[17] T. Carell, *Angew. Chem.* **1995**, *107*, 2697–2700; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2491–2494.
[18] G. B. Sancar, M. S. Jorns, G. Payne, D. J. Fluke, C. S. Rupert, A. Sancar, *J. Biol. Chem.* **1987**, *262*, 492–498.
[19] T. Carell, L. T. Burgdorf, L. M. Kundu, M. K. Cichon, *Curr. Opin. Chem. Biol.* **2001**, 491–498.
[20] J.-S. Taylor, *Acc. Chem. Res.* **1994**, *27*, 76–82.
[21] M. G. Debije, M. T. Milano, W. A. Bernhard, *Angew. Chem.* **1999**, *111*, 2926–2930; *Angew. Chem. Int. Ed.* **1999**, *38*, 2752–2755.
[22] A. Pezeshk, M. C. R. Symons, J. D. McClymont, *J. Phys. Chem.* **1996**, *100*, 18562–18566.
[23] A. Messer, K. Carpenter, K. Forzley, J. Buchanan, S. Yang, Y. Razskazovskii, Z. Cai, M. D. Sevilla, *J. Phys. Chem. B* **2000**, *104*, 1128–1136.
[24] Z. Cai, Z. Gu, M. D. Sevilla, *J. Phys. Chem. B* **2000**, *104*, 10406–10411.
[25] C. A. M. Seidel, A. Schulz, M. H. M. Sauer, *J. Phys. Chem.* **1996**, *100*, 5541–5553.
[26] S. Steenken, J. P. Telo, H. M. Novais, L. P. Candeias, *J. Am. Chem. Soc.* **1992**, *114*, 4701–4709.
[27] A. Schwögler, L. T. Burgdorf, T. Carell, *Angew. Chem.* **2000**, *112*, 4082–4085; *Angew. Chem. Int. Ed.* **2000**, *39*, 3918–3920.
[28] A. Schwögler, T. Carell, *Org. Lett.* **2000**, *2*, 1415–1418.
[29] S. Nadji, C.-I. Wang, J.-S. Taylor, *J. Am. Chem. Soc.* **1992**, *114*, 9266–9269.
[30] D. A. Vivic, D. T. Odom, M. E. Nunez, D. A. Gianolio, L. W. McLaughlin, J. K. Barton, *J. Am. Chem. Soc.* **2000**, *122*, 8603–8611.
[31] R. Epple, E.-U. Wallenborn, T. Carell, *J. Am. Chem. Soc.* **1997**, *119*, 7440–7451.
[32] R. Epple, T. Carell, *J. Am. Chem. Soc.* **1999**, *121*, 7318–7329.
[33] D. Ly, Y. Kan, B. Armitage, G. B. Schuster, *J. Am. Chem. Soc.* **1996**, *118*, 8747–8748.
[34] P. K. Bhattacharya, J. K. Barton, *J. Am. Chem. Soc.* **2001**, *123*, 8649–8656.
[35] K. J. Breslauer, *Methods Enzymol.* **1987**, *259*.
[36] J. Kemmink, R. Boelens, T. Koning, G. A. van der Marel, G. A. van Boom, R. Kaptein, *Nucleic Acids Res.* **1987**, *15*, 4645–4653.
[37] K. McAteer, Y. Jing, J. Kao, J.-S. Taylor, M. A. Kennedy, *J. Mol. Biol.* **1998**, *282*, 1013–1032.
[38] J.-S. Taylor, D. S. Garrett, I. A. Brockie, D. L. Svoboda, J. Tesler, *Biochemistry* **1990**, *29*, 8858–8866.
[39] J.-K. Kim, D. Patel, B.-S. Choi, *Photochem. Photobiol.* **1995**, *62*, 44–50.
[40] D. B. Hall, R. E. Holmlin, J. K. Barton, *Nature* **1996**, *382*, 731–735.
[41] E. Meggers, M. E. Michel-Beyerle, B. Giese, *J. Am. Chem. Soc.* **1998**, *120*, 12950–12955.
[42] K. Fukui, K. Tanaka, *Angew. Chem.* **1998**, *110*, 167–170; *Angew. Chem. Int. Ed.* **1998**, *37*, 157–161.
[43] S. Hess, M. Götz, W. B. Davis, M. E. Michel-Beyerle, *J. Am. Chem. Soc.* **2001**, *123*.
[44] M. P. Scannel, D. J. Fenick, S.-R. Yeh, D. E. Falvey, *J. Am. Chem. Soc.* **1997**, *119*, 1971–1977.
[45] H. Slaper, G. J. M. Velders, J. S. Daniel, F. R. deGruijl, J. C. van den Leun, *Nature* **1996**, *384*, 256–258.
[46] J.-S. Taylor, *J. Chem. Educ.* **1990**, *67*, 835–841.

A Highly Specific Ca^{2+}-Ion Sensor: Signaling by Exciton Interaction in a Rigid–Flexible–Rigid Bichromophoric "H" Foldamer[**]

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The design of chemosensors which are specific for the detection of biologically relevant cations, such as Na^+, K^+, Mg^{2+}, and Ca^{2+}, is a topic of considerable interest.[1] Selective detection of one of these cations in the presence of others, particularly the sensing of Ca^{2+} ions in the presence of Na^+, K^+, and Mg^{2+} ions, is a challenging task. Crown-ether based binding sites, which are integrated into the signaling units of organic chromophores, are the usual configuration of a chemosensor.[1b] A recognition event is signaled by perturbation in the absorption or emission properties of the chromophore, which are highly sensitive and easy to detect.[2] Even though a variety of crown-ether and related macrocycle-based chemosensors are known, the corresponding acyclic-polyether- (podand-) based sensors are relatively rare.[3] In most of the latter systems, the binding of a metal ion forces the attached donor and the acceptor moieties to come close enough to interact, thereby triggering either a charge-transfer, electron-transfer, or energy-transfer process, except in a recent report where conformational restrictions and charge transfer are invoked for a dual signaling of cation binding.[3h]

Herein we describe a different approach to the design of a highly specific Ca^{2+} ion sensor, which exploits the principle of a metal-ion induced conformational folding of a rigid–flexible–rigid bichromophore **3** (Scheme 1) to form an "H" foldamer,[4] thereby leading to dramatic perturbations in the optical properties as a result of exciton interactions. To our knowledge, this is the first report of a cation sensor based on the exciton interaction of a Ca^{2+} foldamer, in which the tethered chromophores are positioned akin to the "H" aggregate of an organic dye.

The rationale behind the design of the new sensor is based on the formation of "H" and "J" aggregates of cyanines and squaraines, which show distinctly different optical properties under appropriate conditions.[5, 6] According to the exciton theory of Kasha, the excited-state energy level of a monomeric dye splits into two upon aggregation, one level being lower and the other higher in energy than the monomer excited states.[7] Studies related to the aggregation of squar-

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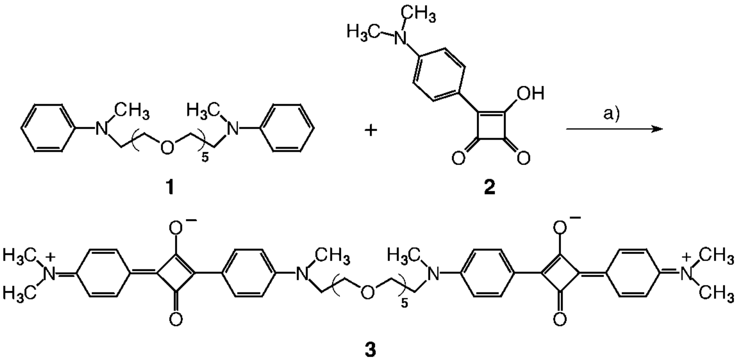
aine dyes show that they prefer to form "H" aggregates in the appropriate solvents.[6] In this context, Liang et al. have reported the exciton interaction in tethered squaraine dyes.[8] However, this property has never before been exploited in the design of sensors for the selective detection of metal ions. Although squaraine-dye-based fluoroionophores have been reported, none of them show any selectivity towards Ca^{2+} ions in the presence of Na^{+}, K^{+}, or Mg^{2+} ions.[9, 10]

A rigid–flexible–rigid bichromophore **3**, which contains a squaraine dye as the rigid signaling unit and an oxyethylene chain as the flexible recognition moiety, was chosen as the sensor (see Scheme 1 for synthetic procedure). The bisaniline derivative **1** was prepared according to standard procedures starting from *N*-methylaniline. The 3-cyclobuten-1,2-dione **2** was obtained by heating *N*,*N*-dimethylaniline under reflux with squaryl chloride.[11] Reaction of **1** and **2** in 2-propanol, in the presence of tributylorthoformate, gave the bichromophore **3** in 24% yield, which was characterized by spectral analyses.

In acetonitrile, the bichromophore **3** showed an absorption maximum at 630 nm with a weak shoulder around 570 nm (Figure 1a), and an emission maximum at 652 nm (Figure 1b). Interestingly, addition of Na^{+} and K^{+} ions did not alter the absorption or emission properties of **3**. In contrast, addition of Ca^{2+} ions to the acetonitrile solution of **3** (1.7×10^{-5} M) showed a color change visible to the naked eye, from light blue ($\lambda_{max} = 630$ nm) to an intense purple-blue ($\lambda_{max} = 552$ nm). The intensity of the absorption maximum at 630 nm decreased with the concomitant growth of a hypsochromically shifted band at 552 nm, through an isosbestic point at 580 nm. Apart from these changes, the fluorescence emission of **3**, when excited at 580 nm ($\lambda_{max} = 652$ nm, 1.7×10^{-5} M in CH$_3$CN, $\Phi_f = 0.03$), underwent considerable quenching upon addition of Ca^{2+} ions ($\Phi_f = 0.008$; Figure 1b). The Benesi–Hildebrand plot (not shown) was in agreement with a 1:1 complexation between **3** and Ca^{2+} ions. A stability constant (K_s) of 1.9×10^4 M^{-1} was estimated from this plot, which is reasonably high for an acyclic polyether. Addition of other metal ions, such as Mg^{2+}, Sr^{2+}, and Ba^{2+} showed only marginal changes to the absorption and emission of **3** when compared to those with Ca^{2+} ions. In a separate experiment, a mixture of a threefold excess each of Na^{+} and K^{+} ions was added to a solution of **3** in CH$_3$CN, which did not change its absorption or emission properties. Addition of Ca^{2+} ions to this solution caused the same kind of changes in the absorption and emission behavior as shown in Figure 1a and 1b, respectively. These observations show the unique ability of **3** to detect Ca^{2+} ions selectively, which is evident from Figure 2.



Scheme 1. Synthesis of the foldamer **3**; a) 2-propanol, tributylorthoformate, 80°C, 24%.

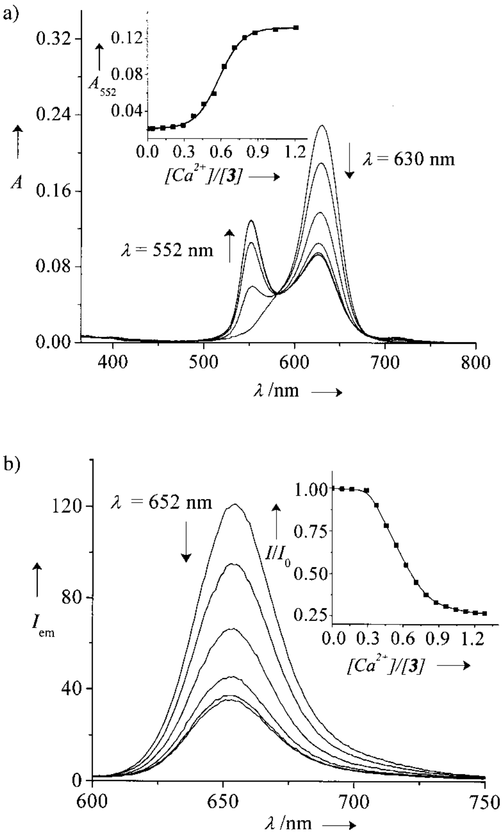


Figure 1. Changes in a) the absorption and b) emission ($\lambda_{ex} = 580$ nm) spectra of **3** upon addition of Ca^{2+} ions. Arrows indicate the changes that result from progressively increasing the concentration of Ca^{2+} ions relative to **3** in acetonitrile (**3**: Ca^{2+}; 1:0, 1:0.48, 1:0.65, 1:0.83, 1:1, 1:1.2). Insets: a) Variation of absorbance at 552 nm and b) fluorescence intensity of **3** with increasing Ca^{2+}-ion concentration.

The observed changes in the absorption and emission behavior of **3** in the presence of Ca^{2+} ions can be

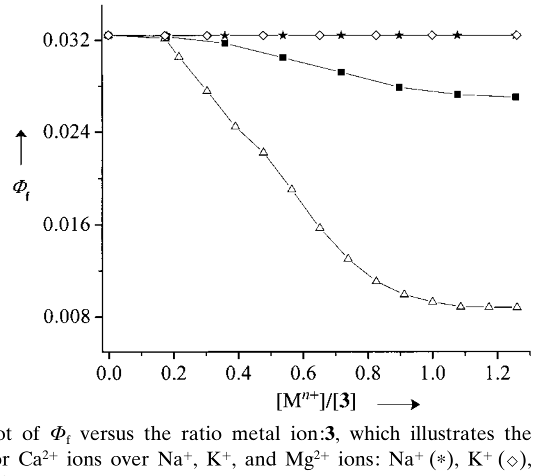


Figure 2. Plot of Φ_f versus the ratio metal ion:**3**, which illustrates the selectivity for Ca^{2+} ions over Na^{+}, K^{+}, and Mg^{2+} ions: Na^{+} (*), K^{+} (◇), Mg^{2+} (■), Ca^{2+} (△).

rationalized on the basis of the metal-ion-induced folding of the chromophore to form a face-to-face stacked foldamer **4**, which is analogous to the "H" aggregates of squaraine dyes (Figure 3). The blue-shifted band of **4** matches the absorption spectra of the "H" aggregates of *N,N*-dialkylaniline derived squaraine dyes.[12] The fluorescence of **4** is weaker than that of the unfolded **3**, because the internal conversion from an upper excited state into a lower one occurs immediately, and the emission from a lower excited state is theoretically forbidden (inset, Figure 3). Changes in the ^{1}H NMR spectrum of **3** before and after the addition of Ca^{2+} ions support the proposed folded conformation **4** (see Supporting Information). On the other hand, addition of Na^+ or K^+ ions did not cause any considerable change in the ^{1}H NMR spectrum of **3**. Unlike in macrocyclic crown ethers, the ionic size of the cations does not play a crucial role when they bind to noncyclic polyethers. The binding in such cases will depend mainly upon the charge density and the coordination number of the cation, which may be the reasons for the specific binding of Ca^{2+} ions with **3**.[3d]

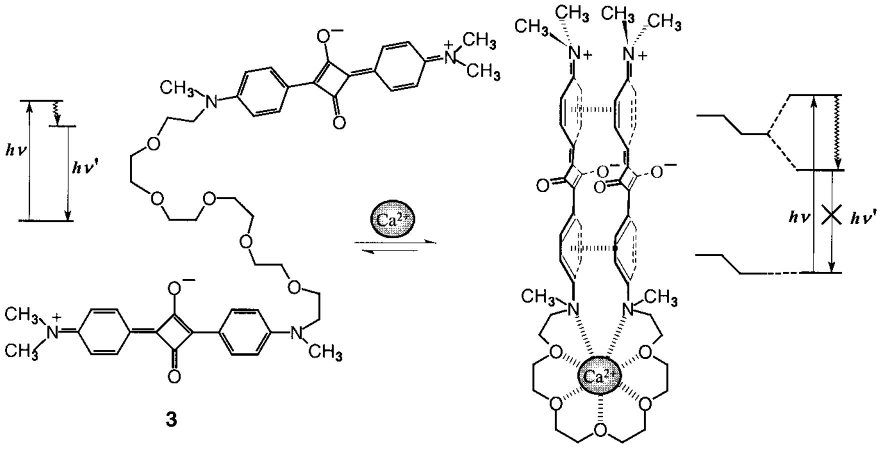
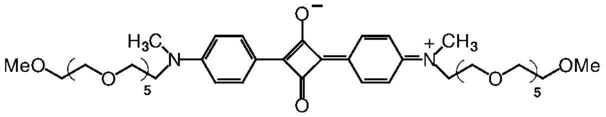


Figure 3. Ca^{2+}-ion-induced folding of **3** to the "H" foldamer **4**. Insets show the corresponding allowed and forbidden transitions in the two conformations.

To confirm the involvement of a folded conformation of the bichromophore **3** upon Ca^{2+}-ion binding, a monochromophore **5** of the flexible–rigid–flexible type was synthesized and mixed with various metal ions. None of the metal ions could produce any change to the absorption or emission properties of **5**.



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In conclusion, a Ca^{2+}-ion selective rigid–flexible–rigid type bichromophoric sensor is described, which works on the principle of Ca^{2+}-ion-steered folding, and the consequent exciton coupled signal transduction.

Experimental Section

Fluorescence quantum yields were determined in spectroscopic grade CH_3CN, by use of optically matching solutions of bis[4-(dimethylamino)-phenyl]squaraine in chloroform ($\Phi_f = 0.70$) as a standard, at an excitation wavelength of 580 nm. Metal-ion titrations were carried out by adding small volumes (1–5 μL) of the metal solutions (10^{-5} M in CH_3CN, 4 mL) in a quartz cuvette. The stability constant K_s was determined from absorption spectral changes using Equation (1), where ε_L and ε_{ML} are the molar extinction coefficients of the ligand and the complex, respectively. The quantity $A_0/(A_0 - A)$ is plotted versus $[M^{-1}]$, and the stability constant is then given by the ratio intercept:slope. K_s was also determined from the emission-spectral changes using Equation (2), where ϕ_L and ϕ_{ML} are the fluorescence quantum yields of the ligand and the complex, respectively. The quantity $I_F^0/(I_F^0 - I_F)$ is plotted versus $[M^{-1}]$, and the stability constant is then given by the ratio intercept:slope.

$$\frac{A_0}{A_0 - A} = \frac{\varepsilon_L}{\varepsilon_L - \varepsilon_{ML}}\left(\frac{1}{K_s\,[M]} + 1\right) \qquad (1)$$

$$\frac{I_F^0}{I_F^0 - I_F} = \frac{\varepsilon_L \phi_L}{\varepsilon_L \phi_L - \varepsilon_{ML} \phi_{ML}}\left(\frac{1}{K\,[M]} + 1\right) \qquad (2)$$

Bichromophore **3**: *N,N*-(dimethylaminophenyl)-4-hydroxy-3-cyclobuten-1,2-dione (**2**; 117 mg, 0.54 mmol) and tributylorthoformate (1 mL) were added to a 100-mL round-bottomed flask containing isopropanol (50 mL) and **1** (100 mg, 0.22 mmol). The reaction mixture was then heated to reflux for 20 h. The hot reaction mixture was filtered and the solid was washed with isopropanol until the filtrate was almost colorless. Column chromatography (chloroform:methanol 9:1) of the crude product on neutral alumina gave pure **3** (45 mg, 24%) as a green powder. M.p. 225–227°C; FTIR (KBr): $\tilde{\nu} = 1593$, 1401, 1367, 1182, 1122, 937, 830, 784.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 3.18$ (s, 18H, -NCH_3), 3.59–3.69 (m, 24H, -NCH_2 and -OCH_2), 6.74–6.79 (dd, 8H, $J = 1.2$, 9.2 Hz, aromatic), 8.33–8.38 ppm (dd, 8H, $J = 2.8$, 9.1 MHz, aromatic). MS (ESI, 4 kV): 859.7 [MH^+].

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[1] a) G. W. Gokel, *Crown Ethers and Cryptands*, CRC Press LLC, Boca Raton, **1991**, pp. 99–128; b) B. Valeur in *Topics in Fluorescence Spectroscopy, Vol. 4* (Ed.: J. R. Lakowicz), Plenum Press, New York, **1994**, pp. 21–48.

[2] a) L. Fabbrizzi, A. Poggi, *Chem. Soc. Rev.* **1995**, 197–202; b) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566; c) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537–2574; d) B. Valeur, I. Leray, *Coord. Chem. Rev.* **2000**, *205*, 3–40; e) A. P. de Silva, D. B. Fox, A. J. M. Huxley, T. S. Moody, *Coord. Chem. Rev.* **2000**, *205*, 41–57.

[3] a) J. P. Dix, F. Vögtle, *Chem. Ber.* **1980**, *113*, 457–470; b) H.-G. Löhr, F. Vögtle, *Chem. Ber.* **1985**, *118*, 914–921; c) Y. Kakizawa, T. Akita, H. Nakamura, *Chem. Lett.* **1993**, 1671–1674; d) Y. Suzuki, T. Morozumi, H. Nakamura, M. Shimomura, T. Hayashita, R. A. Bartsh, *J. Phys. Chem. B* **1998**, *102*, 7910–7917; e) T. Morozumi, T. Anada, H. Nakamura, *J. Phys. Chem. B* **2001**, *105*, 2923–2931; f) B. Valeur, J. Pouget, J. Bourson, M. Kaschke, N. P. Ernsting, *J. Phys. Chem.* **1992**, *96*, 6545–6549; g) F. Vögtle, E. Webber, *Angew. Chem.* **1979**, *91*, 813–837; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 753–776; h) J. V. Mello, N. S. Finney, *Angew. Chem.* **2001**, *113*, 1584–1586; *Angew. Chem. Int. Ed.* **2001**, *40*, 1536–1538.

[4] Foldamers are molecules designed to utilize noncovalent interactions to stabilize a well-defined conformation in solution. a) S. H. Gellman,

Acc. Chem. Res. **1998**, *31*, 173 – 180; b) In the present context, we use the term H foldamer to describe the folded conformation of a dimerlike bichromophore, the optical properties of which are analogous to the H aggregates of an organic dye.

[5] a) T. Katoh, Y. Inagaki, R. Okazaki, *J. Am. Chem. Soc.* **1998**, *120*, 3623 – 3628; b) L. Lu, R. J. Lachicotte, T. L. Penner, J. Perlstein, D. G. Whitten, *J. Am. Chem. Soc.* **1999**, *121*, 8146 – 8156; c) E. N. Ushakov, S. P. Gromov, O. A. Fedorova, Y. V. Pershina, M. V. Alfimov, F. Barigelletti, L. Flamigni, V. Balzani, *J. Phys. Chem. A* **1999**, *103*, 11188 – 11193; d) F. Würthner, S. Yao, *Angew. Chem.* **2000**, *112*, 2054 – 2057; *Angew. Chem. Int. Ed.* **2000**, *39*, 1978 – 1981; e) S. Zeena, K. G. Thomas, *J. Am. Chem. Soc.* **2001**, *123*, 7859 – 7865.

[6] a) K. Liang, K.-Y. Law, D. G. Whitten, *J. Phys. Chem.* **1994**, *98*, 13379 – 13384; b) H. Chen, M. S. Farahat, K.-Y. Law, D. G. Whitten, *J. Am. Chem. Soc.* **1996**, *118*, 2584 – 2594; c) E. Buncel, A. J. McKerrow, P. M. Kazmaier, *J. Chem. Soc. Chem. Commun.* **1992**, 1242 – 1243; d) S. Das, T. L. Thanulingam, K. G. Thomas, P. V. Kamat, M. V. George, *J. Phys. Chem.* **1993**, *97*, 13620 – 13624; e) S. Das, K. G. Thomas, K. J. Thomas, V. Madhavan, D. Liu, P. V. Kamat, M. V. George, *J. Phys. Chem.* **1996**, *100*, 17310 – 17315.

[7] The allowed and the forbidden transitions to the excitons are governed by the tilt angle (α) of the transition moments, with respect to the line of centers. When α is less than 54°, transition to the lowest excited level is allowed, which results in a bathochromically shifted absorption caused by head-to-tail J aggregates. If α is greater than 54°, transition to the highest excited level is favored, which leads to hypsochromically shifted absorption corresponding to the head-to-head H aggregates. M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371 – 392.

[8] K. Liang, M. S. Farahat, J. Perlstein, K.-Y. Law, D. G. Whitten, *J. Am. Chem. Soc.* **1997**, *119*, 830 – 831.

[9] a) S. Das, K. G. Thomas, K. J. Thomas, P. V. Kamat, M. V. George, *J. Phys. Chem.* **1994**, *98*, 9291 – 9296; b) K. G. Thomas, K. J. Thomas, S. Das, M. V. George, *Chem. Commun.* **1997**, 597 – 598; c) C. R. Chenthamarakshan, A. Ajayaghosh, *Tetrahedron Lett.* **1998**, *39*, 1795 – 1798; d) C. R. Chenthamarakshan, J. Eldo, A. Ajayaghosh, *Macromolecules*, **1999**, *32*, 5846 – 5851.

[10] a) U. Oguz, E. U. Akkaya, *Tetrahedron Lett.* **1997**, *38*, 4509 – 4512; b) U. Oguz, E. U. Akkaya, *Tetrahedron Lett.* **1998**, *39*, 5857 – 5860.

[11] D. Keil, H. Hartmann, *Dyes Pigm.* **2001**, *49*, 161 – 179.

[12] The aggregation of *N,N*,-dialkylaniline-based squaraine dyes is well-documented. They form blue-shifted H aggregates around 520 – 570 nm (ref. [6]).

Unidirectional Photoinduced Shuttling in a Rotaxane with a Symmetric Stilbene Dumbbell[**]

Carol A. Stanier, Sara J. Alderman, Tim D. W. Claridge, and Harry L. Anderson[*]

Dedicated to Professor Fraser Stoddart
on the occasion of his 60th birthday

A molecular machine is a molecular or supramolecular structure in which the components can be forced to move past each other, to achieve a functional outcome.[1–3] New insights into biological molecular motors[1] have stimulated a surge of activity towards the construction of artificial molecular machines.[2–11] Rotaxanes feature prominently among these prototypes, because they offer the possibility of long-range translational motion of a threaded macrocycle "shuttle" along the length of a dumbbell "rail track".[3–11] This shuttling motion can be driven chemically,[4] electrochemically,[5] or photochemically.[6–11] Use of light as the external stimulus or power source is particularly appealing because it can lead to a fast response without forming by-products. Light-driven translational motion has been achieved in rotaxanes using photoinduced electron transfer,[5, 6] excited-state changes in hydrogen-bonding,[7] and *E*/*Z* photoisomerization of azobenzene dumbbells.[8–11] Here we report the photochemical behavior of the azobenzene and stilbene rotaxanes shown in Scheme 1.[12] One of the stilbene rotaxanes ($\mathbf{3} \subset \alpha$-CD) exhibits unprecedented unidirectional shuttling, with the asymmetry of the cyclodextrin macrocycle determining its direction of motion on a symmetric dumbbell. Comparison of the *E*/*Z* photoisomerization of all four rotaxanes provides some general insights into the workings of a rudimentary molecular machine.

The *E*/*Z* photoisomerism of azobenzene rotaxane $\mathbf{1} \subset$ TM-α-CD, and its dumbbell analogue **1**, were investigated by monitoring the change in absorption during irradiation of the *E* isomers at 361 nm.[13] The dumbbell compound *E*-**1** underwent rapid photoisomerization to give a photostationary *E*/*Z* mixture characterized by the rise of a new absorption maximum at 255 nm, and a decrease in absorption at 361 nm; the photostationary equilibrium can be shifted back towards the *E* isomer by irradiation at 255 nm and displays excellent reversibility. In contrast, irradiation of rotaxane *E*-$\mathbf{1} \subset$ TM-α-CD under identical conditions results in no change in absorption. The cyclodextrin completely prevents $E \rightarrow Z$ photoisomerization. This may seem surprising, as

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