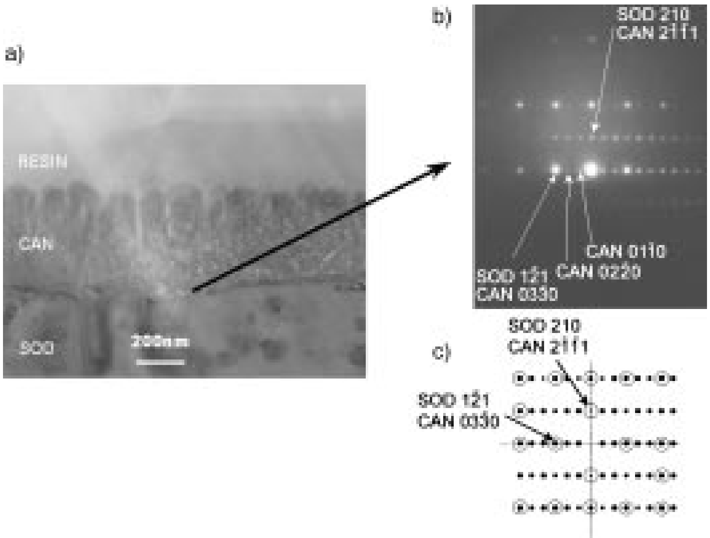

Figure 4. A TEM photograph and an SAED pattern of a cross section of a layer overgrown on a sodalite {111} substrate. a) The substrate is sodalite {111} prepared by mechanical polishing. The cancrinite crystals grow perpendicular to the sodalite {111} substrate. b) An SAED pattern recorded along the sodalite $[1\bar{2}5]$ zone axis. Spots due to cancrinite and sodalite are observed and indexed. c) A composite electron-diffraction simulation along the sodalite $[1\bar{2}5]$/cancrinite $[\bar{2}112]$ zone axis. The spots resulting from superposition of diffracted beams from sodalite and cancrinite crystal planes are circled.

been accomplished. To the best of our knowledge, these results are the first to show the feasibility of preparing in-plane and out-of-plane oriented zeolite films with channels perpendicular to the substrate. These composite structures suggest a pathway toward the fabrication of multidimensional, nanospatial networks.

Experimental Section

The synthesis consists of aging, preheating without sodalite substrates, and growth with sodalite substrates. The starting solution had the composition $34\,SiO_2{:}2\,Al{:}50\,NaNO_3{:}200\,NaOH{:}2000\,H_2O$. First, aluminum powder, 0.1 μm in size, was added to a concentrated solution of NaOH in a Teflon vessel and dissolved completely. In another Teflon vessel, SiO_2 (Cab-O-Sil M-5), $NaNO_3$, and the remaining NaOH and distilled water were mixed until the solution became transparent. Then the former solution was added to the latter, and the mixed clear solution was stirred for 2 h. All these procedures were carried out at 298 K. After this aging step, the solution was heated at 358 K for 18 h without sodalite substrates. Then, sodalite was introduced, and the mixture heated at 358 K for 48 h. The product was washed with distilled water and dried at 358 K. When the preheating phase was shortened by 2 h (Entry 2 in Table 1), heterogeneous nucleation on sodalite was enhanced, and a densely accumulated cancrinite layer was formed.

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Rotaxane-Encapsulation Enhances the Stability of an Azo Dye, in Solution and when Bonded to Cellulose[**]

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Tim D. W. Claridge, and Harry L. Anderson[*]

The groups of Cram and Warmuth have shown that exotic high-energy intermediates such as cyclobutadiene, *ortho*-benzyne, and cycloheptatetraene can be stabilized by encapsulation inside calixarene-based cages.[1] These results inspired us to attempt to encapsulate and stabilize more mundane species such as dyes[2] and conjugated polymers[3] by synthesizing rotaxanes[4] in which the reactive π system of the dye or polymer is protected inside the cavity of a macrocycle. We have previously reported the synthesis of azo dye rotaxanes;[2a–c, 5] however, two key questions remained unanswered: a) Does encapsulation improve the longevity of the azo chromophore? b) Does encapsulation detrimentally prevent the dye from binding to surfaces? Here we address these issues by reporting an efficient synthesis of a

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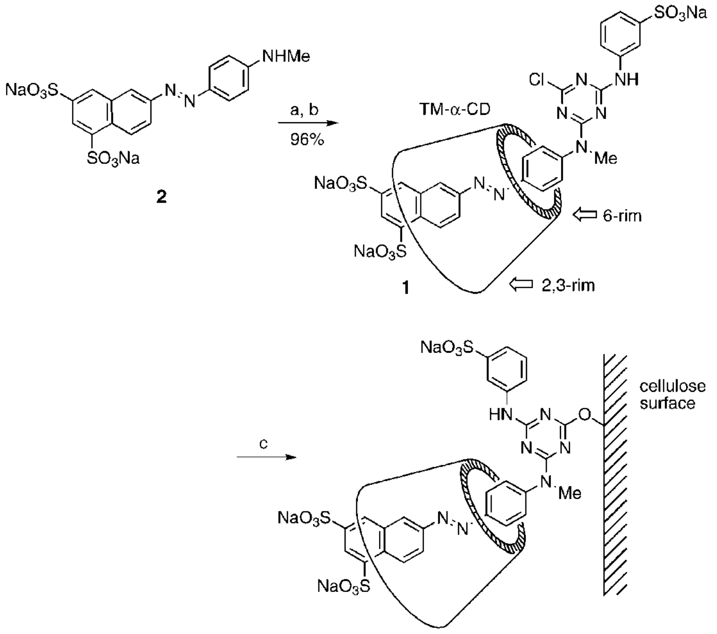
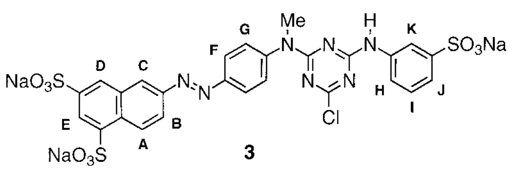
chlorotriazine-functionalized azo dye rotaxane. Encapsulation of this azo dye dramatically increases its stability towards bleaching, and does not prevent it from being covalently attached to cotton cloth (cellulose).

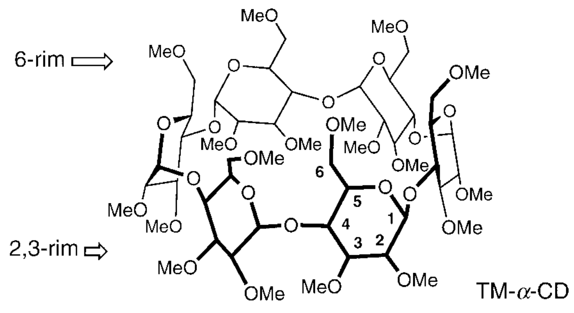
It is often desirable to covalently attach dyes to solid substrates, and this is commonly achieved by reacting an amine-substituted dye with 2,4,6-trichloro-1,3,5-triazine to give a chlorotriazine-functionalized "reactive dye" which couples with nucleophilic surface groups.[6] This chlorotriazine chemistry works well in water, so it is compatible with the use of hydrophobic binding to direct rotaxane formation.[7] The reactive dye rotaxane **1** was synthesized from amine **2** as shown in Scheme 1; the free reactive dye **3** was prepared by the same procedure in the absence of cyclodextrin. Compounds **1** and **3** are bright yellow, with λ_{max} in water at 364 and 350 nm, respectively. A simple dichlorotriazine end group would have been bulky enough to prevent the cyclodextrin from slipping off, but dichlorotriazines are hydrolytically unstable, so we displaced one of the chlorine atoms with 3-aminobenzenesulfonate to facilitate isolation and characterization. The remaining chlorine in **1** and **3** is stable to hydrolysis under neutral conditions, but reacts with cellulose at pH 10.



Scheme 1. Synthesis of rotaxane **1** and its covalent attachment to cellulose. a) TM-α-CD, $C_3N_3Cl_3$, H_2O, 0 °C, pH 6.5; b) 3-aminobenzenesulfonic acid, H_2O, 35 °C, pH 7.6; c) mercerized cotton, H_2O, 20 mM **1**, 0.7 M NaCl, 85 °C, pH 10, 24 h.



We used hexakis(2,3,6-tri-*O*-methyl)-α-cyclodextrin (TM-α-CD) in the synthesis of **1** to prevent coupling between the chlorotriazine and hydroxy groups on the macrocycle. Methylation also extends the cavity,[8] further shielding the encapsulated chromophore. TM-α-CD has the added benefit of binding extremely strongly to **2**,[9] enabling the rotaxane to be prepared in quantitative yield without using a large excess of the cyclodextrin. Analytical thin-layer chromatography shows no sign of the free dye **3**, or any other colored byproducts, in the crude reaction mixture, and rotaxane **1** was isolated in 96 % yield on a 1.5-g scale. A further advantage of the permethylated cyclodextrin is that excess TM-α-CD is readily removed from the reaction mixture by extraction into chloroform.



The conical shape of TM-α-CD results in the possibility of two stereoisomers for rotaxanes such as **1**, however in this case the rotaxane is formed as a single isomer[10] (as shown by its sharp, well-resolved ^1H and ^{13}C NMR spectra, in both D_2O and [D_6]DMSO). COSY and NOESY spectra were used to assign the ^1H NMR spectrum in D_2O and to determine the three-dimensional geometry. The observation of NOEs from H_D, on the naphthalene unit, to H3 and OMe3, on the CD, and from H_E to OMe3 (Figure 1) proves that the wide 2,3-rim of the CD is over the naphthalene unit, whereas the NOEs from $H_{F/G}$ to OMe6, H6, H6′, and H5 show that the narrow 6-rim is over the *para*-phenylene unit, as depicted in Scheme 1. No NOEs are observed from OMe2 to the aromatic protons because these six methoxy groups are directed away from the cavity, as noted by Harata et al.[8] A space-filling representation of the energy-minimized structure of **1** (Figure 2) shows that the azo region of the chromophore is masked by the cyclodextrin.

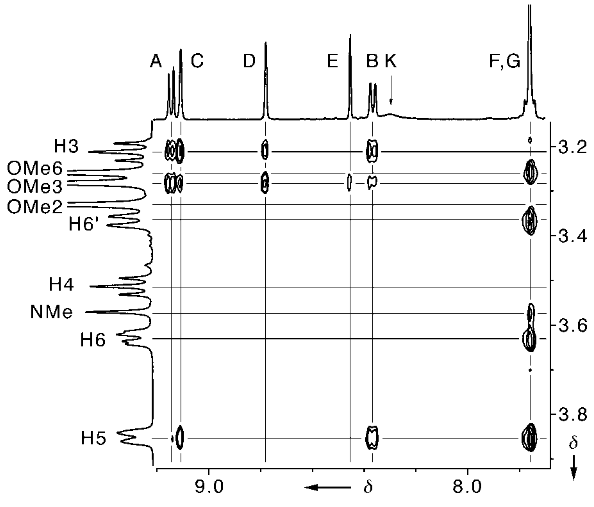


Figure 1. Part of the NOESY spectrum of **1** (500 MHz, D_2O, 298 K, 300 ms mixing time; all NOEs are negative).

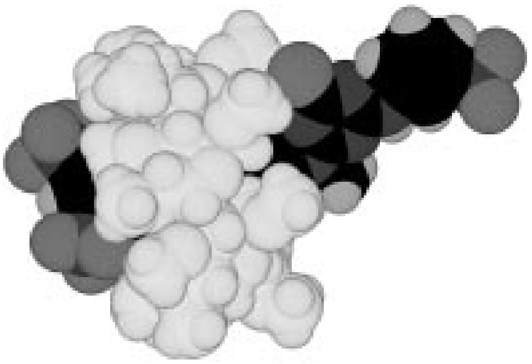


Figure 2. Energy-minimized structure (MM2 force field, CACHe 4.1.1) of rotaxane **1** (same orientation as in Scheme 1, with TM-α-CD pale gray).

The reactivity of rotaxane **1**, and the analogous free dye **3**, towards reductive bleaching was investigated by using aqueous sodium dithionite. This reagent bleaches azo dyes by reducing the azo link first to a hydrazine, then to two amine units.[11] Test tube experiments immediately showed that solutions of the free dye **3** are rapidly bleached by dithionite, whereas the rotaxane **1** is unaffected. The rates of reaction were compared by monitoring the bleaching of solutions of **1** and **3** in UV cuvettes, giving the data plotted in Figure 3. The free dye is essentially destroyed after 15 min, whereas the rotaxane retains 90 % of its absorption even after 9 h. It is difficult to estimate the rate of bleaching for **1** because it is so slow, and the dithionite decomposes before it reacts with the rotaxane. From the initial rates, **1** appears to be more than 100 times less reactive than **3**. We also tested the reactivity of both dyes towards oxidative bleaching with hydrogen peroxide in the presence of catalytic iron(II) sulfate, a mixture known as Fenton's reagent[12] (see decay curves in the Supporting Information). An orange intermediate is observed in both cases (probably an azoxide), followed by complete destruction of the chromophore. The free dye **3** gives an intense coloration after 10 min and is 90 % bleached after 50 min, whereas the rotaxane **1** shows only a slight rise in absorption, and is 90 % bleached after 6 h.

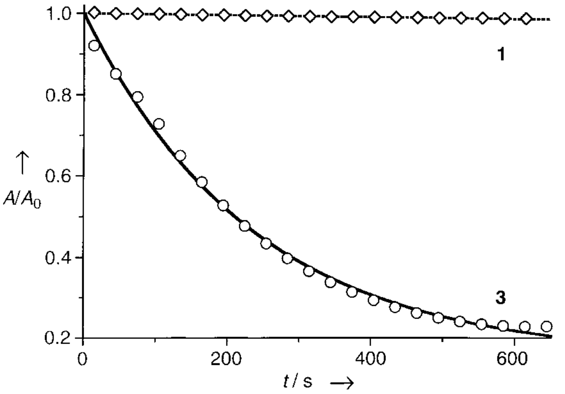


Figure 3. Reductive bleaching of **1** and **3** with aqueous sodium dithionite at 25 °C fitted to pseudo first-order decay curves with $k = 4.2 \times 10^{-3}$ and $2.3 \times 10^{-5}\,\mathrm{s}^{-1}$, respectively; A/A_0 is the normalized absorption at 500 nm; initial concentration of **1** and **3**: 0.1 mM; 0.5 M $Na_2S_2O_4$.

Samples of mercerized cotton were dyed yellow with aqueous solutions of compounds **1** and **3**, whereas no permanent coloration was produced by the nonreactive dye **2**, demonstrating that **1** and **3** bind covalently to cellulose. When cotton is dyed with **1** and **3** under identical conditions, the rotaxane gives a paler color than the free dye. The TM-α-CD evidently hinders coupling to the chlorotriazine, but this is a minor effect, and is easily compensated by using a more concentrated solution of the rotaxane, as illustrated by the photographs of cotton dyed with **1** (25 mM) and **3** (18 mM) in Figures 4a top and bottom, respectively. Images b–e in Figure 4 show the effect of bleaching both samples with sodium dithionite for increasing lengths of time: The sample dyed with **3** is almost completely bleached after 1 h, whereas that dyed with **1** is only slightly paler after 20 h. Treatment of similar cotton samples with Fenton's reagent resulted in a brown coloration of the cloth dyed with **3** after about 1 h, whereas that dyed with **1** was almost unaffected. Light-stability tests were carried out on a commercial fadeometer and showed that the cellulose-bound free dye underwent photo-bleaching about ten times faster than the cellulose-bound rotaxane.[13]

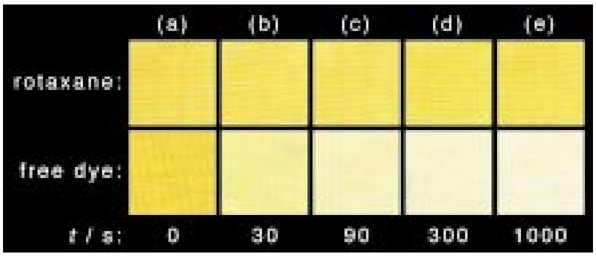


Figure 4. Photographs of cotton samples dyed with rotaxane **1** (top) and free dye **3** (bottom), before (a) and after different times *t* of bleaching with $Na_2S_2O_4$ (1 M): b) $t = 30$, c) $t = 90$, d) $t = 300$, e) $t = 1000$ s.

The synthesis of a reactive azo dye rotaxane as a single isomer in quantitative yield on a gram scale and the demonstration that this rotaxane exhibits dramatically enhanced stability towards reductive bleaching, oxidative bleaching and photo-bleaching suggest that rotaxane-encapsulated dyes may have potential applications in areas where chromophore degradation needs to be prevented.

Experimental Section

1: Crushed ice (5 g) was added to a rapidly stirred solution of 2,4,6-trichloro-1,3,5-triazine (154 mg, 0.833 mmol) in acetone (5 mL). The resulting fine suspension was added dropwise to a solution of **2** (380 mg, 0.817 mmol) and TM-α-CD (1.16 g, 0.95 mmol) in water (50 mL) at 0 °C, while maintaining the pH at 6.5 (using HCl and $NaHCO_3$). After the pH of the solution ceased to fall the mixture was stirred for 20 min, adjusted to pH 7.6 and filtered while cold. A solution of sodium 3-aminobenzenesulfonate (163 mg, 0.833 mmol) in water (5 mL) was added to the reaction mixture, then the temperature was taken to 35 °C for 1 h, while the pH was maintained at 7.6. The mixture was washed with chloroform (5 × 50 mL), ultrafiltered in water (1.5 L) for 17 h using a membrane with a nominal molecular weight cut-off of 1000 (YM1, regenerated cellulose, from Millipore Ltd.), then evaporated to dryness to yield rotaxane **1** as an orange solid (1.58 g, 96 %). ^1H NMR (500 MHz, D_2O): $\delta = 9.12$ (d, $J = 9$ Hz, 1 H), 9.08 (d, $J = 2$ Hz, 1 H), 8.76 (d, $J = 1$ Hz, 1 H), 8.44 (d, $J = 1$ Hz, 1 H), 8.35 (dd, $J' = 9$, $J'' = 2$ Hz, 1 H), 8.28 (br s, 1 H), 7.73 (AA'BB' q, 4 H), 7.57 (d, $J=7$ Hz, 1H), 7.48 (d, $J=7$ Hz, 1H), 7.40 (t, $J=7$ Hz, 1H), 5.00 (d, $J=3$ Hz, 6H), 3.83 (d, $J=9$ Hz, 6H), 3.61 (dd, $J'=10$, $J''=3$ Hz, 6H), 3.52 (s, 3H), 3.49 (t, $J=10$ Hz, 6H), 3.34 (d, $J=10$ Hz, 6H), 3.31 (s, 18H), 3.26 (s, 18H), 3.24 (s, 18H), 3.19 (t, $J=10$ Hz, 6H), 3.01 (dd, $J'=10$, $J''=3$ Hz, 6H); ^{13}C NMR (125 MHz, D_2O): $\delta=169.1$, 165.4, 164.0, 150.7, 150.5, 147.7, 143.8, 141.8, 141.5, 138.5, 133.9, 133.1, 131.7, 129.94, 129.93, 129.7, 128.9, 128.1, 124.9, 123.7, 121.3, 118.5, 117.4, 100.0, 82.4, 81.4, 81.1, 71.4, 71.1, 62.5, 59.0, 57.6, 39.1; UV/Vis (H_2O): $\lambda_{max}=364$ nm, $\lg\varepsilon=4.3$; ES-MS (negative): m/z: 964.2 [$M^{3-}+Na^+$].

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[9] UV/Vis titrations in water at 298 K showed that the complex **2**·TM-α-CD has a stability constant of $(5\pm1)\times10^5\,\text{M}^{-1}$ compared to only $(1.1\pm0.1)\times10^4\,\text{M}^{-1}$ for **2**·α-CD. It is difficult to obtain an accurate value of K_1 for **2**·TM-α-CD because a weak complex **2**·2TM-α-CD is also formed, $K_2\approx100\,\text{M}^{-1}$. For other work on the stability of azo dye CD complexes, see: N. Yoshida, *J. Chem. Soc. Perkin Trans. 2* **1995**, 2249–2256.

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[13] Light-fastness was measured in conformance with International Standard ISO 105-B02 in a Xenotest 150 fadeometer, using a xenon arc lamp to mimic daylight. The degree of fading was assessed against ISO blue wool standards, irradiated simultaneously. Cotton samples dyed with rotaxane **1** had a light-fastness rating of 5, whereas those dyes with free dye **3** had a rating of 3–4.

2-Pyridyldimethylsilyl as a Removable Hydrophilic Group in Aqueous Diels–Alder Reactions**

Kenichiro Itami, Toshiki Nokami, and
Jun-ichi Yoshida*

During the last two decades water has been rediscovered as a most intriguing medium for organic synthesis.[1] However, the execution of organic reactions in water is not straightforward since many organic compounds, reagents, and catalysts are insoluble or unstable in it. Therefore, many of the reported aqueous organic reactions have had to rely on the use of organic co-solvents at the expense of the many inherent advantages and unique properties of water, such as hydrophobic effects, hydrogen-bonding interactions, and high polarity.[1]

During the course of our study on the development of multifunctional phase tags for solution-phase synthesis it was found that organic molecules bearing the 2-pyridyldimethylsilyl (2-PyMe$_2$Si) group are miscible with water when HCl is added.[2, 3] Molecular aggregation seems to be involved in their dissolution so as to minimize the energetically unfavorable contact between water molecules and nonpolar carbon chains. In addition, we have also established that the 2-PyMe$_2$Si group can be easily removed from organic molecules by oxidation with H_2O_2 to afford the corresponding alcohols.[4]

We envisioned that if the 2-PyMe$_2$Si group works as a removable hydrophilic group and induces molecular aggregation in water, organic reactions in aqueous molecular aggregates should be possible when the reaction site is located on a hydrophobic side chain of the 2-PyMe$_2$Si-substituted molecule (Figure 1).[5] The advantage of using the 2-PyMe$_2$Si

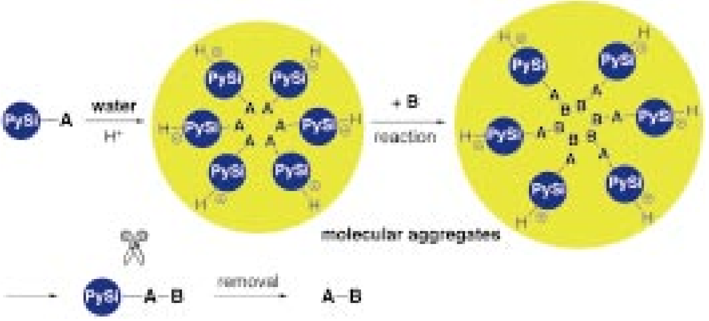

Figure 1. New strategy for aqueous organic reactions using a removable hydrophilic group.

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