COMMUNICATION

Regio- and stereospecific [2+2] photocyclodimerization of a crown-containing butadienyl dye *via* cation-induced self-assembly in solution†

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Self-assembled pseudocyclic structures consisting of two molecules of a crown-containing butadienyl dye and two Mg²⁺ ions readily undergo regio- and stereospecific [2+2] photocycloaddition in MeCN to produce a single cyclobutane stereoisomer in almost quantitative yield.

Self-organization into supramolecular structures *via* noncovalent interactions such as hydrogen bonding, host–guest interactions, ion association or stacking interactions, makes it possible to control excited-state reactions of organic molecules.[1] In the early nineties we reported a dramatic effect of molecular self-assembly on the photochemistry of a styryl dye containing a 15-crown-5 ether fragment and a benzothiazole residue with 3-sulfonatopropyl *N*-substituent (dye **1**, Scheme 1).[2]
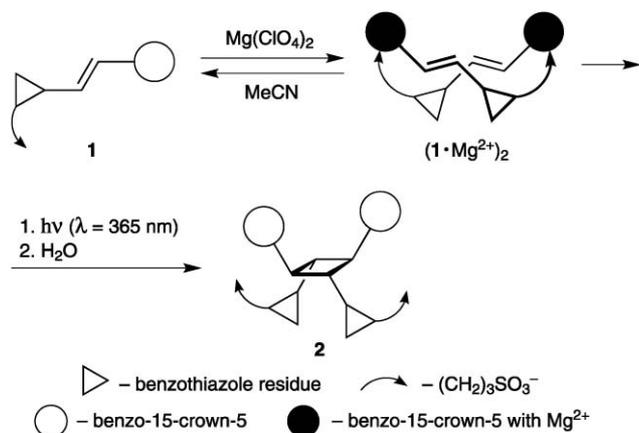
Scheme 1 Self-assembly into dimeric complexes leading to stereospecific [2+2] photocycloaddition of styryl dye **1**.

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† Electronic supplementary information (ESI) available: Absorption spectroscopy data for a cationic analogue of dye **5**; global analysis of spectrophotometric titration data (factor analysis, discussion on complexation stoichiometry, parameterized modelling of absorption spectra); molecular mechanics and DFT modelling of dimers (**5**·Mg²⁺)₂. See DOI: 10.1039/c0pp00227e

In aprotic solvents dye **1** binds Mg²⁺ ions to form pseudocyclic 2:2 complexes in which the sulfonate anion of one dye molecule coordinates with the metal cation located in the crown ether cavity of another and *vice versa*. The dye molecules in these complexes undergo selective *anti*-head-to-tail [2+2] photocycloaddition (PCA) to afford a single cyclobutane stereoisomer (**2**, Scheme 1). Irradiation at 365 nm led to almost quantitative conversion of dye **1** into cyclobutane **2**. In metal-free solutions dye **1** does not undergo PCA even at a relatively high concentration (~1 mM).

The effect of different structural factors on the cation-induced PCA of crown-containing styryl dyes has been studied.[3] In particular, it was found that changing to a 4-styrylquinolinium chromophore altered the PCA pattern (*syn*-head-to-tail *vs.* *anti*-head-to-tail).[3d]

Other supramolecular approaches that have been used to control intermolecular PCA of olefins in solution include duplex formation *via* hydrogen bonds,[4] dimerization within the cavities of γ-cyclodextrin,[5] cucurbit[8]uril[6] and calixarenes,[7] encapsulation within self-assembled coordination cages,[8] hydrogen bonding with molecular templates,[9] self-assembly into pseudorotaxane structures,[10] preorganization *via* multiple noncovalent interactions.[11] In a few cases supramolecular assistance to PCA provided almost quantitative conversion of an olefin into a single cyclobutane isomer.

In comparison with olefins, 1,3-butadienes can be involved in a broader spectrum of photochemical reactions.[12] This makes it more difficult to control their photochemical behaviour by supramolecular methods. It is known that topochemical PCA of butadienes can result not only in cyclobutanes[13] but also in [3]ladderanes through a stepwise process.[14] A few studies have been published on supramolecular control of the solid-state intermolecular PCA of butadienes. For instance, the photochemical syntheses of [3]ladderanes from butadienes were reported[15] in which proper molecular packing of the reactants were provided by weak noncovalent interactions. However, the potential of supramolecular chemistry with respect to controlling the solution-phase intermolecular PCA of 1,3-butadienes remains unexplored.

We assumed that for stereospecific PCA of two butadiene molecules to occur in solution, the reactant must be properly preorganized by means of relatively strong noncovalent interactions, such as two-centre ion pairing in complexes (**1**·Mg²⁺)₂.[16] To test this assumption we synthesized a butadiene analogue of styryl dye **1**, *viz.*, the crown-containing butadienyl dye **5** (Scheme 2).
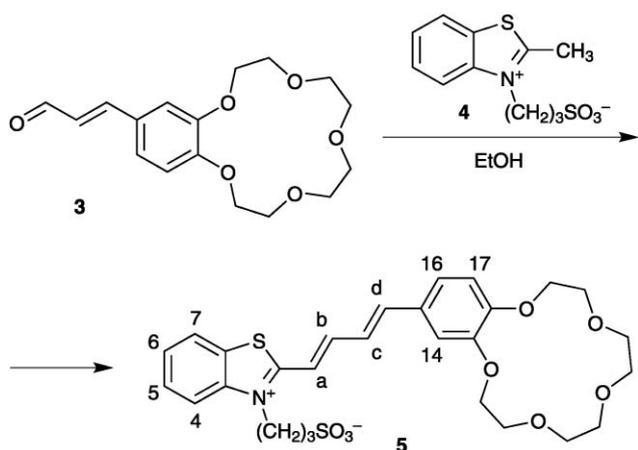
Scheme 2 Synthesis of butadienyl dye **5**.

Dye **5** was obtained in 43% yield by condensation of cinnamaldehyde **3** (ref. 17) with quaternary salt **4** (ref. 3b) on long-term heating in absolute ethanol. The structure assigned to **5** is confirmed by elemental analysis and ^{1}H NMR spectroscopy.‡

Fig. 1 shows the absorption spectra of dye **5** in MeCN/0.01 M Bu$_4$NClO$_4$ as a function of the concentration of added magnesium perchlorate. The strong hypsochromic effect observed on addition of Mg(ClO$_4$)$_2$ indicates Mg^{2+} coordination to the 15-crown-5 ether moiety of dye **5**.[18] The spectrum measured at a 20% excess of Mg(ClO$_4$)$_2$ over the dye (spectrum B in Fig. 1) is attributable to a fully complexed form of **5** because a subsequent increase in the metal salt concentration by an order of magnitude did not induce any spectral changes. This spectrum has a specific profile with a pronounced long-wavelength shoulder, which points to H-type aggregation of dye molecules.[19] To interpret this feature, we assume that dye **5**, similarly to styryl dye **1**, forms 2 : 2 complexes with Mg^{2+} *via* two-centre ion pairing. Factor analysis[20] showed that other complexes most likely make an insignificant contribution to the spectra represented in Fig. 1. This enabled us to assign spectrum B to the dimers (**5**·Mg^{2+})$_2$.
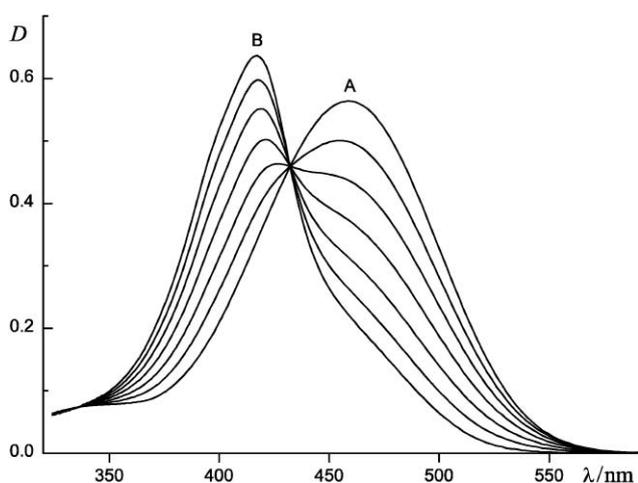
Fig. 1 Absorption spectra of dye **5** in MeCN/0.01 M Bu$_4$NClO$_4$ as a function of the concentration of added magnesium perchlorate (C_M): 1 cm cell, the concentration of **5** $C_D = 1.2 \times 10^{-5}$ M, $C_M/C_D = 0$ (A), 0.18, 0.36, 0.53, 0.71, 0.87 and 1.2 (B); spectrum B is assigned to complex (**5**·Mg^{2+})$_2$.

Table 1 Electronic absorption and emission spectroscopy data for dye **5** and complex (**5**·Mg^{2+})$_2$ in MeCN[21]

Compound	λ_{max}^{abs}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{max}^{em}/nm	φ_{lum}
5	459	47000	626	0.017
(**5**·Mg^{2+})$_2$	417	106000	587	0.0008

φ_{lum} – luminescence quantum yield.

The main absorption and luminescence characteristics of dye **5** and complex (**5**·Mg^{2+})$_2$ are listed in Table 1. Note that the formation of 2 : 2 complexes between **5** and Mg^{2+} leads not only to significant changes in the absorption spectrum but also to luminescence quenching.

Fig. 2 shows the effect of irradiation with low-intensity 436 nm light on the absorption spectra of (**5**·Mg^{2+})$_2$ in MeCN. The irradiation results in rapid disappearance of the long-wavelength absorption band associated with (**5**·Mg^{2+})$_2$. The product obtained after 15 min photolysis was tested for the presence of *Z* photoisomers of **5** using a four-stage procedure, as described previously for styryl dyes.[3d] This test showed that the photolysis led to complete consumption of dye **5**, presumably owing to very efficient PCA reaction between dye molecules in the dimeric complexes (**5**·Mg^{2+})$_2$. The PCA quantum yield was estimated to be about 0.3.
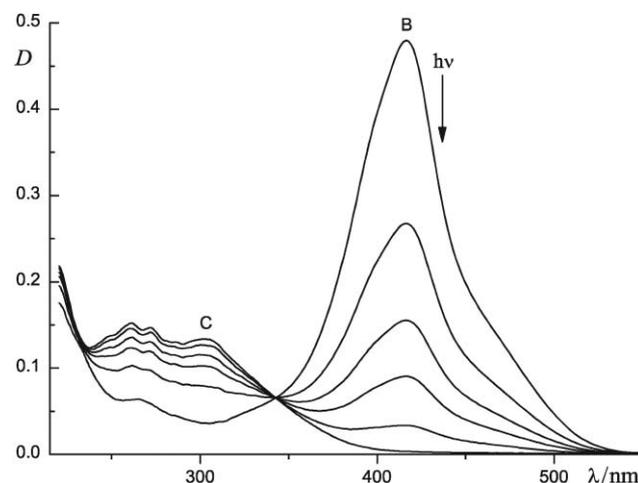
Fig. 2 Photolysis of dye **5** (9.1×10^{-6} M) in MeCN in the presence of Mg(ClO$_4$)$_2$ (1×10^{-4} M), as monitored by spectrophotometry: 1 cm cell, irradiation at 436 nm, light intensity 5×10^{14} cm^{-2} c^{-1}, irradiation time 0 (B), 0.5, 1.0, 1.5, 2.5 and 15 (C) min; spectrum C is assigned to complex **6**·(Mg^{2+})$_2$.

The photolysate obtained from (**5**·Mg^{2+})$_2$ was studied in a MeCN-d_3/D$_2$O solution by ^{1}H NMR spectroscopy.§ Water was added in order to preclude complex formation between the photolysate and Mg^{2+}. The ^{1}H NMR spectrum of the uncomplexed photolysate (Fig. 3) revealed that the PCA reaction in complexes (**5**·Mg^{2+})$_2$ occurs regio- and stereospecifically to afford a single cyclobutane isomer (cyclobutane *rtct*-**6**, Scheme 3). The photolysate contained no other detectable components, *i.e.*, the cyclobutane **6** is obtained from dye **5** in almost quantitative yield (>95%).

In the aromatic region, the ^{1}H NMR spectrum of **6** exhibits four signals from the ethylene protons H(a′)–H(d′) and a set of signals from the protons of two non-equivalent benzothiazole residues and two non-equivalent benzo-15-crown-5 ether fragments. The

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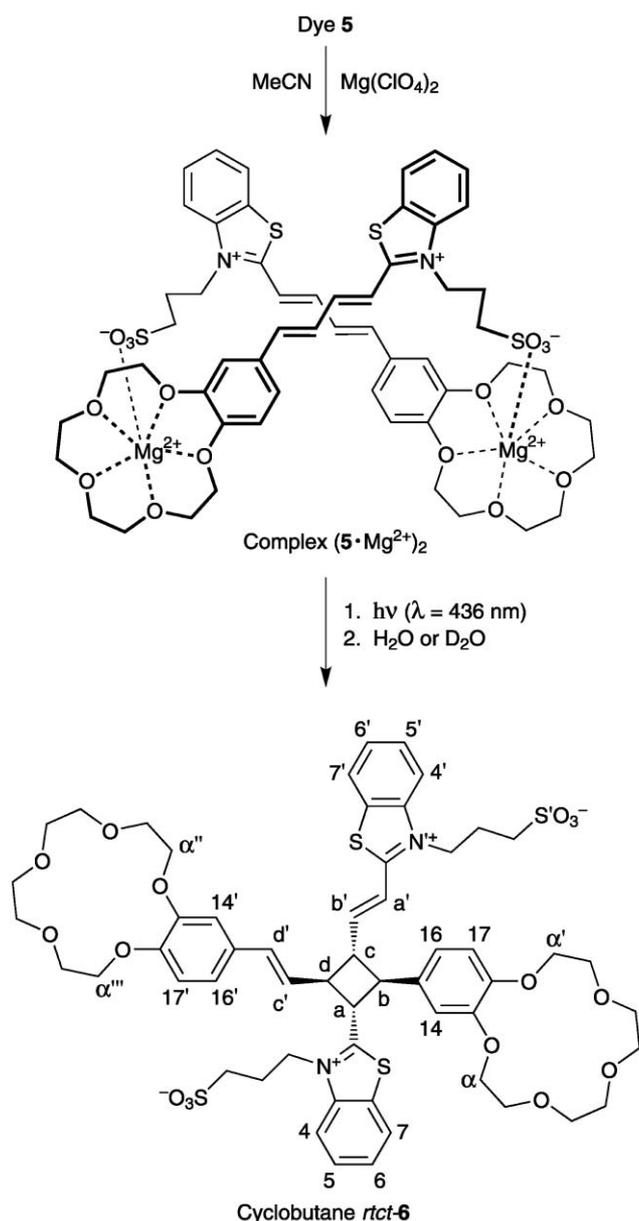
Scheme 3 Regio- and stereospecific synthesis of cyclobutane *rtct*-**6**.

Fig. 3 ^{1}H NMR spectrum of cyclobutane *rtct*-**6** in a MeCN-d_3/D$_2$O solution (10 : 1 v/v): (a) aromatic and (b) aliphatic regions.

protons of cyclobutane ring, H(a)–H(d), give four signals between 3.6 and 4.8 ppm.[22] These facts indicate that the substituents in the 1,2,3,4-tetrasubstituted cyclobutane **6** differ from each other in structure. The relative position of these substituents was derived from analysis of the 2D COSY and NOE spectra of **6**. The cyclobutane protons H(a) and H(b) show two triplet signals at 4.73 and 4.01 ppm with ^3J = 9.5 and 9.7 Hz, respectively. The triplet structure of these signals as well as the magnitudes of vicinal coupling constants are indicative of the *rtct*-configuration of the cyclobutane moiety in **6**.[3a–c] The structure assigned to cycloadduct **6** suggests an *anti*-head-to-tail alignment of the two dye molecules in the precursor complexes (**5**·Mg^{2+})$_2$ (Scheme 3). This alignment is confirmed by molecular mechanics and DFT calculations of (**5**·Mg^{2+})$_2$ (see ESI†).

In summary, the self-assembly of butadienyl dye **5** into 2 : 2 complexes with Mg^{2+} *via* two-centre ion paring in MeCN leads to

very efficient regio- and stereospecific [2+2] photocycloaddition affording cyclobutane *rtct*-**6** in almost quantitative yield. This result demonstrates for the first time that intermolecular PCA of 1,3-butadienes can be effectively controlled in solution by supramolecular methods. The approach we developed can be used to design novel supramolecular systems with high functionality.

Notes and references

(d, J = 8.6 Hz, 2H, H(4), H(4′)), 8.21 (d, J = 8.1 Hz, 1H, H(7′)), 8.30 (d, J = 8.2 Hz, 1H, H(7)).

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