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1,3-Bicyclo[1.1.1]pentanediyl: The Shortest Rigid Linear Connector of Phenylated Photochromic Units and a 1,5-Dimethoxy-9,10-di(phenylethynyl)anthracene Fluorophore

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Abstract: An excess of bis-1,3-(4-iodophenyl)bicyclo[1.1.1]pentane, prepared in 63 % yield by iodination of 1,3-diphenylbicyclo[1.1.1]pentane, was selectively mono-coupled with 9-ethynyl-1,5-dimethoxy-10-phenylethynylanthracene (**26**), and subsequently with the zinc derivatives of 1-(2-methyl/methoxy-4-methyl-5-phenylthiophen-3-yl)-2-(2-methyl/methoxy-4-methylthiophen-3-yl)perfluorocyclopentenes (**38**-H–**41**-H). Regioselective synthesis of the 2-unsubstituted thiophenes **38**-H–**41**-H required intermediate preparation of 2-trimethylsilyl-3,5-dimethyl-4-bromothiophene (**37**) or 2-trimethylsilyl-5-methoxy-3-methyl-4-bromothiophene (**40**). Protection of the α-position of the thiophene ring with a 2-trimethylsilyl group blocks the rearrangement of the 4-lithio derivatives into the corresponding 2-lithiated thiophenes. With the bicyclo[1.1.1]pentane fragment linking the photochromic units **1**–**3** and 1,5-dimethoxy-9,10-di(phenylethynyl)anthracene as a fluorescent part, quantitative resonance energy transfer between the excited state of the fluorophore (donor) and the closed form of the photochromic units **1**–**3** (acceptors) was observed. The closed forms of the methoxy-substituted photochromic units **2** and **3** are less resistant to UV light (313 nm) than the closed form of **1**.

Keywords: bicyclo[1.1.1]pentane · fluorescence · molecular switches · photochromism · thiophenes

Introduction

Bicyclo[1.1.1]pentane and its derivatives are not only of theoretical interest, but have attracted particular attention of organic and physical-organic chemists as peculiar fragments in oligomers, liquid crystalline compounds, supramolecular aggregates and monolayers, as well as compounds for drug design, etc.[1] 1,3-Disubstituted derivatives—bicyclo[1.1.1]-pentanes with blocked bridgehead positions—are rigid rod-like molecules which, in spite of their high strain energy, are remarkably thermally stable, resistant to oxygen and organometallic reagents. Bicyclo[1.1.1]pentane is transparent in the UV and visible light region, and because of its very short C^1–C^3 distance of approximately 1.87 Å, it can serve as a unique linker or bridge between two unsaturated molecular fragments, if their close proximity, yet without any significant π-conjugation, is desired. According to previous work from our own[2] as well as from another group,[3] 1,3-diarylbicyclo[1.1.1]pentanes can be prepared. Thus, it ought to be possible to incorporate the bicyclo[1.1.1]pentane unit between any two aromatic systems, for example, between a fluorescent group and a photochromic part (Figure 1). Mate-

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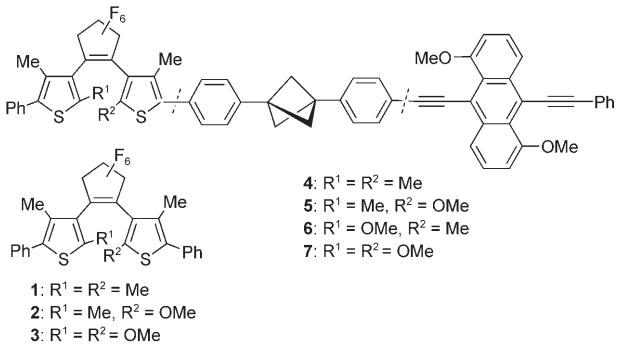
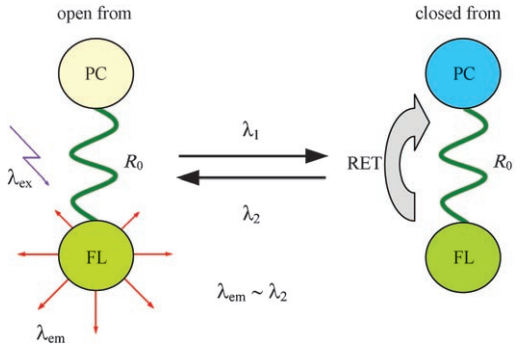


Figure 1. Photochromic compounds **1**–**3** and bicyclo[1.1.1]pentane-bridged assemblies thereof **4**–**7** with 1,5-dimethoxy-bis(9,10-phenylethynyl)anthracene.

rials containing covalently bound photochromes and fluorophores have been proposed as (rewritable) data storage media, in which fluorescence is reversibly switched "on" and "off", depending on the state of the photochromic part (Scheme 1). Moreover, a new concept of far-field optical imaging and writing recently emerged, attaining diffraction-unlimited spatial resolution through molecular photoswitching.[4]

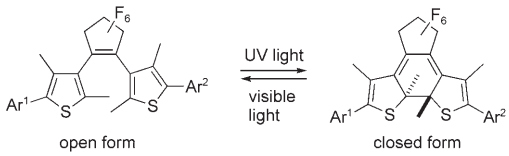


Scheme 1. Resonance energy transfer (RET) between the closed form of the photochromic unit (PC) and the fluorophore (FL) connected by a bridge with length R_0: λ_1 (UV light), which "closes" the PC and switches off the fluorescence; λ_2 (visible light), which restores the initial state of the PC unit and switches on the fluorescence; λ_{ex} (excitation light), which probes fluorescence; λ_{em} (emitted light). Fluorescence is efficiently quenched, if λ_{max} of the closed form (λ_2) is near to λ_{em} and $R_0 < R_F$, where R_F is the Foerster radius (distance between PC and FL, where the efficiency of the energy transfer (E_{RET}) is 50%); $E_{RET} \approx R_F^6/(R_F^6 + R_0^6)$.[5]

This novel lens-based optical microscopy concept has the potential to visualize subcellular components in biology with the resolution of a fraction of the wavelength of light, as well as the optical writing of nanostructured patterns down to the size of a few molecules.[4a] In fact, breaking the diffraction barrier in fluorescence microscopy has been demonstrated by other "switchable" optical transitions between a fluorescent and a non-fluorescent state, such as the de-excitation by stimulated emission of a fluorophore from the fluorescent state to the ground state. Referred to as stimulated emission depletion (STED), this microscopy modality has so far produced a resolution of 16 nm in the focal plane with light intensities of about 1 GW per cm^2.[4b] These high intensities can be drastically reduced if the lifetime of the (conformational) state capable of emitting fluorescence photons and to be switched-off is increased.[4c] Reversibly photoswitchable fluorescent dyes that feature long-lived or even fully stable states, allow a reduction of several orders of magnitude in the applied intensities.[4d] To provide subdiffraction resolution, the switchable dyes should possess a high fluorescence modulation and a large photostability. High fluorescence quantum yields (Φ_{Fl}) are also desirable to increase the sensitivity of the method and to reduce the imaging times.

A convenient and flexible way to achieve fluorescence modulation[6] is to connect a photochromic compound[7] to a fluorescent dye. The two moieties may be attached without any linker,[8] or through a spacer.[9] The mechanism of the fluorescence modulation is resonance energy transfer (RET)[5] from the fluorescent dye selectively to one of the isomers of the photochromic switch. Only this isomer (acceptor) should have an absorption band, which overlaps with the emission band of the fluorophore (donor). Most often it is the closed form (CF). This kind of overlap means that the corresponding transition energies of the donor and acceptor units are similar, and, therefore, the effective RET from the excited state of the donor (fluorophore) to the CF of the acceptor quenches the emission of light (Scheme 1).

Diheteroarylethenes display excellent photochromic properties, such as low fatigue, good chemical and thermal stability, and can be reversibly switched between a colorless open form (OF) and a colored CF.[7a] The forward reaction is performed with UV light, while the reversal is performed with green or red light (Scheme 2).



Scheme 2. Photochromism of 1,2-bis(thiophen-3-yl)hexafluorocyclopentenes.

Surprisingly, up to now only four reports deal with fluorophores, which have been connected to the photochromic 1,2-bis(thiophen-3-yl)perfluorocyclopentenes by way of a linker.[9] Meanwhile, this modular approach allows one to construct various combinations of donors and acceptors with great flexibility. A linker, for example, a bicyclo[1.1.1]pentane unit, breaks π-conjugation between them, and thus the regularities of RET in the molecular design may be used, without any unpredictable perturbations caused by the overlapping of the π-systems.[5]

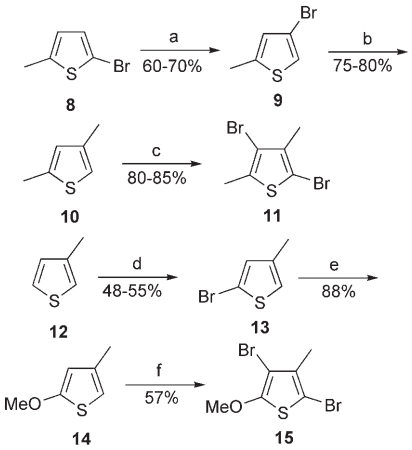
For example, when anthracene was bound through a CH_2 group to an acceptor, 87% conversion to the non-fluores-

cent CF was observed at the photostationary state (PS) at 355 nm.[9a] Irie et al. used a 1,3-adamantanediyl bridge and studied in detail the single molecule properties of highly fluorescent 2,5-dimethoxybis(9,10-phenylethynyl)anthracene linked with two photochromic units—a symmetrical 1,2-bis(2-methoxy-4-methyl-5-phenylthiophen-3-yl)perfluorocyclopentane and a nonsymmetrical derivative with a methyl group at C-2 and a methoxy group at C-2′.[9c] The symmetrical compound with two methoxy groups has one of the lowest photocycloreversion quantum yields ever reported ($<10^{-4}$ in toluene at 630 nm), while the non-symmetrical assembly has a higher value (1.5×10^{-3} at 600 nm). No quantitative data on the residual fluorescence in solution have been published. The closed form of the symmetrical adduct was found to be "almost nonfluorescent".[9c] The spectral properties and the behavior of the photochromic unit **2** also have not yet been reported.[11b] In another study,[9b] an assembly in which a relatively long and flexible cadaverine linker acylated with succinic or butanoic acid residues connected the Lucifer Yellow with different acceptors, the decrease in fluorescence was found to be 65 or 84% in the PS state (in MeOH, at 313 and 320 nm, respectively). Interestingly, the photochromic units alone, without the fluorophore, were converted to the closed forms nearly quantitatively by irradiation even at the band edge (340 nm; 92 and 97% conversion for 2-methyl- and 2-methoxybenzo[*b*]thiophene derivatives, respectively).[9b]

In order to be able to select appropriate high-performing photoswitchable fluorescent compounds for utilization in microscopy techniques with sub-diffraction resolution, it was necessary to first identify stable photochromic units with full conversion to the closed form. Towards this goal, we prepared the photochomic compound **2**, studied its photoreactions in solution in comparison with those of the previously known derivatives **1**[10] and **3**,[11] and then connected all of them by way of a bicyclo[1.1.1]pentane bridge with the fluorophore, 1,5-dimethoxy-bis(9,10-phenylethynyl)anthracene (Figure 1). The latter has a bright yellow-green fluorescence with a high $\Phi_{Fl}=72\%$,[9c,12] and its emission maximun (537 nm) overlaps with the absorption bands of the compounds **1**–**3** in the CFs. The rigid bicyclo[1.1.1]pentane fragment is the shortest linear non-π-system linker ever possible. A very short distance and the favorable mutual orientation of the dipole transition moments of the donor and the acceptor provides the RET efficiency to be as high as possible (even if there will be no perfect overlap of the donor and acceptor absorption bands).[5] From the non-symmetrical photochromic unit **2** we prepared two mono-methoxy substituted photoswitches **5** and **6**. We hoped that one methoxy group would be sufficient for the quantitative photocyclization and good fluorescence modulation at the photostationary state, and at the same time the quantum yield of the ring-opening reaction would not be too low, so that numerous cycles might be performed in a reasonable time.

Results and Discussion

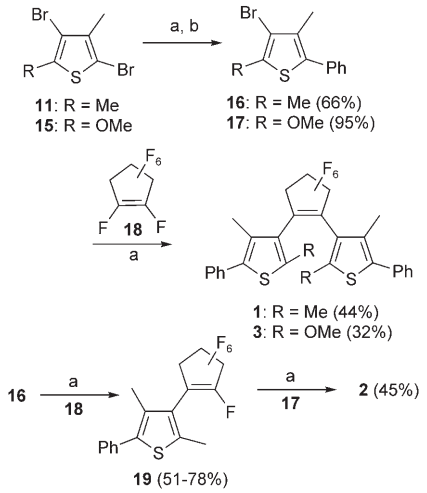
Synthesis of the photochromic unit 2 and the fluorescent switches 4–7: A general approach to the symmetrical photochromic compounds **1** and **3** has been reported,[10,11] and towards those 2,4-dibromothiophene derivatives **11** and **15** had to be prepared. They may, in fact, be easily obtained from the 2,4-disubstituted thiophenes **10** and **14**. However, no well established preparation of 2,4-dimethylthiophene (**10**) could be found in the literature. Several routes leading to **10** were tried,[13] and the best one was found to be that based on the so-called "halogen dance" in 2-bromo-5-methylthiophene (**8**)[14] followed by a Kumada coupling of the resulting 4-bromo-2-methylthiophene (**9**) with methylmagnesium chloride (Scheme 3).[15]



Scheme 3. Preparation of 2,4-dimethylthiophene (**10**), 2-methoxy-4-methylthiophene (**14**), 2,4-dibromo-3,5-dimethylthiophene (**11**) and 2,4-dibromo-3-methyl-5-methoxythiophene (**15**): a) LDA (1.0 equiv), THF, −78°C, then MeOH; b) MeMgCl, [Ni(dppp)Cl_2], Et_2O/THF, 0°C → reflux; c) Br_2, AcOH, NaOAc; d) *n*BuLi (2.5 M in hexanes), TMEDA, Et_2O, RT → reflux, then CBr_4, Et_2O, −78°C → RT; e) MeONa, MeOH, CuBr, reflux; f) NBS, CCl_4, 0°C → RT, 2 h.

2-Methoxy-4-methylthiophene (**14**) is most conveniently prepared from 3-methylthiophene (**12**), which may be selectively deprotonated at the 5-position, followed by quenching of the resulting 2-lithio-4-methyl derivative with CBr_4.[16] Substitution of the bromine atom in **13** by a methoxy group proceeded according to the standard protocol.[17] Bromination of **10** to yield the dibromide **11** had previously been reported.[10] Bromination of **14** occurred smoothly only under conditions, which had previously been used for the preparation of the corresponding dibromide from 2-methoxythiophene.[18] Both dibromides **11** and **15** are low-melting solids, which should be kept at low temperature to avoid decomposition, if storage for prolonged time is desired.

To complete the synthesis of the photochromic compounds **1**–**3**, the phenylated thiophenes **16** and **17** were prepared first, and then they were coupled with perfluorocyclopentene (Scheme 4). Slow addition of a perfluorocyclopentene solution (1 equiv) to the lithiated intermediates **16** and

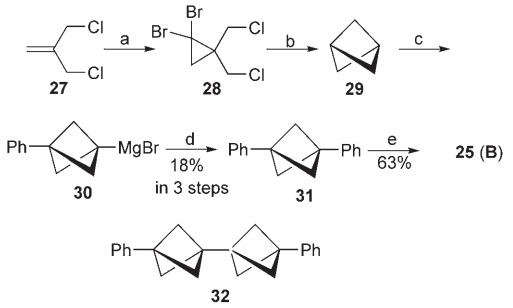


Scheme 4. Synthesis of the photochromic compounds **1**–**3**: a) *n*BuLi (2.5 M in hexanes), THF, −78 °C; b) $ZnCl_2$ (1 M in Et_2O), −78 → 0 °C, then PhI with [Pd(dba)$_2$] (4 mol %), Ph_3P, THF, 0 → 50 °C.

17 (2 equiv) at −78 °C produced the symmetrical compounds **1**[10] and **3**,[11] while the reverse mode of addition, that is, of the lithiated precursor **16** to an excess of **18**, gave first the crystalline mono-coupling product **19**,[19] which was isolated and coupled with the thiophene derivative **17** to produce the unsymmetrical photochromic unit **2**. Compounds **1**–**3** were isolated from the reaction mixtures by column chromatography, and then recrystallized several times from methanol in the dark.

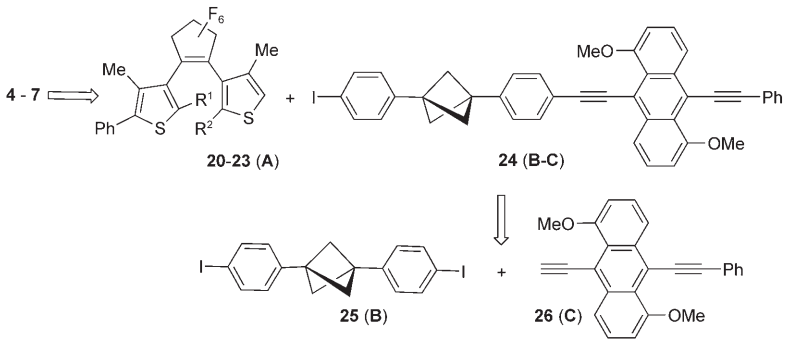
For the assembly of the whole molecules **4**–**7**, the envisaged strategy was to first connect the fluorophore **26** (fragment **C**) to the 1,3-diphenylsubstituted linker **25** (fragment **B**) and then couple the resulting **24** (fragment **B**–**C**) to the photochromic molecules **1**–**3** (fragments **A**). This strategy (Scheme 5) required 1,3-bis-(4-iodophenyl)bicyclo[1.1.1]-pentane (**25**) as a key building block.

For an acceptable overall yield of **31**, the reaction sequence (**28** → **30** → **31**) must be performed in diethoxymethane (or in solvent mixtures, in which diethoxymethane prevails). 1,3-Diphenylbicyclo[1.1.1]pentane (**31**) was isolated by column chromatography and recrystallized from methanol. It contained some 3,3′-diphenyl[2]staffane (**32**) as an impurity, which could easily be removed at the last step. Iodination of **31** with iodine in the presence of a strong oxidizing agent—PhI(OCOCF$_3$)$_2$[20]—afforded, after recrystallization from chloroform, analytically pure diiodide **25**. The moderate preparative yield in the iodination step is not surprising and rationalized with the formation of considerable amounts of regioisomeric iodides as by-products, due to the unsufficient steric shielding of the *ortho*-positions in the phenyl groups by the relatively small bicyclo[1.1.1]pentyl fragment. According to the recently developed protocol, the dibromocyclopropane **28** (Scheme 6) can easily be prepared in a quantity of 100 g (or even more) in one run,[21] and therefore several grams of the pure diiodide **25** may easily be produced at the end.

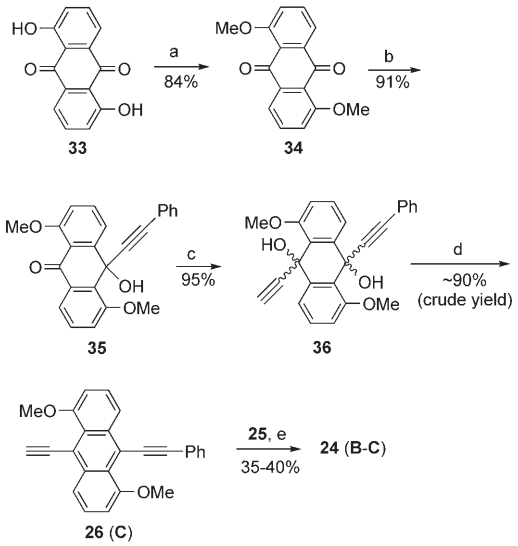


Scheme 6. Synthesis of bis-1,3-(4-iodophenyl)bicyclo[1.1.1]pentane (**25**): a) $CHBr_3$, 50 % aq. NaOH; b) MeLi (3 M in $(EtO)_2CH_2$), $(EtO)_2CH_2$, −40 to −30 °C, then RT, 1 h; c) PhMgBr (3 M in Et_2O), $(EtO)_2CH_2$, RT, 6 d; d) PhI, [Pd(dppf)Cl$_2$]·CH_2Cl_2 (2 mol %), dioxane/$(EtO)_2CH_2$, RT, 2 d; e) I_2, PhI(OCOCF$_3$)$_2$, CCl_4, 0 °C → RT.

The building block **26** (fragment **C**) was prepared from commercially available 1,5-dihydroxyanthraquinone (anthrarufin, **33**). After two-fold methylation with methyl iodide in the presence of silver oxide in dichloromethane,[22a,b] conditions for the addition of phenylacetylene were screened (Scheme 7). The best results were obtained in liquid ammonia at low concentration (0.05 M) of 1,5-dimethoxyanthraquinone (**34**) with 2.5 equivalents of lithium phenylacetylide.[23] Subsequent addition of a large excess of lithium acetylide afforded the two-fold adduct **36**. Simple recrystallization from a chloroform/pentane mixture provided a single diastereomer (presumably *trans*) in very high yield. Aromatization of **36** by treatment with stannous chloride and acetic acid in tetrahydrofuran[24] afforded the 9,10-dialkynylanthracene **26** with one terminal acetylene unit. This compound, which exhibits a strong green-yellow fluorescence, is not very stable and partially decom-



Scheme 5. Building blocks **A**, **B**–**C**, **B** and **C**, emerging from a retrosynthetic analysis of the target molecules **4**–**7**.

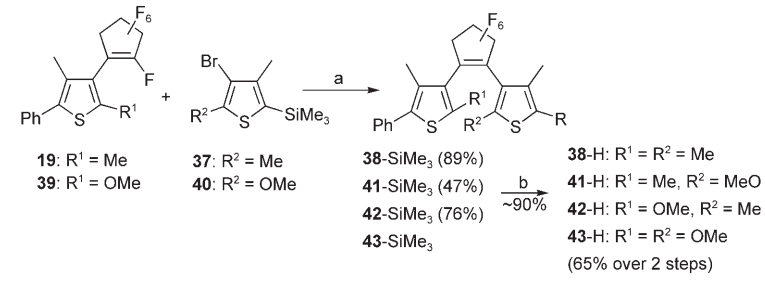


Scheme 7. Preparation of the building blocks **26** (fragmet **C**) and **24** (fragments **B**–**C**): a) MeI, Ag_2O, CH_2Cl_2, 30–35 °C; b) Li, liq. NH_3, PhC≡CH, then **34**, −40 °C, 10 h; c) Li, liq. NH_3, HC≡CH, −40 °C; d) $SnCl_2$, THF/HOAc, 0 °C; e) $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, THF, 40 °C, 36 h.

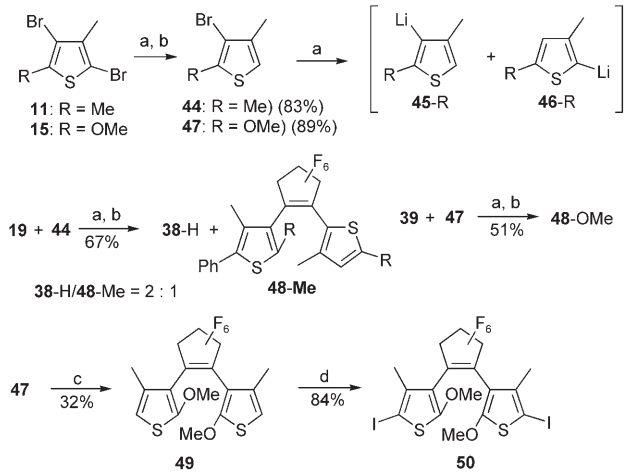
posed on exposure to silica gel. Therefore it was used in the cross-coupling with **25** after precipitation from the reaction mixture without further purification. Sonogashira coupling of **26** with a two-molar excess of the diiodide **25** only gave the mono-coupling product **24**. This reaction, however, was complicated by the formation of an intensely red-colored, poorly soluble by-product, which turned out to be a dehydrodimer of the terminal acetylene **26** (with two conjugated triple bonds).[25] Nevertheless, the target monoiodide **24** can be separated from this impurity by chromatography and isolated as a bright orange solid.

The photochromic building blocks **38**-H–**43**-H (fragments **A**) were prepared from (heptafluorocyclopentenyl)thiophene derivatives **19**,[19] **39**[9c] and the 2-trimethylsilyl-protected thiophenes **37**, **40**,[9c] which were, in turn, straightforwardly obtained in high yields (83–93 %) from the dibromothiophenes **11** and **15**, respectively (Scheme 8).

Protection of the α-positions in thiophenes **37** and **40** with a trimethylsilyl group was found to be very important, though this group has to be removed later from the coupling products **38**-$SiMe_3$–**43**-$SiMe_3$, in order to create the reaction site for the final coupling with the monoiodide **24**. The necessity for this α-protection became evident, when the corresponding transformations were tried without it (Scheme 9).



Scheme 8. Synthesis of the non-symmetric photochromic building blocks **38**-H–**43**-H: a) *n*BuLi (2.5 M in hexanes), THF, −78 °C; b) nBu_4NF (1 M in THF), 0 °C → RT.



Scheme 9. Bromine–lithium exchange in monobromothiophenes **44** and **47**: a) *n*BuLi (2.5 M in hexanes), THF, −78 °C; b) MeOH, −78 °C → RT; c) *n*BuLi (2.5 M in hexanes), Et_2O, −78 °C, then 0.5 equiv of C_5F_8; d) I_2/HgO, C_6H_6, RT, 1 h.

Monobromothiophenes **44**[10,26] and **47** can be readily obtained and isolated in good yields, but their further reactions with *n*-butyllithium are complicated by rearrangements and always give mixtures of monolithiated thiophenes **45**-R and **46**-R (R = Me, OMe), as corroborated by an analysis of the products of the reactions with the (heptafluorocyclopentenyl)thiophenes **19** and **39**. After bromine–lithium exchange (in THF), 3-bromo-2,4-dimethylthiophene (**44**) and heptafluoride **19** produced an inseparable 2:1 mixture of the "normal" product **38**-H and the compound **48**-Me stemming from the rearranged intermediate. Moreover, 3-bromo-2-methoxy-4-methylthiophene (**47**) and the derivative **39**, under the same conditions, afforded only the rearrangement product **49**.

A strong solvent effect was observed in this case: the normal product **43**-H was isolated in moderate yield (39 %), when the reaction between **47** and **39** was performed in diethyl ether. An analogous treatment of the monobromide **47** with *n*BuLi and subsequently with perfluorocyclopentene in diethyl ether also gave the expected symmetrical 1,2-di(thiophen-3-yl)perfluorocyclopentene derivative **49**. Obviously, the rate of equilibration between the lithiated thiophenes **45** and **46** strongly depends upon the nature of the solvent.

It was not trivial to establish the correct structures of the products **38**-H, **48**-Me, **48**-OMe

and **49** by spectroscopy only, especially in the case of the inseparable mixture of **38**-H and **48**-Me).[27] Therefore, the structures of the derivative **38**-$SiMe_3$ and the diiodide **50**, which was obtained from the coupling product **49**, were prooved by single crystal X-ray analyses.[28] These results further confirmed the assignments for **38**-H and **49**.

Diarylethenes are known to undergo photochromic transformations not only in solution, but also in the crystalline state.[29] In the crystal, the possibility of a photochemical ring-closure depends on the fixed conformation of the molecule. According to the Woodward–Hoffmann rules,[30] this kind of photochemical process is allowed in a conrotatory fashion. For steric reasons, only the *anti* conformer with two thiophene rings possessing local C_2 symmetry (like in compound **50**; Figure 2) may undergo photocyclization in the crystal.[31] On the contrary, if only *syn* conformers are present in the crystalline packing, the conrotatory ring-closure is impossible for steric reasons. This kind of local symmetry with a mirror plane is observed for compound **38**-H in the crystal. In $CDCl_3$ solution, an equilibrium between equal amounts of two conformers was observed.

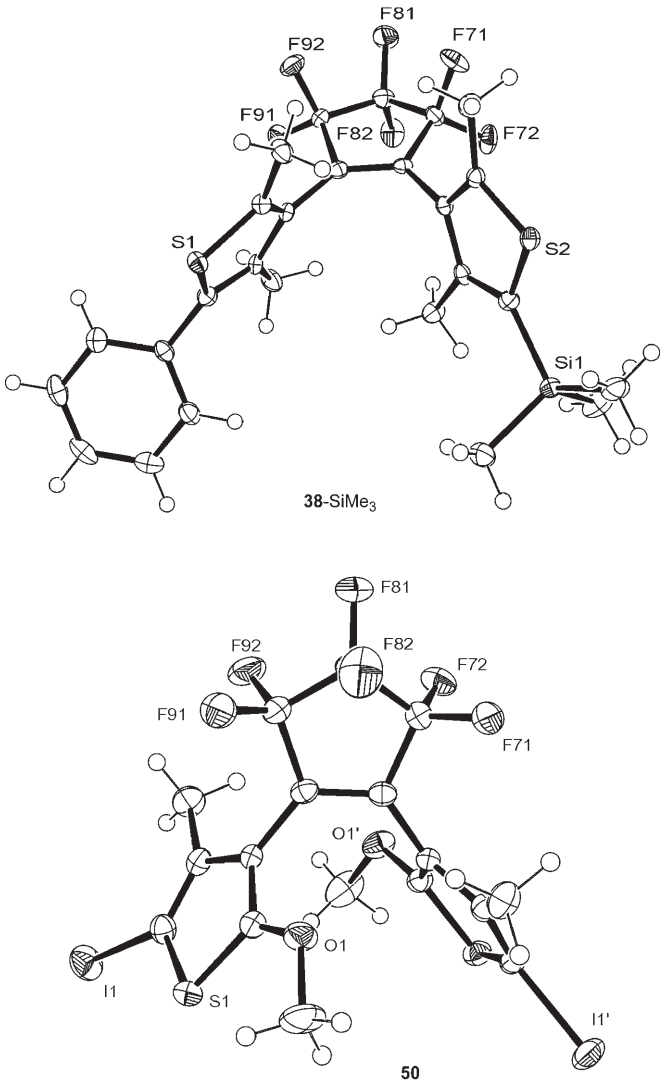
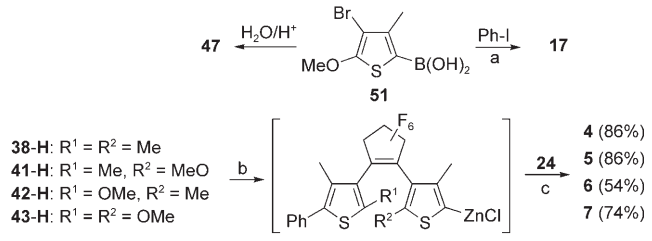


Figure 2. Structures of the compounds **38**-$SiMe_3$ and **50** in the crystals.[28]

With all the building blocks at hand, two alternatives for the final coupling, that is, via α-thiopheneboronic acids[9c] or zinc derivatives,[10] were briefly checked. Towards that goal, the model boronic acid **51** was prepared and its reaction with iodobenzene was tested (Scheme 10). Relatively pure



Scheme 10. Spontaneous protiodeboronation of the thiophenylboronic acid **51** and final coupling of the (iodophenyl)bicylo[1.1.1]pentane derivative **24** with α-unsubstituted thiophenes **38**-H–**41**-H via their α-zinc derivatives: a) 20% aq. Na_2CO_3, THF, $[Pd(dba)_2]$, Ph_3P, reflux, 16 h; b) LiTMP (3 equiv), THF, −78 °C; then 1 M $ZnCl_2$ in Et_2O, −78 → 0 °C; c) THF, $[Pd(dba)_2]$, Ph_3P, RT → 40 °C, 16–24 h.

thiophenylboronic acid **51** was obtained as a wet solid from the dibromothiophene **15** by selective α-bromine–lithium exchange, quenching of the reaction mixture with $(i\text{PrO})_3B$, extractive work-up with 1 M aqueous sodium hydroxide, followed by careful acidification of the aqueous phase up to pH 5–6. Unfortunately, however, this compound looses its boronic acid residue on drying, and thus mixtures of **51** and the thiophene **47** were always obtained. Quenching of the reaction mixture (after adding $(i\text{PrO})_3B$) with 20% aq. Na_2CO_3, addition of iodobenzene, $[Pd(dba)_2]$, Ph_3P, followed by heating under reflux overnight, afforded the coupling product in 40% analytical yield (NMR), along with the thiophene **47** (48%). These results indicate that the boronic acid **51** is unstable, and thus the boronic acids derived from the α-unsubstituted thiophenes **38**-H–**41**-H would probably also be unstable.[32]

Therefore, the shorter route utilizing the Negishi coupling of thiophenylzinc derivatives, obtained by lithium-zinc exchange, was chosen. The lithiothiophenes were generated by deprotonation of the α-unsubstituted thiophenes with a three-fold excess of lithium 2,2,6,6-tetramethylpiperidide (LiTMP), and the exchange was initiated by addition of three equivalents of zinc chloride in Et_2O. This reaction mixture was added at 0 °C to the (iodophenyl)bicyclopentane derivative **24** in the presence of the catalyst ($[Pd(dba)_2]$, Ph_3P). To complete the reaction in a reasonable time (16–24 h at 38 °C) and to provide high yields of the coupling products **4**–**7**, up to a seven-fold excess of each of the substrates **38**-H–**41**-H was used. The reaction proceeded cleanly, and the starting materials (**38**-H–**41**-H) could easily be recovered after solvolysis of the unreacted zinc organyls with methanol. The products **4**–**7** could be isolated by chromatography, provided that full conversion of the (iodophenyl)bicy-

clopentane **24** had occurred. Interestingly, this deprotonation–transmetallation–coupling sequence worked well even in the case of the β-unsubstituted **48**-OMe (probably due to the activating effect of the neighboring methoxy group, which enhances the deprotonation rate).

Compound **4** in solution exists as a 1:1 mixture of two conformers, one with *syn* and one with *anti* orientation of the pairs of methyl groups in the central part of the photochromic unit. Compounds **5**–**7** have at least one methoxy group at the inner carbon atoms involved in the cyclization reaction. A methoxy group is sterically less demanding than a methyl, and therefore, the rotational barrier between the two conformers should be lower. In full agreement with this, compounds **5**–**7** displayed only one set of signals for the methyl groups in the ^{1}H NMR spectra, yet broadening of the corresponding singlets at room temperature was observed.

Physical properties of photochromic compounds 1–3 and the fluorescent switches 4–7: The properties of all the compounds were studied in acetonitrile solutions. Absorption and fluorescence spectra were recorded before and during irradiation cycles with UV and visible light at 313 and 575 nm, respectively. Conversions in the photostationary state after irradiation with UV light were measured by HPLC on a reversed phase. Since the peaks of the closed forms always had higher retention times and were well separated from the peaks of the open forms, the equilibrium constants could be obtained by integration of the corresponding peak areas, provided that the UV detection was made at the isobestic point, where both forms have the same absorbance.

The properties of the photochromic units **1**–**3** in acetonitrile are not any different from those in apolar solvents such as hexane or toluene (Table 1). Replacement of one or two methyl by methoxy substituents had no effect on the quantum yield of the photocyclization ($\Phi_{OF\rightarrow CF}$), but the quantum yield of the ring opening reaction ($\Phi_{CF\rightarrow OF}$) decreased by one order of magnitude per one methoxy group. The main absorption bands of both isomers are red-shifted within the series **1**–**2**–**3**, and this effect is more pronounced in the closed form. The conversion to the closed form in the photostationary state (α_{PS}) increases in the sequence **1**–**2**–**3**. The conversion to the closed form in the photostationary state ($\alpha_{PS} = [CF]/C_0$, where $C_0 = [OF]+[CF]$) increases in the series **1**–**2**–**3**.

Table 1. Spectroscopic and photochromic properties of compounds **1**–**3** in acetonitrile.[a]

Compound	ε [M^{-1}cm^{-1}]/ λ [nm] open form	ε [M^{-1}cm^{-1}]/ λ [nm] closed form	$\Phi_{OF\rightarrow CF}$	$\Phi_{CF\rightarrow OF}$	α_{PS}	R_0 [Å]
1	3.0×10^4/270	1.1×10^4/572	0.46	1.5×10^{-2}	0.80	45
2	2.6×10^4/276	1.2×10^4/591	0.46	1.8×10^{-3}	0.96	44
3	2.2×10^4/287	9.7×10^3/624	0.46	1.3×10^{-4}	1.00	40

[a] Definitions for $\Phi_{OF\rightarrow CF}$, $\Phi_{CF\rightarrow OF}$ and α_{PS} are given in the text; for the definition of the Foerster radius (R_0) see Scheme 1 and ref. [5].

The bicyclo[1.1.1]pentane unit was selected to link both components and isolate their π systems, thus their optical properties should remain the same as in the unconnected units. However, the spectra of the fluorescent switches **4**–**7** were found to be slightly different from the simple superposition of the spectra of the photochromic units **1**–**3** and the fluorophore, 1,5-dimethoxy-9,10-bis(phenylethynyl)anthracene. The bicyclic substituent attached to the fluorophore causes a small bathochromic shift of 3 nm for both the absorption and emission maxima in acetonitrile. It is not surprising, because the bicyclo[1.1.1]pentyl substituent is a weak σ donor, and its +I effect is responsible for the observed bathochromic shifts. However, the fluorescence quantum yields (Φ_{Fl}) of compounds **4**–**7** do not differ from that of the fluorophore alone, indicating that there is no appreciable energy transfer from the fluorophore to the non-cyclized photochromic parts when excited with blue light (460–490 nm). The photochromic properties of the switches **4**–**7** (Table 2) were quite different from the photochromic properties of the compounds **1**–**3**.

Table 2. Photochromic properties of the fluorescent switches **4**–**7** in acetonitrile.

Compound	$\Phi_{OF\rightarrow CF}$	$\Phi_{CF\rightarrow OF}$	α_{PS}	Fluorescence modulation
4	5.6×10^{-2}	1.3×10^{-2}	0.55	0.58
5	6.3×10^{-2}	1.8×10^{-3}	0.90	0.90
6	0.11	1.5×10^{-3}	0.95	0.96
7	0.12	8×10^{-5}	1.00	1.00

The fluorescent switch **4** displayed a considerably smaller conversion α_{PS} than the corresponding photochromic building block **1**. This difference between compound **5** and the building block **2** is less pronounced, and no difference was observed for compounds **6** and **7** compared with building blocks **2** and **3**, respectively. The most interesting difference is that observed between compounds **5** and **6**, which indicates that the position, where the fluorophore is attached to the non-symmetric photochromic unit, influences the photochromic properties quite distinctly. The decrease in $\Phi_{CF\rightarrow OF}$ for the assemblies **4**–**7** compared with the corresponding values for the photochromic units **1**–**3** had previously been attributed to the fact that the fluorophore absorbs part of the light at the irradiation wavelength (313 nm), which does not contribute to photocyclization.[9c] The tendency observed here is consistent with this interpretation: the red shift in the absorption of the open form (OF) leads to a smaller fraction of the light being absorbed by the fluorophore in the sequence of the units **3** < **2** < **1**, and therefore, a smaller difference between the values of $\Phi_{OF\rightarrow CF}$ observed for the assembly and the corresponding photochromic building block is recorded. The only exception is the assembly **5**, in which other factor(s) may affect its properties. The smaller value of $\Phi_{OF\rightarrow CF}$ for this compound compared with that of compound **6** must be responsible for the lower conversion in the photostationary state. The quantum yields for the ring-

opening reaction ($\Phi_{CF\rightarrow OF}$) are almost unaltered for compound **4** on one hand and for compounds **5** and **6** on the other hand in comparison with the photochromic units **1** and **2**, respectively, but slightly reduced for the assembly **7** in comparison with the photochromic unit **3**. Regarding the fluorescent switching properties, all compounds showed a RET efficiency of close to 100% from the fluorophore to the CF, regardless of the differencies in spectral overlap (Figure 3a). This conclusion follows from the equal values of

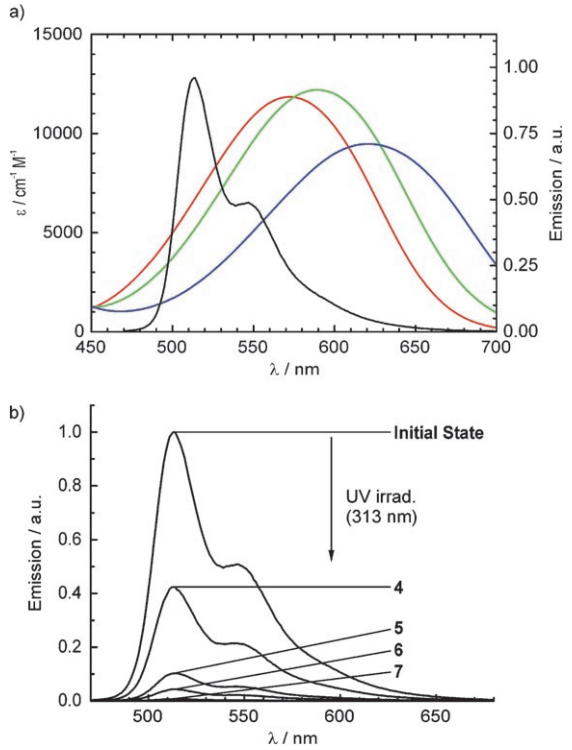


Figure 3. a) Emission of the fluorophore (solid line, right axis) and absorption coefficients (left axis) of the closed isomers **1** (red line), **2** (green line) and **3** (blue line); b) fluorescence modulation of the switches **4**–**7**. The signal was normalized to the one in the initial state, and the spectrum in the photostationary state after irradiation at 313 nm is shown for each compound (excitation wavelength 460 nm).

the conversion to the closed form (CF) in the photostationary state (α_{PS}) and fluorescence modulation (Table 2), confirming the applicability of the selected linker unit. The bicyclo[1.1.1]pentane moiety provides the shortest possible distance between the two components (1.87 Å) and a favorable angle of 180° for RET; the estimated Foerster radius (R_0) is much wider for all compounds (Table 1). Moreover, the absorption of the CF can be changed in a relatively wide range (about 50 nm), according to the desired application, and with no sacrifice in the intrinsic efficiency of the CF as the RET acceptor. The residual fluorescence is only limited by the conversion to the CF in the photostationary state (Figure 3b). The value of α_{PS} for the fluorescent switches **4**–**7** strongly depends only on the nature of the photochromic building block, which also determines the conversion rates in both directions, thus allowing to change them according to the desired application.

An important issue in most applications of molecular switches (e.g. optical memories, diffraction-unlimited resolution, etc.) is the fatigue resistance of the system. The number of cycles that can be performed with the switch before 10% of the signal is lost, is normally used as a figure of merit.[7a] In view of the long times required to complete the ring-opening reaction, in particular for the photochromic unit **3** and its fluorescent derivative **7** (ca. several hours with the isolated line of 577 nm of a 200 W mercury lamp), and in view of the fact that photobleaching occurs mainly in the closed isomer, the photoresistances of the closed forms to the UV light were evaluated. To this end, solutions of compounds **1**–**3** were irradiated at 313 nm (Figure 4), and after the photostationary state had been reached, irradiation was continued, while the absorption of the closed isomers in the visible range was monitored.

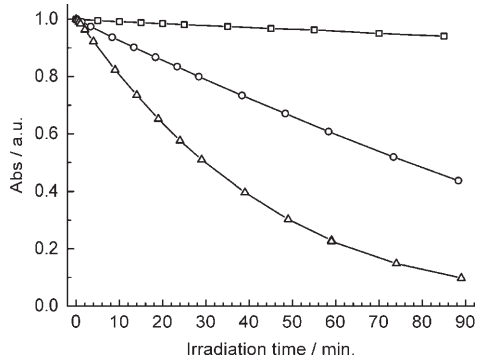


Figure 4. Normalized (with respect to the same initial absorption at 313 nm) absorptions at the maximum of the visible band of the closed forms **1** (□), **2** (○), **3** (△) versus time of irradiation at 313 nm.

It is obvious that the CFs of compounds **2** and **3** with one and two methoxy substituents, respectively, are increasingly less resistant to UV light irradiation. The same tendency was observed for the fluorescent assemblies **5**–**7**. Irradiation of their solutions with UV light was not only accompanied by the appearance of the CFs, but small amounts of unidentified by-products were also detected in the HPLC analysis.

Conclusion

New 2-methoxy-4-methylthiophene has been shown to be a valuable precursor in the preparation of various photochromic compounds. The strategy of this study may be applied for the stepwise incorporation of the bicyclo[1.1.1]pentane fragment between two phenyl rings, one of which belongs to the photochromic unit and the other one to the fluorescent part. For this, bis-1,3-(4-iodophenyl)bicyclo[1.1.1]pentane (**25**) may serve as a "building block" to introduce the bicyclo[1.1.1]pentane unit. Reduced photostability of the methoxy substituted photochromic units **2** and **3** (compared

with that of **1**) may limit their use in fatige-resistant optical switches.

The properties of the fluorescent assemblies (like **5** and **6**) derived from the asymmetrical photochromic compounds (e.g. **2**) may depend on the position of the linker, which anchors the fluorophore.

Experimental Section

General remarks: Melting points (uncorrected) were determined in capillaries using an SMP 10 device (BIBBY STERLING LTD, UK) or Büchi apparatus according to Dr. Tottoli. Routine NMR spectra were recorded with Varian MERCURY 300 and Bruker AM 250 spectrometers at 300 (^{1}H) and 75.5 MHz (^{13}C and APT), as well as at 250 (^{1}H) and 62.9 MHz (^{13}C and DEPT), respectively. ^{1}H NMR spectra were also recorded with Varian INOVA 500 or 600 (600 MHz) instruments. All spectra are referenced to tetramethylsilane as an internal standard ($\delta = 0$ ppm) using the signals of the residual protons of $CHCl_3$ in $CDCl_3$ (7.26 ppm) or [D_5]DMSO (2.50 ppm). Multiplicities of signals are described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, m_c = centrosymmetrical multiplet. Coupling constants (J) are given in Hz. Multiplicities in the ^{13}C NMR spectra were determined by DEPT (Distortionless Enhancement by Polarization Transfer) or APT (Attached Proton Test) measurements. IR spectra were recorded on a Bruker IFS 66 spectrometer and measured as KBr pellets or as oils between KBr plates. Low resolution mass spectra (EI at 70 eV or DCI with NH_3) were obtained with Finnigan MAT 95 and ESI-MS, with LCQ spectrometers. High resolution mass spectra (EI-HRMS) were obtained on a Finnigan MAT 95 spectrometer with preselected-ion peak matching at $R \approx 10000$ to be within ± 2 ppm of the exact masses. HPLC system (Knauer): Smartline pump 1000 (2×), UV detector 2500, column thermostat 4000, mixing chamber, injection valve with 20 and 100 μL loop for the analytical and preparative columns, respectively; 6-port-3-channel switching valve; analytical column: Eurospher-100 C18, 5 μm, 250×4 mm; preparative column: Eurosphere-100 C18, 5 μm, 250×8 mm; solvent MeCN + 0.1% v/v TFA. Injections of the irradiated solutions in EtOH allowed the direct measurements of the ratios of the open and closed forms at the photostationary state (detection at the isobestic point). Analytical TLC was performed on MERCK ready-to-use plates with silica gel 60 (F_{254}) and developed with a molybdatophosphoric acid acid solution (5% in EtOH). Flash chromatography: Merck silica gel, grade 60, 0.04–0.063 mm; fraction collector Retriever II (ISCO). Elemental analyses were carried out at Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen. DMF and CH_2Cl_2 were distilled from CaH_2. Et_2O and THF were freshly distilled from sodium/benzophenone. Organic solutions were dried over $MgSO_4$. All reactions were carried out with magnetic stirring under positive argon pressure using the standard technique with a vacuum-inert gas manifold, unless stated otherwise. Absorption and fluorescence stationary measurements were carried out with a Varian Cary 4000 UV/Vis spectrophotometer, and with a Varian Cary Eclipse fluorescence spectrophotometer, respectively. Sealed quartz cuvettes of 1 cm path length were used in all experiments. Emission spectra were corrected for instrument response. Photochromic reactions were performed with styrring by irradiation with a 200 W Mercury lamp (LOT-Oriel GmbH, Darmstadt, Germany) equipped with a monochromator and a system of filters to select the appropriate wavelengths. The analysis of the kinetic data to extract the values of the quantum efficiencies of the isomerization reactions ($\Phi_{OF\rightarrow CF}$ and $\Phi_{CF\rightarrow OF}$) was described elsewhere.[33]

2-Bromo-5-methylthiophene (8) was prepared in 80% yield according to the published procedure.[34]

4-Bromo-2-methylthiophene (9) was synthesized adopting a published procedure employing a "halogen dance":[35] nBuLi (2.5 M in hexanes, 68.0 mL, 170 mmol) was added dropwise to a solution of iPr$_2$NH (17.2 g, 170 mmol) in THF (100 mL) at 0 °C within 30 min. The resulting solution of LDA was left to warm-up to room temperature. In another dry 500 mL flask equipped with a dropping funnel and an argon inlet tube, a solution of 2-bromo-5-methylthiophene (30.0 g, 169 mmol) in THF (100 mL) was prepared. The LDA solution was transferred to the dropping funnel under Ar and added dropwise at −78 °C within about 2 h to the solution in the flask. Then MeOH (20 mL) were slowly added to quench the remaining lithiothiophene. After warming-up to room temperature, 2 M aq. HCl (100 mL) was added (100 mL), followed by Et_2O (400 mL). The organic layer was separated, washed with water (200 mL), brine (100 mL) and dried. After removal of the solvents in vacuo, the residue was purified by distillation to yield 4-bromo-2-methylthiophene as a colorless oil (24.0 g, 80%). B.p. 67–68 °C (20 Torr); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.47$ (d, $J = 1.3$, 3H), 6.69 (d, $J = 1.3$, 1H), 6.98 ppm (m, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.3$ (Me), 108.9, 120.3, 127.8, 141.1 ppm.

2,4-Dimethylthiophene (10) was synthesized according to the published method.[15] ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.2$ (Me), 15.6 (Me), 118.1 (CH), 127.6 (CH), 137.48, 139.5 ppm.

2,4-Dibromo-3,5-dimethylthiophene (11) was synthesized from 2,4-dimethylthiophene according to the published bromination procedure[10] with addition of two equivalents of AcONa. B.p. 120–125 °C (2 mm Hg); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.17$ (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.4$ (Me), 16.1 (Me), 104.7 (C-Br), 111.3 (C-Br), 133.8, 136.2 ppm; IR (film): $\tilde{\nu} = 2918$, 2852, 1653, 1554, 1437, 1379, 1329, 1022, 952, 758 cm^{-1}; MS (EI): m/z (%): 272 (35) [$M(^{81}Br_2)^+$], 270 (90) [$M(^{81}Br+^{79}Br)^+$], 268 (35) [$M(^{79}Br_2)^+$], 110 (100).

2-Methoxy-4-methylthiophene (14): Into a 100 mL-three-necked flask, equipped with a thermometer and a reflux condenser, was added sodium methoxide (13.8 g, 256 mmol), then anhydrous methanol (22 mL). Subsequently, 2-bromo-4-methylthiophene[16] (27.3 g, 154 mmol) and copper(I) bromide (2.8 g, 19 mmol) were added, and the mixture was heated at reflux for 8 h (bath temp. 120 °C). The reaction mixture was cooled to room temperature, and sodium cyanide (10 g, in 100 mL water, **CAUTION! Poison!** Well ventilated hood is required!) was added under vigorous stirring. The aqueous layer was extracted with Et_2O (5×50 mL). Before disposal, the aqueous solution was decontaminated by addition of $KMnO_4$: The combined organic layers were dried, and after evaporation of the solvent in vacuo, the residue was distilled to yield the title compound as a colorless oil (17.3 g, 88%). B.p. 72–73 °C (80 Torr); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.17$ (d, $J = 1.1$, 3H), 3.86 (s, 3H), 6.03 (d, $J = 1.8$, 1H), 6.13 ppm (dq, $J \approx 1.2$ and 1.8, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 16.7$ (Me), 60.0 (Me), 106.0 (CH), 106.4 (CH), 135.2 (C), 166.0 ppm (C); IR (film): $\tilde{\nu} = 2937$, 2825, 1564, 1496, 1426, 1219, 1203, 1133, 1004, 704 cm^{-1}; MS (EI): m/z (%): 128 (60) [M^+], 114 (25), 113 (50), 85 (55), 69 (24), 45 (100).

2,4-Dibromo-5-methoxy-3-methylthiophene (15): To a stirred solution of **14** (15.3 g, 0.120 mol) in CCl_4 (20 mL) was added in small portions within 1 h with external ice-cooling a suspension of *N*-bromosuccinimide (42.7 g, 0.24 mol) in CCl_4 (200 mL). The reaction mixture was stirred at room temperature for 2 h, then it was cooled down again to 0 °C, filtered, and the filtrate was concentrated in vacuo. The dark oily residue was dissolved in hexane, and the solution filtered through 100 g of silica gel (which was placed as a suspension in hexane into a fritted-glass filter). The filter cake was washed with hexane (TLC control). The filtrate was evaporated in vacuo, and the oily residue was kept at +5 °C overnight. Crystalline material (colorless needles) was filtered-off with suction to give the first crop (11 g). The liquid fraction was distilled to give the second crop (8.5 g, b.p. 88–90 °C, 1 Torr) as a yellow oil, which gradually crystallized. Total yield 19.5 g (57%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.14$ (s, 3H, Me), 3.92 ppm (s, 3H, OMe); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.8$, 61.8, 93.5, 94.4, 134.2, 157.2 ppm; IR (film): $\tilde{\nu} = 2918$, 1718, 1653, 1559, 506, 1249, 1239, 1153, 993, 940, 812, 633 cm^{-1}; MS (EI): m/z (%): 288 (30) [$M(^{81}Br_2)^+$], 286 (60) [$M(^{81}Br+^{79}Br)^+$], 284 (30) [$M(^{79}Br_2)^+$], 271 (100), 243 (40); elemental analysis calcd (%) for $C_6H_6Br_2OS$ (285.99): C 25.20, H 2.11; found: C 25.09, H 1.97.

Photochromic unit 2: To a solution of compound **17**[9c] (425 mg, 1.50 mmol) in anhydrous THF (5 mL) was added dropwise at −78 °C

*n*BuLi (2.5 M in hexanes, 0.70 mL, 1.75 mmol). The mixture turned yellow, and after 15 min a solution of **19**[19] (540 mg, 1.42 mmol) in THF (3 mL) was added dropwise. At first, the reaction mixture turned green, and when the addition was complete yellow again. After 30 min, the reaction was quenched by adding MeOH (0.5 mL), and the mixture then diluted with hexane (100 mL). The combined organic solutions were washed with water (50 mL), brine (50 mL) and dried. After evaporation of the solvents, the oily residue was applied on top of a column with silica gel (100 g), and the title compound (360 mg, 45%) was eluted with hexane/CH_2Cl_2 5:1. An analytical sample with m.p. 120°C was obtained after several recrystallizations from MeOH (in the dark). The product is a colorless solid which turns to blue upon exposure daylight; HPLC: t_R (open form) = 5.3 min, t_R (closed form) = 6.2 min (25°C, 1 mL per min, detection at the isobestic point of 313 nm); ^{1}H NMR (250 MHz, $CDCl_3$, open form): δ = 2.119 (s), 2.123 (s) (Σ 6H), 2.32 (s, 3H), 3.78 (s, 3H), 7.29–7.43 ppm (m, 5H); ^{1}H NMR (250 MHz, $CDCl_3$, closed form): δ = 2.03 (s), 2.04 (s) (Σ 6H), 2.43 (s, 3H), 3.64 (s, 3H), 7.41 ppm (m, 5H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.2 (Me×2), 14.6 (Me), 61.1 (MeO), 109.2, 124.6, 125.5, 127.2 (CH), 127.3 (CH), 128.5 (CH×4), 128.96, 129.0 (CH), 129.2 (CH), 129.8, 133.9, 134.2, 135.6, 163.8 ppm; IR (KBr): $\tilde{\nu}$ = 3056, 3018, 2961, 2926, 1559, 1507, 1458, 1398, 1341, 1263, 1192, 1146, 1100, 1054, 1033, 988, 756, 690 cm^{-1}; MS (EI): *m*/*z* (%): 566 (16)/565 (30)/564 (100) [M^+], 533 (28) [M^+–MeO], 518 (31) [M^+–Me–MeO], 329 (18), 282 (12), 121 (15); elemental analysis calcd (%) for $C_{29}H_{22}F_6OS_2$ (564.61): C 61.69, H 3.93; found: C 61.48, H 3.78.

Bis-1,3-(4-iodophenyl)bicyclo[1.1.1]pentane (25): To a solution of iodine (1.74 g, 7.00 mmol) in CCl_4 (100 mL) was added compound **31**[2,3] (1.54 g, 7.00 mmol), and the mixture was cooled with stirring to 0°C. Then PhI-$(OCOCF_3)_2$ (3.1 g 7.2 mmol) was added in one portion, and stirring at 0°C was continued for 30 min. The cooling bath was removed, and the mixture was stirred overnight at room temperature. It was concentrated in vacuo to ca. 25 mL, cooled to 0°C and filtered. The precipitate was washed with cold MeOH (15 mL), and dried to yield the crude product (1.8 g), which was contaminated with regioisomeric diiodides and monoiodides. It was recrystallized from $CHCl_3$ (20–25 mL) to yield the first crop (1.1 g) with m.p. 269–272°C. Concentration of the mother liquids afforded the second crop (0.25 g). Total yield 1.35 g (63%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 6H), 7.02 (d, *J* = 8.8, 2H), 7.64 ppm (d, *J* = 8.8, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 40.8 (C), 53.9 (CH_2), 91.9 (C-I), 128.2 (CH), 137.2 (CH), 140.2 (C); IR (KBr): $\tilde{\nu}$ = 2968, 2902, 2868, 1480, 1184, 1001, 832, 797 cm^{-1}; MS (EI): *m*/*z* (%): 471 (13) [M^+–H], 346 (16), 345 (100) [M^+–I], 219 (41); elemental analysis calcd (%) for $C_{17}H_{14}I_2$ (472.10): C 43.25, H 3.93; found: C 43.61, H 3.06.

1,5-Dimethoxyanthraquinone (34): To a suspension of anthrarufin **33** (16 g, techn. grade (85%), 66.6 mmol of the pure substance) in CH_2Cl_2 (1.8 L) was added Ag_2O (100 g, 0.43 mol), then MeI (212 g, 93 mL, 1.49 mol). The suspension was stirred in the dark at 30–35°C for one week. When all of the starting material and the intermediately formed 5-hydroxy-1-methoxyanthraquinone (R_f = 0.15, $CHCl_3$) had disappeared (TLC), the mixture was filtered through Celite, the filter cake was washed with warm CH_2Cl_2 (300 mL), and the solution concentrated to about 100 mL. The residue was gradually diluted with pentane (0.9 L) with ice-cooling and stirring. The precipitated bright yellow solid was removed by flitration and air-dried to afford the title compound as fine yellow needles (15 g, 84%). M.p. 236–237°C (lit:[22c] 236–237°C (EtOH)); R_f = 0.1 ($CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3094, 2950, 2839, 1664, 1597, 1466, 1261, 1071, 975, 807, 768, 713 cm^{-1}.

9,10-Dihydro-10-hydroxy-10-(phenylethynyl)-1,5-dimethoxyanthracen-9-one (35): In a dry 500 mL flask, equipped with a cooling trap with dry ice and acetone, was collected at −60°C 200 mL of liquid NH_3, and then at this temperature lithium metal (70 mg, 10 mmol) was added. The solution turned blue, and it was stirred at −40°C for 2 h. Then neat phenylacetylene (1.02 g, 10 mmol) was carefully added with a syringe at −60°C, and the solution turned grey. It was stirred at −40°C for 2 h, then the solid compound **34** (1.07 g, 4.0 mmol) was added at −60°C, and stirring was continued at −40°C for another 10 h. The cooling bath was removed, and the ammonia was evaporated at room temperature. Sat. aq. NH_4Cl (100 mL) was added, the mixture was extracted with $CHCl_3$ (3×50 mL), the combined organic solutions were dried, filtered, and the solvent was evaporated. The residue was subjected to chromatography on silica gel (50 g, column 2×20 cm, $CHCl_3$) to yield **35** as a colorless solid (1.35 g, 91%). R_f = 0.20 ($CHCl_3$); m.p. 177°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.08 (s, 3H), 4.10 (s, 3H), 5.53 (s, 1H), 7.05 (d, *J* = 8.3, 1H), 7.31–7.22 (m, 5H), 7.49 (t, *J* = 8.3, 1H), 7.67 (t, *J* = 8.0, 1H), 7.82 (d, *J* = 7.8, 1H), 7.93 ppm (d, *J* = 8.0, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 56.2, 55.6, 64.4, 91.8, 111.5, 115.8, 120.16, 120.22, 128.1, 122.3, 128.4, 129.4, 130.0, 131.6, 131.9, 134.9, 146.3, 156.5, 159.9, 182.4 ppm; IR (KBr): $\tilde{\nu}$ = 3466, 3025, 2962, 2935, 2833, 1661, 1589, 1465, 1374, 1328, 1268, 1181, 1035, 994, 825, 795, 762, 725, 698 cm^{-1}; MS (EI): *m*/*z* (%): 370 (48) [M^+], 355 (100), 311 (16), 279 (6), 239 (8), 149 (12), 102 (44; elemental analysis calcd (%) for $C_{24}H_{18}O_4$ (370.40): C 77.82, H 4.90; found: C 77.75, H 4.83.

9-Ethynyl-9,10-dihydro-9,10-dihydroxy-10-(phenylethynyl)-1,5-dimethoxyanthracene (36): In a dry 500 mL flask, equipped with a cooling trap with dry ice and acetone, was collected at −60°C 400 mL of liquid ammonia, and then at this temperature lithium metal (896 mg, 128 mmol) was added in small pieces. The solution turned blue, and it was stirred at −40°C for 2 h. Then acetylene gas was introduced at a rate of 1–2 mL per s at −60°C for 10 min, and the solution was stirred for 2 h at −40°C. Then the system was cooled to −60°C again, and a solution of compound **35** (1.58 g, 4.27 mmol) in anhydrous THF (10 mL) was carefully added with syringe, and the mixture was stirred at −40°C for 24 h. The flask was warmed up to room temperature, until the ammonia had completely evaporated, then sat. aq. NH_4Cl (200 mL) was added, and the mixture was extracted with $CHCl_3$ (3×50 mL). The combined organic solutions were dried, filtered, the solvent was evaporated in vacuo, and the residue was recrystallized from $CHCl_3$/pentane mixture to give the title product (1.60 g, 95%) as a colorless solid. M.p. 228°C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.51 (s, 1H, ≡CH), 4.04 (s, 3H, OMe), 4.05 (s, 3H, OMe), 4.96 (s, 1H, OH), 5.08 (s, 1H, OH), 7.05–7.00 (m, 2H), 7.26–7.22 (m, 3H), 7.30–7.28 (m, 2H), 7.80–7.81 (m, 2H), 7.47 ppm (t, *J* = 8.0, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.3 (OMe), 56.5 (OMe), 64.9 (C-O), 65.5 (C-O), 71.5 (≡CH), 83.4 (≡C), 88.6 (≡C), 94.3 (≡C), 111.6 (C), 111.9 (C), 121.8 (C), 122.3 (CH), 123.3 (C), 124.8 (C), 125.2 (C), 128.0 (CH), 128.1 (CH, 2C), 129.5 (CH), 129.6 (CH), 131.5 (CH, 2C), 137.1 (C), 137.5 (C), 157.0 (C), 157.3 ppm (C); IR (KBr): $\tilde{\nu}$ = 3496, 3241 cm^{-1}; MS (EI): *m*/*z* (%): 397 (4)/396 (24) [M^+], 381 (80), 365 (70), 348 (24), 321 (16), 305 (20), 276 (20), 270 (100), 255 (40), 167 (30), 149 (72), 83 (88); elemental analysis calcd (%) for $C_{26}H_{20}O_4$ (396.43): C 78.77, H 5.09; found: C 78.90, H 5.09.

9-Ethynyl-1,5-dimethoxy-10-phenylethynylanthracene (26): To a suspension of compound **36** (198 mg, 0.500 mmol) in THF (3 mL), was added dropwise at 0 → +5°C a solution of anhydrous $SnCl_2$ (142 mg, 0.75 mmol) in distilled water (0.5 mL) with HOAc (120 mg) was added dropwise. The starting material gradually dissolved, and the mixture became fluorescent. After stirring at 0 → +15°C for 2 h, TLC indicated that the starting material had been consumed. Ice water (5 mL) was added dropwise to the stirred reaction mixture at 0 → +5°C within 30 min, and the suspension was stirred for 1 h. The precipitate was filtered off and washed with water. It was taken up in anhydrous THF (5–6 mL), the mixture filtered, and the filtrate evaporated in vacuo. After drying under reduced pressure over P_2O_5, a red-brown powder (170 mg corresponding to 94% yield) was obtained, and it displayed one spot on the TLC with bright yellow fluorescence. R_f = 0.6 ($CHCl_3$/hexane 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.08 (s, 3H, OMe), 4.10 (s, 1H, ≡CH), 4.11 (s, 3H, OMe), 6.90 (d, *J* = 7.5, 2H), 7.53–7.38 (m, 5H), 7.74–7.70 (m, 2H), 8.55–8.46 ppm (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.4 (OMe), 55.8 (OMe), 83.5 (≡C), 89.6 (≡CH), 90.3 (≡C), 102.3 (≡C), 105.1 (CH), 105.4 (CH), 114.1 (C), 116.0 (C), 119.85 (CH), 119.99 (CH), 124.4 (C), 125.1 (C), 125.8 (C), 126.4 (CH), 126.7 (CH), 128.2 (CH), 128.4 (CH), 131.3 (CH), 134.4 (C), 135.3 (C), 156.4 (C), 156.6 ppm (C); IR (KBr): $\tilde{\nu}$ = 3066, 2933, 2832, 1618, 1534, 1458, 1261, 1034, 785, 674 cm^{-1}; MS (EI): *m*/*z* (%): 363 (16)/362 (55) [M^+], 316 (10), 274 (10), 256 (4), 223 (4), 181 (4), 71 (62), 42 (100); HRMS (ESI): *m*/*z*: calcd for $C_{26}H_{19}O_2$: 363.1385; found: 363.1377 [M+H]$^+$.

1,5-Dimethoxy-9-[4-[1-(4-iodophenyl)bicyclo[1.1.1]pent-3-yl]phenyl]-10-phenylethynylanthracene (24): The alkyne **26** (250 mg, 0.69 mmol), diio-

dide **25** (942 mg, 2.0 mmol), $Pd(Ph_3P)_2Cl_2$ (68 mg, 96 μmol), CuI (20 mg, 105 μmol) and Ph_3P (50 mg, 190 μmol) were placed in a flame-dried round-bottomed flask (25 mL) with a side-arm. The flask was closed with a septum, evacuated, filled with nitrogen, and this cycle was repeated two more times. Then anhydrous THF (12 mL) was introduced through the septum, the mixture was stirred at room temperature for 10 min, and Et_3N (0.5 mL) was added. The mixture was stirred at 38 °C for 36 h, diluted with $CHCl_3$ (50 mL), washed with sat. aq. NH_4Cl containing 2% (v/v) of 25% aq. NH_3 (20 mL), water (20 mL), 1 M aq. HCl (20 mL) and brine (20 mL). The organic layer was dried, evaporated in vacuo, the residue was taken up in hot $CHCl_3$ and applied on top of a column with flash silica gel (200 g). Elution with a $CHCl_3$/hexane mixture (1:3 → 3:1) afforded first the unreacted diiodide **25** (ca. 0.5 g), then the orange band with the title compound (230 mg) followed by a red band, which contained the by-product. Recrystallization from $CHCl_3$ gave **24** (171 mg, 35%). M.p. 270 °C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.33$ (s, 6H), 4.09 (s), 4.10 (s) (Σ 6H), 6.90 (d, $J = 7.8$, 2H), 7.04 (d, $J = 7.8$, 2H), 7.32 (d, $J = 7.8$, 2H), 7.35–7.42 (m, 3H), 7.46 (t, $J = 7.8$, 2H), 7.63–7.73 (m, 6H), 8.52 ppm (dd, $J = 7.8$ and 3, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.7$ (C), 41.0 (C), 54.1 (CH_2), 56.1 (MeO), 90.7 (C≡), 91.8 (C-I), 102.2 (C≡), 102.3 (C≡), 105.6 (CH), 115.4, 115.6, 120.2 (CH), 122.9, 124.7, 125.5, 126.3 (CH), 126.5(CH×2), 128.2 (CH), 128.3 (CH×2), 128.5 (CH×2), 131.3 (CH×2), 131.4 (CH×2), 134.9, 137.3 (CH×2), 140.5, 140.8, 156.9 ppm; IR (KBr): $\tilde{\nu}$ = 2925, 2360, 2340, 1264,, 1185, 1034, 756, 694, 517 cm^{-1}; MS (EI): *m*/*z* (%): 708 (3)/707 (33)/706 (92) [M^+], 582 (8), 581 (42), 580 (100) [M^+−I+H], 142 (58); elemental analysis calcd (%) for $C_{43}H_{31}IO_2$ (706.61): C 73.09, H 4.42; found: C 73.32, H 4.79.

3-Bromo-2,4-dimethyl-5-trimethylsilylthiophene (37):[38] To a solution of the thiophene **11** (2.15 g, 7.96 mmol) in anhydrous THF (20 mL), was added t at −78 °C *n*BuLi (2.5 M in hexanes, 3.3 mL, 8.25 mmol). During the addition, the solution turned yellow, then green and then brown. After 10 min, freshly distilled Me_3SiCl (1.26 mL, 1.09 g, 10 mmol) in THF (5 mL) was added dropwise to the reaction mixture, and the mixture was left to warm up to room temperature. It was diluted with hexane (50 mL), the mixture washed with brine (50 mL), the organic phase was dried and concentrated. The title compound was isolated from the oily residue (2.09 g) by chromatography on silica gel (125 g) eluting with hexane ($R_f \approx 0.75$), yield **37** as a colorless liquid (1.54 g, 74%), which was used in the next step without further purification. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.34$ (s, 9H), 2.28 (s, 3H), 2.41 ppm (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -0.5$ (Me_3Si), 15.3 (Me), 17.1 (Me), 115.1, 129.7, 138.2, 143.1 ppm; IR (KBr): $\tilde{\nu}$ = 2945, 2924, 2902, 2864, 1250, 1048, 839 cm^{-1}; MS (EI): *m*/*z* (%): 264/262 (24) [M^+], 249/247 (100) [M^+−Me], 138/136 (20).

4-[2-(2,4-Dimethyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-3,5-dimethyl-2-trimethylsilylthiophene (38-SiMe$_3$): To a solution of the thiophene **37** (363 mg, 1.38 mmol) in anhydrous THF (2.0 mL), was added slowly at −78 °C *n*BuLi (2.5 M in hexanes, 0.56 mL, 1.40 mmol), and the mixture was stirred at this temperature for 30 min. A solution of compound **19**[36] (500 mg, 1.32 mmol) in anhydrous THF (2.0 mL) was added slowly at −78 °C. The reaction mixture was allowed to warm-up to room temperature, stirred for 30 min, diluted with Et_2O (100 mL), and washed with water (50 mL). After drying, the solvents were removed in vacuo. The residue was subjected to chromatography on silica gel (50 g, column 2×20 cm, pentane) to give the title compound as a colorless solid (476 mg, 66%). $R_f = 0.75$ (pentane); m.p. 120–122 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 2 rotamers): $\delta = 0.28$ (s, 9H), 2.047 (s), 2.053 (s), 2.067 (s), 2.073 (s) (Σ 3H), 2.086 (s), 2.094 (s), 2.117 (s), 2.123 (s) (Σ 3H), 2.30 (s, 3H), 2.32 (s), 2.33 (s) (Σ 3H), 7.30–7.39 ppm (m, 5H); ^{13}C NMR (62.9 MHz, $CDCl_3$):[37] $\delta = 0.3$, 14.6, 14.89, 14.95, 16.3, 127.2, 127.4, 128.5, 129.1, 131.1, 132.0, 134.1, 136.1, 138.7 (d, $J = 1.9$), 143.2, 144.5 ppm (d, $J = 15.7$); IR (KBr): $\tilde{\nu} = 3022$, 2956, 2928, 1653, 1443, 1269, 1251, 1192, 1141, 1109, 1066, 1026, 990, 945, 839, 757, 704 cm^{-1}; MS (EI): *m*/*z* (%): 544 (100) [M^+]; elemental analysis calcd (%) for $C_{26}H_{26}F_6S_2Si$ (544.69): C 57.33, H 4.81; found: C 57.59, H 5.05.

Crystal structure analysis of compound **38**-SiMe$_3$:[28] Crystal size 0.30×0.20×0.20 mm^3, triclinic, $a = 1063.85(9)$, $b = 1175.17(10)$, $c = 1238.74(11)$ pm, $\alpha = 63.963(10)$, $\beta = 75.887(10)$, $\gamma = 69.7010(8)$°, $V = 1.29736(2)$ nm^3, $Z = 2$, space group $P\bar{1}$, $Mo_{K\alpha}$ radiation at 71.073 pm, $T = 100(2)$ K, $\rho = 1.394$ Mg m^{-3}, absorption coefficient: 0.308 mm^{-1}, $F_o = 564$, θ range for data collection: 2.05 to 24.4°, reflections collected: 5303, independent reflections: 5303 [$R_{int} = 0.0000$], completeness to $\theta = 26.40$°: 99.6%, max. and min. transmission: 0.9410 and 0.9133, refinement method: full-matrix least squares on F^2, data/restraints/parameters: 5303/0/323, goodness of fit on F^2: 1.396; final *R* indices [$I > 2\sigma(I)$]: $R_1 = 0.0731$, $wR_2 = 0.1420$; *R* indices (all data): $R_1 = 0.0758$, $wR_2 = 0.1431$; largest diff. peak and hole: 0.493 and −0.424 e Å^{-3}.

4-[2-(2,4-Dimethyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-3,5-dimethylthiophene (38-H): To a solution of **38**-SiMe$_3$ (350 mg, 0.64 mmol) in anhydrous THF (8.0 mL), was added slowly at room temperature Bu_4NF (1.0 M in THF, 1.2 mmol, 1.2 mL), and stirring was continued for 10 min. The mixture was diluted with Et_2O (100 mL), washed with water (50 mL), dried and filtered. The solvents were removed in vacuo, and the title compound (280 mg, 93%) was isolated by chromatography (50 g silica gel, column 2×20 cm, pentane) as a colorless oil. $R_f = 0.48$ (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.06$ (s, 6H), 2.32 (s, 6H), 6.73 (s, 1H), 7.42–7.28 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$):[37] $\delta = 14.58$, 14.63, 14.8, 15.19, 116.2, 119.4, 127.4, 128.5, 129.19, 132.0, 134.0, 136.2, 136.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -133.4$ to −133.3 (m, 2F), −110.7 to −110.15 ppm (m, 4F); IR (film): $\tilde{\nu} = 2959$, 2929, 2867, 1473, 1442, 1342, 1274, 1191, 1144, 1114, 1057, 989, 874, 758, 697 cm^{-1}; MS (EI): *m*/*z* (%): 472 (100) [M^+]; elemental analysis calcd (%) for $C_{23}H_{18}F_6S_2$ (472.51): C 58.46, H 3.84; found: C 58.63, H 3.95.

4-[2-(2,4-Dimethyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-5-methoxy-3-methylthiophene (41-H) was obtained from heptafluorocyclopentyl derivative **19**[36] (0.60 g, 1.6 mmol) and the 3-thienyl bromide **40**[9c] (1.8 mmol) in two steps and isolated as an oil (327 mg, 42%) as described above for compound **38**-H. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.08$ (s, 3H), 2.11 (d, $J = 1$, 3H), 2.29 (s, 3H), 6.25 (q, $J = 1$, 1H), 7.29–7.41 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$):[37] $\delta = 14.1$ (Me), 14.2 (Me), 16.3 (Me), 60.9 (MeO), 107.4 (CH), 107.8, 126.9, 127.3 (CH), 128.5 (CH), 128.5 (CH), 129.0 (CH×2), 132.3, 134.2, 134.5, 135.6, 138.6, 165.5 ppm; IR (film): $\tilde{\nu}$ = 3023, 2968, 2928, 2864, 1600, 1557, 1494, 1448, 1395, 1341, 1278, 1192, 1142, 1112, 1060, 1022, 982, 906, 871, 758, 698, 539, 505 cm^{-1}; MS (ESI, positive mode): *m*/*z* (%): 491 (10)/490 (24)/489 (100) [M+H]$^+$; HRMS (ESI): *m*/*z*: calcd for $C_{23}H_{19}F_6OS_2$: 489.07815, found: 489.07728 [M+H]$^+$.

4-[2-(2-Methoxy-4-methyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-3,5-dimethylthiophene (42-H):[38] 4-[2-(2-Methoxy-4-methyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-3,5-dimethyl-2-trimethylsilylthiophene (**42**-SiMe$_3$)[9c] was synthesized from the thiophenes **37** (438 mg, 1.66 mmol) and **39** (555 mg, 1.40 mmol) as described above for the compound **38**-SiMe$_3$, to yield **42**-SiMe$_3$ a pale blue solid (600 mg, 76%). $R_f = 0.65$ (pentane); m.p. 85–87 °C; ^{13}C NMR (75.4 MHz, $CDCl_3$):[37] $\delta = -0.18$, 14.29, 14.55, 15.87, 60.98, 124.39, 127.16, 128.53, 129.15, 129.79, 133.95 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -114.9$ to −106.1 (br m, 2F), −113.0 (s, 2F), −133.4 ppm (s, 2F); IR (KBr): $\tilde{\nu}$ = 3007, 2957, 2928, 1602, 1560, 1486, 1450, 1394, 1345, 1273, 1253, 1191, 1147, 1104, 1061, 1021, 942, 922, 839, 762, 702 cm^{-1}; MS (EI): *m*/*z* (%): 560 (100) [M^+]; elemental analysis calcd (%) for $C_{26}H_{26}F_6OS_2Si$ (560.69), C 55.70, H 4.67; found: C 55.94, H 4.59.

Compound **42**-H was synthesized from **42**-SiMe$_3$ (500 mg, 0.89 mmol) as described above for the compound **38**-H, to obtain a colorless oil (397 mg, 91%) which gradually crystallized into a pale blue solid. M.p. 99–101 °C; $R_f = 0.35$ (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.078$ (s, 3H), 2.083 (s, 3H), 2.31 (s, 3H), 3.78 (s, 3H), 6.71 (br s, 1H), 7.27–7.41 ppm (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$):[37] $\delta = 14.5$, 14.6, 15.0, 61.1, 109.2, 118.7, 124.5, 125.5, 127.2, 128.52, 129.2, 129.7, 133.9, 137.1, 163.8 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -112.4$ to −108.8 (br m, 4F), −133.2 ppm (s, 2F); IR (film): $\tilde{\nu}$ = 2959, 2929, 2872, 1600, 1559, 1501, 1448, 1395, 1341, 1275, 1228, 1191, 1143, 1111, 1059, 1022, 985, 920, 758, 698 cm^{-1}; MS (EI): *m*/*z* (%): 488 (100) [M^+]; HRMS: *m*/*z*: calcd for $C_{23}H_{18}F_6OS_2$: 488.0748; found: 488.0748 [M+H]$^+$.

4-[2-(2-Methoxy-4-methyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-5-methoxy-3-methythiophene (43-H):[38] To a solution of the thiophene **40** (558 mg, 2.00 mmol) in anhydrous THF (4.0 mL),

was added slowly at −78 °C *n*BuLi (2.5 M in hexanes, 0.80 mL, 2.00 mmol) and, after stirring at this temperature for 30 min, a solution of compound **39** (396 mg, 1.0 mmol) in anhydrous THF (2.0 mL) was added slowly at −78 °C. The mixture was allowed to warm up to room temperature and stirred for 30 min, then nBu$_4$NF (1.0 M in THF, 2.0 mL, 2.0 mmol) was added slowly. After 2 h of stirring, the mixture was diluted with Et$_2$O (100 mL), washed with water (50 mL), dried and filtered. After removal of the solvents, the residue was subjected to chromatography on silica gel (50 g, column 2×20 cm, pentane/ethyl acetate 10:1) to yield the title compound as an oil (330 mg, 65 % over two steps). R_f = 0.35 (pentane/diethyl ether 20:1); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.08 (s, 3H), 2.083 (d, J = 1, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 6.25 (q, J = 1, 1H), 7.28–7.41 ppm (m, 5H); ^{13}C NMR (75.4 MHz, CDCl$_3$):[37] δ = 14.0, 15.7, 61.1, 61.3, 107.1 (CH), 108.7, 110.4, 124.4, 127.0 (CH), 128.5 (CH), 129.1 (CH×2), 130.4, 134.1, 135.1, 163.3, 165.0 ppm; IR (film): $\tilde{\nu}$ = 2961, 2924, 2850, 1559, 1511, 1456, 1397, 1339, 1276, 1241, 1190, 1165, 1138, 1106, 1063, 1032, 979, 919, 758, 698 cm^{-1}; MS (ESI, positive mode): m/z (%): 507 (9)/506 (25)/505 (100) [M+H]$^+$; HRMS (ESI): m/z: calcd for $C_{23}H_{19}F_6O_2S_2$: 505.0775, found: 505.07221 [M+H]$^+$.

3-Bromo-2-methoxy-4-methylthiophene (47): *n*BuLi (2.3 M in hexanes, 8.8 mL, 20.2 mmol) was added at −78 °C to a solution of 2,4-dibromo-5-methoxy-3-methylthiophene (**15**, 5.75 g, 20.1 mmol) in anhydrous Et$_2$O (50 mL). After stirring at −78 °C for 30 min, MeOH (3 mL) was added dropwise, and the reaction mixture was poured into ice water (50 mL). The organic layer was separated, and the aqueous phase was extracted with Et$_2$O (3×20 mL). The combined organic solutions were washed with sat. aq. NH$_4$Cl (50 mL) and dried. After removal of the solvent, the residue was distilled (b.p. 140–147 °C (10 Torr) or purified by column chromatography (3×20 cm column with silica gel, R_f = 0.50 in pentane), and the title compound was isolated as a colorless liquid (3.51 g, 84 %). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.16 (brs, 3H), 3.95 (s, 3H), 6.37 ppm (brs, 1H); ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 16.3, 61.1, 94.2, 106.0, 134.4, 158.2 ppm; IR (film): $\tilde{\nu}$ = 3100, 3010, 2936, 2916, 2828, 1559, 1497, 1430, 1380, 1235, 1149, 1056, 997, 968, 810, 701 cm^{-1}; MS (EI): m/z (%): 208 (80) [M(^{81}Br)$^+$], 206 (78) [M(^{79}Br)$^+$], 193 (100), 191 (98), 165 (39), 163 (40), 84 (70), 45 (64); elemental analysis calcd (%) for C_6H_7BrOS (207.09): C 34.80, H 3.41; found: C 34.70, H 3.12.

5-[2-(2-Methoxy-4-methyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopenten-1-yl]-2-methoxy-4-methythiophene (48-OMe): *n*BuLi in hexane (2.3 M, 5.2 mL, 12.0 mmol) was added dropwise at −78 °C to a solution of the compound **47** (2.46 g, 11.9 mmol) in THF (20 mL). After stirring for 1 h, a solution of the compound **39**[9c] (3.2 g, 8.1 mmol) in THF was added slowly. The color of the reaction mixture changed to red-brown. After stirring at −78 °C for 15 min, TLC showed that **39** had been consumed completely. The reaction was quenched by adding MeOH (1 mL), the mixture was diluted with Et$_2$O (100 mL) and washed with sat. aq. NH$_4$Cl (50 mL). The organic layer was separated and dried. After removal of the solvents in vacuo, the residue was purified by chromatography on silica gel (200 g), elution with a hexane/CHCl$_3$ mixture (5:1 → 3:1) to afford a yellowish oil, which readily crystallized to give a colorless solid (2.1 g, 51 %). M.p. 77 °C; R_f = 0.4 (hexane/CHCl$_3$ 3:1); ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.92 (s, 3H), 1.96 (s, 3H), 3.87 (s, 3H), 3.92 (s, 3H), 5.99 (s, 1H), 7.28–7.40 ppm (m, 5H); ^{13}C NMR (75.4 MHz, CDCl$_3$):[37] δ = 13.9, 16.3, 59.9, 61.6, 108.2 (CH), 109.8, 110.7, 125.1, 127.1 (CH), 128.5 (CH), 129.1, 130.2, 134.1, 140.6, 161.1, 169.0 ppm; IR (KBr): $\tilde{\nu}$ = 2360, 1559, 1521, 190, 1457, 1419, 1250, 1125, 1001, 839, 755, 693 cm^{-1}; MS (ESI, positive mode): m/z (%): 505 (74) [M+H]$^+$, 473 (100), 242 (71); elemental analysis calcd (%) for $C_{23}H_{18}F_6O_2S_2$: C 54.76, H 3.60, found: C 54.48, H 3.39.

1,2-Bis-(2-methoxy-4-methylthiophen-3-yl)perfluorocyclopentene (49): To a solution of the thiophene **47** (1.03 g, 5.0 mmol) in anhydrous Et$_2$O (20 mL), was added slowly at −78 °C *n*BuLi (2.3 M in hexanes, 2.2 mL, 5.0 mmol), and the mixtute was stirred at this temperature for 2 h. Perfluorocyclopentene (2.4 mol, 0.31 mL) was added at −78 °C. The reaction mixture was further at −30 °C stirred for an additional 5 h, then it was allowed to warm up to room temperature. After stirring for additional 2 h, Et$_2$O (40 mL) was added, and the mixture was washed with diluted aq. HCl (1 % v/v, 50 mL), sat. aq NaHCO$_3$ (50 mL) and water (50 mL). The combined organic solutions were dried, filtered and evaporated. The residue was purified by chromatography (3×20 cm column with silica gel, R_f = 0.15 in pentane) to give the title compound (400 mg, 39 %) as an oil. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.02 (s, 6H), 3.75 (s, 6H), 6.21 (s, 2H); ^{13}C NMR (62.9 MHz, CDCl$_3$):[37] δ = 15.6, 53.4, 61.1, 107.0, 108.8, 135.0, 164.9 ppm; IR (film): $\tilde{\nu}$ = 2926, 1734, 1685, 1653, 1559, 1496, 1456, 1395, 1339, 1277, 1249, 1033, 908, 736 cm^{-1}; MS (EI): m/z (%): 428 (100) [M^+]; HRMS: m/z: calcd for $C_{17}H_{14}F_6O_2S_2$: 428.0339; found: 428.0339 [M+H]$^+$.

1,2-Bis-(5-iodo-2-methoxy-4-methylthiophen-3-yl)perfluorocyclopentene (50): To a solution of the compound **49** (1.38 g, 3.22 mmol) in benzene (40 mL), were added alternatingly in small portions yellow HgO (1.68 g, 7.74 mmol) and I$_2$ (7.74 mmol, 1.97 g) during 30 min, and the mixture was stirred for an additional 1 h. It was filtered, the filter-cake was washed with benzene (100 mL), and the combined solutions were washed with a sat. aq. Na$_2$S$_2$O$_3$ (20 mL) and water (20 mL). After drying and evaporation of the solvent, the residue was purified by chromatography (3×20 cm column with silica gel, R_f = 0.10 in pentane) to afford the title compound (1.84 g, 84 %) as a blue solid. M.p. 131–132 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.96 (s, 6H), 3.77 ppm (s, 6H); ^{13}C NMR (62.9 MHz, CDCl$_3$):[37] δ = 17.9, 59.4, 61.3, 108.1, 139.3, 167.4 ppm; ^{19}F NMR (282 MHz, CDCl$_3$): δ = −117.6 to −105.3 (brm, 4F), −132.8 ppm (s, 2F); IR (KBr): $\tilde{\nu}$ = 2965, 2934, 1559, 1487, 1456, 1392, 1339, 1276, 1235, 1143, 1112, 1066, 1030, 984, 909, 735 cm^{-1}; MS (EI): m/z (%): 680 (100) [M^+]; elemental analysis calcd (%) for $C_{17}H_{12}F_6I_2OS_2$ (680.21): C 30.02, H 1.78; found: C 30.29, H, 1.66.

Crystal structure analysis of compound **50**:[28] Crystal size 0.30×0.30×0.30 mm^3, orthorhombic, a = 899.91(3), b = 1538.08(6), c = 1565.37(7) pm, α = 90, β = 90, γ = 90°, V = 2.16668(15) nm^3; Z = 4, space group $P\bar{1}$, T = 133(2) K, ρ = 2.085 Mg m^{-3}, absorption coefficient = 3.157 mm^{-1}, F(000) = 1288, θ range for data collection = 1.86 to 24.78°, reflections collected: 33403, independent reflections: 3683 [R_{int} = 0.0379], data/restraints/parameters = 3683/0/266, goodness of fit on F^2: 1.087, final R indices [I > 2σ(I)]: R_1 = 0.0146, wR_2 = 0.0361; R indices (all data): R_1 = 0.0150, wR_2 = 0.0363; largest diff. peak and hole = 0.360 and −0.281 e Å^{-3}.

4-Bromo-5-methoxy-3-methylthiopheneboronic acid (51) and its coupling with iodobenzene: To a solution of the thiophene **15** (1.5 g, 5.2 mmol) in Et$_2$O (12 mL), was added dropwise at −78 °C *n*BuLi (2.3 M in hexanes, 2.3 mL, 5.3 mmol), and after 15 min neat (*i*PrO)$_3$B (1.5 g, 8.0 mmol) was added slowly. The mixture was allowed to warm up to room temperature, stirred overnight, cooled again to 0 °C, and 1 M aq. NaOH (25 mL) was slowly added. The aqueous layer was separated, washed with Et$_2$O (25 mL) and carefully acidified at 0 °C up to pH 5–6 by addition of 5 % aq. KHSO$_4$. The precipitated product was filtered off, washed with ice-water (5 mL) and pressed between several sheets of filter paper to yield about 1.0 g of the title compound, which contained the monobromide **47** as an impurity. ^{1}H NMR (250 MHz, [D$_6$]DMSO + CDCl$_3$): δ = 2.27 (s, 3H), 3.88 (s, 3H), 4.3 ppm (brs, OH); ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 16.4, 61.3, 95.6, 106.6, 143.4, 161.9 ppm. The content of **47** increased upon drying, and a third set of signals appeared, probably due to the formation of the corresponding cyclic anhydride. To an analogously obtained reaction mixture from **15** (0.99 g, 3.5 mmol), *n*BuLi (2.3 M in hexanes, 1.5 mL, 3.5 mmol) and (*i*PrO)$_3$B (1.1 g, 5.6 mmol) in THF (8 mL), 20 % aq. Na$_2$CO$_3$ (8 mL) was added, followed by the solution prepared from PhI (385 μL, 705 mg, 3.45 mmol), [Pd(dba)$_2$] (80 mg, 0.14 mmol) and Ph$_3$P (150 mg, 0.57 mmol) in THF (5 mL), and the mixture was heated at reflux for 16 h (bath temp. 95 °C). The organic layer was separated, washed with brine (10 mL) and evaporated in vacuo. An internal standard (*p*-MeOCH$_2$OC$_6$H$_4$OCH$_2$OMe) was added to the residue, and the yields of **17** (40 %) and **47** (48 %) were estimated by integration of the corresponding singlets in the ^{1}H NMR spectrum (250 MHz, CDCl$_3$).

Coupling of the iodide 24 with α-unsubstituted thiophenes 38-H–41-H via their α-zinc derivatives, synthesis of the assemblies 4–7: 2,2,6,6-Tetramethylpiperidine (180 mg, 1.27 mmol) and anhydrous THF (1 mL) were introduced through a septum into a flame-dried round-bottomed 10 mL flask (no. 1) with a side arm, which had been filled with argon. *n*BuLi (2.5 M in hexanes, 0.5 mL, 1.25 mmol) was added to this solution at −78 °C, and stirring was continued for 10 min. Then a solution of the dried α-unsubstituted thiophene (**38**-H–**41**-H, 0.5 mmol) in THF (1 mL),

which was prepared under Ar in a flame-dried Schlenk 10 mL flask (no. 2), was added carefully at −78 °C, and the mixture was stirred for 30 min. After that a solution of anhydrous $ZnCl_2$ (1 M in Et_2O, 1.3 mL, 1.3 mmol) was added carefully at −78 °C, the cooling bath was removed, and the reaction mixture was allowed to warm up to 0 °C. (It may contain a precipitate.) In a separate dry flask (no. 3), a mixture of the iodophenylbicyclopentane **24** (43 mg, 60 μmol), [Pd(dba)$_2$] (4 mg, 7 μmol) and Ph_3P (7 mg, 30 μmol) was prepared under Ar. Anhydrous THF (5 mL) was introduced through a septum, and the yellow-orange suspension was stirred at room temperature for 10 min. Then the solution (or suspension) of the α-zinc derivative was taken from the flask (no. 1) with a syringe with an appropriately thick needle and added dropwise with stirring into the flask (no. 3). The reaction mixture was stirred at 35–38 °C for 16–24 h, until no spot of the starting iodide was detected on the TLC. Then it was diluted with $CHCl_3$ (50 mL), washed with sat. aq. NH_4Cl (20 mL), and dried. After evaporation of the sovent, the residue was taken up in a minimal amount of hot $CHCl_3$ and applied onto a column with silica gel (200 g). The unreacted starting thiophene and the corresponding coupling product were eluted with a hexane/$CHCl_3$ mixture (4:1 → 1:2). The final products were obtained as orange solids, washed with a hexane/ether mixture and, if necessary to further improve their purity, additionally recrystallized from a $CHCl_3$/hexane mixture.

Assembly 4: Yield 54 mg (86 %); HPLC: t_R (open form) = 28.2 min, t_R (closed form) = 45.0 min (40 °C, 1 mL per min, detection at the isobestic point of 298 nm); ^{1}H NMR (600 MHz, $CDCl_3$, open form, mixture of two isomers): δ = 2.06/2.08 (3H), 2.09 (3H), 2.33 (3H), 2.35/2.36 (3H), 2.37 (6H), 4.09 s, 4.10 (s, 6H), 6.89 (d, J = 7.6, 2H), 7.28–7.38 (m, 7H), 7.42 (t, J = 7.0, 2H), 7.49 (dd, J = 7.6 and 8.8, 2H), 7.67 (d, J = 8.2, 2H), 7.71 (dd, J = 1.2 and 8.2, 2H), 8.52 ppm (ddd, J = 1.2, 4.4 and 8.5, 2H); IR (KBr): $\tilde{\nu}$ = 2961, 2928, 2855, 1617, 1533, 1398, 1341, 1263, 1192, 1146, 1096, 1032, 787, 690, 472 cm^{-1}; MS (CI/NH_3): m/z (%): 1068 (20) $[M+NH_4]^+$, 1051 (100) $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{66}H_{49}F_6S_2O_2$: 1051.3079, found: 1051.3077 $[M+H]^+$.

Assembly 5: Yield 55 mg (86 %); HPLC: t_R (open form) = 23.4 min, t_R (closed form) = 28.2 min (40 °C, 1 mL per min, detection at the isobestic point of 305 nm); ^{1}H NMR (600 MHz, $CDCl_3$, open form): δ = 2.09 (brs), 2.11 (s) (Σ 6H), 2.31 (brs, 3H), 2.37 (s, 6H, CH_2), 3.76 (brs, 3H), 4.09 (s), 4.10 (s) (Σ 6H), 6.90 (d, J = 7.6, 2H), 7.30–7.38 (m, 12H), 7.42 (t, J = 7.3, 2H), 7.49 (t, J = 8.2, 2H), 7.67 (d, J = 8.2, 2H), 7.71 (d, J = 7.0, 2H), 8.52 ppm (dd, J = 4.7 and 8.8, 2H); ^{1}H NMR (500 MHz, $CDCl_3$, closed form): δ = 2.01/2.027/2.034 (s, 9H), 2.39 (s, 6H), 3.67 (s, 3H), 4.09 (s), 4.10 (s) (Σtotal 6H), 6.90 (d, J = 7.3, 2H), 7.31–7.45 (m, 9H), 7.49 (t, J = 8.2, 2H), 7.68 (d, J = 8.0, 2H), 7.71 (d, J = 7.1, 2H), 8.52 ppm (dd, J = 5.2 and 8.8, 2H); IR (KBr): $\tilde{\nu}$ = 2960, 2926, 2867, 1533, 1458, 1395, 1340, 1262, 1192, 1142, 1096, 1031 cm^{-1}; MS (CI/NH_3): m/z (%): 1067 (100) $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{66}H_{49}F_6S_2O_3$: 1067.3027; found: 1067.3021 $[M+H]^+$.

Assembly 6: Yield 35 mg (54 %), R_f = 0.3 (hexane/CH_2Cl_2, 2:1), HPLC: t_R (open form) = 23.8 min, t_R (closed form) = 28.4 min (40 °C, 1 mL per min, detection at the isobestic point of 308 nm); ^{1}H NMR (300 MHz, $CDCl_3$, open form): δ = 2.08 (s, 6H), 2.32 (s, 3H), 2.39 (s, 6H), 3.76 (s, 3H), 4.095 (s), 4.105 (s) (Σ 6H), 6.88 (d, J = 8, 2H), 7.30–7.54 (m, 16H), 7.66–7.74 (m, 4H), 8.52 ppm (dd, J = 1 and 8, 2H); ^{1}H NMR (500 MHz, $CDCl_3$, closed form): δ = 2.01/2.02/2.03 (s, 9H), 2.38 (6H), 3.62 (s, 3H), 4.09 (s), 4.10 (s) (Σ 6H), 6.90 (d, J = 7.3, 2H), 7.31–7.44 (m, 9H), 7.49 (t, J = 7.9, 2H), 7.67 (d, J = 8.0, 2H), 7.71 (dd, J = 1.4 and 6.9, 2H), 8.52 ppm (dd, J = 4.4 and 8.7, 2H); IR (KBr): $\tilde{\nu}$ = 2963, 2907, 2868, 2829, 1653, 1559, 1539, 1457, 1263, 1192, 1144, 1112, 1033 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{66}H_{49}F_6S_2O_3$: 1067.3027; found: 1067.3024 $[M+H]^+$.

Assembly 7: Yield 49 mg (74 %), HPLC: t_R (open form) = 23.3 min, t_R (closed form) = 24.7 min (40 °C, 0.8 mL per min, detection at the isobestic point of 315 nm); ^{1}H NMR (300 MHz, $CDCl_3$, open form): δ = 2.08 (s, 6H), 2.37 (s, 6H), 3.76 (s, 6H), 4.09 (s), 4.10 (s) (Σ 6H), 6.90 (d, J = 7.4, 2H), 7.29–7.45 (m, 9H), 7.49 (dd, J = 7.9 and 8.6, 2H), 7.67 (d, J = 8.1, 2H), 7.71 (dd, J = 1.3 and 7.9, 2H), 8.53 ppm (dd, J = 2.1 and 8.7, 2H); IR (KBr): $\tilde{\nu}$ = 2968, 2935, 2908, 2869, 1559, 1525, 1472, 1437, 1262, 1096, 1031 cm^{-1}; MS (CI/NH_3): m/z (%): 1100 (18) $[M+NH_4]^+$, 1183 (100) $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{66}H_{49}F_6S_2O_4$: 1083.2976; found: 1083.2967 $[M+H]^+$.

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[13] Deprotonation of 3-methylthiophene with *n*BuLi/TMEDA in a hexane-ether mixture (see ref. [16]) followed by quenching with MeI, gave an inseparable mixture of 2,4- and 2,3-dimethylthiophenes (ca. 4:1). Kumada coupling of 2-bromo-4-methylthiophene (its preparation is described in the main text) with MeMgCl is low-yielding (probably this is a general drawback of all 2-halothiophenes). The previously published procedure of M. Takeshita, M. Tashiro, *J. Org. Chem.* **1992**, *57*, 746–748) requires 2,5-dibromothiophene as a starting material, methyl chloromethyl ether as a reagent and CS_2 as a solvent, and the intermediately formed 2,4-dibromo-3,5-di(chloromethyl)thiophene could not be reduced easily and cleanly with $LiAlH_4$ in THF to pure 2,4-dibromo-3,5-dimethylthiophene. Two-fold bromine–lithium exchange in the expensive 2,4-dibromothiophene followed by methylation with an excess of $(MeO)_2SO_2$ (M. Janda, J. Šrogl, I. Stibor, M. Nìmec, P. Vapatrna, *Synthesis* **1972**, 545–547) is very difficult to control, and this protocol also does not afford a reasonably pure product.
[14] A procedure similar to a previously reported method was used; see: J. Froehlich, C. Hameter, W. Kalt, *Monatsh. Chem.* **1996**, *127*, 325–330.
[15] a) M. Kumada, K. Tamao, K. Sumitani, *Org. Synth.* **1978**, *58*, 127–133; b) M. Takeshita, M. Tashiro, *J. Org. Chem.* **1991**, *56*, 2837–2845.
[16] G. Consiglio, D. Spinelli, S. Gronowitz, A.-B. Hoernfeldt, B. Maltesson, R. Noto, *J. Chem. Soc. Perkin 2* **1982**, 625–630.
[17] M. A. Keegstra, T. H. A. Peters, L. Brandsma, *Tetrahedron* **1992**, *48*, 3633–3652. An alternative preparation of **14** is much more difficult and gave worse results. Thus, 2,4-dibromothiophene in the presence of CuBr (20 mol%) reacted with MeONa in MeOH to give predominantly 4-bromo-2-methoxythiophene, which could be isolated in 41% yield by a difficult chromatographic separation from the regioisomer and the unreacted starting material. Kumada coupling of 4-bromo-2-methoxythiophene with MeMgCl then afforded the required compound **14**.
[18] A. Hallberg, S. Gronowitz, *Chem. Scr.* **1980**, *16*, 38–41.
[19] S. Kobatake, M. Irie, *Tetrahedron* **2003**, *59*, 8359–8364.
[20] For a recent example of applying $PhI(OCOCF_3)_2$ with iodine for the iodination of aromatics, see: Q. Li, A. V. Rukavishnikov, P. A. Petukhov, T. O. Zaikova, J. F. W. Keana, *Org. Lett.* **2002**, *4*, 3631–3634. In our hands other oxidizing agents gave poorer results.
[21] K. M. Lynch, W. P. Dailey, *Org. Synth.* **1997**, *75*, 98–105.
[22] These reagents were used for the monomethylation of 1-hydroxy-5-methoxy-9,10-anthraquinone: a) S. Laugraud, A. Guingant, C. Chassagnard, J. d′Angelo, *J. Org. Chem.* **1988**, *53*, 1557–1560; methylation of anthrarufin (Aldrich, techn. grade, ≈85% purity) with $(MeO)_2SO_2$ in DMF with NaH at 80°C for 24 h gave the desired product in 75% yield after column chromatography (cf.: b) H. Quast, H.-L. Fuchbauer, *Chem. Ber.* **1986**, *119*, 1016–1038); c) P. N. Preston, *J. Chem. Soc. Perkin Trans. 1* **1983**, 1439–1441.
[23] See: W. Ried, W. Donner, W. Schlegelmilch, *Chem. Ber.* **1961**, *94*, 1051–1058.
[24] W. Chodkiewicz, P. Cadiot, *C. R. Chim.* **1958**, *247*, 2383–2385.
[25] It may not only arise by an oxidative coupling of **26**, but also from the corresponding tin acetylide, which may be present as an impurity in the crude starting material **26**.
[26] a) J. Sice, *J. Org. Chem.* **1954**, *19*, 70–73; b) S. Gronowitz, K. Lawitz, *Chem. Scr.* **1983**, *22*, 265- 266; c) H.-J. Bertram, M. Guentert, R. Hopp, H. Sommer, P. Werkhoff, *New J. Phys.* **2006**, *8*, 275–284.
[27] Chemical shifts of the thiophene proton in the rearranged compounds **48**-Me and **48**-OMe are δ 6.50 and 5.98 ppm, respectively (δ 6.72 and 6.22 ppm in **38**-H and **43**-H, respectively). The difference of 0.2 ppm is diagnostically important: the proton signal of the "normal" regioisomer is always found at a higher field. Moreover, the closed form of the wrong substance **48**-OMe absorbs light with a maximum at about 500 nm, and its solutions turned red upon irradiation with UV light. The right compound **43**-H has a much longer π-conjugation path in the closed form leading to a $\lambda_{max}\approx600$ nm, and its solutions turned blue (cf.: K. Yagi, C. F. Soong, M. Irie, *J. Org. Chem.* **2001**, *66*, 5419–5423).
[28] CCDC-290971 and -290972 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[29] M. Morimoto, M. Irie, *Chem. Commun.* **2005**, 3895–3905 and references therein.
[30] R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, VCH, Weinheim, **1970**.
[31] This prerequisite is not sufficient: M. Irie et al. reported that if the distance between the reactive carbon atoms in the antiparallel orientation exceeds 4.2 Å, the photocyclization does not occur. If this distance is shorter than 4.0 Å, the ring-closing reaction may be efficient: a) S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Commun.* **2002**, 2804–2805; b) K. Shibata, K. Muto, S. Kobatake, M. Irie, *J. Phys. Chem. A* **2002**, *106*, 209–214.
[32] The boronic acids **42**-$B(OH)_2$ and **43**-$B(OH)_2$, which were obtained from the bromides **42**-Br/**43**-Br and further treated (without isolation) with an excess of 1,3-bis-(4-iodophenyl)adamantane, were reported to give the corresponding mono-coupling products in 28 and 18% yield, respectively (ref. [9c]).
[33] M. H. Deniel, D. Lavabre, J. C. Micheau, in *Organic Photochromic and Thermochromic Compounds, Vol 2: Physicochemical Studies, Biological Applications, and Thermochromism* (Eds.: J. C. Crano, R. J. Guglielmetti), Kluwer Academic, Plenum Publishers, New York, **1999**, pp. 167–209.
[34] a) Y. Goldberg, H. Alper, *J. Org. Chem.* **1993**, *58*, 3072–3075; b) M. J. Marsella, G. Piao, F. S. Tham, *Synthesis* **2002**, 1133–1135.
[35] This procedure is similar to the method previously reported, see: J. Froehlich, C. Hameter, W. Kalt, *Monatsh. Chem.* **1996**, *127*, 325–330.
[36] S. Kobatake, M. Irie, *Tetrahedron* **2003**, *59*, 8359–8364.
[37] Signals of the fluorinated carbon atoms were not registered, due to low intensity.
[38] This compound had previously been prepared by M. Irie et al. and used for further reactions without characterization (see Supporting Information of ref. [9c]).

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