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Sulfhydryl-functionalized diarylethenes: synthesis, photoswitching, and fluorescent properties

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Sulfhydryl group (SH) plays important roles in reactions with various functional groups, especially in biologically active systems. Photoswitchable diarylethene (DAE) derivatives have demonstrated applications in many research fields. Among the many classes of diarylethene derivatives, thiol derivatives have not been extensively explored. In this study, we systematically synthesized and characterized a series of bis-thiol functionalized dithienylethene derivatives. The thiol groups in this series are attached directly to the thiophene, or through a phenyl or methylene linker. Each series incorporated both dithienyl cyclopentene and hexafluorocyclopentene bridges and total six thiol substituted diarylethenes were synthesized. Among the six sulfhydryl DAE derivatives, four compounds were synthesized for the first time. Due to the reactivity of the thiol, they were prepared and stored as the corresponding thiol acetates. The photoswitching properties of the acetylated thiol derivatives were characterized. Three new thiol derivatives exhibited intriguing 'turn-on' fluorescence behavior, where the open isomers are non-fluorescent, while the closed isomers display fluorescence. These compounds represent a new class of fluorescent diarylethenes that do not require additional fluorophores. The thiol functional group offers potential for biological conjugation reactions and application as fluorescent probes.

Introduction

Thiol derivatives are important compounds with many different applications as chemical reagents and reaction intermediates. Thiol group is an excellent functional group for the formation of other derivatives especially in biologically important systems.[1] They are also useful as catalysts for transfer hydrogenation reactions.[2–4] Diarylethene (DAE) based photochromic compounds have been studied extensively during the past several decades due to their interesting photochemical properties and a wide range of applications.[5–8] DAE dicarboxylic acid derivatives were used to functionalize quantum dots, which resulted in interesting new materials.[9,10] Recently, thiol functional groups have been incorporated into DAE core structures, and the resulting water-soluble salt derivatives have demonstrated photochromic behavior.[11] Thiol-containing diarylethene derivatives represent a unique class of compounds that can be conjugated with various organic or inorganic functionalities, as well as with metal surfaces. Among the various classes of diarylethene derivatives, thiol substitution on the thiophene side chain remains relatively underexplored, with research largely limited to nanoparticle formation. Typically, reported thiol derivatives are synthesized with acetyl-protected thiol groups, which are then deprotected *in situ* before being attached to gold or other surfaces.[12] Feringa *et al.* have reported the synthesis and characterization of several thiol-containing dithienylethene (DTE) derivatives designed for photochromic and electrochromic molecular wires.[13] Due to the interesting properties of thiol derivatives, we set out to systematically study sulfhydryl substituted DAEs, specifically examining the effect of varying the distance between the sulfhydryl group and the thiophene moiety. Varying the distance between the sulfhydryl group and the thiophene moiety is important because it can significantly influence the compounds' photochromic behavior, electronic properties, and their efficiency in conjugation with other molecules or surfaces. Understanding this relationship allows for better design and optimization of diarylethene-based materials for applications in molecular electronics, sensing, and bio-conjugation. The targeted thiol derivatives, compounds **1–6**, are illustrated in Fig. 1 .

Although diarylethenes have been extensively studied, the sulfhydryl derivatives **1** and **2** have only been reported in computational theoretical studies[14] and no experimental preparations and characterization data can be found in the literature, to the best of our knowledge. The photoswitching properties of compounds **1** and **2** and their gold conjugates were studied theoretically *via* DFT modeling by Staykov.[15,16] The mercaptomethyl derivatives **3** and **4** have not been reported yet, although a different analog containing a thiol-methylene moiety has been reported.[17] The synthesis of these four

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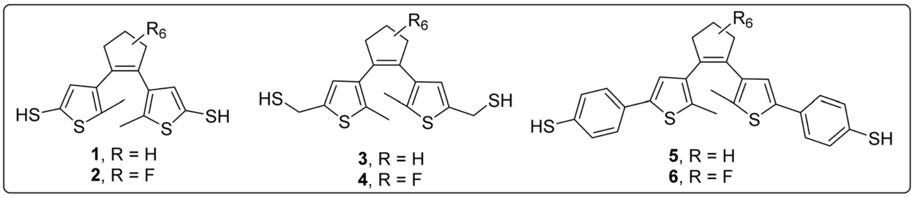


Fig. 1 Thiol derivatives synthesized in this work.

compounds (**1–4**) will provide access to valuable thiol functionalized diarylethenes and their characterizations can lead to the discovery of functional photochromic compounds with practical applications. Compounds **5** and **6**, which contain phenylthiol groups, have been previously reported in theoretical studies.[14,18] Feringa *et al.* reported the synthesis of several diarylethene derivatives, including the SAc derivative of compound **5**, whose properties were subsequently investigated.[19,20] They have also synthesized and studied several mono phenylthiol and thiophene thiol derivatives. Typically, the sulfhydryl group was protected as a thioacetate and deprotected *in situ* before attachment to gold surfaces.[13,21,22] Recently, the thiomethyl ether derivatives of compounds **5** and **6** were synthesized and characterized,[23] the methyl thioether was deprotected using *tert*-butylthiolate and followed by treatment with HCl to remove the *t*-butyl group *in situ*. The free thiol derivatives **5** and **6** were not isolated and the deprotected products were directly attached to gold surfaces as self-assembled monolayers (SAMs). Other mono- and bis-thiophenyl derivatives have also been reported, along with studies on their conductivity following the formation of networks by DAE thiols on gold nanoparticles.[24–26] An asymmetrical diarylethene containing a phenyl thiol group immobilized on a gold surface has also been studied, where the corresponding thioacetate derivative was found to spontaneously adsorb onto the gold surface.[27]

Fluorescent molecules with photoswitching properties are important compounds with many practical applications, as shown in recent reviews.[7,28] Diarylethene based photochromic compounds often exhibit "turn-off" fluorescence in which the open form is fluorescent and the closed form has weak or no fluorescence.[29,30] DAEs with intrinsic fluorescence, meaning no additional fluorophores are incorporated, have also been recently reported to exhibit turn-on mode fluorescence. Most of these compounds are the oxidation products of thiophene groups, typically forming sulfone derivatives.[27] DAE sulfone derivatives synthesized through oxidation reactions exhibited strong fluorescence, indicating potential for bioconjugation applications.[31,32] Fluorescent DAEs exhibiting turn-on mode fluorescence are valuable for imaging applications and are promising candidates for photoactivation localization microscopy (PALM).[33,34] Numerous DAE sulfone derivatives have been synthesized and studied, with their photoswitchable fluorescence properties explored for applications in sensing, bioimaging, and related fields.[35–38] Related fluorescent DAEs featuring various bridges, such as triangle terarylenes, have also been synthesized and utilized for photopatterning applications.[39,40] In addition to DAEs with intrinsic fluorescence, numerous derivatives incorporating other fluorescent moieties have been extensively studied and applied in various fields.[28] Several diarylethene compounds exhibit photochromic and fluorescent responses to Cu^{2+} and CN^- ions,[40] and photo-erasable fluorescent diarylethene derivatives have been explored as molecular turnstiles.[41,42]

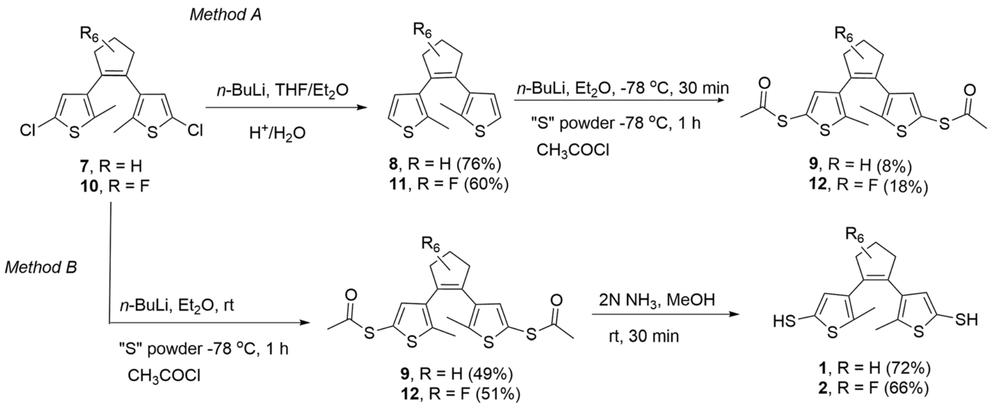
We are intrigued by the fact that the simple DAE compounds **1–4** have never been synthesized, and none of the six free thiol (SH) derivatives **1–6** have been isolated or characterized thus far. Since these compounds feature interesting structures that can act as reactive species through thiol functionalization, their experimental photochromic properties are likely to attract significant interest from chemists. Although these compounds have been reported in the literature, they were mostly used *in situ* and not fully characterized. Therefore, we aimed to synthesize and thoroughly characterize them.

Results and discussions

Synthesis of thiol derivatives

To synthesize the thiol derivatives **1** and **2**, several different methods for thiolation reactions were explored, but a majority of these reactions failed to produce the desired product. Thioacetylation on phenyl iodide and substituted phenyl iodide has been reported using CuI and KSAc.[43] We also tried to use CuI as a catalyst to convert iodo derivatives to the corresponding thiol group, as these worked for phenyl iodide and other aryl iodides.[44–46] However, none of these conditions worked for the dithienylethene derivatives. After these reactions did not lead to satisfactory results, we focused on lithiation, followed by the addition of sulfur powder directly. As shown in Scheme 1, the chloro derivatives **7** and **10** were prepared following literature procedures, and they can be converted to the dehalogenated thiophene derivatives **8** and **11**, respectively. Lithiation on compounds **8** or **11** followed by sulfurization and acetylation afforded the corresponding thioacetates **9** or **12** in low isolated yields. Alternatively, starting from the chloro derivatives **7** and **10**, we carried out a one-pot reaction of lithiation, sulfurization, and acetylation to afford the products **9** and **12** in moderate yields. The reactions are reproducible to afford the desired products. The thioacetate was then deprotected under very mild conditions using 2 N ammonia in methanol. Other basic conditions, such as using K_2CO_3 led to intractable byproducts and the free thiol derivatives **1** and **2** could not be isolated.

The primary thiol derivatives **3** and **4** have a methylene linker between the thiophene ring and the mercapto group. The



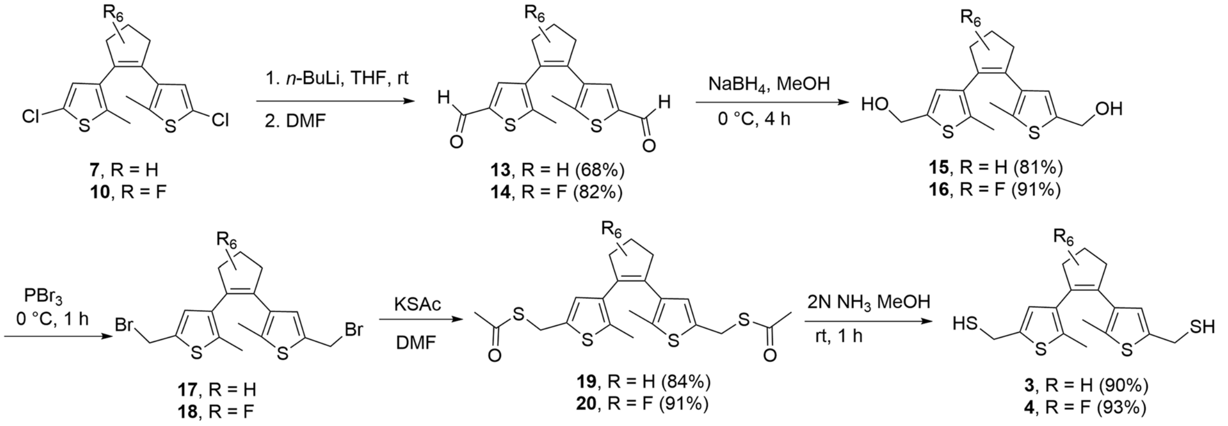
Scheme 1 Synthesis of DTE-SH compounds **1**, **2**.

synthesis of these compounds proceeded smoothly as shown in Scheme 2. The formyl derivatives **13** and **14** were prepared from the corresponding chlorothiophene derivatives, and the reduction of the aldehyde afforded the corresponding primary alcohols **15** and **16**. Bromination with PBr_3 afforded the bromo intermediates **17** and **18**,[47] which were directly converted to the corresponding thioacetates **19** and **20** by nucleophilic substitution reaction (S_N2). Deprotection of the acetyl group with ammonia in methanol afforded the thiol derivatives **3** and **4** smoothly.

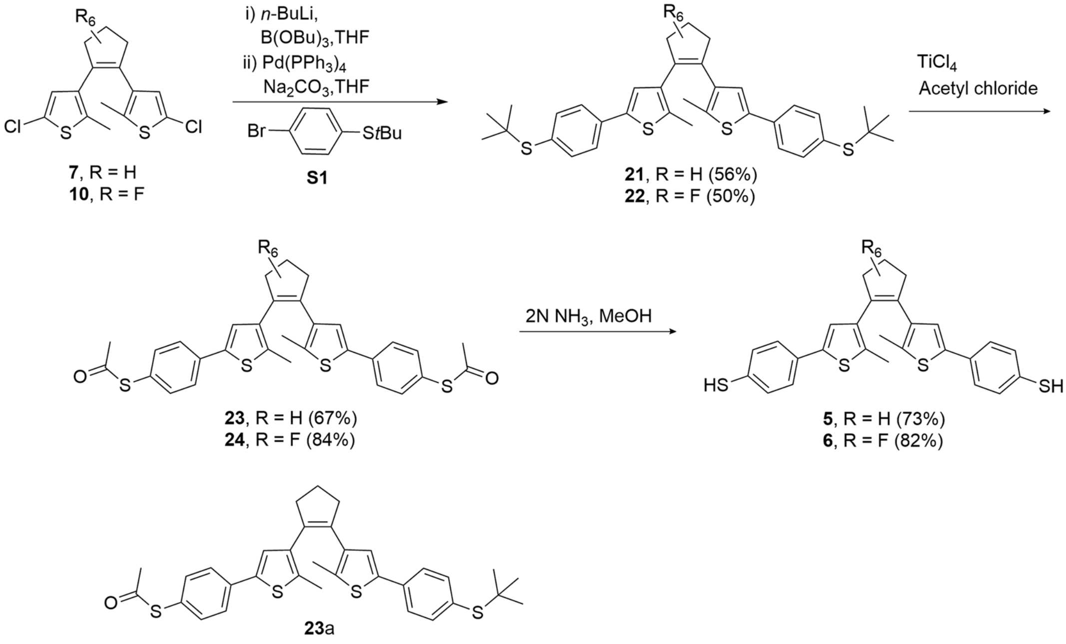
The synthesis of compounds **5** and **6** is shown in Scheme 3. We first synthesized the *t*-butylthioether derivatives **21** and **22** using the Suzuki coupling method reported in the literature.[19] The *t*-butylthioethers were deprotected using $TiCl_4$ to produce the corresponding thioacetates **23** and **24**.[12] The acetyl group was removed to afford the free thiol derivatives **5** and **6**. These two compounds have only been reported as intermediates following deprotection, but they were neither isolated nor characterized. Interestingly, during the deprotection of the *t*-butyl ether, we also obtained a small amount of mono-deprotected product **23a**, which contains an electron donating group and electron withdrawing group on opposite sides of the conjugated system.

Photo switching properties

These compounds represent an interesting class of thiol-containing photoswitches. With these compounds in hand, we conducted photoirradiation studies on the six derivatives and demonstrated their ability to form photo-cyclized closed forms upon UV irradiation. However, the free thiol groups were prone to oxidation, leading to instability during light exposure. The perfluorinated bridged derivatives **2**, **4**, **6** were found to be more stable compared to the perhydrogenated bridged compounds **1**, **3**, and **5**. Due to the instability and reactivity of the free thiols, and since the thioacetates were shown to be suitable as precursors of thiol after mild base deprotection, we focused our studies on thioacetate derivatives for photoswitching experiments. These compounds exhibited more stable photoswitching properties compared to the free thiol derivatives. The UV-vis spectra of the thioacetate compounds **9**, **12**, **19**, **20**, **23**, **23a**, and **24** are shown in Fig. 2–5 and S1–S4. Compound **12** was converted to the cyclized form with a new signal at 560 nm reaching maximum intensity after 2 minutes irradiation, as shown in Fig. 2, the open form has λ_{max} at 246 nm. At approximately 5 minutes UV treatment, the cyclized closed form reached maximum absorptions at 362 and 560 nm,



Scheme 2 Synthesis of F6-DTE-CH_2SH compounds **3** and **4**.



Scheme 3 Synthesis of DTE-PhSH compounds **5** and **6**.

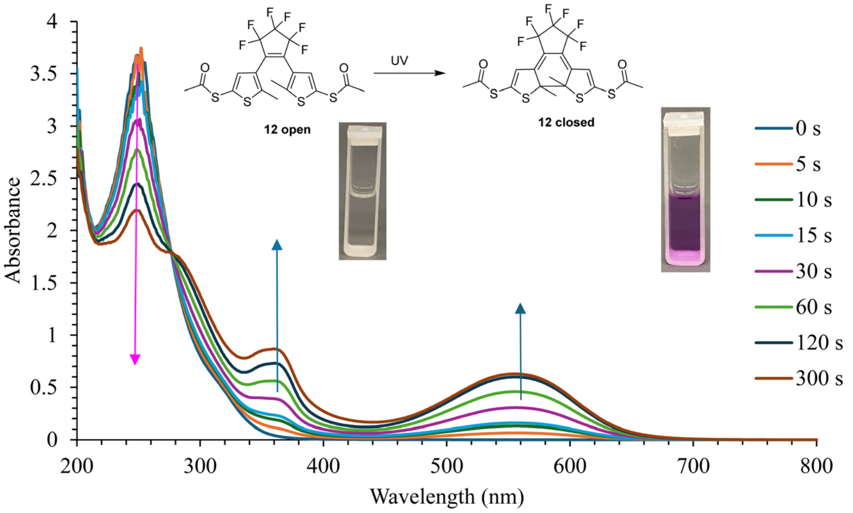


Fig. 2 UV-vis absorption spectra of compound **12** in acetonitrile (0.1 mM) after exposure at 302 nm at different time.

and the solution appeared light purple. The fluorinated derivative **20** also exhibited photoswitching properties. The compound cyclized after 2 minutes of UV irradiation and reached maximum absorptions at 350 and 530 nm and the solution appeared red colored (Fig. 3). The ^{1}H NMR spectrum of the photoswitched compound **20** was obtained and included in Fig. S7. Due to higher concentrations required for NMR spectroscopy, longer irradiation time was necessary to cyclize the open forms. Using DMSO-d_6, compound **20** reached approximately 80% conversion from the open to the closed forms after 25 minutes irradiation.

The photoswitching properties of compound **23a** were studied and the results are shown in Fig. 4. The compound exhibited fast switching between the open and the cyclized forms. The open form showed two main peaks at λ_{max} 290 and 320 nm. After 15 s irradiations, the cyclized form reached maximum absorptions at 378 and 545 nm. The fluorinated compound **24** showed a little more complex UV absorption spectra after treatment with UV light, the closed form had several absorptions at 370, 390, and 600 nm and the solution appeared blue (Fig. 5). The UV signals and the colors of the photocyclized forms are included in Table 1. The color change of the materials could be useful in visual sensors and certain switches.

The relative rate of photocyclizations for these compounds were compared using the UV-vis spectra. Compounds **9** and **19**

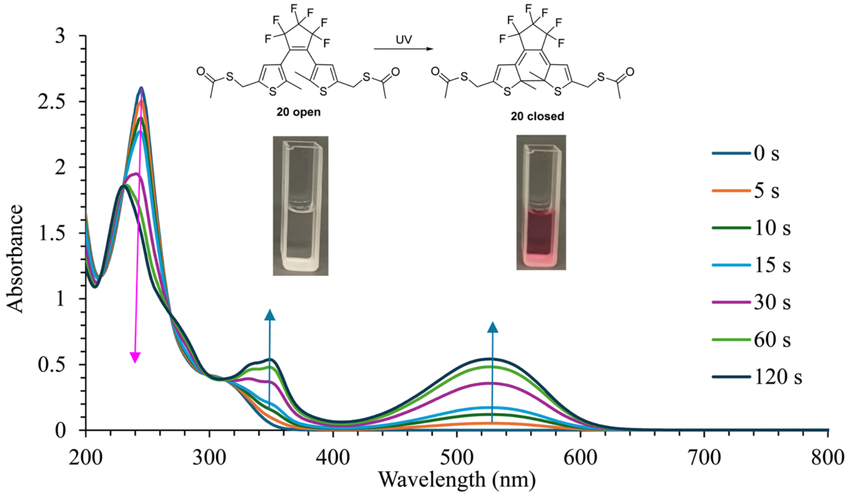


Fig. 3 UV-vis absorption spectra of compound **20** in acetonitrile (0.1 mM) after exposure at 302 nm at different time.

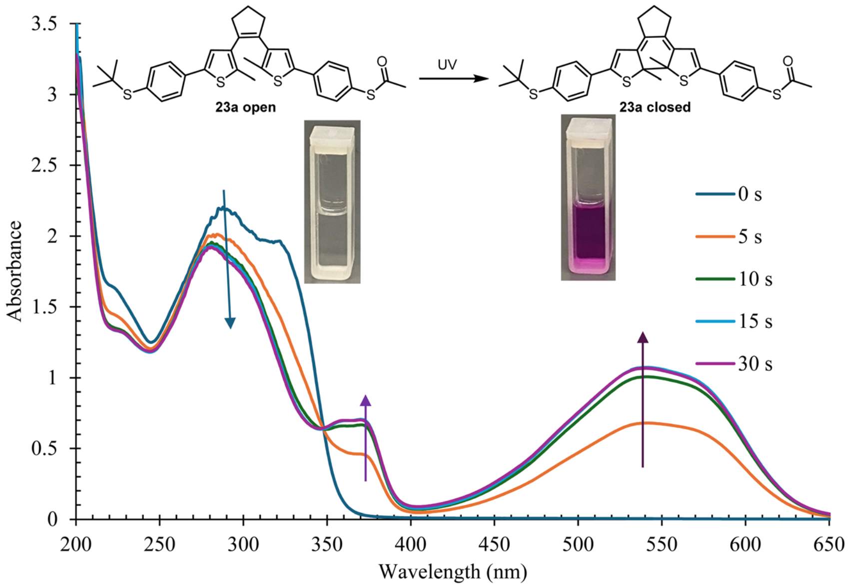


Fig. 4 UV-vis absorption spectra of compound **23a**, at 0.10 mM in acetonitrile after exposure at 302 nm at different times.

were slower to cyclize, typically requiring over 5 minutes. The rates of cyclization reaction for compounds **12**, **20**, **23**, **23a**, **24** were calculated using the UV absorbance of the samples after irradiation at given time *versus* the maximum absorbance, these are shown in Fig. S6a–e. The fluorinated analogs **12** and **20** took about 2 minutes to reach full conversion, and the compounds with phenyl spacer **23a**, **23** and **24** were faster switching, which only took about 15, 60, and 60 seconds, respectively. Compound **23a** was found to be the fastest switching compound in the series, perhaps due to the opposite electronic effect of the substituents.

Fluorescent properties

The fluorescent properties of the thiol derivatives in the open and closed forms were characterized. It was interesting to find that three DAE thiol derivatives **9**, **19**, and **20** exhibited "turn-on" fluorescence upon UV light exposures; while compounds **12**, **23** and **24** did not exhibit significant fluorescence in either open or the closed forms. The perhydrogenated cyclopentene bridged compounds **9** and **19** exhibited intriguing fluorescent properties: their closed forms exhibited strong fluorescence, while the open forms were non-fluorescent, as illustrated in Fig. 6 and 7. These compounds represent a new type of turn-on fluorescence among DAEs, as most turn-on fluorescent DAE systems reported to date have a structure containing benzothiophene sulfone moieties.[29,37,48] Compound **9** does not exhibit fluorescence in acetonitrile in its open form; however, upon UV irradiation for 5 minutes, the closed form displays strong fluorescence around 500 nm. The fluorescence intensity increased with continued UV exposure, reaching a maximum

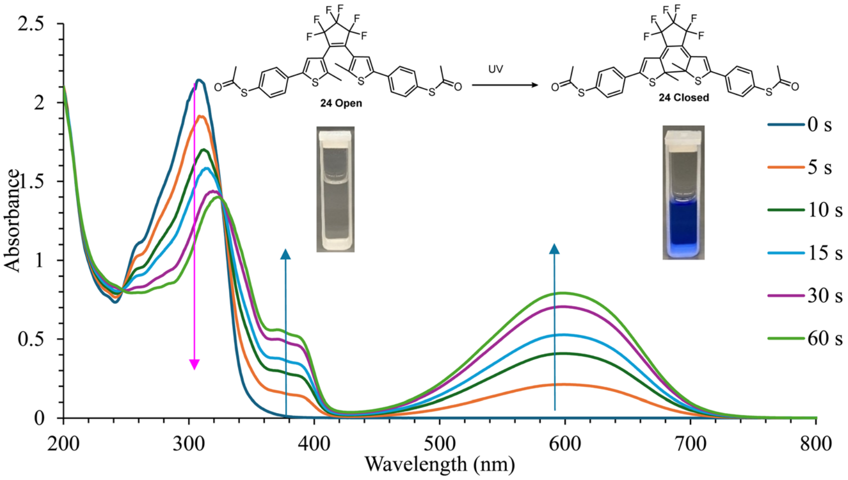


Fig. 5 UV-vis absorption spectra of compound **24** in 0.05 mM, after exposure at 302 nm at different times. λ_{max}, open form 308 nm, shifting to 325 nm after 1 min; cyclized form showed 3 peaks at 370, 390, 600 nm.

after 20 minutes. The compound also exhibited turn-on fluorescence at a higher concentration of 0.2 mM, showing the reproducible results (Fig. S9). In contrast to this observation, as shown in Fig. S11, the fluorinated derivative **12** showed a minor difference between its open and closed forms. Both the open and closed form exhibited weak fluorescence at 468 nm. However, the closed form also displayed enhanced fluorescence at 575 nm compared to the open form. Interestingly, the thioacetate derivative with the CH_2 spacer, compound **19**, exhibited a similar trend of "Turn-on" fluorescence like compound **9**, as shown in Fig. 7. After 3 minutes of UV irradiation, the cyclized closed form exhibited maximum fluorescence intensity, showing strong emission around 534 nm. In the absence of UV treatment, the open form displayed no fluorescence. The

Table 1 The λ_{max} of the open and closed forms

Compound number	CH_3CN, mM	Isosbestic point, nm	λ_{max} open form, nm	λ_{max} closed form, nm	Color of the closed form	Appearance cuvette
9	0.10	289	245	375, 495	Yellow	
12	0.10	275	246	560, 360	Purple	
19	0.10	274	237	380	Yellow	
20	0.10	242	268	530, 350	Red	
23	0.10	250	319, 297	540, 363	Purple	
23a	0.10	349	320, 290	545, 372	Purple	
24	0.05	325, 246	306	600, 390, 370	Blue	

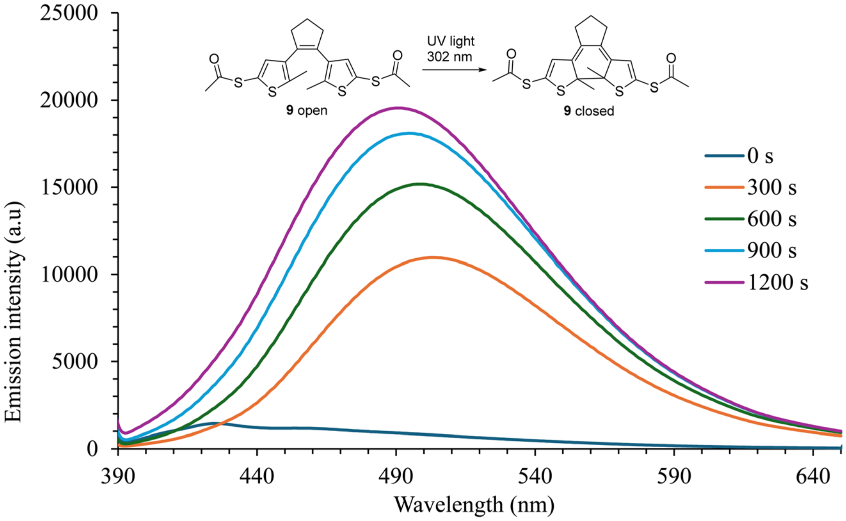


Fig. 6 Fluorescence spectra of compound **9**, 0.1 mM in acetonitrile, $\lambda_{ex} = 375$ nm.

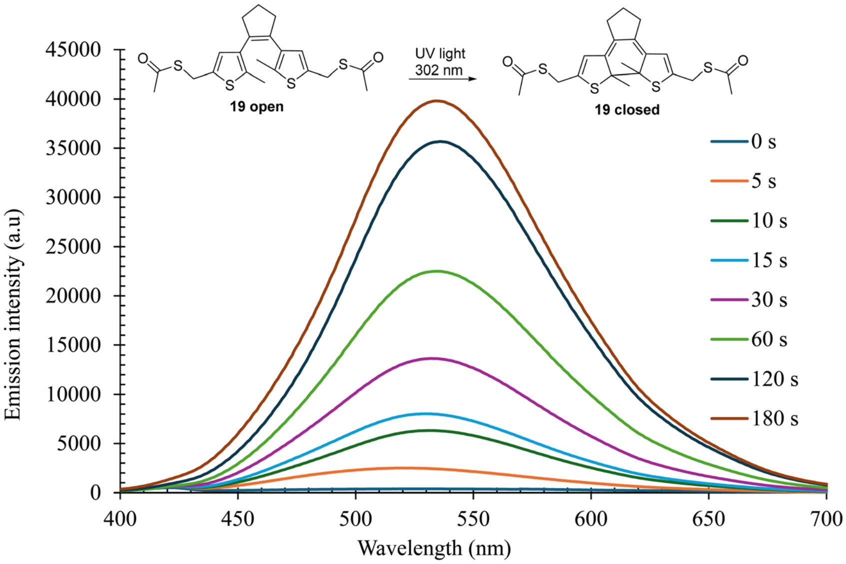


Fig. 7 Fluorescence spectra of compound **19**, 0.05 mM in acetonitrile, $\lambda_{ex} = 375$ nm.

perfluorinated cyclopentene bridged compound **20** exhibited more complex "turn-on" fluorescence upon UV irradiation (Fig. S13). At 5 minutes of irradiation, two weak signals centered at 492 nm and 620 nm appeared. Longer irradiation time led to the enhancement of the 492 nm peak and reduced intensity for the peak at 620 nm, reaching maximum around 15 minutes. The fluorescent properties of compounds **23** and **24** which contain a phenyl ring spacer showed no difference between the open and the closed forms, both exhibited weak fluorescence at the same wavelengths. Upon UV treatment, there were no significant changes in the fluorescence emission spectra (Fig. S15–16 and S18).

Compounds **9** and **19** contain the cyclopentene bridge, while compounds **12** and **20** contain the electron withdrawing perfluorinated cyclopentene bridge. In compounds **9** and **12**, the electron withdrawing SAc groups are directly attached to the conjugated system, which increases the structural rigidity. Compounds **19** and **20** both contain a flexible methylene spacer between the thiophene ring and the thioacetate functional groups. The open forms of compounds **9**, **19**, and **20** showed no fluorescence; upon photocyclizations, the closed forms exhibited extended conjugations which contributed to the enhanced fluorescence. We have also analyzed the fluorescence spectra of the cyclized forms of compounds **9** and **19** at different concentrations as shown in Fig. 8 and S19. The UV absorbance of the cyclized form was measured after irradiation had proceeded to the point of maximum cyclization, as confirmed by UV-vis spectra; fluorescence spectra were then recorded. Their fluorescent quantum yields (QYs) were determined using 7-diethylamino-4-methylcoumarin as a standard.[49] The fluorescent

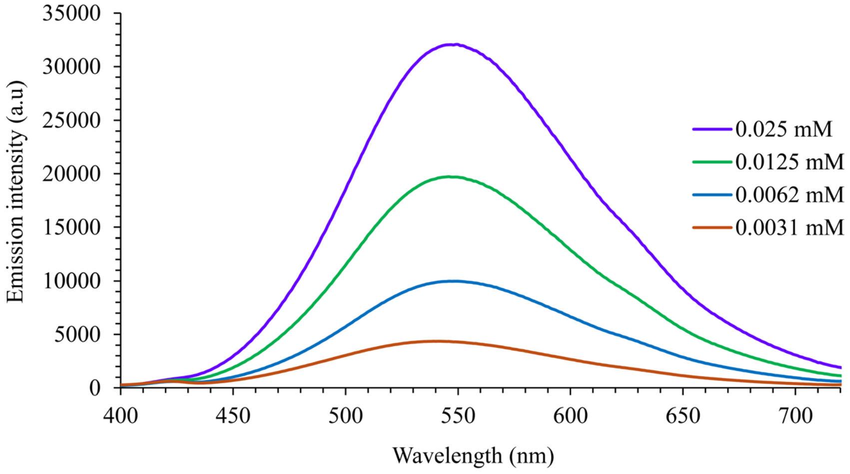


Fig. 8 Fluorescence spectra of compound **19** (closed form) in acetonitrile at different concentrations, $\lambda_{ex} = 375$ nm.

QYs of closed forms of compounds **9** and **19** are 0.043 and 0.054, respectively. Both compounds exhibited enhanced fluorescence at higher concentrations. Comparing the fluorescence intensities of the two compounds at 0.025 mM concentration, compound **19** with the methylene spacer exhibited more than 6-fold stronger fluorescence than compound **9**.

Conclusions

A series of six bis-mercapto methyl and sulfhydryl substituted diarylethenes were systematically synthesized and characterized. Among the six thiol derivatives, compounds **1–4** were synthesized for the first time and their photoswitching and fluorescent properties have been studied. The photochromic properties were studied using the corresponding acetyl protected thiol compounds due to better stability. In general, the fluorinated derivatives are more robust than the hydrogenated derivatives during the photoswitching experiments. The cyclopentene bridged derivatives **9** and **19** exhibited turn-on fluorescence, in which the open forms were not fluorescent, but the closed forms exhibited strong fluorescence. The perfluorinated bridged compound **20** exhibited more complex turn-on fluorescence emissions after UV treatment. The perfluorinated bridged compound **12** and compounds **23**, **24** with thiophenyl substituents are almost non-fluorescent in their open forms and did not exhibit much difference after UV treatment. These indicated that the "turn-on" fluorescence is affected by the nature of the bridge between the two thiophenes as well as the flexible spacer between the thiophene and the thioacetate functions. The thioacetate can be deprotected *in situ* to afford the free thiols and which can be used for different reactions, expanding the applications of these compounds. The unique "Turn-on" fluorescence observed for these compounds can be applied for sensing applications for detection of light irradiation and bioimaging. These compounds are expected to have applications for optical imaging and sensing as well as useful reagents for photoswitchale bioconjugation *via* the free thiol function.

Experimental section

General methods

All reactions were carried out under normal conditions (1 atm pressure, without catalyst unless otherwise mentioned, rt or heated with specified temperature), reagents and solvents were obtained from commercial suppliers from Sigma-Aldrich, VWR, and Fisher and used directly without any purifications. All reactions unless otherwise noted were carried out in oven dried glassware under nitrogen atmosphere. All purification was conducted by flash chromatography using 230–400 mesh silica gel with a gradient of solvent systems. Thin-layer chromatography (TLC) analysis was performed with aluminum or glass backed TLC plates (Sigma-Aldrich) with UV and fluorescence indicator and visualized using UV lamp at 254 nm then stained with PMA solution. ^{1}H NMR and proton-decoupled ^{13}C NMR spectra were obtained with Bruker 400 MHz spectrometers in DMSO-d_6 or $CDCl_3$. The chemical shifts were reported using $CDCl_3$/DMSO-d_6 as internal standard at 7.26/2.50 ppm and at 77.0/39.5 ppm, respectively. 2D NMR experiments (HSQC, COSY) were also conducted to assist the compound structure assignment. Melting point measurements were carried out using a Fisher Jones melting point apparatus. UV-vis analysis was performed using Shimadzu UV Spectrophotometer (UV-1800) and Fluorescence spectra were obtained using Shimadzu Spectro Fluorophotometer (RF-6000) with single scan mode, slit width of 1.0 nm and scan speed of 600 nm min^{-1}. High resolution mass spectra (HRMS) were obtained on a Thermo Scientific LTQ Discovery spectrometer using ESI+ and reported for the molecular ion $[M + Na]^+$.

Photoswitching studies

The compounds were dissolved in acetonitrile to prepare a solution at typically 0.1 mM concentration. To perform a photoswitching study, the solution was irradiated using UVM-16 EL Series UV Lamp (6 watt, 302 nm and white light, P/N 95-0273-01, 0.12 Amps, 115 V, 60 Hz) at different time points and

UV absorbance was measured using a Shimadzu UV Spectrophotometer (UV-1800).

Fluorescence experiments

A Shimadzu Spectro Fluorophotometer (RF-6000) was used to study the fluorescence emission of the solutions in acetonitrile. The fluorescent excitation wavelengths were determined first, then the emission spectra were recorded at different time points of UV irradiation. Open form emission was measured under normal daylight. To obtain the closed form, 302 nm light was used to treat the sample solution for a certain amount of time, and the emission spectra of the closed forms were measured.

Quantum yield measurement

The relative fluorescent quantum yield (QY) was determined using 7-diethylamino-4-methylcoumarin as the standard and a Shimadzu RF-6000 spectrofluorophotometer. Solutions of the standard and compounds **9** and **19** at different concentrations in acetonitrile were prepared. The UV-vis spectra were then recorded using a Shimadzu UV-1800 spectrophotometer. The solutions of the samples were irradiated with UV lamp to obtain the photocyclized closed forms. Using an excitation wavelength of 369 nm, the QYs of the closed forms of compounds **9** and **19** were determined relative to the coumarin standard (QY $\sim$ 1).

Synthesis and characterizations of compounds 8–24

Synthesis of compound 8. Compound **8** has been synthesized by different methods in the literature.[50,51] To a stirred solution of compound **7** (200 mg, 0.607 mmol, 1.0 eq.) in THF (5 mL) was added dropwise *n*-BuLi (1.95 M in hexanes, 0.84 mL, 1.641 mmol, 2.7 eq.). The reaction mixture was allowed to stir for 1 hour at rt. After 1 hour, the reaction was quenched with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and removed under reduced pressure. The crude product was purified by column chromatography using hexane to obtain a viscous liquid as the desired compound **8**, 76% (120 mg). $R_f = 0.6$ in hexane. ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, $J = 5.2$ Hz, 2H), 6.74 (d, $J = 5.2$ Hz, 2H), 2.79 (t, $J = 7.4$ Hz, 4H), 2.10–2.00 (m, 2H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 134.5, 134.4, 128.2, 121.1, 38.4, 23.0, 14.0.

Synthesis of compound 9

*Method **A**.* To a stirred solution of compound **8** (310 mg, 1.192 mmol, 1.0 eq.) in THF (5 mL) was added dropwise *n*-BuLi (1.95 M in hexanes, 1.58 mL, 3.0992 mmol, 2.6 eq.) at −78 °C. The reaction mixture was allowed to stir for 0.5 hours at the same temperature. After 0.5 hours, sulfur powder (114 mg, 3.576 mmol, 3 eq.) was added, and the reaction was stirred at −78 °C for 1.0 hours, after this, acetyl chloride (0.25 mL, 3.576 mmol, 3 eq.) was added to the reaction and the mixture was continued stirring at −60 °C to rt for 1 hour. The reaction was monitored by TLC. The reaction was quenched with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and reduced pressure, 8% (40 mg, $R_f = 0.25$ in 5% EtOAc/hexanes).

*Method **B**.* Compound **7** (200 mg, 0.61 mmol, 1 equiv.) was dissolved in anhydrous diethyl ether (3 mL) in a dried and argon-flushed round-bottomed flask. *n*-Butyl lithium (1.95 M in hexanes, 0.78 mL, 1.52 mmol, 2.5 equiv.) was added dropwise at 0 °C, and the reaction was stirred for 1 hour at rt. Then, sulfur (59 mg, 1.83 mmol, 3 equiv.) was added in one portion at −78 °C and the mixture was stirred for 2 hours and warmed to 0 °C. Acetyl chloride (0.13 mL, 1.83 mmol, 3 equiv.) was added to the flask and the reaction was statured for 1 h. TLC and ^1H NMR were used to monitor the reaction. The reaction was quenched with water and extracted with 20 mL EtOAc. Then the organic layer was dried and the solvent was removed under reduced pressure. Column chromatography was performed using 0–2% EtOAc/hexane to afford a viscous semisolid product compound **9**. Yield: 121 mg (49%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.76 (t, $J = 7.4$ Hz, 4H), 2.35 (s, 6H), 2.08–2.00 (m, 2H), 1.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 141.9, 137.0, 136.6, 134.6, 120.6, 38.4, 29.3, 23.0, 14.5. HRMS (ESI+) *m*/*z* calcd for $[C_{19}H_{20}O_2S_4Na]^+$ $[M + Na]^+$: 431.0238, found 431.0238.

Synthesis of compound 1. Compound **9** (50 mg, 0.122 mmol, 1 equiv.) was dissolved in anhydrous 2 N NH_3 in MeOH (2 mL) in a dried 50 mL round-bottomed flask and stirred for 1 hour. After the addition of 2 N ammonia solution, yellow color precipitate was formed. Then the reaction was monitored by ^1H NMR and TLC. Methanol was removed under reduced pressure and diluted with 5 mL DCM. The organic layer was washed with 4 mL (2 mL × 2) DI water. The organic layer was dried with anhydrous sodium sulphate. The crude was further purified using a finger column with 100% hexane to afford the desired compound as a white solid, 28 mg (72%). $R_f = 0.5$ in 5% EtOAc/hexanes. ^1H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 2.74 (t, $J = 7.4$ Hz, 4H), 2.16 (s, 6H), 2.07–1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.0, 136.2, 134.5, 131.5, 37.8, 23.3, 15.1.

Synthesis of compound 11. Compound **11** was prepared in the literature by different methods.[52,53] To a stirred solution of compound **10** (80 mg, 0.183 mmol, 1.0 eq.) in Et_2O (5 mL) was added dropwise *n*-BuLi (1.95 M in hexanes, 0.25 mL, 0.494 mmol, 2.7 eq.). The reaction mixture was allowed to stir for 1 hour at rt. After 1 hour, the reaction was quenched with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, reduced under reduced pressure. The crude was purified by column chromatography using 100% hexane to afford the desired compound **11** as a viscous liquid in 60% yield (40 mg, $R_f = 0.6$ in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, $J = 5.4$ Hz, 2H), 7.05 (d, $J = 5.4$ Hz 2H), 1.88 (s, 6H).

Synthesis of compound 12. Using the same method **A** described above, compound **11** (100 mg, 0.271 mmol, 1.0 eq.) in Et_2O (4 mL) was added dropwise *n*-BuLi (1.95 M in hexanes, 0.36 mL, 0.706 mmol, 2.6 eq.) at −78 °C, sulfur powder (26 mg, 0.813 mmol, 3 eq.) was added, and followed by acetyl chloride (0.057 mL, 0.813 mmol, 3 eq.) The crude product was purified by using column chromatography using 2–5% EtOAc/hexane to afford compound **12** in 18% (25 mg) yield.

Using the same method **B** described above for compound **9**, only the quantities are given here for the synthesis of compound **12**.

Compound **10** (200 mg, 0.457 mmol, 1.0 eq.) in Et_2O (8 mL) was added dropwise *n*-BuLi (2.3 M in hexanes, 0.5 mL, 1.18 mmol, 2.6 eq.) at −78 °C. Sulfur powder (87 mg, 2.74 mmol, 6 eq.) was added to the flask and the reaction was stirred at −78 °C for 4 hours. Acetyl chloride (0.098 mL, 1.37 mmol, 3 eq.) added to the reaction and continued stirring at −60 °C for 2 hours. The organic layer was dried over Na_2SO_4 and removed under reduced pressure. The crude was purified by column chromatography using 2–5% EtOAc/hexanes to obtain the desired product compound **12** as a viscous liquid in 51% (120 mg), $R_f = 0.6$ in 10% EtOAc/hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H), 2.40 (s, 6H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 148.4, 135.1, 125.4, 123.8, 29.5, 14.6. HRMS (ESI+) *m*/*z* calcd for $[C_{19}H_{14}F_6O_2S_4Na]^+$ $[M + Na]^+$: 538.9673, found 538.9641.

Synthesis of compound 2. Compound **12** (35 mg, 0.067 mmol, 1 equiv.) was dissolved in anhydrous 2 N NH_3 in MeOH (1.5 mL) in a dried 50 mL round-bottomed flask and stirred for 1 hour. Then the reaction was monitored by ^{1}H NMR and TLC. Methanol was removed under reduced pressure and diluted with 5 mL DCM. Organic layer was washed with 4 mL (2 mL × 2) DI water. The organic layer was dried with anhydrous sodium sulphate. The organic solvent was removed under reduced pressure to afford compound **2** as an off white solid, 19 mg (66%). $R_f = 0.5$ in 5% EtOAc/Hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (s, 2H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 135.1, 134.6, 125.5, 15.2. ^{19}F NMR (400 MHz, $CDCl_3$): δ −109.75 (s, 4F), −132.96 (s, 2F).

Synthesis of compound 17. Compound **15** (200 mg, 0.63 mmol, 1 equiv.) was dissolved in anhydrous DCM (3 mL) in a dried 25 mL round-bottomed flask. The temperature was reduced to 0 °C *via* an ice bath and phosphorus tribromide (48 mg, 1.26 mmol, 2 equiv.) which was dissolved in anhydrous DCM (1 mL) was added to the reaction mixture dropwise. After addition of PBr_3, color changed to dark green. Then the reaction was stirred for 1 hour and monitored by ^{1}H NMR. Then the reaction was quenched by addition of 3 mL DI water. Then aqueous layer was extracted with DCM (5 mL × 3) and combined, dried with anhydrous sodium sulphate. The crude was used in subsequent reactions without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 2H), 4.61 (s, 4H), 2.74 (t, J = 7.4 Hz, 4H), 2.08–1.95 (m, 2H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.1, 135.5, 134.5, 129.3, 38.2, 27.6, 22.9, 14.4.

Synthesis of compound 19. Compound **17** was dissolved in 3 mL anhydrous DMF in a 50 mL round-bottomed flask. Potassium thioacetate (175 mg 1.53 mmol, 3.0 equiv.) was added to the reaction mixture all at once. The reaction was stirred overnight at rt. The reaction was quenched with cold DI water. The mixture was extracted with ethyl acetate (5 mL × 3). The organic layer was combined and dried over anhydrous sodium sulfate to afford the desired compound **19** as a viscous brown semisolid, 188 mg (84%). $R_f = 0.2$ in 5% EtOAc/hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.17 (s, 4H), 2.71 (t, J = 7.4 Hz, 4H), 2.34 (s, 6H), 2.04–1.95 (m, 2H), 1.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 135.3, 135.2, 134.49, 134.47, 127.7, 38.7, 38.2, 30.3, 28.2, 22.9, 14.1. HRMS (ESI+) *m*/*z* calcd for $[C_{21}H_{24}O_2S_4Na]^+$ $[M + Na]^+$: 459.0551, found 459.0576.

Synthesis of compound 3. Compound **19** (50 mg, 0.115 mmol, 1 equiv.) was dissolved in anhydrous 2 N NH_3 in MeOH (3 mL) in a dried 50 mL round-bottomed flask and stirred for 2 hours. Then the reaction was monitored by ^{1}H NMR and TLC. Methanol was removed under reduced pressure and diluted with 5 mL DCM. The organic layer was washed with 4 mL (2 mL × 2) DI water and then dried with anhydrous sodium sulfate. The organic solvent was removed under reduced pressure to afford compound **3** as a white solid of 36 mg (90%). $R_f = 0.5$ in 5% EtOAc/Hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 3.81 (d, J = 7.4 Hz, 2H), 2.73 (t, J = 7.4 Hz, 4H), 2.05–1.96 (m, 2H), 1.91 (s, 6H), 1.89 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 135.2, 134.6, 134.0, 126.3, 38.2, 23.6, 23.0, 14.2.

Synthesis of compound 20. Compound **16** (175 mg, 0.41 mmol, 1 equiv.) was dissolved in anhydrous DCM (3 mL) in a dried 25 mL round-bottomed flask. The flask was cooled to 0 °C *via* an ice bath and phosphorus tribromide (219 mg, 0.81 mmol, 2 equiv.) dissolved in anhydrous DCM (1 mL) was added to the reaction mixture dropwise. After the addition of PBr_3, the color changed to dark green. Then the reaction was stirred for 1 hour and monitored by ^{1}H NMR for completion. The reaction was quenched by the addition of 3 mL DI water. The aqueous layer was extracted with DCM (5 mL × 3) combined and dried with anhydrous sodium sulfate. The solvent was removed, and the product obtained (**18**) was used for the next step. Compound **18** was dissolved in 3 mL anhydrous DMF in a 50 mL round-bottomed flask. Potassium thioacetate (140 mg, 1.23 mmol, 3.0 equiv.) was added to the reaction mixture all at once. The reaction was stirred at rt overnight. The reaction was quenched with cold DI water. The mixture was extracted with ethyl acetate (5 mL × 3). The organic layer was combined, dried over anhydrous sodium sulfate. The crude was further purified using 0–10% EtOAc/Hexane to afford a sticky semisolid of 203 mg (91%) as the desired product compound **20**. $R_f = 0.2$ in 10% EtOAc/hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 4.20 (s, 4H), 2.35 (s, 6H), 1.82 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 194.4, 141.6, 138.5, 126.1, 124.3, 30.28, 27.8, 14.2. HRMS (ESI+) *m*/*z* calcd for $[C_{21}H_{18}O_2F_6S_4Na]^+$ $[M + Na]^+$: 566.9986, found 567.0007.

Synthesis of compound 4. Compound **20** (66 mg, 0.15 mmol, 1 equiv.) was dissolved in anhydrous 2 N ammonia in methanol (3 mL) in a dried 50 mL round-bottomed flask and stirred for 1 hour. TLC indicated that the starting material was consumed. The reaction mixture stopped, and methanol was removed under reduced pressure. Then the residue was diluted with 5 mL DCM and washed with 4 mL water (2 mL × 2). The organic layer was dried with anhydrous Na_2SO_4 and the solution was removed under reduced pressure to afford compound **4** as a white solid of 52 mg (93%). $R_f = 0.5$ in 10% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.85 (d, J = 7.6 Hz, 4H), 1.96 (t, J = 7.6 Hz, 2H), 1.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.3, 124.7, 124.4, 23.3, 14.4.^{19}F NMR (400 MHz, $CDCl_3$): δ −110.17 (t, J = 5.4, 4F), −131.93–132.00 (m, 2F).

Synthesis of compound 21. Compound **21** was prepared following the literature procedure.[19] Compound **7** (100 mg, 0.30 mmol, 1 eq.) was dissolved in THF (4 mL) in a 50 mL round-bottom flask under nitrogen, *n*-BuLi (0.45 mL, 0.82 mmol, 2.7 eq., 1.8 M in hexanes) was added dropwise at 0 °C. The solution was stirred at rt for 30 min, followed by the addition of $B(OBu)_3$

(0.26 mL, 0.91 mmol, 3 eq.), stirring for another hour. In another flask, 4-bromo-tertbutylsulfanylbenzene (**S1**) (0.223 g, 0.911 mmol, 3 eq.) was dissolved in THF (3 mL), and Pd(PPh_3)$_4$ (0.017 g, 0.0151 mmol, 0.1 eq.) was added, and the reaction was stirred at rt for 15 min, then heated to 80 °C. An aqueous solution of Na_2CO_3 (2.4 mL, 2 M) and a previously prepared boronic ester solution were then added to the second flask, and the reaction mixture was stirred at 80 °C for 16 h. The reaction was completed after 16 h as indicated by TLC monitoring. The reaction was quenched with water and extracted with ethyl acetate and dried over Na_2SO_4. The crude was further purified by column chromatography using 1–2% EtOAc/Hexane to obtain 200 mg (56%) desired product compound **21** as a brown solid (R_f = 0.2 in 5% EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 4H), 7.44 (d, J = 8.5 Hz, 4H), 7.06 (s, 2H), 2.84 (t, J = 7.4 Hz, 4H), 2.13–2.04 (m, 2H), 2.00 (s, 6H), 1.29 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.8, 136.8, 135.1, 134.8, 134.7, 131.2, 125.1, 124.5, 46.1, 38.5, 31.0, 23.0, 14.5.

Synthesis of compound 23. $TiCl_4$ (0.11 mL, 1.120 mmol, 2.2 eq.) was added in a dropwise fashion to a solution of compound **21** (300 mg, 0.509 mmol, 1 eq.), acetyl chloride (0.080 mL, 1.120 mmol, 2.2 eq.) in DCM at 0 °C. The resulting mixture was stirred at rt for 20 minutes. The progress of the reaction was monitored by TLC and indicated completion at this point. The reaction was quenched with water and extracted with DCM. The DCM layer was dried over Na_2SO_4 and then removed using a rotary evaporator. The crude product was purified by column chromatography using 2–3% hexane/ethyl acetate to afford the desired product **23** in 67% (190 mg, R_f = 0.1 in 5% EtOAc) yield, and a small amount (6 mg) of mono acetylated compound **23a** was also isolated. Compound **23**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 4H), 7.36 (d, J = 8.5 Hz, 4H), 7.06 (s, 2H), 2.84 (t, J = 7.4 Hz, 4H), 2.44 (s, 6H), 2.13–2.08 (m, 2H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 138.6, 136.8, 135.7, 135.5, 134.8, 134.7, 126.1, 125.9, 124.9, 38.4, 30.2, 23.0, 14.5. HRMS (ESI+) m/z calcd for $[C_{31}H_{28}O_2S_4Na]^+$ $[M + Na]^+$: 583.0864, found 583.0888. Compound **23a**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 3.0 Hz, 2H), 2.84 (s, 2H), 2.84 (t, J = 7.4 Hz, 4H), 2.42 (s, 3H), 2.13–2.08 (m, 2H), 2.01 (s, 3H), 1.99 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 139.0, 138.6, 137.8, 136.9, 136.8, 135.7, 135.5, 135.2, 134.84, 134.80, 134.6, 131.2, 126.1, 125.9, 125.1, 124.9, 124.5, 46.1, 38.5, 38.4, 31.0, 29.7, 23.0, 14.5, 14.4.

Synthesis of compound 5. Compound **23** (31 mg, 0.055 mmol, 1 equiv.) was dissolved in anhydrous 2 N NH_3 in MeOH (3 mL) in a dried 50 mL round-bottomed flask and stirred for 1 hour. Then the reaction was monitored by ^{1}H NMR and TLC. Methanol was removed under reduced pressure and diluted with 5 mL DCM. The organic layer was washed with 4 mL (2 mL × 2) DI water. The organic layer was dried with anhydrous sodium sulfate. The organic solvent was removed under reduced pressure to afford compound **5** as a white solid of 19 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 4H), 7.23 (d, J = 8.5 Hz, 4H), 6.97 (s, 2H), 3.44 (s, 2H), 2.82 (t, J = 7.4 Hz, 4H), 2.12–2.01 (m, 2H), 1.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 136.7, 134.7, 134.5, 132.2, 129.9, 129.1, 125.9, 123.9, 38.4, 23.0, 14.5.

Synthesis of compound 22. Compound **10** (250 mg, 0.571 mmol, 1 eq.) was dissolved in Et_2O (5 mL) in a 50 mL RBF under nitrogen, n-BuLi (0.79 mL, 1.543 mmol, 2.7 eq., 1.95 M in hexanes) was added dropwise at 0 °C. The solution was stirred at rt for 30 minutes. Then, B(OBu)$_3$ (0.49 mL, 1.713 mmol, 3 eq.) was added in one portion and stirred at rt for 1 h. In the meanwhile, compound **S1** (411 mg, 1.713 mmol, 3 eq.) was dissolved in THF (5 mL) and Pd(PPh_3)$_4$ (70 mg, 0.0571 mmol, 0.1 eq.) was added and reaction was stirred at rt for 15 min then heated to 80 °C. Finally, an aqueous solution of Na_2CO_3 (1.2 g, 2 M) and previously prepared borylated solution were added and the reaction mixture was stirred at 80 °C for 16 h. After 16 hours, progress of the reaction was monitored by TLC, which showed consumption of compound **10.** The reaction was quenched with water and extracted with ethyl acetate and dried over Na_2SO_4. The crude was further purified by column chromatography using 1–2% EtOAc/Hexane to obtain compound **22** in 50% (200 mg, R_f = 0.2) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.47 (m, 8H), 7.31 (s, 2H), 1.98 (s, 6H), 1.31 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.5, 137.9, 133.6, 132.6, 126.0, 125.4, 122.9, 46.3, 31.0, 14.6.

Synthesis of compound 24. $TiCl_4$ (0.066 mL, 0.632 mmol, 2.2 eq.) was added in a dropwise fashion to a solution of compound **22** (200 mg, 0.287 mmol, 1 eq.), acetyl chloride (0.044 mL, 0.632 mmol, 2.2 eq.) in DCM at 0 °C. The resulting mixture was stirred at rt for 15 minutes, and TLC indicated completion of reaction. The reaction mixture was quenched with water and extracted with EtOAc. The solvent was dried over Na_2SO_4 and removed under reduced pressure. The crude was further purified by column chromatography using 3–4% EtOAc/Hexanes to obtain the desired product compound **24** in 84% (162 mg) yield, R_f = 0.1 in 5% EtOAc/Hexanes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.5 Hz, 4H), 7.42 (d, J = 8.5 Hz, 4H), 7.31 (s, 2H), 2.44 (s, 6H), 1.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 142.1, 141.2, 135.0, 134.4, 127.4, 126.2, 126.0, 123.3, 30.2, 14.6.

Synthesis of compound 6. Compound **24** (20 mg, 0.03 mmol, 1 equiv.) was dissolved in anhydrous 2 N NH_3 in MeOH (3 mL) in a dried 50 mL round-bottomed flask and stirred for 1 hour. Then the reaction was monitored by ^{1}H NMR and TLC. Methanol was removed under reduced pressure and diluted with 5 mL DCM. The organic layer was washed with 4 mL (2 mL × 2) DI water. The organic layer was dried with anhydrous sodium sulphate. The organic solvent was removed under reduced pressure to afford compound **6** as an off white solid of 14 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 8.5 Hz, 4H), 7.21 (s, 2H), 3.49 (s, 2H), 1.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 141.1, 130.9, 130.7, 129.8, 126.2, 125.9, 122.3, 14.5.^{19}F NMR (400 MHz, $CDCl_3$): δ −110.03 (t, J = 5.4, 4F), −131.80–131.96 (m, 2F).

Data availability

The data supporting this article have been included in the experimental section and also as part of the supplementary information (SI). The experimental section in the main text included characterization and NMR data for all new compounds. Supplementary information: additional experimental details for the synthesis of intermediates, ^{1}H, ^{13}C, some ^{19}F and 2D NMR spectra, additional photoswitching experiments and UV-vis spectra and fluorescence spectra. See DOI: https://doi.org/10.1039/d5ra08492j.

Conflicts of interest

There are no conflicts to declare.

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