Design, Synthesis and Evaluation of a New Diarylethene with A Quinoline Formaldehyde Unit

Xiaodong Zhang *

Department of Ecology and Environmental Protection, Linyi Vocational University of Science and Technology, Linyi, 276025, P. R. China

* Corresponding Author Email: zhangxiaodong@lyvust.edu.cn

Abstract. A new asymmetrical diarylethene (1O) with a quinoline formaldehyde unit was synthesized by click chemistry reaction. Its photochromic and fluorescence performances by the stimulation of light was investigated in detail. The results showed that the compound exhibits good photochromism with UV/Vis light irradiation. The diarylethene 1O changed the color from colorless to purple upon irradiation with 297 nm UV light, in which absorption maxima were observed at 367 and 552 nm.

Keywords: Diarylethene, Fluorescence, Photochromism.

1. Introduction

Photochromic materials have attracted much attention as most promising candidates for optical memories, photo-switches, logic circuit, and chemical sensors [1–2]. Among all photochromic compounds, Diarylethene derivatives are have received extensive attention due to their excellent thermal stability [3, 4], remarkable fatigue resistance [5–7], and non-destructive. Upon alternating irradiation with UV and visible light, the diarylethene derivatives can undergo the reversible cyclization/cycloreversion photochromic reactions between the open-ring and the closed-ring isomers [8]. In the past several decades, many new diarylethene systems with different heteroaryl moieties were explored. In this paper, an unsymmetrical photochromic diarylethene (1O) has been synthesized, and we not only examined its photochromic properties but also studied fluorescence properties in solution. The photochromic reaction of 1O is shown in Figure 1.

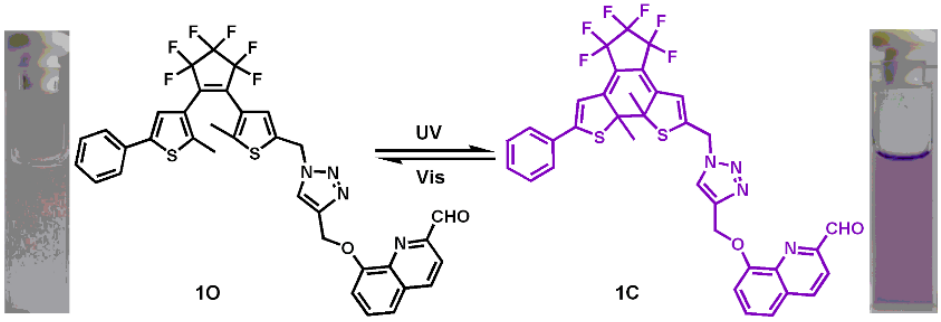

Figure 1. Photochromism of diarylethene 1

2. Experimental

2.1. Material and Methods

All solvents and reagents involving in experiments were purchased from commercial suppliers and directly used without any further purification. The solution of 1 was dissolved in DMSO at a concentration of 10 mM as the stock solution. ^{1}H NMR spectra were recorded on a Bruker 500 spectrometer. Mass spectrometric data were achieved with HP1100LC/MSD MS and an LC/Q-TOF-MS instruments.

2.2. Synthesis

The synthetic route to the target diarylethene, [1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-(2-quinoline formaldehyde-methoxyl-(1, 2, 3-triazole)) methyl)-3-thienyl)] perfluoro cyclopentene (1O), is shown in Figure 1. Compounds 2 [9-10] and 3 [11] were facilely synthesized in high yield by the procedure as published in the literature.

To a stirred solution THF (40 mL) of compound 2 (0.50 g, 1.00 mmol) and compound 3 (0.21 g, 1.00 mmol) was added water (5 mL) containing NaVc (0.04 g, 0.20 mmol) and $CuSO_4$ (0.025 g, 0.10 mmol) at room temperature. The reaction mixture was stirred for 12 h at room temperature. After being extracted with CH_2Cl_2, the organic phase was dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 1/1) as the eluent to afford 0.42 g compound 1O as a pale yellow solid in 67% yield. m.p. 363–364 K; ^{1}H NMR (DMSO-d6, 400 MHz), δ (ppm): 1.83 (s, 3H), 1.95 (s, 3H), 5.51 (s, 2H,), 5.90 (s, 2H), 7.31 (s, 1H), 7.37 (t, 1H, J = 8.0 Hz), 7.35-7.39 (m, 3H), 7.60-7.65 (m, 3H),7.72 (t, 1H, J = 8.0 Hz), 7.76 (t, 1H, J = 8.0 Hz), 8.04 (d, 1H, J = 8.0 Hz), 8.42 (s, 1H), 8.59 (d, 1H, J = 8.0Hz), 10.14 (s, 1H); 13C NMR (DMSO-d6, 100 MHz): 13.24, 13.41, 28.64, 47.41, 62.16, 109.92, 110.04, 116.84, 119.31, 120.53, 120.90, 121.07, 121.45, 121.83, 122.27, 122.99, 123.69, 123.92, 124.48, 124.72, 124.96, 126.86, 126.95, 127.97, 128.65, 130.32, 132.02, 133.33, 136.30, 138.98, 140.04, 141.44, 142.80, 143.22, 150.44, 153.52, 192.47.

3. Results and Discussion

The synthesis routes are shown in Figure 2. The structure of compound 1O was confirmed by 1H NMR and MS.

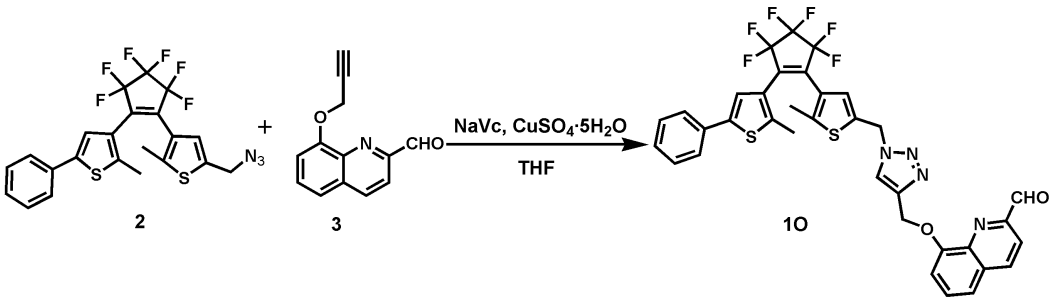

Figure 2. Synthetic route of diarylethene 1O

The UV-vis absorption and fluorescence spectral changes of 1O induced by photoirradiation were measured in acetonitrile (2.0×10^{-5} mol L^{-1}) at room temperature, and the results are shown in Figure 3. As shown in Figure 3A, its open-ring isomer 1O exhibited a sharp absorption peak at 289 nm due to $\pi \rightarrow \pi^*$ [12-13] transition. Upon irradiation with 297 nm light, a new absorption band centered at 552 nm was observed and the color changed from colorless to purple due to the formation of the closed-ring isomer 1C. Reversely, the purple solution could be completely bleached upon irradiation with visible light (λ> 450 nm), and the absorption spectrum was converted to its initial state. When arrived at the photostationary state (PSS), the isosbestic point was observed at 302 nm, which clearly indicates a two-component photochromic reaction [14].

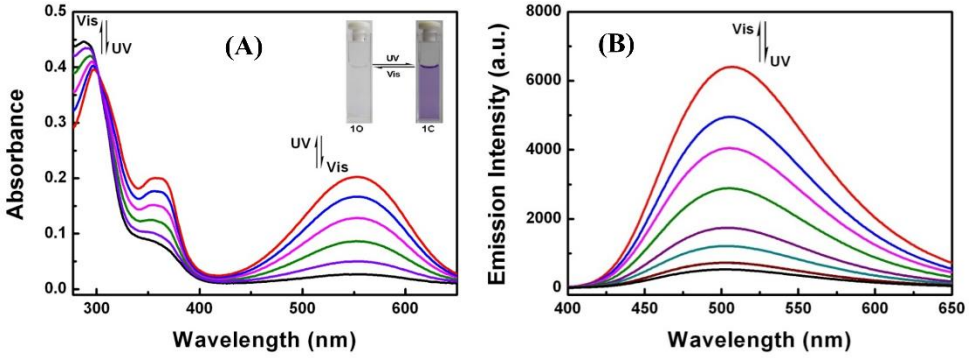

Figure 3. Changes in the absorption and fluorescence spectra of 1O upon alternating irradiation with UV and visible light in acetonitrile (2.0×10^{-5} mol L^{-1}): (A) absorption spectral change; (B) fluorescence change, excited at 297 nm

Figure 3B shows the fluorescence spectral change of 1O in acetonitrile upon photoirradiation. When excited at 297 nm, weak fluorescence centered at 507 nm can be seen and the fluorescence quantum yield was determined to be 0.067. Upon irradiation with 297 nm UV light, distinct fluorescence quenching was observed along with the occurrence of the photocyclization reaction. When arriving at the PSS, the fluorescence intensity of 1O was quenched to ca. 8%. The residual fluorescence in the photostationary state may be attributed to the incomplete cyclization reaction and existence of parallel conformation isomer 1O [15]. Reversely, the fluorescence of 1O could be restored by irradiation with appropriate visible light ($\lambda > 450$ nm).

4. Conclusion

In summary, a new asymmetrical diarylethene with a quinoline formaldehyde unit has been synthesized, and its photochromism and ions sensing properties were investigated systematically. The results showed that this compound exhibited reversible photochromism.

References

[1] M. Irie. Chem. Rev. 2000, 100, pp. 1685.

[2] H. Tian, S. Yan. J. Chem. Soc. Rev. 2004, 33, pp. 85.

[3] Y.N. Li, Q. Li. Org. Lett. 2012, 14, pp. 4362.

[4] X. Y. Lv, M. S. Wang, C. Yang, G. E. Wang, S. H. Wang, R. G. Lin, G. C. Guo. Inorg. Chem. 2012, 51, pp. 4015.

[5] S. J. Chen, L. J. Chen, H. B. Yang, H. Tian, W. H. Zhu. J. Am. Chem. Soc. 2012, 134, pp. 13596.

[6] C. Sciascia, R. Castagna, M. Dekermenjian, R. Martel, A. S. Kandada, F.D. Fonzo, A. Bianco, C. Bertarelli, M. Meneghetti, G. Lanzani. J. Phys. Chem. C. 2012, 116, pp. 19483.

[7] Y. Ishibashi, T. Umesato, S. Kobatake, M. Irie, H. Miyasaka. J. Phys.Chem. C. 2012, 116, 4862Hanahan, D.; Weinberg, R. A. The hallmarks of cancer. Cell, 2000, 100, pp. 57−70.

[8] T. Yamaguchi and M. Irie: J. Photochem. Photobiol. A. Chem. 2006, 178, pp. 162.

[9] Pu SZ, Ding HC, Liu G, Zheng CH, Xu HY. Multiaddressing fluorescence switch based on a new photochromic diarylethene with a triazole-linked Rhodamine B unit. The Journal of Physical Chemistry C. 2014, 118, pp. 7010-7017.

[10] Ding HC, Liu G, Pu SZ, Zheng CH. Multi-addressable fluorescent switch based on a photochromic diarylethene with triazole-bridged methylquinoline group. Dyes and Pigments. 2014, 103, pp. 82-88.

[11] Chereddy N R, Thennarasu S, Mandal A B. Incorporation of triazole into a quinoline-rhodamine conjugate imparts iron (III) selective complexation permitting detection at nanomolar levels. Dalton Transactions, 2012, 41, pp. 11753-11759.

[12] Yam VWW, Lee JKW, Ko CC Zhu NY. Photochromic diarylethene-containing ionic liquids and N-heterocyclic carbenes. J Am Chem Soc., 2009, 131, pp. 912-913.

[13] Liu G, Pu SZ, Wang XM. Synthesis and the effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit. J Photochem Photobiol A Chem., 2010, 214, pp. 230-240.

[14] Li ZX, Liao LY, Sun W, Xu CH, Zhang C, Fang CJ, Yan CH. Reconfigurable cascade circuit in a photo- and chemical-switchable fluorescent diarylethene derivative. J. Phys. Chem. C., 2008, 112, pp. 5190-5196.

[15] Fan CB, Pu SZ, Liu G, Yang TS. Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms. J. Photochem. Photobiol. A Chem., 2008, 194, pp. 415-425.