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Synthesis and Photoswitching Studies of Difurylperfluorocyclopentenes with Extended π-Systems

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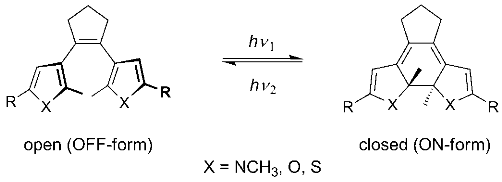
Abstract: In an attempt to design molecular optoelectronic switches functioning in molecular junctions between two metal tips, we synthesized a set of photochromic compounds by extending the π-system of 1,2-bis-(2-methyl-5-formylfuran-3-yl)perfluorocyclopentene through suitable coupling reactions involving the formyl functions, thereby also introducing terminal groups with a binding capacity to gold. Avoiding the presence of gold-binding sulphur atoms in the photoreactive centre, as they are present in the frequently used analogous thienyl compounds, the newly synthesized compounds should be more suitable for the purpose indicated. The kinetics of reversible photoswitching of the new compounds by UV and visible light was quantitatively investigated in solution. The role of conformational flexibility of the π-system for the width of the UV/Vis spectra was clarified by using quantum chemical calculations with time-dependent (TD)-DFT. As a preliminary test of the potential of the new compounds to serve as optoelectronic molecular switches, monolayer formation and photochemical switching on gold surfaces was observed by using surface plasmon resonance.

Keywords: electrocyclic reactions · molecular electronics · photochromism · photoswitches · surface plasmon resonance

Introduction

Molecular switches have been vastly investigated in the last two decades due to promising applications in molecular electronics, in particular, optoelectronics, optical data storage or self-assembling polymeric systems.[1–2] Of particular interest for molecular electronics applications are molecules that can be reversibly switched between two well-defined states through optical activation. These can be contacted in a two-wire geometry and do not require a third (control) electrode. Among a great variety of types of molecular switches,[3–4] diarylethenes, in particular, substituted bis(hetaryl)cycloalkenes,[5] have figured most prominently in recent years. They exhibit moderate to good quantum yields of photocyclization–photocycloreversion reactions (e.g. "on–off" switching, Scheme 1) and high fatigue resistance. Because the switching process goes along with only minor length change, they are suitable as a molecular bridge between two metal contacts,[6] thus providing a break-junction molecular unit, the conductance of which can be optically controlled.[7] Also interesting is the immobilization of the functionalized switches on a gold surface: reversible switching by light of appropriate wavelengths has been demonstrated for an asymmetrically substituted dithienylcyclopentene with one anchoring group under such conditions.[8]



Scheme 1. Switching process of diheteroarylethenes induced by light of different wavelengths.

Molecular junctions of the diarylethene type have been investigated before. However, their switching properties were reported to be non-reversible when closely embedded between two metal electrodes.[9] The molecules switched reversibly when attached to only one electrode though.[8] It has been argued that photoisomerization did not occur because the photoexcited state was quenched in the presence of the metal. An alternative explanation of the irreversibility could be undesired bonding of the sulphur atoms in the thio-

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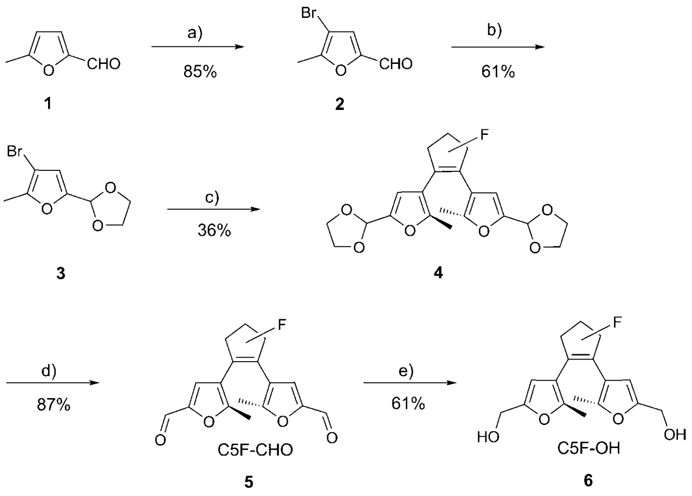
phene rings to the metal surface (gold is the most commonly used electrode metal in molecular electronics).

To avoid this undesired mode of adsorption, we synthesized a series of molecular switches of the difurylethene type. These are sulphur-free in their switching unit but have heteroatom-modified side chains, hence allowing to bridge metal contacts. Another reason for the choice of furans is that their diene character is more pronounced than that of thiophenes. Therefore, an enhanced reactivity in pericyclic reactions may be expected.

So far, the photoswitching properties of only two difurylethenes have been thoroughly studied by Yamaguchi and Irie.[10] They compared the properties of 1,2-diarylperfluorocyclopentene derivatives with either aryl = thienyl or furyl (X = S or O) and R = methyl or phenyl. In the short-hand notation that will be used for our compounds in the remainder of the paper, the furyl compounds would be assigned the codes C5F-Me and C5F-Ph, respectively, C5F representing the central bridging perfluorinated five-membered ring, Me coding for methyl and Ph for phenyl substituents at the 5-position of the furan rings. As was described in reference [10], the thienyl and furyl derivatives exhibit very similar switching properties. The closed forms of the phenyl derivatives of both types of photochromic molecules have long thermal half lives and stand more than 150 switching cycles before deteriorating to a level below 80%. These results encouraged us to go ahead with the synthesis of photochromic furyl compounds with more extended π-systems, including terminal groups capable of bonding to a gold surface, thus opening a pathway to the controlled molecular design and tuning of the photochemical properties.

Results and Discussion

Synthesis: Several routes to difuryl-substituted ethenes have been described in the literature. Among these are reductive coupling of carbonyl precursors according to the McMurry reaction[11] with TiCl$_4$/Zn as the reducing system,[12–14] Stille coupling,[15] and Suzuki cross-coupling.[13] For our purposes, the coupling of brominated aryl moieties to the double bond in perfluorinated cyclopentene with nBuLi as used in reference [10] was the method of choice. In general, furans are known to be labile molecules relative to the corresponding thiophene derivatives since the furan ring shows more diene-like rather than aromatic properties. Moreover, acidic conditions may lead to protonation and further destruction of the furan rings, especially in the case of electron-rich ones. To avoid this, the electron-poor furaldehyde C5F-CHO (**5**) was synthesized as a common starting compound (Scheme 2), for which further extension of the π-system can be easily achieved.



Scheme 2. Synthetic pathway to the key intermediate, dialdehyde **5**: a) Br$_2$, AlCl$_3$, neat; b) ethylene glycol, p-toluensulfonic acid, toluene, reflux; c) tBuLi, THF, −78 °C, then C$_5$F$_8$; d) HCl$_{aq.}$, acetone/THF 1:1, 24 h, RT; e) LiAlH$_4$, Et$_2$O, reflux.

The structure of the protected aldehyde **4** was characterized by X-ray crystallographic structure determination. Suitable single crystals were grown by slow diffusion of n-hexane into a saturated solution of **4** in diethyl ether.[16] The compound crystallizes in the monoclinic system in the centrosymmetric space group $C2/c$ with half a molecule in the asymmetric unit with carbon atom C7 located on a two-fold rotation axis. In the crystalline state, the molecule adopts the antiparallel conformation with both furan rings pointing away from the central hexafluorocyclopentene. With a value of 11.46° the torsion angle (C4-C5-C4^i-C5^i) between the furan rings is much larger than the corresponding angle in the two other structurally related furan derivatives known so far (7.21 for C5F-Ph and 6.95° for C5F-Me).[17] However, in the crystal a distance of 3.59 Å between the reactive carbon atoms C8 and C8^i in **4** (Figure 1) is in surprisingly good accord with the data from reference [17] (3.54 for C5F-Ph and 3.74 Å for C5F-Me), for which a value of 4.2 Å

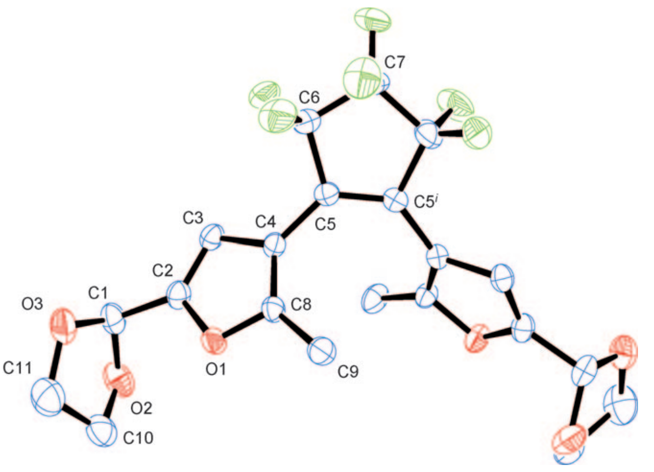
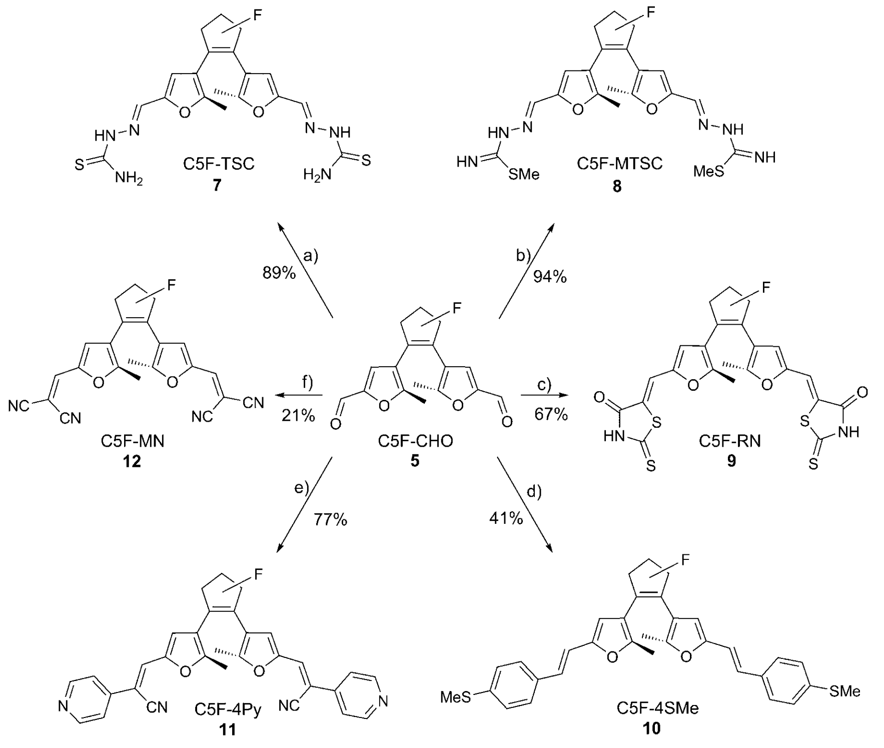


Figure 1. X-ray crystal structure of the protected aldehyde **4**. Thermal ellipsoids are drawn at the 50% probability level. Main occupancy is shown for disordered fluorine atoms; hydrogen atoms are omitted for clarity.

is given as a condition sufficient for photochromic ring closure in the crystal.

The reactive aldehyde groups of compound **5** offer various pathways of modification of the switching unit to vary its coupling strength to the metal's electronic system. Thereby a wide range of possibilities is opened up for modifications (extending the π-system, prolonging an aliphatic side chain to increase solubility, connecting with chelating ligands with further metal coordination, etc.). In this work, we synthesized the thiosemicarbazones **7** and **8** and the compounds **9**–**12** carrying vinylogous π-systems attached to the furan rings (Scheme 3). All the N and S atom containing endgroups bear the affinity to bind to gold, thereby providing suitable anchoring of the switches between two gold contacts.



Scheme 3. Synthesis of functionalized molecular switches based on either the formation of an azomethine (**7**–**8**), a Knoevenagel-approach (**9**, **11** and **12**) or a Wittig-reaction (**10**): a) thiosemicarbazide, MeOH, RT, 24 h; b) methylthiosemicarbazide, MeOH, RT, 24 h; c) rhodanine, dichloromethane, piperidine, RT, 12 h; d) [4-(methylthio)benzyl]triphenylphosphonium bromide, MeOH, MeONa, RT, 36 h; e) 2-(pyridin-4-yl)acetonitrile hydrochloride, K_2CO_3, MeOH, RT, 48 h; f) malodinitrile, cat. piperidine, benzene, RT, 4 h.

The synthesis of thiosemicarbazone C5-TSC (**7**) and methylthiosemicarbazone C5F-MTSC (**8**) was achieved in good yield by azomethine formation with aldehyde **5** and the respective hydrazine derivatives in methanolic solution at room temperature (Scheme 3). Switches **9**, **11** and **12** were synthesized by Knoevenagel condensation of the rather CH-active rhodanine (**9**), 2-(pyridin-4-yl)acetonitrile (**11**) and malodinitrile (**12**) with aldehyde **4** under mild basic conditions. The 4-thioanisyl derivative C5F-pSMe (**10**) was prepared by a classical Wittig approach by starting from the ylide accessible by sodium methoxide induced deprotonation of [*p*-(methylthio)benzyl]triphenylphosphonium bromide.

UV/Vis spectra: For solubility reasons, all spectral and photokinetic investigations were carried out in MeOH except for the aldehyde C5F-CHO (**5**), for which the formation of the acetal was observed on irradiation. Therefore $CDCl_3$ was used in that case, which also allowed us to observe the NMR spectrum of irradiated solutions in the same solvent. The general picture of the UV/Vis absorption spectra of the new molecular switches appears as expected for this class of compounds. In the open form, the first absorption band is in the UV to blue spectral range, whereas the first absorption band of the closed form is in the visible region. The positions of these bands move to longer wavelength as the length of the conjugated π-system increases. The spectra of two examples (**6**, C5F-OH and **9**, C5F-RN) demonstrating this effect are shown in Figure 2. The wavelengths and absorption coefficients of all synthesized new photochromic compounds are summarized in Table 1 (for the UV/Vis spectra see the Supporting Information).

To account for the influence of the substituents on the absorption spectra and to test if a rational design of the substituents for specific applications is possible, theoretical spectra were calculated by using TD-DFT (B3LYP/6-31++g(d,p)).[18–20] For an easier comparison with the experiment, the obtained absorption energies were broadened by a Gaussian distribution (full-width half-maximum: 3000 cm^{-1}). The influence of solvents on the transition energies was tested by an implicit solvent model (IEF-PCM[21–22]). The polarization due to different solvents yielded a shift of the absorption frequencies to larger wavelengths of less than 50 nm (data not shown). Since we were only interested in a qualitative description of the influences of the substituents, we restricted the discussion to calculations in vacuo.

The results for C5F-OH (**6**) and C5F-RN (**9**) are shown in Figure 2. For the smaller conjugated system C5F-OH, reasonable agreement between experiment and calculations is found. In particular, the most important lowest-energy transition is nicely reproduced. The shift to longer wavelengths

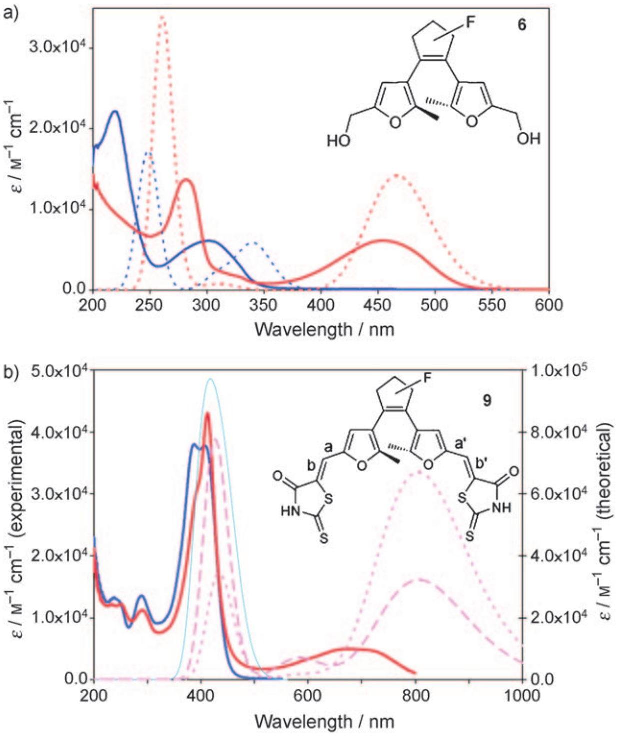


Figure 2. UV/Vis spectra of open and closed forms in MeOH: a) C5F-OH (**6**) (——: exptl. closed; ——: exptl. open; -----: theor. closed; -----: theor. open), b) C5F-RN (**9**) (——: exptl. closed; ——: exptl. open; ——: theor. open; – – –: theor. closed conf. 1; -----: theor. closed conf. 2). Conformation 1 is as shown in the graph, conformation 2 is rotated by 180 degrees around bonds a and a′. There is only a minor effect of this rotation in the open form.

Table 1. Absorption maxima and photoconversion quantum yields.[a]

Compound	λ_{max} (open) [nm]	ε_{max} (open) [$M^{-1}cm^{-1}$]	λ_{max} (closed) [nm]	ε_{max} (closed) [$M^{-1}cm^{-1}$]	$\phi_{o\to c}$ (λ_1)	$\phi_{c\to o}$ (λ_2)
C5F-CHO (**5**)	289	2.40×10^4	533	0.95×10^4	0.40[b,c]	0.11[d]
C5F-OH (**6**)	299	0.59×10^4	455	0.75×10^4	0.42[b]	0.42[d]
C5F-Me[10]	302	0.61×10^4	449	0.87×10^4	0.35	0.32
C5F-Ph[10]	285	3.87×10^4	525	1.65×10^4	0.53	0.077
C5F-TSC (**7**)	327	5.46×10^4	576	1.54×10^4	0.28[b]	4.9×10^{-3}[f]
C5F-MTSC (**8**)	329	5.98×10^4	575	1.79×10^4	0.38[b]	3.2×10^{-3}[f]
C5F-RN (**9**)	388[h]	3.80×10^4	667	0.50×10^4	0.0015[e]	7.2×10^{-5}[g]
C5F-4SMe (**10**)	341	4.72×10^4	592	1.29×10^4	0.69[b]	1.6×10^{-3}[f]
C5F-4Py (**11**)	360	2.87×10^4	612	0.62×10^4	–[i]	–[i]
C5F-MN (**12**)	361	3.67×10^4	–[j]	–[j]	–[j]	–[j]

[a] All data for MeOH as the solvent, except for **5**·C5F-CHO, in which $CDCl_3$ was used. [b] Irradiation wavelength: 313 nm, [c] For the aldehyde **5**, the switching reaction is photoreversible at 313 nm with $\phi_{c\to o}(313)=0.12$. [d] 438 nm. [e] 366 nm. [f] 576 nm. [g] 633 nm (He/Ne-Laser). [h] This compound shows a double maximum at 388/409 nm. [i] More-step photoreaction, quantum yield not determined. [j] Photoirradiation of the open form does not yield characteristic single maximum in the visible region.

with increasing conjugated system is also well predicted. But for the largest systems, such as C5F-RN, the very flat and broad absorption at larger wavelengths cannot be reproduced. One possible explanation for this broadening is the steric freedom of the extended conjugated chain. For example, a change from the *transoid* to the *cisoid* configuration at the formal single bonds designated a and a′ in Figure 2 brings about considerable changes of spectral intensity in the region between 500 and 1000 nm. Spectral broadening may not only be due to different configurations for fully conjugated, planar forms of the central part and the substituents. Due to thermal fluctuations, the substituents could rotate relative to the central part, partially disrupting the conjugated system. Thereby shifts of the lowest-energy transition to shorter wavelengths are expected. To test this assumption, we rotated one of the substituents of C5F-RN around the formal single bond, optimized all other variables and calculated the absorption spectra according to the method described above. The dependence of the lowest-energy absorption with the torsion angle is shown in Figure 3. It can be clearly seen that for 0 and 180°, which correspond to full conjugation, the longest wavelengths are obtained and with 90° the conjugate system is divided into two parts without the possibility of overlapping *p*-orbitals resulting in shorter wavelengths. In the calculations only one of the two substituents is rotated whilst the other one is kept in the optimal planar arrangement, so that an even broader range is expected for the experiment in which both substituents are flexible. Thus we can conclude that the calculations are able to qualitatively reproduce the absorption spectra and that the broad peaks of the larger conjugated systems are caused by conformational averaging of the flexible substituents. Similar calculations can now be used to

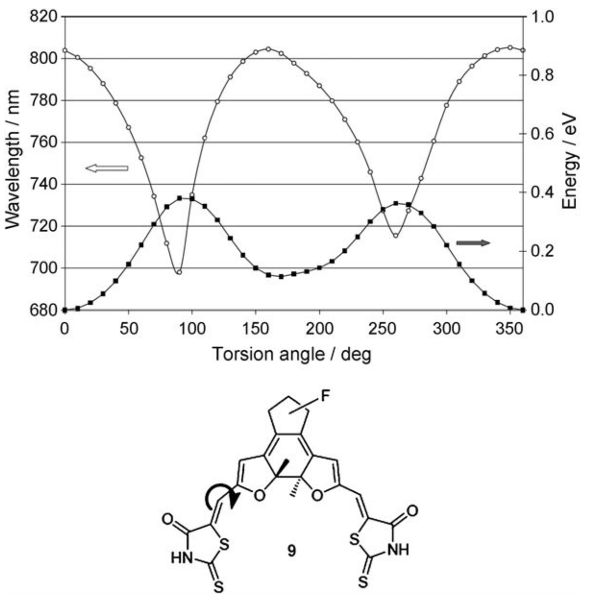


Figure 3. Theoretical dependence of wavelength of lowest energy transition on internal rotation coordinate for C5F-RN (**9**).

design substituents with desired properties as, for example, absorption in a specific frequency range, but the introduction of more rigid connections to the central part should also be considered to obtain more narrow spectra. More rigid molecules may probably also be of advantage for obtaining higher photochemical quantum yields due to fewer routes of radiationless deactivation.

Photokinetic behaviour in solution: All synthesized compounds undergo reversible photoswitching in solution. The switching process goes along with a pronounced colour change (cf. Table 1). The transformations from the open to the closed form and back can be nicely followed and quantified by UV/Vis spectrophotometry. An example of a spectrokinetic series for C5F-MTSC (**8**) is given in Figure 4.

A similar behaviour was found for compounds **6**–**10** (for the spectra see the Supporting Information). Isosbestic points and linear absorption/absorption correlation diagrams for pairwise combinations of different wavelengths (not shown) indicate the uniformity of the process, that is, the absence of side reactions during the switching. Within an irradiation series, the spectra converge to a photostationary state after long times. In case of the ring-closing reaction it is not possible from the UV/Vis spectra alone to determine the open/closed ratio in this situation. Therefore, the photoreactions were also followed by NMR spectroscopy. An example is shown in Figure 5. It was found that, except for the aldehyde C5F-CHO (**5**), the photostationary state for shortwave illumination of the open form resulted in complete switching to the closed form. In MeOH, the aldehyde **5** showed a hypsochromic shift of the newly developing band in the visible region during irradiation. This can be assigned to the formation of the acetal of **5.** To avoid this reaction and to be able to measure the composition of the photostationary state in the same solvent by NMR spectroscopy, we used $CDCl_3$ as a solvent in this case. An open/closed ratio of 2:5 corresponding to 71.4% closed form could be assessed from the integral values of the pertinent proton signals. When irradiating the open forms in the visible region, a complete reversion to the closed form was achieved in all cases. It is of interest to note that for compounds C5F-Me and C5F-Ph, derivatives investigated in the Irie group,[10] all the data for C5F-Me resemble closely those of C5F-OH (**6**) and the data for C5F-Ph those of C5F-CHO (**5**), which is very gratifying in view of the electronic similarity of these pairs of compounds.

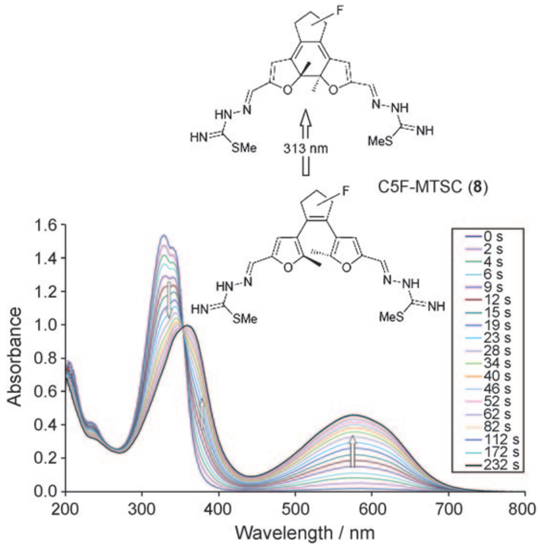


Figure 4. Spectrokinetic series for irradiation of C5F-MTSC (**8**) in MeOH at 313 nm. Time intervals of irradiation are given in the figure. Concentration $c_0 = 2.57 \times 10^{-5}$ M, photon irradiance $I_0 = 7.9 \times 10^{-9}$ Einstein cm^{-2} s^{-1}.

Compounds C5F-4Py (**11**) and C5F-4MN (**12**) showed somewhat irregular behaviour (see the Supporting Information). In both cases, even the open form shows a weak, long-tailed absorption in the visible region. For compound **11**, the photochemical switching to the coloured form and back did not occur in a uniform reaction (no clear isosbestic points, non-monotonic shift of maximum in the UV region), so that an evaluation of the quantum yield was difficult. In case of compound **12**, the absorption in the visible region increases, but does not develop a clear single maximum.

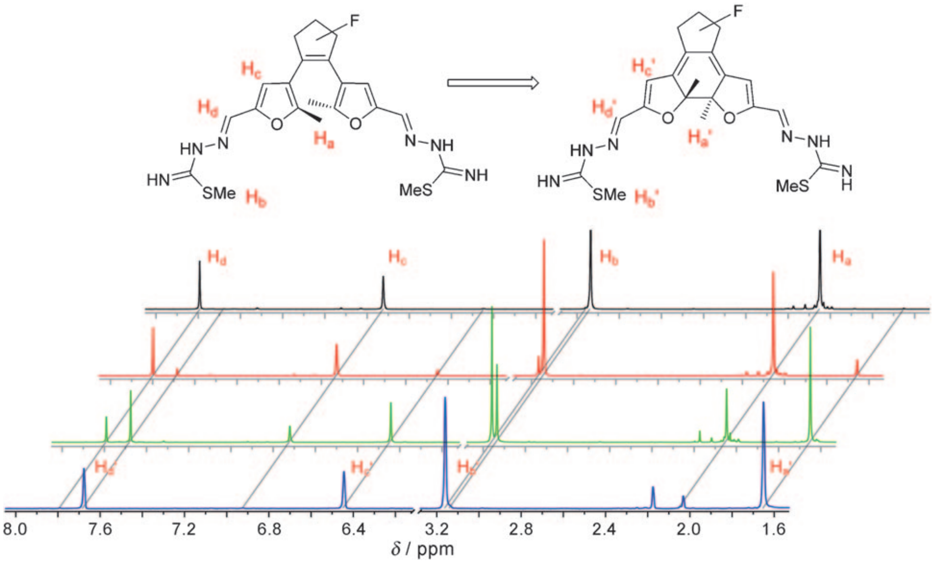


Figure 5. ^{1}H NMR spectra of **8** (400 MHz, [D$_4$]MeOD, 10^{-3} M) recorded at different time intervals of irradiation with 366 nm. Spectra are shown top down: 0 (——), 45 (——) and 220 min (——). As a reference, the bottom spectrum (——) shows the completely closed form, isolated by column chromatography from a reaction mixture. The spectral region from $\delta = 3.3$ to 6.1 ppm has been omitted for clarity.

From the photokinetics of compounds **5**–**10** under continuous irradiation, the quantum yields of closing and opening the central ring were evaluated according to the method described by Gauglitz (see the Supporting Information).[23–24] The resulting values are listed in Table 1. In general, the quantum yields of closing are much higher than for re-opening. This observation is in line with what was reported in Irie's review,[5] in which it was also pointed out that the quantum yield of ring closure seems to be limited by the fraction of molecules that are present in the "antiparallel" conformation (i.e. with C_2 symmetry of the photoreactive group), whereas the "parallel" conformation (with σ_v symmetry) cannot undergo this reaction. Thus a value of 0.5 for the ring-closing reaction seems to be a natural limit. In fact, for the compounds listed in Table 1, most of the quantum yields $\phi_{o\rightarrow c}$ are below although rather near 0.5. As exceptions we note C5F-4SMe (**10**), which is clearly above 0.5 and C5F-RN (**9**), with a very low quantum yield of 0.0015. Without further studies it cannot be decided whether this is due to the conformational distribution or to photophysical reasons.

With the exceptions of C5F-OH (**6**) and C5F-CHO (**5**), the quantum yields of the cycloreversion, that is, re-opening the switch by irradiation in the visible region, are quite small. As has already been remarked by Irie,[5] the quantum yields of this reaction are generally found to be much smaller than those of the closing reaction, and that the cycloreversion quantum yields were dependent on the π-conjugation length of the aryl groups. As an explanation, it is suggested that in the excited singlet state the antibonding nature of the central photogenerated carbon–carbon bond decreases with the extension of the π-conjugation. We add that by the inclusion of rotational flexibility in the π-system the tendency for radiationless deactivation may be also increased with the effect of lowering the quantum yield of photoinduced cycloreversion. In line with this reasoning is the finding of a very high cycloreversion quantum yield for the aldehyde **5** and still higher for the alcohol **6**, the latter approaching a value of 1. If the internal flexibility of the conjugated π-system is primarily responsible for the low quantum yields of cycloreversion, one may hope that in a situation in which the ends of the π-system are anchored to gold contacts, the flexibility of the chain might be reduced and the quantum yield thereby increased. Alternatively, one might choose to design photochemical switches with a short aliphatic interruption of the π-system to approach the favourable properties of the alcohol **5**.

Surface plasmon resonance (SPR): Preliminary experiments for testing the photoswitching potential of the newly synthesized molecules in contact with gold were performed by using SPR.[25–26] In this method, the resonance angle α detectable at the minimum of the resonance curve when scanning the reflectivity of a gold layer on a glass prism under conditions of total reflectance is very sensitive to adlayers of molecules chemisorbed to the gold surface.[27] Such an adlayer causes a shift $\Delta\alpha$ of the resonance angle that is proportional to the optical path length of the adlayer given as nd, the product of its refraction index n and thickness d.

Adlayers of the closed forms of several of the new compounds were prepared by adsorbing them from a droplet of MeOH solutions of the samples ($4.2–9.5\times10^{-5}$ M), pre-irradiated at 365 nm. After an incubation time of 24 h, washing away of the unbound molecules and further illuminating with 365 nm light to make sure that complete conversion to the closed form is achieved, the SPR resonance curves shown in Figure 6a were obtained. In all cases, a shift of the resonance angle α on the order of 0.05° to higher values with reference to a clean gold surface was observed. To assess the thickness of the adsorbed adlayers, we calculated the theoretical value of the resonance angle α as a function of the thickness d of a layer with a refractive index of 1.58,[5] a value applying to thin films of some thiazolyl analogues. They should be reasonably applicable also to the present furanyl derivatives. The results of the theoretical simulations yield a linear correlation between $\Delta\alpha$ and d with a slope of about $0.04\,^{\circ}\,\mathrm{nm}^{-1}$ (cf. Figure 6b). Placing the experimental data points with their observed $\Delta\alpha$ values on this line (cf. —), would indicate that the adlayers formed correspond to a dense packing in a layer of an apparent thickness of 1–1.5 nm. For an interpretation of the molecular ordering within the adlayers, these values should be compared to some characteristic molecular length parameter. As such, we chose the distance between the terminal heteroatoms of compounds **7**, **9**, **10** and **11**. The geometries were derived from molecular mechanics calculations based on the Universal Force Field.[28] The starting geometries were chosen such that in the closed forms double bonds of the terminal π-chains in direct conjugation with the furan rings were oriented in a *trans* configuration. The distance of the terminal heteroatoms was measured after geometry optimization. The theoretical length parameters thereby obtained are represented by the horizontal positions of the data points in Figure 6b. It appears that the experimental data points for compounds **7** and **9** are close to the theoretical $\Delta\alpha$ (d) line. This means that the molecules seem to form a fairly dense monolayer (the refraction index corresponds to that of a compact film) with the main extension of the molecule directed perpendicular to the surface. For **10** and **11**, the data points fall somewhat below the theoretical line, which could mean that the monolayer is less dense. It may be less well ordered in these cases, perhaps because a certain fraction of the molecules is attached with both termini on the gold surface.

For demonstrating the switching functionality, we repeatedly irradiated the molecular film with light suitable for inducing the ring-opening or -closing reaction, respectively. In Figure 6c) we show how the SPR signal of the closed form of C5F-4Py (**11**) (as already presented in Figure 6a) changes after irradiation with visible light ($\lambda=633$ nm). A clear shift of the SPR angle $\Delta\alpha_{\mathrm{switch}}=0.020°$ is observed.[29] In Figure 6d) we plot the reflectance at a fixed angle of $\alpha=42.2°$ as a function of time for compound C5F-4Py (**11**). The shaded areas indicate the irradiation periods with UV and visible light, respectively. A small, but recurrent variation of

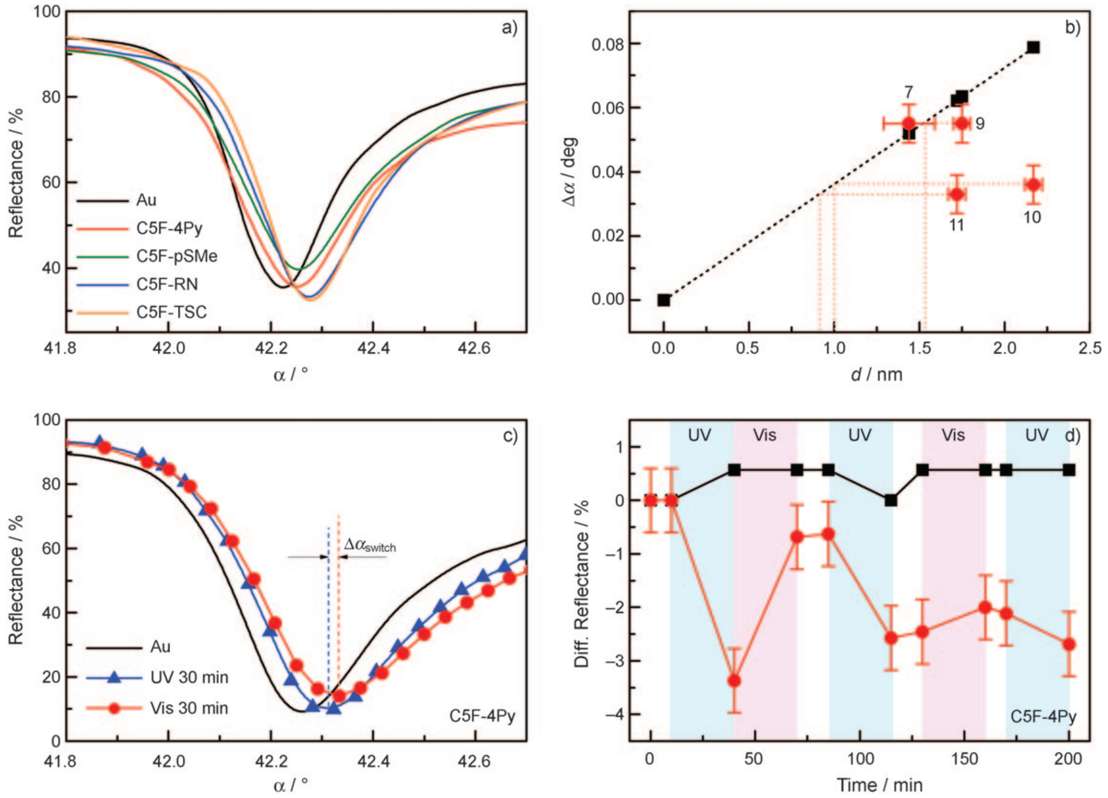


Figure 6. a) SPR curves obtained for a clean Au surface and Au with adlayers of closed forms of **11** (C5F-4Py), **10** (C5F-pSMe), **9** (C5F-RN) and **7** (C5F-TSC), respectively. b) Shift $\Delta\alpha$ of resonance angle as a function of layer thickness. Black squares: theoretical simulation, red dots: experimental $\Delta\alpha$ values from (a) versus geometrical length parameter of the respective molecule (for details see text). c) Effect of illumination by visible light (633 nm) on the SPR curve for C5F-4Py. Blue: curve from a), Red: curve after illumination with visible light. The angular shift between the SPR curves is 0.02°. d) Differential reflectance of **11**, C5F-4Py, (red dots) recorded at 42.2° as a function of irradiation time. The reflectance changes of clean Au (black squares) are small and independent of the irradiation wavelength, which indicates that temperature or humidity changes do not dominate the SPR shift of the molecular layer.

the reflectance with maximal amplitude on the order of 3.5% reflectance change is observed, which indicates that the molecules switch reversibly while chemically bonded to the metal surface. The amplitude of the signal becomes smaller for further repetitions signalling ageing effects in the film. For estimating the influence of potential artefacts, such as the effects of temperature or humidity changes on the reflectance, we also show the behaviour of a clean Au surface under the same irradiation conditions (——). The reflectance change of the pure Au layer is in the order of 0.6% and has no systematic dependence on the irradiation wavelength or time. Its stochastic variation amplitude represents the noise of the measurement.

Considering the supposedly small difference in refraction index of open and closed form and the overall geometric similarity of both forms, the observed size of the photoeffect on the resonance angle of SPR appears quite pronounced. Further studies to understand and model these effects quantitatively are in progress.

Conclusion

By starting with the dialdehyde C5F-CHO (**5**), a systematic synthetic access to photoswitchable difurylethenes with extended π-systems is opened up. Whereas switching of the compounds from the open, less conductive form (off-state) to the closed, better conductive form (on-state) by UV light is achieved with high quantum yields, the quantum yields for re-opening the switches by the reverse photoreaction when irradiating with visible light are very low for the fully conjugated extended π-systems. Interrupting the conjugation by an sp^3 centre adjacent to the furan ring might be a way to improve the quantum yield for the reverse switching process without losing too much contrast in conductance between the on- and off-state.

As a proof of principle, SPR experiments have demonstrated that the new molecules do have the potential to act as photoreversible optoelectronic switches in contact with gold.

Experimental Section

Syntheses: The compounds used were purchased from Sigma–Aldrich, Fluka, Acros, ABCR and Fluorochem. Compound **3** was synthesized as described in the literature.[30] TLC was performed on Polygram Sil G/UV$_{254}$ plates. A UV lamp (254 nm) was used for detection. Elemental analyses were performed on a CHN-analyzer Heraeus (CHN-O-RAPID) by the Microanalysis laboratory of Konstanz University. IR spectra were recorded on a Perkin–Elmer 100 Series FTIR spectrometer. GCMS was performed on an Agilent GCMS 7890A/5975C instrument (EI, 70 eV). HRMS ESI/FTICR spectra were recorded on a Bruker APEX II FTICR instrument. FABMS were performed on a Finnigan MAT 8200 instrument. MALDI-TOF spectra were recorded on a Bruker Biflex III instrument with pulsed nitrogen-laser (337 nm). UV/Vis spectra were recorded on a Cary 50 spectrophotometer. NMR spectra were recorded on a Bruker Avance DRX600 (600 MHz) and a Jeol ECP-Eclipse 400 (400 MHz).

1,2-Bis[5-(1,3-dioxolan-2-yl)-2-methylfuran-3-yl]perfluorocyclopentene (4): *t*BuLi (52.5 mL, 79 mmol, 1.5 M/hexane) was added dropwise to a solution of **3** (7.58 g , 32.7 mmol) in dry THF (50 mL) at −78 °C under N_2 and the reaction mixture was stirred for 30 min at −78 °C. A solution of octafluorocyclopentene (2.2 mL, 16.4 mmol) in dry THF (5 mL) was added dropwise over a period of 5 min and the reaction mixture was brought to RT and stirred overnight. After quenching with aqueous NH_4Cl, the organic solvent was removed in vacuo, water (100 mL) was added and the oily residue was extracted with diethyl ether (3 × 100 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo yielding a brown oil. After column chromatography, crude **4** (2.84 g) was obtained as a yellow oil and was used for the next step. The compound was obtained in an analytically pure form as light-brown crystals after recrystallization from *n*-hexane. Yield: 36 %; $R_f = 0.31$ (silica, hexanes/EtOAc 2:1); m.p. 98–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.96$ (s, 6H; CH_3), 3.93–4.01 (m, 4H; CH_2), 4.04–4.11 (m, 4H; CH_2), 5.80 (s, 2H; CH (acetal)), 6,42 ppm (s, 2H; Ar-H (furyl)); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 13.51$ (CH_3), 65.25 (CH_2), 97.27 (CH (acetal)), 109.30 (C-4), 109.49 (C-3), 110.9 (m, $CF_2CF_2CF_2$), 116.25 (tt, ^{1}J(C,F) = 257, ^{2}J(C,F) = 24 Hz; $CF_2CF_2CF_2$), 132.37 (t, ^{2}J(C,F) = 24 Hz; CCF_2), 150.60 (C-5), 153.88 ppm (C-2); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -110.10$ (t, ^{3}J(F,F) = 5.2 Hz, 4F; $CF_2CF_2CF_2$), −131.63 ppm (m, 2F; $CF_2CF_2CF_2$); IR: $\tilde{\nu} = 2896$, 1685, 1612, 1292, 1279 cm^{-1}; MS: *m*/*z*: 480 $[M]^+$, 435, 73; HRMS: *m*/*z*: calcd for $C_{21}H_{19}F_6O_6$: 481.1080 $[M+1H]^+$; found: 481.1069; elemental analysis calcd (%) for $C_{21}H_{18}F_6O_6$: C 52.51, H 3.78; found: C 52.48, H 3.95.

1,2-Bis(2-methyl-5-formylfuran-3-yl)perfluorocyclopentene (5): Compound **4** (0.78 g, 1.63 mmol) was dissolved in THF (50 mL). Acetone (50 mL) and conc. HCl (3 mL) were added and the solution was stirred overnight at RT. The reaction was monitored by TLC analysis. After complete deprotection, the organic solvents were removed in vacuo and the residue was brought to pH 9 by adding aqueous $NaHCO_3$. After extraction with diethyl ether (3 × 50 mL) the combined organic fractions were dried with $MgSO_4$ and the solvent was removed in vacuo. The oily residue was purified by column chromatography thus giving of **5** (0.55 g). Analytically pure **5** was obtained after recrystallization from diethyl ether as light-brown crystals. Yield: 87 %; $R_f = 0.26$ (hexanes/EtOAc 5:2); m.p. 116–118 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 2.11$ (s, 6H; CH_3), 7.23 (s, 2H; Ar-H), 9.59 ppm (s, 2H; CHO); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 13.96$ (CH_3), 110.55 (m, $CF_2CF_2CF_2$), 111.70 (C-3), 115.80 (tt, ^{1}J(C,F) = 256, ^{2}J(C,F) = 24 Hz; $CF_2CF_2CF_2$), 120.71 (C-4), 132.80 (t, ^{2}J(C,F) = 24 Hz; CCF_2), 152.15 (C-2), 158.95 (C-5), 176.93 ppm (CHO); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -110.10$ (t, ^{3}J(F,F) = 4.9 Hz, 4F; $CF_2CF_2CF_2$), −131.63 ppm (m, 2F; $CF_2CF_2CF_2$); correlations confirmed by ^{1}H-^{13}C-HSQC, ^{1}H-^{13}C-HMBC, 19F-^{13}C-HSQC and ^{19}F-^{13}C-HMBC experiments; IR: $\tilde{\nu} = 3136$, 2880, 1672 (C=O), 1651, 1590, 1537 cm^{-1}; MS: *m*/*z*: 392 $[M]^+$, 377, 307; HRMS: *m*/*z*: calcd for $C_{17}H_{11}F_6O_4$: 393.0556 $[M+1H]^+$; found: 393.0529; elemental analysis calcd (%) for $C_{17}H_{10}F_6O_4$: C 52.05, H 2.57; found: C 52.39, H 2.93; closed form isomer of **5**: dark-pink crystals; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.71$ (s, 6H; CH_3), 6.61 (s, 2H; CH (furyl)), 9.71 ppm (s, 2H; CHO); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 16.18$ (CH_3), 93.76 (CCH_3), 111.24 (CH (furyl)), 164.94 (CCHO), 181.71 ppm (CHO); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -114.51$ (m, 4F; $CF_2CF_2CF_2$), −133.61 ppm (m, 2F; $CF_2CF_2CF_2$).

1,2-Bis(2-methyl-5-hydroxymethylfuran-3-yl)perfluorocyclopentene (6, C5F-OH): Compound **5** (0.21 g, 0.54 mmol) was dissolved in dry diethyl ether (100 mL) and the solution was cooled to 0 °C. $LiAlH_4$ (0.2 g, 5.36 mmol) was added in portions while keeping the temperature at 0 °C and the reaction mixture was brought to RT. After refluxing for 5 h (reaction monitored by TLC analysis) the mixture was cooled down, quenched with water and the organic phase was separated. After drying with $MgSO_4$, the organic solvent was removed in vacuo and 0.13 g of analytically pure yellow oil was obtained (product solidified over several weeks into brown crystals). Yield: 61 %; m. p. 97–99 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 1.96$ (s, 6H; CH_3), 2.21 (brs, 2H; OH), 4.52 (s, 4H; CH_2), 6.27 ppm (s, 2H; Ar-H (furyl)); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 13.58$ (CH_3), 57.3 (CH_2), 108.52 (C-4), 109.86 (C-3), 111.03 (m, $CF_2CF_2CF_2$), 116.37 (tt, ^{1}J(C,F) = 255, ^{2}J(C,F) = 24 Hz; $CF_2CF_2CF_2$), 132.46 (t, ^{2}J(C,F) = 24 Hz; CCF_2), 153.37 (C-2), 153.55 ppm (C-5); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -109.94$ (m, 4F; $CF_2CF_2CF_2$), −131.53 ppm (m, 2F; $CF_2CF_2CF_2$); IR: $\tilde{\nu} = 3268$ (brs; OH), 1579, 1423, 1342, 1278 cm^{-1}; MALDI-TOF-MS: *m*/*z*: 396.3 $[M]^+$, 379.4.

1,2-Bis{2-methyl-5-[(*E*)-(2-thiocarbamoylhydrazono)methyl]furan-3-yl}-perfluorocyclopentene (7, C5F-TSC): Compound **5** (50 mg, 0.13 mmol) and thiosemicarbazide (23 mg, 0.26 mmol) were dissolved in hot EtOH (10 mL) with a few drops of pure acetic acid. The reaction mixture was stirred for 24 h at RT and then poured into water (30 mL) and filtered. After washing with cold EtOH (3 mL) and drying dark-brown crystals (61 mg) were obtained. Yield: 89 %; m.p. 203 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C): $\delta = 1.95$ (s, 6H; CH_3), 7.07 (s, 2H; Ar-H (furyl)), 7.74 (brs, 2H), 7.89 (s, 2H; *H*C-6), 8.25 (brs, 2H), 11.50 ppm (brs, 2H; *H*NN); ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C): $\delta = 13.58$ (CH_3), 110.68 (C-3), 110.84 (m; $CF_2CF_2CF_2$), 112.11 (C-4), 116.06 (tt, ^{1}J(C,F) = 254, ^{2}J(C,F) = 24 Hz; $CF_2CF_2CF_2$), 131.80 (C-6), 132.16 (t, ^{2}J(C,F) = 24 Hz; CCF_2), 149.62 (C-5), 155.14 (C-2), 177.83 ppm (C=S); ^{19}F NMR (376 MHz, DMSO, 25 °C): $\delta = -109.37$ (br, 4F; $CF_2CF_2CF_2$), −130.78 ppm (br, 2F; $CF_2CF_2CF_2$); IR: $\tilde{\nu} = 3422$, 3526, 3144, 2962, 1590, 1504, 1275 cm^{-1}; FAB-MS: *m*/*z*: 539 $[M+1H]^+$, 462, 389; HRMS: *m*/*z*: calcd for $C_{19}H_{16}F_6N_6O_2S_2$: 539.0753 $[M+1H]^+$; found: 539.0750; elemental analysis calcd (%) for $C_{19}H_{20}F_6N_6O_4S_2$ $[M+2H_2O]^+$: C 39.72, H 3.51, S 11.16; found: C 39.58, H 3.36, S 11.23; closed form isomer of **7**: dark-blue crystals; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.64$ (s, 6H; CH_3), 6.44 (s, 2H; CH (furyl)), 7.70 ppm (s, 2H; *H*C-6); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 16.55$ (CH_3), 94.11 (CCH_3), 107.10 (CH (furyl)), 132.33 (C=N), 148.39 (C-3), 167.28 (C-5), 180.98 ppm (C=S); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -115.43$ (m, 4F; $CF_2CF_2CF_2$), −135.13 ppm (m, 2F; $CF_2CF_2CF_2$).

1,2-Bis{2-methyl-5-[(*E*)-(1-methylthio-1-iminomethylhydrazono)methyl]-furan-3-yl}perfluorocyclopentene (8, C5F-MTSC): Compound **5** (50 mg, 0.13 mmol) and methylthiosemicarbazide (27 mg, 0.26 mmol) were dissolved in hot EtOH (10 mL) with a few drops of pure acetic acid. The reaction mixture was stirred for 24 h at RT and was poured into water (30 mL) and filtered. After washing with cold EtOH (3 mL) and drying blue crystals (68 mg) were obtained. Yield: 97 %; m.p. 157 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C): $\delta = 1.97$ (s, 6H; CH_3), 2.98 (s, 6H; SC*H*$_3$), 7.04 (s, 2H; Ar-H (furyl)), 7.90 (s, 2H; *H*C-6), 8.29 (brs, 2H; C=N*H*), 11.51 ppm (brs, 2H; *H*NN); ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C): $\delta = 13.42$ (CH_3), 30.87 (SCH_3), 110.51 (C-3), 110.69 (m; $CF_2CF_2CF_2$), 111.62 (C-4), 115.79 (tt, ^{1}J(C,F) = 255, ^{2}J(C,F) = 24 Hz; $CF_2CF_2CF_2$), 131.05 (C-6), 132.07 (t, ^{2}J(C,F) = 24 Hz; CCF_2), 149.63 (C-5), 154.85 (C-2), 177.51 ppm (C=N); ^{19}F NMR (376 MHz, DMSO, 25 °C): $\delta = -109.33$ (br, 4F; $CF_2CF_2CF_2$), −130.77 ppm (br, 2F; $CF_2CF_2CF_2$); IR: $\tilde{\nu} = 3138$, 2940, 1540, 1277, 1243 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{21}H_{20}F_6N_6O_2S_2$: 567.1066 $[M+1H]^+$; found: 567.0986; closed form isomer of **8**: dark-blue crystals; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.63$ (s, 6H; CH_3), 3.14 (s, 6H; SCH_3), 6.43 (s, 2H; CH (furyl)), 7.66 ppm (s, 2H; *H*C-6); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 16.59$ (CH_3), 94.05 (CCH_3), 106.41 (CH (furyl)), 131.29 (HC=N), 148.50 (C-3), 150.18 (C=NH), 167.64 ppm (C-5);

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -115.37$ (m, 4F; $\mathrm{C}F_2\mathrm{CF_2C}F_2$), -135.07 ppm (m, 2F; $\mathrm{CF_2C}F_2\mathrm{CF_2}$).

1,2-Bis{2-methyl-5-[(*E*)-4-oxo-2-thioxothiazolidin-5-ylidenemethyl]lfuran-3-yl}perfluorocyclopentene (9, C5F-RN): Piperidine (0.2 mL) was added to a solution of **5** (0.2 g, 0.51 mmol) and rhodanine (0.13 g, 1 mmol) in CH_2Cl_2 (30 mL). The reaction was stirred for 24 h at RT, the organic solvent was removed in vacuo and the residue was purified by column chromatography on silica thus giving gold-brown crystals (0.21 g). Yield: 67 %; $R_f = 0.43$ (hexanes/EtOAc 1:1); m.p. 106 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 2.12$ (s, 6H; CH_3), 4.30 (brs, 2H; NH), 6.67 (s, 2H; Ar-H (furyl)), 7.20 ppm (s, 2H; C-6); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 14.19$ (CH_3), 110.85 (m; $\mathrm{CF_2}C\mathrm{F_2CF_2}$), 112.52 (C-3), 115.35 (C-6), 116.00 (tt, $^1J(\mathrm{C,F}) = 257$, $^2J(\mathrm{C,F}) = 24$ Hz; $C\mathrm{F_2CF_2}C\mathrm{F_2}$), 116.82 (C-4), 128.39 (C-7), 132.78 (t, $^2J(\mathrm{C,F}) = 24$ Hz; $C\mathrm{CF_2}$), 150.11 (C-5), 157.18 (C-2), 174.65 (C=O), 200.04 ppm (C=S); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -109.91$ (t, $^3J(\mathrm{F,F}) = 5.4$ Hz, 4F; $\mathrm{C}F_2\mathrm{CF_2C}F_2$), -131.44 ppm (m, 2F; $\mathrm{CF_2C}F_2\mathrm{CF_2}$); correlations confirmed by ^{1}H-^{13}C-HSQC and ^{1}H-^{13}C-HMBC (^3J(H, C=O) = 21 Hz) experiments; IR: $\tilde{\nu} = 3101$, 2849, 1686 (C=O), 1607, 1421 cm^{-1}; EIMS: m/z: 622 $[M]^+$, 535; HRMS: m/z: calcd for $C_{23}H_{12}N_2S_4F_6O_4$ $[M+1\mathrm{H}]^+$: 622.9657; found: 622.9660; elemental analysis calcd (%) for $C_{23}H_{12}N_2S_4F_6O_4$: C 44.37, H 1.94, N 4.50; found: C 44.28, H 2.93, N 4.48.

1,2-Bis[2-methyl-5-(*E*)-(4-methylthiostyryl)furan-3-yl]perfluorocyclopentene (10, C5F-4SMe) (mixture of diastereomers): [4-(Methylthio)benzyl]-triphenylphosphonium bromide (0.67 g, 1.4 mmol) was dissolved in dry MeOH (50 mL) containing MeONa (0.17 g, 3.15 mmol). After stirring for 15 min, compound **5** (0.25 g, 0.64 mmol) was added and the whole stirred overnight. The reaction mixture was neutralized with aqueous NH_4Cl and concentrated in vacuo. The remaining dark-blue oily residue was mixed with dichloromethane (150 mL) and water (50 mL). The organic phase was separated, dried with $MgSO_4$ and the solvent removed in vacuo. Dark-blue crystals (0.17 g) were obtained. Yield: 41 %; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 2.03$ (m, 6H; CH_3), 2.50 (m, 6H; SCH_3), 6.23 (m, 1H), 6.31 (m, 2H), 6.43 (m, 1H), 6.77 (m, 1H), 6.99 (m, 1H), 7.20 (m, 4H), 7.36 ppm (m, 4H); ^{19}F NMR (376 MHz, DMSO, 25 °C): $\delta = -109.857$ (m, 4F; $\mathrm{C}F_2\mathrm{CF_2C}F_2$), -131.49 ppm (m, 2F; $\mathrm{CF_2C}F_2\mathrm{CF_2}$); MALDI-TOF-MS: m/z: 634, 633, 632.

1,2-Bis(2-methyl-5-{(*Z*)-[2-cyano-2-(pyridin-4-yl)vinyl]}furan-3-yl)perfluorocyclopentene (11, C5F-4Py): Compound **5** (0.1 g, 0.25 mmol) and pyridine-4-acetonitrile hydrochloride (0.08 g, 0.5 mmol) were dissolved in dry MeOH (10 mL). After the addition of K_2CO_3 (0.176 g, 1.27 mmol), the reaction mixture was stirred for 48 h at RT. After addition of diethyl ether (50 mL) the mixture obtained was washed consecutively with water (30 mL), aqueous K_2CO_3 (30 mL) and again with water (30 mL). The organic fraction was dried with $MgSO_4$, the solvent removed in vacuo and the dark residue purified by filtering through a silica column by using hexanes/EtOAc 1:1 as the eluent, thus giving brown crystals (0.12 g). Yield: 77 %; m.p. 182 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 2.24$ (s, 6H; CH_3), 7.24 (s, 2H; Ar-H (furyl)), 7.47 (s, 2H; C-6), 7.51 (dd, ^3J(H,H) = 4.6, ^4J(H,H) = 1.7 Hz), 4H; C-9), 8.69 ppm (dd, ^3J(H,H) = 4.6, ^4J(H,H) = 1.7 Hz), 4H; C-10); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 14.02$ (CH_3), 106.63 (C-7), 110.82 (m; $\mathrm{CF_2}C\mathrm{F_2CF_2}$), 112.30 (C-3), 115.90 (m; $C\mathrm{F_2CF_2}C\mathrm{F_2}$), 116.31 (CN), 117.23 (C-4), 119.60 (C-9), 128.91 (C-6), 132.90 (t, $^2J(\mathrm{C,F}) = 24$ Hz; $C\mathrm{CF_2}$), 140.75 (C-8), 149.07 (C-5), 150.78 (C-10), 157.01 ppm (C-2); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -109.94$ (m, 4F; $\mathrm{C}F_2\mathrm{CF_2C}F_2$), -131.46 ppm (m, 2F; $\mathrm{CF_2C}F_2\mathrm{CF_2}$); IR: $\tilde{\nu} = 3048$, 2216 (C≡N), 1591, 1415, 1275 cm^{-1}; FAB-MS: m/z: 592 $[M]^+$, 506; HRMS: m/z: calcd for $C_{31}H_{19}F_6N_4O_2$: 593.1407 $[M+1\mathrm{H}]^+$; found: 593.1394.

1,2-Bis[2-methyl-5-(2,2-dicyanovinyl)furan-3-yl]perfluorocyclopentene (12, C5F-MN): Piperidine (2 drops) was added to a solution of **5** (50 mg, 0.13 mmol) and malodinitrile (18 mg, 0.28 mmol) in benzene (5 mL) and the mixture was stirred for 48 h. The organic solvent was removed in vacuo and the oily residue was filtered through a silica column by using hexanes/EtOAc 1:1 as the eluent. Violet crystals (13 mg) were obtained. Yield: 21 %; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 2.25$ (s, 6H; CH_3), 7.25 (s, 2H; Ar-H (furyl)), 7.41 ppm (s, 2H; C-6); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 14.40$ (CH_3), 79.94 (C-7), 110.60 (m, $\mathrm{CF_2}C\mathrm{F_2CF_2}$), 112.32 (CN (*trans* to *H*C-6)), 113.20 (C-3), 113.35 (CN (*cis* to *H*C-6)), 115.66 (tt, $^1J(\mathrm{C,F}) = 256$, $^2J(\mathrm{C,F}) = 24$ Hz; $C\mathrm{F_2CF_2}C\mathrm{F_2}$), 122.27 (C-4), 133.14 (t, $^2J(\mathrm{C,F}) = 24$ Hz; $C\mathrm{CF_2}$), 141.89 (C-6), 147.69 (C-5), 160.43 ppm (C-2); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -109.99$ (t, $^3J(\mathrm{F,F}) = 4.8$ Hz, 4F; $\mathrm{C}F_2\mathrm{CF_2C}F_2$), -131.47 ppm (m, 2F; $\mathrm{CF_2C}F_2\mathrm{CF_2}$); correlations confirmed by ^{1}H-^{13}C-HSQC and ^{1}H-^{13}C-HMBC (*cis*-^3J(H,CN) = 7.2, *trans*-^3J(H,CN) = 13 Hz) experiments; IR: $\tilde{\nu} = 3059$, 2237 (C≡N), 2225 (C≡N), 1615 cm^{-1}; FAB-MS: m/z: 511 $[M+\mathrm{Na}]^+$, 489 $[M+\mathrm{H}]^+$.

For further experimental details see the Supporting Information.

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[1] For a selection of review articles, see the special issue on "Photochromism: Memories and Switches", *Chem. Rev.* (Ed.: M. Irie) **2000**, *100*, Issue 5.

[2] M. Irie, *Chem. Rev.* **2000**, *100*, 1683–1684, Editorial to special issue.

[3] *Photochromism: Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**.

[4] *Dynamic Studies in Biology: Phototriggers, Photoswitches, and Caged Biomolecules* (Eds.: M. Goeldner, R. Givens), Wiley-VCH, Weinheim, **2005**.

[5] M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.

[6] A. Staykov, K. Yoshizawa, *J. Phys. Chem. C* **2009**, *113*, 3826–3834.

[7] F. L. E. Jakobsson, P. Marsal, S. Braun, M. Fahlmann, M. Berggren, J. Cornil, X. Crispin, *J. Phys. Chem. C* **2009**, *113*, 18396–18405.

[8] N. Katsonis, T. Kudernac, M. Walko, S. J. van der Molen, B. J. van Wees, B. L. Feringa, *Adv. Mater.* **2006**, *18*, 1397–1400.

[9] D. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402.

[10] T. Yamaguchi, M. Irie, *J. Mater. Chem.* **2006**, *16*, 4690–4694.

[11] J. E. McMurry, *Acc. Chem. Res.* **1983**, *16*, 405–411.

[12] M. Irie, M. Mohri, *J. Org. Chem.* **1988**, *53*, 803–808.

[13] M. Dubernet, V. Caubert, J. Guillard, M.-C. Viaud-Massuard, *Tetrahedron* **2005**, *61*, 4585–4593.

[14] Z.-N. Huang, B.-A. Xu, S. Jin, M.-G. Fan, *Synthesis* **1998**, 1092–1094.

[15] X. Deng, L. S. Liebeskind, *J. Am. chem. Soc.* **2001**, *123*, 7703–7704.

[16] Crystal data for **4**: $C_{21}H_{18}F_6O_6$; $M = 480.35$; $T = 173(2)$ K; monoclinic; space group $C2/c$; $a = 21.390(4)$, $b = 8.9727(10)$, $c = 10.6721(18)$ Å; $\beta = 93.767(13)°$; $V = 2043.8(5)$ Å^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.561$ g cm^{-3}; $\mu\mathrm{Mo}_{K\alpha} = 0.148$ mm^{-1}; 2117 reflections measured; 1998 independent reflections ($R_{\mathrm{int}} = 0.0182$); R_1 $(I > 2\sigma(I)) = 0.0512$, wR_2 (all data) = 0.1534. CCDC-801309 contains 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.

[17] The relevant structures of the open forms described in reference [10] have been retrieved from the Cambridge Structural Database. Identifier: CESWED for C5F-Ph and CESWON for C5F-Me.

[18] R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, *109*, 8218–8224.

[19] R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454–464.

[20] M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439–4449.

[21] E. Cances, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032–3041.

[22] B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158.

[23] G. Gauglitz, *J. Photochem.* **1976**, *5*, 41–47.

[24] G. Gauglitz, S. Hubig, *J. Photochem.* **1981**, *15*, 255–257.

[25] H. Raether, *Springer Tracts in Modern Physics, Vol. 111, Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer-Verlag, Berlin, **1988**.
[26] W. Knoll, *Annu. Rev. Phys. Chem.* **1998**, *49*, 569–638.
[27] T. Geldhauser, P. Leiderer, J. Boneberg, S. Walheim, T. Schimmel, *Langmuir* **2008**, *24*, 13155–13160.
[28] ArgusLab 4.0.1, Planaria Software LLC, M. A. Thompson, Seattle, http://www.arguslab.com.
[29] The repeated switching experiments shown in Figure c have been performed in a somewhat different optical setup than the measurements shown in Figure a. This results in a slightly different shape of the SPR resonance but has no influence on the value of the resonance angle.
[30] M. Gorzynski, D. Rewicki, *Liebigs Ann. Chem.* **1986**, 625–637.

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