**Photoisomerization**

The Catalytic Z to E Isomerization of Stilbenes in a Photosensitizing Porous Coordination Network**

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The tris(4-pyridyl)triazine ligand (1) is an important organic building block for self-assembled coordination cages and networks. Typically employed because of its rigid planarity, triangular shape, and commercial availability, ligand 1 is extremely electron-deficient and, upon coordination of the pyridyl arms, 1 can become electro- and photochemically active. Guest interactions with the low-lying lowest unoccupied molecular orbital (LUMO) of 1 in triazine-based hosts regularly generate host–guest charge-transfer complexes, and photoradiation can induce efficient energy transfer or, in some cases, photoinduced electron transfer.

We hypothesized that network 2, which is generated from 1 and ZnI₂, could display similar photochemistry in the solid state; thus we examined the photoinduced isomerization of stilbene within coordination network 2 (Scheme 1a). Encapsulated within the pores of 2, (Z)-stilbene selectively isomerized to (E)-stilbene under visible light irradiation (Scheme 1b); the Z/E equilibrium ratio typical for the photostationary state (Z/E = 92:8 at λ_ex = 313 nm) was not obtained. As guest molecules can freely diffuse from the pores of 2 into the solution, crystals of 2 efficiently catalyzed the one-way Z→E isomerization of stilbene in cyclohexane.

The porous network complex \([([\text{ZnI}_2]_3(1)_{3a} \cdot x(\text{C}_6\text{H}_5\text{NO}_2))]_n\), \((2, x \approx 5.5)\) employed in this work was prepared according to the reported procedure. When the as-synthesized network 2 was soaked in a solution of (Z)-stilbene (3a) in cyclohexane, the crystals immediately turned from pale to bright yellow. Elemental analysis showed the inclusion of approximately one molecule of (Z)-3a per unit with a formula of \([([\text{ZnI}_2]_3(1)_{3a} \cdot x(\text{C}_6\text{H}_5\text{NO}_2)))_n\), \((2^*, x \approx 1.1, y \approx 1.0)\). The diffuse reflectance UV/Vis spectrum showed a new, broad charge-transfer (CT) band at approximately 450 nm. Since this CT band was not observed in a solution of ligand 1 and (Z)-3a in toluene, coordination of 1 to zinc(II) ions and proximity of the guest with 1 in the network pore play a crucial role in inducing effective CT interactions.

Crystals of 2', which were suspended in a solution of (Z)-3a in cyclohexane, were photoirradiated with a Xe lamp (λ_ex = 400–500 nm) for 83 h. This procedure resulted in greater than 98% conversion into (E)-3a in both the crystal and in the supernatant, as determined by 1H NMR spectroscopy. To analyze the stilbene contained in network 2', the crystals were decomposed with hydrochloric acid and extracted with CHCl₃. No other photo-by-products, for example, dihydrophenanthrene or photooxidized products, were detected. Finally, X-ray diffraction analysis of the photoirradiated network 2' provided convincing evidence of the formation of (E)-3a in the pores of network 2' (Figure 1 and the Supporting Information). Encapsulated molecules of (E)-3a exhibited only minor disorder and are distributed over three non-equivalent positions, one of which interacts with a nearby triazine moiety 1 by aromatic–aromatic interactions (interplanar distance ca. 3.4 Å; Figure 1b).

Based on the following observations, we believe the selective photoisomerization of (Z)-3a to (E)-3a only occurs within the pores of 2': 1) In the absence of network 2, photoisomerization did not occur and even the individual network component(s) (ligand 1 and/or ZnI₂) were insufficient to catalyze the conversion. 2) When crystals of 2' were removed during photoradiation, isomerization stopped. 3) Photoisomerization was dramatically retarded when pyrene, which is strongly bound by 2'[a] and inhibits guest exchange, was added to the reaction mixture. 4) The E/Z ratio of stilbene increases faster within the crystals of 1 than in the supernatant[b] (Figure 2). These results demonstrate that

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[b] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001902.
photoisomerization first occurs within the pores of 2\(^*\) and, once formed, the (E)-stilbene in the pores rapidly exchanges with unreacted (Z)-stilbene in solution. These equilibrium processes continue until nearly all (>98%) of stilbene is converted into the E isomer.

A variety of stilbene derivatives was converted to the E isomer in the presence of catalytic quantities of 2 (Scheme 2). When a solution of stilbene 3b in cyclohexane (30 mm; 45:55 E/Z mixture)\(^{[7]}\) was irradiated in the presence of a catalytic amount of crystalline 2 for 3 days, almost-pure (E)-3b was obtained (>98% conversion). 4,4’-Dibromostilbene 3c (90:10 E/Z)\(^{[7]}\) also isomerized to the E isomer with greater than 98% conversion. However, no conversion was observed for the electron-poor 4,4’-dinitrostilbene (3d; 85:15 E/Z)\(^{[7]}\) which is a poor guest for network 2 and was not included, thus further supporting that the reaction occurs within the porous network 2.\(^{[8–10]}\)

In conclusion, the electron-deficient triazine moieties 1 in coordination network 2 are photoactive and catalyze the Z \(\rightarrow\) E photoisomerization of stilbenes under visible light. The photoisomerization occurs within the pores of 2 and the resulting (E)-stilbene rapidly exchanges with (Z)-stilbene in solution so that only a few crystals suffice to completely convert the entire solution. Although free ligand 1 is photochemically inert, it becomes photoactive when incorporated into three dimensional coordination cages and porous networks. We believe that photoelectron-transfer catalysis by porous-network solids holds great promise, and we are currently investigating further applications.

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\[\text{Scheme 2. Selective conversion of } E/Z \text{ mixtures of 3 into the } E \text{ isomer with a catalytic amount of crystals 2 (ca. 20 mol % of the } [(ZnI}_2)_3(N}_3)_2 \text{ unit).}\]


[7] Obtained from irradiating the commercially available E isomer at 366 nm for 18 h.

[8] The Z — E isomerization of aromatic olefins, such as stilbene, involves a radical cation mechanism and the generation of cation radicals through electron transfer to photoexcited electron acceptors is well known. We thus believe that a similar mechanism operates within the pores of network 2' where the proximity of 3 and acceptor 1, which is evidenced by the CT band in the UV/Vis spectrum and by X-ray analysis, facilitates excited state electron transfer (refs [9,10]).
