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Photochromism of Asymmetrical Diarylethenes with a Pyrrole Unit: Effects of Aromatic Stabilization Energies of Aryl Rings

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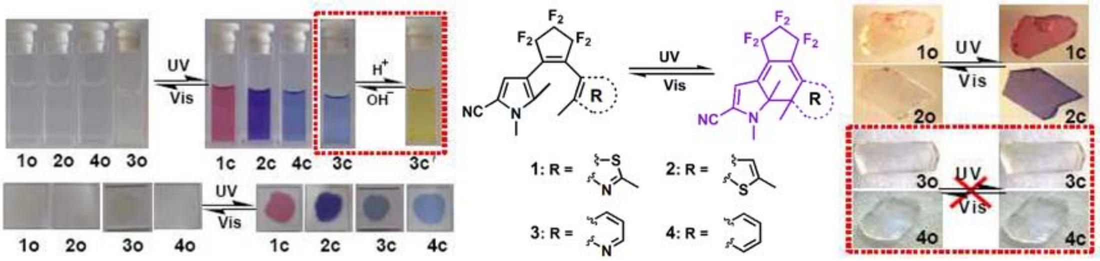
ABSTRACT



Four novel asymmetrical diarylethenes with a pyrrole and a variable aryl unit have been synthesized. Their crystal structures and photochromic performance were systematically studied to elucidate the effects of the aromatic stabilization energy (ASE) of aryl units. Experimental results showed that their thermal stability as well as cyclization quantum yield, photoconversion ratio, fluorescence modulation efficiency, and fatigue resistance exhibited a strong correlation with ASE.

Photochromic materials have attracted considerable attention due to their wide applications in optical memory media and photo-optical switching devices.[1] Among various photochromic materials, the diarylethenes with heteroaryl groups are one of the most promising candidates for their excellent thermal stability and photochemical reactivity.[2] The structural diversity originating from a variation of a bridge and two aryl units offer a unique chance for chemists to expand the library of diarylethenes and seek the ones with ideal photochromic properties.

In the past several decades, significant advancement has been made in the synthesis of novel diarylethene structures.[3] It has been revealed that the nature of the aryl ring imposes significant influence on their properties.[4] Based on the study of a series of symmetrical diarylethenes with two phenyl, pyrrolyl, furyl, and thienyl groups, Irie pointed out that aromaticity of the aryl groups, which well correlates with the ground-energy difference of the open- and

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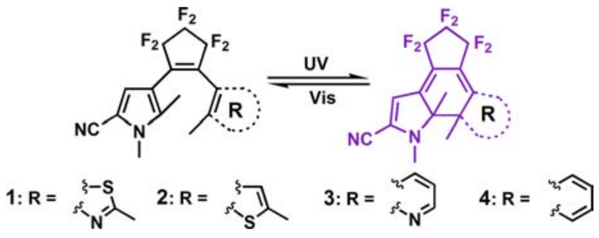
closed-ring forms, is the key molecular property that determines the thermal stability of the closed-ring isomers.[1a] While the diarylethenes with two thiophenes, furans, and thiazoles exhibit excellent thermal stability, the ones with two indoles, pyrrols, and benzenes are thermally unstable. It was concluded that introduction of heteraryl groups with low aromatic stabilization energy (ASE) is the design principle of thermally irreversible diarylethenes. But the effects of the ASE of aryl units on more complicated unsymmetrical diarylethenes, especially those containing aryl groups of both high and low aromatic stabilization energies, remain unclear.

Analysis of our previous research on novel asymmetrical perfluorodiarylethenes indicated that the heteroaryl groups with low aromaticity stabilization energies (e.g., thiazyl and thienyl groups) affected not only thermal stability but also, more importantly, certain photochromic properties of asymmetcial diarylethenes, such as cyclization quantum yield, photoconversion ratio, and fluorescence modulation efficiency.[5] For instance, a hybrid of a thiazole and benzene possessed significantly improved thermal stability and photochromic features compared with the diphenylethene, which is unreactive to photoirradiation.[5a] Similarly, when one pyrrol unit of thermally unstable dipyrrolylethene was replaced with a phenylthiophene, the new diarylethene exhibited much better properties.[4d] However, the effects of the aromatic stabilization energy of aryl moieties on the photochromic performance of asymmetrical diarylethenes has not been systematically investigated.

In this research work, we designed and synthesized four novel asymmetrical pyrrole-containing diarylethenes, which have a thiazole, thiophene, pyridine, and benzene moiety, respectively (Scheme 1). Their photochromic properties in different states and crystallographic structures were studied and compared to elucidate the effects of the ASE of aryl rings on the thermal stability and photochromism of asymmetrical diarylethenes.

Scheme 1. Photochromism of Diarylethenes **1o**−**4o**



Diarylethenes **1o**−**4o** were synthesized according to known procedures[4d] and characterized by NMR, elemental analysis, and IR spectroscopy. All four diarylethenes cyclized with notable solution color change upon UV irradiation. The thermal stability of the closed-ring isomers (**1c**−**4c**) was evaluated in ethyl acetate at different temperatures (Figure S1, Supporting Information (SI)). According to Irie's and Fishtik's research,[1a,6] the aromatic stabilization energy of the aryl units increases in order of thiazyl < thienyl (4.7 kcal/mol) < pyrrolyl (13.8 kcal/mol) < pyridyl < phenyl (27.7 kcal/mol). As shown in Figure 1, the thermal cycloreversion rates of **1c**−**4c** at 293 K accelerated, when ASE of the variable aryl unit is elevated. This result indicated that Irie's design principle of thermally irreversible diarylethenes is very applicable to asymmetrical ones.

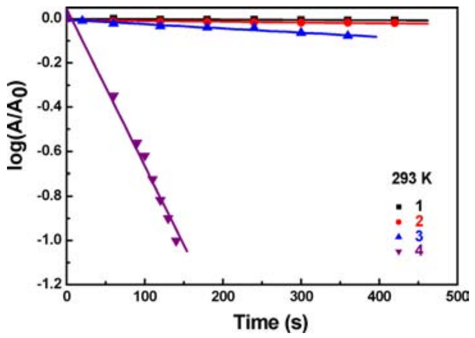


Figure 1. Thermal fading of **1c**−**4c** at 293 K in ethyl acetate.

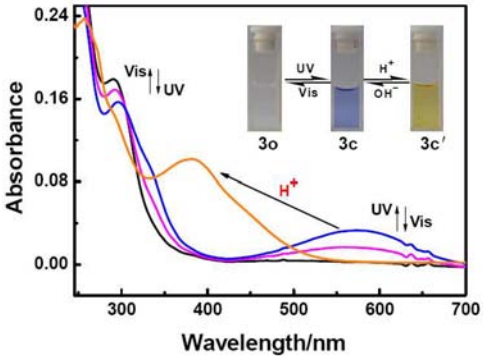


Figure 2. Absorption spectrum and the color changes of diarylethene **3** with stimulation of acid/base and light in hexane (2.0×10^{-5} mol L^{-1}) at room temperature.

The absorption spectrum of **1o**−**4o** in both hexane and PMMA films were recorded with a UV/vis spectrometer (Figure S2, SI). The absorption maxima of both open-ring and closed-ring isomers of **1**−**4** were summarized in Table 1. As shown in Figure 2, **3o** exhibited a sharp absorption peak at 291 nm in hexane corresponding to a $\pi \rightarrow \pi^*$ transition.[7] Upon irradiation with UV light, a new visible absorption band centered at 573 nm emerged due to the formation of closed-ring isomer **3c**, with a solution color change from colorless to blue. The blue color was bleached by irradiation with visible light ($\lambda > 450$ nm), and the absorption spectrum

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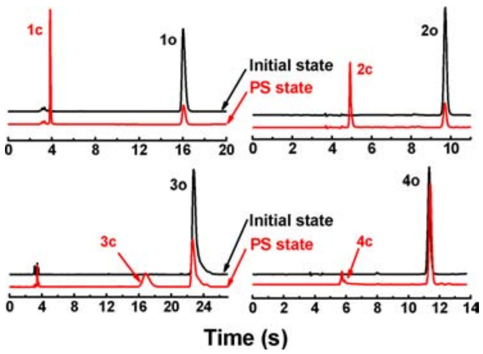

Figure 3. Photoconversion ratios of **1**−**4** in the photostationary state in hexane by HPLC analysis.

returned to the initial state of **3o**. Furthermore, addition of trifluoroacetic acid to the solution of **3c** produced the protonated **3c′** whose absorption maximum shifted from 573 to 382 nm, accompanied with a notable solution color change from blue to pale yellow.

As shown in Table 1, cyclization quantum yields ($\Phi_{\text{o-c}}$) and photoconversion ratios in the photostationary state (PR) of **1**−**4** showed trends that were similar to their thermal stability. The $\Phi_{\text{o-c}}$ of **1**−**4** decreased (0.15 for **1**, 0.13 for **2**, 0.065 for **3**, and 0.041 for **4**) incrementally with the ASE of the variable aryl group. In the photostationary state, the photoconversion ratios of **1**−**4** from the open-ring to closed-ring isomers were determined by HPLC analysis with values of 79% for **1**, 78% for **2**, 48% for **3**, and 16% for **4**, which is in accordance with the increasing order of the ASE of the variable aryl rings (Figure 3). It is noteworthy that when the asymmetrical diarylethenes are composed of both low and high ASE aryl units, their $\Phi_{\text{o-c}}$ and PR are significantly better than those with two high ASE aryl rings.

Table 1. Photochromic Parameters of Diarylethenes **1**−**4** in Hexane (2.0×10^{-5} mol L^{-1}) at Room Temperature

	$\lambda_{\text{c,max}}$/nm[a] (ε/L mol^{-1} cm^{-1})	$\lambda_{\text{c,max}}$/nm[b] (ε/L mol^{-1} cm^{-1})	Φ[c]		
			$\Phi_{\text{o-c}}$	$\Phi_{\text{c-o}}$	PR[d] (%)
1	243 (2.36×10^4)	509 (4.36×10^3)	0.15	0.23	79
2	238 (2.59×10^4)	553 (4.39×10^3)	0.13	0.14	78
3	291 (8.95×10^3)	573 (1.65×10^3)	0.065	0.30	48
4	290 (1.26×10^4)	572 (1.08×10^3)	0.041	0.27	16

[a] Absorption maxima of open-ring isomers. [b] Absorption maxima of closed-ring isomers. [c] Quantum yields of cyclization reaction ($\Phi_{\text{o-c}}$) and cycloreversion reaction ($\Phi_{\text{c-o}}$). [d] Photoconversion ratios of diarylethenes **1**−**4** in the photostationary state.

Single crystals of **1o**−**4o** were obtained via slow evaporation of their solutions and subjected to X-ray diffraction analysis (Figure S3 and Table S1, SI). Their ORTEP drawings and photochromic processes in the crystalline phase are shown in Figure 4. **1o** and **2o** were packed in *anti*-parallel conformations, and the distances between the two reactive carbons were shorter than 4.2 Å (3.589 Å for **1o** and 3.628 Å for **2o**, Table S2, SI). As expected, the crystals of **1o** and **2o** exhibited a notable color change upon irradiation with 297 nm light.[8] In contrast, exposure to visible light entirely bleached the colors of **1c** and **2c**. The photochromism of **1** and **2** was highly consistent in the crystalline phase even after 200 repeated cycles, which is favorable for applications in optoelectronic devices.[9] Though the crystals of **3o** and **4o** were also packed in *anti*-parallel conformations and the distances between bond-forming carbons were 4.054 Å for **3o** and 3.829 Å for **4o**, they still showed no photochromism. The above results showed that other than the conformation and distance factors, the heteroaryl unit with low ASE played a pivotal role in the photochromism of asymmetrical diarylethenes in the crystalline phase. Our previous research on benzene-based diarylethenes is also consistent with this point.[10] When both aryl units are of high ASE, such as diphenylethene and **4o**, their crystals showed no photoreactivity. When aryl units in the diarylethene system were a low ASE thiophene and a high ASE pyridine, their crystals exhibited excellent photochromic activity.[5b]

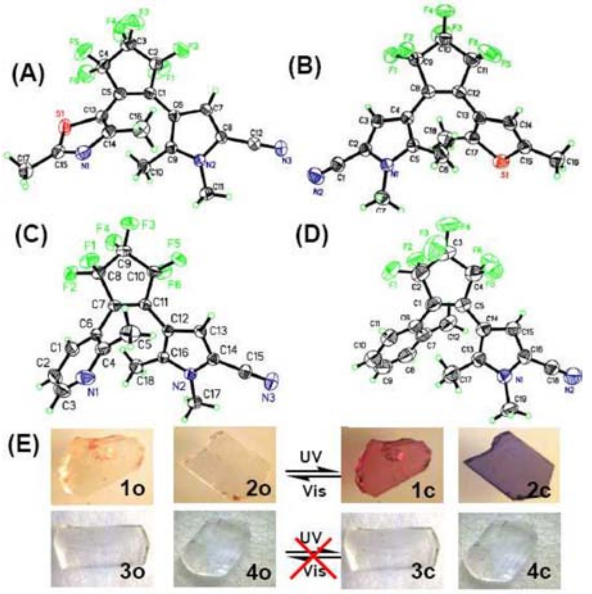

Figure 4. ORTEP drawings (ellipsoids are drawn at 30% level): (A) **1o**; (B) **2o**; (C) **3o**; (D) **4o**; (E) photographs demonstrating their photochromic processes in the crystalline phase.

The fluorescence spectra of **1o**−**4o** (Figure 5) and the emission intensity changes induced by photoirradiation

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(Figure S4, SI) were measured in hexane and PMMA films. The parameters of their fluorescence behaviors (Table 2) showed that **1o** is the best in terms of emission intensity and fluorescence quantum yield, **2o** and **3o** are of medium level, and **4o** has the lowest values in both hexane and PMMA films. The results suggested that introduction of a nitrogen atom to the variable aryl ring (**1o** vs **2o**, **3o** vs **4o**) has a remarkable impact on their fluorescence performance. Due to the fact that the fluorosecence change of diarylethene upon UV irradiation is dependent on photoconversion ratio,[11] the fluorescence modulation efficiency (η) of **1**–**4** should also correlate with the ASE of the variable heteroaryl unit. The η values determined for **1**–**4** in both hexane and PMMA films demonstrated this hypothesis well. The fluorescence modulation efficiencies of the diarylethenes with at least one low ASE unit (74/79% for **1o**, 69/69% for **2o**) are significantly higher than those of the diarylethenes with two high ASE units (21/30% for **3o**, 16/21% for **4o**).

In addition, the fatigue resistance of **1**–**4** was also determined (Figure S5, SI). In PMMA films, the diarylethenes with one low ASE unit exhibited much better fatigue resistance (93% for **1o** and 91% for **2o** after 150 repeat cycles) than those with two high ASE units (84% for **3o** and 80% for **4o** after 150 repeat cycles) due to the lowered ground state energy of the closed-ring isomers. When exposed to air in the solution phase, the fatigue resistance of **1**–**4** was remarkably reduced, which could be possibly ascribed to the presence of a pyrrole unit in these compounds.[12]

In summary, four novel diarylethenes with a pyrrole unit and a variable aryl unit have been synthesized to study the effects of ASE of aryl rings on their thermal and photochromic behaviors. Experimental results showed that the thermal stability of **1**–**4** correlates with the ASE of the variable aryl rings. Thermal fading of the closed-ring isomer was significantly suppressed by the introduction of a low ASE aryl unit, which is in good accordance with Irie's principle. Furthermore, their photochromic properties closely related to the ground-energy difference of the open- and closed-ring isomers, such as cyclization quantum yield, photoconversion ratio, photochromism in the crystalline phase, fluorescence modulation efficiency, and fatigue resistance, also exhibited a similar dependence on ASE. Although a more detailed investigation on more structural analogs is required to completely elucidate the structure–properties relationship for diarylethenes, the results of our research provided new insights into the effects of aryl moieties, which is valuable for the design of novel asymmetrical diarylethenes with ideal thermal and photochromic properties.

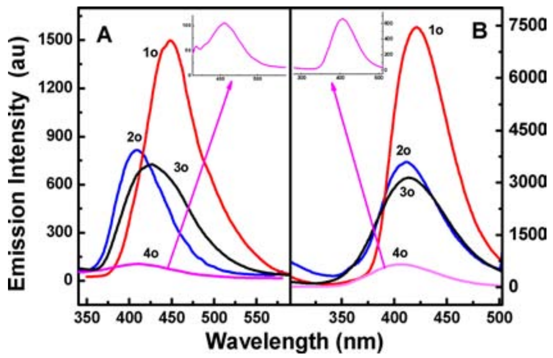

Figure 5. Fluorescence emission spectra of diarylethenes **1o**–**4o** in both hexane (A) and PMMA films (B) at room temperature.

Table 2. Fluorescence Parameters of Diarylethenes **1**–**4** in Both Hexane (2.0×10^{-5} mol L^{-1}) and PMMA Films

	hexane			PMMA			
	λ_{em}[a]	I_f[b]	η[c] (%)	λ_{em}	I_f	η (%)	Φ_f
1o	448	1500	74	421	7449	79	0.085
2o	409	817	69	408	4088	69	0.054
3o	426	725	21	414	3145	30	0.039
4o	411	105	16	406	657	21	0.031

[a] Emission peak. [b] Emission intensity. [c] Fluorescence modulation efficiency in the photostationary state.

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Supporting Information Available. Experimental procedures, characterization data, and CIF files for **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.