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Visible-light triggered photoswitching systems based on fluorescent azulenyl-substituted dithienylcyclopentenes

Eugenia Andreea Dragu,[a] Adrian E. Ion,[b] Sergiu Shova,[c] Daniela Bala,[d] Constantin Mihailciuc,[d] Mariana Voicescu,[e] Sorana Ionescu[d] and Simona Nica[a*]

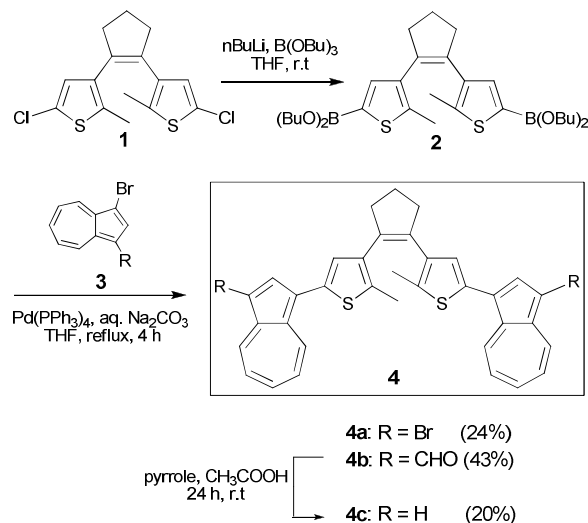**Novel azulenyl functionalized dithienylethenes were synthesized, and their photochromic reactivity, fluorescent and electrochemical properties were investigated. By tailoring the conventional dithienylcyclopentene chromophore with azulene groups, the photocyclization occurred with 405 nm wavelength light irradiation. These compounds exhibited relatively strong fluorescence at 524 nm when excited at 360 nm, which decreased along with the photocyclization. Furthermore, their electrochemical oxidation induced cyclization.**

Molecular switches that can reversibly change their properties upon excitation with light or other external stimuli have recently received considerable attention due to their potential applications for molecular electronic devices such as memories and switches.[1] Among various types of organic photoswitches, diarylethene bearing two thiophene or benzothiophene rings are the most promising candidates owing to their excellent thermal stability and remarkable fatigue resistance.[2] Attempts to modulate the photochromic properties of diarylethenes have led to structural variations in both the heterocyclic rings and the unsaturated bridge between.[3] So far, the most commonly used diarylethenes are the dithienylperfluorocyclopentenes which exhibit good photochromic behaviour and high thermal stability during photocyclization.[4] However, the expensive and rather volatile octafluorocyclopentene starting material is a major disadvantage. Furthermore, Feringa et al. reported that the photochromic behavior of perhydro- and perfluorocyclopentene switches is remarkably similar.[3a] Therefore, diheteroarylethenes with a cyclopentene bridge possess attractive photochromic properties and can be considered as promising alternative to diarylperfluorocyclopentenes. Although the field of molecular switches is rapidly growing,[5] several key challenges remain to be addressed, such as the development of photochromic systems that can be triggered by irradiation using visible and/or near-IR light. In this context, substitution of the dithienylethene photochromic system with various chromophores may represent a new way of tuning the optical properties of molecular switches.[6] The unique electronic and optical characteristics of azulene, prompted us to develop novel azulene-substituted dithienylcyclopentene switches. The design of these systems combines the photoswitching ability of the photochromic dithienylcyclopentene unit with azulene property to absorb in the visible region in order to access visible light-triggered cyclization. We report herein, the synthesis and photochromic behaviour of novel azulenyl functionalized dithienylethenes **4** (Scheme 1). Furthermore, because of azulene "anomalous" $S_2 \rightarrow S_0$ fluorescence emission[7] and interesting electrochemical properties,[8] we also investigated the feasibility of fluorescence and electrochemical switching of these compounds.

As shown in Scheme 1, the target compounds **4a** and **4b** were synthesized in 24% and 43% yields, respectively, by Suzuki–Miyaura coupling reaction. The boronate ester **2**, which was prepared through the lithiation and borylation of dichloride **1**, was coupled with the appropriate azulenyl bromides using 3 mol% Pd(PPh$_3$)$_4$ as catalyst and aqueous Na$_2$CO$_3$ as base.

4a: R = Br   (24%)
4b: R = CHO (43%)
4c: R = H   (20%)

Scheme 1. Synthesis of azulenyl functionalized dithienylcyclopentenes **4**.

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This synthetic protocol could not, however, be used for the preparation of dithienylethene **4c** because the 1-bromoazulene precursor cannot be obtained separately by azulene bromination, but rather as an inseparable mixture with 1,3-dibromoazulene. Nevertheless, dithienylethene **4c** was prepared in 20% yield by decarbonylation of **4b** with pyrrole in acetic acid media (Scheme 1).[9] The photoswitching behavior of compounds **4** was monitored by UV-Vis spectroscopy and the results are illustrated in Figure 1. Compounds **4** showed absorption changes typical of photochromic diarylethene derivatives. Irradiation of dichloromethane solutions of the ring-open isomers **4(o)** with 405 nm wavelength light triggered the photocyclization reaction and generated the ring-closed isomers **4(c)** (Figure 1). The visual demonstration of this photoreaction was the change in colour of the solutions from yellow-greenish to purple-bluish due to the formation of the extended π-conjugated backbone in the ring-closed isomers. The absorption maxima and molar extinction coefficients of both the ring-open and ring-closed isomers are summarized in Table S1 (ESI).
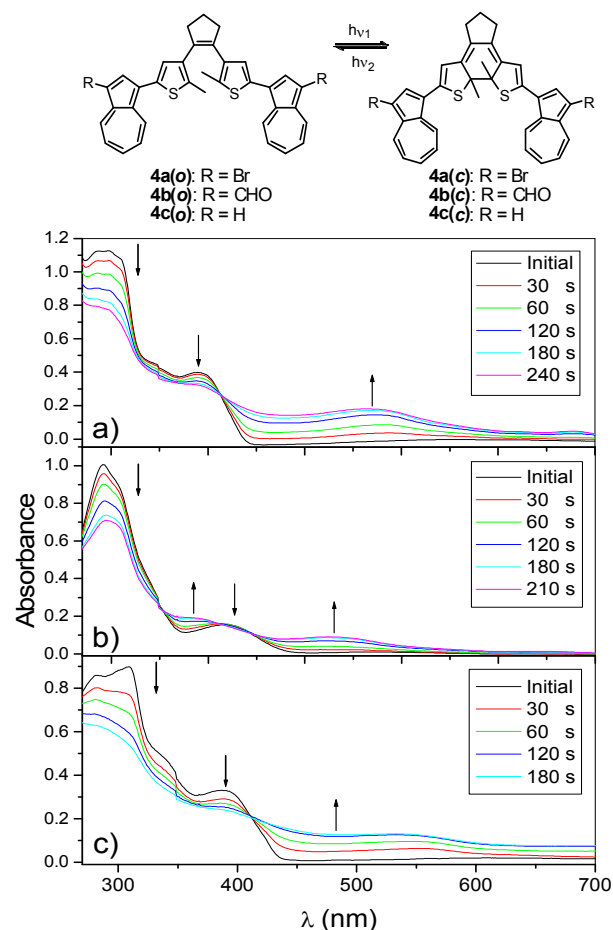

Figure 1. Absorption spectral changes of dichloromethane solutions of (a) **4a** (1.55×10^{-5} M), (b) **4b** (1.16×10^{-5} M) and (c) **4c** (2.74×10^{-5} M) at different irradiation time.

In the open state, the absorption spectra of compounds **4** showed intense bands in the UV domain at wavelengths below 310 nm. Tailoring the thiophene rings with azulene moieties resulted in an additional band in the range between 380 and 420 nm, which is significantly red-shifted as compared to those of related dithienylcyclopentene derivatives.[2,3] Photocyclization to the ring-closed isomers was demonstrated by the appearance of a new absorption band in the visible region located above 520 nm,

accompanied by a significant decrease in the absorbances at shorter wavelengths. The photostationary state was reached within several minutes with the photocyclization quantum yields varying from 0.45 in the case of **4a** to 0.39 for **4b** and 0.40 for **4c**, respectively (Table S1, ESI). Upon exposure to visible light for around two hours, using a normal bulb (tungsten, 100 W, 1340 lumen, 230 V), the initial UV-Vis spectra were recovered for all three compounds, showing the reversibility of the photocyclization reaction. In the case of compound **4a**, ^{1}H NMR spectra before and after irradiation provide further evidence for the proposed photocyclization reaction. The thiophene protons resonate at 6.94 ppm in the starting **4a(o)**, while upon irradiation a decrease of this signal accompanied by new resonance at 5.97 ppm was observed, in accordance with the formation of **4a(c)** isomer. The ring-closed isomers of compounds **4a** and **4b** are stable at room temperature in dichloromethane solution for more than 10 h when kept in the dark, whereas in the case of compound **4c(c)**, a considerable decrease of the visible absorption maxima was observed within 30 minutes. Preliminary investigations showed that compounds **4a(c)** and **4b(c)** are also thermally stable at 50 °C in chloroform solutions for short periods of time, the half-life of these compounds being 8.5 min and 7.4 min, respectively. These results show that adequate substitution of the azulenyl moieties can be used to tune the thermal stability of this type of photoswitching compounds. The photochemical ring-opening/-closing experiments were performed with compound **4a** which performed well five cycles, but further photoswitching for ten cycles lead to a decrease of the monitored absorbances to around 30 % (Figure S7, ESI).

In the crystalline form,[*] **4a** consists of two symmetrically related thiophene rings in antiparallel conformation (Figure 2). The distance between the active carbons is 3.453(7) Å, significantly shorter than 4.2 Å. As reported earlier,[10] this condition along with the antiparalell configuration of the methyl groups are crucial for the photochromic properties of such materials. The molecule as a whole is essentially non-planar, the dihedral angle between two symmetrically related thiophene and bromo-azulene rings are equal to 51.88(8)° and 30.08(8)°, respectively. An interesting feature of the crystalline structure is the one-dimensional supramolecular aggregates formed through π-π stacking interaction of 3.486 Å between centro-symmetrically related bromo-azulene rings (Figure S8, ESI).

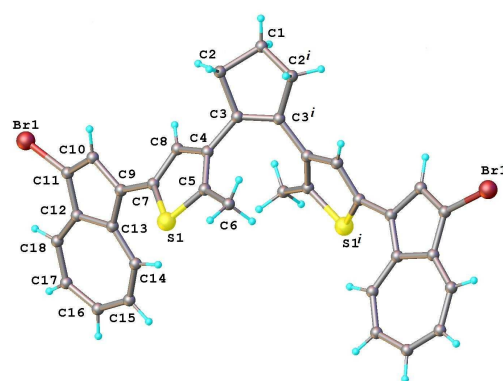**Figure 2.** The molecular structure of compound **4a** along with the atomic labelling scheme. Only the major component of disordered cyclopentene ring is shown. Symmetry code: *i*) $1 - x$, y, $3/2 - z$.

Next, we evaluated whether fluorescence switching of compounds **4** could be achieved by photocyclization. The ring-open isomers **4(o)** exhibit strong fluorescence at 524 nm, due to characteristic $S_2 \rightarrow S_0$
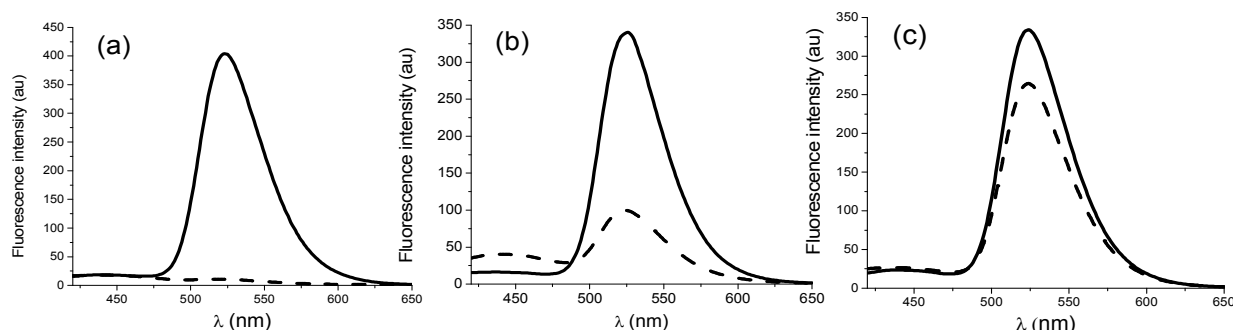
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Figure 3. Fluorescence emission spectra (λ_{exc} = 360 nm) of compounds **4a** (a), **4b** (b), and **4c** (c) in CH$_2$Cl$_2$ (1.65×10^{-6} M) in the open form (solid line) and at the photostationary state under irradiation with 405 nm wavelength light (dashed line).

fluorescence emission of azulene when excited at 360 nm. The fluorescence quantum yields of **4a-c** were determined as 0.21, 0.20 and 0.17, respectively, using quinine bisulfate (0.1 N solution in sulfuric acid as a reference[11] (Table S1, ESI).Thus, it is clear that the substituent of the azulenyl moiety has a significant effect on the emission intensity, but does not affect the position of the emission peak. Upon irradiation with 405 nm wavelength light, different degrees of fluorescence quenching were observed. The emission intensity of **4b** and **4c** in the photostationary state was quenched to ca. 38% and 20% respectively, whereas in the case of bromo-derivative **4a**, nearly total quenching of fluorescence emission took place (Figure 3). These results suggest that the photochromic fluorescence switching of azulenyl-functionalized dithienylcyclopentenes of type **4** can be finely-controlled by varying the substituents attached to the azulene rings. Recently, the reversible fluorescence switching of diarylethenes has attracted considerable attention, as these compounds might have potential applications in the design of erasable ultra-high density optical memory media.[12] The ring-open isomer is the "ON" state and the ring-closed isomer is the "OFF" state. If the ratio of the two isomers is not influenced by the excitation wavelength, the fluorescence readout method is non-destructive. In the case of compound **4a**, simple irradiation with 405 nm wavelength caused photocyclization which, in turn, quenched the fluorescence. Because neither cyclization nor cycloreversion are induced by excitation with 360 nm light, **4a** can be potentially used for non-destructive recording.

Finally, the possibility of electrochemical switching between the open and closed states of compounds **4** was examined by cyclic voltammetry. All compounds showed similar cyclic voltammogram profiles with oxidative ring-closure of the dithienylethene group above 1.7 V. For each compound, in the second cycle, an additional anodic peak appeared corresponding to the ring-closed isomer. For the ring-open isomer **4a(o)**, the cyclic voltammograms (Figure 4) shows three anodic (0.76, 1.21 and 1.77 V) and two cathodic peaks (0.09 and 0.83 V) (Table S2, ESI) in the first cycle. In the second one, additional anodic peak appeared at ca. 0.20 V corresponding to the ring-closed isomer **4a(c)**. By comparison with the redox potentials of 1,3-dibromoazulene (Table S2, ESI), the first two anodic peaks were attributed to the sequential oxidation of the two azulenyl moieties bonded to the thiophene rings in **4a(o)**, whilst the peak at 1.77 V was tentatively assigned to the two-electron oxidative ring-closure of the dithienylethene group. This latter assignment is

supported by previous reports[13] and, furthermore, by the fact that when the oxidation potential was restricted to +1.0 and +1.4 V, respectively, the anodic peak at +0.2 V became negligible. The cyclic voltammetry results also suggest that the ring-closure occurs after the two-electron oxidation of the open form, that is, from **4a(o)**$^{2+}$ to **4a(c)**$^{2+}$. The electrochemical ring-closure of **4a(o)** was further confirmed by spectroelectrochemistry (Figure S10, ESI). Oxidation at 1.9 V (i.e., at a potential more anodic than the ring-closing peak at 1.77 V) led to an increase in the intensity of the absorption band at 633 nm, which is indicative of the formation of the ring-closed isomer. In the case of compounds **4b** and **4c** (Figure S9, ESI), the oxidative ring-closure of the dithienylethene group occurred around 1.8 V. In the second cycle, additional anodic peaks were observed at 0.30 and 0.18 V (Table S2, ESI, Entries 6 and 8) corresponding to the ring-closed isomers **4b(c)** and **4c(c)**, respectively.
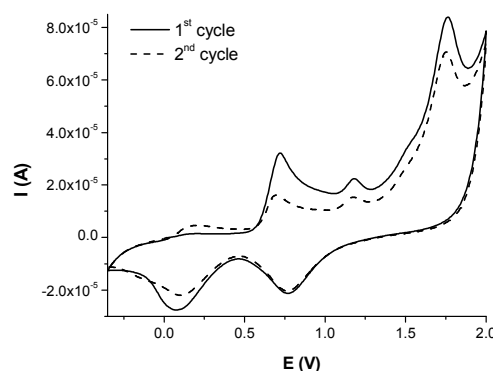

Figure 4. Cyclic voltammetry of **4a** in dichloromethane (10^{-3} M) at 100 mV/s in the 0.5 - 2.0 V potential range.

The electrochemical data can be qualitatively explained by the quantum chemical calculations. The relative stability of **4a(o)** and **4a(c)** changes in different oxidation states (Table S4, ESI). The neutral **4a(o)** is 10.48 kcal/mol lower in energy than **4a(c)**. **4a(o)** needs an energy of 5.10 eV to ionise and its monocation becomes less stable than **4a(c)**$^{1+}$ by 5.69 kcal/mol. The barrier to ring-closing is nonetheless still high (20.21 kcal/mol) and the process highly improbable. With an additional 5.71 eV the second ionization takes place and not only does the dication **4a(o)**$^{2+}$ become 22.66 kcal/mol

higher in energy than $4a(c)^{2+}$, but the barrier drops to 2.60 kcal/mol. The ring-closing can take place, $4a(c)^{2+}$ forms and the ring-opening process has a low probability, due to the high energy barrier of 25.26 kcal/mol, so that the equilibrium is shifted towards the dicationic $4a(c)^{2+}$. The oxidation energy of $4a(c)$ is 0.70 eV lower than that of $4a(o)$, meaning that it will oxidize earlier, as seen from the signal at 0.2 V in the voltammogram. The calculated difference between the first and second ionization steps for $4a(o)$ is 0.61 eV *vs.* 0.45 V in the voltammogram ($E_{pa3}-E_{pa2}$), whereas the difference between the third and second ionization steps is 0.39 eV vs. the experimental value of 0.56 V ($E_{pa4}-E_{pa3}$). The correlation holds also for compound **4c**, where the calculated differences between the oxidation potential of $4c(c)$ and $4c(o)$ is 0.70 eV (Table S4, ESI). The relative energies and activation barriers for compounds **4a** and **4c** present less than 4 kcal/mol difference when compared with phenyl substituted dithienylcyclopentene.[14] Therefore, substitution with azulene does not greatly change the relative stability of the species or the barriers.

Conclusions

In summary, we have synthesized novel azulene-substituted dithienylethenes **4** for which the photocyclization reaction proceed by irradiation with visible light. These compounds function also as fluorescent switches, exhibiting strong fluorescence in the ring-open state. According to the azulenyl substituent, different degree of fluorescent quenching occurs upon photocyclization. Furthermore, electrochemical investigations, correlated with quantum chemical calculations, have demonstrated that oxidative ring-closure of **4a** occurs *via* dicationic species $4a(c)^{2+}$ resulting from the cyclization of $4a(o)^{2+}$. Further investigations regarding the influence of the azulenyl substitution on the photochromic properties of this novel system are underway.

Notes and references

a Institute of Organic Chemistry "C. D. Nenitzescu" of the Romanian Academy, Splaiul Independentei, 202B, 060023, Bucharest, Romania Fax: +4021 3121 601; Tel: +4021 3167 900; E-mail: snica@cco.ro
b Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie, no. 23, 020464, Bucharest, Romania
c "Petru Poni" Institute of Macromolecular Chemistry of the Romanian Academy, Grigore-Ghica Voda Alley, no. 41A, 700847, Iasi, Romania
d Physical Chemistry Department, Faculty of Chemistry, University of Bucharest, Regina Elisabeta, no. 4-12, 030018, Bucharest, Romania.
e "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Splaiul Independentei 202, 060021, Bucharest, Romania

* Crystal data for compound **4a**: $C_{35}H_{26}Br_2S_2$, Mr = 670.50 g mol^{-1}, size 0.45×0.10×0.01 mm^3, monoclinic, space group $C2/c$, a = 24.2712(7) Å, b = 8.3649(3) Å, c = 14.4048(6) Å, β = 93.305(3)°, V = 2919.68(19) Å^3, Z = 4, ρ_{calcd} = 1.525 g cm^{-3}, μ(MoKα) = 2.943 mm^{-1}, $F(000)$ = 1352, 8962 reflections in h(-29/29), k(-10/10), l(-17/17), measured in the range 5.16 ≤ Θ ≤ 51.98, T = 200 K, completeness Θ_{max}=99.91%, 2871 independent reflections, R_{int} = 0.0413, 178 parameters, 0 restraints, R_{1obs}=0.0438, wR_{2obs} = 0.0936, R_{1all} = 0.0655, wR_{2all} = 0.1019, GoF = 1.036, largest difference peak and hole: 0.55/-0.34 e A^{-3}. CCDC-983049 contains the supplementary crystallographic data and can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

Electronic Supplementary Information (ESI) containing synthesis, characterization, spectroelectrochemistry and quantum calculations are available.

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