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Acid-catalysed thermal cycloreversion of a diarylethene: a potential way for triggered release of stored light energy?

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Upon addition of catalytic amounts of acid, a closed diarylethene derivative carrying a fluorenol moiety undergoes facile thermal ring opening. The underlying thermodynamics and kinetics of the entire system have been analysed experimentally as well as computationally. Our work suggests that general acid catalysis provides a useful tool to bypass thermal barriers, by opening new reaction pathways, and to efficiently trigger the release of light energy stored in photoswitches.

The use of a molecular photoswitch that can be reversibly isomerised by sunlight constitutes a promising approach to chemically store solar energy and subsequently convert it to thermal energy on demand. To store light energy efficiently, the molecular system has to fulfil certain design criteria: (1) a high energy difference between the isomers combined with a low molecular mass to maximise the energy storage density; (2) a photoreaction with high quantum yield (and no photochemical back reaction); (3) a matching absorption spectrum of the low energy isomer with the solar spectrum; (4) sufficient thermal stability of the high energy isomer; (5) high fatigue resistance to ensure recycling of the system. While progress has been made in optimising the energy storage density as well as long-time energy storage, we will focus on the issue of how to release the stored light energy using well-established diarylenes (DAEs).

DAEs are photochromic compounds, which undergo a 6π-electrocyclisation upon UV irradiation with high quantum yields, while cycloreversion is induced by visible light, yet occurring with much lower quantum yields. For this reason, illumination of DAEs with sunlight, which contains a UV portion, leads to preferential cycloreversion in the solar photostationary state (PSS). Typically, DAEs show no thermal cycloreversion and are therefore considered so called “P-type” photochromic molecules, thus enabling long time energy storage. By introducing proper substitution, DAEs can be rendered highly fatigue resistant, even in solution.

From the pioneering work of Irie and coworkers, it is known that the closed DAE is a thermodynamically less stable isomer and the thermal back reaction is kinetically hindered due to an activation barrier, which increases upon decreasing the ground state energy difference. DFT calculations of the thermal cycloreversion indicate the strong biradical character of the transition state and therefore suggest a homolytic C-C-bond cleavage. It has been reported that the thermal stability decreases upon introduction of one or more aromatic moieties, which maximise the ground state energy difference, or upon substitution with electron-withdrawing groups or by protonation of basic nitrogen atoms.

Here, we show that in situ generation of a positive charge due to dehydration of a fluorenol moiety induces rapid thermal ring opening and requires only catalytic amounts of acid. Therefore, general acid catalysis is used to efficiently trigger the release of energy stored in the closed DAE isomer (Fig. 1). Note that the use of various chemical stimuli to modulate photoswitching behaviour is often referred to as “gated” photochromism.

Target compound (Fig. 1, bottom) was designed to feature the advantageous properties of DAEs while incorporating the possibility of generating a positive charge within the π-framework to effectively lower the thermal barrier. For this purpose, a 3,3′-(3,3,3,4,5,5-hexafluoro-1-cyclopentene-1,2-diyl)(bis(2-methylthiophene) core was substituted with a 4-methoxyphenyl unit on the one side and a 9-fluorenol moiety on the other side. Acid-driven dehydration leads to the formation of a tertiary carbenium ion in both the open and closed isomers, respectively. The thienyl moiety adjacent to the fluorenol unit carries a β-methyl group to prevent side reactions of the free carbenium ion.

Comparing the two open closed equilibria, the relative destabilisation upon ring closure should be more pronounced for the neutral isomers than for the charged isomers (1a ‒ 1c), which counterbalance this destabilisation to some degree by the effective stabilisation of the positive charge only in the closed isomer 1c. This should lead to a significant difference in the associated equilibrium constants (Kc and Kc).

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Interestingly, irradiation of the strongly acidified solution does not induce any spectral changes, suggesting that the observed absence of photochromic behaviour originates from this competing charge transfer. This is furthermore supported by transient absorption measurements, showing that the absence of the photoreaction is caused by thermal relaxation of the excited (charge transfer) state (ESI†). Titration of 1o in acetonitrile containing 1 vol% water with a 2 M TfOH solution in the same solvent mixture at 25 °C allowed us to determine the equilibrium constant for dehydration accompanied by formation of 1o+ (Ko = 4.3 ± 0.4, see Fig. 2b). Surprisingly and key to this work, TfOH-induced dehydration of the closed isomer 1c does not result in the formation of the illusive closed charged form 1c+ but in thermal ring opening. This acid-induced ring opening is accompanied by recovery of the absorption spectrum of 1o and is clearly supported by UPLC-MS experiments. It is for this reason that the equilibrium constant for the closed isomer 1c (Kc) could not be determined. To get more insight into the observed acid-induced thermal ring opening, the dependence of the kinetics on TfOH concentration was investigated by monitoring the decay of the band at 576 nm of 1c at 60 °C (Fig. 3a). An acceleration of the reaction with increasing acid concentration was observed and in all cases, the reaction was of pseudo first order. Direct conversion to the neutral open form 1o was observed, whereas the charged open form 1o+ could not be detected over the employed concentration window (10⁻³ M ≤ [TfOH] ≤ 10⁻² M), which is below the one needed for dehydration (see Fig. 2b). Studying the reverse process, i.e. the UV-induced ring closure of 1o in the presence of TfOH, shows a clear dependence of the PSS composition on acid concentration (Fig. 3b). Increasing amounts of TfOH lead to a faster attainment of the PSS while the amount of the closed isomer 1c steadily shrinks in the PSS. Evaluating the photokinetic data using the Runge–Kutta algorithms shows a reciprocally proportional decrease of the molar fraction of 1c at the PSS. The rate constant of the thermal back reaction increases linearly, while the rate constant of the photochemical ring closure remains constant (Fig. 3c).

Importantly, the thermal ring opening reaction is observed well below the presence of one equivalent of TfOH, illustrating the catalytic nature of the process. Considering the overall reaction cycle (see Fig. 1), we can derive the following eqn (1), (for derivation, see the ESI†) describing the dependence of the molar fraction of 1c at the PSS (x_{PSS}(H⁺)) on the acid concentration:

\[
\frac{1}{x_{\text{PSS}}(\text{H}^+)} = z[\text{H}^+] + \frac{1}{x_{\text{PSS}}} \tag{1}
\]

where \(x_{\text{PSS}}\) is the molar fraction of 1c at the PSS without acid; [H⁺] is the acid concentration and \(z\) is a linearity factor. Upon plotting the experimentally determined PSS compositions as a function of acid concentration, we indeed find a linear relationship (Fig. 3c), thereby proving the validity of our mechanistic proposal (ESI†).

Furthermore, it should be mentioned that even after several reaction cycles, including irradiation to the PSS and thermal back reaction, only marginal fatigue was observed (ESI†).

The energetics of the catalytic cycle, i.e. the stability of the involved intermediates, and the key transition state of the
thermal back reaction were investigated by DFT calculations at the UB3LYP 6-31G* SCRF SMD level in an acetonitrile–water (90 : 10) mixture (Fig. 3d).\textsuperscript{11,21,22} The photochemical 6π electrocyclic ring closing reaction of 1o to 1c leads to an increase in...
the Gibbs free energy ($+76 \text{kJ mol}^{-1}$). The following dehydration of $1c$ to $1c^+$ is more or less balanced ($-2 \text{kJ mol}^{-1}$) as calculated using a triphenylmethanol reference and is driven by the following reaction (ESI†). Upon ring opening of the charged closed form $1c^+$, a significant amount of energy is released ($-62 \text{kJ mol}^{-1}$). Hydration of $10^*$ represents a slight down-hill reaction ($-12 \text{kJ mol}^{-1}$) and closes the cycle. The calculated numbers support our overall mechanistic proposal. In order to rationalise the significantly lower barrier for thermal ring opening in the charged form ($1c^+ \rightarrow 10^*$), we investigated the corresponding transition state, which showed an imaginary frequency of the dissociating bond between both thiophene moieties. In comparison to the uncharged transition state ($TS$), the charged one ($TS^*$) is computed to be significantly lower in energy ($\Delta G^* = -59 \text{kJ mol}^{-1}$). Electrostatic charge population analysis21 shows a highly charged $\pi$-carbon atom of the cationic fluorenol substituted thiophene, while analysis of the spin density shows no biradical character.24,25 Both of these findings are strong indications for a change from the homolytic mechanism in the neutral form to a heterolytic bond cleavage in the charged form.

Title compound 1 shows robust photochromism with a high fatigue resistance against (photo)chemical side reactions in both the uncharged and the charged forms. The photochromism could be gated by an excess of acid due to formation of the charged open isomer, which is not photoreactive. Importantly, could be gated by an excess of acid due to formation of the both the uncharged and the charged forms. The photochromism fatigue resistance against (photo)chemical side reactions in

Significant amounts of energy ($60-50 \text{kJ mol}^{-1}$) is released ($60 \text{kJ mol}^{-1}$) via a heterolytic transition state. The light energy stored in the closed isomer ($\Delta H_{\text{c-o}}$) amounts to $59 \text{kJ mol}^{-1}$ giving rise to an energy density of $81 \text{J g}^{-1}$. This value clearly is not optimal for light energy storage as other photoresponsive materials, such as norbornadienes ($1042 \text{J g}^{-1}$) and even normal azobenzenes ($228 \text{J g}^{-1}$), perform much better.4 Nevertheless, our work shows an alternative and promising pathway to catalystically trigger the release of the stored energy and efficiently recover the system. Importantly, the rate of the energy release can be tuned by the amount of acid added and the uncharged closed isomer is fully stable over a long time. Future work will be focused on applying our concept to other photochromic systems to maximise the energy that can be stored while proper substitution should allow us to minimise the amount of acid needed for energy release and ensure a better match with the solar spectrum.

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Notes and references

14. The only example in the literature using substoichiometric amounts of acid is reported in: T. Nagakawa, C. L. Serpentini, C. Coudret, J. C. Micheau and T. Kawai, *Dyes Pigm.*, 2011, 89, 271. However, relatively large amounts of acids are needed to induce a rather slow thermal cycloreversion and the inherent thermal stability of the uncharged closed isomer is limited.
20. For common DAEs e.g. 1,2-bis[2,4-dimethyl-5-phenylthiophen-3-yl]perfluorocyclopentene, no acid induced ring opening has been observed (60 °C, 10–5 M DAE, 0,001 M TTOH).