

- [9] a) Single-crystal X-ray experiments were performed on either a Nonius kappaCCD diffractometer (**1**) or a Bruker SMART1000 CCD diffractometer (**2,3**) both equipped with an Oxford Cryosystems open-flow cryostat (graphite-monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). All structures were solved by direct methods^[11] and all non-hydrogen atoms were located by using subsequent difference Fourier methods.^[12] b) Crystals of **1** were grown by the following procedure: Lanthanum triflate hydrate (0.029 g , $5 \times 10^{-5} \text{ mol}$), and 2,2'-bipyridine- N,N' -dioxide (0.010 g , $5 \times 10^{-5} \text{ mol}$) were dissolved in MeOH (10 mL). After 24 h 4,4'-bipyridine- N,N' -dioxide hydrate (0.022 g , $1 \times 10^{-4} \text{ mol}$) in MeOH (10 mL) was added. After about three days a crystalline product **1**, suitable for X-ray diffraction was formed. Crystal data for **1**, $\text{C}_{47.2}\text{H}_{48.8}\text{F}_9\text{LaN}_8\text{O}_{21.2}\text{S}_3$, $M_r = 1473.43$, tetragonal, $P4c2$, $a = 25.9970(4) \text{ \AA}$, $c = 26.7847(6) \text{ \AA}$, $V = 18102.3(6) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 12$, $\rho_{\text{calcd}} = 1.622 \text{ Mg m}^{-3}$, $F(000) = 8923$, $\mu(\text{MoK}\alpha) = 0.920 \text{ mm}^{-1}$. Crystal morphology: colorless block. Crystal dimensions: $0.20 \times 0.20 \times 0.11 \text{ mm}$. A total of 19471 unique reflections were collected ($R_{\text{int}} = 0.325$), $\theta_{\text{max}} = 27.48^\circ$. Semiempirical absorption correction from equivalents. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.199P)]$, where $P = [\max(F_o^2, 0) + 2F_o^2]/3$. Goodness-of-fit on F^2 was 1.025, $R1$ (for 6414 reflections with $I > 2\sigma(I)$) = 0.132, $wR2 = 0.309$. Data/parameters 19471/650. Largest difference Fourier peak and hole 2.87 and $-1.15 \text{ e \AA}^{-3}$, respectively. c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154975 (**1**), CCDC-154976 (**2**), and CCDC-154977 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [10] Crystals of **2** were grown by the following procedure: Lanthanum perchlorate hydrate (0.022 g , $4 \times 10^{-5} \text{ mol}$) and sodium tetraphenylborate (0.028 g , $8 \times 10^{-5} \text{ mol}$) were dissolved in MeOH (15 mL). 4,4'-Bipyridine- N,N' -dioxide hydrate (0.033 g , $1.5 \times 10^{-4} \text{ mol}$) in MeOH (10 mL) was added. The mixture produced a white precipitate, which transformed into pale yellow plate crystals over a period of about seven days. Crystal data for **2**, $\text{C}_{66.75}\text{H}_{63}\text{BCl}_2\text{LaN}_8\text{O}_{18.75}$, $M_r = 1497.87$, monoclinic, $P2_1/n$, $a = 13.2242(11) \text{ \AA}$, $b = 38.366(3) \text{ \AA}$, $c = 13.2515(11) \text{ \AA}$, $\beta = 99.752(1)^\circ$, $V = 6626(2) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.501 \text{ Mg m}^{-3}$, $F(000) = 3062$, $\mu(\text{MoK}\alpha) = 0.805 \text{ mm}^{-1}$. Crystal morphology: yellow triangular plate. Crystal dimensions: $0.17 \times 0.06 \times 0.04 \text{ mm}$. A total of 12705 unique reflections were collected ($R_{\text{int}} = 0.095$), $\theta_{\text{max}} = 27.15^\circ$. Semiempirical absorption correction from equivalents. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.261P)]$, where $P = [\max(F_o^2, 0) + 2F_o^2]/3$. Goodness-of-fit on F^2 was 0.902, $R1$ (for 6541 reflections with $I > 2\sigma(I)$) = 0.062, $wR2 = 0.096$. Data/parameters 12705/861. Largest difference Fourier peak and hole 1.55 and $-0.99 \text{ e \AA}^{-3}$, respectively.^[9c]
- [11] Crystals of **3** were grown by the following procedure: Lanthanum chloride hydrate (0.012 g , $3 \times 10^{-5} \text{ mol}$) and $\text{Na}[\text{Co}(\text{C}_2\text{H}_{11}\text{B}_9)]$ (0.035 g , $1 \times 10^{-4} \text{ mol}$) were dissolved in MeOH (10 cm^3). 4,4'-Bipyridine- N,N' -dioxide hydrate (0.033 g , $1.5 \times 10^{-4} \text{ mol}$) in MeOH (10 cm^3) was added, producing a white emulsion-like precipitate, from which large yellow plate crystals grew in about three days. Crystal data for **3**, $\text{C}_{52.5}\text{H}_{100}\text{B}_{54}\text{Co}_3\text{LaN}_8\text{O}_{8.5}$, $M_r = 1878.85$, orthorhombic, $P2_12_12_1$, $a = 17.5705(14) \text{ \AA}$, $b = 18.571(2) \text{ \AA}$, $c = 13.3355(11) \text{ \AA}$, $V = 4351.4(10) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 1.434 \text{ Mg m}^{-3}$, $F(000) = 1894$, $\mu(\text{MoK}\alpha) = 1.098 \text{ mm}^{-1}$. Crystal morphology: yellow plate. Crystal dimensions: $0.34 \times 0.12 \times 0.03 \text{ mm}$. A total of 10175 unique reflections were collected ($R_{\text{int}} = 0.067$), $\theta_{\text{max}} = 28.69^\circ$. Semiempirical absorption correction from equivalents. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0156P)]$, where $P = [\max(F_o^2, 0) + 2F_o^2]/3$. Goodness-of-fit on F^2 was 0.919, $R1$ (for 7301 reflections with $I > 2\sigma(I)$) = 0.044, $wR2 = 0.061$. Data/parameters 10175/575. Flack parameter = 0.027(12). Largest difference Fourier peak and hole 0.98 and $-0.71 \text{ e \AA}^{-3}$, respectively.^[9c]
- [12] SHELXS-97: G. M. Sheldrick, *Acta Crystallogr. Sect. A*. **1990**, *46*, 467.
- [13] G. M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, **1997**.
- [14] A. R. Al-Karaghoul, R. O. Day, J. S. Wood, *Inorg. Chem.* **1978**, *17*, 3702.
- [15] D.-L. Long, A. J. Blake, N. R. Champness, M. Schröder, *Chem. Commun.* **2000**, 2273.
- [16] For example see: a) C. Viñas, S. Gomez, J. Bertran, F. Teixidor, J.-F. Dozol, H. Rouquette, *Chem. Commun.* **1998**, 191; b) V. V. Romanovskii, D. W. Wester, *Sep. Sci. Technol.* **1999**, *34*, 2141; c) R. M. Chamberlin, K. D. Abney, *J. Radioanal. Nucl. Chem.* **1999**, *241*, 437; d) I. B. Sivaev, V. I. Bregadze, *Collect. Czech. Chem. Commun.* **1999**, *64*, 783; e) for example of sodium salt polymer of cyclotrimeratrylene see: M. J. Hardie, C. L. Raston, *Angew. Chem.* **2000**, *112*, 3993; *Angew. Chem. Int. Ed.* **2000**, *39*, 3835.
- [17] D.-L. Long, A. J. Blake, N. R. Champness, M. Schröder, unpublished results.
- [18] For the europium analogue of **3**, elemental analysis calcd for $\text{C}_{52.5}\text{H}_{100}\text{B}_{54}\text{Co}_3\text{EuN}_8\text{O}_{8.5}$ (%): C 33.33, H 5.33, N 5.92; found: C 32.75, H 5.16, N 5.78; cell dimensions: orthorhombic, $a = 17.4254(3) \text{ \AA}$, $b = 18.6346(3) \text{ \AA}$, $c = 13.2015(2) \text{ \AA}$, $V = 4289.7(2) \text{ \AA}^3$. For the holmium analogue of **3**, elemental analysis calcd for $\text{C}_{52.5}\text{H}_{100}\text{B}_{54}\text{Co}_3\text{HoN}_8\text{O}_{8.5}$ (%): C 33.10, H 5.29, 5.88; found: C 32.76, H 5.65, N 6.05; cell dimensions: orthorhombic, $a = 17.363(7) \text{ \AA}$, $b = 18.715(5) \text{ \AA}$, $c = 13.184(5) \text{ \AA}$, $V = 4284(2) \text{ \AA}^3$.

Working Supramolecular Machines Trapped in Glass and Mounted on a Film Surface**

Shinye Chia, Jianguo Cao, J. Fraser Stoddart,* and Jeffrey I. Zink*

Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

The concept of a macroscopic machine can be realized^[1] in solution at a supramolecular level in complexes where the self-assembly^[2] of the components can be reversed upon quelling temporarily the molecular recognition that exists between the matching components. Thus, a supramolecular machine can be defined as an assembly of two or more molecular components designed to perform mechanical-like motions with respect to each other in response to some energy supply—for example, chemical, electrochemical, or photochemical—that can be switched on and off at will. One of the most highly investigated classes of supramolecular machines^[1,3] are those based on the complexes known as pseudorotaxanes.^[4] The reason for this is that the dethreading and rethreading movements of a thread through the center of a ring are reminiscent of the action of a linear motor. Numerous artificial supramolecular machines,^[1] based on pseudorotaxanes,^[4] exist that can be induced to undergo conformational change^[5] by chemical,^[6] electrochemical,^[7] and photochemical^[8–10] means. They have been demonstrated^[1] to operate efficiently in solution, albeit in an incoherent manner. In order to realize the full potential of these supermolecules in a machine-shop setting, they have to be organized at interfaces^[11] or deposited on surfaces^[12] so that they can be made to operate in unison. Herein we describe two solid-state supramolecular machines in action: one in which the machines are trapped physically in a rigid, nanoporous, optically transparent matrix, and the other in which

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one component of the machine is tethered onto the surface of a silica film.

In [2]pseudorotaxanes, which are stabilized (in part at least) by π -donor/ π -acceptor interactions—for example, such as those present^[8] when the naphthalenedioxy donor ring system in 1,5-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (BHEEN) is threaded through the middle of the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) with its two accepting bipyridinium units—charge-transfer (CT) absorption bands are evident in the visible region of the spectrum. Excitation of these bands leads^[1, 8] formally to the transfer of an electron from the donor to one of the two acceptors, thus nullifying the CT and C–H...O interactions^[8] responsible for the pseudorotaxane formation in the first place. However, photochemical reduction of the bipyridinium units in CBPQT⁴⁺ requires^[1, 8] additional ingredients, such as a photosensitizer *P* (9-anthracenecarboxylic acid, ACA) to serve as a photoactivated reductant, and a sacrificial reagent added to prevent fast back-electron transfer. Since the emission of BHEEN is quenched when it is threaded through CBPQT⁴⁺, the change in the emission intensity of BHEEN can be used to follow the dethreading and rethreading upon oxygenation of the solution (Scheme 1).

Our first solid-state device was prepared by condensation of a sol–gel^[13] silica framework^[14] around the [2]pseudorotax-

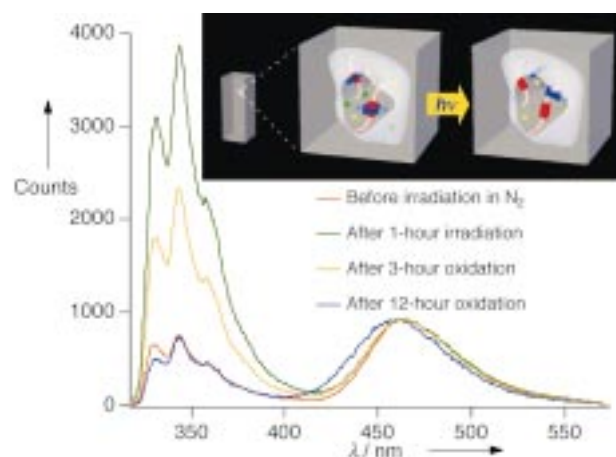
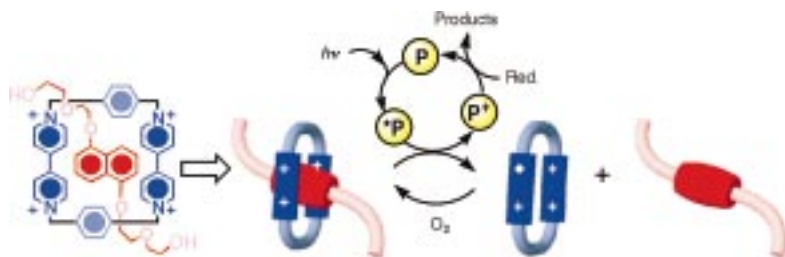


Figure 1. Illustration of a supramolecular machine in action in an interior pore of a sol–gel monolith. Shown are the emission spectra of BHEEN in the sol–gel monolith before irradiation (red), and complete (12 h, green) photoinduced reduction and dethreading of CBPQT⁴⁺ to give free BHEEN, and following oxidation by dioxygen which diffuses through the pores and causes partial (yellow) and complete rethreading (blue). The peaks observed between 300 and 400 nm arise from BHEEN emission and that at 400 nm from the reference standard (coumarin 480). The insert shows a $0.8 \times 0.8 \times 3.5$ cm³ transparent monolith. The magnification shows a pore (<100 nm) containing CBPQT⁴⁺ (blue), BHEEN (red and pink) in threaded form, together with ACA (yellow) and EDTA (green). After irradiation (*hν*), the pseudorotaxanes become dissociated.



Scheme 1. Light-driven dethreading in aqueous solution of the [2]pseudorotaxane (BHEEN $\subset$ CBPQT⁴⁺) by excitation of the external photosensitizer, 9-anthracenecarboxylic acid (ACA), in the presence of a sacrificial reductant (Red. = triethanolamine). Dioxygen is used to effect rethreading. See ref. [8].

ane (BHEEN $\subset$ CBPQT⁴⁺), ACA (the photosensitizer), and a sacrificial reagent (ethylenediaminetetraacetate, EDTA). An aged monolithic sample (dimensions $0.8 \times 0.8 \times 3.5$ cm³) was placed under an atmosphere of nitrogen. Light of wavelength 365 nm from a 100-W Hg lamp was used to irradiate the photosensitizer, thus reducing the CBPQT⁴⁺ cyclophane. Molecules of BHEEN are excited by the 308-nm wavelength light from a XeCl excimer laser. The emission is monitored and used as an indicator of threading and dethreading processes. After one hour of irradiation, the initially pink sample with a charge transfer band at 520 nm becomes either clear or pale blue at the irradiated spot. The fading of the pink color indicates dissociation of the pseudorotaxane, while the appearance of the blue color comes from bipyridinium units in the cyclophane which have been reduced to radical cations. The increased emission following irradiation (Figure 1) proves that BHEEN and CBPQT⁴⁺ have dissociated.^[8] The emission intensity after 12 hours of oxidation in air decreased to its initial level as a consequence of the reformation of the

pseudorotaxane. The dethreading process was roughly an order of magnitude slower in the gel than in solution, probably because of the interaction between the negatively charged pore walls of the silicate matrix and the oppositely charged tetracationic cyclophane. The spatial confinement within the nanopores could also contribute to the decrease in molecular mobility. Prolonged and localized irradiation leads to decomposition of the molecular ingredients (including the sacrificial reagent) so that the second dethreading is only 15% of that of the first under the concentration conditions of the experiment.

The second device we report is one involving (Figure 2) the operation of a supramolecular machine on the surface of a solid support. We reasoned that attaching the BHEEN derivative BHEEN—which has an extra ethoxy unit in each polyether chain, one of which is terminated with a benzyl ether group^[15]—onto a solid support would allow CBPQT⁴⁺ to be captured on threading and then to be released again upon dethreading. The surfaces of the sol–gel film have silanol groups which can be treated (Scheme 2) with a suitably functionalized silicon alkoxide for subsequent molecular anchoring of the monobenzylated BHEEN. In this investigation, we used silicon substrates that were dip-coated to give a sol–gel film of 150-nm thickness.^[16] All spectra were recorded from the derivatized surface. These films were functionalized by treating the surface silanol groups with isocyanatopropyltriethoxysilane (ICPES) by using a vapor-phase reaction which is known^[17] to result in the tethering of the lower boiling monomeric silane to the film.^[18] The monobenzylated BHEEN was then coupled (Scheme 2) to the isocyanate groups on the surface, which resulted in the

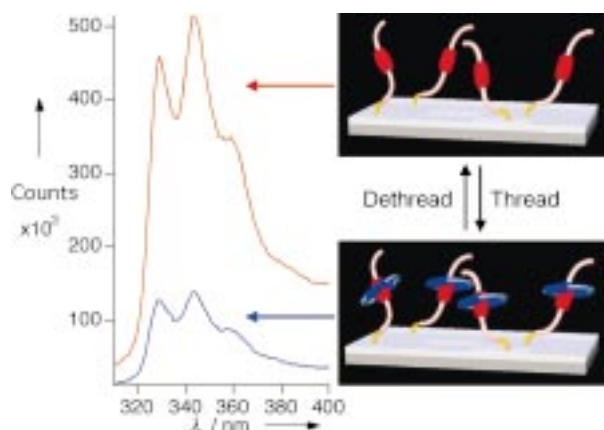


Figure 2. Illustration of the threading and dethreading of a supramolecular machine in action on a sol-gel surface. The emission spectrum (blue) arises from the small proportion of “unthreaded” monobenzylated BHEEN after treatment of the derivatized surface with CBPQT·4Cl. The emission spectrum (red) from the surface corresponds to the increase in dethreaded monobenzylated BHEEN following irradiation in the presence of ACA and EDTA.

formation of carbamates. The derivatized films were placed firstly in an aqueous solution of CBPQT·4Cl for two days. This immersion treatment had the effect (see T1 in Figure 3a) of reducing the emission intensity of the film at 344 nm from 100 % down to 4%. The film was immersed in an aqueous solution (ca. 3.5 mL) containing ACA (ca. 30 μ M) and EDTA (ca. 30 mM) and then irradiated with light of wavelength 365 nm for 2–4 hours. The observed 14 % emission (see D1 in Figure 3a) is a result of the combined emission for 1) the 4 % base of unthreaded units, 2) units that have been dethreaded photochemically, and 3) units that become dethreaded as a result of re-equilibration. The degree of dethreading as a result of this re-equilibration was estimated from a control experiment by soaking a separate film in water and comparing its emission intensity with that of the photochemically reduced film. Three threading and dethreading redox cycles (T1/D1–T2/D2–T3/D3; Figure 3a) are shown and the relative amounts of the photochemically induced dethreading diminish a little with each cycle. This trend could be attributed to decomposition or to the loss of

the BHEEN-containing units on prolonged irradiation and/or

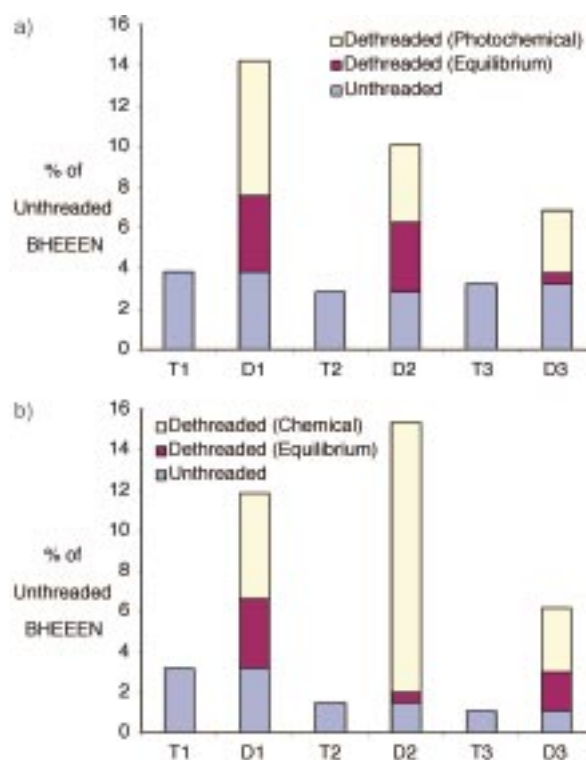
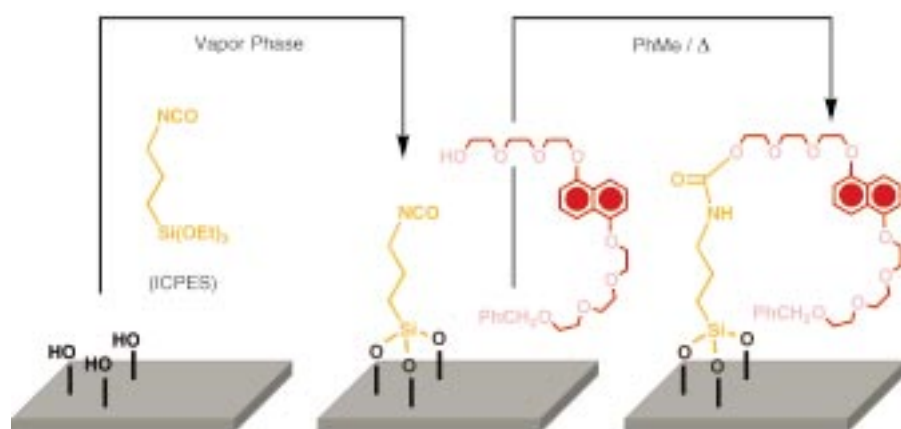


Figure 3. Histograms recording relative luminescent intensities after three sequential threading (T) and dethreading (D) cycles by supramolecular machines on a sol-gel surface. In (a) the machines are photochemically driven and in (b) they are chemically driven.

soaking. Chemical reductions with NaBH_4 caused (Figure 3b) dethreading of the supramolecular machines mounted on films in the same manner^[19] as for the photochemical experiments.

In summary, we have trapped pseudorotaxanes in a silica monolith and mounted them on a silica film. We have also demonstrated threading and dethreading of the pseudorotaxanes in and on these solid supports. The method of attachment of machine components that we have chosen, namely,

derivatization with trialkoxysilane groups, has general applicability. In principle, supramolecular machines can be attached, not only to silica, but also to oxidized silicon surfaces and many metal oxide surfaces, thus facilitating the formation of other types of superstructures and different kinds of activation, such as direct electrical reduction. The sol-gel support that we have chosen for this proof of principle also offers a lot of opportunities for fabrication. Its structure cannot only be provided in the form of macroscopic monolithic blocks or as thin films, as demonstrated here, but it can also be presented in the form of



Scheme 2. The two-step procedure used to anchor monobenzylated BHEEN onto the surface of a sol-gel film.

fibres and templated porous materials with long-range order. The ability to encapsulate molecules in a synthetic framework will allow us to position the power supply, for example, a photosensitizer as the transducer, in the proximity of the machine.^[20] In addition, the use of templated silica will enable ordered arrays of machines and other functional materials to be constructed.

Experimental Section

CBPQT·4PF₆,^[21] 1,5-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (BHEEN),^[22] and 1,5-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene (BHEEN)^[23] were prepared as described in the literature.

The water-soluble tetracationic cyclophane CBPQT·4Cl was obtained from its tetrakis(hexafluorophosphate) salt^[21] as follows: Bu₄NCl (134 mg, 0.48 mmol) was added to a solution of CBPQT·4PF₆ (133 mg, 0.12 mmol) in MeNO₂ (5 mL). The solution was stirred for 24 h at room temperature. The precipitate was filtered off and washed (MeNO₂) to afford CBPQT·4Cl as a white solid (78 mg, 98%). ¹H NMR (400 MHz, D₂O, 300 K): δ = 5.76 (s, 8H), 7.53 (s, 8H), 8.18 (d, *J* = 7 Hz, 8H), 9.00 (d, *J* = 7 Hz, 8H). BHEEN was monobenzyllated as follows: BHEEN (424 mg, 1.00 mmol) in THF (30 mL) was added to a suspension of NaH (36 mg, 1.50 mmol) in dry THF (30 mL) under Ar. The solution was stirred for 30 min at room temperature and then for a further 30 min under reflux. A solution of PhCH₂Br (172 mg, 1.00 mmol) in THF (20 mL) was added dropwise during 15 min and then the reaction mixture was heated under reflux for 12 h. It was then cooled and MeOH (5 mL) was added. The solvents were removed and the oily residue was dissolved in CH₂Cl₂ (50 mL) before being washed with saturated aqueous Na₂CO₃ solution (2 × 50 mL) and H₂O (2 × 50 mL). The organic layer was dried (MgSO₄), filtered, and the CH₂Cl₂ was removed under vacuum. The resulting oil was subjected to column chromatography on silica gel using MeOH/EtOAc (5/95) as the eluant to afford a yellow oil of monobenzyllated BHEEN (235 mg, 46%). ¹H NMR (360 MHz, CDCl₃, 300 K): δ = 2.89 (brs, 1H), 3.55–3.68 (m, 12H), 3.72–3.77 (m, 4H), 3.90–3.95 (m, 4H), 4.22 (t, *J* = 5 Hz, 4H), 4.52 (s, 2H), 6.78 (d, *J* = 8 Hz, 2H), 7.23–7.34 (m, 7H), 7.84–7.87 (dd, *J* = 3, 8 Hz, 2H); ¹³C NMR (90 MHz, CDCl₃, 300 K): δ = 61.4, 63.0, 67.0, 68.9, 69.2, 69.5, 70.3, 71.0, 72.3, 72.9, 105.4, 114.3, 124.8, 125.7, 126.5, 127.2, 128.0, 138.0, 154.0, 154.1; liquid secondary ion MS (LSI-MS): *m/z*: 515 [*M*+H]⁺; elemental analysis calcd (%) for C₂₉H₃₈O₈ (514.26): C 67.70, H 7.39; found: C 67.18, H 7.21.

The silicate sol was prepared by stirring a mixture of tetraethylorthosilicate, EtOH, H₂O, and HCl (molar ratios: 1/4/16/8 × 10⁻⁴) at 70 °C for 1 h. BHEEN (40 μL, 1 mM in EtOH), CBPQT·4Cl (40 μL, 1 mM in H₂O), ACA (4 μL, 1 mM in EtOH), and EDTA (0.1 M, 0.4 mL in H₂O) were added to the silicate sol (2 mL) in distilled H₂O (1.52 mL). The mixture was allowed to gel in a sealed polystyrene cuvette (1 × 1 × 4 cm) for 1 week. The seal was punctured to allow slow evaporation of the solvent over 2 weeks, which resulted in an aged monolithic sample (~0.8 × 0.8 × 3.5 cm³).

The sol–gel silica films were prepared by dip-coating silicon substrates with the sol mixture,^[16] followed by sintering. The silicon substrates were cut into 1-cm wide strips and cleaned using a H₂O₂/H₂SO₄ (1/4 by volume) solution, followed by rinsing with boiling H₂O. The films were loaded into an apparatus similar to the one described in ref. [17] and then heated to 120 °C for 1 h under a dynamic vacuum. ICPEs (1 mL) and dry PhMe (20 mL) were added to the apparatus under N₂. The reaction mixture was heated under reflux for 6 h. The functionalized films were soaked in PhMe for 1 day to remove free ICPEs. The monobenzyllated BHEEN was coupled to the functionalized films by heating the monobenzyl derivative (40 μL) of BHEEN in PhMe (25 mL) for 4 h. The films were then rinsed with PhMe and H₂O, followed by soaking in H₂O for 1 day prior to carrying out any threading–dethreading experiments.

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[1] a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391;

- b) R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Acc. Chem. Res.* **2001**, *34*, 445–455.
- [2] a) J. S. Lindsey, *New J. Chem.* **1991**, *15*, 153–180; b) D. Philp, J. F. Stoddart, *Synlett* **1991**, 445–458; c) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1155–1196; d) M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401; e) L. F. Lindoy, I. M. Atkinson, *Self-Assembly in Supramolecular Systems* (Ed.: J. F. Stoddart), Royal Society of Chemistry, Cambridge, **2000**.
- [3] For an impressive example of a real-space observation of single-molecule (hexa-*tert*-butyldecacyclene) rotors surrounded by like molecules that form a supramolecular bearing on an atomically clean Cu(100) surface, see J. K. Gimzewski, C. Joachim, R. R. Schlitter, V. Langlais, H. Tang, I. Johannsen, *Science* **1998**, *281*, 531–533.
- [4] Pseudorotaxanes are complexes (supermolecules) that resemble rotaxanes by virtue of being comprised of wheel-like and axle-like components, but their components are free to dissociate from each other; see P. R. Ashton, D. Philp, N. Spencer, J. F. Stoddart, *J. Chem. Soc. Chem. Commun.* **1991**, 1677–1679.
- [5] We have advocated the use of the term co-conformation to designate the different three-dimensional spatial arrangements of the constituent parts in supramolecular systems, for example, pseudorotaxanes; see M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1997**, *109*, 2158–2160; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2068–2070.
- [6] a) M. Asakawa, S. Iqbal, J. F. Stoddart, N. D. Tinker, *Angew. Chem.* **1996**, *108*, 1054–1056; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 976–978; b) A. Credi, V. Balzani, S. J. Langford, J. F. Stoddart, *J. Am. Chem. Soc.* **1997**, *119*, 2679–2681; c) A. Credi, M. Montalti, V. Balzani, S. J. Langford, F. M. Raymo, J. F. Stoddart, *New J. Chem.* **1998**, *22*, 1061–1065; d) E. Ishow, A. Credi, V. Balzani, F. Spadola, L. Mandolini, *Chem. Eur. J.* **1999**, *5*, 984–989; e) V. Balzani, A. Credi, G. Matternsteig, O. A. Matthews, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Org. Chem.* **2000**, *65*, 1924–1936; f) V. Balzani, P. Ceroni, A. Credi, M. Gómez-López, C. Hamers, J. F. Stoddart, R. Wolf, *New J. Chem.* **2001**, *25*, 25–31.
- [7] a) A. Mirzozian, A. E. Kaifer, *Chem. Eur. J.* **1997**, *3*, 1052–1057; b) P. R. Ashton, V. Balzani, J. Becher, A. Credi, M. C. T. Fyfe, G. Matternsteig, S. Menzer, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 3951–3957; c) V. Balzani, J. Becher, A. Credi, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, A. M. Talarico, M. Venturi, *J. Org. Chem.* **2000**, *65*, 1947–1956; d) for a really fine account of the emerging field of supramolecular electrochemistry, see A. E. Kaifer, M. Gómez-Kaifer, *Supramolecular Electrochemistry*, Wiley-VCH, Weinheim, **1999**.
- [8] a) R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, *Angew. Chem.* **1993**, *105*, 1362–1364; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1301–1303; b) P. R. Ashton, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, M. T. Gandolfi, M. Gómez-López, S. Iqbal, D. Philp, J. A. Preece, L. Prodi, H. G. Ricketts, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 152–170.
- [9] a) P. R. Ashton, R. Ballardini, V. Balzani, E. C. Constable, A. Credi, O. Kocian, S. J. Langford, J. A. Preece, L. Prodi, E. R. Schofield, N. Spencer, J. F. Stoddart, S. Wenger, *Chem. Eur. J.* **1998**, *4*, 2413–2422; b) P. R. Ashton, V. Balzani, O. Kocian, L. Prodi, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1998**, *120*, 11190–11191.
- [10] a) A. C. Benniston, A. Harriman, D. Philp, J. F. Stoddart, *J. Am. Chem. Soc.* **1993**, *115*, 5298–5299; b) A. C. Benniston, A. Harriman, D. S. Yufit, *Angew. Chem.* **1997**, *109*, 2451–2454; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2356–2358; c) A. C. Benniston, A. Harriman, V. M. Lynch, *J. Am. Chem. Soc.* **1995**, *117*, 5275–5291; d) M. Seiler, H. Dürr, I. Willner, E. Joselevich, A. Doren, J. F. Stoddart, *J. Am. Chem. Soc.* **1994**, *116*, 3399–3404; e) M. Kropf, E. Joselevich, H. Dürr, I. Willner, *J. Am. Chem. Soc.* **1996**, *118*, 655–665; f) E. David, R. Born, E. Kaganer, E. Joselevich, H. Dürr, I. Willner, *J. Am. Chem. Soc.* **1997**, *119*, 7778–7790.
- [11] For examples of Langmuir films of pseudorotaxanes, see a) R. C. Ahuja, P.-L. Caruso, D. Möbius, G. Wildburg, H. Ringsdorf, D. Philp, J. A. Preece, J. F. Stoddart, *Langmuir* **1993**, *9*, 1534–1544; b) R. C. Ahuja, P.-L. Caruso, D. Möbius, D. Philp, J. A. Preece, H. Ringsdorf, J. F. Stoddart, G. Wildburg, *Thin Solid Films* **1996**, *284/285*, 671–677.

- [12] For recent examples of supramolecular systems deposited on surfaces, see a) P. Laitenberger, C. G. Claissens, L. Kuipers, F. M. Raymo, R. E. Palmer, J. F. Stoddart, *Chem. Phys. Lett.* **1997**, 279, 209–214; b) G. Ashkenasy, G. Kalyuzhny, J. Libman, I. Rubenstein, A. Shanzer, *Angew. Chem.* **1999**, 111, 1333–1336; *Angew. Chem. Int. Ed.* **1999**, 38, 1257–1261; c) M. Lahav, L. Leiserowitz, *Angew. Chem.* **1999**, 111, 2691–2694; *Angew. Chem. Int. Ed.* **1999**, 38, 2533–2536; d) A. Semenov, J. P. Spatz, M. Müller, J.-M. Lehn, B. Sell, D. Schubert, C. H. Weidl, U. S. Schubert, *Angew. Chem.* **1999**, 111, 2701–2705; *Angew. Chem. Int. Ed.* **1999**, 38, 2547–2550; e) N. Bampos, C. N. Woodburn, M. E. Welland, J. K. M. Sanders, *Angew. Chem.* **1999**, 111, 2949–2953; *Angew. Chem. Int. Ed.* **1999**, 38, 2780–2783; f) H. Imahori, H. Yamada, S. Ozawa, K. Ushida, Y. Sakata, *Chem. Commun.* **1999**, 1165–1166; g) D. Ryan, S. N. Rao, H. Rensmo, D. Fitzmaurice, J. A. Preece, S. Wenger, J. F. Stoddart, N. Zaccheroni, *J. Am. Chem. Soc.* **2000**, 122, 6252–6257; h) M. Lahav, A. N. Shipway, I. Willner, M. B. Nielsen, J. F. Stoddart, *J. Electroanal. Chem.* **2000**, 482, 217–221; i) G. Cooke, F. M. A. Duclairoir, V. M. Rotello, J. F. Stoddart, *Tetrahedron Lett.* **2000**, 41, 8163–8166.
- [13] C. J. Brinker, G. W. Scherer, *Sol–Gel Science*, Academic Press, San Diego, **1990**.
- [14] A silica sol–gel provides a stable transparent matrix for encapsulating molecules physically in a macroscopic solid; see a) B. Dunn, J. I. Zink, *Chem. Mater.* **1997**, 9, 2280–2291; b) D. Avnir, *Acc. Chem. Res.* **1995**, 28, 328–334; c) B. Dunn, J. I. Zink, *J. Mater. Chem.* **1991**, 1, 903–913. The sol–gel process is a synthetic technique for preparing oxide gels, glasses, and inorganic compounds at far lower temperatures than is possible by conventional synthesis. The approach is based on the hydrolysis and condensation of molecular precursors such as metal alkoxides. It has received considerable attention because it possesses a number of desirable characteristics in terms of producing materials of high purity and excellent homogeneity. Moreover, since the sol–gel approach is a solution-based method, it is readily adaptable to producing thin films and fibres as well as bulk materials. The flexible solution chemistry associated with the synthesis of sol–gels makes it possible to incorporate a large variety of organic molecules in the inorganic oxide matrix. The optical properties of the molecular dopants are then imparted upon the solid derived from the sol–gel. Hence this process gives rise to a large number of materials with interesting and unique properties. The interconnected nanopores in sol–gels are filled with liquid which can provide supramolecular machines with a local solution environment in which large molecular movements (co-conformational changes) can be performed, with the silicate framework providing the macroscopic support. The silicate matrix is also transparent to visible light and this transparency makes it possible to study a photoactivated system inside its pores.
- [15] This particular BHEEEN derivative with four oxygen atoms present in each of its polyether chains is well suited to maximizing the C–H...O interactions with CBPQT⁴⁺; see M. Asakawa, W. Dehaen, G. L'abbé, S. Menzer, J. Nouwen, F. M. Raymo, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **1996**, 61, 9591–9595.
- [16] a) M. H. Huang, H. M. Soyee, B. Dunn, J. I. Zink, *Chem. Mater.* **2000**, 12, 231–235; b) F. Nishida, J. McKiernan, B. Dunn, J. I. Zink, C. J. Brinker, A. J. Hurd, *J. Am. Ceram. Soc.* **1995**, 78, 1640–1648.
- [17] I. Haller, *J. Am. Chem. Soc.* **1978**, 100, 8050–8055.
- [18] The derivatization of the silica surface by using monomeric ICPES is important as the first step in the anchoring of the monobenzylated BHEEEN derivative. If this derivative is treated first of all with ICPES prior to silanization, then undesired oligomers are formed on the silica surface.
- [19] The derivatized films were immersed in an aqueous solution of CBPQT·4Cl for two days. The residual percentage (ca. 3.4%) of unthreaded BHEEEN is shown by T1 in Figure 3b. Dethreading, was effected by immersing the film in an aqueous solution (ca. 4 mL) of NaBH₄ (ca. 2 mM) for 2–3 h. The resulting luminescent intensity is shown in D1 in Figure 3b. Threading and dethreading was demonstrated over three redox cycles, namely, T1/D1–T2/D2–T3/D3.
- [20] Ordered arrays of molecular motors are essential to the life of a cell; see a) R. A. Cross, *Nature* **2000**, 406, 839–840; b) T. Hasson, R. E. Cheney, *Curr. Opin. Cell Biol.* **2001**, 13, 29–35.
- [21] P.-L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, 114, 193–218.
- [22] D. B. Amabilino, P.-L. Anelli, P. R. Ashton, G. R. Brown, E. Córdova, L. A. Godínez, W. Hayes, A. E. Kaifer, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, M. S. Tolley, D. J. Williams, *J. Am. Chem. Soc.* **1995**, 117, 11 142–11 170.
- [23] P. R. Ashton, J. Huff, S. Menzer, I. W. Parsons, J. A. Preece, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, 2, 31–44.

Helical Superstructures of a C₂-Symmetric Molecule Exhibiting Strong Second Harmonic Generation in the Solid-State**

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The design of molecular materials for quadratic nonlinear optical (NLO) applications involves optimization of the structure at both the molecular and the materials level.^[1] Molecular design aims at the maximization of the hyperpolarizability (β) as well as the incorporation of structural features that facilitate suitable assembly in the bulk phase. The latter features include hydrogen-bonding functionalities,^[2] ionic groups,^[3] optimally long alkyl chains,^[4] and chirality.^[5, 6] Of these, only chirality ensures noncentrosymmetric organization, an essential prerequisite for the observation of quadratic NLO effects. However, even though the basic symmetry requirement is satisfied, efficient exploitation of the inherently strong molecular nonlinear response is rarely achieved at the bulk level. An exceptionally successful case is that of *N*-4-nitrophenyl-(*S*)-prolinol (NPP).^[6] We previously investigated the strategic placement of stereogenic centers in push-pull quinonoid molecules to achieve enhanced second harmonic generation (SHG).^[7] A logical extension of this study is that an axial chiral system having a strong β component coincident with the symmetry axis would be a promising candidate. We also envisaged that C₂-symmetric molecules could potentially form helical assemblies, the chirality of which extends over the whole molecular superstructure. Recent studies have demonstrated enhanced NLO effects arising from supramolecular chirality in polymers,^[8] mesoscopic systems,^[9] and Langmuir–Blodgett films.^[10] Helical

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