

Photoswitches

Diaryltriazolium Photoswitch: Reaching a Millisecond Cycloreversion with High Stability and NIR Absorption

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Abstract: The exceptional thermal stability of diarylethene closed isomers enabled many applications but also prevented utilization in photochromic systems that require rapid thermal reversibility. Herein, we report the diaryltriazolium (DAT⁺) photoswitch undergoing thermal cycloreversion within a few milliseconds and absorption of the closed form in the near-infrared region above 900 nm. Click chemistry followed by alkylation offers modular and fast access to the electron-deficient DAT⁺ scaffold. In addition to excellent fatigue resistance, the introduced charge increases water solubility, rendering this photoswitch an ideal candidate for exploring biological applications.

Diarylethenes (DAEs) were developed by Irie and co-workers in 1988,^[1,2] and since then constitute the most exploited class of photochromic compounds together with azobenzenes.^[3–7] The selection of a molecular photoswitch for a particular application is determined by the targeted modulation of the material system's physicochemical properties upon photoisomerization. On the molecular level, azobenzenes are mainly applied to induce geometrical changes, whereas DAEs are primarily used to alter electronic properties between the open and closed isomers. One must, however, consider numerous (photo)physical and (photo)chemical properties of the chosen photoswitch to accomplish the desired photomodulation successfully. De-

spite decades of extensive development and a current broad palette of photoswitches,^[3,7–14] all photochromic compounds have their weaknesses associated with the type of application. For instance, poor solubility and aggregation tendency of DAEs in aqueous media limit their utilization in biological environments. To circumvent this issue, an extensive structural adaptation of their aryl units is required.^[15–19]

Upon UV light exposure, open DAEs undergo photochemical 6 π -electrocyclization, yielding strongly colored closed DAEs due to the formation of an extended π -system. While the open isomers mainly absorb in the UV region, the closed isomers' absorption maxima (λ_{max}) are in the visible range typically between 500 and 650 nm (see DAEs 1–4 in Figure 1).^[4,6,20–22] Closed DAEs with absorption maxima $\lambda_{\text{max}} > 700$ nm are scarce, and to our best knowledge, the push-pull system prepared by the Lehn group has the highest red-shift with a $\lambda_{\text{max}} = 828$ nm in the NIR region in benzene (see DAE 5 in Figure 1).^[23]

Regarding the thermal stability of the closed isomers, DAEs have intentionally been designed as P-type photoswitches, i.e., open and closed isomers are thermodynamically stable at operating, typically room temperature, and can only be interconverted using light. The majority of DAEs have thermal half-lives of the closed isomer at room temperature in the range of years (see DAEs 1–2 in Figure 1). Although exceptional thermal stability enabled many previously impossible applications,^[9,10,20,24] this feature has hindered the application of DAEs when a significant electronic change is required only for a short period.

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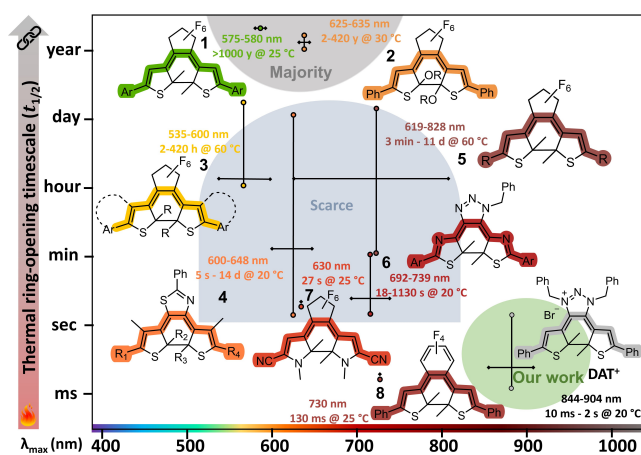


Figure 1. Scope of closed DAEs according to thermal half-lives ($t_{1/2}$) and lowest absorption maxima (λ_{max}). The range for thermal half-lives (\circ) and λ_{max} (\blacklozenge) depends on both the substitution pattern and environment (solvent).

Therefore, the fast thermal bleaching reaction of the closed and thus colored isomer would open new avenues for applying these photoswitchable compounds. Extensive research over the past decades yielded a handful of thermally reversible DAEs, reducing half-lives from years to hours and seconds (see DAEs **3–7** in Figure 1).^[23,25–29] The general design concept for obtaining T-type DAEs is based on Hammond's postulate and aims to increase the energetic driving force for ring-opening by destabilizing the closed relative to the open isomer. This has been achieved by (i) introducing sterically bulky substituents at the reactive 2-positions (**2, 3**),^[21,28] (ii) introducing push-pull or pull-pull substituents on the two termini of the thiophene moieties (**5, 7**),^[23,26] (iii) exchanging the thiophene with pyrrole, indole, or phenyl moieties that have higher aromatic stabilization energies (**7**),^[25] and (iv) replacing the (typically cyclic) olefin bridge with an aromatic moiety (**4, 6, 8**).^[6,20,27,29–31] However, only relatively recently, the study of the aryl-bridged **DAB** (1,2-diarylbenzene) by the Kobatake group revealed the first photochromic system with a ring-opening timescale below seconds, taking DAEs to the millisecond regime (see compound **8** in Figure 1).^[30]

Transient DAE-based photochromic systems could be an exceptionally beneficial tool for obtaining high temporal as well as spatial resolution in various material, biophysical, and medical applications, among them real-time holography,^[34–36] super-resolution imaging,^[16,37] photopharmacology,^[32,33] and many others.^[24,38,39] Crucial requirements for such photochromic systems include (i) facile and modular synthesis providing rapid access to structural variants, (ii) large spectral changes between the open and closed isomers, and (iii) high fatigue resistance as well as (iv) absorption in the biological window (far-red or NIR) and (v) water solubility, both in the context of a biological application. Here, we report a water-soluble diaryltriazolium photoswitch (**DAT**⁺, Figure 1) with the largest bathochromic shift of the closed isomer's lowest

energy transition ($\lambda_{max} > 900$ nm) and fastest thermal ring-opening ($t_{1/2} = 10$ ms) thus far.

To establish a straightforward and modular synthetic approach to **DAT**⁺, we envisioned the use of click chemistry followed by simple alkylation.^[40] The alkyne-azide cycloaddition provides convenient access to the diaryltriazole (**DAT**) photoswitch from non-photochromic precursors in a single step. Despite being remarkably effective and allowing to “click” the photoswitch, only recently has this method been utilized for the preparation of DAEs incorporating a triazole as the bridge^[27] or the terminus.^[41] Yokoyama and coworkers first replaced an alkyne with a triazole bridge using a Ru(I)-catalyzed cycloaddition (**6**, Figure 1) using thiazole as a photoreactive heteroaromatic moiety. Expectedly, these photoswitches were thermally labile, however, their ring-opening took place on a time scale of seconds to minutes ($18 \text{ s} \leq t_{1/2} \leq 19 \text{ min}$) with a significant bathochromically shifted absorption maximum of the closed isomer ($690 \text{ nm} \leq \lambda_{max} \leq 740 \text{ nm}$), both in toluene. Fatigue of the **DAT** photoswitches was not disclosed,^[27] while the triazole-terminated DAEs were reported to exhibit severe photobleaching.^[41]

We chose phenyl-substituted dithienylalkyne and commercially available benzyl azide as simple, structurally not optimized cycloaddition partners (Figure 2A). Optimization of the click reaction conditions included screening temperature, solvents, and catalysts, leading to a moderate conversion (65 %) but almost quantitative yield (97 %) based on recovered starting material. For synthetic details, see the Supporting Information. Prepared **DAT** was subjected to alkylation with benzyl bromide to obtain a desired symmetrical **DAT**⁺ photoswitch in high yield (82 %, Figure 2A).

With both compounds in hand, photochemical and photophysical properties were assessed. Subjecting **DAT** to photoisomerization with UV light (313 nm) in dichloromethane showed no changes in the absorption spectrum (0–25 °C). Only upon cooling the sample below –15 °C photo-switching was observed, with a visible band rising at $\lambda_{max} = 745$ nm (Figure 2B). While the absorption maximum of the closed isomer **DAT**_c was slightly red-shifted compared to the previously reported diaryltriazoles,^[27] the ring-opening reaction was significantly faster. Inspection of the spectral region around the isosbestic point at 315 nm showed that **DAT** undergoes noticeable photodegradation (Figure 2B). In strong contrast - and to our pleasant surprise - irradiation of the **DAT**⁺ photoswitch led to the formation of the corresponding closed isomer **DAT**_c⁺ with an outstanding bathochromic shift of $\lambda_{max} = 904$ nm, an even faster thermal backreaction (than **DAT**), and, importantly, a clean isosbestic point pointing to high fatigue resistance (Figure 2C).

To gain further insight into these surprising experimental observations, the origin of the strong red shift of **DAT**_c and **DAT**_c⁺ was investigated by quantum chemical calculations and compared with **DAB 8** and DAE **1Ph** (see Figure 1). The absorption band was assigned predominantly to the HOMO–LUMO excitation for all systems considered. The experimental trend was reproduced, and **DAT**_c⁺ indeed showed the largest red-shift among the investigated photoswitches (see Page S8 and Figure S5 in the Supporting

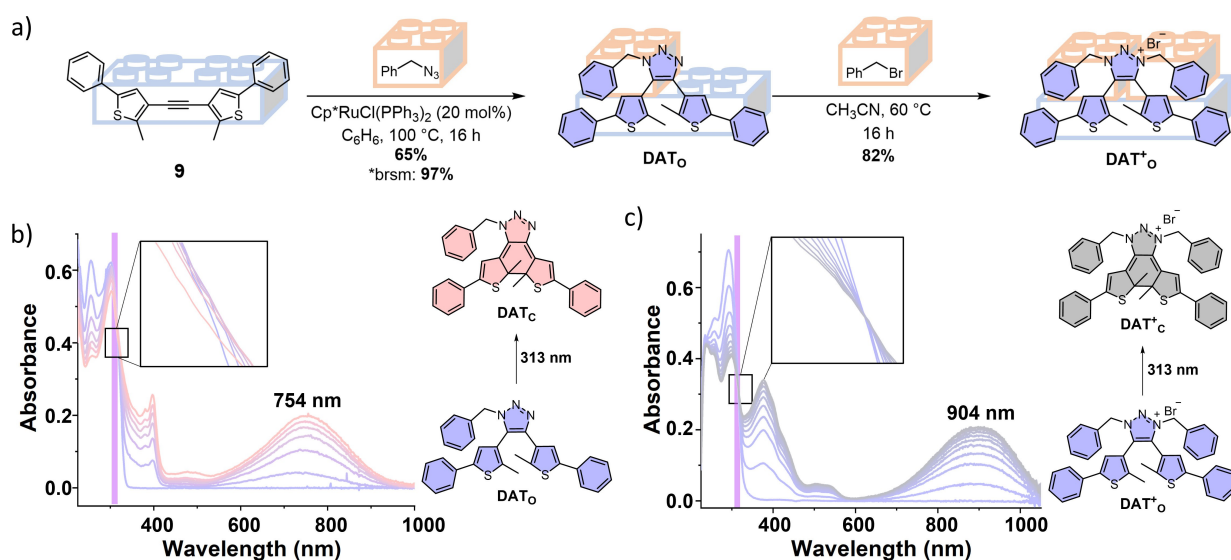


Figure 2. Synthesis and photochromism of **DAT** and **DAT**⁺. Preparation of **DAT** via click chemistry followed by benzoylation (a). Photoisomerization of **DAT** (b) and **DAT**⁺ (c) upon irradiation with 313 nm light (zooms show irradiation spectra around isosbestic point). Irradiation spectra were taken every 16 s at -50°C in 20 μM CH_2Cl_2 solution. * brsm = based on recovered starting material

Information). We attempted to rationalize this trend in the HOMO–LUMO gap with a fragment orbital analysis between the triazol(ium) bridge and both thiophenes. Based on a simple linear model, we could infer that the LUMO of the bridge moiety mainly impacts the positioning of the HOMO of the photoswitch, while the LUMO of the latter is affected by the bridge HOMO (see Figures S1–S4). The additional red shift in **DAT**⁺ compared to **DAT** originates from a lowering of the HOMO in triazolium compared to triazole, which in turn lowers the LUMO of the photoswitch. Regarding the thermal stability, a barrier of 17.7 kcal/mol and 19.0 kcal/mol was calculated for **DAT**⁺ and **DAT**, respectively ($\omega\text{B97X-V}/\text{def2-QZVP}/\text{PBEh-3c}^{[42-46]}$ with thermal^[47] and solvent corrections:^[48-49] MeCN for **DAT** and EtOH for **DAT**⁺, see Figures S8,9 and Tables S3–S10 in the Supporting Information). These barriers are in agreement with the experimental observation that **DAT**⁺ generally has shorter lifetimes. By inspecting the $\langle S^2 \rangle$ expectation values, we noticed that the electronic structures of **DAT** and **DAT**⁺ are characterized by a multi-reference character in the closed isomers and the transition state structures for thermal ring opening. A similar observation was previously made for DABs.^[50] This indicates that the closed isomers are rather unstable and that distortion, i.e., ring opening, is required to generate a stable closed-shell molecule, similar to distortions of anti-aromatic compounds. A thorough computational investigation of these systems involving a detailed study of the underlying excitation mechanism will be presented in the near future.

Due to the thermally labile nature of the closed isomers, it was not possible to estimate their composition in the photostationary state (PSS). However, temperature-dependent photoisomerization clearly showed that at lower temperatures, a higher content of the closed isomer is formed (see Figures S10–S35 in the Supporting Information). The tem-

perature-dependent PSS composition demonstrates a kinetic competition between photocyclization and thermal ring-opening. Additionally, **DAT** shows less pronounced solvatochromism ($\Delta\lambda = 28$ nm, 0.062 eV) than **DAT**⁺ ($\Delta\lambda = 60$ nm, 0.098 eV) (see Figures S36–S37 in the Supporting Information). Both closed isomers have a more pronounced red-shift in halogenated solvents such as CH_2Cl_2 or CHCl_3 and a blue-shift in non-polar media such as hexane.

To quantify the half-lives and investigate the influence of the solvent polarity, the decay of the absorption maximum λ_{max} of the closed isomers was followed over time at different temperatures (see Figures S38–S97 in the Supporting Information). For this purpose, solutions containing **DAT** or **DAT**⁺ were brought to the PSS by UV light irradiation, and then the decrease in absorbance was followed after the light was turned off (Figure 3A). The thermal ring-opening curves initially follow first-order kinetics, but at lower temperatures, one or more processes slower than cycloreversion become competitive to the ring-opening. The disentanglement of these processes and their dynamics is part of an ongoing study in our group and will be reported separately. The kinetic analysis illustrates a strong solvent effect on the cycloreversion rate and renders **DAT**⁺ the fastest photoswitch of its kind (Figure 3B, Table 1). The thermal half-lives of **DAT** vary between a few hundred milliseconds in halogenated solvents to a few seconds in non-polar solvents (Table 1). A similar trend for cycloreversion was observed in the case of the **DAT**⁺ but with even faster kinetics. A half-life of approximately 1 s was observed in non-polar solvents, whereas in dichloromethane, the thermal half-life decreased to 10 ms, which to the best of our knowledge is the fastest cycloreversion reported to date. Faster ring-opening of **DAT**⁺ also correlates with its experimentally and computationally

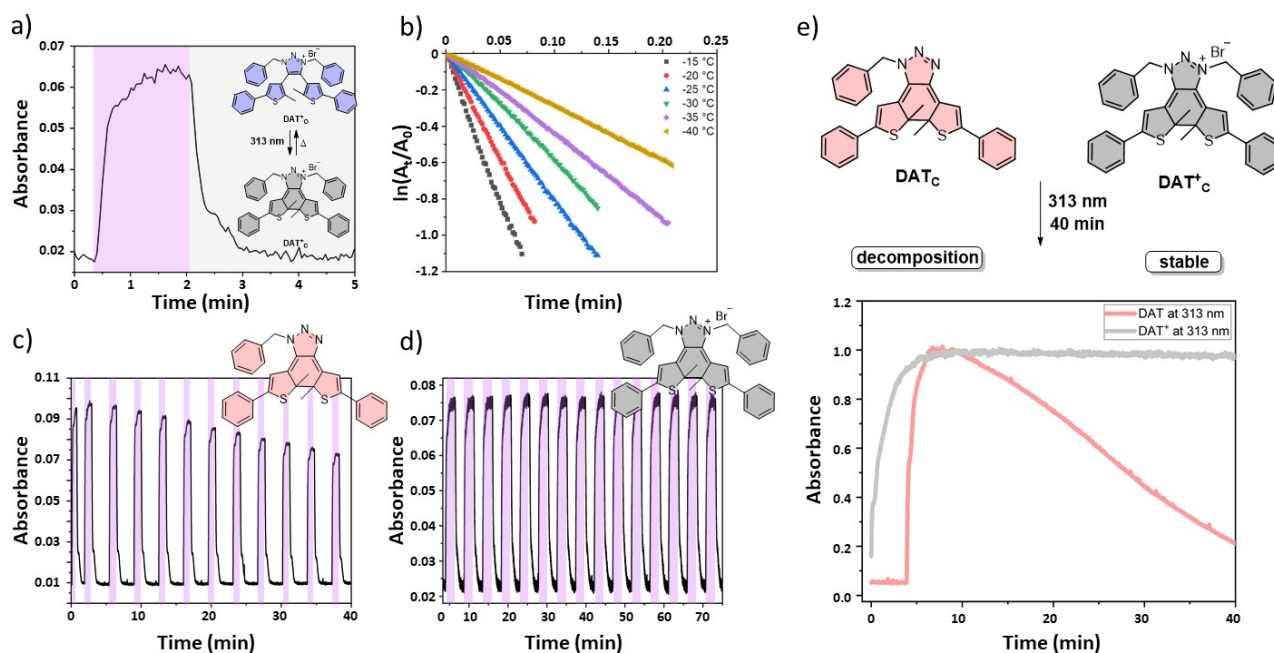


Figure 3. (a) Representative example of time-dependent absorbance change at λ_{max} for **DAT⁺** (20 μM in EtOH at -30°C ; magenta shading symbolizes UV-light irradiation at 313 nm, while grey shading represents thermal ring-opening). (b) First order kinetics of thermal ring-opening (initial slope method) at different temperatures for **DAT⁺** (20 μM in hexane). Fatigue resistance of (c) **DAT** and (d) **DAT⁺** photoswitches upon repetitive photochemical and thermal isomerization or (e) at prolonged UV light irradiation (313 nm, 243 K, 20 μM , EtOH). All the measurements were performed without degassing and in the presence of oxygen.

Table 1: Absorption maxima, thermal half-lives, and activation energy ΔG^\ddagger of closed isomers **DAT_c** and **DAT⁺_c** in various solvents.

Solvent	DAT_c			DAT⁺_c			$\Delta\Delta G^\ddagger$
	λ_{max} [nm]	$t_{1/2}^{25^\circ\text{C}}$ [ms]	ΔG^\ddagger [kcal mol ⁻¹]	λ_{max} [nm]	$t_{1/2}^{25^\circ\text{C}}$ [ms]	ΔG^\ddagger [kcal mol ⁻¹]	
CH ₃ CN	734	1072	15.3	ND ^[a]	ND ^[a]	ND	ND
EtOAc	733	1594	15.5	844	493	14.8	0.7
EtOH	740	520 ^[c]	14.8	856	105 ^[c]	13.9	0.9
MeOH	736	1665 ^[c]	15.5	848	209 ^[c]	14.3	1.2
n-C ₆ H ₁₄	732	8974	16.5	855	2052	15.7	0.8
PhMe	ND ^[b]	ND ^[b]	ND	853	1060	15.2	ND
THF	742	1916	15.6	850	76 ^[c]	13.7	1.9
CH ₂ Cl ₂	754	833	15.1	904	10	14.4	0.7
CHCl ₃	760	523	14.8	898	ND ^[d]	ND	ND

[a] Photoisomerization of **DAT⁺** occurs below the freezing point of CH₃CN; [b] Compound was not soluble enough to perform photochemical studies; [c] Parallel processes taking place at low temperatures; [d] Parallel processes complicate kinetic analysis.

obtained lower activation energy ΔG^\ddagger (Table 1, Figures S8–S9).

In addition, we investigated the resistance to fatigue during photoisomerization in the presence of oxygen. As mentioned, **DAT** showed noticeable changes in the spectral range around the isosbestic point, indicative of fatigue. Repetitive switching cycles consisting of UV light and thermal cycloreversion show a significant decrease in absorption of the **DAT** photoswitch (Figure 3C, see also Figures S98–S100 in the Supporting Information). On the contrary, **DAT⁺** shows no observable fatigue after more than 10 cycles (Figure 3D, see also Figure S102 in the Supporting Information). The same observation was made in the presence of acid or base (see Figures S101–S103 in the

Supporting Information). To further test the fatigue, we exposed both photoswitches to UV light of 313 nm for over 40 min. While the absorbance of **DAT** almost entirely vanished over this time frame, the absorbance of **DAT⁺** remained unchanged (Figure 3E). These spectral observations were substantiated by UPLC-MS analysis at the end of the irradiation experiment, which shows various **DAT** side products yet almost no change in the case of **DAT⁺** (see Figures S104–S107 in the Supporting Information). We attribute the exceptional fatigue resistance of **DAT⁺** to the electron-deficient nature of the triazolium cation.^[51]

Lastly, we doped polymethyl methacrylate (PMMA) with both photoswitches and tested its responsiveness upon UV light irradiation (Figure 4). Photoisomerization with a

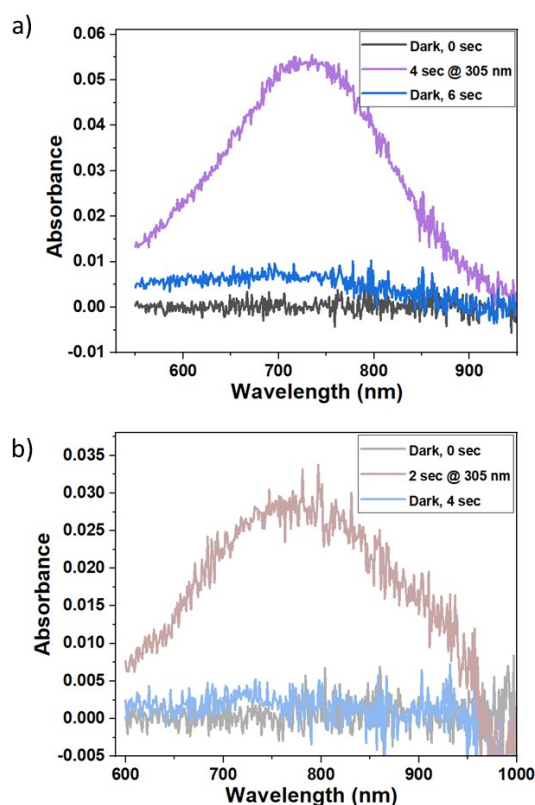


Figure 4. Photoisomerization of (a) **DAT** and (b) **DAT**⁺ in PMMA. For the irradiation, UV light (305 nm) was used, and the experiments were performed at room temperature or $-10...0^{\circ}\text{C}$, respectively.

slightly slower thermal back-reaction than in solution was observed but still significantly faster than the DAE photoswitches. It has been shown again that ring-opening of **DAT**⁺ is faster than **DAT**. Additionally, the great water-solubility of **DAT**⁺ enabled us to observe the formation of **DAT**⁺_c in a frozen aqueous matrix (Figure S110). The possibility of photoisomerization in a solid state with a fast thermal back-reaction shows the application potential of the **DAT/DAT**⁺ photochromic system in materials.

In summary, we have designed and studied the new DAE-derived photoswitch **DAT**⁺ exhibiting unique photo-physical properties. **DAT**⁺ was prepared from non-photochromic alkyne and commercially available azide precursors using modular and effective click chemistry followed by simple alkylation. The introduced charge mediates solubility in water ($>1\text{ mM}$), thereby opening the door for utilizing these photoswitches in an aqueous environment without any extensive modifications. Related investigations in aqueous media need to be performed above the freezing point of water and thus require reasonably fast time-resolved spectroscopy methods, specifically time-resolved absorption measurements in a collaborative effort to be reported in due course. Due to the enormous red-shift of the transient closed isomer's absorption ($\lambda_{\text{max}} > 840\text{ nm}$) in the biological window and the ability to adjust its thermal half-life, **DAT**⁺ photoswitches offer a great starting point for the development of photochromic systems suitable for biological applications.

Since materials and life science applications require repetitive and clean photocycling, **DAT**⁺ should moreover prove advantageous due to its high fatigue resistance. In view of all these unique features, we expect that our **DAT**⁺ photoswitches disclosed herein will open opportunities for DAE-based photoswitches that were previously not possible.

Acknowledgements

D.K. thanks Dr. Ellen Teichmann and Svante Ihrig for their help with the low-temperature measurements and insightful discussions. We also thank Dr. Björn Kobin for the preparation of the PMMA block doped with **DAT** photoswitch. Financial support from the Leibniz Collaborative Excellence Program via the project “Light-driven molecular machines in active materials (LightForce)” is gratefully acknowledged. C.B. acknowledges funding from the Federal Ministry of Education and Research (BMBF) and the Ministry of Culture and Science of the German State of North Rhine-Westphalia (MKW) under the Excellence Strategy of the Federal Government and the Länder (*RWTH JPI Fellowship*) as well as funding from the MKW via the *NRW Rückkehrprogramm*. S.H. is indebted to the Einstein Foundation Berlin for generous support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Click Chemistry · Diarylethenes · Diaryltriazolium · Photochromism · Photoswitches

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Manuscript received: November 24, 2023

Accepted manuscript online: December 20, 2023

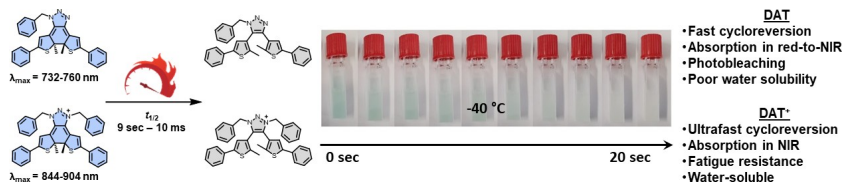
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Communications

Photoswitches

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Diaryltriazolium Photoswitch: Reaching a
Millisecond Cycloreversion with High
Stability and NIR Absorption



Diaryltriazolium photoswitch (**DAT⁺**) was prepared by alkyne-azide cycloaddition followed by alkylation. Due to a charged heterocyclic bridge, the closed isomer of **DAT⁺** exhibits the most bathochromically shifted absorption maxi-

mum and the shortest thermal half-life reported for any diarylethene thus far. The new photoswitch exhibits excellent fatigue resistance and is well water-soluble.