# Photocontrolled dispersibility of colloidal silica by surface adsorption of a calix[4]resorcinarene having azobenzene groups

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A novel calix[4]resorcinarene (4-AzCRA) having four *p*-butylazobenzene residues attached to the upper rim of the cyclic framework has been prepared and subjected to adsorption on the surface of colloidal silica particles. The *trans–cis* photoisomerization of 4-AzCRA went almost to completion without being affected by the adsorption on the surface. UV irradiation of a homogeneous dispersion of surface-modified silica particles in cyclohexane enhanced the sedimentation owing to the increase in surface polarity, leading to the formation of porous precipitates. Subsequent visible light irradiation regenerated a dispersed state, displaying photocontrol of the reversible alternation between dispersed and aggregated states of the silica particles.

Organic photochromic compounds undergo reversible colour changes owing to their molecular structural modification upon light irradiation, accompanied by the alteration of their physical properties other than electronic absorption spectra, such as molecular shape, polarity, and so on. Photoinduced reversible changes have attracted extensive interest because of their applicability to versatile photoregulation of molecular systems by appropriate combination of photochromic molecules with various materials.[1] In these systems, photoactive molecules are reasonably referred to as 'commander molecules' since their photofunctionality does not arise from the spectroscopic modification in the visible range, but from triggering structural as well as orientational alteration of a number of molecules or residues surrounding the photoactive molecules which are referred to as 'soldier molecules'.[2] This kind of molecular system is essentially associated with molecular amplification, as discussed in our earlier paper.[2] One of the typical amplification systems generated by photosensitive commander molecules is the surface-assisted photoregulation of liquid crystal alignment by photochromic molecules which are localized at an uppermost surface of substrate plates.[3–5]

We have reported a novel approach to the surface-assisted dispersibility photocontrol of colloidal silica in non-polar solvents by chemical modification of a particle surface with a photochromic spirobenzopyran as a commander molecule.[6–8] The ring opening of a spiropyran to form a zwitterionic merocyanine structure brings about a decrease in the affinity between the particle surfaces and the non-polar solvent molecules, resulting in the aggregation of silica particles as soldier molecules which lead to sedimentation. The *trans*-to-*cis* photoisomerization of azobenzene is the other well known photochromism process and causes a marked change in the hydrophobicity of the molecule because of a large dipole moment developed across the azo bond. *cis*-Azobenzene has a larger dipole moment of 3.1 D in contrast to the much smaller value of *trans*-azobenzene (0.5 D or less).[9] Many reports have demonstrated that the properties of material can be photocontrolled by using polarity-changeable azobenzene molecules. In a solution of a polymer with azobenzene side chains, light-induced changes affect the solution viscosity,[10,11] the sol–gel transition,[12] solubility,[13] and so on. Therefore, it would be expected that the dispersibility of colloidal silica can be photoregulated by surface treatment with photochromic azobenzene molecules without any photoinduced charge generation. We report here that a dipole moment change of azobenzene units on a surface of colloidal particles results in the photocontrol of their dispersibility in non-polar solvents.

## Experimental

### Materials

**Silica particles.** Monodispersed silica particles were a gift from Tokuyama Corp.; particle diameter 150 nm, BET surface area 48 $m^2\ g^{-1}$.

**4-[4-(4-Butylphenylazo)phenoxy]butanal diethylacetal (4-Az).** A mixture of 1.50 g of 4-butyl-4′-hydroxyazobenzene, 1.10 g of 4-chlorobutanal diethylacetal and 3.0 g of powdered potassium carbonate in 23 ml of DMF was stirred for 8 h at 80 °C (Fig. 1). The reaction mixture was treated with 50 ml water and 50 ml hexane to separate the organic layer which was washed with water, followed by drying over magnesium sulfate. Evaporation of the solvent afforded a crystalline mass which was purified by chromatography on silica gel using a 9:1 mixture of hexane and ethyl acetate as eluent to give 1.79 g (76.1% yield) of orange plates, mp 38.5–40.5 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.95 [3H, t, $\mathrm{C}\mathit{H}_3(\mathrm{CH}_2)_3$], 1.24 (6H, t, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2\mathrm{O}$), 1.06 [4H, br, $\mathrm{CH}_3(\mathrm{C}\mathit{H}_2)_2\mathrm{CH}_2$], 1.90 [4H, br, $\mathrm{OCH}_2(\mathrm{C}\mathit{H}_2)_2\mathrm{CH}$], 2.70 (2H, t, $\mathrm{PhC}\mathit{H}_2\mathrm{CH}_2$), 3.57 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 4.06 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_2$), 4.65 (1H, t, CH), 6.9–8.0 (8H, m, Ar). Calc. for $C_{24}H_{34}N_2O_3$, C, 72.33; H, 8.60; N, 7.03%. Found: C, 71.62; H, 8.63; N, 6.94%.

**2,8,14,20-Tetrakis{3-[4-(4-butylphenylazo)phenoxy]propyl}-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (4-AzCRA).** A solution of 3.00 g of 4-Az and 0.83 g of resorcinol in 50 ml of 2-methoxyethanol containing 2 ml of conc. HCl was stirred for 8 h at 80 °C (Fig. 1). After standing at room temperature for one day, the precipitated orange crystals were collected by filtration, washed succesively with ethanol and water and finally with ethanol, and dried *in vacuo* to yield 1.28 g of crude product. Recrystallization from a mixed solvent of ethanol and chloroform gave 0.99 g of orange crystals which did not melt below 300 °C. MS [$M^+$H] 1666. $^1$H NMR ($CDCl_3$): $\delta$ 0.91 (12H, t, $CH_3$), 1.34 (8H, m, $CH_2$), 1.58 (8H, m, $CH_2$), 1.86 (8H, br s, $CH_2$), 2.47 (8H, br s, $CH_2$), 2.61 (8H, br t, $ArCH_2$), 4.07 (8H, br s, $ArOCH_2$), 4.45 (4H, br s, CH), 6.17 (4H, br s, Ar-$H^b$), 6.94 (8H, d, ArH of azobenzene), 7.19 (8H, d, ArH of azobenzene), 7.32 (4H, br s, Ar-$H^c$), 7.75 (16H, dd, ArH of azobenzene), 9.45 (4H, br s, OH), 9.71 (4H, br s, OH). Calc.

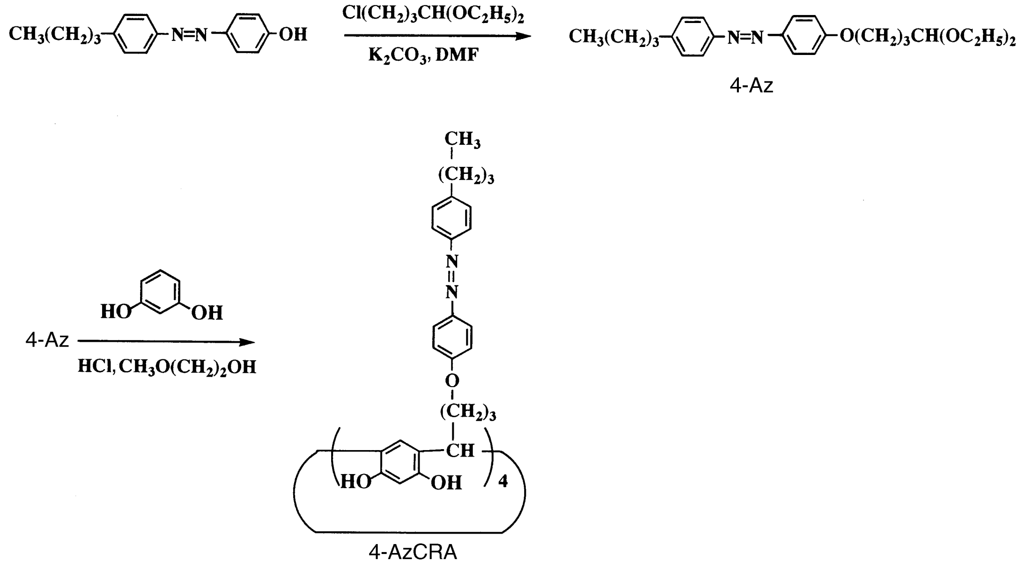

**Fig. 1** Synthetic pathways to 4-Az and 4-AzCRA

for $C_{104}H_{112}N_8O_{12}$: C, 74.97; H, 6.78; N, 6.73%. Found: C, 74.53; H, 6.62; N, 6.64%.

### Adsorption of azobenzenes

Silica particles with two different adsorbed amounts of 4-AzCRA were prepared (CRA-CS1 and CRA-CS2). The adsorption on the surface of silica particles was carried out as follows. To a dispersion of silica particles (0.50 g) in chloroform (10 ml) was added 55.4 mg (for CRA-CS1) or 300 mg (for CRA-CS2) of 4-AzCRA, and the mixture was stirred for 1 h at room temperature. After being centrifuged, the supernatant was discarded. The residual colloidal silica was washed repeatedly with toluene, then rinsed with cyclohexane until no UV absorption bands of 4-AzCRA were observed in the supernatant cyclohexane, and dried at 60 °C under vacuum for 8 h. The amount of adsorbed 4-AzCRA was determined by means of electronic absorption measurements in a cyclohexane dispersion using the absorption coefficient ($\varepsilon$) of 4-AzCRA: 113000 $dm^3\ mol^{-1}\ cm^{-1}$ at 350 nm. Average densities were estimated to be one 4-AzCRA molecule in a silica surface area of 21 $nm^2$ for CRA-CS1 and 9 nm for CRA-CS2, respectively. The densities are quite low for both cases, when compared with the cross-sectional area of an azobenzene moiety of 0.25 nm.

Silica particles with adsorbed 4-Az (Az-CS) were also prepared by the same procedure. The absorption spectra of Az-CS dispersed in cyclohexane were recorded using cyclohexane as a reference. The average density was estimated to be one 4-Az molecule in an area of 16 $nm^2$ using $\varepsilon = 30\,000\ dm^3\ mol^{-1}\ cm^{-1}$ for 4-Az.

### Photoirradiation

The photochromism experiments were carried out by irradiation with 365 nm and 440 nm light at room temperature using a Jasco CRM-FA irradiator equipped with a 2 kW xenon arc lamp with a monochromator. Absorption spectra were taken on a diode-array spectrometer (Hewlett Packard HP8452A).

### Sedimentation measurement

Surface-modified silica particles (200 mg) were dispersed in 100 ml of carbon tetrachloride or cyclohexane. A sample (4 ml) of each dispersion was placed in a cell (10 mm × 10 mm × 50 mm) and exposed to 365 nm light. The dispersion was shaken and subsequently placed in the cell holder of a spectrometer and allowed to stand at room temperature. The cell was exposed to the probe light through a circular window of diameter 7 mm, which was set on a cell wall 15 mm from the bottom of the cell as shown in Fig. 2, to measure the absorbance at an isosbestic point (304 nm) during the sedimentation.

### Physical measurements

SEM photographs were taken by a JEOL JSM-6400F.

## Results and Discussion

### Preparation and surface adsorption of a calixarene with azobenzene residues

We determined the following requirements for the optimization of a polarity change due to the geometrical photoisomerization of azobenzenes on a silica surface. First, the molecular axes of azobenzene molecules tethered to a silica surface orient in the same direction as much as possible, so that cancellation of the dipole moment of the chromophores is expected to be minimized. Secondly, an azobenzene chromophore is substituted with an alkyl residue at the *p*-position to enhance the hydrophobicity of the *trans* isomer. Considering these conditions, we noted the unique molecular structure of a crown conformer of calix[4]resorcinarene (CRA) which possesses eight phenolic OH groups on the lower rim of the cyclic skeleton, whereas four alkyl residues are attached to the upper rim.[14] Thus, CRA is a cyclic amphiphile and is expected to adsorb readily onto a polar silica surface through hydrogen bonds. In fact, CRA displays Langmuir-type adsorption from non-polar solvents, as revealed by our work which will be reported in detail elsewhere.[15] This adsorption mode fulfils one of the requirements concerning molecular orientation on a

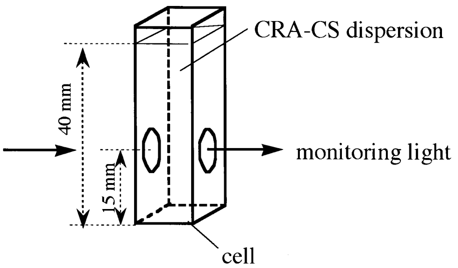

**Fig. 2** Cell for the photoinduced sedimentation of azo-modified colloidal silica

solid surface. The molecular design based on these consideration led us to prepare CRA having *p*-butylazobenzene residues at the upper rim (4AzCRA) (Fig. 1).

It has been reported that CRA is readily prepared by the condensation of resorcin with an aldehyde in ethanol containing hydrochloric acid.[16,17] The formation of a crown conformer needs prolonged heating[16] because the thermodyamically stable crown isomer is formed selectively as a result of acid-catalysed isomerization of the other conformers. The reaction of resorcin with an equimolar amount of an azobenzene acetal (4-Az) in ethanol in the presence of hydrochloric acid resulted in the precipitation of a product at an early stage of heating so that the transformation into the crown compound was inefficient. In order to enhance the solubility of the condensation product, the solvent was replaced by 2-methoxyethylethanol to carry out the reaction in a homogeneous solution at an elevated temperature. On cooling the reaction mixture, 4AzCRA was precipitated and purified conveniently by recrystallization. A spot of 4AzCRA on a silica gel TLC plate did not move at all with less polar eluent solvents, suggesting that the cyclic compound adsorbs firmly on a silica surface. Structural elucidation was carried out by means of NMR spectroscopic studies. The phenolic OH groups of 4AzCRA were separated at $\delta$ 9.45 and 9.71, respectively, because half of the OH groups are subjected to intramolecular hydrogen bonding to stabilize the cyclic structure.[17] The signals of two hydrogen atoms of benzene rings ($H^b$ and $H^c$ in the structural presentation) originated from resorcin are well separated and appear at $\delta$ 6.17 and 7.32, respectively, indicating that the molecule has $C_{4v}$ symmetry.

## Absorption spectra of 4-Az and 4-AzCRA

Monodispersed colloidal silica particles of diameter 150 nm were employed here because of their large surface area which will adsorb a sufficient amount of 4AzCRA, and because of the availability of a transparent dispersion in cyclohexane owing to good refractive index matching which enabled us to carry out spectroscopic analysis. The adsorption was performed in a chloroform solution because of good solubility of the calixarene, followed by washing out with toluene. For comparison, a monomer model, 4-Az, was also subjected to the adsorption experiment.

Fig. 3(*a*) and (*b*) show the absorption spectra of the colloidal silica particles modified with 4-Az and 4-AzCRA, respectively, which were dispersed in cyclohexane. The n–$\pi^*$ transitions of both 4-Az and 4-AzCRA adsorbed on silica particles are blue-shifted so that the absorption bands appear as a shoulder at *ca.* 420 nm. It should be noted that the n–$\pi^*$ absorbance of 4-AzCRA is smaller than that for 4-Az. The blue shift is ascribed to hydrogen bonding between the azo group and silanols and/or water molecules on the silica surfaces. As discussed in our previous papers, the increase in the n–$\pi^*$ absorbance can be reasonably explained in terms of the distortion of the azobenzene moiety which leads to the mixing of forbidden n orbitals with allowed p orbitals.[18,19] Therefore, 4-Az molecules on silica particles are intimately adsorbed on the silica surface through hydrogen bonds between the azo group and silanols, which cause the mixing of n orbitals of the azo group with $\pi$ orbitals. On the other hand, 4-AzCRA molecules adsorbed on a silica surface display no marked molecular deformation since it is very likely that the physical adsorption is mainly due to the hydrogen bonding between the phenolic OH groups, which are oriented in the same direction, and the silanol groups on the silica surface. A structural model of these two azobenzene chromophores on the surface of silica are shown in Fig. 4.

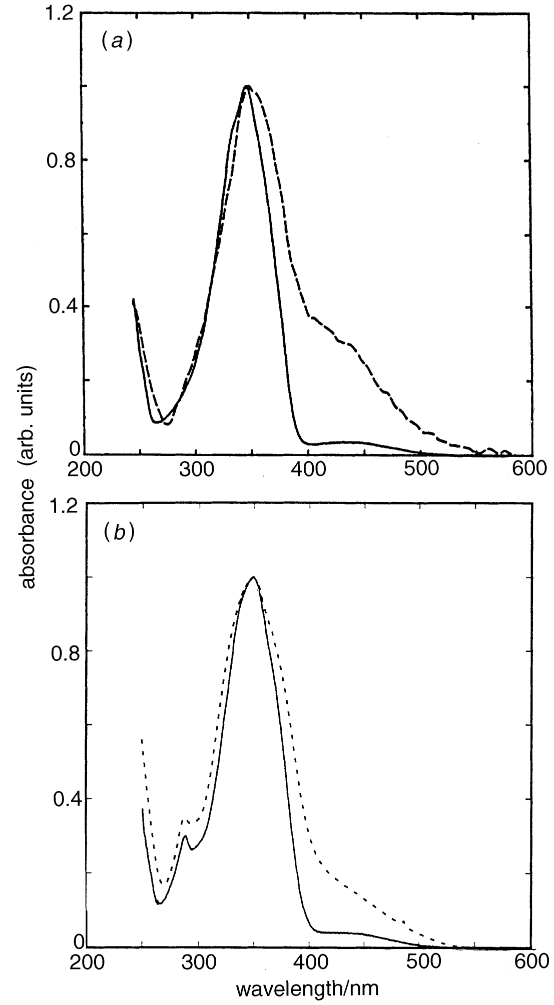

**Fig. 3** Absorption spectra of azobenzenes: (*a*) —, 4Az in a cyclohexane solution; ···, 4Az adsorbed on silica particles dispersed in cyclohexane; (*b*) —, 4AzCRA in a THF solution; ···, 4AzCRA adsorbed on silica particles dispersed in cyclohexane

## Photocontrolled aggregation of silica particles physisorbed with 4-AzCRA

In order to obtain a transparent dispersion, carbon tetrachloride ($n = 1.457$) and cyclohexane ($n = 1.426$) meet the requirements for refractive index matching with silica ($n \approx 1.45$) and are convenient for following the photochromic reaction of the modified silica particles spectroscopically. The desorption of 4-AzCRA from the silica surface was found to be negligible because essentially no UV absorption band due to the chromophore was detected in the supernatant obtained by centrifuging dispersions before and after the photoisomerization. As shown in Fig. 5, the *trans–cis* photoisomerization of 4-AzCRA adsorbed on silica particles went almost to completion without being affected by the surface adsorption. The appearance of isosbestic points indicates that the *trans*-to-*cis* photoisomerization proceeds without any side reactions.

The sedimentation behaviour of silica particles with different surface densities of 4AzCRA (CRA-CS1 and CRA-CS2) was determined by following the decrease in the absorbances at an isosbestic point (304 nm) appearing during the photochromic reaction of dispersions of the particles. A monitoring light was passed through a cell (*ca.* one-third of the way up) filled with the dispersion. Fig. 6 shows the absorbance changes of dispersions in non-polar solvents showing good refractive index matching before and after UV irradiation. In carbon tetrachloride, UV irradiation resulted in the enhancement of sedimentation of azo-modified silica particles while the sedimentation rate was influenced by the degree of surface coverage with 4AzCRA [Fig. 6(*a*) and (*b*)]. The slower rate for CRA-CS2 clearly reflects the stabilizing effect of surface 4AzCRA on the dispersion owing to its hydrophobicity.

Much more unequivocal results were obtained when silica

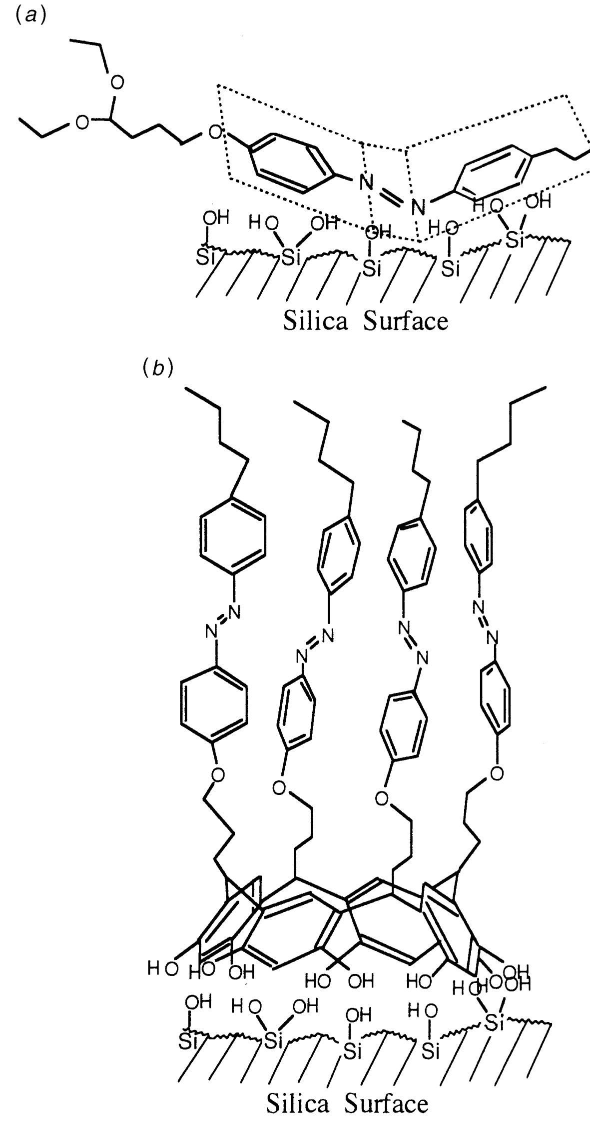

**Fig. 4** Illustrative representation of (*a*) 4Az and (*b*) 4AzCRA on a silica surface

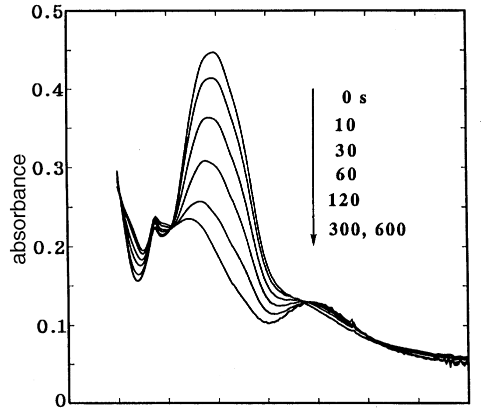

**Fig. 5** Changes in absorption spectra of a dispersion of silica particles adsorbing 4AzCRA during irradiation with 365 nm light at room temperature for the times indicated

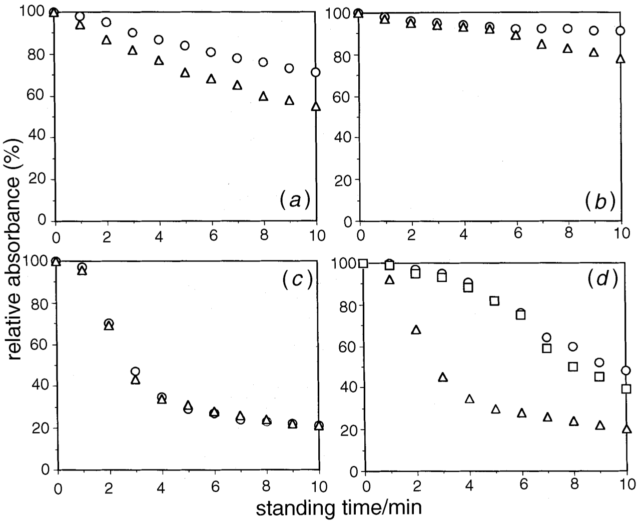

**Fig. 6** Sedimentation behaviour of colloidal silica adsorbing 4AzCRA: (*a*) CRA-CS1 in carbon tetrachloride; (*b*) CRA-CS2 in carbon tetrachloride; (*c*) CRA-CS1 in cyclohexane; (*d*) CRA-CS2 in cyclohexane. ○, Before UV irradiation; △, after UV irradiation; □, with subsequent visible light irradiation.

particles were dispersed in cyclohexane. Although the sedimentation took place relatively rapidly and was not affected by UV photoirradiation [Fig. 6(*c*)], the rate of sedimentation of CRA-CS2 was reduced owing to greater surface coverage with azobenzene. As shown in Fig. 6(*d*), the sedimentation is markedly accelerated by UV irradiation. The reversion of the *cis* to the *trans* form with 440 nm light irradiation regenerated a light-yellow dispersion after ultrasonical treatment, leading to sedimentation behaviour similar to that of the original dispersion. This implies that dispersion and precipitation are interchangeable by means of surface photoisomerization. It should be noted here that surface coverage with 4AzCRA is quite low, at 21 nm$^2$ and 9 nm$^2$ per 4AzCRA molecule for CRA-CS1 and

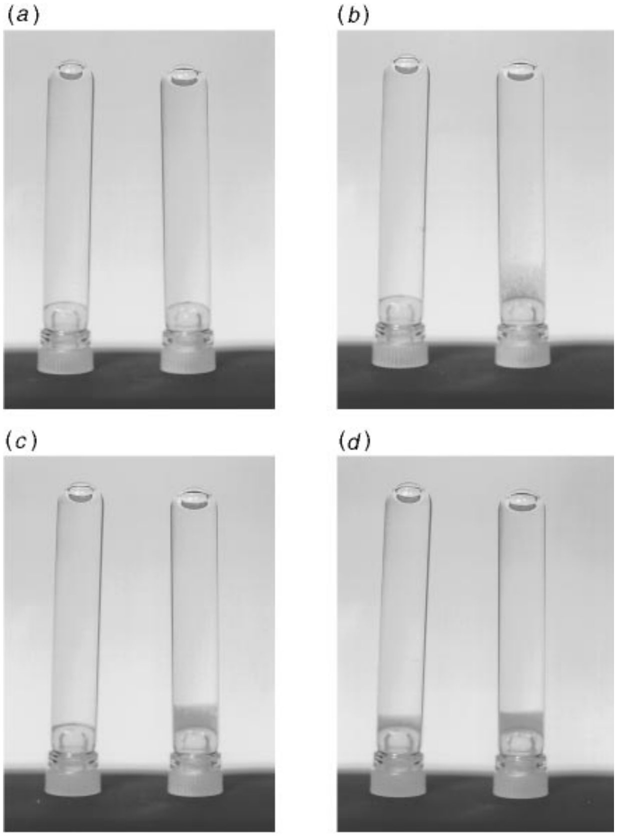

**Fig. 7** Pictures of a CRA-CS2 dispersion in cyclohexane (concentration: 2.0 g dm$^{-3}$) in microtubes (inner diameter 6 mm, length 50 mm): (*a*) 0 min standing; (*b*) 2 min standing; (*c*) 5 min standing; (*d*) 15 min standing. The right- and left-hand tubes in each picture are the dispersion with and without UV irradiation, respectively.

CRA-CS2, respectively. The base area of the cylindrical CRA skeleton is *ca.* 1.3 nm$^2$ according to a $\pi$–$A$ isotherm measurement on a water surface, being in line with that estimated with use of a space-filling molecular model.[20,21] In the case of CRA-CS1, such a low surface density of azobenzene displays no stabilizing effect on the dispersion so that the aggregation of particles occurs readily after ultrasonic treatment.

The different sedimentation behaviour of cyclohexane and carbon tetrachloride is interpreted as follows.[7] The sedimentation rate ($v$) of spherical particles of diameter $D$ is expressed by the Stokes equation:

$$v = \frac{(\rho - \rho_0)gD^2}{18\eta}$$

where $\rho$ and $\rho_0$ are the densities of the particles and the solvent (which has viscosity $\eta$), respectively, and $g$ is gravitational acceleration. The slow sedimentation in carbon tetrachloride ($\rho_0 = 1.584$ g cm$^{-3}$ at 25 °C) is brought about, at least partially, as a result of the smaller density difference ($\rho - \rho_0$) when compared with that for cyclohexane ($\rho_0 = 0.774$ g cm$^{-3}$ at 25 °C).

The photoinduced enhancement of particle sedimentation of CRA-CS2 is ascribable to the dramatic increase in the surface polarity owing to the conversion from *trans*-azobenzene to *cis*-azobenzene with more polar character. Closely related work has been reported on the UV induced precipitation of a polystyrene with azobenzene derivatives as pendant groups in cyclohexane, because of the decrease in the polymer–solvent interaction caused by the generation of polar pendant groups.[22,23] UV irradiation induces the change in surface polarity, which causes abrupt reduction of the interaction between the silica surface and the non-polar solvent molecules, resulting in an attractive force between the silica particles.

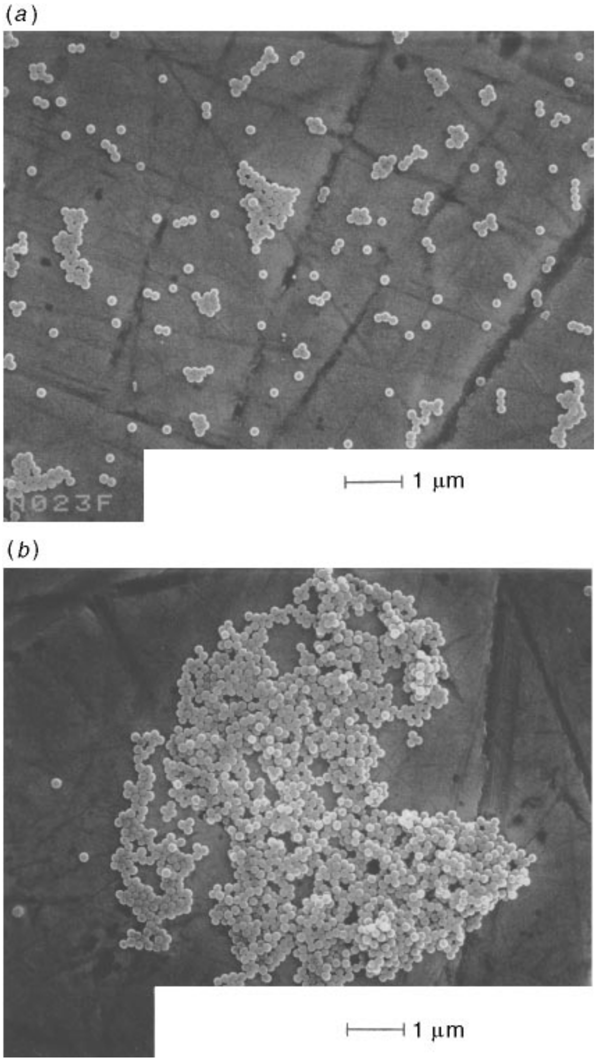

**Fig. 8** Scanning electron micrographs of CRA-CS2 (*a*) before and (*b*) after UV irradiation

Fig. 7 shows photographs of dispersions of CRA-CS2 in cyclohexane. The sedimentation of yellow particles was observed when a dispersion was exposed to UV light and subsequently kept standing at room temperature. After sedimentation was complete, the sample was irradiated with 440 nm light to reverse the *trans*-form to the *cis*-form. A homogeneous dispersion was obtained again with the aid of ultrasonic treatment, thereby displaying reversible alternation between dispersed and aggregated states of silica particles. Fig. 7 also shows that the volume of the *cis*-form precipitate is approximately double that of the *trans*-form precipitate after 15 min standing in the dark. This implies that the *cis*-form precipitate has a highly porous structure due to flocculation of the particles. This was confirmed by scanning electron microscopy of samples prepared by evaporating a solvent of the dispersion before and after UV irradiation. As shown in Fig. 8, after UV irradiation the particles form highly porous aggregates. Similar results have been obtained for silica particles, the surface of which was modified with a spiropyran.[5,6]

In summary, the photoisomerization of 4AzCRA adsorbed on silica particles triggers reversible dispersion–sedimentation cycles, just as in the case of the photochromic reaction of surface spiropyran, even though the surface density of azobenzene is low. This provides a novel system for molecular amplification of photonic information.

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