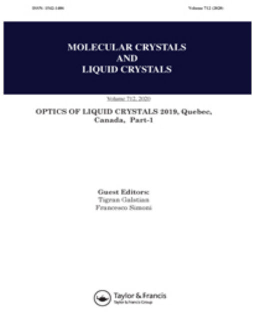

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Substituent position effect on photochromic properties of aldehyde-functionalized dithienylethenes

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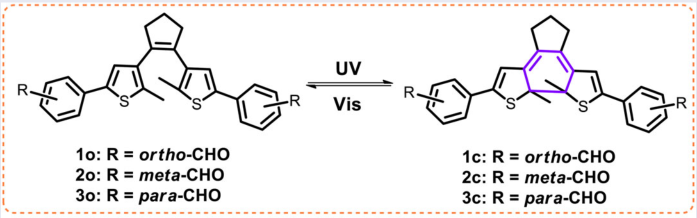
ABSTRACT

Three symmetrical dithienylethenes bearing two electron-withdrawing aldehyde groups have been synthesized. And their structures were confirmed by ^{1}H NMR, ^{13}C NMR and HRMS (ESI). Investigation on photochromic properties indicated that they had good photochromic behavior with excellent fatigue resistance upon irradiation with UV or visible light. And it was found that the aldehyde substituent position had a significant effect on their photochromic properties. The DFT calculations further validated those experimental results for their photochromic behavior. Furthermore, they may be used as versatile building blocks to construct novel photochromic materials.



1. Aldehyde substituent position effect;

2. Novel Building Blocks for Photochromic Materials.

KEYWORDS
Aldehyde; dithienylethene; photochromism; substituent position effect

Introduction

In recent decades, photochromic compounds, such as spiropyran, azobenzene, diarylethene and so on, have drawn increasing attention due to potential applications in molecular devices and optical memory systems [1,2]. Among them, diarylethenes with heterocyclic aryl groups, especially those bearing two thiophene groups have been extensively investigated because of their excellent irreversible thermal stability, high sensitivity and remarkable fatigue resistance [3–11]. The photochromic properties of the dithienylethene depended on several factors, such as the conformation of the ring-open isomer, electron donor/acceptor substituents, and the π-conjugation length of the heteroaryl groups, etc [12–14]. Among these factors, the effect of electron substituents was the most direct and practicable one for the design of a photoactive dithienylethene with

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tunable properties [15–18]. Dithienylethenes bearing phenyl groups were the most common class of examples which can be substituted by different electron-withdrawing/donating substituents at different positions of the benzene ring in order to modulate their photochromic properties [19]. Apart from the fact that various substituent groups had great influence on the photochromic behaviors of dithienylethenes, the position of the substituent groups could affect its photochromism significantly, which can be utilized for the fine tuning of the optical properties of dithienylethenes [20–24]. Nevertheless, searching new dithienylehene scaffolds with excellent regulation of photochromism is still highly desirable due to their potential application. To the best of our knowledge, the aldehyde group is a strong electron-withdrawing moiety which have been used in many functional materials. In additon, the formyl group can function as not only electron acceptor (A) but a classical reaction moiety to carry on a series of reaction, such as Reduction, Oxidation, Aldol condensation, Knoevenagel condensation, etc. Herein, three symmetrical dithienylethenes bearing two aldehyde groups were presented in order to: (1) evaluate the effect of the position of the CHO substitution on dithienylethene; (2) utilization as potential building blocks to construct novel functional photochromic materials. As expected, investigation on photochromic properties indicated that dithienylethenes **1–3** had good photochromic behavior with excellent fatigue resistance upon irradiation with UV or visible light. Moreover, results showed that the aldehyde substituent position had a significant effect on their photochromic properties.

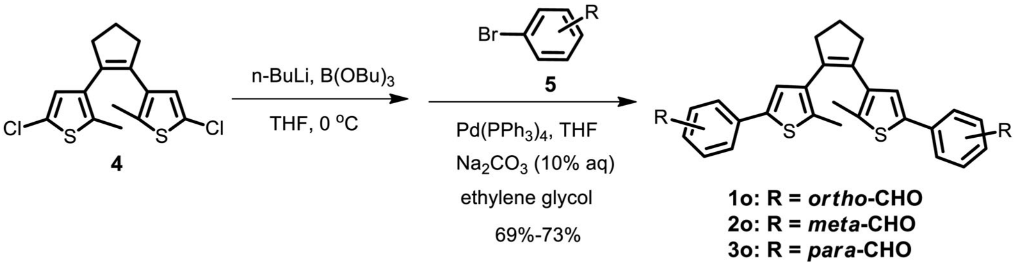
Experimental

General procedures and materials

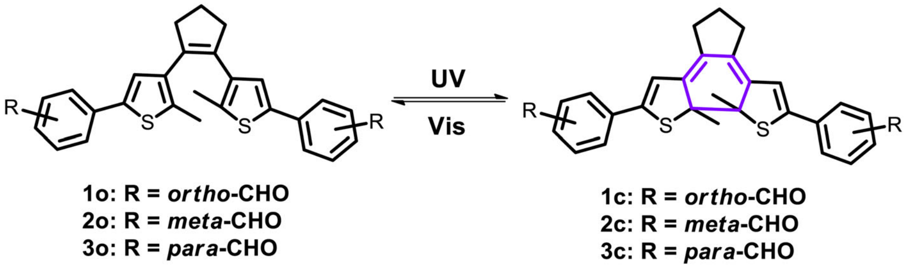
All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques unless otherwise stated. THF was distilled under nitrogen from sodium/benzophenone. 1, 2-bis (5-chloro-2-methylthiophen-3 -yl)cyclopent-1-ene **2** [25] and dithienylethenes **1** [26] and **3** [27] were prepared by modified literature methods. All other starting materials were obtained commercially as analytical-grade and used without further purification. The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 1, 2-bis (2-methyl-5-phenyl-3- thienyl)perfluorocyclopentene [28]. ^{1}H and ^{13}C NMR spectra were collected on German BRUKER AVANCE III 400 MHz. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS. High resolution mass spectra were obtained on Thermo Scientific TM Q ExactiveTM (ESI mode). UV-vis spectra were obtained on a Persee TU-1810 UV-Vis spectrophotometer. In the photoisomerization reaction, UV light irradiation (254 nm) was carried out using a ZF5UV lamp, and visible light was irradiated using a LZG 220 V 500 W tungsten lamp ($\lambda > 402$ nm) with cutoff filters.

Synthesis of dithienylethene (2)

To a solution of **4** (537 mg, 1.0 mmol) in anhydrous THF (10 mL) was added *n*-BuLi (0.88 mL of 2.5 M solution in hexane, 2.2 mmol) under nitrogen at 0 °C and stirred for 2 h at 0 °C. Then $B(OBu)_3$ (0.82 mL, 3.0 mmol) was added slowly and stirred for 6 h at room temperature, which was used in the following Suzuki cross coupling reaction



Scheme 1. Synthetic route of dithienylethenes **1-3**.



Scheme 2. Photochromism of dithienylethenes **1-3**.

without any workup. Then, the resulting reddish solution was added dropwise to a flask containing **5** (368 mg, 2.0 mmol), $Pd(PPh_3)_4$ (100 mg, 0.082 mmol) in THF (15 mL) and Na_2CO_3 solution (15 mL, 2 M) at 60 °C. Subsequently, the mixture was refluxed for 24 h under an N_2 atmosphere. The solution was cooled to room temperature and extracted with EA (3 × 40 mL), and the combined organic layer was washed with the saturated NaCl solution (2 × 50 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. And the residue was purified by column chromatography (PE: EA = 9:1) to afford compound **2** as a gray solid in a yield of 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 2H), 8.02 (s, 2H), 7.77 – 7.74 (m, 4H), 7.52 (t, $J = 8.0$ Hz, 2H), 7.16 (s, 2H), 2.89 (t, $J = 8.0$ Hz, 4H), 2.17 – 2.10 (m, 2H), 2.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.08, 138.07, 136.91, 136.87, 135.59, 135.44, 134.76, 130.96, 129.49, 128.18, 125.98, 124.99, 38.45, 23.01, 14.45. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{24}O_2S_2$ 468.1218; Found 468.1227.

Results and discussion

Photochromic properties of dithienylethenes 1–3

The photoisomerization behavior of the dithienylethenes **1–3** in CH_2Cl_2 was investigated at room temperature. These dithienylethene derivatives underwent photoisomerization between ring-open isomers and ring-closed isomers upon alternating irradiation with UV light (254 nm) and visible light (> 402 nm), as illustrated in Scheme 2. As shown in Figure 1A, the absorption maximum of dithienylethene **one** was observed at 246 nm ($\varepsilon = 8.38 \times 10^4$ L mol^{-1} cm^{-1}), which was ascribed to intramolecular π - π^* transition [29]. Upon irradiation with 254 nm UV light, a new absorption band at

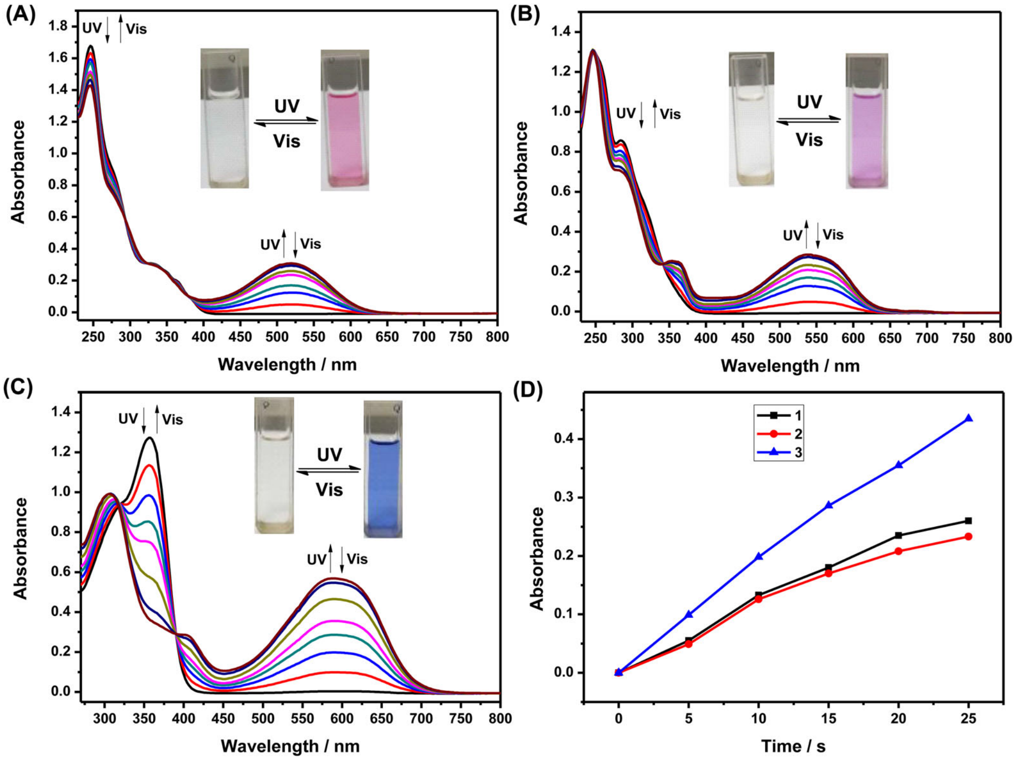


Figure 1. Absorption spectral changes of dithienylethenes **1-3** with 254 nm UV and >402 nm Vis light irradiation in DCM (2.0×10^{-5} mol/L), (A) spectral changes for **1**; (B) spectral changes for **2**; (C) spectral changes for **3**; (D) optical response rate monitored at the maximum absorption wavelength in the visible region for ring-closed isomers **1c-3c**.

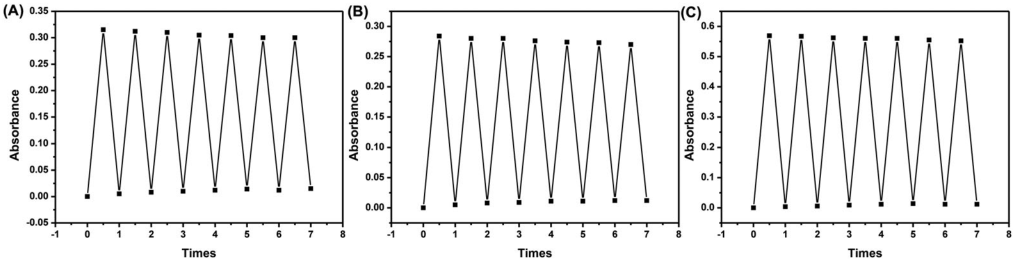


Figure 2. Fatigue resistance of dithienylethenes **1-3** with 254 nm UV and >402 nm Vis light irradiation in DCM (2.0×10^{-5} mol/L), (A) fatigue resistance for **1** (518 nm); (B) fatigue resistance for **2** (544 nm); (C) fatigue resistance for **3** (596 nm).

518 nm ($\varepsilon = 1.59 \times 10^4$ L mol^{-1} cm^{-1}) appeared along with an obvious color change from colorless to pink, as a result of formation of the corresponding ring-closed isomer **1c**. Furthermore, a well-defined isosbestic point was observed at 293 nm, which revealed that **1o** was cleanly converted to the photocyclized product. Upon irradiation with $\lambda > 402$ nm visible light, the pink ring-closed isomer **1c** underwent a cycloreversion reaction and returned to the initial ring-open isomer **1o**. In particular, dithienylethene **one** showed very good reversibility and no apparent deterioration (about 3%) was

Table 1. Photochromic parameters of dithienylethene **1-3** in DCM at 298 K (2.0×10^{-5} mol/L).

Compounds	λ_{max}/nm[a] ($\varepsilon \times 10^4$) Open	λ_{max}/nm[b] ($\varepsilon \times 10^4$) PSS[d]	Φ[c]	
			$\varphi_{\text{o-c}}$	$\varphi_{\text{c-o}}$
1	246 (8.38)	518 (1.59)	0.356	0.0079
2	247 (6.58)	544 (1.47)	0.232	0.0065
3	357 (6.40)	596 (2.85)	0.526	0.0092

[a] Absorption maxima of open-ring isomers;.
[b] Absorption maxima of closed-ring isomers;.
[c] Quantum yields of open-ring ($\varphi_{\text{c-o}}$) and closed-ring isomers ($\varphi_{\text{o-c}}$);.
[d] Photostationary state, respectively.

observed after repeating the above process eight times, indicating excellent fatigue resistance (Figure 2A). The cyclization and cycloreversion quantum yields of **1** were 0.356 ($\varphi_{\text{o-c}}$) and 0.0079 ($\varphi_{\text{c-o}}$), respectively (Table 1). Similar photochromic properties were obtained when solution of dithienylethenes **2** and **3** in DCM was irradiated with the same light, as shown in Figures 1B,C and 2B,C and Table 1. The absorption spectral parameters of dithienylethenes **1–3** in DCM were summarized in Table 1. These data showed that the aldehyde substituent position had a significant effect on their photochromic properties, mainly including maximum absorption wavelength, molar absorption coefficients, optical response rate and quantum yields. Among these three isomers, the absorption maximum of the *para*-substituted derivative **3c** (596 nm) is the longest in DCM, while that of *ortho*-substituted derivative **1c** (518 nm) is the shortest, which exhibited 78 nm red-shifts. However, these results were inconsistent with those for methoxy substituents where the absorption maximum of *meta*-substituted diarylethene was the shortest, and that of *ortho*-substituted one was the longest [20]. As presented in Table 1, the molar absorption coefficients of ring-closed isomers **1c–3c** increased in the order of *meta*- $<$ *ortho*- $<$ *para*- substitution by the aldehyde group. Furthermore, their optical response rate was compared, and it was found that the response rate of *para*-substituted derivative was the fastest and that of *meta*- substituted one was the slowest (Figure 1D). As shown in Table 1, the cyclization quantum yields of dithienylethenes **1–3** were much higher than their corresponding cycloreversion quantum yields. The cyclization quantum yield of the *para*-substituted derivative **one** was the biggest ($\varphi_{\text{o-}c} = 0.526$), that of the *meta*-substituted derivative **two** is the smallest ($\varphi_{\text{o-}c} = 0.232$).

DFT theoretical calculation

In order to gain an insight into the electronic features and photoreactivity of **1–3**, their optimized molecular geometries and electron densities have been calculated by dependent density functional theory (DFT) in Gaussian 09 B3LYP/6-31G* level [30–32]. As shown in Figure 3, the open-isomers of **1o–3o** presented classical antiparallel conformation. Moreover, the HOMO orbital energy of **1o–3o** was mainly localized on the central dithienylethene unit, while the orbital energy of the LUMO was largely distributed over the thiophene and formyl substituted benzene moieties due to great effect of electron deficient formyl group, which exhibited Acceptor-DTE-Acceptor type molecular skeleton. And higher HOMO-LUMO band gap (3.35 eV for **1o**, 3.54 eV for **2o**, and 3.53 eV for **3o**) for their ring-open isomers was obtained. For the ring-closed isomers **1c**–3**c**, they presented an almost planar conjugated skeleton, and their HOMO and

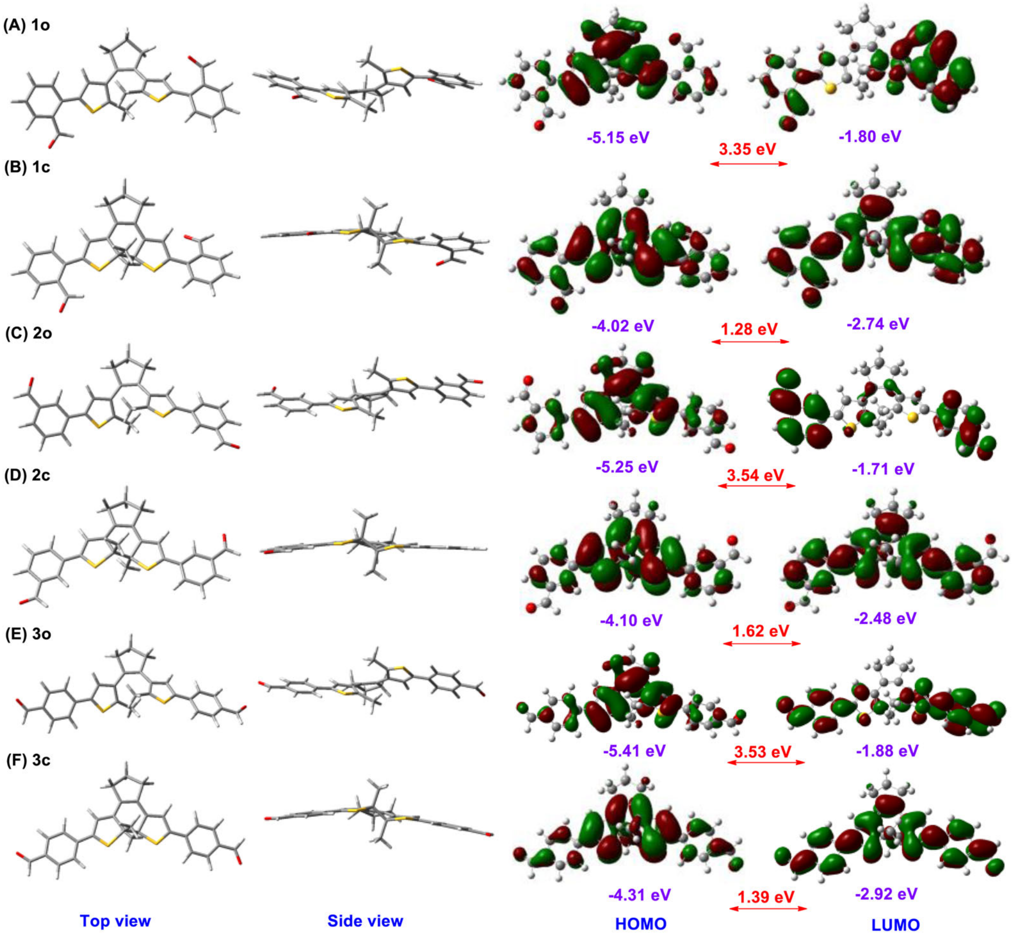


Figure 3. The energy-minimized structures and Frontier molecular orbital profiles of ring-open and ring-closed isomers of **1-3** based on DFT calculations at the B3LYP/6-31G* level by using the Gaussian 09 program.

LUMO coefficient was nearly delocalized on the whole molecular backbone. As expected, **1c**–3**c** presented a narrower energy band gap (1.28 eV for **1c**, 1.62 eV for **2c**, and 1.39 eV for **3c**) compared with that of the corresponding ring-open isomers due to the extended π conjugation system. Accordingly, the theoretical calculations further validated the above experimental results of the photochromic behaviors for **1–3**.

Conclusion

In summary, three dithienylethene derivatives appending two electron-withdrawing aldehyde groups were prepared. They displayed good photochromic behaviors and excellent fatigue resistance upon irradiation with UV or visible light. And it was found that the aldehyde substituent position had a remarkable effect on their photochromic properties, mainly including maximum absorption wavelength, molar absorption coefficients, optical response rate and quantum yields. The DFT theoretical calculations further validated these experimental results for photochromic behaviors. Moreover, they can be utilized as versatile building blocks to construct novel photochromic materials.

References

[1] B. L. Feringa, *Molecular Swiches* (Wiley-VCH: Weinheim, Germany, 2001).
[2] S. Kawata, and Y. Kawata, *Chem. Rev.* ***100*** (5), 1777 (2000). doi:10.1021/cr980073p
[3] M. Irie, *Chem. Rev.* ***100*** (5), 1685 (2000). [Database] doi:10.1021/cr980069d
[4] H. Tian, and S. Yang, *Chem. Soc. Rev.* ***33*** (2), 85 (2004). doi:10.1039/b302356g
[5] Z. Li *et al.*, *Dyes Pigm* ***148***, 130 (2018). doi:10.1016/j.dyepig.2017.09.001
[6] M. Irie *et al.*, *Chem. Rev.* ***114*** (24), 12174 (2014). doi:10.1021/cr500249p
[7] S.-Z. Pu *et al.*, *J. Mater. Chem. C.* ***4*** (15), 3075 (2016). doi:10.1039/C6TC00110F
[8] Z. Li *et al.*, *Dyes Pigm.* ***160***, 597 (2019). doi:10.1016/j.dyepig.2018.08.034
[9] Z. Li *et al.*, *Dyes Pigm.* ***162***, 339 (2019). doi:10.1016/j.dyepig.2018.10.049
[10] A. S. Lubbe, W. Szymanski, and B. L. Feringa, *Chem. Soc. Rev.* ***46*** (4), 1052 (2017). doi:10.1039/c6cs00461j
[11] Y. Wang *et al.*, *J. Chem. Res.* ***42*** (10), 531 (2018). doi:10.3184/174751918X15386526000173
[12] M. Irie, and M. Mohri, *J. Org. Chem.* ***53*** (4), 803 (1988). doi:10.1021/jo00239a022
[13] S. Nakamura, and M. Irie, *J. Org. Chem.* ***53*** (26), 6136 (1988). doi:10.1021/jo00261a035
[14] S. Z. Pu *et al.*, *Tetrahedron Lett.* ***44*** (5), 1011 (2003). doi:10.1016/S0040-4039(02)02739-9
[15] S. Z. Pu *et al.*, *Tetrahedron* ***61*** (27), 6623 (2005). doi:10.1016/j.tet.2005.04.044
[16] X. Li, W. Jiang, and Y. Son, *Mol. Cryst. Liq. Cryst.* ***602*** (1), 1 (2014). doi:10.1080/15421406.2014.940804
[17] X. Li *et al.*, *Mol. Cryst. Liq. Cryst.* ***654*** (1), 115 (2017). doi:10.1080/15421406.2017.1355715
[18] S. Y. Huang *et al.*, *Dyes Pigm.* ***92*** (3), 961 (2012). doi:10.1016/j.dyepig.2011.08.005
[19] S. Hermes *et al.*, *Tetrahedron Lett.* ***50*** (14), 1614 (2009). doi:10.1016/j.tetlet.2009.01.102
[20] S. Z. Pu *et al.*, *Dyes Pigm.* ***84*** (1), 25 (2010). doi:10.1016/j.dyepig.2009.06.018
[21] S. Z. Pu, W. J. Liu, and W. J. Miao, *J. Phys. Org. Chem.* ***22*** (10), 954 (2009). doi:10.1002/poc.1545
[22] S. Z. Pu *et al.*, *J. Photochem. Photobio. A Chem.* ***196*** (1), 84 (2008). doi:10.1016/j.jphotochem.2007.11.016
[23] S. Z. Pu *et al.*, *Tetrahedron Lett.* ***47*** (36), 6473 (2006). doi:10.1016/j.tetlet.2006.06.073
[24] S. Z. Pu *et al.*, *Org. Lett.* ***9*** (11), 2139 (2007). doi:10.1021/ol070622q
[25] L. N. Lucas *et al.*, *Eur. J. Org. Chem.* ***2003*** (1), 155 (2003). doi:10.1002/1099-0690(200301)2003:1<155::AID-EJOC155>3.0.CO;2-S
[26] P. Jin *et al.*, *Dyes Pigm* ***132***, 151 (2016). doi:10.1016/j.dyepig.2016.04.043
[27] M. Akazawa *et al.*, *Org. Biomol. Chem.* ***6*** (9), 1544 (2008). doi:10.1039/b802580k
[28] M. Irie *et al.*, *J. Am. Chem. Soc.* ***122*** (20), 4871 (2000). doi:10.1021/ja993181h
[29] Z. Li *et al.*, *J. Phys. Chem. C.* ***112*** (13), 5190 (2008). doi:10.1021/jp711613y
[30] M. J. Frisch *et al.*, *Gaussian 09, Revision B.01* (Gaussian, Inc., Wallingford CT, 2010).
[31] A. D. Becke, *J. Chem. Phys.* ***98*** (7), 5648 (1993). doi:10.1063/1.464913
[32] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* ***54*** (2), 724 (1971). doi:10.1063/1.1674902