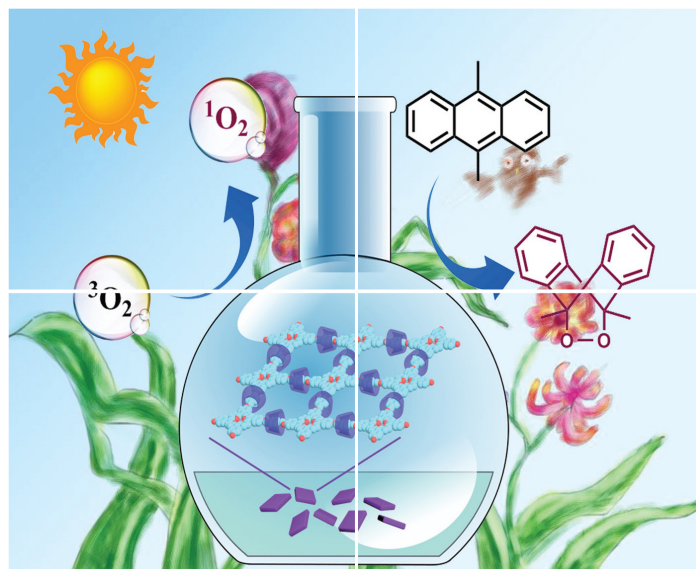


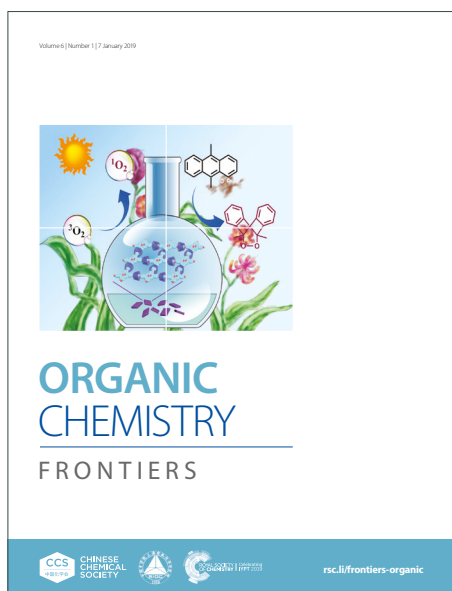
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Biphenylene-based all-carbon analogues of dithienylethene photoswitchesView Article Online
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Abstract

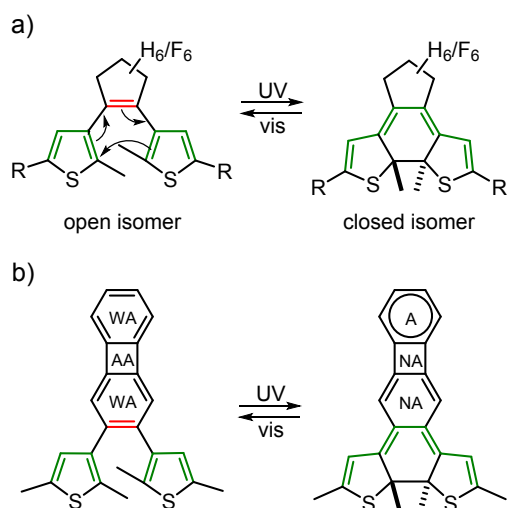
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We report the exploration of novel diarylethene photoswitches constructed through the successive incorporation of the biphenylene ring system at key structural positions. The low aromatic character of the benzene rings in biphenylene enables observable photoswitching even when all three double bonds that are involved in the electrocyclization reaction are embedded within biphenylene subunits. Replacing a single thienyl group in the well-known dithienylethene having a perfluorocyclopentene bridge with a biphenylene unit leads to a P-type photoswitch that responds to longer-wavelength light and exhibits improved fatigue resistance compared to the parent photoswitch. Incorporation of two biphenylene units as the aryl groups provide a thermally stable switch ($t_{1/2} = 780$ h), while the terbiphenylene analogue is a T-type system that undergoes rapid thermal ring opening ($t_{1/2} \approx 20$ min) at room temperature. The changes in the aromatic character of the biphenylene units associated with photochemical ring closing were quantified by NICS calculations for each photoswitch in both the open and closed forms of the molecules.

Introduction

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Photochromic molecular switches are key components in the development of smart materials with light-controlled properties and functions.^{1,2} A guiding design principle is the amplification of their reversible structural and electronic changes beyond the core switching units, enabling macroscopic or device-level effects.³⁻⁷ The most frequently used photochromic motifs include azobenzenes,⁸ spiropyrans,⁹ and dithienylethenes¹⁰ (DTEs, more generally diarylethenes – DAEs), which exhibit reversible changes in molecular length, polarity, and π -conjugation, respectively. In azobenzenes and spiropyrans, photoisomerization is typically accompanied by significant conformational rearrangements. In contrast, the light-induced conrotatory electrocyclization of DTEs involves minimal structural reorganization but leads to substantial changes in conjugation (Figure 1a). This unique combination of structural rigidity and conjugation modulation makes DTEs especially attractive for organic optoelectronic and molecular electronic applications.^{6,11,12} Accordingly, photoinduced switching of conductance in DTE-based molecular wires has been demonstrated,¹³⁻¹⁶ and numerous photoswitchable wire-like systems incorporating DTE units have been synthesized and characterized.¹⁷⁻²⁵ These systems often feature DTEs connected through π -conjugated linkers, typically acetylene or (oligo)phenylene fragments. However, π -extension by embedding DTEs into polycyclic conjugated frameworks is comparatively less common.²⁶ Extension of the thienyl fragment typically does not go beyond benzothiophene,¹⁰ although incorporation of the ethene bridge into various (hetero)aromatic rings has been explored.²⁷⁻³⁴ Furthermore, it has been argued that the use of sulfur-containing DTEs in molecular wires may hinder the switching process due to of strong binding to metal electrodes; therefore, sulfur-free analogues have been proposed.^{35,36} Our group has recently reported that biphenylene (BP) is a suitable bridging unit in DTE photoswitches (Figure 1b).³⁷ Due to the presence of a four-membered ring with some antiaromatic character in BP³⁸ the aromaticity of the adjacent benzene rings is alleviated, and upon photochemical ring closure, the resulting closed isomer exhibits enhanced thermal stability compared to dithienylbenzene.³¹ Furthermore, the reversible alteration of π -conjugation during the electrocyclization process allows for modulation of the local (anti)aromaticity within the BP framework.³⁷



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Figure 1. (a) General structure and photoisomerization of DTE-type photoswitches. (b) Photoisomerization of a photoswitch having a BP bridge. (WA – weakly aromatic, AA – antiaromatic, A – aromatic, NA – non-aromatic)

The applicability of BP as a π -extended bridging unit in DTE photoswitches prompted us to systematically investigate how its incorporation at different positions within the DAE scaffold affects the photochemical and thermal behavior of the resulting photochromes (Figure 2). As, in the most extreme case, the generally used “aryl” and “ethene bridge” distinctions correspond to identical BP structures (structure **3**), we hereafter use the notions of “bridge” and “pillar” (Figure 2) to facilitate the discussion. The integration of BP can be considered a π -extension of the double bonds that participate in the 6π -electrocyclization reaction central to DAE switching. This structural modification lays the foundation for the development of two- and three-terminal, wire-like all-carbon photoswitchable systems.

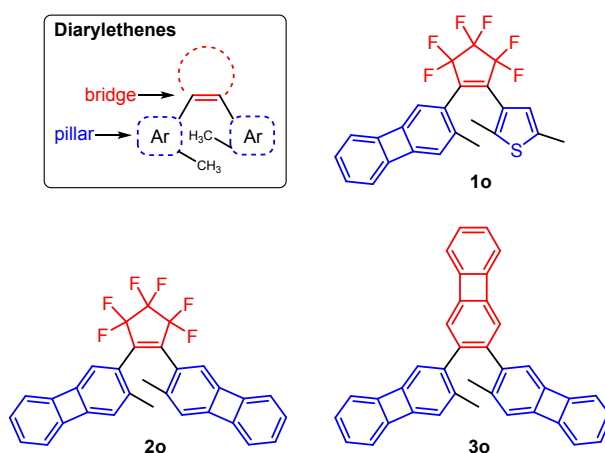


Figure 2. Targeted BP-containing DAEs having different “bridge” and “pillar” units.

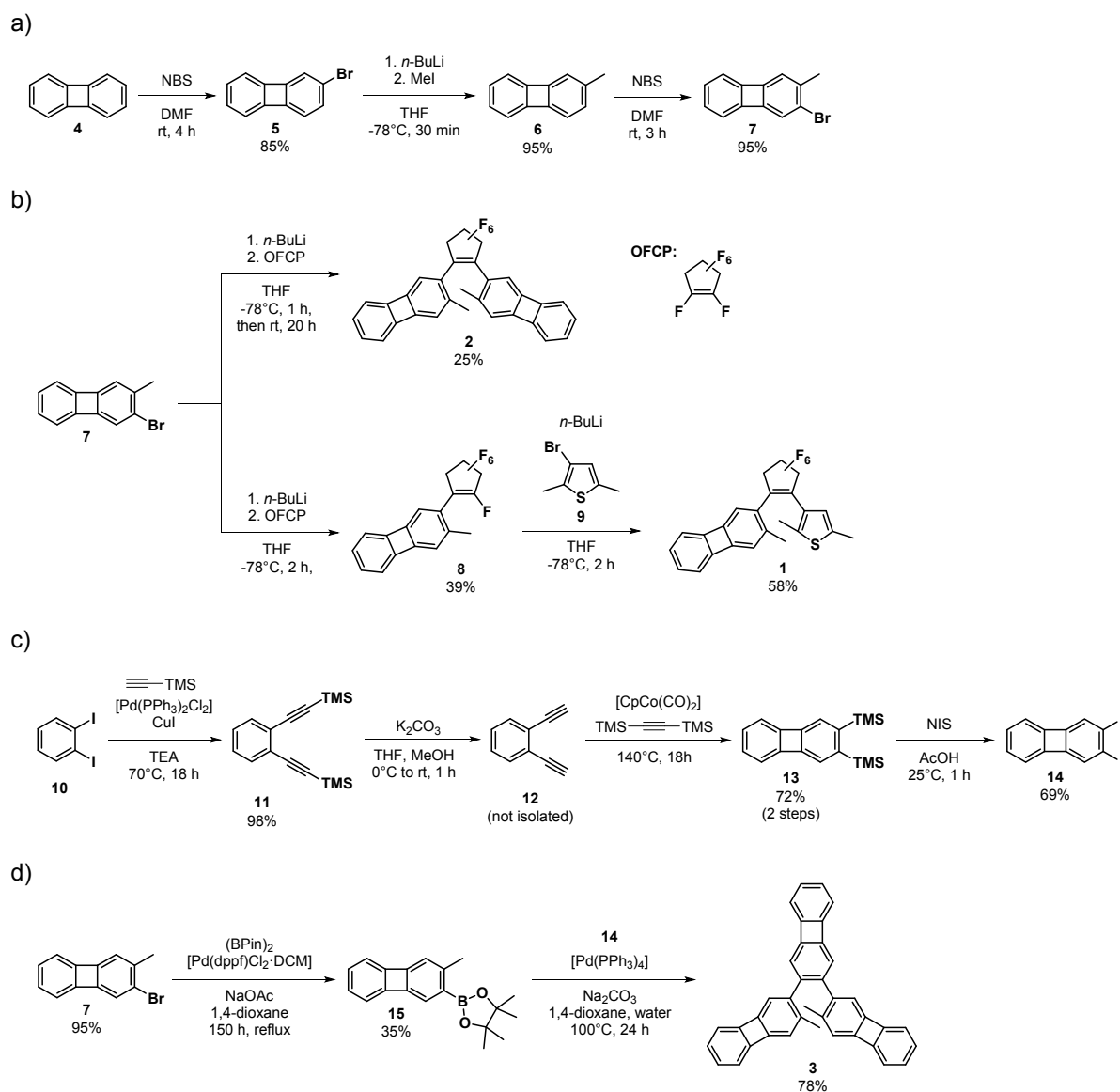


Results and discussion

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First, we describe the synthesis of compounds **1-3** followed by the description of their photochemical and thermal properties. Then comparisons are drawn between the newly prepared and existing photoswitches to highlight the novel properties of the new compounds. Finally, we present computational results that aim to quantify the aromaticity changes within the different BP units upon isomerization.

The synthesis of the three novel photoswitches **1-3** is outlined in Scheme 1. Pivotal to all three molecules is the efficient synthesis of **7** as a key intermediate bearing an *ortho* methyl group. Methyl substituents on the “pillar” units prevent oxidation/aromatization of the closed form,³⁹ thus ensure the reversibility of the photoisomerization.



Scheme 1. Convergent synthesis of compounds **1-3**. a) Synthesis of key BP pillar unit **7**. b) Synthesis of photoswitches **1** and **2**. (c) Synthesis of BP bridge unit **14**. (d) Synthesis of photoswitch **3**.

The synthesis of **7** from BP (**4**) had been described previously⁴⁰ and this route only required some optimization to produce **7** reliably in good yields. BP was synthesized based on the work of our group.⁴¹ Subsequently, it was brominated by NBS to access compound **5**, then the bromine was removed in a halogen-lithium exchange reaction, and the resulting lithium salt was methylated with iodomethane to yield **6**. Compound **6** was then brominated by NBS to access structure **7** with good selectivity, as the methyl group of **6** is *ortho*-directing, and the C1-position of biphenylene is not well suited for electrophilic attacks.⁴²

The synthesis of switches **1** and **2** was achieved by substitution of fluorine on a vinyl carbon center with an appropriate aryl lithium compound. In case of **2** the procedure was straightforward; octafluorocyclopentene (OFCP) was injected into a solution of excess (3-methylbiphen-2-yl)lithium prepared from **7**. Gratifyingly, it was possible to quench this reaction after the first substitution by reversing the addition order of the reactants and omitting the overnight warm-up to room temperature. In this case intermediate **8** was produced in moderate yield (39%), along with the target switch **2** as a significant side product (12% yield). Importantly, compound **8** proved to be a suitable platform to produce unsymmetrical diarylethenes, as demonstrated by the synthesis of switch **1**. In this latter case, the lithium salt of dimethylthiophene **9** was used to replace the remaining vinyl fluorine of **8**.⁴³

Photoswitch **3** was prepared by the double Suzuki coupling between diiodobiphenylene **14** and boronic ester **15**. The synthesis of **14** proceeded according to literature^{37,44} from 1,2-diiodobenzene **10**, which was coupled with trimethylsilylacetylene in a twofold Sonogashira reaction, followed by the removal of the trimethylsilyl groups under basic conditions. The resulting diacetylene **12** was used without isolation – due to its instability under an oxygen atmosphere – in a cobalt-catalyzed [2+2+2] cycloaddition reaction with bis(trimethylsilyl)acetylene^{44,45} to form biphenylene **13**. Finally, compound **14** was accessed from **13** using a new method, based on the work of Kirschner *et al*⁴⁶ by reacting **13** with NIS in glacial acetic acid at room temperature for 1 h. This reaction offers a slightly higher yield (69% vs. 63%), faster reaction time (1 h vs. 74 h), and a milder iodinating agent NIS (instead of iodine monochloride) than the typically employed condition for this transformation.^{37,44} For the synthesis of **3** it was necessary to prepare a boronic ester from **7**, as we planned to produce **3** from diiodobiphenylene **14** and the appropriate boronic ester compound in a Suzuki coupling



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reaction. The Suzuki reaction itself proceeded smoothly in good yields, however the preceding borylation of **7** has not. We tested a number of conditions to access **15** (including lithiation and subsequent borylation with boronic esters, and Miyaura-type borylation⁴⁷) and found that the method presented here (Scheme 1 d) is the most efficient one, even with its long reaction time and modest yield. Notably, as evidenced by NMR spectroscopy (Figure S48, SI), compound **3** formed as a mixture of two isomers; one with a photoactive antiparallel and one with a non-photoactive parallel conformation (about 1 :1 ratio).

The optical properties of the three new photoswitches were monitored by UV-vis spectroscopy (Figure 3a). The spectra of the open forms **1o-3o** showed similar absorption profiles with maxima below 400 nm (Figure 3a, left). Notably, the absorbance intensities increased with the number of BP units in the molecule. Irradiation of the switches in toluene solutions using a 365 nm light-source (1 W) led to substantial changes in their spectra associated with the formation of the closed forms **1c-3c** (Figure 3a, middle). The samples were irradiated until no further change was observed in their spectra. In each case a new, broad absorption band appeared in the visible region (with maxima at 513 nm, 510 nm and 582 nm, respectively, for **1c**, **2c** and **3c**) in accordance with the color change of the compounds from pale yellow to red for **1c** and **2c** and to blue for **3c**. This new band was considerably redshifted and less intense in the case of **3c** compared to the other two compounds. While the more extended conjugation in **3c** can be responsible for the redshifted spectrum, the lower intensity can indicate the lower ratio of **3c** in the photostationary state. We explored the effect of a range of solvents on the **3o**-to-**3c** photoswitching by UV-vis spectroscopy, but the results were similar to those found in toluene (see section S3.1, SI). The changes in color and absorption profile were found reversible in each case, and the original spectra could be restored by irradiating the samples with visible light (520 nm for **1** and **2** and 590 nm for **3**) (Figure 3a, right).

To demonstrate the reversibility of the photoswitching process and to explore the fatigue resistance of the molecules, all three photoswitches were put through multiple irradiation cycles using alternating UV (365 nm) and visible light irradiation at room temperature (Figure 3b). The samples were irradiated until no further changes were observed in their UV-vis spectra. During these cycles, no significant degradation trend was observed in any of the cases.



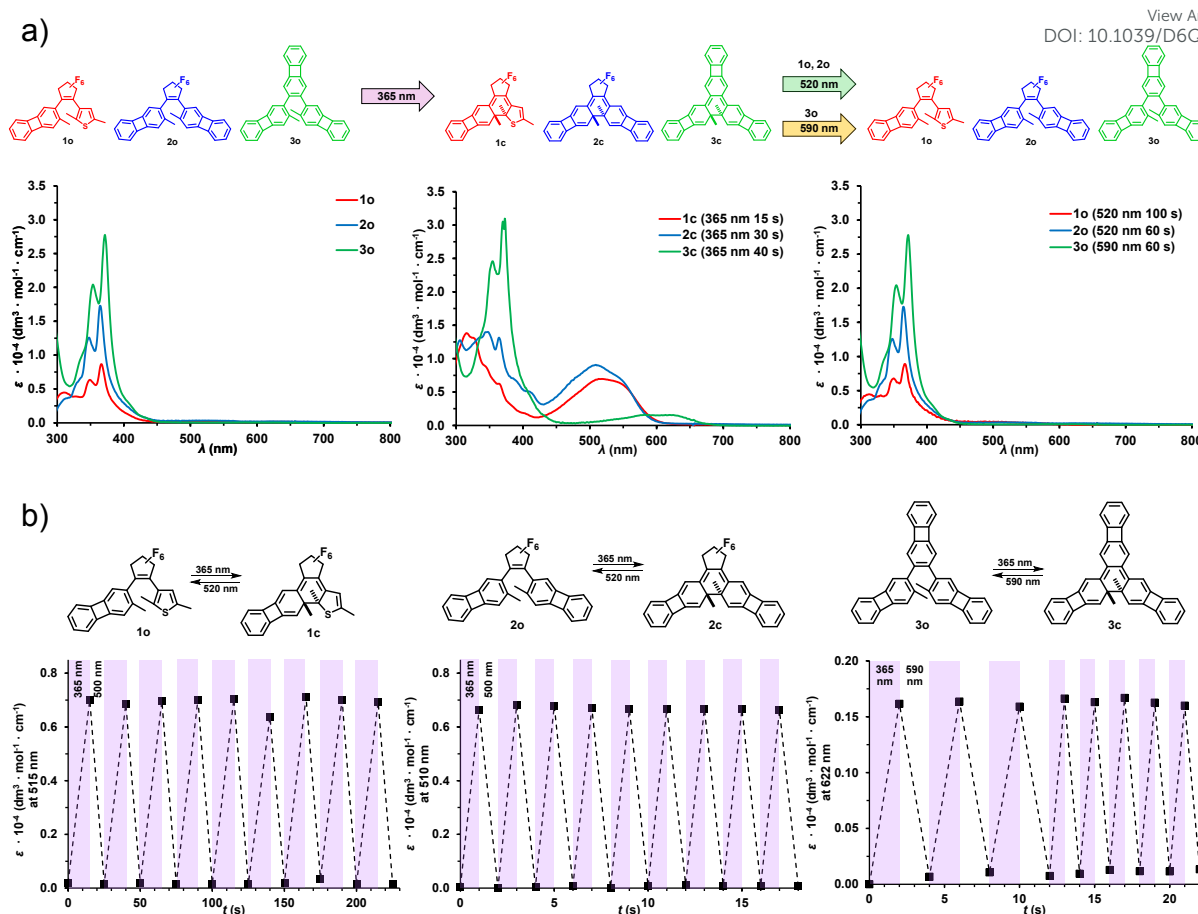


Figure 3. a) UV-vis spectra of **1-3** ($c = 3 \cdot 10^{-5} \text{ M}$, toluene, rt, N_2) before irradiation (left), after irradiation with 365 nm (1 W) light (middle), and then visible light (right) showing the reversible photoisomerization. Note that the molar extinction coefficients presented after the UV irradiations are apparent coefficients representing the PSS under the given conditions and are not the photospectra of isolated closed forms. b) Fatigue resistance of the three new compounds demonstrated through multiple photoswitching cycles with varying irradiation times, represented by the absorbance changes at their characteristic isomerization wavelengths ($c = 3 \cdot 10^{-5} \text{ M}$, toluene, rt, N_2). (During fatigue measurements, for the irradiation of compound **1** 1 W LEDs, while for the irradiation of compounds **2** and **3** 30 W LEDs were used.)

Further investigation of photostability was done by continuous irradiation of the samples with high intensity UV light (30 W, 365 nm LED) under both aerobic and inert conditions in toluene solutions (see section S3.3, SI). These experiments revealed that compounds **1** and **3** do not show significant degradation under an inert atmosphere in toluene. However, all three photoswitches are oxygen-sensitive, and compound **2** degrades even under an inert atmosphere, with an approximate half-life of 30 minutes under the irradiation conditions (assuming first-order kinetics). However, the nature of the degradation process requires further investigations.



During the UV-vis spectroscopic monitoring of the irradiation experiments it became clear that these switches have a rather rapid photoresponse in both the ring-closing and ring-opening direction. To further explore this, we performed measurements with low-power (1 W) LEDs and high sampling rate (every 2 s). The results are shown in Figure 4a (see also section S3.2, SI). Upon irradiation with UV-light, compound **2** reached the highest molar extinction coefficient (around $9\,000\text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) with the fastest photoresponse, reaching the photostationary state in 18 s. Similarly, compound **2** showed the fastest ring-opening (about 28 s) upon irradiation with visible light, while it took roughly 90 s for the other two switches. The comparably slow ring closing of compound **3** is likely due to the presence of a non-photoactive conformer, which reduces the likelihood of photoisomerization. Compounds **1o** and **2o** underwent ring closing reaction even when irradiated with 400 nm light. In these cases, the extinction coefficients of the photostationary states were somewhat lower (68% and 48%, respectively, of the values reached upon 365 nm irradiation of **1** and **2**) (Figure 4 c,b), but it is significant that these DAEs can photoisomerize even with visible (blue) light irradiation.

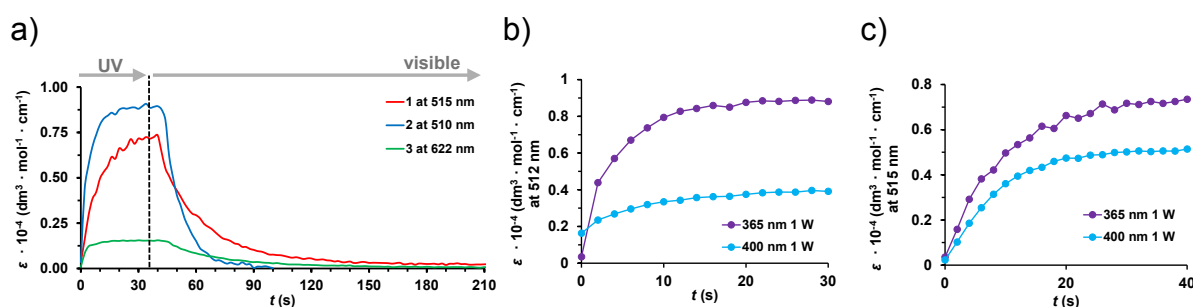


Figure 4. a) The rates of photoresponse of **1o-3o** upon irradiation with UV and visible light, monitored through the absorbance changes at their characteristic isomerization wavelengths (spectra were recorded in every 2 s). The photostationary states were reached using a 365 nm 1 W LED. The dashed line indicates the end of irradiation with UV light and the start of the ring-opening process with visible light irradiation ($c = 3 \cdot 10^{-5}$ M, toluene, rt, N_2). Comparison of the ring closing reactions of b) **2** and c) **1** when irradiated with 365 nm and 400 nm light.



Table 1. Summary of the properties of photoswitches **1**, **2** and **3**.View Article Online
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Compound no.	$\lambda_{\text{max,open}}$ (nm)	$\epsilon_{\text{max,open}}$ ($\text{M}^{-1} \cdot \text{cm}^{-1}$)	$\lambda_{\text{max,closed}}$ (nm)	$\epsilon_{\text{max,PSS}}$ ($\text{M}^{-1} \cdot \text{cm}^{-1}$)	$t_{1/2}^{25^\circ\text{C}}$ (h)	PSS composition ^[a] (% closed)
1	350	6 340	315	13 800	-[b]	67
	366	8 660	513	6 970		
2	349	12 600	349	14 000	780	41
	365	17 300	510	9 060		
3	353	20 400	354	24 600	0.36	3
	372	27 800	373	31 000		
			583	1 580		
			619	1 570		

^[a] Determined by ¹H-NMR spectroscopy.^[b] No thermal ring opening was observed after 5 h at 100°C.

The closed forms could isomerize back to the open form thermally as well at different rates, that was dependent on the structure. While the ring opening of **1c** was not observed even after 5 h at 100 °C in toluene, the half-lives of **2c** and **3c** were determined to be 780 h (32.5 days) and about 20 min, respectively (at 25 °C in toluene) (see also section S3.4, SI). This finding is in line with the lower intensity of the UV-vis absorptions in the case of **3** and highlights how the thermal properties can be tuned by varying the subunits of the BP based photoswitches. Notably, the analogue of **2** with benzene pillar units has been reported.⁴⁸ The thermal half-life of its closed isomer was on the scale of a few minutes due to the strongly aromatic pillars compared to those in compound **2**. Quantum yields (Φ) of the light-induced ring closing (Φ_{RC}) and ring opening (Φ_{RO}) reactions for P-type switch **1** were determined^{49,50} to be $\Phi_{RC} = 0.16$ and $\Phi_{RO} = 0.44$ (see also section S7, SI). Higher quantum yields for the ring opening directions have been documented for DAEs with six-membered aryl pillars due to rearomatization.^{48,51}

¹H NMR spectroscopy was used to characterize the structure of the closed forms and to quantify their ratios in the photostationary states (Figure 5 and section S4, SI). Samples were irradiated with high-power LEDs (30 W) at room temperature (a water bath was used to prevent the heating of the sample) in C₆D₆ for different time periods. In each case, a new set of absorptions appeared in the spectra that could be assigned to the closed forms of the switches. No signs of significant degradation were detected during the time of the measurements. Indicative of the ring-closing process were the downfield shifts of the Hs on the terminal benzene rings of the BP units and the upfield shifts of the methyl Hs (Figure 5). The former indicates the increased



aromaticity of the terminal benzene rings in BP upon photochemical ring closing, while the latter corresponds to a loss of the aromatic ring current adjacent to the methyl groups. Among the structures the highest ratio of the closed form was observed for compound **1**, approximately 67% after 5 min irradiation in toluene. For **2** and **3**, the ratios of the closed forms were 41% and 3%, respectively. The very low ratio of the closed form for compound **3** can be explained by the presence of a non-photoactive conformer and rapid thermal ring opening in this case. Note that the PSS values are approximative as about 2-3 minutes passed between the end of the irradiation of the samples and the measurement due to instrument setting. The spectral, photochemical and thermal properties of compounds **1-3** are summarized in Table 1.

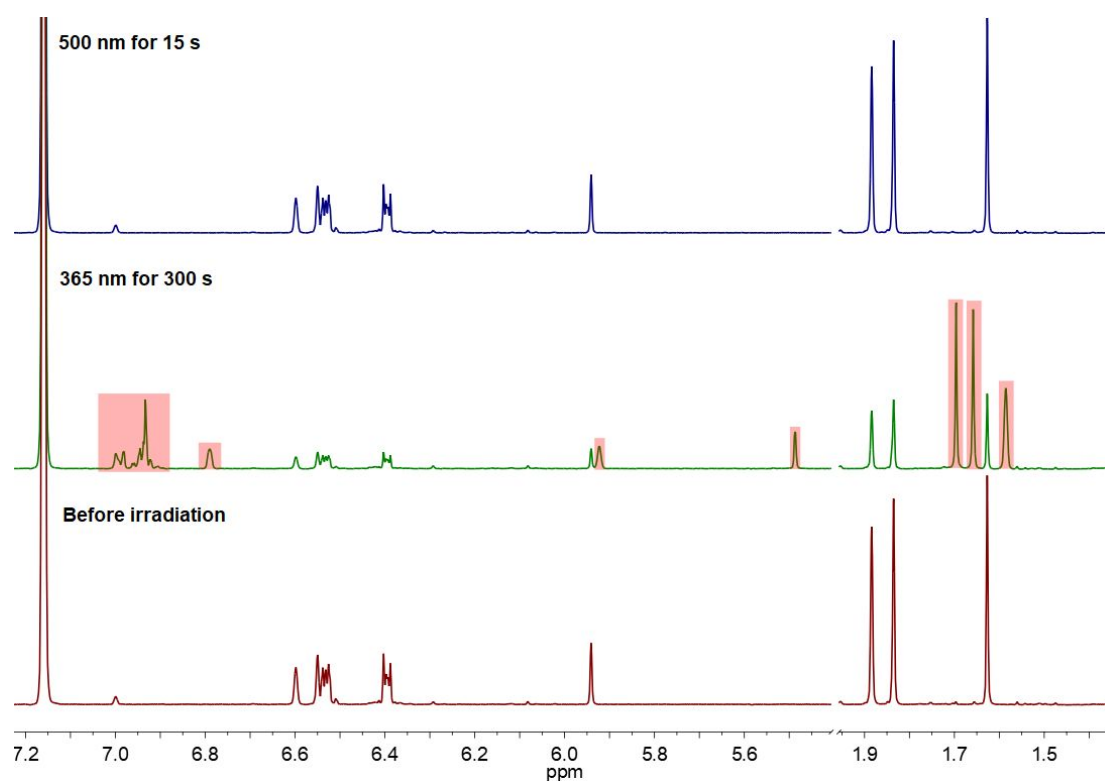


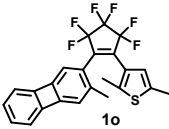

Figure 5. ^1H NMR (500 MHz, C_6D_6 , $c = 1.4 \cdot 10^{-2}$ M, 3 mm diameter tube) spectral changes upon irradiation of **1o** with UV (365 nm, 30 W LED) and visible (500 nm, 30W LED) light. The new peaks associated with **1c** after the UV irradiation step are highlighted in red. (Note that the low-intensity signal at 7.0 ppm is the higher-field satellite signal of the residual $\text{C}_6\text{D}_5\text{H}$ in the solvent.)

An apparent benefit of all BP-based photoswitches prepared thus far (including the previous work of our research group)³⁷ is that the wavelength at which the ring closing reaction can be triggered is significantly redshifted towards the visible range, compared to DAEs with



the more general thiophene containing pillars.¹⁰ A brief comparison of compound **1** having a BP and a thiophene pillar with the well-described photoswitch **16**⁵² (Table 2) shows that while **16o** requires UV light for its photoisomerization, **1o** possesses a redshifted absorption band, and can be photoisomerized even with 400 nm light, as shown in Figure 4b. This change can be attributed to the BP moiety, as biphenylenes usually have absorption bands around 365 nm owing to their decreased aromatic stabilization. Furthermore, unlike **2** and **3**, the closed form of **1** shows high thermal stability, along with solid-state photochromism (Figure S14, SI); features that are similar to **16**. The latter is another interesting point, as it seems that two BP pillars (as in **2** and **3**) are too bulky to allow the conrotation in solid phase, but only one (as in **1**) can still manage. Importantly, replacement of one of the thiophene pillars in **16** to BP, as in **1**, leads to improved fatigue resistance.

Table 2. Comparison of the basic properties of BP-containing **1o** and well-known **16o**.

		
Excitation (nm) ^[a]	365, 400	254, 313
Thermal stability ^[b]	stable	stable
Solid-state switching	yes	yes
Fatigue resistance	improved	limited

^[a] Irradiation wavelength to trigger ring closing.

^[b] Thermal stability of the closed form.

Since the closed forms of the switches are significantly different conjugated systems compared to their open isomers, it is instructive to computationally explore these structures to gain a deeper understanding of the aromaticity changes associated with the ring-closing process. All calculations were performed with the ORCA 6.1 suite of programs.⁵³⁻⁵⁷ Nucleus Independent Chemical Shift (NICS) calculations⁵⁸⁻⁶⁰ were carried out for all switches both in their open and closed forms (Figure 6 and section S6, SI). In an applied magnetic field positive NICS values indicate paratropic ring currents associated with antiaromaticity, while negative NICS values indicate diatropic ring currents associated with aromatic character. NICS_{zz} values were calculated at the center of each ring both at the ring plane [NICS(0.0)_{zz}] and 1.70 Å above the rings [NICS(1.7)_{zz}]. We found that the NICS(0.0)_{zz} values of the symmetric pillar groups were identical, and the differences between the NICS(1.7)_{zz} values were insignificant. To further validate the single-point NICS_{zz} values, NICS-XY-scans were performed at 1.7 Å above



the plane of the BP subunits of both **1** and **3** (see section S6, SI). These scans also revealed systematic NICS changes between the rings. It is generally accepted that NICS(1.7)_{zz} values indicate antiaromaticity at values greater than 5.0 ppm, and aromaticity below -5.0 ppm. Between -5.0 ppm and 5.0 ppm the ring is considered non-aromatic.⁶⁰ We further divided the values associated with aromatic rings into three arbitrary sections to better represent the aromaticity changes in the specific case of these photoswitches. Below -17 ppm we refer to the rings as being “strongly aromatic” to indicate the strongest aromatic ring currents observed. We then drew another distinction at a value of -12 ppm to indicate the difference between the inner (C/C') and outer (A/A') benzene rings of the BP subunits.

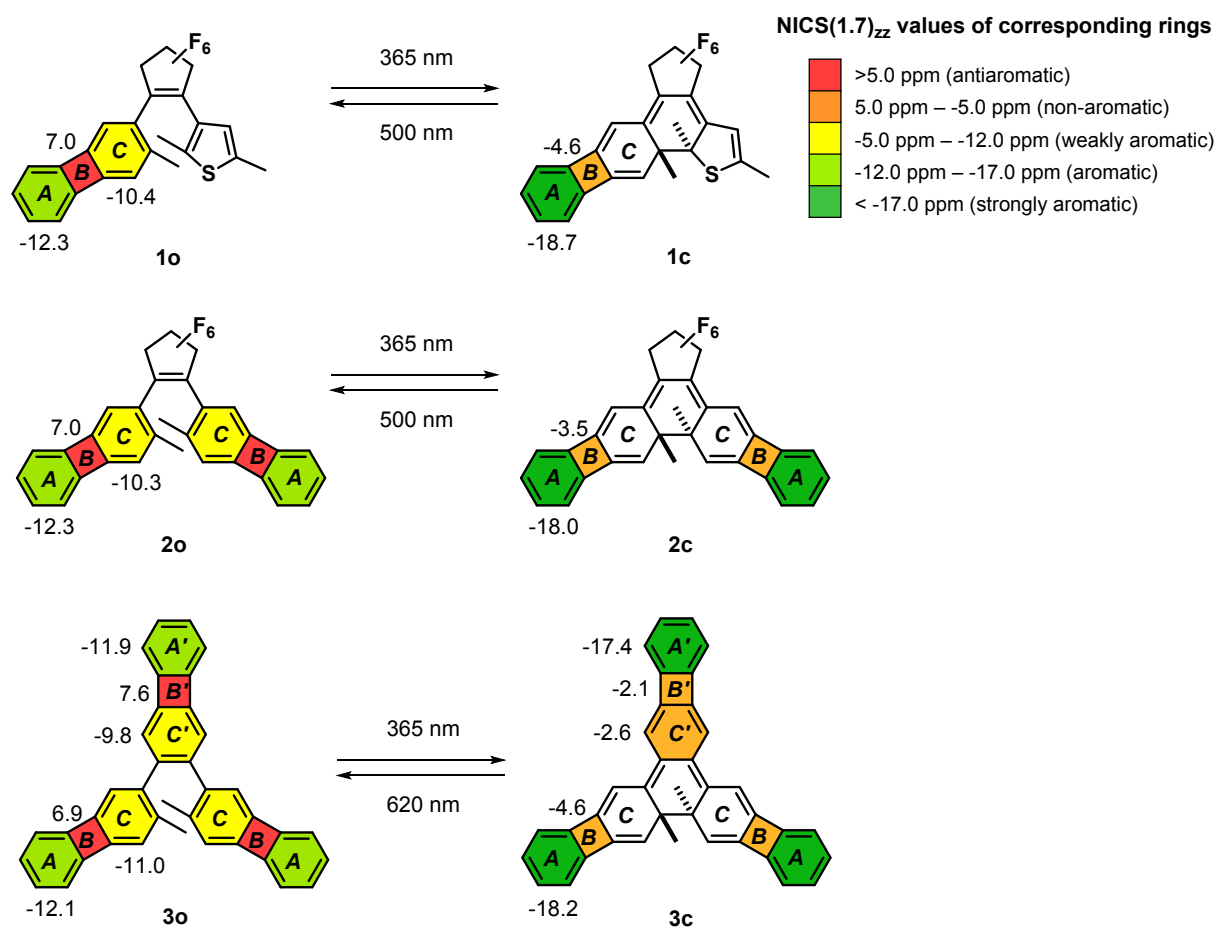


Figure 6. Differences in (anti)aromaticity between the open and closed forms of switches **1-3**. NICS(1.7)_{zz} values next to the rings are given in ppm units.

The calculations show that the BP subunits in open forms **1o-3o** have NICS values similar to those of the BP molecule. Specifically, the benzene rings are weakly aromatic, while the central 4-membered rings have some antiaromatic character. Photochemical ring closing changes this situation strongly. In the closed forms **1c-3c** the outer benzene rings (A/A') reach NICS(1.7)_{zz} values of about -18 ppm indicating aromaticity gain. The increase in aromaticity is independent



of whether the BP unit functions as a bridge or a pillar. This finding is in line with $^1\text{H NMR}$ spectroscopic data that show the downfield shift of the Hs on the outer benzene rings of the BP units upon ring closing. The region between the strongly aromatic outer benzene rings (A/A') is non-aromatic in each case, based on the NICS values. The presence of these extended non-aromatic sp^2 carbon frameworks is likely the reason for the degradation of the closed forms upon extended UV irradiation. Note that NICS indices were not calculated for rings C in **1c** and **2c** and **3c**, since the newly formed ring systems involving these rings can only be considered as olefinic due to the sp^2 to sp^3 hybridization change that occurs during the electrocyclization reaction.

Conclusions

We have prepared and thoroughly characterized three novel diarylethene-type photoswitches with the aim of establishing biphenylene as a viable structural motif for all functional parts of this family of compounds, best demonstrated by **3**. We found these compounds to be fast switches that are reasonably resistant to photofatigue. Our results demonstrate that variation of the “bridge” unit in this type of photoswitches has far-reaching effects on the properties of these compounds, while varying the “pillar” units is also a viable way to fine-tune them. The biphenylene motifs offer a number of advantages, perhaps most importantly the general shift towards reversible visible light-only isomerization, and access to all-carbon photoswitches. Furthermore, the ability to reversibly change the aromaticity of the biphenylene units on photoisomerization is retained even when the biphenylenes act only as “pillar” groups. This could be exploited in the future in functionalized switches for controlling various molecular properties.

Author contributions

Barnabás Zsignár-Nagy and Bence Pál performed the syntheses. Barnabás Zsignár-Nagy and Attila Kunfi performed the UV-vis measurements and the kinetic studies. Barnabás Zsignár-Nagy and Péter J. Mayer performed the calculations. Gábor London conceptualized the research. Barnabás Zsignár-Nagy and Gábor London wrote the manuscript. All authors contributed to the final version of the manuscript.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available.

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Data Availability Statement

View Article Online
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The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available.



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