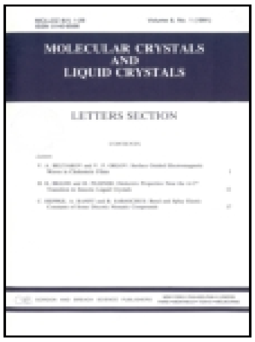

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Investigation of a Photochromic Diarylethene with Electron-acceptor Attached

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In this contribution, an electron acceptor attached diarylethene derivative was synthesized and fully characterized. The photochromic behavior was investigated in THF. Under exposure of UV and visible light cycles, the solution color can be switched between colorless and yellow smoothly. Fatigue resistance measurements could be repeated 50 times with an acceptable degradation. Due to the electron acceptor attached to the framework of diarylethene, the photo- and thermal-stability were enhanced both. A full-photo mode switch can be established based on the well-defined states by external excitation. The molecular structures of ring-open and ring-closed form were optimized by Dmol^3. The distance between photocyclizing atoms in aptiparallel conformation meets the requirement for photochromic reaction. And the calculated absorption wavelengths were also in agreement with the experimental values.

Keywords: diarylethene; photochromism; fatigue resistance; photo- and thermal-stability; photocyclizing atoms

Introduction

Small functional molecules play vital roles in material science and bio-technology development. It has been well documented and developed toward the application in molecular logic [1], emission materials [2–6], fluorescent sensors and bioprobes [7–12], photoelectronic conversion devices [13–16], and optical switches [17–20]. Optical switches are powerful tools for signal conversion in molecular level, which is potential for super massive information storage media, biomedical signal/image processing, and microprocessors. Among various types of optical switches, diarylethenes (**DAE**s) is the promising candidate due

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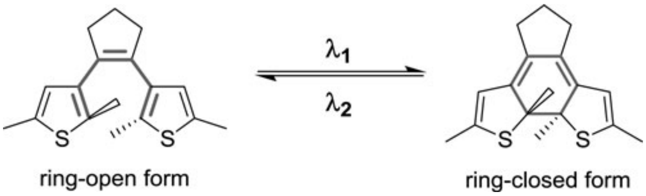
to its high quantum yield in conversion between bistable state, favorable photo-thermal stability, and highly fatigue resistance [21].

The framework of **DAE**s possesses a hexatriene framework, with which a reversible conrotatory 6π-cyclization photocyclization reaction can proceed efficient upon suitable light stimuli (Scheme 1). Up to now, the rational design of symmetric or asymmetric **DAE**s has been fully development and investigated by modifying the aromatic rings, mainly the thiophene rings [22]. In addition, it is should not to be neglected that the central ethane bridges is also a key element for the versatility the **DAE**s architectures. To date, the central bridge units of most **DAE**s varied but limited to five-membered cyclopentene unit or its strong electron-withdrawing analogues, such as perfluorocyclopentene, maleic anhydride, maleic imide, and other five membered heteroaromatics. Six membered aromatic ring also can be an alternative selection as the central bridge unit, such as cyclohexene, 1,10-phenanthroline, benzothiadiazole, and naphthalimide units. However, highly degree of aromaticity of the six-membered central bridge ring facilitates the undesirable thermal back reaction in the dark as a result of the significant loss of aromatic stabilization energy upon photocyclization form the open to the closed isomers. Therefore, low aromaticity of the central ethene bridge unit (five-membered central bridging) is expected to lead to a higher thermal stability of the closed isomers. In addition, five-membered central bridging ethene units can enhance the quantum yield in its closed-ring isomer and longer absorption. Here, we report a **DAE** derivative with a strong electron-withdrawing group attached and investigate its photo-physical properties.



Scheme 1. Photochromic reaction of diarylethenes.

Experimental

General Procedures and Materials

The solvents used in the reaction were carefully dried according to the standard procedure and stored over 4Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC. (South Korea) and used without further purification. All the synthesized compounds were routinely characterized by TLC and NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

^{1}H and ^{13}C NMR Spectroscopy

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in $CDCl_3$. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz.

Mass and High Resolution Mass Spectra (HRMS)

The mass spectra measured on a LC-MS (Waters UPLC-TQD) mass spectrometer. High resolution mass spectra (HRMS) were measured on a Brucker microOTOF II Focus instrument.

UV-Vis and Emission Spectra

The absorption spectra were measured with a PERSEE TU-1900 and an Agilent 8453 spectrophotometer. Emission spectra were measured with Shimadzu RF-5301PC fluorescence spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds (2×10^{-3} M) was prepared in THF, and a fixed amount of these concentrated solutions were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.

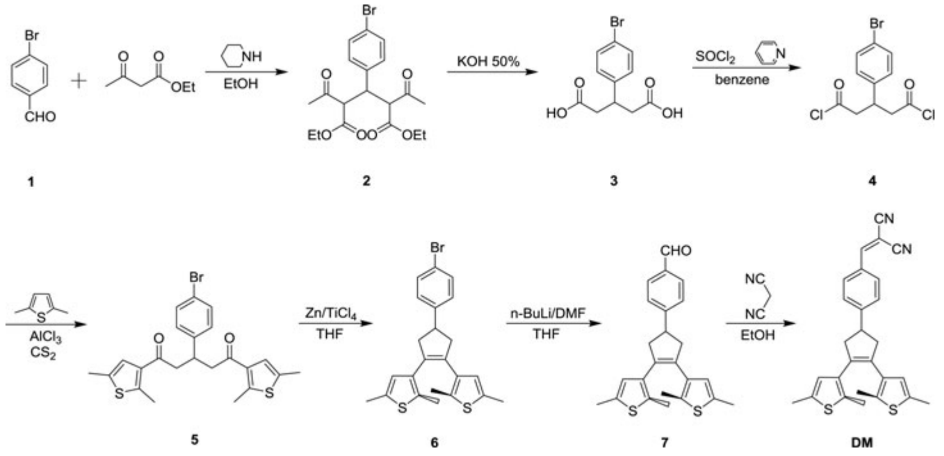
Theoretical Calculations

For the theoretical study of excited state photo-physics of the compound, the *DMol*^{3} program packaged in *Material Studio* (Accelrys Software Inc., United States) was used [23, 24]. The ground state geometries and the frontier molecular orbital of the compound were calculated using the density function theory (DFT) with the B3LYP hybrid functional and the double numerical plus *d*-functions (DNP) atomic orbital basis set.

Synthesis

The synthesis of target diarylethene, 2-(4-(3,4-bis(2,5-dimethylthiophen-3-yl)cyclopent-3-en-1-yl)benzylidene) malononitrile (abbreviated as **DM**), derivative was outlined in Scheme 2. The total synthesis was started from 4-bromobenzaldehyde (**1**), a very cheap commercial chemical. Firstly, 4-bromobenzaldehyde was condensed with ethyl acetoacetate at room temperature with piperidine as catalyst and gave **2**. β-arylglutaric (**3**) was obtained by hydrolysis under 50% KOH aqueous solution. Refluxing **3** and sulfoxide chloride in benzene gave diacid chloride (**4**). Acylation of 2,5-dimethylthiophene with **4** yielded 1,5-diketone (**5**). Diarylethene backbone was formed by a ring-closure reaction of 1,5-diketone via McMurry coupling reaction, yielding **6**. The active Br atom of **6** can be transformed to aldehyde (**7**) with *n*-BuLi/DMF. The totally synthesis form **1** to **7** is based on our previous experience [25].

7 (80 mg, 0.2 mmol) and malononitrile (20 mg, 0.3 mmol) dissolved in toluene (20 mL). One drop of piperidine and a catalytic amount of acetic acid were added to the above mixture. The mixture was refluxed until **7** disappeared on TLC plate. The mixture was poured into dichloromethane 50 mL. It was washed with water (20 mL × 3). The organic layers were combined, dried over anhydrous $MgSO_4$, and the solvent was evaporated in vacuum. The crude product was purified by column chromatography (Silica gel, EtOAc/hexane) afforded **DM** (67 mg, 76%).



Scheme 2. Synthesis of 2-(4-(3,4-bis(2,5-dimethylthiophen-3-yl)cyclopent-3-en-1-yl)benzylidene) malononitrile (**DM**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.74 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 6.43 (s, 2H), 3.69 (m, 1H), 3.26 (dd, J = 8.0 Hz, 2H), 2.86 (dd, J = 8.0 Hz, 2H), 2.36 (s, 6H), 1.89 (s, 6H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 159.5, 155.3, 135.4, 134.4, 132.8, 132.7, 131.2, 128.9, 128.1, 125.7, 113.9, 112.8, 81.4, 46.0, 42.6, 15.1, 14.1. EI$^+$/MS m/z 440[M]$^+$. HRMS calcd for $C_{27}H_{24}N_2S_2$ 440.1381, found 440.1384.

Result and Discussion

The photochromic behavior of **DM** was investigated in THF solution with the concentration 4.5×10^{-5} M at room temperature. The absorption change was shown in Figure 1a irradiated with 254 nm (hand-held UV lamp, 8W). Before irradiation with 254 nm light, the longest absorption maximum was observed at 254 nm ($\varepsilon = 2.4 \times 10^4$ M^{-1}cm^{-1}), which was exactly match to the hand-held UV lamp (254 nm), generally used in the lab for TLC detection. Together with the shoulder peak (287 nm, $\varepsilon = 6.6 \times 10^3$ M^{-1}cm^{-1}), all the absorption bands were shorter than 325 nm, locating in the invisible region. Therefore, the solution color was colorless. Upon irradiation with 254 nm UV light, a new absorption band appeared between 400 and 500 nm, centered at 447 nm. At the same time, the 254 nm absorption decreased accompanied with the increase of 447 nm absorption. At last, a plateauing of the 447 nm band at 150s of 254 nm irradiation was observed, corresponding to the photostationary state (PSS, A = 0.126) (Figure 1b). The solution color changed from colorless to yellowish. Irradiating with visible light (broad-band light greater than 400 nm), the absorption band in the visible (400-500 nm) decreased until the totally disappearance of this absorption band. The resulting yellowish solution color decolorized to colorless. Obvious isosbestic points ($\lambda = 236, 272$ nm) were found and suggest the existence of only two species in solution, which in this case are the ring-open and ring-closed isomers of **DM**. Based on the character mentioned above, a full-photo mode switch could be established according to the well-distinguished states by external excitation.

The photochromic reaction upon alternating irradiation of UV/Vis was shown in Scheme 3. Generally, the absorption of the ring-open form appeared at a shorter wavelength, while that of the ring-closed form would shift to longer wavelength due to the

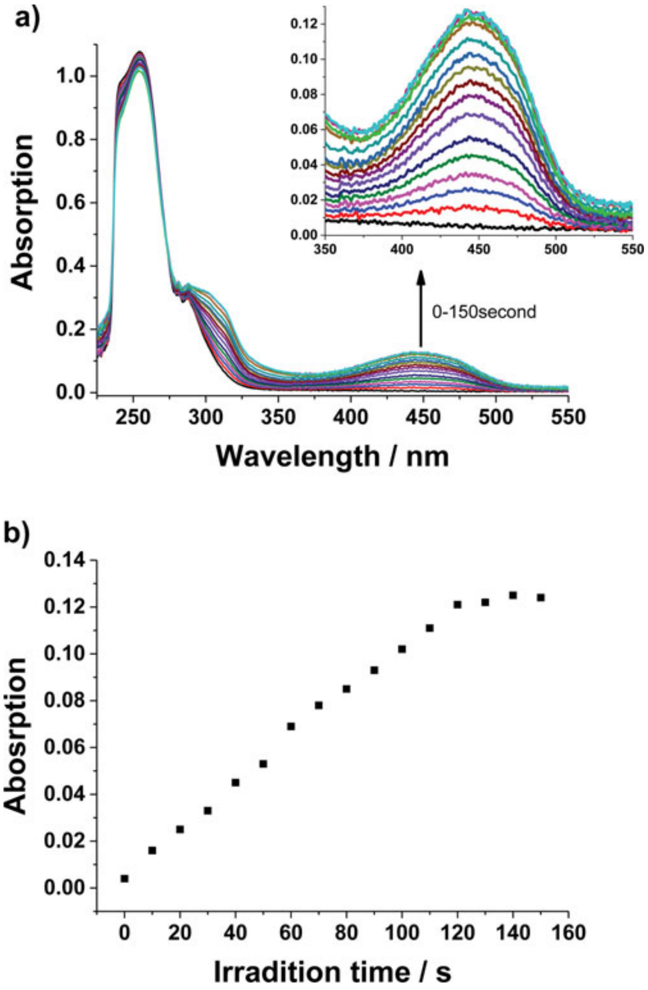
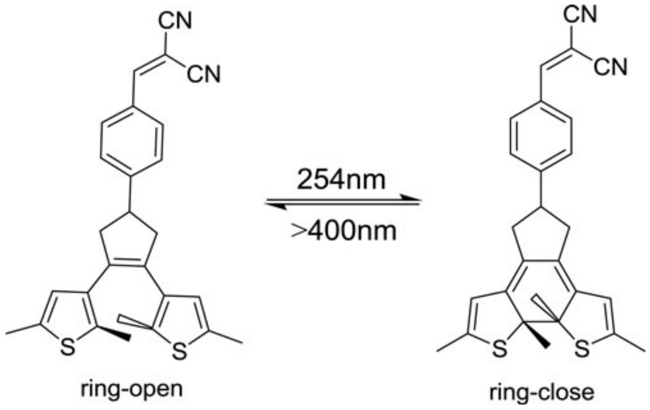


Figure 1. a) Absorption change of **DM** in THF (4.5×10^{-5} M) upon irradiation with 254 nm light. Insert: Enlarged absorption change of **DM** in the 350–500 nm. B) Increase of absorbance at 447 nm with respect to irradiating time.

delocalized π-electrons. In theory, the dithienylethene molecule has two conformations with the two thiophene rings in mirror symmetry (parallel conformation) and in C_2 symmetry (anticonformation). The photoisomerization can only proceed from the antiparallel confirmation. In general, the population ration of the two conformations in solution is 1:1. According to the well-defined isosbestic point, the relative conversion of photocyclization was determined to be 0.33 at the photostationary state [26].

The fatigue resistance of **DM** was investigated at room temperature. In THF, **DM** was irradiated alternatively with 254 nm and visible light (<400 nm), respectively. In each cycle, PSS state was reached with 254 nm irradiation and then bleached to colorless completely. As shown in Figure 2a, the coloration/decoloration could repeat 50 cycles with 17% degradation, indicating an excellent fatigue resistance. Photo-stability measurements were performed under the UV light exposure. A gradual decrease of absorbance at 272 nm



Scheme 3. Photochromic reaction of **DM**.

was observed indicating the degradation of **DM** upon exposure to UV light (Figure 2b). Totally, 19% of **DM** degraded after 10h hour's exposure of UV light, corresponding to moderate photo-stability. Thermal stability of the ring-closed forms was also investigated with the temperature ranged from room temperature to 50°C in the dark. Figure 2c shows the thermal induced absorption decrease at 447 nm. In the dark, the ring-closed form is stable and the solution color can maintain more than one day. With the temperature rising, the thermal induced cycloreversion rate speeds up. The solution color decolorized to colorless rapidly, reverting back to the ring-open form. Therefore, the ring-closed form is not only visible light-sensitive but also thermo-sensitive.

To better comprehend the geometrical, electronic, and optical properties of **DM**, we undertook a comprehensive computational investigation on the platform of Material Studio. To reduce the run times in the first instance, the ground-state energy-minimized structures were calculated using DFT and LDA/DN basis set. Further refinement and optimization on structures were then undertaken using DFT/B3LYP/DNP basis set.

Figure 3 shows the optimized structure of **DM**. Due to the conformation requirement, only the geometric structure of antiparallel conformation was optimized. A key factor for the reactivity of conrotatory cyclization is the distance between the photocyclizing carbon atoms. According to the optimized structure, the distance between the two carbon atoms involved in the cyclization is 3.649Å, which is meet the requirement for photochromism (distance less than 4.2 Å) [27, 28]. With the distance of photocyclizing carbon atoms larger than 4.2 Å, the photochromic reaction will be suppressed completely. The absorption spectra of ring-open and ring-closed form for **DM** were also calculated based on the optimized ground state (Figure 4). For ring-open form of **DM**, the transition HOMO→LUMO is possible with the oscillator strength (*f*) 0.547, corresponding to 272 nm absorption. It is in agreement with experimental value (254 nm). The molecular ortibals (MO) topologies of the ring-open form (Figure 4a) indicates that the HOMO and LUMO have π shapes. In HOMO of ring-open form, the electron density distributed over the photochromic core totally. Contrary to the HOMO distribution, the LUMO distribution of ring-open form transferred to benzylidenemalononitrile unit due to the electron-withdrawing character. For the ring-closed form, the electron transition is dominated by HOMO-1→LUMO+1 with the oscillator strength (*f*) 0.823. Once the ring-closed, the energy gap for electron transition was lowered to 2.77eV ($\Delta E_{\text{HOMO-1}\rightarrow\text{LUMO+1}}$) and led to the absorption band shift to longer wavelength. The calculated absorption wavelength of ring-closed form is identical to that

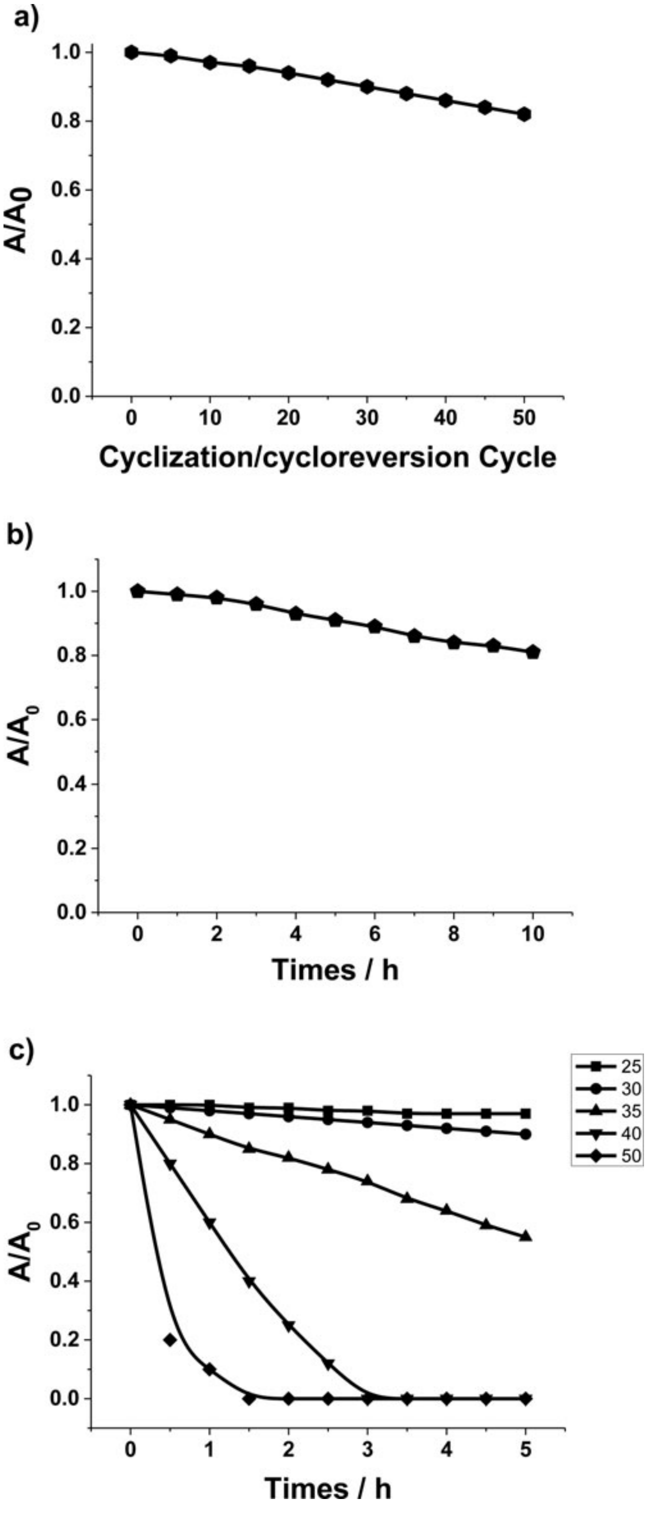


Figure 2. a) Fatigue resistance of **DM** in THF at room temperature. b) Photo-stability of **DM** upon exposure to UV light. c) Absorption change versus time with the temperature ranged from 25–50°C.

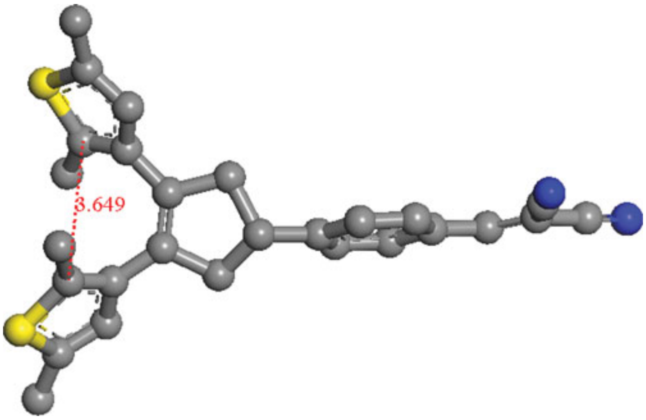


Figure 3. Optimized structure of **DM** and the distance between reactive carbon atoms.

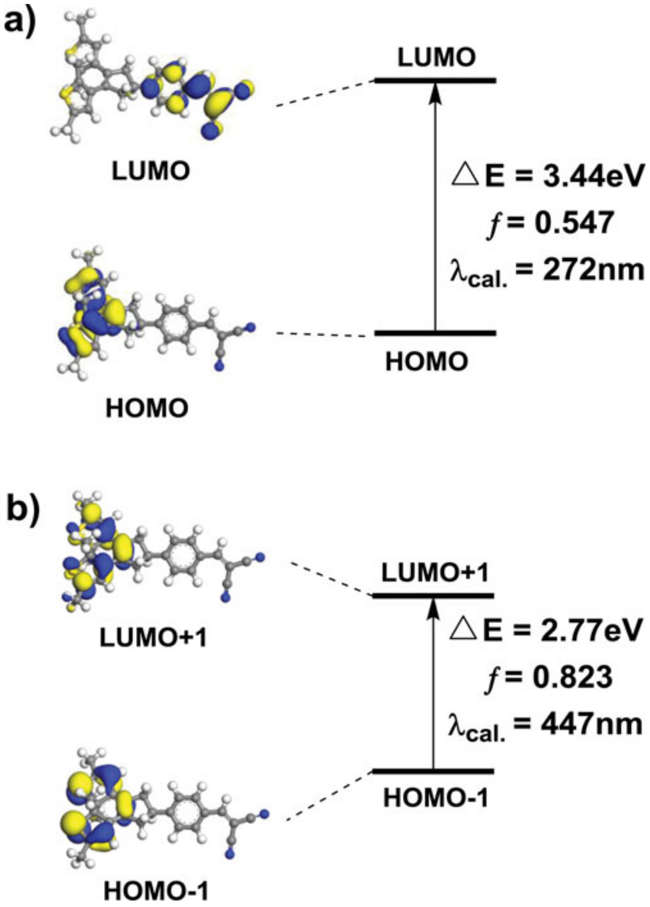


Figure 4. Frontier orbitals for **DM**. a) ring-open form; b) ring-closed form.

of the experimental value (447) mentioned above. In addition, the electron density gathered around in the photochromic core in the HOMO and LUMO distribution. By comparison of the MO topologies between the ring-open and ring-closed form, the introduction of strong electron acceptor unit enhanced the sensitivity toward 254 nm light. It also enhanced the fatigue resistance of **DM** in solution.

Conclusions

In summary, a photochromic diarylethene derivative was designed and synthesized, and was fully characterized with the NMR and mass spectra. Photochromic behavior was investigated in THF solution in details. The longest absorption maximum of ring-open form of **DM** was estimated to be 254 nm, which corresponds to our generally used hand-held UV lamp. Upon irradiation with 254 nm light, the solution color changed from colorless to yellowish. Visible light irradiation could decolorize the yellowish solution to the original state. Under cycles of UV and Visible light exposure, the coloration/decoloration cycles could be repeated 50 times with an acceptable degradation, attesting the excellent fatigue resistance. Photo- and thermal-stability measurements show that **DM** in THF is stable at room temperature. The ring-closed form of **DM** is thermal sensitive. Temperature rising will lead to the cycloreversion accelerated. Based on the optimized antiparallel conformation, the distance between the photocyclizing carbon atoms was estimated and shorter than the threshold (4.2 Å), which is critical to the photochromic reactivity of diarylethenes. The calculated MOs demonstrated the inherent relationship between fatigue resistance/photo-/thermal-stability and the attaching of electron acceptor. Based on the principles, newly designed functional diarylethenes were synthesized in progress.

Acknowledgments

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