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Photoswitching of Cation Complexation with A Monoaza-crown Dithienylethene Photochrome

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The design and synthesis of functional molecules that could serve as molecular devices for sensing, switching, and signal transduction, particularly from optical inputs, is an area of intense activity and of tremendous potential significance.[1]

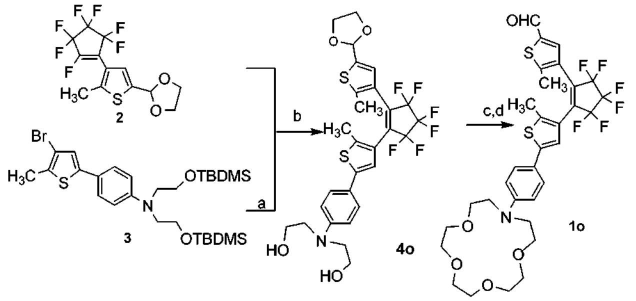
In the course of our program of developing integrated (intrinsic) fluoroionophores we demonstrated that photoinduced intramolecular charge transfer from the ionophore to the π-conjugated system led to release of the cation during the excited-state lifetime of the probe,[2] but the mean diffusion length of the cation is only 10 Å for 1 ns,[3] and the switching action is quickly reversed as the system loses its excitation energy and returns to the original ground state. We thought that a fast and complete cation release could be achieved from a photoionochromic if one photochromic form only involves the ionophore conjugation with an electron-withdrawing group.

For that purpose we report the synthesis, the photochemical and photophysical properties, and the cationic binding ability of a new photochromic crown ether **1** composed of the 1,2-bis(3-thienyl) perfluorocyclopentene substituted at the positions 5 and 5′ by a *p*-phenylaza-15-crown-5 as the ionophore and a formyl group as a strong electron-withdrawing group. The synthetic route to compound **1** followed the scheme defined for dissymmetric 1,2-dithienyl perfluorocyclopentene,[4] but we built the azacrown group after the organometallic step to avoid reported difficulties to generate lithiated thiophene in the presence of a strongly cation coordinating group[5] (Scheme 1).

All the intermediates and the photochrome **1** were characterized by ^{1}H NMR and UV−vis spectroscopies and mass spectrometry.

To follow the electronic effect of the different fragments of the photochrome upon the binding unit we measured the absorption and fluorescence spectra and the oxidation potentials of the photochrome **1**, of its analogue **4** with the protected and hence ineffective electron-accepting group (the *N*,*N*-diethanol group should reproduce the electronic property of the azacrown receptor), and of the ionophore branch **3** (Table 1). The absorption spectra of the open chromophores **1o** and **4o** show the long-wavelength band the same as that of **3**. The first oxidation potential of **3** is slightly lower than those of **1o** and **4o** which are similar to the oxidation potential of *N*,*N*-dimethylaniline.[6] This denotes that thiophene is rather electron-donating, while covalent linking to the perfluorocyclopentene group slightly reduces this electronic effect without noticeable effect from the substituent in position 5′. As a whole these results are evidence for the absence of conjugation between the two thiophene groups in the open form of the photochromes[7] and the binding ability of the ionophore should not be strongly altered by insertion into **1**. Indeed the logarithm of the complex stability constants, log K_s, obtained by titrating 10^{-6} M solutions of **1o** with stock solutions of the metal perchlorates and after a least-squares analysis[8] of the resulting titration curves are 2.3, 5.4, and 2.95 for Na^+, Ca^{2+}(in acetonitrile), and Ag^+(in methanol), respectively. These values compare with those obtained from phenylazacrowns substituted by an electron-donating group.[9]

Scheme 1 [a]



[a] (a) ^{t}BuLi, THF, −78 °C; (b) ^{n}Bu$_4$NF, THF; (c) ^{t}BuONa, ^{t}BuOH, triethyleneglycolditosylate; (d) pyridinium *p*-toluene sulfonate, acetone.

Table 1. UV−Visible Spectroscopy (λ_{max} (nm)) and Electrochemical Data for Compounds **1**, **3**, **4** in Acetonitrile

	λ_{abs} nm	λ_{exc} nm	λ_{em}	log $K_{Ca^{2+}}$	Φ_f	F_c	epa[a]
1o	332	375	523	5.4	0.006[b] 0.0007[c]	0.0005[b] 0.005[c]	0.78
1c	675			1.7			0.71
3	337	338	400		0.003[c]		0.71
4o	332	370	512		0.12[b] 0.004[c]		0.74
4c	588	-	-				0.62

[a] Cyclic voltammetry in acetonitrile (0.1 M, nBu$_4$NBF$_4$), scan rate 200 mV·s^{-1}, all potentials vs SCE; irreversible process for **1**c and **4**c. [b] λ_{exc} = 390 nm. [c] λ_{exc} = 330 nm.

If the conformation of the open photochrome **1** prevents the electronic communication between the two thiophene groups in the ground state, long-range processes are available from the excited state. The two photochromes **1o** and **4o** show fluorescence which shift to the red with more polar solvents, indicating a higher dipole moment in the excited state than that in the ground state. The bathochromic shift of the fluorescence is large and not significantly different for the two photochromes (**1o**: 2906 cm^{-1}, **4o**: 3042 cm^{-1} from hexane to acetonitrile), while it is much smaller for **3** (2248 cm^{-1}). The large charge-transfer character of the excited state could result from the rather low-lying LUMO of the perfluorocyclopentene group which allows electron-transfer from the electron-rich ionophore branch in the excited state. Irie first found that the fluorescence of 1,2-bis(2,4,5-trimethylthiophene-3-yl)-maleic anhydride was red-shifted and that its intensity was reduced in polar solvents.[10] This led him to propose that the photocyclization could occur from a planar conformation which, in polar solvent, deactivates to a twisted form (TICT state) which fluoresces. Accordingly the ring-closure quantum yield decreased with the increasing solvent polarity but this solvent dependence was not observed when the

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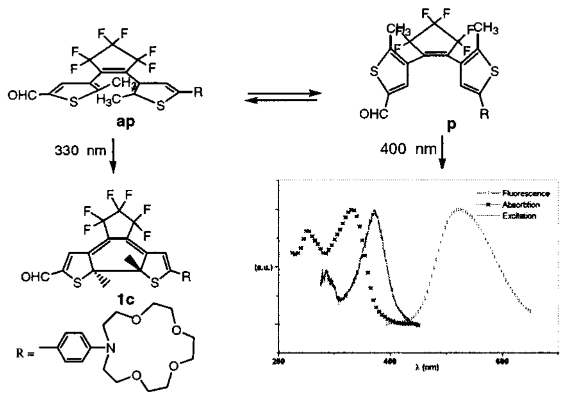

Figure 1. Photochemistry and spectroscopic properties of **1o** two conformers in acetonitrile.

acid anhydride moiety was replaced with perfluorocyclopentene. Nevertheless, it has been shown that dithienylethene derivatives exist in two different conformations already in the ground state: the so-called antiparallel (**ap**) conformation with C_2 symmetry and the parallel conformation (**p**) with C_s symmetry.[11] The photocyclization reaction can proceed only from the **ap** conformation and it was observed that it occurred in the picosecond time scale[12] while it is the conformer **p** which eventually fluoresces. This specific photochemical behavior of the two conformers has been pointed out recently for 1,2-bis [5-anthryl-2-methylthien-3-yl] perfluorocyclopentene, and it was argued that it was a requirement for applications relying on efficient switching of the fluorescence.[13]

A striking result from the emission measurements of the two photochromes **1o** and **4o** is the large red-shift of the excitation spectra relative to the absorption spectra, particularly in polar solvents (Figure 1), while the excitation and absorption spectra of **3** are superimposable. This indicates that the fluorescent conformer **p** absorbs at wavelengths longer than those for reactive conformer **ap** and this feature should allow a nondestructive readout capability from this photochrome. Indeed the fluorescence quantum yield (Φ_f) of **1o** and **4o** increases 10 times or more, while the cyclization quantum yield (F_c) decreases approximately 10 times when the excitation wavelength is shifted from the absorption maximum (330 nm) beyond the excitation maximum (390 nm). Other dithienylethenes with dithieno-(thiophene)[14] or porphyrinic macrocycle[15] attached to the photochrom exhibit this property but were assigned to energy-transfer modulation rather than dual behavior of conformers. The large solvatochromism of the excitation spectrum and its location at the red end of the absorption spectrum denote a forbidden transition involving an electron transfer from the ionophore branch to the quasi-perpendicular perfluorocyclopentene. The emission arises from the excited state in the same conformation which accordingly can be regarded as TICT state.

Upon irradiation at 254 nm the photochromes **1o** and **4o** show new absorption bands at longer wavelengths which are ascribed to the closed-ring isomers **1c** and **4c**. The photochemical interconversion properties were monitored directly by both ^{1}H NMR and electronic spectroscopy. By irradiation at 254 nm up to 90% conversion to the closed forms was obtained, while irradiation with visible light completely regenerated the open form. The electronic effect of the formyl group is shown by the red-shift of the long-wavelength band of the closed form of **1** relative to that of **4** (675 vs 588 nm in acetonitrile), but the slightly lower solvatochromism from hexane to acetonitrile (570 vs 600 cm^{-1}) is evidence of polar ground state. Indeed values of the ground-state dipole moments, $\mu_g = 4.9$ D for **4c** and 7.5 D for **1c,** have been calculated using the AM1 method.

From the closed form of the photochrome **1**, the logarithm of the complex stability constant, log K_s, obtained as described for the open form, is 1.7 for Ca^{2+} (1.6 and 1.74 for Na$^+$ and Ag$^+$, respectively) corresponding to a binding inhibition of almost 4 orders of magnitude, which means that all the complexed cations from the open chromophore can be released by photocyclization. Such a large decrease of the binding ability for calcium has been obtained by the electronic transition from the ground state (log $K_s = 6.9$) to the excited state (log $K_s^* = 3.2$) of Fura-2.[16] This lowered binding ability is the result of the large decrease of the charge density on the amino group which is a coordinating site for calcium and at the same time an electron-donating group in the closed photochrom as in the excited state of Fura-2. The importance of the electrostatic factor is illustrated by the smaller change in the binding constant for the monocharged alkali metal ion (Na$^+$) and, in addition for Ag$^+$, by the partial covalent interaction with the nitrogen atom. Other photoionochromics such as bis(crown) azobenzene[17] and diarylethene[5,18] have been used to carry out active transportation of cations, but the "bis(crown) effect" for the binding of cations is rather modest and poorly understood.[5]

We have shown, from the photoionochromic **1o** and its electronic analogue **4o**, that it was possible to trigger the fluorescence at wavelengths which were inactive for the cyclization. We have realized an efficient optical release of calcium ions in acetonitrile, and we believe that the photophysical results reported show that integrated supramolecular systems combining the 1,2-bis(3-thienyl) perfluorocyclopentene photochrome and a specific electron-rich ionophore which bears a binding atom which is also active in the closed photochrome furnish the suitable electronic configuration for a large change in the cation-binding ability from one photoisomer to the other. In addition the interdependent photocyclization and binding-switch processes can be followed by fluorescence without perturbing the equilibrium, on account of the different absorption spectra of the emitting and reacting conformers.

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