Photochromism of Spiropyran−Cyclodextrin Inclusion Complexes on Au(111)

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This paper reports on the switching characteristics of a spiropyran−cyclodextrin inclusion complex on a Au(111) surface. The switching behavior in acetone/water and ethanol/water solution is compared with that of the complex as thin film (∼100 layers) on gold and with the complex in a microcrystalline form. For the inclusion complex, we find a significantly increased switching time from the closed spiro to the open merocyanine conformation as compared to a solution of pure spiropyran. The thin film has a similar switching time as the solution of the inclusion complex. For the microcrystalline form, on the other hand, the switching times are considerably shorter. The back reaction exhibits a switching time for the solution of the inclusion complex which is similar to the pure spiropyran solution whereas the microcrystalline sample switches faster and the thin film of the inclusion complex slower than all the other ones. Furthermore, reversible switching of an adsorbed layer of the complex on gold could be observed. The switching characteristics can be explained in a model considering steric and compressive strain.

Introduction

A molecular switch is a challenging option to control the properties of a system by an external stimulus on the nanometer scale. Much research interest is focused on photochromic switches due to the possibility of an easy and fast read-out of the molecular state.[1,2] In the endeavor to miniaturize electronic devices, molecule-based bottom-up approaches have complemented silicon-based technology. Molecular-electronic devices adopt function as wires,[3] rectifiers, modulators, transistors, and switches.[4] Optical read-out is used especially in memories, switches, and signal processing (logic gates).[5] Spiropyrans can serve as elements in gated organic thin-film transistor,[6] in half-adders,[7] and in data storage.[8,9] For assembly of molecular-electronic elements, molecules have to be integrated in solid-state devices, in polymer matrices, or assembled on metallic nanoparticles. This environment significantly changes their properties such as switching rates[10] or the equilibrium state.[11] One possibility to retain or adapt certain properties is molecular encapsulation of the active molecules which can in addition enhance chemical stability and fine-tune photophysical properties of photochromes and conducting polymers. The latter serve as wires and can be 'insulated' by threading macrocycles such as cyclodextrin onto the polymers.[12] In this work, encapsulation has been performed with spiropyran in cyclodextrin.

Spiropyrans undergo a ring-opening reaction upon irradiation with ultraviolet (UV) light into a colored merocyanine state.[13,14] Temperature and time, as well as illumination with visible (VIS) light, induce the back reaction into the spiro state of the molecule.[9,15,16] Spiropyrans have attracted much attention due to the large change in molecular properties; while merocyanine has a large planar conjugated π-system and a high dipole moment due to its zwitterionic nature, spiropyran is not fully conjugated, has perpendicular planes, and is neutral with a small dipole moment.[17−22] These changes make spiropyrans an interesting candidates for gates and switches in molecular electronics.

Directly on a gold surface, spiropyran adsorbs in an ordered fashion forming 2D domains.[23] In this state it has been shown to undergo a thermally induced (irreversible) ring-opening reaction.[11] However, usage in molecular electronic solid-state devices presupposes retention of the switching capability of spiropyran. Partial decoupling from the surface is necessary for the process. This can be realized by a spacer−linker concept, i.e., spiropyrans bound via a linker unit to a silicon surface and separated from adsorption by spacious molecules[24] or spiropyrans tethered to a gold electrode[25] can be switched. An alternative approach to the spacer−linker concept is encapsulation by supramolecular structures. One prevalently used system for encapsulation is cyclodextrin (CD), with its hydrophobic interior and different sizes of the ring system (α-, β-, γ-CD) makes it applicable for various classes of molecules.[26] Spiropyran (SP) forms an inclusion complex with γ-CD.[27−32] The host−guest complex SP@CD in its crystallized form showed photochromism.[27,33] Furthermore, it was found that the UV stability of spiropyran in γ -CD was enhanced compared with spiropyran in a PMMA matrix.[27] However, the rate of the back reaction from the merocyanine state to the spiro state was also increased in the complex.[33]

There are at least two possibilities to link cyclodextrin to surfaces. One approach is to thiolate one or more of the hydroxyl groups to form a defined self-assembled monolayer with a Au(111) surface,[34,35] but also by adsorption from aqueous solution, a monolayer of cyclodextrin on Au(111) is obtained.[36,37] In such a monolayer the cyclodextrin, adsorbs arbitrarily on the Au(111) surface.

In this paper, the concept of encapsulation is adapted to surfaces establishing a novel way of controlling switching properties while retaining close proximity to the surface. In detail, we report on the optical switching process of a spiropyran inclusion complex in cyclodextrin on Au(111) surfaces. The switching behavior in solution is compared with that of the SP@CD complex as a thin film (∼100 layers) and as an adsorbed monolayer on Au(111) surfaces.

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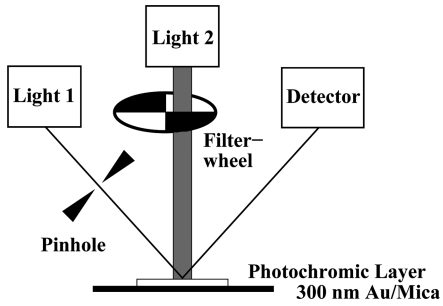

Figure 1. Experimental setup. Light 1: halogen lamp for detecting the state of the molecular switch. The white light is focused on a 20 μm pinhole which is imaged onto the sample. Light 2: Xe lamp used for switching the sample. The detection unit is composed of a spectrograph and a CCD camera.

Experimental Methods

Preparation of the Inclusion Complex and of Thin Films. According to ref 32, a 50 mmol/L solution of γ-cyclodextrin (Wacker, CAS 17465-86-0) and 50 mmol/L solution of 1′,3′,3′-trimethyl-6-nitrospiro[1-(*H*)-benzopyran-2,2′-indoline (TCI Europe, CAS 1498-88-0) in EtOH/H_2O (40:1) was prepared and stirred in the dark overnight. The precipitate was filtered, washed twice, and dried. The composition of the complex was confirmed by X-ray analysis and ^{1}H nuclear magnetic resonance (NMR).

Microcrystalline samples were obtained on Au(111)/mica substrates by drying a droplet of a 2.5 mM solution. The crystals could be seen by the naked eye and were of the order of several hundred micrometers in size.

For thin films, a 2.5 10^{-4} mol/L solution of the complex was prepared, spread on an Au(111)/mica surface, and dried for 2 h. This procedure should result in films of an average thickness of ~100 layers on the gold surface.

Adsorbed layers of the complex on Au(111)/mica were prepared by mounting a clean Au(111) mica substrate vertically for 24 h into a 2.5 10^{-4} mol/L solution of SP@CD in acetone/H_2O. After removing from solution samples were dried in a desiccator for 1 h and immediately measured.

Optical Setup. Figure 1 shows the setup for the measurement of switching kinetics. Optical absorption and transmission spectra have been measured with slight modifications of this setup. The sample was illuminated by a halogen lamp focused onto a 20 μm spot on the sample. For transmission experiments, sample solution was placed in a 10 mm cuvette with detection optics behind the sample (not shown) while for experiments on surfaces, the detection pathway was setup in line with the reflected beam. The reflected and the transmitted beam are detected by a combination of a flat-field spectrograph (Triax 320, Jobin Yvon) with a charge-coupled device (CCD) camera (Newton EM-CCD, Andor; front-illuminated chip, cooled to −50 °C) that allows acquisition of a spectrum for wavelengths in the range of 500−760 nm in a single shot. Through a second beam path, filtered light from a Xe shortarc lamp (PE300BUV, Perkin-Elmer; at 11 A leading to an integrated power of 3.6 mW at the sample position in the range 525−537 nm) was directed onto the same spot of the sample to induce photoswitching. A filter suppressing visible light in the range of 420−680 nm (UG1, Schott) and a 515 nm edge filter to eliminate UV light (OG515, Schott) were used to excite the transition to the merocyanine state and back to the spiropyran state, respectively. To avoid artifacts in the transmission spectrum caused by scattered light, the second beam was blocked by a chopper during spectrum acquisition. For kinetic measurements of switching behavior, a cycle was used which consisted of a short illumination period subsequently followed by a measuring period. After a certain number of illumination/measurement cycles, the switching light was changed from UV to visible light and back. For thermal relaxation measurements one long illumination period with either UV (30 s) or vis light (90 s) was followed by one measurement period. The exact cycle times and numbers are described with the individual experiments.

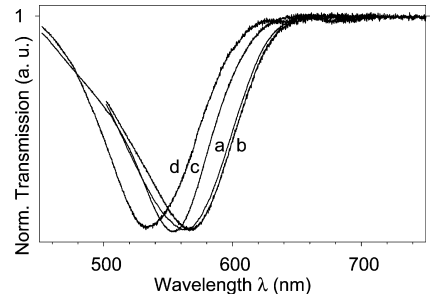

Figure 2. Difference spectra of the vis-generated merocyanine state and the uv generated spiro state show the merocyanine absorption band of (a) free SP and (b) SP@CD in EtOH/H_2O, (c) free SP, and (d) SP@CD in acetone/H_2O.

Results and Discussion

Experiments in Solution. The complex SP@CD could be dissolved well in acetone/H_2O and slightly in EtOH/H_2O. In Figure 2 the absorption band of the inclusion complex in two different solvents is compared with the absorption of the free spiropyran in the same solvents. Plotted are difference spectra of the absorption of the merocyanine and the spiro form, i.e., spectra after vis and after UV radiation. In such spectra only the absorption of the π, π* transition of the merocyanine state shows up. The change of intensity of this absorption band will be used further on for identification of the merocyanine state and thereby for characterization of the switching process. The absorption band of the SP@CD complex in EtOH/H_2O (Figure 2, curve b) has its maximum at 568 nm which is slightly shifted from the absorption maximum of free SP in EtOH/H_2O at 562 nm (Figure 2, a). In addition, the shoulder visible at 530 nm in the spectrum of SP in EtOH/H_2O is lost in the spectrum of the inclusion complex. A blue-shift of the absorption maximum to 530 nm we also found for pure SP in EtOH/H_2O at higher concentration and attribute it to aggregation of merocyanin. Blue-shifted maxima and shoulders blue-shifted from the maximum, respectively, have been reported for aggregated merocyanines.[38−40] Therefore, the disappearance of the shoulder for the inclusion complex shows that formation of aggregates is prevented.

In acetone/H_2O, the shift between the free SP (Figure 2, c) which absorbs at 555 nm, and the complex (Figure 2, d) which absorbs at 542 nm[20,41] is much more pronounced. The position of the absorption maxima depends cardinally on the polarity of the solvent such that a less-polar environment shifts the maximum of 6-nitrospiropyran to longer wavelength[42] but also the opposite, i.e., a shift to shorter wavelength is reported for very similar spiropyrans.[43] In addition, aggregation of the merocyanine can lead to a significant shift (blue-shift for H aggregates, red-shift for J aggregates) of the absorption.[44,9]

In ethanol the absorption maximum of nitrobenzospiropyran is reported at 537 nm,[42] which significantly differs from the value found in the ethanol/water mixture used here. No data exist on nitrospiropyran in water since it does not dissolve. However, the solvation of binary mixtures depends not only on the polarity and proticity of the mixture but also on the microenvironment and, hence, is not trivial.[45,46]

TABLE 1: Time Constants τ_1 and τ_2 and Ratio of Amplitudes A_1/A_2 for the Switching Processes Resulting from Fitting the Experimental Data with a Biexponential Model $I(t) - I_{uv} = A_1 \exp^{-t/\tau_1} + A_2 \exp^{-t/\tau_2} + y_{offset}$[a]

		SP → MC			MC → SP		
compd	environment	τ_1 (s)	τ_2 (s)	A_1/A_2	τ_1 (s)	τ_2 (s)	A_1/A_2
free SP	soln EtOH/H_2O	10	26	[1:1]	12	−	
free SP	soln acetone/H_2O	9	52	[0.92:1]	7	0.3	[1:0.06]
SP@CD	soln EtOH/H_2O	20	101	[0.67:1]	10	−	
SP@CD	soln acetone/H_2O	90	−		6	−	
SP@CD	microcrystalline	4.8	26	[1:0.73]	1.9	−	
SP@CD	thin film	27	139	[0.65:1]	3.9	29	[0.77:1]

[a] SP and MC denote the spiro and merocyanine state, respectively.

TABLE 2: Time Constants τ_i for Thermal Coloration (SP → MC) and Thermal Fading (MC → SP) after Illumination Back to an Equilibrium State

			SP → MC	MC → SP	
compd	environment	light[a]	τ	τ_1	τ_2
free SP	soln acetone/H_2O	10 V	2925 s	3850 s	−
SP@CD	sol. acetone/H_2O	10 V	358 min	156 min	−
SP@CD	microcrystalline	10 V	[b]	318 s	82 s
SP@CD	microcrystalline	extr.	[b]	1159 s	82 s
SP@CD	thin film	10 V	612 s	840 s	−
SP@CD	thin film	extr.	1381 s	2137 s	−

[a] Absorption was measured with a halogen lamp (10 V). If measuring light had a strong influence on the time constant, relaxation was measured for several light intensities and then extrapolated to zero intensity (extr.). [b] No data obtained.

The rate of the switching process of the SP@CD complex in two different solvents is compared with switching rates of free SP in the same solvents. Rates are determined by fitting the intensity change of the merocyanine absorption band with a biexponential decay function or, if possible, single exponential. Time constants and amplitude ratios for all switching processes are listed in Table 1. Time constants for thermal decay are listed in Table 2.

Concerning the behavior in acetone/H_2O solution, the switching process of the SP@CD complex could be fitted with a first-order exponential function (Table 1). Conversion from the spiro (SP) to the merocyanine (MC) state is retarded for the SP@CD complex as compared to free spiropyran, i.e., the fast component of the process is no longer observable. Regarding the reaction MC → SP induced by visible light, one time constants is similar for SP@CD and for free SP in acetone/H_2O whereas the faster second component, which is present in free SP, vanishes.

In EtOH/H_2O, switching to the merocyanine state is described by a biexponential process for SP@CD, as well as for free SP. This is consistent with the model in which the excited singlet state of spiropyran can directly convert to merocyanin or relax into an excited triplet state which than relaxes into the merocyanin form, thus yielding two time constants.[47,17] Similar to the case of the acetone/H_2O solution, the process is significantly retarded for the inclusion complex. For the reverse reaction, which follows a single-exponential decay process, time constants are similar.

In general, rates of the conversion from the spiro to the merocyanine state are for the SP@CD complex much slower than for free SP in solution. This could be due to increased steric hindrance by entrapment of the spiropyran within cyclodextrin. For spiropyran enclosed in β-cyclodextrin switching is not possible due to strongly hindered rotational mobility of the both parts of the dye molecule. Spiropyran requires an ∼90° rotation of one-half of the molecule when switching between clear and colored state; therefore, surroundings have a large effect on the switching speed.[48] To investigate the influence of inclusion on the lifetime of the states, thermal relaxation of SP@γ-CD was determined from the spirostate and from the merocyanin state to thermal equilibrium (Table 2). Both rates are decreased for the inclusion complex, for thermal coloration by a factor of 7. Thermal fading MC → SP on the other hand is retarded only by a factor of 2.5 by formation of the inclusion complex, whereas the rate constants for the switching process, however, are very similar and only slightly accelerated for the SP@CD complex compared with free SP. Since the merocyanine state has a length of 14 Å, it extends out of the cyclodextrin cavity, which has a length of ∼9 Å into the solvent. It is, thus, less influenced than the spiro form, which has a length of 10 Å and is mostly buried within the cavity. The small but not negligible acceleration of rate constants for the inclusion complex in both solvents compared with free spiropyran again points to a steric influence of the cyclodextrin cage which destabilizes the merocyanine state.

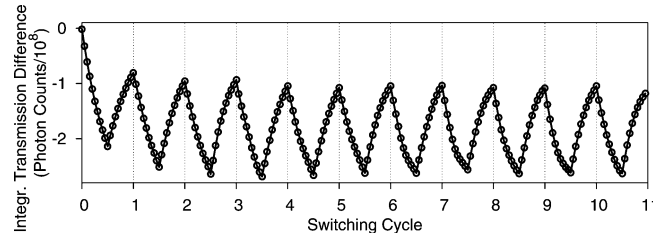

Figure 3. Reversible switching of a solution of SP@CD in aceton/H_2O between the spiro and the merocyanine state over 11 cycles. Total illumination time was 10 × 5 s and 10 × 0.5 s for one UV and one vis cycle, respectively. Absorption intensity was integrated between 480 and 580 nm.

Reversible switching between the two states was possible over many cycles almost without any degradation as shown in Figure 3. After the first cycle, 16% of the integrated signal is lost. Within the following 10 cycles, however, less than 10% of the integrated signal and, therefore, of the participating molecules is lost. Whereas the reduction at the very beginning is presumably due to some drift effects, UV degradation most likely accounts for the small decrease after ten cycles. Obviously, degradation is much smaller for the guest−host complex of spiropyran in cyclodextrin than for free spiropyran. This finding is in agreement with the suggestion by Iyengar[33] that the inclusion complex is more stable with respect to UV irradiation.

Experiments on Thin Films on Au(111)/Mica. The switching behavior of thin films of SP@CD on Au(111)/mica substrates with a thickness of ∼100 layers was measured and compared with results obtained on microcrystalline samples and in solution.

Microcrystals of SP@CD on a gold surface show a spectral behavior which is dominated by the absorption coefficient and, therefore, is comparable with transmission spectra of bulk substance (spectra not shown). The spectral change between 500 and 750 nm was recorded in reflection.

Spectra of thin films (Figure 4), on the other hand, show a much more complex structure since the reflection at the air/material interface becomes comparable with the transmission through the substance. Despite the noise, the change in signal intensity due to switching is clearly visible in the range between 530 and 630 nm.

The switching curves (Figure 5) were fitted with exponential decay functions. While in solution switching could be partially

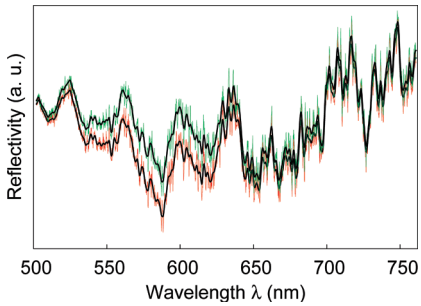

Figure 4. Reflectivity spectra of ~100 layer thick films of SP@CD on Au(111)/mica. Red, after UV irradiation; green, after vis irradiation. The black line is a guide to the eye. For the switching curves (Figures 5 and 7), a spectral range from 530 to 630 nm was integrated.

described as a monoexponential process, two time constants were necessary in most cases for the switching of films.

The reaction from the spiro to the merocyanine state comprises a short time constant of 27 s and a long time constant of 139 s which are comparable to the time constants found for the complex when dissolved in an EtOH/H_2O solution (see Table 1 and Figure 6a, curves **6** and **3**, respectively). This is in contrast to the switching behavior of microcrystals where instead of a long time constant a fast component ($\tau = 4.8$ s) is involved (Figure 6a, **5**). Therefore, in thin films other processes dominate the reaction than in the microcrystalline state.

For microcrystals, the back reaction from the merocyanine to the spiro state is very fast (1.9 s) (Figure 6b, **5**) and even accelerated compared with the solution of the complex (Figure 6b, curves **3** and **4**). This is consistent with earlier results which claim a destabilization of the merocyanine state of nitrospiropyran in cyclodextrin shown by lifetime studies of the photogenerated state.[33] Here, thermal decay shows a biexponential behavior where the smaller time constant is independent of the intensity of measuring light. The larger time constant is in the same order of magnitude as reported by Iyengar,[33] differences are likely attributable to solvent molecules which are build into the crystal structure and are different for their and our crystals.

For thin films, the back reaction has two components (3.9, 29 s) and is, therefore, retarded compared with SP@CD in solution as shown in Figure 6 (curves **3**, **4**, and **6**, respectively). Thermal fading is monoexponential and faster than for the complex in solution.

Comparing the forward with the back reaction in thin films, one finds that the UV-induced switching SP → MC is slower. This is in contrast to results for thin layers of pure spiropyran on MgO where time constants for the UV-induced reaction are much smaller than for the vis-light-induced reactions.[49] One explanation for this behavior would be the formation of merocyanine aggregates upon evaporation on the MgO substrate. Such aggregates were found to be stable and to increase the lifetime of the merocyanine state significantly.[50] A second explanation would be the destabilization of a transition state in the photoreaction from merocyanine in the inclusion complex. A strong indication supporting this theory are the circular dichroism spectra of the SP@CD inclusion complex.[27,51] There, the theoretically achiral merocyanine state exhibits optical activity in the region between 500−600 nm,[27] corresponding to its absorption band, as well as in the UV region where the pattern is similar to the spiro state.[51] Such induced chirality may lead to a preferential formation of one spiro isomer;[51−53] therefore, the chiral environment can lift the degeneracy of the transition state of the photoreaction. Thermal decay seems to follow another reaction pathway and thus is independent of that transition state, showing different changes in its rate constants. Thermal decay is much faster for the thin film than for solution but slower for the decay of the merocyanine form in thin film than for the relaxation of the spiro state to equilibrium. In addition, because the merocyanine state is elongated as compared to the spiro state, the elongation will induce compressive strain when embedded in a well-ordered crystal lattice of cyclodextrin as is the case in the microcrystalline samples. The effect is reduced in—less ordered—thin films yielding longer switching for the back reaction MC→SP compared with microcrystalline samples. Also, thermal decay of the merocyanine state is much faster for microcrystals than for thin films. No compressive strain is present in SP@CD in solution which leads to even longer time constants for the back reaction then for SP@CD as solid.

Finally, the long time constant for the pure spiropyran solution in EtOH/H_2O can be explained by a stabilization of the merocyanine state due to dipole interaction with the solvent.

Reversible switching was obtained in SP@CD microcrystals, as well as in thin films of SP@CD, as shown in Figure 7. In microcrystals, the switching amplitude is reduced by less than 16% after eight cycles, in a nearly linear decline, 2% of the signal is lost per switching cycle. In thin films, the change of the integrated signal varies strongly from cycle to cycle. Up to 30% of the signal is lost but also recovered such that an overall decrease of the signal due to UV degradation cannot be extracted from the experimental data.

Experiments on Adsorbed Layers on Au(111)/Mica. Preliminary results were obtained on adsorbed layers of SP@CD on Au(111)/mica. The samples exhibited a very weak absorption signal. However, a strong indication of reversible switching could be found a shown in Figure 8. Nevertheless, degradation of the layer is very fast, limiting the switching ex situ to a few cycles. Although we were not able to determine the thickness of the adsorbed layer, it is unlikely that it will be more than a couple of monolayers. Pure cyclodextrin adsorbed on gold under similar conditions resulted in formation of monolayers but without a preferential orientation of the cyclodextrin.[36,37] Therefore, this result gives a strong indication that reversible switching of spiropyran adsorbed on a surfaces is possible in contrast to earlier findings where monolayers adsorbed on a Au(111) surface could not reversibly switched.[11]

Conclusions

We have investigated the switching behavior of the inclusion complex of spiropyran in γ-CD in solution, in a microcrystalline form, as thin films and as adsorbed layer on Au(111)/mica substrates. A significantly increased switching time from the closed spiro to the open merocyanine state is found for the inclusion complex compared with a solution of pure spiropyran. Also, thermal life times are considerably enhanced upon inclusion of spiropyran. The thin film has a similar switching time as the solution of the inclusion complex. For the microcrystalline form, on the other hand, switching times are considerably shorter. Changes in switching times can be explained by increased steric hindrance due to entrapment of spiropyran within CD.

The back reaction exhibits a switching time for the solution of the inclusion complex which is slightly faster than that of the pure spiropyran solution. The microcrystalline sample switches even faster than SP@CD in solution, whereas for the thin film the rate is significantly retarded. This can be explained by a destabilization of a transition state in the photoreaction of

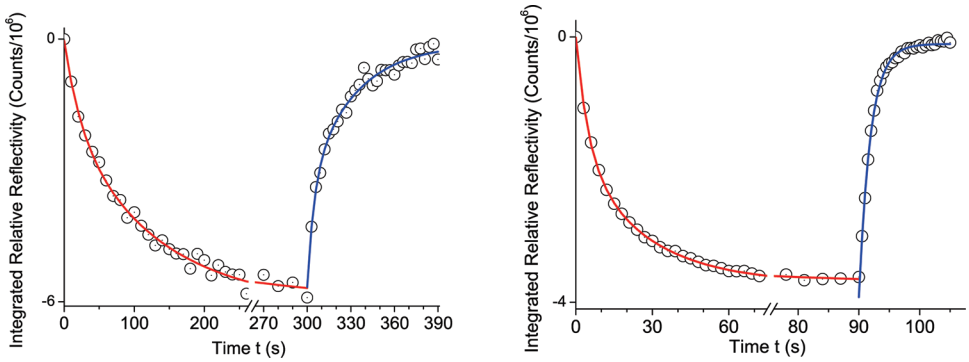

Figure 5. Switching of SP@CD on Au(111)/mica. Left, thin film (∼100 layers); right, microcrystalline sample. ⊙, data points; solid line, best fit, biexponential decay. Note the change of scale in the *x*-axis.

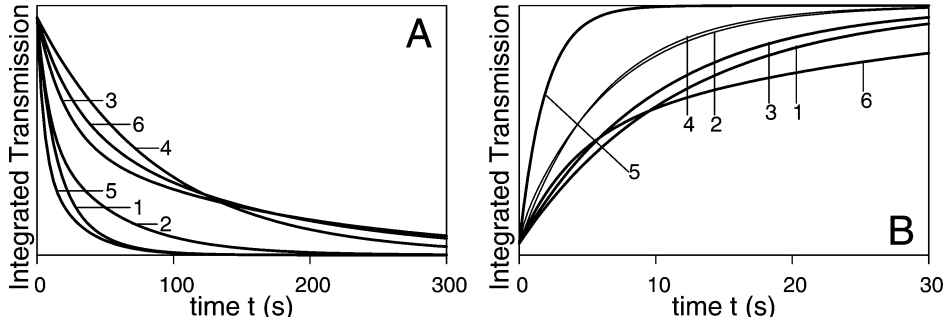

Figure 6. Comparison of exponential fits of switching from (A) spiro to merocyanine and (B) merocyanine to spiro state: (1) free SP dissolved in EtOH/H_2O, (2) free SP dissolved in acetone/H_2O, (3) SP@CD dissolved in EtOH/H_2O, (4) SP@CD dissolved in acetone/H_2O, (5) SP@CD microcrystalline, and (6) SP@CD thin film.

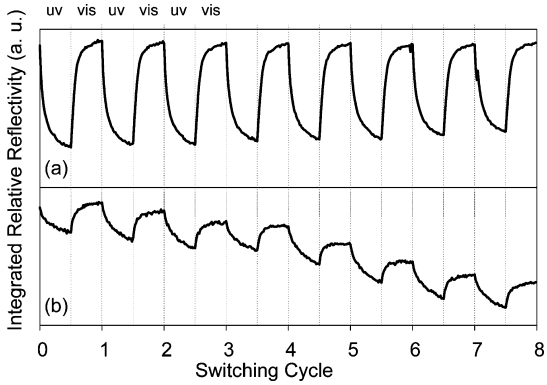

Figure 7. Switching of spiropyran to merocyanine and back over eight cycles. (a) Microcrystalline SP@CD on Au(111)/mica, illumination times were 30 × 3 s for one UV and 30 × 0.5 s for one vis cycle, (b) thin film of SP@CD (ca. 100 layers) on Au(111)/mica, for one UV cycle illumination time was 30 × 10 s, for one vis cycle illumination time was 30 × 3 s. Intensity change was recorded between 530 and 630 nm.

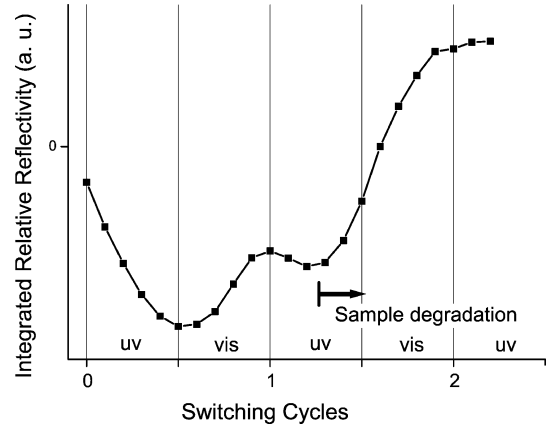

Figure 8. Switching and degradation of an adsorbed layer of SP@CD on Au(111)/mica.

merocyanine in CD caused by steric strain due to the cyclodextrin enclosure. The steric strain on SP@CD is enhanced by compressive strain in microcrystals due to fixed lattice positions of the complex further decreasing switching time. Finally, an indication of reversible switching of an adsorbed layer of the SP@CD complex on gold could be observed accompanied by a rapid degradation of the layer. In conclusion, using inclusion complexes might open a new route to decouple optical switches from the surface in a controlled way sustaining reversible switching and modulating the switching characteristics. Furthermore, the pro-chiral structure of the merocyanine in the cyclodextrin can be used for detection of the state via circular dichroism. In the future this will allow a true separation between initiation of the switching process and detection of the molecular state.

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