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ARTICLE

Photoswitching the Mechanical Properties in Langmuir Layers of Semifluorinated Alkyl-Azobenzenes at the Air-Water Interface

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Semifluorinated alkyl-azobenzene derivatives (SFAB) can form stable Langmuir layers at the air-water interface. These systems combine the amphiphobic character of the semifluorinated alkyl units as structure-directing motif with a photochromic behavior based on the well-known, reversible *cis-trans* isomerization upon irradiation with UV and visible light. Here, we report on our investigations of the structural and dynamic tunability in these SFAB layers at the air-water interface in response to an external light stimulus. The monolayer structures and properties are studied for [4-(heptadecafluorooctyl)phenyl](4-octylphenyl)diazene (F8-azo-H8) and bis(4-octylphenyl)diazene (H8-azo-H8) by neutron reflectivity, surface pressure-area isotherms with compression-expansion cycles, and interfacial rheology. We find that UV irradiation reversibly influences the packing behavior of the azobenzene molecules, and interpret it as a transition from organized layer structures with the molecular main axis vertically oriented in the *trans* form to random packing of the *cis* isomer. Interestingly, this *trans-cis* isomerization leads to an increase of surface pressure, which is accompanied by a decrease of viscoelastic moduli. These results suggest ways for tailoring the properties of responsive fluid interfaces.

I.   Introduction

The term "reconfigurable" or "programmable" soft matter represents an emerging concept in science and technology, where the chemical, physical and functional properties of materials can be switched between well-defined states by external stimulation, for example by irradiation with light.[1] Manifold examples are found in the animate nature, such as phototaxis of plants (like the head of the sunflower following the sun), and at present the challenge exists in research to harness such powerful behaviour in artificial matter by

merging the specific responsive functionality of molecules with a complex structural hierarchy. One strategy to achieve this goal targets the ability of certain types of compounds to self-assemble into complex super-structures and to implement this behaviour with appropriate responsive molecules and polymers.[2] For such systems the final structure of the assembly depends on the presence or absence of the stimulus. Lower dimensional systems made or such responsive materials, like 2D layer architectures or interdigitating phases, possess a large interface between the different phases and are of particular interest for their structural organization, since here the interaction between the stimulus and the responsive material is enhanced compared to the bulk.

Semifluorinated alkanes (SFAs) containing fluorinated alkyl chains besides hydrogenated alkyl moieties constitute a specific class of materials that can organize into ordered structures due to the mutual incompatibility of the fluorinated and hydrogenated segments. Based on this structure-guiding motif they have received attention over the last years, for example for their ability to form different mesophases in the bulk upon decreasing temperature[3] and stable Langmuir layers

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at the air-water interface via hierarchical self-assembly, despite the hydrophobicity of both fluorinated and alkane moieties.[4] The specific challenges with fluid interfaces coated with SFAs is the manipulation of their properties using external stimuli, specifically with light. An appropriate materials class that responds to irradiation with light are photochromic molecules, with one of the most prominent members of this class being azobenzene compounds.

Photosensitive azobenzene derivatives reversibly undergo *cis-trans* isomerization upon light irradiation, that is formation of the kinked *cis*-isomer by exposure to short wavelength UV radiation and reconfiguration into the *trans* isomer by visible light. They can exhibit photo-induced optical anisotropy (becoming dichroic and/or birefringent) and thus are potential candidates for various electro-optical applications[5,6,7] such as photosensitive devices[8], photonics[9], reversible optical data storage[10] and high density data storage films [11]. Ikeda et al.[12] developed azobenzene liquid crystal (LC) films with a nematic phase of the *trans*-isomers (generated by irradiation with laser light) and no LC phase in the *cis* form. Photosensitive materials in general find applications in pharmacotherapy[13] by incorporating photoswitchable groups into the molecular structure of bioactive compounds.

Photoinduced material transport in thin films was for example shown with azobenzene-modified polymers by surface plasmon near field radiation from surface nanostructured coated with this polymer,[14] or by far field irradiation to yield topographic patterns with >100 nm height variation.[15] Furthermore, the expansion factor of single microgel particles in aqueous suspension could be reversibly controlled by light irradiation at different wavelengths upon mixing of the microgels with azobenzene surfactants.[16]

Wustneck et al.[17] investigated the *cis-trans* photoisomerization of monolayers with an azobenzene-containing trifluoromethoxy-substituted methacrylate copolymer at fluid interfaces using surface pressure-area isotherms with the pendant drop technique. It was found that the minimum area demand per repeat unit in the *trans* configuration was smaller than that of the *cis* isomer. Concomitantly, the aggregation tendency was higher in the *trans* configuration at low surface coverage. The restoration of the *trans* configuration depended on the surface pressure[11].

Ultrathin films of two novel azobenzene-functionalized 1,3,5-triazine-4,6-dithiols were investigated by Muzikante et al.[18]. Switching from *trans*- to *cis* configuration was observed by measuring the surface potential using the Kelvin probe technique while alternating irradiation on the self-assembled quasi-monolayer with UV or visible light. In the literature, most investigated systems are self-assembled monolayers (SAMs) of azobenzene-containing alkanethiols. [19,20]

Fuller et al.[21] studied the interfacial rheology of photosensitive monolayers using azobenzene-containing fatty acids. It was found that the *trans*-configuration yielded a well-packed film with non-Newtonian behaviour while the *cis*-configuration resulted in a structureless Newtonian film that could not be oriented by surface flows. Recently, Monteux et al.[22] studied the adsorption dynamics of azobenzene-based charged

surfactants between the air-water interface and the subphase and found that the *cis*-isomer adsorbed 10 times faster than the *trans*-isomer, whereas on the other hand the *cis* isomer also desorbed 300 times faster. As a result the surface was enriched in the *trans*-isomer within a few seconds, and upon illumination with UV or blue light part of the *trans*-population was converted into the *cis*-configuration leading to a rapid rise of the surface tension. Further studies support the higher surface affinity of *trans*-isomers and their ability to stabilize foams[23]. In addition, Shang et al.[24] measured neutral surfactants containing one azobenzene group in their tail and showed changes in the surface tension and the critical micellar concentration. The temperature dependence of aggregation and dynamic surface tension in a photoresponsive surfactant system at the air-water interface for the *cis*- and *trans*-isomers was investigated by Cicciarelli et al.[25,26]

Regarding the kinetics of *trans-cis* isomerization in azobenzene-containing systems, as studied in Langmuir–Blodgett (LB) films, it was found to be of first order, [27] while in a solid glass deviations have been reported. [28] Kumar et al.[29] studied the kinetics from *trans*- to *cis*-photoisomerisation in a Langmuir monolayer composed of mesogenic azobenzene dimers at the water-air interface and also found deviation from first-order kinetics. This effect was attributed to the simultaneous photoisomerisation of *trans*-isomers to form *cis*-isomers and the reverse thermal isomerization of the metastable *cis*-isomers to form stable *trans*-isomers. Finally, LB films of amphiphilic azobenzene derivatives have been used as motifs for macroscopic reorganization in liquid-crystal thin films.[30]

From the above it is evident that fluid interfaces decorated with azobenzene moieties exhibit interesting photo-responsive properties and are promising candidates in electro-optical thin-film applications. However, despite the work done so far, a clear link between interfacial structure and 2D-mechanical properties in such responsive materials is missing. This is especially true for systems with the ability to exhibit different levels of hierarchical self-assembly at interfaces, such as semifluorinated alkanes.

In the present study we address the above challenge by investigating the effects of UV stimulus on the interfacial properties of a novel azobenzene derivative of semifluorinated alkane[4-(heptadecafluorooctyl)phenyl](4-octylphenyl)diazene (in short F8-azo-H8) and its fully hydrogenated analogue bis(4-octylphenyl)diazene (abbreviated here as H8-azo-H8). The semifluorinated alkyl-azobenzene (SFAB) derivative F8-azo-H8 combines the structure-guiding motif of mutual incompatibility between fluorinated and hydrogenated alky chains with the photochromic property to switch molecular configuration by external stimulation with light. This water-insoluble compound can be spread at the air-water interface as stable Langmuir layers to control the mechanical behaviour of this interface in response to light. For both azobenzene derivatives we probe the interfacial organization by means of neutron reflectivity and surface pressure isotherms in a Langmuir trough, whereas the interfacial viscoelasticity is investigated using a magnetic rod interfacial stress rheometer (ISR). Changes of these

properties are examined systematically in response to UV and visible light irradiation, which is shown to dramatically influence the interfacial packing of the azobenzene molecules. The obtained data suggest a UV light-induced transition of packing structures with vertically oriented molecular main axis to a featureless amorphous film.

II. Experimental

II.1. Materials

The azobenzene derivative[4-(heptadecafluorooctyl)phenyl](4-octylphenyl)diazene (F8-azo-H8) with one fluorinated and one hydrogenated alkyl chain was synthesized by asymmetric coupling of the 1-nitroso-4-octylbenzene (from oxidation of 4-octylaniline with potassium peroxomonosulfate) with 4-perfluorooctylaniline.[31] Coupling of 1-nitroso-4-octylbenzene with 4-octylaniline yielded bis(4-octylphenyl)diazene (H8-azo-H8). The thermodynamic, optical, structural, and dynamic properties of these materials have been reported by Stangenberg et al. and the absorption spectra in the *trans* and *cis* configuration are provided in the Supporting Information, Figure S12.[32]
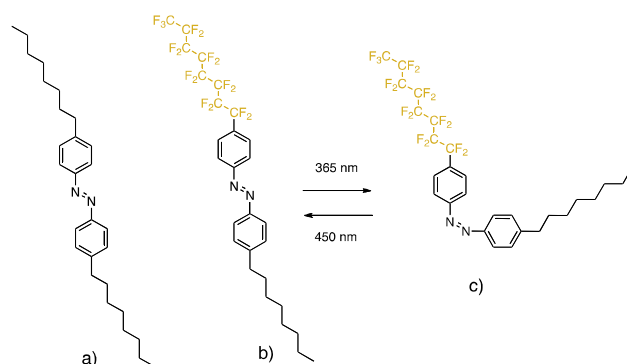

Figure 1: Chemical structures of (a) bis(4-octylphenyl)diazene (abbreviated **H8-azo-H8**), (b) [4 (heptadecafluorooctyl)phenyl](4-octylphenyl)diazene (abbreviated **F8-azo-H8**) and (c) light-induced change of configuration from *trans* to *cis*.

II.2. Methods

II.2.1. Surface pressure-area isotherms

Surface pressure (Π) -area (A) isotherms were measured with a commercial Langmuir trough (Mini trough 4, KSV Instruments, Finland) made of hydrophobic Teflon with movable barriers of hydrophilic polyoxymethylene. An amount of 1 mg ml^{-1} of the SFAB compound to be deposited was dissolved in hexane and the solution was spread with a Hamilton glass syringe onto the subphase (consisting of ultrapure water). In the case of F8-azo-H8 100μl of solution was spread in the dark (experimental data labelled "dark") or in the experiments indicated with the label "UV" 50 μl of the SFAB solution was irradiated inside the spreading syringe with UV light of 365 nm wave length before spreading. The photo-conversion of the compounds was

achieved with a Spectroline UV lamp (365 nm, 6 Watt tube, irradiated for 10 minutes at a distance of 8 cm, experimental details see Supporting Information). For H8-azo-H8 200μl of solution was spread to obtain the whole isotherm under dark and 50 μl was spread under UV irradiation (same conditions as syringe irradiation). The solvent was let to evaporate for at least 10 minutes and subsequently the barriers were compressed / expanded with a speed of 5 to 25 mm min^{-1}. A Wilhelmy-plate balance measured the surface pressure while the temperature of the water subphase was maintained at 20°C in all experiments by means of a water bath circulator. The same set-up was also used for performing compression-expansion cycles in order to examine the mechanical stability of the Langmuir films.

II.2.2. Interfacial rheology

The Langmuir trough was further equipped with an interfacial stress rheometer (ISR), originally developed by Brooks et al.[33] Two Helmholtz coils in the center of the trough generated a homogeneous magnetic field with the field lines parallel to the air-water interface. A sinusoidal, time-dependent gradient was induced to the magnetic field by modulating the applied voltage amplitude in the frequency range of 0.01 to 4 Hz with a frequency generator. A Teflon-coated, magnetized rod floating at the air-water interface in a small channel in the centre of the trough served as the rheological probe. The horizontal displacement of the rod by the field oscillation was monitored as a function of time using a CCD camera (SONY XC-HR50). The rod was positioned at the air-water interface in the channel before spreading the SFAB sample solution. The measurement protocol involved dynamic frequency sweep measurements in the linear viscoelastic regime (checked via selected dynamic time and strain sweep tests) at various positions of the barriers during compression and expansion cycles, with the light (UV or visible light, respectively) either switch on or off.

II.2.3. Neutron reflectivity

Neutron reflectivity measurements were performed at the air-water interface using the Langmuir trough on the AMOR reflectometer of the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institute, Switzerland. Barrier motion allowed reflectivity measurements at different surface pressures as described in section II.2.1. The subphase consisted of D$_2$O. Further details of the instruments and the procedures used are described elsewhere.[34,35] Measurements were made at three incident angles (0.6°, 1.4° and 2.4°) which gave a range of momentum transfer Q, ($Q = (4\pi \sin \theta) / \lambda$, with λ being the wavelength and θ the angle of incidence) from 0.1 to 1.5 nm^{-1}. The obtained reflectivity data were analysed using the Parratt32 software, version 1.6 (Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany).[36] Taking into account the different possible packing models by variation of the structural parameters (number of layers, and for each layer, layer thickness, scattering length density and surface roughness) the scattering density profile is calculated. For each case, three numbers of layers are tried (1 layer, 2 layers and 3 layers). Detailed results for these different fitting models are

provided in the supporting information. The scattering length density of each layer is calculated using the NIST's scattering length density calculator[37] assuming the density of the layer to be the bulk density of each material (for example the bulk density for the fluorinated alkyl chain is taken equal to the density of polytetrafluoroethylene, while the hydrogenated alkyl chain is represented by polyethylene data, the aromatic core is approximated by toluene data). For each case, we used as fixed parameters the number of layers and the scattering length density while layer thickness and surface roughness were treated as variable parameters for the minimization. In the first step the layer thicknesses was fixed to the expected value of the model, and in the second step this value was then optimized.

II.2.4. Scanning force microscopy

For scanning force microscopy (SFM) the SFAB films were transferred from the water-air interface to plasma-cleaned silicon wafer substrates (10 min Argon plasma). For the layer transfer the silicon wafers were located at the bottom of the trough (KSV Minitrough, KSV Instruments Ltd., Finland) with a small tilt angle of around 7º and the water was removed by a peristaltic pump (Minipuls 3, Abimed, Gilson Inc., United States) at a speed of approximately 10 mL·min^{-1}. The films that were investigated under UV irradiation were initially compressed to a surface pressure of 2 mN m^{-1} and then illuminated with UV light for around 60 min followed by the film transfer as described above. For the films prepared under visible light, the SFAB was spread and compressed up to a surface pressure of 2 mN m^{-1} in the dark, then irradiated with UV light for 60 min, kept in the dark for 60 min and then white light was switched on. After several hours, the films were transferred onto the silicon wafer.

Directly after the transfer each sample was analyzed by SFM (MFP-3D, Asylum Research, USA) in intermittent contact mode. We used silicon cantilevers (Olympus OMCL-AC240TS, nominal tip radius <7 nm, resonance frequency 50 - 90 kHz, spring constant 0.7-3.8 N m^{-1}). The cantilevers were put on a glass coverslip and cleaned in an Argon plasma (Plasma Cleaner/Sterilizer PDC-002, 200W, Harrick Scientific Corp., United States) for 30 s at a pressure of approximately 1.6 mbar. The SFM data were flattened and analyzed using Gwyddion Software (www.gwyddion.net).

III. Results and Discussion

III.1. Characterisation of the semifluorinated F8-azo-H8 Langmuir layers.

The surface pressure (Π)-molecular area (A) isotherm of F8-azo-H8 measured at the air-water interface is shown in Figure 2 for different illumination conditions. As a plausibility check, the measured molecular surface area between 40-50 mN m^{-1} of the SFAB Langmuir film (*trans* configuration for the "DARK"

experiment) was compared with the theoretical surface requirement calculated from the molecular projection area perpendicular to the long molecular axis in *trans* configuration corresponding to configuration in the "DARK" experiment. The agreement of these two numbers suggested the formation of a true monolayer with the alkyl chain axis being oriented predominantly perpendicular to the air-water interface (and in good agreement to the surface requirement of simple semifluorinated alkanes).[4] After thermal equilibration of the Langmuir film in the absence of light the azobenzene units of the SFAB molecules are predominantly in the *trans* configuration. The *trans*-to-*cis* configurational change of the azobenzene units upon irradiation with UV light, which can be reverted by exposure to visible light (above ca. 450 nm wavelength), has a direct consequence on the surface pressure isotherms, as shown in Figure 2. During the measurement under UV irradiation (the isotherm labelled "UV") the F8-azo-H8 molecules predominantly exists in the *cis* configuration (about 70 % in the photostationary equilibrium) and apparently occupy a molecular area at the onset of the pressure increase (say about 2 mN m^{-1}), which is about three times larger than that in the *trans* configuration (measurements performed in the absence of light, isotherm labelled "DARK"). This is directly linked to the molecular reorganization, as will be discussed below based on the neutron reflectivity data. Under visible light, the situation is intermediate, as most molecules revert from the *cis* to the *trans* form. Moreover, we note that the isotherm compression/expansion is completely reversible in the dark while showing a slight hysteresis under UV or visible light irradiation. Nevertheless, these compression-expansion cycles suggest that even at the highest pressures reached (18 mN m^{-1}) there was no signature of an irreversible film collapse or other degradative effects discernible in the isotherms, hence the applied films deformation is fully reversible.
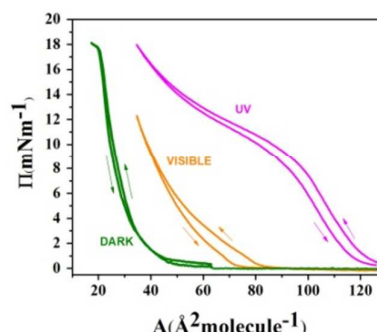

Figure 2: Surface pressure (Π) versus molecular area (A) isotherms of F8-azo-H8 monolayers at the air-water interface at 20 °C, under different irradiation conditions: UV light inducing predominantly *cis* configuration (right curve in purple, labelled "UV"), visible light with *cis* and *trans* configurations (middle curve, orange, "VISIBLE") and in the dark with *trans* configurations (left curve, green, "DARK"). The arrows indicate compression and expansion directions with negligible hysteresis.

The modulation of the internal strain (as expressed by surface pressure variation in the isotherm of Fig. 3) of the F8-azo-H8 monolayers was examined upon exposure to different light stimuli. The measurement started at a surface pressure of 2 mN m^{-1} in the dark (corresponding to the onset of the slope in Fig. 2) and after about 1 hour the UV lamp was switched on. During this irradiation the surface pressure increased and reached a maximum value of about 16 mNm^{-1} within about 1 hour. Then the monolayer was exposed to visible light. There the surface pressure dropped to 4 mNm^{-1} after 3 hours.
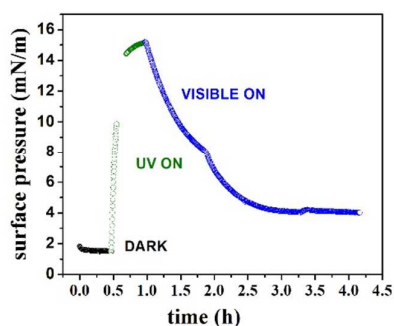
Figure 3: Variation of the surface pressure over time for a F8-azo-H8 monolayer for different light stimuli (pure water subphase, 20 °C) under dark (green), UV (purple), dark (black) and visible light (blue) conditions.

The responsiveness of the F8-azo-H8 monolayer to light irradiation conditions is also reflected by the concomitant modulation of its viscoelastic properties. This is demonstrated with dynamic time sweep measurements in Fig. 4, depicting the UV-induced change of the storage (G') and loss (G'') moduli.
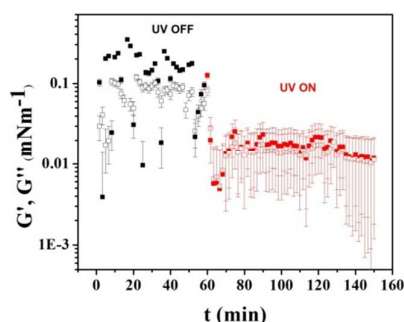

Figure 4: Dynamic time sweep measurement of storage (G', closed symbols) and loss (G'', opened symbols) moduli for a F8-azo-H8 monolayer at the air-water interface at a temperature of 20 °C, frequency $\omega = 0.6$ rad s^{-1} and strain amplitude $\gamma_0 = 0.1$ % using the magnetic rod interfacial stress rheometer. The measurement started at a surface pressure of 12 mNm^{-1}. Light conditions: UV off (first 60 min), then UV on.

In the course of the experiment the conditions changed from dark (at a surface pressure of 12 mNm^{-1}) to UV irradiation. This resulted in a change of the surface pressure (increasing to 17 mN m^{-1}), which is apparently caused by a structural

reorganization of the F8-azo-H8 film (discussed further below) leading to a decrease of G' and G'' by about one order of magnitude when UV is switched on. Note that the moduli response is almost instantaneous when changing irradiation, while for static lighting conditions the moduli are constant. It is worth mentioning that the moduli are very weak (in fact barely resolved) and the response of the F8-azo-H8 monolayers is liquid-like. This is further confirmed by analysis of the apparent Poisson ration of the films. The compression modulus, $\varepsilon = -A \, d\Pi / dA$, extracted from the pressure area isotherms, is of the order of 10 mN m^{-1}, essentially orders of magnitude higher than the shear modulus (Fig. 4). Hence, the Poisson ratio of the 2D layer is $\nu = \varepsilon - G / \varepsilon + G \approx 1$, which is the expected value for a liquid interface.[38]

A series of viscoelasticity measurements for different combinations of surface pressures and irradiation conditions (UV versus dark) is presented in Fig. 5. As a general trend we find that the G' modulus is reduced upon UV irradiation (consistent with Fig. 4) while at the same time the surface pressure increases (consistent with Fig. 3). From these results it can be further concluded that the lower the initial surface pressure in the dark, the larger the surface pressure jump and the lower the modulus decrease when UV is switched on. These results raise the question which structural change upon irradiation is related to this surface pressure and moduli shift. A potential answer may be given by the SFM results presented further below (Fig. 8), which indicate a tendency of the *cis* conformer for 3D aggregate formation at confined surface area (and consequent surface pressure increase) under UV irradiation. Thus, we discuss below the structural analysis of the films, which was performed by neutron reflectivity measurements.
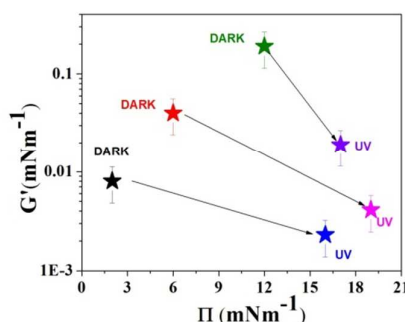

Figure 5: Storage modulus (G') versus surface pressure of the F8-azo-H8 monolayer at the air-water interface showing the order of magnitude decrease of the elastic modulus under UV irradiation for three different starting surface pressure (Π), $\Pi=2$mNm^{-1}, $\Pi=6$mNm^{-1} and $\Pi=12$mNm^{-1}.

The results from the neutron reflectivity experiments are depicted in Fig. 6, where the scattering curves are shown as normalized intensity versus q for the F8-azo-H8 layer in comparison to the bare D$_2$O subphase in the dark (Fig. 6a) and under UV irradiation (Fig. 6b). In the upper insets of these figures we show the same data in a more sensitive

representation (normalized intensity (NR) * q^4 versus q) that allows to better distinguish the small, albeit unambiguous structural effect of the F8-azo-H8 layer at the air-water interface. This is consistent with the scattering length density profiles of the lower insets. From the best fitting we can extract the scattering length density profile and the proposed molecular packing model for the interfacial arrangement of the F8-azo-H8 molecules in the monolayer. As schematically illustrated in Fig. 7, it is suggested that in the dark the F8-azo-H8 molecules in their *trans* configuration organize with their long axis perpendicular to the air-water interface (consistent with the isotherm analysis and the findings of reference [39]). For this case, a two-layer model with a hydrocarbon and a fluorocarbon segment is suggested with total layer thickness of 4.37 nm with the CF-blocks pointing towards the subphase. This model gives the best match in the fitting procedure with the Parratt32 software. Data for other packing and fitting models are provided in the Supporting Information, which resulted in inferior matches between the measurements and fits.
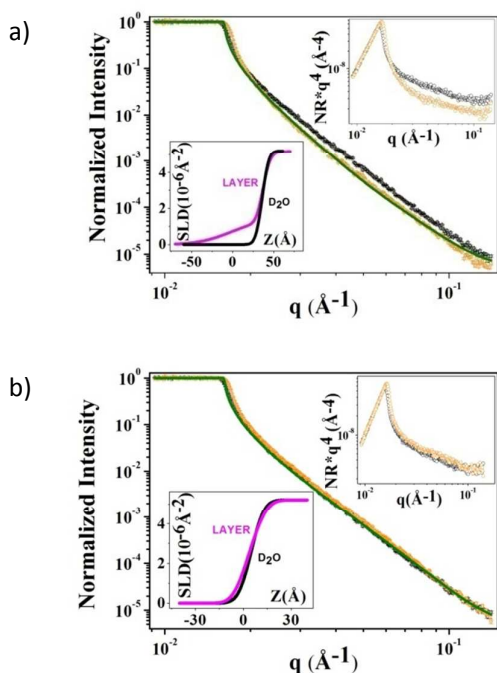

a)

b)

Figure 6: Neutron reflectivity curves (normalized intensity vs q) of the F8-azo-H8 monolayer on a D_2O subphase, lower insets: scattering length density profiles, upper inset: normalized intensity (NR) * q^4 versus q. Colour legend: D_2O (black), F8-azo-H8 layer (orange) and fit (green). (a) Dark experiment (surface pressure= 2 mN m^{-1}). (b) Under UV irradiation (surface pressure= 12mN m^{-1}).

Under UV irradiation the induced *trans*-to-*cis* isomerization gives rises to a random, structureless arrangement. A layer thickness of 0.96 nm is found for a structureless film with random molecular orientation. Assuming a regular orientation in the *cis* cofiguration with the azobenzene moieties in contact with the water subphase and both the fluorocarbon and

hydrocarbon chains pointing towards the air did not provide a satisfactory fit result (see Supporting Information). This configuration-induced change of packing order is accompanied by a decrease of interfacial viscoelastic moduli and a concurrent increase of surface pressure, as documented by the experimental results reported further up.
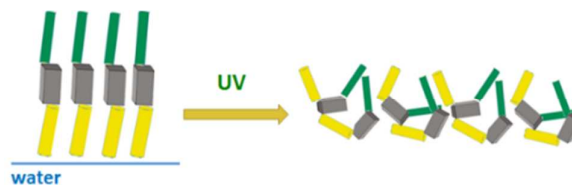

Figure 7: Model proposed for F8-azo-H8 monolayer at the water-air interface before and after its exposure to UV light.

In order to visualize more details of the layer structure SFM measurements were performed on samples that were transferred from the air-water interface onto solid supports. In samples transferred under white light illumination (*trans* configuration) we observed a partial coverage of the Si surface with a thin film (Fig. 8a). A line profile across those steps revealed a film thickness of 4.1 nm (Fig. 8b), which is about 10 % thinner than the layer thickness derived from the neutron reflectometry results (4.4 nm). We attribute this marginal decrease in film thickness to drying effects during the transfer. In samples which were transferred directly after illumination with UV light (*cis* configuration) we observed island structures being up to 160 nm in height and 2 μm in width. In between the island structures no steps were observed which indicates a full coverage of the substrate with a monolayer film. However, on top of the islands a patchy structure was observed (Fig. 8c). A height analysis of the patchy structures revealed a thickness of 0.8 nm (Fig. 8d). The latter indicates that the UV light can induce a conformational change into *cis* resulting in a film thicknesses < 1 nm that was also concluded by neutron reflectometry.
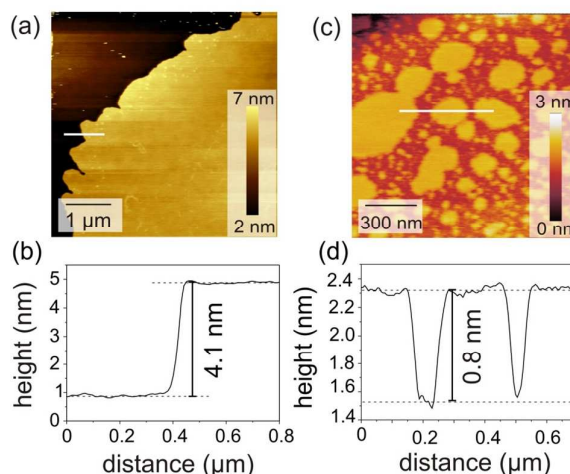

Figure 8: SFM images of the F8-azo-H8 layers transferred onto a Si wafer. (a) Topography of a film in *trans* configuration transferred

under white light illumination at a surface pressure of 2 mN m^{-1}. (b) Line profile at one edge of the film in (a). (c) Topography on a 2 µm wide crystal of a sample that was transferred under UV irradiation (*cis* configuration). (d) Line profile across the island structures of (c).

III.2. Characterisation of the hydrogenated H8-azo-H8 Langmuir layers.

The specific molecular structure of the F8-azo-H8 is apparently responsible for the observed behaviour and in particular the responsiveness with resulting tunability of the monolayer by light irradiation. It turns out that the fluorocarbon component of the F8-azo-H8 molecule has a vital role as it is responsible for the presence of a string dipole in the F-H direction and therefore, along with extended and stiff molecular shape of the azobenzene moiety in the *trans* configuration, yields the perpendicular order as indicated in Fig. 7. When the azobenzene fragment changes its configuration to *cis* under the influence of UV light, an additional strong dipole is generated by the *cis*-azobenzene moiety, which may destructively interfere with the strong dipole, and in combination with the substantial change of molecular shape leads to the loss of the specific molecular order. To verify the particular structure-guiding character of the fluorocarbon chain, we performed experiments under similar conditions with the analogous non-fluorinated azobenzene derivative H8-azo-H8, which contains two identical hydrocarbon chains instead of a fluorocarbon chain. In the *trans* configuration under dark conditions the H8-azo-H8 molecule does not possess a strong dipole moment and due to its low polarity is not strongly interacting with the water subphase. Hence, these molecules have an enhanced tendency to aggregate into 3D structures (preferentially at the barrier wall upon compression), which is reflected in the very low apparent surface area visible in the compression-expansion trace of Figure 9 (green curve labeled "DARK"). Upon UV irradiation the H8-azo-H8 molecules switch to the more polar *cis* form, leading to a much stronger attraction to the water subphase. Accordingly, as visible from the surface pressure-area isotherms the molecules occupy an area about three times larger in the *cis* configuration under UV irradiation compared to the *trans* isomer in the dark (Fig. 9). Under visible light illumination the molecular surface requirement lies between the UV and dark conditions, which may be caused by the photostationary equilibration between the *cis* and the *trans* configuration with both forms being present simultaneously. In all cases the compression-expansion cycles show no significant hysteresis (as for F8-azo-H8), indicating full reversibility of the layer deformation during compression on the time scale of the experiment.
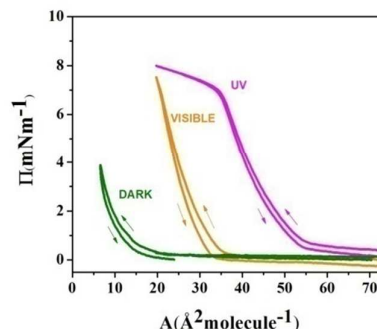

Figure 9: Surface pressure (Π) versus molecular area (A) isotherms of non-fluorinated H8-azo-H8 monolayers at the air-water interface at 20 °C mesured under UV light (right curve in purple, labelled "UV"), under visible light (middle curve, orange, "VISIBLE") and in the dark (left curve, green, "DARK").

The time-resolved surface pressure change under varying illumination conditions (dark - UV irradiation - dark) is presented in Fig. 10. As in the case for F8-azo-H8 above (although not as high values), a significant pressure increase is observed when switching on the UV irradiation, which is explained by the substantially increased surface requirement of the molecules switching from the *trans* (in the dark) to the *cis* configuration (UV). The curve rapidly reaches saturation, and when switching off the light after about 1 h of irradiation, the pressure stays constant (as measured for 1/2 h). The data indicates that the H8-azo-H8 monolayer is stable under these experimental conditions.
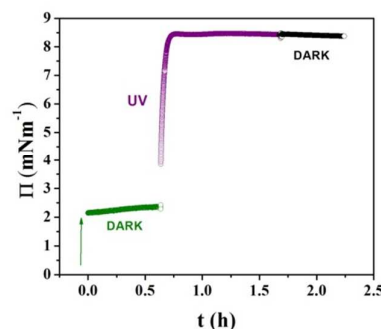

Figure 10: Surface pressure (Π) versus time (t) of a H8-azo-H8 monolayer at the air-water interface at 20 °C, Under dark (left curve in green, labelled "DARK"), UV (middle curve, purple, "UV"), dark (right curve segment, black, "DARK").

Further, the neutron reflectivity results in different representations (as in Fig. 6 above) are reported in Fig. 11, and suggest a different model for the molecular arrangement of H8-azo-H8 (Fig. 12). The molecular packing providing the best fit to the reflectivity curves indicate a loose random organization of the molecules and a layer thickness of 0.65 nm with no significant effect of light irradiation on the level of organization. Interestingly, the H8-azo-H8 interface has a viscous rheological response indistinguishable from the water subphase (data not shown).
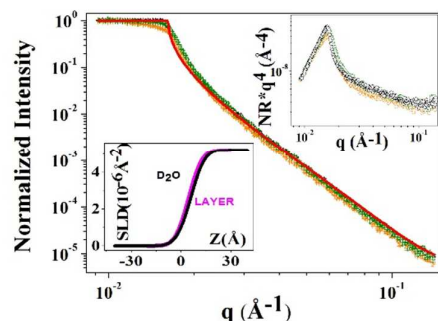
Figure 11: Neutron reflectivity curve (normalized intensity vs q) of the H8-azo-H8 monolayer on a D_2O subphase in the absence of light and under UV irradiation along with the scattering length density profile in the lower inset. Upper inset: normalized intensity (NR) * q^4 versus q. Colour legend: D_2O (black), H8-azo-H8, dark (orange), H8-azo-H8, UV (green) and fit (red). Surface pressure = 2 mN m^{-1} for dark and surface pressure = 8 mN m^{-1} for UV.
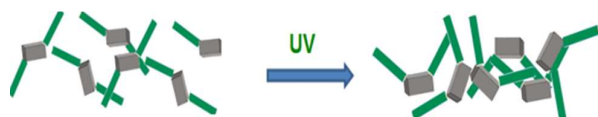

Figure 12: Model proposed for the H8-azo-H8 monolayer at the air-water interface before and after its exposure to UV light.

IV. Conclusions

We have investigated the structural and rheological properties of semifluorinated and fully hydrogenated azobenzene derivatives at the water-air interface under different conditions of light irradiation. Building on earlier studies with related SFA systems, which have demonstrated the intriguing ability of these molecules to hierarchically self-assemble at fluid interfaces, we have examined here the role of UV light as specific trigger on the properties and stability of the SFAB F8-azo-H8 and its non-fluorinated analogue H8-azo-H8 monolayers. UV irradiation was found to significantly influence the interfacial organization and viscoelasticity of the SFAB derivative F8-azo-H8 with the structure-guiding motif of the fluorinated alkyl chain, whereas it had a significantly weaker effect on the symmetric hydrocarbon derivative H8-azo-H8. Based on the well-known effect of UV- and visible light irradiation on the *cis-trans* isomerization, such light exposure drastically influences also the packing behaviour of the SFA azobenzene molecules in a reversible way. We conclude that the combination of this effect and the F-chain associated dipole in F8-azo-H8 yields a transition from well-organized vertically oriented structures to random packing, accompanied by a decrease of the viscoelastic moduli and increase in surface pressure. These findings confirm the reconfigurability of such responsive interfaces and provide the means to tailor their mechanical properties at wish by exploiting the sensitivity of molecular configuration to UV irradiation. This behavior might be exploited in responsive fluid interfaces for potential application such as light-triggered 2D actuation layers and photoswitchable lubrication films.

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