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Switching-Properties of a Spiropyran-Cucurbit[7]uril Supramolecular Assembly: Usefulness of the Anchor Approach

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Abstract

A nitrospiropyran, which was modified with a cadaverine-derived anchor, was investigated with respect to its thermally-induced isomerizations, hydrolytic stability of the merocyanine form, and the photochromic ring closure. The host-guest complexation of the anchor by the cucurbit[7]uril macrocycle, evidenced by absorption titration, NMR spectroscopy, and electrospray ionization mass spectrometry, produced significant improvements of the switching properties of the photochrome: a) a *ca*. 70 times faster appearance of the merocyanine form, b) a practically unlimited hydrolytic stability of the merocyanine (two and a half days without any measureable decay), and c) a fast, clean, and fatigue-resistant photoinduced ring-closure back to the spiro form. The importance of an adequate molecular design of the anchor was demonstrated by including control experiments with spiropyrans with a shorter linker or without such structural asset.

Keywords: photochromism · acidochromism · host-guest chemistry · switching · hydrolysis

Introduction

Cucurbiturils (CBs) are a recently widely explored class of water-soluble macrocyclic host compounds[1] with applications in chemosensing assemblies,[2-7] label-free enzyme assays,[8] nanovalves,[9] molecular self-sorting,[10] dye encapsulation and stabilization,[11-13] supramolecular catalysis,[14, 15] drug delivery,[5, 16-21] molecular logic and switches,[22-25] *etc*. CBs are composed of a variable number of *n* glycouril units (*n* = 5, 6, 7, 8, 10) which are linked by methylene bridges.[26] Their structure is characterized by two carbonyl-laced portals and an inner cavity with low polarity and low polarizability.[27] Hence, preferred organic guests carry positive charges or contain protonable nitrogens which support ion-dipole interactions with the portals,[28] while hydrophobic parts are immersed into the inner cavity.

It is widely accepted that the encapsulation of organic guest dyes by macrocyclic host compounds can alter their photophysical and photochemical properties in a dramatic manner.[13] The underlying reasons for such modulations are often related to changes in the microenvironment, confinement effects, or host-induced guest protonation. This has been demonstrated for the direct encapsulation of a large number of organic fluorophores.[13] A conceptually different approach toward switching guest properties is the use of anchors which bind to CBs but the covalently linked photophysically or -chemically active unit remains exposed to the bulk aqueous phase. Given an appropriate molecular design, anchor and fluorophore can communicate *via* internal charge transfer or photoinduced electron transfer and thus, enable the fluorescence monitoring of the host-guest complexation.[23, 24, 29]

The use of photochromic compounds in the context of cucurbituril chemistry has been rarely investigated. Recently, the partial inclusion of a spiropyran photochrome[30, 31] in cucurbit[*n*]urils (*n* = 7 and 8, CB7 and CB8, respectively) was reported.[32, 33] On the one hand, it was shown that CB8 contributes to a higher hydrolytic stability of the ring-opened merocyanine isomeric form as compared to the absence of the host.[32] As a disadvantage the light-induced conversion of the merocyanine (MC) back to the spiropyran (SP) form was slowed down due to the confined surrounding of the photochrome. This imposes serious limitations in the context of applications which require the efficient recycling between ring-opened and -closed spiropyran forms. On the other hand, CB7 binds selectively to the protonated merocyanine form (MCH), which can be photoisomerized efficiently back to the spiro form.[33] However, the required conditions (pH 2.3) were far from physiological conditions encountered in bio-relevant contexts. Indeed, the photochromic properties of spiropyrans are of elevated interest for the photocontrol of biological functions,[34-40] bioimaging,[41-45] optical signal processing and photoswitching in general,[46-55] as well as chemosensing.[56-61]

In order to overcome the handicap of a limited photochromic performance of spiropyrans upon direct encapsulation in cucurbiturils we devised herein a novel strategy based on the use of anchor-substituted spiropyrans as guests of cucurbit[7]uril (CB7). This approach led to the observation of an impressive

long-term protection of the merocyanine against hydrolytic degradation. Importantly, a confinement of the photoactive spiropyran itself was avoided and hence, the inherent photochromic switching properties of the spiropyran were effectively maintained.

Results and Discussion

The spiropyrans **1**–**3**, which are shown in Chart 1, were used in the present study. However, the main focus was on spiropyran **1**, while the compounds **2** and **3** were included for the sake of comparison. The derivatives **1** and **2** contain the photochromic 3',3'-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2'-indoline] moiety and an *N*,*N*-dimethylaminoalkyl derived anchor. The compounds differ in the number of methylene units contained in the anchor: **1** has five CH_2 units, while compound **2** integrates only three CH_2 units. Because of the protonable terminal dimethylamino function both derivatives show sufficient water solubility at neutral and acidic pH. The anchor design of spiropyran **1** was inspired by the strong binding of protonated cadaverine (1,5-diaminopentane) by CB7 (structure of CB7 in Chart 1; $K = 1.4 \times 10^7$ M^{-1}),[8] which we expected to occur analogously for the twice positively charged anchor in the merocyanine forms of **1** (**1MC** and **1MCH** in Scheme 1). The synthesis of a spiropyran analogous to **1**, but with a primary terminal NH_2 amino group (as in cadaverine), was attempted. However, the synthesis was not successful, which is tentatively explained by the occurrence of an intramolecular Mannich cyclization.[62] Spiropyran **3** contains an amidinium substituent in 6-position, which guaranteed a sufficient water solubility while the electron withdrawing character was maintained (as compared to the nitro substitution). The analogue 6-nitrospiropyran with an *N*-methylindoline is commercially available, but has limited solubility in water.

Acido- and Photochromic Behavior of Spiropyran 1 in Aqueous Solution

In the following the acido- and photochromic behaviour of spiropyran **1** as well as its hydrolytic stability[63] will be discussed in detail. The corresponding processes are illustrated in Scheme 1. Noteworthy, these functional characteristics of the photochrome were not altered significantly by the length of the anchor and thus, were very similar for compounds **1**–**3** (see kinetic data for thermal processes in Table 1). The absorption spectra of the different implicated forms are shown in Figure 1. In aqueous solution at pH 7 (10 mM phosphate buffer) the spiro form of **1** (**1SP**) showed an absorption maximum at 353 nm ($\varepsilon = 7800$ $M^{-1}cm^{-1}$). This form converted thermally in a ring opening process to the merocyanine form (**1MC**) with a maximum conversion of *ca*. 90% as verified by ^1H NMR spectroscopy. The kinetic data were extracted by bi-exponential fitting of the time-dependent absorbance of **1MC**, observed at its absorption maximum (501 nm, $\varepsilon = 30100$ $M^{-1}cm^{-1}$); see Figure 2. Similar kinetics with a

biexponential "rise and decay" behaviour have been reported for related spiropyrans.[63, 64] In our case this fitting yielded a rise time constant of τ_1 = 6.5 h, corresponding to a rate constant of $k_1 = 4.3 \times 10^{-5}$ s^{-1}. In a first approximation[65] this rate constant corresponds to the sum of the rate constants for ring opening (**1SP→1MC**) and closing (**1MC→1SP**), $k_{opening}$ and $k_{closing}$, respectively (see Scheme 1). The decay time constant τ_2 = 47.4 h ($k_2 = 5.3 \times 10^{-6}$ s^{-1}) corresponds mainly to the hydrolytic decomposition of the merocyanine **1MC**.[65] This process was significantly slower for the herein used **1** than recently reported for the nitrospiropyran **4**, for which τ_2 *ca.* 7 h was determined at pH 7.[63]

With general character, the discussed hydrolytic instability is one of the limiting factors for the application of spiropyrans in aqueous medium. For example, this may be a problem for the storage capability of the merocyanine during long-term experiments in water. The hydrolysis is known to be initiated by nucleophilic attack at the ene-iminium cation, which is followed by a retro-aldol reaction, leading to Fischer's base (**6**) and 4-nitrosalicyladehyde (**7**);[63] see structures in Scheme 1.

At pH ≤ 3 the **1MC** form is transformed into the protonated merocyanine **1MCH**, which is accompanied by a hypsochromic shift of the long-wavelength absorption maximum (λ_{max} = 405 nm, ε = 26600 $M^{-1}cm^{-1}$, pK_a = 4.2). In contrast to **1MC**, at the low pH required for the formation of **1MCH** the hydrolysis is suppressed and thus, no signs of decay were observed within 24 hours.

The irradiation of **1MCH** at 430 nm or **1MC** at 503 nm (see Experimental Section) induced ring closure to yield **1SP**. The time constants τ for these photoprocesses are in the order of a few seconds under the chosen irradiation conditions (see Experimental Section): 5.0 s for **1MC** and 5.1 s for **1MCH**. Noteworthy, for **1MC** the competing hydrolysis (see Table 1 for a rate constant) is considerably slower. The quantum yield for the photoinduced **1MC→1SP** ring closure was determined to $\Phi_{\mathbf{1MC\rightarrow 1SP}}$ = 0.03, while the conversion **1MCH→1SP** proceeded with $\Phi_{\mathbf{1MCH\rightarrow 1SP}}$ = 0.04.

Supramolecular Interaction with Cucurbit[7]uril (CB7)

The spiropyran **1**, in its various forms (**1SP**, **1MC**, and **1MCH**), was investigated with respect to the supramolecular interaction of the cadaverine-derived anchor with CB7. For this purpose absorption titrations were performed. In the presence of CB7 the spiro form **1SP** converted rapidly into **1MC** (see below). This hampered our attempts to obtain clear-cut data for the binding of this isomer. Continuous irradiation with visible light (465 nm long pass filter), and thereby steadily converting formed **1MC** back to **1SP**, enabled to follow at least some spectral changes of the UV absorption of the spiro form on addition of the macrocycle (at pH 7). A bathochromic shift by *ca.* 13 nm (λ_{max} = 365 nm for **1SP•**CB7) was observed, which lends some qualitative support to the complexation by CB7.

On the other hand, the inherently stable protonated merocyanine form **1MCH** allowed the convenient monitoring of the UV/vis absorption titration with CB7 at pH 2.5 (see Supporting Information). The

titration can be divided in two phases: *i*) an initial decrease of the absorption band at 405 nm accompanied by a slight hypsochromic shift by *ca*. 2–3 nm and *ii*) the growth of a bathochromically shifted band with a maximum at 420 nm accompanied by an isosbestic point at *ca*. 409 nm. The global fitting according to the consecutive complexation of two CB7 macrocycles by **1MCH** yielded the following binding constants: $K_1 = 7.9 \times 10^5$ M^{-1} and $K_2 = 1.3 \times 10^3$ M^{-1}. The constant K_1 is tentatively assigned to the binding of the anchor by CB7. The second binding constant K_2 may be associated with the obviously rather hindered formation of an *exo* complex with the indolenium part. The **1MC** form was also stable enough (see above) on the timescale of an UV/vis absorption titration experiment (see Figure 3). A similar behaviour as noted for **1MCH** was observed. Namely, the long-wavelength band decreased and shifted bathochromically by *ca*. 4 nm in a first phase of the titration. This was followed by a further shift of the absorption maximum to 526 nm, which was accompanied by a hyperchromic effect. The global fitting (consecutive formation of 1:1 and 1:2 complexes) yielded $K_1 = 1.2 \times 10^5$ M^{-1} and $K_2 = 8.6 \times 10^3$ M^{-1} for **1MC**. The somewhat lower binding constant K_1 in comparison to **1MCH** reflects assumingly the negative charge at the nearby phenolic oxygen, which disfavoured the interaction of the anchor with the high-electron density carbonyl-laced CB7 portals. Job's plots for both ring open forms at a total concentration of 10 μM yielded a maximum at 0.5, which corroborated the formation of a 1:1 complex in a low concentration regime (Supporting Information).

Complementary evidence for the formation of a complex between the anchor and CB7 was obtained by ^{1}H NMR spectroscopy (see Supporting Information). Of particular interest are the protons of the anchor (H_f–H_k) and the aromatic protons of the indolenium ring (H_m–H_p); see Chart 2 for letter codes. The terminal methylene protons of the anchor were observed as isolated triplets at 4.48 and 3.09 ppm for H_f and H_j, respectively. The ammonium methyl protons (H_k) were assigned to a singlet at 2.82 ppm. The aromatic protons H_m–H_p showed up as a group of multiplets in the range of 7.5–7.8 ppm. In agreement with the immersion of the anchor into the CB7 cavity a broadening and substantial upfield shifts of the corresponding **1MC** signals (H_f–H_k) were observed on addition of the macrocycle. For example, the H_j and H_k protons underwent clear upfield shifts by 0.72 and 0.81 ppm, respectively. Interestingly, signal broadening was much less evident for the aromatic H_m–H_p protons and no upfield shifts were noted. This supports our notion that the preferential CB7 complexation site is constituted by the anchor.

The mass spectrometric characterization (electrospray ionization mass spectrometry, ESI-MS) of separately prepared free **1MCH** (see Experimental Section) and its complex with CB7 yielded further interesting insights. The free guest showed signals at m/z = 422 and 211, with isotope spacings of Δm = 1.0 and 0.5, consistent with singly and doubly charged ions, respectively (Figure 4a). We assign these ions to **1MC** and **1MCH** (see charge status in Scheme 1 and caption of Figure 4), respectively. This observation points to a partial deprotonation of **1MCH** upon ionization. The fragmentation (MS^2) of m/z

422 yielded major peaks at *m*/*z* = 325 and 160 (see Supporting Information). These data indicated that the 4-nitro-2-vinylphenol moiety as well as the *N*,*N*-dimethylaminoalkyl derived anchor were released upon fragmentation (see Scheme 2). The fragmentation of the *m*/*z* 211 ion was more complex and less conclusive (see Supporting Information).

The presence of CB7 changed the ESI-MS spectrum significantly (Figure 4b). The free deprotonated guest **1MC** (*m*/*z* = 422) was present together with ions peaking at *m*/*z* 1163 and 793. The former ion was readily assigned to the single protonated CB7,[66] while the doubly charged ion (Δm = 0.5) at *m*/*z* 793 belongs to the 1:1 complex between **1MCH** and CB7. The merocyanine guest prevails as MCH form in the complex, most likely due to a disfavoured deprotonation (compare stronger CB7 binding of **1MCH** *versus* **1MC**, see above). The MS^2 fragmentation of *m*/*z* 793 yielded a main peak at *m*/*z* = 711 (see Supporting Information), which indicated the loss of the 4-nitro-2-vinylphenol moiety. However, no fragmentation at the anchor was seen, which pointed to a protective effect of CB7 in the gas phase.

The CB complexation of organic guests with protonable functions is known to impose shifts of the protonation constants, known as host-assisted guest protonation.[12, 16, 18, 21, 23] Invariably, the complexation by CBs leads to higher guest pK_a values. In the present case the phenolic moiety has a pK_a of 4.2 for the uncomplexed guest which shifts to pK_a' = 5.0 for the CB7 complex, i.e., $\Delta pK_a = pK_a' - pK_a$ = 0.8 (Figure 5). The increased basicity of the phenolic oxygen is in line with the somewhat stronger binding of **1MCH** by CB7 as compared to **1MC** (see above). Additional evidence for the role of the CB7 macrocycle in the shift of protonation equilibria can be obtained by the application of the four-state thermodynamic cycle[67] shown in Scheme 3, which yields $K_1(MCH)/K_1(MC) = 10^{\Delta pK_a}$. With the CB7 binding constants of **1MC** and **1MCH** (see above), a pK_a shift of 0.8 units was predicted, which is in excellent agreement with the experimentally verified shift.

The indoline nitrogen of the spiro form **1SP**, but not of the ring opened forms, can be protonated as well.[68] However, the pH titrations of **1SP** are complicated by the thermal ring opening (**1SP**→**1MC**) and therefore the experiments had to be performed under steady irradiation with visible light (λ > 465 nm) which reconverts any formed merocyanine back to the spiro form. Under these conditions protonation constants of pK_a = 1.4 and pK_a' = 3.2 were determined in the absence and presence of CB7, respectively (see Supporting Information). The decrease of pH yielded the disappearance of the typical absorption of the spiro form at around 350 nm and the build-up of a new band with a maximum at 310 nm, which we ascribe to the protonated spiro form **1SPH** (see Figure 1).[68] The pK_a shift of almost two units corroborates the close interaction between the protonated indoline nitrogen and one of the CB7 portals. Thus, it can be assumed that the CB7 ring is capable of slipping completely over the anchor, accommodating one protonated nitrogen on each portal. Furthermore, it is highly reasonable to forecast that for two positively charged nitrogens (indolenium and ammonium) in the ring-opened forms **1MC** and

1MCH the same situation applies. This lends indirect support to our assumption of a complete immersion of the anchor into the CB7 cavity.

Spiropyran Ring Opening and Merocyanine Stability in the Presence of CB7

The above discussed CB7 complexation of the spiropyran anchor has interesting consequences for the thermally-induced ring opening of **1SP** and the hydrolytic stability of the formed **1MC**. Importantly, the hydrolytic stability of the merocyanine form is a crucial precondition for potential applications of spiropyrans in aqueous media.

In the presence of CB7 (20 equivalents) a considerable acceleration of the **1SP→1MC** ring opening was observed. The rise time constant for the appearance of the merocyanine form was obtained from monoexponential fitting as τ_1 = 5.2 min (see rate constants in Table 1 and corresponding graph in Figure 2).[69] This was about 70 times faster than in the absence of CB7 (see above). This rate-acceleration effect has been noted in related contexts of cucurbituril chemistry.[16, 32] However, for spiropyran **5** no kinetic effect of CB7 on the thermal ring-opening at acidic pH was observed in a recent work.[33] This underlines the importance of the herein adopted anchor approach for the observation of a catalyzed ring opening. The composition of the equilibrium mixture was determined by ^{1}H NMR spectroscopy as [**1MC•**CB7]/[**1SP•**CB7] > 95/5, corresponding to the virtual absence of the spiro form in the spectrum. The observed acceleration of **1MC** formation is explained by the presence of the positively charged indolenium nitrogen as integral part of the anchor. This positive charge probably develops already partially in the transition state of the ring opening, which hence experiences stabilization in the presence of CB7. This argumentation was corroborated by temperature-dependent kinetic measurements of the conversion of **1SP** to **1MC**. The Arrhenius-type analysis (see Supporting Information) of the data yielded an apparent activation energy E_a of 109 kJ mol^{-1} (pre-exponential factor $A = 1.4 \times 10^{15}$ s^{-1}; T = 293.15 – 320.15 K, 6 points, r^2 = 0.998) in the absence of CB7, which compares well with data reported in the literature.[70] However, in presence of CB7 (20 equivalents) the activation energy was considerably lower: E_a = 88 kJ mol^{-1} (pre-exponential factor $A = 1.2 \times 10^{13}$ s^{-1}; T = 293.15 – 315.15 K, 5 points, r^2 = 0.999). These complementary data support the observed kinetic effects of CB7 in the thermally-induced formation of **1MC**.

The beneficial effects of CB7 complexation extend further to a dramatically increased stability of the merocyanine form against undesired hydrolysis. While, as discussed above, the free merocyanine **1MC** underwent considerable degradation on the timescale of hours, the **1MC•**CB7 complex showed impressive and unmatched long-term stability. In practice no decay of the characteristic merocyanine absorption was observed after 2.5 days standing at 20 °C (see Figure 2). In contrast, in the same time period already *ca*. 40% of uncomplexed **1MC** were irreversibly hydrolyzed. Noteworthy, the known stability of the protonated merocyanine form of spiropyrans (**1MCH** in our case) is not altered by CB7. In

the absence as well as in the presence of the host macrocycle practically no change of the **1MCH** absorption spectrum was noted during 24 hours.

In order to show that it is really the supramolecular host-guest complexation with CB7 which causes the observed effects, a control experiment with an efficient competitor for the macrocycle was performed. The well-reported preference of CB7 for cadaverine ($K = 1.4 \times 10^7$ M^{-1} at pH 6; 10 mM ammonium acetate buffer)[8] was used to remove the macrocycle from the anchor in a competitive complexation. As shown in Figure 6, the release of the photochrome resulted in an increased vulnerability toward hydrolysis which followed the same kinetics as observed for **1MC** in the absence of CB7. Importantly, cadaverine itself has no influence on the decomposition kinetics of uncomplexed **1MC**.

The importance of the anchor design was corroborated by including the spiropyrans **2** and **3** in our study. In compound **2** the anchor is shortened by two methylene groups. Based on reported data for the complexation of 1,*n*-bisammoniumalkanes by the homologous CB6 it can be anticipated that $n = 5–6$ is an ideal situation for strong complexation, while $n = 3$ would lead to complexes with inferior stability.[28] Hence, different effects based on a weaker supramolecular interaction with CB7 may be expected for compound **2** (see Table 1 and Figure 2). The rise time constant for merocyanine formation ($\tau_1 = 5$ h) of the uncomplexed photochrome was very similar to the one observed for spiropyran **1**. However, in contrast to **1** the addition of 20 equivalents CB7 to spiropyran **2** led to a much less pronounced rate acceleration factor of just 7 for merocyanine formation ($\tau_1 = 44$ min); compare with a factor of *ca*. 70 for **1** (see above). Also the hydrolytic stability of **2** in presence of CB7 was inferior: $\tau_2 = 36.5$ h. Note that for **1MC•**CB7 the hydrolysis time constant τ_2 is practically infinite. In fact, spiropyran **3**, which contains no anchor but a positively charged amidinium group in 6 position showed a slightly increased rate for **3MC** formation upon addition of CB7 (factor of *ca*. 2.5) and a practically unchanged hydrolysis rate (see rate constants in Table 1 and kinetic traces in Figure 2). These control experiments corroborated that the observed effects are related to the supramolecular encapsulation of the anchor. Noteworthy, the recently reported partial encapsulation of spiropyran **5** by cucurbit[8]uril (CB8) yielded a *ca*. 6-fold slower hydrolysis rate as compared to the uncomplexed photochrome.[32] This corresponds roughly to the effects observed herein for photochrome **2** with a moderately efficient anchor. Based on these data it becomes clear that the described molecular design based on an anchor approach constitutes a viable strategy for extraordinary merocyanine stabilization.[32, 64, 71] This becomes even more evident when considering the highly desirable conservation of the photochromic properties as will be discussed in the following section.

Photoswitching with Visible Light

In order to test the influence of the anchor complexation on the photoreactivity of the open forms (**1MC** and **1MCH**), samples of the uncomplexed and the CB7-complexed guests were irradiated under identical conditions. Neither the complexed merocyanine nor the protonated merocyanine form showed a significantly slower photoreaction as compared to the absence of CB7. The time constants for the photoinduced ring closing of **1MC** and **1MCH** in presence of CB7 were determined to τ *ca*. 3.5 and 6.0 s, respectively, which is comparable with the kinetics observed for the uncomplexed guests (see above). The photoreaction in presence of CB7 macrocycle is accompanied by the observation of the following quantum yields: $\Phi_{\mathbf{1MC}\bullet\mathrm{CB7}\rightarrow\mathbf{1SP}\bullet\mathrm{CB7}} = 0.06$ and $\Phi_{\mathbf{1MCH}\bullet\mathrm{CB7}\rightarrow\mathbf{1SPH}\bullet\mathrm{CB7}} = 0.04$. These results are in sharp contrast to the reported behaviour of the CB8 complex of the merocyanine form of **5**, for which the photochromic ring closing was slowed down considerably due to a confinement effect.[32] This drawback was successfully eliminated by the herein adopted anchor approach, which will not impose any confinement effect as the photochromic unit is not encapsulated in the CB7 cavity. It should be noted that it was shown in a very recent work that the partial CB7 inclusion of the protonated merocyanine form (MCH) of **5** led even to a slightly enhanced photoisomerization rate to the spiro form (SP) under acidic conditions.[33] However, no data on the merocyanine (MC) at neutral pH are available due to the missing binding to the host.

It is worth commenting that for the irradiation of **1MC•**CB7, the typical absorption spectrum of the spiro form as photoproduct was observed (see Supporting Information). However, the irradiation of **1MCH•**CB7 yielded a product absorption spectrum (λ_{max} = 310 nm) which corresponded to the protonated spiro form (**1SPH**). According to the protonation constant of the free **1SPH** (pK_a = 1.4) the photoirradiation of **1MCH** at pH 2.5 in the absence of CB7 yielded the unprotonated **1SP**. On the other hand, the phototransformation of **1MCH•**CB7 at pH 2.5 resulted in CB7-complexed **1SPH** (pK_a = 3.2).

After having demonstrated that the photochromic properties were maintained in the complexes we finally aimed to show that the CB7-modulated fast thermal SP to MC conversion and the photoinduced back reaction can be recycled repeatedly. The result of this experiment is shown in Figure 7. The thermal **1SP→1MC** transformation in presence of CB7 (20 equivalents) was run for 30 min which was enough to reach the maximum conversion to **1MC**. After that 40 s of visible light irradiation (λ > 465 nm, 1.67 Wcm^{-2}) were applied which yielded back the **1SP** form. Remarkably, in ten cycles no fatigue effect of the photochromic system was noted, which is the joint result of a clean thermal ring opening, the high hydrolytic stability of the merocyanine, and an efficient photoinduced back isomerization.

Conclusions

We have devised a much improved supramolecular strategy for the rate-accelerated formation of the merocyanine form of an anchor-substituted photo- and acidochromic spiropyran in the presence of the macrocyclic cucurbit[7]uril host. The commonly observed hydrolytic instability of the merocyanine form in aqueous solution is totally suppressed in the presence of the host, showing impressive long-term persistence (no sign of any decay during 2.5 days). The observed kinetic and thermodynamic effects can be rationalized with a strong binding of the macrocycle to the cadaverine-derived anchor of spiropyran **1**. The importance of an adequate anchor design is underlined by the much less pronounced benefits for spiropyran **2**, which has a shorter anchor. The absence of an anchor, as in spiropyran **3**, turns the system into a "normal" spiropyran with commonly observed hydrolytic instability. Importantly, contrary to other efforts to stabilize the merocyanine form by inclusion in supramolecular macrocycles the photoinduced back conversion to the spiro form was not negatively affected by the presence of the host macrocycle. The remarkable hydrolytic stability and the conserved photoswitching performance of the supramolecular assembly may provide a new drive for the further application of spiropyrans in aqueous solutions.

Experimental Section

Materials. The synthesis of *N*,*N*-dimethyl-*N*-[5-[3″,3″-dimethyl-6′-nitrospiro[(2*H*)-1-benzopyran-2′,2″-indoline]-1″-yl]-*n*-pentyl]amine hydrobromide (**1**) and 1′,3′,3′-trimethyl-6-amidinospiro[2*H*-1-benzopyran-2,2′-indoline] hydrochloride (**3**) was performed according to herein slightly modified literature procedures which are outlined in the Supporting Information. *N*,*N*-Dimethyl-*N*-[3-[3″,3″-dimethyl-6′-nitrospiro[(2*H*)-1-benzopyran-2′,2″-indoline]-1″-yl]-*n*-propyl]amine hydrobromide (**2**) is a known compound which was available from a study published earlier.[39] Cucurbit[7]uril (CB7) was a gift from Prof. W. M. Nau (Jacobs University Bremen, Germany) and was prepared according to a published procedure.[72] The ring-opened forms of the spiropyran **1** (merocyanine **1MC** and protonated merocyanine **1MCH**) were prepared by heating the spiro form **1SP** in an aqueous solution containing 0.1% trifluoroacetic acid at 80 °C for three minutes according to a described method and if required (for **1MC**) this was followed by an adjustment of pH if required.[63]

Photophysical measurements. The spectroscopic measurements were performed in mQ water or phosphate buffer (pH 7, 10 mM). For pH determination a Jenway 3510 pH meter was employed; pH adjustments were made with HCl and NaOH. The absorption measurements were carried out on a Cary Bio 50 UV/Vis spectrometer equipped with a Varian PCB 1500 Water Peltier System thermostat for temperature control. Typically the measurements were performed at 20 °C. The visible light was

generated by a 500 W Xe lamp equipped with a hot mirror (A = 1.8 at 900 nm) to reduce IR intensity and suitable optical filters. For quantum yield determinations interference filters (maximum transmission at 503 nm for MC isomerization and maximum transmission at 430 nm for MCH isomerization) were used. This yielded power densities of *ca*. 33 $mWcm^{-2}$ and *ca*. 28 $mWcm^{-2}$ for the application of the 503 nm filter and 430 nm filter, respectively. Around half of the sample volume was exposed to light at any given time. For the cycling experiment 20 equivalents of CB7 were added to a 10 μM spiropyran solution (t = 0 s) in 10 mM phosphate buffer (pH 7). The thermal ring opening was monitored for 30 min at λ_{obs} = 526 nm. This was followed by a 40 s irradiation period with simultaneous UV/vis absorption monitoring (500 W Xe lamp with 465 nm long-pass filter, power density of 1.67 Wcm^{-2}). The thermal ring opening / photoinduced ring closing cycle was repeated ten times.

The titration experiments with CB7 were done by administering aliquots of a CB7 stock solution to quartz cuvettes (1 cm optical pathlength) containing the photochrome guest (in its MC or MCH form). After each addition the UV/vis absorption spectrum was recorded. The binding constants were determined by a global fit according to a model of consecutive 1:1 and 1:2 (guest:CB7) complexation.[73] Attempts to fit the data only with a 1:1 binding model or according to a 2:1 (guest:CB7) complexation yielded unsatisfactory fits or physically meaningless data. The Job´s plots were performed according to published methods.[74] The following errors are estimated for the different kinetic and thermodynamic data obtained in this work: binding constants 20%; activation energies 5%; protonation constants ± 0.1 pH unit; kinetic rate constants 15%; quantum yields 40%.

^{1}H NMR spectroscopy of free guest and its CB7 complex. The ^{1}H NMR (400 MHz) spectrum of a saturated spiropyran solution in D_2O was recorded on a JEOL Eclipse 400 spectrometer at *ca*. 20 °C. The solution was allowed to reach the maximum conversion (90%) to the merocyanine form by thermal ring opening and measured before notable hydrolysis was taking place. For the characterization of the CB7 complex an excess of the macrocycle was added to a saturated photochrome solution. The chemical shifts (δ/ ppm) were referenced to the residual HOD solvent peak at 4.78 ppm for D_2O.

Electrospray ionization mass spectrometry (ESI-MS). ESI-MS spectra were obtained on a Bruker Daltonics HCT ultra mass spectrometer (ion trap), equipped with an ESI source (Agilent) and using a nickel-coated glass capillary (inner diameter of 0.6 mm). The ions were continuously generated by infusing the aqueous sample solution (4 μL/min) into the source with the help of a syringe pump (KdScientific, model 781100, USA). The solutions contained 10 μM **1MCH** at pH 2.5 in absence or presence of 10 μM CB7 and were studied in the positive polarity mode. Typical experimental conditions were: capillary voltage (CE): 3.5 kV; capillary exit voltage: 75 V; skimmer voltage: 15 V; drying gas:

300 ºC at 6 L/min; nebulizer gas pressure: 20 psi. The host-guest complexes were stable in the gas phase and can be seen in a wide range of CE potentials (50–300 V).

Acknowledgements

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Captions of Figures and Schemes

Chart 1. Structures of spiropyrans **1**–**3** (in their SP form) and cucurbit[7]uril (CB7). The spiropyrans **4** and **5** are related structures from previous studies (see text).

Chart 2. Structure of **1MC** and letter coding for protons as discussed in the text for the ^{1}H NMR studies.

Scheme 1. Thermal, photochromic, and acidochromic interconversion between the three different forms of spiropyran **1** (**1SP**, **1MC**, and **1MCH**) and the structures of the hydrolysis products **6** and **7** are shown.

Scheme 2. Proposed fragmentations of **1MC** and **1MCH•**CB7 in the gas phase.

Scheme 3. Four-state model for the complexation of **1MC** and **1MCH** by CB7. Note that only 1:1 complexation with the anchor moiety was considered.

Figure 1. Absorption spectra of **1SP** (full triangles), **1SPH** (open triangles), **1MC** (full dots), and **1MCH** (open dots).

Figure 2. Kinetic traces (monitored at the respective UV/vis absorption maxima) of a) **1**, b) **2**, and c) **3**, reflecting the thermal ring opening of the SP form and subsequent hydrolysis of the MC form in the absence (full lines) and presence (dotted lines) of 20 equivalents CB7. All traces were measured at 20 °C.

Figure 3. Absorption titration of **1MC** (*ca*. 9 μM) with CB7 at pH 7. Inset: Absorption changes at λ = 511 nm upon CB7 addition. The full line shows the fit according to a consecutive complexation of two CB7 macrocycles.

Figure 4. ESI-MS spectra (full scans) of a) free **1MCH** and b) **1MCH•**CB7 complex at pH 2.5. The insets show the corresponding isotope patterns. Assignments with charge indication: *m*/*z* 211.6 [**1MCH**]$^{2+}$; 422.4 [**1MC**]$^{+}$; 793.4 [**1MCH•**CB7]$^{2+}$; 1163.4 [CB7H]$^{+}$.

Figure 5. pH titration of **1MC** in the presence of 20 equivalents CB7. Inset: Titration curves for the MC absorption maximum in the presence (open circles) and absence (full circles) of 20 equivalents CB7.

Figure 6. Thermal ring opening of **1SP** in the presence (dotted line) and absence (full line) of 20 equivalents CB7. At *t* = 24 h 100 equivalents of cadaverine were added to both samples.

Figure 7. Thermo-photonic reversible switching between **1SP** and **1MC** in the presence of 20 equivalents CB7. The absorbance was monitored at 526 nm.

Table

Table 1. Rate constants for the rise (k_1) and decay (k_2) of the merocyanine forms of **1**, **2**, and **3** in 10 mM phosphate buffer (pH 7) at 20 °C.

	1	**2**	**3**
k_1 [s^{-1}]	4.3×10^{-5}	5.5×10^{-5}	2.7×10^{-5}
k_2 [s^{-1}]	5.3×10^{-6}	7.2×10^{-6}	2.2×10^{-6}
k_1 (CB7)[a] [s^{-1}]	3.2×10^{-3}	3.8×10^{-4}	7.0×10^{-5}
k_2 (CB7)[a] [s^{-1}]	0	1.8×10^{-6}	1.6×10^{-6}

[a] In presence of 20 equivalents CB7.

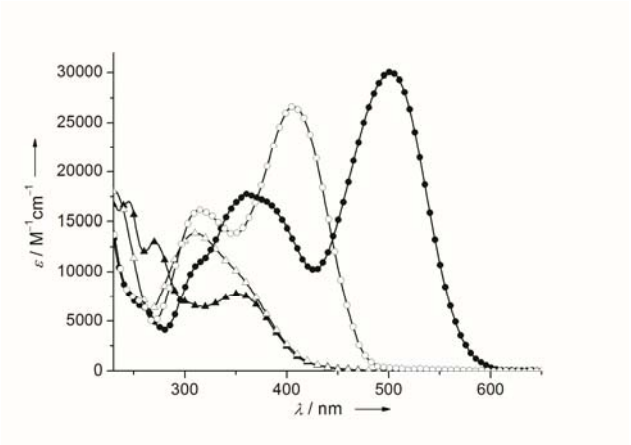


Figure 1.

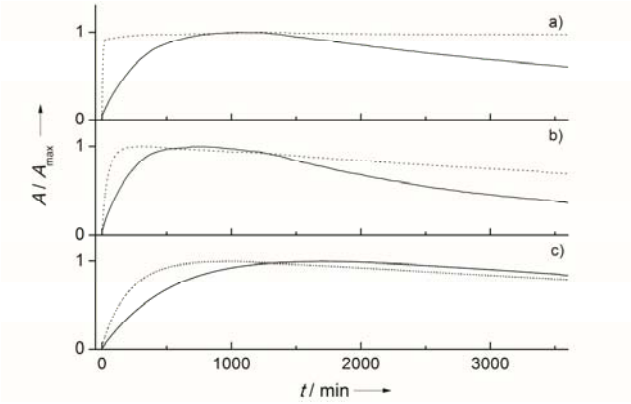


Figure 2.

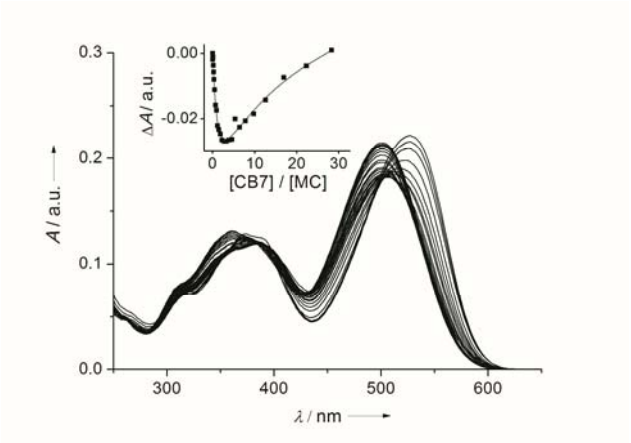


Figure 3.

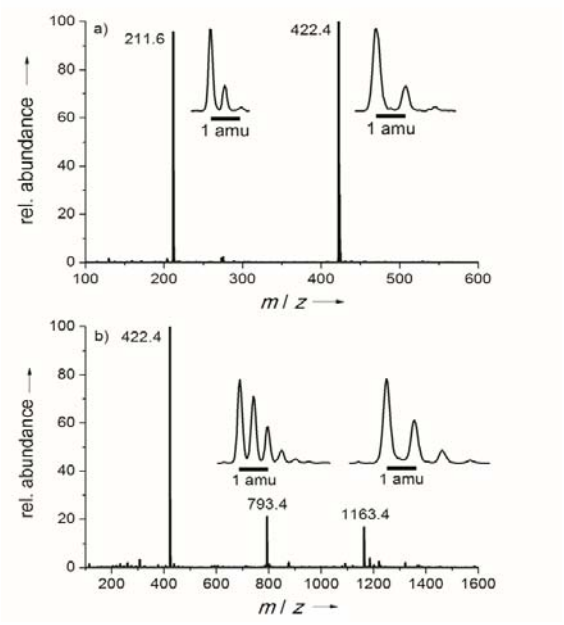


Figure 4.

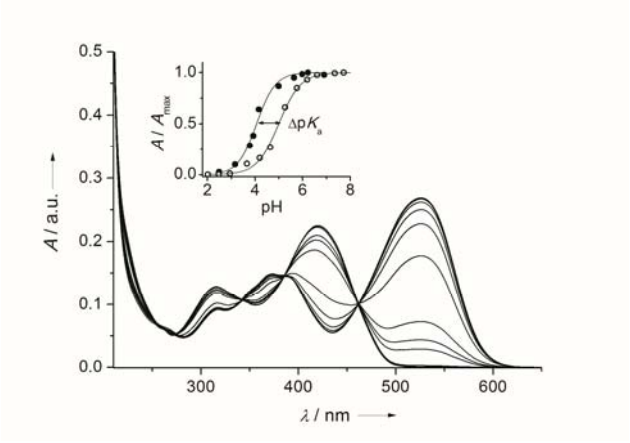


Figure 5.

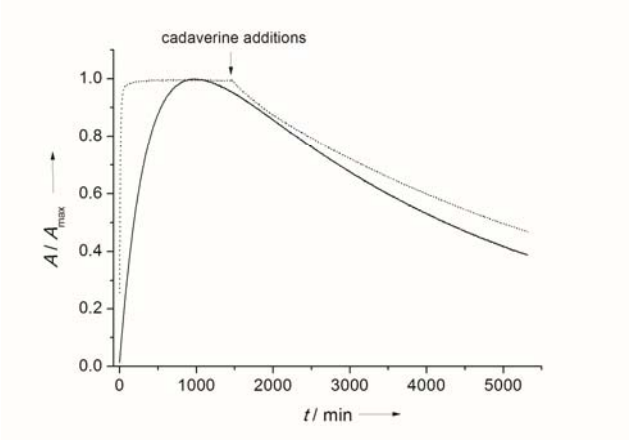


Figure 6.

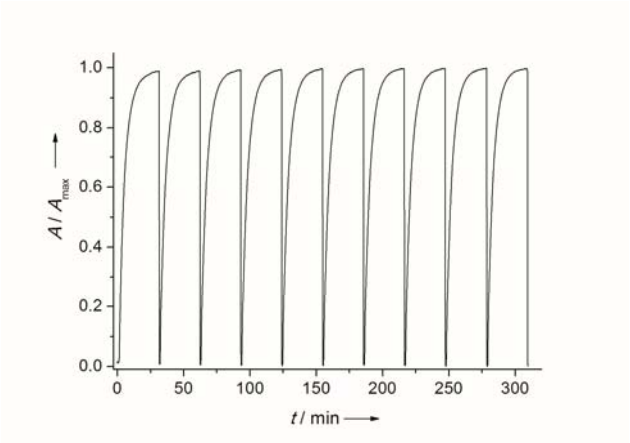
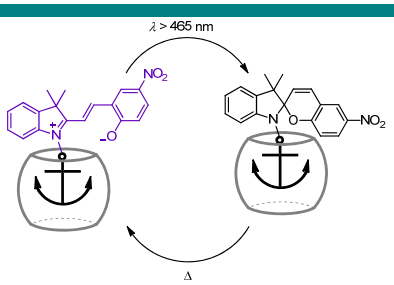


Figure 7.

Entry for the Table of Contents

ARTICLES

The switching properties of anchor-substituted photo- and acidochromic spiropyrans in presence of the cucurbit[7]uril macrocycle as host were investigated. The supramolecular encapsulation of the anchor results in a dramatically accelerated ring opening to the merocyanine form. This isomer is highly stable in presence of the host and can be efficiently photoswitched back to the spiro form with high fatigue resistance.



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Switching-Properties of a Spiropyran-Cucurbit[7]uril Supramolecular Assembly: Usefulness of the Anchor Approach