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Synthesis, thermal stability, light emission, and fluorescent photopatterning of poly(diphenylacetylene)s carrying naphthalene pendant groups

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Abstract

Naphthalene (Nap)-containing poly(diphenylacetylene)s with different spacer lengths ($-\{C_6H_5C{=}C[C_6H_4O(CH_2)_mO{-}Nap]\}_n-$; **P1**($m$), $m = 4$, 6, 8) are synthesized. The monomers are prepared by etherifications of 1,m-dibromoalkanes with 1-naphthol and 1-(4-hydroxy)phenyl-2-phenylacetylene and are polymerized by $TaCl_5$–n-Bu_4Sn and WCl_6–Ph_4Sn catalysts. Whereas the tantalum-based catalyst gives insoluble products in low yields, the tungsten-based catalyst furnishes soluble polymers with high molecular weights (M_w up to 5.0×10^4) in satisfactory yields (up to 62%). The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, UV, PL, and EL analyses. All the polymers are thermally stable: while the polymers lose 5% of their weights at ~420 °C under nitrogen, no decreases in molecular weights are found after they have been annealed at 200 °C for 2 h in air. When their THF solutions are photoexcited, the polymers emit strong green lights with high efficiencies (up to 98%). No significant shifts in the photoluminescence spectra are observed when the polymers are cast into thin solid films, suggestive of little involvement of aggregative or excimeric emission. A multilayer EL device with a configuration of ITO/**P1**(8):PVK/BCP/Alq_3/LiF/Al is constructed, which emits a green light of 520 nm with a maximum external quantum efficiency of 0.16%. The spectral stability is outstanding: no recognizable change is observed in the EL spectrum when the device current is raised. Irradiation of a film of **P1**(8) through a mask photooxidizes and quenches the emission of the exposed regions, resulting in the formation of two-dimensional luminescent photopatterns.

Keywords: Light emission; Photopatterning; Polyacetylene

1. Introduction

Design and synthesis of new conjugated polymers have attracted much attention in recent years because of their potential applications in optics and electronics such as field-effect transistors and light-emitting diodes [1,2]. While light emissions of poly(fluorene)s, poly(phenylene vinylene)s, and poly(p-phenylene)s have been the focus of intensive research in the area [3–11], polyacetylene, being the best-known conjugated polymer [12–14], has received little interest because it is insoluble, thermally unstable, and weakly luminescent in the infrared region [15]. Structural modifications to the polymer by substitution chemistry have solved these problems and have generated soluble, stable, mono- and disubstituted polyacetylenes with efficient light emissions [16–25].

Our group has recently succeeded in synthesizing an array of blue light-emitting polyacetylenes [16,17]. To achieve full-color displays, strong green and red emitters are also needed. Incorporation of chromophoric groups into poly(diphenylacetylene) structure may generate efficient green luminophors because of the favorable energy transfer from the pendant groups

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to the polymer backbone. This kind of polymers has, however, been rare. The limitation may lie in the synthetic difficulty. To link appendages to the polymer backbone, one unavoidably has to use functional groups to join them together. The functional groups, however, are usually toxic to the catalysts used for the polymerizations of diphenylacetylenes. In this paper, we report the synthesis of a group of green light-emitting poly(diphenylacetylene)s bearing naphthalene appendages. We describe how the polymers are prepared and what properties they exhibit (Chart 1).

2. Experimental section

2.1. Materials

Toluene (BDH) was pre-dried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine was distilled and dried over potassium hydroxide. Phenylacetylene, copper(I) iodide, triphenylphosphine, and molybdenum(V) chloride were purchased from Acros. 1,4-Dibromobutane, 4-iodophenol, 1-naphthol, 1,6-dibromohexane, 1,8-dibromooctane, dichlorobis(triphenylphosphine)palladium(II), tungsten(VI) chloride, tantalum(V) chloride, niobium(V) chloride, tris(8-hydroxyquinolinolato)aluminum (Alq_3), poly(9-vinyl carbazole) (PVK), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Aldrich and used without further purification.

2.2. Instrumentation

IR spectra were measured on a Perkin Elmer 16 PC FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer with chloroform-*d* ($CDCl_3$) as a solvent and tetramethylsilane (TMS; $\delta = 0$) as an internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer and 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 with methane as carrier gas. Molecular weights of the polymers were estimated in THF by a Waters associated gel permeation chromatography (GPC) system. A set of monodisperse polystyrene standards covering the molecular weight range of 10^3–10^7 were used for the molecular weight calibration. Thermal stability of the polymers was evaluated on a Perkin Elmer TGA 7 under dry nitrogen at a heating rate of 20 °C/min. Photoluminescence (PL) spectra of the polymers in THF and solid state (thin film) were recorded on an SLM 8000 C spectrofluorometer. The polymer films for the solid-state PL measurements were prepared by spin-coating toluene solutions of the polymers onto quartz substrates. Cyclic voltammetry was performed on a Princeton Applied Research (PAR) model 273A potentiostat in 0.1 M tetrabutylammonium hexafluorophosphate dichloromethane solution. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively. The highest occupied molecular orbital (HOMO) energy levels of the polymers were determined from their onset oxidation potentials, with the assumption that the energy level of ferrocene/ferrocenium is 4.8 eV below vacuum [26]. Electroluminescence (EL) spectra were obtained on a Kollmorgen Instrument PR 650 photospectrometer. The luminescence area was 12.6 mm^2. Current–voltage characteristics were obtained using a Hewlett–Packard HP 4145B semiconductor analyzer.

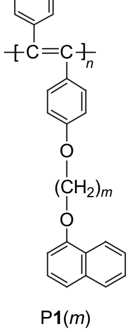

P**1**(*m*)
m = 4, 6, 8

Chart 1. Poly(diphenylacetylene)s carrying naphthalene pendant groups.

2.3. Quantum yield measurement

PL efficiency of the polymers in THF solutions was measured using the literature procedure as described previously [27,28]. The sample (polymer) and reference (Rhodamine B solution) were excited at the same wavelength (398 nm) to avoid possible errors caused by neglecting the difference between the excitation light intensities of different wavelengths. The quantum yield (Φ_F) for Rhodamine B in water was assumed to be 68% when excited at 398 nm.

2.4. Device preparation

Multilayer EL device of P**1**(8) was prepared by spin-coating toluene solution of the polymer and PVK onto ITO glass (cf., inset of Fig. 8; for illustration only, layer thicknesses were not in proportion to those actually used in this study). Film thickness was controlled by the polymer solution concentration (~10 mg/mL) and spinning rate (~2500 rpm). The thickness of the polymer layer was measured by a surface profiler (Tencor P-10) and was determined to be 60 nm. The ratio of the polymer and PVK was fixed at 1:4 by weight [29]. BCP [hole-blocking layer (HBL); 20 nm], Alq_3 [electron-transporting layer (ETL); 30 nm], LiF [electron-injection layer (EIL); 0.8 nm], and Al were successively deposited under vacuum (2×10^{-6} Torr).

2.5. Photopatterning

Photooxidation of the polymer film was conducted in air at room temperature (~23 °C) for 2 min using 365 nm UV light with an intensity ~30 mW/cm^2. The polymer film was prepared by spin-coating the polymer solution (~2 wt% in

1,2-dichloroethane) at 2000 rpm for 1 min on silicon wafer. The film was dried in a vacuum oven at room temperature overnight. The fluorescent image was generated using a Cu-negative mask and taken on a fluorescent optical microscope (Olympus BX4) using a 330–385 nm broad range UV source.

2.6. Synthesis of monomers

Monomers **1**(*m*) were synthesized by two etherifications of 1,*m*-dibromoalkanes with 1-naphthol and 1-(4-hydroxy)-phenyl-2-phenylacetylene (Scheme 1). Typical experimental procedures for the synthesis of **1**(4) are given below as examples.

2.6.1. 1-(4-Hydroxy)phenyl-2-phenylacetylene (*2*)

Into a 250 mL round bottom flask were added copper(I) iodide (3 mg, 16 μmol), dichlorobis(triphenylphosphine) palladium(II) (0.42 g, 0.6 mmol), and 4-iodophenol (6.6 g, 30 mmol) in 100 mL of triethylamine. After stirring for 15 min, 6.6 mL (60 mmol) of phenylacetylene was added. The mixture was stirred for 24 h at room temperature. After filtration and solvent evaporation, the crude product was purified on a silica-gel column using chloroform/acetone mixture (10:1 by volume) as eluent. Light brown solid; yield 88%.

2.6.2. 1-[4-(1-Naphthoxy-4-butyloxy)]phenyl-2-phenylacetylene [*1(4)*]

Into a 500 mL Erlenmeyer flask equipped with a condenser were dissolved 1.44 g (10 mmol) of 1-naphthol and 0.55 g of KOH (10 mmol) in 250 mL ethanol/water mixture (10:1 by volume) under gentle heating and stirring. To the homogeneous solution were added 2.2 g (10 mmol) of 1,4-dibromobutane and a catalytic amount of potassium iodide. The resulting mixture was then refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into 200 mL water and acidified with 10 mL of 37% hydrochloric acid. The mixture was extracted with chloroform. After solvent evaporation, the crude product was purified on a silica-gel column using chloroform/hexane mixture (1:3 by volume) as eluent. The desired intermediate was obtained in 1.8 g (6.5 mmol) as a colorless liquid. The intermediate was further etherified with 1-(4-hydroxy)-phenyl-2-phenylacetylene (1.6 g, 8.2 mmol) using the same procedures described above to yield **1**(4).

2.6.3. Characterization data of 1-[4-(1-naphthoxy-4-butyloxy)]phenyl-2-phenylacetylene [*1(4)*]

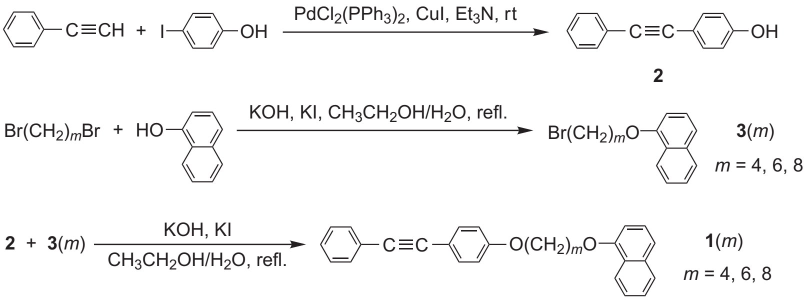
Pale yellow liquid; yield 45.3%. IR (KBr), ν (cm^{-1}): 2218 (C≡C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.27 [d, 1H, Naphthalene (Nap)–H at 8 position], 7.80 (d, 1H, Nap–H at 5 position), 7.49 (m, 6H, Nap–H at 6 and 7 positions, Ph–H *ortho* to C≡C, and Ph–H *meta* to OCH_2), 7.35 (m, 5H, Ph–H *para* and *meta* to C≡C and Nap–H at 3 and 4 positions), 6.89 (d, 2H, Ph–H *ortho* to OCH_2), 6.73 (d, 1H, Nap–H at 2 position), 4.22 (t, 2H, Nap–OCH_2), 4.11 (t, 2H, Ph–OCH_2), 2.12 [m, 4H, $(CH_2)_2$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.0, 154.6, 134.5, 133.0, 131.4, 128.3, 127.9, 127.4, 126.4, 125.9, 125.1, 123.6, 122.0, 120.1, 115.3, 114.5, 104.5, 89.4 (Ph–C≡*C*), 88.0 (Ph–*C*≡C), 67.54, 67.52, 26.2, 26.0. MS (CI): *m/e* 393.2 [$(M+1)^+$].

2.6.4. 1-[4-(1-Naphthoxy-6-hexyloxy)]phenyl-2-phenylacetylene [*1(6)*]

Pale yellow liquid; yield 40.1%. IR (KBr), ν (cm^{-1}): 2214 (C≡C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.28 (d, 1H, Nap–H at 8 position), 7.74 (d, 1H, Nap–H at 5 position), 7.48 (m, 6H, Nap–H at 6 and 7 positions, Ph–H *ortho* to C≡C, and Ph–H *meta* to OCH_2), 7.33 (m, 5H, Ph–H *para* and *meta* to C≡C and Nap–H at 3 and 4 positions), 6.81 (d, 2H, Ph–H *ortho* to OCH_2), 6.74 (d, 1H, Nap–H at 2 position), 4.06 (t, 2H, Nap–OCH_2), 3.89 (t, 2H, PhO–CH_2), 1.88 (m, 2H, Nap–OCH_2CH_2), 1.76 (m, 2H, PhO–CH_2CH_2), 1.54 [m, 4H, $(CH_2)_2$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.1, 154.7, 134.4, 133.0, 131.4, 128.2, 127.8, 127.4, 126.3, 125.8, 125.6, 125.0, 123.6, 122.0, 119.9, 115.1, 114.4, 104.5, 89.5 (Ph–C≡*C*), 88.0 (Ph–*C*≡C), 67.8, 29.13, 29.07, 26.0, 25.8. MS (CI): *m/e* 421.2 [$(M+1)^+$].

2.6.5. 1-[4-(1-Naphthoxy-8-octyloxy)]phenyl-2-phenylacetylene [*1(8)*]

Pale yellow solid; yield 35.8%. IR (KBr), ν (cm^{-1}): 2213 (C≡C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.28 (d, 1H, Nap–H at 8 position), 7.77 (d, 1H, Nap–H at 5 position), 7.48 (m, 6H, Nap–H at 6 and 7 positions, Ph–H *ortho* to C≡C, and Ph–H *meta* to OCH_2), 7.35 (m, 5H, Ph–H *para* and *meta* to C≡C and Nap–H at 3 and 4 positions), 6.86 (m, 3H, Nap–H at 2 position and Ph–H *ortho* to OCH_2), 4.14 (t, 2H, Nap–OCH_2), 3.96 (t, 2H, PhO–CH_2), 1.94



Scheme 1. Synthesis of diphenylacetylenes containing naphthalene moieties.

(m, 2H, $\mathrm{Nap{-}OCH_2C}H_2$), 1.79 (m, 2H, $\mathrm{PhO{-}CH_2C}H_2$), 1.53 [m, 8H, $(CH_2)_4$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.2, 154.8, 134.4, 133.0, 131.4, 128.3, 127.8, 127.4, 126.3, 125.9, 125.7, 125.0, 123.6, 122.0, 119.9, 115.1, 114.5, 104.5, 89.5 ($\mathrm{Ph{-}C{\equiv}}C$), 88.0 ($\mathrm{Ph{-}}C\mathrm{{\equiv}C}$), 68.0, 67.9, 29.3, 29.2, 29.1, 26.2, 25.9. MS (CI): *m/e* 449.2 $[(M+1)^+]$.

2.7. Polymerization

All the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or in 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**(4) are as follows.

Into a baked 20 mL Schlenk tube with a stopcock in the sidearm was added 320 mg (0.8 mmol) of **1**(4). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (2 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 15.9 mg of tungsten(VI) chloride and 34.4 mg of tetraphenyltin in 2 mL of toluene. The two tubes were aged at 80 °C for 15 min and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 80 °C under nitrogen for 24 h. The solution was cooled to room temperature, diluted with 10 mL of chloroform, and added dropwise to 500 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered with a sintered glass filter. The polymer was washed with methanol and dried in a vacuum oven to a constant weight.

2.7.1. Characterization data of poly{1-[4-(1-naphthoxy-4-butyloxy)]phenyl-2-phenylacetylene} [P**1**(4)]

Greenish-yellow solid; yield 45.1%. M_w 22 000; M_w/M_n 1.7 (Table 1, no. 6). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.21, 7.71, 7.31, 6.69, 6.18, 4.00, 1.92. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 156.7, 154.5, 145.2 (=CPhO), 143.7 (PhC=), 136.6, 134.3, 130.9, 127.9, 127.3, 126.2, 125.7, 125.5, 125.0, 121.9, 120.0, 104.4, 67.4, 26.1, 26.0. UV (THF, 6.4×10^{-5} M), λ (nm)/ε (mol^{-1} L cm^{-1}): 294.2/1.44×10^4, 360.4/0.49×10^4, 425/0.42×10^4.

Table 1
Polymerization of 1-[4-(1-naphthoxy-4-butyloxy)]phenyl-2-phenylacetylene **1**(4)[a]

No.	Catalyst	Temperature (°C)	Yield (%)	M_w[b]	M_w/M_n[b]
1	$TaCl_5$—n-Bu_4Sn	80	5.5	Insoluble	
2	$NbCl_5$—n-Bu_4Sn	80	0		
3	WCl_6—n-Bu_4Sn	80	0		
4	$TaCl_5$—Ph_4Sn	80	Trace		
5	$NbCl_5$—Ph_4Sn	80	0		
6	WCl_6—Ph_4Sn	80	45.1	22 000	1.7
7[c]	WCl_6—Ph_4Sn	80	41.6	24 300	1.8
8[c]	WCl_6—Ph_4Sn	100	28.6	21 800	4.6

[a] Carried out under nitrogen in toluene for 24 h; $[M]_0 = 0.2$ M, [cat.] = 10 mM, [cocat.] = 20 mM.

[b] Determined by GPC in THF on the basis of a polystyrene calibration.

[c] [cocat.] = 10 mM.

Table 2
Polymerization of naphthalene-containing diphenylacetylenes[a]

No.	Catalyst	Temperature (°C)	Yield (%)	M_w[b]	M_w/M_n[b]
Monomer **1**(6)					
1	$TaCl_5$—n-Bu_4Sn	80	Trace		
2	$NbCl_5$—n-Bu_4Sn	80	0		
3	WCl_6—n-Bu_4Sn	80	0		
4	$TaCl_5$—Ph_4Sn	80	5.9	Insoluble	
5	$NbCl_5$—Ph_4Sn	80	2.5	Insoluble	
6	WCl_6—Ph_4Sn	80	36.3	20 300	1.6
7[c]	WCl_6—Ph_4Sn	80	47.3	18 400	1.7
8[c]	WCl_6—Ph_4Sn	100	21.4	7600	1.7
Monomer **1**(8)					
9	$TaCl_5$—n-Bu_4Sn	80	10.5	Insoluble	
10	$NbCl_6$—Ph_4Sn	80	0		
11	WCl_6—Ph_4Sn	80	61.7	38 400	2.5
12[c]	WCl_6—Ph_4Sn	80	44.8	19 200	1.8
13[c]	WCl_6—Ph_4Sn	100	37.6	49 500	3.2

[a] Carried out under nitrogen in toluene for 24 h; $[M]_0 = 0.2$ M, [cat.] = 10 mM, [cocat.] = 20 mM.

[b] Determined by GPC in THF on the basis of a polystyrene calibration.

[c] [cocat.] = 10 mM.

2.7.2. Poly{1-[4-(1-naphthoxy-6-hexyloxy)]phenyl-2-phenylacetylene} [P**1**(6)]

Greenish-yellow solid; yield 36.3%. M_w 20 300; M_w/M_n 1.6 (Table 2, no. 6). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.24, 7.73, 7.49, 7.37, 7.20, 6.86, 6.83, 6.64, 6.15, 4.21, 4.13, 4.02, 3.99, 3.97, 3.73, 1.86, 1.52. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 156.8, 154.8, 144.4 (=CPhO), 143.8 (PhC=), 136.8, 134.5, 128.3, 127.4, 126.3, 125.9, 125.7, 125.0, 122.6, 122.0, 105.2, 104.5, 67.9, 29.3, 27.1. UV (THF, 5.6×10^{-5} M), λ (nm)/ε (mol^{-1} L cm^{-1}): 293.5/1.24×10^4, 361.9/0.41×10^4, 427.5/0.31×10^4.

2.7.3. Poly{1-[4-(1-naphthoxy-8-octyloxy)]phenyl-2-phenylacetylene} [P**1**(8)]

Greenish-yellow solid; yield 61.7%. M_w 38 400; M_w/M_n 2.5 (Table 2, no. 11). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.26, 7.74, 7.40, 6.98, 6.88, 6.13, 4.04, 3.87, 3.72, 1.87, 1.40. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 156.8, 154.8, 145.1 (=CPhO), 143.9 (PhC=), 136.7, 134.5, 131.0, 128.0, 127.4, 126.3, 125.9, 125.7, 125.0, 122.0, 119.9, 114.2, 114.1, 112.7, 104.5, 68.0, 29.4, 29.3, 26.2. UV (THF, 6.9×10^{-5} M), λ (nm)/ε (mol^{-1} L cm^{-1}): 291.6/1.43×10^4, 365.9/0.42×10^4, 425.0/0.34×10^4.

3. Results and discussion

3.1. Monomer synthesis

Almost all the poly(diphenylacetylene)s prepared so far contain no chromophoric pendants [30–32]. With a view of synthesizing polymers with efficient green light emissions, we attached naphthalene ring as pendant to the diphenylacetylene structure through different lengths of methylene spacer by two etherifications of 1,*m*-dibromoalkanes with 1-naphthol and then with 1-(4-hydroxy)phenyl-2-phenylacetylene (**2**; cf., Scheme 1). All the reactions have proceeded smoothly and the desirable monomers are obtained in moderate yields (36–45%) after purification by column chromatography. We characterized the products by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures are obtained (see Section 2 for details).

3.2. Polymerization by transition-metal catalysts

We first tried to polymerize our monomers by $TaCl_5$–*n*-Bu_4Sn, an effective catalyst for the polymerizations of diphenylacetylenes [33–35]. Reaction of **1**(4) catalyzed by $TaCl_5$–*n*-Bu_4Sn in toluene at 80 °C, however, gives a greenish-yellow polymer in a low yield (Table 1, no. 1). The catalyst may be poisoned by the ether functionalities in the monomer, leading to the failure in the polymerization reaction. The polymer is insoluble in any organic solvents, preventing us from estimating its molecular weight by GPC as well as elucidating its molecular structure by "wet" spectroscopic techniques. Changing the catalyst to $NbCl_5$–*n*-Bu_4Sn and WCl_6–*n*-Bu_4Sn has also ended up in disappointment: no polymeric products are obtained after precipitation of their toluene solutions into acetone.

Although the results mentioned above are poor, we did not give up. We changed the cocatalyst to Ph_4Sn to see whether any improvement can be made. $TaCl_5$– and $NbCl_5$–Ph_4Sn are again unable to polymerize **1**(4). Although there have been no successful examples reported in the literature for using WCl_6 as catalyst for the polymerizations of diphenylacetylene derivatives [34,35], we found that **1**(4) can be converted into a soluble polymer in a satisfactory yield (45.1%) at 80 °C by WCl_6–Ph_4Sn catalyst (Table 1, no. 6). Lowering the amount of Ph_4Sn affects little the results but the yield becomes lower when the polymerization is carried out at a higher temperature (100 °C).

Similar to **1**(4), **1**(6) undergoes sluggish polymerizations when $TaCl_5$–, $NbCl_5$–, and WCl_6–*n*-Bu_4Sn are used as catalysts (Table 2, nos. 1–3). Small amounts of polymeric products are obtained by $TaCl_5$– and $NbCl_5$–Ph_4Sn but they are insoluble. Delightfully, WCl_6–Ph_4Sn works for the polymerization at 80 °C, furnishing a soluble polymer in ~36% yield. Decreasing the catalyst/cocatalyst ratio to 1:1 increases the polymer yield but at the expense of the molecular weight. Attempts to improve the results by raising the temperature to 100 °C failed and a polymer with a lower molecular weight is isolated in a much lower yield.

The polymerization behavior of **1**(8) is analogous to that of **1**(4). While no soluble polymer is obtained by $TaCl_5$–*n*-Bu_4Sn catalyst, the situation is even worse in $NbCl_5$–Ph_4Sn, with no product isolated at all. WCl_6–Ph_4Sn, however, is still effective for the polymerization and produces a high molecular weight polymer of over 60% yield. Unlike in **1**(6), both the yield and molecular weight decrease as the catalyst/cocatalyst ratio becomes lower. The molecular weight, however, is boosted more than two times when the polymerization is performed at 100 °C.

3.3. Structural characterization by spectroscopic methods

The molecular structures of the polymers are characterized by spectroscopic methods and all give satisfactory data corresponding to their expected molecular structures (see Section 2 for details). An example of the IR spectrum of P**1**(8) is shown in Fig. 1; for comparison, the spectrum of its monomer **1**(8) is also given in the same figure. The monomer shows a characteristic C≡C stretching absorption at 2218 cm^{-1}. This peak, however, is not observed in the spectrum of P**1**(8), suggesting that the triple bond of the monomer is completely consumed during the polymerization.

Fig. 2 depicts the ^1H NMR spectra of P**1**(8) and its monomer **1**(8) in chloroform-*d*. The phenyl protons of the diphenylacetylene structure of **1**(8) absorb at δ 7.48, 7.35, and 6.87. These absorption peaks, however, disappear after polymerization. The transformation of the acetylene triple bond of the monomer to the double bond of the polyene by the polymerization reaction downfield-shifts the ethynylphenyl proton resonances, which are now observed at δ 6.93, 6.71, and 6.10. No other unexpected signals are observed and all the peaks can be readily assigned, proving that the molecular structure of the polymeric product is indeed P**1**(8), as shown in Chart 1.

The structures of the polymers are further characterized by ^{13}C NMR spectroscopy (Fig. 3). The spectrum of P**1**(8) shows no acetylene carbon resonances of **1**(8) at δ 89.4 and 88.0. On the other hand, two small peaks associated with the olefin carbon resonances in the newly formed poly(diphenylacetylene) backbone are observed at δ 145.1 and 143.8.

3.4. Thermal stability

Unsubstituted polyacetylene is insoluble in common organic solvents, infusible before thermal decomposition, and degradable upon exposure to air. Our polymers, however, are soluble in $CHCl_3$, THF, and toluene and enjoy high thermal

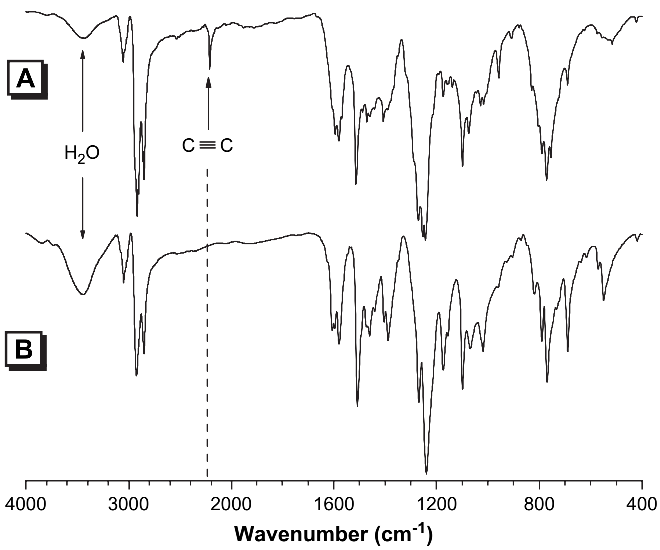


Fig. 1. IR spectra of (A) **1**(8) and (B) its polymer P**1**(8) (sample from Table 2, no. 12).

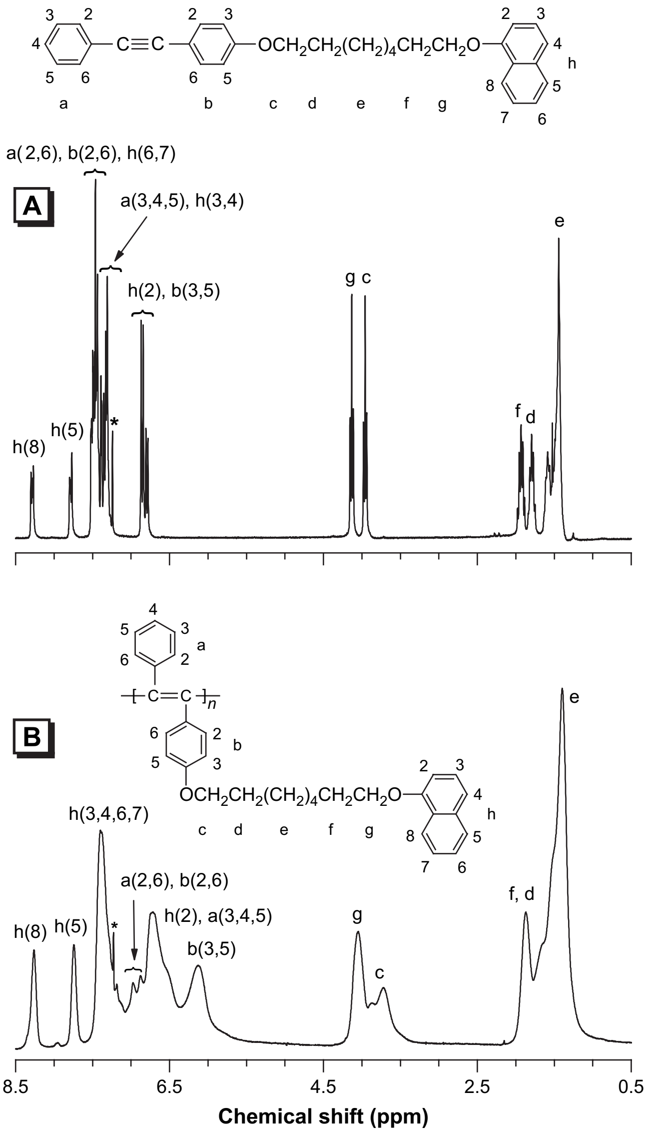


Fig. 2. ^{1}H NMR spectra of chloroform solutions of (A) **1**(8) and (B) its polymer P**1**(8) (sample from Table 2, no. 12). The solvent peak is marked with an asterisk.

stability. As shown in Fig. 4, P**1**(4) shows a 5% weight loss at a temperature as high as 420 °C. The enhanced thermal stability should be due to the jacket effect [36,37] contributed by the phenyl rings linked to the polyacetylene backbone plus the 1-naphthoxy pendants, which well wrap the polymer chains and thus limit their perturbation by heat and/or attack by the degradative species. The thermal stability of the polymers is insensitive to the length of the methylene spacer and both P**1**(6) and P**1**(8) degrade at a temperature similar to that of P**1**(4).

To further evaluate the stability of the polymers, we checked the changes of their molecular weight with temperature. We annealed the polymers in air for 2 h at different temperatures and plotted their M_w against temperature (Fig. 5). Almost no changes in the molecular weights are observed when the polymers are annealed up to 150 °C, while the molecular weights of P**1**(4) and P**1**(6) are increased when heated at 200 °C. This further confirms that the polymers are resistant to the chain scission caused by thermolytic oxidation.

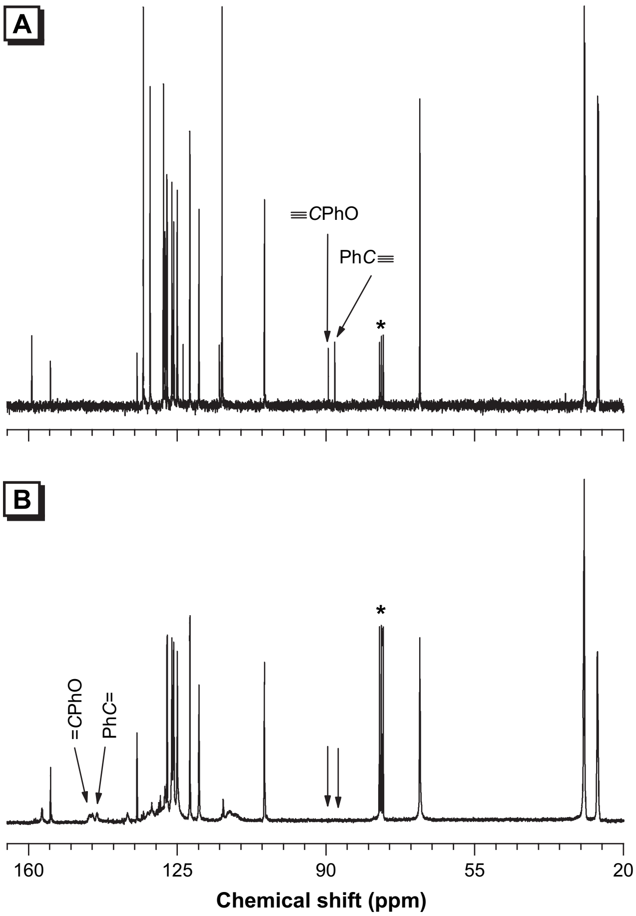


Fig. 3. ^{13}C NMR spectra of (A) **1**(8) and (B) its polymer P**1**(8) (sample from Table 2, no. 12) in chloroform-*d*. The solvent peaks are marked with asterisks.

3.5. Electronic transition

The absorption spectra of the polymers in THF are given in Fig. 6. While the strong absorption at 295 nm is due to the E_2 band of the 1-naphthoxy pendants of P**1**(4) [38], the backbone absorption is found at wavelengths longer than 330 nm with high intensities. The polymer segment may take a more planar conformation owing to the planar and bulky phenyl and naphthalene appendages. The planar backbone allows better conjugation of the alternating double bond and hence makes the polymer more absorptive in the longer wavelength regions. The spacer length exerts little influence on the ground-state electronic transitions of the polymers: the UV spectra of P**1**(6) and P**1**(8) are similar to that of P**1**(4). The band gap and the HOMO energy level of the polymers are estimated from their absorption onset wavelengths and cyclic voltammetry measurements and are found to be ~2.61 and ~5.06 eV, respectively.

3.6. Photoluminescence

Disubstituted polyacetylenes such as poly(diphenylacetylene)s and poly(1-phenyl-1-alkyne)s are strong light emitters. For example, poly[1-(4-butylphenyl)-2-phenylacetylene]

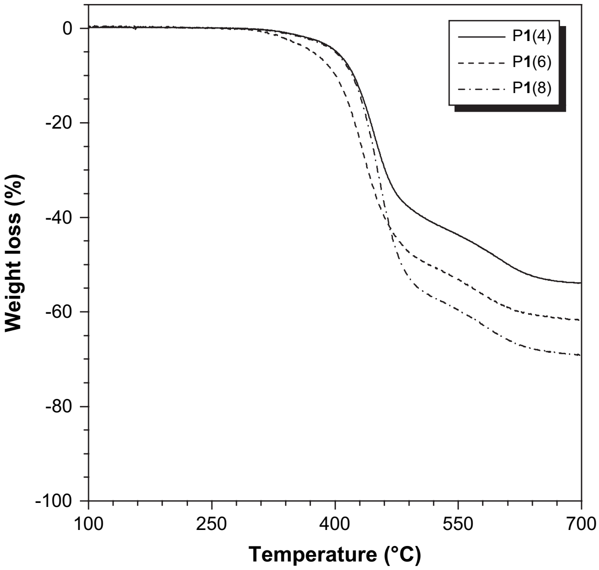


Fig. 4. TGA thermograms of polymers **P1**(4) (sample from Table 1, no. 7), **P1**(6) (Table 2, no. 7), and **P1**(8) (Table 1, no. 12) recorded under nitrogen at a heating rate of 20 °C/min.

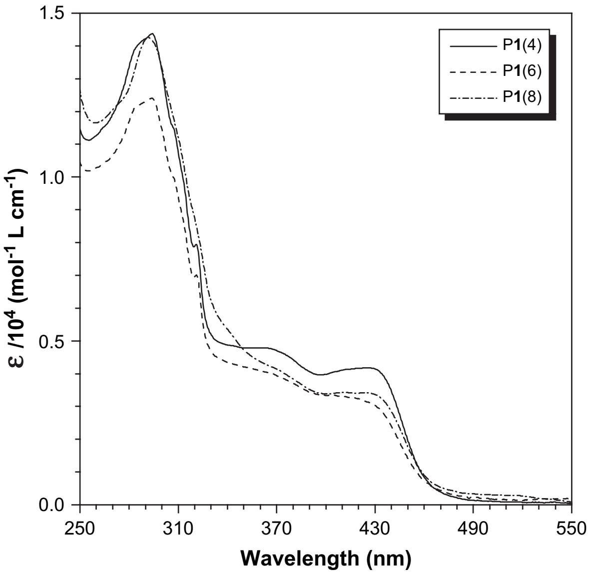


Fig. 6. UV spectra of THF solutions of polymers **P1**(4) (sample from Table 1, no. 7), **P1**(6) (Table 2, no. 7), and **P1**(8) (Table 2, no. 13).

$-\{(C_6H_5)C{=}C[C_6H_4(CH_2)_3CH_3]\}_n-$ (PBPPA) emits a strong green light of 520 nm with a Φ_F of 43% when photoexcited [39]. Since **P1**(m) are structural congeners of PBPPA with naphthalene pendant groups, it is of interest to check whether our polymers are also strong emitters. Fig. 7A shows the PL spectra of the polymers in THF. Upon UV irradiation, **P1**(4) emits a green light of 510 nm. Since the emission of the naphthalene moiety of its monomer is found at 340 nm, the peak at 510 nm should have originated from the PL of the poly(diphenylacetylene) backbone. Using Rhodamine B as the standard, the Φ_F value of the polymer is calculated to be 94%, which is more than two times higher than that of PBPPA, thanks to the energy transfer from the pendant groups to the polymer main chain and the reduction of the interchain interaction by the long aliphatic chain and bulky naphthalene side groups. This indicates that the optical properties of polyacetylenes are sensitive to their molecular structures and that the attachment of chromophoric moieties to the poly(diphenylacetylene) backbone is an effective methodology to boost the emission efficiency of the polymer. The emissions of **P1**(6) and **P1**(8) are found at similar wavelength regions, with **P1**(8) showing the highest Φ_F of 98%.

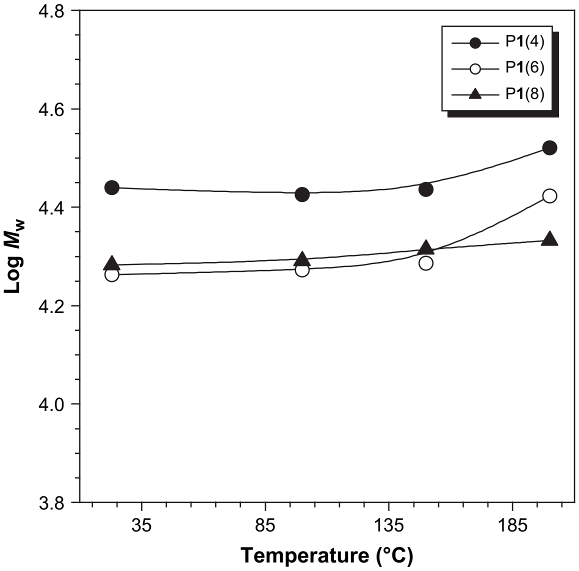


Fig. 5. Effect of temperature on the molecular weight (M_w) of **P1**(4) (sample from Table 1, no. 7), **P1**(6) (Table 2, no. 7), and **P1**(8) (Table 2, no. 12). The polymer samples were annealed in air at given temperatures for 2 h.

Many conventional conjugated polymers emit intensely in solution but become almost nonluminescent when fabricated into thin films. This is mainly caused by strong interchain interaction [40,41]. In the solid state, the polymer strands aggregate together and form less emissive species such as excimers, leading to red-shifted emissions with low efficiencies. Would our polymers become non-emissive in the solid state? Delightfully, the thin films of the polymers still emit strongly upon photoexcitation, although we do not know their Φ_F values due to the technical difficulty. Compared to those in THF, no significant shift in the emission maximum is observed (Fig. 7B), suggesting that few or no excimeric species are involved in the light emission process in the solid state.

3.7. Electroluminescence

The efficient PL of our polymers prompts us to study their EL performance. We chose **P1**(8), the best PL emitter, for this study. We fabricated an EL device with a configuration of ITO/**P1**(8):PVK(1:4 w/w)/BCP/Alq$_3$/LiF/Al, which emits a green light of 510 nm (Fig. 8A). The EL spectrum is single-peaked and symmetrically shaped, with no sidebands associated with such emitting species as excimers. The pattern is similar to its PL spectrum, indicating that the PL and EL originate from the radiative decay of the singlet excitons induced by photoexcitation and charge recombination. The changes in the

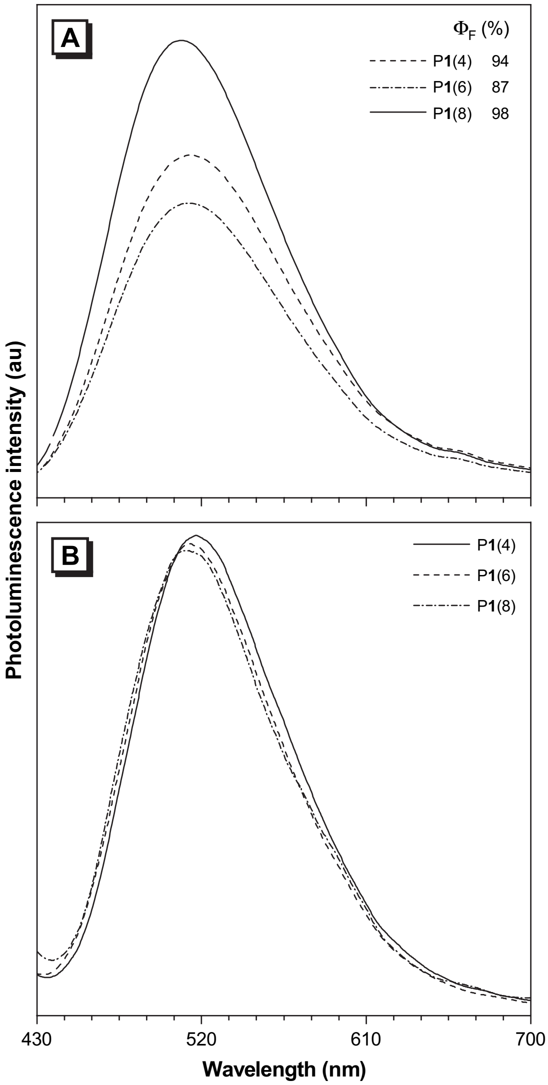


Fig. 7. Photoluminescence spectra of **P1**(4) (sample from Table 1, no. 7), **P1**(6) (Table 2, no. 7), and **P1**(8) (Table 2, no. 12) in (A) THF solutions and (B) solid thin films. Concentration: 0.05 mM; excitation wavelength: 398 nm.

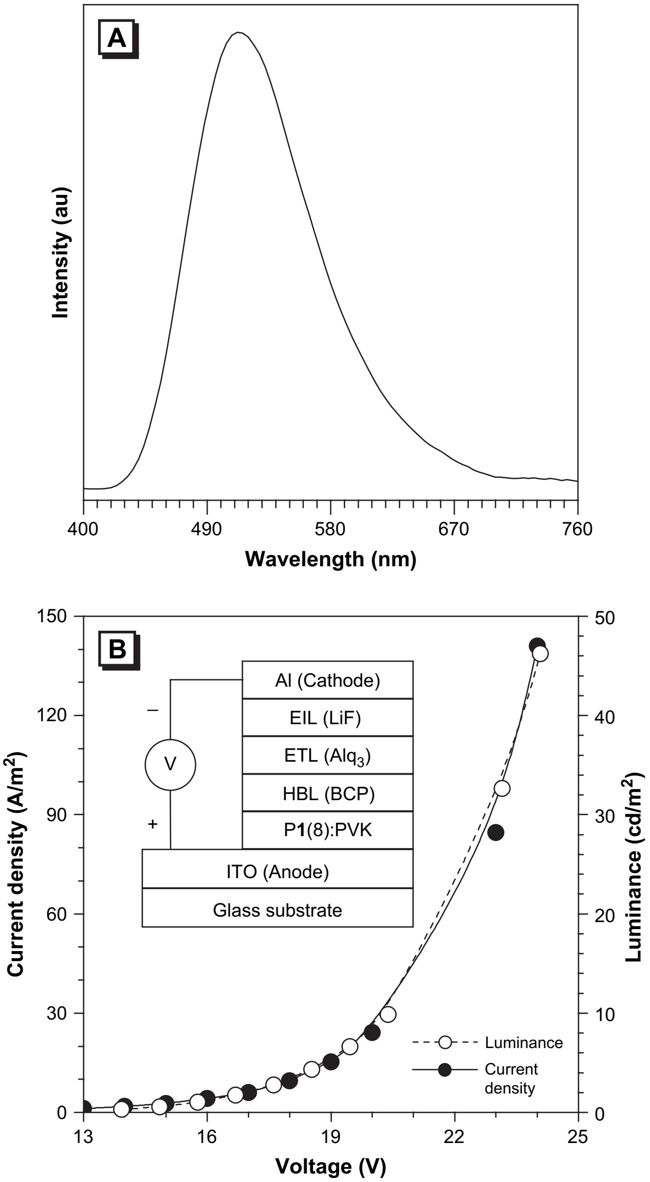


Fig. 8. (A) Electroluminescence spectrum and (B) changes in the current density and luminance with the applied voltage in a multilayer light-emitting diode of **P1**(8) with a device configuration of ITO/**P1**(8):PVK(1:4 w/w)/BCP/Alq_3/LiF/Al (inset).

current density and the luminance with the voltage of the EL device are shown in Fig. 8B. The current flowing through the device is low until its turn-on voltage (13 V) is reached. Afterwards, it increases exponentially. A similar exponential increase in luminance against the applied voltage is observed. The device reaches its maximum luminance at 46 cd/m^2 at 24 V. The quantum efficiency at this voltage is ~0.16%. This suggests that the device configuration is yet to be optimized.

3.8. Spectral stability

Although poly(fluorene)s are the best-known luminescent conjugated polymers, their EL devices suffer from poor spectral stability [42–44]. Upon raising the bias voltage, the emission changes from blue to undesirable bluish green. Our polymers, however, enjoy good spectral stability. Fig. 9 shows the EL spectra of **P1**(8) at different currents. Little shift in the peak maximum is observed when the current is raised from 0.06 to 1.3 mA. Even when the current is increased to 5.4 mA, the EL spectrum experiences little change, indicative of its excellent stability.

3.9. Fluorescence imaging

Since the polymers are efficient PL emitters, we tried to utilize them for the fabrication of fluorescence patterns. Due to photooxidation of the polymer chains [45], UV irradiation of a film of **P1**(8) in air through a mask quenches the luminescence of the exposed regions (black lines), while the unexposed areas remain emissive (Fig. 10). A fluorescent photoimage is thus directly drawn without going through a developing process.

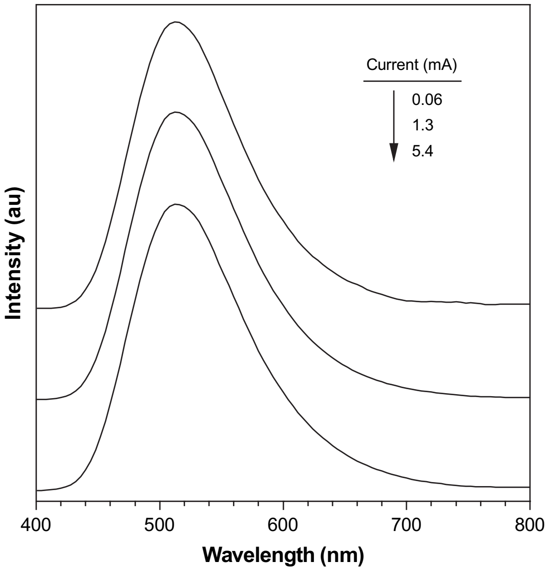


Fig. 9. Stability of the electroluminescence spectra of P**1**(8) against applied voltage. (The device configuration is the same as that given in Fig. 8).

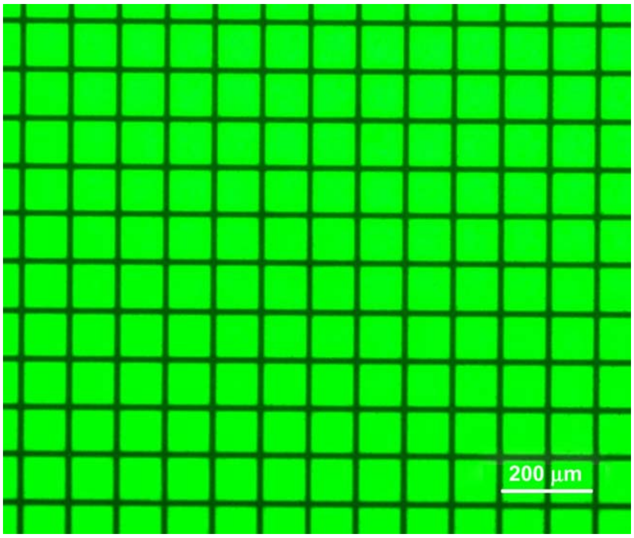


Fig. 10. Fluorescence photopattern generated by photooxidation of P**1**(8) (sample from Table 2, no. 12) imaged under a handheld UV lamp.

4. Conclusions

In this work, we designed and synthesized a group of naphthalene-containing poly(diphenylacetylene)s with different spacer lengths and studied their thermal and optical properties. Our findings can be summarized as follows:

(1) The monomers are prepared by two substitutions of 1,*m*-dibromoalkanes in moderate yields. Although $TaCl_5$–*n*-Bu_4Sn is the most widely used catalyst for the polymerization of diphenylacetylenes, it is inactive in polymerizing the monomers. WCl_6–Ph_4Sn, on the other hand, produces high molecular weight polymers (up to 5.0×10^4) in satisfactory yields (up to 62%).

(2) All the polymers possess high thermal stability. They start to lose their weights at ~400 °C in nitrogen. They are also stable towards thermolysis up to 200 °C in air, thanks to the protective jacket effect contributed by the phenyl and the naphthalene pendants.

(3) Upon photoexcitation, the polymers emit strong green lights of 510 nm in THF in high quantum efficiencies (up to 98%). Little or no shift in the peak maximum is observed in the PL spectra of the polymer thin films, suggesting that no excimeric species are involved in the light emission process in the solid state.

(4) Multilayer EL device with a configuration of ITO/P**1**(8)/BCP/Alq_3/LiF/Al is constructed, which gives a green emission at 510 nm with a maximum quantum efficiency of 0.16%. The stability of the EL spectrum is outstanding: almost no change in the peak maximum is observed when the current is raised.

(5) The polymers are sensitive to photooxidation. UV irradiation of the polymers in air through a mask quenches the light emission of the exposed regions, resulting in the formation of light-emitting photopatterns.

Acknowledgments

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