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[16] Ru loading is calculated from the mass increase which accompanies functionalization of the glass surface. ICP-MS analysis for Ru was also carried out for the supported catalyst. However, the former is more reproducible and reliable.

[17] See the Supporting Information for all experimental details.

[18] Analysis of the 400 MHz ^1H NMR spectrum of the unpurified reaction mixtures indicated no difference in reaction efficiency among the three catalysts.

[19] Five hours for cycle 5, six hours for cycles 6 and 7, seven hours for cycle 8, eight hours for cycles 9 and 10, nine hours for cycle 11, ten hours for cycle 12, twelve hours for cycle 13 and fourteen hours for cycles 14 and 15.

[20] Elemental analyses were not obtained for product samples in cycles 5–8, since multiple ROCM products are produced in these reactions along with substantial amounts of uncharacterized oligomers (derived from ROMP of **13**). Similar product distributions are obtained by the monomeric **2**.

Host–Guest Chemistry Aids and Abets a Stereospecific Photodimerization in the Solid State**

Dafni G. Amirsakis, Miguel A. Garcia-Garibay,*
Stuart J. Rowan, J. Fraser Stoddart,*
Andrew J. P. White, and David J. Williams*

In memory of Donald J. Cram

The ability to preorganize olefins for their solid-state photochemical dimerization[1] within a crystalline lattice is a challenging problem.[2] It has been ascertained[3] that, in order for such reactions to occur, the olefinic functions need to be aligned in a parallel manner and to have centroid–centroid separations of about 3.5–4.2 Å. The utilization of supramolecular assistance toward the alignment of stilbenes[4] in the solid state offers a potential solution to this problem of preorganization. To date, examples of this methodology include 1) double-stranded complexes of stilbenes bound within the torus of γ-cyclodextrin,[5, 6, 7] 2) the functionalization of the aromatic units of stilbenes to encourage donor–acceptor π–π stacking interactions,[8, 9] and 3) the incorporation of hydrogen-bond acceptors into a stilbene derivative that are capable of forming a noncovalent macrocycle upon cocrystallization with a hydrogen-bond donor.[10] Herein we demonstrate that cocrystallization of a crown ether with a bis(dialkylammonium) salt—which contains a central *trans*-stilbenoid unit—generates a 2:2 complex within which the two (*E*)-olefinic bonds are aligned in an appropriate geometry that facilitates subsequent stereospecific solid-state photochemical dimerization.

Supramolecular complexes with pseudorotaxane-like architectures that are formed spontaneously from dialkylammonium ions and crown ethers have been studied extensively.[11] It has been demonstrated[12] that the bis(dialkylammonium ion)-containing threadlike dication $\mathbf{1}\text{-}H_2\cdot 2\,PF_6$ and the crown ether bis-*p*-phenylene[34]crown-10 (BPP34C10) form a doubly encircled and doubly threaded 2:2 complex $[(BPP34C10)_2\cdot(\mathbf{1}\text{-}H_2)_2][PF_6]_4$ (Scheme 1) upon cocrystallization in the solid state. This result suggested to us a method for aligning stilbene derivatives in the solid state. By replacing the *p*-phenylene unit of $\mathbf{1}^{2+}$ with a *trans*-stilbenoid unit (namely, producing *trans*-$\mathbf{2}\text{-}H_2\cdot 2\,PF_6$) we anticipated that a 2:2 complex $[(BPP34C10)_2\cdot(\mathbf{2}\text{-}H_2)_2][PF_6]_4$ would form upon cocrystallization in which adjacent *trans*-stilbene olefinic bonds

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[*] Prof. M. A. Garcia-Garibay, Prof. J. F. Stoddart, D. G. Amirsakis, S. J. Rowan
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-1843
E-mail: mgg@chem.ucla.edu, stoddart@chem.ucla.edu

Prof. D. J. Williams, Dr. A. J. P. White
Chemical Crystallography Laboratory
Department of Chemistry, Imperial College
South Kensington, London, SW7 2AY (UK)
Fax: (+44) 207-594-5835

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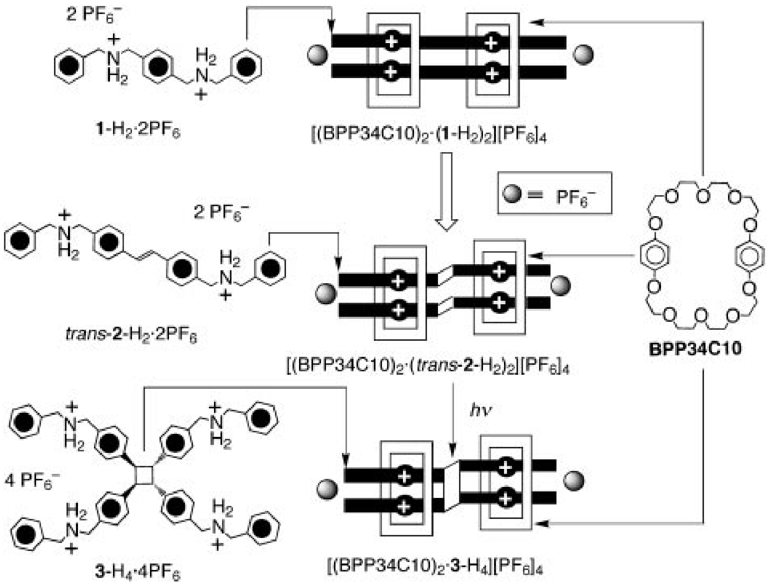


Scheme 1. The complexation of threads **1**-$H_2 \cdot 2PF_6$ and *trans*-**2**-$H_2 \cdot 2PF_6$ with BPP34C10 generates the 2:2 complexes $[(BPP34C10)_2 \cdot (\mathbf{1}\text{-}H_2)_2][PF_6]_4$ and $[(BPP34C10)_2 \cdot (\textit{trans}\text{-}\mathbf{2}\text{-}H_2)_2][PF_6]_4$ in the solid state, respectively. Irradiation of $[(BPP34C10)_2 \cdot (\textit{trans}\text{-}\mathbf{2}\text{-}H_2)_2][PF_6]_4$ in the solid state yields the 2:1 complex $[(BPP34C10)_2 \cdot \mathbf{3}\text{-}H_4][PF_6]_4$.

would be aligned in a manner suitable for a solid-state [2+2] cycloaddition to occur. Depending upon the alignment of the two *trans*-stilbenoid units in the complex, a single diastereoisomer of a tetrasubstituted cyclobutane derivative should be isolable after photochemical irradiation.

The bis(dialkylammonium) salt *trans*-**2**-$H_2 \cdot 2PF_6$ was synthesized by the substitution reaction between *trans*-4,4′-bis(bromomethylstilbene)[6] and benzylamine followed by counterion exchange. Single crystals of the complex $[(BPP34C10)_2 \cdot (\textit{trans}\text{-}\mathbf{2}\text{-}H_2)_2][PF_6]_4$ were obtained by vapor diffusion of $i\text{Pr}_2\text{O}$ into a solution of an equimolar mixture of *trans*-**2**-$H_2 \cdot 2PF_6$ and BPP34C10 in Me_2CO/CH_2Cl_2. The complex $[(BPP34C10)_2 \cdot (\textit{trans}\text{-}\mathbf{2}\text{-}H_2)_2][PF_6]_4$ adopts a classic centrosymmetric doubly threaded, doubly encircled [4]pseudorotaxane geometry in the solid state[13, 14] (Figure 1) analogous to that exhibited by those formed between BPP34C10 and, for example, α,α'-bis(benzylammonium)-*p*-xylene[12] and bis(benzylammonium-*p*-toluic acid).[15] The dicationic threads are each hydrogen bonded through their ammonium centers to oxygen atoms in the polyether loops of the crown ether components, the latter having distinctly cupped conformations, with their hydroquinone rings inclined by approximately 51° to one another. The central *trans*-stilbenoid portions of the dicationic threads have near-planar conformations, the torsional twists about the bonds linking the phenyl rings to the central *trans*-olefinic unit being only approximately 3 and 11°, respectively. There are weak interthread π–π stacking interactions between the laterally offset *trans*-stilbene units, with mean interplanar and centroid–centroid separations of 3.57 and 4.33 Å, respectively, between adjacent phenylene rings, and of 3.60 and 4.20 Å, respectively, between the *trans*-olefinic components. Adjacent dumbbell-shaped supermolecules pack end-to-middle (Figure 2). One of the PF_6^- ions is trapped within the cleft formed between the outwardly folded pairs of terminal *N*-benzyl units of one supermolecule and the sheared *trans*-stilbenoid units of the other. The shortest associated contact to a fluorine atom is only 2.24 Å from one of the *trans*-stilbene aryl *ortho* hydrogen atoms that is *syn* to the double bond; the associated C···F distance and C–H···F angle are 3.14 Å and 155°, respectively. This positioning of a PF_6^- ion in the cleft formed between the

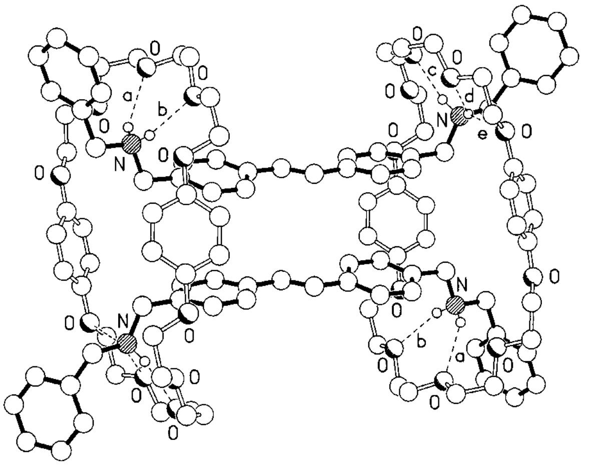


Figure 1. The solid-state supramolecular structure of the doubly threaded, doubly encircled [4]pseudorotaxane $[(BPP34C10)_2 \cdot (\textit{trans}\text{-}\mathbf{2}\text{-}H_2)_2]^{4+}$. Hydrogen-bonding N···O, H···O distances [Å] and N–H···O angles [°], are a) 2.96, 2.27, 133; b) 3.02, 2.18, 155; c) 2.90, 2.04, 161; d) 2.94, 2.26, 131; and e) 3.17, 2.34, 154.

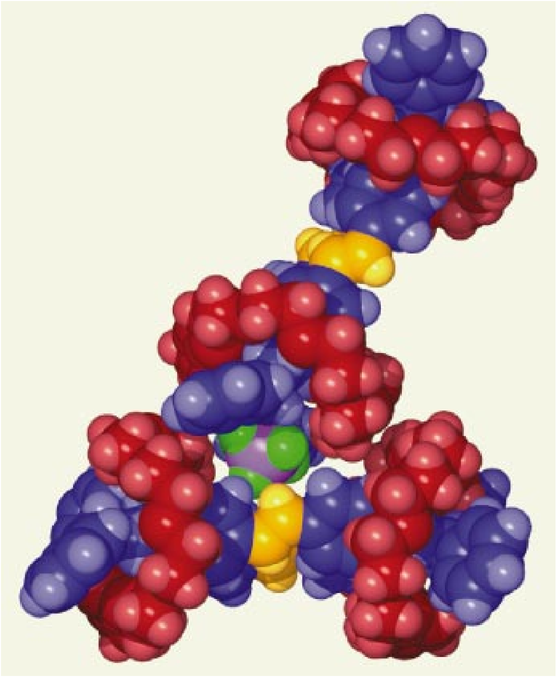


Figure 2. Space-filling representation of the end-to-middle arrangement of adjacent supermolecules of $[(BPP34C10)_2 \cdot (\textit{trans}\text{-}\mathbf{2}\text{-}H_2)_2]^{4+}$ showing the strategic location of one of the PF_6^- ions (P: purple and F: green) between the two 2:2 complexes (BPP34C10 is shown in red and the *trans*-**2**-H_2^{2+} in blue with the central *trans*-olefinic units highlighted in orange).

terminal *N*-benzyl rings and proximal to the NH_2^+ centers of the dications is directly analogous to that observed, for example, in the BPP34C10-based [4]pseudorotaxanes formed with α,α'-bis(benzylammonium)-p-xylene[12] and with bis(benzylammonium-p-toluic acid).[15] This packing motif extends in a jigsawlike manner to form the closely packed sheet illustrated in Figure 3. The upper and lower surfaces of these sheets are essentially hydrophobic, being populated by the hydrogen atoms of the polyether and terminal *N*-benzyl groups. The other unique PF_6^- ion and the included Me_2CO solvent molecules are located in small pockets formed between adjacent sheets.

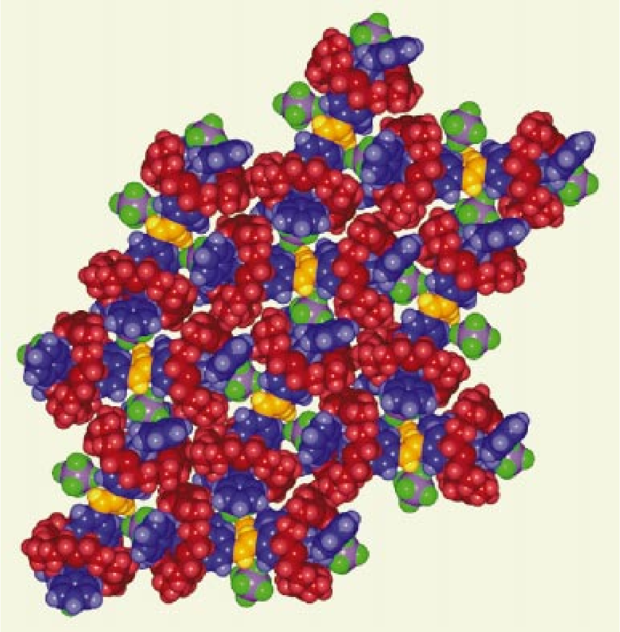


Figure 3. Space-filling representations of the jigsawlike sheets of supermolecules (with strategically located, embedded PF_6^- ions) present in the solid-state supramolecular structure of $[(\text{BPP34C10})_2\cdot(\textit{trans}\text{-}\mathbf{2}\text{-H}_2)_2]^{4+}$. The color code for the various atoms and components is identical to that described in the caption to Figure 2.

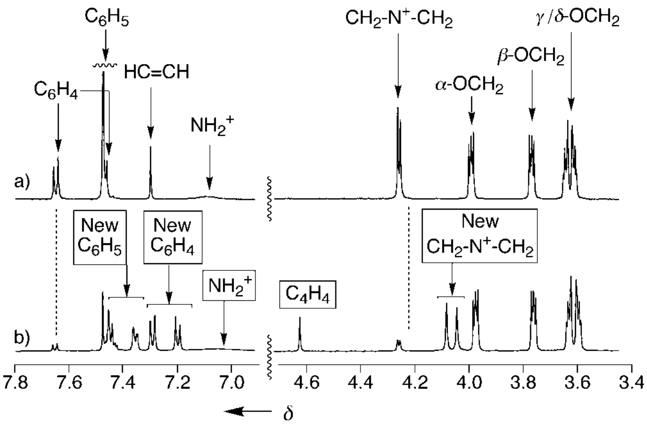
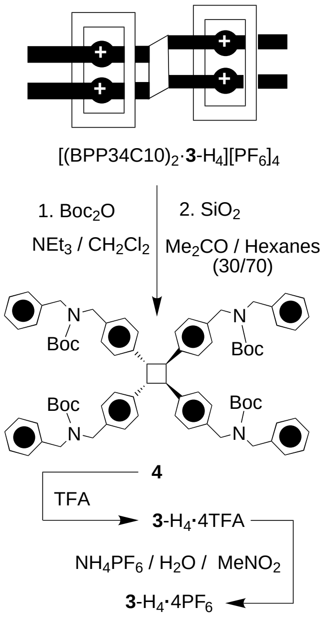


Figure 4. Partial ^1H NMR spectra (400 MHz, CD_3CN) obtained a) before and b) after solid-state irradiation of $[(\text{BPP34C10})_2\cdot(\textit{trans}\text{-}\mathbf{2}\text{-H}_2)_2][\text{PF}_6]_4$. The new signal at $\delta = 4.58$ is diagnostic of the *syn-anti-syn* diastereoisomer of $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$.

The complexation of two *trans*-$\mathbf{2}^{2+}$ dications with two BPP34C10 crown ethers forces the stilbene threads containing a dialkylammonium ion into a suitable co-conformation for a photochemical [2+2] cycloaddition; that is, the two adjacent stilbene olefin groups of $[(\text{BPP34C10})_2(\textit{trans}\text{-}\mathbf{2}\text{-H}_2)_2][\text{PF}_6]_4$ are aligned in an eclipsed co-conformation with respect to one another and are ideally set up for the solid-state [2+2] photocycloaddition. A powdered crystalline sample (421 mg) of $[(\text{BPP34C10})_2(\textit{trans}\text{-}\mathbf{2}\text{-H}_2)_2][\text{PF}_6]_4$ was irradiated[16] for 30 h with UV light from a Hanovia lamp in a rotating Pyrex tube attached to a Kugelrohr apparatus. A ^1H NMR spectrum (400 MHz, CD_3CN) of the irradiated sample is shown in Figure 4b, along with a spectrum (Figure 4a) of the sample prior to irradiation. The spectrum of the photoaddition product reveals the presence of a new singlet at δ 4.58 (which corresponds to the cyclobutane ring protons of $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$) and the almost complete disappearance of the singlet at δ 7.28 (which corresponds to the alkene protons of *trans*-$\mathbf{2}\text{-H}_2\cdot2\,\text{PF}_6$). Integration of peaks associated with the cyclobutane and stilbene derivatives suggests an approximate 80% conversion of *trans*-$\mathbf{2}\text{-H}_2\cdot2\,\text{PF}_6$ to $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$. The presence of *only one* new signal corresponding to the cyclobutane methine protons suggested that *only one* diastereoisomer of $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$ was formed.[17] The irradiated sample of $[(\text{BPP34C10})_2\cdot(\textit{trans}\text{-}\mathbf{2}\text{-H}_2)_2][\text{PF}_6]_4$ was characterized by electrospray ionization (ESI) mass spectrometry where peaks were found at *m*/*z* 837 and 536. These peaks correspond to the $\mathbf{3}\text{-H}^+$ ion of the photodimer and the BPP34C10 crown ether, respectively. No peaks were observed in the gas phase for any complex formed between the photodimer and BPP34C10; this observation is not unexpected, however, since higher order complexes with this crown ether are not always observed.[18]



Scheme 2. The isolation of $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$ from the BPP34C10 crown ethers after photoirradiation of the crystalline complex $[(\text{BPP34C10})_2\cdot(\textit{trans}\text{-}\mathbf{2}\text{-H}_2)_2][\text{PF}_6]_4$ in the solid state. Boc = *tert*-butoxycarbonyl, TFA = trifluoroacetic acid.

The cyclobutane derivative $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$ was separated from the BPP34C10 crown ethers in good yield[19] by a process (Scheme 2) involving: 1) deprotonation of $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$, followed by protection of the amino groups with di-*tert*-butyldicarbonate to give the Boc-protected derivative **4**, 2) separation of **4** from BPP34C10 by column chromatography on silica gel, 3) removal of the Boc groups from **4** with trifluoroacetic acid (TFA) to give $\mathbf{3}\text{-H}_4\cdot4\,\text{TFA}$, and 4) counterion exchange with NH_4PF_6 to regenerate $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$. The free cyclobutane derivative $\mathbf{3}\text{-H}_4\cdot4\,\text{PF}_6$ was characterized by ^{1}H NMR and ^{13}C NMR spectroscopies,[20] as well as by ESI mass spectrometry, where the peak of the highest mass (*m*/*z* 1276) corresponded to the cyclobutane derivative having lost one PF_6^- counterion. The *syn-anti-syn* stereochemistry of the cyclobutane derivative was confirmed unambiguously by X-ray crystallographic analysis[14, 21] of **3**-$H_4 \cdot 4$TFA (Figure 5a). This study also showed the tetracation to have inversion symmetry. The four NH_2^+ centers are each involved in N–H $\cdots$ O hydrogen-bonding interactions with the trifluoroacetate anions. Adjacent lattice-translated tetracations are linked by π–π stacking and C–H $\cdots$ π hydrogen-bonding interactions to form tapes (Figure 5b).

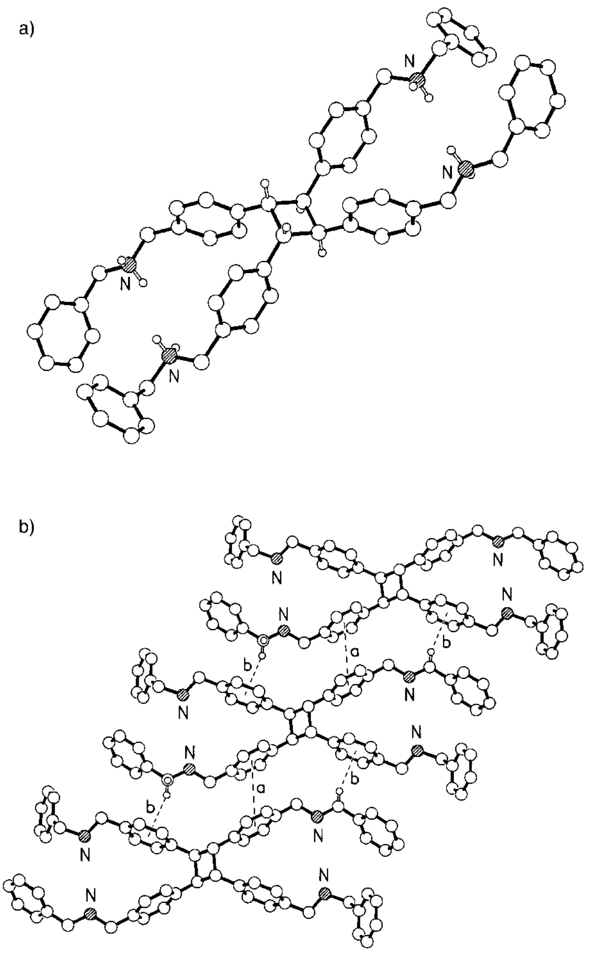


Figure 5. a) The solid-state molecular structure of **3**-H_4^{4+} showing the tetrasubstituted cyclobutane ring with the *syn-anti-syn* configuration. b) Part of one of the tapes present in the solid-state structure of **3**-$H_4 \cdot$ 4TFA. The centroid–centroid distance and mean interplanar separation (a) are 4.12 and 3.60 Å, respectively; the C–H $\cdots$ π interaction (b) has H $\cdots$ π 2.78 Å and C–H $\cdots$ π 136°.

In order to demonstrate that the BPP34C10 macrocycles are necessary to achieve the photodimerization, a powdered sample (30 mg) of *trans*-**2**-$H_2 \cdot 2PF_6$ was placed between two Pyrex slides and irradiated for a period of 5 h. No photoproduct was obtained and the only peaks observed in the ^{1}H NMR spectrum of the irradiated material corresponded to *trans*-**2**-$H_2 \cdot 2PF_6$. Photochemical studies conducted in CD_3CN solutions (30 mM) of *trans*-**2**-$H_2 \cdot 2PF_6$—either alone or in the presence of an equimolar amount of BPP34C10—resulted in *trans* to *cis* isomerization of the olefinic unit to yield the *cis*-stilbene derivative[22] *cis*-**2**-$H_2 \cdot 2PF_6$. Irradiation of *trans*-**2**-$H_2 \cdot 2PF_6$ in CD_3OD[23] (20 mM) resulted predominantly in isomerization to *cis*-**2**-$H_2 \cdot 2PF_6$, in addition to the formation of small amounts of the *syn-anti-syn* dimer **3**-$H_4 \cdot 4PF_6$, and the formation of other unidentified products.

We have demonstrated that the solid-state [2+2] photodimerization[24] of the doubly threaded and doubly encircled pseudorotaxane $[(BPP34C10)_2 \cdot (\mathbf{2}\text{-}H_2)_2][PF_6]_4$ proceeds efficiently to yield a single diastereoisomer of **3**-$H_4 \cdot 4PF_6$. The *syn-anti-syn* stereochemistry of the cyclobutane derivative, which is preordained[25] by the solid-state superstructure of the 2:2 complex,[26] was confirmed by X-ray crystallography and ^{1}H NMR spectroscopy. In the future we hope to widen the scope of this technique of solid-state supramolecular assistance by preparing other doubly threaded and doubly encircled pseudorotaxanes (formed between constitutionally asymmetric, olefin-containing dialkylammonium salts and BPP34C10) that might undergo both regiospecific and stereospecific photochemical dimerizations.

Experimental Section

4,4′-Bis(bromomethyl)stilbene[6] (1.98 g, 5.37 mmol) was dissolved in DMF (20 mL) and then benzylamine (1.26 g, 11.8 mmol) was added. The solution was stirred for 1 h and the white precipitate that formed was filtered off and then suspended in Me_2CO (20 mL). Small portions of a saturated aqueous solution of NH_4PF_6 were added until all of the white solid dissolved, and then an excess of H_2O was added to this solution. This process resulted in the formation of a white precipitate, which was filtered off and dried to yield *trans*-**2**-$H_2 \cdot 2PF_6$ (700 mg, 18%). ^{1}H NMR (CD_3CN, 500 MHz, 298 K): $\delta = 4.51$ (s, 8H), 7.15 (s, 2H), 7.32 (s, 10H), 7.43 (d, $J = 8.2$ Hz, 4H), 7.53 (d, $J = 8.2$ Hz, 4H); ^{13}C NMR ($(CD_3)_2CO$, 125 MHz, 298 K): $\delta =$ 51.0, 51.3, 127.0, 128.8, 128.9, 129.3, 130.0, 130.5, 130.7, 131.3, 138.2; MS (FAB): *m*/*z* (%): 565 (50) $[trans\text{-}\mathbf{2}\text{-}H_2PF_6]^+$, 419 (100) $[trans\text{-}\mathbf{2}\text{-}H]^+$. Crystals suitable for X-ray cystallography and photochemical irradiation were grown by vapor diffusion of *i*Pr_2O into a solution of a mixture of *trans*-**2**-$H_2 \cdot 2PF_6$ (553 mg, 0.78 mmol) and BPP34C10 (418 mg, 0.78 mmol) in Me_2CO/CH_2Cl_2, (99/1) to yield $[(BPP34C10)_2 \cdot (trans\text{-}\mathbf{2}\text{-}H_2)_2][PF_6]_4 \cdot (Me_2CO)_4$ (960 mg, 90%). These crystals (421 mg, 0.169 mmol) were powdered and then irradiated for 30 h with UV light from a Hanovia lamp in a rotating Pyrex tube attached to a Kugelrohr apparatus. The irradiated solid was suspended in CH_2Cl_2 (20 mL), and then Et_3N (210 mg, 2.07 mmol), di-*tert*-butyldicarbonate (776 mg, 3.56 mmol), and 4-dimethylaminopyridine (DMAP, 1 mg, 8 μmol) were added. The solution was washed after 10 min with H_2O (1 × 30 mL) and 1N HCl (3 × 30 mL), and then the combined aqueous phases were extracted with CH_2Cl_2. The CH_2Cl_2 solutions were combined, dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (SiO_2, Me_2CO/hexanes (3/7)) to yield **4** as a clear oil (93 mg, 49%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K): $\delta = 1.46$ (s, 36H), 4.30–4.36 (br m, 16H), 4.51 (s, 4H), 6.95 (br s, 8H), 7.15–7.20 (m, 16H), 7.21–7.52 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): $\delta = 28.0$, 47.2, 49.0, 50.1, 79.6, 127.0, 127.2, 127.6, 128.2, 128.3, 135.7, 138.1, 139.6, 155.6; MS (FAB): *m*/*z* (%): 1137 (20) $[\mathbf{4}\text{-H} - t\text{Bu} - CO_2]^+$, 1081 (25) $[\mathbf{4}\text{-H} - 2\,t\text{Bu} - CO_2]^+$, 1025 (35) $[\mathbf{4}\text{-H} - 3\,t\text{Bu} - CO_2]^+$, 925 (40) $[\mathbf{4}\text{-H} - 4\,t\text{Bu} - 2\,O_2]^+$. TFA (2 mL, 26 mmol) was added to a solution of **4** (93 mg, 75 μmol) in CH_2Cl_2 (10 mL). The mixture was evaporated to dryness after 1 h to yield **3**-$H_4 \cdot 4$TFA as a white solid. Crystals suitable for X-ray crystallographic analysis were grown by layer diffusion of hexane into a solution of **3**-$H_4 \cdot 4$TFA (2 mg, 2 μmol) in CH_2Cl_2/TFA (99/1). The remainder of **3**-$H_4 \cdot 4$TFA was suspended in $MeNO_2$ (20 mL) and washed with saturated aqueous NH_4PF_6 (20 mL) and H_2O (2 × 20 mL). The $MeNO_2$ extract was dried ($MgSO_4$), filtered, and concentrated to yield **3**-H$_4$·4F$_6$ (90 mg, 86%) as a light-brown solid. ^{1}H NMR (CD$_3$CN, 500 MHz, 298 K): $\delta = 4.03$ (s, 8H), 4.06 (s, 8H), 4.60 (s, 4H), 7.21 (d, $J = 10.2$ Hz, 8H), 7.28 (d, $J = 10.2$ Hz, 8H), 7.38–7.45 (m, 20H); ^{13}C NMR (CD$_3$CN, 125 MHz, 298 K): $\delta = 46.4$, 50.7, 51.1, 128.1, 128.9, 129.1, 129.7, 129.8, 130.1, 130.3, 141.9; MS (FAB): m/z (%): 1276 (10) [**3**-H$_4$·3PF$_6$]$^+$, 1129 (27) [**3**-H$_3$·2PF$_6$]$^+$, 983 (35) [**3**-H$_2$·PF$_6$]$^+$, 837 (70) [**3**-H]$^+$.

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[14] 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-116797 [(BPP34C10)$_2$·(*trans*-**2**-H$_2$)$_2$][PF$_6$]$_4$·(Me$_2$CO)$_4$] and -116798 [**3**-H$_4$·4TFA]. 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).

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[17] The chemical shift of this signal at $\delta = 4.58$ is consistent with the *syn-anti-syn* isomer **3**-H$_4$·4PF$_6$ since other *syn-anti-syn* tetraaryl-substituted cyclobutane derivatives have been reported to exhibit resonance of the corresponding ring proton in the range $\delta = 4.10$ to 5.00. In contrast, the *all-trans* tetraaryl-substituted isomer is expected to contain cyclobutane ring protons resonating between $\delta = 3.50$ and 3.80; see a) references [7], [9], and [10]; b) H. Shechter, W. J. Link, G. V. D. Tiers, *J. Am. Chem Soc.* **1963**, *85*, 1601–1605; c) W. H. Laarhoven, T. J. H. M. Cuppen, R. J. F. Nivard, *Tetrahedron* **1970**, *26*, 1069–1083; d) B. S. Green, L. Heller, *J. Org. Chem.* **1974**, *39*, 196–201; e) Y. Ito, T. Kajita, K. Kunimoto, T. Matsuura, *J. Org. Chem.* **1989**, *54*, 587–591.

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[19] Since the photoreaction of [(BPP34C10)$_2$·(*trans*-**2**-H$_2$)$_2$][PF$_6$]$_4$·(Me$_2$CO)$_4$ to [(BPP34C10)$_2$·**3**-H$_4$][PF$_6$]$_4$·(Me$_2$CO)$_4$ was determined by ^{1}H NMR spectroscopy to have proceeded in an 80% conversion, the overall yield of 42% (that is, 49% for Boc protection and 86% for deprotection and counterion exchange) corresponds to the isolation of 53% of **3**-H$_4$·4PF$_6$.

[20] A ^{1}H NMR chemical shift of $\delta = 4.60$ was observed for the cyclobutane proton of the free **3**-H$_4$·4PF$_6$ after its separation from the crown ethers. This δ value is consistent with the *syn-anti-syn* configuration as described in ref. [17]. The observed ^{13}C NMR chemical shift of $\delta = 46.4$ corresponds to the expected δ value for a cyclobutane carbon atom. A ^1J(C,H) value of 132 Hz, which is consistent with the expected value for this coupling in a cyclobutane ring, was obtained when broad-band decoupling was turned off; see H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH, Weinheim, **1993**, p. 95–95.

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[22] Prolonged irradiation of these solutions resulted in the production of unidentified by-products, which could correspond to dihydrophenanthrene and phenanthrene derivatives formed by the electrocyclic ring closure of *cis*-**2**-H$_2$·2PF$_6$, see C. O. Parker, P. E. Spoerri, R. E. Buckles, *J. Am. Chem. Soc.* **1955**, *77*, 1040–1041.

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[25] The pivotal role of the PF$_6^-$ counterions in determining the formation of the supermolecules in the solid state has been noted previously in related systems, see a) P. R. Ashton, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 12514–12524; b) P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 577–589; c) P. R. Ashton, M. C. T. Fyfe, M.-V. Martínez-Díaz, S. Menzer, C. Schiavo, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 1523–1534; d) P. R. Ashton, S. J.

Cantrill, J. A. Preece, J. F. Stoddart, Z.-H, Wang, A. J. P. White, D. J. Williams, *Org. Lett.* **1999**, *1*, 1917–1920; e) S. J. Cantrill, J. A. Preece, J. F. Stoddart, Z.-H. Wang, A. J. P. White, D. J. Williams, *Tetrahedron* **2000**, *56*, 6675–6681. The present research provides yet another beautiful example of anion-orchestrated self-assembly in the solid state.

[26] The thought processes that led to the design and synthesis of this 2:2 host–guest complex had their origins in the seminal work done by Cram in the 1970s on the face-to-face complexation of crown ethers with primary alkylammonium ions, see a) D. J. Cram, J. M. Cram, *Science* **1974**, *183*, 803–809; b) D. J. Cram, J. M. Cram, *Acc. Chem. Res.* **1978**, *11*, 5–14; c) "Container Molecules and Their Guests": D. J. Cram, J. M. Cram in *Supramolecular Chemistry* (Ed.: J. F. Stoddart, Royal Society of Chemistry, Cambridge, **1994**.

Novel Calcium Half-Sandwich Complexes for the Living and Stereoselective Polymerization of Styrene[**]

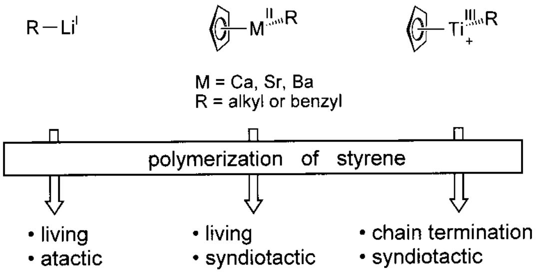
Sjoerd Harder,[*] Florian Feil, and Konrad Knoll

The many advantages of the anionic living polymerization of styrene (chain-length control, narrow molecular-weight distribution, chain-end functionalization, and particularly block-copolymerization) makes this technique the method of choice in the rational design of new styrene-based polymers.[1] The only disadvantage of this method is the lack of control of the polymers tacticity; control of tacticity offers many advantages in plastic material design.[2] Although stereoregular isotactic polystyrene was made in 1955 by use of classical Ziegler–Natta catalysts,[3] it never found any commercial application because of its extremely slow crystallization rate (crystallization times can be several days!). The discovery of its fast crystallizing syndiotactic form, obtained by polymerization with a titanocene half-sandwich complex, was therefore a revolution in polystyrene chemistry.[4] Syndiotactic polystyrene shows a low glass-transition temperature (104 °C) but high melting point (273 °C) with a high modulus and combines good electrical properties with an excellent solvent resistance.[5] The only disadvantage of stereocontrolled styrene polymerization by titanocene half-sandwiche complexes, however, is the lack of living character.

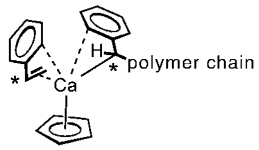
Research to combine the favorable properties of anionic living polymerization and stereocontrolled coordination polymerization has come from both sides. Anionic polymerization with *n*BuLi initiators under certain reaction conditions can produce isotactic polystyrene,[6] but traces of water seem to be essential.[7] This observation has led to the use of mixed *n*BuLi/Li-alkoxide initiators; polymerizations, however, have to be carried out in apolar solvents at −30 °C and polymerization times can take up to 5 days with only 50 % conversion.[8] Only 15 % of the chains are highly isotactic, which indicates the presence of more than one reactive site at the proposed alkoxide initiator cluster. Recently it was discovered that a mixture of living polyisoprenyllithium and LiOH polymerizes styrene with high isotacticity and without atactic parts.[9]

Attempts to make stereocontrolled coordination polymerization living are also under investigation. Under certain conditions, the polymerization of *para*-methylstyrene by titanium half-sandwich complexes shows living features, however, the system was not suitable for the living syndiotactic polymerization of styrene.[10]

Our approach to enable a living and a syndiospecific polymerization of styrene is based on "cross-breeding" the catalysts (RLi) used for classical anionic styrene polymerization and that for coordination polymerization (Scheme 1). A proposed catalytic species for coordination polymerization is a cationic Ti^{III} complex with a cyclopentadienyl spectator ligand and a growing chain. Syndiotactic stereocontrol proceeds through communication of the chiral chain-end and the stereogenic center on the coordinated monomer (**1**). A similar isolobal Group II metal compound could initiate the anionic (living) polymerization of styrene with syndiotactic insertions. We expect the polymerization to be living because of the considerable ionic (alkali metal like) character of the heavier alkaline-earth metals.[11] Syndiotactic insertion is anticipated on the basis of the very similar structure of [CpTiR$^+$] and the proposed Group II species. The use of non- or weak-coordinating solvents is a prerequisite for a coordination polymerization mechanism.



Scheme 1.



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The apparent simplicity of the desired catalyst, CpM^{II}R (Cp = C_5H_5), is in contrast to the inherent problems associated with this type of compound: a) the synthesis of reactive

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[*] Dr. S. Harder, Dipl-Chem. F. Feil
Fachbereich Chemie
Universität Konstanz
Postfach 5560, M738, 78457 Konstanz (Germany)
Fax: (+49) 7531-883137
E-mail: harder@chemie.uni-konstanz.de
Dr. K. Knoll
Kunststofflaboratorium, BASF AG
67056 Ludwigshafen (Germany)

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