



## Basic enemies of photochromism: irreversible transformation of fluorinated diarylethenes to polyenic enamines and enols

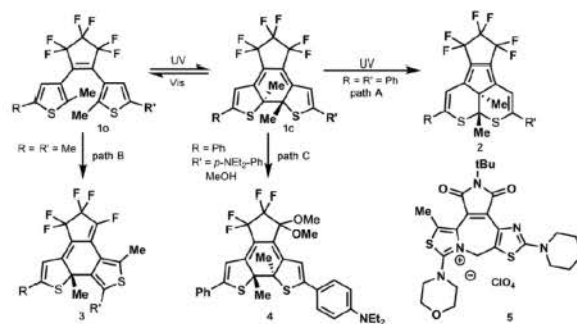
Dmytro Sysyoyev  ‡ and Thomas Huhn  \*

Non-photochemical degradation of perfluorinated photochromic diarylethenes (DAE) under Knoevenagel, Sonogashira or Wittig conditions was discovered. This base promoted formation of strongly colored non-photochromic byproducts has an impact in the field of molecular electronics due to the basic conditions often employed during deacylation and desilylation of the protected thiol anchoring groups of functionalized DAE. The products were identified as seven-membered ring systems of the bicyclo[5.3.0] deca-1,7-diene type. Their formation was rationalized by a tentative two-step reaction mechanism.

### Introduction

Photochromic diarylethenes<sup>1</sup> (DAE) are one of the most promising classes of organic photoswitches with potential applications in different areas such as optical memory media,<sup>2</sup> charge transport at the single molecule level,<sup>3</sup> photo-control of biological systems,<sup>4</sup> self-healing of polymers<sup>5</sup> and super-resolution microscopy.<sup>6,7</sup> Besides their photophysical properties like absorption wavelength, quantum yield and reversibility of the switching process, fatigue resistance is an important area of concern. Benzothiophene-<sup>8</sup> or 3-methyl-substituted thiophene-derived perfluorinated cyclopentenes<sup>9</sup> are best fulfilling the demands of thermal irreversibility of the switching process and high fatigue resistance.<sup>10,11</sup> Substituting DAE with electron withdrawing groups has been recently found to be another way to enhance fatigue resistance.<sup>12</sup> Perfluorocyclopentene derived DAE are known to exhibit high fatigue resistance when irradiated in the crystalline phase or

under the exclusion of oxygen in polymer films.<sup>13</sup> However, DAE might suffer from different types of fatigue mechanisms, ultimately leading to products with impaired ability to switch and hence degraded device performance. A list of prominent fatigue products of DAE includes annelated dihydrothiopyran **2**<sup>9</sup> formed upon UV-irradiation of the closed ring isomer **1c** by a proposed radical migration in the  $\pi$ -conjugated system (Scheme 1, path A).<sup>14</sup> The minor byproduct **3** is formed upon prolonged UV irradiation of the 2,5-dimethylthienyl derivative of **1o** by photocyclization *via* C3 instead of C1 and the concomitant elimination of HF (Scheme 1, path B).<sup>14</sup> The photochromic byproduct **4** was obtained *via* a step-wise ionic release of fluoride from the closed form of the non-symmetrical donor substituted DAE **1c** (Scheme 1, path C).<sup>15</sup> A non-photochemical fatigue product was detected in bis (morpholinethiazolyl) maleimide DAE operating with redox potential and light as stimuli. Oxidative ring closure rapidly led to deactivation due to incorporation of one methyl group into the seven-membered ring of non-photochromic product **5**.<sup>16</sup>



**Scheme 1** Light driven switching of photochromic DAE **1** from open (**1o**) to closed (**1c**) form and selected products **2**, **3**, **4**, and **5** formed by photochemical (paths A and B) or non-photochemical (path C and **5**) degradation.

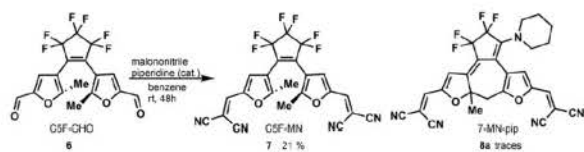
Fachbereich Chemie, Universität Konstanz, Universitätsstr. 10, 78464 Konstanz, Germany. E-mail: [thomas.huhn@uni-konstanz.de](mailto:thomas.huhn@uni-konstanz.de)

‡Current address: Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences Flemingovo nam. 2, 16610 Prague (Czech Republic).

## Results and discussion

Non-photochemical degradation mechanisms of DAE came to our attention while investigating the base-catalyzed Knoevenagel condensation of aldehyde **6** with CH-acidic malononitrile derivatives towards  $\pi$ -extended DAE for application as light-driven single-molecular switches in mechanical-break junction measurements in the field of molecular electronics.<sup>17–19</sup> While  $\pi$ -extended DAE are formed as the main product, inevitably the formation of small amounts of deeply colored byproducts have been observed. The side reaction took place even in the dark and hence had to follow a different path from the above UV-light-induced transformations. We were intrigued by the fact that basic conditions are also required for deacylation by ammonia or accompany desilylation of protected thiols when tetrabutyl ammonium fluoride is used. Deprotected thiols are commonly used for contacting of gold electrodes in single molecule electronics.<sup>20,21</sup> Will the *in situ* deprotection also give rise to the formation of byproducts?

Elongation of the  $\pi$ -system of aldehyde **6** by using the Knoevenagel protocol with malononitrile and catalytic amounts of piperidine resulted in the formation of  $\pi$ -extended switch **7** (21%) (Scheme 2). Upon closer inspection of the <sup>1</sup>H-NMR spectrum, trace amounts of deeply colored seven-membered ring **8a** were identified which were initially missed (Fig. S26 in the ESI† shows the original <sup>1</sup>H-NMR spectrum of **7** with the minor signals of **8a**).<sup>17</sup> For isolation and identification, larger amounts of **8a** were needed. Using a 10-fold molar excess of piperidine gave a mixture of **7** (20%) in its open state and non-photochromic byproduct **8a** (33%). While switch **7** in its open-state was a colorless solid, **8a** was deeply violet. A precipitate formed during the reaction was identified as piperidine hydrofluoride by <sup>19</sup>F-NMR spectroscopy. According to FAB-MS measurement, **8a** has a molecular weight of 534, which implied a formula “C<sub>5</sub>F-MN + piperidine – HF<sub>2</sub>”, or C<sub>28</sub>H<sub>19</sub>F<sub>4</sub>N<sub>5</sub>O<sub>2</sub>. The <sup>1</sup>H-NMR spectrum of **8a** showed two distinct singlets of the two dicyanovinyl protons, a single methyl-group signal more shielded than in **7** and a pair of doublets of the diastereotopic methylene protons. Furthermore, the signals of the furan protons appeared as two signals, *i.e.* one singlet and one triplet (*J*<sub>HF</sub> = 2.3 Hz). Evidently, the proton signal was split by through-space coupling by the neighboring CF<sub>2</sub> group. In the <sup>19</sup>F-NMR spectrum of **8a**, a set of four doublets with intensities of 1:1:1:1 were found in contrast to a triplet and quintet with intensities of 4:2 in the parent **7**. The



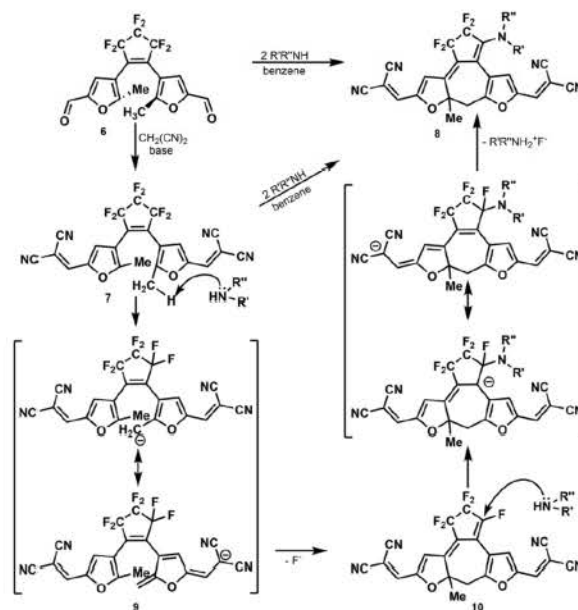
**Scheme 2** Formation of the bicyclo[5.3.0]deca-1,7-diene system **8a** during  $\pi$ -system elongation of **6** with malononitrile and piperidine as the base.

above data imply the formation of an apparently less symmetric molecule than **7** and furthermore provide a hint to the plausible structure of **8a**, a bicyclo[5.3.0]deca-1,7-diene core with the furan rings fused with the seven-membered ring. To rule out the influence of light and oxygen, and to check whether aldehyde **6** or the primary condensation product **7** is vulnerable under the above conditions, two control experiments were performed. To pure colorless  $\pi$ -elongated **7** dissolved in dry degassed benzene was added piperidine (10 eq.) at room temperature in the dark. Aliquots of the mixture showed increasing coloration over time accompanied by a precipitation of piperidine hydrofluoride. Finally, the unreacted **7** and enamine **8a** were identified by NMR spectroscopy. In the second experiment **6** was exposed to piperidine under the above conditions. This led to no detectable changes and the starting material was recovered quantitatively.

### Mechanistic discussion

The reaction apparently starts with the condensation of **6** with malononitrile under Knoevenagel conditions to form the target molecule, the  $\pi$ -elongated **7**. Inevitably, the amine now deprotonates at one of the methyl groups to form the stabilized anion **9** which *via* conjugate addition to the second furan ring closes the seven-membered ring to give vinyl fluoride **10** with a concomitant loss of the first equivalent amine hydrofluoride. The excess amine now acts as a nucleophile and attacks vinyl fluoride *via* a conjugate addition/elimination to form enamine **8** which is stable under the reaction conditions (Scheme 3).

A similar mechanism was identified by Heller *et al.* during the intended base promoted *Z/E*-isomerization of photochromic



**Scheme 3** Tentative mechanism for the formation of seven-membered ring enamines **8a–f** starting from either **6** or **7**.

mic 2,5-disubstituted 3-thienyl and 3-furyl fulgides.<sup>22</sup> During reflux in pyridine, the fulgide isopropylidene group was deprotonated and the resultant resonance stabilized anion then attacked position 2 of the heterocycle by an intramolecular 1,6-addition closing a 7-membered ring. In contrast to the above described DAE, here no leaving-group is available to discharge the anion and consequently re-protonation results in the irreversible formation of strongly colored, non-photo-chromic cyclohepta[b]furan (thiophene) derivatives.

### Base screening

Base screening with several secondary amines in the reaction with **7** in benzene at room temperature gave variable amounts of seven-membered ring annealed enamines **8a-f** together with small amounts of starting material **7**. Using either pyrrolidine (Table 1, entry b) or dicyclohexylamine (Table 1, entry e), the reaction resulted in an almost exclusive formation of strongly colored enamines **8b** and **8e** while only trace amounts of functionalized switch **7** remained. Utilizing either piperidine, methylbutylamine or methylallylamine (Table 1, entries a, c and d), no clear preference in product composition for either the unchanged starting material **7** or the formation of enamines **8a**, **c**, and **d** was detectable. The  $\{^1\text{H}, ^{19}\text{F}\}$ -HOESY spectra of **8c** (Fig. S36, ESI†) and **8b** (Fig. S32, ESI†) showed the interactions of one  $\text{CF}_2$  group with the proton of one furan ring, while the other  $\text{CF}_2$  group interacts with the  $\text{CH}_2$  group of the amine and the furan proton. This, together with HMBC data (Fig. S37, ESI†), unambiguously proved the connectivity of the amine fragment at the perfluorocyclopentene ring in **8**. According to our tentative mechanism, the reaction of **7** with a tertiary, non-nucleophilic base like DIPEA should lead to the intermediate cyclization product **10** (Scheme 3) with the  $\text{Csp}^2\text{-F}$  fragment still untouched. However, upon reaction under standard conditions (benzene, r.t., 10 eq. of base) of **7** with DIPEA, only trace amounts of starting material **7** were isolated, the remainder being an inseparable mixture of polar degradation products (Table 1, entry h). Apparently, the intermediate vinyl fluoride **10** is not stable under the reaction conditions. Using DIPEA, aldehyde **6** and 1.1 eq. of malononitrile in benzene, the reaction mixture turned deep-green instead of

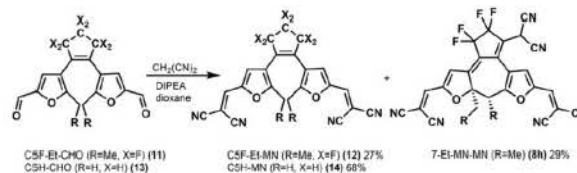
violet as with the secondary amines. Besides **7** (4%), the highly polar blue addition product **8g** (9%) of malononitrile to vinyl fluoride **10** was isolated from the tarry degradation products (Table 1, entry g). The  $^1\text{H}$  NMR spectrum of **8g** shows the characteristic signals of the seven-membered ring compounds **8**. The apparently deprotonated malononitrile is now the nucleophile substituting vinyl fluoride.<sup>23</sup> To completely suppress the unfavorable formation of the seven-membered ring product, the less basic pyridine ( $\text{p}K_a$  of the conjugate acid: 5.2 vs. 10.8 of DIPEA) was employed next. In strong contrast to the reaction of **7** with DIPEA, the reaction of **7** with pyridine under standard conditions resulted in 90% recovery of the starting material (Table 1, entry i). Apparently, pyridine is not capable of initiating the formation of the bicyclo[5.3.0]deca-1,7-diene system and hence much less degradation products were formed compared to the reaction with DIPEA as the base. Gratifyingly, the condensation of aldehyde **6** with malononitrile in benzene using pyridine resulted in an almost exclusive formation of pure **7** as a colorless solid in 92% yield. Apparently, both DIPEA and pyridine are capable of initiating the Knoevenagel condensation between aldehyde and malononitrile towards **7**. However, DIPEA is able to deprotonate the furyl-bound methyl group to give the bicyclo[5.3.0]deca-1,7-diene system **10**, whereas pyridine is not able to do so (Scheme 3). **10** now suffers a nucleophilic attack by the deprotonated malononitrile, ultimately leading to seven-membered ring **8g**. A further proof of this reactivity is found in the reaction of **11**, the ethyl-homologue of aldehyde **6** with two eq. of malononitrile and catalytic amounts of pyridine giving **12** (92%), whereas the same reaction using DIPEA instead of pyridine yielded seven-membered ring **8h** (29%) besides **12** (27%) (Scheme 4). To confirm the necessity of perfluorocyclopentene for seven-membered ring formation, non-fluoro **13** was used. In the above reaction with DIPEA, the Knoevenagel product **14** was the only product isolated in 68% yield.<sup>24,25</sup>

The above reaction is not limited to furan derived DAE with more diene-like character compared to thiophenes with higher degree of aromaticity. When the thiophene homologue of **11** and pyrrolidine as a catalyst were used for the condensation of bisaldehyde with malononitrile to give **15**<sup>26</sup>, the green color of the reaction mixture was observed (Scheme 5). The formation of **8f** was detected by NMR and the experiment was repeated with 10 eq. of pyrrolidine in dry degassed benzene with the exclusion of light. As before, the solution turned deep-green

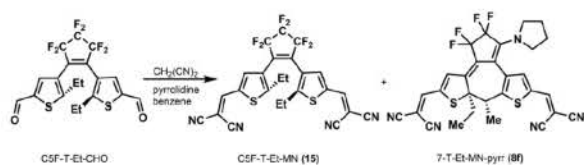
**Table 1** Base screening in the formation of enamines **8a-e** from  $\pi$ -elongated **7** and **8f** in benzene at room temperature

Entry	Amine	Recovered <b>7</b> <sup>a</sup>	Enamines <b>8</b> [yield] <sup>a</sup>
a	Piperidine	22%	<b>8a</b> [35%]
b	Pyrrolidine	Traces	<b>8b</b> [88%]
c	Methylbutylamine	27%	<b>8c</b> [44%]
d	Methylallylamine	14%	<b>8d</b> [21%]
e	Dicyclohexylamine	Traces	<b>8e</b> [65%]
f	Pyrrolidine	22% <sup>b</sup>	<b>8f</b> [40%]
g	DIPEA <sup>c</sup>	4%	<b>8g</b> [9%]
h	DIPEA	Traces <sup>d</sup>	—
i	Pyridine	90%	—

<sup>a</sup> Isolated yield. <sup>b</sup> recovered **15**. <sup>c</sup> from **6** and 1.1 eq. of malononitrile. <sup>d</sup> by NMR.



**Scheme 4** Comparison of hexafluoro- vs. hexahydro DAE **12** and **14** in the base-induced C-F bond cleavage with subsequent addition of the C-nucleophile.

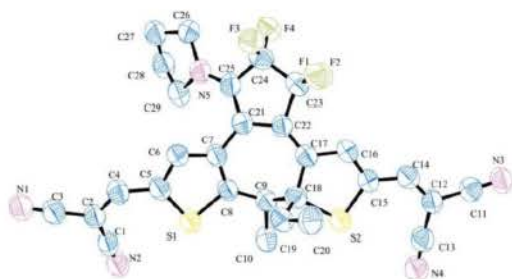


**Scheme 5** Product composition depending on base equivalents employed. Using catalytic amounts of pyrrolidine,  $\pi$ -extended **15** contaminated with trace amounts of **8f** was obtained in 52% yield. Employing 10 eq. of pyrrolidine **8f** (40%) was the sole product except for recovered starting material (22%).

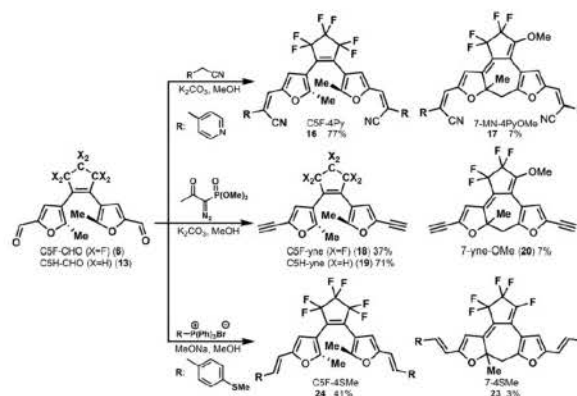
and after work-up a mixture of the starting material (22%) and **8f** (40%) was isolated (Fig. 1). A single diastereomer was formed during ring closure, placing the methyl and ethyl groups in *cis* configuration at the newly formed seven-membered ring. Crystals suitable for X-ray diffraction were grown by slow evaporation from a saturated solution of **8f** in dichloromethane. **8f** in the solid state has two separate, almost flat  $\pi$ -systems. A linear one stretches from N3/N4 over C12/C14, C15/C16, C17/C22 to C21/C25, while the other ranges from N1/N2 over C2/C4 to C5/C6 and C7/C8 of thiophene. Furthermore, both  $\pi$ -systems are in cross conjugation *via* C7/C21. Both  $\pi$ -systems are almost parallel to each other and are separated by the seven-membered ring which introduces a kink along quaternary C18 and C9 and separates the planes of both  $\pi$ -systems by around  $\sim 0.96$  Å. The ethyl group occupies the pseudo-axial position, and the methyl group occupies the pseudo-equatorial position.

#### Implications for other reactions

The above formation of the non-photochromic bicyclo[5.3.0] deca-1,7-diene system during the base-catalyzed reactions of perfluorinated DAE seems to be rather general and is not limited to organic bases. Using potassium carbonate in the condensation of 2-(pyridin-4-yl)acetonitrile with **6** to give **16**<sup>17</sup> leads to a contamination of the desired product with colored seven-membered ring enol ether **17** (7%) (Scheme 6). The amount of **17** depends strongly on the reaction time but is inevitable since its formation starts already before the consumption of all starting materials, *i.e.* before the completion of the main reaction. Apparently, trace amounts of methoxide initiate ring closure and substitution of fluoride (*vide supra*).

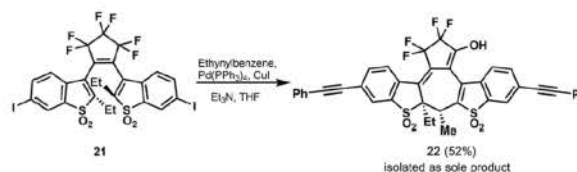


**Fig. 1** ORTEP of **8f** with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.



**Scheme 6** Formation of bicyclo[5.3.0]deca-1,7-diene type enol ethers **17**, **20** and vinyl fluoride **23** during base promoted functionalization of aldehydes **6** and **13**.

A further example is the synthesis of the alkynyl-substituted **18** and **19** (Scheme 6).<sup>27</sup> The mono- or bisalkyne is conveniently accessible by the Bestmann–Ohira homologation on a small scale.<sup>17</sup> However, upscaling to gram quantities proved difficult in the case of **6**.<sup>28</sup> Upon longer reaction time necessary to drive the upscaled reaction to completeness, transient enol ether **20** formed already before complete consumption of **6**. **20** itself is not stable under these conditions and decomposes over time. However, the initially formed **20** was isolated and its structure elucidated by MS and NMR-spectra. The EI-mass spectrum ( $m/z$  376, 100%), the <sup>1</sup>H-NMR spectrum (3.25 and 3.41 ppm; <sup>2</sup> $J_{HH}$  = 15.9 Hz; 6.32 ppm;  $J_{HF}$  = 2.1 Hz) and the <sup>19</sup>F-NMR spectrum (−107, −110, −114, and −115 ppm; <sup>2</sup> $J_{FF}$  = 248 Hz and 258 Hz) are in accordance with the structure of **20**. We believe that the reaction proceeds *via* proton abstraction on one of the methyl groups followed by ring-closure and fluoride expulsion. The rapid decomposition of **20** upon a longer reaction time is then a consequence of the acidity of the terminal acetylenes and employment of excess of methoxide. The attack of the formed nucleophilic alkynylide to the polyene system of **20** with concomitant elimination of fluoride leads then to products of higher molecular mass identified by MS. When ethynylbenzene was used in the Sonogashira alkylation of benzothiophene derived DAE **21** to access a switchable fluorescence emitter,<sup>29</sup> only the formation of enol **22** (52%) was observed upon workup (Scheme 7). Attempts to isolate the primary product of the formed seven-membered ring, *i.e.* vinyl fluoride, were unsuccessful.



**Scheme 7** Attempted Sonogashira coupling of 6-iodobenzothiophene-derived DAE **21**.

The substrate has a profound influence on the outcome of the base-driven degradation of DAE which is documented in the Wittig reaction of **6** in the presence of sodium methylate. Besides the Wittig product **24**<sup>17</sup> (41%), the seven-membered ring **23** (3%) was isolated (Scheme 6). The <sup>1</sup>H,<sup>19</sup>F-HOESY data of **23** showed distinct through-space interactions of the CF<sub>2</sub>- and CF-groups with each of the furan protons (Fig. S69, ESI†). In contrast to the above Sonogashira reactions in which either methanol or water was the nucleophile substituting the primarily formed vinyl fluoride, **23** is not attacked by either methoxide or water. We explain this by the donor ability of the 4-methylthio group which lowers the electrophilicity of **23**.

## Conclusion

In summary, the formation of non-photochromic rearrangement products with a bicyclo[5.3.0]deca-1,7-diene core is a general reaction upon chemical manipulations of perfluorinated DAE when strong bases are employed. Depending on the electronic properties of the substrate, either vinyl fluoride or the addition products of the used base and/or solvent are isolated, and a tentative mechanism is presented. The reaction is insensitive to light and oxygen, tolerates furan, thiophene and oxidized benzothiophenes as the arene part of DAE, and can dominate product formation. This is of special importance in molecular electronics at the single molecule level where even trace impurities due to byproduct formation can render a device non-functional or to malfunction. This reaction might also play a role in base-promoted deprotection of DAE bearing acetyl protected thiols as anchoring groups for use in single molecular electronics.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We gratefully acknowledge the financial support from the DFG (HU 1682/3-1). We thank Anke Friemel and Ulrich Haunz of the NMR-core facility of the University of Konstanz for support with the NMR measurements and Dr Inigo Göttker gen. Schnetmann for support with the X-ray diffraction studies.

## Notes and references

- M. Irie, Photochromism of diarylethene molecules and crystals, *Proc. Jpn. Acad., Ser. B*, 2010, **86**, 472–483.
- H. Tian and Y. Feng, Next step of photochromic switches?, *J. Mater. Chem.*, 2008, **18**, 1617–1622.
- S. J. van der Molen and P. Liljeroth, Charge transport through molecular switches, *J. Phys.: Condens. Matter*, 2010, **22**, 133001.
- W. Szymański, J. M. Beierle, H. A. V. Kistemaker, W. A. Velema and B. L. Feringa, Reversible Photocontrol of Biological Systems by the Incorporation of Molecular Photoswitches, *Chem. Rev.*, 2013, **113**, 6114–6178.
- A. Fuhrmann, R. Göstl, R. Wendt, J. Kötteritzsch, M. D. Hager, U. S. Schubert, K. Brademann-Jock, A. F. Thünemann, U. Nöchel, M. Behl and S. Hecht, Conditional repair by locally switching the thermal healing capability of dynamic covalent polymers with light, *Nat. Commun.*, 2016, **7**, 13623.
- E. Siemes, O. Nevskiy, D. Sysoiev, S. K. Turnhoff, A. Oppermann, T. Huhn, W. Richtering and D. Wöll, Nanoscopic Visualization of Cross-Linking Density in Polymer Networks with Diarylethene Photoswitches, *Angew. Chem., Int. Ed.*, 2018, **57**, 12280–12284.
- O. Nevskiy, D. Sysoiev, J. Dreier, S. C. Stein, A. Oppermann, F. Lemken, T. Janke, J. Enderlein, I. Testa, T. Huhn and D. Wöll, Fluorescent Diarylethene Photoswitches—A Universal Tool for Super-Resolution Microscopy in Nanostructured Materials, *Small*, 2018, **14**, 1703333.
- M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluorocycloalkene derivatives, *J. Chem. Soc., Chem. Commun.*, 1992, 206–207.
- M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, Fatigue resistant properties of photochromic dithienylethenes: by-product formation, *Chem. Commun.*, 1999, **35**, 747–750.
- M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators, *Chem. Rev.*, 2014, **114**, 12174–12277.
- M. Irie, Diarylethenes for Memories and Switches, *Chem. Rev.*, 2000, **100**, 1685–1716.
- M. Herder, B. M. Schmidt, L. Grubert, M. Pätzelt, J. Schwarz and S. Hecht, Improving the Fatigue Resistance of Diarylethene Switches, *J. Am. Chem. Soc.*, 2015, **137**, 2738–2747.
- J. C. Owrutsky, H. H. Nelson, A. P. Baronavski, O. K. Kim, G. M. Tsivgoulis, S. L. Gilat and J. M. Lehn, Optical properties and dynamics of a photochromic bithienylethene in solution and in a polymer film, *Chem. Phys. Lett.*, 1998, **293**, 555–563.
- K. Higashiguchi, K. Matsuda, S. Kobatake, T. Yamada, T. Kawai and M. Irie, Fatigue Mechanism of Photochromic 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2389–2394.
- S. Kobatake, S. Imao, Y. Yamashiro and Y. Terakawa, Photoswitching of an alcohol-sensitive photochromic diarylethene, *Tetrahedron Lett.*, 2011, **52**, 1905–1908.
- M. Herder, M. Utecht, N. Manicke, L. Grubert, M. Patzelt, P. Saalfrank and S. Hecht, Switching with orthogonal stimuli: electrochemical ring-closure and photochemical ring-opening of bis(thiazolyl)maleimides, *Chem. Sci.*, 2013, **4**, 1028–1040.

- 17 D. Sysoiev, A. Fedoseev, Y. Kim, T. E. Exner, J. Boneberg, T. Huhn, P. Leiderer, E. Scheer, U. Groth and U. E. Steiner, Synthesis and Photoswitching Studies of Difurylperfluorocyclopentenes with Extended  $\pi$ -Systems, *Chem. – Eur. J.*, 2011, **17**, 6663–6672.
- 18 Y. Kim, T. J. Hellmuth, D. Sysoiev, F. Pauly, T. Pietsch, J. Wolf, A. Erbe, T. Huhn, U. Groth, U. E. Steiner and E. Scheer, Charge Transport Characteristics of Diarylethene Photoswitching Single-Molecule Junctions, *Nano Lett.*, 2012, **12**, 3736–3742.
- 19 B. M. Briechele, Y. Kim, P. Ehrenreich, A. Erbe, D. Sysoiev, T. Huhn, U. Groth and E. Scheer, Current–voltage characteristics of single-molecule diarylethene junctions measured with adjustable gold electrodes in solution, *Beilstein J. Nanotechnol.*, 2012, **3**, 798–808.
- 20 L. A. Zotti, T. Kirchner, J.-C. Cuevas, F. Pauly, T. Huhn, E. Scheer and A. Erbe, Revealing the Role of Anchoring Groups in the Electrical Conduction Through Single-Molecule Junctions, *Small*, 2010, **6**, 1529–1535.
- 21 E. Leary, A. La Rosa, M. T. González, G. Rubio-Bollinger, N. Agrait and N. Martín, Incorporating single molecules into electrical circuits. The role of the chemical anchoring group, *Chem. Soc. Rev.*, 2015, **44**, 920–942.
- 22 S. L. Bowden, S. A. Harris, H. G. Heller and M. J. E. Hewlins, Photochromic heterocyclic fulgides. Part 6. Base-catalysed cyclizations of 1-(2,5-dimethyl-3-furyl and 2,5-dimethyl-3-thienyl)ethylidene(isopropylidene)succinic anhydrides and related compounds, *J. Chem. Soc., Perkin Trans. 1*, 1992, 725–728.
- 23 T. Nakamura and Y. Kawanishi, Reaction and sensing of octafluorocyclopentene with 1,5-diazabicyclo[4,3,0]non-5-ene, *Tetrahedron Lett.*, 2017, **58**, 1176–1180.
- 24 S. Wang, Y. Zhou, L. Zhu, J. Zhang, Q. Zou, T. Zeng and W. Chen, A photochromic prototype based on difurylperhydrocyclopentene with remarkable photoswitching behavior and in vivo application, *Chem. Commun.*, 2017, **53**, 9570–9573.
- 25 Q. Zou, T. Zheng and W. Chen, Preparation of organic light emitting switch material and application in detecting cyanide ion, bioimaging and biosensing, CN109232486, 2019.
- 26 S.-Z. Pu, T.-S. Yang, R.-J. Wang and J.-K. Xu, 1,2-Bis[5-(2,2-dicyanovinyl)-2-ethyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene, a new photochromic diarylethene compound, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, o4077–o4079.
- 27 D. Kim, H. Jeong, W.-T. Hwang, Y. Jang, D. Sysoiev, E. Scheer, T. Huhn, M. Min, H. Lee and T. Lee, Reversible Switching Phenomenon in Diarylethene Molecular Devices with Reduced Graphene Oxide Electrodes on Flexible Substrates, *Adv. Funct. Mater.*, 2015, **25**, 5918–5923.
- 28 J. Wolf, I. Eberspächer, U. Groth and T. Huhn, Synthesis and Photoswitching Studies of OPE-Embedded Difurylperfluorocyclopentenes, *J. Org. Chem.*, 2013, **78**, 8366–8375.
- 29 O. Nevskiy, D. Sysoiev, A. Oppermann, T. Huhn and D. Wöll, Nanoscopic Visualization of Soft Matter Using Fluorescent Diarylethene Photoswitches, *Angew. Chem., Int. Ed.*, 2016, **55**, 12698–12702.