Supplementary Material (ESI) for Chemical Communications
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Electronic supplemental information for

Reversible photoisomerisability and particle size changes of azobenzene crystals mill-dispersed in water

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Preparation of aqueous dispersions of Az crystals

A suspension of Az crystals (150 mg) in 10 g of poly(vinyl alcohol) (PVA) (D. P. = 500) was placed in a zirconia vessel (20 mL) and milled with aid of a table-top plenary mill (Frisch; P-7) in the presence of zirconia beads (ca. 20 g) of a diameter of 0.1 mm at 600 rpm for 1 hr. After removing the beads by filtration, an aqueous suspension was subjected to centrifugation at 3500 rpm for 10 min to obtain a slightly turbid dispersion. Particle size distribution was recorded on a Nano-Z (Sysmex), and an averaged particle size was 252±2 nm.

Extraction of Az in aqueous dispersions with hexane

One mL of a dispersed solution of Az before or after photoirradiation was extracted with 5 mL of hexane in a sealed test tube by vigorous shaking, and a hexane layer was dried over magnesium sulfate after removing the aqueous solution and employed for measurements of electronic absorption spectra after appropriate dilution with hexane. Figure S1 shows absorption spectra of Az in an aqueous dispersion and a hexane extract of the dispersion. The concentration of Az was diluted five times to take absorption spectra.

Determination of water-solubility of Az

A suspension of about 50 mg of Az in 10 mL of deionized water was stirred gently overnight and filtered with a filter paper. A saturated concentration of Az in water was estimated by using absorbance of a filtrate of 0.349 at λ_{max} of 315 nm and molar absorption coefficient of 2.06 x 10^4 at 320 nm in a 1:1 (v/v) mixture of methanol and water.

Changes of first derivative spectra of Az during photoirradiation

Absorption spectra taken on a diode array spectrometer, a MultiSpec-1500 (Shimadzu) were

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converted into first derivative spectra. Figure S2 shows changes of derivative spectra of Az in a hexane solution during irradiation with 313 nm light, whereas Figure S3 displays changes of derivative spectra of Az in an aqueous dispersion upon exposure to 313 nm light and 435 nm light.

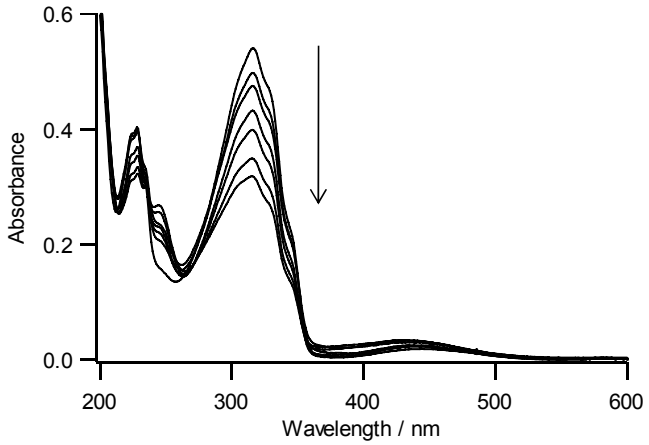

Figure S1 Absorption spectra of hexane solutions of hexane extracts of Az dispersed in water after exposure to 313 nm light for 0 sec, 20sec, 40 sec, 90sec, 180 sec, 720 sec and 1800 sec.

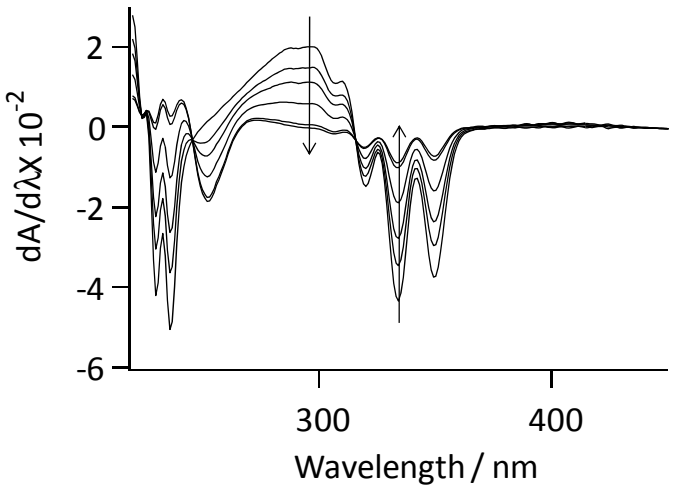

Figure S2 First derivative spectra of Az in hexane during irradiation with 313 nm light.

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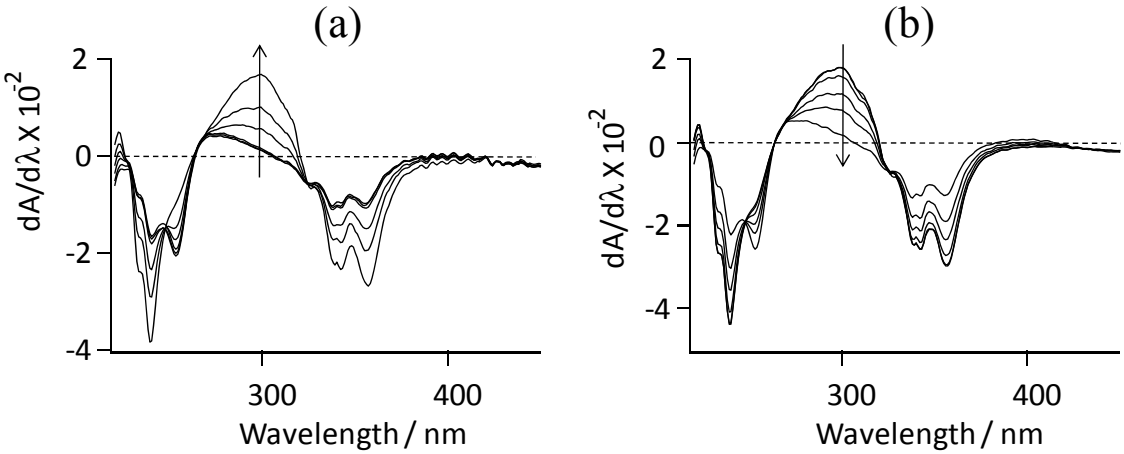

Figure S3 First derivative spectra of Az in an aqueous dispersion during irradiation (a) with 313 nmlight and (b) subsequently during irradiation with 435 nm light.