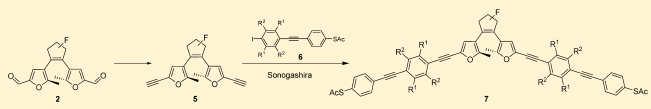# Synthesis and Photoswitching Studies of OPE-Embedded Difurylperfluorocyclopentenes

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S *Supporting Information*

ABSTRACT: We report the synthesis and photochemical behavior of five photochromic molecular switches **7a–e** with attached molecular wires based on differently substituted oligo(phenylene ethynylene) (OPE) building blocks. The switchable molecular wires **7a–e** were built in a convergent approach from substituted iodotolans **6a–e** and 1,2-bis(2-methyl-5-ethynylfuran-3-yl)perfluorocyclopentene **5** by 2-fold Sonogashira coupling. Compound **5** was prepared from the corresponding bis-aldehyde **2** by Wittig-type olefination with [PPh$_3$CHBr$_2$]Br·CH$_3$CN, followed by elimination to the bromoalkyne under mild phase-transfer conditions at 0 °C. Halogen–metal exchange with *i*-PrMgCl·LiCl and hydrolysis furnished **5** in good overall yield. Substituents R^1 and R^2 in the OPE portion were either electron-withdrawing or electron-donating, and their influence on the photostability and photoswitching characteristics of **7a–e** was studied. All resulting molecules show reversible photochromism between the colorless off and the deeply colored on states when irradiated with light of 313 and 576 nm wavelengths, respectively. The quantum yields of these photoreactions increased when electron-withdrawing groups were used. This was further corroborated by reversible protonation/deprotonation of **7e** (R^1 = NMe$_2$, R^2 = H) for which the ring-closing quantum yield increased 10-fold upon switching off the donor by protonation.

INTRODUCTION

In order to realize functionality beyond charge transport in molecular electronics by single molecules, bistable building blocks that can be switched between two well-defined states are essential. Diarylperfluorocyclopentenes belong to the class of photochromic molecular switches and are particularly suitable for this task since they are thermally stable and highly fatigue resistant. Furthermore, light as the driving force for switching produces no waste or other side products.[1] Since photoisomerization in diarylethenes[2] occurs with only a minor length change,[3] these molecules can bridge two metal electrodes without introducing a geometrical strain, yielding a light-controlled current-modulation through a single molecular junction. Molecular switches of the diarylethene-type have been studied in break junction geometries before, but switching was nonreversible with the molecule bridging two gold electrodes.[4] It has been argued that a strongly coupled switch causes leakage of the photogenerated exciton from the molecule into the metal electrodes on a time scale faster than the time needed for switching.[5] Decoupling of the switch from the metal electrodes therefore presents a desirable way to prevent fast exciton deactivation. Furthermore, thiophene-based switches might disturb such measurements since their sulfur-atoms offer additional binding sites to metal electrodes directly at the switching moiety. Therefore, they are prone to undesired deactivation during the stimulation process. Recently, we reported on a series of difurylperfluorocyclopentenes[6] and difurylperfluorocyclobutenes[7] with attached π-systems. These furan-based molecular switches[8] cannot interfere with measurements due to unspecific binding, since only their heteroatom-substituted conjugated side chains bind to gold electrodes.

Charge-transport measurements in a mechanically controlled break junction setup (MCBJ) showed that the closed form of the switches exhibits up to 38 times higher conductance values compared with their open-ring isomers.[9] For molecules with more than one heteroatom anchoring group, multiple small conductance peaks were recorded, while a single and much more pronounced conductance value was found for a molecule with a stiff phenylene(ethynylene)-linker and a thiol anchoring group. To further investigate this kind of conformational rigid photochromic molecules, we combined a sulfur-free switch with oligo(phenylene ethynylene) linkers having donor or acceptor groups[10,11] to give a new type of switchable molecular wire (SMW) with terminal thiol groups for binding to metal electrodes. This combination of a tunable and conductive spacer with a furan based switch leads to a family of conformational rigid photochromic molecular wires which might show distinct on–off ratios and different conductance in transport measurements. Due to the spatial separation of the switch from the electrodes by two OPE units, the switching blockade caused by fast exciton leakage into the electrode might be overcome. Five SMWs were synthesized by a convergent strategy and the dependence of their photochromic properties on electronic effects was investigated in different solvents by UV–vis and NMR spectroscopy.
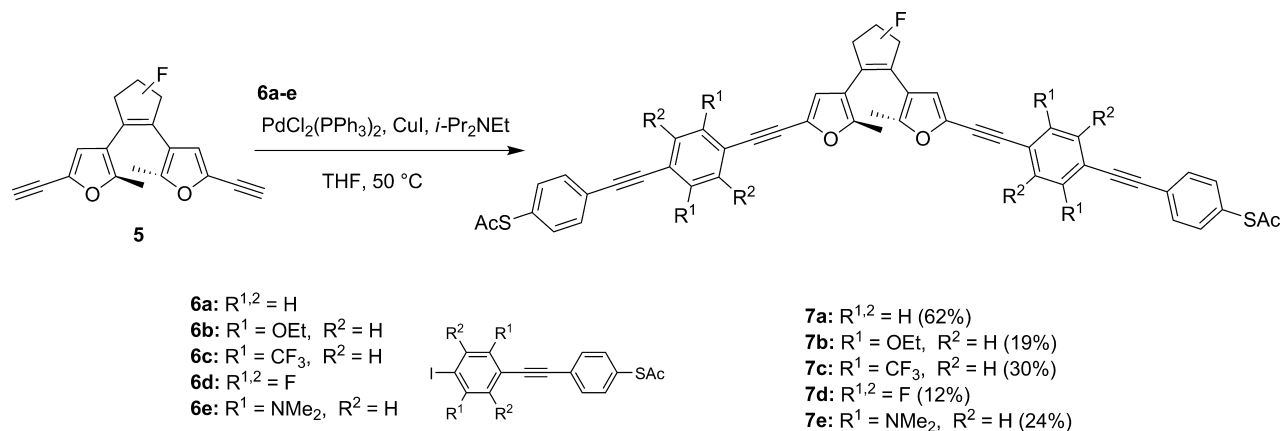
RESULTS AND DISCUSSION

Synthesis. Key compounds for the convergent synthesis of SMWs are bisalkyne **5** and the suitable substituted tolans **6a–e**,
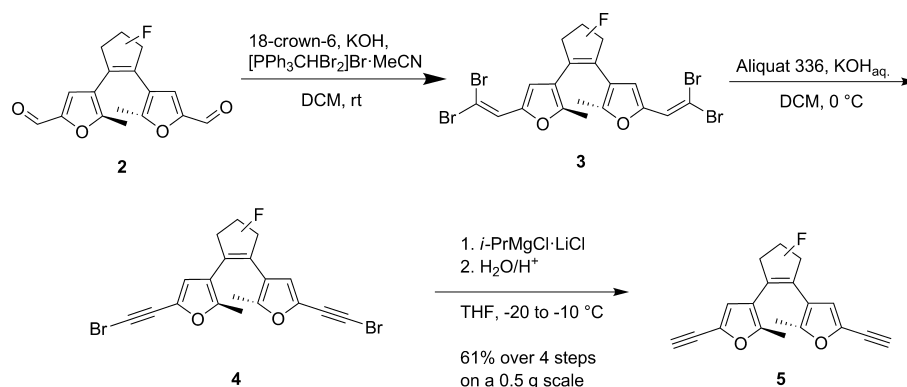
Scheme 1. Convergent Approach toward SMWs 7a−e

6a: R^{1,2} = H
6b: R^1 = OEt, R^2 = H
6c: R^1 = CF$_3$, R^2 = H
6d: R^{1,2} = F
6e: R^1 = NMe$_2$, R^2 = H

7a: R^{1,2} = H (62%)
7b: R^1 = OEt, R^2 = H (19%)
7c: R^1 = CF$_3$, R^2 = H (30%)
7d: R^{1,2} = F (12%)
7e: R^1 = NMe$_2$, R^2 = H (24%)

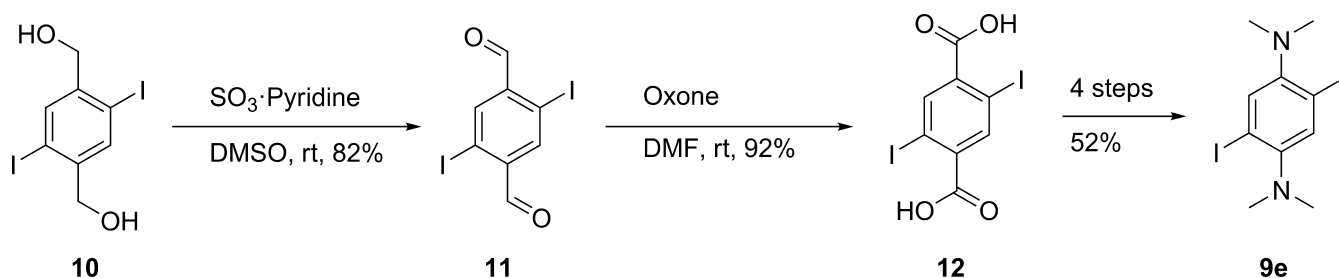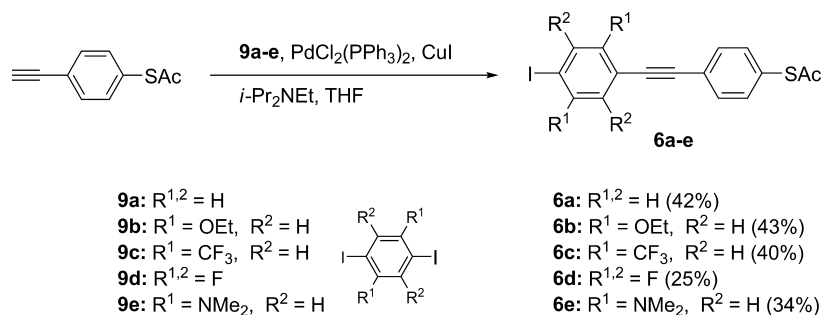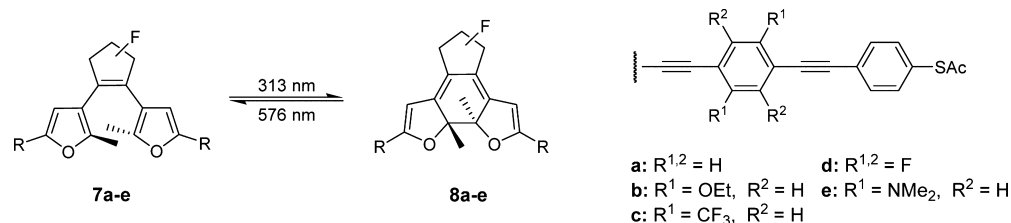**Scheme 2. Bisalkynylation of Dialdehyde 2**

supplying the molecular switch and the wires, respectively. In the final stage of the synthesis both are "welded" together by double-Sonogashira coupling (Scheme 1).

For the synthesis of **5**, we utilized bis-furaldehyde **2**, which in turn was obtained in four steps starting from 5-methylfurfural.[6] Bromination in the 4-position, protection of the aldehyde as 1,3-dioxolane with subsequent halogen−lithium exchange, and coupling with octafluorocyclopentene gave after deprotection bis-furaldehyde **2**. Compared to our original protocol,[6] modifications like steam distillation for the isolation of 4-bromo-5-methyl furfural and an improved workup procedure of the coupling reaction turned out to be beneficial for a synthesis of **2** on a multigram scale.

Transformation of bis-furaldehyde **2** to the pivotal diyne **5** in reasonable amounts proved to be more challenging than initially anticipated. Alkynylation under classical Corey−Fuchs conditions[12] led to decomposition of the starting aldehyde **2**. Seyferth−Gilbert homologation using the Bestmann−Ohira reagent[13] resulted in decomposition of the formed product, probably due to methanolate, and was only useful for very small batches with their comparatively short reaction times.[9] The decomposition of larger batches can be understood with respect to the sensitivity of the furan itself and the formed triple bonds toward the nucleophilic and strongly basic agents present under these reaction conditions. Thus, an alternative strategy avoiding concentrated strong bases was developed. The isolation of the intermediate of the Corey−Fuchs alkynylation, namely the bis-dibromoalkene **3**, was successful when [PPh$_3$CHBr$_2$]Br·CH$_3$CN was utilized in a formal Wittig reaction on aldehyde **2**.[14] Elimination of the resulting vinyl dibromide **3** under

classical conditions using *n*-BuLi led to decomposition of the starting material with no alkyne formation detectable. Diyne **5** was finally accessible by a two-step procedure via bromoalkyne **4**. Elimination of **3** was accomplished under very mild Aliquat 336 phase-transfer conditions using KOH in DCM/water at 0 °C. The obtained bromoalkyne **4** was subjected to halogen−metal exchange at −78 °C with various reagents commonly used, but only *i*-PrMgCl·LiCl[15] between −20 and −10 °C gave successful metalation without side reactions. Lithium-based reagents like *n*-BuLi, *t*-BuLi, or LiTEMP produced a mostly insoluble black mass that probably resulted from polymerization of the attacked and ring-opened furan, whereas LDA showed no reaction. The obtained di-Grignard was hydrolyzed during aqueous workup, yielding the desired alkyne **5** in an overall yield of 61% with respect to furaldehyde **2** on a 0.5 g scale (Scheme 2). This procedure is highly reproducible and does not require tedious purification in between the three consecutive steps.

The tolan building blocks **6** (Scheme 1) were available by cross-coupling a phenylacetylene with five differently substituted 1,4-diiodobenzenes **9a−e** under Sonogashira conditions. Substituents were chosen in a way to cover the whole range from electron withdrawing (**9c−d**) over moderately electron donating (**9b**) to the strongly donating dimethylamino-group (**9e**). 1,4-Diethoxy-2,5-diiodobenzene (**9b**) was obtained by alkylation of hydroquinone, followed by iodination in analogy to reference[16] in 62% overall yield. 1,4-Bis(trifluoromethyl)-2,5-diiodobenzene (**9c**) was synthesized by iodination of 1,4-bis(trifluoromethyl)benzene.[17] 1,4-Bis-(dimethylamino)-2,5-diiodobenzene (**9e**) (Scheme 3) was

Scheme 3. Synthesis of 1,4-Bis(dimethylamino)-2,5-diiodobenzene (9e)

Scheme 4. Synthesis of Tolans 6a−e

9a: $R^{1,2}$ = H
9b: R^1 = OEt, R^2 = H
9c: R^1 = CF$_3$, R^2 = H
9d: $R^{1,2}$ = F
9e: R^1 = NMe$_2$, R^2 = H

6a: $R^{1,2}$ = H (42%)
6b: R^1 = OEt, R^2 = H (43%)
6c: R^1 = CF$_3$, R^2 = H (40%)
6d: $R^{1,2}$ = F (25%)
6e: R^1 = NMe$_2$, R^2 = H (34%)

Scheme 5. Reversible Photoswitching of 7a−e

a: $R^{1,2}$ = H   d: $R^{1,2}$ = F
b: R^1 = OEt, R^2 = H   e: R^1 = NMe$_2$, R^2 = H
c: R^1 = CF$_3$, R^2 = H

prepared in six steps starting from 2,5-diiodo-1,4-bis-(hydroxymethyl)benzene (**10**),[18] which was first oxidized to 2,5-diiodoterephthalicaldehyde (**11**) under Parikh−Doering conditions.[19] Treatment of the aldehyde with Oxone gave 2,5-diiodoterephthalic acid (**12**) as the sole product in almost quantitative yield. This procedure starting from diol **10** is clearly superior to the oxidation of 1,4-diiodo-2,5-dimethylbenzene which in our hands yields variable amounts of an inseparable mixture of diiodo-4-tolylic acid and diiodoterephthalic acid.[20,21]

Diiodoterephthalic acid (**12**) was transformed into the acid chloride.[20] Treatment with sodium azide in dichloroethane enabled the direct Curtius rearrangement without isolation of the azide.[22] The obtained bis-isocyanate was decomposed to the *p*-phenylenediamine.[23] Reductive amination[24] finally gave 1,4-bis(dimethylamino)-2,5-diodobenzene (**9e**) in an overall yield of 52% over four steps with respect to carboxylic acid **12**. The five iodotolans **6a−e** were then prepared by Sonogashira coupling of diiodobenzenes **9a−e** with acetylsulfanyl-4-(ethynyl)benzene[25] in a THF/*i*-Pr$_2$NEt mixture (Scheme 4). To favor the formation of iodoalkynes **6** over the OPE byproduct, a 2−3-fold molar excess of diiodobenzenes **9a−e** was used.

Synthesis of SMWs 7a−e. With alkyne **5** and the iodotolans **6a−e** in hand, the aspired switchable wires **7** were finally built up by Sonogashira coupling (Scheme 1). To grant sufficient solubility of reactants the reaction was run at 50 °C in a THF/*i*-Pr$_2$NEt mixture. Yields of **7a−e** were strongly

dependent on the nature of the iodotolan and ranged from 12% (**6d**) to 62% (**6a**). The reactions were monitored by TLC and run until total consumption of the alkyne **5**. Even though stoichiometric amounts of **5** and **6** were used in all cases remaining iodo-tolans **6** but no monocoupled product was recovered during column chromatography. This indicates that either alkyne **5** or the intermediate monoaddition product decomposes under these reaction conditions.

UV−vis Absorption Spectra and Photochromism in Solution. All synthesized SMWs **7a−e** underwent reversible photochromism in solution as depicted in Scheme 5.

Figure 1 shows the absorption spectra of **7a−e** and of the protonated form **7e*H$^+$** in acetonitrile. For all compounds spectra of the open form **7**, as well as spectra at their respective photostationary state (PSS) **8** are given. The transformation **7** to **8** was achieved by irradiation with light of 313 nm wavelength, the cycloreversion was initiated by irradiation with 576 nm light (spectra in chloroform and spectrokinetic measurements cf. Supporting Information). Table 1 summarizes the photophysical properties of all molecules estimated in both solvents.

In the open form, all molecules showed an absorbance maximum in the short-wavelength region around 330−380 nm. Upon irradiation in the short-wavelength region, the closed isomer with its typical long-wavelength band around 560 nm was formed and the solutions took on a deep violet color. The closed-ring isomers **8a−d** were readily formed in acetonitrile with high conversions between 82% and 98% at the
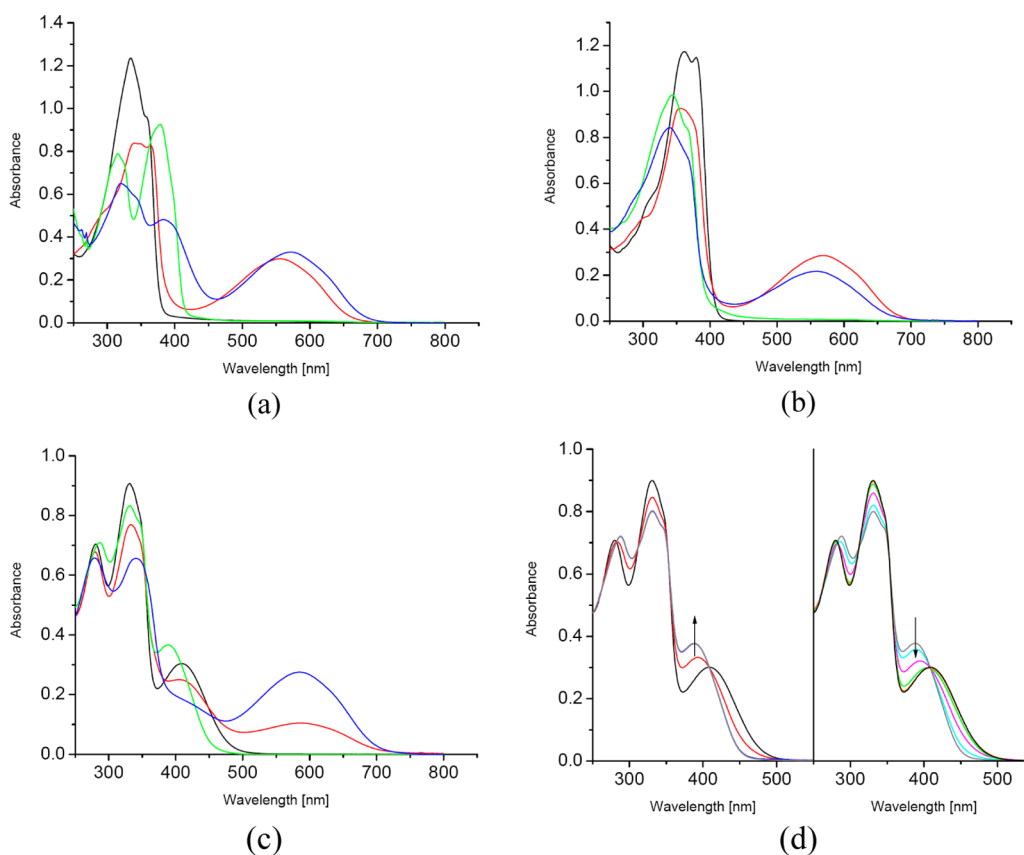
Figure 1. (Panels a−c) UV−vis absorption spectra in acetonitrile of the open forms **7** (black and green lines) and of the photostationary states **8** after irradiation with light of 313 nm wavelength (red and blue lines): (a) **7a/8a** (black/red) and **7b/8b** (green/blue); (b) **7c/8c** (black/red) and **7d/8d** (green/blue); (c) **7e/8e** (black/red) and **7e*H⁺/8e*H⁺** (green/blue). **7e*H⁺** and **8e*H⁺** measured in the presence of 70 equiv of TFA. (Panel d) Short-wavelength region of the absorption spectra of **7e** upon addition of either 0 (black), 10 (red), 60 (blue), or 70 equiv (gray) of TFA (left) and **7e*H⁺** upon backward titration with either 0 (gray), 10 (cyan), 30 (magenta), 50 (green), and 70 equiv (red) of Et₃N (right). For comparison, the spectrum of an untreated sample of **7e** is superimposed in black in the right panel. All spectra were recorded in acetonitrile ($c = 1.2 \times 10^{-5}$ M).

Table 1. Photophysical Properties of Difurylethenes 7a−e and 8a−e in Chloroform and Acetonitrile[a]

compd	open form (**7**)		closed form (**8**)		$\phi_{o\text{-}c}$[c]	$\phi_{c\text{-}o}$[c]	$\phi_{c\text{-}o}$[d]	conversion[c] (% closed)
	λ_{max} (nm)	ε_{max} (M⁻¹cm⁻¹)	λ_{max} (nm)	ε_{max} (M⁻¹cm⁻¹)				
a[b]	334	10.3×10^4	556	2.72×10^4	0.15	0.01	0.02	96
b[b]	378	7.71×10^4	571	3.00×10^4	0.23	0.01	0.01	98[e]
c[b]	361	9.75×10^4	569	2.89×10^4	0.08	0.02	0.01	82
d[b]	344	8.20×10^4	559	1.97×10^4	0.14	0.01	0.02	92
e[b]	331	7.56×10^4	589	1.87×10^4	0.004	0.006	0.01	46[e]
e*H⁺[b]	331	6.94×10^4	586	2.17×10^4	0.05	0.005	0.005	95
a[f]	338	9.37×10^4	559	2.65×104	0.29	0.07	0.01	88
b[f]	380	7.89×10^4	575	3.02×10^4	0.22	0.03	0.005	90
c[f]	362	9.25×10^4	572	2.54×10^4	0.30	0.03	0.01	93
d[f]	347	8.02×10^4	565	1.79×10^4	0.33	0.02	0.02	95
e[f]			decomposition					

[a]ε_{max}(**8**) is given with respect to the concentration of the closed-ring isomers in the PSS. The quantum yields ϕ of closing and opening the central ring were evaluated according to the method described by Gauglitz.[27,28] The photon irradiance at 313 nm was determined by azobenzene actinometry.[27,28] At 576 nm *meso*-diphenylhelianthrene was used as the actinometer.[29] The conversion at the photostationary state was determined by ¹H-NMR spectroscopy in MeCN or CDCl₃ and verified by HPLC if applicable. [b]Solvent MeCN. [c]Estimated at 313 nm. [d]Estimated at 576 nm. [e]Determined by HPLC. [f]Solvent CHCl₃.

photostationary state (PSS). The composition at the PSS was determined by recording ¹H NMR-spectra. In cases where the conversion was higher than the NMR detection limit (5%), HPLC was used to determine the ratio directly from the solutions used for optical spectroscopy (cf. Supporting Information). Quantum yields for the ring-closing reaction in acetonitrile were on the order of 15% for **7a** and 23% for the moderately electron enriched **7b**, whereas the electron-depleted SMW **7c** and **7d** showed somewhat lower values on the order of 10%. The molecule with the strongest donor, the
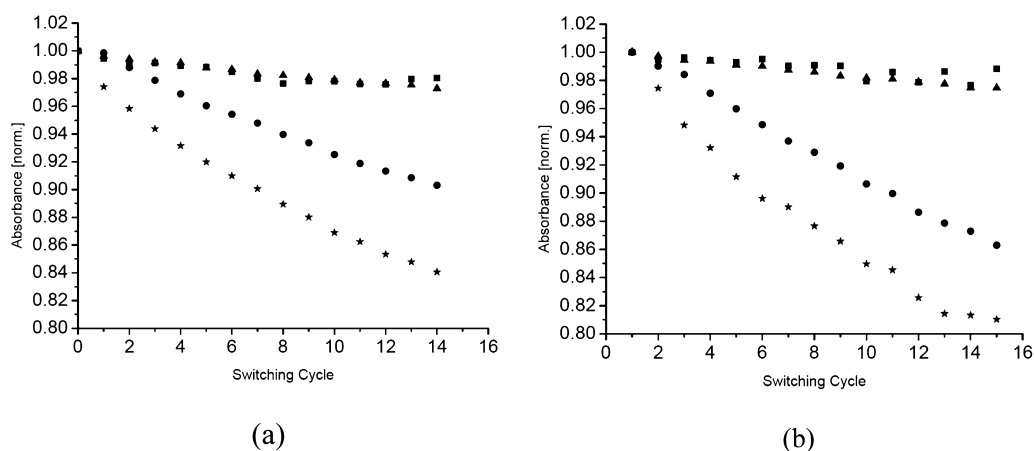
Figure 2. Photostability of difurylethenes **7** and **8** under ambient conditions. The normalized absorbance values of irradiation experiments after each cycle and half-cycle are shown. Squares = **7/8a**; circles = **7/8b**; triangles = **7/8c**; stars = **7/8d**. Panel (a) shows the absorbance of **7** after 3 min irradiation with visible light (open form maxima);[30] data at switching cycle 0 represents untreated samples as reference. Panel (b) shows the absorbance of **8** in the PSS after 3 min irradiation with 313 nm light (closed form maxima). Experimental conditions: t_{cycle} = 3 min, $I_{0(313\ nm)}$ = 1.047 × 10^−8 E cm^−2 s^−1, $I_{0(576\ nm)}$ = nd (long pass filter), c = 2.0 × 10^−5 M in DCM.

dimethylamino-modified **7e**, behaved remarkably different. It showed an unusually small quantum yield of 0.4% for the ring-closing reaction. This was accompanied by only 46% conversion of **7e** to its closed-form **8e** at the PSS.

The quantum yields of the ring-opening reaction showed only a small variation when **8a–e** were irradiated with visible light of 576 nm in acetonitrile. However, with values in the range of 1% to 2% for **8a–e** they showed enhanced quantum yields for the ring-opening process compared with other thiophene[26] and furan[6,7] based switches with extended π-systems. Cycloreversion quantum yields are generally smaller than those of the closing reaction and drop far below 1% when conjugation is extended beyond the limits of the switching core itself. This effect has been partly explained by an decrease of the antibonding nature of the central photogenerated carbon–carbon bond in the excited singlet state with an increase of the π-conjugation[26] and by the conformational flexibility of the π-conjugated groups which results in a tendency for radiationless deactivation of the excited state.[6] OPE molecules in general show only a limited conformational flexibility because of their rigid triple bonds interconnecting the arene rings. Even though they have some rotational degree of freedom reducing the π–π-orbital overlap, broken conjugation cannot explain the enhanced quantum yields of **8a–e** for the ring-opening process. Compared to 1,2-bis(2-methyl-5-((4-(acetylthio)phenyl)-ethynyl)furan-3-yl)perfluorocyclopentene[9] which has in its closed state an absorption maximum at 500 nm, **8a–e** clearly exhibit a larger degree of π-conjugation as manifested by a bathochromic shift of more than 50 nm of the long wavelength absorption band.

To gain more insight into the dependency of the quantum yields on the electronic effects of the SMWs side groups, we "switched"-off the electron-donating dimethylamino groups by titrating **7e** in acetonitrile with a strong non-nucleophilic acid. Upon addition of trifluoroacetic acid (TFA), a spectral shift which figures most prominently at the long wavelength absorption band of the open form becomes apparent (Figure 1d). After the addition of 70 equiv of TFA, the spectral shift approaches a saturation limit. At this point, the molecule exists predominantly in a protonated form **7e*H⁺** in which the ring closing quantum yield increased more than 10-fold to 5%. The

quantum yield of the cycloreversion from **8e*H⁺** to **7e*H⁺** was not significantly affected by the protonation. The protonation was fully reversed after addition of an equimolar amount of triethylamine. **7e** was completely recovered as was evident by UV–vis-spectroscopy. Furthermore, the back-titrated sample exhibited the same cyclization quantum yield as a fresh untreated sample. The other molecular wires did not show any response to the addition of TFA. A detailed study of the protonation equilibrium in acetonitrile is currently underway and will be reported elsewhere.

The solvent influence on the photochemistry was investigated by recording a second set of data in chloroform. As before, quantum yields for the photoisomerization of SMWs **7a–e** were estimated from irradiation experiments in the 10^−5 mol concentration regime. SMW **7e** decomposed to an unknown switchable species under these conditions even when degassed chloroform solutions were employed. This was attributed to traces of hydrochloric acid which are always present in chloroform exposed to ambient conditions. However, higher concentrated NMR samples of **7e** in chloroform showed no decomposition over time. The quantum yields for the ring-closing reaction increased from 22% for the electron-rich molecule **7b** to 33% for the extremely electron-poor tetrafluoro-substituted **7d**. This trend compares quite well with the data acquired in acetonitrile. Quantum yields for the ring-opening reaction showed a similar trend as for the ring-closing reaction. The electron rich compound **7b** showed the smallest quantum yield of 0.5% and an increase to 2% was observed for the electron poor **7d**. The other two SMWs bridge these two extremes as expected with quantum yields of 1% for both **7a** and **7c**. None of the closed-ring isomers **8a–e** showed thermal reversibility of switching at room temperature or even at 80 °C within 48 h, except for the tetrafluoro SMW **7d**, which underwent 6% of thermally activated back reaction to the open form during that time.

Photostability. The photochemical stability of **7a–d** was investigated in nondegassed solutions to study the fatigue resistance of the SMWs. Samples of **7a–d** were successively closed and opened by repeated irradiation. As before, light of 313 nm was used for initiating ring closing. In contrast to the above experiments, a long pass filter with a transmission

window for wavelengths greater than 495 nm was used for the opening process achieving a higher irradiance, thus warranting a complete transformation of the closed to the open form within a reasonable time.[30] Even though the PSS was usually reached within less than 150 s for the slowest photoreactions, irradiation was continued for a total of 3 min at each wavelength. The experimental conditions and the measured decay curves are shown in Figure 2. The degree of decomposition was estimated from the decay in absorbance of the open and closed form at their respective λ_{max}. **7a−d** decomposed fast compared to most of the known diarylethenes which allow for 10000 or even more switching cycles in the absence of oxygen.[2,3] The decay was addressed to decomposition of the extended π-system due to photobleaching, most probably due to oxidation. The well-known fatigue mechanism that leads to a photochemically inactive six-membered ring byproduct[31,32] was not observed on the experiment's time scale. Depending on the side chains present in the molecule, different photostabilities were observed. **7a** and **7c** which exhibited similar switching behavior, showed the highest photostability of all compounds with approximately 2% of decay during the 15 cycles performed (90 min total irradiation time). In contrast, more than 10% of the ethoxy derivative **7b** had decomposed after the 14th switching cycle. **7d**, the molecule with the strongest electron withdrawing substituents exhibited the fastest decay and its UV-absorption decreased to 90% of the initial value after the sixth switching cycle.

■ CONCLUSION

We successfully attached pairs of substituted OPE-like molecular wires on bisfurylethene-based photochromic switches in a convergent synthetic approach with good overall yield. The convergent approach allowed us an efficient construction of differently substituted derivatives from common starting materials. En route to 2,5-diiodo-1,4-phenylendiamine, an improved high-yielding synthesis of 2,5-diiodo-1,4-terephthalic acid, a valuable building block in OPE chemistry, was devised. Electron-donating or electron-withdrawing functionalities in the OPE part of these new switchable wires modulated the quantum yield of the ring-opening and -closing reaction in solution while maintaining a nearly quantitative conversion in the photostationary state. Reversible chemical gating and its influence on the quantum yield of the ring-closing and -opening reaction was demonstrated by protonation/deprotonation of **7e** carrying a methylated phenylendiamine. With their sulfur termini at both ends these molecules are capable of bridging 4 nm wide gaps making them ideal candidates for transport measurements in mechanical break junctions and other experimental setups (using gold electrodes) where defined contacting is a necessity.

In summary, this new class of furan-based functionalized photochromic switches is accessible in good yield and shows a more balanced switching behavior, namely an enhanced ring-opening quantum yield when compared with other diarylethene switches with extended π-systems and switch thermally irreversibly.

■ EXPERIMENTAL SECTION

General Methods. THF and DCM were distilled from Na/K-alloy and CaH$_2$, respectively. All experiments requiring dry atmosphere were carried out under nitrogen using Schlenk techniques. All other solvents and all commercially available reagents were used without any purification. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 600/

400, 125/100, and 376 MHz, respectively. Deuterated solvents where purchased in sealed ampules and dried where necessary according to standard procedures.[33] IR spectra were recorded on an FTIR spectrometer. GCMS measurements were conducted on a 50 m fused silica capillary column with 5% phenylarylene, 95% dimethylpolydisiloxane phase, and He as carrier gas. UV−vis spectra were recorded in 1.0 cm quartz cuvettes.

Continuous Irradiation in Solution. A high-pressure mercury lamp (HBO 200 W/2) was used. The light was passed through a heat filter (optical length 5 cm, filled with a saturated aqueous solution of CuSO$_4$), a collimating lens, and an electronic shutter. Irradiations were done in a setup equipped with a 313 or 576 nm interference filter, a thermostated optical cell holder with a quartz-cell of 1 cm path length equipped with a magnetic stirring bar and filled with 3 mL of probe solution. At 313 nm the photon irradiance I_0 was determined by azobenzene actinometry,[27,28] at 576 nm actinometry with *meso*-diphenylhelianthrene[29] was used. The samples were not degassed. UV−vis absorption spectra were recorded before and after irradiation on a UV−vis spectrophotometer.

1,2-Bis[5-(1,3-dioxolane-2-yl)-2-methylfuran-3-yl]perfluorocyclopentene (1). 2-(4-Bromo-5-methyl-2-furyl)-1,3-dioxolane (7.53 g, 32.3 mmol) was dissolved in THF (50 mL) and cooled to −78 °C. *t*-BuLi (46 mL, 79 mmol, 1.7 M in pentane) was slowly added at this temperature. After complete addition, the mixture was stirred for 0.5 h before octafluorocyclopentene (3.43 g, 2.2 mL, 16.2 mmol) was added dropwise in a manner that the temperature of the reaction mixture did not exceed −45 °C. After complete addition, the cooling bath was adjusted to −45 °C, and the mixture was slowly thawed inside the cooling bath until it reached 5 °C. At this point, TLC showed complete conversion. The reaction was terminated by the addition of a saturated aqueous NH$_4$Cl solution (5 mL), and all volatiles were removed. The remaining slurry was redissolved in dichloromethane (150 mL) and filtered before silica gel (10 g) was added. The solvent was removed, and the obtained powder was charged onto a silica gel column (300 g SiO$_2$). Elution with petroleum ether/EtOAc 7/3 gave the title compound as a pale brown solid (4.8 g, 10.0 mmol, 61%). Analytical data of difurylethene **1** were identical to the data reported in ref 6.

1,2-Bis(5-ethynyl-2-methylfuran-3-yl)perfluorocyclopentene (5). 1,2-Bis(2-methyl-5-formylfuran-3-yl)perfluorocyclopentene (2) (0.47 g, 1.19 mmol), [Ph$_3$PCHBr$_2$]Br*CH$_3$CN (2.0 g, 3.57 mmol), and a catalytic amount of 18-crown-6 were dissolved in DCM (50 mL). The mixture was vigorously stirred, and freshly ground KOH (0.47 g, 8.33 mmol) was added. After being stirred for 1 h, TLC showed complete conversion, and the solvent was removed on a rotary evaporator. The residue was dissolved in DCM, and silica gel (3 g) was added. The solvent was removed, and the powder was charged onto a plug of silica gel. The product was eluted with hexane until switching (color change) was no longer observed on a TLC plate. Removal of the solvent gave the bis-dibromoalkene **3** (0.72 g, 1.02 mmol) as a waxy material in sufficient purity for the next step. An analytical sample was obtained by column chromatography (SiO$_2$, hexane), mp <35 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 (s, 2H), 6.91 (s, 2H), 2.00 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 153.12, 149.50, 132.51 (t, $^2J_{(C,F)}$ = 20 Hz, CCF$_2$), 125.36, 116.05 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 111.43, 110.87, 110.87 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 88.95, 13.55. ^{19}F NMR (376 MHz, CDCl$_3$): δ −110.02 (t, J = 5 Hz), −131.52 (quint, J = 5 Hz). IR (neat ATR): 3033, 2919, 2849, 1270, 1110 cm^{-1}. Anal. Calcd for C$_{19}$H$_{10}$Br$_4$F$_6$O$_2$: C, 32.42; H, 1.43. Found: C, 32.54; H, 1.66.

Bis-dibromoalkene **3** (0.72 g, 1.02 mmol) was dissolved in DCM (40 mL), and Aliquat 336 (0.46 g) was added. After the mixture was cooled to 0 °C, aqueous KOH (4.6 g KOH in 30 mL H$_2$O) was added. The mixture was vigorously stirred until TLC showed complete conversion (1 h). The phases were separated, and the aqueous phase was further extracted with DCM. The combined organic layers were dried with MgSO$_4$, silica gel (3 g) was added, and the solvent was removed. The obtained powder was charged onto a plug of silica gel, and the product was eluted with hexane until switching (color change) was no longer observed of a sample on a TLC plate. Removal of the

solvent gave the bromoalkyne **4** (0.53 g, 0.97 mmol) as a waxy solid in sufficient purity for the next step. An analytical sample was obtained by column chromatography (SiO$_2$, hexane), mp <35 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.59 (s, 2H), 1.98 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 154.32, 136.57, 132.33 (t, $^2J_{(C,F)}$ = 20 Hz, CCF$_2$), 116.03, 116.03 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 110.84 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 109.97, 69.84, 57.49, 13.78. ^{19}F NMR (376 MHz, CDCl$_3$): δ −110.13 (t, J = 5 Hz), −131.54 (quint, J = 5 Hz). IR (neat ATR): 3140, 2919, 2201, 1275, 1109 cm^{-1}. Anal. Calcd for C$_{19}$H$_8$Br$_2$F$_6$O$_2$: C, 42.10; H, 1.49. Found: C, 42.33; H, 1.58.

Bromoalkyne **4** (0.53 g, 0.97 mmol) was dissolved in THF (75 mL), and the solution was cooled to −20 °C. *i*-PrMgCl·LiCl (3.0 mmol, 4.5 mL, 0.67 M in THF) was added dropwise, followed by carefully warming the solution to −10 °C. The mixture was stirred at this temperature until TLC showed complete conversion. Water was added, and the phases were separated. The aqueous phase was further extracted with diethyl ether. The combined organics were dried with MgSO$_4$ and the solvents were removed. The crude product was purified by column chromatography (40 g SiO$_2$, hexane) giving the title compound **5** as a colorless to slightly pink (traces of closed form) solid (0.276 g, 0.73 mmol, 61% over three steps). The alkyne prepared via this route may be stored under nitrogen at −20 °C without decomposition. Analytical data of **5** were identical to data reported in ref 9.

Iodo-4-(2-(4-acetylsulfanylphenyl)ethynyl)benzene (6a). A solution of 1,4-diiodobenzene (**9a**) (1.67 g, 5.05 mmol) and acetylsulfanyl-4-(ethynyl)-benzene (0.29 g, 1.68 mmol) in THF (9 mL) and *i*-Pr$_2$NEt (1.7 mL, 10.1 mmol) was degassed. [PdCl$_2$(PPh$_3$)$_2$] (23.6 mg, 0.033 mmol) and CuI (3.2 mg, 0.016 mmol) were added, and the mixture was stirred at 50 °C until the alkyne was completely consumed. All volatiles were removed in vacuo, and the residue was dissolved in diethyl ether and filtered through a plug of silica gel. The solvent was removed, and the residue was purified by column chromatography (150 g SiO$_2$, hexane/diethyl ether 7/3) giving 0.26 g (0.71 mmol, 42%) of the title compound as a colorless solid, mp 107−108 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, J = 8 Hz, 2H), 7.54 (d, J = 8 Hz, 4H), 7.40 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 193.50, 137.74, 134.39, 133.29, 132.30, 128.54, 124.31, 122.59, 94.64, 90.22, 90.15, 30.44. MS (EI) m/z (rel intensity): 336.2, 378.1 (M$^+$), 208.2. IR (neat ATR): 2924, 1703, 1630 cm^{-1}. Anal. Calcd for C$_{16}$H$_{11}$IOS: C, 50.81; H, 2.93; S, 8.65. Found: C 50.58; H 3.16; S, 8.65.

Iodo-2,5-bis-ethoxy-4-(2-(4-acetylsulfanylphenyl)ethynyl)-benzene (6b). A solution of 1,4-diiodo-2,5-diethoxybenzene (**9b**) (2.1 g, 5.05 mmol) and acetylsulfanyl-4-(ethynyl)benzene (0.29 g, 1.68 mmol) in THF (9 mL) and *i*-Pr$_2$NEt (1.7 mL, 10.1 mmol) was degassed. [PdCl$_2$(PPh$_3$)$_2$] (23.6 mg, 0.033 mmol) and CuI (3.2 mg, 0.016 mmol) were added, and the mixture was stirred at 50 °C until the alkyne was completely consumed. All volatiles were removed in vacuo, and the residue was dissolved in diethyl ether and filtered through a plug of silica gel. The solvent was removed, and the residue was purified by column chromatography (150 g SiO$_2$, hexane/diethyl ether 9/1) giving 0.33 g (0.73 mmol, 43%) of the title compound as a colorless solid, mp 98−99 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 (d, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.32 (s, 1H), 6.91 (s, 1H), 4.09−4.03 (m, 4H), 2.43 (s, 3H), 1.48−1.44 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 193.58, 154.46, 152.00, 134.33, 132.26, 128.22, 124.78, 124.27, 116.47, 113.52, 93.57, 88.32, 87.39, 66.01, 65.72, 30.42, 15.01, 14.99. MS (EI) m/z (rel intensity): 466.5 (M$^+$), 424.3, 367.2. IR (neat ATR): 2975, 2930, 2890, 1697 cm^{-1}. Anal. Calcd for C$_{20}$H$_{19}$IO$_3$S: C, 51.51; H, 4.11; S, 6.88. Found: C, 51.38; H, 4.25; S, 6.88.

Iodo-2,5-bis-trifluoromethyl-4-(2-(4-acetylsulfanylphenyl)-ethynyl)benzene (6c). A solution of 1,4-bis(trifluoromethyl)-2,5-diiodobenzene (**9c**) (1.3 g, 2.82 mmol) and acetylsulfanyl-4-(ethynyl)benzene (0.25 g, 1.41 mmol) in THF (5 mL) and *i*-Pr$_2$NEt (1.4 mL, 8.46 mmol) was degassed. [PdCl$_2$(PPh$_3$)$_2$] (19.6 mg, 0.028 mmol) and CuI (2.6 mg, 0.014 mmol) were added, and the mixture was stirred at 50 °C until the alkyne was completely

consumed. All volatiles were removed in vacuo, and the residue was dissolved in diethyl ether and filtered through a plug of silica gel. The solvent was removed, and the residue was purified by column chromatography (100 g SiO$_2$, petroleum ether/EtOAc:20/1) giving 0.29 g (0.56 mmol, 40%) of the title compound as a colorless solid. An analytical sample was obtained by recrystallization from hexane, mp 138−140 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30 (s, 1H), 7.89 (s, 1H), 7.58 (d, J = 8 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 193.21, 139.72 (q, J = 5 Hz), 137.07 (q, J = 32 Hz), 134.98 (q, J = 32 Hz), 134.47, 132.49, 132.43 (q, J = 6 Hz), 129.88, 127.06, 123.26 (q, J = 16 Hz), 123.03, 121.81, 120.52 (q, J = 16 Hz), 97.33, 90.16 (q, J = 1 Hz), 85.15, 30.51. ^{19}F NMR (376 MHz, CDCl$_3$): δ −63.09, −63.70. MS (FAB) m/z (rel intensity): 472.1, 516.2 (M + H)$^+$. IR (neat ATR): 3057, 2217, 1694, 1389 cm^{-1}. Anal. Calcd for C$_{18}$H$_9$F$_6$IOS: C, 42.04; H, 1.76; S, 6.24. Found: C, 42.22; H, 1.55; S, 6.58.

Iodo-2,3,5,6-tetrafluoro-4-(2-(4-acetylsulfanylphenyl)-ethynyl)benzene (6d). A solution of 1,4-diiodotetrafluorobenzene (**9d**) (3.0 g, 7.5 mmol) and acetylsulfanyl-4-(ethynyl)benzene (0.66 g, 3.7 mmol) in Et$_3$N (15 mL) was degassed. [PdCl$_2$(PPh$_3$)$_2$] (52 mg, 0.075 mmol) and CuI (7.0 mg, 0.037 mmol) were added and the mixture was stirred at 50 °C until the alkyne was completely consumed. All volatiles were removed in vacuo, and the residue was dissolved in diethyl ether and poured on a plug of silica gel. 1,4-Diiodotetrafluorobenzene was eluted with a 1/1 mixture of DCM and diethyl ether. The product was eluted with DCM. The solvent of the DCM fraction was removed, and the crude product was transferred into a sublimation vessel. Remaining 1,4-diiodotetrafluorobenzene was carefully removed by sublimation (30 °C, 2 × 10^{-2} mbar, approximately 30 min). The remaining solid was purified by column chromatography (200 g SiO$_2$, petroleum ether/EtOAc 9/1), giving the title compound as a colorless crystalline solid (0.42 g, 0.93 mmol, 25%), mp 94−97 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.62 (d, J = 8 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 2.45 (m, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 193.08, 147.23 (dm, $^1J_{(C,F)}$ = 248 Hz), 146.19 (dm, $^1J_{(C,F)}$ = 255 Hz), 134.44, 132.61, 130.16, 122.76, 105.40 − 105.15 (m), 101.70, 76.09, 73.69 − 73.33 (m), 30.51. ^{19}F NMR (CDCl$_3$, 376 MHz, 25 °C): δ (−120.06) − (−120.19) (m), (−134.49) − (−134.60) (m). MS (FAB) m/z (rel intensity): 409.0, 281.7, 451.3 (M + H)$^+$. IR (neat ATR): 2218, 1690, 1474, 963 cm^{-1}. Anal. Calcd for C$_{16}$H$_7$F$_4$IOS: C, 42.69; H, 1.57; S, 7.12. Found: C, 42.28; H, 1.24; S, 6.66.

2,5-Diiodoterephthalaldehyde (11). To a solution of 2,5-diiodo-1,4-bis(hydroxymethyl)benzene (**10**) (4.0 g, 10.2 mmol) in dry DMSO (40 mL) was added Et$_3$N (12.4 g, 17.6 mL, 123 mmol). SO$_3$·pyridine (9.9 g, 62.2 mmol) was added in small portions. The mixture was stirred until TLC indicated complete conversion (2 h). Water (240 mL) was added, and the mixture was stirred for 5 min. The mixture was extracted with small portions of DCM (in total 400 mL), the combined organic phases were washed with brine twice, and the solution was dried with MgSO$_4$. The crude product obtained after evaporation of the solvent (600 mL), and water (160 mL) was added to the boiling solution. The mixture was slowly cooled to rt and stored at 0 °C overnight. The formed crystalline solid was collected by filtration. Further crops were obtained from the mother liquor by partially removing the solvent on a rotary evaporator until crystallization set in, followed by storage at 0 °C until crystallization had finished. The title compound was obtained as a bright yellow microcrystalline solid (3.15 g, 8.8 mmol, 82%), mp 198−199 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.93 (s, 2H), 8.24 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 193.43, 141.65, 139.04, 98.53. MS (EI) m/z (rel intensity): 386.0 (M$^+$), 258.0, 130.9, 75.0, 356.9. IR (neat ATR): 3346, 3063, 2962, 2868, 2852, 1673 cm^{-1}. Anal. Calcd for C$_8$H$_4$I$_2$O$_2$: C, 24.90; H, 1.04. Found: C, 24.87; H, 1.17.

2,5-Diiodoterephthalic Acid (12). To a solution of 2,5-diiodoterephthalaldehyde (**11**) (2.0 g, 5.2 mmol) in dry DMF (52 mL) was added Oxone (6.37 g, 20.7 mmol, monopersulfate compound). The mixture was stirred at rt until TLC showed complete conversion (16 h). Water (125 mL) and 2 N HCl (25 mL) were added, and the mixture was extracted three times with 150 mL of diethyl ether. The combined organics were washed with brine (100

mL) and extracted four times with 50 mL of 2 N NaOH each. The aqueous phase was washed with diethyl ether (100 mL) before it was reacidified with concentrated HCl. The precipitate was allowed to aggregate for one hour before it was collected on a sintered glass frit (P4). The colorless solid was dried over phosphorus pentoxide in a vacuum desiccator, yielding 2.0 g (4.8 mmol, 92%) of the acid. Analytical data of 2,5-diiodoterephthalic acid (**12**) was identical to data reported in ref.[20]

1,4-Diiodo-2,5-*N*,*N*-dimethylaminobenzene (9e). The following operations were carried out behind a blast shield. Following ref 22, a solution of 2,5-diiodoterephthalic dichloride[20] (2.58 g, 5.67 mmol) in 1,2-dichloroethane (30 mL) was added dropwise to an ice-cold solution of NaN$_3$ (0.81 g, 12.5 mmol) in water (10 mL). After the addition, the ice bath was removed and the mixture stirred at rt until complete conversion. The conversion was monitored by the appearance of a new ^{1}H NMR singlet at 8.39 ppm observed in aliquots dissolved in CDCl$_3$. After 3 h, 1,2-dichloroethane (20 mL) and water (15 mL) were added and the phases were separated. The organic layer was washed with water (15 mL), dried over MgSO$_4$ and slowly heated to 85 °C, provoking the rearrangement to the isocyanate. The reaction was monitored by the consumption of the azide via ^{1}H NMR samples in CDCl$_3$. After 1.5 h, the mixture was cooled to rt. At this time, the sample was no longer considered to be explosive. The solvent was evaporated under reduced pressure, yielding 1.55 g (3.76 mmol, 66%) 2,5-diiodo-1,4-diisocyanatobenzene as a colorless solid that was directly used for the next step. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (s, 2H).

A solution of 2,5-diiodo-1,4-diisocyanatobenzene (1.46 g, 3.54 mmol) in benzene (30 mL) was heated to 45 °C, and aqueous KOH (50%, 30 mL) was added dropwise.[23] The resulting slurry was stirred for 25 min before it was cooled to rt. Concentrated HCl (25 mL) was added dropwise until the solution turned acidic. The mixture was stirred for 15 min before it was neutralized with a saturated solution of NaHCO$_3$. The precipitate was collected, washed with water and dried over KOH, giving 1.21 g (3.36 mmol, 95%) of 2,5-diiodophenylenediamine that was directly used for the next step. Analytical data of 2,5-diiodophenylenediamine was identical to data reported in ref.[23]

A slurry of 2,5-diiodophenylenediamine (1.21 g, 3.36 mmol) and freshly ground NaBH$_4$ (1.81 g, 47.9 mmol) in THF (28 mL) was added batchwise to a mixture of formalin (4 mL), H$_2$SO$_4$ (3 M, 5.5 mL) and THF (28 mL) under ambient conditions.[24] The mixture was stirred at rt for 1.5 h while the pH was repeatedly adjusted to be acidic by the addition of 3 M H$_2$SO$_4$, before a second portion of formalin (4 mL) was added. Stirring was continued for 17 h before the mixture was brought to pH 10 by means of aqueous KOH. The mixture was extracted with diethyl ether and the organic phase was dried over MgSO$_4$. The solvent was removed under reduced pressure, yielding 1.24 g (2.98 mmol, 89%) of the title compound as an off white solid, mp 134−136 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.47 (s, 2H), 2.70 (s, 12H). ^{13}C NMR (101 MHz, CDCl$_3$): δ151.90, 131.57, 97.57, 45.25. IR (neat ATR): 2981, 2946, 2855, 2824, 2724, 1470 cm^{-1}. Anal. Calcd for C$_{10}$H$_{14}$I$_2$N$_2$: C, 28.87; H, 3.39; N, 6.73. Found: C, 29.22; H, 3.75; N, 7.00.

Iodo-2,5-bis-*N*,*N*-dimethylamino-4-(2-(4-acetylsulfanyl-phenyl)ethynyl)benzene (6e). A solution of 1,4-diiodo-2,5-*N*,*N*-dimethylaminobenzene (**9e**) (1.24 g, 2.98 mmol) and acetylsulfanyl-4-(ethynyl)benzene (**10**) (0.26 g, 1.50 mmol) in THF (10 mL) and *i*-Pr$_2$NEt (1.52 mL, 8.94 mmol) was degassed. [PdCl$_2$(PPh$_3$)$_2$] (20.9 mg, 0.030 mmol) and CuI (282 mg, 0.015 mmol) were added, and the mixture was stirred at 50 °C until the alkyne was completely consumed. All volatiles were removed in vacuo, and the residue was dissolved in diethyl ether/DCM (1:1) and filtered through a plug of silica gel. The solvent was removed and the residue was purified by column chromatography (300 g SiO$_2$, petroleum ether/EtOAc 9/1) giving 0.24 g (0.51 mmol, 34%) of the title compound as a yellow solid, mp 116−117 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.61 (d, J = 8 Hz, 2H), 7.47 (d, J = 8 Hz, 2H), 7.43 (s, 1H), 7.25 (s, 1H), 2.94 (s, 6H), 2.67 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, acetone-d_6): δ 193.10, 152.87, 149.07, 135.39, 132.45, 129.54, 129.42, 126.16, 125.38, 116.23, 100.83, 95.05, 90.83, 45.37, 43.61, 29.84 (COCH$_3$,

superimposed by solvent signal). MS (FAB) m/z: 465.3 (M + H)$^+$. IR (neat ATR): 2978, 2940, 2863, 2827, 2780, 2205, 1708 cm^{-1}. Anal. Calcd for C$_{20}$H$_{21}$IN$_2$OS: C, 51.73; H, 4.56; N, 6.03; S, 6.91. Found: C, 51.84; H, 4.61; N, 6.19, S, 6.86.

1,2-Bis(5-(2-(4-(2-(4-acetylsulfanylphenyl)ethynyl)phenyl)-ethynyl)-2-methylfuran-3-yl)perfluorocyclopentene (7a). A solution of 1,2-bis(5-ethynyl-2-methylfuran-3-yl)perfluorocyclopentene (**5**) (77 mg, 0.2 mmol) and iodo-4-(2-(4-acetylsulfanylphenyl)-ethynyl)benzene (**6a**) (151 mg, 0.4 mmol) in THF (2.8 mL) and *i*-Pr$_2$NEt (154 mg, 200 µL, 1.2 mmol) was degassed. CuI (0.4 mg, 2 × 10^{-6} mol) and [PdCl$_2$(PPh$_3$)$_2$] (2.8 mg, 4 × 10^{-6} mol) were added, and the mixture was stirred at 50 °C for 17 h, after which all volatiles were removed in vacuo. The residue was dissolved in DCM and filtered through a plug of silica gel. The crude product obtained after removing the solvent was purified by column chromatography (30 g SiO$_2$, hexane/DCM 1/1), yielding 120 mg (0.14 mmol, 62%) of the title compound, mp 192−193 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 (d, J = 8 Hz, 4H), 7.53−7.48 (m, 8H), 7.41 (d, J = 8 Hz, 4H), 6.70 (s, 2H), 2.44 (s, 6H), 2.07 (s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 193.56, 154.57, 136.77, 134.41, 132.35, t C=CCF$_2$ at ca. 132 ppm superimposed by other signals, 131.86, 131.49, 128.58, 124.25, 123.71, 121.88, 116.13 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 24 Hz, CF$_2$CF$_2$CF$_2$), 115.64, 110.88 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 110.51, 94.31, 91.10, 90.61, 80.21, 30.47, 13.91. ^{19}F NMR (376 MHz, CDCl$_3$): δ −110.01 (t, J = 5 Hz), −131.46 (quint, J = 5 Hz). MS (FAB) m/z (rel intensity): 885.9 (M + H)$^+$, 842.6, 462.2. IR (neat ATR): 2963, 2916, 2208, 1704, 1261 cm^{-1}. Anal. Calcd for C$_{51}$H$_{30}$F$_6$O$_4$S$_2$: C, 69.22; H, 3.42; S, 7.25. Found: C, 69.34; H, 3.17; S, 7.10.

1,2-Bis(5-(2-(2,5-bisethoxy-4-(2-(4-acetylsulfanylphenyl)-ethynyl)phenyl)ethynyl)-2-methylfuran-3-yl)perfluorocyclo-pentene (7b). A solution of 1,2-bis(5-ethynyl-2-methylfuran-3-yl)perfluorocyclopentene (**5**) (63 mg, 0.164 mmol) and iodo-2,5-bis-ethoxy-4-(2-(4-acetylsulfanylphenyl)ethynyl)benzene (**6b**) (150 mg, 0.32 mmol) in THF (3 mL) and *i*-Pr$_2$NEt (133 mg, 170 µL, 1.03 mmol) was degassed. CuI (0.31 mg, 1.6 × 10^{-6} mol) and [PdCl$_2$(PPh$_3$)$_2$] (2.3 mg, 3.3 × 10^{-6} mol) were added, and the mixture was stirred at rt for 40 min. To complete the reaction, the flask was heated to 50 °C for 16 h, after which all volatiles were removed in vacuo. The residue was dissolved in DCM and filtered through a plug of silica gel. The crude product obtained after removing the solvent was purified by column chromatography (25 g SiO$_2$, hexane/DCM 1/1), yielding 33 mg (0.031 mmol, 19%) of the title compound, mp 96−98 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56 (d, J = 8 Hz, 4H), 7.40 (d, J = 8 Hz, 4H), 7.01 (s, 2H), 6.99 (s, 2H), 6.69 (s, 2H), 4.12−4.07 (m, 8H), 2.44 (s, 6H), 2.06 (s, 6H), 1.49−1.44 (m, 12H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 193.56, 154.42, 153.65, 153.58, 137.04, 134.34, 132.31, t C=CCF$_2$ at ca. 132 ppm superimposed by other signals, 128.36, 124.69, 117.18, 117.03, 116.17 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 24 Hz, CF$_2$CF$_2$CF$_2$), 115.44, 114.74, 112.84, 110.92 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$) 110.53, 94.67, 91.32, 87.58, 83.53, 65.40, 65.39, 30.43, 15.02, 14.95, 13.89. ^{19}F NMR (376 MHz, CDCl$_3$): δ −109.99 (t, J = 5 Hz), −113.75 (t, J = 5 Hz closed form), −131.45 (quint, J = 5 Hz), −133.27 (quint, J = 5 Hz, closed form). MS (FAB) m/z: 1062.0 (M + H)$^+$. IR (neat ATR): 2980, 2929, 2873, 2208, 1705, 1275 cm^{-1}. Anal. Calcd for C$_{59}$H$_{46}$F$_6$O$_8$S$_2$: C, 66.78; H, 4.37; S, 6.04. Found: C, 66.64; H, 4.46; S, 5.74.

1,2-Bis(5-(2-(2,5-bis-trifluoromethyl-4-(2-(4-acetylsulfanyl-phenyl)ethynyl)phenyl)ethynyl)-2-methylfuran-3-yl)perfluoro-cyclopentene (7c). A solution of 1,2-bis(5-ethynyl-2-methylfuran-3-yl)perfluorocyclopentene (**5**) (77 mg, 0.2 mmol) and iodo-2,5-bis-trifluoromethyl-4-(2-(4-acetylsulfanylphenyl)ethynyl)benzene (**6c**) (205 mg, 0.4 mmol) in THF (3 mL) and *i*-Pr$_2$NEt (154 mg, 198 µL, 1.2 mmol) was degassed. CuI (0.4 mg, 2 × 10^{-6} mol) and [PdCl$_2$(PPh$_3$)$_2$] (2.8 mg, 4 × 10^{-6} mol) were added. The flask was heated to 50 °C for 16 h before a second portion of CuI and catalyst was added (amount same as above). Stirring was continued at 50 °C for 24 h before all volatiles were removed in vacuo. The residue was dissolved in DCM and filtered through a plug of silica gel. The crude product obtained after removing the solvent was purified by column

chromatography (30 g SiO$_2$, gradient hexane/DCM 7/3 (500 mL), then hexane/DCM 6/4), yielding 70 mg (0.06 mmol, 30%) of the title compound, mp 122−125 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (s, 2H), 7.95 (s, 2H), 7.59 (d, J = 8 Hz, 4H), 7.54 (d, J = 8 Hz, 4H), 6.83 (s, 2H), 2.45 (s, 6H), 2.09 (s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 193.17, 155.74, 135.93, 134.58 (q, J = 31.5 Hz), 134.47, 133.95 (q, J = 31.5 Hz), 132.55, t C=CCF$_2$ at ca. 132 ppm superimposed by other signals, 131.60 (q, J = 4.5 Hz), 131.26 (q, J = 4.5 Hz), 129.99, 123.02, 122.62 (q, J = 273 Hz), 122.56 (q, J = 273 Hz), 121.77 (q, J = 1.5 Hz), 120.00 (q, J = 1.5 Hz), 117.56, 116.05 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 24 Hz, CF$_2$CF$_2$CF$_2$), 110.82 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 110.75, 98.21, 98.70, 86.88, 85.67, 35.51, 30.49, 14.00. ^{19}F NMR (376 MHz, CDCl$_3$): δ −63.05, −63.20, −110.06 (t, J = 5 Hz), −131.48 (quint, J = 5 Hz). MS (FAB) m/z (rel intensity): 1158.4 (M + H)$^+$, 1073.4. IR (neat ATR): 2956, 2927, 2215, 1698, 1420 cm^{-1}. Anal. Calcd for C$_{55}$H$_{26}$F$_{18}$O$_4$S$_2$: C, 57.10; H, 2.27; S, 5.54. Found: C, 56.97; H, 2.20; S, 5.64.

1,2-Bis(5-(2-(2,3,5,6-tetrafluoro-4-(2-(4-acetylsulfanyl-phenyl)ethynyl)phenyl)ethynyl)-2-methylfuran-3-yl)perfluoro-cyclopentene (7d). A solution of 1,2-bis(5-ethynyl-2-methylfuran-3-yl)perfluorocyclopentene (5) (77 mg, 0.2 mmol) and iodo-2,3,5,6-tetrafluoro-4-(2-(4-acetylsulfanylphenyl)ethynyl)benzene (6d) (180 mg, 0.4 mmol) in i-Pr$_2$NEt (4 mL) was degassed. CuI (0.8 mg, 4 × 10^{-6} mol) and [PdCl$_2$(PPh$_3$)$_2$] (5.6 mg, 8 × 10^{-6} mol) were added. The flask was heated to 50 °C for 16 h before a second portion of CuI and catalyst was added (half the amount as above). Stirring was continued at 50 °C for 40 h before all volatiles were removed in vacuo. The residue was dissolved in DCM and filtered through a plug of silica gel. The crude product obtained after removing the solvent was purified by column chromatography (30 g SiO$_2$, gradient hexane/DCM 7/3 (500 mL), then hexane/DCM 6/4, then hexane/DCM 1/1), yielding 25 mg (0.024 mmol, 12%) of the title compound, mp 83 °C under decomp. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.63 (d, J = 8 Hz, 4H), 7.45 (d, J = 8 Hz, 4H), 6.88 (s, 2H), 2.45 (s, 6H), 2.09 (s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 193.09, 155.89, 146.69 (dd, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 15 Hz), 146.47 (dd, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 15 Hz), 135.64, 134.46, 132.66, 132.31 (t, $^2J_{(C,F)}$ = 14 Hz, C=CCF$_2$), 130.30, 128.15, 122.66, 117.85, 116.04 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 24 Hz, CF$_2$CF$_2$CF$_2$), 110.80 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 110.72, 105.74 − 105.52 (m), 103.97 − 103.74 (m), 102.88, 91.21, 80.41, 76.10, 30.53, 14.01. ^{19}F NMR (376 MHz, CDCl$_3$): δ −110.06 (t, J = 5 Hz), −131.46 (quint, J = 5 Hz), (−136.14) − (−136.41) (m). MS (FAB) m/z (rel intensity): 646.3, 835.2, 1029.0 (M + H)$^+$. IR (neat ATR): 2926, 2849, 2216, 1713, 1488, 1277 cm^{-1}. Anal. Calcd for C$_{51}$H$_{22}$F$_{14}$O$_4$S$_2$: C, 59.54; H, 2.16; S, 6.23. Found: C, 59.31; H, 2.20; S, 5.98.

1,2-Bis(5-(2-(2,5-bis-N,N-dimethylamino-4-(2-(4-acetyl-sulfanylphenyl)ethynyl)phenyl)ethynyl)-2-methylfuran-3-yl)-perfluorocyclopentene (7e). A solution of 1,2-bis(5-ethynyl-2-methylfuran-3-yl)perfluorocyclopentene (5) (77 mg, 0.2 mmol) and iodo-2,5-bis-N,N-dimethylamino-4-(2-(4-acetylsulfanylphenyl)-ethynyl)benzene (6e) (186 mg, 0.4 mmol) in i-Pr$_2$NEt (4 mL) was degassed. CuI (0.8 mg, 4 × 10^{-6} mol) and [PdCl$_2$(PPh$_3$)$_2$] (5.6 mg, 8 × 10^{-6} mol) were added. The flask was heated to 50 °C for 4 h before a second portion of CuI and catalyst was added (half the amount as above). Stirring was continued at 50 °C for 20 h before all volatiles were removed in vacuo. The residue was dissolved in DCM and filtered through a plug of silica gel. The crude obtained after removing the solvent was purified by column chromatography (30 g SiO$_2$, petroleum ether/EtOAc 9/1), yielding 50 mg (0.047 mmol, 24%) of the title compound, mp 122−124 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.57 (d, J = 8 Hz, 4H), 7.40 (d, J = 8 Hz, 4H), 7.08 (s, 2H), 7.06 (s, 2H), 6.69 (s. 2H), 2.92 (s, 12H), 2.91 (s, 12H), 2.43 (s, 6H), 2.06 (s, 6H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 193.54, 154.31, 149.16, 149.12, 137.21, 134.34, 132.07, t C=CCF$_2$ at ca. 132 ppm superimposed by other signals, 128.22, 124.86, 122.99, 122.59, 117.33, 116.17 (tt, $^1J_{(C,F)}$ = 255 Hz, $^2J_{(C,F)}$ = 24 Hz, CF$_2$CF$_2$CF$_2$), 115.66, 115.07, 110.91 (tt, $^1J_{(C,F)}$ = 271 Hz, $^2J_{(C,F)}$ = 25 Hz, CF$_2$CF$_2$CF$_2$), 110.52, 95.52, 93.99, 90.45, 84.52, 44.11, 43.97, 30.41, 13.90. ^{19}F NMR (376 MHz, CDCl$_3$): δ −109.97 (t, J = 5 Hz), −131.43 (quint, J = 5 Hz). MS (FAB) m/z

(rel intensity): 1058.0 (M + H)$^+$, 802.6. IR (neat ATR): 2940, 2929, 2876, 2838, 2789, 2209 cm^{-1}. Anal. Calcd for C$_{59}$H$_{50}$F$_6$N$_4$O$_4$S$_2$: C, 67.03; H, 4.77; N, 5.30, S, 6.07. Found: C, 66.83; H, 4.59; N, 5.47; S, 6.33.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes
The authors declare no competing financial interest.

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