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New Photochromic Dithienylethenes through a Click Chemistry Approach

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Symmetric dithienylethenes **9**–**12** bearing a variety of substituents were synthesized by a click chemistry approach. The starting material, diacetylene **4**, was obtained through Wittig reaction of dialdehyde **1** with dibromomethyltriphenylphosphonium bromide (**2**) and subsequent treatment with a lithium base (Corey–Fuchs reaction). Triazoles **11** and **12** with covalently linked fluorophore moieties show reversible quenching of fluorescence in solution.

Introduction

Photochromism describes the light-induced reversible interconversion of two isomers that have different absorption spectra.[1] Along with their color, photochromic systems also change their physical and chemical properties, for example, structures, refractive indices, or oxidation/reduction potentials, which makes them interesting candidates for optical memories and switches.[2] Among the numerous photochromic compounds, dithienylethenes specifically have drawn considerable attention because of their promising characteristics, such as P-type photochromism, thermal stability, and high fatigue resistance.[3]

There has been much effort in the past years to covalently combine photochromic dithienylethenes with functionalized building blocks (e.g., crown ethers,[4] terpyridines,[5] gelators,[6] polymers,[7] liquid crystals,[8] fluorophores[9]) to obtain new photoswitchable functional materials. So far the synthetic strategies used to build up these photochromic compounds involve the whole bandwidth of modern synthetic organic chemistry, except for copper-catalyzed azide–alkyne cycloaddition (CuAAC). This powerful click method (a Huisgen-type 1,3-dipolar cycloaddition[10]) has become a very efficient tool in organic synthesis.[11] Although photochromic diacetylene **4** was reported in the literature almost a decade ago[12] it has surprisingly not been employed in copper-mediated click reactions with organic azides so far. Since the availability of a vast number of azide building blocks makes CuAAC chemistry highly modular, its combination with a suitable dithienylethene would give access to various photoswitchable functional materials. In this paper we present an alternative synthetic pathway to compound **4**, a protocol for its use in CuAAC reactions with a variety of azides and the photochromic properties of obtained triazoles **9**–**12**.

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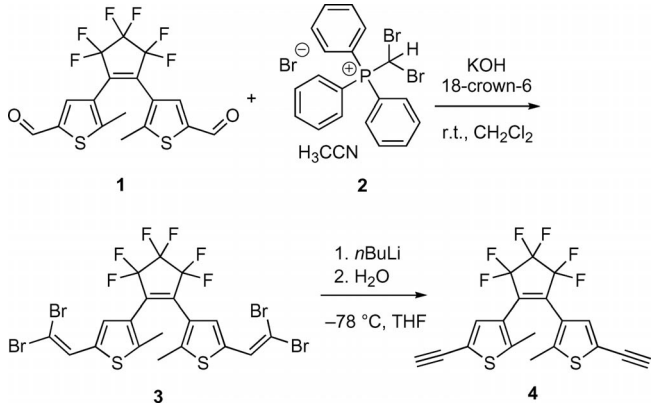
Results and Discussion

Synthesis

The synthetic pathway to diethynyl-substituted dithienylethene **4** is outlined in Scheme 1. Dialdehyde **1**, which was synthesized in four steps in 44% overall yield starting from commercially available 5-methyl-2-thiophenecarbaldehyde,[12,13] was treated under phase-transfer catalysis conditions[14] with dibromomethyltriphenylphosphonium bromide (acetonitrile complex, **2**)[15] to give brominated olefin **3** in 77% yield. Subsequent reaction with an excess amount of *n*-butyllithium and quenching with water afforded diacetylene **4** in 70% yield.

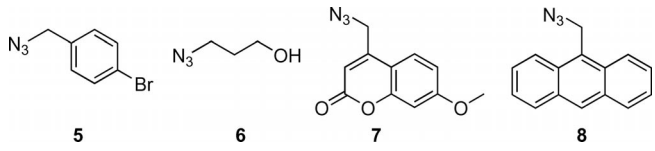


Scheme 1. Synthesis of diacetylene **4**.

The two-step reaction sequence from **1** to **4** follows the well-known Corey–Fuchs reaction pathway, a modification of the Wittig reaction.[16] Classically, the aldehyde component is treated directly with triphenylphosphane, zinc, and tetrabromomethane at low temperatures to obtain the corresponding dibromoolefin. Applied to dithienylethene **1**,

this procedure unfortunately only led to decomposition of the starting material. Although the reaction sequence from 5-methyl-thiophenecarboxaldehyde to **4** over six steps is longer than the route reported by Irie and co-workers (four steps, 25% overall yield),[12] the overall yield is comparable (24%). Also, the Corey–Fuchs approach avoids the use of expensive, air-sensitive palladium-mediated cross-coupling with trimethylsilylacetylene.

Azides **5**–**8** (Scheme 2) were prepared from the corresponding chloro or bromo compounds through substitution of the halide with sodium azide: 4-bromobenzyl azide (**5**) was prepared in almost quantitative yield from commercially available 4-bromobenzylbromide following a procedure describing the analogous synthesis of 4-fluorobenzyl azide.[17] 3-Azido-1-propanol (**6**) was synthesized in 70% yield following the method of Stenzel et al.[18] 4-Azidomethyl-7-methoxycoumarin (**7**)[19] was prepared in 58% yield from the corresponding 4-chlorocoumarin, which was prepared in 77% yield from 3-methoxyphenol following a slightly altered literature procedure.[20] 9-(Bromomethyl)-anthracene[21] was converted into 9-(azidomethyl)anthracene (**8**) in nearly quantitative yield by a similar procedure.[19]

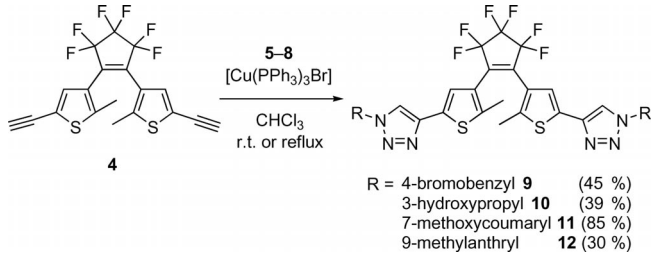


Scheme 2. Azides applied in click reactions.

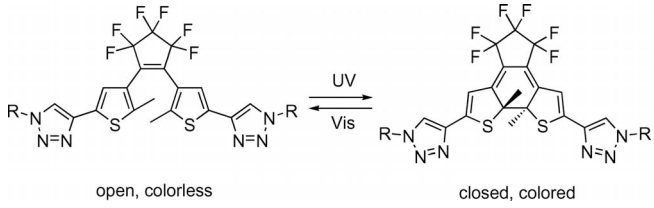
The copper-catalyzed azide–alkyne cycloadditions were carried out in chloroform solution and gave desired triazoles **9**–**12** in moderate to good yields (Scheme 3). We chose $[Cu(PPh_3)_3Br]$ as the catalyst, because it is quickly prepared from inexpensive copper(II) bromide and triphenylphosphane, and it is air stable and easy to handle.[22] The synthetic protocol for the cycloadditions involved stirring diacetylene **4**, the corresponding azide **5**–**8** (2–8 equiv.), and the catalyst (ca. 15 mol-%) in chloroform. All reactions were carried out at ambient temperature except for the reaction employing **8**, which required reflux conditions. Once the reactions were finished, no workup was necessary: after removal of the solvent the products were directly purified by column chromatography on silica gel (see the Experimental Section for details). To show the generality of the protocol, a benzylic, an aliphatic, and two fluorogenic functional building blocks were chosen.

Photochromism

All four triazole-substituted dithienylethenes **9**–**12** show P-type photochromism in solution. Upon irradiation with UV light the open-ring isomer is converted into the closed form (Scheme 4) and the solution becomes blue or purple. In all cases decoloration can be achieved by irradiation with 590 or 620-nm light.



Scheme 3. Copper-catalyzed azide–alkyne cycloadditions.



Scheme 4. Photochemical switching of dithienyl triazoles.

Benzyl-substituted triazole **9** (Figure 1a) and hydroxypropyl dithienylethene **10** (Figure 1b) have very similar absorption spectra with two absorption bands at 230 and 274 nm (Table 1), respectively, and a shoulder above 310 nm (for clarity, spectra in Figure 1 are scaled, see Supporting Information for full-scale spectra). A hypsochromic shift can be observed compared to the absorption of dialdehyde **1**[14b] and methyl-substituted 1,2-bis(2,5-dimethylthien-3-yl)perfluorcyclopentene (see ref.[23]). The open-ring isomers of **9** and **10** can be converted into the colored forms by irradiation with 254-nm light and new broad bands at around 570 nm arise.

Dicoumarin **11** shows absorption bands at 274 and 324 nm, the latter being attributed to the coumarin moieties (Figure 1c).[24] The ring-closing reaction can be triggered with 300-nm light, and the colored isomer shows the same broad absorption band at 572 nm as **9** and **10** do. Anthracene-substituted compound **12** has a similar absorption spectrum with a strong band at 260 nm and additionally shows the typical anthracene absorption pattern around 370 nm (Figure 1d). Although the dithienylethene scaffold has only weak absorption at 350 nm, as can be seen in the spectra of **9** and **10** (Figure 1a,b), **12** can be transformed into its colored isomer by irradiation with 365-nm light where only the fluorophore is expected to absorb. In the closed-ring form, a new broad band at 590 nm arises and irradiation at this wavelength gives the decolored isomer again. The UV/Vis data of compounds **9**–**12** are summarized in Table 1.

The emission spectra of **11** and **12** are given in Figures 2 and 3. Both are excited at isosbestic points to make sure that the same number of photons is absorbed by the fluorophore in both open and closed isomers. Dicoumarin **11** is excited with 325-nm light and emits at 400 nm in the open form (Figure 2). When the solution is irradiated with 300-nm light for 5 s the closed ring isomer is formed and acts as a quencher for the fluorescence. The intensity of emission therefore drops to 35% of the starting value. Additional

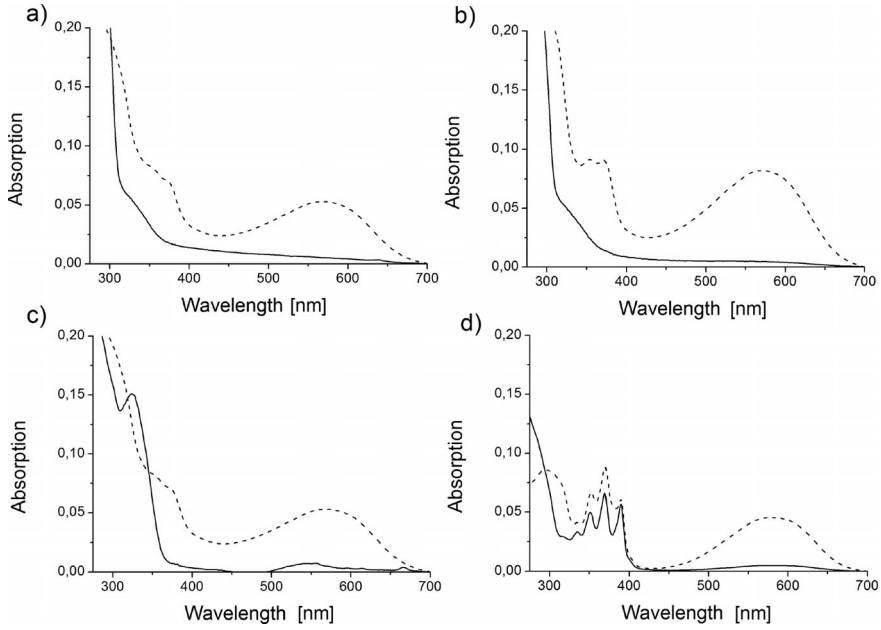


Figure 1. Solid lines: UV/Vis spectra of compounds **9** (a, 3.4×10^{-6} M), **10** (b, 1.8×10^{-5} M), **11** (c, 3.5×10^{-5} M), and **12** (d, 1.4×10^{-6} M) in dichloromethane. Dashed lines: after 1 min irradiation with UV light: (a,b) 254 nm, (c) 300 nm, and (d) 365 nm.

Table 1. UV/Vis data of **9**–**12**.

Compound	λ_{max} [nm]	ε [10^3 M^{-1}cm^{-1}]	Compound[a]	λ_{max} [nm]	ε [10^3 M^{-1}cm^{-1}]
9 open	230	67	**9** irradiated	230	72
	274	47		277	24
				572	5
10 open	230	95	**10** irradiated	229	100
	274	47		277	31
				572	8
11 open	274	21	**11** irradiated	230	72
	324	15		274	24
				572	5
12 open	258	200	**12** irradiated	258	190
	351	10		352	13
	369	13		370	18
	389	11		389	12
				584	9

[a] For irradiation wavelengths see Figure 1.

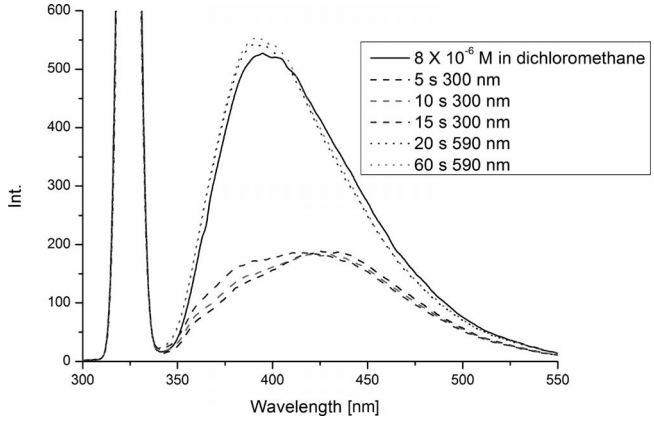


Figure 2. Emission spectra of **11**, λ_{ex} = 325 nm; solid line: 8×10^{-6} M in dichloromethane, dashed lines: after irradiation with 300 nm (5,10, and 15 s), dotted lines: after irradiation with 590 nm (20 and 60 s).

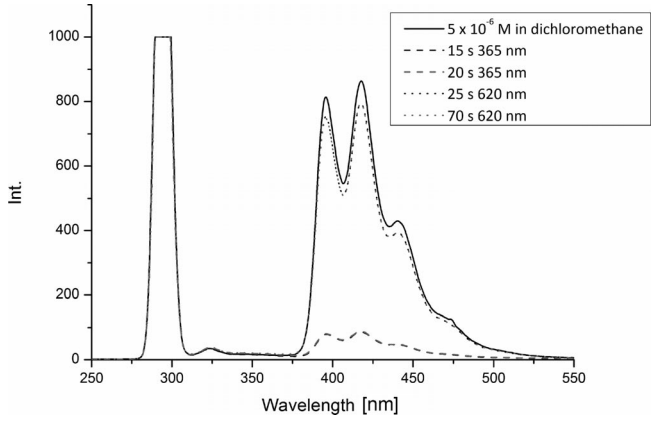
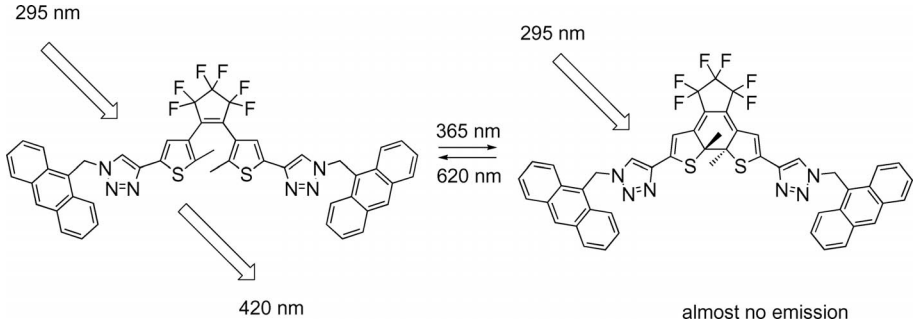


Figure 3. Emission spectra of **12**, λ_{ex} = 295 nm; solid line: 5×10^{-6} M in dichloromethane, dashed lines: after irradiation with 365 nm (15 and 20 s), dotted lines: after irradiation with 620 nm (25 and 70 s).

irradiation with 300 nm for 5 s and 10 s changes the fluorescence insignificantly, suggesting that a photostationary state like condition was already reached.[25] After irradiation with 590 nm for 20 s the fluorescence intensity rises again to a value slightly higher than the original intensity, possibly due to degradation of **11** under irradiation with energy-rich 300-nm light. Additional irradiation with 590 nm does not affect the fluorescence further.

Compound **12** shows a more efficient fluorescence quenching performance (Scheme 5, Figure 3). When excited at the isosbestic point with 295-nm light, **12** gives a typical anthracene emission spectrum with bands centered around 425 nm. After irradiation with 365-nm light for 15 s the anthracene fluorescence drops to 10% of the starting value. Additional irradiation with 365-nm light does not alter the emission intensity, indicating a photostationary state like



Scheme 5. Fluorescence switching of dianthryldithienylethene **12**.

situation. After irradiation with 620 nm for 25 or 60 s the emission is restored to ca. 95% of the starting value. In contrast to **11** this cycle can be repeated several times even in nondegassed solution.

To assess the mechanism of the fluorescence switching processes, the overlap integrals J and the Förster radii R_0 for **11** and **12** were determined from the measured absorption spectra and the corresponding emission spectra. The values were calculated to be $J = 1.14 \times 10^{14}\ nm^4\,cm^{-1}\,M^{-1}$ and $R_0 = 14$ Å for **11** closed and $J = 9.00 \times 10^4\ nm^4\,cm^{-1}\,M^{-1}$ and $R_0 = 0.2$ Å for **11** open, indicating that quenching through a resonance energy transfer (RET) mechanism is possible in the closed isomer. The values for **12** are $J = 7.24 \times 10^{13}\ nm^4\,cm^{-1}\,M^{-1}$ and $R_0 = 26$ Å for the closed form and $J = 4.22 \times 10^{13}\ nm^4\,cm^{-1}\,M^{-1}$ and $R_0 = 24$ Å for the open form, respectively (see ref.[26] and the Supporting Information for details). This indicates that for dianthracene **12** fluorescence quenching is not likely to proceed through RET, but possibly through photoinduced electron transfer (PET). For **11**, a PET mechanism cannot be excluded, as we did not calculate the exact free energy change (ΔG_{PET}) for the emission quenching of **11** and **12**.[27]

Conclusions

In summary we have synthesized the previously known dithienylethene **4** by an alternative synthetic route. For the first time we have used this precursor in alkyne–azide click reactions to obtain novel photochromic materials including fluorophores. Specifically, photoswitchable fluorophore **12** showed efficient reversible quenching of fluorescence in solution possibly through a PET mechanism.

Experimental Section

General Remarks: NMR spectra were measured at room temperature with a Bruker DRX 500 spectrometer (500 MHz). $CDCl_3$, CD_2Cl_2, and [D_6]DMSO were used as internal standards for ^1H and ^{13}C NMR spectra. Mass spectra (ESI) were recorded by using a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer Bruker APEX III. EI mass spectra were recorded by using an Autospec X magnetic sector mass spectrometer with EBE geometry equipped with a standard EI source. Absorption spectra were recorded with Perkin–Elmer Lamda 25 and Lamda 40 spectrometers. Fluorescence spectra were recorded with a Perkin–Elmer LS50B spectrometer. Irradiations at 254 and 300 nm were done in a rayonet reactor and irradiations at 365, 590, and 620 nm were carried out with LEDs.

Materials: Triphenylphosphane, tetrabromomethane, 18-crown-6, 4-bromobenzyl bromide, 3-methoxyphenol, and 4-chloroacetoacetate are commercially available and were used as received. 1,2-Bis-(5-formyl-2-methylthiophen-3-yl)hexafluorocyclopentene (**1**),[12] 3-azido-1-propanol (**6**),[18] 9-(bromomethyl)anthracene,[21] and [$Cu(PPh_3)_3Br$][22] were prepared according to literature procedures. Solvents were of analytical grade and dried according to standard procedures prior to use, except for chloroform, which was used as received.

Safety: Azides should always be handled carefully. Organic azides, particularly those of low molecular weight, or with high nitrogen content, are potentially explosive.[28] Any reactions with azides should involve precautions against explosions.

Dibromomethyltriphenylphosphonium Bromide·CH_3CN (2):[15] Triphenylphosphane (17.0 g, 64.81 mmol) and tetrabromomethane (10.0 g, 30.15 mmol) were stirred in dichloromethane (160 mL) for 0.5 h at room temperature. To this solution was added water (50 mL), and the phases were separated. The aqueous layer was extracted with dichloromethane (50 mL). The combined organic layers were washed with brine (50 mL), dried with sodium sulfate, filtered, and concentrated in vacuo. To the oily residue was added acetonitrile (100 mL), and the flask was subjected to ultrasonic irradiation until the oil solidified (ca. 30 min). The solid was filtered, washed with acetonitrile several times, and dried to give **2** as a solvate with one equivalent of acetonitrile. Yield: 15.7 g, 28.2 mmol, 88%; colorless solid. ^1H NMR (CD_2Cl_2): $\delta = 1.97$ (s, 3 H, acetonitrile), 7.70–7.74 (m, 6 H, ArH), 7.84–7.87 (m, 3 H, 4′-ArH), 8.14–8.20 (m, 6 H, ArH), 10.37 (d, $J = 1.9$ Hz, 1 H, $PCHBr_2$) ppm. MS (ESI+): $m/z = 434.9$ [M – CH_3CN – Br]$^+$.

1,2-Bis[5-(2,2-dibromoethenyl)-2-methylthiophen-3-yl]hexafluorocyclopentene (3): Dialdehyde **1** (0.424 g, 1.00 mmol), phosphonium salt **2** (1.67 g, 3.00 mmol), and 18-crown-6 (0.010 g, 0.04 mmol) were suspended in dichloromethane (30 mL). To this mixture was added freshly ground potassium hydroxide (0.360 g, 6.00 mmol), and the mixture was stirred at room temperature for 1 h. After filtration, the solvent was removed in vacuo. The remainder was passed through a pad of silica gel (cyclohexane/ethyl acetate, 7:3) until a sample of the last filtrate showed no color change on TLC material upon irradiation with UV light. The solvent was removed in vacuo to give **3** as a yellow green solid. Yield: 0.570 g, 0.77 mmol, 77%. ^1H NMR ($CDCl_3$): $\delta = 1.87$ (s, 6 H, CH_3), 7.14 (s, 2 H, ArH), 7.53 (s, 2 H, $CHCBr_2$) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 14.7$, 88.3, 124.5, 128.7, 129.6, 130.3, 132.1, 132.3, 132.4, 133.1 ppm. HRMS (EI): calcd. for $C_{19}H_{10}S_2Br_4F_6^+$ [M]$^+$ 731.68616; found 731.68860.

1,2-Bis(5-ethynyl-2-methylthiophen-3-yl)hexafluorocyclopentene (4):[12] Tetrabromide **3** (0.57 g, 0.77 mmol) was dissolved in dry ethyl ether (30 mL) under an argon atmosphere. To this solution was added *n*-butyllithium (1.6 M in hexanes, 2.50 mL, 4.00 mmol) at –78 °C, and the mixture was stirred at this temperature for 1.5 h and additionally for 1 h at room temperature. Water (30 mL) and a few drops of 2 M hydrochloric acid were added; the phases were separated, and the aqueous layer was extracted with ethyl ether (20 mL). The combined organic layers were washed with brine (50 mL), dried with sodium sulfate, and concentrated in vacuo. The remainder was passed through a pad of silica gel (cyclohexane/ethyl acetate, 7:3) until the filtrate was nearly colorless. The dark yellow solution was concentrated to dryness to give **4** as a sticky dark brown solid. Yield: 0.223 g, 0.54 mmol, 70%. ^{1}H NMR ($CDCl_3$): δ = 1.88 (s, 6 H, CH_3), 3.34 (s, 2 H, CH), 7.21 (s, 2 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.4, 75.7, 82.3, 120.6, 124.5, 132.54, 143.6 ppm.[29] HRMS (EI): calcd. for $C_{19}H_{10}S_2F_6^+$ $[M]^+$ 416.01281; found 416.01256.

4-Bromobenzyl Azide (5): 4-Bromobenzyl bromide (1.25 g, 5.00 mmol) and sodium azide (0.49 g, 7.50 mmol) were stirred in water (20 mL) and acetone (80 mL) at room temperature for 60 h. The mixture was extracted with dichloromethane (3 × 50 mL), the combined organic layers were dried with sodium sulfate, and the solvent was removed in vacuo to give the product as a yellow liquid. Yield: 1.04 g, 4.90 mmol, 98%. ^{1}H NMR ($CDCl_3$): δ = 4.31 (s, 2 H, CH_2), 7.20 (d, J = 8.3 Hz, 2 H, ArH), 7.52 (d, J = 8.4 Hz, 2 H, ArH) ppm. MS (EI, 70 eV): *m/z* (%) = 211.0 (30) $[M]^+$, 184.0 (50) $[M - N_2]^+$, 171.0 (100) $[M - N_3]^+$, 155.0 (30) $[M - CH_2N_3]^+$.

4-Azidomethyl-7-methoxycoumarin (7)[19]

Pechmann Condensation: 3-Methoxyphenol (2.48 g, 20.00 mmol) and 4-chloroacetoacetate (3.62 g, 22.00 mmol) were mixed with concentrated sulfuric acid (15 mL), and the mixture was stirred at room temperature for 3 h. The mixture was poured into water (200 mL), and the pink precipitate was collected by filtration, washed with additional water, dried in air, and recrystallized (ethanol) to give 4-chloromethyl-7-methoxycoumarin[20] as a slightly pink solid. Yield: 3.26 g, 14.55 mmol, 73%. ^{1}H NMR ([D$_6$]-DMSO): δ = 3.86 (s, 3 H, OCH_3), 4.99 (s, 2 H, CH_2Cl), 6.50 (s, 1 H, CHC=O), 7.01 (m, 1 H, ArH), 7.04 (d, J = 2.5 Hz, 1 H, ArH), 7.76 (d, J = 8.8 Hz, 1 H, ArH) ppm.

Reaction with Sodium Azide: 4-Chloromethyl-7-methoxycoumarin (1.00 g, 4.46 mmol) was added to a suspension of sodium azide (2.60 g, 36.92 mmol) in acetone (60 mL) and acetonitrile (60 mL). The mixture was heated to reflux for 4 h, and then the volume was reduced to 50%. Ethyl acetate (50 mL) was added, and the precipitate was removed by filtration. The filtrate was dried with sodium sulfate, and the solvents were removed in vacuo. The residue was recrystallized (methanol) to give **7** as a colorless solid. Yield: 0.60 g, 2.60 mmol, 58%. ^{1}H NMR ([D$_6$]DMSO): δ = 3.87 (s, 3 H, OCH_3), 4.84 (d, J = 0.9 Hz, 2 H, CH_2N_3), 6.36 (s, 1 H, CHC=O), 7.01 (m, 1 H, ArH), 7.05 (d, J = 2.5 Hz, 1 H, ArH), 7.66 (d, J = 8.8 Hz, 1 H, ArH) ppm. MS (ESI+): *m/z* = 253.9 $[M + Na]^+$, 484.8 $[2M + Na]^+$.

9-(Azidomethyl)anthracene (8): 9-(Bromomethyl)anthracene[21] (0.81 g, 2.99 mmol) and sodium azide (1.95 g, 30.00 mmol) were suspended in acetone (60 mL) and acetonitrile (60 mL). The mixture was heated to reflux for 2 h, and the solvents were then removed in vacuo. The residue was passed through a pad of silica gel (cyclohexane/ethyl acetate, 7:3), and the filtrate was concentrated to dryness to give **8** as an orange-brown solid. Yield: 0.68 g, 2.91 mmol, 97%. ^{1}H NMR ($CDCl_3$): δ = 5.33 (s, 2 H, CH_2N_3), 7.52 (m, 2 H, ArH), 7.49 (m, 2 H, ArH), 8.06 (d, J = 8.8 Hz, 2 H, ArH), 8.30 (d, J = 8.5 Hz, 2 H, ArH), 8.51 (s, 1 H, ArH) ppm. MS (EI, 70 eV): *m/z* (%) = 233.1 (25) $[M]^+$, 204.1 (80) $[M - N_2]^+$, 191.1 (100) $[M - N_3]^+$, 176.1 (30) $[M - CH_2N_3]^+$.

Bis(bromobenzyl)dithienylethene (9): Diacetylene **4** (35 mg, 0.08 mmol) was dissolved in chloroform (20 mL). To this solution was added **5** (34 mg, 0.16 mmol) and $[Cu(PPh_3)_3Br]$ (5 mg, 0.005 mmol). After 4 h of stirring at room temperature, the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate, 9:1 to 7:3 mixture). Yield: 30 mg, 0.036 mmol, 45%; grey solid. ^{1}H NMR ($CDCl_3$): δ = 1.91 (s, 6 H, CH_3), 5.50 (s, 4 H, CH_2), 7.19 (d, J = 8.3 Hz, 4 H, ArH), 7.27 (s, 2 H, thiophene), 7.53 (d, J = 8.3 Hz, 4 H, ArH), 7.58 (s, 2 H, triazole) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.7, 53.8, 119.1, 123.3, 123.6, 125.4, 129.9, 131.2, 132.6, 133.4, 141.9, 142.6 ppm.[29] HRMS (ESI): calcd. for $C_{33}H_{23}N_6S_2Br_2F_6^+$ $[M + H]^+$ 838.96911; found 838.96905.

Bis(hydroxypropyl)dithienylethene (10): Diacetylene **4** (52 mg, 0.13 mmol) was dissolved in chloroform (20 mL). To this solution was added **6** (101 mg, 1.000 mmol) and $[Cu(PPh_3)_3Br]$ (20 mg, 0.02 mmol). After 16 h of stirring at room temperature the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate, gradient 0 to 100% ethyl acetate; then ethyl acetate/methanol, 3:1). Yield: 30 mg, 0.050 mmol, 39%; brown solid. ^{1}H NMR ($CDCl_3$): δ = 1.98 (s, 6 H, CH_3), 2.16 (m, 4 H, $CH_2CH_2CH_2OH$), 3.68 (t, J = 5.7 Hz, 4 H, $CH_2CH_2CH_2OH$), 4.56 (t, J = 6.7 Hz, 4 H, $CH_2CH_2CH_2OH$), 7.25 (s, 2 H, thiophene), 8.01 (s, 2 H, triazole) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.6, 32.6, 47.3, 58.7, 116.2, 120.1, 123.7, 125.4, 131.3, 136.2, 141.9, 142.0, 162.8 ppm. HRMS (ESI): calcd. for $C_{25}H_{25}N_6O_2S_2F_6^+$ $[M + H]^+$ 619.13791; found 619.13927.

Dicoumaryldithienylethene (11): Diacetylene **4** (52 mg, 0.13 mmol) was dissolved in chloroform (20 mL). To this solution was added **7** (116 mg, 0.500 mmol) and $[Cu(PPh_3)_3Br]$ (20 mg, 0.02 mmol). After 16 h of stirring at room temperature the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate, 9:1 to 1:3). Yield: 93 mg, 0.11 mmol, 85%; yellow solid. ^{1}H NMR ([D$_6$]DMSO): δ = 1.91 (s, 6 H, CH_3), 3.86 (s, 6 H, OCH_3), 5.96 (s, 4 H, CH_2N), 5.98 (s, 2 H, CHC=O), 7.01 (m, 2 H, ArH), 7.07 (d, J = 2.4 Hz, 2 H, ArH), 7.50 (s, 2 H, thiophene), 7.75 (d, J = 8.9 Hz, 2 H, ArH), 8.72 (s, 2 H, triazole) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 14.1, 49.6, 56.1, 101.2, 110.6, 111.6, 112.5, 122.1, 123.1, 124.5, 125.9, 131.5, 141.2, 141.4, 155.2, 159.9, 162.8 ppm.[29] HRMS (ESI): calcd. for $C_{41}H_{29}N_6O_6S_2F_6^+$ $[M + H]^+$ 879.14887; found 879.14914.

Dianthryldithienylethene (12): Diacetylene **4** (67 mg, 0.16 mmol) was dissolved in chloroform (20 mL). To this solution was added **8** (150 mg, 0.64 mmol) and $[Cu(PPh_3)_3Br]$ (20 mg, 0.02 mmol). After 5 h of stirring at reflux, the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate, 7:3). Yield: 43 mg, 0.05 mmol, 30%; yellow solid. ^{1}H NMR ($CDCl_3$): δ = 1.71 (s, 6 H, CH_3), 6.56 (s, 4 H, CH_2N), 7.02 (s, 2 H, thiophene), 7.17 (s, 2 H, triazole), 7.55 (m, 4 H, ArH), 7.62 (m, 4 H, ArH), 8.10 (d, J = 8.5 Hz, 4 H, ArH), 8.32 (d, J = 8.5 Hz, 4 H, ArH), 8.59 (s, 2 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.4, 46.6, 118.6, 122.8, 123.0, 123.3, 125.0, 125.5, 127.9, 129.6, 130.1, 130.8, 131.2, 131.4, 141.4, 142.0 ppm.[29] HRMS (ESI): calcd. for $C_{49}H_{33}N_6S_2F_6^+$ $[M + H]^+$ 883.21068; found 883.20983.

Supporting Information (see footnote on the first page of this article): Details on calculations of overlap integrals and Förster radii, full scale UV/Vis spectra of compounds **9**–**12**, enlarged emission spectra of compounds **11** and **12**.

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