# **Electronic Supplementary Information**

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

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## **Table of contents**

1.	GENERAL METHODS	2
2.	EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA	3
3.	COPIES OF NMR	6
4.	PHOTOCHROMIC AND FLUORESCENCE PROPERTIES	.12
5.	CRYSTAL DATA	. 13
6.	CYCLIC VOLTAMMETRY	.14
7.	SPECTROELECTROCHEMISTRY	.15
8.	COMPUTATIONAL DETAILS	.15
9.	REFERENCES	.19

### 1. General methods

#### 1.1. Materials

Chemical reactions were carried out under argon atmosphere. Anhydrous tetrahydrofuran (THF) was distilled under argon atmosphere from LiAlH<sub>4</sub> and stored over sodium. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was freshly distilled from CaH<sub>2</sub> before use. CH<sub>2</sub>Cl<sub>2</sub> for fluorescence measurements was purchased from CHIMACTIV S.R.L, Bucharest. CH<sub>2</sub>Cl<sub>2</sub> for cyclic voltammetry was purchased from Sigma-Aldrich and used as received. All other solvents were also used as received. Column chromatography was carried out on 40-63 mesh silica gel. Analytical thin layer chromatography was performed on Merck silica gel 60–F plates. Visualization was accomplished with UV light.

#### **1.2. Instrumentation**

Melting points were determined with Koehler Automatic Melting Point Range Apparatus (K90190). Elemental analyses were performed with Perkin Elmer CHN 240B analyzer. NMR spectra were recorded in deuteriochloroform (CDCl<sub>3</sub>) containing TMS as internal standard with the following instruments: Bruker Fourier (1H: 300.18 MHz, 13C: 75.48 MHz) and Bruker Avance DRX 400 (1H: 400 MHz, <sup>13</sup>C: 100.62 MHz); chemical shifts ( $\delta$ ) are expressed in ppm, and J values are given in Hz. The splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. The numbering of atom positions used for the characterization of the products is described in Figures S1, S3 and S5, respectively. UV-Vis spectra were recorded on a Varian Cary 100 spectrophotometer. The fluorescence emission and excitation spectra were recorded with a Jasco FP-6500 Spectrofluorometer equipped with a 150 W Xenon Lamp. The excitation wavelength was 360 nm. The fluorescence quantum yield was determined by comparison to dilute quinine bisulfate solution in 0.1 N H<sub>2</sub>SO<sub>4</sub>. Photochemical reactions were all carried out in a 10-mm path length guartz cell. Photoirradiation with 405-nm wavelength light was carried out using a 500 W high-pressure mercury lamp enclosed in a water glass mantle separated by a L-39 glass filter.<sup>1</sup> Photoirradiation with >500 nm light was carried out with a normal bulb (tungsten, 100 W, 1340 lumen, 230 V at around 15 cm distance),<sup>2</sup> by mentaining the volume constant to 3 mL. The measurements that required longer time were performed on solutions kept in the refrigerator overnight, at temperature around 5 °C. Photoswitching properties of compound 4a were performed by recording the absorbance at 390 nm and 565 nm, respectively. Quantum yields were determined according to the method described in literature.<sup>3</sup> Electrochemical measurements were carried out on a potentiostat-galvanostat system AutoLabPGStat 12, controlled by GPES (General Purpose Electrochemical System) electrochemical interface for Windows (version 4.9.007). Three electrodes in one-compartment cell (10 mL) were used in all experiments. Platinum disk electrode (Metrohm, 3 mm in diameter) served as working electrode. The counter electrode was a Pt wire of large area. All experimental potentials were referred to Ag wire (Metrohm), used as quasi-reference electrode. The electrochemical measurements were carried out in anhydrous acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The solutions containing the electroactive species and the supporting electrolyte were purged with argon for 15 minutes in order to remove the oxygen, and low pressure inert gas atmosphere was maintained above the solution during the electrochemical experiments. The spectroelectrochemical measurements were carried out using chronoamperometry coupled with UV-Vis spectroscopy. Chronoamperometry was performed on a Voltalab-40 electrochemical device. UV-Vis spectroelectrochemical spectra were recorded on the Unicam Helios- $\alpha$  UV-Vis spectrophotometer using a three electrode optical cell equipped with an optical transparent electrode (SnO<sub>2</sub> on glass) as working electrode, Pt as counter electrode and Ag/Ag<sup>+</sup> as reference electrode.

## 2. Experimental procedures and characterization data

The synthetic route of photoswitches 4a and 4b is shown in Scheme S1. 1,2-bis(5-chloro-2-methylthiopheb-3-yl)cyclopent-1-ene<sup>4</sup> (1) and 1,3-dibromoazulene (3a) and 3-bromoazulene-1-carbaldehyde (3b)<sup>5</sup> were obtained as described in the literature.



Scheme S1. Synthetic scheme to prepare photoswitches 4a and 4b.

Synthesis of photoswitches 4a and 4b:

To a solution of compound **1** (165 mg, 0.5 mmol) in THF (5 mL) under Ar atmosphere, nBuLi (0.56 mL of 2 M solution in hexane, 1.1 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 30 min, then B(OBu)<sub>3</sub> (0.4 mL. 1.5 mmol) was added at once and the resulting mixture was stirred for 1 h to produce the intermmediate bis-boronic ester **2**. In a separate flask, under Ar atmosphere, the corresponding azulenyl bromide **3a** or **3b** (1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) and THF (10 mL) were stirred for 15 minutes at room temperature, then aqueous Na<sub>2</sub>CO<sub>3</sub> 2 M (2.5 mL) and ethylene glycol (2 drops) were added. The resulting mixture was preheated at 60 °C and the bisboronic ester **2** was added dropwise. The reaction mixture was heated under reflux for 4 h, then cooled to room temperature and diluted with water (25 mL) and diethyl ether (50 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under strong vacuum. The residue was purified by silica gel column chromatography to afford the desired products **4a** and **4b**.

**1,2-bis(5-(3-bromoazulen-1-yl)-2-methylthiophen-3-yl)cyclopent-1-ene (4a):** Column elution with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (10:1) first gave the unreacted 1,3-dibromoazulene (**3a**) followed by the product **4a** (81 mg, 24 %). Green solid, m.p. 150-153° C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.11-2.18 (m, 2H, 3-CH<sub>2</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 2.91 (t, 4H, *J* = 7.4 Hz, 2,4-CH<sub>2</sub>), 6.94 (s, 2H, H-thiophene), 6.98 (t, 2H, *J* = 9.8 Hz, 5'-H), 7.14 (t, 2H, *J* = 9.8 Hz, 7'-H), 7.49 (t, 2H, *J* = 10.0 Hz, 6'-H), 7.92 (s, 2H, 2'-H), 8.26 (d, 2H, *J* = 9.6 Hz, 4'-H), 8.44 (d, 2H, *J* = 9.6 Hz, 8'-H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.4, 23.2, 38.1, 104.3, 122.9, 123.6, 124.2, 126.7, 133.6, 134.6, 134.9, 135.1, 136.4, 136.6, 136.7, 136.9, 137.1, 139.7 ppm. Anal. calcd. for C<sub>35</sub>H<sub>26</sub>Br<sub>2</sub>S<sub>2</sub> (670.52): C, 62.69; H, 3.91; found: C, 62.67; H, 3.95.

<sup>1</sup>H NMR at the photostationary state (**4a**(o) + **4a**(c)):  $\delta$  = 2.15-2.18 (m, CH<sub>2</sub>, CH<sub>3</sub>), 2.23 (s, CH<sub>3</sub>), 2.91 (t, J = 7.4 Hz, CH<sub>2</sub>), 5.97 (s, H-thiophene), 6.94 (s, H-thiophene), 6.99 (t, J = 9.8 Hz, 5'-H), 7.14 (t, J = 9.8 Hz, 7'-H), 7.49 (t, J = 9.2 Hz, 6'-H), 7.92 (s, 2'-H), 8.27 (d, J = 9.0 Hz, 4'-H), 8.44 (d, J = 9.6 Hz, 8'-H) ppm.

**3,3'-(4,4'-(cyclopentene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))diazulene-1-carbaldehyde** (4b): Gradient column elution with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (1:0  $\rightarrow$  10:1) first gave the unreacted 3-bromoazulene-1carbaldehyde (**3b**) followed by the product **4b** (122 mg, 43%). Green solid, m.p. 111-113° C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.12-2.17$  (m, 2H, 3-CH<sub>2</sub>), 2.27 (s, 6H, CH<sub>3</sub>), 2.92 (t, 4H, J = 7.4 Hz, 2,4-CH<sub>2</sub>), 7.00 (s, 2H, H-thiophene), 7.33 (t, 2H, J = 9.8 Hz, 5'-H), 7.54 (t, 2H, J = 9.8 Hz, 7'-H), 7.71 (t, 2H, J =9.6 Hz, 6'-H), 8.32 (s, 2H, 2'-H), 8.66 (d, 2H, J = 9.6 Hz, 4'-H), 9.53 (d, 2H, J = 9.2 Hz, 8'-H), 10.37 (s, 2H, CHO) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 14.4$ , 23.3, 38.0, 124.7, 124.9, 127.3, 128.6, 129.8, 133.3, 134.9, 135.2, 136.7, 137.9, 140.7, 140.9, 141.3, 141.4, 186.5 ppm. Anal. calcd. for C<sub>37</sub>H<sub>28</sub>O<sub>2</sub>S<sub>2</sub> (568.75): C, 78.14; H, 4.96; found: C, 78.17; H, 4.95. Synthesis of 1,2-bis(5-(azulen-1-yl)-2-methylthiophen-3-yl)cyclopent-1-ene (4c):



Scheme S2. Synthesis of the photoswitch 4c

To a stirred suspension of **4b** (114 mg, 0.2 mmol) in glacial acetic acid (1.2 mL) under argon, pyrrole (0.4 mL, 6 mmol) was added dropwise. The resulting mixture stirred at room temperature for 24 h in the dark, then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The combined organic layers were successively washed with water (3 × 50 mL), 5% aqueous Na<sub>2</sub>CO<sub>3</sub> solution (3 × 20 mL), and again with water (3 × 50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. The residue was purified by alumina column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:2) to give product **4c** (20 mg, 20%) as a green oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.08-2.18 (m, 2H, 3-CH<sub>2</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 2.92 (t, 4H, *J* = 7.4 Hz, 2,4-CH<sub>2</sub>), 6.95-7.09 (m, 6H, H-thiophene, 5',7'-H), 7.34 (t, 2H, *J* = 3.9 Hz, 3'-H), 7.45 (t, 2H, *J* = 9.8 Hz, 6'-H), 7.84 (d, 2H, *J* = 3.9 Hz, 2'-H), 8.24 (d, 2H, *J* = 9.3 Hz, 4'-H), 8.55 (d, 2H, *J* = 9.9 Hz, 8'-H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.4, 23.2, 38.1, 117.6, 123.2, 123.4, 123.7, 126.1, 133.9, 134.5, 135.0, 135.1, 135.9, 136.5, 136.7, 137.1, 138.4, 142.1 ppm. Anal. calcd. for C<sub>35</sub>H<sub>28</sub>S<sub>2</sub> (512.73): C, 81.99; H, 5.50; found: C, 82.02; H, 5.48.

# 3. Copies of NMR



Figure S1. <sup>1</sup>H-NMR spectrum of 4a



Figure S2. <sup>13</sup>C-NMR spectrum of 4a.



Figure S3. <sup>1</sup>H-NMR spectrum of 4b



Figure S4. <sup>13</sup>C-NMR spectrum of 4b



Figure S5. <sup>1</sup>H-NMR spectrum of 4c



Figure S6. <sup>13</sup>C-NMR spectrum of 4c

## 4. Photochromic and fluorescence properties

Compd.	Ring-open form		<b>Ring-closed form</b>			
1	$\lambda_{abs} [nm] (\log \varepsilon)$	$\Phi_{\mathbf{F}}$	$\lambda_{abs} [nm] (\log \varepsilon)$			
<b>4</b> a	257 (4.94), 298 (4.86), 389 (4.41)	0.215	286 (4.16), 386 (4.41), 566 (4.16)	0.45		
<b>4b</b>	291 (4.94), 418 (4.12)	0.206	294 (4.13), 383 (4.56), 525 (4.24)	0.39		
<b>4</b> c	282 (4.50), 310 (4.52), 389 (4.08)	0.174	280 (4.17), 385 (4.56), 533 (4.29)	0.40		

Table S1. Photophysical properties of compounds 4a-c

[a]  $\lambda_{\text{max}}$ , absorption maximum;  $\varepsilon$ , absorption coefficient;  $\Phi_{\text{F}}$ , fluorescence quantum yield under excitation at 360 nm;  $\Phi_{\text{o}\rightarrow\text{c}}$ , cyclization quantum yield.



**Figure S7.** Photoswitching properties of compound **4a** showing changes in absorbance monitored at 390 nm and 565 nm, respectively upon alternative exposure to 405 nm wavelength light (180 sec) and visible light of a tungsten bulb (100 W, 1390 lumen, 230 V) (2h).

## 5. Crystal data

Single crystals of **4a** suitable for X-ray diffraction were isolated within one week by slow evaporation of dicloromethane/acenotrile solution (5:2) at room temperature. Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer. Single crystal was positioned at 40 mm from the detector and 343 frames were measured each for 60 s over 1° scan width. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.<sup>6</sup> The structures were solved by direct methods using Olex2<sup>7</sup> software with the SHELXS<sup>8</sup> structure solution program and refined by full-matrix least-squares techniques. Atomic displacements for non-hydrogen, atoms were refined using an anisotropic model. H atoms were placed at calculated positions and refined as riding atoms in the subsequent least-squares model refinements. Three of five carbon atoms of the cyclopentene ring were found to be desordered over two resolvable positions with refined site occupancy ratio of 0.58(2):0.42(2). The positional parameters of these atoms were refined in combination with PART and SADI restrains using isotropic model for non-H atoms and the displacement parameters for paired components were constrained to be equivalent. The molecular plots were obtained using the Olex2 program.



**Figure S8.** 1D supramolecular chain in the crystal structure **4a**. Centroid-to-centroid distances (3.486 Å) are shown wit dashed lines.

## 6. Cyclic voltammetry



Figure S9. Cyclic voltammetry of 4b (a) and 4c (b) in  $CH_2Cl_2$  (10<sup>-3</sup> M) containing 0.1 M TBAP at 100 mV/s.

Entry	Compound	Cycle	E <sub>pa1</sub> (V)	E <sub>pa2</sub> (V)	E <sub>pa3</sub> (V)	E <sub>pa4</sub> (V)	E <sub>pc1</sub> (V)	E <sub>pc2</sub> (V)	E <sub>pc3</sub> (V)
1	4.0	1	_	0.76	1.21	1.77	0.09	0.83	_
2	<del>4</del> a	2	0.20	0.76	1.20	1.78	0.10	0.82	_
3	1,3-	1	_	-	1.18	_	0.10	0.67	0.91
4	dibromoazulene	2	_	0.75			1.17	_	0.91
5	4h	1	_	0.93	_	≈1.83	0.05	0.16	0.86
6	40	2	0.30	0.99	_	≈1.86	0.06	0.17	0.83
7		1	_	0.77	1.21	1.80	0.04	0.58	0.86
8	<b>4c</b>	2	0.18	0.74	1.26	1.72	0.04	0.58	0.85

Table S2. Redox properties of compounds 4a–c and 1,3-dibromoazulene.

The anodic peak potentials recorded in DPV experiments for all three compounds are listed in Table S<sup>3</sup>. The DPV study was performed in order to confirm the presence of the fourth anodic peak of compound **4b** appearing as an ill-defined shoulder in the cyclic voltammogram. All data from DPV study refer only to the first scan performed in the anodic direction. For this reason, the anodic peaks assigned to the oxidation of the ring-closed isomers in the second scan do not appear.

Table S3. Redox	properties	s of compoun	ds 4a-c from	1 DPV 6	experiments
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Entry	Compound	E <sub>pa1</sub> (V)	E <sub>pa2</sub> (V)	E <sub>pa3</sub> (V)	E <sub>pa4</sub> (V)
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1	4a	-	0.69	0.89	1.67
2	<b>4b</b>	-	0.87	0.03	1.79
3	<b>4</b> c	-	0.64	0.11	1.59

## 7. Spectroelectrochemistry



**Figure S10**. Absorption spectral changes of **4a**(o) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 × 10<sup>-4</sup> M) at an applied potential of 1.9 V. The spectra were recorded every minute, before (black line) and after 1 (red), 2 (green), 3 (blue), 4 (magenta) and 5 (purple) minutes of oxidation.

## 8. Computational details

All the calculations were performed in the frame of the DFT method, with a B3LYP functional and a TZVP basis set. The solvent, dichloromethane, was considered as a polarizable continuum through the PCM model. The transition states (TS) were located using the QST3 procedure and checked for one imaginary frequency. The only significant atom displacements in the transition vector were those of C5 and C5' and the adjacent hydrogen atoms. Two IRC calculations, towards the reactants and products, were performed in order to univocally assign the TS to the ring closing process. The starting geometries for the TS were taken as the highest points on the section through the potential energy surface (PES) build along the C5-C5' distance. The first, second and third oxidation energy,  $E_{ox1}$ ,  $E_{ox2}$  and  $E_{ox3}$  (Table S4), were determined as  $-E_{HOMO}$  for the neutral, mono- and dianionic species, respectively, and alternatively as  $E_{ox1}=E_{M+}$  -  $E_M$ ;  $E_{ox2}=E_{M2+}$  -  $E_{M+}$ ;  $E_{ox3}=E_{M3+}$  -  $E_{M2+}$  in an adiabatic process.

It must be stated that within 1 kcal/mol several conformers are possible for 4a(o) in solution, but only the most stable one was taken into account. The conformers differ in the values of the dihedral angles between the cyclopentene and thiophene planes and between the thiophene and azulene fragments. The relative stability of 4a(o) and 4a(c) changes in different oxidation states (Table S4). The neutral 4a(o) is 10.48 kcal/mol lower in energy than 4a(c) and the energy barriers are 41.92 kcal/mol and 52.40 kcal/mol for the ringopening and closing, respectively.

Species	E <sub>rel</sub> (kcal/mol)	–E <sub>HOMO</sub> (eV)	E <sub>ox</sub> (eV)	E <sub>a</sub> (kcal/mol)
4a(o)	0.00	5.26	5.10	52.40
4a(c)	10.48	4.63	4.40	41.92
$4a(o)^{1+}$	5.69	5.73	5.71	20.21
$4a(c)^{1+}$	0.00	5.23	4.97	25.90
$4a(o)^{2+}$	22.66	6.00	6.10	2.60
$4a(c)^{2+}$	0.00	6.94	6.79	25.26
4c( <i>o</i> )	0.00	5.16	5.00	52.41
4c( <i>c</i> )	10.02	4.52	4.29	42.40
$4c(o)^{1+}$	6.34	5.69	5.62	19.85
$4c(c)^{1+}$	0.00	5.13	4.87	26.19
$4c(o)^{2+}$	23.73	6.24	6.07	2.06
4c(c)2 <sup>+</sup>	0.00	6.99	6.85	25.79

Table S4. Relevant calculated parameters

The section through the PES along the C5-C5' distance, which represents the main (but not the only) internal coordinate that changes during the ring closing process is presented in Figure S14 for the neutral and S15 for dicationic states. In Figure S14 one can see two branches of the section through PES due to a second internal coordinate that governs the ring closing process both in the ground and the excited states, i.e. the dihedral angle between the cyclopentene and thiophene fragments, as was previously shown by Staykov et al. for phenyl substituted compounds.<sup>9</sup> The values of this dihedral are noted for each branch.





**Figure S11.** Relaxed section through the PES along the C5-C5' distance in the neutral states for **4a** and **4c**. The respective closed (blue square), open (green rhombus) and TS (red triangle) species are also shown.



**Figure S12.** Relaxed section through the PES along the C5-C5' distance in the dicationic states for **4a** and **4c**. The respective closed (blue square), open (green rhombus) and TS (red triangle) species are also shown.

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