Supporting Information

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

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Neutron Reflectivity

In the following section various models and corresponding fit parameters are compared for the analysis of the neutron reflectivity data using the Parratt32 program. In each case the number of layers is defined by three parameters: thickness (d), scattering length density (rho) and roughness (sigma). D_2O is the bulk phase and the upper phase is air. On the right side of the parameter table the bulk density of each layer is reported. The abbreviation HUP refer to the H-alkyl chain pointing towards the air, FUP means fluorocarbon chain pointing towards the air.

F8-azo-H8 under dark conditions

In the first graph, Fig. S1 the best fitting parameters for F8-azo-H8 measured in the dark (*trans* configuration) are presented, as reported in the manuscript in Fig. 6a. The corresponding layer model assumes the molecules oriented with their long axis vertical to the air-D_2O interface and with the H-alkyl chains pointing up towards the air.

2 LAYER_ HUP

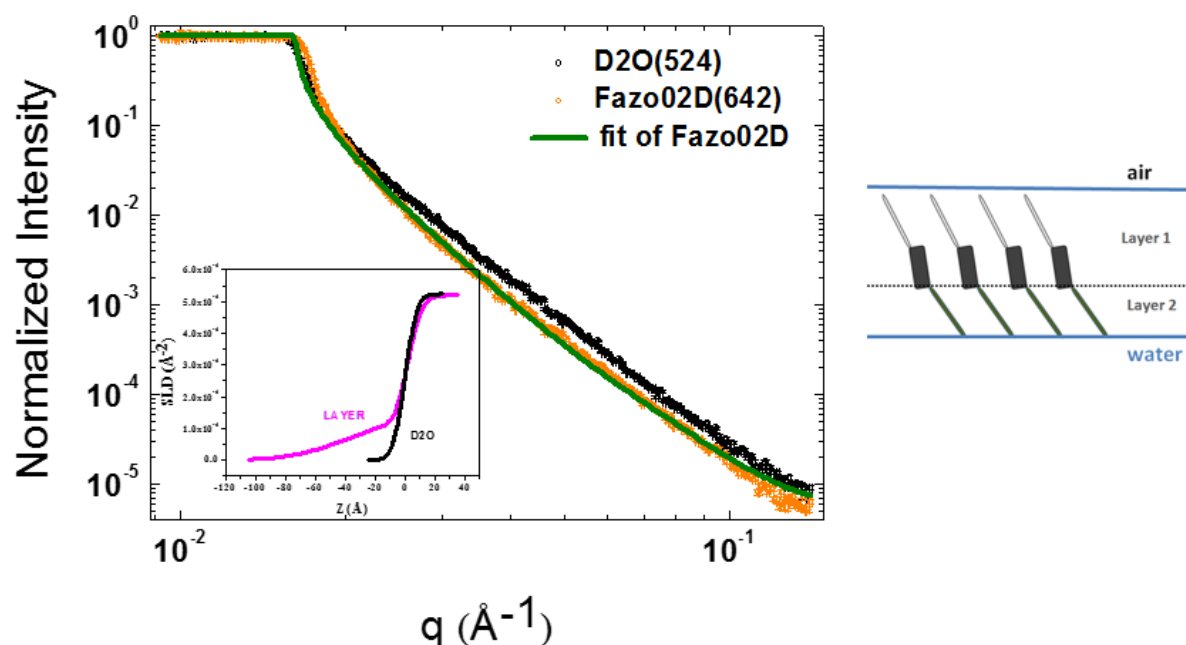|	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	36.321	1.46E-6	4.5E-11	32.635
2	7.364	4.72E-6	4.5E-11	6.388
bulk	N/A	5.232E-6	4.5E-11	6.388

$C20H25N2$ $\rho = 1.46 g/cm^3$
$C8F17$ $\rho = 2.2 g/cm^3$

Figure S1: *Model, reflectivity data and scattering length density profile of F8-azo-H8 measured in the dark - two-layer fit model with H-alkyl chains pointing towards the air. Surface pressure 2 mN m^{-1}. This layer model provides the best convergence of the fit with the measured data, as reported in Fig. 6a of the manuscript.*

For comparison, in Fig. S2 the same data of F8-azo-H8 in the dark are fitted assuming one layer model with random orientations. We fixed the scattering length density parameter while the thickness and the roughness of the layer were left as floating parameters for the fit procedure. At high q we observe a bad convergence of this model.
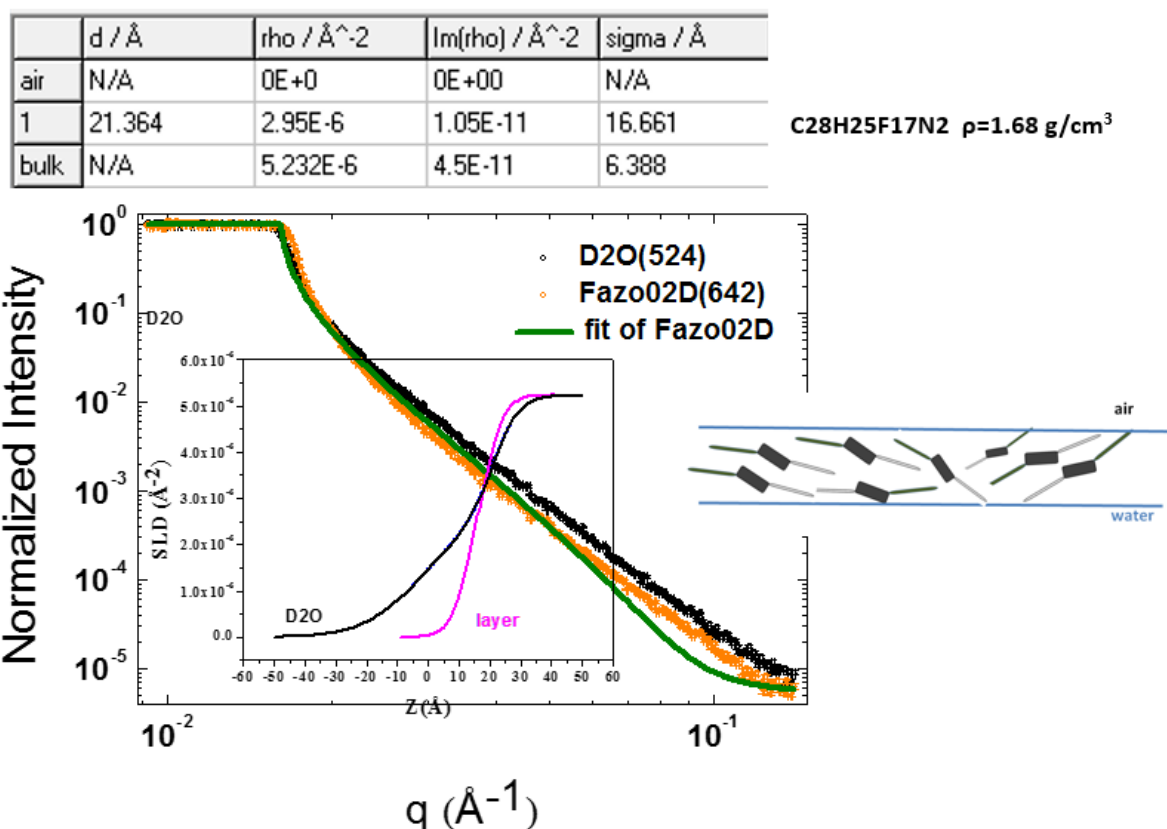
1 LAYER_ mixed

	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	21.364	2.95E-6	1.05E-11	16.661
bulk	N/A	5.232E-6	4.5E-11	6.388

$C_{28}H_{25}F_{17}N_2$ $\rho = 1.68$ g/cm^3

Figure S2: *Model, reflectivity data and scattering length density profile of F8-azo-H8 in the dark. A single mixed layer model was applied. A stronger divergence of the fit from the measured data is observed at larger q-values.*

In Fig. S3 (F8-azo-H8 in the dark) a third model is applied with three sublayers. The first layer consists of the fluorocarbons that point towards the water, the second layer comprises the azobenzene moieties and the third layer contains the alkyl chains. The parameters of thickness and roughness are left floating during fitting. In this case the data do not converge due to a minimum of the normalized intensity at q = 0.06 Å^{-1}.

3 LAYER_ FUP

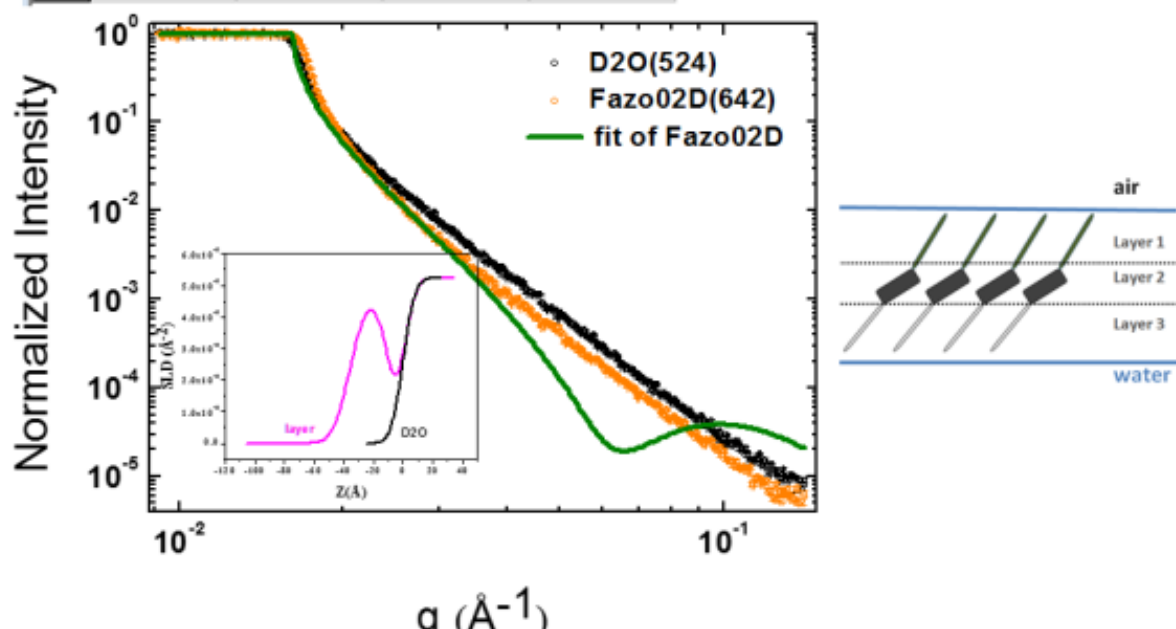|	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	22.31	4.72E-6	4.5E-11	9.155
2	6.778	2.5E-6	4.5E-11	6.175
3	6.485	-3.89E-7	4.5E-11	5.478
bulk	N/A	5.232E-6	4.5E-11	6.388

$C8F17$ $\rho = 2.2$ g/cm^3

$C12H8N2$ $\rho = 1.09$ g/cm^3

$C8H17$ $\rho = 0.703$ g/cm^3

Figure S3: *Model, reflectivity data and scattering length density profile of F8-azo-H8 under dark. 3 layer model with the fluorocarbon chains pointing towards the air. This fit result in a minimum around q = 0.06 Å^{-1}, which is not present in the actual experimental data.*

Fig. S4 provides the data analysis utilizing the same molecular packing model as in Fig. S3, but applying only two sublayers with separated C-F- and C-H-fragments. Keeping again the scattering length density fixed, this model leads to a bad fit of the data with a minimum at q = 0.09 Å^{-1}.

2 LAYER_ FUP

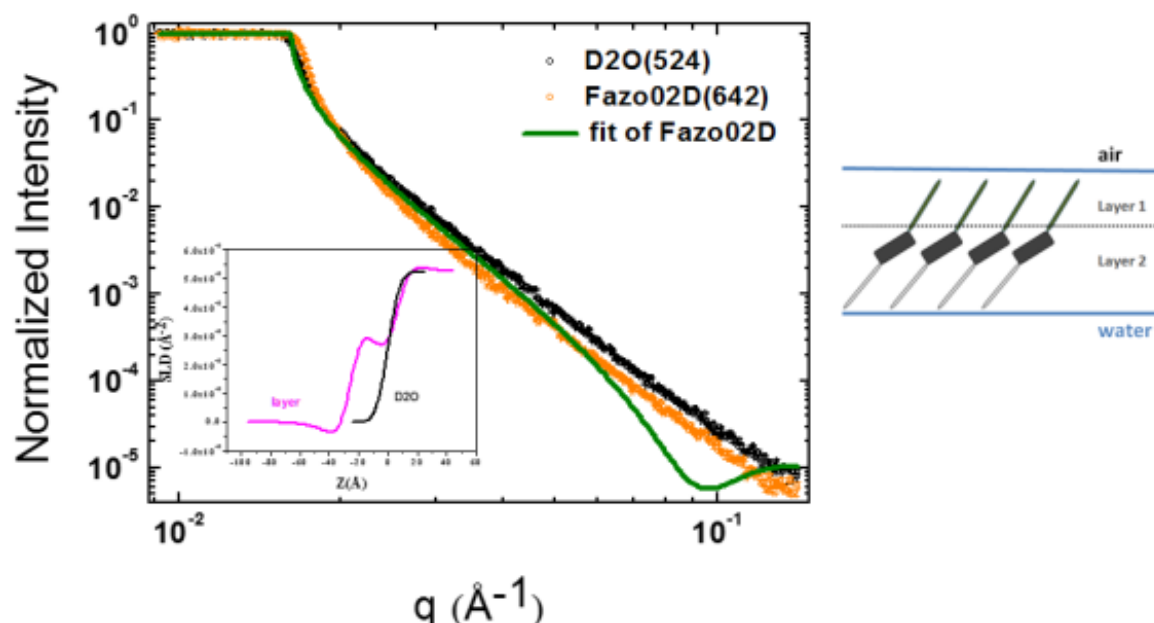|	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	11.35	4.72E-6	4.5E-11	6.388
2	20.8	1.46E-6	4.5E-11	22.076
bulk	N/A	5.232E-6	4.5E-11	6.388

C8F17 ρ=2.2 g/cm^3

C20H25N2 ρ=1.46g/cm^3

Figure S4: *Model, reflectivity data and scattering length density profile of F8-azo-H8 in the dark dark. A two layer model with the fluorocarbons to point towards the air is applied, assuming the same molecular packing as in Fig. S3. This fit show a strong deviation to the measured data by a dip around q = 0.09 Å^{-1}.*

In Fig. S5 a model is used where the fluorocarbon chains are in contact with the D$_2$O phase. In this case, three sublayers are applied in the model. Fixing the scattering length density of each layer we vary the thickness and roughness and obtain a reasonable fit of the normalized intensity. This fit could be further improved by applying the same packing model, but using a two sublayer fit model, as shown in Fig. S1 and reported in the main text (Fig. 6a).

3 LAYER_ HUP

	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	10.732	-3.89E-7	4.5E-11	6.388
2	12.36	2.5E-6	4.5E-11	6.388
3	17.326	4.72E-6	4.5E-11	13.365
bulk	N/A	5.232E-6	4.5E-11	6.388

C8H17 ρ=0.703 g/cm^3
C12H8N2 ρ=1.09 g/cm^3
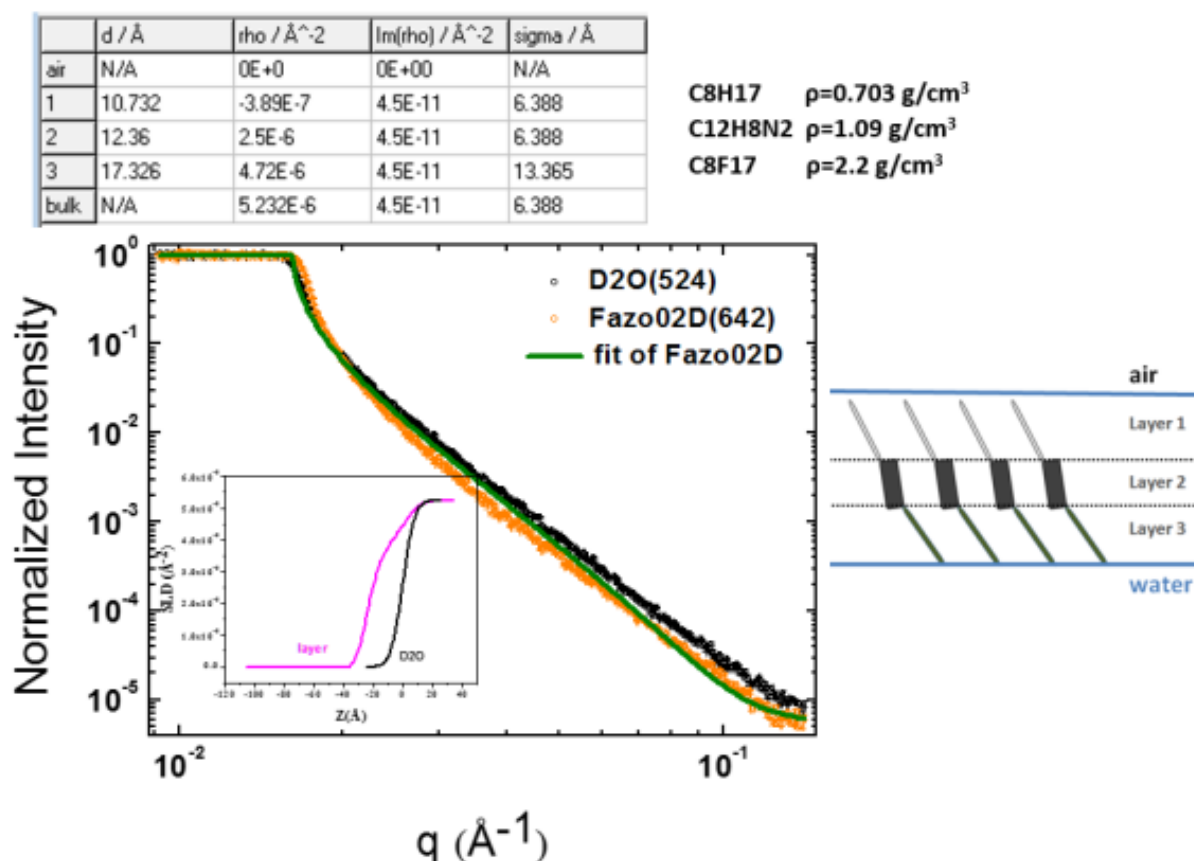C8F17 ρ=2.2 g/cm^3

Figure S5: *Model, reflectivity data and scattering length density profile of F8-azo-H8 in the dark. 3 layer model with the fluorocarbons in contact with the D$_2$O phase. Surface pressure= 2mNm^{-1}.*

F8-azo-H8 under UV irradiation

Under UV irradiation the azobenzene unit converts into the *cis* configuration, which provides the SFAB molecule with a kinked shape and a stronger dipole moment. Assuming a single layer model with disordered molecular arrangement provided the best fit of the neutron reflectivity data. The curve for this fit model was reported in Fig. 6b of the manuscript and the detailed fit data is provided here in Fig. S6.
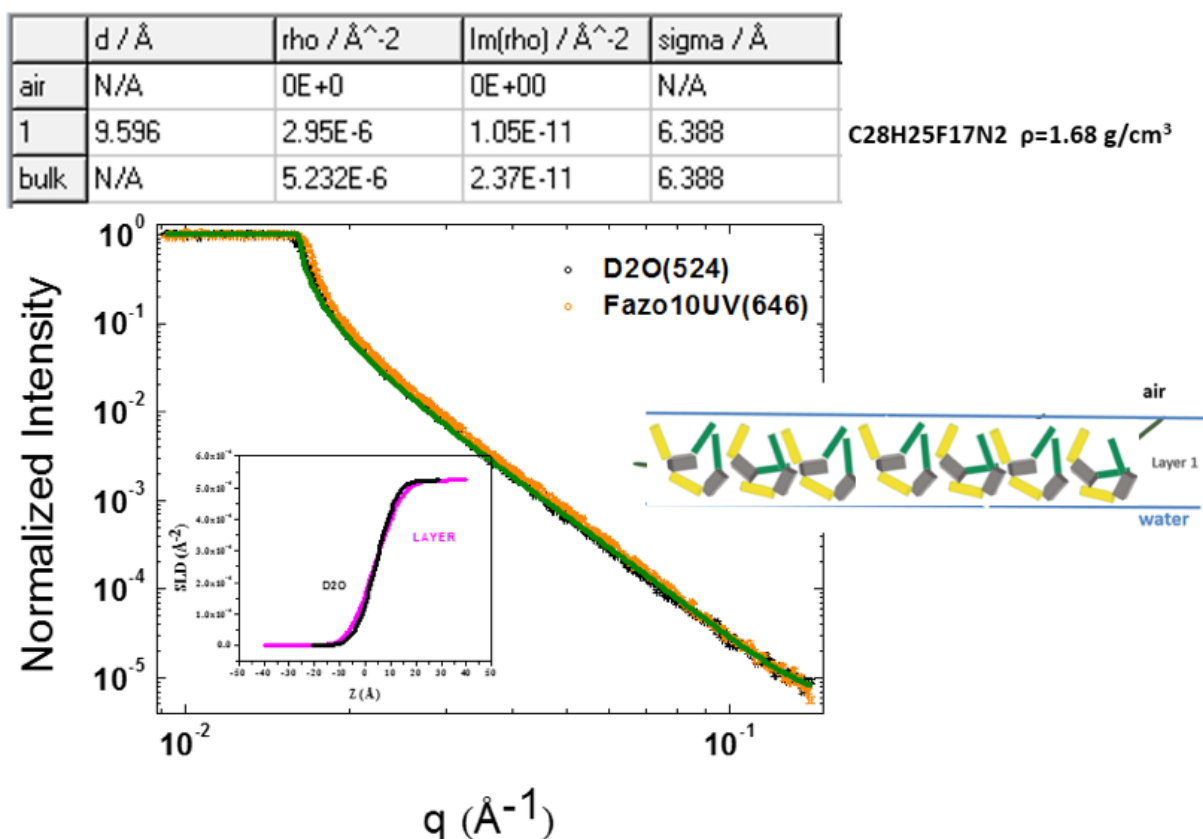
1 LAYER_ mixed

	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	9.596	2.95E-6	1.05E-11	6.388
bulk	N/A	5.232E-6	2.37E-11	6.388

C28H25F17N2 ρ=1.68 g/cm³

Figure S6: *Model, reflectivity data and scattering length density profile of F8-azo-H8 measured under UV irradiation - single-layer fit model with disordered molecular arrangement. Surface pressure 12 mN m^{-1}. This layer model provides the best convergence of the fit with the measured data, as reported in Fig. 6b of the manuscript.*

As alternative model for the F8-azo-H8 layer under UV irradiation we fitted the neutron reflectivity data with a structure assumption where the azobenzene moieties in *cis* configurations are in contact with the D_2O subphase, as it is shown in Figure S7. A two-layer model separating the azobenzene moieties from the alkyl side chains is used and the fit is also close to the experimental data. Nevertheless, a better fit was obtained with the single-layer model, as reported in Fig. 6b of the main text and Fig. S6 above with a mixed layer of unknown orientations of the molecules.
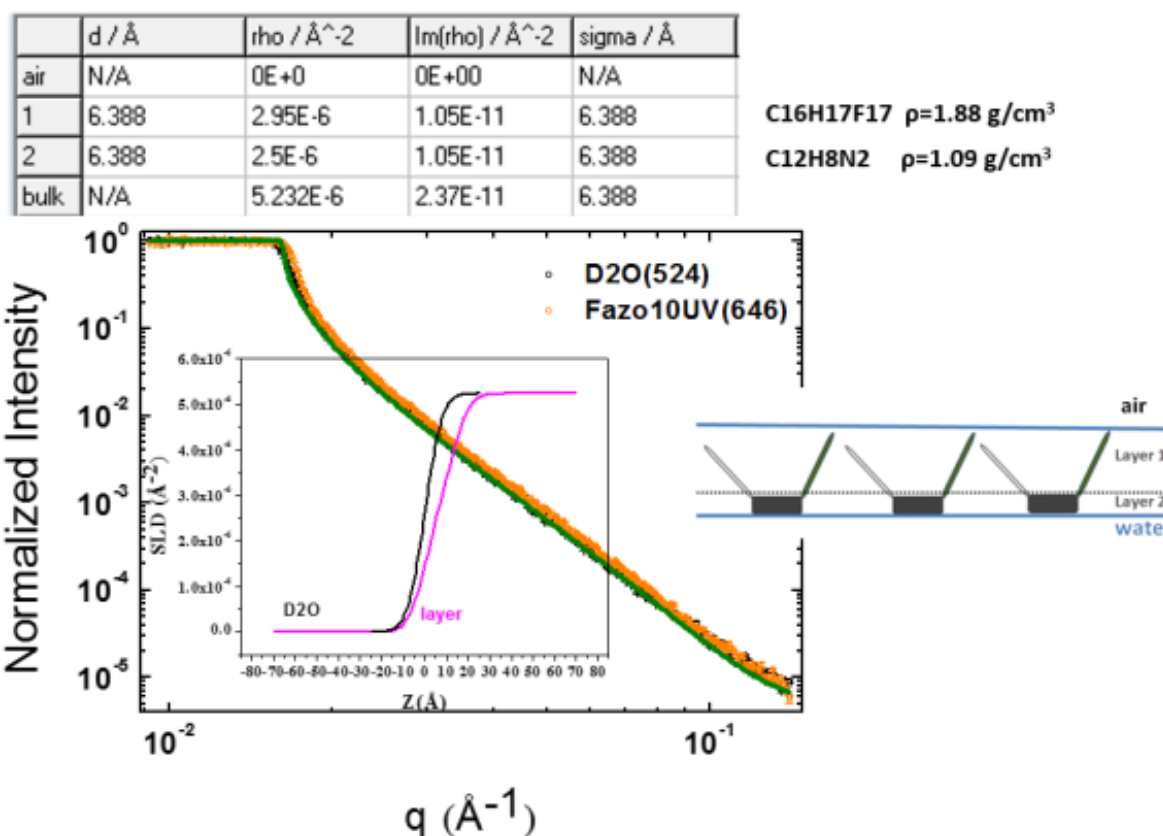
2 LAYER_ cisUP

	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å
air	N/A	0E+0	0E+00	N/A
1	6.388	2.95E-6	1.05E-11	6.388
2	6.388	2.5E-6	1.05E-11	6.388
bulk	N/A	5.232E-6	2.37E-11	6.388

$C_{16}H_{17}F_{17}$ $\rho=1.88$ g/cm³

$C_{12}H_8N_2$ $\rho=1.09$ g/cm³

Figure S7: Model, reflectivity data and scattering length density profile of F8-azo-H8 under UV irradiation. A two-layer model with the azobenzene group in contact with the D_2O subphase is assumed here. Surface pressure = 12 mN m⁻¹.

Interfacial Rheology

Fig. S8 depicts the dynamic time sweep measurement of F8-azo-H8 monolayer at the air-water interface at 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 6 mN m⁻¹ with the UV light OFF and after 60 min the UV was switched ON. Within 20 min the surface pressure increased to SP = 19 mN m⁻¹, while for the interfacial storage modulus a one order of magnitude drop was observed.
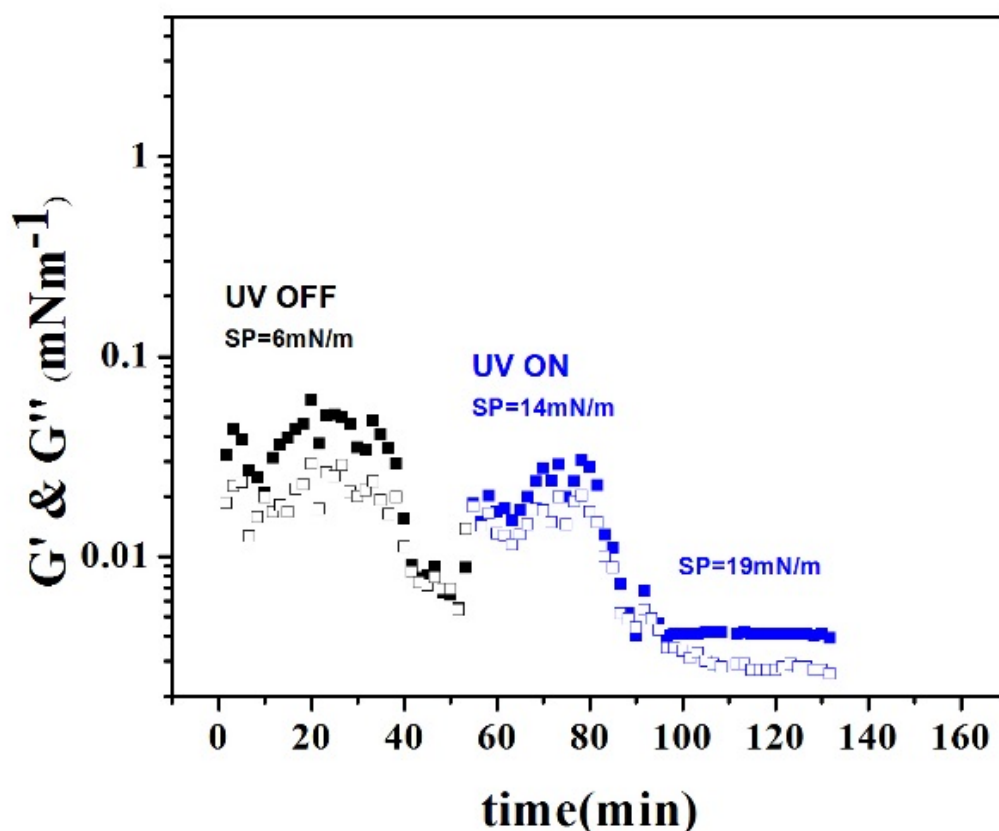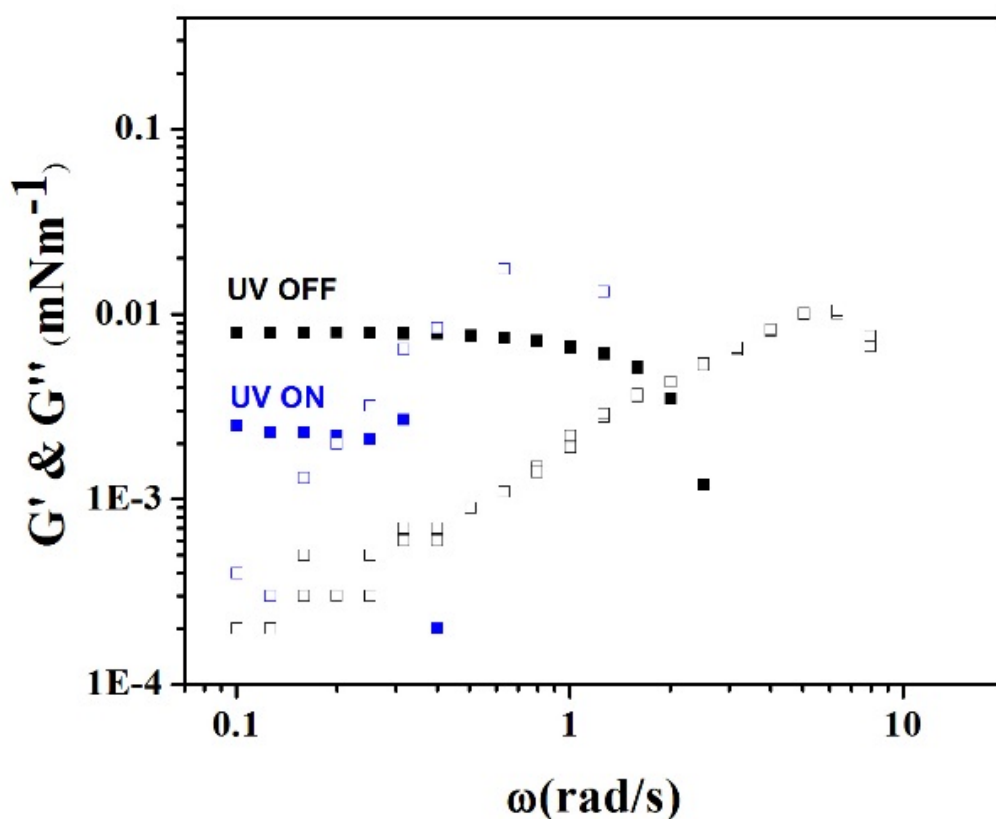
Figure S8: *Dynamic time sweep measurement of storage (G', closed symbols) and loss (G'', opened symbols) moduli for a F8-azo-H8 monolayer at the air-water interface at a temperature of 20 °C, frequency ω = 0.6 rad s^{-1} and strain amplitude γ$_0$ = 0.1 % using the magnetic rod interfacial stress rheometer. The measurement started at a surface pressure of 6 mN m^{-1}.*

Fig. S9 shows dynamic frequency sweep measurements of H8-azo-H8 at γ$_0$ = 0.1 %. The first DFS measurement is performed with the UV light OFF at SP = 2 mN m^{-1}. After the end of this experiment the UV light is turned ON and the surface pressure increased to SP = 8 mN m^{-1}. A drop of the interfacial storage modulus is observed from 0.008 mN m^{-1} to 0.002 mN m^{-1}.

Figure S9: *Dynamic time sweep measurement of storage (G', closed symbols) and loss (G'', opened symbols) moduli for a H8-azo-H8 monolayer at the air-water interface at a temperature of 20 °C, frequency ω = 0.6 rad s⁻¹ and strain amplitude γ₀ = 0.1 % using the magnetic rod interfacial stress rheometer. The measurement started at a surface pressure of 2 mN m⁻¹.*

Irradiation - Experimental Details

Fig. S10 shows a schematic representation of the experimental details for the irradiation of the spreading solution with a Spectroline UV lamp of 365 nm (6 Watt tube, 0.7 mW cm⁻² @ 15 cm, corresponding to about 10¹⁵ photons cm⁻² sec⁻¹) irradiated at a distance of 8 cm for 10 minutes. For white light irradiation a 12 W halogen lamp at a distance of 10-15 cm was used.
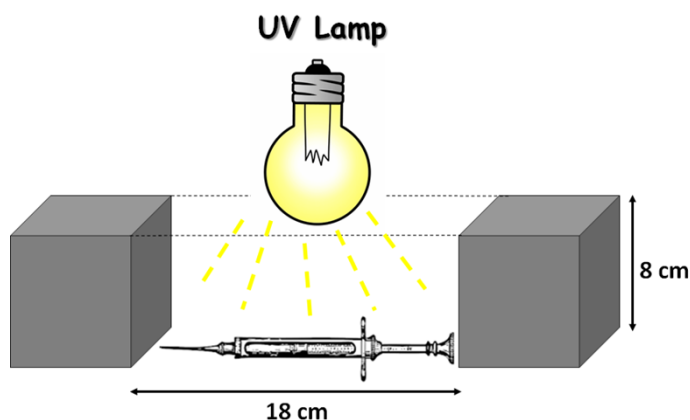

Figure S10: *Schematic representation of the irradiation of the solutions before spreading at the air-water interface.*

The spectral properties of the azobenze derivatives in the dark (*trans*) and after UV irradiation (*cis*) are provided for their solutions in THF in Fig. S12.
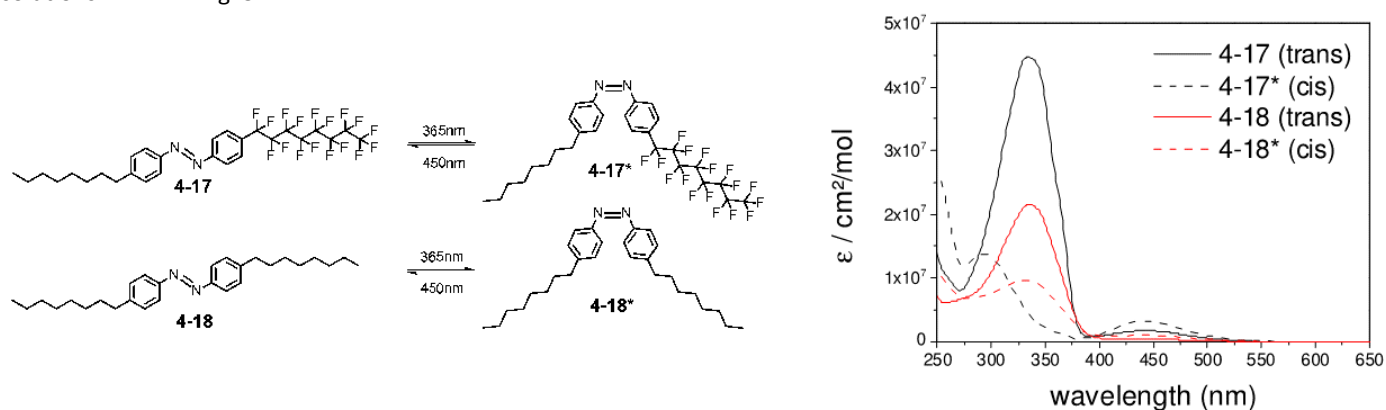

Figure S12: *UV-VIS absorption spectra of F8-azo-H8 (black) and H8-azo-H8 (red). The azobenzene derivatives were dissolved in THF with c=3.2x10⁻⁵g/ml before (black lines) and after (dashed lines) irradiation at 365 nm for 2 min. The data are reproduced from the PhD Thesis of Rene Stagenberg, Johannes Gutenberg-University of Mainz, 2013, pages 139 & 140.*