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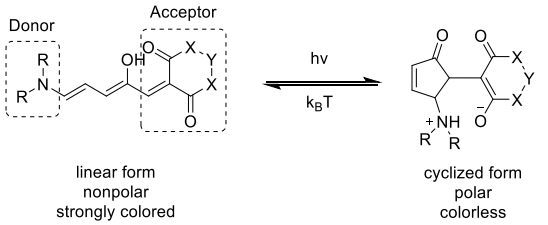
It's a Trap: Thiol-Michael Chemistry on a DASA Photoswitch

Jessica Alves, [§a] Sandra Wiedbrauk, [§a] David Gräfe,[a] Sarah L. Walden,[a] James P. Blinco,*[a] and Christopher Barner-Kowollik*[a]

Abstract: Donor-Acceptor Stenhouse Adducts (DASA) are popular photoswitches capable of toggling between two isomers depending on the light and temperature of the system. The cyclized polar form is accessed via visible light irradiation, while the linear nonpolar form is recovered in the dark. Upon the formation of the cyclized form, the DASA contains a double bond featuring a β-carbon prone to nucleophilic attack. Here, we present an isomer selective thiol-Michael reaction between the cyclized DASA and a base-activated thiol. The thiol-Michael addition was carried out with an alkyl (1-butanethiol) and an aromatic thiol (*p*-bromothiophenol) as reaction partners, both in the presence of base. Under optimized conditions, the reaction proceeds preferentially in the presence of light and base. The current study demonstrates that DASAs can be selectively trapped in their cyclized state.

Molecular photoswitches undergo reversible isomerization upon irradiation with light, and sometimes in combination with a different stimulus, e.g. temperature.[1] Light, as a readily available and adjustable reaction trigger, is particularly interesting for implementing spatiotemporal control on reaction outcomes. For example, photoswitches are employed for biomedical and biochemical processes including targeted drug delivery and chemical/biological sensing applications.[2–5] Photoswitches, such as derivatives of the Donor-Acceptor Stenhouse Adduct (DASA), coexist in an equilibrium between two isomeric forms. One isomer is constituted of an intensely colored (blue, purple or orange) nonpolar linear form, while the other isomer is cyclized, polar, colorless and commonly zwitterionic (Scheme 1).[6–9] The equilibrium between the two forms is determined by the solvent environment and the structural motifs of the DASA derivatives, consisting of an electron donor as well as an acceptor moiety, resulting in a push-pull system. Upon irradiation, the equilibrium is shifted towards the ring cyclized isomer (cyclized form) and — upon thermal relaxation — returns to the initial conjugated state (linear form). The cyclization mechanism has been clarified in a careful study by *Feringa* and *Buma* where density functional theory calculations and transient absorption kinetics measurements were employed.[32] The current consensus on the cyclization process involves isomerization of the double bonds, followed by a bond rotation, and finally a thermal conrotatory 4π electrocyclization leading to the cyclized ring, commonly stabilized by its zwitterionic form through a proton transfer.[10–13] Clarification of the cyclization mechanism resulted in a pool of DASA photoswitches bearing a variety of acceptor and donor functionalities as well as an improved knowledge of factors influencing the switching process.[8,9,14,15]



Scheme 1. The photoswitching of DASA between the linear and cyclized form, depicted for a general structural motif. The acceptor group may be altered by substituting X and Y, while the donor properties are adjustable via the amino functionality R.

The inherent advantages of DASA photoswitches, which includes negative photochromism, inexpensive starting materials, modular synthesis, tunable absorption spectrum, visible light switches, and good fatigue resistance, are appealing for a range of applications. To date, polarity and color are the main adjustable properties of DASAs explored for applications including micelles formation targeting biomedical applications,[4,16] pH and temperature sensors,[5,17] and visible light responsive devices.[18–20]

The isomerization of DASAs is dependent on the prevailing conditions, such as solvent, temperature, concentration or pH.[21] The effect of the solvent on the switching behavior of the DASA has been previous reported in the literature.[7,10,21] DASAs are commonly categorized according to the different generations. The first generation DASAs — the focus of the present study — are stabilized in the cyclized form with protic solvents, whereas halogenated solvents encourage the linear form.[10,21] For first generation DASAs, aromatic solvents are known for allowing reversible switching upon irradiation, followed by a fast, thermally induced reversion to the linear form in the absence of light.[10,21] Second generation DASAs have been reported in the literature, however, the equilibrium in the dark consists of a mixture between linear and cyclized form without allowing the control of equilibrium ratio with light. Therefore, the present work focuses exclusively on a first generation DASA. Precisely, we used **D1** in this study.

To the best of our knowledge, ligation reactions of DASA photoswitches have not been reported so far and the reactivity as well as selectivity of this molecule class remain unknown. Selectively gated reactions are uncommon, with only a few successful systems known.[22–24] The ability of molecules to

[a] J. Alves, Dr. S. Wiedbrauk, Dr. D. Gräfe, Dr. S. L. Walden, Dr. J. P. Blinco, and Prof. Dr. C. Barner-Kowollik
School of Chemistry, Physics and Mechanical Engineering
Queensland University of Technology
2 George Street, Brisbane, QLD 4000 Australia
E-mail: christopher.barnerkowollik@qut.edu.au; j.blinco@qut.edu.au

§ These authors contributed equally to the work

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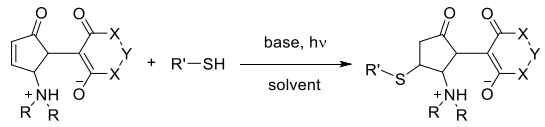
react selectively in only one of its isomeric states is promising for the development of advanced materials, e.g. for the use as inks in direct laser writing.[22] Upon irradiation, the conjugated linear DASA forms a substituted cyclopentenone. The formation of an α,β-unsaturated carbonyl makes the β-carbon prone to nucleophilic attack in a (1,4) addition such as the thiol-Michael reaction. Since its first report in 1964 by *Allen et al*.[25] the thiol-Michael addition, being classified as a 'click-reaction', has been extensively used in organic and polymer synthesis.[26–29] The reaction commonly does not form any side-product, features a high selectivity and proceeds to high yields.[26–28] As the DASA isomerization and the thiol-Michael addition requires specific conditions (e.g. base and light), a screening of the reaction conditions is required to assess the potential of a respective ligation reaction. Herein, we show that the DASA photoswitches are a suitable class of compounds for a selective reaction with a thiol via a thiol-Michael addition of the DASA in its cyclized form (Scheme 2).

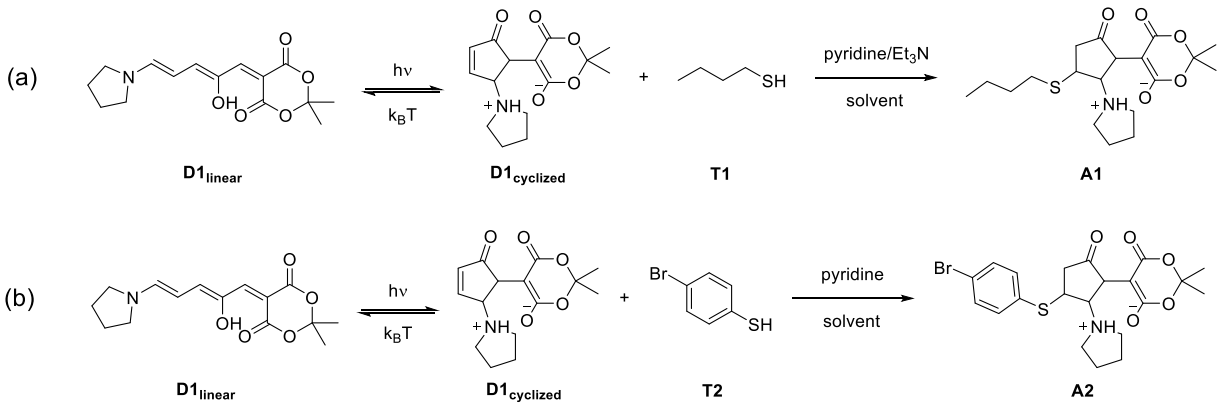


Scheme 2. A DASA photoswitch in the cyclized form can undergo a thiol-Michael addition at the activated double bond of the furan ring. Herein, reactivity was observed with both aromatic and alkyl thiols R'-SH.

The synthesis of the DASA photoswitch employed for the current study was adapted from the literature.[7,30] The photoswitch was obtained in quantitative yields as a red solid. The reaction of **D1** with the model thiols 1-butanethiol (**T1**) or *p*-bromothiophenol (**T2**) in the presence of a base, either pyridine or triethylamine (Et_3N), leads to the formation of **A1** and **A2**, respectively, as depicted in Scheme 3.

The photoinduced ligation reactions were performed in different solvents such as toluene, DCM, or methanol. In methanol the cyclization undergoes independently of light, in DCM reversible switching behavior is possible.[7,10,21] Toluene was selected as the solvent as it is well known to enable reversibility of the switching process of DASA compounds upon irradiation.[7] Further, the dark equilibrium of **D1** in toluene and DCM lies almost completely on the linear form (100% and 96%, respectively). The ligations were performed in toluene with 1.3 eq. of thiol under constant irradiation with green LEDs (λ_{max} = 525 nm, 3 mW·cm^{-2}). Structural proof for the successful ligation was obtained after column chromatography *via* nuclear magnetic resonance (NMR) spectroscopy and is supported *via* liquid chromatography coupled to electrospray ionization mass spectrometry (LC-MS).

LC-MS results of the unpurified reaction mixture between **D1** and **T1**, after irradiation for 2 hours, is shown in Figure 1 and indicates the formation of the thiol-Michael product **A1**.



Scheme 3. Switching of the DASA, initially in the linear form (**$D1_{linear}$**) upon light irradiation allows the formation of a cyclized species containing a cyclopentenone (**$D1_{cyclized}$**). The double bond formed is a suitable reaction partner for a thiol-Michael reaction in presence of pyridine or Et_3N with either (a) 1-butanethiol (**T1**) or (b) *p*-bromothiophenol (**T2**). The resulting thiol-Michael adducts are depicted as **A1** and **A2**, respectively.

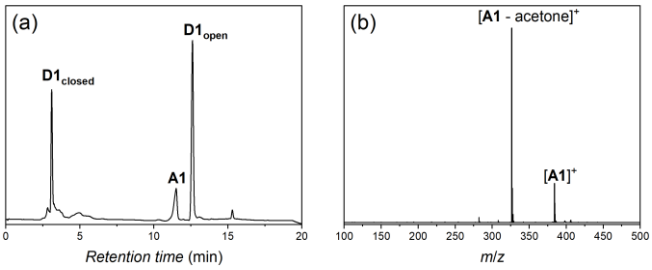


Figure 1. LC-MS analysis of the reaction between the DASA **D1** and 1-butanethiol (**T1**) upon irradiation (λ_{max} = 525 nm, 2 hours, 3 mW·cm^{-2}) in presence of pyridine in DCM. (a) Chromatogram and (b) MS spectrum at RT = 10.2 – 10.4 min of the thiol-Michael product **A1**. Refer to supplementary information for details on the mass accuracy.

Structural proof for **A1** was obtained via ^{1}H NMR spectroscopy (Figure 2). A recent study showed that the DASA switching was affected when the DASA concentration changed from 1 M to 0.003 M in toluene, demonstrating that the DASA switch is drastically inhibited at higher concentrations.[31] As a conventional ^{1}H NMR spectrum requires a concentration of approximately 0.01 M, the switching yield towards the cyclized form is limited. Therefore, to ensure sufficient conversion to the thiol-Michael product **A1** even at high DASA concentrations, the reaction was performed in methanol (MeOH), where the cyclized form is favored, even in the dark and with a greater excess of **T1** and

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Et_3N. The reaction consisted of dissolving 70.6 µmol of **D1**, 5.6 eq. of **T1** and 8.5 eq. of Et_3N in 5 mL methanol. The reaction mixture was stirred under ambient conditions for 48 hours. The thiol-Michael product **A1** was isolated by reverse phase column chromatography using a mixture of MeOH and acetonitrile (ACN).

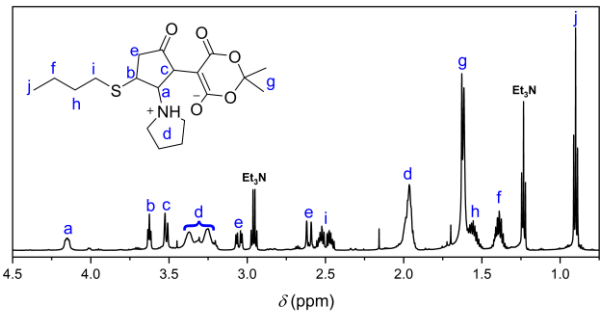

Figure 2. ^{1}H NMR spectrum (600 MHz, 25 °C) assignment in $CDCl_3$ of **A1**. The reaction between the DASA (**D1**) and 1-butanethiol (**T1**) in the presence of Et_3N under ambient conditions for 48 hours and purified by reverse column chromatography results in **A1**.

After purification of the thiol-Michael product **A1**, the reappearance of **D1$_{linear}$** and **D1$_{cyclized}$** was observed after some time. To investigate this, the stability of **A1** was assessed *via* ^{1}H NMR spectroscopy (Figure 3). The product was obtained via the aforementioned procedure using methanol as the solvent. ^{1}H NMR spectra were recorded as a function of time. Initially, the product **A1** comprises 94 % of the total species in the solution (**D1$_{linear}$**, and **D1$_{cyclized}$**). Over a period of more than 50 hours, an equilibrium between the species, **A1**, **D1$_{cyclized}$** and **D1$_{linear}$**, was observed. **D1$_{linear}$**, initially non-existent, was reformed while the quantity of **D1$_{cyclized}$** increases substantially (from 5 % to 20 % in the same timeframe). **D1$_{cyclized}$** is known to exist in several different isomers, shown by *Feringa* and *Buma et al.* recently.[32] So far little is known about the individual stability of these different isomers. It is hypothesized that the reaction of **T1** with one particular isomer of **D1$_{cyclized}$** is not stable in solution. Therefore, the bond once formed between **T1** and the less stable **D1$_{cyclized}$** is cleaved in solution, leading to the formation of both starting materials. However, further research is needed to full understanding.

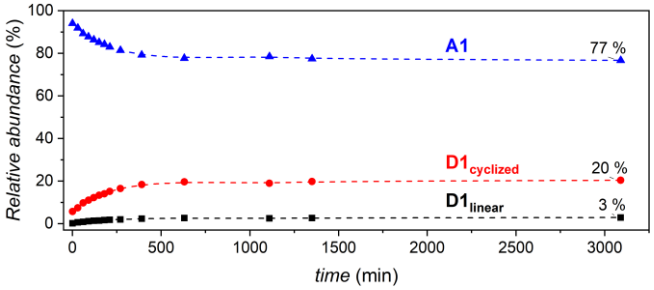

Figure 3. Reaction between the DASA **D1** and 1-butanethiol (**T1**) upon irradiation (λ_{max} = 525 nm, 3 mW·cm^{-2}) in the presence of Et_3N led to the formation of adduct **A1**. The stability of **A1** was assessed by ^{1}H NMR spectroscopy in $CDCl_3$. Details on the ^{1}H NMR signals used are available in the supplementary information.

Hemmer et al. observed previously that the dissociation constant (determined *via* the pK_a) of the precursor amine significantly affects the equilibrium between the linear and cyclized forms in DCM.[8] Further to this, we observed that the basicity of the solution, due to the quantity of base present, also affected the switching. A high pK_a base (e.g., Et_3N), in particular at high concentrations, strongly affects the formation of **A1**. In Figure 4a-c, three solutions of **D1** in CD_2Cl_2 (33.33 µmol·mL^{-1}) with 1.3 eq. **T1** and 1 eq., 5 eq. or 9 eq. of Et_3N were prepared. Irradiation was performed for 6 hours (shaded area in Figure 4a-d). When 1 eq. of base is used, the rate of ring closure is reduced, and the thiol-Michael product is not formed (Figure 4a). Due to precipitation of salt formation of **D1$_{cyclized}$** with the base the overall yield is around 20%. Little effect is observed when the base equivalence is increased from 5 eq. to 9 eq. (Figure 4b and c, respectively). In both cases, nearly full conversion of **A1** was observed after irradiation. A comparison of the abundance of product **A1** in all three situations is presented in Figure 4d. The findings suggest that — at high concentrations of DASA — non-stoichiometric equivalence of base is required for **A1** formation. Considering the dependence of the DASA switching on the solvent and the base equivalence, and also recalling that the base needs to be of a sufficient pK_a to deprotonate the thiol, one can tune the reactivity of the DASA.

In addition to the ligation with 1-butanethiol (**T1**), *p*-bromothiophenol (**T2**) also led to successful formation of the product using the standard procedure. Figure 5 shows the LC-MS analysis of **D1** reaction with **T2** under different conditions. The reaction in the presence of base and light proved to be most efficient, leading to efficient formation of the expected product **A2** (Figure 5a, bottom spectrum). Since there are two stable forms of **D1**, which elute at different times from the column, two **D1** peaks are observed in the LC trace. One around 3 minutes corresponding to the cyclized isomer and another close to 13 minutes, assigned to the linear isomer.

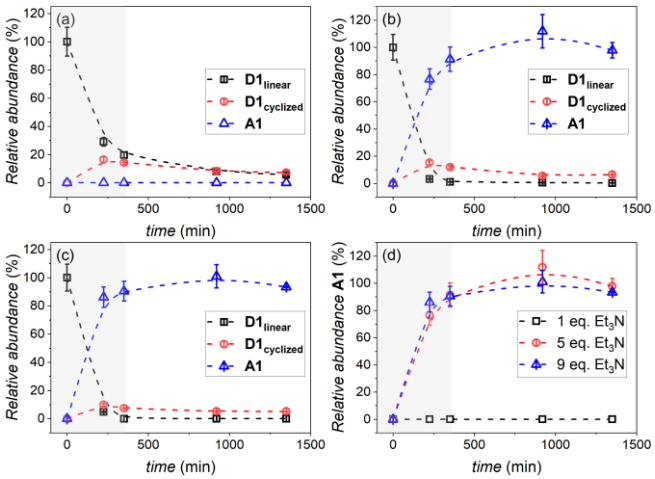

Figure 4. Irradiation (λ_{max} = 525 nm, 6 mW·cm^{-2}, 6 hours) of the DASA **D1** with 1-butanethiol **T1** (1.3 eq.) in presence of (a) 1 eq., (b) 5 eq. or (c) 9 eq. Et_3N in CD_2Cl_2 affects the product **A1** formation. **A1** is not formed when 1 eq. of Et_3N is used. (d) Comparison of **A1** formation with respect to different base equivalencies shows that an excess of base is required. CD_2Cl_2 was the selected solvent as it does not affect the switching behavior and allows high solubility of the species. The integrals were calculated using an internal standard (1,3,5-trimethoxybenzene). The error bars were determined by the percentage error between the two standard signals for each NMR spectrum and applied for each integral of **D1$_{linear}$**, **D1$_{cyclized}$** and **A1**. Note that the lines in the graphs are a guide for the eye only.

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Control experiments of the ligation reaction with **T2** were performed to determine the robustness of the thiol-Michael reaction. Without light (λ_{max} = 525 nm), the UV-Vis trace at 280 nm of the respective LC-MS measurement showed no conversion of **A2** within a 3 hour period (Figure 5a, top spectrum). Upon irradiation, but without base, the formation of **A2** was limited to 40 % of the fraction initially obtained when base is present — even after additional reaction time (Figure 5a, blue line spectrum). In this case, **A2** formation can still occur possibly due to the basicity of the DASA moiety and the low pK_a value of *p*-bromothiophenol **T2**. However, the combination of light and base is essential for high yields of the desired adduct **A2**. The stability of **A2** was tested via HPLC measurements, where two different isomers were observed. The stability was tested over 20 hours in acetonitrile and a decrease about 58% was observed of one isomer. The other isomer was stable without any noticeable degradation over 20 hours.

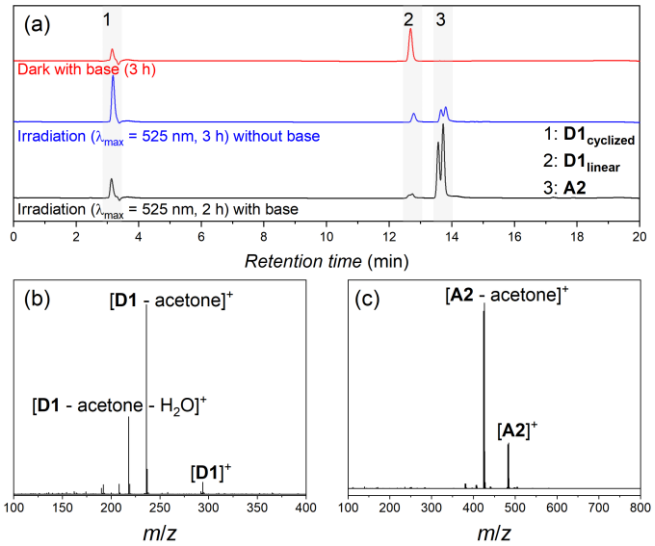

Figure 5. Reactivity of the DASA **D1** and the *p*-bromothiophenol (**T2**) assessed via liquid chromatography coupled to mass spectrometry (LC-MS). In (a), the experimental conditions — without light (red, c = 7.5 µmol·mL^{-1}), without base (pyridine, blue, c = 4.1 µmol·mL^{-1}), and irradiation with base (pyridine, black, c = 2.1 µmol·mL^{-1}) — were changed to access the effect on product formation of **A2**. Note that the peak corresponding to the product **A2** is split due to the presence of diastereomers. The *m/z* values for the peaks shown in (a) correspond to those expected for (b) **D1** (RT = 2.5 – 3 min and 12.5 – 13 min) and (c) **A2** (RT = 13.5 – 14 min).

In summary, the reactivity of the cyclized form **D1$_{cyclized}$** was assessed. A first generation DASA was successfully trapped with 1-butanethiol (**T1**) and *p*-bromothiophenol (**T2**) leading to the respective products at high yields. The light promotes the cyclisation of the DASA at low concentrations, which subsequently reacts with a thiol in the presence of a base towards the thiol-Michael product. At high concentrations, the base has a significant effect on the product formation and switching rate. In solution, the product **A1** has an inherent equilibrium with the DASA starting material. These new ligations properties, in addition to the well-established tunability of the DASA properties based on donor and acceptor type and solvent environment allow for the prospect of fine tuning, not just the switching, but also the reactivity of the DASA. We thus highlight a pathway for selectively controlling the reactivity of a cyclized DASA and its subsequent trapping.

Experimental Section

The thiols used, 1-butanethiol (**T1**) and *p*-bromothiophenol (**T2**), as well as the bases used: pyridine and Et_3N, were obtained from commercially available sources. The standard procedure for the reaction consists of dissolving 1.7 µmol of **D1**, 1.3 eq. of the thiol and 1.3 eq. of base in 0.9 mL of dry toluene, constantly stirred during irradiation with 8 x 525 nm green LEDs in a photoreactor for a minimum of 2 hours. For the detailed description, refer to supplementary information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: selective reactions • thiol-Michael addition • molecular switch • Donor-Acceptor Stenhouse Adducts • photogated reactivity

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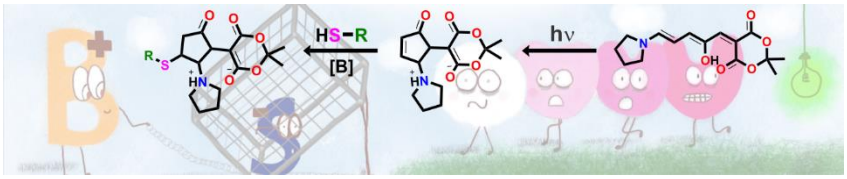

It's a trap: DASAs are well-known photoswitches that reversibly isomerize from a strongly colored linear to a colorless cyclized form upon visible light irradiation. We herein show that the cyclized form can be readily trapped *via* a base-mediated thiol-Michael addition. The reactivity of the closed DASA towards thiol addition was found to be strongly dependent on the reaction conditions. Tuning of the conditions allows to selectively control the DASA's reactivity in its cyclized form.

Jessica Alves, Sandra Wiedbrauk, David Gräfe, Sarah L. Walden, James P. Blinco, Christopher Barner-Kowollik**

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It's a Trap: Thiol-Michael Chemistry on a DASA photoswitch