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Sterically Crowding the Bridge of Dithienylcyclopentenes for Enhanced Photoswitching Performance

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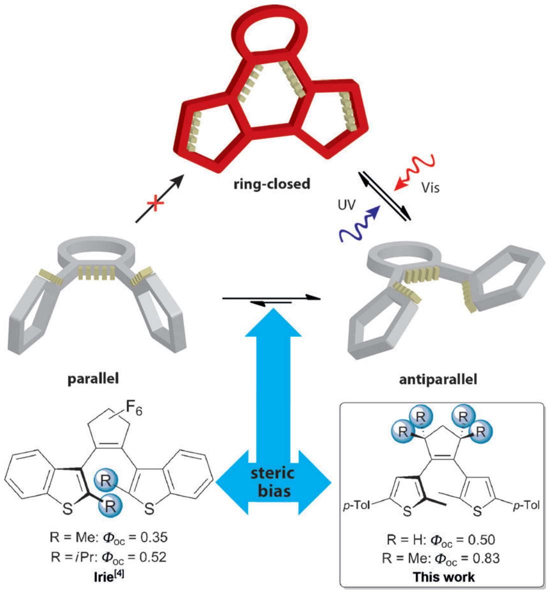
Diarylethenes (DAEs) are photochromic molecules with outstanding physicochemical properties. DAEs undergo a reversible 6π electrocyclic reaction upon irradiation with light.[1] They are ideal for incorporation into materials for optoelectronics because of their superior switching properties, in particular their thermal stability and high fatigue resistance, together with the large optical and electronic changes that occur upon their switching between ring-open and ring-closed forms.[2] However, further improvement of their switching efficiency[3] and reversibility[4] is of fundamental concern in view of their application in real devices. The efficiency of the photocyclization reaction is governed by its quantum yield (Φ_{oc}), which is dependent on the equilibrium between the parallel (p) and the antiparallel (ap) conformation (Scheme 1, top).[5,6] The quantum yield, Φ_{oc}, is intrinsically limited to 0.5 for conventional DAEs because photocyclization can take place in a conrotatory manner from the ap conformation only. To achieve higher photocyclization quantum yields it is necessary to bias the conformational equilibrium and several approaches towards this goal have been reported.

In one approach, mechanical locking of DAEs in the ap conformation was achieved either by incorporating the photochromic unit into a polymer backbone[7] or by covalently connecting bridging and aryl moieties.[8] However, these methods are not generally applicable for small molecules and do not allow versatile functionalization of the aryl moieties. Alternatively, extraordinarily high photocyclization quantum yields could be realized by incorporating attractive hydrogen-bonding and sulfur–nitrogen interactions between the bridge moiety and aryl termini of the switch.[3,9] Yet, a fundamental drawback of using these directed noncovalent interactions is their intrinsic solvent dependency, which is reflected in the varying Φ_{oc} values.[3,9] In contrast, steric repulsion, which is largely independent of the environment, can also be used to influence the equilibrium between p and ap conformation. Sterically demanding substituents can either be introduced at the terminal aryl moieties or in the bridge. The research group of Irie used the former approach to obtain higher Φ_{oc} values for one distinct type of derivative (Scheme 1, bottom left).[5] However, the latter approach has thus far not been systematically explored. Introducing steric bias in the bridge should enable flexible functionalization of the termini, an ability that is essential to realize and optimize optoelectronic property changes (Scheme 1, bottom right).



Scheme 1. Schematic representation of the photocyclization of DAEs, as governed by the equilibrium between parallel (p) and antiparallel (ap) conformations (top). Steric repulsion can be used to bias the conformational equilibrium, through the introduction of bulky groups at either the thiophene termini (bottom left) or in the bridge (bottom right).

Herein, we report a synthetically straightforward method for introducing bulky substituents into the bridge moiety of dithienylcyclopentenes, thus leading to derivatives exhibiting higher photocyclization quantum yield. We focused on DAEs consisting of 3-thienyl termini linked by a cyclopentene bridge because these systems are by far the most widely employed.[1] The five-membered cyclopentene bridge has been established to have the best balance of switching performance and spectral differences between the two interconverting isomers.[10] Instead of the common perfluorocyclopentene bridging motif,[1] dithienylperhydrocyclopen-

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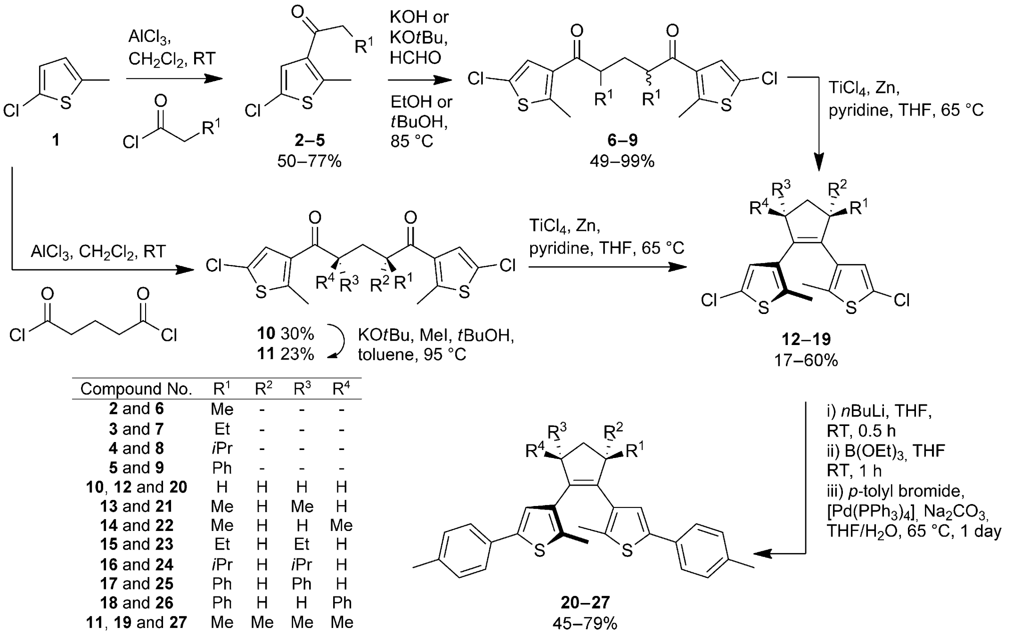


Compound No.	R^1	R^2	R^3	R^4
2 and **6**	Me	-	-	-
3 and **7**	Et	-	-	-
4 and **8**	*i*Pr	-	-	-
5 and **9**	Ph	-	-	-
10, **12** and **20**	H	H	H	H
13 and **21**	Me	H	Me	H
14 and **22**	Me	H	H	Me
15 and **23**	Et	H	Et	H
16 and **24**	*i*Pr	H	*i*Pr	H
17 and **25**	Ph	H	Ph	H
18 and **26**	Ph	H	H	Ph
11, **19** and **27**	Me	Me	Me	Me

Scheme 2. Synthesis of dithienylethenes **20**–**27**.

tenes[11] were chosen because they are readily accessible through McMurry cyclization of the corresponding 1,5-diketone precursors and their α-chlorothienyl termini allow for modular postfunctionalization.[11]

Our synthesis of the target photochromes **20**–**27** is based on the easily accessible key α,α′-di- and α,α,α′,α′-tetrasubstituted 1,5-diketone intermediates **6**–**11** (Scheme 2). Starting from 2-chloro-5-methyl-thiophene (**1**), alkanoylated compounds **2**–**5** were easily obtained by employing Friedel–Crafts acylation. Aldol condensation of **2**–**5** with formaldehyde afforded the corresponding α,β-unsaturated ketones, which served as Michael acceptors in a conjugate addition reaction with **2**–**5** to give α,α′-disubstituted diketones **6**–**9** in moderate to excellent yields.[12] The transformation of ketones bearing bulky substituents at the α position necessitated the use of a stronger base (KO*t*Bu instead of KOH) to achieve sufficiently efficient enolization. Notably, derivatives bearing tertiary alkyl groups at the α position, such as *t*Bu, could not be prepared because the corresponding α,β-unsaturated ketone was not formed; only the aldol addition product was isolated in this case. The α,α,α′,α′-tetramethyl derivative **11** was obtained by methylation of precursor **10**. McMurry condensation of 1,5-diketones **6**–**11** gave dichloro-substituted dithienylcyclopentenes **12**–**19**, which were subsequently transformed into the target compounds **20**–**27** through in situ borylation followed by Suzuki cross-coupling with *p*-tolyl bromide. In principle, any aryl halide could be employed in this versatile late-stage functionalization reaction. Notably, for the α,α′-disubstituted compounds, our synthesis provides access to the target photochromes, which were obtained as a mixture of *cis* and *trans* diastereomers of varying composition; these diastereomers could be separated successfully and characterized by NMR analysis.

To investigate the effect of substitution on the switching efficiency, quantum yields of cyclization (Φ_{oc}) and ring-opening (Φ_{co}) were determined by absorption measurements upon irradiation with either UV or visible light, respectively (Table 1). From the data it is clear that compounds containing α,α′-disubstituted cyclopentene moieties have higher quantum yields ($\Phi_{oc} \approx 0.6$) than the parent unsubstituted compound **20**. Interestingly, neither the steric demand of these α substituents, that is, whether the substituent is a methyl group (**21** and **22**), an ethyl group (**23**), an isopropyl group (**24**), or a phenyl group (**25** and **26**), nor the identity of the diastereomer (**21** versus **22** and **25** versus **26**) has a measurable effect on Φ_{oc}. However, α,α,α′,α′-tetrasubstituted product **27** has the remarkably high Φ_{oc} value of 0.83.

Table 1. Photocyclization (Φ_{oc}) and ring-opening (Φ_{co}) quantum yields of diarylcyclopentenes **20**–**29** in different solvents.

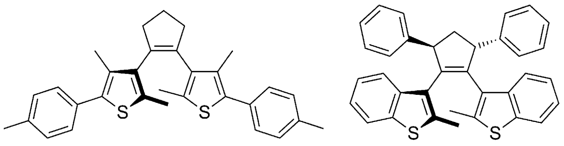
Compound	Φ_{oc}[a]	Φ_{co}[b]	pss [%][c]
20[d]	0.50	0.01	92
21[d]	0.57	0.01	94
22[d]	0.57	0.01	84
23[d]	0.63	0.01	85
26[d]	0.64	0.01	92
27[d]	0.83	0.01	93
24[e]	0.58	0.01	86
25[e]	0.61	0.01	90
28[d]	0.32	0.04	64
29[d]	0.25[f]	0.54[g]	62

[a] $\lambda_{irr}=313$ nm. The uncertainty of measurements is estimated as being ±0.05 for ring closure. [b] $\lambda_{irr}=546$ nm. The uncertainty of measurements is estimated as being ±0.005 for ring opening. [c] Fraction of the ring-closed isomer in the photostationary state (pss) as determined by ultra-high-performance liquid chromatography (UPLC). [d] In MeCN. [e] In MeCN, CH$_2$Cl$_2$, MeOH, toluene, and cyclohexane. [f] $\lambda_{irr}=280$ nm. [g] $\lambda_{irr}=436$ nm.

Most importantly, the large quantum yield of cyclization was found to be independent of the polarity of the solvent, the solvents tested being nonpolar, such as cyclohexane, to polar, such as acetonitrile and the protic solvent, methanol.

The observed increase in the quantum yields of cyclization upon substitution can be rationalized by considering the increased steric repulsion between the α substituents of the cyclopentene bridge and both the α-methyl and β-hydrogen substituents of the adjacent terminal thienyl moieties, a repulsion that would shift the conformational equilibria in favor of the reactive ap conformer.

To verify this assumption, ring-open forms of unsubstituted dithienylethene **20** and α,α,α′,α′-tetrasubstituted derivative **27** were investigated using variable-temperature ^{1}H NMR spectroscopy. For compound **20**, we were unable to directly determine the ratio of the two conformers by integration of the respective signals since the signals derived from the p and ap conformation were overlapping, even at temperatures as low as −80 °C. For the best-performing compound, dithienylethene **27**, however, a nonlinear shifting of various signals was observed upon temperature variation. When the approach of Coudret and co-workers[13] was used, the fraction of the ap conformer in the ring-open form at 25 °C was estimated as being 81 ± 10 % (see the Supporting Information). This value is in good agreement with the experimentally determined quantum yield of cyclization, Φ_{oc} = 0.83, and supports the underlying hypothesis that biasing the conformational equilibrium towards the ap form is the key mechanism that determines the improvement of photocyclization quantum yields of dithienylethenes.



Scheme 3. DAEs **28** and **29** with blocked α positions and increased steric strain.

To gain further insight into the steric repulsion between substituents, dithienylcyclopentene **28**, which contains methyl groups only at the 3- and 5-positions of the thiophene termini,[14] as well as dibenzothienylcyclopentene **29**, which contains substituents on both the bridge moiety and the thiophene termini, were prepared and investigated (Scheme 3). For **28**, the photocyclization quantum yield was only 0.32 (see Table 1), which is significantly lower than that of **27** and indicates either unfavorable steric or electronic interactions; these data are in agreement with known β-methyl substituted perfluorocyclopentenes, which show similar behavior.[15] Surprisingly, for **29**, the photocyclization quantum yield, Φ_{oc}, was similarly low, thus suggesting that the advantageous effect of the α substituents is negated by the substituents on the thiophene termini, presumably because of excessive steric strain. This assumption is supported by the absorption spectra of the different photoswitches **20** and **27**–**29** (Figure 1). With increasing steric interactions between the substituents in the bridge and the thiophene termini, the absorption maxima in the spectra of both the ring-open and ring-closed isomers show considerable hypsochromic shifts (see also the Supporting Information, Table S-1). These shifts suggest that in the ring-open and the ring-closed forms of diarylcyclopentenes **28** and **29**, the π conjugation is heavily disturbed. Because **28** and **29** have photostationary states that are composed of lower amounts of the ring-closed form relative to that of **27**, and the quantum yields for ring opening are much higher (as high as 0.5), it is reasonable to assume that the lower photocyclization quantum yields result from lower thermodynamic stability of the ring-closed isomers.

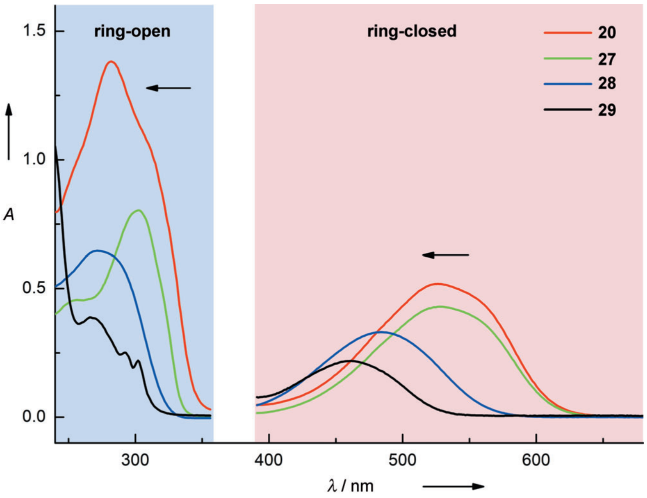


Figure 1. Maxima in the absorption spectra of ring-open (left) and ring-closed (right) isomers of DAEs **20** and **27**–**29** (25 °C, ca. 10^{-5} M in MeCN) with steric strain increasing in the direction of the arrow.

In contrast, the introduction of substituents at the α and α′ positions of the cyclopentene bridge does not affect the absorption spectra, the spectra of derivatives **20**–**27** being almost identical and showing absorption maxima at around 530 nm (see also the Supporting Information, Figure S-1 and S-2). In addition, the quantum yields of ring opening, Φ_{co}, of these dithienylcyclopentenes can be considered constant and independent of the substitution pattern of the bridge moiety.

Considering the above data, tetramethylsubstituted derivative **27** exhibits the optimum substitution pattern for maximizing photocyclization quantum yield without compromising on other switching attributes.

Most importantly, the improved switching performance does not lead to changes in optical and redox properties of the two switching states, properties that are crucial for gating optoelectronic functionality.[16] This key point is illustrated by a comparison of the absorption spectra and the first reversible oxidation potentials of the ring-open and ring-closed forms of the investigated photochromes

(Table 2). The large spectral separation between the ring-open and ring-closed isomers of about 250 nm remains constant throughout the series, that is, the absorption spectra do not change upon varying the bridge substitution. Notably, there is only a slight influence of the orientation of the α and α′ substituents on the relative intensity of the two vibronic bands in the ring-open form. In addition, the large difference between the first oxidation potentials of both switching states in the range of 0.73–0.82 V is hardly affected.

Table 2. Oxidation potentials and absorption maxima of ring-open and -closed dithienylcyclopentenes **20**–**27** and their difference.

Compound	Ring-open form		Ring-closed form		Difference Δ_{oc}	
	E_p^{a} [V][a]	λ_{max} [nm][b]	E_p^{a1} [V][a]	λ_{max} [nm]	ΔE_p^{a1} [V][a]	$\Delta\lambda_{max}$ [nm]
20	0.73	282	−0.02	527	0.75	245
21	0.74	282	−0.03	524	0.77	242
22	0.71	282	−0.03	526	0.74	244
23	0.75	283	−0.04	529	0.79	246
24	0.76	284	−0.06	537	0.82	253
25	0.80	285	0.04	532	0.76	247
26	0.79	284	0.05	529	0.73	245
27	0.78	283	−0.01	529	0.79	246

[a] The data are given in reference to the ferrocene redox couple (Fc/Fc^+), in MeCN, 0.1 M Bu_4NPF_6, 25 °C. [b] Mean of both vibronic bands, associated with transoid and cisoid orientation of the α and α′ substituents.

In conclusion, we have successfully developed a strategy to improve the switching performance of DAE photochromes. By introducing bulky substituents in the bridge moiety of dithienylcyclopentenes, derivatives exhibiting enhanced photocyclization quantum yield were obtained, the quantum yield being independent of the environment (solvent). The improved switching efficiency was achieved without compromising on the differences in the optical and redox properties of the ring-open and ring-closed states, thus rendering the new photoswitches ideal candidates for applications in light-gated optoelectronic devices. Investigations on the origin of the observed effect, on resolving the conformational equilibrium, and on the diastereoselectivity of the ring-closing reaction are currently underway in our laboratories. Furthermore, the improved switches are being implemented in optically addressable thin-film transistors.

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Keywords: aldol reaction • diarylethenes • photochromism • quantum yield • steric hindrance

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