# Synthesis and Photochromism studies of 1,2-bis-[2-methyl-5-(9,9-diethyl-5H-fluorene)-3-thienyl] perfluorocyclopentene

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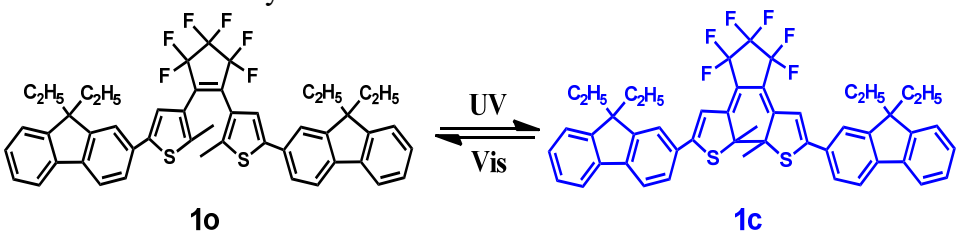
**Abstract.** A novel photochromic diarylethene which called 1, 2 – bis - [ 2- methyl -5- (9 ,9 -diethyl-5H- fluorene ) -3-thienyl ] perfluorocyclopentene was designed and constructed successfully. In the meantime, its photochromism and fluorescent properties have been discussed systematically. This compound exhibited excellent photochromism, changing from colorless to blue after irradiation with UV light in solution. The diarylethene also showed obviously fluorescence switch property.

## Introduction

Organic photochromic compounds have caught much attention. Duing to the fact of widespread potential application in photonic devices, the design and synthesis of these types of compounds has become significant research [1]. Recently, there are many kinds of photochromic compounds that have been synthesized, like diarylethenes [2] and phenoxynaphthacene-quinones [3]. Among various kinds of photochromic compounds, diarylethenes are the most promising candidates for the photochromic materials [4–6], for examples, in optical memory and molecular switch, because of their high fatigue resistance, good thermal stability, and rapid response time [6]. Though organic substance with fluorene ring has high luminous efficiency, owing to fluorene having a rigid planar biphenyl structure, there are very few compounds on diarylethene with fluorene has been reported.

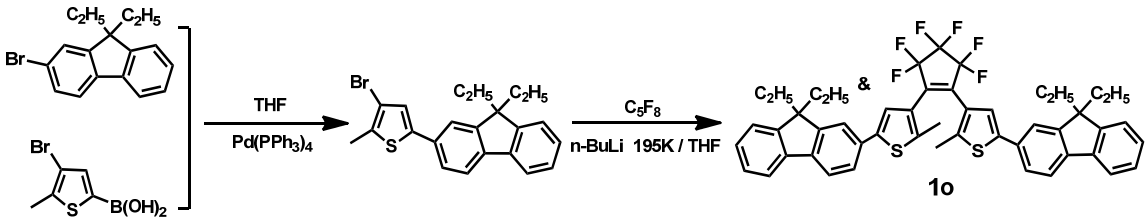
Learning in process of the research, we successfully synthesized a novel diarylethene with fluorene ring, 1,2-bis-[2-methyl-5-(9,9-diethyl-5H-fluorene)-3-thienyl]perfluorocyclopentene (*1o*). Then, we discussed and investigated its photochromic properties and fluorescence properties at length. The photochromism of diarylethene *1o* is shown in Scheme 1.




Scheme 1. Photochromism of diarylethene *1o*

## Experiments

**Synthesis of diarylethene *1o*.** The synthesis of compound *1o* used the similar method as previous reported [7]. The synthetic route of *1o* was shown in Scheme 2. The structure of compound *1o* was confirmed by NMR spectroscopy. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J$ = 12.4 Hz, 2H, phenyl-H), 7.78 (d, $J$ = 12.0 Hz, 2H, phenyl-H), 7.69 (s, 2H, phenyl l-H), 7.62 (d, $J$ = 5.2 Hz, 2H, phenyl-H), 7.47 (d, $J$ = 8.8 Hz, 2H, phenyl-H), 7.44 (t, $J$ = 11.2 Hz, 2H, phenyl-H), 7.22 (t, $J$ = 10.0 Hz,2H, phenyl-H), 7.19 (s, 2H, thienyl-H), 2.34 (s, 6H, -$CH_3$), 1.95-2.00 (m, 8H,-$CH_2$), 1.65 (t, $J$ = 7.6 Hz, 12H, -$CH_3$).




Scheme 2. Synthetic route for the compound *1o*

## Results and Discussion

**Synthesis of diarylethene *1o*.** The changes in the absorption spectra of *1o* induced by photo-irradiation in acetonitrile solution ($2.0 \times 10^{-5}$ mol·L$^{-1}$). As shown in Fig. 1, it can be seen that the photochromic compound *1o* showed an absorption peak at 333 nm ( $\varepsilon = 8.0\times10^{4}$ L·mol$^{-1}$·cm$^{-1}$) in acetonitrile, arising from π→π* transition [8]. A new visible absorption band at 613 nm ( $\varepsilon = 2.3\times10^{4}$ L·mol$^{-1}$·cm$^{-1}$) emerged after irradiation with 297 nm light, while the original peak at 333 nm decreased, indicating the formation of the closed-ring isomer *1c*. Correspondingly, the color changed from blue to colorless when irradiation with visible light ( $\lambda$ > 500 nm), while we could observe a clear isosbestic point at 347 nm.

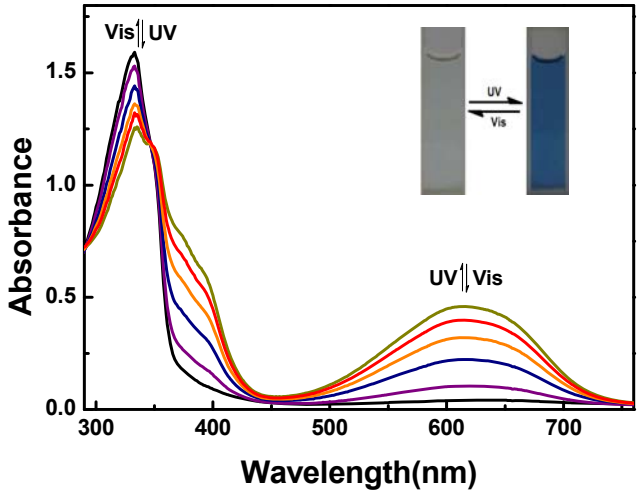
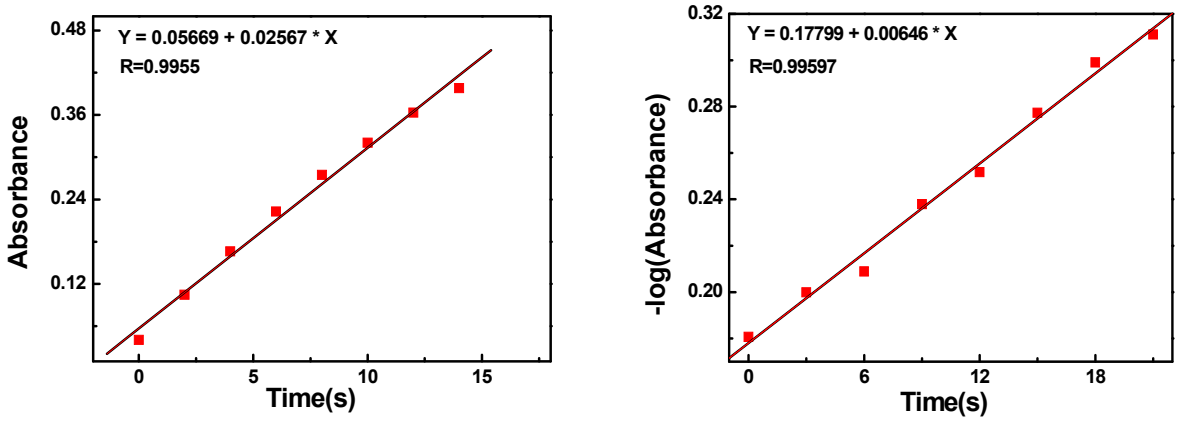



Fig.1 Absorption spectral and color changes of *1o* in acetonitrile ($2.0 \times 10^{-5}$ mol·L$^{-1}$)

**Photochromic reaction kinetics in solution**. Fig.2 shows the absorption spectral and color changes of *1o* when it was induced by alternating irradiation with UV and visible light. The symmetrical photochromic compound *1o* has good photochromic behavior and can switch between its colorless ring-open and blue ring-closed forms with appropriate wavelengths of light. The result indicates that the cyclization process of *1o* belong to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. As shown in Fig.2B, during the cycloreversion of *1c*, the relationship between –log(Absorbance) and exposal time also behave perfect linearity, indicating that the cycloreversion process belong to the first order reaction. The *k* of cycloreversion ($k_{c\text{-}o}$, $10^{-3}$) process of *1c* can be easily obtained, which is 6.46 mol·L$^{-1}$·s$^{-1}$ in acetonitrile solution. It is demonstrated that *1o* could show good photochromic behavior in solution.




(A) (B)

Fig.2 The photochromic cyclization (A) and cycloreversion (B) kinetics curves of *1o*

**Fluorescence of diarylethene**. In our work, the fluorescence properties of *1o* in acetonitrile solution were measured. Fig.3 showed that the photocyclization reaction was carried out and the non-fluorescent closed-ring form of the diarylethene were produced when irradiated by light of 297 nm. When arrived at photostationary state, the emission intensity was quenched to ca. 50%. The open-ring isomer *1o* could regenerate and recover to the original emission intensity when *1c* was irradiated with appropriate visible light. On account of its reversible changes of the emission intensity, it is extremely useful for compound *1o* that it can be applied as the fluorescence switches. As fluorescence readout method, diarylethene *1o* can be potentially applied to optical memory because of its unique properties [9].

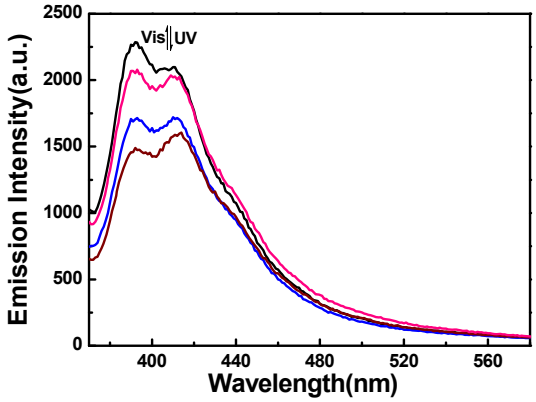



Fig.3 Fluorescent intensity changes of *1o* in acetonitrile solution ($2.0 \times 10^{-5}$ mol·L$^{-1}$)

## Summary

In brief, a novel diarylethene has been synthesized successfully and has carried on the investigation of its photochromic and fluorescence properties. We can draw a conclusion that the compound has good reversible photochromism in acetonitrile. It has excellent photochromic properties and good fluorescence behavior. In addition, it is suggesting that it will be helpful in designing new diarylethenes for further potential applications.

## Acknowledgement

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