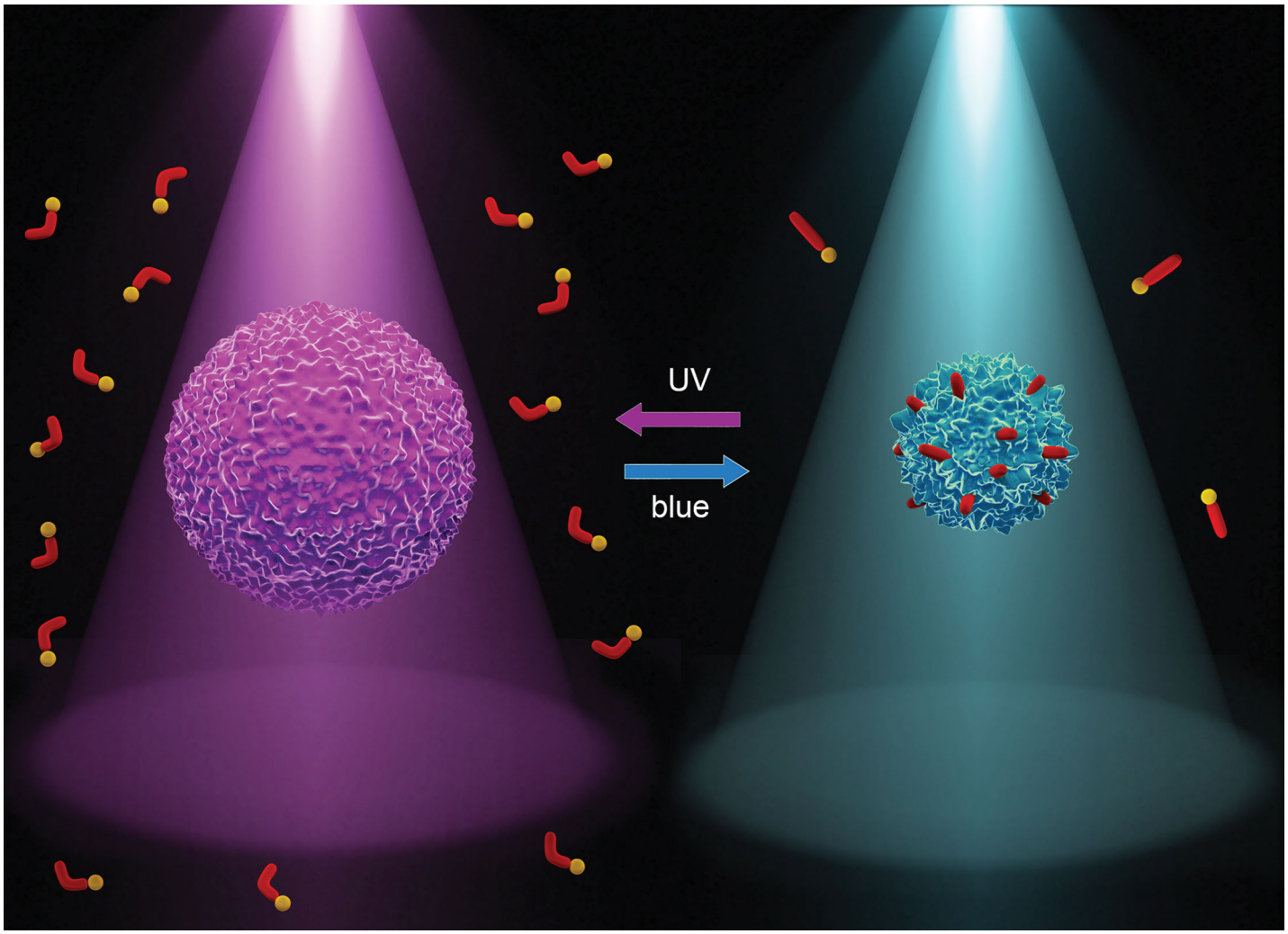

Showcasing work from a joint team of three groups: Svetlana Santer (experimental physics, Potsdam, Germany), Regine von Klitzing (physical chemistry, Berlin, Germany) and Elena Kramarenko (theoretical physics, Moscow, Russia).

Photosensitive microgels containing azobenzene surfactants of different charges

This paper reports light induced reversible switching of microgel size in the presence of azobenzene-containing surfactants with different charges. By periodically applying irradiation of two wavelengths, the microgel volume is reversibly changed more than five times within a few seconds.

As featured in:

See Svetlana Santer *et al.*, *Phys. Chem. Chem. Phys.*, 2017, **19**, 108.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/pccp

Registered charity number: 207890

PCCP

PAPER

View Article Online
View Journal | View Issue

Cite this: *Phys. Chem. Chem. Phys.*, 2017, **19**, 108

Photosensitive microgels containing azobenzene surfactants of different charges†

Selina Schimka,[a] Nino Lomadze,[a] Maren Rabe,[a] Alexey Kopyshev,[a] Maren Lehmann,[b] Regine von Klitzing,[b] Artem M. Rumyantsev,[c] Elena Yu. Kramarenko[c] and Svetlana Santer*[a]

Received 29th June 2016,
Accepted 20th September 2016

DOI: 10.1039/c6cp04555c

www.rsc.org/pccp

We report on light sensitive microgel particles that can change their volume reversibly in response to illumination with light of different wavelengths. To make the anionic microgels photosensitive we add surfactants with a positively charged polyamine head group and an azobenzene containing tail. Upon illumination, azobenzene undergoes a reversible photo-isomerization reaction from a *trans*- to a *cis*-state accompanied by a change in the hydrophobicity of the surfactant. Depending on the isomerization state, the surfactant molecules are either accommodated within the microgel (*trans*-state) resulting in its shrinkage or desorbed back into water (*cis*-isomer) letting the microgel swell. We have studied three surfactants differing in the number of amino groups, so that the number of charges of the surfactant head varies between 1 and 3. We have found experimentally and theoretically that the surfactant concentration needed for microgel compaction increases with decreasing number of charges of the head group. Utilization of polyamine azobenzene containing surfactants for the light triggered remote control of the microgel size opens up a possibility for applications of light responsive microgels as drug carriers in biology and medicine.

Introduction

Stimuli-sensitive microgel particles consisting of cross-linked polymers have received increasing attention due to their ability to encapsulate and/or release compounds upon controlled external triggers. This is related to the ability of microgels to undergo a volume transition in response to changes in pH, temperature, chemical composition of the solvent as well as application of light or static magnetic and electric fields.[1–12] These properties make microgels a promising material class for applications in many scientific and industrial fields such as sensor design,[13,14] optics, colloidal crystals,[15] bio-medicine, or fabrication of pharmaceuticals, cosmetics, and food products.[16–21]

In order to make microgels responsive to stimuli outlined above one typically modifies the microgels with functional groups or nanoparticles. For instance, one can incorporate semiconductor-, metal- or magnetic nanoparticles within the microgel, which in turn becomes responsive to optical or magnetic fields.[22–26] Microgels made of, for instance, PNIPAM, PEO, PVCL or weak polyelectrolytes augmented with acidic or basic functional groups exhibit temperature or pH sensitivity.[27–30]

One of the most convenient external triggers for the remote control of microgel size is light. In order to make microgels photo-responsive one may exploit the photo-thermal effect. Here, a thermo-responsive microgel is modified with nanoparticles converting optical energy into heat in order to induce phase transition accompanied by a pronounced change in volume.[31] Another possibility is to attach photosensitive groups such as spiropyran or azobenzene covalently to the microgel and make use of the light induced changes in polarity of the photosensitive groups, thus controlling the swelling behavior of the gel.[32,33]

Recently it was proposed to use azobenzene containing surfactants for rendering microgel particles photo-sensitive.[34–37] The advantage of this approach is that any charged microgel particle can be made photo-responsive by immersing it into a solution with oppositely charged photosensitive surfactants. When azobenzene is incorporated into the hydrophobic tail of a surfactant molecule, the hydrophobicity of the whole surfactant can be switched by illumination with UV or blue light, between a more hydrophobic (*trans*-) and a rather hydrophilic (*cis*-) isomer.[38] The physical mechanism of light responsive behavior of microgel particles can be described as follows.[39] Microgel particles (for instance, negatively charged) are in a swollen state when they are dissolved in water at room temperature. Upon adding cationic surfactants, one can first achieve

[a] *Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany. E-mail: santer@uni-potsdam.de*
[b] *Institute of Chemistry, Technical University Berlin, 10623 Berlin, Germany*
[c] *Faculty of Physics, Lomonosov Moscow State University, Moscow, 119991, Russia*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cp04555c

compaction because the surfactant diffuses into the particle, and replaces the counter ions at the charged groups of the gel. The counterions are subsequently expelled from the particle. The resulting drop in osmotic pressure induced by the micellization of surfactants within the gel in combination with screening of electrostatic interactions finally causes microgel particles to collapse and reduce their hydrodynamic radius significantly. Upon UV irradiation the surfactant molecules photo-isomerize to their *cis*-conformation and are thus rendered sufficiently hydrophilic to become non-aggregated and leave the particle, causing re-entering of counterions and re-swelling of the particle back to its initial size. This process can be reverted by stimulating fast back-relaxation to the *trans* isomer upon exposure to blue light. During this process, there is a fast transport of considerable amounts of surfactant molecules into and out of the particle.[34,35,38]

Here we propose to use azobenzene containing polyamine surfactants in order to realize light driven control of microgel particles. The microgel is based on *N*-isopropylacrylamide and co-monomer allyl acetic acid (NIPAM-AAA). The presence of two of these groups introduces thermo-responsive and pH-sensitive behavior of microgels.[29,40–42] We work at neutral pH at which the microgels are found to be negatively charged. Their charge is distributed within and on the surface of the particles. Surfactants with polyamines as a head group are cationic and bear a valence depending on the number of amine groups and pH of the surroundings. In our study we utilize three molecules with 2, 3 and 4 amino groups in the surfactant head, which then acquires 1.5+, 2+ and 3+ charges at neutral pH, respectively. Synthetic polyamines are similar to the well-known natural compacting agent spermidine and have been used, *e.g.*, in DNA compaction for transfection applications.[41,43] Modified with azobenzene they have also recently been applied to achieve reversible compaction/decompaction of DNA molecules.[44] Here we show experimentally and theoretically that negatively charged microgels can be shrunken by photosensitive polyamine surfactants as well. The critical concentration needed for a microgel to deswell increases with decreasing number of charges at the head group. The light-triggered remote control of the microgel size is achieved for all studied surfactants by periodic illumination with light of two different wavelengths: UV and blue. It is shown that upon irradiation it is possible to change the volume of the microgels by up to a factor more than 4 within only a few seconds. These unique properties of photosensitive microgels might be very attractive for biological applications, where the microgel can serve, for instance, as a container, which being in its compacted state, can deliver a substance and release it during subsequent decompaction triggered by irradiation with the appropriate wavelength.

Materials and methods

Synthesis of photosensitive azobenzene containing polyamines

Cationic azo-polyamines were synthesized according to the published procedure in ref. 44. First, azocoupling of 4-butylaniline with phenol and a subsequent reaction with 1,6-dibromohexane were carried out, followed by quaternization with trimethylamine (Fig. 1d) or by the reaction with either ethylenediamine (Fig. 1a), diethylenetriamine (Fig. 1b) or tris(2-aminoethyl)amine (Fig. 1c). The resulting azobenzene containing polyamines differ in the number of amine groups in the head (2 to 4, Fig. 1).[45] The polyamines were dissolved in water (Milli-Q) and kept in the dark for several days to ensure complete relaxation to the *trans*-state. The dependence of the amine charge on pH was calculated (ESI,† Fig. S1) from the Henderson–Hasselbach equation and local amine-pK_a values were determined using Marvin Sketch.[46] All experiments were performed at pH = 7, fixing the charge of **Azo-En** to 1.5, of **Azo-Deta** to 2.0 and of **Azo-Tren** to 3.0.

Synthesis of the microgel

The microgel particles were synthesized as described elsewhere.[36] In short, *N*-isopropylacrylamide (NIPAM, Aldrich, 97%), 5 mol% (with respect to the mass of NIPAM) of *N*,*N*′-methylenebisacrylamide

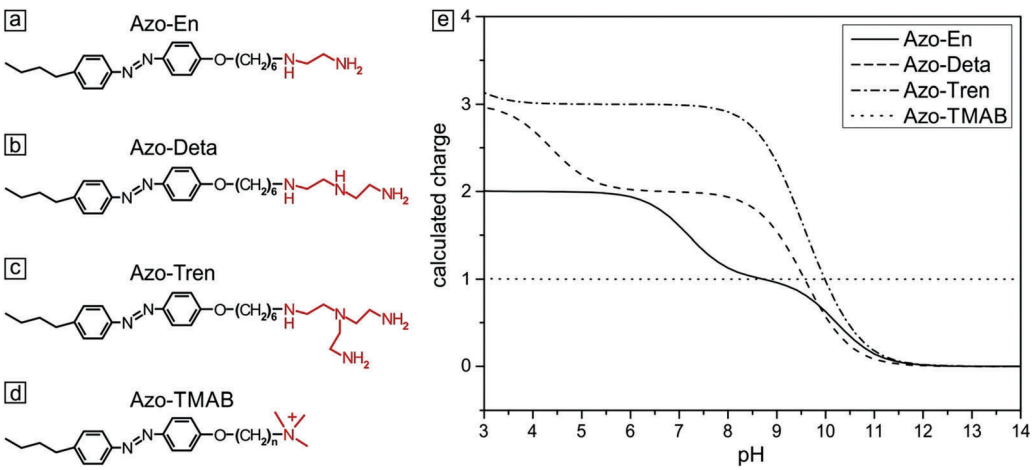

Fig. 1 Chemical structures of the studied surfactants: (a) **Azo-En**, (b) **Azo-Deta**, (c) **Azo-Tren**. (d) Shows the chemical structure of the **Azo-TMAB** cationic surfactant. (e) Dependence of the valence of the head group on the pH value for three different molecules: **Azo-En** (solid line), **Azo-Deta** (dashed line), **Azo-Tren** (dot-dashed line), **Azo-TMAB** (dotted line).

(BIS, Aldrich, 99,5%), and 50 mol% (with respect to the mass of NIPAM) of the co-monomer allyl acetic acid (AAA, Aldrich, 97%) were dissolved in 100 mL Milli-Q water, heated to 70 °C under a constant nitrogen stream. Polymerization was initiated by the addition of 1 mg KPS. After synthesis the microgel was dialyzed for 14 days with Milli-Q water to remove oligomers and excess educts, and freeze-dried.

Photoisomerization behavior of polyamines

The photoisomerization behavior of the polyamines was found to be similar to a previously described cationic surfactant (azobenzene-containing trimethylammonium (TMAB), Fig. 1). This was expected since they share the same azobenzene containing tail.[47–49] The *trans* isomer of all compounds discussed in this work has a characteristic absorption band (π–π* transition) with a maximum at 351 nm. The spectrum of the *cis* isomer is characterized by two absorption bands with maxima at 313 nm (π–π* transition) and at 437 nm (n–π* transition).

Sample preparation

The microgel and the azobenzene containing surfactants were dissolved in de-ionized water (Milli-Q) to obtain initial solutions with concentrations of 2×10^{-5} M and 2×10^{-4} M, respectively. Both polyamines and microgel solutions were diluted prior to mixing to obtain a certain value of the molar ratio, MR, determined by the ratio between the total concentration of polyamine [Polyamine] and carboxylic groups [AAA]: MR = [Polyamine]/[AAA]. The concentrations of polyamine surfactants were kept far below their CMC, which is 0.11 mM, 0.14 mM, 0.18 mM for **Azo-En**, **Azo-Deta**, **Azo-Tren**, respectively. The CMC was determined using the Wilhelmy plate method (Kibron-Tensiometer, Kibron MicroTroughXL) as described in the ESI,† Fig. S4. The ionic strength was kept constant at 5 mM NaCl. All preparations and measurements in solution were carried out at 20 °C and under yellow light to avoid unwanted isomerization of the photosensitive substances.

Preparation of samples for SEM measurements

SEM samples were prepared by pipetting microgel/polyamine solution on a silicon wafer followed by drying under ambient conditions.

Methods

UV-Vis spectra were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer (Varian Inc.) in quartz cuvettes with 10 mm length of the optical pathway.

The dynamic light scattering (DLS) characterization of the microgel-surfactant complexes was performed in micro UV-Cuvettes using a Zetasizer Nano ZS (Malvern Instruments Ltd) at a scattering angle of 173°.

Electron micrographs were acquired using a transmission electron microscope, type JEM-1011 (JEOL Ltd, Japan) and a SEM device (Ultra Plus, Zeiss, Germany).

The lamps (VL-4.L, Vilber Lourmat, 365 nm, $I = 1.2$ mW cm^{-2}; LED Spot Luxeon Royal Blue, P453E-PR09, 453 nm, 7 mW cm^{-2}, Conrad Electronic) were used for the irradiation of the samples, at a duration of typically 10 min to guarantee the steady state behavior of the surfactant molecules.

An inverted optical microscope (Olympus IX71) equipped with two lasers (Samba 532 nm, Cobolt, Sweden; and 355 nm, Genesis CX, Coherent Inc., USA) is used to acquire images at a speed of 1 frame per second.

Theoretical considerations

Following ref. 39, the microgel is assumed to consist of ν flexible subchains each containing N monomer units. Some fraction f of the monomer units is ionic, so that both the total number of charges on the network and the number of microgel counterions equal νNf. Microgel swelling is described by the dimensionless swelling ratio $\alpha = R/R_0$, which is the ratio between the equilibrium microgel radius R, and the microgel radius R_0 in the reference state. The reference state implies Gaussian coil conformations of the network subchains such that $R_0 = aN^{1/2}\nu^{1/3}$, a being a monomer unit size. The microgel concentration in solution is defined by the average distance between the centers of adjacent particles $2R_{out} = 2R_0/\gamma$ with a dimensionless parameter $\gamma \ll 1$ for diluted solutions.

If δ is the charge of the surfactant ion and all other charged species in the system (microgel ionized groups, microgel and surfactant counterions) carry unit charges, the total number of surfactant molecules in the solution is $ZfN\nu/\delta$; δ can assume fractional values in the case of pH-dependent surfactants. As in ref. 39, we use a two-zone model to account for the redistribution of ions between the microgel interior and the outer solution, resulting in the uncompensated microgel charge of $Q/e = \nu Nf(1 - \beta + sZ - tZ)$, where e is the elementary charge while s, β and t denote the fractions of surfactant molecules, network counterions and surfactant counterions, respectively, that are kept within the microgel. Thus, the charge binding ratio equals Zs.

We restrict our considerations to the case of relatively low surfactant concentration, not exceeding the CMC in the outer solution. Nevertheless, under these conditions micelle formation inside the microgel is still possible due to a reduction of the CMC within the oppositely charged polyelectrolyte network, as compared to a pure surfactant solution.[39,50,51] This effect can most likely be attributed to the neutralization of an excess micelle charge by the oppositely charged microgel subchains so that surfactant counterions, neutralizing the micellar charge in the outer solution, are now able to leave the micelle vicinity gaining extra translational entropy.[39]

The free energy of the solution per microgel is given by:

$$F_{tot} = F_{el} + F_{el-st} + F_{tr}^{nc} + F_{tr}^{sc} + F_{int} + F_{tr}^{s} + F_{agg} \quad (1)$$

The first term is the energy of elastic deformation of the microgel subchains

$$\frac{F_{el}}{k_B T} = \frac{3}{2}\nu\left(\alpha^2 + \frac{1}{\alpha^2}\right) \quad (2)$$

The subsequent term accounts for the excess Coulomb energy of the charged microgel and the outer solution, treated as the

energy of a spherical capacitor with R and R_{out} as the radii of the internal and the external plates, respectively:

$$F_{el-st} = \frac{Q^2}{\varepsilon}\left(\frac{1}{R} - \frac{1}{R_{out}}\right), \quad (3)$$

where ε is the relative dielectric permittivity of the solvent.

The terms F_{tr}^{nc} and F_{tr}^{sc} are responsible for the translational entropy of the microgel and the surfactant counterions, which are regarded as ideal gases both inside and outside the microgel:

$$\frac{F_{tr}^{nc}}{k_B T} = fN\nu\left[\beta \ln(\beta f \Phi) + (1-\beta)\ln\left(\frac{(1-\beta)f\Phi\gamma^3}{\Phi N^{1/2} - \gamma^3}\right)\right] \quad (4)$$

$$\frac{F_{tr}^{sc}}{k_B T} = ZfN\nu\left[t \ln(Ztf\Phi) + (1-t)\ln\left(\frac{Z(1-t)f\Phi\gamma^3}{\Phi N^{1/2} - \gamma^3}\right)\right] \quad (5)$$

Here $\Phi = \nu N a^3/R^3$ is the polymer volume fraction inside the microgel.

The free energy of van der Waals' interactions is written in the form of a virial expansion

$$F_{int} = k_B T N \nu\left[\frac{B}{a^3}\Phi^2 + \frac{C}{a^6}\Phi^3\right] \quad (6)$$

where the second and the third virial coefficients can be estimated as $B \sim \tau a^3$ and $C \sim a^6$, respectively, and τ is the relative temperature deviation from the Θ-point.

Finally, the last two terms are the surfactant contributions to the free energy. Since surfactant molecules are able to aggregate within the microgel, the last term corresponding to the aggregation energy

$$\frac{F_{agg}}{k_B T} = \frac{N\nu Zfs}{\delta}\left[\ln(1-q) + \frac{m-1}{m}q\right] \quad (7)$$

should be added to the ideal gas entropy of surfactant ions both inside and outside the microgel written as

$$\frac{F_{tr}^{sc}}{k_B T} = \frac{ZfN\nu}{\delta}\left[s \ln\left(\frac{Zsf\Phi}{\delta}\right) + (1-s)\ln\left(\frac{Z(1-s)f\Phi\gamma^3}{\delta(\Phi N^{1/2} - \gamma^3)}\right)\right] \quad (8)$$

The fraction of surfactants q aggregated into micelles with aggregation number m is defined by the law of mass action:

$$\frac{q}{(1-q)^m} = \left(\frac{\Phi s Z f}{\delta}\right)^m m e^{\Delta F m}, \quad (9)$$

where ΔF is the energy gain per surfactant ion due to micellization inside the microgel. In order to find the equilibrium microgel state, the free energy function $F_{tot}(\alpha, \beta, s, t)$ was minimized with respect to its four parameters. The values of $\nu = 10^8$, $N = 15$, $f = 0.33$, $\gamma = 0.015$, $\tau = 0$, $e^2/\varepsilon a k_B T = 1$ corresponding to the microgels investigated experimentally are fixed. For all surfactants m is assumed to be 50, which is known to be a typical aggregation number of surfactants in spherical micelles. In fact, the exact numerical value of $m \gg 1$ hardly influences theoretical conclusions. Owing to large microgel dimensions and a high content of ionic groups, the ratio between the excess microgel charge and the total charge of the network is close to zero, and condition $1 - \beta + sZ - tZ \approx 0$ valid for macroscopic networks is fulfilled.

Results and discussion

To study the influence of photosensitive surfactants on the microgel compaction we synthesized a set of azobenzene containing molecules with different numbers of amine groups (Fig. 1a–c). The valence of charges on the head group depends on the pH. At pH 7 for instance, **Azo-En**, **Azo-Deta**, **Azo-Tren** have 1.5+, 2+ and 3+ charges per molecule (Fig. 1e). In this paper, for comparison we also discuss the cationic surfactant (azobenzene-containing trimethylammonium bromide) (**Azo-TMAB**) (Fig. 1d), the interaction of which with the microgels was published elsewhere.[35] This surfactant carries 1 positive charge per molecule.

All the four surfactants discussed here have similar UV-Vis absorption spectra (Fig. 2 shows the spectrum of **Azo-Deta**). The absorption spectra depend on the pH value (see ESI†, Fig. S1). For the present study, however, the pH was fixed at a value of 7. The *trans* isomer of all discussed compounds has a maximum adsorption at 351 nm, while the *cis* isomer is characterized by two absorption bands at 313 nm and at 437 nm (Fig. 2). The irradiation of the *cis*-isomers with blue light does not completely return the surfactant into its initial dark state (Fig. 2, blue curve). It was found that after irradiation with λ = 453 nm for 10 minutes *ca.* 66% of all the molecules are converted to the *trans*-state,[35] while after irradiation with UV-light only 12% of the *trans*-isomer was detected following the absorption at 376 nm. The lifetime of the *cis* isomer in water is ~72 hours; therefore, the spectra do not change considerably after the irradiation is turned off (see ESI,† Fig. S2). The transition from *trans*- to *cis*- and back to the *trans*-state triggered by irradiation with UV (λ = 365 nm) and blue (λ = 453 nm) light, respectively, takes place within only a few seconds.

The complexes between the microgel particles and polyamine surfactants were prepared by mixing a water solution of both substances at a certain molar ratio. For this, the microgel concentration was kept constant (two concentrations were used in this study, their values expressed in concentrations of [AAA] units in the solution are 1×10^{-5} M and 5×10^{-6} M), while the

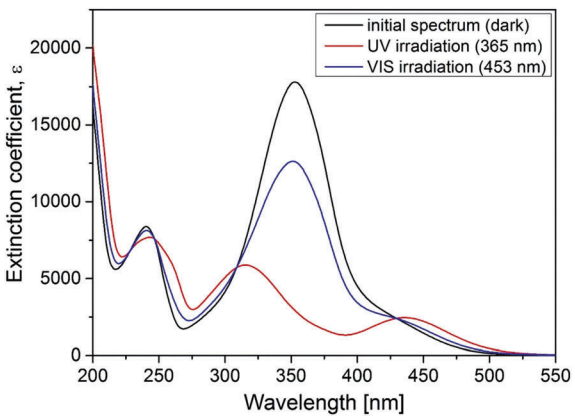

Fig. 2 UV-VIS absorption spectra of **Azo-Deta**: recorded in dark (black curve), *i.e.* after 4 days of relaxation, after irradiation with light of λ = 365 nm for 10 minutes (red curve), after irradiation with light of λ = 453 nm (blue curve).

surfactant concentration was varied between 5×10^{-7} M and 2×10^{-4} M. Fig. 3 shows the dependence of the hydrodynamic diameter of the microgel on the molar ratio between a total concentration of the polyamine surfactant [Polyamine] and the carboxylic groups [AAA] of the microgel defined as MR = [Polyamine]/[AAA].

When dissolved in water the microgel is in a swollen state with a hydrodynamic diameter of (1.4 ± 0.2) μm (Fig. 3). At a low surfactant concentration, the microgel is still in its swollen state up to some critical concentration at which contraction commences. For all the four surfactants the character of the size change is similar: with increasing surfactant concentration the size of the microgel decreases. Depending on the number of charges on the head group the contraction starts at varying molar ratio MR. A small amount of surfactant is needed to initiate the shrinkage of the microgel in the presence of molecules carrying 3 positive charges (**Azo-Tren**, Fig. 3c and d), while larger amounts of surfactant are required for 1.5 (**Azo-En**) and 2 (**Azo-Deta**) positive charges in the head group to induce the onset of microgel contraction. A further increase in the concentration results in a gradual decrease of the particle size down to (700 ± 100) nm at which the saturation of the microgel contraction occurs (Fig. 3). Also the onset of the saturation value depends on the valence of the surfactant head group: more surfactant is needed at smaller valences. The results for the **Azo-TMAB** surfactant interacting with the microgel are shown in Fig. 3d for comparison. A Boltzmann fit is applied to analyze the microgel size change with the inflection points of 0.23, 0.38, 0.70 and 1.10 for **Azo-Tren**, **Azo-Deta**, **Azo-En** and **Azo-TMAB**, respectively (Fig. 3d). These results indicate that with increasing number of charges on the surfactant head group smaller concentrations are required in order to induce the shrinkage of the microgel. The microgel-surfactant complexes are colloidal stable in the concentration range presented here.

Similar behavior is observed for smaller microgel concentration, $c = 5 \times 10^{-6}$ M (see ESI,† Fig. S3). For the case of smaller concentrations, the inflection point for all surfactants shifts to a larger molar ratio. The fact that in more concentrated solutions microgel collapse occurs at lower values of MR is fully supported by the theoretical calculations.[39] An explanation is a higher entropy loss of surfactant molecules under their accumulation within the microgel at lower microgel concentrations (*i.e.* lower values of γ).[39]

To examine the impact of the ionic surfactant charge on the swelling behavior of the microgel, we modify the theoretical approach developed by us earlier for monovalent surfactants.[39] A short description of the theory is presented in the Materials and methods section.

In the absence of surfactant molecules microgel swells due to the osmotic pressure generated by the counterions, and the

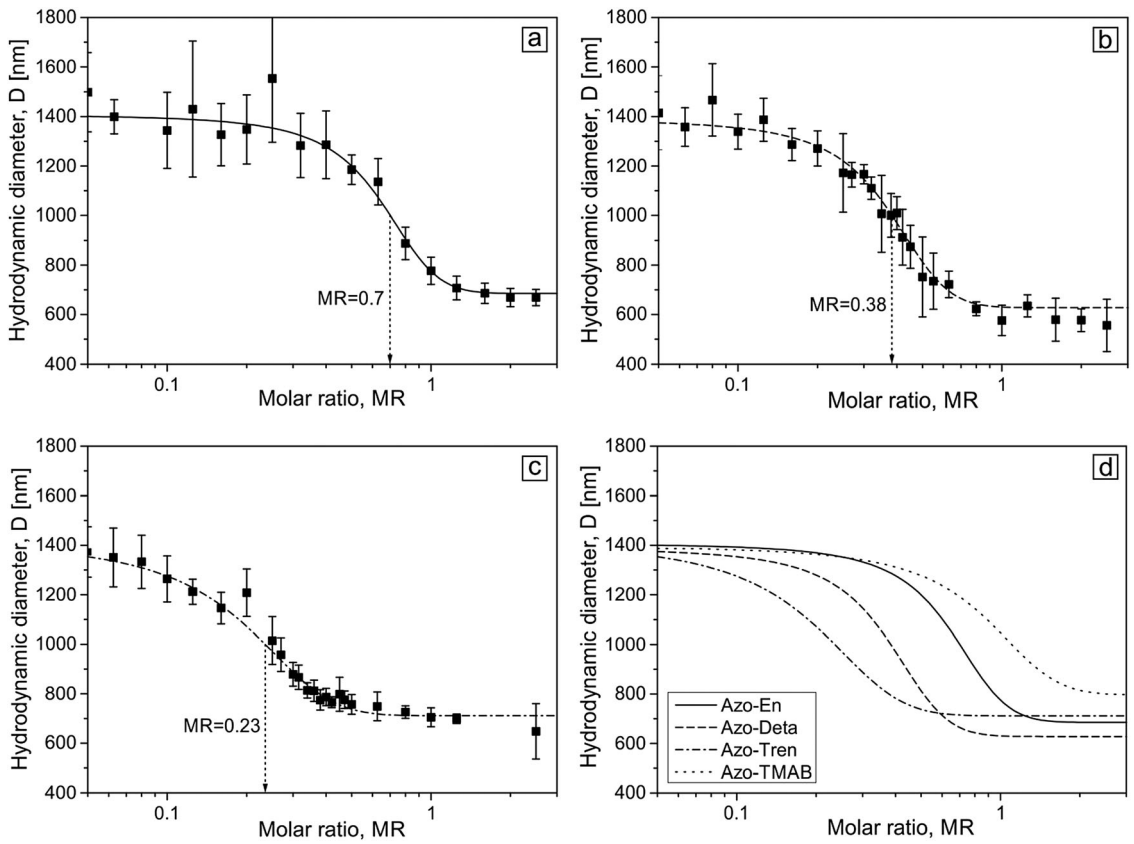

Fig. 3 Hydrodynamic diameter of the microgels as a function of molar ratio for (a) **Azo-En** (solid line), (b) **Azo-Deta** (dashed line) and (c) **Azo-Tren** (dot-dashed line). In (d), the fitted lines of (a)–(c) are reproduced to facilitate their comparison. The concentration of the microgel is $c = 10^{-5}$ M.

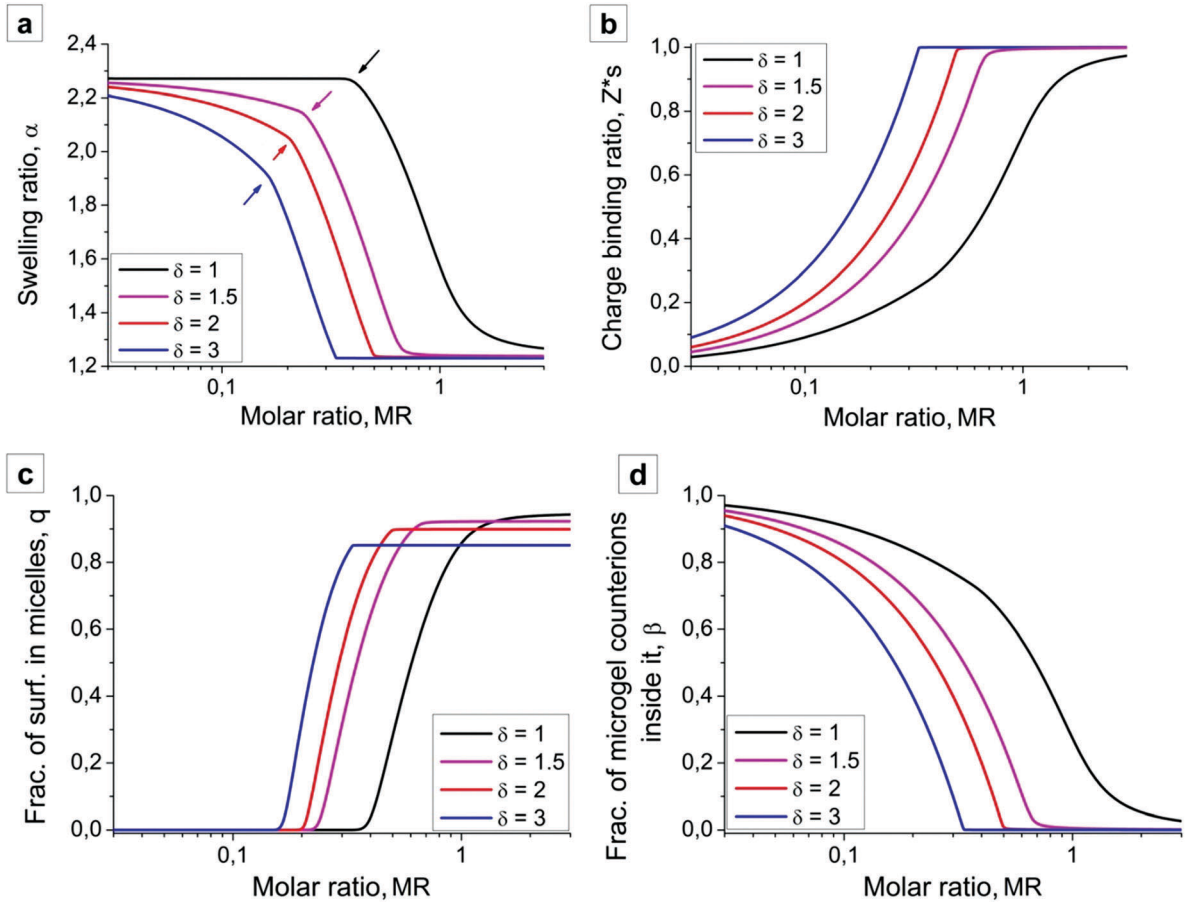

Fig. 4 Swelling ratio α (a), charge binding ratio Z^*s (b), fraction of surfactant molecules aggregated into micelles inside the gel q (c) and fraction of network counterions inside the gel β (d) as a function of the molar ratio. The effect of surfactant charge is illustrated by combining curves for δ = 1, 1.5, 2 and 3, respectively. Surfactant hydrophobicity ΔF = 6.

swelling ratio is given by $\alpha = \sqrt{Nf} \approx 2.2$ (see Fig. 4a, low values of the MR). Surfactant addition causes microgel contraction, and each swelling curve of the microgel (Fig. 4a) can be divided into three regions, depending on the fractions of the aggregated surfactant within the microgel (Fig. 4c). In the first region there is no micelle formation within the microgel, $q = 0$, and its contraction takes place only at $\delta > 1$. In the course of ion exchange δ-valent surfactant ions substitute δ "native" counterions of the network (Fig. 4d) with their release to the outer solution, and thus some gain in translational entropy. Consequently, the amount of mobile ions within the microgel decreases, exerting osmotic pressure drops and microgel volume decays. The higher the value of δ, the steeper the microgel volume diminution. Microgel volume remains unchanged at $\delta = 1$ because of (i) the constant total number of mobile ions (both "native" network counterions plus surfactant ions) within the network and (ii) low surfactant concentration outside the microgel. Indeed, the concentration of ions outside the microgel is manifold (approx. $1/Z\gamma^3$ times) lower than that inside it, so that the Donnan salting out effect is negligible.[51]

In the second region, *i.e.* at intermediate values of MR, an intense micelle formation within the microgel sets in, Fig. 4a. Arrows in Fig. 4a point at the sharp bend in swelling curves corresponding to the border between the first and the second regimes. Since micelles containing $m \gg 1$ surfactants almost do not create osmotic pressure, microgel volume in this region rapidly goes down until all network counterions are substituted by surfactants. Microgel volume reaches values close to that of a neutral counterpart.

In the third region further surfactant addition hardly influences both the microgel dimensions and the internal structure; swelling ratio α (Fig. 4a) and the fraction of aggregated surfactants q (Fig. 4c) remain unchanged.

The results of our theoretical analysis coincide quite well with experimental observations. First, increasing surfactant charge leads to a shift of the swelling curves and microgel contraction at lower values of the surfactant molar ratio. Second, the shapes of the experimental and theoretical swelling curves (Fig. 3 and 4a) qualitatively coincide: in the first region microgel volume is almost unchanged in the solution of the univalent **Azo-TMAB** surfactant ($\delta = 1$), while microgel contraction in the presence of **Azo-Deta** and **Azo-Tren** surfactants takes place even at their low concentrations, $Z < 0.2$. Finally, the theory containing the only adjusting parameter ΔF reproduces quantitatively not only the range of microgel contraction but also its amplitude: in the collapsed state the microgel radius is twice lower than that in the swollen state.

Assumption on the equal values of ΔF, *i.e.* equal CMCs of all surfactants, was adopted in order to reveal the effect of the surfactant charge rather than surfactant hydrophobicity. In fact, the CMC in water increases from 0.1 mM for **Azo-TMAB** to 0.18 mM for **Azo-Tren** as measured experimentally using the Wilhelmy plate (see ESI,† Fig. S4). However, it should be primarily ascribed to the repulsion of charged head groups of the surfactant in the water, while in the microgel interior it is largely neutralized by oppositely charged network subchains, and the identical hydrophobic moiety of all surfactants makes our presumption on the equal values ΔF rather justified.

Light driven remote control of the microgel size

Since the surfactant molecules are photosensitive, the contraction of the microgel can be altered by illumination. To realize the light-induced reversible swelling/shrinkage process a sample in the compaction range with MR = 0.60 (**Azo-Deta**) was exposed periodically to irradiation with UV and blue light. The light-induced changes in microgel hydrodynamic diameter are shown in Fig. 5. One observes a completely reversible contraction/swelling transition of the microgel triggered by light. The change in the diameter of a microgel particle between ~700 nm and 1200 nm corresponds to more than a four-fold change in volume.

We should mention that the hydrodynamic diameter of the light induced decompacted state (1200 nm) is smaller than that of the swollen particles without surfactants (1400 nm). This is related to the fact that surfactants act as the salt suppressing gel swelling in accordance with the Donnan equilibrium and not all of them undergo photo-isomerization to the *cis*-state. In a previous publication[35] we have found that under illumination with UV light *ca.* 12% of the surfactants are in the *trans*-state. At an overall molar ratio, MR = 0.60, the specific molar ratio of the *trans*-isomers is MR_{eff}^{UV} = 0.07 (MR_{eff} = 0.60 × 12%). This value of MR corresponds to the range of a gradual decrease in the microgel size (Fig. 3b).

Using the same argument we estimate that under irradiation with blue light the effective concentration of *trans*-isomers is MR_{eff}^{blue} = 0.42 ($MR_{eff}^{blue} = MR_{eff}^{UV} + MR_{cis}$ 66%, where MR_{cis} = 0.60 − 0.07 = 0.53),

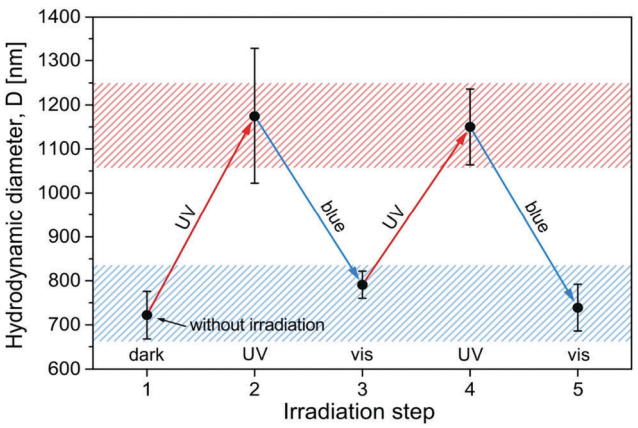

Fig. 5 Reversible changes of the effective hydrodynamic diameter for the microgel loaded with the **Azo-Deta** surfactant at MR = 0.6 and [AAA] = 1×10^{-6} M after UV and blue light (red and blue arrows, respectively) irradiation.

corresponding to the range of incomplete contraction where the microgel diameter is *ca.* 800 nm.

A similar behavior was found for all surfactants studied here (see ESI,† Fig. S5). Only in the case of **Azo-Tren** with three charges the light induced swelling of the microgels is smaller than for other surfactants (*ca.* 1000 nm, Fig. S5c, ESI†). This phenomenon is discussed below.

Since the change in the size of the micorgels is significant, one can easily observe it microscopically. Fig. 6 shows the SEM micrographs of the microgels (**Azo-Deta** complexes at different Z values and under irradiation conditions). At MR = 0.1, the microgels are in a swollen state (see for comparison Fig. 3b) with a diameter of D = 1200 nm (Fig. 6a). The diameter was measured as the average distance between the microgel particle centers. With increasing MR the diameter decreases down to a value of *ca.* 330 nm (Fig. 6b, MR = 2). Under irradiation with UV light, the particles swell again and the diameter increases to 440 nm (Fig. 6c shown for MR = 1), while upon irradiation with blue light, the diameter drops down to 300 nm (Fig. 6d).

The microgel particles were adsorbed on a silicon wafer from solutions of certain values of MR after irradiation with either UV or blue light and dried prior to measurement. Therefore, one cannot directly compare the diameter of the particles acquired from SEM micrographs and DLS measurements, however, the qualitative trend is similar in both cases, *i.e.* the diameter decreases for a larger value of MR, and increases upon UV irradiation.

The swelling/shrinkage process can directly be observed with optical microscopy (Fig. 7).

Tracking the diameter change of the single microgel particles using an optical microscope is a difficult task, since the particles are small, mobile and transparent. But one can see the change in the size and shape of physisorbed aggregates consisting of

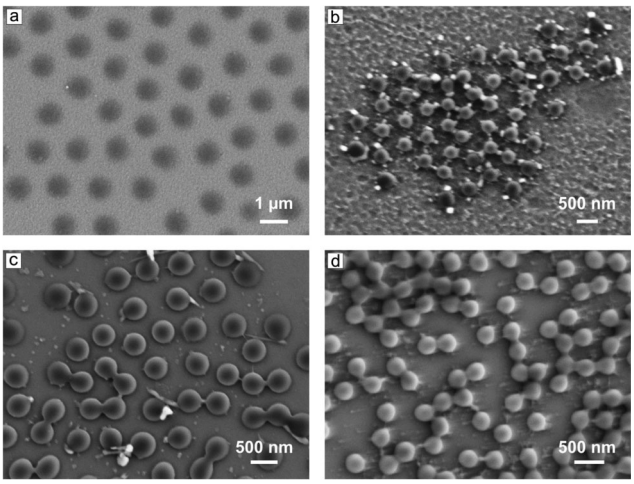

Fig. 6 SEM micrographs of microgels loaded with the **Azo-Deta** surfactant. (a) At MR = 0.1, the microgel particles are still in a swollen state with a diameter of D = 1200 nm. (b) At MR = 2 the particles are contracted to D = 330 nm. (c and d) The change in the microgel diameter (MR = 1) triggered by light: (c) swollen state (D = 440 nm) after irradiation with UV light, (d) shrunken microgel particles with D = 300 nm under exposure with visible light.

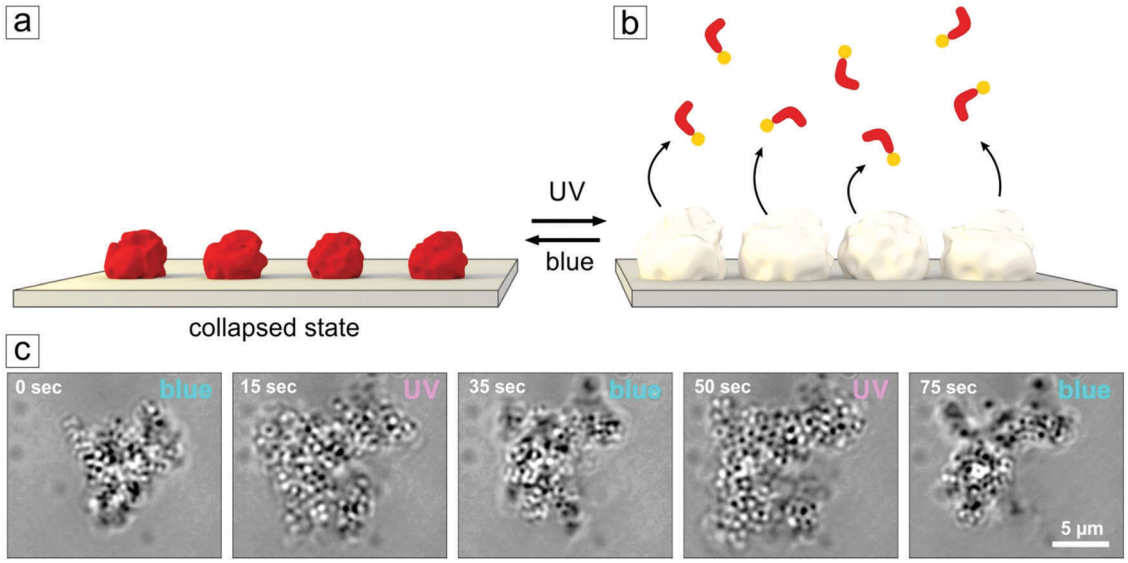

Fig. 7 (a) Schematic view of the adsorbed microgel particles loaded with photosensitive surfactants. (b) Upon UV irradiation, the surfactants leave the microgel, particles assume a swollen state. (c) Snapshots of the swelling/deswelling process (video recording available in the ESI,† Fig. S7). Here a cluster of microgel particles is attached to a glass surface and shows a significant and fast change in volume in response to alternating exposure to UV and blue irradiation.

lumps of microgel particles (Fig. 7). Here we make use of aggregate formation that occurs in aged solutions. Those containing photosensitive surfactants (shown for **Azo-TMAB**, at MR = 3) were irradiated periodically with UV and blue light within the setup of the optical microscope. Significant and reversible changes in the size of the aggregate could then be detected while changing the illumination conditions (Fig. 7).

The light driven compaction/decompaction process within the microgels loaded with photosensitive surfactants can also be described within the theoretical model discussed above. The surfactant hydrophobicity is included through the free energy gain upon micelle formation ΔF. In Fig. 8 we plot the swelling curves calculated for two different values of ΔF. With increasing ΔF, *i.e.* with increasing hydrophobicity of the surfactant tail, the surfactant concentration required for microgel shrinkage decreases (Fig. 8). This is related to the fact that the CMC reduces with the increase of surfactant hydrophobicity. Since our model of microgel shrinkage is based on the drop of osmotic pressure during the formation of micelles, the reduction of the CMC with increasing hydrophobicity results in a shift of the transition region between the swollen and collapsed state toward smaller surfactant concentrations. The hydrophobicity of the surfactant can be altered by irradiation, *i.e.* in the *trans*-state the surfactant is more hydrophobic than in the *cis*-state. According to ref. 52–55, the ratio between the CMCs of *cis*- and *trans*-isomers isomers of the same azobenzene-containing surfactants varies over a broad range from *ca.* 2 to 20 depending on the surfactant structure and solution temperature. Since the CMC inside the microgel is estimated as $\exp(-\Delta F - 1)$,[38] the difference between free energy gains under micellization for *trans*- and *cis*-isomers is $0.7 \leq (\Delta F_{trans} - \Delta F_{cis}) \leq 3$. Thus, at the same absolute value of the surfactant concentration there is a range of Z at which the microgel is swollen in the presence of *cis*-isomers, and shrunken when loaded with *trans*- (Fig. 8).

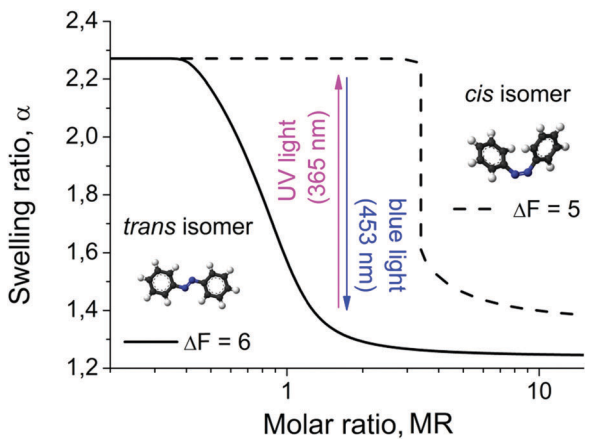

Fig. 8 Dependence of the swelling ratio α on the Z value for two surfactants differing in hydrophobicity: the *trans*-isomer is more hydrophobic (solid curve) than the *cis*-isomer (dashed curve). Model parameters are $\delta = 1$, $\Delta F_{cis} = 5$ and $\Delta F_{trans} = 6$.

In other words, under irradiation with UV light the micelles consisting of *trans*-isomers are disturbed, since *trans*- goes to the *cis*-state. The more hydrophilic *cis*-isomers leave the microgel, resulting in an uptake of counterions and thus the swelling of the particle. Upon irradiation with blue light, the *cis*-isomers photo-isomerise to the *trans*-conformation, thus diffusing back into the microgel and aggregating into micelles therein. At a certain concentration collapse of the microgel occurs. The process can be reversed by changing the irradiation wavelength. The change of the microgel size upon consequent UV and blue light irradiation decreases with increasing charge of the surfactant head group (see Fig. S5 and S6, ESI†). This tendency is especially pronounced for the case of the **Azo-Tren** surfactant. A probable

reason for this behavior is the following. As we discussed above, multivalent ions induce the contraction of the microgel at smaller surfactant concentrations and the extent of the gel contraction is higher because with multivalent ions the drop in osmotic pressure within microgels becomes considerable even without surfactant micellization. The higher the value of the surfactant charge δ, the more counterions are released into the solution, and thus the gel adopts more shrunken conformations. As a result, the CMC within the gel is reached earlier (at a smaller molar ratio MR). Thus, if we choose (MR) in the region where the microgel with a single-charge surfactant is close to the transition between swollen and shrunken states (see Fig. S6a, ESI†), a small change in the surfactant hydrophobicity can induce a considerable change in the swelling ratio resulting from the reversible formation and destruction of micelles within the gel. At the same (MR) the microgel with a triple-charge surfactant is already far from the transition and switching between *trans*- and *cis*-isomers could only slightly change the amount of aggregated surfactants, thus, the variations in the gel volume upon irradiation are smaller. Moreover, the gel volume after blue light irradiation hardly depends on the surfactant charge (see Fig. S5 and S6, ESI†) because micelles comprising *trans*-form surfactants scarcely create exerting osmotic pressure within the gel, so that the amplitude of volume changes is governed by the gel volume after UV irradiation when *cis*-isomers are in the non-aggregated state.

Conclusions

We studied the interaction between anionic microgel particles and azobenzene-containing cationic surfactants. All surfactants considered in this work share the same type of hydrophobic tail, the incorporated photosensitive group and differ only in the head group, which can acquire average charges of 1+, 1.5+, 2+ and 3+. The presence of the azobenzene group in the hydrophobic tail allows for photo-induced switching of the hydrophobicity of the surfactant. It was shown that upon increasing the surfactant concentration the microgel undergoes a transition from a swollen to a collapsed state. The larger the number of charges at the head group, the smaller the surfactant concentration required to trigger the transition. This observation has been supported/explained theoretically. Two consequent stages of microgel shrinking, corresponding to the absence and presence of micelle formation within the microgel, were shown up. Indeed, at a low surfactant concentration surfactant absorption by the microgel appears as a result of an ion exchange between counterions initially trapped within the microgel and surfactant ions. At that, the microgel volume remains unchanged in the solution of a univalent surfactant while goes down in the event of multivalent ions due to moderate osmotic pressure diminution. Increasing the surfactant concentration results in the formation of micelles within the microgel at which most of the counterions are expelled from the interior and the microgel charges are largely compensated by micelles. At this stage the osmotic pressure drops significantly, and the microgel undergoes a transition to a collapsed state in the solutions of both univalent and multivalent surfactants. The concentration, at which this two-stage transition occurs, decreases with increasing number of charges in the head group since more counterions can be replaced by one surfactant molecule at once.

During irradiation, the hydrophobicity of the surfactant tail is switched between a hydrophilic state (UV irradiation) and hydrophobic one (blue irradiation). The hydrophilic surfactant allows the microgel and the particles to swell, while the interaction of *trans*-isomers with the microgel results in its contraction. This process is completely reversible and can be carried out many times.

The light triggered reversible contraction/swelling behavior of the microgel induces a microscopic osmotic loading of the particles with surrounding solution, an effect which might be utilized for many applications such as artificial muscles, adaptive micro-fluidic devices and drug delivery systems.

Acknowledgements

This research is supported by the International Max Planck Research School on Multiscale Bio-Systems (IMPRS), Potsdam, German-Russian Interdisciplinary Science Center (G-RISC), Germany and Russian Foundation for Basic Research. M. L. and R. v. K. acknowledge the German Research Council (DFG) for financial support (KL 1165/12).

References

1 S. Nayak and L. A. Lyon, *Angew. Chem., Int. Ed.*, 2005, **44**, 7686–7708.
2 M. Das, H. Zhang and E. Kumacheva, *Annu. Rev. Mater. Res.*, 2006, **36**, 117–142.
3 L. A. Wells and H. Sheardown, *Eur. J. Pharm. Biopharm.*, 2007, **65**, 329–335.
4 H. Dou and M. Jiang, *Polym. Int.*, 2007, **56**, 1206–1212.
5 D. Klinger and K. Landfester, *Soft Matter*, 2011, **7**, 1426–1440.
6 Y. Wang, J. Nie, B. Chang, Y. Sun and W. Yang, *Biomacromolecules*, 2013, **14**, 3034–3046.
7 W. Richtering and A. Pich, *Soft Matter*, 2012, **8**, 11423.
8 J. B. Thorne, G. J. Vine and M. J. Snowden, *Colloid Polym. Sci.*, 2011, **289**, 625–646.
9 A. Pich and W. Richtering, *Adv. Polym. Sci.*, 2011, **234**, 1–37.
10 for instance review: M. Motornov, Y. Roiter, I. Tokarev and S. Minko, *Prog. Polym. Sci.*, 2010, **35**, 174–211.
11 K. Gawlitza, C. Wu, R. Georgieva, D. Wang, M. B. Ansorge-Schumacher and R. von Klitzing, *Phys. Chem. Chem. Phys.*, 2012, **14**, 9594–9600.
12 C. Scherzinger, O. Holderer, D. Richter and W. Richtering, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2762–2768.
13 I. Tokarev, I. Tokareva, V. Gopishetty, E. Katz and S. Minko, *Adv. Mater.*, 2010, **22**, 1412–1416.
14 M. Karg, I. Pastoriza-Santos, J. Pérez-Juste, T. Hellweg and L. M. Liz-Marzán, *Small*, 2007, **3**, 1222–1229.
15 J. D. Debord and L. A. Lyon, *J. Phys. Chem. B*, 2000, **104**, 6327–6331.

16 M. Hamidi, A. Azadi and P. Rafiei, *Adv. Drug Delivery Rev.*, 2008, **60**, 1638–1649.
17 N. A. Peppas and W. Leobandung, *J. Biomater. Sci., Polym. Ed.*, 2004, **15**, 125–144.
18 A. M. Kloxin, A. M. Kasko, C. N. Salinas and K. S. Anseth, *Science*, 2009, **324**, 59–63.
19 T. Dvir, M. R. Banghart, B. P. Timko, R. Langer and D. S. Kohane, *Nano Lett.*, 2010, **10**, 250–254.
20 M. A. Moses, H. Brem and R. Langer, *Cancer Cell*, 2003, **4**, 337–341.
21 D. A. LaVan, D. M. Lynn and R. Langer, *Nat. Rev. Drug Discovery*, 2002, **1**, 77–84.
22 M. Das, S. Mardyani, W. C. W. Chan and E. Kumacheva, *Adv. Mater.*, 2006, **18**, 80–83.
23 B. Brugger and W. Richtering, *Adv. Mater.*, 2007, **19**, 2973–2978.
24 M. Karg, Y. Lu, E. Carbó-Argibay, I. Pastoriza-Santos, J. Pérez-Juste, L. M. Liz-Marzán and T. Hellweg, *Langmuir*, 2009, **25**, 3163–3167.
25 A. O. Govorov and H. H. Richardson, *Nano Today*, 2007, **2**, 30–38.
26 N. S. Satarkar, D. Biswal and J. Z. Hilt, *Soft Matter*, 2010, **6**, 2364.
27 A. Z. Pich and H.-J. P. Adler, *Polym. Int.*, 2007, **56**, 291–307.
28 I. Berndt, J. S. Pedersen and W. Richtering, *Angew. Chem., Int. Ed.*, 2006, **45**, 1737–1741.
29 M. Karg, I. Pastoriza-Santos, B. Rodriguez-González, R. von Klitzing, S. Wellert and T. Hellweg, *Langmuir*, 2008, **24**, 6300–6306.
30 Y. Hertle and T. Hellweg, *J. Mater. Chem. B*, 2013, **1**, 5874.
31 I. Gorelikov, L. M. Field and E. Kumacheva, *J. Am. Chem. Soc.*, 2004, **126**, 15938–15939.
32 A. Garcia, M. Marquez, T. Cai, R. Rosario, Z. Hu, D. Gust, M. Hayes, S. A. Vail and C.-D. Park, *Langmuir*, 2007, **23**, 224–229.
33 L. Zhu, C. Zhao, J. Zhang and D. Gong, *RSC Adv.*, 2015, **5**, 84263–84268.
34 M. Richter, Y. Zakrevskyy, M. Eisele, N. Lomadze, S. Santer and R. v. Klitzing, *Polymer*, 2014, **55**, 6513–6518.
35 Y. Zakrevskyy, M. Richter, S. Zakrevska, N. Lomadze, R. von Klitzing and S. Santer, *Adv. Funct. Mater.*, 2012, **22**, 5000–5009.
36 K. Fan, M. Bradley and B. Vincent, *J. Colloid Interface Sci.*, 2012, **368**, 287–291.
37 M. Bradley, B. Vincent, N. Warren, J. Eastoe and A. Vesperinas, *Langmuir*, 2006, **22**, 101–105.
38 Y. Zakrevskyy, J. Roxlau, G. Brezesinski, N. Lomadze and S. Santer, *J. Chem. Phys.*, 2014, **140**, 044906.
39 A. M. Rumyantsev, S. Santer and E. Y. Kramarenko, *Macromolecules*, 2014, **47**, 5388–5399.
40 R. v. Klitzing, *J. Mater. Chem.*, 2010, **20**, 3502–3507.
41 A. Burmistrova, M. Richter, C. Uzum and R. v. Klitzing, *Colloid Polym. Sci.*, 2011, **289**, 613–624.
42 A. Burmistrova, M. Richter, M. Eisele, C. Üzüm and R. von Klitzing, *Polymers*, 2011, **3**, 1575–1590.
43 V. Vijayanathan, T. Thomas and T. J. Thomas, *Biochemistry*, 2002, **41**, 14085–14094.
44 A. Venancio-Marques, A. Bergen, C. Rossi-Gendron, S. Rudiuk and D. Baigl, *ACS Nano*, 2014, **8**, 3654–3663.
45 A. Kopyshev, C. J. Galvin, J. Genzer, N. Lomadze and S. Santer, *Polymer*, 2016, **98**, 421–428.
46 Marvin (MarvinSketch) was used for drawing, displaying and characterizing chemical structures, substructures and reactions, Marvin 6.1.3, 2013, ChemAxon (http://www.chemaxon.com).
47 Y. Zakrevskyy, E. Titov, N. Lomadze and S. Santer, *J. Chem. Phys.*, 2014, **141**, 164904.
48 Y. Zakrevskyy, A. Kopyshev, N. Lomadze, E. Morozova, L. Lysyakova, N. Kasyanenko and S. Santer, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **84**, 021909.
49 Y. Zakrevskyy, P. Cywinski, M. Cywinska, J. Paasche, N. Lomadze, O. Reich, H.-G. Löhmannsröben and S. Santer, *J. Chem. Phys.*, 2014, **140**, 044907.
50 A. R. Khokhlov, E. Y. Kramarenko, E. E. Makhaeva and S. G. Starodubtzev, *Die Makromol. Chemie, Theory Simulations*, 1992, **1**, 105–118.
51 A. R. Khokhlov, E. Y. Kramarenko, E. E. Makhaeva and S. G. Starodubtsev, *Macromolecules*, 1992, **25**, 4779–4783.
52 L. Yang, N. Takisawa, T. Hayashita and K. Shirahama, *J. Phys. Chem.*, 1995, **99**, 8799–8803.
53 H. Kang, B. Lee, J. Yoon and M. Yoon, *J. Colloid Interface Sci.*, 2000, **231**, 255–264.
54 T. Shang, K. A. Smith and T. A. Hatton, *Langmuir*, 2003, **19**, 10764–10773.
55 B. A. Cicciarelli, J. A. Elia, T. A. Hatton and K. A. Smith, *Langmuir*, 2007, **23**, 8323–8330.