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Synthesis, crystal structure and photochromism of new diarylethenes with a benzene moiety



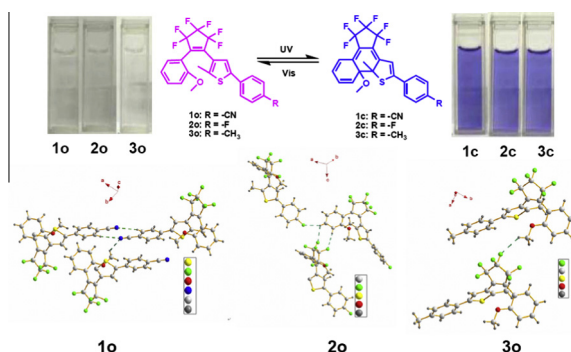
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HIGHLIGHTS

- Three new diarylethenes with thiophene and benzene moieties were synthesized.
- Their crystal structures and photochromic features were investigated systematically.
- Computational studies were performed.

GRAPHICAL ABSTRACT



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ABSTRACT

Three unsymmetrical diarylethenes with both thiophene and benzene moieties were synthesized. Their crystal structures and photochromic features were investigated systematically to elucidate the substituent effects of the terminal phenyl group on photochromism. Computational studies were performed to provide further insight into their frontier molecular orbitals and spatial distributions of electronic density. Each compound exhibited favorable photochromism in hexane and functioned as notable fluorescent photo-switches with fluorescence quenching efficiency of ~96% induced by the intensity change of UV/vis light. Among the three diarylethenes, the cyano group on the terminal phenyl group significantly decreased the distance of the two reactive carbon atoms and strengthened the intermolecular hydrogen bond stacking interactions, resulting in improved stability in crystal state. Furthermore, it exhibited a red-shifted absorption maximum, an enhanced molar absorption coefficient, cyclization quantum yield, and fluorescence quantum yield in solution.

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Introduction

In the past several decades, various types of photochromic compounds have been synthesized for applications in multifunctional optoelectronic fields [1,2], such as optical switch devices, optical data storage [3–9], fluorescence sensing of specific ions [10–13], photo-switchable probe for imaging living cells [14], organic

memory [15], and solar cells [16]. Diarylethene derivatives are the most promising candidates for such applications because of their excellent photochromic characteristics [17]. In addition, the photochromic properties of diarylethene can be predictably improved by structure variation to meet a special functional requirement.

Two structural features strongly influence the photochromic properties of diarylethene, including the heteroaryl moieties and the terminal aryl moieties. There are a number of reports on the effect of the heteroaryl moieties [17,18–22]. For example, diarylethenes bearing thiophene/benzothiophene moieties exhibited

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notable thermal stability and remarkable fatigue resistance [23–25], whereas diarylethenes bearing two pyrrole groups were thermally unstable and returned to the open-ring isomers even in the dark [26]. It was found by our group that diarylethenes bearing both thiazole and benzene moieties had poor fatigue resistance with 88% of closed ring isomers destroyed after 10 repeat cycles [27]. This result was in agreement with the explanation that the heteraryl groups of aromatic stabilization energy (ASE) level determined the thermal stability of the closed-ring isomers [17,22]. However, diarylethene with thienyl group, which has low ASE, and the other aromatic heterocyclic moieties also exhibited good photochromic properties [28–34]. For instance, diarylethenes bearing thiophene and isoxazole moieties exhibited remarkable photochromism which functioned as a fluorescent photoswitch in solution. Diarylethenes bearing both thiophene and benzofuran showed good thermal stability as well [31,32]. Another example is diarylethene containing thiophene moiety and six-membered pyridine unit, which exhibited good photochromism both in solution and in the crystalline phase by permitting the pyridine unit to participate in the photoinduced cyclization reaction [33]. In our previous research, it was found that diarylethenes based on thiophene moiety and a hybrid structure of six-membered naphthalene exhibited good photochromism and notable fatigue resistance, which was applied as fluorescent photoswitches in solution [34]. Based on these results, it is postulated that unsymmetrical diarylethenes containing thiophene moiety of low ASE should be able to effectively improve the properties of photochromism.

The effect of the other structural feature, i.e. the electron-donating/withdrawing substituents at the terminal groups in the aryl moieties, has also been studied, including its impact on the diarylethene absorption peaks, cyclization and cycloreversion quantum yields, and the fluorescence emission peaks [35,36]. Jeong et al. reported that the introduction of acetyl groups at the 6,6'-positions and heptyl groups at the 2,2'-positions in disulfonyl diarylethene gave rise to an increase in the fluorescence quantum yield and fluorescence lifetime [37]. In the study of a series of diarylethenes containing different electron-donating/withdrawing groups, it was found that the electron-donating groups significantly increased the cyclization quantum yield, depressed the cycloreversion quantum yield, red-shifted the emission peak, and decreased the fluorescence quantum yield in solution; while the electron-withdrawing groups functioned as an inverse action for these diarylethene derivatives [28–32].

So far, there have been a few examples of photochromic diarylethenes bearing thiophene moieties and aryl moieties [38]. To the best of our knowledge, for these diarylethenes bearing thiophene moieties and aryl moieties, the effects of the electro-donating or electro-withdrawing groups on their photochromism and crystal packing properties have not been reported.

Herein, we have designed and synthesized a new class of photochromic diarylethene derivatives, with different groups at the terminal of diarylethenes and a benzene ring as an aryl moiety,

i.e., {1-[2-methyl-5-(4-cyanophenyl)-3-thienyl]-2-(2-methoxyphenyl)}perfluorocyclopentene (**1o**), {1-[2-methyl-5-(4-fluorophenyl)-3-thienyl]-2-(2-methoxyphenyl)}perfluorocyclopentene (**2o**), and {1-[2-methyl-5-(4-methylphenyl)-3-thienyl]-2-(2-methoxyphenyl)}perfluorocyclopentene (**3o**), all of which showed good reversible photochromism in hexane solution. The scheme showing the photochromism of **1–3** is presented in Scheme 1.

Results and discussions

Photochromism in solution

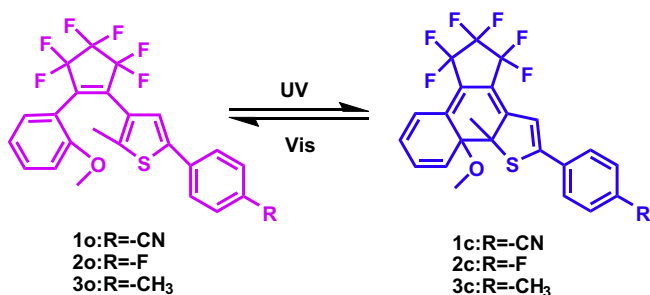
The photochromic behaviors of diarylethenes **1–3** were examined in solution ($c = 3.0 \times 10^{-5}$ mol/L) at room temperature. The changes in the absorption spectra of **1–3** induced by alternating irradiation with UV and visible light in hexane are shown in Fig. 1.

In hexane, the colorless solution of diarylethene **1o** exhibits a sharp absorption peak at 313 nm corresponding to a $\pi \rightarrow \pi^*$ transition [39]. Upon irradiation with 313 nm light, a new absorption band in the visible region centered at 591 nm emerged with a color change from colorless to blue due to the formation of the closed-ring isomer **1c** for S_0-S_1 transition [40]. Alternatively, the blue solution could bleach to colorless upon irradiation with visible light ($\lambda > 450$ nm), and the absorption spectrum return to the initial state **1o** (Fig. 1A and D). The coloration-decoloration cycles could be repeated many times and a clear isosbestic point was observed at 337 nm. Just like diarylethene **1**, diarylethenes **2** and **3** also show good photochromism in hexane (Fig. 1B and C). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions of **2o** and **3o** turned blue due to the cyclization reactions leading to the closed-ring isomers **2c** and **3c**, respectively. These compounds had absorption maxima in the visible region at 584 and 589 nm, respectively. The blue solutions of **2c** and **3c** could be decolorized upon irradiation with visible light ($\lambda > 450$ nm), indicating the return to initial state of **2o** and **3o**.

To further investigate the optical properties of **1o–3o**, molecular orbital calculations at the B3LYP/6-31G(d) level of density functional theory (DFT) were used [41,42]. Fig. 2 shows the calculated spatial distributions of the HOMO and LUMO levels of diarylethenes **1o–3o**. It could be easily seen that the HOMO levels of **1o–3o** are π orbitals concentrated on the central thiophene–phenyl moiety. For LUMO levels, **1o** with a strong electron-withdrawing cyano group is not concentrated on the central active part, but **2o** and **3o** are still concentrated on the central active part. The result is well consistent with that of the reported diarylethenes [43].

The DFT results indicate that the features of the frontier molecular orbital change significantly with different substituents. The calculated HOMO–LUMO gaps of **1o–3o** follow the descending order of **2o** (397.78 kJ/mol) > **1o** (395.35 kJ/mol) > **3o** (390.83 kJ/mol), indicating that the HOMO–LUMO gap of **3o** is the smallest among the three diarylethene derivatives. The possible reason is that the electron-withdrawing groups as in compound **1o** and **2o** tend to induce broader energy gaps, thus can stabilize the molecule significantly. On the contrary, the electron-donating groups as in **3o** lower the HOMO–LUMO energy gap resulting in weakened chemical stability.

The absorption spectral parameters of diarylethenes **1–3** in hexane solution are summarized in Table 1. The cyclization and cycloreversion quantum yields of **1–3** were measured by comparison of them to 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [44] under identical conditions (Table 1). As shown in Table 1, cyano terminated diarylethene **1** in the open-ring isomer state has the largest maximum absorption wavelength of 313 nm among the three diarylethenes. The molar absorption coefficient of the



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

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