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Supramolecular Catalysis of Olefin [2 + 2] Photodimerization

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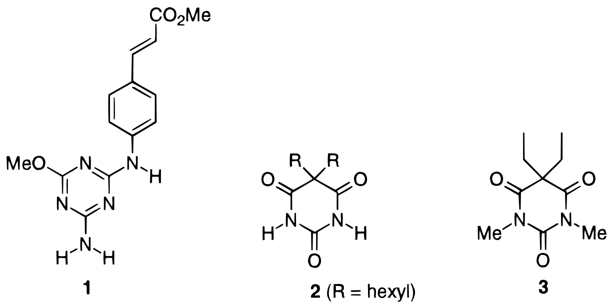
Supramolecular catalysis differs from conventional catalysis by reversibly binding the reagents to further control their reactivity and, in this regard, bears resemblance to enzymatic catalysis.[1] Because of the short-lived nature of electronically excited states, photophysical processes are particularly prone to profit from pre-organization of the reactive centers, and important organizational effects have been observed for photoinduced electron and energy transfer in ordered assemblies.[2] On the other hand, the use of supramolecular architectures to control photochemical reactions in solution is rare,[3,4] despite the remarkable potential of using light to trigger specific reaction centers within complex supramolecular structures. To test this concept, we have designed a supramolecular hydrogen-bonded assembly based on a cinnamic ester derivative covalently linked to a diaminotriazine moiety. The latter serves as a molecular recognition unit, used as a handle to position the photosensitive cinnamate chromophores.

Chart 1



Cinnamic acid has long been known for undergoing topochemically controlled photodimerization in the solid,[5] whereas the ester derivatives undergo moderately efficient dimerization only in the absence of solvent[6] or in the presence of a Lewis acid catalyst.[7] The hydrogen-bonding pattern of the diaminotriazine unit in **1**[8] is complementary to that of barbituric acid and in the presence of **2** various hydrogen-bonded dimers and trimers may be formed. In one of these trimers, the photoactive cinnamates are held face-to-face, a geometry known to favor cyclodimerization[9] (Figure 1). Thus, whereas irradiation of **1** in solution should result in the slow formation of various cyclobutane dimers, as is generally the case for cinnamate esters, the addition of **2**, acting as a molecular scaffold, is expected to exert a catalytic effect for the selective formation of *syn* photodimers. Provided the templated reaction is faster, the equilibrium mixture will shift toward the templated products.

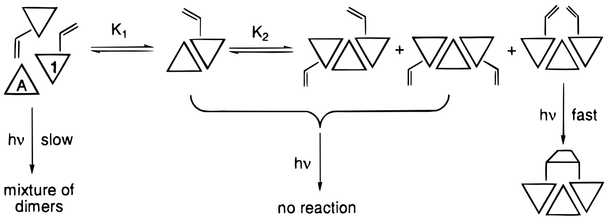


Figure 1. In the presence of a suitable molecular template (A) such as **2**, **1** may form several hydrogen-bonded assemblies (two dimers, only one shown, and three trimers), of which one places two photoreactive cinnamate chromophores in close proximity, favoring the formation of *syn* photodimers. In its absence, or in the presence of an unsuitable template (e.g. **3**), the slow formation of a mixture of photodimers is expected.

The binding of **1** to **2** is moderately strong, as evidenced by NMR titration experiments. Addition of aliquots of **2** to a solution of **1** (6 mM in $CDCL_3$) causes a displacement of the primary and secondary N−H protons of the aminotriazine moiety, as well as of the barbiturate N−H protons. The data are best fit[10] by a 2:1 binding isotherm with binding constants $K_1 = 620\ M^{-1}$ and $K_2 = 410\ M^{-1}$.[11] Crystal structures of structurally related compounds forming hydrogen-bonded tapes[12] can be used as a basis for molecular modeling of the possible hydrogen-bonded structures. In the energy-minimized structure of the trimer in which the cinnamates are proximal, the two chromophores are held face to face with the reactive double bonds 4.4 Å apart. Although this distance is slightly larger than the optimum distance yielding photodimers in the solid (~3.7 Å),[13] flexibility within the framework is expected to allow the reactive centers to approach.

Degassed solutions of **1** (10^{-2} M in dichloromethane) were irradiated on an optical bench with 350 nm monochromatic light (or on a RAYONET reactor equipped with 350 nm lamps for preparative irradiations) to selectively excite the 4-aminocinnamate chromophore, and analyzed by HPLC. Upon irradiation, rapid *Z*, *E* isomerization leads to a photostationary state composed of a 2:1 mixture of *Z*-: *E*-cinnamate isomers. Upon prolonged irradiation, the emergence of one major and six new minor peaks is detected, corresponding to the formation of photoproducts. Under identical irradiation conditions, solutions of **1** containing 0.5 equivalents of **2** displayed enhanced rates of formation for three of the photoproducts. Compounds corresponding to these peaks (**4a**, **4b**, and **4c**) were isolated by preparative HPLC and

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(8) Compound **1** was prepared by Heck coupling between 2-amino-4-(4-iodophenyl)amino-6-methoxy[1, 3, 5]triazine and methylacrylate in 68% yield. Experimental details will be published elsewhere.

(9) Dimerization efficiencies of > 80% have been observed in suitably constructed cinnamophanes: Greiving, H.; Hopf, H.; Jones, P. G.; Bubenitschek, P.; Desvergne, J.-P.; Bouas-Laurent, H. *Liebigs Ann.* **1995**, 1949.

(10) The program EQNMR was used to fit the experimental data. Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

(11) These values are comparable to those reported for analogous imide-diaminotriazine receptors: Park, T. K.; Schroeder, J.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5125.

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characterized by ^{1}H NMR and mass spectroscopy. Many of the cinnamate photodimers have been previously characterized,[6,7,14] and this facilitates their structural assignment. In the case of the major product **4a**, spectral data indicates a symmetrical head-to-head (truxinic) dimer with a cis orientation of the phenyl groups. Because no dimerization originates from excited *Z*-cinnamates,[6] **4a** is assigned the β-truxinate geometry. Interestingly, this contrasts the preference for the δ-truxinate dimer observed in neat ethylcinnamate, and may be an indication of a predominantly singlet state dimerization mechanism. Compound **4b** is an unsymmetrical neotruxinate dimer, originating from the dimerization of an *E*- and a *Z*-cinnamate in an *endo* head-to-head approach. Finally, **4c** is attributed the ϵ-truxillate structure, resulting from an *endo* head-to-tail dimerization of two *E*-cinnamate chromophores.

The formation of **4c** is intriguing, as head-to-tail dimers are normally disfavored in cinnamate photodimerizations.[6,15] The origin of this regioselectivity is proposed to lie in the structure of the supramolecular assembly responsible for the catalysis, as illustrated in Figure 2. Rotational freedom about the phenyl-ethenyl C—C bond in the ternary complex in which the two cinnamates are face to face generates two conformers that lead to syn head-to-head (**4a**) or syn head-to-tail (**4c**) dimers. Ternary complexes containing one *Z*-cinnamate isomer give rise to neotruxinate dimer **4b**.

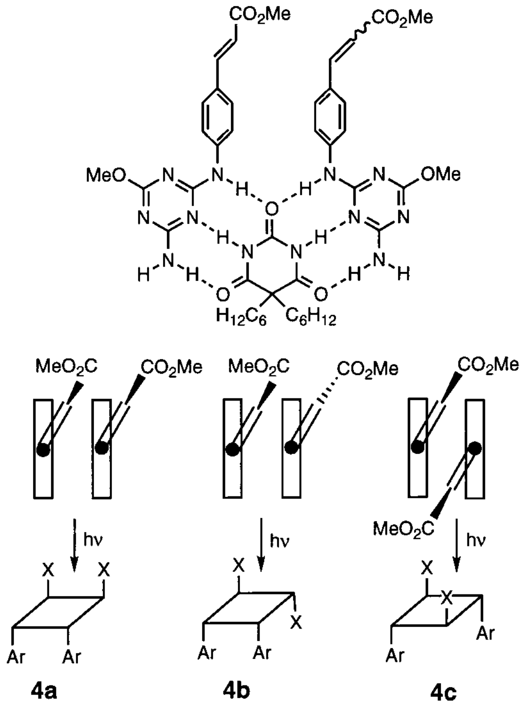

Figure 2. Proposed origin of the observed regioselectivity in the photodimerization of **1** in the presence of **2**: The reactive trimer in which the cinnamates are held face-to-face may place the double bonds *syn* or *anti*. The former yields dimers **4a** or **4b** (in the case of two *E*-cinnamates, or one *E*- and one *Z*-cinnamate isomers, respectively), whereas the latter leads to the formation of a head-to-tail ϵ-truxillate dimer (**4c**). Bottom: View along the phenyl-ethenyl C—C bond illustrating the mutual orientation of the reactive double bonds.

To confirm the supramolecular nature of the catalytic activity, and to exclude a change in reaction mechanism due to the presence of **2**, irradiations were conducted in the presence of **3**, in which the hydrogen-bonding N—H sites are blocked by methyl groups. Table 1 presents the quantum yields of the isolated photoproducts in the absence and presence of **2** or **3**. Whereas the presence of **2** exerts a catalytic effect on the formation of **4**, quantum yields in the absence of **2** or in the presence of **3** are within experimental error. A 3- to 10-fold yield enhancement for the formation of dimers **4** is observed in the presence of **2**. From K_1 and K_2, and assuming a statistical distribution of trimers, one may estimate the quantum yield for the dimerization of two *E*-cinnamates in the supramolecular assembly (leading to the formation of **4a** or **4c**) to be ~0.06, a 75-fold increase with respect to solution.[16]

Table 1. Quantum Yields^a of Photodimers$\cdot 10^3$

	1 alone^c	0.5 equiv of **2**^{b}	0.5 equiv of **3**^{c}
4a	0.7	2.3	0.7
4b	0.1	0.6	0.1
4c	<0.1	0.8	<0.1

^{a} Measured at low conversion and corrected for absorption by the unreactive *Z*-isomer at $[\mathbf{1}] = 10^{-2}$ M in degassed (freeze−pump−thaw) dichloromethane solutions at 20 °C. ^{b} Determined using Aberchrome actinometry at 350 nm. ^{c} Estimated by comparison to quantum yield determined in the presence of 0.5 equiv of **2**.

Transposition of the topochemical nature of cinnamate photodimerization from the solid to solution is particularly interesting, and one would expect the dimers formed to retain the predimerization organization present in the supramolecular assembly. This indeed appears to be the case, as evidenced by the "capture" through dimers **4a**, **4b**, and **4c** of different geometrical isomers within the supramolecular assembly. The photoproducts display molecular recognition capabilities due to their tweezer-like shape, induced by the template molecule. For example, titration of **4a** with **2** indicates the formation of a 1:1 complex with $K_{\mathrm{ass}} = 6800$ M^{-1}, consistent with binding of the barbiturate within the cleft formed by the two aminotriazine units.[17]

In conclusion, we have shown that supramolecular catalysis, operating through molecular recognition, can be used to promote and control excited-state reactions. The rigid cyclobutane structures formed can be used to advantageously capture the organization induced by supramolecular architectures, providing a photochemical alternative to olefin metathesis. Additionally, the preferential formation of photoproducts that are receptors of the template is an example of substrate-induced receptor synthesis. The extension of this work to the formation of two-dimensional polymeric ribbon structures is in progress.

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Supporting Information Available: Details of binding constant measurements, and characteration of photodimers **4a**, **4b**, and **4c**: ^{1}H, ^{13}C NMR, COSY, HMQC, EI-MS for **4a**, ^{1}H NMR, FAB- and EI-MS for **4b** and **4c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Ben Efraim, D. A.; Green, B. S. *Tetrahedron* **1974**, *30*, 2357.

(15) The formation of head-to-tail dimers is more commonly observed in the solid. Crystal engineering can favor the formation of the ϵ-truxillate dimer [Ito, Y.; Borecka, B.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1995**, *36*, 6083], as can the use of Lewis acids in solution [ref 6].

(16) This presumably leads to an underestimation, as the reactive trimer is calculated to be least-favored energetically (PM3 calculations). Overall, 9 different trimers can be formed, and their interconversion becomes slow on the NMR time scale at 193 K (CH_2Cl_2, 400 MHz).

(17) The observed binding constant is comparable to that reported in ref 9, but lower than those for tailored barbiturate receptors [Chang, S. K.; Van Engen, D.; Fan, E.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 7640].