

# Synthesis, Characterization, and Photochemical Properties of Chromophores Containing Photoresponsive Azobenzene and Stilbene

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**ABSTRACT:** In this article, we describe the synthesis of two azobenzene and two stilbene-based diacetylene chromophores containing terminal electron-donating ( $-\text{OCH}_3$ ) and electron-withdrawing ( $-\text{NO}_2$ ) terminal groups with esterification reactions. The target compounds were characterized by NMR, X-ray diffraction (XRD), absorption, and photoluminescence spectroscopies. We investigated the structural effects of these photochromic compounds on the E–Z photoisomerization and 1,4-addition under UV irradiation. 4-[(4-Nitrophenyl)-diazenyl]phenyl pentacos-10,12-dienoate, incorporating the electron-withdrawing nitro group ( $-\text{NO}_2$ ), underwent the fastest rate of Z-to-E isomerization in darkness via a rotation mechanism. Our results demonstrate that

self-assembled azobenzene Z isomers exhibited enhanced fluorescence under UV irradiation. XRD spectroscopy identified bilayer packing by the polydiacetylene films after 1,4-addition. Chromophores comprising the diacetylene group presented moderate photochromic stability upon 1,4-addition, changing from their original yellowish color to form a blue phase. These synthesized compounds may be useful in the development of new and unique functional materials that exhibit bistable photochromism. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4193–4205, 2012

**Key words:** addition polymerization; photochemistry; synthesis; UV–vis spectroscopy

## INTRODUCTION

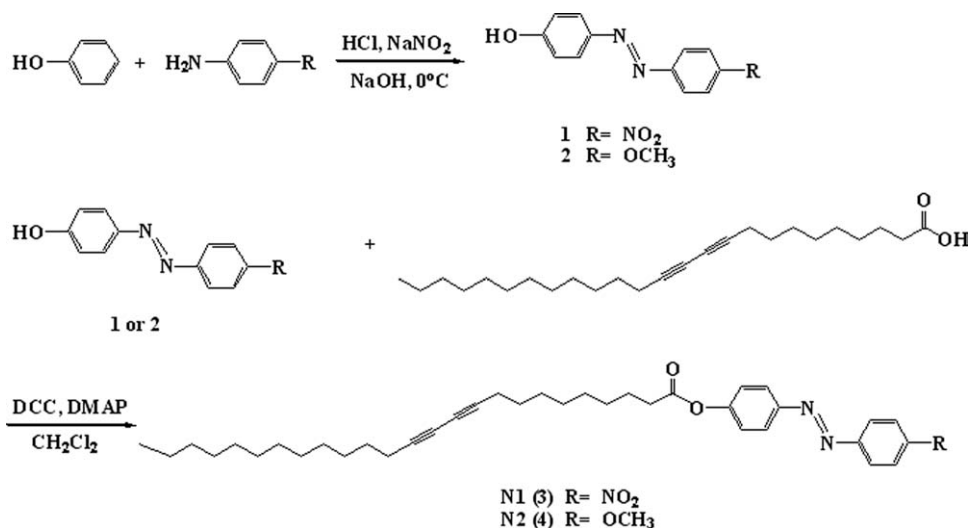
Photoresponsive polymers have promising practical applications in areas such as reversible optical data storage<sup>1–3</sup> and surface relief gratings.<sup>4–6</sup> UV-light-induced configuration changes in polymer chains, resulting in the E–Z isomerization or disorganization of azobenzene and stilbene fragments, can be used to provide a motor function for contractions in photoresponsive materials.<sup>7</sup> Configuration changes are often accompanied by changes in the orientation or optical properties. This opens possibilities for the preparation of so-called photorecorded films, with locally variable supramolecular structures and optical properties. Several groups have reported the preparation and applications of photoresponsive materials that are composed of fast photochemical segments.<sup>8–11</sup> Our system is based on configuration changes in azobenzene- or stilbene-based chromophores. Azobenzene-containing chromophores undergo isomerization from the E

isomer to the Z form under irradiation by light, whereas the Z isomer can return to the E form either by photochemical or thermal stimulus.<sup>12</sup> Polydiacetylenes also attract attention because of their tendency toward topochemical polymerization, their ability to form well-defined nanostructures, and their optical and chromic properties. This class of compound has a wide range of applications in chemistry, including biosensors, optical materials, and Langmuir–Blodgett films.<sup>13–15</sup> The topochemical polymerization of diacetylene can be achieved photochemically, thermally, or even by the application of pressure. Polydiacetylene films are obtained by the 1,4-addition polymerization of diacetylene monomer. The polymerization proceeds only when the monomers are arranged with appropriate geometry relative to the translation axis, that is, a distance ( $d$ ) of 5 Å and an orientation angle ( $\theta$ ) of 45°. <sup>16,17</sup> In addition to photochromism, polyacetylenes also exhibit thermochromic properties, and this feature was researched by Peng et al.<sup>18</sup>

In a previous study,<sup>19</sup> we demonstrated that the cinnamoyl (C=C) group, present in polyacrylates, is insensitive to 365-nm UV light and undergoes very little E–Z photoisomerization. In this study, we examined the influence of photochromic compound structures on the photoreactivity of polymers bearing multiple photochromic groups. We also investigated

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**Scheme 1** Synthetic routes of azobenzene-based chromophores N1 and N2.

the association between the optical behavior and the molecular structure. We report here on the synthesis, characterization, and E–Z isomerization properties of a series of photoresponsive azobenzene- or stilbene-based diacetylene chromophores containing various terminal groups. The optical properties of the photochromic compounds were studied by ultraviolet–visible (UV–vis) and photoluminescence (PL) spectroscopy. The molecular structures obtained after the 1,4-addition reaction were investigated by X-ray diffraction (XRD).

## EXPERIMENTAL

### Measurements

All new compounds were identified by NMR, Fourier transform infrared (FTIR) spectra, and elemental analysis (EA). <sup>1</sup>H-NMR (400-MHz) and <sup>13</sup>C-NMR (100.6-MHz) spectra were recorded on a Bruker AMX-400 Fourier transform NMR spectrometer (Darmstadt, Germany), and chemical shifts are reported in parts per million with tetramethylsilane as an internal standard. FTIR spectra were recorded with KBr disks with a Jasco VALOR III FTIR spectrometer (Tokyo, Japan); 32 scans were collected at a resolution of 1 cm<sup>-1</sup>. EA was carried out on a Heraeus CHN-O rapid elemental analyzer (Darmstadt, Germany). UV/Visible absorption spectra were measured using a Jasco V-550 spectrophotometer (Tokyo, Japan) and photoluminescence (PL) spectra were obtained using a Jasco FP-750 fluorescence spectrophotometer (Tokyo, Japan). Thermal analysis was performed using a differential scanning calorimeter (Perkin Elmer DSC 7, PerkinElmer Cetus Instrument, USA) at a scanning rate of 10 K/min under nitrogen atmosphere. Characterization of polyacetylene films by XRD measurement was recorded on a Rigaku RINT 2500 X-ray diffractometer (Tokyo, Japan) with Ni-filtered CuKα radiation ( $\lambda = 0.154056$

nm). The tube current and voltage were 30 mA and 40 kV, respectively.

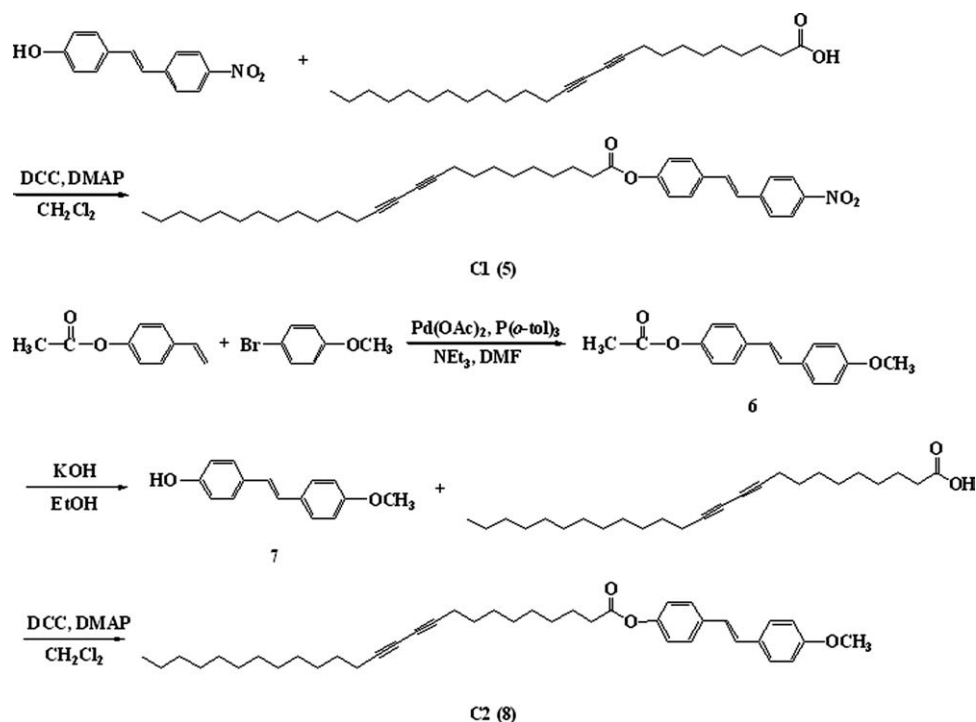
### Materials

The synthetic routes for the target photochromic compounds are shown in Schemes 1 and 2. The intermediates, 4-hydroxy-4'-nitroazobenzene (1) and 4-hydroxy-4'-methoxyazobenzene (2), were synthesized according to processes reported in the literature.<sup>20–22</sup> 4-Hydroxy-4'-methoxystilbene (7) and the following photochromic compounds consisting of diacetylene groups were synthesized according to similar procedures described in the literature.<sup>19,23</sup> The obtained products were purified and identified with FTIR and NMR spectroscopy and EA. All organic solvents and reagents were purchased from Acros (Geel Belgium), Alfa Aesar (Ward Hill, MA, USA), and Aldrich (Steinheim, Germany) Chemical Co. and were used without further purification. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled over calcium hydride under argon immediately before use. Dimethylformamide (DMF) was dried with appropriate drying agents (Na or CaCl<sub>2</sub>), then distilled under reduced pressure, and stored over 4-Å molecular sieves before use. Analytical thin-layer chromatography was conducted on Merck aluminum plates with 0.2 mm of silica gel (60F-254). Anhydrous sodium sulfate was used to dry all of the organic extracts.

### Synthesis of the photochromic compounds (Schemes 1 and 2)

Synthesis of 4-[(4-nitrophenyl)-diazenyl]phenyl pentacosadiynoic acid (3 or N1)

10,12-Pentacosadiynoic acid (1.56 g, 4.0 mmol), 1 (0.97 g, 4.0 mmol), and 50 mL of dry CH<sub>2</sub>Cl<sub>2</sub> were added to a two-necked glass reactor. *N,N'*-



Scheme 2 Synthetic routes of stilbene-based chromophores C1 and C2.

Dicyclohexylcarbodiimide (1.24 g, 6.0 mmol) and 4-dimethylaminopyridine (48.9 mg, 0.4 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and then added to the solution under a nitrogen atmosphere. The reaction mixture was stirred for 24 h at 30°C. A solid *N,N'*-dicyclohexyl urea was precipitated and filtered off. The resulting solution was washed with water, dried with anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>).

Yield: 56.8%. Melting temperature ( $T_m$ ) = 66.0°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ, ppm): 0.87 (t, 3H, CH<sub>3</sub>), 1.25–1.54 (m, 30H, CH<sub>2</sub>), 1.75–1.78 [m, 2H, –C(=O)CH<sub>2</sub>CH<sub>2</sub>–], 2.22–2.26 (t, 4H, –C≡C–CH<sub>2</sub>–), 2.59–2.61 [t, 2H, –C(=O)CH<sub>2</sub>–], 7.27–7.29 (d, 2H, Ar–H), 7.99–8.02 (d, 4H, Ar–H), 8.36–8.38 (d, 2H, Ar–H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 14.07 (CH<sub>3</sub>); 19.16, 22.64, 24.77, 28.25, 28.31, 28.69, 28.82, 28.84, 28.97, 29.03, 29.05, 29.30, 29.43, 29.85, 31.87 (CH<sub>2</sub>); 34.34 [C(=O)CH<sub>2</sub>]; 65.35, 77.60 (C≡C); 122.45, 123.69, 124.67 (aromatic); 148.69, 149.86, 153.86, 155.57 (aromatic quaternary); 171.72 (C=O). ANAL. Calcd for C<sub>37</sub>H<sub>49</sub>N<sub>3</sub>O<sub>4</sub>: C, 74.02%; H, 8.17%; N, 7.00%. Found: C, 73.96%; H, 8.14%; N, 6.97%.

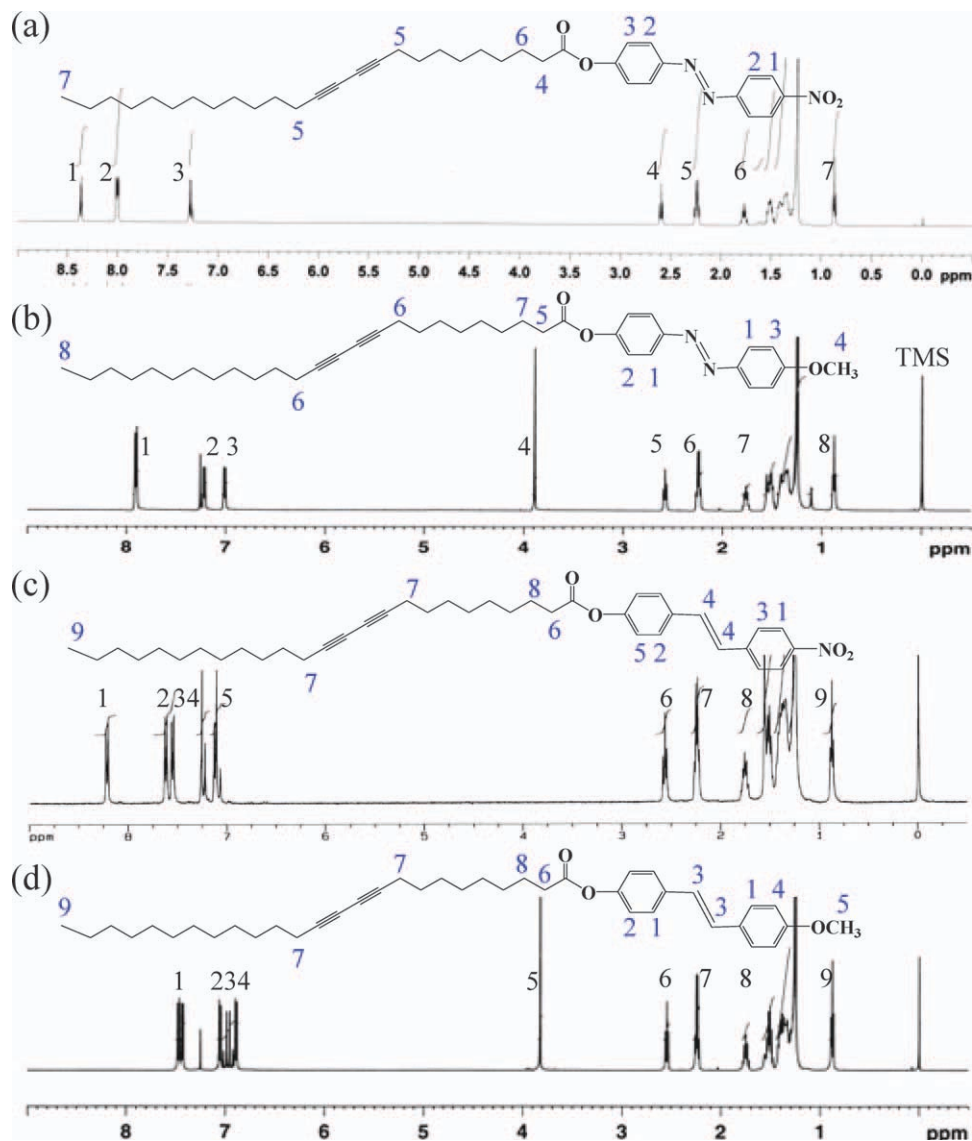
Synthesis of 4-[(4-methoxyphenyl)-diazenyl]phenyl pentacosano-10,12-diyenoate (4 or N2)

The synthesis procedures of N2, 4-(4-nitrostyryl)phenyl pentacosano-10,12-diyenoate (5 or C1), and 4-(4-methoxystyryl)phenyl pentacosano-10,12-diyenoate (8 or C2) were analogous to that of N1.

Yield: 52.2%.  $T_m$  = 81.0°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ, ppm): 0.89 (t, 3H, CH<sub>3</sub>), 1.11–1.55 (m, 30H, CH<sub>2</sub>), 1.73–1.79 [m, 2H, –C(=O)CH<sub>2</sub>CH<sub>2</sub>–], 2.22–2.26 (t, 4H, –C≡C–CH<sub>2</sub>–), 2.56–2.59 [t, 2H, –C(=O)CH<sub>2</sub>–], 3.89 (s, 3H, OCH<sub>3</sub>), 7.00–7.02 (d, 2H, Ar–H), 7.20–7.22 (d, 2H, Ar–H), 7.89–7.91 (d, 4H, Ar–H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 19.22 (CH<sub>3</sub>); 22.70, 24.88, 28.31, 28.38, 28.76, 28.88, 28.91, 29.05, 29.11, 29.35, 29.49, 29.62, 29.64, 29.66, 29.71, 31.26, 31.93, 34.42 (CH<sub>2</sub>); 38.17 [C(=O)CH<sub>2</sub>]; 55.60 (OCH<sub>3</sub>); 65.26, 77.65 (C≡C); 114.24, 122.14, 123.71, 124.77 (aromatic); 146.98, 150.35, 152.30, 162.12 (aromatic quaternary); 171.99 (C=O). ANAL. Calcd for C<sub>38</sub>H<sub>52</sub>N<sub>2</sub>O<sub>3</sub>: C, 77.97%; H, 8.89%; N, 4.79%. Found: C, 77.92%; H, 8.92%; N, 4.76%.

Synthesis of 5 (C1)

Yield: 48.6%.  $T_m$  = 58.7°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ, ppm): 0.86 (t, 3H, CH<sub>3</sub>), 1.27–1.47 (m, 30H, CH<sub>2</sub>), 1.74–1.77 [m, 2H, –C(=O)CH<sub>2</sub>CH<sub>2</sub>–], 2.23–2.25 (t, 4H, –C≡C–CH<sub>2</sub>–), 2.58–2.61 [t, 2H, –C(=O)CH<sub>2</sub>–], 7.11–7.14 (2H, d, Ar–H), 7.23–7.26 (2H, dd, vinyl CH=CH), 7.55–7.57 (2H, d, Ar–H), 7.62–7.64 (2H, d, Ar–H), 8.21–8.23 (2H, d, Ar–H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): 14.08 (CH<sub>3</sub>); 18.30, 22.67, 25.71, 28.61, 28.70, 29.11, 29.20, 29.29, 29.36, 29.48, 30.12, 31.92 (CH<sub>2</sub>); 34.01 [C(=O)CH<sub>2</sub>]; 67.39, 76.75 (C≡C); 121.01, 124.47, 128.11, 129.07 (aromatic); 124.68, 127.50 (vinyl C=C); 133.44, 139.74, 147.57, 149.32 (aromatic quaternary); 171.35 (C=O). ANAL. Calcd for C<sub>39</sub>H<sub>51</sub>NO<sub>4</sub>: C, 78.28%; H, 8.53%; N, 2.34%. Found: C, 78.34%; H, 8.48%; N, 2.35%.



**Figure 1**  $^1\text{H-NMR}$  spectra of (a) N1, (b) N2, (c) C1, and (d) C2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The organic layer was washed with distilled water and dried with anhydrous  $\text{MgSO}_4$

A mixture of 4-bromoanisole (1.87 g, 10.0 mmol), 4-acetoxystyrene (1.95 g, 12.0 mmol), palladium(II) acetate (44.9 mg, 0.2 mmol), tri-*o*-tolylphosphine (0.33 g, 1.1 mmol), and triethylamine (2.02 g, 20.0 mmol) was dissolved in 30 mL of dry DMF. The reaction mixture was stirred at  $100^\circ\text{C}$  for 48 h under a nitrogen atmosphere. The reaction was poured into distilled water and extracted with chloroform. The organic layer was washed with distilled water and dried with anhydrous  $\text{MgSO}_4$ . The precipitate was filtered, dried, and recrystallized from ethanol to produce 6.

Yield: 50.6%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.31 [s, 3H,  $\text{CH}_3\text{C}(=\text{O})$ ], 3.83 (s, 3H,  $\text{OCH}_3$ ), 6.88–6.92 (2H, d, Ar–H), 6.96–7.05 (dd, 2H, vinyl  $\text{CH}=\text{CH}$ ), 7.06–7.09 (d, 2H, Ar–H), 7.42–7.50 (d, 4H, Ar–H).

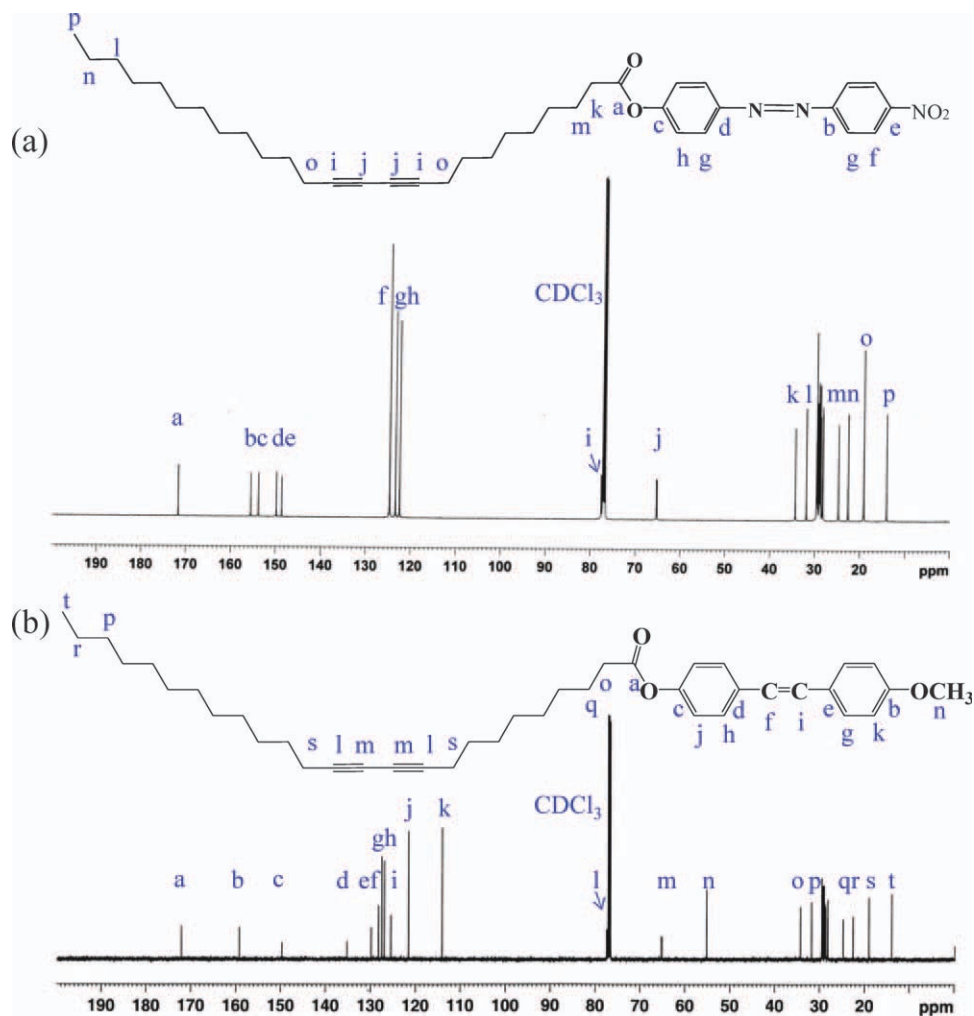
#### Synthesis of 7

A mixture of 6 (0.511 g, 0.9 mmol), KOH (0.169 g, 3.0 mmol), and ethanol (30 mL) was stirred at  $80^\circ\text{C}$  for 4 h under a nitrogen atmosphere. After it was cooled to room temperature, the mixture was poured into water. The precipitate was collected by filtration, dried, and recrystallized from ethanol to provide 7.

Yield: 67.6%.  $^1\text{H-NMR}$  (acetone- $d_6$ ,  $\delta$ , ppm): 3.79 (s, 3H,  $\text{OCH}_3$ ), 6.81–6.83 (d, 2H, Ar–H), 6.89–6.91 (d, 2H, Ar–H), 6.98–6.99 (2H, vinyl  $\text{CH}=\text{CH}$ ), 7.39–7.41 (d, 2H, Ar–H), 7.46–7.48 (d, 2H, Ar–H), 8.50 (s, 1H, OH).

#### Synthesis of 8 (C2)

Yield: 45.2%.  $T_m = 51.6^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.87 (t, 3H,  $\text{CH}_3$ ), 1.31–1.56 (m, 30H,  $\text{CH}_2$ ), 1.72–1.77 [m, 2H,  $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2-$ ], 2.22–2.24 (t, 4H,  $-\text{C}\equiv\text{C}-\text{CH}_2-$ ),



**Figure 2**  $^{13}\text{C}$ -NMR spectra of (a) N1 and (b) C2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

2.53–2.56 [t, 2H,  $-\text{C}(=\text{O})\text{CH}_2-$ ], 3.82 (3H, s,  $\text{OCH}_3$ ), 6.88–6.90 (2H, d, Ar–H), 6.92–7.04 (2H, dd, vinyl  $\text{CH}=\text{CH}$ ), 7.06–7.08 (2H, d, Ar–H), 7.42–7.48 (4H, d, Ar–H).  $^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ): 14.08 ( $\text{CH}_3$ ); 19.22, 22.70, 24.92, 28.32, 28.38, 28.77, 28.88, 28.92, 29.06, 29.10, 29.12, 29.36, 29.50, 29.62, 29.65, 29.66, 29.72, 31.94 ( $\text{CH}_2$ ); 34.41 [ $\text{C}(=\text{O})\text{CH}_2$ ]; 55.33 ( $\text{OCH}_3$ ); 65.27, 77.64 ( $\text{C}\equiv\text{C}$ ); 114.17, 121.76, 127.11, 127.73, (aromatic); 125.67, 128.41 (vinyl  $\text{C}=\text{C}$ ); 130.05, 135.39, 149.88, 159.39 (aromatic quaternary); 172.27 ( $\text{C}=\text{O}$ ). ANAL. Calcd for  $\text{C}_{40}\text{H}_{54}\text{O}_3$ : C, 82.35%; H, 9.26%. Found: C, 82.31%; H, 9.28%.

### Fabrication of the polymer films

The diacetylene films for optical measurements were prepared by the casting of a solution of the synthesized compound in toluene onto a glass substrate. Before film casting, the substrates were cleaned with a detergent solution and washed under ultrasonic stimulation in water for 30 min and in acetone for 60 min. The substrates were then dried *in vacuo*. Toluene solu-

tions (10 wt %) were stirred for 12 h before they were cast onto the substrate and further dried *in vacuo* at  $50^\circ\text{C}$  for 48 h. The polymer films were obtained after UV exposure ( $254\text{ nm}$ ,  $6\text{ mW}/\text{cm}^2$ ) and were examined for their optical properties.

## RESULTS AND DISCUSSION

### Synthesis and characterization

Two azobenzene- and two stilbene-based diacetylene chromophores containing terminal electron-donating ( $-\text{OCH}_3$ ) and electron-withdrawing ( $-\text{NO}_2$ ) moieties were prepared to investigate the effects of E–Z photoisomerization on the absorption and PL spectra under UV irradiation. The four chromophores were synthesized by the esterification of 10,12-pentacosadiynoic acid and analogous compounds with alcohol groups with *N,N'*-dicyclohexylcarbodiimide as a condensation agent and 4-dimethylaminopyridine as a catalytic reagent in a dry  $\text{CH}_2\text{Cl}_2$  solution at  $30^\circ\text{C}$ . The reactive intermediate, **7**, bearing a hydroxyl

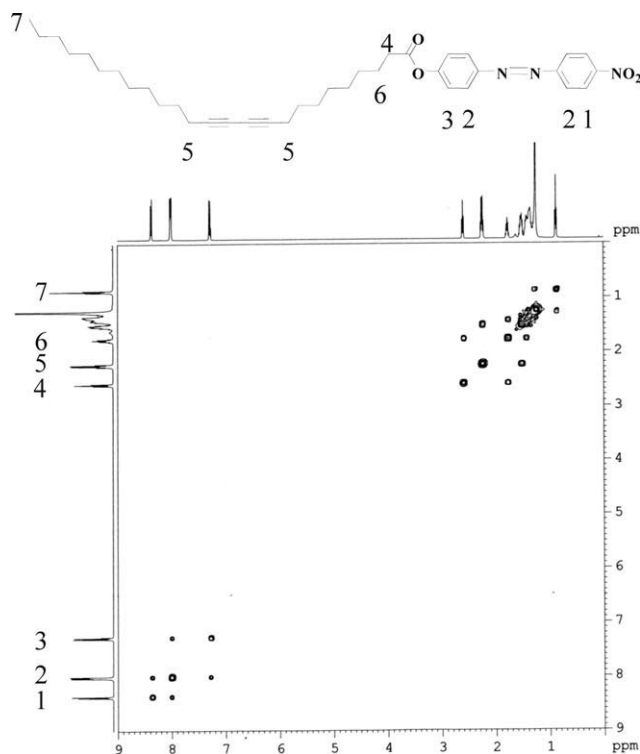


Figure 3 H–H COSY spectrum of N1 in  $\text{CDCl}_3$ .

moiety, was synthesized in two steps, starting from the palladium-catalyzed Heck coupling reaction of 4-acetoxystyrene and 4-bromoanisole (Scheme 2). The chemical structures and constitutional compositions of the synthesized compounds were confirmed by EA, FTIR spectroscopy,  $^1\text{H}$ -NMR spectroscopy,  $^{13}\text{C}$ -NMR, correlation spectroscopy (COSY) NMR, and heteronuclear multiple quantum coherence (HMQC)-NMR spectroscopy. Figure 1 shows the  $^1\text{H}$ -NMR spectra of the synthesized diacetylene chromophores. The  $^{13}\text{C}$ -NMR spectra of two representative compounds (N1 and C2) in  $\text{CDCl}_3$  are also shown in Figure 2. Carbon and proton peaks are labeled alphanumerically, as shown in these figures. As shown in Figure 1(a), the  $^1\text{H}$ -NMR spectrum of N1, incorporating the azobenzene chromophores, verified the characteristic chemical shifts at 7.27–8.38, 2.59–2.61, 2.22–2.26, 1.75–1.78, and 0.87 ppm corresponding to protons of the aromatic,  $-\text{C}(=\text{O})\text{CH}_2-$ ,  $-\text{C}\equiv\text{C}-\text{CH}_2-$ ,  $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2-$ , and methyl groups, respectively. The aromatic protons at  $\text{H}_1$  appeared the most downfield (8.36–8.38 ppm) as a doublet. However, the aromatic protons at  $\text{H}_3$  and  $\text{H}_4$  [Fig. 1(b,d)] exhibited a higher field (7.01 and 6.89 ppm) than the other aromatic protons for N2 and C2, respectively, because of the existence of their adjacent electron-donating ( $-\text{OCH}_3$ ) terminal groups. The  $^{13}\text{C}$ -NMR spectrum [Fig. 2(a)] confirmed that four resonance peaks at 155.57, 153.86, 149.86, and 148.69 ppm resulted from quaternary carbons ( $\text{C}_b$ ,  $\text{C}_c$ ,  $\text{C}_d$ , and  $\text{C}_e$ ) of N1.

The  $-\text{C}=\text{O}-$ ,  $-\text{C}\equiv\text{C}-\text{CH}_2-$ ,  $-\text{C}\equiv\text{C}-\text{CH}_2-$ ,  $-\text{C}(=\text{O})\text{CH}_2-$ , and methyl carbons of N1 appeared at 171.72, 77.25–77.60, 65.21–65.35, 34.34, and 14.07 ppm, respectively. In addition, H–H COSY and C–H HMQC measurements were adapted to confirm the structure of N1. Figure 3 shows the H–H COSY spectrum of N1. The overlapping pairs of doublets, centered between 8.37 and 8.01 ppm and between 8.01 and 7.28 ppm, were assigned to protons 1–3 on the aromatic core of azobenzene. Accordingly, the triplet and multiple signals at 2.60 and 1.76 ppm were assigned to aliphatic protons 4 and 6 ( $\text{H}_4$  and  $\text{H}_6$ ), respectively. The aliphatic protons of the methyl group ( $\text{H}_7$ ) appeared upfield as a triplet at 0.87 ppm [Fig. 1(a)]. A full assignment of the resonances of the aromatic protons and carbons was assisted by the HMQC experiments (Fig. 4), and the HMQC spectrum was in good agreement with the proposed molecular structure of N1. Figure 4 shows connected pairs of doublets located at positions  $\text{H}_1/\text{C}_f$ ,  $\text{H}_2/\text{C}_g$ , and  $\text{H}_3/\text{C}_h$ . The remaining proton resonances in the C–H HMQC spectrum were well correlated with their corresponding  $^{13}\text{C}$  resonances. The molecular structures of the synthesized compounds were also supported by EA.

#### This shift resulted from conjugation between the aromatic rings and the lone pair on nitrogen atoms

We studied the E–Z isomerization and 1,4-addition of photochromic compounds to explore the

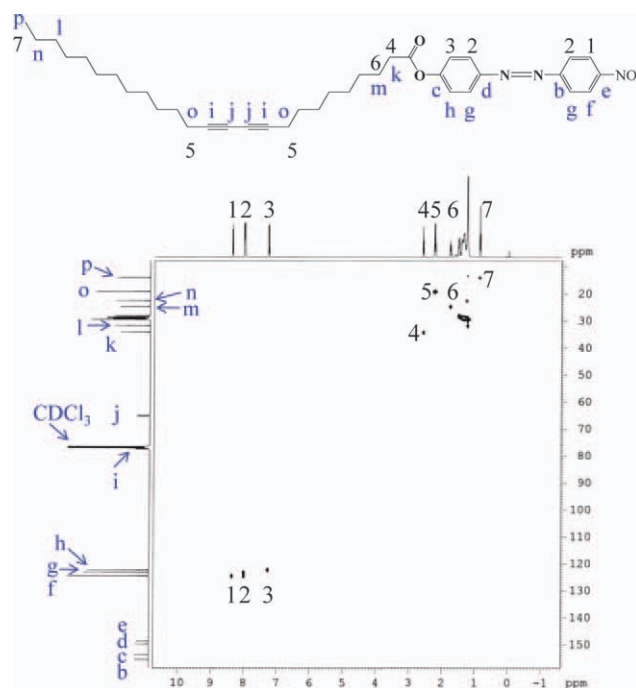


Figure 4 C–H HMQC spectrum of N1 in  $\text{CDCl}_3$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TABLE I  
UV-Vis Absorption of the Photochromic Compounds

Compound	UV-vis $\lambda_{\max}$ (nm) <sup>a</sup>	PL $\lambda_{\max}$ (nm) <sup>b</sup>	Isosbestic points (nm) <sup>c</sup>	$t_{365}$ (s) <sup>d</sup>	$t_{\text{dark}}$ (h) <sup>e</sup>	$t_{254}$ (min) <sup>f</sup>
N1	336	407	293, 400	$3.0 \times 10^2$	5	—
N2	347	409	301, 408	$3.0 \times 10^2$	60	—
C1	335	368, 405, 523	262, 436	$1.2 \times 10^2$	— <sup>g</sup>	15
C2	337	403	277, 355	90	— <sup>g</sup>	20

<sup>a</sup> Maximum wavelength of the  $\pi$ - $\pi^*$  transition of the compounds in  $\text{CHCl}_3$  solution; concentration =  $1 \times 10^{-5}$  M.

<sup>b</sup> The excitation wavelengths were the absorption maxima in the UV spectra.

<sup>c</sup> Time reached the photostationary state of UV irradiation (365 nm).

<sup>d</sup> Isosbestic points in absorption during UV irradiation (365 nm).

<sup>e</sup> Time to reach the photostationary state in the dark after UV irradiation of 365 nm.

<sup>f</sup> Time to reach the photostationary state of UV irradiation (254 nm).

<sup>g</sup> An absorption intensity change was not observed under darkness.

photoreactivity of these azobenzene- and stilbene-based photochromic compounds substituted with diacetylene groups. The optical properties were investigated with UV-vis and PL spectroscopy. E-Z photoisomerization of azobenzene and stilbene

derivatives was recorded by UV absorption spectroscopy in  $\text{CHCl}_3$  with irradiation at 365 nm.<sup>22,24,25</sup> In addition, 254-nm UV light was used to investigate the Z-to-E photoisomerization of the stilbene-based compounds.<sup>26,27</sup> Table I summarizes the data of

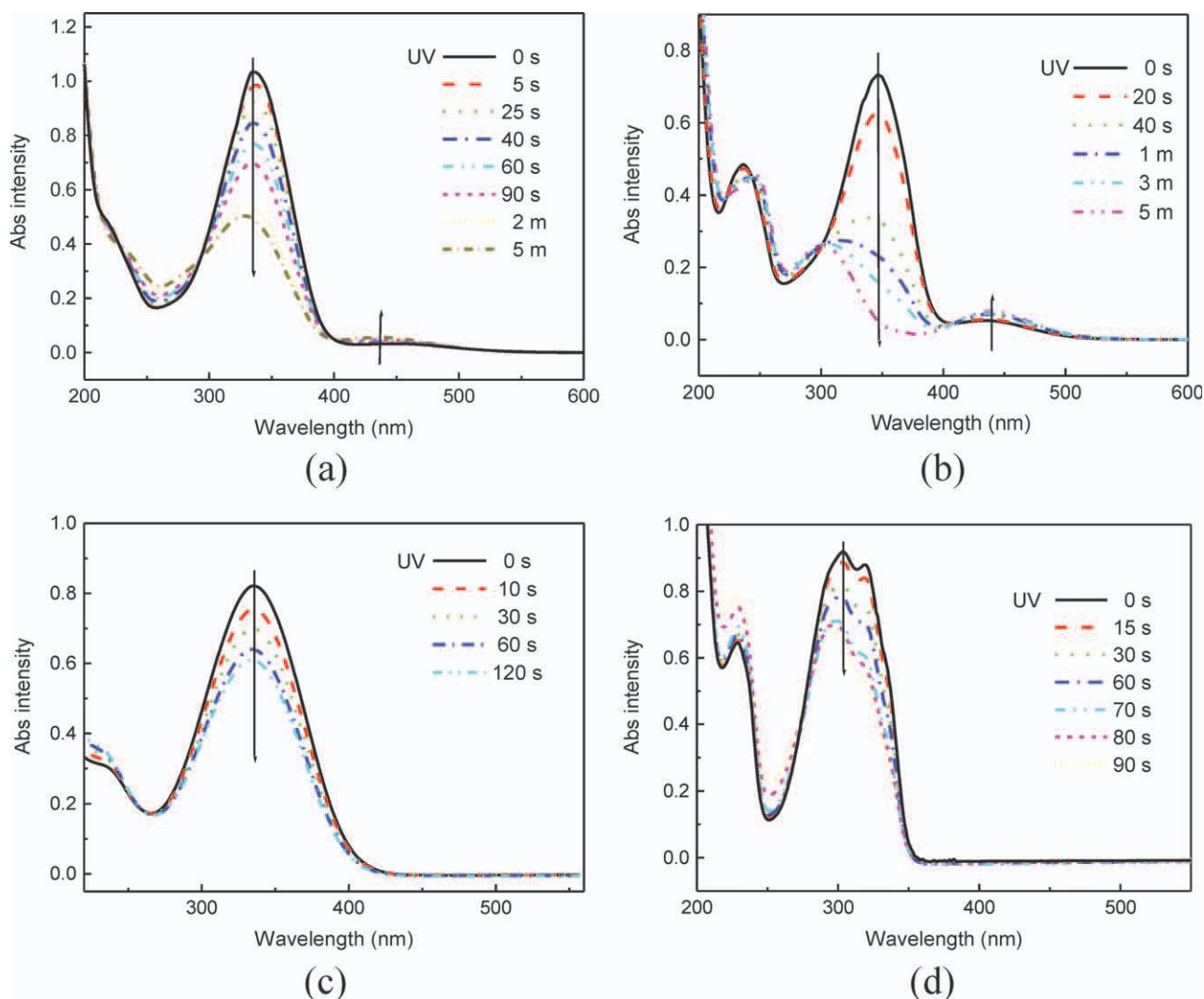
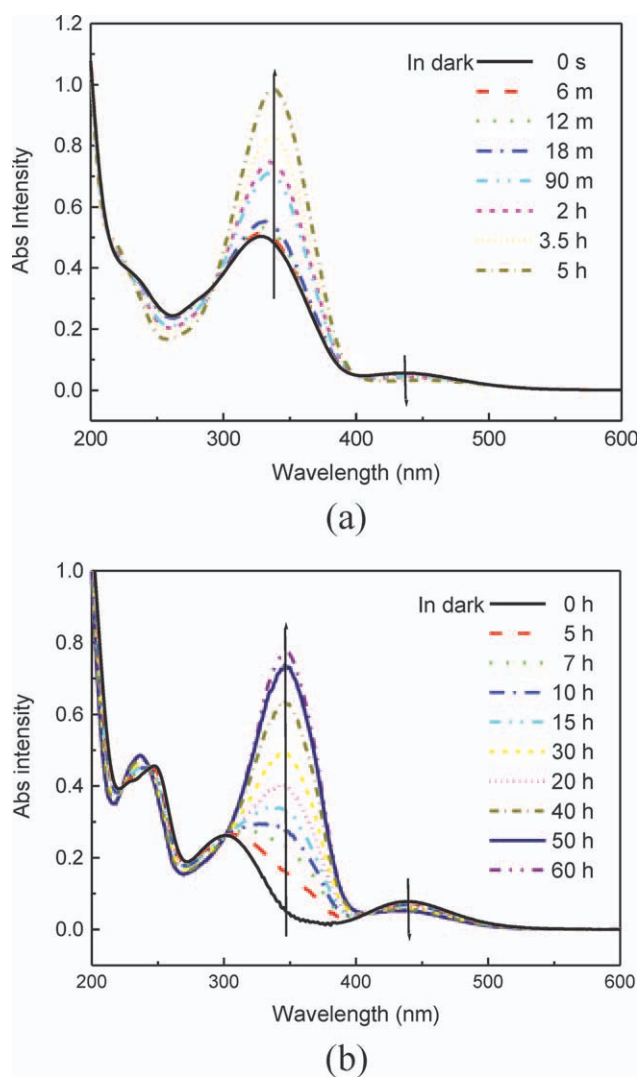


Figure 5 UV-vis spectra before and after UV irradiation with 365 nm for (a) N1, (b) N2, (c) C1, and (d) C2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

absorption and the isosbestic points of the photochromic compounds during UV irradiation. These compounds exhibited strong UV-vis absorption bands at 335–347 nm, which were attributed to a  $\pi$ - $\pi^*$  transition of the E isomer of the chromophores. Weak absorption bands around 435–440 nm resulted from an  $n$ - $\pi^*$  transition of the E isomer for compounds **N1** and **N2**, which each contained azobenzene groups. The absorption maximum of **N1**, incorporating the electron-withdrawing nitro group ( $-\text{NO}_2$ ), was located at 336 nm, slightly blueshifted (ca. 11 nm) relative to compound **N2**, which incorporated the electron-donating methoxy group ( $-\text{OCH}_3$ ). This shift resulted from conjugation between the aromatic rings and the lone pair on nitrogen atoms. The E isomer is generally more stable than the Z isomer is, but each isomer is interconvertible under exposure to UV light of the appropriate wavelength. Figures 5(a) and 6(a) show the variation with irradiation time in the UV-vis spectra of **N1** under 365-nm irradiation. The figures also illustrate the stability of compound **N1** in darkness. UV irradiation induced a decrease in the absorption intensity around 336 nm and an increase at about 435 nm during irradiation. As shown in Figure 5(a), an E-Z photostationary state was obtained within 5 min of irradiation. Isosbestic points of **N1** were observed at 293 and 400 nm, which corresponded to E-Z photoisomerization. Additionally, the  $\pi$ - $\pi^*$  transition shifted to a shorter wavelength, and the  $n$ - $\pi^*$  absorption intensity increased. The observed variation of the absorptions might have been ascribed to the geometric change from the E isomer to the Z isomer of the azo compounds. Thermal stability for the Z-E isomerization of **N1** in darkness was achieved in 5 h, as shown in Figure 6(a). These results suggest that the geometric Z form might have gradually converted back to the E form, even in the absence of UV irradiation. As seen from Table I and Figure 6(b), a steady state for Z-E isomerization was achieved in 60 h for compound **N2**; this implied that **N1**, which incorporated the electron-withdrawing nitro group ( $-\text{NO}_2$ ), used a rotation mechanism with a low potential energy profile to achieve a faster rate of Z-E isomerization in darkness than **N2** did.<sup>20</sup> Furthermore, the stilbene-containing compounds (**C1** and **C2**) illustrated different photoisomerization mechanisms. Figure 5(c,d) shows the UV-vis spectral dependence of the two stilbene-containing compounds at 365-nm irradiation for various irradiation times. **C1** and **C2** exhibited an absorption maximum around 335–337 nm, which resulted from  $\pi$ - $\pi^*$  transitions within the E isomer. UV irradiation caused a decrease in the absorption intensity around 335–337 nm. Accordingly, under darkness, the absorption intensities of the stilbene-based compounds (**C1** and **C2**) did not return to their initial

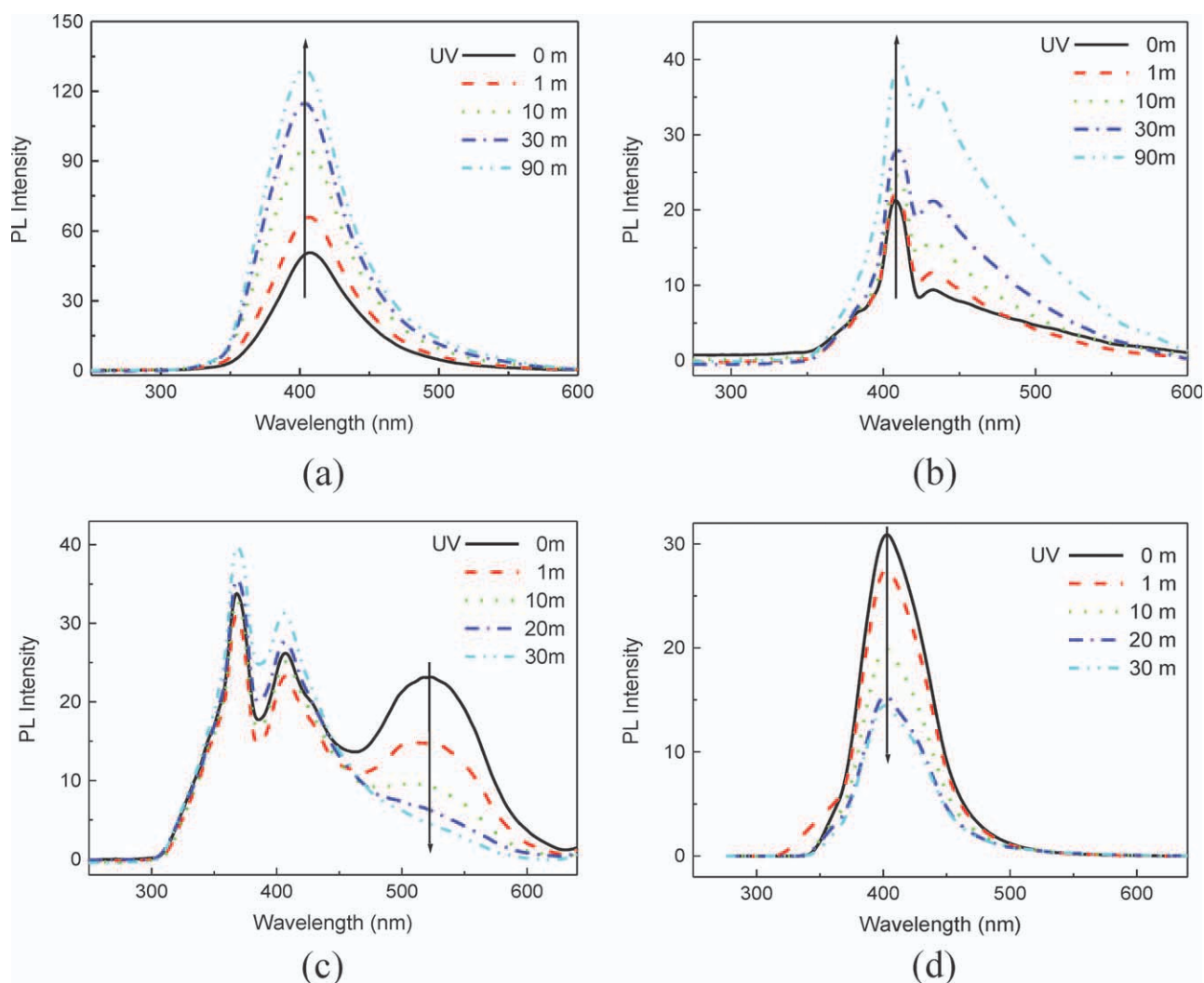


**Figure 6** Stability of UV-vis spectra of (a) **N1** and (b) **N2** in the dark. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

intensities because of the higher potential energy of the Z isomer. After irradiation at 254 nm, the  $\pi$ - $\pi^*$  band absorption intensities recovered to their initial levels in 15 and 20 min for **C1** and **C2**, respectively. Taking into account the previous discussion, we may be able to control the photoisomerization of photochromic compounds by the selection of an appropriate wavelength of irradiating light.

As shown in Table I and Figure 7, the fluorescence spectra of the photochromic compounds in  $\text{CHCl}_3$  at ambient temperatures exhibited emission maxima around 403–409 nm. However, the fluorescence spectral maxima of **C1** were located at 368, 405, and 523 nm; these might have been due to the electronic states from different vibrational-rotational levels of excited states to ground the electronic state. Figure 7 shows the dependence of the fluorescence spectra of the azobenzene- and stilbene-based chromophores in





**Figure 7** Dependence of 365 nm exposure on PL spectra of (a) N1, (b) N2, (c) C1, and (d) C2 in chloroform with various irradiation times. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

dilute solutions with 365-nm irradiation for various irradiation times. UV irradiation induced a gradual decrease in the fluorescence intensity for the stilbene-containing compounds (C1 and C2) with increasing UV irradiation time. These results indicate that the Z isomer of the chromophores caused lower fluorescence intensities and quantum yields because of the presence of nonplanar molecular structures, as compared with the planar rod-shaped E form. By contrast, when N1 and N2 solutions were excited at their absorption maxima, we observed weak fluorescence around 407–409 nm. However, after continuous UV irradiation for 90 min, the fluorescence intensities gradually increased, as shown in Figure 7(a,b). The data shown in Figure 7(a,b) indicate that the self-assembled Z isomers of azobenzenes experienced fluorescence enhancement upon UV irradiation.<sup>28–30</sup> This also implied that other reactions, such as photoreaction

or aggregation, could have occurred together with E–Z photoisomerization. NMR spectra confirmed that no decomposition of the aromatic rings of azobenzenes or diacetylene groups occurred upon exposure to UV light. The results are, thus, consistent with the dramatic changes seen in the fluorescence intensity; this suggested that the fluorescence enhancement seen during UV light exposure originated from the formation of aggregates.<sup>31–33</sup> Han et al.<sup>30</sup> demonstrated that the Z isomer of azobenzene was more hydrophilic than the E isomer, whereas the long alkyl chain was hydrophobic. Such a Z isomer of azobenzene with a longer alkyl chain might function as an amphiphilic molecule and assemble into aggregates upon UV irradiation.

To understand the photoresponsive behaviors of the diacetylene monomer with azobenzene or stilbene segments during 1,4-addition, we prepared polydiacetylene films with 254-nm irradiation. The

**TABLE II**  
Optical Properties of the Photochromic Compounds

Compound	$\lambda_{\max}$ (nm) <sup>a</sup>	$l$ (nm) <sup>b</sup>	$d$ (nm) <sup>c</sup>	Tilt angle (°) <sup>d</sup>
N1	628	4.18	6.03	43.8
N2	641	4.25	6.10	44.1
C1	623	4.20	6.02 <sup>m</sup> , 4.28, 3.13, 2.10	44.2
C2	653	4.27	6.06	44.8

<sup>a</sup> Maximum wavelength of the  $\pi$ - $\pi^*$  transition of the compounds after 254 nm of irradiation (1,4-addition).

<sup>b</sup> Molecular length of the compounds in the all-trans model of the most extended conformation with CS Chem3DPro, with MM2 energy parameters.

<sup>c</sup>  $d$ -Spacing value after 1,4-addition polymerization. The superscript  $m$  indicates the main  $d$ -spacing value in the XRD measurements.

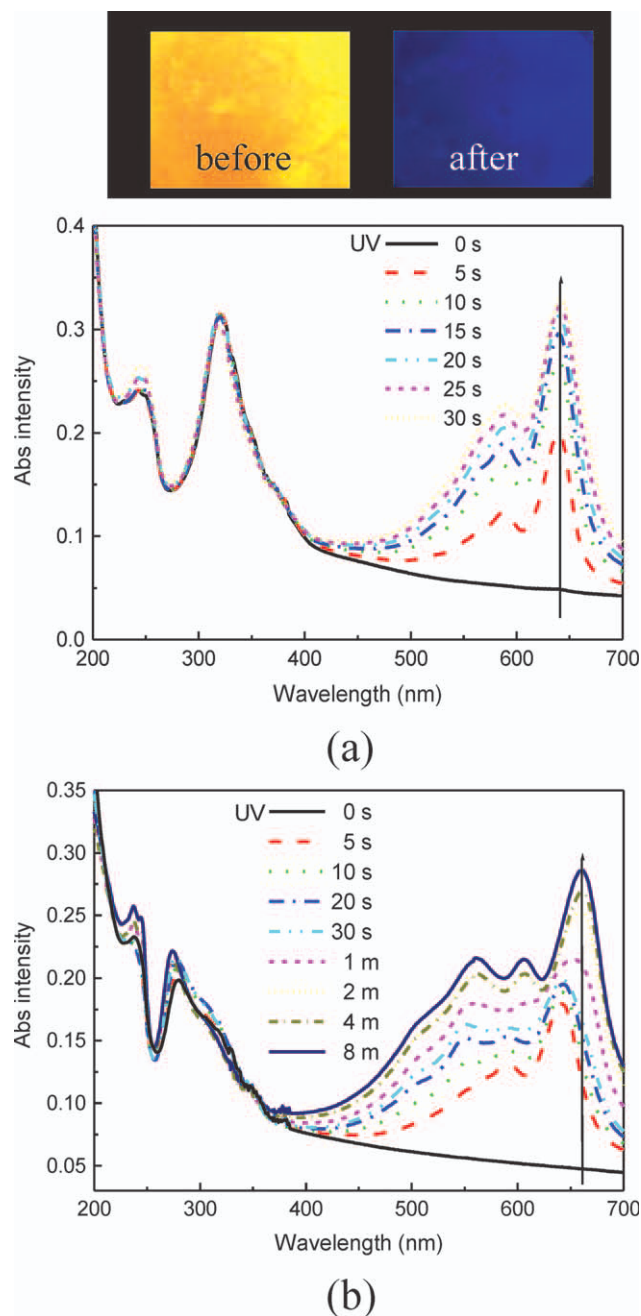
<sup>d</sup> Tilt angle of the polydiacetylene films relative to the translation axis.

optical properties of polydiacetylene films are summarized in Table II. The diacetylene films derived from our synthesized compounds predominantly polymerized into blue phases associated with a maximum absorption wavelength around 640–660 nm, as shown in Figure 8. The photostationary state for N2 during 1,4-addition was achieved in 30 s. We confirmed the occurrence of 1,4-addition for N2 by <sup>13</sup>C-NMR spectroscopy by monitoring the decrease in the chemical shift integrals at 65.35 and 77.60 ppm, points that corresponded to the diacetylene sp-hybridized carbon atoms. Other important evidence for 1,4-addition was the fact that the intense absorption band between 480 and 700 nm did not recover to its initial absorption level, even under UV irradiation. Real images of the N2 polydiacetylene film, recorded before and after UV irradiation, are shown in Figure 8(a). However, the photostationary state during 1,4-addition for C2 was stable for nearly 8 min, as shown in Figure 8(b), probably because of the greater chemical bonding energy during 1,4-addition. This also implied that the distinctive polymerization behavior was associated with the difference in molecular structure and intermolecular interactions between the two different side chains.

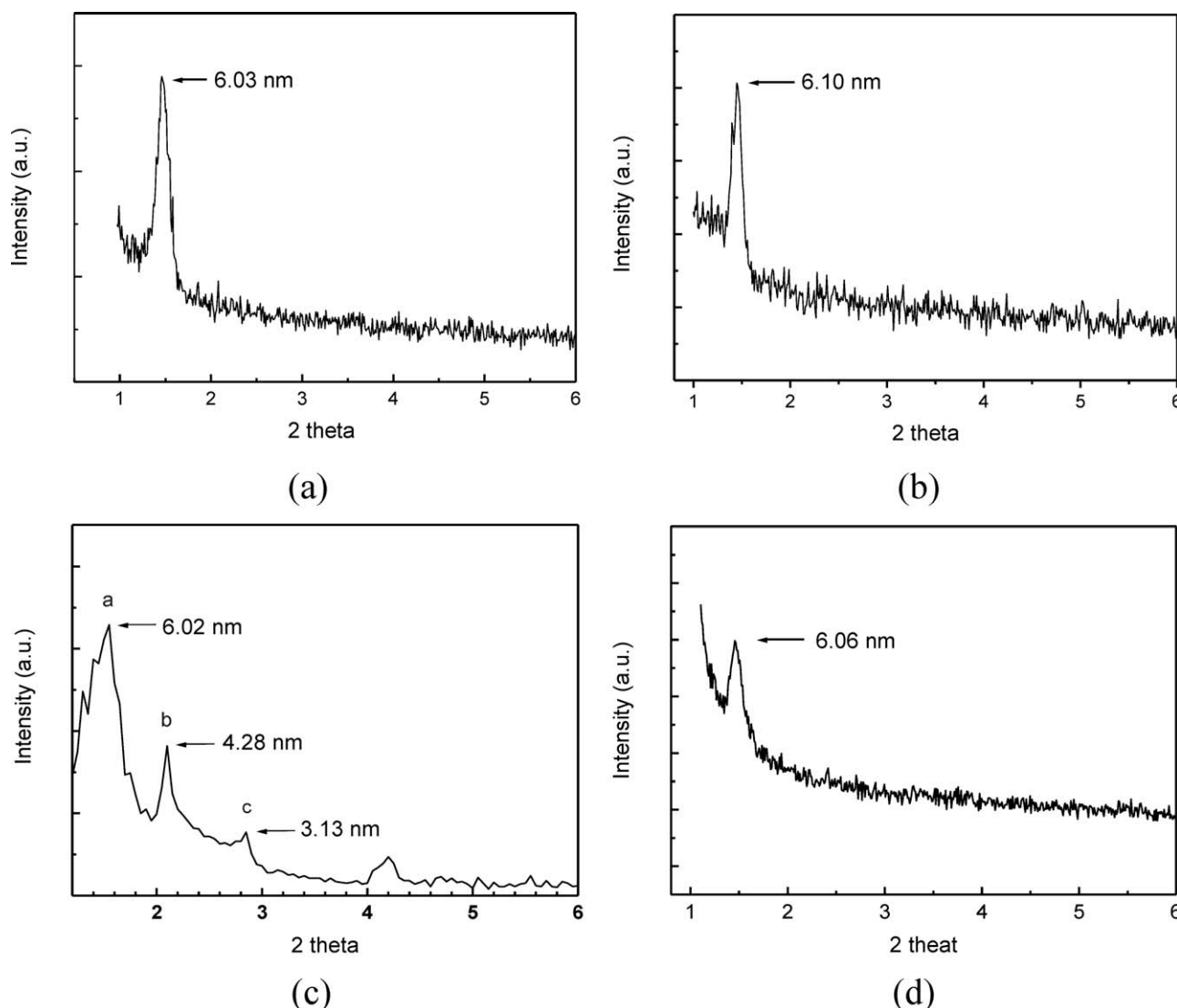
### XRD of the polydiacetylene films

To obtain information on the molecular packing after 1,4-addition, we made XRD measurements of the polydiacetylene films. Figure 9 shows the XRD curves for four polydiacetylene films after UV irradiation. These X-ray patterns showed the presence of a sharp and strong peak at a small-angle region at  $2\theta = 1.44$ – $1.47^\circ$ ; this corresponded to a layer  $d$ -spacing value of 60.2–61.0 Å. According to molecular modeling calculations (CS Chem3DPro, Cambridge, MA

with molecular mechanics (MM2) energy parameters), the estimated all-trans molecular lengths ( $l$ 's), of the most extended conformation of the diacetylene monomers, were around 41.8, 42.5, 42.0, and 42.7 Å for N1, N2, C1, and C2, respectively. The orientation of the diacetylene moiety following 1,4-addition was estimated with these results. The calculated tilt angles of the diacetylene moieties upon polymerization are



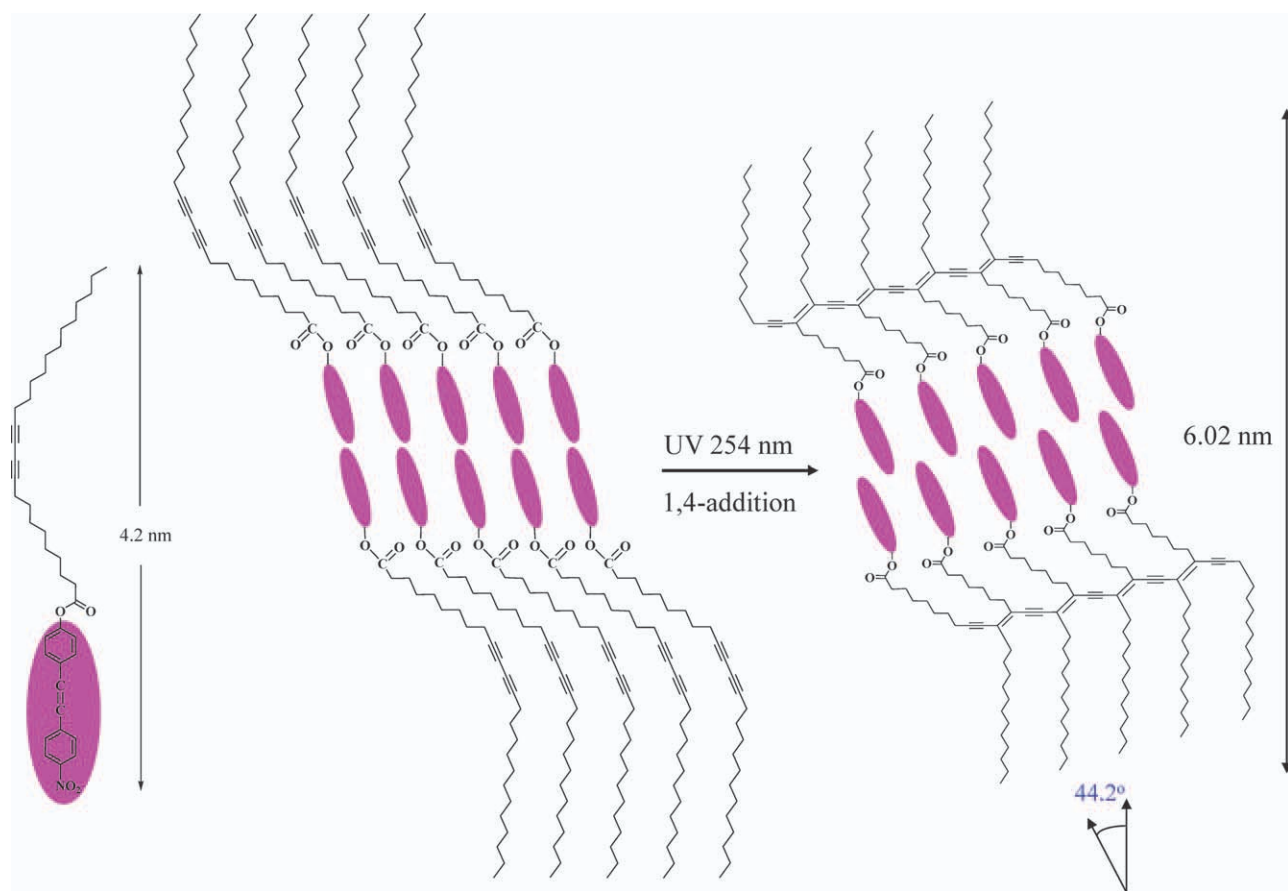
**Figure 8** Variation of the UV-vis spectra of (a) N2 and (b) C2 thin film with various irradiation times during 254 nm irradiation. Inset: Real color image of N2 film recorded after 1,4-addition polymerization; size: 2 × 2.5 cm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9** Small-angle XRD pattern of (a) N1, (b) N2, (c) C1, and (d) C2 film after UV irradiation.

summarized in Table II. The diacetylene function tilt angle, relative to the translation axis, was about  $43.8\text{--}44.2^\circ$ . The data of the tilt angle for the blue phases between the diacetylene groups and the axis connecting the centers of the adjacent diacetylene moieties was appropriately  $45^\circ$  during polymerization, which was consistent with literature values.<sup>16,17</sup> XRD data indicated that a major layer structure was bilayered side-chain packing. All of the diacetylene films exhibited similar bilayer side-chain packing. We visualized the central region of the bilayered side-chain packing as being composed of azobenzene moieties through their strong  $\pi\text{-}\pi$  stacking interaction and the outer regions of the bilayered packing containing the alkyl side chains. The assembly of the azobenzene moieties into a rigid core by  $\pi\text{-}\pi$  stacking was a prerequisite for the formation of the layered architecture, which was required for the topochemical 1,4-addition po-

lymerization of diacetylene units. Moreover, Figure 9(c) shows other peaks around  $2\theta = 2.06, 2.82,$  and  $4.21^\circ$ , assignable to the layer  $d$ -spacing values of 42.8, 31.3, and 21.0 Å, respectively. This indicated that the peaks at 2.06, 2.82, and  $4.21^\circ$  were due to the diacetylene crystals contained as a disordered structure, which had a different crystal packing from that of the main part of the bilayer packing. A schematic representation of the proposed major bilayer packing scheme for the supramolecular organization of the C1 film is shown in Figure 10. It was reported previously<sup>34</sup> that polar electron-withdrawing ( $-\text{NO}_2$  or  $-\text{CN}$ ) groups tend to induce the formation of a more ordered antiparallel or interdigitated packing because of strong dipole-dipole interactions between the terminal groups. We found that the structural effect of terminal groups on the molecular packing of diacetylene films upon 1,4-addition polymerization was of



**Figure 10** Schematic representation of the proposed bilayered packing for the resultant supramolecular assemblies of C1 film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

minor importance for extended orientations because of the long alkyl side chains. The molecular packing might have also contributed to stabilization through van der Waals interactions. Johal et al.<sup>35</sup> reported that quantum chemical simulations suggested that the molecular packing of films has a complex relationship between molecular dipole moments,  $\pi$ - $\pi$  interactions, and internal dipole moments of terminal groups.

Taking into account our spectroscopic results, one could control the isomerization of various photochromic groups by altering the wavelength of the irradiating light. Accordingly, while selecting the wavelength, one might cause selected photochemical reactions (e.g., 1,4-addition or isomerization), either of diacetylene ( $C\equiv C-C\equiv C$ ) or stilbene ( $C=C$ )/azobenzene ( $N=N$ ) photochromic groups, to occur. The characteristic properties of such photochromic compounds possess great potential to advance the research of polymer matrices. A detailed investigation of the temperature dependence of the diacetylene films under UV irradiation and scanning electron microscopy morphologies of self-assembled chromophore Z isomers is now in progress.

## CONCLUSIONS

We successfully synthesized and characterized four photochromic diacetylene compounds containing azobenzene- or stilbene-substituted groups. The optical properties of the photochromic compounds comprising either  $N=N$  or  $C=C$  bonds were evaluated with UV-vis spectroscopy. The 1,4-addition polymerization of diacetylene bonds of the newly photochromic compounds were also investigated. The molecular packing of the azobenzene- or stilbene-substituted polydiacetylene films were characterized by small-angle XRD. We demonstrated that polydiacetylene films containing two different photoisomerizable groups sensitive to discrete light wavelengths are of value in the study of photochromic processes in polymer materials with dual photochromism.

## References

- Häckel, M.; Kador, L.; Kropp, D.; Frenz, C.; Schmidt, H. W. *Adv Funct Mater* 2005, 15, 1722.
- Breiner, T.; Kreger, K.; Hagen, R.; Häckel, M.; Kador, L.; Müller, A. H. E.; Kramer, E. J.; Schmidt, H. W. *Macromolecules* 2007, 40, 2100.
- Häckel, M.; Kador, L.; Kropp, D.; Schmidt, H. W. *Adv Mater* 2007, 19, 227.

4. Natansohn, A.; Rochon, P. *Chem Rev* 2002, 102, 4139.
5. You, F. X.; Paik, M. Y.; Häckel, M.; Kador, L.; Kropp, D.; Schmidt, H. W.; Ober, C. K. *Adv Funct Mater* 2006, 16, 1577.
6. Gao, J.; He, Y.; Xu, H.; Song, B.; Zhang, X.; Wang, Z.; Wang, X. G. *Chem Mater* 2007, 19, 14.
7. Wu, Y.; Mamiya, J.; Shiono, T.; Ikeda, T.; Zhang, Q. *Macromolecules* 1999, 32, 8829.
8. Chang-Chien, G. P. *J Polym Sci Part A: Polym Chem* 1998, 36, 2849.
9. Hogan, P. M.; Tajbakhsh, A. R.; Terentjev, E. M. *Phys Rev E* 2002, 65, 041720.
10. Yu, Y.; Nakato, M.; Ikeda, T. *Nature* 2003, 425, 145.
11. Li, M. H.; Keller, P.; Li, B.; Wang, X. G.; Brunet, M. *Adv Mater* 2003, 15, 569.
12. Tamai, N.; Miyasaka, H. *Chem Rev* 2000, 100, 1875.
13. Ma, G.; Müller, A. M.; Bardeen, C. J.; Cheng, Q. *Adv Mater* 2006, 18, 55.
14. Rangin, M.; Basu, A. *J Am Chem Soc* 2004, 126, 5038.
15. Kuriyama, K.; Kikuchi, H.; Kajiyama, T. *Langmuir* 1998, 14, 1130.
16. Sarkar, A.; Okada, S.; Matsuzawa, H.; Matsuda, H.; Nakanishi, H. *J Mater Chem* 2000, 10, 819.
17. Lim, C.; Sandman, D. J.; Sukwattanasinitt, M. *Macromolecules* 2008, 41, 675.
18. Peng, H.; Tang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. *J Am Chem Soc* 2005, 127, 12782.
19. Yang, P. C.; Wu, M. Z.; Liu, J. H. *Polymer* 2008, 49, 2845.
20. Ho, C. H.; Yang, K. N.; Lee, S. N. *J Polym Sci Part A: Polym Chem* 2001, 39, 2296.
21. Liu, J. H.; Yang, P. C. *J Appl Polym Sci* 2004, 91, 3693.
22. Liu, J. H.; Wu, F. T. *J Appl Polym Sci* 2005, 97, 721.
23. Lee, C. C.; Yeh, K. M.; Chen, Y. *Polymer* 2009, 50, 410.
24. Liu, J. H.; Hsieh, C. D. *J Appl Polym Sci* 2006, 99, 2443.
25. Lub, J.; Ferrer, A.; Larossa, C.; Malo, B. *Liq Cryst* 2003, 30, 1207.
26. Ogasawara, S.; Saito, I.; Maeda, M. *Tetrahedron Lett* 2008, 49, 2479.
27. Giménez, R.; Piñol, M.; Serrano, J. L.; Viñuales, A. I.; Rosenhauser, R.; Stumpe, J. *Polymer* 2006, 47, 5707.
28. Deans, R.; Kim, J.; Machacek, M. R.; Swager, T. M. *J Am Chem Soc* 2000, 122, 8565.
29. Han, M.; Hara, M. *J Am Chem Soc* 2005, 127, 10951.
30. Han, M. R.; Hirayama, Y.; Hara, M. *Chem Mater* 2006, 18, 2784.
31. An, B. K.; Kwon, S. K.; Jung, S. D.; Park, S. Y. *J Am Chem Soc* 2002, 124, 14410.
32. Zebger, I.; Rutloh, M.; Hoffmann, H.; Stumpe, J.; Siesler, H. W.; Hvilsted, S. *J Polym Sci Part A: Polym Chem* 2002, 106, 3454.
33. Lim, S. J.; An, B. K.; Jung, S. D.; Chung, M. A.; Park, S. Y. *Angew Chem Int Ed* 2004, 43, 6346.
34. Schleek, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. *J Polym Sci Part A: Polym Chem* 1993, 31, 1859.
35. Tang, Z.; Johal, M. S.; Scudder, P.; Caculitan, N.; Magyar, R. J.; Tretiak, S.; Wang, H. L. *Thin Solid Films* 2007, 516, 58.