Crystallographic observation of an olefin photodimerization reaction that takes place *via* thermal molecular tumbling within a self-assembled host†

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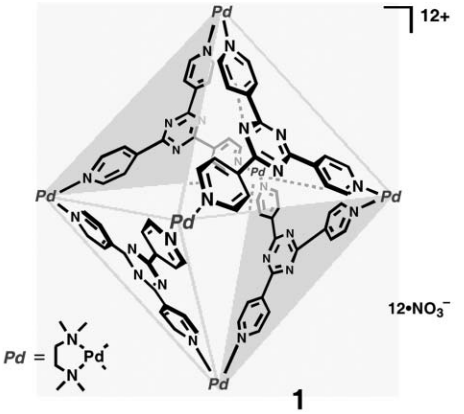
***In situ* crystallography reveals that the solid state [2 + 2] photodimerization of acenaphthylene in a coordination cage takes place smoothly without preorganizaiton of reaction centers at a preferred geometry, because the substrate tumbles thermally in the large hollow of the cage.**

Photochemical reactions in organic crystals often take place efficiently with high reactivity and selectivity because the substrate geometry around reaction centers is strictly controlled by the solid state environment.[1–3] However, reactions are normally allowed to proceed only if the reaction centers of the substrates are mutually well-oriented in close proximity, typically within 4.2 Å as required by the Schmidt rule.[4] We assume that preorganization of the reaction centers is not required if the substrates are accommodated in the cavity of a large hollow cage compound because they are allowed to tumble thermally in the cavity even in the solid state. Therefore, various solid state photoreactions are expected to proceed without preorganization, like a solution state reaction. In addition, such a solution-like behavior of the substrates can be directly observed by X-ray crystallographic analysis if the rigid cage framework prevents the crystal from deteriorating during the reaction. To demonstrate this idea, [2 + 2] photoaddition of acenaphthylene (**2**)[5] within the cavity of a cage-like coordination host (**1**)[6] in the solid state was selected as a model reaction because the host–guest complexation of **1** with **2** and the subsequent [2 + 2] photoaddition in aqueous media have been previously studied.[7] We show that, despite the very unfavorable orientation of the substrates in the cavity of **1**, the [2 + 2] photodimerization cleanly proceeds in a single-crystal-to-single-crystal fashion. The reaction completely differs from common solid state photoreactions in that the reaction centers are not preorganized, but the reaction proceeds *via* thermal tumbling of the substrates.

As described previously,[7a] a 1 : 2 encapsulation complex ($\mathbf{1} \supset (\mathbf{2})_2$) was formed in a quantitative yield by simply suspending powdered **2** in an aqueous solution of **1** at 353 K. Single crystals were obtained by the slow evaporation of the yellow solution of $\mathbf{1} \supset (\mathbf{2})_2$ at 298 K for 2 d. The diffraction data were collected at 240 K.‡ X-Ray analysis reveals the presence of two crystallographically independent coordination cages (hereafter, $\mathbf{1}_\mathrm{A}$ and $\mathbf{1}_\mathrm{B}$). Cage $\mathbf{1}_\mathrm{A}$ encapsulates two acenaphthylene molecules (Fig. 1a) while $\mathbf{1}_\mathrm{B}$ includes only one which is not modeled because of severe disorder.[8] Outside the cage, a free acenaphthylene molecule is found, which is presumably expelled from cage $\mathbf{1}_\mathrm{B}$ during crystallization to form better crystal packing. In cage $\mathbf{1}_\mathrm{A}$, the two guests are disordered and located at three positions with occupancies of 0.82, 0.66, and 0.54 (Fig. 1b). All acenaphthylene molecules are stacked on the triazine ligands of the cage *via* π– π interactions with 3.3–3.5 Å face-to-face distances, indicating donor–acceptor interactions between electron-rich acenaphthylene and the electron-deficient triazine ligand. The center-to-center distances between C=C bonds among the three disordered acenaphthylene guests are 9.0, 8.4, and 8.3 Å, far larger than the 4.2 Å within which the Schmidt rule allows topochemical [2 + 2] coupling in the solid state. In addition to the unfavorable distances, two of any C=C bonds are not parallel at all.[9] This means that the photoreaction requires considerably large molecular motion. Therefore, the [2 + 2] photoaddition is not expected to occur according to numerous empirical observations in the past.[10,11]



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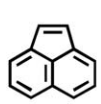

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Nevertheless, the [2 + 2] photoaddition took place cleanly in the cage when the crystal was irradiated (300–365 nm) on a diffractometer at 240 K for 1 h.[12] The color of the crystal turned from yellow to reddish-yellow. After irradiation, diffraction data were collected at 240 K.§ Very small changes in the lattice parameters were observed and the single-crystallinity remained intact, displaying the structure of a [2 + 2] adduct in cage $\mathbf{1}_\mathrm{A}$ after irradiation. The most remarkable feature in the X-ray structure after irradiation was that the [2 + 2] photoaddition quantitatively took place in cage $\mathbf{1}_\mathrm{A}$ to give only the *syn*-dimer **3** (Fig. 2).[13]

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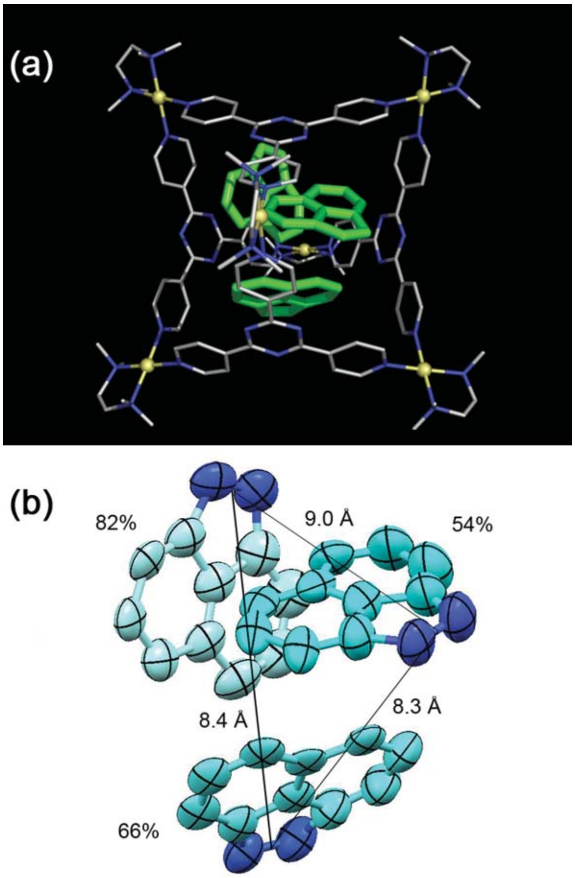

Fig. 1 (a) The crystal structure of $\mathbf{1}\supset(\mathbf{2})_2$ at 240 K. Counter ions, solvents of crystallization, and a free acenaphthylene molecule (per two cages) stacking to the outside of the cage are omitted. (b) ORTEP drawing (30% probability) of the two guests disordered at three positions in $\mathbf{1}_\mathrm{A}$. Percentages indicate the occupancies of the guests. The center-to-center distances between C=C bonds are also indicated.

Interestingly, product **3** was not disordered and was fixed at a single position in cage $\mathbf{1}_\mathrm{A}$ despite the disorder of **2** at three positions before irradiation.[14] We suggest that, though being unfavorably oriented in the crystal structure, they are dynamically disordered. Namely, they are allowed to tumble thermally in the cage to undergo the [2 + 2] photodimerization. The rigid framework of the cage seems to prevent the crystal from deteriorating during the reaction, keeping the cell parameters almost unchanged. Therefore, we emphasize that, in contrast to conventional photochemical reactions in the crystalline state, the large void of the cage allows non-topochemical reactions accompanied by dynamic molecular motion without losing single-crystallinity.

The crystalline state photoreaction in the cage requires thermal activation[15] (240 K) to bring about the mobility of the substrate in the cage. In fact, no reaction took place when the crystal was irradiated at 90–210 K. The structure of the inclusion complex at 90 K was also successfully solved (Fig. S6†).[16] The two acenaphthylene molecules were disordered at three positions. They were reoriented in such a way that the shortest distance between the reaction centers was only 4.8 Å. Despite such a closer proximity of the reaction centers, no reaction took place at 90 K. This result clearly showed that the substrate geometry was completely frozen at this temperature to follow the Schmidt rule like common solid state reactions. The rigid network of the surrounding water molecules developed at low temperature may also suppress the solution-like behavior of acenaphthylene molecules in the cavity of **1**.

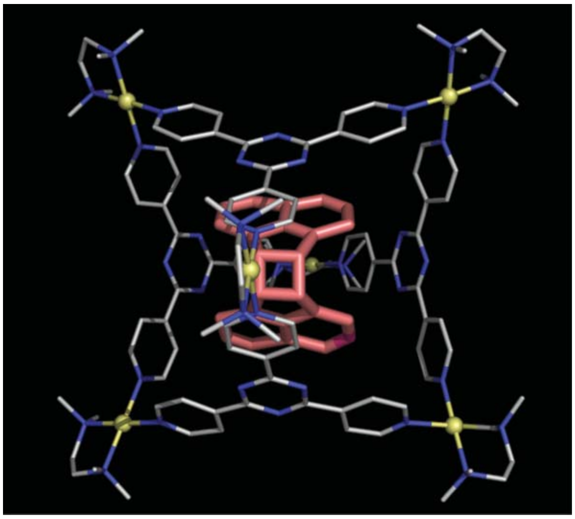

Fig. 2 The crystal structure of $\mathbf{1}_\mathrm{A}\supset\mathbf{3}$. Counter ions, solvents of crystallization, $\mathbf{1}_\mathrm{B}\supset\mathbf{2}$ complex that remained unchanged upon irradiation, and a free acenaphthylene molecule (per two cages) are omitted.

Encapsulation of **2** in **1** produced a broad charge-transfer absorption band derived from π–π stacking interactions between the host and guests in the range of 350 to 500 nm (Fig. 3). Basically photolysis with light in the range of 300 to 436 nm resulted in quantitative *syn*-dimer formation, although longer wavelength excitations were less efficient. Photolysis of **1** without cage **2** produces a mixture of the *syn*- and *anti*-dimer with different ratios depending upon excitation conditions in either solution or the solid state.[5] This fact means that the highly stereoselective photoreaction is due to the cage effects including steric and/or electronic effects.

In conclusion, we have shown that the cavity of cage **1** provides organic substrates with a solution-like environment even in the crystalline state. Due to the rigid framework of the cage, the crystallinity remains unchanged even after 100% conversion of the reactant in the cage, allowing the *in situ* crystallographic

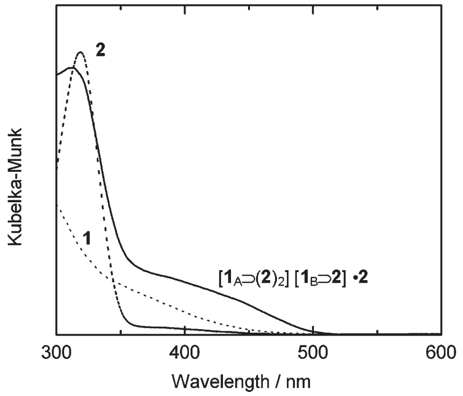

Fig. 3 Diffuse reflectance UV-vis spectra of **1**, **2** and $[\mathbf{1}_\mathrm{A}\supset(\mathbf{2})_2][\mathbf{1}_\mathrm{B}\supset\mathbf{2}]\cdot\mathbf{2}$ in $BaSO_4$ at 293 K.

observation of the photochemical transformation. Substrates behave like a solute in a solution and the reaction is not restricted by the Schmidt rule because of their thermal motion. Thus, the fluid character of the void allows guest molecules to tumble within the host cavity at 240 K, the temperature at which the X-ray structure relevant to the photodimerization is acquired.

Notes and references

‡ X-Ray single crystal analysis of $[\mathbf{1}_{\mathrm{A}}\supset(\mathbf{2})_2][\mathbf{1}_{\mathrm{B}}\supset\mathbf{2}]\cdot\mathbf{2}$ at 240 K (before irradiation). The diffraction data were measured on a Bruker APEX-II/CCD diffractometer equipped with a micro-focused rotating anode system combined with an X-ray focusing mirror (MoKα radiation $\lambda = 0.71073$ Å) with a cryostat system equipped with a N_2 generator (Japan Thermal Eng. Co., Ltd.). The diffraction data of the crystal before irradiation were collected at 240 K. *Crystal data at 240 K (before irradiation)*: triclinic, space group $P\bar{1}$, $a = 25.82(2)$ Å, $b = 26.03(2)$ Å, $c = 31.71(2)$ Å, $\alpha = 97.03(1)^\circ$, $\beta = 96.03(1)^\circ$, $\gamma = 102.16(1)^\circ$, $V = 20436(26)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.343$ g cm^{-3}, $\mu = 0.593$ mm^{-1}, 60682 unique reflections out of 22100 with $I > 2\sigma(I)$, 2399 parameters, final R factors $R_1 = 0.1357$, wR_2 (all data) = 0.3535, and GOF = 1.020. CCDC 290223. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600812g

§ X-Ray single crystal analysis of $[\mathbf{1}_{\mathrm{A}}\supset\mathbf{3}][\mathbf{1}_{\mathrm{B}}\supset\mathbf{2}]\cdot\mathbf{2}$ at 240 K (after irradiation). The X-ray crystallographic measurement was performed on PF-AR NW2 beamline (λ(synchrotron) = 0.6890 Å) at High Energy Accelerator Research Organization (KEK), Japan. Diffraction data were collected at 240 K (after irradiation). The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Hydrogen atoms were fixed at calculated positions and refined using a riding model. *Crystal data at 240 K (after irradiation)*: triclinic, space group $P\bar{1}$, $a = 25.669(1)$ Å, $b = 25.782(1)$ Å, $c = 31.995(1)$ Å, $\alpha = 97.702(1)^\circ$, $\beta = 96.5334(9)^\circ$, $\gamma = 101.117(3)^\circ$, $V = 20376.3(11)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.236$ g cm^{-3}, $\mu = 0.595$ mm^{-1}, 63792 unique reflections out of 20951 with $I > 2\sigma(I)$, 2544 parameters, final R factors $R_1 = 0.1310$, wR_2(all data) = 0.4131, and GOF = 1.041. CCDC 277006. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600812g

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12 Photolysis of $[\mathbf{1}_{\mathrm{A}}\supset(\mathbf{2})_2][\mathbf{1}_{\mathrm{B}}\supset\mathbf{2}]\cdot\mathbf{2}$ was performed for 1 h at 240 K with a 350 W high-pressure mercury lamp (SAN-EI ELECTRIC UVF-352S), equipped with a band path filter (TOSHIBA, UV-D33S), to give $[\mathbf{1}_{\mathrm{A}}\supset\mathbf{3}][\mathbf{1}_{\mathrm{B}}\supset\mathbf{2}]\cdot\mathbf{2}$. The crystal was rotated on the diffractometer about the phi axis during UV irradiation.

13 Two guests in $\mathbf{1}_{\mathrm{A}}$ dimerized, whereas one in $\mathbf{1}_{\mathrm{B}}$ and another outside **1** did not. In total, two of four guests in the crystal participated in the dimeziation. The ^{1}H NMR study of an aqueous solution of the photolyzed crystal clearly resulted in *syn*-dimer formation in *ca.* 50% yield, in good agreement with X-ray analysis. This also indicated that the [2 + 2] photodimerization in the cavity of $\mathbf{1}_{\mathrm{A}}$ proceeded quantitatively, whereras photoirradiation in solution resulted in 98% *syn*-dimerization as reported in ref. 7*a*.

14 The distance between $\mathbf{1}_{\mathrm{A}}$ and **3** was larger than the sum of the van der Waals radii, indicating that the intermolecular interaction between the host and the guest molecules was less efficient after irradiation than the structure before irradiation.

15 For the temperature dependence of the reaction rate of [2 + 2] photodimerization, see: K. Honda, F. Nakanishi and N. Feeder, *J. Am. Chem. Soc.*, 1999, **121**, 8246.

16 X-Ray Single Crystal Analysis of $[\mathbf{1}_{\mathrm{A}}\supset(\mathbf{2})_2][\mathbf{1}_{\mathrm{B}}\supset\mathbf{2}]\cdot\mathbf{2}$ at 90 K (before irradiation). The X-ray crystallographic measurement was performed by using synchrotron radiation. *Crystal data at 90 K (before irradiation)*: triclinic, space group P-1, $a = 27.3274(5)$ Å, $b = 27.5977(5)$ Å, $c = 32.1815(7)$ Å, $\alpha = 100.824(1)^\circ$, $\beta = 91.953(1)^\circ$, $\gamma = 107.373(1)^\circ$, $V = 22645.7(8)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.343$ g cm^{-3}, $\mu = 0.563$ mm^{-1}, 104975 unique reflections out of 38153 with $I > 2\alpha(I)$, 3903 parameters, final R factor $R_1 = 0.1019$, wR_2 (all data) = 0.3282, and GOF = 0.948. CCDC 277005. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600812g.