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New photochromic diarylethenes bearing a pyridine moiety

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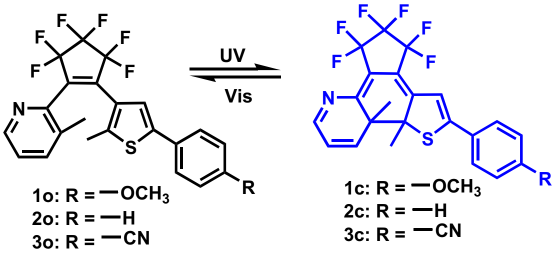
ABSTRACT

A new class of diarylethenes bearing a pyridine unit has been firstly developed and their properties such as photochromism, fatigue resistance, and fluorescence have been discussed. The pyridine unit was connected directly to the central cyclopentene ring as one aryl moiety and availably participated in the photoinduced cyclization reaction even in the crystalline phase. All of these diarylethenes exhibited excellent photochromism, remarkable fatigue resistance, and notable fluorescence photoswitches both in solution and in poly(methylmethacrylate) films. Moreover, the different substituents had a significant effect on their properties. The results indicated that the electron-donating substituent could significantly enhance the cyclization quantum yield and depress the cycloreversion quantum yield while the electron-withdrawing group had a notable contribution to the cycloreversion quantum yield and fluorescence quantum yield for these diarylethenes.

Due to the widespread potential application in photonic devices such as recording media and photoswitches, the exploration of photochromic diarylethenes has aroused a surge of interest in materials science.[1] Among diarylethenes hitherto reported, there are many theses on cationic diarylethenes containing pyridinium cation units as the side group connected to the photoreactive thienyl moieties.[2] It is because pyridine groups are widely used for the interaction with carboxylic acids to form intermolecular hydrogen bonds,[3] which would result in the generation of novel structures such as organogels,[4] nanostructures,[5] and optical textures in liquid crystal materials.[3c–e,6]

Nowadays, the design of new diarylethene skeletons with different aryl moieties has become an active area of research. As is well known, studies on the hexatriene backbone of diarylethenes are mainly confined to the five-membered heteroaryl moieties, and the diarylethene designs are generally limited to the addition of functional units to the aryl rings and the substitution of the central ethene group.[7] In the case of six-membered rings as aryl moieties, only a few symmetrical diarylethene derivatives bearing two phenyl/naphthyl groups have been reported.[8] The majority of these derivatives are thermally reversible with poor photochromism. In previous works,[9] we reported a new class of diarylethene derivatives bearing both five-membered and six-membered moieties, which showed some new characteristics differing from diarylethenes containing five-membered aryl rings. Among the diarylethenes bearing a six-membered aryl moiety hitherto reported, the six-membered unit has been only limited to the benzene ring.[9] Although they showed good photochromism both in solution and in poly(methylmethacrylate) (PMMA) film, they exhibited no photochromism in the crystalline phase.[9a] As far as we are aware, photochromic hybrid diarylethenes bearing other six-membered moieties, which exhibit good photochromism in the crystalline phase have not hitherto been reported.

Based on the above aspects, in this Letter, we have developed a new class of photochromic diarylethene derivatives in which a six-membered pyridine group is connected directly to the central ethene unit as an aryl moiety and participates in the photochromic hexatriene–cyclohexadiene reaction (Scheme 1). The synthesized diarylethenes are 1-(3-methyl-2-pyridyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1-(3-methyl-2-pyridyl)-2-(2-methyl-5-phenyl-3-thienyl)per-fluorocyclopentene (**2o**), and 1-(3-methyl-2-pyridyl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluorocyclopentene (**3o**). All of these diarylethenes showed good photochromism in solution, in amorphous PMMA films and in the crystalline phase. They are, to the best of our knowledge, the first example of photochromic diarylethene derivatives bearing a pyridine moiety.



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

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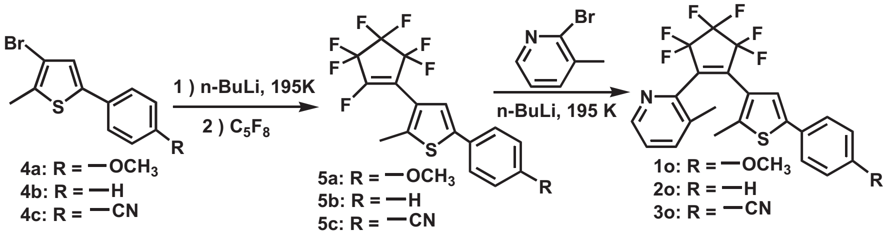

Scheme 2. Synthetic route for diarylethenes **1o**–**3o**.

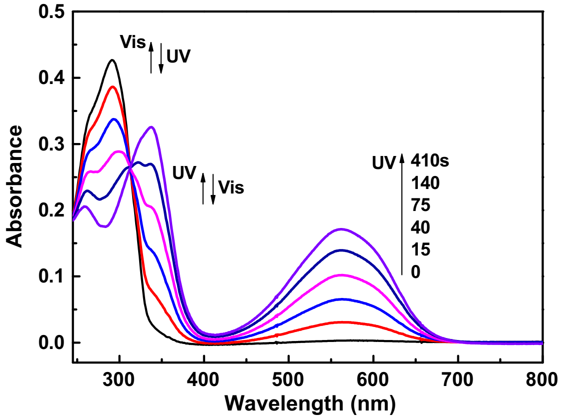

Figure 1. Absorption spectral changes of diarylethene **1** by photoirradiation in hexane (2.0×10^{-5} mol L^{-1}) at room temperature.

The synthetic route for diarylethenes **1o**–**3o** is shown in Scheme 2. First, three phenylthiophene derivatives (**4a**–**4c**)[10] were lithiated and coupled with octafluorocyclopentene to give three mono-perfluorocyclopentene derivatives (**5a**–**5c**). Finally, 2-bromo-3-methylpyridine was lithiated and then separately coupled with **5a**–**5c** to give diarylethenes **1o**–**3o**, respectively. The structures of **1o**–**3o** were confirmed by elemental analysis, NMR, and IR.[11]

Reversible absorption spectral changes of diarylethenes **1o**–**3o** were observed in hexane at room temperature, and each of them presented an isosbestic point which supported the reversible two component photochromic reaction schemes.[12] Figure 1 shows the absorption spectral changes of diarylethene **1** with the photochromic reaction as a typical example. In hexane, compound **1o** exhibited a sharp absorption peak at 291 nm (ε, 2.13×10^4 L mol^{-1} cm^{-1}) in hexane, as a result of a $\pi \rightarrow \pi^*$ transition.[13] Upon irradiation with 297 nm light, a new visible absorption band centered at 563 nm (ε, 1.07×10^4 L mol^{-1} cm^{-1}) emerged while the original peak at 291 nm decreased, indicating the formation of the closed-ring isomer **1c**. This could be seen with the naked eyes, as the colorless solution of **1o** turned violet (Fig. 2A). The photostationary state is achieved upon irradiation with 297 nm light for 410 s. Alternatively, **1c** could return to the initial state **1o** upon irradiation with visible light (λ >450 nm) for 60 s. Just like diarylethene **1**, the spectral changes of diarylethenes **2o** and **3o** were similar to that of **1o**. The absorption maxima of diarylethenes **2c** and **3c** were observed at both 555 nm, which was 8 nm shorter than that of **1c**. In the photostationary state, the isosbestic points of diarylethenes **1**–**3** were observed at 313, 298, and 335 nm, respectively. The photostationary state is achieved by irradiation 425 s for **2** and 420 s for **3**, and the bleaching time is 40 s for **2** and 33 s for **3**, respectively. In addition, the photoconversion ratios of the three derivatives were analyzed by HPLC in the photostationary state, with the value of 80% for **1**, 74% for **2**, and 85% for **3**, respectively (Table 1). In PMMA amorphous film, diarylethenes **1**–**3** also showed good photochromism similar to samples in solution (Fig. 2B). Upon irradiation with 313 nm light, the colors of the diarylethene/PMMA films **1**–**3** changed from colorless to violet, with the appearance of a new broad absorption band centered at 581, 569 and 571 nm, respectively. This band was assigned to the formation of the closed-ring isomers **1c**–**3c**. All colored diarylethene/PMMA films reverted to colorless upon irradiation with visible light (λ >450 nm). As has been observed for most of the reported diarylethenes,[14] the maximum absorption peaks of **1c**–**3c** are found at longer wavelengths in PMMA film than those in hexane solution. This red shift phenomenon may be attributed to the polar effect of the polymer matrix in solid state.[15] The spectral properties of diarylethenes **1**–**3** are summarized in Table 1. Also, we have tested the response of the molecules to acidic condition according to the references.[16] The photochromic reactivity of diarylethenes **1**–**3** is controlled by the addition of acid (trifluoroacetic acid) and base (diethylamine) in corresponding CH_3CN solutions. With the addition of acid to the solutions of **1c**–**3c** in photostationary state, the colors changed to green for **1c** and blue to **2c** and **3c** by protonation, and their absorption maxima exhibited a remarkable bathochromic shift similar to that of the reported diarylethenes.[16] The neutralization with base could regenerate the original absorption spectra and colors of **1c**–**3c**. It should be noted here that diarylethenes **1o**–**3o** showed excellent photochromism in the crystalline phase, too (Fig. 2C). They could be colored and bleached repeatedly more than 200 times by alternating irradiation with UV light and visible light with appropriate wavelength. The result is completely reverse to that reported for diarylethenes bearing a benzene moiety, where they showed no photochromism in the crystalline phase.[9a] To the best of our knowledge, this is the first class of diarylethenes with a six-membered ring moiety which they could exhibit good photochromism in the crystalline phase.

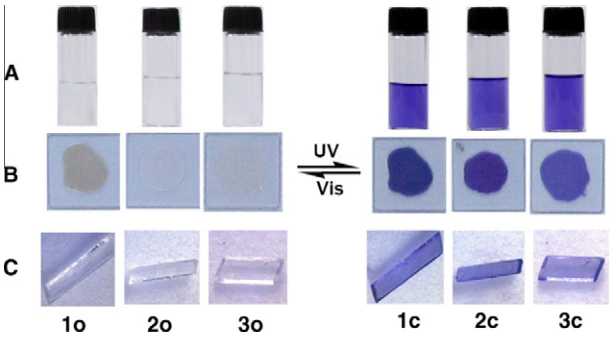

Figure 2. The color changes of diarylethenes **1**–**3** by photoirradiation in different media at room temperature: (A) in hexane, (B) in PMMA film, and (C) in crystalline phase.

The quantum yields were determined by comparing the reaction yields of diarylethenes **1**–**3** against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane at room

Table 1
Absorption spectral properties of diarylethenes **1**–**3** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA film (10%, w/w) at room temperature

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]		PR/%[d]
	Hexane	PMMA	Hexane	PMMA	Φ_{o-c}	Φ_{c-o}	
1	291(2.13×10^4)	291	563(1.07×10^4)	581	0.43	0.088	80
2	284(1.70×10^4)	285	555(6.59×10^3)	569	0.33	0.096	74
3	311(2.66×10^4)	313	555(8.25×10^3)	571	0.37	0.16	85

[a] The maximum absorption peak of the open-ring isomers.
[b] The maximum absorption peak of the closed-ring isomers.
[c] Quantum yields of cyclization (Φ_{o-c}) and cycloreversion (Φ_{c-o}), respectively.
[d] Photoconversion ratios of diarylethenes **1**–**3** (PR%) in the photostationary state.

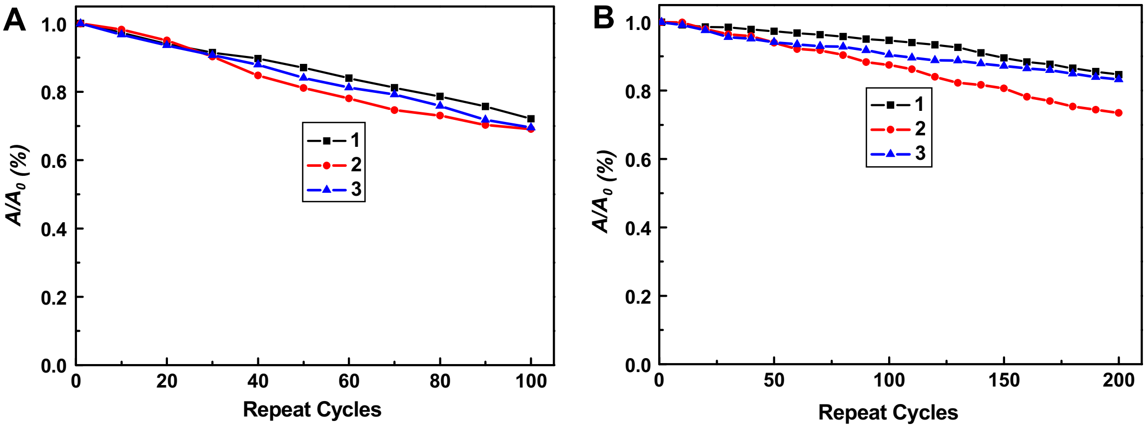

Figure 3. Fatigue resistance of diarylethenes **1**–**3** in hexane and in PMMA film in air atmosphere at room temperature: (A) in hexane, (B) in PMMA film. Initial absorbance of the sample was fixed to 1.0.

temperature,[17] and the results are also listed in Table 1. These data illuminated that altering the substituents had a significant effect on the photochromic features of diarylethenes **1**–**3** such as the absorption maxima, molar absorption coefficients and quantum yields. Among diarylethenes **1**–**3**, the molar absorption coefficients of the two isomers and its cyclization quantum yield of the unsubstituted parent compound **2** are the smallest. When replacing with a methoxy group at the *para*-position of the terminal phenyl ring, the molar absorption coefficients and the cyclization quantum yield increased notably, but the cycloreversion quantum yield showed a slight reduction. When the same position instead contains a cyano group, all of the photochromic parameters except the absorption maxima of the closed-ring isomer have notably increased. The result indicated that the electron-donating methoxy group could be effective to increase the molar absorption coefficient and to decrease the cycloreversion quantum yield, which is consistent with that of dithienylethenes reported by Irie et al.[18] Compared to that of **3c**, the absorption maximum of **1c** is red-shifted by 8 nm and its molar absorption coefficient is larger, which may be attributed to the more marked intramolecular charge transition (ICT).[10a] Moreover, the pyridine moiety has also a significant effect on the photochromic properties of diarylethenes 1–3. When replacing the pyridine moiety with the benzene moiety in the same molecular skeleton of diarylethenes, the cyclization quantum yield markedly decreased and the cycloreversion quantum yield showed the reverse trend.[9a] Similarly, when the same molecular skeleton instead contains other aryl moieties such as thiophene, thiazole, pyrazole, and pyrrole, among others,[9,10,19] their photochromic features are very different in comparison with those of diarylethenes bearing a pyridine moiety.

The thermal stabilities of the open-ring and closed-ring isomers of diarylethenes **1**–**3** were tested in hexane both at room temperature and at 80 °C. Storing these solutions in hexane at room temperature in the dark and then exposing them to air for more than 10 days, we found that no changes in the UV/vis spectra of diarylethenes **1**–**3** were observed. At 80 °C, diarylethenes **1**–**3** still showed good thermal stabilities for more than 5 h. The result suggests that these diarylethene derivatives have notable thermally irreversible photochromic behaviors, which are different from the dithienylethenes having pyridinium ions that undergo thermally reversible photochromic reactions.[7a] Besides this, the photogenerated closed-ring isomers of diarylethenes with six-membered benzene rings are also thermally unstable, which may be attributed to the relatively high aromatic stabilization energy.[7a,9a]

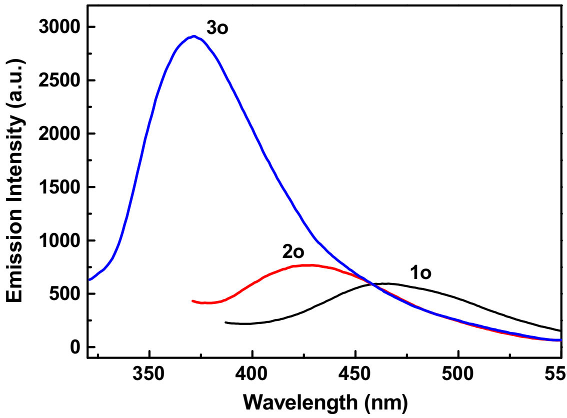

Figure 4. Emission spectra of diarylethenes **1**–**3** in hexane (2.0×10^{-5} mol L^{-1}) at room temperature when excited at 300 nm.

The fatigue resistances of diarylethenes **1**–**3** were examined both in hexane and in PMMA films by alternating irradiating with

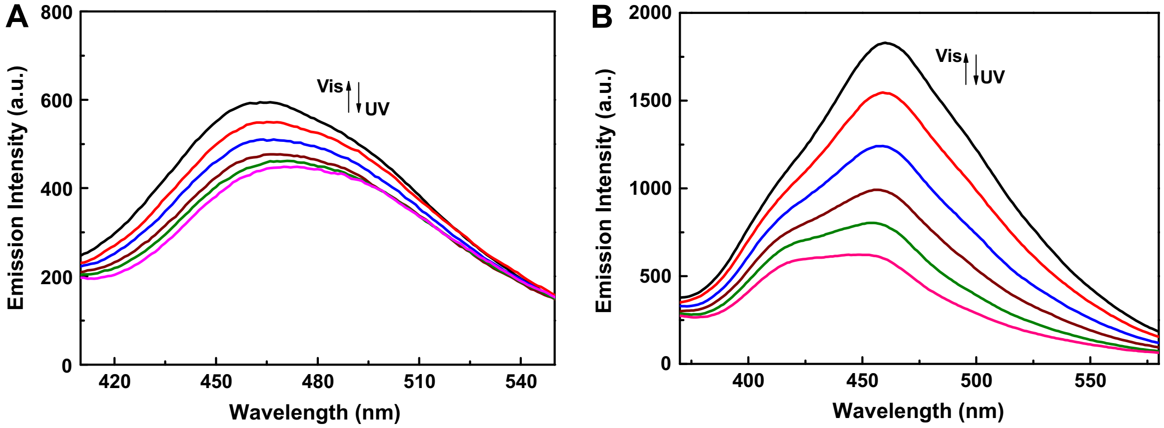

Figure 5. Emission intensity changes of diarylethenes **1** both in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA film (10%, w/w) by photoirradiation at room temperature: (A) in hexane (λ_{ex} = 300 nm), (B) in PMMA film (λ_{ex} = 350 nm).

UV and visible light in air at room temperature, as shown in Figure 3. In hexane, the coloration and decoloration cycles of diarylethenes **1–3** can be repeated at least 10 times with almost no photodegradation. However, 28% of **1c** and 31% of both **2c** and **3c** were destroyed after 100 repeat cycles in the same condition, which may be ascribed to degradation resulting from the formation of an epoxide.[20] The fatigue resistance of diarylethenes **1**–**3** in PMMA films is much stronger than that in solution. After 200 repeated cycles, these compounds still showed good photochromism with only ca. 15% degradation of **1c**, 27% of **2c**, and 17% of **3c**, respectively. This remarkable improvement may result from effectively suppressing the oxygen diffusion.[7a] Compared to diarylethenes bearing a benzene moiety,[9] the fatigue resistances of the diarylethenes bearing a pyridine moiety are much better both in hexane and in PMMA films, which may be attributed to the lower aromatic stabilization energy of the pyridine ring. In addition, the fatigue resistance of diarylethene with an electron-donating group (such as in compound **1**) is slightly stronger than that of diarylethene with an electron-withdrawing group (such as in compound **3**) both in hexane and in PMMA films. The result is completely contrary to that reported for analogs bearing a benzene moiety, where fatigue resistance markedly increased with the increase of electron-withdrawing ability.[9]

The fluorescence spectra of diarylethenes **1o**–**3o** both in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) were measured at room temperature. The fluorescent emission peaks of diarylethenes **1o**–**3o** were observed at 463, 429 and 372 nm when excited at 300 nm in hexane (Fig. 4), and were observed at 460, 452, and 465 nm when excited at 350 nm in PMMA films. Compared to those in hexane, the emission peaks of diarylethenes **2o** and **3o** showed a remarkable bathochromic shift in PMMA film, which is well consistent with those of their maxima absorption wavelengths. But to the diarylethene **1o**, its emission peak is almost constant in PMMA film. As shown in Figure 4, it could be clearly seen that the electron-donating methoxy group shifted the emission peak to longer wavelength and notably decreased the emission intensity; while the cyano group could be effective to increase the emission intensity and shifted the emission peak to a shorter wavelength, compared with the unsubstituted parent diarylethene **2o**. By using anthracene as the reference, the fluorescence quantum yields of diarylethenes **1o**–**3o** were determined to be 0.0078, 0.0083 and 0.015, respectively. The results suggested that the electron-withdrawing cyano substituent could effectively increase the fluorescence quantum of diarylethene bearing a pyridine unit. This is completely contrary to those of the diarylethenes bearing a biphenyl unit whose fluorescence quantums increased with the electron-donating ability.[21]

Diarylethenes **1**–**3** exhibited a notable fluorescent photoswitch on changing from the open-ring isomers to closed-ring isomers by photoirradiation both in hexane and in PMMA film, just like most of the reported diarylethenes.[1c,d,19] During the process of photoisomerization, diarylethene **1** exhibited changes in its fluorescence both in hexane and in PMMA film as shown in Figure 5. Upon irradiation with 297 nm UV light, the sample arrived at the photostationary state, in which its emission intensity quenched to ca. 75% in hexane and 34% in PMMA film, respectively. Back irradiation of the appropriate wavelength of visible light regenerated the open-ring isomer **1o** and duplicated the original emission spectra. The phenomena are useful for application as the fluorescence switches.[22] Similarly, diarylethenes **2** and **3** also functioned as a notable fluorescent switch upon photoirradiation both in hexane and in PMMA films. In the photostationary state, their emission intensities were quenched ca. 46% for **2** and 48% for **3** in solution and ca. 32% for **2** and 38% for **3** in PMMA films. The incomplete cyclization reaction and the existence of parallel conformations with relatively strong fluorescence may be the main cause for the lower fluorescent conversion.[14]

In conclusion, three new unsymmetrical diarylethenes based on a six-membered pyridine ring have been firstly developed and their properties have been discussed. This new photochromic system showed good photochromism in solution, in PMMA films, and in crystalline phase. This is the first example of diarylethenes bearing a six-membered moiety which exhibited good photochromism in the crystalline phase. The pyridine moiety induced some new dramatic properties differing from other diarylethenes with five-membered and six-memered aryl moieties reported so far. The results will be helpful for the synthesis of efficient photoactive diarylethene derivatives with new molecular skeletons and to design new photochromic systems for further potential applications in optoelectronic devices.

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References and notes

1. (a) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990; (b) Brown, G. H. *Photochromism*; Wiley-Interscience: New York, 1971; (c) Tian, H.; Yang, S. J. *Chem. Soc. Rev.* **2004**, *33*, 85–87; (d) Tian, H.; Feng, Y. L. *J. Mater. Chem.* **2008**, *18*, 1617–1622; (e) Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14843–14849; (f) Pu, S. Z.; Zhang, F. S.; Xu, J. K.; Shen, L.; Xiao, Q.; Chen, B. *Mater. Lett.* **2006**, *60*, 485–489.
2. (a) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439–1442; (b) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 275–284; (c) Kawai, S. H.; Gilat, S. L.; Lehn, J.-M. *Eur. J. Org. Chem.* **1999**, 2359–2366; (d) Kawai, T.; Koshido, T.; Nakazono, M.; Yoshino, K. *Chem. Lett.* **1993**, 697–700; (e) Koshido, T.; Kawai, T.; Yoshino, K. *J. Phys. Chem.* **1995**, *99*, 6110–6114; (f) Baron, R.; Onopriyenko, A.; Katz, E.; Lioubashevski, O.; Willner, I.; Wang, S.; Tian, H. *Chem. Commun.* **2006**, 2147–2149; (g) Matsuda, K.; Shinkai, Y.; Yamaguchi, T.; Nomiyama, K.; Isayama, M.; Irie, M. *Chem. Lett.* **2003**, *32*, 1178–1179; (h) 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; (i) Tan, W. J.; Zhang, Q.; Zhang, J. J.; Tian, H. *Org. Lett.* **2009**, *11*, 161–164.
3. (a) Wang, Y. J.; Tang, L. M.; Wang, Y. *Chem. Lett.* **2006**, *35*, 548–549; (b) Luo, X. F.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Macromolecules* **1998**, *31*, 3251–3254; (c) Lu, X.; He, C.; Griffin, A. C. *Macromolecules* **2003**, *36*, 5195–5200; (d) Xu, J.; Toh, C. T.; Liu, X.; Wang, S.; He, C.; Lu, X. *Macromolecules* **2005**, *38*, 1684–1690; (e) Bazuin, C. G.; Brandys, F. A. *Chem. Mater.* **1992**, *4*, 970–972.
4. Bao, C. Y.; Lu, R.; Jin, M.; Xue, P. C.; Tan, C. H.; Liu, G. F.; Zhao, Y. Y. *Org. Biomol. Chem.* **2005**, *3*, 2508–2512.
5. Li, R.; Yang, X.; Li, G.; Li, S.; Huang, W. *Langmuir* **2006**, *22*, 8127–8133.
6. (a) Kato, T.; Frechet, J. M. J. *Macromolecules* **1989**, *22*, 3818–3819; (b) Lee, M.; Cho, B.-K.; Kang, Y.-S.; Zin, W.-C. *Macromolecules* **1999**, *32*, 8531–8537.
7. (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716; (b) Matsuda, K.; Irie, M. *Chem. Lett.* **2006**, *35*, 1204–1209; (c) Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781–792; (d) Belser, P.; De Cola, L.; Hartl, F.; Adamo, V.; Bozic, B.; Chriqui, Y.; Iyer, V. M.; Jukes, R. T. F.; Kühni, J.; Querol, M.; Roma, S.; Salluce, N. *Adv. Funct. Mater.* **2006**, *16*, 195–208; (e) Nakashima, T.; Atsumi, K.; Kawai, S.; Nakagawa, T.; Hasegawa, Y.; Kawai, T. *Eur. J. Org. Chem.* **2007**, 3212–3218; (f) Kawai, S.; Nakashima, T.; Atsumi, K.; Sakai, T.; Harigai, M.; Imamoto, Y.; Kamikubo, H.; Kataoka, M. *Chem. Mater.* **2007**, *19*, 3479–3483; (g) Kühni, J.; Belser, P. *Org. Lett.* **2007**, *9*, 1915–1918; (h) Laurent, A. D.; André, J.-M.; Perpète, E. A.; Jacquemin, D. *J. Photochem. Photobiol., A* **2007**, *192*, 211–219.
8. (a) Takeshita, M.; Ogawa, M.; Keisuke, M.; Yamato, T. *J. Phys. Org. Chem.* **2003**, *16*, 148–151; (b) Uchida, K.; Nakamura, S.; Irie, M. *Res. Chem. Intermed.* **1995**, *21*, 861–876; (c) Liu, X. D.; Tong, Q. X.; Shi, M.; Zhang, F. S. *Sci. China, Ser. B* **2006**, *49*, 517–521.
9. (a) Pu, S. Z.; Fan, C. B.; Miao, W. J.; Liu, G. *Tetrahedron* **2008**, *64*, 9464–9470; (b) Pu, S. Z.; Li, H.; Liu, G.; Liu, W. J. *Tetrahedron Lett.* **2010**, *51*, 3575–3579.
10. (a) Pu, S. Z.; Liu, G.; Shen, L.; Xu, J. K. *Org. Lett.* **2007**, *9*, 2139–2142; (b) Peters, A.; Vitols, C.; McDonald, R.; Branda, N. R. *Org. Lett.* **2003**, *5*, 1183–1186; (c) Liu, G.; Pu, S. Z.; Wang, X. M. *J. Photochem. Photobiol., A* **2010**, *214*, 230–240; (d) Pu, S. Z.; Fan, C. B.; Miao, W. J.; Liu, G. *Dyes Pigm.* **2009**, *84*, 23–35; (e) Pu, S. Z.; Liu, W. J.; Liu, G. *Dyes Pigm.* **2010**, *87*, 1–9.
11. Data for **1o**: mp 103–104 °C; calcd for $C_{23}H_{17}F_6NOS$: C, 58.85; H, 3.65; N, 2.98. Found: C, 58.89; H, 3.72; N, 2.94; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.95 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-OCH_3$), 6.89 (d, 2H, *J* = 8.0 Hz, phenyl–H), 7.06 (s, 1H, thienyl–H), 7.25 (t, 1H, pyridyl–H), 7.41 (d, 2H, *J* = 8.0 Hz, phenyl–H), 7.49 (d, 1H, *J* = 8.0 Hz, pyridyl–H), 8.63 (d, 1H, *J* = 4.0 Hz, pyridyl–H); ^{13}C NMR(100 MHz, $CDCl_3$, ppm): δ 14.4, 18.3, 55.4, 114.4, 121.3, 124.1, 124.9, 126.1, 126.9, 133.5, 138.5, 141.0, 142.1, 147.7, 159.5; IR (KBr, ν, cm^{-1}): 738, 792, 825, 876, 951, 992, 1037, 1069, 1109, 1131, 1185, 1257, 1340, 1383, 1456, 1516, 1572, 1609, 1655, 1703, 2046, 2838, 2931, 2962, 3011, 3133, 3186, 3261, 3331, 3429, 3690. Data for **2o**: mp 117–118 °C; Calcd for $C_{22}H_{15}F_6NS$: C, 60.13; H, 3.44; N, 3.19. Found: C, 60.21; H, 3.39; N, 3.15; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.98 (s, 3H, $-CH_3$), 1.99 (s, 3H, $-CH_3$), 7.17 (s, 1H, thienyl–H), 7.23–7.30 (m, 2H, Ar–H), 7.36 (t, 2H, *J* = 7.5 Hz, Ar–H), 7.48 (d, 3H, *J* = 8.0 Hz, Ar–H), 8.63 (d, 1H, *J* = 4.3 Hz, pyridyl–H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.4, 18.3, 122.4, 124.2, 125.6, 127.9, 129.0, 132.9, 133.5 138.6, 141.9, 142.3, 147.8; IR (KBr, ν, cm^{-1}): 787, 882, 995, 1072, 1139, 1168, 1278, 1344, 1401, 1454, 1613, 1663, 2316, 2376, 2620, 3188, 3336, 3438, 3745. Data for **3o**: mp 176–177 °C; Calcd for $C_{23}H_{14}F_6N_2S$: C, 59.48; H, 3.04; N, 6.03. Found: C, 59.69; H, 3.00; N, 6.12; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.99 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 7.27 (t, 1H, pyridyl–H), 7.30 (s, 1H, thienyl–H), 7.50 (d, 1H, *J* = 8.0 Hz, pyridyl–H), 7.57 (d, 2H, *J* = 8.0 Hz, phenyl–H), 7.65 (d, 2H, *J* = 8.0 Hz, phenyl–H), 8.64 (d, 1H, *J* = 4.4 Hz, pyridyl–H); ^{13}CNMR (100 MHz, $CDCl_3$, TMS): δ 14.6, 18.3, 111.1, 118.6, 124.4, 124.7, 125.8, 132.8, 133.3, 137.4, 138.7, 139.8, 147.9; IR (KBr, ν, cm^{-1}): 738, 801, 832, 874, 993, 1068, 1137, 1191, 1276, 1341, 1379, 1472, 1511, 1629, 1749, 2226, 3136, 3230, 3305, 3377, 3511. Data for **1c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.89 (s, 3H, $-CH_3$), 2.08 (s, 3H, $-CH_3$), 3.87 (s, 3H, $-OCH_3$), 5.98 (d, 1H, *J* = 7.2 Hz, pyridyl–H), 6.25 (d, 1H, *J* = 5.4 Hz, pyridyl–H), 6.60 (s, 1H, thienyl–H), 6.93 (d, 2H, *J* = 8.8 Hz, phenyl–H), 7.53 (d, 2H, *J* = 8.4 Hz, phenyl–H), 7.60 (s, 1H, pyridyl–H); Data for **2c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.89 (s, 3H, $-CH_3$), 2.09 (s, 3H, $-CH_3$), 5.99 (d, 1H, *J* = 6.4 Hz, pyridyl–H), 6.27 (d, 1H, *J* = 9.6 Hz, pyridyl–H), 6.70 (s, 1H, thienyl–H), 7.42–7.45 (m, 3H, phenyl–H), 7.56–7.59 (m, 2H, phenyl–H), 7.63 (s, 1H, pyridyl–H); Data for **3c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.90 (s, 3H, $-CH_3$), 2.10 (s, 3H, $-CH_3$), 6.03 (d, 1H, *J* = 6.4 Hz, pyridyl–H), 6.29 (d, 1H, *J* = 5.6 Hz, pyridyl–H), 6.76 (s, 1H, thienyl–H), 7.64 (d, 1H, *J* = 2.4 Hz, phenyl–H), 7.66 (d, 1H, *J* = 2.4 Hz, phenyl–H), 7.68 (s, 1H, phenyl–H), 7.70 (s, 1H, phenyl–H), 7.72 (s, 1H, pyridyl–H).
12. Kawai, S.; Nakashima, T.; Atsumi, K.; Sakai, T.; Harigai, M.; Imamoto, Y.; Kamikubo, H.; Kataoka, M.; Kawai, T. *Chem. Mater.* **2007**, *19*, 3479–3483.
13. Li, Z. X.; Liao, L. Y.; Sun, W.; Xu, C. H.; Zhang, C.; Fang, C. J.; Yan, C. H. *J. Phys. Chem. C* **2008**, *112*, 5190–5196.
14. (a) Pu, S. Z.; Yang, T. S.; Xu, J. K.; Shen, L.; Li, G. Z.; Xiao, Q.; Chen, B. *Tetrahedron* **2005**, *61*, 6623–6629; (b) Fan, C. B.; Pu, S. Z.; Liu, G.; Yang, T. S. *J. Photochem. Photobiol., A* **2008**, *194*, 333–343; (c) Fan, C. B.; Pu, S. Z.; Liu, G.; Yang, T. S. *J. Photochem. Photobiol., A* **2008**, *197*, 415–425.
15. Kasatani, K.; Kambe, S.; Irie, M. *J. Photochem. Photobiol., A* **1999**, *122*, 11–15.
16. (a) Yumoto, K.; Irie, M.; Matsuda, K. *Org. Lett.* **2008**, *10*, 2051–2054; (b) Liu, H. H.; Chen, Y. *J. Mater. Chem.* **2009**, *19*, 706–709.
17. Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876.
18. Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309.
19. (a) Yun, C.; You, J.; Kim, J.; Huh, J.; Kim, E. *J. Photochem. Photobiol., C* **2009**, *10*, 111–129; (b) Pu, S. Z.; Yang, T. S.; Xu, J. K.; Chen, B. *Tetrahedron Lett.* **2006**, *47*, 6473–6477.
20. Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, 1358–1359.
21. Pu, S. Z.; Miao, W. J.; Cui, S. Q.; Liu, G.; Liu, W. J. *Dyes Pigm.* **2010**, *87*, 257–267.
22. (a) Chen, B. Z.; Wang, M. Z.; Wu, Y. Q.; Tian, H. *Chem. Commun.* **2002**, 1060–1061; (b) Tian, H.; Chen, B. Z.; Tu, H. Y.; Müllen, K. *Adv. Mater.* **2002**, *14*, 918–923.