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The effects of phenyl-bridged glucosyltriazolyl groups on the properties of water-soluble diarylethene derivatives

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ABSTRACT

Three water-soluble diarylethenes with glycosyltriazolyl groups and variable phenyl units have been synthesized, and their properties, such as water solubility, photochromism, and fluorescence have been discussed. Upon alternating irradiation with UV and visible light, each of the diarylethenes exhibited favorable photochromism and functioned as fluorescent switches in water. Experimental results showed that their water solubility as well as absorption features, cyclization quantum yields, photoconversion ratios, thermal stability, and fatigue resistance exhibited a strong correlation with the number of phenyl-bridged glucosyltriazolyl groups in diarylethene systems. The absorption maximum, thermal stability, and fatigue resistance were significantly improved, but the water solubility and fluorescent modulation efficiency were suppressed with the increase of the number of phenyl-bridged glucosyltriazolyl groups for these diarylethene derivatives.

1. Introduction

Organic photochromic molecules have gained much attention for potential applications in optical memories and photoswitches.[1–3] In recent decades, considerable attention has been focusing on photochromic diarylethenes due to high conversion efficiency of reversible photochromic reactivity, excellent thermal stability of both isomers, and remarkable fatigue resistance.[4–7] On one hand, diarylethenes have shown great promise as new materials for optoelectronic devices and molecular switches.[8–12] On the other hand, their biological applications have not yet been extensively explored, although a few precedent works have been reported.[13] For biological applications, it is necessary for diarylethenes to undergo photocyclization and cycloreversion reactions in aqueous solution. Solubility in water is a very important property to be applied in biological fields, such as biosensors or drug deliveries. However, most of the reported works are carried out in organic systems, including the newly developed fluorescent photochromic diarylethenes for labeling biomolecules.[14] During the past decade, much effort has been focusing on designing and synthesizing water-soluble diarylethenes, since they have potential applications in biological field.

So far, several amphiphilic photochromic diarylethenes exhibited favorable photochromism upon irradiation with UV and visible light in aqueous solution.[10a,15] For example, Yi and co-workers prepared a new amphiphilic diarylethene, which exhibited switchable fluorescence and formed stable vesicle nanostructures in aqueous solution.[15a] Irie and co-workers synthesized diarylethene derivatives with hexaethylene glycol side chains and investigated their self-assembling photochromic behavior in organic solvents and water.[10a,15b,c] But their solubility in water was relatively small and the aqueous solutions easily turned turbid upon heating. Irie and co-workers also developed a simple non-covalent approach to improve the water solubility of the perfluorinated diarylethenes.[15e] The water-insoluble diarylethenes could be encapsulated into a water-soluble nanocavitand to induce photochromic performance in aqueous solution. However, this method is not easy to achieve due to its difficulty in selecting a perfect cavitand for each diarylethene molecule. In order to capsulate hydrophobic diarylethenes into a cavitand, the entrance diameter and volume of cavitand should be very large. Belov and co-workers reported a water-soluble photochromic diarylethene, but the synthetic method was very complex and the total yield was only about 3%.[15f] As mentioned above, it is strongly desired to develop simple methods to explore new photochromic systems with good water solubility.

In a previous work, we have reported that a diarylethene with two glucosyltriazolyl groups exhibited favorable photochromism in both water and a PMMA solid film.[16] The result inspired us to do a consecutive research in this work. We have a strong desire to understand what the relationship is between the molecular structures and the water solubility of diarylethenes with

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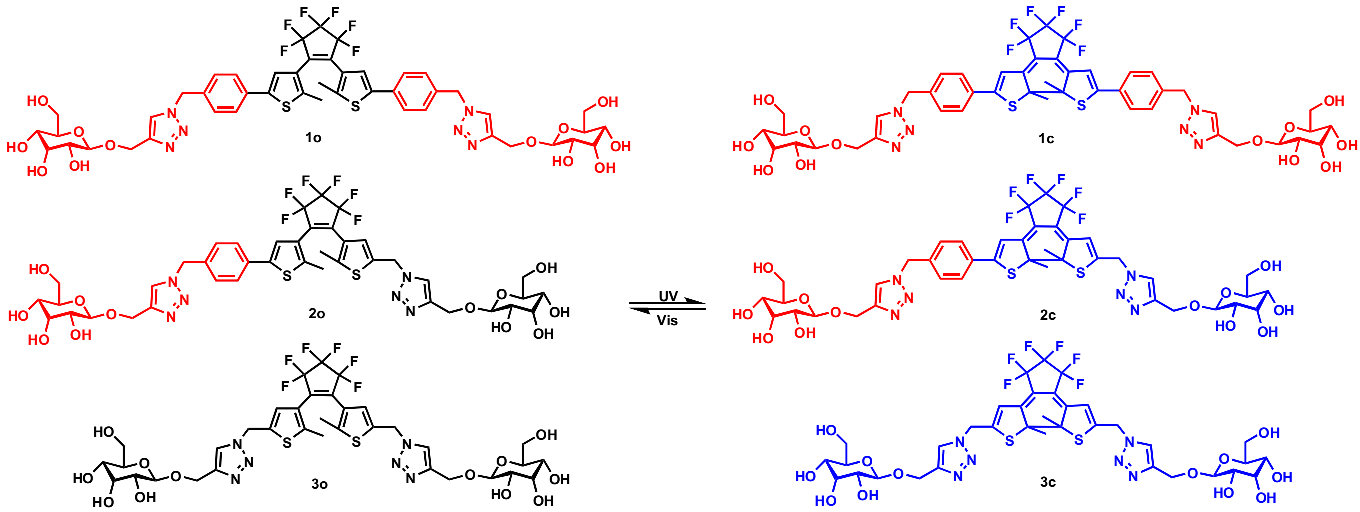
glucosyltriazolyl groups. Therefore, three diarylethenes (**1o**–**3o**) with glucosyltriazolyl groups were synthesized to investigate the effects of phenyl-bridged glucosyltriazolyl groups on the properties of these diarylethene derivatives. All of these diarylethene derivatives showed favorable photochromism in both aqueous solution and PMMA amorphous films. The photochromic reactions of **1o**–**3o** are shown in Scheme 1.



Scheme 1. Photochromism of **1**–**3**.

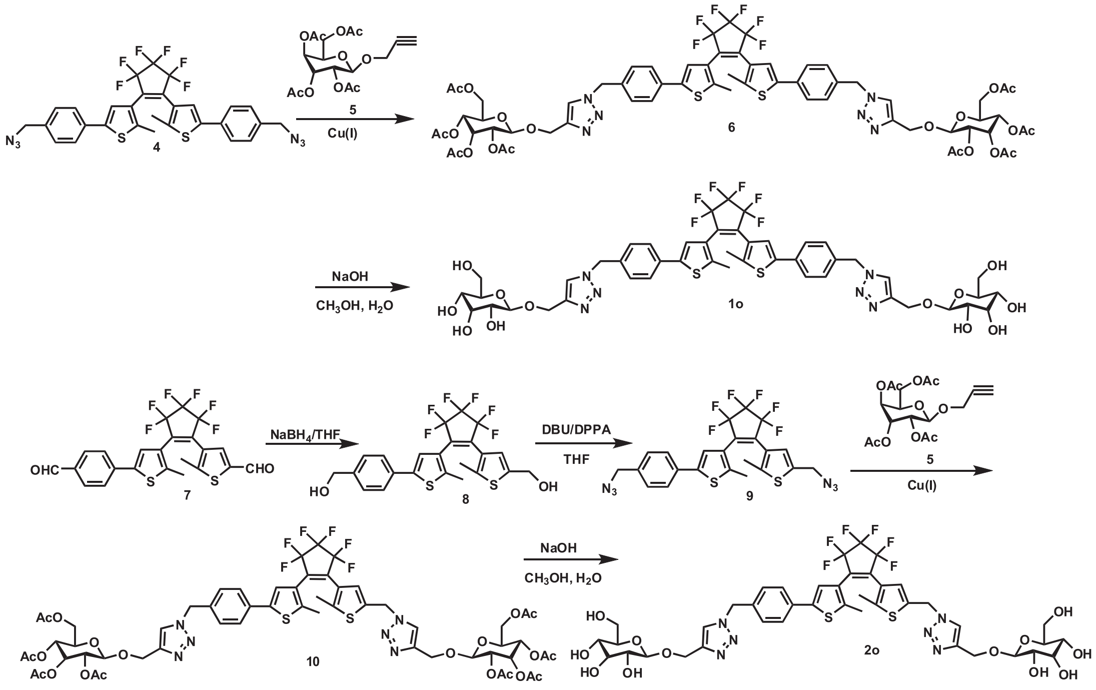
2. Experimental

2.1. General

Melting points were taken on a WRS-1B melting point apparatus. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ and tetramethylsilane as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Elemental analysis was measured with an elemental analyzer labeled the PE CHN 2400 analyzer. Fluorescent spectra were measured using a Hitachi F-4500 fluorimeter. Absorption spectra were measured using an Agilent 8453 UV/vis spectrophotometer. Photoirradiation was carried out using an SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 Visible lamp. The required wavelength was isolated by the use of the appropriate filters. The quantum yields of cyclization/cycloreversion were determined by comparing the reaction yield of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane.[17] Dissolved ultrasonically 10 mg of diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the film was prepared by spin-coating on the surface of quartz substrate.

2.2. Synthesis

Diarylethene **3o** was synthesized by the reported method.[16] The synthesis route for diarylethenes **1o** and **2o** is shown in Scheme 2.



Scheme 2. Synthetic route for **1o** and **2o**.

*2.2.1. 1,2-Bis{2-methyl-5-{4-[5-(2,3,4,6-tetraacetyl-β-D-glycoside)-3-(1,2,3-triazole)]methyl}phenyl-3-thienyl}perfluorocyclopentene (**6**).* To a stirred THF (90 mL) of compound **4** (0.70 g, 1.3 mmol) and 2-propynyl-2,3,4,6-tetraacetyl-β-D-glucoside (**5**)[16] (1.10 g, 2.6 mmol) was added 10.0 mL water containing NaVc (0.03 g, 0.2 mmol) and $CuSO_4$ (0.01 g, 0.1 mmol) at room temperature. The reaction mixture was stirred for 12 h at room temperature and then extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered and evaporated. Column chromatography on SiO_2 with petroleum ether/ethyl acetate (1 : 5) as the eluent afforded 1.13 g of **6** as a light blue solid in 62% yield. Mp 367–368 K; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.90 (s, 6H), 1.95 (s, 6H), 1.99 (s, 6H), 2.02 (s, 6H), 2.07 (s, 6H), 3.72 (m, 2H), 4.13 (d, 2H, J=12.8 Hz), 4.23 (d, 1H, J=4.8 Hz), 4.26 (d, 1H, J=3.2 Hz), 4.66 (d, 2H, J=7.6 Hz), 4.81 (d, 2H, J=12.4 Hz), 4.91 (d, 2H, J=12.8 Hz), 4.98 (t, 2H, J=8.8 Hz), 5.08 (t, 2H, J=9.6 Hz), 5.19 (t, 2H, J=9.2 Hz), 5.53 (s, 4H), 7.30 (d, 6H, J=9.2 Hz), 7.48 (s, 2H), 7.54 (d, 4H, J=8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 14.49, 20.52, 20.67, 53.75, 61.82, 63.02, 68.35, 71.24, 71.93, 72.76, 99.96, 122.60, 122.98, 125.94, 126.23, 127.54, 128.41, 128.80, 133.89, 134.07, 141.17, 141.82, 144.77, 169.27, 169.36, 170.12, 170.55.

*2.2.2. 1,2-Bis{2-methyl-5-{4-[5-(2,3,4,6-tetrahydroxyl-β-D-glycoside)-3-(1,2,3-triazole)]methyl}phenyl-3-thienyl}perfluorocyclopentene (**1o**).* To a stirred methanol solution (90.0 mL) containing compound **6** (0.80 g, 0.6 mmol) was added 10.0 mL aqueous solution containing sodium hydroxide (0.24 g, 6.0 mmol) at room temperature. The reaction mixture was stirred for 24 h at room temperature and then evaporated. Column chromatography on SiO_2 with methanol as the eluent afforded 0.59 g of **1o** as a blue solid in 93% yield. Mp 361–362 K; Anal. Calcd for $C_{47}H_{48}F_6N_6O_{12}S_2$ (%): C, 52.90; H, 4.53; N, 7.88, found: C, 52.98; H, 4.57; N, 7.91; ^1H NMR ($(CD_3)_2SO$, 400 MHz), δ (ppm): 1.96 (s, 6H), 2.97 (t, 2H, J=8.4 Hz), 3.06 (d, 2H, J=8.8 Hz), 3.14 (m, 4H), 3.47 (m, 2H), 3.70 (d, 2H, J=11.6 Hz), 4.26 (d, 2H, J=7.6 Hz), 4.62 (d, 2H, J=12.4 Hz), 4.85 (d, 2H, J=12.0 Hz), 5.61 (s, 4H), 7.38 (d, 4H, J=8.0 Hz), 7.50 (s, 2H), 7.64 (d, 4H, J=8.0 Hz), 8.20 (s, 2H); ^{13}C NMR ($(CD_3)_2SO$, 100 MHz), δ (ppm): 14.44, 52.84, 61.63, 62.03, 70.60, 73.85, 77.16, 77.48, 102.75, 123.32, 124.76, 125.44, 126.12, 129.38, 132.80, 136.31, 141.57, 141.93, 144.73; IR (KBr, ν, cm^{-1}): 661, 744, 792, 897, 989, 1020, 1053, 1079, 1112, 1194, 1229, 1273, 1339, 1415, 1567, 3428; MS calcd for $C_{47}H_{48}F_6N_6O_{12}S_2Na^+$ $[M+Na]^+$: 1089.2, found 1089.2.

*2.2.3. 1-(2-Methyl-5-hydroxymethyl-3-thienyl)-2-[2-methyl-5-(4-hydroxymethyl)phenyl-3-thienyl]perfluorocyclopentene (**8**).* To a stirred THF of compound **7** (1.00 g, 2.0 mmol) and sodium borohydride (0.15 g, 4.0 mmol) was refluxed for 2 h. After stopping the reaction, the mixture was washed sequentially by aqueous $NaHCO_3$. The product was extracted with ether, dried with $MgSO_4$, filtrated, and evaporated in vacuo. Column chromatography on SiO_2 with petroleum ether/ethyl acetate (1 : 1) as the eluent afforded 0.91 g of **8** as a silver gray solid in 90% yield. Mp 408–409 K; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.91 (s, 3H, $-CH_3$), 1.92 (s, 3H, $-CH_3$), 4.72 (d, 2H, J=4.8 Hz, $-CH_2-$), 4.78 (d, 2H, J=5.6 Hz, $-CH_2-$), 6.99 (s, 1H, thiophene-H), 7.39 (d, 2H, J=8.0 Hz, benzene-H), 7.54 (d, 2H, J=8.0 Hz, benzene-H).

*2.2.4. 1-(2-Methyl-5-azidomethyl-3-thienyl)-2-[2-methyl-5-(4-azidomethyl)phenyl-3-thienyl]perfluorocyclopentene (**9**).* Compound **9** was prepared by a method similar to that used for compound **4**. Column chromatography on SiO_2 with petroleum ether/ethyl acetate (4:1) as the eluent afforded 0.81 g of **9** as a green solid in 91% yield. Mp 368–369 K; ^1H NMR ($CDCl_3$, 100 MHz), δ (ppm): 1.92 (s, 3H, $-CH_3$), 1.94 (s, 3H, $-CH_3$), 4.36 (s, 2H, $-CH_2-$), 4.43 (s, 2H, $-CH_2-$), 7.04 (s, 1H, thiophene-H), 7.28 (s, 1H, thiophene-H), 7.34 (d, 2H, J=8.4 Hz, benzene-H), 7.56 (d, 2H, J=8.4 Hz, benzene-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):14.51, 14.55, 48.90, 54.37, 120.19, 122.62, 125.27, 127.19, 128.93, 129.73, 129.22, 133.30, 135.09, 135.59, 141.78, 143.30.

*2.2.5. 1-{2-Methyl-5-[5-(2,3,4,6-tetraacetyl-β-D-glycoside)-3-(1,2,3-triazole)]methyl-3-thienyl}-2-{2-methyl-5-{4-[5-(2,3,4,6-tetraacetyl-β-D-glycoside)-3-(1,2,3-triazole)]methyl}phenyl-3-thienyl}perfluorocyclopentene (**10**).* Compound **10** was prepared by a method similar to that used for compound **6** using compound **9** instead of **4**. Column chromatography on SiO_2 with petroleum ether/ethyl acetate (1:5) as the eluent afforded 1.17 g of **10** as a gray solid in 68% yield. Mp 355–356 K; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.89 (s, 3H), 1.91 (s, 3H), 1.95 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 3.72–3.74 (m, 2H), 4.10–4.17 (m, 2H), 4.24–4.28 (m, 2H), 4.66 (d, 1H, J=2.8 Hz), 4.68 (d, 1H, J=2.8 Hz), 4.81 (d, 2H, J=12.4 Hz), 4.92 (m, 2H), 4.99 (m, 2H), 5.09 (m, 2H), 5.18 (m, 2H), 5.54 (s, 2H), 5.64 (s, 2H), 7.12 (s, 1H), 7.25 (s, 1H), 7.30 (d, 2H, J=8.0 Hz), 7.49 (s, 1H), 7.53 (d, 3H, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 14.17, 14.42, 14.47, 20.52, 20.54, 20.70, 21.00, 48.42, 53.74, 60.36, 61.75, 61.79, 63.02, 63.04, 68.31, 71.18, 71.20, 71.90, 71.94, 72.71, 72.73, 99.94, 100.06, 122.28, 122.63, 122.83, 124.93, 125.70, 126.23, 127.78, 128.81, 133.76, 134.14, 134.62, 141.34, 141.76, 143.80, 144.75, 144.84, 169.29, 169.39, 170.14, 170.59.

*2.2.6. 1-{2-Methyl-5-[5-(2,3,4,6-tetrahydroxyl-β-D-glycoside)-3-(1,2,3-triazole)]methyl-3-thienyl}-2-{2-methyl-5-{4-[5-(2,3,4,6-tetrahydroxyl-β-D-glycoside)-3-(1,2,3-triaz-ole)]methyl}phenyl-3-thienyl}perfluorocyclopentene (**2o**).* Compound **2o** was prepared by a method similar to that used for compound **1o** using compound **10** instead of **6**. Column chromatography on SiO_2 with methanol as the eluent afforded 0.56 g of **2o** as an orange solid in 95% yield. Mp 350–351 K; Anal. Calcd for $C_{41}H_{44}F_6N_6O_{12}S_2$ (%):C, 49.69; H, 4.48; N, 8.48, found: C, 49.76; H, 4.54; N, 8.56; ^1H NMR ($(CD_3)_2SO$, 400 MHz), δ (ppm): 1.87 (s, 6H), 2.96 (m, 2H), 3.05 (d, 2H, J=10.4 Hz), 3.10 (m, 4H), 3.45 (m, 2H), 3.68 (d, 2H, J=11.6 Hz), 4.24 (d, 2H, J=11.6 Hz), 4.61 (d, 2H, J=12.0 Hz), 4.83 (m, 2H), 5.61 (s, 2H), 5.80 (s, 2H), 7.27 (s, 1H, thiophene-H), 7.37 (d, 2H, J=8.0 Hz, benzene-H), 7.47 (s, 1H, thiophene-H), 7.63 (d, 2H, J=8.0 Hz, benzene-H), 8.17 (s, 1H), 8.20 (s, 1H); ^{13}C NMR ($(CD_3)_2SO$, 100 MHz), δ (ppm): 14.16, 14.20, 23.96, 47.39, 48.84, 52.63, 61.42, 61.68, 61.82, 70.38, 73.66, 76.99, 77.32, 102.48, 102.56, 123.02, 124.23, 124.58, 125.92, 127.32, 129.18, 132.58, 136.12, 137.09, 141.39,143.32, 144.53; IR (KBr, ν, cm^{-1}): 531, 644, 990, 1021, 1051, 1080, 1110, 1275, 1342, 1415, 1559, 1642, 3433; MS calcd for $C_{43}H_{47}F_6N_6O_{14}S_2^-$ $[M+CH_3COO]^-$: 1049.2, found 1049.7.

3. Results and discussion

3.1. Solubility in water

The solubility of diarylethenes **1o**–**3o** in water were measured at room temperature according to the known method.[18] When reached a saturation state in water at 300 K, the solubility of **1o**–**3o** was 0.056, 47.0, and 750 mg mL^{-1}, respectively, indicating that the water solubility increased with the decrease in the number of phenyl-bridged glucosyltriazolyl groups in diarylethene systems. Consequently, the solubility of **1o** is the smallest and that of the **3o** is the biggest in water among the three diarylethene derivatives.

3.2. Photochromism of diarylethenes

The photochromic behaviors of **1**–**3** induced by photoirradiation were measured at room temperature in both water and PMMA films. The absorption spectral change of **1** and the color changes of **1**–**3** induced by photoirradiation in water are shown in Fig. 1. **1o** exhibited a sharp absorption peak at 292 nm (ε_{max}=2.5×10^4 L mol^{-1} cm^{-1}) in water, which arose from $\pi\rightarrow\pi^*$ transition.[19] Upon irradiation with

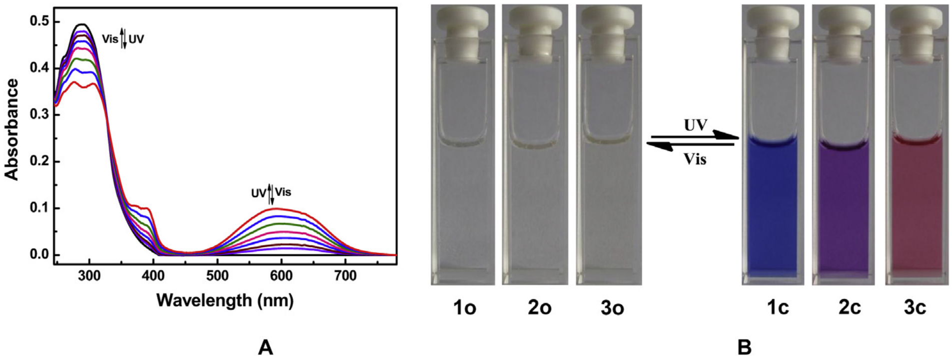


Fig. 1. Absorption spectral changes of **1** and color changes of **1**–**3** upon alternating irradiation with UV and visible light in water at room temperature: (A) spectral changes of **1** (2.0×10^{-5} mol L^{-1}); (B) color changes of **1**–**3**.

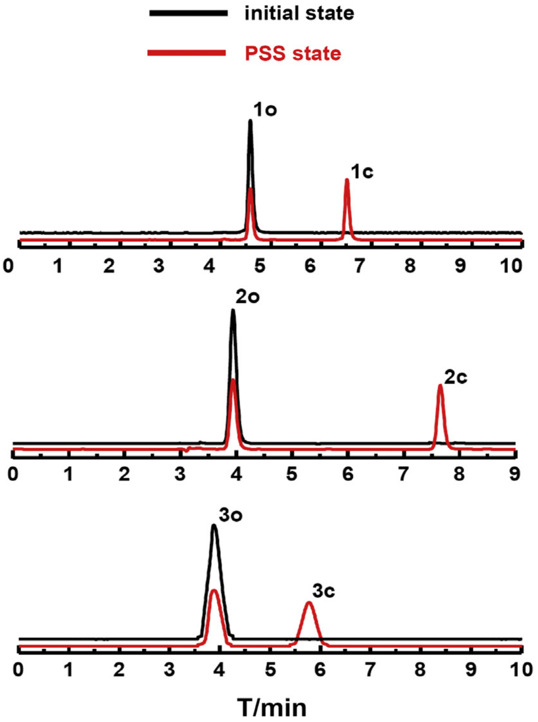


Fig. 2. Photoconversion ratios of **1**–**3** in the photostationary state in methanol measured by HPLC analysis.

297 nm light, a new visible absorption band centered at 592 nm ($\varepsilon_{max}=4.4\times10^3$ L mol^{-1} cm^{-1}) emerged, while the original peak at 292 nm decreased due to the formation of the closed-ring isomer **1c**. This could be seen with the naked eyes, as the colorless solution of **1o** turned blue. Alternatively, the blue solution could be bleached completely upon irradiation with visible light ($\lambda>450$ nm), indicating that **1c** returned to the initial state **1o**. In the photostationary state, the isosbestic point of **1** was observed at 328 nm, which was in agreement with the reversible two-component photochromic reaction scheme. Similar to **1**, diarylethenes **2** and **3** also exhibited favorable photochromism in water. Upon irradiation with 297 nm light, the colorless solution of **2o** turned purple, and that of **3o** turned red due to the formation of the closed-ring isomers **2c** and **3c**, respectively (Fig. 1B). The absorption maxima of **2c** and **3c** in water were observed at 551 and 516 nm, respectively. In the photostationary state, the isosbestic points of **2** and **3** were observed at 315 and 261 nm, respectively. In the photostationary state, the photoconversion ratios from the open-ring to the closed-ring isomers of the three derivatives were measured by HPLC analysis in methanol (Fig. 2). It was calculated that the photoconversion ratios of **1**–**3** were 54% for **1**, 48% for **2**, and 40% for **3** in the photostationary state. Compared to diarylethenes with a pyrrole moiety,[20] the photoconversion ratios of **1**–**3** decreased significantly in solution, but were much larger than those of diarylethenes with six-membered aryl units.[21]

In PMMA films, **1**–**3** also showed similar photochromism as observed in water. The absorption spectral changes of **1** and the color changes of **1**–**3** are shown in Fig. 3. Upon irradiation with 297 nm UV light, the colorless **1o**/PMMA film turned blue with the absorption maximum observed at 594 nm. The colorless **2o**/PMMA film turned purple and **3o**/PMMA film turned red by irradiating with UV light. In the photostationary state, the absorption maxima of **2c** and **3c** in PMMA films were observed at 557 and 520 nm, respectively. All colored diarylethene/PMMA films could be bleached completely by irradiating of visible light with appropriate wavelength. Compared to those in water, the absorption maxima of the closed-ring isomers **1c**–**3c** in PMMA films were at longer wavelengths, with the redshift values of 2 nm for **1c**, 6 nm for **2c**, and 4 nm for **3c**. The redshift may be attributed to the polar effect of the polymer matrix as observed for most of the reported diarylethenes.[22]

The photochromic parameters of **1**–**3** in both water and PMMA films are summarized in Table 1. The results showed that the number of phenyl-bridged glucosyltriazolyl groups in diarylethene systems had a significant effect on the photochromic properties of these water-soluble diarylethenes, including the absorption maxima, molar absorption coefficients, and quantum yields of cyclization/cycloreversion. Among the three compounds, **1**, which contained two phenyl-bridged glucosyltriazolyl groups, had the longest absorption maximum in both water and a PMMA film. When the number of phenyl-bridged glucosyltriazolyl groups decreased, the absorption maxima of the diarylethenes shifted to a shorter wavelength in both water and PMMA films due to reducing the π-conjugation in diarylethene systems. As a result, **3**, which contained no phenyl-bridged glucosyltriazolyl groups, had the shortest absorption maximum in both water and a PMMA film. Compared to those of **3c**, the absorption maximum of **1c** was redshifted by 76 nm in water, and by 74 nm in a PMMA film. The molar absorption coefficients of the open-ring isomers **1o**–**3o** increased in the order of **2o**<**3o**<**1o**, and those of **1c**–**3c** increased in the order of **3o**<**2o**<**1o** in water. Compared to that of **3c**, the molar absorption coefficient of **1c** was twofold larger in water. For **1** with two phenyl-bridged glucosyltriazolyl groups, the cyclization quantum yield was 0.30 and its cycloreversion quantum yield was 0.011. In water, the cyclization quantum yields of **1**–**3** increased in the order of **2**<**1**<**3**, and their cycloreversion quantum yields increased in the order of **1**<**3**<**2**. Therefore, the cycloreversion

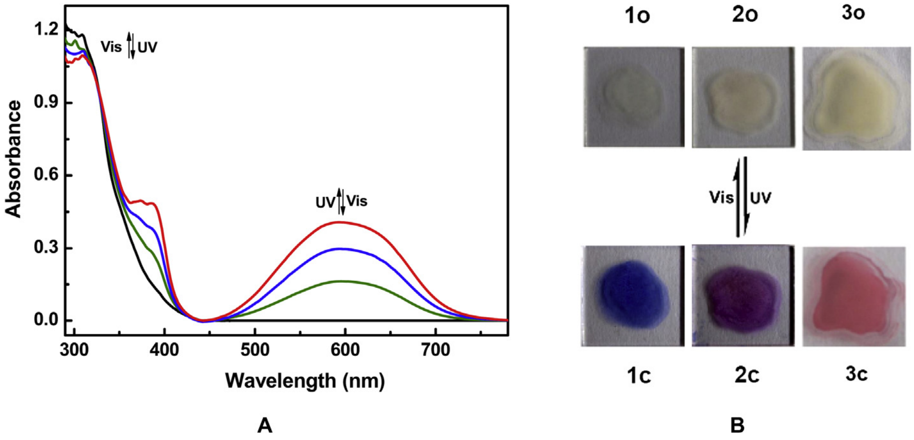


Fig. 3. Absorption spectral changes of **1** and color changes of **1**–**3** upon alternating irradiation with UV and visible light in PMMA films (10%, w/w) at room temperature: (A) spectral changes of **1**; (B) color changes of **1**–**3**.

Table 1
Absorption spectral properties of **1**–**3** in both water and PMMA films

Compd	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		Conversion at PSS in hexane (%)
	Water	PMMA film	Water	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	292 (2.5×10^4)	308	592 (4.4×10^3)	594	0.30	0.011	54
2	293 (5.9×10^3)	260	551 (2.2×10^3)	557	0.27	0.046	48
3	239 (1.1×10^4)	247	516 (2.1×10^3)	520	0.33	0.020	40

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

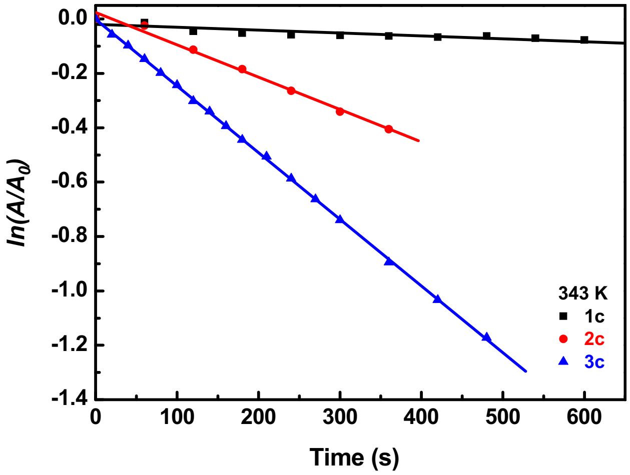


Fig. 4. Thermal fading of **1c**–**3c** at 343 K in water.

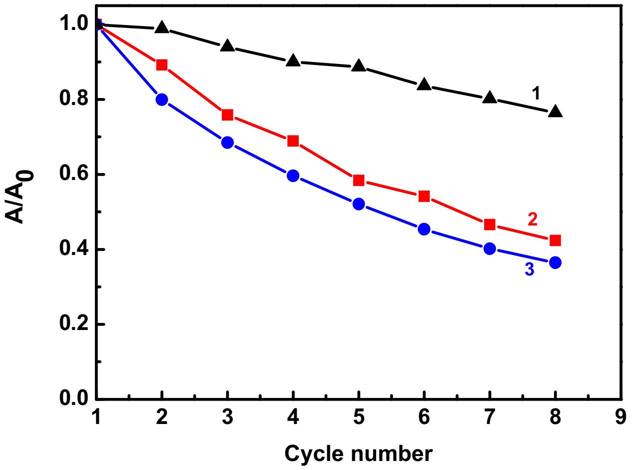


Fig. 5. Fatigue resistance of **1**–**3** in water in air atmosphere at room temperature. Initial absorptance of the sample was fixed to 1.0.

quantum yield of **2** with mono-phenyl-bridged glucosyltriazolyl group is the largest, and the cyclization quantum yield of **3** with non-phenyl-bridged glucosyltriazolyl group is the largest among the three derivatives. As mentioned above, the number of phenyl-bridged glucosyltriazolyl groups had a great effect on the photoreactivity of these diarylethene derivatives.

The thermal stability of the open-ring and closed-ring isomers of **1**–**3** was tested in water at room temperature and 343 K, respectively. After storing these solutions in water at room temperature in the dark and then exposing them to air for more than 30 days, no changes were detected in colors and UV/Vis spectra for **1**–**3**. No decomposition was detected, when these derivatives were exposed to air for more than three months. To investigate the effect of phenyl-bridged glucosyltriazolyl groups on the thermal stability of the closed-ring isomers **1c**–**3c**, the thermal cycloreversion kinetics of **1c**–**3c** at 343 K was examined by the reported method[5a,23] (Fig. 4). It could be clearly seen that the thermal fading rate of **3c** was the fastest and that of **1c** was the slowest at 343 K. The result suggested that the number of phenyl-bridged glucosyltriazolyl groups could be effective to enhance the thermal stability of these diarylethenes. In addition, the fatigue resistance of **1**–**3** was examined in water by alternating irradiation with UV and visible light in air at room temperature (Fig. 5). The irradiation time was long enough for coloration to reach the photostationary state. In water, the coloration/decoloration cycles of **1**–**3** could be repeated for more than eight times with 24% degradation of **1c**, 58% degradation of **2c**, and 64% degradation of **3c**. The result indicated that the number of phenyl-bridged glucosyltriazolyl groups could effectively enhance the fatigue resistance of these diarylethenes. Compared to the reported diarylethenes,[24] the fatigue resistance of **1**–**3** was much poorer, but better than that of diarylethenes with a benzene moiety.[25]

3.3. Fluorescence of diarylethenes

The fluorescence of **1**–**3** in water was measured at room temperature. As shown in Fig. 6, the emission peaks of **1o**–**3o** were observed at 504, 406, and 430 nm in water (5.0×10^{-5} mol L^{-1}), when excited at 418, 323, and 259 nm, respectively. Among the three compounds, the emission peak of **1o** with two phenyl-bridged glucosyltriazolyl groups was the longest and that of **2** was the shortest in water. Compared to that of **2o**, the emission peak of **1o** was red-shifted by 98 nm in water. **1**–**3** behaved as a weak fluorescent switch, when transformed from the open-ring isomers to the closed-ring isomers by photoirradiation in water. The emission intensity changes of **1**–**3** during the process of photoisomerization are shown in Fig. 7. Upon irradiation with 297 nm UV light, the photocyclization reaction occurred and the emission intensity of **1** decreased due to the formation of the closed-ring isomer **1c**. When arrived at the photostationary state, its emission intensity was quenched to ca. 82% in water. Back irradiation with visible light of appropriate wavelength regenerated the open-ring isomer **1o** and recovered the original emission intensity. Similar to **1**, diarylethenes **2** and **3** displayed analogous fluorescent switch property by alternating irradiation with UV and visible light. In the photostationary state, the emission intensity was quenched to ca. 91% for **2** and 70% for **3**, respectively. Compared to the diarylethenes with two thiophene moieties,[22c,26] the fluorescent modulation efficiency of **1**–**3** decreased remarkably in solution. The reason could be possibly attributed to the incomplete cyclization reaction in water as well as to the existence of inactive **1o**, **2o**, and **3o** in parallel conformations.[26,27]

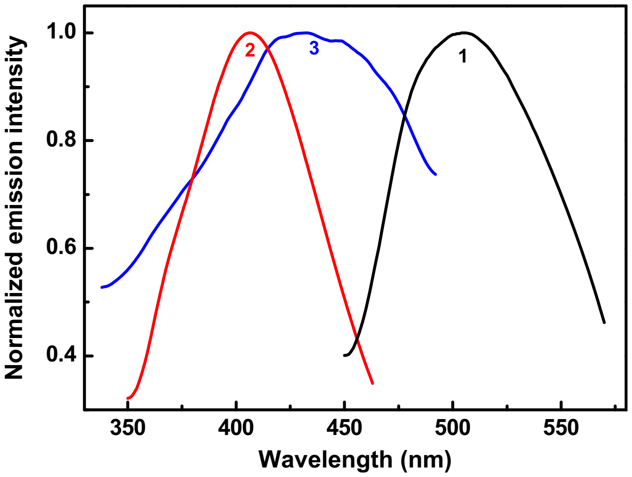


Fig. 6. Normalized fluorescence emission spectra of **1**–**3** in water at room temperature.

4. Conclusions

In summary, a new class of water-soluble diarylethenes with glycosyltriazolyl groups and variable phenyl units has been synthesized to study the effect of the number of phenyl units on their water solubility, photochromism, and fluorescent behavior. With the increase of the number of phenyl-bridged glycosyltriazolyl groups, their photochromic properties, including the absorption maximum, photoconversion ratio, thermal stability, and fatigue resistance were significantly enhanced. However, their water solubility and fluorescent modulation efficiency were remarkably suppressed. Though a more detailed study on more structural analogs is required to completely elucidate the molecular structure–property relationship for these water-soluble diarylethenes, the present results are valuable for the design of novel diarylethenes with good water solubility and photochromic properties.

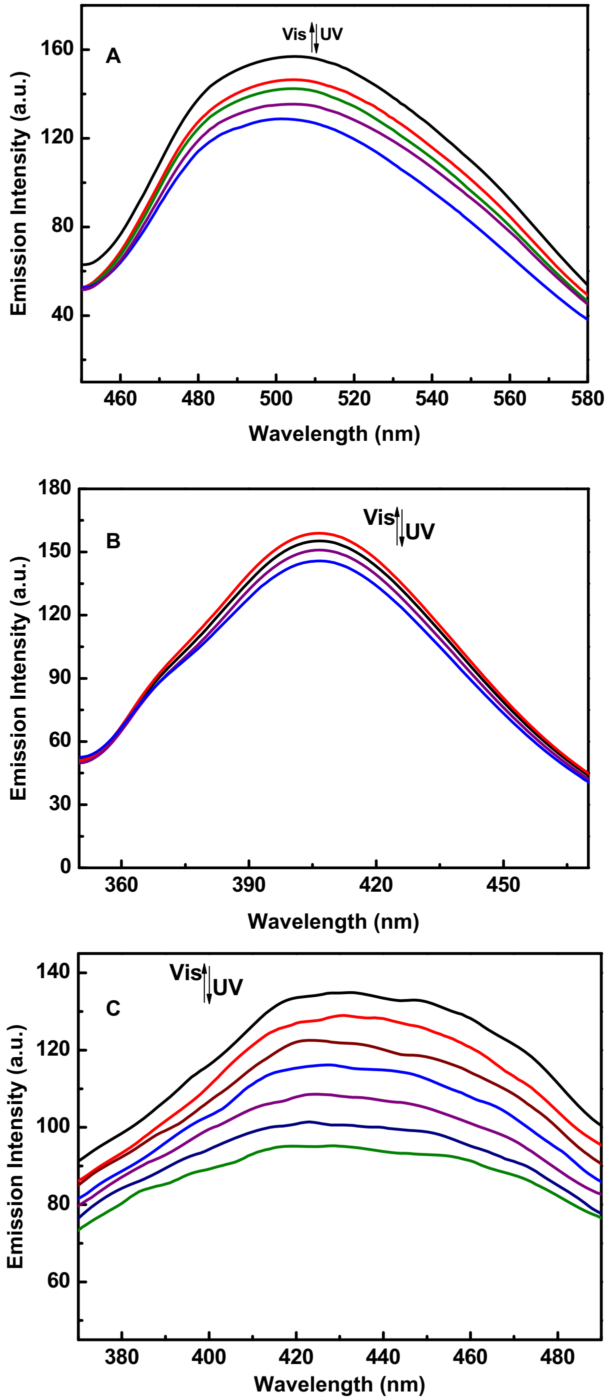


Fig. 7. Emission intensity changes of **1**–**3** in water (5.0×10^{-5} mol L^{-1}) by photoirradiation at room temperature: (A) **1**; (B) **2**; (C) **3**.

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References and notes

1. (a) Kodani, T.; Matsuda, K.; Yamada, T.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 9631–9637; (b) Shiozawa, T.; Hossain, M. K.; Ubukata, T.; Yokoyama, Y. *Chem. Commun.* **2010**, 4785–4787; (c) Lin, H.; Xu, W.; Zhu, D. B. *J. Mater. Chem.* **2010**, *20*, 884–890.
2. Guo, X. F.; Zhang, D. Q.; Wang, T. X.; Zhu, D. B. *Chem. Commun.* **2003**, 914–915.
3. Gilat, S. L.; Kawai, S. H.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439–1442.
4. Tian, H.; Qin, B.; Yao, R. G.; Zhao, X. L.; Yang, S. J. *Adv. Mater.* **2003**, *15*, 2104–2107.
5. (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716; (b) Barachevsky, V. A.; Strokach, Y. P.; Puankov, Y. A.; Krayushkin, M. M. *J. Phys. Org. Chem.* **2007**, *20*, 1007–1020; (c) Tian, H.; Yang, S. J. *Chem. Soc. Rev.* **2004**, *33*, 85–97.
6. Zou, Y.; Xiao, S. Z.; Yi, T.; Zhang, H. J.; Li, F. Y.; Huang, C. H. *J. Phys. Org. Chem.* **2007**, *20*, 975–980.
7. Takata, A.; Yokojima, S.; Nakagawa, H.; Matsuzawa, Y.; Murakami, A.; Nakamura, S.; Irie, M.; Uchida, K. *J. Phys. Org. Chem.* **2007**, *20*, 998–1006.
8. Ikeda, M.; Tanifuji, N.; Yamaguchi, H.; Irie, M.; Matsuda, K. *Chem. Commun.* **2007**, 1355–1357.
9. (a) Hirose, T.; Irie, M.; Matsuda, K. *Adv. Mater.* **2008**, *20*, 2137–3141; (b) Zheng, H. Y.; Zhou, W. D.; Yuan, M. J.; Yin, X. D.; Zuo, Z. C.; Ouyang, C. B.; Liu, H. B.; Li, Y. L.; Zhu, D. B. *Tetrahedron Lett.* **2009**, *50*, 1588–1592.
10. (a) Hirose, T.; Irie, M.; Matsuda, K. *Chem.—Asian J* **2009**, *4*, 58–66; (b) Jiang, Y. G.; Wang, Z. Q.; Yu, X.; Shi, F.; Xu, H. P.; Zhang, X. *Langmuir* **2005**, *21*, 1986–1990.
11. (a) Wang, C.; Chen, Q.; Xu, H.; Wang, Z. Q.; Zhang., X. *Adv. Mater.* **2010**, *22*, 2553–2555; (b) Wang, Y.; Han, P.; Xu, H.; Wang, Z.; Zhang, X.; Kabanov, A. V. *Langmuir* **2010**, *26*, 709–715; (c) Herder, M.; Patzel, M.; Grubert, L.; Hecht, S. *Chem. Commun.* **2011**, 460–462; (d) Matsumoto, S.; Yamaguchi, S.; Ueno, S.; Komatsu, H.; Ikeda, M.; Ishizuka, K.; Iko, Y.; Tabata, K. V.; Aoki, H.; Ito, S.; Noji, H.; Hamachi, I. *Chem.—Eur. J.* **2008**, *14*, 3977–3986.
12. (a) Jiang, Y. G.; Wang, Y. P.; Ma, N.; Wang, Z. Q.; Smet, M.; Zhang, X. *Langmuir* **2007**, *23*, 4029–4034; (b) Huang, C. S.; Li, Y. L.; Yang, J. E.; Cheng, N.; Liu, H. B.; Li, Y. *Chem. Commun.* **2010**, 3161–3163; (c) Wu, D. Q.; Zhi, L. J.; Bodwell, G. J.; Cui, G. L.; Tsao, N.; Mülen, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5417–5420; (d) Xia, F.; Feng, L.; Wang, S. T.; Sun, T.; Song, W. L.; Jiang, W. H.; Jiang, L. *Adv. Mater.* **2006**, *18*, 432–434.
13. (a) Berns, M. W.; Krasieva, T.; Sun, C.-H.; Dvornikov, A.; Rentzepis, P. M. *J. Photochem. Photobiol., B* **2004**, *75*, 51–56; (b) Kocer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. *Science* **2005**, *309*, 755–759; (c) Loudwig, S.; Bayley, H. *J. Am. Chem. Soc.* **2006**, *128*, 12404–12405; (d) Willner, I.; Rubin, S. *Angew. Chem., Int. Ed.* **1996**, *35*, 367–385; (e) Sakata, T.; Yan, Y.; Marriott, G. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4759–4764; (f) Saito, M.; Musha, K.; Yokoyama, Y.; Yokoyama, Y. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2423–2429.
14. Soh, N.; Yoshida, K.; Nakajima, H.; Nakano, K.; Imato, T.; Fukaminato, T.; Irie, M. *Chem. Commun.* **2007**, 5206–5208.
15. (a) Hirose, T.; Matsuda, K.; Irie, M. *J. Org. Chem.* **2006**, *71*, 7499–7508; (b) Hirose, T.; Irie, M.; Matsuda, K. *New J. Chem.* **2009**, *33*, 1332–1334; (c) Zou, Y.; Yi, T.; Xiao, S. Z.; Li, F. Y.; Li, C. Y.; Gao, X.; Wu, J. C.; Yu, M. X.; Huang, C. H. *J. Am. Chem. Soc.* **2008**, *130*, 15750–15751; (d) Zhou, X. H.; Duan, Y. L.; Yan, S. H.; Liu, Z. H.; Zhang, C. J.; Yao, L. S.; Cui, G. L. *Chem. Commun.* **2011**, 6876–6878; (e) Saitoha, M.; Fukaminato, T.; Irie, M. *J. Photochem. Photobiol., A* **2009**, *207*, 28–31; (f) Polyakova, S.; Belov, V.; Bossi, M.; Hell, S. *Eur. J. Org. Chem.* **2011**, *18*, 3301–3312.
16. Tong, Z. P.; Pu, S. Z.; Xiao, Q.; Liu, G.; Cui, S. Q. *Tetrahedron Lett.* **2013**, *54*, 474–477.
17. Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876.
18. Li, Q. S.; Li, Z.; Wang, S. *J. Chem. Eng. Data* **2007**, *52*, 151–153.
19. Li, Z. X.; Liao, L. Y.; Sun, W.; Xu, C. H.; Zhang, C.; Fang, C. J. *J. Phys. Chem. C* **2008**, *112*, 5190–5196.
20. Liu, G.; Pu, S. Z.; Wang, X. M. *J. Photochem. Photobiol., A* **2010**, *214*, 230–240.
21. Wang, R. J.; Pu, S. Z.; Liu, G.; Cui, S. Q.; Liu, W. J. *Tetrahedron Lett.* **2012**, *53*, 320–324.
22. (a) Kasatani, K.; Kambe, S.; Irie, M. *J. Photochem. Photobiol., A* **1999**, *122*, 11–15; (b) Hoshino, M.; Ebisawa, F.; Yoshida, T.; Sukegawa, K. *J. Photochem. Photobiol., A* **1997**, *105*, 75–81; (c) Fan, C. B.; Pu, S. Z.; Liu, G.; Yang, T. S. *J. Photochem. Photobiol., A* **2008**, *194*, 333–343.
23. (a) Nakagawa, T.; Hasegawa, Y.; Kawai, T. *J. Phys. Chem. A* **2008**, *112*, 5096–5103; (b) Nakashima, T.; Atsumi, K.; Kawai, S.; Nakagawa, T.; Hasegawa, Y.; Kawai, T. *Eur. J. Org. Chem.* **2007**, *19*, 3212–3218.
24. (a) Liu, G.; Liu, M.; Pu, S. Z.; Fan, C. B.; Cui, S. Q. *Tetrahedron* **2012**, *68*, 2267–2275; (b) Liu, G.; Liu, M.; Pu, S. Z.; Fan, C. B.; Cui, S. Q. *Dyes Pigm.* **2012**, *95*, 553–562; (c) Pu, S. Z.; Yan, P. J.; Liu, G.; Miao, W. J.; Liu, W. J. *Tetrahedron Lett.* **2011**, *52*, 143–147.
25. (a) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309; (b) Pu, S. Z.; Fan, C. B.; Miao, W. J.; Liu, G. *Tetrahedron* **2008**, *64*, 9464–9470.
26. (a) Fan, C. B.; Pu, S. Z.; Liu, G.; Yang, T. S. *J. Photochem. Photobiol., A* **2008**, *197*, 415–425; (b) Tsujioka, T.; Kume, M.; Irie, M. *J. Photochem. Photobiol., A* **1997**, *104*, 203–206.
27. (a) Pu, S. Z.; Tong, Z. P.; Liu, G.; Wang, R. J. *J. Mater. Chem. C* **2013**, *1*, 4726–4739; (b) Pu, S. Z.; Liu, G.; Shen, L.; Xu, J. K. *Org. Lett.* **2007**, *9*, 2139–2142.