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**Compact “push–pull” photochromic diaryethenes (DAEs) with unsymmetric oxidation pattern of the benzothiophene core display multicolour fluorescence switching, as a result of dual emission from both “open” and “closed” forms. These DAEs also present an unprecedented photo-fatigue resistance.**

Photochromic compounds have isomeric states interconvertible by alternate irradiation with ultraviolet (UV) and visible light *via* a shared (singlet) excited state.<sup>1</sup> They attract great attention in life and materials science.<sup>2</sup> The optical properties of two distinct structures are drastically different, and the switching is controllable by changing the irradiation wavelengths. Due to the high sensitivity of fluorescence, as the state-reporting signal, optical systems with fluorescent photochromic units are particularly promising.<sup>3</sup> The photoswitching of fluorescence is promising for molecular memories,<sup>4</sup> bio-imaging<sup>5</sup> and, in particular, as a tool for cutting-edge nanoscopy techniques.<sup>6</sup>

Due to thermal stability of the two isomers and efficient photo-conversion, diaryethenes (DAEs) have emerged as a versatile platform for constructing fluorescent photochromic compounds.<sup>7</sup> Current fluorescent DAEs can be divided into two categories: Turn-Off<sup>3,4,8</sup> and Turn-On modes.<sup>9</sup> In the former case, DAE is connected with an additional fluorophore (forming a dyad), and the mechanism of fluorescence modulation is based on energy/electron transfer, usually to the closed form. This molecular design is versatile and applicable to various types of fluorophores. The latter case relies on the intrinsic fluorescence of the photogenerated closed-ring isomers<sup>9</sup> of the highly fluorescent 1,2-[bis-(2-alkyl-1-benzothiophene-1,1-dioxide-6-aryl-3-yl)]perfluorocyclopentenes.<sup>10</sup>

## Multicolour fluorescent “sulfide–sulfone” diarylethenes with high photo-fatigue resistance†

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Another intriguing category is dual fluorescence systems. Although dual-emissive assemblies combining more than two fluorescent components (*e.g.* a fluorescent dye, a fluorescent diarylethene, and fluorescent dots) have been reported,<sup>11</sup> photochromic compounds that exhibit fluorescence in both isomers are still very rare.<sup>12</sup> Due to simple chemistry which is favourable for labelling biomolecules, the compact molecular switches have advantages over complex multicomponent hybrid materials.

Here, we report a series of unique push–pull fluorescent DAEs with unsymmetric oxidation pattern in the benzothiophene core (**MeO-H**, **MeO-CN**, **MeO-CN2**) that not only exhibit reversible blue-to-red multicolour fluorescence switching, but also undergo over 10 000 cycles (in acetonitrile) without exclusion of air oxygen (Scheme 1).

In brief, **MeO-H** was synthesized *via* methylation of compound **1**<sup>13</sup> followed by selective oxidation of the  $\pi$ -electron-rich benzothiophene unit bearing methoxy group. **MeO-CN** was obtained by selective oxidation of compound **3**<sup>14</sup> with mCPBA followed by transformation of aromatic iodide into cyanide using  $\text{Zn}(\text{CN})_2/\text{Pd}(\text{PPh}_3)_4$ . Dicyanovinyl substituted diarylethene (**MeO-CN2**) was prepared by formylation of unoxidized DAE **MeO-H** followed by condensation with malonodinitrile (Scheme 2).<sup>13</sup>

To study the photophysical properties, we first measured photoinduced UV-Vis spectral changes of **MeO-H**, **MeO-CN**, and **MeO-CN2**. Upon irradiation with UV light (365 nm) in toluene, the colourless solutions of all compounds turned reddish. The absorption maxima ( $\lambda_{\text{max,OF}}$ ) of the open-ring forms of **MeO-H**, **MeO-CN**, and **MeO-CN2** were observed at 338 nm, and the corresponding absorption maxima of the closed-ring forms

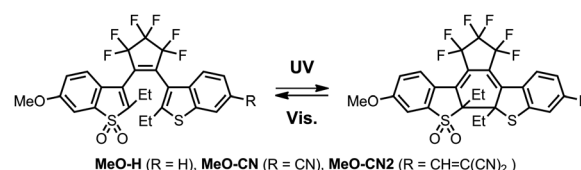
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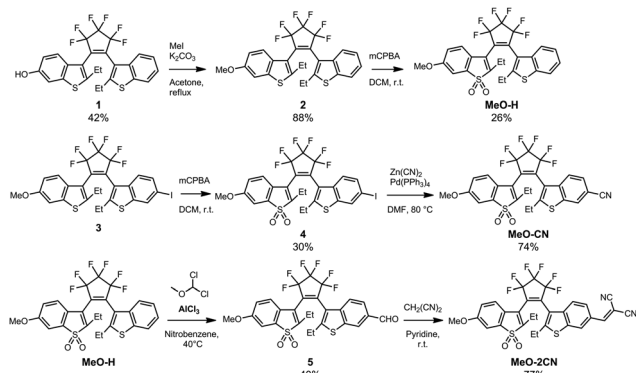
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 Scheme 1 Photochromic reactions of **MeO-H**, **MeO-CN** and **MeO-CN2**.

Scheme 2 Synthesis of "sulphide-sulfones" MeO-H, MeO-CN and MeO-CN2.

( $\lambda_{\text{max}}^{\text{CF}}$ ) were 514 nm, 509 nm, and 540 nm respectively (Fig. S8, ESI<sup>†</sup>). The photocyclization quantum yields ( $\Phi_{\text{OF} \rightarrow \text{CF}}$ ) of MeO-H and MeO-CN were 0.50 and 0.44; similar to the values reported for analogs.<sup>15,16</sup> The value of  $\Phi_{\text{OF} \rightarrow \text{CF}}$  found for MeO-CN2 was one order of magnitude smaller. Upon exposure to visible light (505 nm), the coloured solutions (containing mixtures of both forms) were fully converted to colourless open forms. The photocycloreversion quantum yields ( $\Phi_{\text{CF} \rightarrow \text{OF}}$ ) in toluene for MeO-H,

MeO-CN, and MeO-CN2 were found to be 0.02, 0.18 and 0.06, which are several orders of magnitude higher than the ring-opening efficiencies reported for another red-emissive fluorescent DAEs.<sup>17</sup> In all cases, the values of the isomerization quantum yields measured in acetonitrile and toluene were almost identical. Therefore, the photoconversion degree of DAEs with unsymmetric oxidation patterns is scarcely influenced by the solvent polarity.

The photoinduced changes in the emission spectra in toluene and acetonitrile solutions and the main photophysical data are given in Fig. 1 and Table 1. In contrast to "oxidized" fluorescent DAEs<sup>9,10,14</sup> with a high ratio of isomerization quantum yields ( $\Phi_{\text{OF} \rightarrow \text{CF}}/\Phi_{\text{CF} \rightarrow \text{OF}} > 100$ ), now the photostationary states (PSS<sub>365nm</sub>) contain mixtures of both isomers in comparable amounts. Thus, the optical properties of the UV-irradiated solutions depend on absorption/emission spectra of both isomers, the degree of conversion, and the excitation wavelength.

We next studied the multicolour fluorescence properties of MeO-H, MeO-CN, and MeO-CN2. Irradiation of the solutions of MeO-H and MeO-CN in toluene with UV light (365 nm) rapidly changed the initial blue emission to red (Table 1 and TOC graph). The emission maximum ( $\lambda_{\text{fl}}^{\text{max}}$ ) and the fluorescence quantum yield ( $\Phi_{\text{fl}}$ ) of the open form MeO-H were found to be 535 nm and 0.5%, and  $\lambda_{\text{fl}}^{\text{max}}$  and  $\Phi_{\text{fl}}$  of the closed form – 622 nm

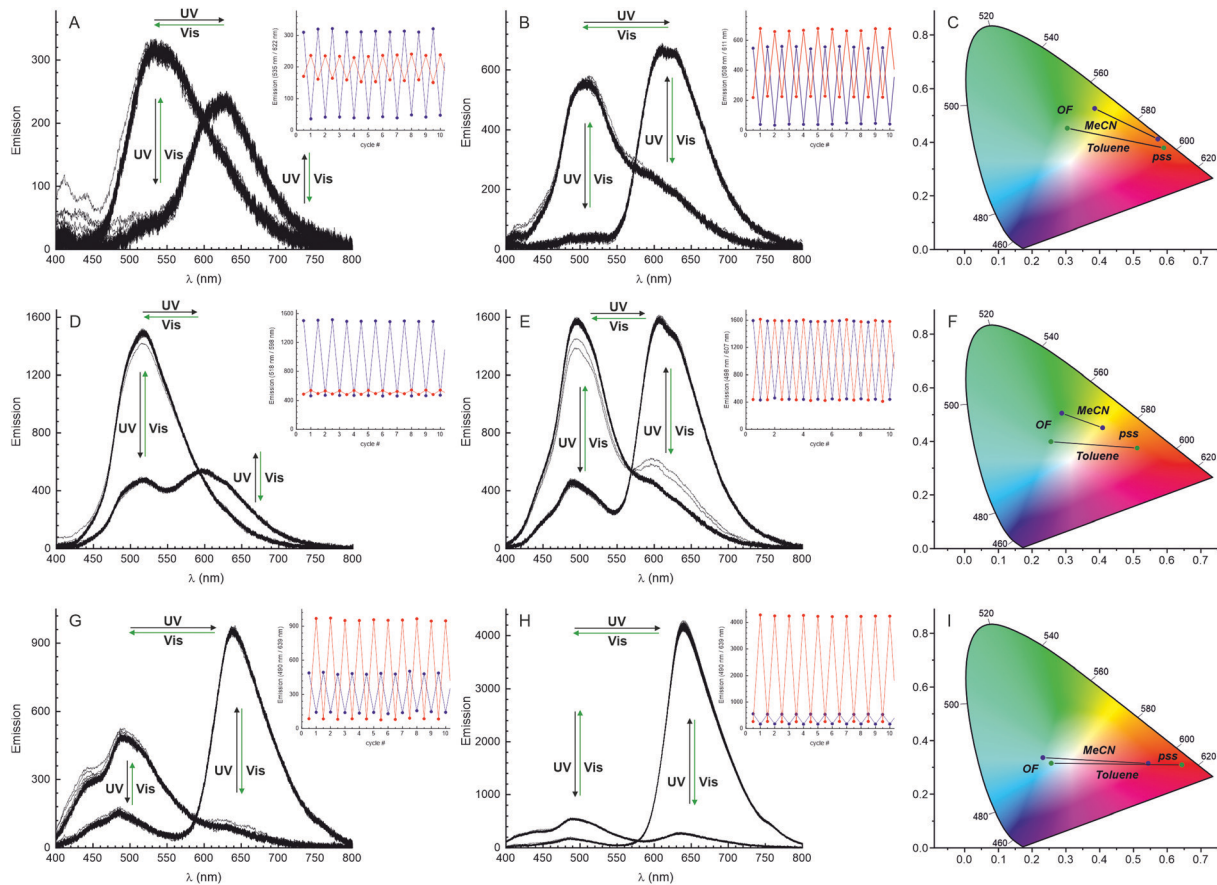


Fig. 1 Emission changes observed for DAEs MeO-H (A–C), MeO-CN (D–F), and MeO-CN2 (G–I) for 10 full cycles of irradiation (365 nm/505 nm), in acetonitrile (A, D, G) and toluene solutions (B, E, H). Light of 365 nm ensures excitation of both isomers. The emission changes at the maxima of each isomer are shown in the insets. The emission colours of both states (PSS-365 and PSS-505) are shown in the CIE chromaticity space (400–800 nm range); see also Fig. S9 and S10 (ESI<sup>†</sup>).



Table 1 The main photophysical data of **MeO-H**, **MeO-CN**, and **MeO-CN2**, in acetonitrile

	$ab\lambda^{\max} [\text{nm}]/\epsilon \times 10^{-3}$ [ $\text{M}^{-1}\text{cm}^{-1}$ ]	$\Phi_{\text{fl}}^{\lambda^{\max}} [\text{nm}]/\Phi_{\text{fl}} [\%]$	$ab\lambda^{\max} [\text{nm}]/\epsilon \times 10^{-3}$ [ $\text{M}^{-1}\text{cm}^{-1}$ ]	$\Phi_{\text{fl}}^{\lambda^{\max}} [\text{nm}]/\Phi_{\text{fl}}^{\text{b}} [\%]$	$\Phi_{\text{OF} \rightarrow \text{CF}}$ (366 nm)	$\Phi_{\text{CF} \rightarrow \text{OF}}$ (470 nm)	$\alpha_{\text{PSS}}$ (365 nm)	Fatigue resistance [ $N_{1/2}$ ]
	Open form		Closed form					
<b>MeO-H</b>	338/4365	535/0.5	514/12 657	622/0.4	0.50	0.02	0.89	23 900
<b>MeO-CN</b>	338/4002	518/1.9	509/12 018	598/3.1	0.44	0.18	0.42	29 300
<b>MeO-CN2</b>	338/25 615	490/0.1	540/19 844	639/6.6	0.03	0.06	0.62	14 500

and 0.4%, respectively. To our surprise, the presence of an electron withdrawing cyano group in compound **MeO-CN** increased the values of  $\Phi_{\text{fl}}$  of both open and closed forms to 2% and 3%, respectively. The dyes presented here have very large Stokes shifts (especially open forms). Remarkably, the introduction of an electron acceptor dicyanovinyl group (**MeO-CN2**) further increased the  $\Phi_{\text{fl}}$  of the closed ring form to 6.6%, though it decreased the  $\Phi_{\text{fl}}$  of the open form to 0.1%. To evaluate the solvent polarity effect on fluorescent properties, we determined  $\Phi_{\text{fl}}$  values and recorded the fluorescence spectra of open- and closed-ring isomers in acetonitrile. Although the emission in acetonitrile was weaker than the emission in toluene, the multicolour fluorescence response was clearly observed. The plots in the CIE chromaticity space show reversible multicolour fluorescence changes of the three compounds in toluene and acetonitrile (Fig. 1C, F and I). The reversible transitions were induced by irradiation with UV and visible light. Furthermore, a distinct difference in the colour transition path in the CIE diagram was observed when solvents with different polarity were used (acetonitrile and toluene).

To explore the effect of solvent polarity on fluorescence properties, we selected **MeO-CN** for further studies, due to its  $\Phi_{\text{fl}}$  values comparable in the open and closed forms. The emission band of the open-ring isomer exhibited red-shift with increasing solvent polarity, which indicates the push-pull electronic effects in this isomer (Fig. 2A and B).<sup>18</sup> The emission band of the closed-ring form underwent only a slight red-shift, even in highly polar solvents (methanol and acetonitrile; Fig. 2C). Thus, the overall push-pull interactions in the closed form are weaker than in the open form.

Based on the recorded fluorescence spectra of **MeO-CN** in various solvents, we plotted CIE diagram describing the colour perception of a human eye (Fig. 2D). The solvatochromism of the open form of **MeO-CN** combined with its photoinduced multicolour fluorescence switching enabled the control of emission colour in a wide chromaticity range (Fig. 2D).

Using the automated optical measurement system,<sup>14</sup> we evaluated the photo-fatigue resistance ("cycling number"  $N_{1/2}$ ) of the compounds in acetonitrile (Fig. 3A and Table 1). For cyclization reactions, irradiation with UV (365 nm) light was continued until the photostationary state (PSS) was reached, which was monitored by an increase in absorption at 518 nm. Then the samples were irradiated with visible light (505 nm), until cycloreversion reactions were fully complete (see Fig. S11–S13 in ESI†). In addition to the standard observation of the colour changes by monitoring the absorption of the CFs (Fig. 3B and C), we also tracked the fluorescence changes (Fig. 3D and E) with UV excitation of both isomers in acetonitrile (Fig. S14–S19, ESI†) and toluene solutions (Fig. S20–S22, ESI†). After one of the photostationary states of the

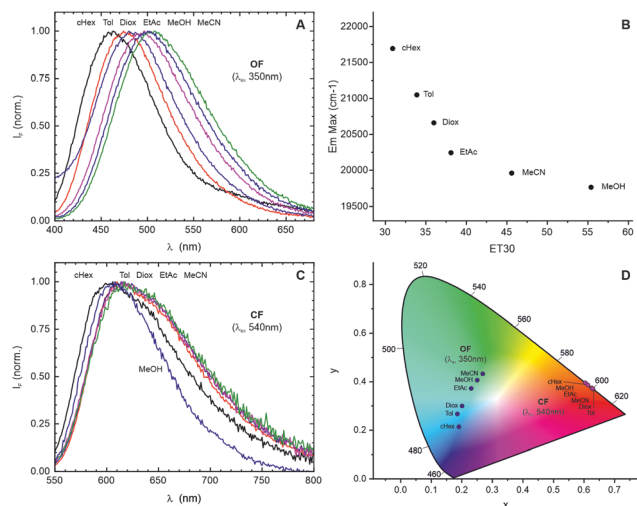
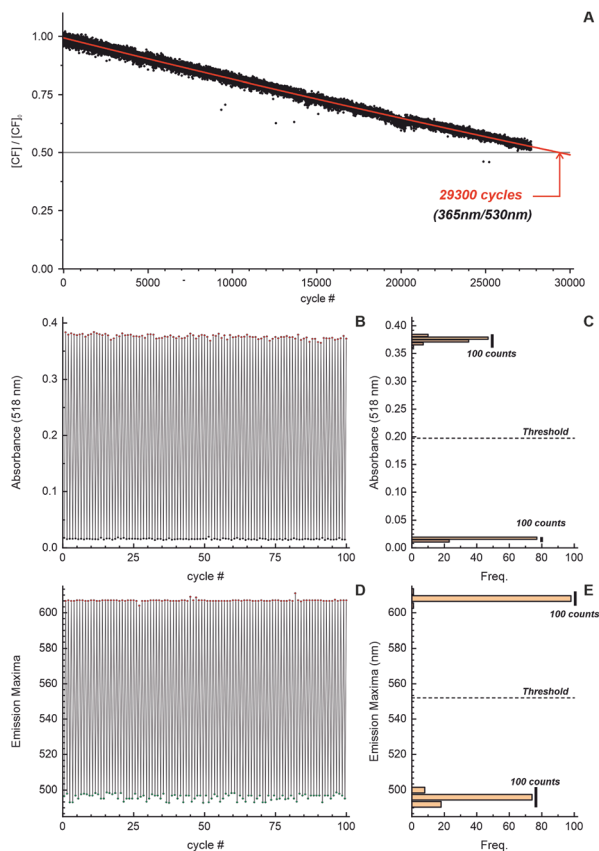


Fig. 2 Normalized fluorescence spectra of the open (A,  $\lambda_{\text{EX}} = 350$  nm) and closed (C,  $\lambda_{\text{EX}} = 540$  nm) forms of **MeO-CN** in cyclohexane, toluene, dioxane, ethyl acetate, methanol and acetonitrile. (B) Emission maxima of the OF vs. ET30 values of the solvents. (D) CIE diagram of the open- and closed-ring isomers of **MeO-CN**.

system was reached (*i.e.* under irradiation with UV or visible light), the emission maximum (wavelength at the maximum of the detected signal) was automatically searched. A plot of such calculated emission maxima  $\Phi_{\text{fl}}^{\lambda^{\max}}$  vs. the number of cycles, along with the histograms of the total obtained values, demonstrates the value of this parameter as an efficient state assignment of the system. An assignment of the system state to the closed or open form was based on absorption (Fig. 3C) or emission maxima (Fig. 3D). For the first 100 cycles, it showed no errors; the threshold was arbitrarily set at the middle point between the two local maximum bins of the corresponding histograms (Fig. 3C and E). Remarkably, the cycling number of **MeO-CN** exceeded 29 000 (50% bleaching, relative to the initial absorbance). The fatigue resistance of **MeO-H** is on the same order ( $> 23$  000 cycles), while compound **MeO-CN2** survived over 14 000 switching cycles. To our knowledge, this is the first report on photochromic fluorescent compounds that endure more than 10 000 switching cycles.

In summary, we introduced three photochromic diaryethenes with unsymmetrically oxidized cores, exhibiting photoswitchable emission signal, with a blue-to-red multicolour fluorescence modulation. Diaryethenes with a distinctive dual fluorescence switching capacities were recently reported by Yokoyama *et al.*<sup>12</sup> Compound **MeO-CN** presented here is advantageous in terms of its improved fluorescence quantum yield in both open/closed





**Fig. 3** Cyclization experiments in acetonitrile. (A) The absorption decay of closed-ring **MeO-CN** in the PSS vs. the number of cycles; (B) absorption changes at the maximum of the CF in the first 100 cycles; (C) the corresponding histogram; (D) emission changes in the first 100 cycles (excitation with 365 nm light) and the corresponding histogram (E).

ring isomers, efficient photocyclization/cycloreversion quantum yields (faster switches), and the compact structure. In addition, it exhibited an outstanding photofatigue resistance, which is essential for all practical applications. While several fluorescent diarylethenes are reported to endure several thousands of photocycles, such highly photostable fluorescent DAEs, as **MeO-H**, **MeO-CN** and **MeO-CN2** are still rare.<sup>14,19</sup> We believe that our work will contribute to the design and facile synthesis of diarylethenes with unsymmetric oxidation patterns and unusual photophysical properties interesting for the optical superresolution techniques.

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## Conflicts of interest

There are no conflicts to declare.

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