Photoisomerization

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

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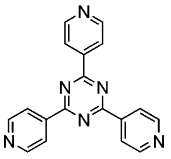
The tris(4-pyridyl)triazine ligand (**1**) is an important organic building block for self-assembled coordination cages[1] and networks.[2] Typically employed because of its rigid planarity, triangular shape, and commercial availability, ligand **1** is extremely electron-deficient and, upon coordination 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 photoirradiation can induce efficient energy transfer[3] or, in some cases, photoinduced electron transfer.[4]



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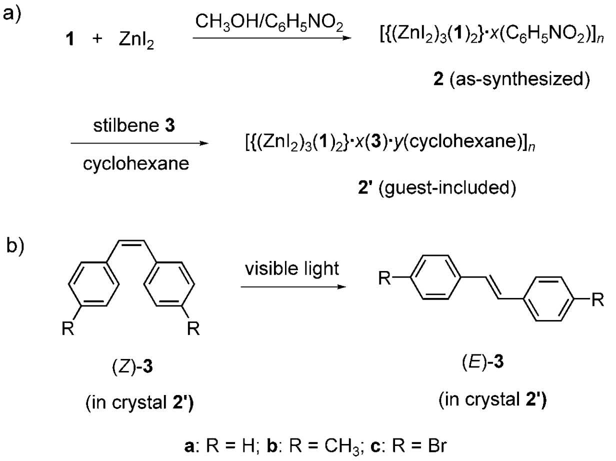
We hypothesized that network **2**, which is generated from **1** and ZnI_2, could display similar photochemistry in the solid state; thus we examined the photoinduced isomerization of stilbene within coordination network **2** (Scheme 1 a). Enclathrated within the pores of **2**, (*Z*)-stilbene selectively isomerized to (*E*)-stilbene under visible light irradiation (Scheme 1 b); the *Z*/*E* equilibrium ratio typical for the photostationary state ($Z/E = 92{:}8$ at $\lambda_{ex} = 313$ 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 $[\{(ZnI_2)_3(\mathbf{1})_2\}\cdot x(C_6H_5NO_2)]_n$ (**2**, $x \approx 5.5$) employed in this work was prepared according to the reported procedure.[5] 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 $[\{(ZnI_2)_3(\mathbf{1})_2\}\cdot x((Z)\text{-}\mathbf{3a})\cdot y(\text{cyclohexane})]_n$ (**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.



Scheme 1. a) Preparation of porous coordination networks **2** and **2′**. b) *Z*→*E* photoisomerization of stilbenes within network **2′**.

Crystals of **2′**, which were suspended in a solution of (*Z*)-**3a** in cyclohexane, were photoirradiated with a Xe lamp ($\lambda_{ex} = 400$–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 ^{1}H NMR spectroscopy. To analyze the stilbene contained in network **2′**, the crystals were decomposed with hydrochloric acid and extracted with $CHCl_3$. 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). Enclathrated 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 1 b).

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 ZnI_2) were insufficient to catalyze the conversion. 2) When crystals of **2′** were removed during photoirradiation, isomerization stopped. 3) Photoisomerization was dramatically retarded when pyrene, which is strongly bound by **2′**[5a] 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[6] (Figure 2). These results demonstrate that

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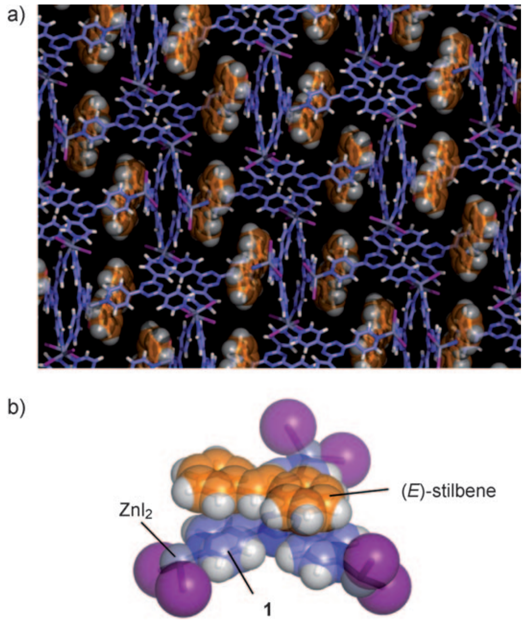


Figure 1. a) X-ray crystal structure of network **2′** with stilbene guest (*E*)-**3 a**, obtained by irradiation of as-synthesized **2** with visible light for 155 h in a solution of (*Z*)-**3 a** in cyclohexane. b) Aromatic–aromatic interactions between triazine moiety **1** and (*E*)-**3 a** formed in situ.

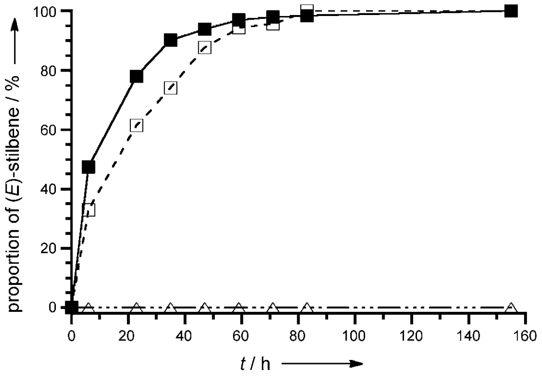
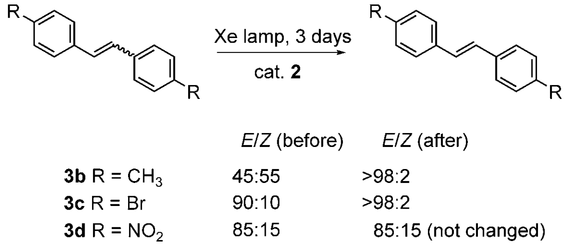


Figure 2. Photoisomerization of pure (*Z*)-**3** upon irradiation with visible light in the presence of crystals of **2**. Proportion of (*E*)-**3 a** within crystals of network **2′** (■) and in the supernatant (□) with increasing irradiation time. △ represents a control experiment in the absence of network **2**.

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]



	E/*Z* (before)	*E*/*Z* (after)
3b R = CH_3	45:55	>98:2
3c R = Br	90:10	>98:2
3d R = NO_2	85:15	85:15 (not changed)

Scheme 2. Selective conversion of *E*/*Z* mixtures of **3** into the *E* isomer with a catalytic amount of crystals **2′** (ca. 20 mol% of the $[(ZnI_2)_3(\mathbf{1})_2]$ unit).

In conclusion, the electron-deficient triazine moieties **1** in coordination network **2** are photoactive and catalyze the *Z*→*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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[6] Similar behavior was also observed in our previous study on the thermal all-E to 13-Z isomerization of retinal within network **2**: K. Ohara, M. Kawano, Y. Inokuma, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 30–31.

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

[8] The $Z \rightarrow E$ 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]).

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