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Efficient Preparation of Photoswitchable Dithienylethene-Linker-Conjugates by Palladium-Catalyzed Coupling Reactions of Terminal Alkynes with Thienyl Chlorides and Other Aryl Halides

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In memory of Herbert Schumann

Abstract: Three photochromic dithienylethene-linker-conjugates with an adamantane core containing different spacer lengths and footprint areas with carboxylic anchoring groups are synthesized. The synthetic routes start either from the ethynylene-linker **5** or the iodo-substituted linker **8**. Reaction conditions for the final Sonogashira coupling step between ethynylene-linker **5** with the chloro-substituted dithienylethene **4** in the presence of $[PdCl_2(CH_3CN)_2]$/X-Phos and Cs_2CO_3 or K_3PO_4 are optimized using 2-chloro-5-methylthiophene (**9**) and triethylsilylacetylene or triisopropylsilylacetylene (**10a**,**b**) as model compounds. Experimental conditions are found to suppress the activation of the C(sp)–Si bond in TIPS-acetylene **10b**, a reaction leading to a subsequent cross-coupling reaction to form by-product **12**. Furthermore, activation of the C(sp)–Si bond in the presence of the fluorinated backbone of the chloro-substituted dithienylethene **4** can also be prevented. The photochromic properties of the conjugate **3** and its precursor dithienylethene **7b** are also investigated.

Keywords: cross-coupling · palladium · photochromism · thiophene · tripodal ligands

Introduction

A major challenge in developing functional modules for molecular electronics, photovoltaics, or biosensor technology is tuning and controlling energy and electron transfer between dye adsorbates and semiconductor and metal substrates.[1–4] A detailed understanding of the elementary processes on the surfaces, and their photoinduced dynamics requires a rational molecular design of model compounds.[5–7] It has been demonstrated that many properties of molecular adsorbate systems already depend upon the surface-immobilization strategy.[4,8] For example, the formation of aggregates strongly depends upon the orientation of single dye molecules and their lateral interaction on the metal or semiconductor surface. Small and large footprint tripodal linkers with three anchoring groups have been used by us and others to bind dyes,[9–11] Ru-bpy,[6] and other metal complexes,[12] as well as photoswitches[3,13–15] to the surface of metal-oxide nanoparticles and metals. Such systems allow control of the dye–surface distance by varying the spacer length.[16] Tripodal linkers are also useful for preventing unwanted aggregate formation, as the coverage of the surface is controllable by the size of the footprint area. The syntheses of tripodal linkers

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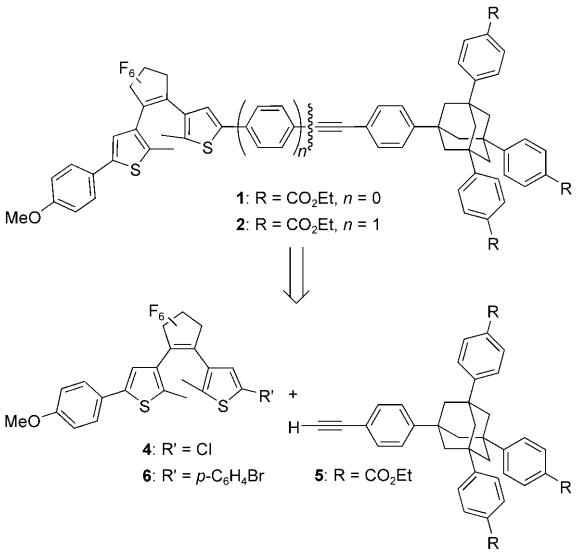
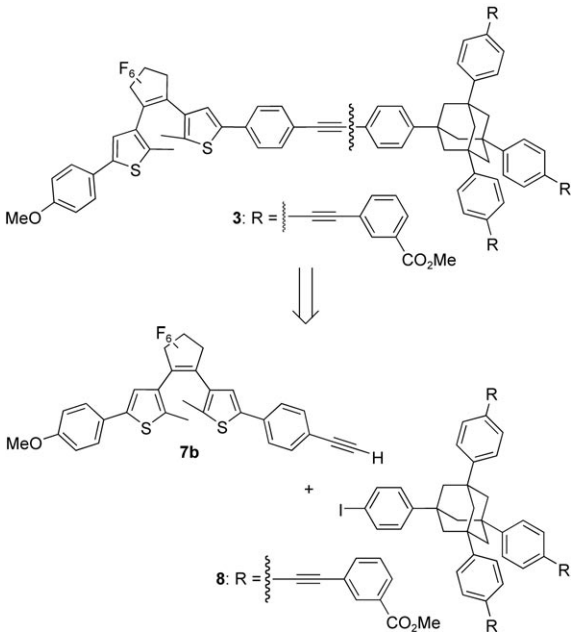
involve Pd-catalyzed cross-coupling reactions as key steps.[13,17,18] Generally, small linker units derived from 1,3,5,7-tetraphenyladamantane having the three binding groups attached to the *para* position of the phenyl residues, already contain an alkyne spacer for the attachment of a chromophore. Then, the chromophore-linker-conjugate is prepared by a Sonogashira coupling reaction of the ethynyl-substituted tripodal linker system with an iodo- or bromo-substituted chromophoric unit.[9,13,14] More recently, linker systems with larger footprints were obtained by an alternative synthetic route, whereby the iodo-substituted linker precursor is coupled with the ethynyl-substituted chromophore.[18] We followed both synthetic routes towards the preparation of the challenging tripodal dithienylethene-linker-conjugates **1**, **2**, (Scheme 1) and **3** (Scheme 2) containing different spacer lengths and footprint areas, and bearing carboxylic acid anchoring groups for the attachment of photoswitches to semiconductor nanoparticles. Such photochromic systems are useful for studying the dynamics of light-controllable interfacial electron transfer. Thus, in a module containing a dye-diarylethene-semiconductor triad, reversible modulation of electronic interactions by light could open access towards new applications. Previously, related concepts were successfully demonstrated in solution for photoswitchable donor–bridge–acceptor systems.[19–23] We herein report the synthesis of dithienylethene-linker-conjugates for long-term studies of the ultrafast dynamics of the electron transfer in dye-diarylethene-semiconductor triad systems.

In view of the recent development of powerful Sonogashira coupling methods that allow cross-coupling of the less reactive aryl chlorides by using electron-rich phosphines,[24] and copper-free conditions to avoid homocoupling,[25] the chloro-substituted dithienylethene **4**[26] and the ethynyl-substituted linker system **5**[6] were used as starting materials for the synthesis of the linker-conjugate **1** (Scheme 1).



Scheme 1. Structures of the dithienylethene-linker-conjugates **1** and **2** and design of their synthesis starting from the ethynylene-linker **5** and the chloro- and bromo-substituted dithienylethenes **4** and **6**.



Scheme 2. Synthetic pathway toward dithienylethene-linker-conjugate **3** with the ethynylene-substituted dithienylethene **7b** and the iodo-substituted linker **8**.

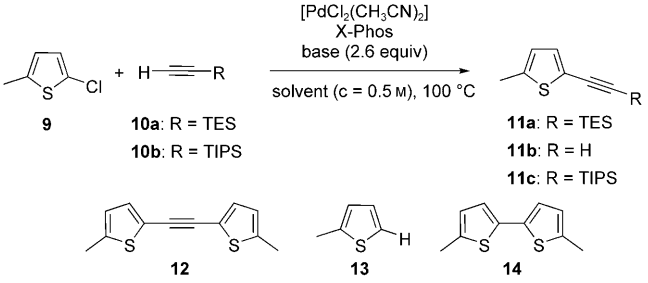
The general and efficient palladium-catalyzed method developed by Gelman and Buchwald involves the use of $[PdCl_2(CH_3CN)_2]$ and X-Phos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) in acetonitrile or dioxane at 70–90 °C, in combination with inorganic bases, such as Cs_2CO_3

Abstract in German: Beschrieben wird die Synthese von drei photochromen Dithienylethen-Linker-Konjugaten, bestehend aus einer zentralen Adamantaneinheit, Carbonsäure-Ankergruppen, sowie variierenden "Spacerlängen" und unterschiedlichen Fußabdrücken. Die synthetischen Routen zu diesen Verbindungen beginnen entweder ausgehend von dem Ethinylen-Linker **5** oder von dem Iod-substituierten Linker **8**. Für die finale Sonogashira-Kupplung wurden dabei Reaktionsbedingungen zwischen dem Ethinylen-Linker **5** und dem Chlor-substituierten Dithienylethen **4** in Gegenwart von $[PdCl_2(CH_3CN)_2]$/X-Phos und Cs_2CO_3 oder K_3PO_4 verwendet, die anhand von Modellstudien mit 2-Chlor-5-methylthiophen (**9**) und Triethylsilylacetylen oder Triisopropylsilylacetylen (**10a**,**b**) optimiert wurden. Dabei wurden experimentelle Bedingungen gefunden, um die Aktivierung der C(sp)-Si-Bindung von TIPS-Acetylen **10b** zu unterdrücken, welche ansonsten zu dem Nebenprodukt **12** führte. Darüber hinaus konnte die Aktivierung der C(sp)-Si-Bindung in Anwesenheit des fluorierten Rückgrats des chlor-substituierten Dithienylethen **4** verhindert werden. Schließlich wurden die photochromen Eigenschaften des Konjugates **3** und der Vorläuferverbindung **7b** untersucht.

or K_3PO_4.[25] In these studies, copper salts were found to enhance the rate of oligomerization of the alkyne and to suppress the coupling process. To prevent this side reaction, either copper-free conditions were employed or the alkyne was added slowly to the reaction mixture. However, thiophene is a π-electron-rich heterocycle. Even though halogenated thiophenes have been frequently employed in cross-coupling reactions,[27] most of the cross-coupling protocols were developed for iodo-substituted or activated bromo- and chloro-substituted thiophenes, that is, substituted with electron-withdrawing groups to facilitate the oxidative addition step. Differences in reactivity between 2-halo- and 3-halothiophenes were not found to be very pronounced. For example, Erker et al. thoroughly investigated the palladium-catalyzed cyanation of thiophene halides employing $Pd_2(dba)_3$ and dppf as catalyst system in the presence of Zn powder and $Zn(CN)_2$ in DMA at 80 °C or 120 °C.[28] Generally, mild reaction conditions for bromo- and chloro-substituted thiophenes are still rare, especially for compounds containing electron-releasing groups.[29,30] More recently, electron-rich 2-methyl-substituted iodo- and bromothiophenes were successfully employed in Suzuki–Miyaura reactions[31] or Heck–Mizoroki coupling procedures at elevated temperature (80-140 °C).[32] Sonogashira reaction methods for a range of alkynes with halothiophenes were thoroughly investigated by Santelli employing 2-iodo-, 2-bromo-, and 3-bromothiophenes by using $[Pd(C_3H_5)Cl]_2$/Tedicyp, K_2CO_3, CuI in DMF at 100 °C for 20 h.[33] Also, copper-free microwave-assisted procedures were developed for aryl chlorides and were successfully applied in the coupling of 2-chlorothiophenes.[34] Again, in most cases, heat was necessary to promote the oxidative addition step to palladium, including cross-coupling reactions involving an electron-rich *N*-heterocyclic-carbene ligand.[32] The copper-free protocol of Gelman and Buchwald was extended by Novák and coworkers by using Pd/C in the presence of X-Phos, and was successfully employed for the coupling of 2-chlorothiophene to phenylacetylene in DMA in the presence of K_2CO_3 at 110 °C.[35] Recently, Beller reported copper-free palladium-catalyzed Sonogashira conditions for the coupling of 3-chlorothiophene using *N*-substituted heteroaryl phosphines at 90 °C in toluene in the presence of Na_2CO_3.[36] This survey of the literature demonstrates the challenges still associated with the coupling of halo-substituted thiophenes. Herein, we report on solutions for Sonogashira coupling reactions of the chloro-substituted dithienylethene **4** for the synthesis of conjugate **1**, and the model compound 2-chloro-5-methylthiophene (**9**) (Table 1). Methods published previously by our groups for the key coupling reactions in the syntheses of the tripodal dithienylethene-linker-conjugates **2** (Scheme 1) and **3** (Scheme 2) were investigated, using common catalysts, for example, $Pd(PPh_3)_4$, $Pd_2(dba)_3$/P(*o*-tol)$_3$, or $[PdCl_2(PhCN)_2]$/$[(tBu)_3PH]BF_4$ with or without CuI as cocatalyst in the presence of NEt_3 or DIPA.[13,14,18]

Accordingly, the bromo-substituted precursor **6** and the linker system **5** were selected as useful starting materials for conjugate **2** (Scheme 1). For the synthesis of conjugate **3**, the alkynyl-substituted dithienylethene **7b** and the iodo-substituted linker building block **8** were chosen (Scheme 2).

Table 1. Model Sonogashira coupling reactions with thiophene **9** and TES- or TIPS-acetylene **10a**,**b**.



Entry	Acetylene	Base	Solvent	*t* [h]	Yield [%][a] **11a/c**
1	**10a**	Cs_2CO_3	CH_3CN	17[b]	76[c,d]
2	**10a**	Cs_2CO_3	CH_3CN	4	63[c,e]
3	**10b**	Cs_2CO_3	CH_3CN	2.5[b]	83[c]
4	**10b**	Cs_2CO_3	DMF	18[f]	30[c,g]
5	**10b**	Cs_2CO_3	dioxane	17[f]	33[c,h]
6	**10b**	Cs_2CO_3	toluene/DMF	18[f]	54[c]
7	**10b**	Cs_2CO_3	toluene/CH_3CN	17[f]	50[c]
8	**10b**	Cs_2CO_3	CH_3CN	2.5[b]	92[i]
9	**10b**	K_3PO_4	CH_3CN	24[f]	67[i]
10	**10b**	K_3PO_4	CH_3CN	24[b,j]	85[i]

[a] Yield of isolated product. [b] Complete conversion according to TLC. [c] Ratio cat/ligand [mol%] = 1:3. [d] Ratio **11a**/**12** = 77:23. [e] Ratio **11a**/**12** = 85:15. [f] No further conversion according to TLC. [g] Ratio **11c**/**14** = 82:18. [h] Ratio **11c**/**12**/**14** = 84:8:8. [i] Ratio cat/ligand [mol%] = 10:30. [j] The reaction was conducted at 80 °C.

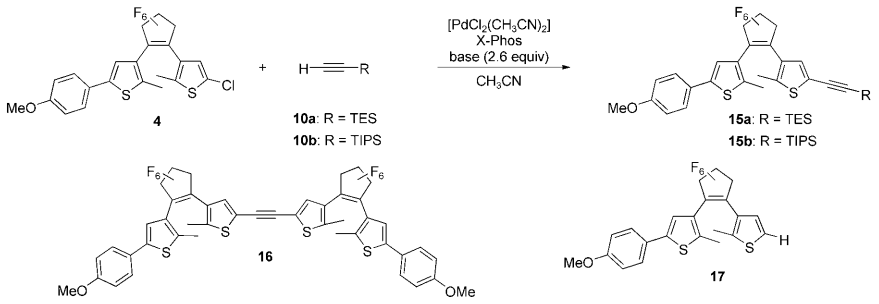
Results and Discussion

To find the optimal reaction conditions for the valuable starting material **4**, we carried out model studies with 2-chloro-5-methylthiophene (**9**) and triethylsilylacetylene (TES-acetylene) (**10a**) or triisopropylsilylacetylene (TIPS-acetylene) (**10b**) (Table 1). The first coupling reaction of **9** and TES-acetylene **10a** (1.3 equiv) was accomplished with $[PdCl_2(CH_3CN)_2]$ (1 mol%), X-Phos (3 mol%), and Cs_2CO_3 (2.6 equiv) in dry acetonitrile (0.5 M) containing <10 ppm water at 100 °C (Table 1, entry 1). The cross-coupling product **11a** was isolated in 76% yield after 17 h reaction time, workup, and flash chromatography. The dithienylethynylene **12** (Table 1, entry 1) was also isolated (ratio **11a**/**12** = 77:23; ^{1}H NMR spectroscopy of the crude product mixture). Exact turnover and the formation of the hydrodehalogenated byproduct **13** was not ascertained by ^{1}H NMR spectroscopy because of the low boiling point of 2-methylthiophene (**13**) (b.p.: 110–113 °C).[37] However, the mass balance was satisfying, and by shortening the reaction times, the amount of byproduct **12** could be minimized at the expense of incomplete turnover. Thus, after 4 h, predominant formation of product **11a** (ratio **11a**/**12** = 85:15) was observed, and **11a** was isolated in 63% yield by flash chromatography (Table 1, entry 2). The formation of compound **12** can be understood as two consecutive Sonogashira reactions, because formation of **12**

takes place in one step without the detection and isolation of the supposed intermediate **11b** (Table 1). A coupled reaction either demands the Pd-mediated activation or the unwanted deprotection of the C(sp)–Si bond. Sila–Sonogashira reactions are usually run in the presence of fluoride ions.[38] However, Pombo–Villar[39] and others[40–42] demonstrated that the C(sp)–$SiMe_3$ bond is also directly activated or deprotected by the appropriate choice of catalysts, additives (Bu_4NX, X = Br, Cl),[39,42] CuI,[39] or other reaction conditions (Cs_2CO_3, 150 °C).[40,41] Interestingly, in this case, the C(sp)–$SiEt_3$ bond was previously observed to be stable under similar reaction conditions, but with shorter reaction times.[25] However, for TIPS-substituted acetylene **10b**, complete conversion of the starting material was observed after 2.5 h, and product **11c** was isolated in 83% yield (Table 1, entry 3). Side products were not detected. When the reaction was carried out in DMF or dioxane, conversion was incomplete (Table 1, entries 4 and 5), and the formation of a new by-product, the homocoupled product **14** (^{1}H NMR), was observed. Furthermore, the formation of dithienylethynylene **12** was also observed (ratio in DMF: **11c**/**14** = 82:18; ratio in dioxane: **11c**/**12**/**14** = 84:8:8; Table 1, entries 4 and 5). The formation of the homocoupled product **14** from the chloro-substituted thiophene **9** was previously observed in the literature in the absence of a transmetallation partner.[43]

The use of a 2:1 mixture of toluene and DMF as the reaction solvent yielded the cross-coupling product **11c** in 54% yield after 18 h without formation of by-products. Moreover, a reaction carried out in a 2:1 mixture of toluene and acetonitrile proceeded without formation of by-products, and **11c** was obtained in 50% yield (Table 1, entries 6 and 7). Actually, the yield of **11c** was increased by using a higher loading of the palladium catalyst (10 mol%) and X-Phos (30 mol%), analogous to a report previously published by Lautens and co-workers for a related catalyst precursor.[44] Finally, in acetonitrile and in the presence of Cs_2CO_3 at 100 °C after 2.5 h workup and flash chromatography, product **11c** was isolated in 92% yield (Table 1, entry 8). Also, reactions with K_3PO_4 were tested (Table 1, entries 9 and 10). Therefore, similar to Cs_2CO_3, also K_3PO_4, derived from Sigma–Aldrich ($K_3PO_4 \cdot 1.5\,H_2O$ and $K_3PO_4 \cdot 7\,H_2O$),[45] was dried for 5 h at 300 °C. By running the reaction at 100 °C for 24 h (TLC monitoring), product **11c** was obtained in 67% yield (Table 1, entry 9). The formation of by-products was not observed. Fortunately, with K_3PO_4 the reaction temperature could be decreased to 80 °C. After 24 h, complete consumption of the starting material was monitored by TLC, and **11c** was isolated in 85% yield after flash chromatography (Table 1, entry 10). The results summarized in Table 1 demonstrate an influence of a) the reaction time and b) the solvent, as the best yields were observed for short reaction times in acetonitrile. Also, the moisture content of the bases and the solvents, and the differences in the solubility and the basicity of the bases, may have contributed to the reaction outcome.[45–47] All these factors similarly affect a palladium-mediated C(sp)–SiR_3 activation, as well as the cleavage[48] of the TES-group and the TIPS-group (Table 1, entry 5). However, in the cases examined, the deprotected alkyne **11b** was not detected by ^{1}H NMR spectroscopy of the crude products.

On route to the photoswitch-linker-conjugate **1**, the synthesis of compounds **15a**,**b** (Scheme 3) was tested, as both compounds are also valuable starting materials for the preparation of additional conjugates with spacer lengths different from **1**–**3.** Thus, the chloro-substituted dithienylethene **4** (Scheme 3) was dissolved in acetonitrile (0.5 mL, 0.2 M solution) and treated with $[PdCl_2(CH_3CN)_2]$ (1 mol%), X-Phos (3 mol%), and Cs_2CO_3 (2.6 equivalents) in the presence of TES-acetylene **10a** (1.3 equivalents) at 90 °C. After 17 h, conversion of the chloride **4** was complete. However, bisthienylethynylene **16** (Scheme 3, Table 2), which was isolated in 40% yield, and the hydrodehalogenated by-product **17** were the only products obtained, and the cross-coupling product **15a** was not observed. When the concentration of compound **4** in anhydrous redistilled acetonitrile was raised



Scheme 3. Synthesis of the ethynylene-dithienylethenes **15a**,**b** by model Sonogashira coupling reactions of the chloro-substituted dithienylethene **4** with the acetylenes **10a**,**b**.

Table 2. Optimization of the Sonogashira coupling reaction of dithienylethene **4** with TES- or TIPS-acetylene **10a**,**b**.

Entry	Acetylene	Base	T [°C]	t [h]	Ratio[a] **15**:**16**:**17**	Yield [%][b] **15**	Yield [%][b] **16**
1	**10a**	Cs_2CO_3	90[c,d]	17	0:82:18	–	40
2	**10b**	Cs_2CO_3	100[e,f]	2.5	0:65:35	–	19
3	**10b**	K_3PO_4	80[e,f]	24	71:18:11	58	10
4	**10b**	K_3PO_4	100[e,f]	24	90:0:10	51	–

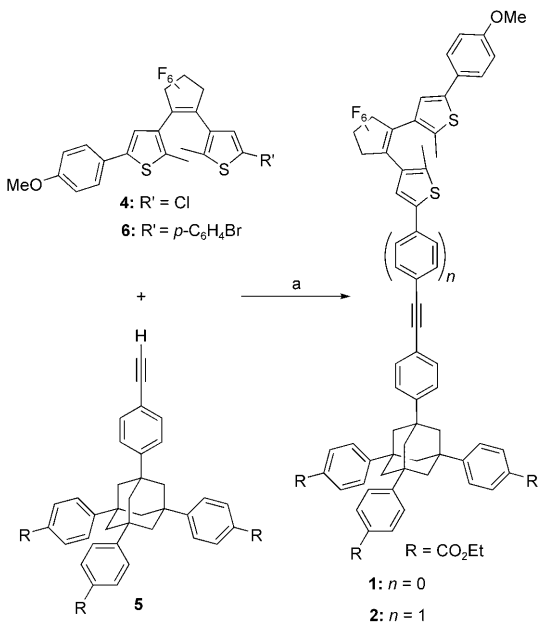
[a] ^{1}H NMR of the crude reaction mixture. [b] Yield of isolated product. [c] 0.2 M solution. [d] Ratio cat/ligand [mol%] = 1:3. [e] 0.5 M solution. [f] Ratio cat/ligand [mol%] = 10:30.

to 0.5 M, the rate of conversion decreased to 22% (^{1}H NMR spectroscopy), and only traces of **16** were isolated. Next, the coupling of the chloro-substituted dithienylethene **4** with TIPS-acetylene **10b** (1.3 equiv) was investigated in the presence of catalyst (10 mol%) and ligand (30 mol%) in combination with Cs_2CO_3 at 100°C in acetonitrile (0.5 M).

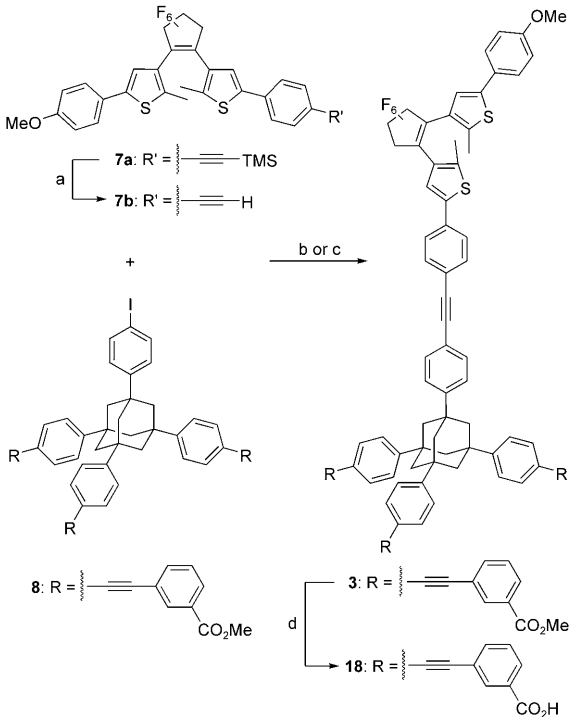
After 2.5 h, complete consumption of the starting material was detected. Surprisingly, the ^{1}H NMR analysis after workup, indicated that product **15b** was not formed, although the more stable TIPS-acetylene **10b** was used. Instead, the dithienylethynylene **16** (Scheme 3) was determined (Table 2, entry 2) besides the hydrodehalogenated by-product **17**. Compound **16** was isolated in 19% yield. However, when using K_3PO_4 instead of Cs_2CO_3, complete consumption of the starting material was observed at 80°C as well as 100°C, and product **15b** was isolated in 58% or 51% yields, respectively (Table 2, entries 3 and 4). In the presence of K_3PO_4, only traces of the by-products **16** and **17** were detected. A possible explanation for the results obtained, is the C–F activation at the perfluorocyclopentene moiety when using Cs_2CO_3, leading to the presence of fluoride ions.[49,50] Then, activation of the TIPS residue of **15b** by fluoride ions and a subsequent Sila–Sonogashira coupling explains the formation of compound **16**. Obviously, this side reaction can be reduced by using K_3PO_4 instead of Cs_2CO_3.

The coupling of the chloro-substituted dithienylethene **4** with the sterically hindered tripodal ethynylene-linker **5** also proceeded well when applying K_3PO_4 in acetonitrile at 80°C for 4 h (Scheme 4).

The predominant formation of product **1** (ratio **1**:**4**:**17** = 78:16:6) was ascertained by ^{1}H NMR spectroscopy. The tripodal dithienylethene-linker-conjugate **1** was isolated in 65% yield after flash chromatography. Furthermore, the bromo-substituted precursor **6** was cleanly and completely coupled with **5** under identical conditions furnishing the conjugate **2** in 76% yield (Scheme 4). The challenging dithienylethene-linker-conjugate **3** with the large footprint was prepared by following a recently published procedure.[18] Dithienylethene **7a** was synthesized starting from literature-known compounds as described in the experimental section. Desilylation with NaOH in methanol at RT gave **7b**[23] in 92% yield. Standard Sonogashira-coupling conditions were employed for the coupling of **8** (0.002 M) with **7b** (2 equiv) by applying a recently published procedure by Galoppini[18] using $Pd_2(dba)_3$ (50 mol%) and P(*o*-tol)$_3$ (300 mol%) in the presence of triethylamine/THF at 60°C for 24 h. After flash chromatography, the yields of conjugate **3** ranged between 25 and 38%. Subsequent deprotection of the methylester functionalities of **3** with NaOH in THF afforded the free acid **18** in 82% yield. For comparison, we also studied the coupling of **7b** with **8** under the aforementioned reaction conditions. Compound **8** (0.1 M) dissolved in acetonitrile was treated with **7b** (1.3 equiv) in the presence of Pd-catalyst (10 mol%), X-Phos (30 mol%), and K_3PO_4 at 80°C for 20 h. After workup and flash chromatography, conjugate **3** was isolated in 25% yield (Scheme 5). Neither longer reaction times (up to 65.5 h), nor an increase in concentration (0.5 M) changed the result. Furthermore, during scale-up by a factor of two, the yield decreased drastically, and product



Scheme 4. Preparation of the dithienylethene-linker-conjugates **1** and **2**. Reagents and conditions: a) 10 mol% $[PdCl_2(CH_3CN)_2]$, 30 mol% X-Phos, K_3PO_4 (2.6 equiv), CH_3CN, 80°C, 4 h, **1**: 65%, **2**: 76%.



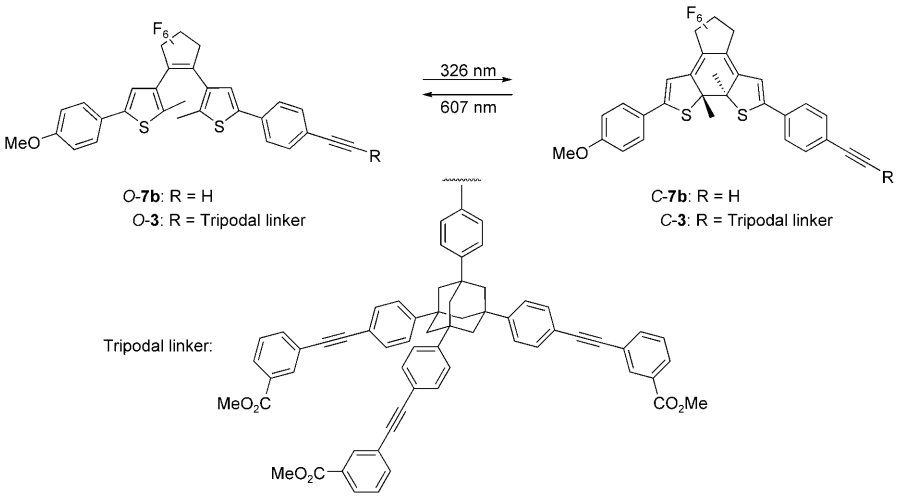
Scheme 5. Synthesis of the dithienylethene-linker-conjugate **3**. Reagents and conditions: a) NaOH, MeOH, RT, 2.5 h, **7b**: 92%; b) 50 mol% $Pd_2(dba)_3$, 300 mol% P(*o*-tol)$_3$, NEt_3, THF, 60°C, 24 h, **3**: 38%; or c) 10 mol% $[PdCl_2(CH_3CN)_2]$, 30 mol% X-Phos, K_3PO_4 (2.6 equiv), CH_3CN, 80°C, 20 h, **3**: 25%; d) NaOH, MeOH, RT, 47 h, **18**: 82%.

3 was isolated in 7% yield. In all coupling reactions with the iodo-substituted linker **8**, establishing turnover numbers and the yield of by-products were difficult because of the similar spectral properties of linker **8** and product **3**, which complicate the determination of the ratios by ^{1}H NMR spectroscopy.

Interestingly, when the commercially available K_3PO_4 was dried to constant weight for the coupling of **8** with **7b** under otherwise identical conditions, the cross-coupling reaction did not proceed. Similar unpredictable influences of the drying procedure were previously reported for bases in palladium- as well as copper-mediated coupling reactions.[45–47]

Photochromism

All dithienylethenes described in this paper were isolated as mixtures of the open-isomer (*O*-isomer) and the closed-isomer (*C*-isomer) in a ratio of *O*/*C*-isomer $\geq$95:5. Pure samples of the open-isomers of compounds **7b** and **3** were prepared by ring-closing with 326 nm light, followed by ring-opening with 607 nm light (Scheme 6).



Scheme 6. Photochromism of the dithienylethene-linker-conjugate **3** and the dithienylethene **7b**.

The UV/Vis data of the open- and closed-isomers of dithienylethene **7b** and the corresponding linker-conjugate **3** in THF at room temperature are shown in Figures 1 and 2, respectively. The absorption maxima of the isomeric forms of both compounds are summarized in Table 3.

The *O*-isomer of compound **7b** shows a maximum at 308 nm, whereas for the *O*-isomer of the dithienylethene-linker-conjugate **3**, two maxima at 290 nm and 306 nm are

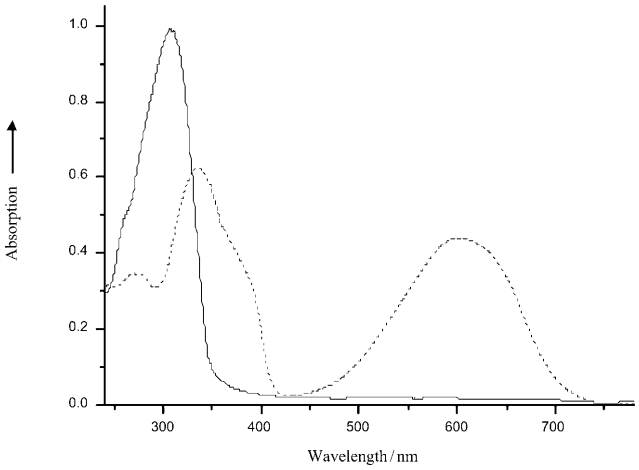


Figure 1. UV/Vis absorption spectrum of dithienylethene **7b** (*O*-isomer = solid line, pss = dotted line, $c = 2.5 \times 10^{-5}$ mol L^{-1}) in THF pss (326 nm) reached after 400 s.

observed. The pericyclic ring-closure to the blue colored *C*-isomer is achieved by irradiation with 326 nm light. For the *C*-isomer of **7b**, two new maxima at 335 nm and 600 nm are monitored, whereas the maxima of the *C*-isomer of conjugate **3** are found at 360 nm and 600 nm. The absorption band at 335 nm of compound **7b** is red-shifted by 25 nm by the tripodal system **3**, and the maximum at 600 nm is slightly broadened. This effect can be assigned to the extended π-system of the linker. The clear conversion of the isomers into each other is indicated by isosbestics points (328 nm for **7b** and at 348 nm for **3**). The reverse ring-opening was investigated by irradiation at 607 nm. The ratios of the two isomers for both compounds in the photostationary state (pss) at 326 nm were determined by ^{1}H NMR spectroscopy in [D$_8$]THF. For compounds **7b** and **3**, ratios of *O*/*C* = 5:95 and *O*/*C* = 11:89 were calculated, respectively.

Table 3. Spectroscopic data of the dithienylethenes **7b** and **3**.

Compound	λ_{max} *O*-isomer[a] (ε)[b]	λ_{max} pss[a] (ε)[b]	λ_{iso}[a]	pss$_{326}$ (*O*/*C*)[c]
7b	308 (38.8)	335 (25.1), 379[d](15.1), 600 (17.5)	328	5:95
3	290 (102.4), 306 (92.3), 333[d](41.9)	290 (91.2), 306 (71.4), 360 (33.5), 390[d](23.5), 600 (20.4)	348	11:89

[a] [nm]. [b] [10^3 cm^{-1} M^{-1}]. [c] Ratios determined by ^{1}H NMR spectroscopy in [D$_8$]THF in the pss upon illumination at 326 nm. [d] Shoulder.

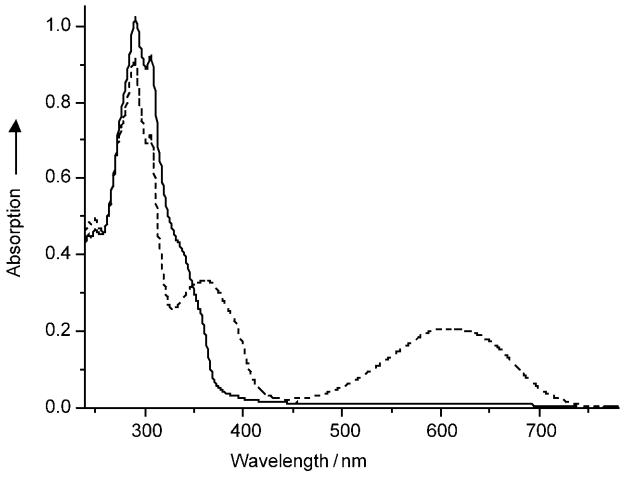


Figure 2. UV/Vis absorption spectrum of conjugate **3** (*O*-isomer = solid line, pss = dashed line, $c = 1.0 \times 10^{-5}$ mol L^{-1}) in THF; pss (326 nm) reached after 540 s.

Conclusions

The dithienylethene-linker-conjugates **1** and **2** have been synthesized from the ethynylene-linker **5**, and the halo-substituted dithienylethenes **4** and **6** by Sonogashira cross-coupling. For the chloro-substituted dithienylethene **4**, model studies were required for the optimization of the reaction conditions in the presence of $[PdCl_2(CH_3CN)_2]$/X-Phos and Cs_2CO_3 or K_3PO_4 to prevent homocoupling of the ethynylene-linker **5**. Dithienylethene **4** and 2-chloro-5-methylthiophene (**9**) were investigated in the model Sonogashira-coupling reactions with TES-acetylene and TIPS-acetylene **10a,b**. A strong influence of the reaction time, the solvent, and the base was observed. Conditions were found for the solvent acetonitrile that allow for suppression of the activation of the C(sp)–Si bond of TIPS-acetylene either in transformations of the electron-rich thiophene **9** or in the presence of the fluorinated backbone of the chloro-substituted dithienylethene **4**. However, in transformations of dithienylethene **4**, the activation of the C(sp)–Si bond and hydrodehalogenation could only be minimized by using K_3PO_4. Finally, conjugate **3** was synthesized from the corresponding iodo-substituted linker **8** and the ethynylene-substituted dithienylethene **7b**, and was successfully deprotected yielding compound **18**. The photochromic properties of the conjugate **3** and its precursor dithienylethene **7b** have also been investigated. Currently, we are investigating the dynamics of the electron transfer through the novel dithienylethene-linker-conjugates reported herein.

Experimental Section

Solvents were purified according to standard procedures.[51] Anhydrous DMF and CH_3CN were purchased from Acros in AcrosSeal bottles. 5-Chloro-2-methylthiophene (**9**, 95.8%) was purchased from Alfa Aesar. Triethylsilylacetylene (**10a**, 96.6%), triisopropylsilylacetylene (**10b**, > 99%), and $[PdCl_2(CH_3CN)_2]$ (99%) were purchased from Acros, and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos) (97%) was commercially available from Sigma–Aldrich. Cs_2CO_3 (catalogue number 441902–50G, 99%) and K_3PO_4 (catalogue number P5629–25G, tribasic ≥98%) were purchased from Sigma–Aldrich and stored in a desiccator. Small portions (1–2 g) were removed and heated in a Schlenk tube under vacuum (2.0×10^{-2} mbar) for five hours at 300 °C before use. When larger amounts of K_3PO_4 were used and dried to constant mass, no conversion to the coupling product could be monitored. Flash column chromatography was performed on silica gel (ICN silica, 32–63 μm, 60 Å, ICN Biomedicals GmbH). Thin-layer chromatography (TLC) was performed on Merck plates (silica gel 60 F_{254}). Melting points were determined with a Büchi SMP-20 or with a Leica Gallen III melting-point apparatus (uncorrected). ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker AM 400 or a Bruker DRX 500 spectrometer at room temperature; residual solvent protons were used as the internal standard {$CDCl_3$: $\delta(^1H) = 7.26$, $\delta(^{13}C) = 77.16$; [D$_8$]THF: $\delta(^1H) = 3.58$, $\delta(^{13}C) = 66.40$}. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and coupling constants in Hz. Overlapping carbon atoms in ^{13}C NMR spectra for the compounds **1**, **2**, **3**, **7b**, and **18** were identified by standard techniques, based on heteronuclear decoupling NMR spectroscopy. The resonances of the carbon atoms of the fluorinated cyclopentene moiety of the compounds **1**, **2**, **3**, **6**, **7a**, **7b**, **15b**, **16**, and **18** could not be observed because of the low intensity and extensive coupling. Low-resolution electron-impact mass spectra (EIMS, 70 eV) or fast atom bombardment mass spectra (FAB) were recorded with a Finnigan MAT 95 SQ. ESI spectra were recorded on an LTQ Orbitrap XL. GC-MS analysis was obtained with an HP-6890 gas chromatograph. IR spectra were recorded with a Nicolet Avatar 360 spectrometer as ATR. Elemental analyses were carried out on a Vario El from Analytik Jena. 3,5-Dibromo-2-methylthiophene[52] was synthesized in 73% yield according to a procedure for the preparation of 3-bromobenzo[*b*]thiophen-2-carbaldehyde.[53] 3-Bromo-2-methylthiophen-5-ylboronic acid[54] was synthesized in 80% yield according to a procedure published for 2,5-dimethylthiophen-3-ylboronic acid.[55] The known precursors 3-bromo-2-methyl-5-(4-methoxyphenyl)-thiophene,[56] 3-bromo-2-methyl-5-[4-(trimethylsilylethynyl)phenyl]thiophene,[57] 1-[5-(4-methoxy-phenyl)-2-methylthien-3-yl]perfluorocyclopentene,[58] and 5-chloro-3-iodo-2-methylthiophene[59] were essentially prepared by literature-known procedures. 1-(4-Ethynylphenyl)-3,5,7-tris-(4-carboethoxyphenyl)adamantane (**5**)[6] and 1-(4-iodophenyl)-3,5,7-[(3-carbomethoxyphenyl)-4-ethynylphenyl]adamantane (**8**)[18] were synthesized by following the published methods. Photoirradiation was carried out using a high-pressure 200 W mercury short arc lamp (HBO, Osram) with a 326 nm interference filter (Amko) and a 1000 W Xe-lamp (XBO, Osram) with a 607 nm interference filter (Amko) until a photostationary state (pss) was reached. UV/Vis spectra were measured on a Shimadzu UV-1601 UV/Visible spectrophotometer.

*X-ray Crystallographic Analysis of **6** (O-isomer)*

$C_{28}H_{19}BrF_6OS_2$: $M_r = 629.46$ g mol^{-1}; crystal size $0.30 \times 0.27 \times 0.16$ mm; monoclinic crystal system with space group $P21/c$ and $Z = 4$, $a = 25.5489(7)$, $b = 9.1126(3)$, $c = 10.9269(3)$ Å; $\alpha = \gamma = 90°$, $\beta = 93.171(3)°$; $V = 2540.07(13)$ Å^3, $\rho_{calcd.} = 1.646$ Mg m^{-3}; $F(000) = 1264$; linear absorption coefficient $\mu = 1.849$ mm^{-1}; type of diffractometer: Siemens SMART CCD; $T = 150(2)$ K; $Mo_{K\alpha}$ radiation; θ range 2.99–25.00°; index ranges $-30 \le h \le 30$, $-10 \le k \le 10$, $-12 \le l \le 12$; reflections collected 16389; independent reflections 4456 ($R_{int} = 0.0468$); observed reflections 346 [$I > 2\sigma(I)$], reflection used for refinement 4456; program system used: SHELXS-97, SHELXL-97, and SHELXTL; empirical absorption correction, direct methods, full-matrix refinement at F^2 with all independent reflections, weighting Scheme SHELXL; goodness-of-fit parameter (based on F^2) S = 0.862; residual densities $\Delta\rho_{max}$ and $\Delta\rho_{min} = 0.598$ and 0.372 e Å^{-3}. Hydrogen atoms: refined with riding model, refined with temperature factor 1.5 times U_{eq} of the carbon atoms; non-hydrogen atoms: refined anisotropically. Data/restraints/parameters: 4456/6/346; R index (all data): wR_2 (based on F^2) = 0.0654; R index (conventional) [$I > 2\sigma(I)$]: R1 (based on F) = 0.0330.[60]

Syntheses

6: 1-[5-(4-Methoxyphenyl)-2-methylthienyl-3-yl]-2-[2-methyl-5-(4-bromophenyl)-thien-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (**6**) was synthesized according to a method described by Feringa and co-workers for related compounds.[61] A solution of **4** (80.0 mg, 0.15 mmol) in Et_2O (2 mL) was slowly treated with *n*-butyllithium (1.6 M in hexane, 0.1 mL, 0.15 mmol, 1.00 equiv) at room temperature. After stirring for 1 h at this temperature, tri-*n*-butylborate (41.4 mg, 0.18 mmol, 1.20 equiv) was added in one portion, and stirring was continued for one hour. Then, 1-bromo-4-iodobenzene (88.0 mg, 0.31 mmol, 2.00 equiv), $Pd(PPh_3)_4$ (7.8 mg, 6.7 μmol, 4.5 mol%), THF (2 mL), and Na_2CO_3 (20% w/w, 1 mL) were added, and the mixture was heated to reflux for 16 h. After this time, TLC monitoring indicated complete conversion of the starting material and the reaction mixture was quenched with water (4 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/CH_2Cl_2 (7:1) to give product **6** as a blue solid (66.0 mg, 0.10 mmol, 66%); mixture of isomers (*O*-isomer/*C*-isomer ≥95:5 as determined by ^{1}H NMR). For X-ray analysis, compound **6** could be separated by recrystallization from CH_2Cl_2 as slightly blue crystals. *C*-isomer: R_f=0.29 (hexane/CH_2Cl_2, 7:1); *O*-isomer: R_f=0.25 (hexane/CH_2Cl_2, 7:1); m.p.: 183–185 °C; IR (ATR): $\tilde{\nu}$=3069, 3002, 2956, 2941, 2919, 2853, 2837, 1704, 1610, 1554, 1515, 1497, 1474, 1466, 1440, 1401, 1394, 1337, 1299, 1274, 1253, 1192, 1180, 1138, 1112, 1092, 1074, 1054, 1036, 1009, 950, 898, 889, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52–7.49 (m, 2H), 7.48–7.45 (m, 2H), 7.42–7.38 (m, 2H) 7.27 (br s, 1H), 7.15 (br s, 1H), 6.94–6.90 (m, 2H), 3.84 (s, 3H), 1.97 (s, 3H), 1.95 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.7, 142.4, 141.9, 141.0, 140.4, 132.5, 132.3, 127.2, 127.1, 126.3, 126.2, 125.8, 123.0, 121.9, 121.4, 114.6, 55.6, 14.7, 14.6 ppm; HRMS (EI): *m*/*z* (%) calcd for $C_{28}H_{19}BrF_6OS_2$: 627.9965; found: 627.9966; elemental analysis: calcd (%) for $C_{28}H_{19}BrF_6OS_2$ (629.47): C 53.43, H 3.04; found: C 53.41, H 3.23.

7a: 1-[5-(4-Methoxyphenyl)-2-methylthienyl-3-yl]-2-{2-methyl-5-[4-(trimethylsilyl-ethynyl)phenyl]thien-3-yl}-3,3,4,4,5,5-hexafluorocyclopentene (**7a**) was prepared analogously to a procedure described by Gust and co-workers:[23] A solution of 3-bromo-2-methyl-5-(4-trimethylsilylethynyl-phenyl)thiophene[57] (192 mg, 0.55 mmol) in THF (4 mL) was cooled to −78 °C under argon atmosphere and treated dropwise with *n*-butyllithium (1.6 M in hexane, 0.34 mL, 0.55 mmol, 1.00 equiv). After stirring for 45 min at −78 °C, a solution containing 1-[5-(4-methoxyphenyl)-2-methyl-thien-3-yl]perfluorocyclopentene[58] (200 mg, 0.50 mmol, 0.90 equiv) in THF (2 mL) was cooled to −78 °C, and added by using a cannula to the lithiated thiophene. The resulting yellow solution was stirred for 4 h at this temperature and then allowed to warm up to room temperature. Stirring was continued for a total of 16 h until TLC monitoring indicated complete conversion of the starting material. The reaction mixture was quenched with HCl (20 mL, 1 M) and then extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with water (25 mL), dried ($MgSO_4$), and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/CH_2Cl_2 (5:1) to give compound **7a** as a blue solid (230 mg, 0.36 mmol, 71%); mixture of isomers (*O*-isomer/*C*-isomer ≥ 95:5 as determined by ^{1}H NMR). *C*-isomer: R_f=0.77 (hexane/CH_2Cl_2, 2:1); *O*-isomer: R_f=0.72 (hexane/CH_2Cl_2, 2:1); m.p.: 80–83 °C; IR (ATR): $\tilde{\nu}$=3076, 3032, 3001, 2959, 2935, 2855, 2837, 2157, 1705, 1610, 1556, 1516, 1475, 1492, 1466, 1441, 1337, 1301, 1273, 1251, 1190, 1179, 1138, 1111, 1092, 1055, 988, 898, 887, 864, 843, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.47–7.45 (m, 6H), 7.30 (br s, 1H), 7.15 (br s, 1H), 6.93–6.90 (m, 2H), 3.84 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 0.27 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.7, 142.4, 142.1, 141.5, 140.4, 133.4, 132.7, 127.1, 126.3, 126.2, 125.8, 125.3, 123.1, 122.6, 121.4, 114.5, 104.8, 95.7, 55.6, 14.8, 14.7, 0.1 ppm; HRMS (EI): *m*/*z* (%) calcd for $C_{33}H_{29}F_6OS_2Si$: 647.1333 [M^++H]; found: 647.1332; elemental analysis: calcd (%) for $C_{33}H_{28}F_6OS_2Si$ (646.78): C 61.28, H 4.36; found: C 61.40, H 4.63.

1-[5-(4-Methoxyphenyl)-2-methylthienyl-3-yl]-2-[2-methyl-5-(4-ethynyl-phenyl)-thien-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (**7b**):[43] To a vigorously stirred solution of the TMS-protected dithienylethene **7a** (100 mg, 0.15 mmol) in MeOH (7 mL), NaOH (45.0 mg, 1.13 mmol, 7.30 equiv) was added. After stirring for 2.5 h at ambient temperature, TLC indicated complete conversion of the starting material. Then, water (10 mL) and CH_2Cl_2 (10 mL) were added to the blue reaction mixture. The aqueous phase was separated and extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/CH_2Cl_2 (2:1) to give product **7b** as a blue solid (82.0 mg, 0.14 mmol, 92%); mixture of isomers (*O*-isomer : *C*-isomer ≥95:5 as determined by ^{1}H NMR). *C*-isomer: R_f=0.65 (hexane/CH_2Cl_2, 2:1); *O*-isomer: R_f=0.60 (hexane/CH_2Cl_2, 2:1); m.p.: 125–127 °C; IR (ATR): $\tilde{\nu}$=3301, 3075, 3032, 3001, 2954, 2924, 2853, 2107, 1717, 1662, 1608, 1572, 1557, 1515, 1492, 1475, 1465, 1440, 1394, 1380, 1338, 1301, 1274, 1252, 1190, 1179, 1138, 1110, 1092, 1055, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.50 (s, 4H), 7.49–7.45 (m, 2H), 7.31 (br s, 1H), 7.16 (br s, 1H), 6.94–6.90 (m, 2H), 3.84 (s, 3H), 3.15 (s, 1H), 1.99 (s, 3H), 1.96 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.7, 142.4, 142.2, 141.4, 140.4, 133.8, 132.9, 127.1, 126.3 (2C), 125.8, 125.5, 123.3, 121.6, 121.4, 114.6, 83.4, 78.5, 55.6, 14.8, 14.6 ppm; MS (70 eV): *m*/*z* (%): 574 (100) [M^+], 559 (22), 544 (20), 151 (10), 69 (10); HRMS (EI): *m*/*z* (%) calcd for $C_{30}H_{20}F_6OS_2$: 574.0860; found: 574.0853.

General procedure for the Sonogashira cross-coupling of 2-chloro-5-methylthiophene (9) with silylprotected acetylenes: A thick-walled Schlenk tube was evacuated, heated under vacuum, and refilled with argon three times. Then, the Schlenk tube was charged with [$PdCl_2(CH_3CN)_2$], X-Phos, and Cs_2CO_3 or K_3PO_4 (2.60 equiv) followed by the thienyl chloride **9** (61.3 mg, 0.46 mmol) and acetonitrile (0.92 mL) under a positive pressure of argon. The yellow suspension was degassed (5 min, ultrasound) and then stirred for 30 min at room temperature. Afterwards, the alkyne (0.60 mmol, 1.3 equiv) was added using a syringe, and the tube was sealed with a teflon valve. The reaction mixture was stirred at the desired temperature for the indicated period of time (TLC monitoring). After complete consumption of the starting material, the resulting suspension was allowed to reach room temperature, was diluted with water (5 mL), and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried ($MgSO_4$), concentrated in vacuo, and the residue was purified by flash chromatography on silica gel (hexane) to provide the desired product.

2-(Triethylsilylethynyl)-5-methylthiophene (**11a**): According to the general procedure, compound **11a** was obtained by the reaction of 2-chloro-5-methylthiophene (**9**) (61.3 mg, 0.46 mmol) with triethylsilylacetylene (**10a**) (84.2 mg, 0.60 mmol, 1.30 equiv), [$PdCl_2(CH_3CN)_2$] (1.2 mg, 4.6 μmol, 1 mol%), X-Phos (6.6 mg, 13.8 μmol, 3 mol%), and Cs_2CO_3 (391 mg, 1.20 mmol, 2.60 equiv) for 17 h at 100 °C in acetonitrile (0.92 mL) to give product **11a** (83.0 mg, 0.35 mmol, 76%) as a yellow oil. R_f=0.49 (hexane); IR (ATR): $\tilde{\nu}$=3074, 2955, 2934, 2912, 2874, 2734, 2143, 1744, 1537, 1458, 1414, 1379, 1236, 1178, 1154, 1018, 1007, 974, 797, 762, 735, 728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.03 (d, J=3.5 Hz, 1H), 6.59 (dq, J=1.0 Hz, 3.4 Hz, 1H), 2.45 (d, J=1.0 Hz, 3H), 1.04 (t, J=7.9 Hz, 9H), 0.67 ppm (q, J=7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.1, 133.0, 125.2, 121.1, 99.3, 95.5, 15.5, 7.6, 4.5 ppm; MS (70 eV): *m*/*z* (%): 236 (30) [M^+], 207 (100), 179 (76), 151 (88); HRMS (EI): *m*/*z* (%) calcd for $C_{13}H_{20}SSi$: 236.1055; found: 236.1065.

2-(Triisopropysilylethynyl)-5-methylthiophene (**11c**): **Method A**: According to the general procedure, compound **11c** was obtained by the reaction of 2-chloro-5-methylthiophene (**9**) (61.3 mg, 0.46 mmol) with triisopropylsilylacetylene (**10b**) (109 mg, 0.60 mmol, 1.30 equiv), [$PdCl_2(CH_3CN)_2$] (12.0 mg, 46.2 μmol, 10 mol%), X-Phos (66.1 mg, 138 μmol, 30 mol%), and Cs_2CO_3 (391 mg, 1.20 mmol, 2.60 equiv) at 100 °C for 2.5 h in acetonitrile (0.92 mL) to give product **11c** as a yellow oil (118 mg, 0.43 mmol, 92%).

Method B: According to the general procedure, compound **11c** was obtained by the reaction of 2-chloro-5-methylthiophene (**9**) (61.3 mg, 0.46 mmol) with triisopropylsilylacetylene (**10b**) (109 mg, 0.60 mmol, 1.30 equiv), [$PdCl_2(CH_3CN)_2$] (12.0 mg, 46.2 μmol, 10 mol%), X-Phos (66.1 mg, 138 μmol, 30 mol%), and K_3PO_4 (255 mg, 1.20 mmol, 2.60 equiv) for 17 h at 80 °C in acetonitrile (0.92 mL) to give product **11c** as a yellow oil (110 mg, 0.39 mmol, 85%). R_f=0.64 (hexane); IR (ATR):

$\tilde{\nu}$ = 3073, 2957, 2936, 2942, 2924, 2891, 2865, 2143, 1744, 1537, 1462, 1383, 1178, 1154, 996, 883, 797, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, J = 3.6 Hz, 1H), 6.60 (dq, J = 1.1 Hz, 3.6 Hz, 1H), 2.45 (d, J = 1.1 Hz, 3H), 1.12 ppm (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 132.7, 125.2, 121.4, 100.0, 94.4, 18.8, 15.5, 11.5 ppm; HRMS (EI): m/z (%) calcd for $C_{16}H_{26}SSi$: 278.1524; found: 278.1517; elemental analysis: calcd (%) for $C_{16}H_{26}SSi$ (278.5): C 69.00, H 9.41; found: C 68.88, H 9.41.

1-[5-(4-Methoxyphenyl)-2-methylthienyl-3-yl]-2-[2-methyl-5-(triisopropylsilyl-ethynyl)thien-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (**15b**): A thick-walled Schlenk tube was evacuated, heated under vacuum, and refilled with argon three times. Then, the Schlenk tube was charged under a positive pressure of argon with dithienylethene **4** (50.0 mg, 98.2 μmol), $[PdCl_2(CH_3CN)_2]$ (2.5 mg, 9.8 μmol, 10 mol%), X-Phos (14.0 mg, 29.4 μmol, 30 mol%), K_3PO_4 (54.1 mg, 255 μmol, 2.60 equiv), and acetonitrile (0.20 mL). The bluish suspension was degassed (5 min, ultrasound) and stirred for 30 min, before triisopropylsilylacetylene (**10b**) (23.2 mg, 127 μmol, 1.3 equiv) was added using a syringe. The Schlenk tube was sealed with a teflon valve, and the resulting suspension was stirred for 24 h at 80 °C (TLC monitoring). The resulting brown suspension was allowed to reach room temperature, was diluted with water (5 mL), and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc (10:1) to give product **15b** as a bluish solid (37.0 mg, 56.5 μmol, 58%) besides by-product **16**; mixture of isomers (*O*-isomer : *C*-isomer ≥ 95:5 as determined by ^1H NMR). *C*-isomer: R_f = 0.73 (hexane/CH_2Cl_2, 2:1); *O*-isomer: R_f = 0.67 (hexane/CH_2Cl_2, 2:1); m.p.: 104–107 °C; IR (ATR): $\tilde{\nu}$ = 2956, 2943, 2865, 2146, 1709, 1610, 1572, 1554, 1515, 1473, 1463, 1441, 1420, 1337, 1300, 1273, 1253, 1192, 1178, 1137, 1112, 1090, 1051, 1037, 987, 883, 823, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 2H), 7.21 (br s, 1H), 7.12 (br s, 1H), 6.93–6.90 (m, 2H), 3.84 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H), 1.12 ppm (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 143.2, 142.5, 140.5, 131.9, 127.1, 126.3, 125.6, 125.0, 122.1, 121.3, 114.5, 98.3, 96.8, 55.6, 18.8, 14.7, 14.6, 11.4 ppm; HRMS (EI): m/z (%) calcd for $C_{33}H_{36}F_6OS_2Si$: 654.1881; found 654.1874; elemental analysis: calcd (%) for $C_{33}H_{36}F_6OS_2Si$ (654.84): C 60.53, H 5.54; found: C 60.49, H 5.80.

16: 1,2-Bis{[5-(4-methoxyphenyl)-2-methylthiophen-3-yl)-2-(5-phenyl-2-methylthiopen-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene}ethyne (**16**) was isolated as a blue solid (4.8 mg, 4.9 μmol, 10%); mixture of isomers (*O*-isomer : *C*-isomer ≥ 95:5 as determined by ^1H NMR). *C*-isomer: R_f = 0.14 (hexane/CH_2Cl_2, 5:1); *O*-isomer: R_f = 0.10 (hexane/CH_2Cl_2, 5:1); m.p.: 160–162 °C; IR (ATR): $\tilde{\nu}$ = 3075, 3033, 3000, 2956, 2924, 2853, 1725, 1706, 1610, 1554, 1515, 1473, 1465, 1440, 1337, 1273, 1253, 1192, 1138, 1113, 1091, 1053, 1035, 986, 899, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.45 (m, J = 8.8 Hz, 4H), 7.29 (br s, 2H), 7.13 (br s, 2H), 6.93–6.91 (m, J = 8.8 Hz, 4H), 3.84 (s, 6H), 1.94 (s, 6H), 1.93 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 144.2, 142.6, 140.5, 132.3, 127.1, 126.3, 125.6, 125.5, 121.3, 120.9, 114.6, 86.1, 55.6, 14.7 ppm (2C); MS (70 eV): m/z (%): 970 (100) [M^+], 546 (10), 312 (22), 191 (15), 130 (20), 119 (62), 105 (70), 91 (20), 77 (18); HRMS (EI): m/z (%) calcd for $C_{46}H_{30}F_{12}O_2S_4$: 970.0937; found: 970.0933.

Dithienylethene-linker-conjugate 1: A thick-walled Schlenk tube was evacuated, heated under vacuum, and refilled with argon three times. Then, the Schlenk tube was charged under a positive pressure of argon with dithienylethene **4** (35.0 mg, 68.7 μmol), **[**$PdCl_2(CH_3CN)_2$] (1.8 mg, 6.9 μmol, 10 mol%), X-Phos (9.8 mg, 20.6 μmol, 30 mol%), K_3PO_4 (38.0 mg, 179 μmol, 2.60 equiv), and acetonitrile (0.14 mL). The bluish suspension was degassed (5 min, ultrasound) and stirred for 30 min before the tripod **5** (60.7 mg, 89.3 μmol, 1.30 equiv) was added. Afterwards, the Schlenk tube was sealed with a teflon valve, and the suspension was stirred for 4 h at 80 °C (TLC monitoring). The resulting suspension was allowed to reach room temperature, and was diluted with water (15 mL) and EtOAc (15 mL). The aqueous phase was separated and extracted with EtOAc (3×15 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc (5:1) to give product **1** as a bluish solid (52.0 mg, 45.1 μmol, 65%); mixture of isomers (*O*-isomer : *C*-isomer ≥ 95:5 as determined by ^1H NMR). *O*/*C*-isomer: R_f = 0.35 (hexane/EtOAc 5:1); m.p.: 119–122 °C; IR (ATR): $\tilde{\nu}$ = 3523, 3059, 3038, 2978, 2929, 2902, 2853, 1714, 1609, 1571, 1553, 1509, 1475, 1464, 1443, 1366, 1338, 1275, 1253, 1188, 1179, 1143, 1104, 1019, 986, 897, 854, 831, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 6H), 7.56 (d, J = 8.5 Hz, 6H) 7.53–7.45 (m, 6H), 7.28 (br s, 1H), 7.14 (br s, 1H), 6.93–6.90 (m, 2H), 4.39 (q, J = 7.1 Hz, 6H), 3.83 (s, 3H), 2.21–2.20 (m, 12H), 1.95 (s, 3H), 1.94 (s, 3H) 1.40 ppm (t, J = 7.1 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 159.7, 153.8, 149.5, 143.4, 142.5, 140.5, 131.7, 131.6, 129.9, 128.8, 127.1, 126.2, 125.6, 125.3, 125.2, 121.8, 121.2 (2C), 120.7, 114.5, 93.8, 81.7, 61.1, 55.5, 46.8 (2C), 39.7, 39.5, 14.7, 14.6, 14.5 ppm; HRMS (EI): m/z (%) calcd for $C_{67}H_{56}F_6O_7S_2$ [M^+−2H]: 1150.3372; found: 1150.3321; elemental analysis: calcd (%) for $C_{67}H_{58}F_6O7S_2$ (1153.29): C 69.78, H 5.07; found: C 70.07, H 5.33.

Dithienylethene-linker-conjugate 2: A thick-walled Schlenk tube was evacuated, heated under vacuum, and refilled with argon three times. Then, the Schlenk tube was charged under a positive pressure of argon with dithienylethene **6** (30.0 mg, 47.6 μmol), $[PdCl_2(CH_3CN)_2]$ (1.2 mg, 4.8 μmol, 10 mol%), X-Phos (6.8 mg, 14.3 μmol, 30 mol%), K_3PO_4 (26.1 mg, 123 μmol, 2.60 equiv), and acetonitrile (0.01 mL). The bluish suspension was degassed (5 min, ultrasound) and stirred for 30 min before compound **5** (42.0 mg, 61.9 μmol, 1.30 equiv) was added. Afterwards, the Schlenk tube was sealed with a teflon valve and the suspension was stirred at 80 °C for 4 h (TLC monitoring). Then, the resulting suspension was allowed to reach room temperature and was diluted with water (15 mL) and EtOAc (15 mL). The aqueous phase was separated and extracted with EtOAc (3×15 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc (5:1) to give compound **2** as a bluish solid (45.0 mg, 36.6 μmol, 76%); mixture of isomers (*O*-isomer : *C*-isomer ≥ 95:5 as determined by ^1H NMR). *O*/*C*-isomer: R_f = 0.32 (hexane/EtOAc, 5:1); m.p.: 140–143 °C; IR (ATR): $\tilde{\nu}$ = 2979, 2932, 2902, 2854, 1716, 1609, 1515, 1336, 1277, 1255, 1188, 1106, 1019, 989, 833, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.8 Hz, 6H), 7.57–7.52 (m, 12H), 7.49–7.45 (m, 4H), 7.31 (br s, 1H), 7.15 (br s, 1H), 6.93–6.90 (m, 2H), 4.38 (q, J = 7.1 Hz, 6H), 3.84 (s, 3H), 2.21 (s, 12H), 1.99 (s, 3H), 1.97 (s, 3H) 1.40 ppm (t, J = 7.1 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 159.7, 153.9, 149.2, 142.4, 142.0, 141.6, 140.4, 133.2, 132.3, 131.9, 130.0, 128.9, 127.1, 126.3 (2C), 125.8, 125.5, 125.24, 125.18, 123.1, 122.8, 121.4 (2C), 114.5, 90.6, 89.2, 61.1, 55.5, 46.9, 46.8, 39.8, 39.5, 14.8, 14.7, 14.5 ppm; MS (70 eV): m/z (%): 1226 (30) [M^+−2H], 712 (10) 655 (10), 549 (17), 433 (10), 368 (17), 278 (15), 214 (18), 163 (20), 139 (42), 97 (57), 71 (65), 57 (100); HRMS (EI): m/z (%) calcd for $C_{73}H_{60}F_6O_7S_2$ [M^+−2H]: 1226.3685; found: 1226.3727.

Dithienylethene-linker-conjugate 3: **Method A**: A flask was charged with iodo-tripod **8** (50.0 mg, 48.0 μmol), dithienylethene **7b** (55.0 mg, 96.2 μmol, 2.00 equiv), $Pd_2(dba)_3$ (22.0 mg, 24.0 μmol, 50 mol%), P(*o*-tol)$_3$ (43.8 mg, 144 μmol, 300 mol%) in Et_3N (7.4 mL), and dry THF (15 mL). The resulting reaction mixture was stirred at 60 °C for 24 h under argon atmosphere (TLC monitoring), then cooled to room temperature and poured into water (20 mL). Then, the reaction mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with water (10 mL), dried ($MgSO_4$), and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc (4:1) to give compound **3** as a blue solid (27.0 mg, 18.1 μmol, 38%); mixture of isomers (*O*-isomer : *C*-isomer ≥ 95:5 as determined by ^1H NMR).

Method B: A thick-walled Schlenk tube was evacuated, heated under vacuum, and refilled with argon three times. Then, the Schlenk tube was charged under a positive pressure of argon with iodo-tripod **8** (25.0 mg, 24.0 μmol), **[**$PdCl_2(CH_3CN)_2$] (0.6 mg, 2.4 μmol, 10 mol%), X-Phos (3.4 mg, 7.2 μmol, 30 mol%), K_3PO_4 (13.3 mg, 62.4 μmol, 2.60 equiv), and acetonitrile (240 μL). The bluish suspension was degassed (5 min, ultrasound) and stirred for 30 min before the dithienylethene **7b** (17.9 mg, 31.2 μmol, 1.30 equiv) was added. Afterwards, the Schlenk tube was sealed with a teflon valve, and the suspension was stirred for 20 h at 80 °C (TLC monitoring). The resulting suspension was allowed to reach room temperature, and diluted with water (5 mL) and EtOAc (5 mL). The aqueous phase was separated and extracted with EtOAc (3×5 mL).

The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using hexane/EtOAc (4:1) to give product **3** as a bluish solid (9.0 mg, 6.0 μmol, 25%); mixture of isomers (*O*-isomer : *C*-isomer ≥ 95:5 as determined by ^{1}H NMR). *O*/*C*-isomer: R_f = 0.19 (hexane/EtOAc, 5:1); m.p.: 111–114 °C; IR (ATR): $\tilde{\nu}$ = 3495, 3068, 3033, 2952, 2923, 2851, 2208, 1908, 1725, 1600, 1579, 1511, 1491, 1463, 1438, 1406, 1357, 1338, 1321, 1304, 1279, 1257, 1191, 1179, 1143, 1112, 1103, 1080, 1054, 1018, 988, 897, 888, 832, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (t, *J* = 1.64 Hz, 3H), 8.00 (dt, *J* = 1.60 Hz, 7.84 Hz, 3H), 7.71 (dt, *J* = 1.48 Hz, 7.80 Hz, 3H), 7.57–7.41 (m, 25H), 7.32 (br s, 1H), 7.16 (br s, 1H), 6.93–6.90 (m, 2H), 3.94 (s, 9H), 3.84 (s, 3H), 2.19 (s, 12H), 1.98 (s, 3H), 1.96 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 159.7, 149.6, 149.5, 142.4, 142.0, 141.6, 140.4, 135.8, 133.2, 132.9, 132.3, 132.0, 131.9, 130.6, 129.3, 128.7, 127.1, 126.30, 126.27, 125.8, 125.5, 125.32, 125.30, 124.0, 123.1, 122.9, 121.4, 121.3, 121.0, 114.6, 90.7, 90.3, 89.2, 88.4, 55.6, 52.4, 47.0 (2C), 39.6 (2C), 14.8, 14.7 ppm; MS (70 eV): *m*/*z* (%): 1490 (100) [M^++3H], 1412 (10), 1253 (20), 1251 (25); HRMS (ESI): *m*/*z* (%) calcd for $C_{94}H_{69}F_6O_7S_2$: 1487.4383; found: 1487.4373.

Dithienylethene-linker-conjugate 18: The methyl ester **3** (5.0 mg, 3.4 μmol) was dissolved in THF (0.8 mL), and NaOH (1 M, 0.2 mL) was added. The resulting solution was stirred at room temperature until TLC monitoring indicated no further conversion of the starting material (47 h). Then, the mixture was extracted with CH_2Cl_2 (3 × 1 mL). Afterwards, the aqueous phase was acidified with HCl (2 M, 0.2 mL) and extracted with $CHCl_3$ (3 × 1 mL). Subsequent evaporation of the solvent in vacuo afforded compound **18** as a blue solid (4.0 mg, 2.8 μmol, 82%); mixture of isomers (*O*-isomer : *C*-isomer ≥95:5 as determined by ^{1}H NMR). *O*/*C*-isomer: R_f = 0.68 (EtOAc/AcOH, 80:1); m.p.: 201–204 °C; IR (ATR): $\tilde{\nu}$ = 3335, 3065, 3034, 2927, 2852, 2616, 2210, 1911, 1704, 1602, 1559, 1511, 1463, 1439, 1386, 1273, 1253, 1180, 1137, 1114, 1054, 1035, 988, 833, 768, 760 cm^{-1}; ^{1}H NMR (400 MHz, [D_8]THF): δ = 8.16 (s, 3H), 7.98 (d, *J* = 7.7 Hz, 3H), 7.70 (d, *J* = 7.8 Hz, 3H), 7.69–7.63 (m, 9H), 7.56–7.44 (m, 17H), 7.27 (br s, 1H), 6.94–6.92 (m, 2H), 3.79 (s, 3H), 2.24 (s, 12H), 2.02 (s, 3H), 2.00 ppm (s, 3H); ^{13}C NMR (100 MHz, [D_8]THF): δ = 165.9, 159.9, 150.3, 150.2, 142.6, 142.0, 141.6, 140.2, 135.0, 132.9, 132.5, 131.9, 131.4, 131.3, 129.1, 128.4, 126.6, 126.0, 125.8 (2C), 125.5, 125.3 (2C), 125.2, 123.7, 123.0, 122.9, 121.0, 120.8, 120.6, 114.2, 90.5, 89.9, 88.5, 87.8, 54.6, 46.5 (2C), 39.5 (2C), 13.6, 13.5 ppm; MS (FAB): *m*/*z* (%): 1444 (10) [M^+], 413 (15), 282 (45), 242 (100); HRMS (ESI): *m*/*z* (%) calcd for $C_{91}H_{61}F_6O_7S_2$ [M^+−H]: 1443.3757; found: 1443.3784.

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