

**Diastereospecific Photochemical Dimerization of a Stilbene-Containing Daisy Chain Monomer in Solution as well as in the Solid State\*\***

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The solid-state [2+2] photochemical dimerization<sup>[1]</sup> of olefins such as stilbenes is a highly efficient method for the stereospecific synthesis of cyclobutanes. In solution, however, the photochemical reactions of such olefins generally result in mixtures of products. For example, irradiation of *trans*-stilbene in solution leads to several products: *trans*-to-*cis* isomerization yields *cis*-stilbene, which then can undergo electrocyclic ring closure to form dihydrophenanthrene, which, in the presence of oxygen, is oxidized to phenanthrene<sup>[2]</sup> while [2+2] cycloaddition of *trans*-stilbene yields<sup>[3]</sup> cyclobutane products with both *syn-anti-syn* and *all-anti* stereochemistries. The reaction rates, yields, and the distribution of products from photochemical reactions are dependent on the choice of solvent.<sup>[4]</sup> For example, in nonpolar solvents, such as benzene, *trans*-to-*cis* isomerization of stilbenes is favored over a very slow dimerization process.<sup>[3]</sup> In more polar solvents, such as methanol or water, hydrophobic interactions and possibly aromatic  $\pi$ - $\pi$  stacking interactions lead to relatively rapid formation of a cyclobutane ring as the major, albeit low-yielding, reaction pathway, but with very little stereo- or regiocontrol.<sup>[4]</sup> Supramolecular assistance has provided solutions to the problem of preorganizing pairs of olefins in solution, such that efficient photochemical [2+2] dimerizations may occur. Examples of such supramolecular assistance in solution include 1) the dimerization of stilbenes within the cavities of  $\gamma$ -cyclodextrins<sup>[5]</sup> and cucurbit[8]uril,<sup>[6]</sup> 2) the use of hydrogen bonding to orchestrate a reaction<sup>[7]</sup> between a bisammonium-substituted dipyrindylethylene and a bis([18]crown-6)-substituted stilbene derivative, 3) using metal cations, such as  $K^+$  and  $Mg^{2+}$ , to template the reaction between the olefinic components of

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derivatized crown ether molecules,<sup>[8]</sup> and 4) the encapsulation and reaction<sup>[9]</sup> of acenaphthylenes and naphthoquinones within self-assembled coordination cages.

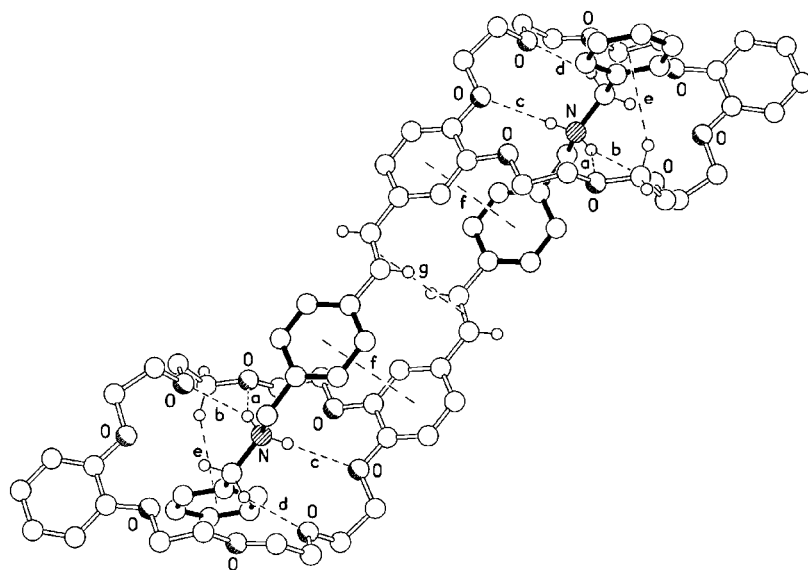
For successful dimerizations to occur in the solid state, the olefinic units must be aligned in a parallel manner with centroid...centroid separations<sup>[10]</sup> of about 3.5–4.2 Å. Supramolecular approaches have been used successfully to align stilbenes in the solid state, and their corresponding cyclobutane products have been obtained stereospecifically after photoirradiation.<sup>[11]</sup> Recently, we reported<sup>[12]</sup> a highly stereospecific, solid-state, [2+2] photocycloaddition between two bis(dialkylammonium ion)-substituted stilbene dications in a crystalline, doubly encircled and double-stranded, 2:2 host–guest complex with bisparaphenylene[34]crown-10. Although this and other examples of supramolecular preorganization in the solid state are highly efficient methods for the diastereospecific preparation of *syn-anti-syn*-substituted cyclobutanes, solid-state reactions do have their drawbacks, such as the need to obtain crystalline substrates, their relatively slow rates of reaction, and the difficulty in scaling reactions up to preparatively useful levels. As a result, it is important to find equally efficient methods for the dimerization of olefins—with both high stereo- and regiospecificity—in solution. Herein we describe a stilbene-containing crown ether/dialkylammonium ion hybrid that self-assembles into a [c2]daisy-chain-like pseudorotaxane both in solution as well as in the solid state. In this complex, the stilbene units are aligned in a head-to-tail manner with their olefinic groups positioned for efficient diastereospecific photochemical dimerizations.

Supramolecular and molecular daisy-chain-like entities<sup>[13]</sup> are becoming increasingly more appealing targets in synthesis. Previously, we demonstrated that **1**·H·O<sub>2</sub>CCF<sub>3</sub>—a self-complementary dialkylammonium salt incorporating a dibenzo[24]crown-8 (DB24C8) unit—forms dimers in a head-to-tail manner, in relatively nonpolar solvents and in the solid state, in which the NH<sub>2</sub><sup>+</sup> unit of one monomer is positioned inside the DB24C8 unit of another, and vice versa.<sup>[14]</sup> As a consequence of the asymmetric nature of the substitution of one of the catechol units of **1**·H·O<sub>2</sub>CCF<sub>3</sub>, two diastereoisomeric [c2]daisy-chain-like complexes (Scheme 1 a) are observed to interconvert slowly on the <sup>1</sup>H NMR time-scale at room temperature. In the solid state, pairs of the trisubstituted catechol rings of **1**·H·O<sub>2</sub>CCF<sub>3</sub> are aligned in a parallel manner with a centroid...centroid separation of 3.55 Å. This observation prompted us to consider replacing the central benzene unit of **1**<sup>+</sup> with a *trans*-stilbenoid unit (namely, to prepare *E*-**2**·H·O<sub>2</sub>CCF<sub>3</sub>) with the anticipation that diastereoisomeric cyclic dimer complexes (*E*-**2**·H)<sub>2</sub>·(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> (Scheme 1 b) would form in which adjacent *trans*-stilbene olefinic groups are aligned in a head-to-tail manner at a distance suitable for a photochemical [2+2] cycloaddition.

The stilbene-containing daisy-chain monomer *E*-**2**·H·O<sub>2</sub>CCF<sub>3</sub> was prepared according to the reaction sequence summarized in Scheme 2. The benzylic alcohol<sup>[15]</sup> **4** was

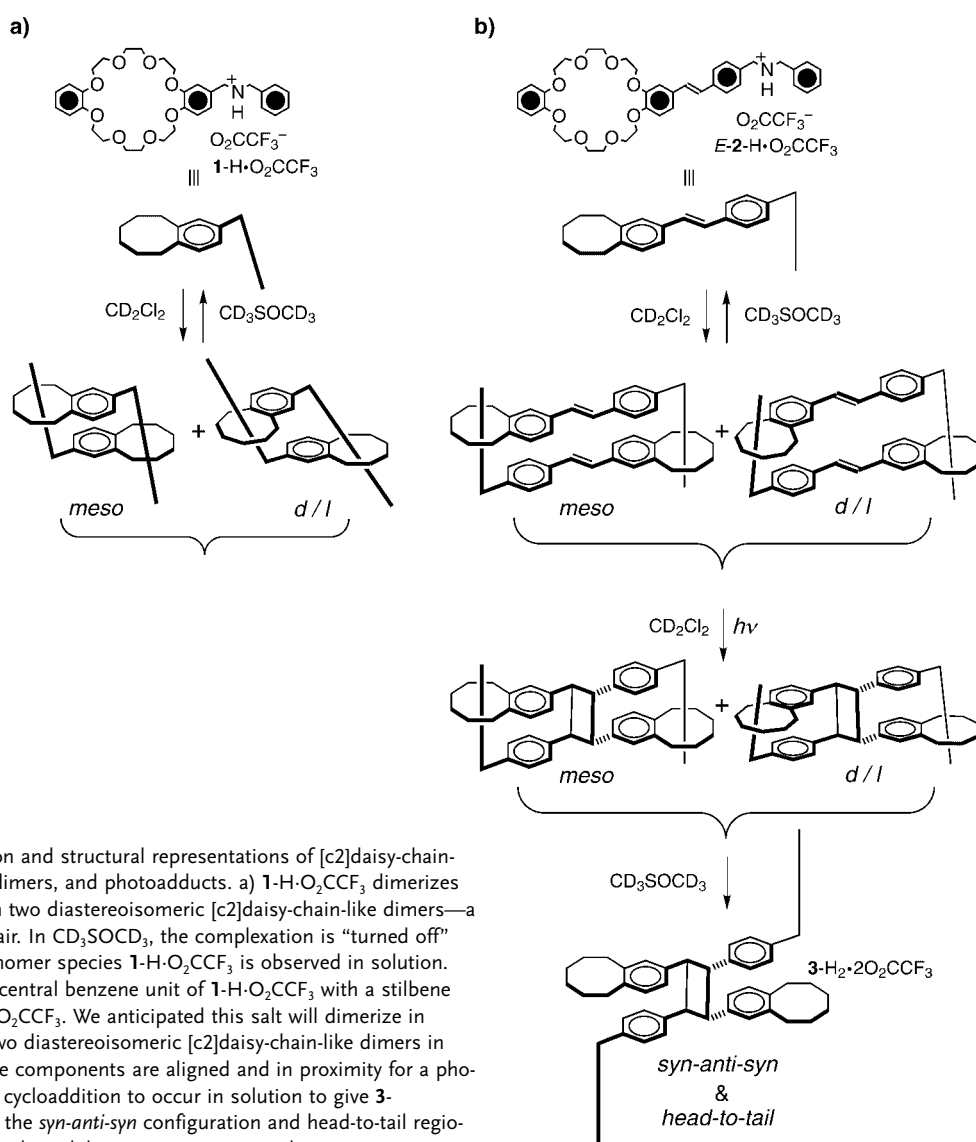
converted using triphenylphosphane and *N*-chlorosuccinimide (NCS) into the chloride **5**, which in turn was converted by a Finkelstein reaction<sup>[16]</sup> into the iodide **6**, which underwent nucleophilic substitution to give the triphenylphosphonium iodide **7**·I. A Wittig reaction<sup>[17]</sup> between **7**·I and (2-formyl)dibenzo[24]crown-8<sup>[14b]</sup> **8** gave the corresponding stilbene derivative *E*-**9**. The Boc protecting groups were removed using trifluoroacetic acid to give *E*-**2**·H·O<sub>2</sub>CCF<sub>3</sub>.

Single crystals were obtained by layer diffusion of hexanes into a solution of *E*-**2**·H·O<sub>2</sub>CCF<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. The X-ray structure<sup>[18]</sup> of *E*-**2**·H·O<sub>2</sub>CCF<sub>3</sub> reveals the formation (Figure 1) of a centrosymmetric [c2]daisy chain wherein the



**Figure 1.** Ball-and-stick representation of the [c2]daisy chain formed by a pair of [*E*-**2**·H]<sup>+</sup> ions. Hydrogen-bonding interactions X...O, H...O [Å], X—H...O [°]: **a**: 2.96, 2.17, 147; **b**: 2.98, 2.25, 138; **c**: 3.25, 2.37, 165; **d**: 3.21, 2.35, 146; the C—H...π interaction **e** has H...π 2.86 Å and C—H...π 153°; the π...π interaction **f** has centroid...centroid and mean interplanar separations of 3.96 and 3.38 Å, respectively, the rings are inclined by approximately 8°; the centroid...centroid distance **g** is 3.94 Å and the planes of the olefinic groups are separated by about 3.29 Å.

dibenzylammonium component of one molecule is threaded through the polyether ring of the other and vice versa (Figure 1). This mutual threading is accompanied by an essentially parallel stacking of the *trans*-stilbene units of the two component molecules such that the centers of the two *trans* olefinic bonds are held at 3.94 Å from each other (see Figure 2)—a geometry that should facilitate subsequent photodimerization. The co-conformation of the [c2]daisy chain is stabilized by a combination of N<sup>+</sup>—H...O, C—H...O, C—H...π, and π...π interactions (interactions **a**–**c**, **d**, **e**, and **f**, respectively, in Figure 1). The dimers form stepped stacks, with the catechol ring in one dimer entering into a parallel π-π stacking interaction with its symmetry-related counterpart in the next; the centroid...centroid and mean interplanar separations are 3.70 and 3.61 Å, respectively. These stacks and their lattice-translated counterparts are arranged to form sheets with the CF<sub>3</sub>CO<sub>2</sub><sup>−</sup> ions and the CH<sub>2</sub>Cl<sub>2</sub> solvent molecules (both of which are disordered) intercalated



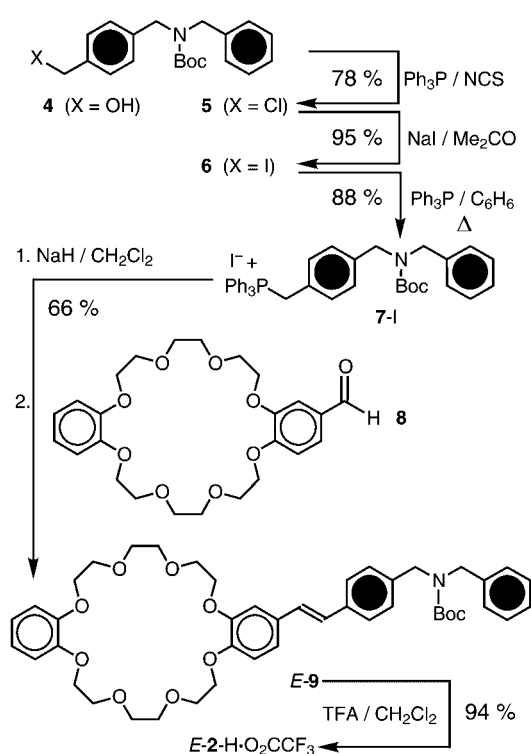
**Scheme 1.** Cartoon and structural representations of [c2]daisy-chain-like monomers, dimers, and photoadducts. a)  $1\text{-H}\cdot\text{O}_2\text{CCF}_3$  dimerizes in  $\text{CD}_2\text{Cl}_2$  to form two diastereoisomeric [c2]daisy-chain-like dimers—a *meso* and a *d/l* pair. In  $\text{CD}_3\text{SOCD}_3$ , the complexation is “turned off” and only the monomer species  $1\text{-H}\cdot\text{O}_2\text{CCF}_3$  is observed in solution. b) Replacing the central benzene unit of  $1\text{-H}\cdot\text{O}_2\text{CCF}_3$  with a stilbene unit gives  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$ . We anticipated this salt will dimerize in  $\text{CD}_2\text{Cl}_2$  to form two diastereoisomeric [c2]daisy-chain-like dimers in which the stilbene components are aligned and in proximity for a photochemical [2+2] cycloaddition to occur in solution to give  $3\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$  with the *syn-anti-syn* configuration and head-to-tail regiochemistry as the sole cyclobutane-containing product.

between adjacent sheets, there being no immediately evident electrostatic cation⋯anion interactions.

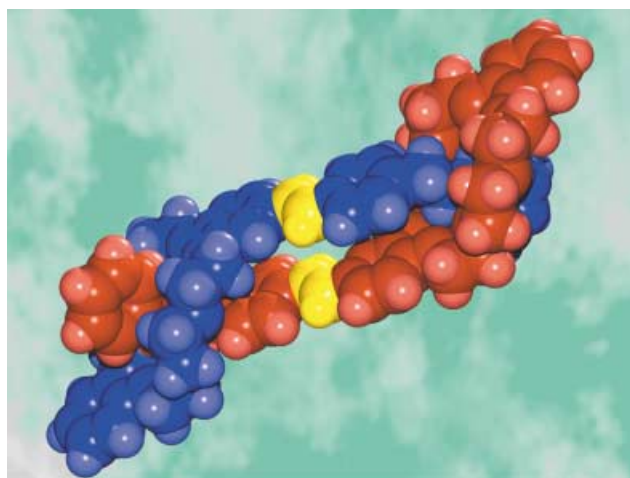
A powdered crystalline sample of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  was placed between two pyrex microscope slides and irradiated for 3 h, after which, an  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{SOCD}_3$ ) spectrum (Figure 3c) of the product displayed a resonance at  $\delta = 4.41$  ppm. The chemical shift of this signal is characteristic of the methine protons of a cyclobutane derivative—presumably  $3\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$ —possessing a *syn-anti-syn* arrangement of its tetraaryl substituents.<sup>[19]</sup> Additionally, the appearance of only one cyclobutane signal in the  $^1\text{H}$  NMR spectrum suggested that only one cyclobutane diastereoisomer had been formed in quantitative yield. This observation confirmed that the pairs of  $3\text{-H}^{2+}$  dications exist in the crystal as [c2]daisy chain dimers with eclipsed stilbene units, as illustrated in the X-ray crystal structure (Figure 1).

A solution (3.8  $\mu\text{M}$ ) of the daisy chain monomer  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  in  $\text{CD}_2\text{Cl}_2$  was studied by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum is very complex (Figure 3a) as a result

of the slow kinetics<sup>[20]</sup> of association and dissociation of the subunits and the existence of diastereoisomeric [c2]daisy-chain-like complexes; for example, two doublets at  $\delta = 6.28$  and 6.43 ppm ( $J = 1.5$  Hz) are observed for the aromatic  $\text{H}_1$  proton, which suggests<sup>[21]</sup> that two diastereoisomeric dimers of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$ —presumably a *meso* one and a *d/l* pair—exist in solution. Additionally, three of the four expected doublets, with coupling constants of 16 Hz, appear between  $\delta = 6.48$  and 6.63 ppm; two of these signals correspond to the olefinic protons of the major diastereoisomer of  $(E\text{-}2\text{-H})_2\cdot(\text{O}_2\text{CCF}_3)_2$  and one to the olefinic protons of the minor one.<sup>[22]</sup> The upfield positioning of these signals suggests that their protons experience a shielding environment, which is expected in the [c2]daisy-chain-like complexes. The  $^1\text{H}$  NMR spectrum of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  in  $\text{CD}_3\text{SOCD}_3$  is much less complicated (Figure 3b) since only the monomer species  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  is expected<sup>[23]</sup> to exist in this highly polar solvent.



**Scheme 2.** Synthesis of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$ . Boc = *tert*-butoxycarbonyl. TFA = trifluoroacetic acid.



**Figure 2.** Space-filling representation of the [c2]daisy chain formed by a pair of  $[E\text{-}2\text{-H}]^+$  ions. One monomer unit is red and the other blue; the stilbenoid carbon-carbon double bond is yellow.

We investigated the [2+2] photoaddition of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  in  $\text{CD}_2\text{Cl}_2$  because of its strong tendency to aggregate to afford cyclic noncovalent dimers in this solvent. Thus, a solution of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  in  $\text{CD}_2\text{Cl}_2$  was placed in a pyrex NMR tube, degassed by sonication, and then irradiated through a cut-off filter ( $\lambda > 350\text{ nm}$ ) for about 20 min. Since the  $^1\text{H}$  NMR spectrum of the reaction mixture in  $\text{CD}_2\text{Cl}_2$  was extremely complex, the solvent was evaporated and the spectrum (Figure 1d) of the product was recorded in

$\text{CD}_3\text{SOCD}_3$ .<sup>[24]</sup> It reveals that a significant change has occurred upon irradiation. Most diagnostically, the signals for the olefinic protons have disappeared and a broad singlet, which represents the *syn-anti-syn* cyclobutane derivative  $3\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$ , has once again appeared at  $\delta = 4.41\text{ ppm}$ . This solution-state photodimerization appears to give rise to only one diastereoisomer of the cyclobutane derivative  $3\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$  with greater than 95% conversion.<sup>[25,26]</sup>

Moreover, the  $^1\text{H}$  NMR spectrum (Figure 3d), obtained after photoirradiation of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$  in a  $\text{CD}_2\text{Cl}_2$  solution is virtually identical to that (Figure 3c) obtained following the solid-state photoirradiation of  $E\text{-}2\text{-H}\cdot\text{O}_2\text{CCF}_3$ . Hence, not only can it be inferred that [c2]daisy-chain-like pseudorotaxanes are formed in solution as well as in the solid state, it can also be concluded that the relative alignment of the stilbenoid double bonds is roughly the same in the reactive solution-state complex—namely, they are eclipsed<sup>[27]</sup>—as it is in the solid-state dimer.

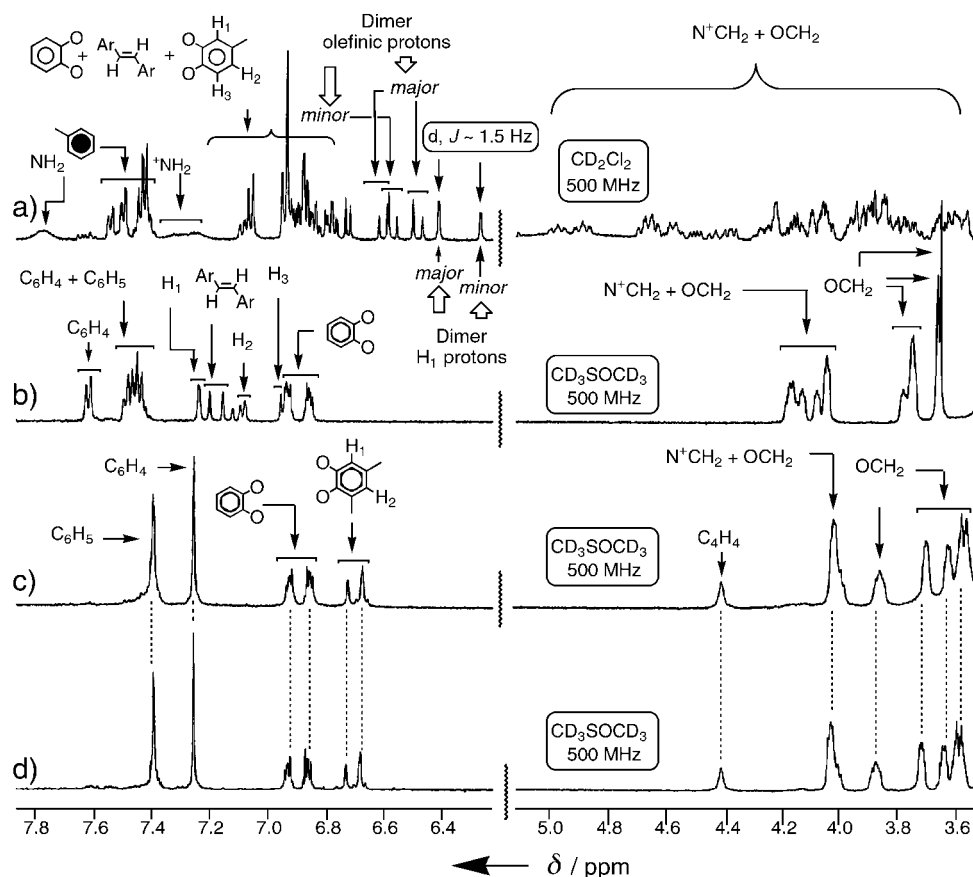
This fundamental investigation has established that supramolecular assistance to the [2+2] photodimerization can be carried out in solution as well as in the solid state, and that the photoreaction occurs with exactly the same stereospecificity in solution as it does in the solid state. This observation is important in designing supramolecular systems with multiple matching reaction centers for the construction of large cluster-like and ribbon-like compounds incorporating functionality.

## Experimental Section

**5:** Addition of a solution of  $\text{PPh}_3$  (1.67 g, 6.40 mmol) in dry THF (32 mL) to a solution of *N*-chlorosuccinimide (NCS) (980 mg, 7.3 mmol) in dry THF (37 mL) resulted in the formation of a white precipitate. A solution of **4**<sup>[15]</sup> (1.0 g, 3.20 mmol) in dry THF (10 mL) was added to the suspension, and the mixture was stirred overnight at room temperature. The THF was evaporated and the residue was subjected to column chromatography ( $\text{SiO}_2$ ; EtOAc/hexanes, 1:10), to afford **5** (890 mg, 78%) as a clear oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 298 K):  $\delta = 1.54\text{ (s, 9H)}$ , 4.38 (brs, 2H), 4.46 (brs, 2H), 4.63 (s, 2H), 7.24 (brs, 2H), 7.27 (brs, 2H), 7.32 (brs, 1H), 7.33 (brs, 1H), 7.36–7.30 ppm (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 298 K):  $\delta = 28.5$ , 31.5, 45.6, 49.0, 79.9, 127.2, 127.4, 127.7, 127.9, 128.3, 128.5, 128.6, 128.8, 129.0, 129.1, 136.4, 155.9 ppm; HR-EIMS calcd for  $\text{C}_{20}\text{H}_{25}\text{ClNO}_2$  [ $M+\text{H}$ ] $^+$ :  $m/z$  346.1496, found: 346.1566.

**6:** A solution of **5** (371 mg, 1.07 mmol) in  $\text{Me}_2\text{CO}$  (10 mL) was added dropwise to a suspension of NaI (176 mg, 1.17 mmol) in  $\text{Me}_2\text{CO}$  (30 mL), and then stirred overnight at room temperature. The salts were filtered off and the solvent was evaporated to give **6** (465 mg, 95%) as a light-brown oil, which was used without further purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 298 K):  $\delta = 1.32\text{ (s, 9H)}$ , 4.12–4.21 (brm, 4H), 4.26 (s, 2H), 6.95–7.08 (brm, 4H), 7.12–7.16 ppm (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 298 K):  $\delta = 5.4$ , 28.1, 29.5, 49.4, 53.5, 127.0, 127.2, 127.6, 128.0, 128.3, 128.6, 128.7, 129.0, 129.1, 138.1, 155.6 ppm; HR-EIMS calcd for  $\text{C}_{20}\text{H}_{25}\text{INO}_2$  [ $M+\text{H}$ ] $^+$ :  $m/z$  448.0852, found: 448.0921.

**7-I:** A solution of **6** (262 mg, 0.60 mmol) and  $\text{PPh}_3$  (173 mg, 0.66 mmol) in benzene (50 mL) was heated under reflux for 2 h. After cooling the reaction mixture down to room temperature, the precipitate was filtered off to give **7-I** (371 mg, 88%) as a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 298 K):  $\delta = 1.45\text{ (s, 9H)}$ , 4.21–4.31 (brm, 4H), 5.24 (d, 2H,  $J = 13.1\text{ Hz}$ ), 6.97–7.26 (brm, 4H), 7.26–7.34 (m, 5H), 7.61–7.69 ppm (m, 15H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 298 K):  $\delta = 28.3$ , 30.6 ( $J_{\text{PC}} = 45.8\text{ Hz}$ ), 48.4, 49.5, 117.5 ( $J_{\text{PC}} = 85.3\text{ Hz}$ ),



**Figure 3.** a) The  $^1\text{H}$  NMR spectrum of  $E\text{-}2\text{-H-O}_2\text{CCF}_3$  in  $\text{CD}_2\text{Cl}_2$  shows two major diastereoisomeric [c2]daisy-chain-like complexes in solution, presumably the *meso* and *d/l* pairs. b) A much simpler  $^1\text{H}$  NMR spectrum of  $E\text{-}2\text{-H-O}_2\text{CCF}_3$  in  $\text{CD}_3\text{SOCD}_3$  where complexation is “turned off”. This spectrum reveals how  $E\text{-}2\text{-H-O}_2\text{CCF}_3$  looks in  $\text{CD}_3\text{SOCD}_3$  before photochemical irradiation. c)  $^1\text{H}$  NMR spectrum of  $3\text{-H}_2\text{-}2\text{O}_2\text{CCF}_3$  after solid-state irradiation of crystalline  $E\text{-}2\text{-H-O}_2\text{CCF}_3$ . d) After irradiation of  $E\text{-}2\text{-H-O}_2\text{CCF}_3$  in  $\text{CD}_2\text{Cl}_2$ , a  $^1\text{H}$  NMR spectrum of the photoproduct taken in  $\text{CD}_3\text{SOCD}_3$  reveals  $3\text{-H}_2\text{-}2\text{O}_2\text{CCF}_3$  as the major product. A singlet centered on  $\delta = 4.41$  ppm corresponds to the methine protons present in a cyclobutane ring with *syn-anti-syn* stereochemistry.

125.6, 127.2, 128.0, 128.2, 128.4, 130.1 ( $J_{\text{PC}} = 12.5$  Hz), 131.6 ( $J_{\text{PC}} = 5.3$  Hz), 134.3 ( $J_{\text{PC}} = 9.8$  Hz), 135.0 ( $J_{\text{PC}} = 2.8$  Hz), 137.6, 138.4, 155.7 ppm; HR-FABMS calcd for  $\text{C}_{38}\text{H}_{39}\text{NO}_2\text{P}^+$  [ $M$ ] $^+$ :  $m/z$  572.2718, found: 572.2713.

**$E\text{-}2\text{-H-O}_2\text{CCF}_3$ :** A mixture of **7-I** (371 mg, 0.53 mmol) and NaH (51 mg, 2.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL) was stirred at ambient temperature for 30 min and then a solution of **8** (253 mg, 0.53 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added slowly. The mixture was stirred for 20 h, before 1N HCl (2 mL) was added to quench the reaction. The mixture was partitioned between  $\text{CH}_2\text{Cl}_2$  (25 mL) and  $\text{H}_2\text{O}$  (20 mL). The organic layer was washed with 1N HCl ( $2 \times 20$  mL), dried ( $\text{MgSO}_4$ ), and then evaporated to dryness. The residue was subjected to column chromatography ( $\text{SiO}_2$ ; EtOAc/hexanes, 3:7) to afford **E-9** as a clear oil (269 mg, 66%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 298 K):  $\delta = 1.50$  (s, 9H), 3.83–3.85 (m, 8H), 3.91–3.96 (m, 8H), 4.13–4.18 (m, 6H), 4.21–4.23 (m, 2H), 4.34 (brs, 2H), 4.44 (brs, 2H), 6.84 (d,  $J = 8$  Hz, 1H), 6.86–6.92 (m, 4H), 6.93 (d,  $J = 16$  Hz, 1H), 6.99 (d,  $J = 16$  Hz), 7.02–7.04 (m, 1H), 7.06 (d,  $J = 1.8$  Hz, 1H), 7.12–7.29 (m, 7H), 7.44 ppm (d,  $J = 8$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 298 K):  $\delta = 28.3$ , 31.5, 69.2, 69.3, 69.4, 69.7, 69.8, 80.0, 111.6, 113.7, 113.9, 120.3, 121.3, 126.3, 127.1, 128.2, 128.4, 130.8, 148.7, 148.8, 148.9, 155.9 ppm; HR-FABMS calcd for  $\text{C}_{45}\text{H}_{55}\text{NO}_{10}\text{Na}^+$  [ $M+\text{Na}$ ] $^+$ :  $m/z$  792.3749, found: 792.3718. TFA (1 mL, 13 mmol) was added to a solution of **E-9** (269 mg,

0.35 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) and the mixture was stirred for 1 h before being evaporated to dryness to yield **E-2-H-O<sub>2</sub>CCF<sub>3</sub>** as a white solid (207 mg, 94%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 500 MHz, 298 K):  $\delta = 3.65\text{--}3.66$  (m, 8H), 3.74–3.79 (m, 8H), 4.04–4.12 (m, 8H), 4.13–4.19 (m, 4H), 6.85–6.87 (m, 2H), 6.93–6.95 (m, 3H), 7.08 (dd,  $J = 8.3$ , 1.5 Hz, 1H), 7.14 (d,  $J = 16.3$  Hz, 1H), 7.22 (d,  $J = 16.3$  Hz, 1H), 7.24 (d,  $J = 1.5$  Hz, 1H), 7.42–7.49 (m, 7H), 7.62 (d,  $J = 8$  Hz, 2H), 9.18 ppm (brs, 2H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 125 MHz, 298 K):  $\delta = 50.4$ , 50.5, 69.0, 69.1, 69.4, 69.5, 70.7, 111.7, 114.0, 114.4, 120.9, 121.5, 125.9, 126.6, 129.0, 129.1, 129.4, 129.7, 130.2, 130.3, 130.4, 130.7, 132.1, 132.2, 138.4, 148.9, 158.3 ppm; HR-FABMS calcd for  $\text{C}_{40}\text{H}_{48}\text{NO}_8$  [ $E\text{-}2$ ] $^+$ :  $m/z$  670.3408, found: 670.3374.

**$3\text{-H}_2\text{-}2\text{O}_2\text{CCF}_3$ :** Irradiation in solution: A solution of **E-2-H-O<sub>2</sub>CCF<sub>3</sub>** (2.6 mg, 3.8  $\mu\text{mol}$ ) in  $\text{CD}_2\text{Cl}_2$  (1 mL) was degassed by sonication in a pyrex NMR tube for about 20 min. The reaction mixture was then irradiated for 20 min with UV light from a Hanovia lamp in the presence of a filter ( $\lambda > 350$  nm). The solvent was evaporated to give **3-2H<sub>2</sub>-2O<sub>2</sub>CCF<sub>3</sub>** as a white solid (2.6 mg, 95%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 500 MHz, 298 K):  $\delta = 3.45\text{--}3.49$  (m, 8H), 3.58–3.59 (m, 8H), 3.64–3.65 (brs, 8H), 3.72 (brs, 8H), 3.88–3.89 (brs, 8H), 3.99–4.03 (brs, 16H), 4.41 (brs, 4H), 6.69 (brs, 4H), 6.74 (brs, 2H), 6.86–6.88 (m, 4H), 6.93–6.95 (m, 4H), 7.27 (s, 8H), 7.40 (s, 10H), 9.09 ppm (brs, 4H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 125 MHz, 298 K):  $\delta =$

46.5, 47.0, 49.9, 50.0, 68.8, 68.9, 69.5, 70.2, 114.4, 121.5, 128.8, 128.9, 129.3, 129.8, 130.2, 132.0, 133.7, 142.3, 146.9, 147.9, 148.8 ppm; HR-FABMS calcd for  $C_{80}H_{95}N_2O_{16} \cdot 2TFA [3-H]^+$ :  $m/z$  1339.6603, found: 1339.6719. Irradiation in the solid state: Crystals were grown by layering hexanes over a solution of *E*-2-H-O<sub>2</sub>CCF<sub>3</sub> (5 mg) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL). The crystals were filtered, air-dried, placed between two pyrex microscope slides, and then irradiated for about 3 h to give 3-2H<sub>2</sub>-O<sub>2</sub>CCF<sub>3</sub> (5 mg, 100%) as a white solid.

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- [19] The chemical shift of this signal at  $\delta$  = 4.41 ppm is consistent with the *syn-anti-syn* isomer 3-H<sub>2</sub>-2O<sub>2</sub>CCF<sub>3</sub>, since other *syn-anti-syn* tetraaryl-substituted cyclobutane derivatives have been reported (see refs. [3], [6], [11f], and [12]) to exhibit resonance of the corresponding ring proton in the range  $\delta$  = 4.10 to 5.00 ppm. In contrast, the *all-anti* tetraaryl-substituted isomer is expected to contain cyclobutane ring protons resonating between  $\delta$  = 3.50 and 3.80 ppm.
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- [21] Although we have depicted (Scheme 1) the major and minor conformations of (*E*-2-H)<sub>2</sub>-(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> to be those in which the olefinic units of each monomer are eclipsed, there exists the

possibility of other co-conformations being populated in which the olefinic units are oriented in staggered arrangements. Since these staggered co-conformations are diastereoisomeric with respect to the eclipsed ones, the well-resolved signals observed for the olefinic protons suggest that if these co-conformations are populated, then they are interconverting rapidly with the eclipsed co-conformations on the  $^1\text{H}$  NMR time-scale at 500 MHz at 300 K.

- [22] We reached this conclusion by analogy to the similar set of two signals for the corresponding  $\text{H}_1$  proton of  $\mathbf{1}\text{-H}\cdot\text{O}_2\text{CCF}_3$  observed in its  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{CN}$ . See ref. [14].
- [23] The FAB mass spectrum of  $E\text{-2-H}\cdot\text{O}_2\text{CCF}_3$  in  $\text{Me}_2\text{SO}$  reveals peaks at  $m/z$  692.52 (100%) and 1339.98 (10%), which correspond to monomeric  $[E\text{-2}+\text{Na}]^+$  and a small amount of the dimeric  $[(E\text{-2})_2\text{-H}]^+$ , respectively. By contrast, the FAB mass spectrum of  $E\text{-2-H}\cdot\text{O}_2\text{CCF}_3$  in  $\text{CH}_2\text{Cl}_2$  reveals peaks at  $m/z$  670.34 (60%) and 692.33 (20%) which correspond to the doubly charged [c2]daisy-chain-like pseudorotaxane  $[(E\text{-2})_2+\text{H}+\text{Na}]^{2+}$  and a small amount of the monomer  $[E\text{-2}+\text{Na}]^+$ , respectively.
- [24] When a solution of  $E\text{-2-H}\cdot\text{O}_2\text{CCF}_3$  (3.8  $\mu\text{mol}$ ) was irradiated in  $\text{CD}_3\text{SOCD}_3$  (1 mL) for 20 min, *trans*-to-*cis* isomerization occurred to yield  $E\text{-2-H}\cdot\text{O}_2\text{CCF}_3$  and  $Z\text{-2-H}\cdot\text{O}_2\text{CCF}_3$  as the only two species present in solution. No cyclobutane derivative was observed in the  $^1\text{H}$  NMR spectrum. This result is not surprising since no dimerization is expected to occur in  $\text{CD}_3\text{SOCD}_3$ . See ref. [20].
- [25] A slight impurity is suggested by the presence of a small signal at  $\delta = 7.6$  ppm in the  $^1\text{H}$  NMR spectrum, but this contaminant also appears to be present in the initial sample of  $E\text{-2-H}\cdot\text{O}_2\text{CCF}_3$ .
- [26] It is worth noting that both the *meso* and *dll* pair of diastereoisomers of  $(E\text{-2-H})_2\cdot(\text{O}_2\text{CCF}_3)_2$  yield the same head-to-head and *syn-anti-syn* diastereoisomer of  $\mathbf{3}\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$ . The *meso* and *dll* diastereoisomeric self-complexes of  $\mathbf{3}\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$  are not observed in  $\text{CD}_3\text{SOCD}_3$  because intramolecular hydrogen-bonding interactions are eradicated. These two self-complexes exist in less polar solvents, a feature that explains the complicated nature of the  $^1\text{H}$  NMR spectrum of  $\mathbf{3}\text{-H}_2\cdot 2\text{O}_2\text{CCF}_3$  in  $\text{CD}_2\text{Cl}_2$ .
- [27] If the staggered co-conformations of  $(E\text{-2-H})_2\cdot(\text{O}_2\text{CCF}_3)_2$  (see ref. [22]) were capable of undergoing [2+2] cycloaddition in solution, we would expect to observe also the formation of the *all-anti* cyclobutane diastereoisomer as a product.