl$_5$– and MoCl$_5$–Ph$_4$Sn completely fail to initiate the polymerization. WCl$_6$–Ph$_4$Sn still works well for the polymerization, and the reaction conducted at 60 °C gives a polymer with an M_w of ∼2.2 × 10^5 in a high yield (∼77%).

Structural Characterization. The polymers are characterized by spectroscopic techniques, and all give satisfactory data corresponding to their expected molecular structures. Since no absorption peaks associated with C≡C stretching vibration at ∼2230 cm^{-1} are observed in the IR spectra of the monomers, the IR spectroscopy offered little information about the structures of the polymers. The NMR analyses, however, prove that the acetylene triple bonds of the monomers have been consumed and transformed to the polyene double bonds of the polymers by the polymerization reactions. An example of the ^{1}H NMR spectra of P**1**(9) is shown in Figure 1; for comparison, the
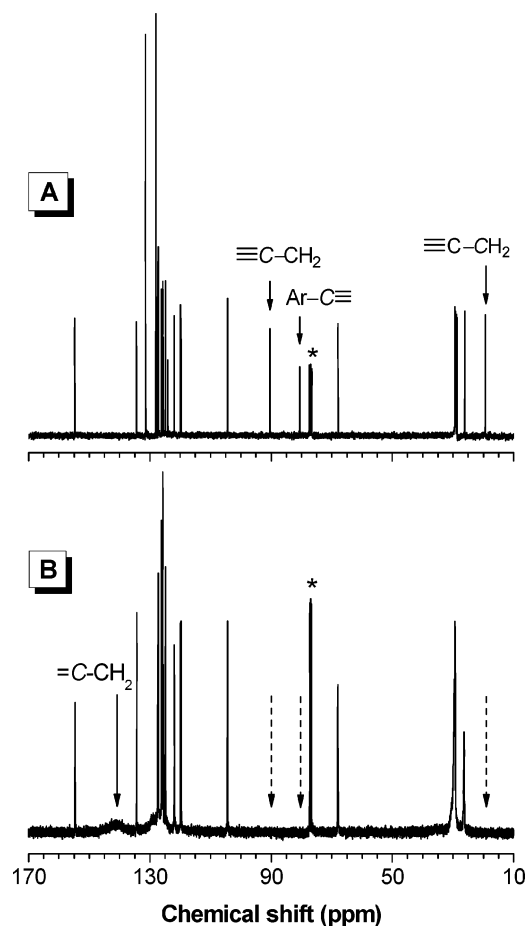
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Figure 2. ^{13}C NMR spectra of (A) **1**(9) and (B) its polymer **P1**(9) (sample from Table 2, no. 10) in chloroform-*d*. The solvent peaks are marked with asterisks.

Figure 3. TGA theromograms of **P1**(3) (sample from Table 1, no. 4), **P1**(4) (Table 2, no. 4), and **P1**(9) (Table 2, no. 10) recorded under nitrogen at a heating rate of 20 °C/min.

Figure 4. Effect of temperature on the molecular weight of **P1**(4) (sample from Table 2, no. 4). The polymer samples are annealed in air at given temperatures for 2 h.

spectrum of its monomer **1**(9) is also given in the same figure. The ethynylphenyl protons of **1**(9) resonate at δ 7.46 and 7.21, which upfield-shift to ~δ 6.8 after polymerization. No other unexpected signals are observed, and all the peaks can be readily assigned, verifying that the molecular structure of the polymeric product is indeed **P1**(9).

The structure of **P1**(9) is further characterized by ^{13}C NMR spectroscopy. The acetylene carbon atoms of **1**(9) absorb at δ 90.4 and 80.6, which are absent in the spectrum of **P1**(9) (Figure 2). The absorption of the propargyl carbon ($\equiv$C$-$CH$_2$) at δ 19.4 also disappears owing to its transformation to the allylic structure in the polymer. A new broad peak is emerged at δ ~140, which may be related to the resonance of the backbone olefin carbon atom linked to the nonyl chain.

Thermal Stability and Electronic Transition. The thermal stability of the polymers is investigated by thermogravimetric analysis. As shown in Figure 3, all the polymers enjoy excellent thermal stability and start to lose weights at temperatures as high as ~430 °C, irrespective of the spacer length. Since poly-(1-phenyl-1-propyne), which may be regarded as a parent form of **P1**(*m*), shows a 5% weight loss at 330 °C,[12b,13] the enhanced resistance of **P1**(*m*) to thermolysis should be due to the "jacket effect" of the 1-naphthoxy pendants,[11c,f] which well wrap the polyene backbones and thus protect them from the attack by the degradative species.

To further evaluate the thermal stability of the polymers, we checked the changes of their molecular weights with temperature. We annealed **P1**(4) in air for 2 h at different temperatures and measured its molecular weight by GPC. Almost no change
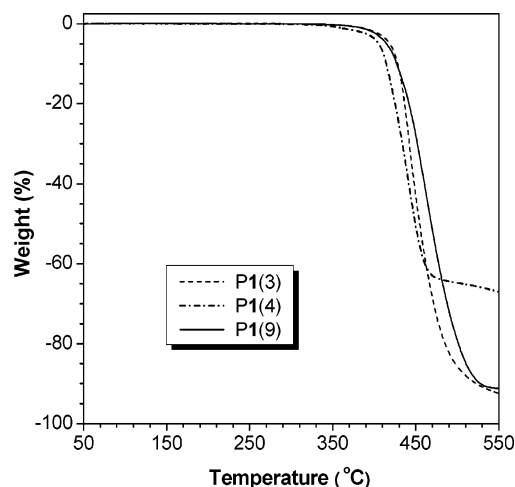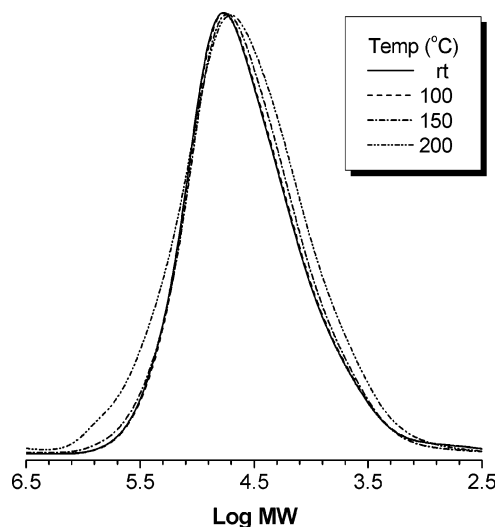
in the molecular weight is observed when the polymer is annealed at temperatures up to 200 °C (Figure 4). This further verifies that the polymer is stable to thermolysis caused by oxidative chain scission.

The absorption spectra of the polymers in THF are given in Figure 5. While the strong absorption observed at 295 nm in the spectrum of **P1**(3) is due to the E$_2$ band of the 1-naphthoxy pendants, the backbone absorption is found at wavelengths longer than 340 nm with high intensities. The polymer segment may take a more planar conformation owing to the steric effects of the phenyl and the 1-naphthoxy pendants.[14] The planar backbone allows better conjugation of the alternating double bonds and hence makes the polymer absorptive in the longer wavelength regions. The spacer length exerts little influence on the ground-state electronic transitions: the absorption spectra of **P1**(4) and **P1**(9) are very similar to that of **P1**(3).

Photoluminescence. Disubstituted polyacetylenes such as PPAs containing long alkyl side chains {$-$[(C$_6$H$_5$)C$=$C(C$_m$H$_{2m+1}$)]$_n$$-$} are strong light emitters:[6,15] PPO (*m* = 6), for example, emits a strong blue PL of 460 nm with a quantum efficiency (Φ_F) of 43% (Figure 6). Since **P1**(*m*) are PPA
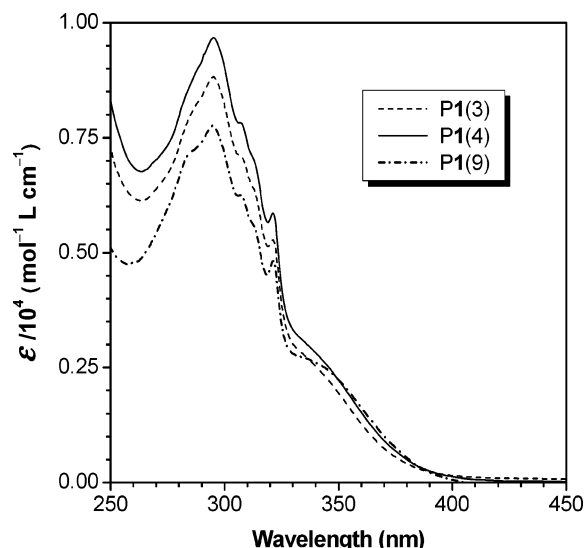
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Figure 5. UV spectra of THF solutions of P**1**(3) (sample from Table 1, no. 4), P**1**(4) (Table 2, no. 4), and P**1**(9) (Table 2, no. 10).
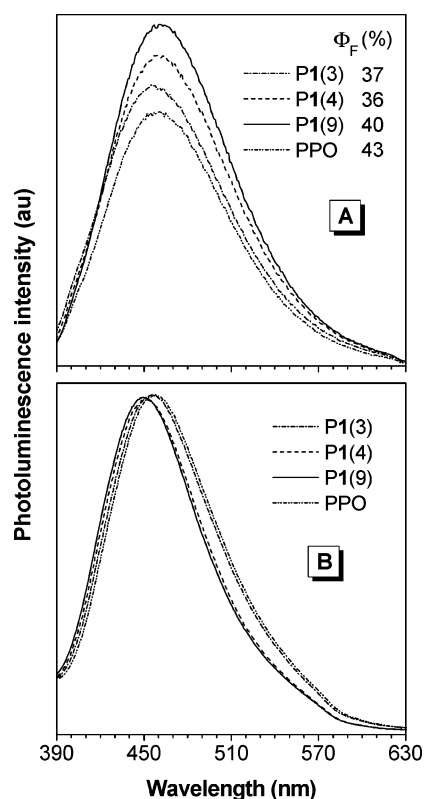

Figure 6. Photoluminescence spectra of P**1**(3) (sample from Table 1, no. 4), P**1**(4) (Table 2, no. 4), P**1**(9) (Table 2, no. 10), and poly(1-phenyl-1-octyne) (PPO) in (A) THF solutions (0.05 mM) and (B) solid states (thin film). Excitation wavelength: 355 nm.

derivatives bearing chromophoric pendant groups, it is of interest to check the effects of the structural variables on their luminescence behaviors.

Upon photoexcitation, P**1**(3) emits in the spectral region similar to that of PPO. Its emission intensity is higher than PPO, but its Φ_F (37%) is slightly lower. The peak maxima of P**1**(4) and P**1**(9) are also located at 460 nm. While the Φ_F of P**1**(4) is similar to P**1**(3), that of P**1**(9) is higher, in agreement with the early observation that longer alkyl chains favor stronger PL and EL in PPAs[6b] owing to the better segregation of the polyene backbones.
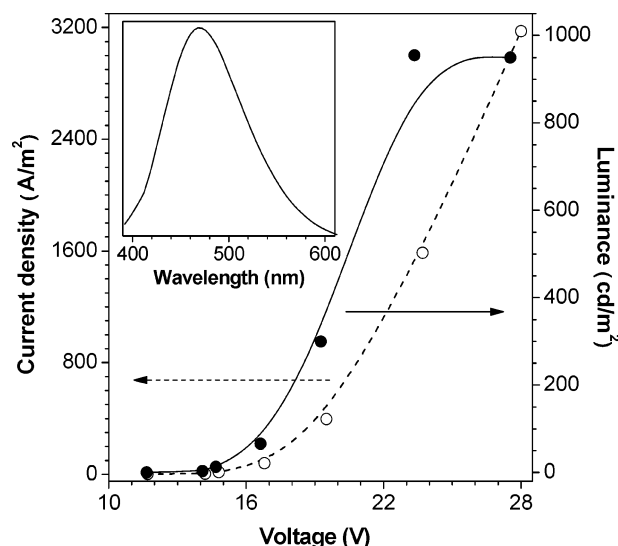

Figure 7. Changes in the current density and luminance with the applied voltage in a multilayer EL device of P**1**(3) (sample from Table 1, no. 4) with a configuration of ITO/P**1**(3):PVK/BCP/Alq$_3$/LiF/Al. The EL spectrum is shown in the inset.

Many conjugated polymers emit intensely in solution but become weak emitters when fabricated into thin solid films.[16] This is mainly caused by strong interchain interaction. In the solid state, the polymer strands aggregate together to form less luminescent species such as excimers, leading to red-shifted emissions with low efficiencies. Would our polymers behave in a similar fashion? Figure 6B shows the PL spectra of solid films of the polymers. Although we have technical difficulty in measuring their Φ_F values in the solid state, no significant shifts in the peak maximum are observed in comparison to those in the solutions. Our recent study of the photophysical processes of the PPAs has revealed that their light emissions are actually enhanced by aggregate formation by increasing the concentrations of their solutions as well as by adding nonsolvents such as water into their solutions, details of which will be published in a separate paper.

Electroluminescence. The efficient PL emission from the polymers prompts us to check their EL behaviors. Because of its simplicity, we first fabricated a single-layer EL device with a configuration of indium tin oxide (ITO)/P**1**:poly(9-vinylcar-bazole) (PVK)/LiF/Al, using a 25 wt % blend of P**1**(3) in PVK as a light-emitting layer (LEL; see Chart 1 in the Experimental Section). The EL from the device is, however, very weak, giving a maximum luminance of 0.43 cd/m^2 and an external quantum efficiency of $\sim$0.001%. The EL data clearly contradict the PL data discussed above, indicating that device configuration is far from optimized. One possible reason for the poor device performance is due to unbalance injection and transport of the charges. The hole transport is probably quite efficient because of the use of PVK, a well-known hole-transporting material. Therefore, we added a thin layer of tris(8-hydroxyquinolinolato)-aluminum (Alq$_3$) on the cathode side to enhance the electron transport. We also added another thin layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) next to the light-emitting layer to prevent the holes from traveling through to reach the cathode. With these engineering modifications, a multilayer EL device with a configuration of ITO/P**1**(3):PVK/BCP/Alq$_3$/LiF/Al is constructed, whose performance is much superior than that of the single-layer device.

The device is turned on at $\sim$10.5 V, emitting a blue EL of $\sim$468 nm. The EL spectrum is single-peaked and symmetrically
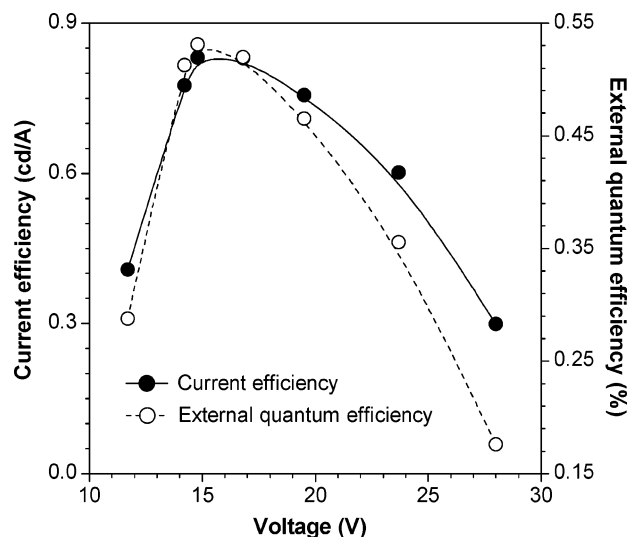
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Figure 8. Current and external quantum efficiencies vs voltage in a multilayer EL device of P**1**(3) (sample from Table 1, no. 4) with a configuration of ITO/P**1**(3):PVK/BCP/Alq$_3$/LiF/Al.
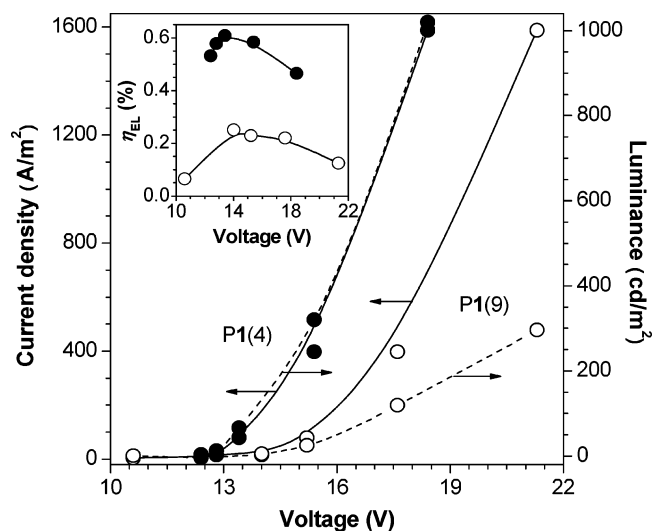

Figure 9. Current density and luminance vs voltage in multilayer EL devices of P**1**(4) (sample from Table 2, no. 4) and P**1**(9) (Table 2, no. 10) with a configuration of ITO/P**1**(m):PVK/BCP/Alq$_3$/LiF/Al. The inset shows the changes in the external quantum efficiency (η_{EL}) with the applied voltage.

shaped (Figure 7). Its peak maximum is close to its PL peak in solution, suggesting that the light emission is truly from the polymer LEL. At an applied voltage of ~24 V, the luminance reaches 955 cd/m^2, which is ~20000-fold higher than that in single-layer device. The maximum current and external quantum efficiencies are 0.83 cd/A and 0.53%, respectively (Figure 8), comparable to some of the results reported by other research groups for blue-emitting LEDs.[17] We also fabricated a diode of PPO with the same device configuration. No light from the PPO layer is, however, emitted. This demonstrates that the superior device performance of P**1**(3) is not merely due to the better design of the device configuration but also related to its molecular structure.

Encouraged by the result from P**1**(3), we further investigated the EL properties of other polymers. Polymer P**1**(4), a structural congener of P**1**(3) with one more methylene spacer, emits a blue EL of 464 nm when the voltage exceeds 12.0 V (Figure 9). Its EL spectrum is again single-peaked with no any sidebands.

At the same voltage, it luminesces more brightly than P**1**(3) with similar or higher efficiencies. The EL performance of P**1**(9) is, however, poorer, with its external quantum yield being only about half of those of P**1**(3) and P**1**(4). The destructive effect of the longer spacer is probably due to the lower mobility of the charge carriers in the insulting alkyl chains, whereas the strong interstrand interaction in the polymers with shorter spacers may have quenched their light emissions to a certain extent.

Concluding Remarks

In this work, we have studied PL and EL of a group of PPAs containing naphthyl pendant groups with different spacer lengths. Our results and findings can be summarized as follows: (1) The monomers are prepared by etherification and coupling reactions of ω-chloro-1-alkynes. Their polymerizations are effected by NbCl$_5$– and WCl$_6$–Ph$_4$Sn catalysts, with the latter giving polymers of high molecular weights in high yields (M_w up to 1.3×10^5 and isolated yield up to 91%). (2) All the polymers possess excellent thermal stability ($T_d \geq 430$ °C), thanks to the jacket effects of by the bulky aryl (phenyl and 1-naphthyl) pendants. (3) Upon photoexcitation, the THF solutions of the polymers emit strong blue lights of ~460 nm with quantum efficiencies of ~40%. The polymer thin films also luminesces intensely at the wavelengths similar to those in the solutions, indicating that the polymers remain emissive in the aggregation state. (4) Multilayer EL devices with a configuration of ITO/P**1**(m):PVK/BCP/Alq$_3$/LiF/Al are constructed, which emit blue lights in high luminance (up to 1019 cd/m^2) and external quantum efficiency (up to 0.61%).

The nonluminescent nature of the unsubstituted polyacetylene and inferior device performances of some previously investigated substituted polyacetylenes have completely quenched the interest of scientists in developing polyacetylene-based light-emitting materials. Our results presented here show that polyacetylenes can be highly emissive with EL performances comparable to those of the best blue-light-emitting polymers. Noticing that a figure of 100 cd/m^2 is considered bright enough for a flat panel display, the high luminescence of the polymers, especially P**1**(3) and P**1**(4), and their easy synthesis and high thermal stability make them promising candidates for luminescent materials to be used in LEDs.

Experimental Section

Instrumentation. The NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane ($\delta = 0$) as internal reference. The UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer, and the molar absorptivity (ϵ) of the polymers was calculated on the basis of their monomer repeat units. The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. The molecular weights of the polymers were estimated in THF by a Waters Associates GPC system. A set of monodisperse polystyrene standards covering the molecular weight range of 10^3–10^7 was used for the molecular weight

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Chart 1. Electroluminescence Device Configuration

Single-layer EL device   Multi-layer EL device
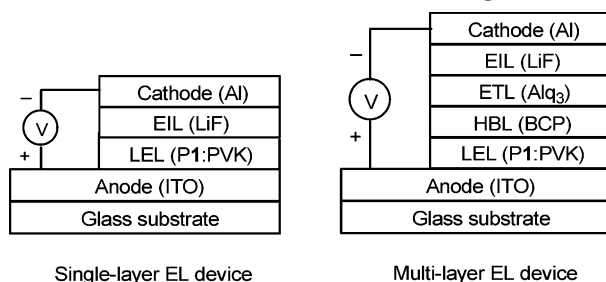
calibration. The thermal stability of the polymers was evaluated on a Perkin-Elmer TGA 7 under dry nitrogen at a heating rate of 20 °C/min. The PL spectra of the polymers in THF and solid state (thin film) were recorded on a SLM 8000C spectrofluorometer. The EL spectra were obtained on a Kollmorgen Instrument PR650 photospectrometer. The luminescence area was 12.6 mm^2. The current−voltage characteristics were obtained using a Hewlett-Packard HP4145B semiconductor analyzer.

PL Quantum Yield Determination. The PL quantum yields of P**1**(*m*) in THF were measured using a literature procedure.[18] Absorbance of the sample solutions was kept below 0.05 to avoid inner filter effect. Measurements were performed at room temperature, with both polymer (sample) and 9,10-diphenylanthracene (reference) solutions excited at the same wavelength (355 nm) to avoid the possible errors caused by neglecting the difference between the light intensities of different wavelengths. The quantum yield for 9,10-diphenylanthracene in cyclohexane was assumed to be 90% when excited at 355 nm.

EL Device Fabrication. The single- and multilayer EL devices based on the PPAs were constructed according to the configurations shown in Chart 1 (for illustration only, layer thickness not in proportion to those actually used in this study).

The single-layer EL devices were prepared by spin-coating toluene solutions of the polymers and PVK onto ITO glasses. The ratio of the polymer and PVK was fixed at 1:4 by weight.[19] The thickness of the resulting polymer films was in the range of ~35−60 nm. LiF [electron-injection layer (EIL); 0.8 nm] and Al were in turn deposited under vacuum (2 × 10^{-6} Torr). Multilayer EL devices utilizing doped P**1**(*m*) as emitting layers were prepared in a similar fashion with the deposition of BCP [hole-blocking layer (HBL); 20 nm] and Alq$_3$ [electron-transporting layer (ETL); 30 nm] inserted into the polymer and LiF layers.

Monomer Synthesis. The 1-phenyl-1-alkyne monomers were prepared by etherification of *ω*-chloro-1-alkynes with 1-naphthol followed by coupling reactions with iodobenzene in the presence of a Pd catalyst. Typical experimental procedures for the synthesis of the monomers are given below.

5-(1-Naphthoxy)-1-pentyne [4(3)]. In a 500 mL Erlenmeyer flask equipped with a condenser were dissolved 5.1 g (35.4 mmol) of 1-naphthol and 1.7 g of KOH (30.4 mmol) in 200 mL of acetone/DMSO mixture (10:1 by volume) under gentle heating and stirring. To the homogeneous solution were added 3.0 g (29.3 mmol) of 5-chloro-1-pentyne and a catalytic amount of potassium iodide. The resulting mixture was then refluxed for 24 h. The reaction mixture was poured into 300 mL water and acidified with 10 mL of 37% hydrochloric acid. The crude product was extracted with chloroform and purified on a silica gel column using chloroform as eluent. Pale yellow liquid was obtained in 83.6% yield (5.1 g). 6-(1-Naphthoxy)-1-hexyne [**4**(4)] and 11-(1-naphthoxy)-1-undecyne [**4**(9)] were prepared by similar procedures and obtained as yellow liquids in 88.0 and 56.1% yields, respectively.

5-(1-Naphthoxy)-1-phenyl-1-pentyne [1(3)]. To a 250 mL two-necked flask were added 0.07 g (0.1 mmol) of PdCl$_2$(PPh$_3$)$_2$, 0.1 mg (0.1 mmol) of CuI, and 150 mL of a triethylamine solution of iodobenzene (1.3 g, 6.4 mmol) under nitrogen. After all the catalysts were dissolved, 5-(1-naphthoxy)-1-phenyl-1-pentyne (1.0 g, 4.8 mmol) was injected into the flask, and the mixture was stirred at room temperature for 24 h. After filtering out the formed salt, the solution

was concentrated by a rotary evaporator. The product was purified by silica gel column chromatography using chloroform/hexane (1:1 by volume) as eluent. 4-(1-Naphthoxy)-1-phenyl-1-hexyne [**1**(4)] and 11-(1-naphthoxy)-1-phenyl-1-undecyne [**1**(9)] were synthesized by similar procedures.

Characterization Data of 1(3): Yellow liquid; yield 82.1%. ^{1}H NMR (300 MHz, CDCl$_3$), *δ* (ppm): 8.29 [m, 1H, naphthalene (Nap)-H at 8-position], 7.80 (m, 1H, Nap-H at 5-position), 7.40 (m, 6H, Nap-H at 3-, 4-, 6-, and 7-positions and Ph−H ortho to C≡C), 7.27 (m, 3H, Ph−H para and meta to C≡C), 6.86 (m, 1H, Nap−H at 2-position), 4.30 (t, 2H, OCH$_2$), 2.74 (t, 2H, ≡CCH$_2$), 2.24 (m, 2H, ≡CCH$_2$C*H*$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), *δ* (ppm): 154.5, 134.5, 131.5 (aromatic carbons ortho to C≡C), 128.2 (aromatic carbons meta to C≡C), 127.6 (aromatic carbons para to C≡C), 127.4, 126.3, 125.8, 125.6, 125.1, 123.7 (aromatic carbon linked with C≡C), 122.0, 120.1, 104.6, 89.2 (≡*C*CH$_2$), 81.2 (Ph*C*≡), 66.5 (OCH$_2$), 28.6 (≡CCH$_2$*C*H$_2$), 16.4 (≡C*C*H$_2$). MS (CI): *m/z* 287.1 [(M + 1)$^+$, calcd 287.1].

1(4): Yellow liquid; yield 79.0%. ^{1}H NMR (300 MHz, CDCl$_3$), *δ* (ppm): 8.30 (m, 1H, Nap−H at 8-position), 7.78 (m, 1H, Nap−H at 5-position), 7.41 (m, 6H, Nap-H at 3-, 4-, 6-, and 7-positions and Ph−H ortho to C≡C), 7.27 (m, 3H, Ph−H para and meta to C≡C), 6.81 (m, 1H, Nap−H at 2-position), 4.20 (t, 2H, OCH$_2$), 2.55 (t, 2H, ≡CC*H*$_2$), 2.13 (OCH$_2$C*H*$_2$), 1.91 (m, 2H, ≡CCH$_2$C*H*$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), *δ* (ppm): 154.6, 134.4, 131.5 (aromatic carbons ortho to C≡C), 128.1 (aromatic carbons meta to C≡C), 127.5 (aromatic carbon para to C≡C), 127.4, 126.3, 125.8, 125.6, 125.0, 123.9 (aromatic carbon linked with C≡C), 122.0, 120.1, 104.4, 89.8 (≡*C*CH$_2$), 81.1 (Ph*C*≡), 67.3 (OCH$_2$), 28.4 (OCH$_2$*C*H$_2$), 25.5 (≡CCH$_2$*C*H$_2$), 19.1 (≡C*C*H$_2$). MS (CI): *m/z* 301.1 [(M + 1)$^+$, calcd 301.1].

1(9): Yellow liquid; yield 72.3%. ^{1}H NMR (300 MHz, CDCl$_3$), *δ* (ppm): 8.29 (m, 1H, Nap−H at 8-position), 7.89 (m, 1H, Nap−H at 5-position), 7.46 (m, 6H, Nap-H at 3-, 4-, 6-, and 7-positions and Ph−H ortho to C≡C), 7.27 (m, 3H, Ph−H para and meta to C≡C), 6.79 (m, 1H, Nap−H at 2-position), 4.13 (t, 2H, OCH$_2$), 2.40 (t, 2H, ≡CC*H*$_2$), 1.93 (OCH$_2$C*H*$_2$), 1.64−1.39 [m, (CH$_2$)$_6$]. ^{13}C NMR (75 MHz, CDCl$_3$), *δ* (ppm): 154.8, 134.5, 131.5 (aromatic carbons ortho to C≡C), 128.1 (aromatic carbons meta to C≡C), 127.41 (aromatic carbon para to C≡C), 127.37, 126.3, 125.9, 125.7, 125.0, 123.9 (aromatic carbon linked with C≡C), 122.0, 119.9, 104.4, 90.4 (≡*C*CH$_2$), 80.6 (Ph*C*≡), 68.0 (OCH$_2$), 29.45, 29.36, 29.26, 28.9, 28.7, 26.2, 19.4 (≡C*C*H$_2$). MS (CI): *m/z* 371.1 [(M + 1)$^+$, calcd 371.1].

Polymerization. All the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done in an open atmosphere. Typical experimental procedures for the polymerization of **1**(3) are given below.

Into a baked 20 mL Schlenk tube with a stopcock in the sidearm was added 460 mg (1.6 mmol) of **1**(3). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (4 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 31.8 mg of tungsten(VI) chloride and 34.4 mg of tetraphenyltin in 4 mL of toluene. The two tubes were aged at 60 °C for 15 min, and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The solution was then cooled to room temperature, diluted with chloroform, and added dropwise to 500 mL of acetone through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered with a Gooch crucible. The polymer was washed with acetone and dried in a vacuum oven to a constant weight.

Characterization Data of Poly[5-(1-naphthoxy)-1-phenyl-1-pentyne] [P1(3)]: Yellow powdery solid; yield 91.2%; M_w 112 700; M_w/M_n 2.4 (GPC; Table 1, no. 2). ^{1}H NMR (300 MHz, CDCl$_3$), *δ* (ppm): 7.58, 7.18 (br, Nap−H and Ph−H), 3.48 (br, OCH$_2$), 2.5−0.5 (br, =CCH$_2$ and =CCH$_2$C*H*$_2$). ^{13}C NMR (75 MHz,

CDV

CDCl$_3$), δ (ppm): 154.4, 140.5 (=C−CH$_2$), 134.2, 127.1, 125.6, 122.0, 119.7, 104.3, 67.9 (OCH$_2$), 29.0 (=CCH$_2$CH$_2$ and =CCH$_2$CH$_2$). UV (THF, 6.6 × 10^{-5} mol/L), $\lambda_{max}/\epsilon_{max}$: 295 nm/0.88 × 10^4 mol^{-1} L cm^{-1}.

*Poly[6-(1-naphthoxy)-1-phenyl-1-hexyne] [P**1**(4)]:* Yellow powdery solid; yield 90.2%; M_w 58 500; M_w/M_n 2.4 (GPC; Table 2, no. 2). ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.02 (br, Nap−H at 8-position), 7.85 (br, Nap−H at 5-position), 7.28 (br, Nap−H at 3-, 4-, 6-, 7-positions), 6.44 (br, Nap−H at 2-position and Ph−H ortho, para, and meta to C=C), 3.50 (OCH$_2$), 2.6−0.4 (br, =CCH$_2$, OCH$_2$CH_2 and =CCH$_2$CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 156.8, 140.1 (=C−CH$_2$), 134.4, 129.1, 128.7, 127.5, 126.5, 126.1, 123.3, 118.4, 67.1, 30.1. UV (THF, 5.0 × 10^{-5} mol/L), $\lambda_{max}/\epsilon_{max}$: 295 nm/0.97 × 10^4 mol^{-1} L cm^{-1}.

*Poly[11-(1-naphthoxy)-1-phenyl-1-undecyne] [P**1**(9)]:* Yellow powdery solid; yield 76.8%; M_w 216 200; M_w/M_n 3.3 (GPC; Table 2, no. 10). ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.22 (br, Nap−H at 8-position), 7.70 (br, Nap−H at 5-position), 7.34 (br, Nap−H at 3-, 4-, 6-, and 7-positions), 6.92 (br, Ph−H ortho, para, and meta to C=C), 6.63 (br, Nap−H at 2-position), 3.93 (br, OCH$_2$), 2.5 (=CCH$_2$), 1.77 (br, OCH$_2$CH$_2$), 1.5−0.5 [br, (CH$_2$)$_6$]. ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 154.6, 142.2 (=C−CH$_2$), 134.4, 127.3, 126.1, 125.8, 125.6, 124.9, 121.9, 119.8, 104.4, 68.0 (OCH$_2$), 29.4, 26.4. UV (THF, 2.6 × 10^{-5} mol/L), $\lambda_{max}/\epsilon_{max}$: 295 nm/0.78 × 10^4 mol^{-1} L cm^{-1}.

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