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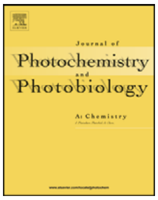

Switching behavior and optical absorbance of azobenzene-functionalized alkanethiols in different environments

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ABSTRACT

Photoswitching of an azobenzene-functionalized alkanethiol has been investigated in different environments. It is found that in solution, in a polymer matrix, in thin layers adsorbed on quartz or silica gel, and in a self-assembled monolayer (SAM) on a rough gold surface the azo compound shows reversible *trans* to *cis* photoisomerization. In contrast, molecules in microcrystalline films are optically inactive. In these systems we observe a blue-shift of the π,π^*-absorption band from about 350 nm to 308 nm, which is attributed to H-aggregate formation. This was confirmed by investigation of the compound in different aqueous ethanolic solutions. When the water content is high enough the absorption pattern and maxima of the H-aggregates are identical to those of the non-switching systems. Furthermore, it is shown that both *trans* and *cis* isomers of the azo derivative exist in an equilibrium with the H-aggregates which depends on the solvent composition. These findings suggest that also in well-ordered SAMs of azobenzene-functionalized alkanethiols formation of aggregates impedes photoswitching by intermolecular coupling.

1. Introduction

Self-assembled monolayers (SAMs) on metal surfaces have been the subject of intense studies during the last two decades because of their great potential for many applications on the nano- and sub-nanoscales [1–14]. These SAMs exhibit novel properties which cannot be generated by traditional top-down methods. One of their outstanding properties is the formation of highly ordered structures. To realize such well-ordered molecular architectures with defined properties we need to understand the chemical and physical characteristics of the molecules within the monolayer and their interactions. Recognizing the relationship between structure and function of the molecular ensemble offers the possibility to control the SAM properties and to tailor thin films for potential applications such as molecular switches for optoelectronic devices. Recently, SAMs of azobenzene-functionalized long chain alkanethiols have attracted much interest since they may offer the possibility for collective photoswitching. Because of the high stability of the N=N-bond against e.g. photochemical degradation and electron impact they are ideal compounds for fundamental research. In azobenzene-functionalized alkanethiols one hydrogen atom of the methyl end-group of an alkanethiol is replaced by an azobenzene unit [15–17].

It is well known that azobenzenes in solution or in a polymeric matrix exist in the thermodynamically stable *trans* form which can undergo *trans*–*cis* photoisomerization and *cis*–*trans* back-reaction [18,19]. The free volume required for the *cis* form is larger than for the *trans* configuration assuming an either inversion or rotation mechanism of the azo bond [20,21]. It is expected that the reversible photoisomerization process also works in azobenzene-functionalized alkanethiol SAMs on gold, where the substrate and the azobenzene unit are sufficiently decoupled by the alkane chain. However up to now no consistent photoswitching behavior has been observed in these systems. Negligible photochemical activity was found in SAMs of simple azobenzene-terminated alkanethiols on gold substrates [15,24–30]. In contrast, reversible photoswitching was detected for similar systems using scanning Kelvin microscopy [23,31,32]. For the same azothiols on gold photoemission experiments suggest only unidirectional laser-induced optical switching [33]. Very recently, a specially designed azo compound based on a biphenylthiol was investigated by scanning tunnelling microscopy and is reported to show reversible photoswitching of sizeable domains of molecules [34]. It is argued that the biphenylthiol with its rigid framework in comparison to the

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flexible alkanethiol chain is responsible for this effect. Photoconversion has been also observed for azobenzene SAMs of asymmetrical disulfides deposited on optically transparent platinum or gold films on quartz slides using UV/Vis absorption spectroscopy [35,36,58], the surface plasmon resonance technique [37], contact angle measurements [30,38–41], and measuring reversible changes in the work function [23].

We have carefully characterized monolayers of azobenzene-substituted alkanethiols with different numbers of methylene groups on (1 1 1)-oriented poly-crystalline gold films on mica by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) [42,43]. However, no photoresponse could be found even after lengthy optical excitation. These obvious discrepancies demand further detailed investigations. Therefore the present study focuses on the relationship between the photoresponse and lateral interactions of the azobenzene-functionalized alkanethiols in different chemical environments. As a selected example, 6-(4-trifluoromethyl-4′-azobenzeneoxy)-hexane-1-thiol (**1**) (Fig. 1) was investigated by UV/Vis absorption spectroscopy. We furthermore present an easily applicable method which can help to decide whether films of 4′-azobenzeneoxy-alkanethiols will show a photoresponse.

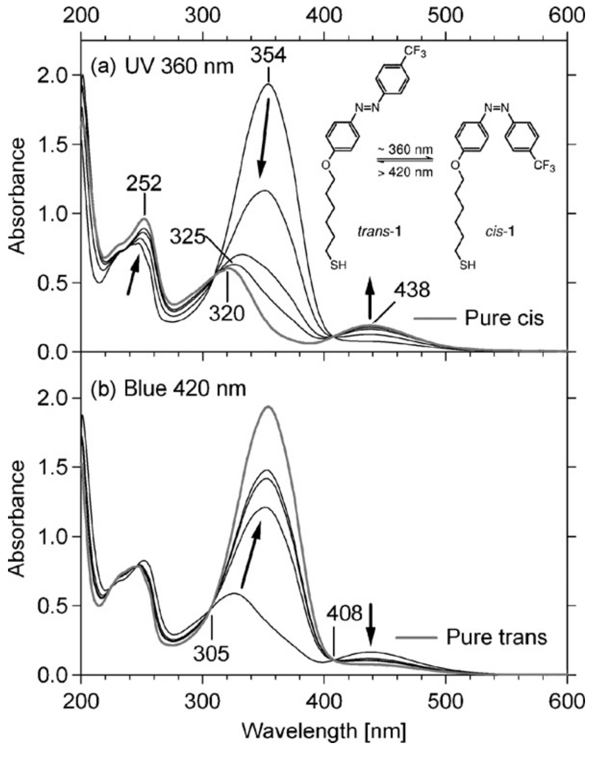

Fig. 1. (a) *trans–cis* photoisomerization of an 7.5×10^{-5} M solution of **1** in ethanol at room temperature by UV illumination for 0 (pure *trans*), 10, 20, 30, and 210 s. The strong π,π^*-absorption at 354 nm rapidly decreases upon illumination to leave a smaller peak at 325 nm, accompanied by the appearance of peaks at 252 nm and 438 nm, characteristic for the *cis* form. By 210 s the solution contains predominantly the *cis* isomer in a photochemical equilibrium with the *trans* form, hence the discrepancy with the pure *cis* spectrum (gray line). As the pure *cis* form had to be prepared independently, its spectrum was scaled to align with the isosbestic points of the illumination experiment, which lie at 408 nm and 305 nm, and indicate that the molecule does not undergo other photochemical reactions. (b) Photochemical *cis–trans* isomerization of the *cis* equilibrium mixture obtained in (a) by illumination at >420 nm for 0, 5, 10, 15 s (photochemical equilibrium predominantly *trans*). Reappearance of the characteristic absorption of the *trans* isomer at 354 nm can be clearly seen, along with a decrease of the *cis* absorption maxima. The isosbestic points at 408 nm and 305 nm are observed as for the *trans* to *cis* conversion. Due to the photochemical equilibrium the starting absorbance of the *trans* form (gray curve) is not completely recovered. Complete thermal recovery occurs in about 200 h.

2. Experimental details

2.1. Materials

Transparent gold substrates for transmission experiments were prepared as follows: Quartz substrates ($10 \times 10 \times 1\ mm^3$), both sides polished (Präzisions Glas & Optik, Iserlohn, Germany) were sonicated in KOH/MeOH, rinsed with water and EtOH, and dried in a stream of argon. On to these gold was evaporated at a rate of approx. 0.1 Å s^{-1} to a nominal thickness of 13 nm or 26 nm. The coating rate and thickness were monitored using a quartz micro-balance. These substrates were stored in ethanol until further use.

2.2. General

All experiments were conducted in the dark using amber or red safelights.

2.3. Preparation of the pure cis form of 1

The pure *cis* form of **1** was prepared by TLC in the dark as follows: A solution of **1** was applied in a stripe onto a standard silica gel 60 TLC sheet. After the sheet had dried it was UV-irradiated for a few minutes using a 366 nm TLC lamp. Following development in benzene the sheet was dried in vacuum. The area containing the *cis* form was then cut out, and eluted with ethanol. This solution was directly used for the reference spectrum in Fig. 1a and for spin-coating.

2.4. Preparation of films of compound 1

2.4.1. Films in polystyrene matrix

A solution of **1** in CH_2Cl_2 was added to a solution of polystyrene in CH_2Cl_2. This mixture was poured into a glass cylinder (both sides open) standing on a glass slide and left to dry for 4 days. The sample was then dried in vacuum for 4 h at 35 °C resulting in an approximately 0.5 mm film which was easily pulled of the substrate.

2.4.2. Films prepared by sublimation

Quartz slides were cleaned in H_2SO_4:H_2O_2:H_2O (1:1:3), rinsed with deionized water (Millipore), and dried in a stream of argon. **1** was evaporated in high vacuum ($<10^{-6}$ mbar) from a glass tube positioned 1–2 cm in front of the substrate at a temperature of 65 °C. To preclude possible thermal degradation, both evaporation residue and deposited films were dissolved in EtOH, analyzed by UV/Vis spectroscopy and TLC, and found to be identical with the original material.

2.4.3. Spin-coated films

Spin-coated films of trans **1** were prepared from 5×10^{-3} to 10^{-4} M solution in benzene or ethanol. Both evaporation and spin-coating result in translucent microcrystalline films.

2.4.4. Dip-coated films

Dip-coated films were prepared by immersion of quartz substrates into 10^{-4} M solution of **1** in ethanol for approximately 1 min and dried it in a stream of argon without prior rinsing.

2.4.5. Preparation of SAMs

After recording a reference spectrum each gold substrate was immersed into a freshly prepared 10^{-4} M solution of **1** for 24 h at room temperature, rinsed with ethanol and dried in a stream of argon.

2.5. Photoisomerization experiments

Two light sources emitting between 320 nm and 400 nm were used for most of the *trans–cis* reactions. For experiments on gold we used a 75 W xenon lamp combined with UV cold-light mirror and UG1 colored glass filter (Schott). For all other *trans–cis* experiments a 300 W xenon arc lamp combined with a water filter and UG1 filter was employed. Illumination with these sources is referred to as "360 nm" throughout the text. In some experiments the 314 nm Hg-line emitted by a 300 W Xe/Hg arc lamp with 314 nm dielectric band-pass filter was used and is referred to as "314 nm". For *cis–trans* isomerization another two sources were used: a blue diode array (λ_{max} = 460 nm, FWHM ≤ 20 nm, <3 W electrical power), referred to as "460 nm", and a 300 W xenon arc lamp combined with a water filter and a GG 420 colored glass long-pass filter (Schott), referred to as ">420 nm"

2.6. UV/Vis spectroscopy

All measurements were conducted using a Perkin Elmer Lambda 900 double beam spectrometer. Absorption spectra of liquid samples were measured using a matched cuvette with the same solvent in the reference path. Spectra of solid samples were measured in transmission mode against air in the reference path and plotted as optical density (OD). For all spectra of thin films a spectrum of a pure substrate has been subtracted (labelled ΔOD). For SAMs on gold each substrate was measured prior to film preparation.

The same spectrometer fitted with a PELA-1020 integrating sphere accessory was used to investigate compound **1** adsorbed on TLC-sheets by diffuse reflection spectroscopy with a piece of uncoated TLC-sheet in the reference path in the same spectrometer. Spectra were converted to absorption measurements by application of the Kubelka-Munk function.

2.7. HPLC–MS experiments

Separation of the non-irradiated and UV-irradiated samples of **1** were performed using an RP C-18 reversed-phase column ($4.6 \times 7.5\ \mathrm{mm}^2$, 3.5 μm) on a Waters (Milford, MA, USA) Alliance HPLC coupled with an 2998 PDA diode-array detector and a 3100 single quadrupole mass spectrometer equipped with an API-source. The mobile phase consisted of water containing 0.1% trifluoro acetic acid (A) and 90% acetonitrile/10% methanol (B). Gradient elution was started with 90% A going to 95% B over 7 min. The flow rate of the mobile phase was 0.8 ml/min, and the injection volume was 20 μl. UV spectra and mass spectra (electrospray, positive ion mode) were simultaneously recorded. Retention times were 10.3 and 8.8 min. for *trans* and *cis* isomers, respectively, showing that the isomers can be completely separated. UV/Vis spectra confirmed their identity by comparison to solution spectra. Mass spectra of the two isomers are identical and show the same main mass peak at [$M+H^+$] $m/e = 383$, indicating no photo-induced fragmentation.

2.8. Synthesis of the azobenzene-functionalized thiol 1

2.8.1. 4-Trifluoromethyl-4′-[(6-bromohexyl)oxy]azobenzene

A mixture of 4.3 g (16 mmol) 4-trifluoromethyl-4′-hydroxyazobenzene (from the coupling reaction of the diazonium salt of 4-trifluoromethylaniline with phenol), 33.8 g (139 mmol) 1,6-dibromohexane, and 2.2 g (16 mmol) potassium carbonate in dried acetone (800 ml) was heated at reflux for 11 h. The reaction was monitored by TLC. Solvent and 1,6-dibromohexane were removed by distillation under reduced pressure. The remaining yellow solid was flash-chromatographed (silica gel 60 (40–63 μm, Merck), eluent toluene/n-hexane 1:1). Yield: 78%, Mp: 72–74 °C. UV/Vis (ethanol), λ_{max} [nm] (lg ε): 438 (3.11), 354 (4.44), 247 (4.06). MS(EI): $m/z = 429$, calculated for $C_{19}H_{20}BrF_3N_2O$, $m/e = 429.3$.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 4H), 7.76 (d, ^3J = 8.3 Hz, 2H), 7.02 (d, ^3J = 9.1 Hz, 2H), 4.06 (t, ^3J = 6.4 Hz, 2H, O–CH_2), 3.44 (t, ^3J = 6.8 Hz, 2H, Br–CH_2), 1.94–1.84 (m, 4H, CH_2), 1.56–1.52 (m, 4H, CH_2).

^{13}C (BB and DEPT) NMR (100 MHz, $CDCl_3$): δ = 162.3 (C_{ar}-O,1C), 154.6 (C_{ar}-N,1C), 146.7 (C_{ar}-N,1C), 126.2 (C_{ar}-H, 2C), 125.2 (C_{ar}-H, 2C), 122.7 (C_{ar}-H,2C), 114.8 (C_{ar}-H,2C), 68.1 (CH_2-O,1C), 33.8 (CH_2-Br,1C), 32.6 (CH_2-O,1C), 29.0 (CH_2,1C), 27.9 (CH_2,1C), 25.3 (CH_2,1C); CF_3 carbon and adjacent ring carbon were not observed [58].

2.8.2. 6-(4-trifluoromethyl-4′-azobenzeneoxy)-hexane-1-thiol 1

In expectation of high yields of **1** the bromo group of the precursor was converted into thiol via the isothiouronium salt by the well-known reaction with thiourea [22]. 859 mg (2 mmol) 4-trifluoromethyl-4′-[(6-bromohexyl)oxy]azobenzene and 213 mg (2.8 mmol) thiourea were dissolved in 100 ml deoxygenated (argon) ethanol and heated at reflux for 15 h. The solvent volume was reduced to approximately 70 ml. To this solution containing the intermediate salt, 1 ml of 5N NaOH purged with argon was added and heating of the mixture is continued under argon for 4.5 h. The solvent was evaporated under reduced pressure and the residue extracted with 40 ml $CHCl_3$. The $CHCl_3$ phase was shaken with 5N HCl until pH 6.0 was reached. After washing three times with water and drying over sodium sulfate the $CHCl_3$ phase containing the free thiol **1** and considerable amounts of its disulfide was concentrated under vacuum. Flash chromatography (silica gel 60 (40–63 μm, Merck), eluent: toluene/n-hexane 70:30) afforded product **1** in 34% yield. TLC and HPLC showed no impurities. Mp.: 72–74 °C. Considerable amounts of the symmetrical disulfide were also obtained (data not given). UV/Vis (ethanol), λ_{max} [nm] (lg ε): 438 (3.11), 354 (4.44), 247 (4.06). MS(EI): $m/z = 382$, calculated for $C_{19}H_{21}F_3N_2OS$, $m/e = 382.4$

^{1}H NMR (400 MHz, $CDCL_3$): δ = 7.96–7.92 (m, 4H), 7.76 (d, ^3J = 8.4 Hz, 2H), 7.02 (d, ^3J = 9.2 Hz, 2H), 4.06 (t, ^3J = 6.4 Hz, 2H, O–CH_2), 2.56 (dd, ^3J = 7.4 Hz, ^3J = 14.6 Hz, 2H,S-CH_2), 1.88–1.81 (m, 2H, CH_2), 1.71–1.64 (m, 2H, CH_2), 1.52–1.49 (m, 4H, CH_2), 1.35 (t, ^3J = 7.8 Hz, 1H, S*H*).

^{13}C(BB and DEPT) NMR (100 MHz, $CDCl_3$): δ = 162.3 (C_{ar}-O,1C), 154.6 (C_{ar}-N,1C), 146.7(C_{ar}-N,1C), 126.2(C_{ar}-H, 2C), 125.2 (C_{ar}-H, 2C), 122.7 (C_{ar}-H, 2C), 114.8 (C_{ar}-H, 2C), 68.2 (CH_2-O,1C), 33.9 (CH_2-SH,1C), 29.0(CH_2,1C), 28.1 (CH_2,1C), 25.5 (CH_2,1C), 24.5(CH_2,1C)); CF_3 carbon and adjacent ring carbon were not observed [58].

3. Results and discussion

3.1. Photoswitching in solution, in a polymer matrix, and adsorbed in silica gel

As shown in Fig. 1a the UV/Vis spectrum of the *trans* configuration of **1** in ethanol at room temperature is dominated by the intense π,π*-transition with a maximum wavelength λ_{max} at 354 nm. The maximum position of the π,π*-transition is not strongly influenced by the polarity of the solvent (351 nm for n-hexane, 355 nm for $CHCl_3$ and 353 nm for CH_3CN). Fig. 1a also includes the UV photoisomerization behavior of **1** in a 7.5×10^{-5} M solution in ethanol at room temperature. Irradiation of the thermodynamically stable *trans* form with UV light results in the appearance of a weak n,π*-transition at 438 nm, and a strong decrease of the π,π*-absorbance accompanied by a blue-shift of the maximum from 354 nm to 325 nm, corresponding to the formation of the *cis* isomer. Similar photoisomerization is observed for a large number of azobenzenes [45]. Both the *cis* and *trans* isomers absorb in the UV and in the blue so that photoisomerization in either direction gives rise to a new equilibrium mixtures of both isomers. Starting with the *trans* form 85 to 90% is converted into the *cis* isomer as seen from a comparison with the absorption spectrum of the pure *cis* form (gray line in Fig. 1a). The pure *cis* form was obtained by separating the *trans* and *cis* isomers chromatographically. Subsequent irradiation of the sample at >420 nm switches back from *cis* to *trans* configuration as shown in Fig. 1b. Again a photostationary equilibrium is reached at which the *trans* form is not completely recovered. The spectrum of the pristine *trans* form is shown as a reference (gray line in Fig. 1b) indicating that a fraction of 25 to 30% of the *cis* form remains. At room temperature *cis*-**1** takes more than 200 h to convert entirely back into *trans*-**1** in the dark. In the course of both the *trans*–*cis* and the *cis*–*trans* photoisomerization the absorption spectra exhibit isosbestic points at 408 nm and 305 nm indicating that the reaction proceeds without forming multiple products. These points are conserved over several cycles of transformations, demonstrating the high stability of **1** to photochemical degradation. This observation is also supported by HPLC–MS which clearly separates the two isomers. Following separation of the photochemical equilibrium mixture, the absorption spectra can be unambiguously assigned to the *trans* and *cis* form and the mass spectra of the two isomers are identical with the correct parent ion peak at $m/e = 383$ $[M+H]^+$.

When molecule **1** is embedded in a rigid polymer matrix such as polystyrene, the absorption spectrum of the *trans* form in the translucent film exhibits a π,π*-absorption maximum at 359 nm. As depicted in Fig. 2 the molecules undergo a *trans* to *cis* transformation upon UV-illumination comparable to the photoisomerization observed in ethanolic solution and other tested solvents in terms of both quantum efficiency and photostationary equilibrium. The inset to Fig. 2 shows the photochemical and thermal back-reaction from the *cis* to the *trans* form, following UV irradiation to generate the *cis* isomer. As in the solution case, the photochemical reaction is only reversible between the two photostationary equilibria, but the thermal *cis*–*trans* reaction goes to completion. We observe the isosbestic points at 415 nm and 315 nm characteristic for a mixture of only two species. The occurrence of isosbestic points indicates in addition that the long alkane chain of **1** and the polymer molecules of the matrix do not hinder the isomerization process, e.g. by steric hindrance.

When going from solution via the polymer matrix to a medium where the molecules will adsorb, the interaction among the dye molecules is increased and therefore changes in the optical properties are to be expected. Nevertheless, it has been shown that azobenzene molecules introduced from the gas-phase into the pore system of molecular sieves can undergo reversible *trans* to *cis* photoisomerization [46]. We have investigated a related substrate system with a large surface, namely silica gel 60 TLC sheets from Merck. Adsorption of *trans*-**1** was established by immersion in either dilute or concentrated ethanolic solution (6×10^{-5} M or 10^{-3} M). The sheet was spectroscopically investigated using an Ulbricht sphere after removing the traces of the solvent in vacuum. As depicted in Fig. 3 the absorption spectrum of **1** on the silica gel closely resembles the measurement in solution. Again irradiation of the adsorbed species shows both *trans*–*cis* and *cis*–*trans* photoisomerization and thermal *cis*–*trans* back-reaction as found in solution (see inset of Fig. 3). It is, however, noteworthy that *cis*-**1** is stable in the adsorbed state for hours.

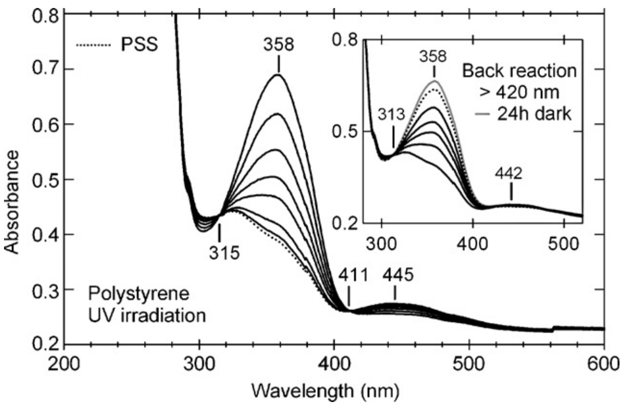

Fig. 2. Photochemical *trans*–*cis* isomerization of **1** embedded in a polystyrene film of 0.6 mm thickness at room temperature by UV-illumination for 0 (pure *trans*), 3, 6, 8, 10, 15, 20, and 25 s (new photostationary state (PSS predominantly *cis*, dotted line). Isosbestic points are observed at 411 nm and 315 nm. Inset: *cis* to *trans* photoisomerization of the film in the *cis* photostationary state by illumination at >420 nm for 0, 2, 4, 6, 10, 20 s (equilibrium predominantly *trans*, dotted line). Thermally the reaction is completely reversible and after 24 h in the dark the initial *trans* concentration is nearly reached (gray line).

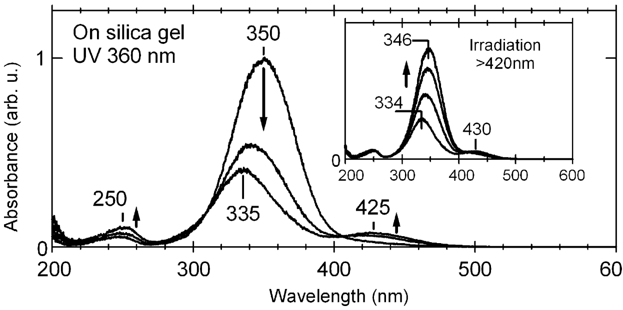

Fig. 3. Photoisomerization of *trans*-**1** adsorbed from 10^{-3} M ethanolic solution onto silica gel 60 (TLC sheet) at room temperature following UV-illumination for 0 (pure *trans*), 10, and 60 s. The absorbance is calculated from diffuse reflection spectra. Inset: reverse reaction by illumination at >420 nm for 0, 3, 10 and 30 s (PSS predominantly *trans*).

3.2. Photoresponse of 1 in microcrystalline films and thin layers on quartz

In contrast to its behavior in the systems described above, the intense π,π*-absorbance seen in solution disappears when **1** is deposited as microcrystalline films on quartz by sublimation in high vacuum. As shown in Fig. 4a we observe instead a broad band at 305 nm. This film did not show any photoreaction following illumination at either 314 nm or >420 nm. A very similar absorption spectrum is observed when spin-coating a film of a few 100 nm thickness (judged from the absorbance) onto the quartz substrate. This film shows likewise no photoreaction (Fig. 4a). Absorption spectra of solutions made by redissolving the films in ethanol before and after light exposure are identical to those taken of a freshly prepared *trans* solution in ethanol. TLC and HPLC also show only the *trans* form in these solutions.

For thinner spin-coated films (30–100 nm) this aggregation seems not to be completed. In addition to the absorption peak at around 312 nm we observe a shoulder at 340 nm, corresponding to the π,π*-absorption band in solution (Fig. 4b). Again, the redissolved films show the absorption spectrum of *trans*-**1** (see inset).

One could argue that the interaction of the molecule **1** with the quartz substrate plays a decisive role in stabilizing the *trans* form in such films and in impeding the *trans*–*cis* photoisomerization. To test this possibility we investigated a quartz slide which was dipped in a solution of **1** in ethanol, and dried in an argon stream. The absorption spectrum, shown in Fig. 4c is similar to that of *trans*-**1** in solution (see Fig. 1). The amplitude of the absorbance of this film indicates that the coverage corresponds to approximately a monolayer of **1** molecules. The film shows a photoresponse when exposed to light at 360 nm which again infers formation of the *cis* isomer. The back-reaction upon illumination at 460 nm proceeds as fast as in solution. These results indicate that it is not

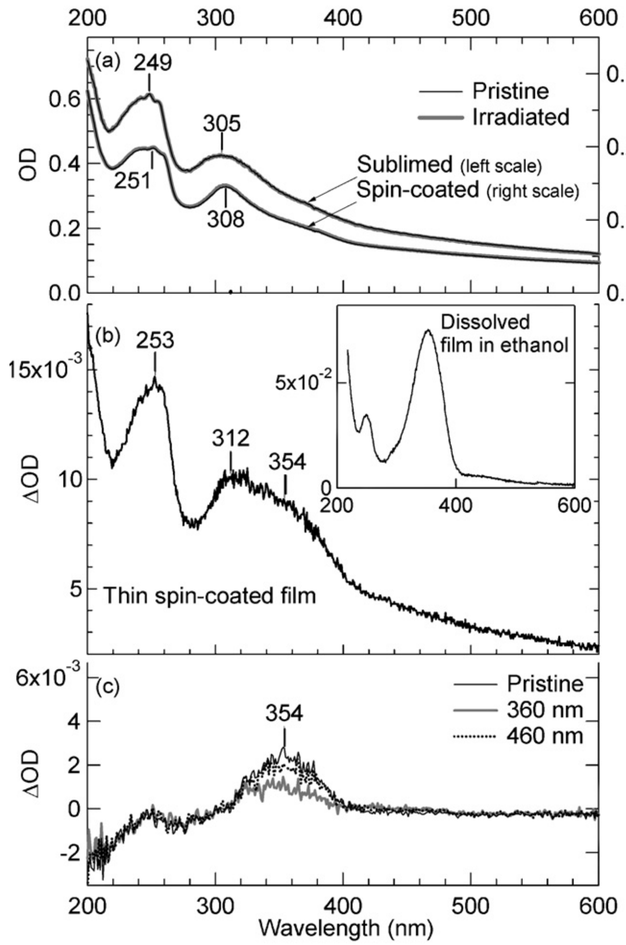

Fig. 4. Photochemistry of sublimed, spin-coated and dip-coated films of **1** on polished quartz substrates. (a) Absorption spectra of sublimed and spin-coated films of a few 100 nm thickness exhibit a new absorption band at around 305 nm. No change is observed upon illumination with 360 nm and >420 nm. (b) Absorption spectrum of a thin spin-coated film of 30–100 nm thickness showing absorption bands at 312 nm with a shoulder at 340 nm which we attribute to a superposition of features from the thicker microcrystalline films in (a) and the adsorbed dip-coated film in (c). (c) Reversible photoswitching of a monolayer-thin film dip-coated in *trans* solution. Changes at around 354 nm are reminiscent of those in solution. Note that the scale is identical to (b).

the interaction between the molecule and the quartz that prohibits switching.

However, there appears to be some surface–molecule interaction for these rather thin films which has impact on the isomerization. In contrast to the stability of *cis*-**1** on silica gel 60 sheets where the surface area is large, on the quartz substrate the *cis* form cannot be stabilized. We coated a thin film of **1** on quartz from a solution containing 90% of the *cis* form. The absorption spectrum of this film was characteristic for films made from solutions of the *trans* form, suggesting that the *cis* form is converted to *trans* upon adsorption, or the residual *trans* form adsorbs preferentially. We also observed similar behavior when preparing SAMs on gold/mica from a solution with molecules predominantly in the *cis* form.

3.3. Photoresponse of 1 in SAMs on transparent gold films

Investigation of SAMs of **1** on transparent gold substrates sheds more light on the switching process. For these films it is well established that the molecules bind with the sulphur head-group to the gold substrate. The azobenzene chromophore end-groups are aligned with the molecular plane nearly vertically to the substrate. Details of the geometric and electronic structure of well-ordered SAMs on gold/mica are discussed elsewhere [42,43]. We expect a similar adsorption on thin transparent gold films. On a 26 nm gold film, the absorption spectrum of the SAMs shows a maximum at 332 nm (Fig. 5a) located between that of the *trans* form in solution (λ_{max} = 354 nm, Fig. 1) and that of the thick spin-coated films (λ_{max} = 308 nm, Fig. 4a). Fig. 5a also includes the changes in the absorption spectrum in response to alternate irradiation by UV and blue light from a LED. These changes are again compatible with a reversible *trans* to *cis* photoisomerization. The experiment was repeated several times using freshly prepared SAMs without a CF_3 head-group on substrates with different gold thickness. For each batch of gold samples we observe either switching or non-switching irrespective of substrate thickness. The non-switching films exhibited an absorption maximum at around 312 nm, as illustrated for a 13 nm thick gold film in Fig. 5b. This absorption is close to that produced by sublimation or in spin-coating of **1** on quartz slides (see Fig. 4a and b). As for the thick sublimed and spin-coated films, irradiation of these films on gold with UV light gave no photoresponse.

Our findings are similar to Ref. [25] where a SAM of an azobenzene-decanethiol on gold on quartz also shows a strongly blue shifted transmission. Those SAMs do not exhibit any photoreaction. We also made this observation for well-ordered SAMs prepared on gold/mica in reflection spectroscopy. The reflection spectra are very similar to those prepared by spin-coating and sublimation. We discuss these results in more detail in Ref. [42].

The blue-shift observed for the microcrystalline films (sublimed or spin-coated) and the SAMs can be interpreted in terms of strong intermolecular interactions in the film leading to formation of H-aggregates. Formation of H-aggregates is well known for a number of dyes and intensively investigated [47–49]. The spectral shifts due to the strong interaction between the neighboring chromophores were explained by the molecular exciton model introduced by Kasha [50]. In H-aggregation the chromophores align in a sandwich

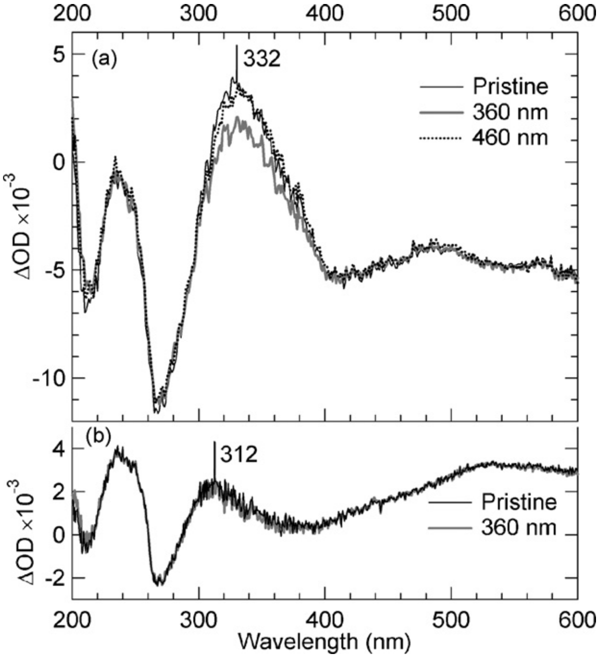

Fig. 5. Photoswitching of differently prepared films on transparent gold substrates observed using UV/Vis transmission mode spectroscopy. (a) SAMs obtained by immersion of a 26 nm gold film on quartz in ethanolic solution of **1**. The spectrum resembles that of *trans*-**1** in solution (see Fig. 1). The film shows reversible photoswitching following UV and blue-light illumination, respectively. (b) Film preparation as for (a) on a 13 nm gold film. The absorption maximum is now shifted to 312 nm. Such films did not show any photoreaction, but this was not correlated to the film thickness.

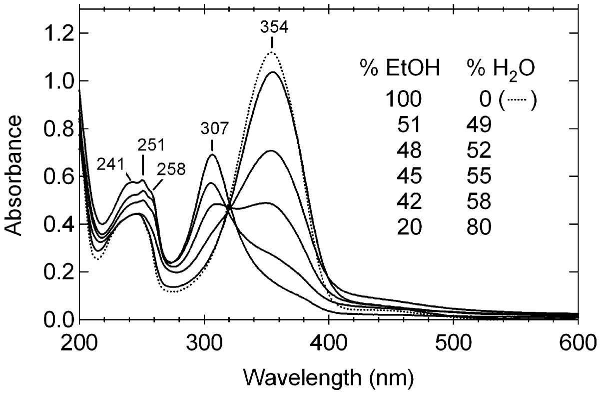

Fig. 6. Molecular aggregation investigated by UV/Vis spectroscopy. Increasing the water content of freshly prepared ethanolic solutions of **1** causes increased aggregation. The concentration of **1** was 4.4×10^{-5} M in each solvent mixture. As the water content increases the absorption spectra exhibit features strongly similar to those of the non-switching films described above. The absorption band at 307 nm gives strong evidence for aggregation, as discussed in the text.

fashion with an angle between the transition dipole moment and distance vector larger than the magic angle (54.7°), leading to an excited state higher in energy than the excited state of the isolated molecule in solution. As a consequence, we observe a blue-shift of the corresponding absorption band [44].

3.4. *Characterization of H-aggregates of **1** in mixtures of water and ethanol*

To understand the coupling of the molecules in more detail we induced aggregation in solution. We found that formation of H-aggregates of **1**, as well as of other alkoxy-azobenzenes with alkanethiol chains of different lengths, proceeds upon addition of water to the ethanolic solution and can be monitored again by UV/Vis spectroscopy. Amphiphilic derivatives of stilbene [53] and azobenzene [54–56] are known to form aggregates in water, in aqueous dispersions or in the presence of saturated and unsaturated phospholipids [57]. In these molecules the hydrophilic substituents are attached to the chromophores either directly or via an alkyl chain. We demonstrate here that the polarity of the thiol group is sufficient to achieve aggregation of **1** in a mixture of ethanol and water. In other solvents no aggregation was found, e.g., even for high concentrations of **1** in n-hexane.

The influence of the water content on aggregation of **1** in an ethanolic solution is illustrated in Fig. 6. With increasing H_2O concentration a new absorption band with its maximum at 307 nm is formed, which we attribute to H-aggregates. These spectra were taken of freshly prepared solutions, in which the thermal equilibrium between the *trans* and aggregated forms is not yet fully established. We note that the new absorption peak at 307 nm falls in the range where the *cis* form of **1** also absorbs. Nevertheless we can distinguish between aggregates and the *cis* isomer since the absorption of the latter is much weaker.

The spectra of fully aggregated solutions (80% H_2O) and do not change if remeasured after a day, while those of the intermediate mixtures clearly show the formation of further aggregates while the amount of *trans* decreases. This process completes on the timescale of hours.

As shown in Fig. 7 irradiation of the aggregate-containing solution with UV light at 314 nm for some minutes does not result in photoisomerization. It should be mentioned that for all the samples where a photoreaction was achieved only a few seconds of irradiation were necessary. Diluting with ethanol either the freshly prepared aggregate solution of **1** or the irradiated sample dissolves the aggregates and results in a complete back formation to *trans*-**1** (see the inset of Fig. 7, black line). This corroborates that aggregation is reversible and the *trans* form in the aggregate is photostable.

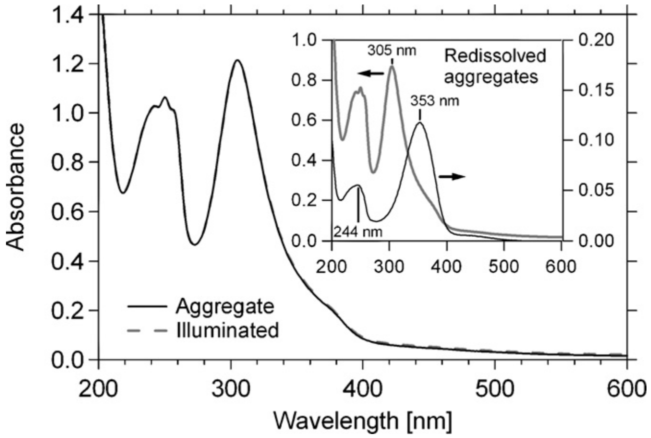

Fig. 7. Absence of photoisomerization in aggregates of **1** in solution in ethanol (20%) and H_2O (80%) measured by UV/Vis spectroscopy. The solution was UV-illuminated for 5 min., but exhibited no change in absorption. Inset: Complete recovery of the *trans* isomer was achieved by increasing the ethanol content of a mixed solution (ethanol 20%, H_2O 80%) containing aggregates, and monitored by UV/Vis spectroscopy. The spectrum of the *trans* isomer is completely recovered, indicating that the aggregation is reversible and the molecules do not undergo any reaction under these conditions. Note that the absorbance has decreased due to dilution while increasing the ethanol content.

To further prove that aggregates do not switch while isolated molecules do, we adjusted the solution to 45% ethanol and 55% water. Under these conditions the absorption spectrum of **1** in a freshly prepared solution shows both the *trans* configuration and the aggregated form with absorption maxima at 349 nm and 307 nm respectively (dotted line in Fig. 8). The ratio of *trans* to aggregates is not at thermal equilibrium. Upon irradiating this mixture at 360 nm the absorption of the *trans* species decreases and an enhancement of the intensity at around 440 nm is observed. This clearly indicates formation of the *cis* form. The intensity of the absorption band at 307 nm decreases by the aggregates partially dissolving when converting the solvated *trans* molecules by light

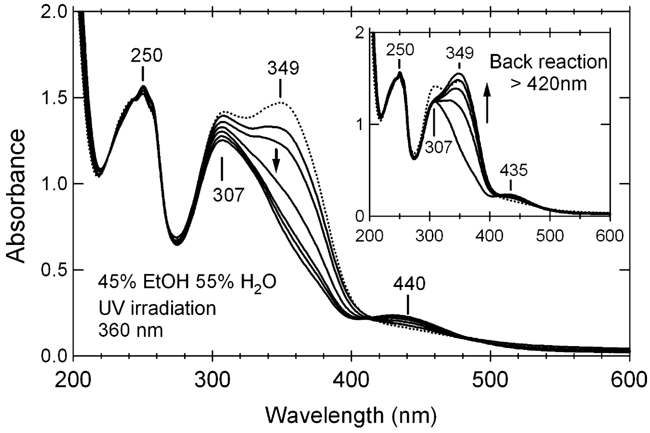

Fig. 8. UV irradiation of a freshly prepared ethanol (45%)/water (55%) solution containing *trans*-**1** (dashed line) and its aggregates. Upon UV irradiation the *trans* isomer is converted into the *cis* isomer, while the aggregates are not photoactive. The absorption by the *cis* isomer is superimposed on that of the aggregates at 307 nm and the residual *trans* form. The increase of the absorption at around 443 nm and the decrease at 349 nm indicates the formation of the *cis* form. Exposure times were 0 s (*trans* form and aggregates, dotted line), 10, 40, 70, 130, and 430 s (*cis* form in the photostationary state with the *trans* form and aggregates). Inset: Photochemical *cis* to *trans* back-reaction induced by light exposure at >420 nm. Exposure times were 0 (predominantly *cis* form and aggregates), 10, 30, and 100 s (predominantly *trans* form and aggregates). For comparison the non-irradiated solution is presented as a dotted line, and indicates a slightly higher *trans* concentration than before illumination.

to the *cis* form, in order to maintain the thermal *trans*-aggregate equilibrium.

After exposure at 360 nm we irradiated the solution with light at >420 nm. As seen from the inset of Fig. 8 exposure to blue light drives the *cis* to *trans* back-photoisomerization. The increased absorption at 349 nm and the decrease at 307 nm in comparison to the initial mixture (dotted line) indicate that the resulting photostationary state between *trans*, *cis* and aggregates differs from that prior to illumination. This is due in part to the presence of the *cis* form at the photstationary point, but also because the reformed *trans* compound has not yet reached thermal equilibrium with the aggregates.

4. Conclusion

We have investigated photoisomerization of **1** in a variety of environments. Photoswitching similar to the reaction in solution was observed when the molecule was embedded in a polymer matrix, adsorbed on silica gel, or dip-coated on quartz. No photoswitching was observed in the case of thick films of **1** made by sublimation or spin-coating. We also found the same behavior for well-ordered SAMs on gold/mica [42,43].

At first glance one might conclude that binding of **1** on quartz and gold is responsible for the differences in the spectra of the films presented. While we believe the molecule to be physisorbed on quartz, SAMs of thiols on gold are known to form a genuine Au–S bond [51,52]. The complex behavior of the films of **1** investigated cannot be simply ascribed to changes of the SAM or film thickness alone. It is most likely that substrate properties and thus the preparation plays an important role for the alignment and lateral ordering of the chromophores in the films.

Whenever the molecules do not show a photoresponse, the π,π^*-absorption band is strongly blue shifted. By measurements in aqueous solution we demonstrate that this blue-shift is very likely caused by formation of H-aggregates. The strong intermolecular coupling in aggregated systems will promote very fast energy relaxation by excitonic transport of the optical excitation, which reduces the switching probability.

We conclude that photoisomerization strongly depends on lateral coupling of the chromophores within the film and thus details of the molecular architecture. What is more the present results show that with a rather simple optical absorption experiment we can test whether or not azobenzene derivatives form aggregate-like assemblies in films. These intermolecular interactions need to be controlled when designing, for example, SAMs having a particular function.

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