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Cavity-Directed Synthesis within a Self-Assembled Coordination Cage: Highly Selective [2 + 2] Cross-Photodimerization of Olefins

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Abstract: Herein reported is the highly selective [2 + 2] cross-photodimerization of olefins within a self-assembled coordination cage that acts as a molecular flask in an aqueous medium. An M_6L_4 coordination nanocage that self-assembles from six Pd(II) complexes and four tridentate ligands accommodates two different kinds of large olefin molecules such as acenaphthylene and 5-ethoxynaphthoquinone in a pairwise selective fashion. This prerequisite recognition mode makes possible the selective [2 + 2] cross-photodimerization of the olefins within the cavity. The reaction is extremely efficient in terms of reaction rate, stereoselectivity, and, most importantly, pairwise selectivity. Maleimide derivatives, which themselves are photochemically inactive under ordinary conditions, are also cross-dimerized with acenaphthylene or dibenzosuberenon quite efficiently. These results are in sharp contrast to those of common photodimerization in organic media, where the yields and selectivities are generally poor to moderate. The key step of the exclusive formation of the cross-dimers stems from the selective formation of ternary complexes before irradiation, which is governed by the size compatibility of the guests with the confined space of the cavity.

Introduction

Rational design of host−guest interactions enables one to realize not only unique physical properties but also highly controlled chemical transformations of the guest molecules within the host molecules.[1,2] To carry out chemical reactions in such environments, the construction of large host molecules that can accommodate two or more substrates in the cavity is particularly important. Recently, nanosized molecular cages have been efficiently synthesized by transition metal-mediated self-assembly.[3] The cavities of the self-assembled cages are large enough to recognize and isolate two or more guest molecules. Therefore, these are regarded as one class of the most promising host systems for promoting chemical transformations.[3−5]

To exploit the self-assembled cages as molecular flasks, the selective encapsulation of two different kinds of guest molecules in one host (i.e., ternary complex formation) is an important step before reaction. However, the selective formation of ternary complexes is in general very difficult to achieve,[6] and hence the subsequent chemical reaction of the guests has been seldom controlled.[7] Recently, we have revealed the facile intermolecular [2 + 2] photodimerization of large olefins in self-assembled coordination cages controlling regio- and stereochemistry by their isolated microenvironment.[8] These results have prompted us to examine the photochemical reaction *between two different types of molecules* within the cage. Of course, managing the selectivity between the cross- and homo-coupling reaction is the most difficult task, when the components are of similar reactivity. There are some reports on the selective [2 + 2] cross-photodimerization of olefins in the crystal state (so-called

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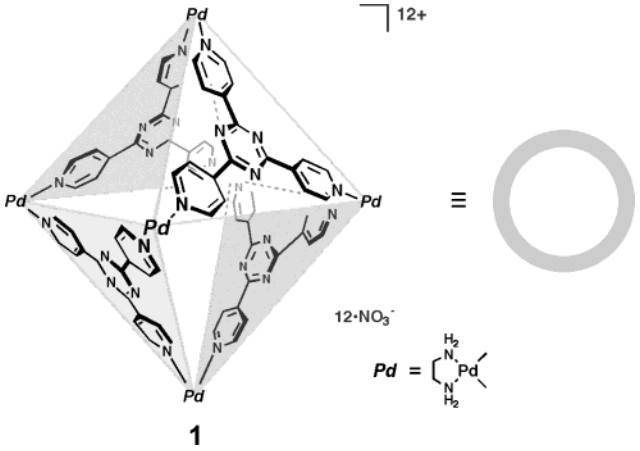
topochemical reaction), where two substrates must align alternatively with suitable geometry for the reaction.[9] In the solution state, however, the selective cross-reaction remains less explored: electrostatic and/or charge-transfer interactions have been examined for the preorganization of two substrates, but the selectivity is generally poor, and an excess of one substrate is required.[10,11]

Here, we report that the self-assembled coordination cage **1**[12] accommodates two different olefin molecules in a pairwise selective fashion, making possible the selective [2 + 2] cross-photodimerization. The reactions we show here are extremely efficient in terms of reaction rate, stereoselectivity, and, most importantly, pairwise selectivity. The key step of the exclusive formation of cross-dimer stems from the selective formation of ternary complex before irradiation, which is governed by the size compatibility of the guests with the restricted space of the cavity.



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Results and Discussion

Cross-Dimerization of Acenaphthylene and Naphthoquinones. Acenaphthylene (**2**) and quinone derivatives are known to form weak charge-transfer complexes (λ_{CT} > 500 nm) in organic media.[11] The cross-dimerization of these two olefins through excitation at the CT band has been examined by Haga et al. However, the homo/hetero selectivity and the stereochemistry of the adduct are still not well controlled.

In expectation of observing high pairwise selectivity by the space restriction effect of the cavity, the photoaddition of acenaphthylene (**2**) and 5-ethoxynaphthoquinone (**3a**) was examined in the presence of cage **1** (**1**:**2**:**3a** = 1:1:1 ratio). When **2** and **3a** were suspended in D_2O solution of **1** at 80 °C, the guests were efficiently accommodated in the cage, and a clear solution resulted within 10 min. The efficient binding of **2** and **3** in the cage was clearly indicated from ^{1}H NMR that showed the remarkably upfield-shifted signals of both guests (Figure 1a). After irradiation (400 W high-pressure mercury lamp, 3 h), the signals of **2** and **3a** completely disappeared, and new signals appeared. After being extracted with $CDCl_3$, the product was analyzed by NMR and MS. Surprisingly, the product analyses showed the exclusive formation of cross syn-dimer **4a**. The yield of **4a** was determined to be 92% based on **2** (Figure 1b). In the NMR spectrum, the cyclobutane protons of **4a** appeared at δ 4.79 and 4.18, and aromatic ring protons of **4a** were found at a significant upfield region (δ 7.30−6.57), characteristic of the syn-configuration.[8] Two methylene protons of 5-ethoxy group of **4a** are diastereotopic, appearing at δ 3.93 and 3.55. No change was observed in the signals of **1** (δ 9.26, 8.63, and 2.98), showing that cage **1** was tolerant to the photoirradiation under this condition.

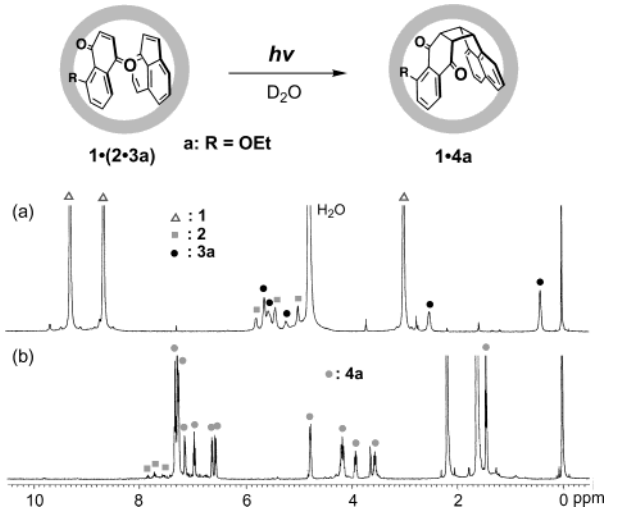

Figure 1. ^{1}H NMR spectra (500 MHz, D_2O, 27 °C). (a) Before irradiation: **1**•(**2**•**3a**) complex in D_2O. (b) After irradiation (400 W) for 3 h and extraction with $CDCl_3$. Triangles, black circles, squares, and gray circles indicate the signals of **1**, **2**, **3a**, and **4a**, respectively.

We assume that the exclusive formation of **4a** is ascribed to the selective formation of ternary complex **1**•(**2**•**3a**) governed by the size compatibility of the guests with the restricted space of the cavity. This assumption was supported by the fact that **1** and **3a** produced a 1:1 complex (**1**•**3a**) but not a 1:2 complex (**1**•(**3a**)$_2$) because of the steric bulkiness of **3a**.[13] However, complex **1**•**3a** still has room for accommodating less sterically demanding **2** to give ternary complex **1**•(**2**•**3a**). Thus, the following hetero/homo equilibration shifts in such a way that all species are complexed (eq 1).

$$\mathbf{1}\cdot(\mathbf{2})_2 + \mathbf{1}\cdot\mathbf{3a} + \text{free } \mathbf{3a} \underset{H_2O}{\rightleftarrows} 2\ \mathbf{1}\cdot(\mathbf{2}\cdot\mathbf{3a}) \qquad (1)$$

The steric effect of the 5-ethoxy substituent is particularly important for controlling the hetero/homo equilibration. When 5-methoxy substituted **3b** was employed in place of **3a**, we still observed the predominant formation of hetero [2 + 2] adduct **4b** (44%), but homo [2 + 2] adducts of **2** and **3b** were also produced in low yields. Probably, homo complexes **1**•(**2**)$_2$ and

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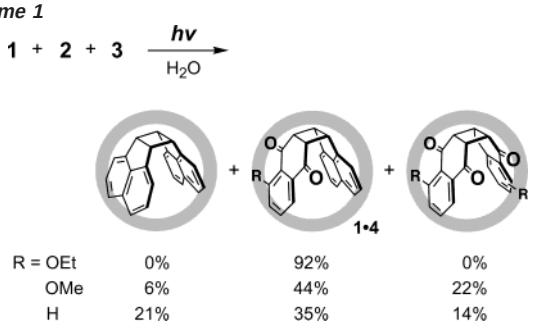
(13) The photoirradiation of an aqueous solution of **1** and **3a** (1:2 ratio) gave no adducts under the same conditions (400 W, 3 h).

Scheme 1



1•(**3b**)$_2$ exist to some extent in the hetero/homo equilibration of eq 2. More dramatically, the use of nonsubstituted **3c** no longer showed the clear selectivity: three products were formed in almost statistical distribution (**4b**:dimer of **2**:dimer of **3c** ≈ 2:1:1). These results demonstrate that two olefins **2** and **3** possess comparable photochemical reactivity and that the exclusive formation of **4** is obviously controlled by steric restriction within the cavity (Scheme 1).

$$\mathbf{1}\cdot(\mathbf{2})_2 + \mathbf{1}\cdot(\mathbf{3b})_2 \underset{H_2O}{\rightleftharpoons} 2\ \mathbf{1}\cdot(\mathbf{2}\cdot\mathbf{3b}) \qquad (2)$$

The selective preorganization of two substrates in the cage is of course an essential event before the photochemical reaction. In the absence of the cage, no cross-dimer was formed from **2** and **3a** even at a very high concentration (150 mM in benzene), but the homo-dimer of **2** was formed in a low yield (32%).

Participation of Otherwise Unreactive Olefins. In addition to the high pairwise selectivity, we also note the activation effect by the cage. Indeed, considerable acceleration has been observed in the [2 + 2] photoaddition of acenaphthylenes, as previously communicated.[8] The most surprising result was the cavity-directed, facile dimerization of 1-methylacenaphthylene, which does not dimerize under ordinary conditions due to the steric hindrance of the methyl group at the reaction site. The synthetic utility of the present cross reaction will be greatly enhanced if photochemically inert substrates can participate. Thus, we examined the cross-dimerization of otherwise unreactive olefins.

A striking result was obtained in the cross photocycloaddition of acenaphthylene (**2**) with *N*-benzylmaleimide (**5a**) within cage **1**. We found that these two olefins were efficiently cross-dimerized only in the presence of **1**. The participation of maleimide **5a** is noteworthy as **5a** itself is a photochemically inert substrate. In fact, free **5a** or even complex **1**•(**5a**)$_2$ never gives the dimeric product upon irradiation.

Again, **2** and **5a** were complexed with **1** in a 1:1:1 stoichiometry and irradiated (400 W, 3 h) in D_2O. In NMR, the signals of **2** and **5a** completely disappeared, and a new set of nine signals appeared (Figure 2a and b). After being extracted with $CDCl_3$, the product was identified as cross syn-dimer **6a** by ^{1}H NMR and MS analyses, and the yield was determined to be 97% based on **2** (Figure 2c).

The exclusive formation of cross-dimer **6a** is again ascribed to the selective formation of ternary complex **1**•(**2**•**5a**) before irradiation, which is interpreted by the size compatibility of the guests in the restricted space of the cavity. Hetero-pair **2**•**5a** fits into the cavity of **1** much better than homo-pairs **2**•**2** or **5a**•**5a**. In fact, when **1**•(**2**)$_2$ and **1**•(**5a**)$_2$ were separately prepared (Figure 3a and b) and mixed at room temperature,

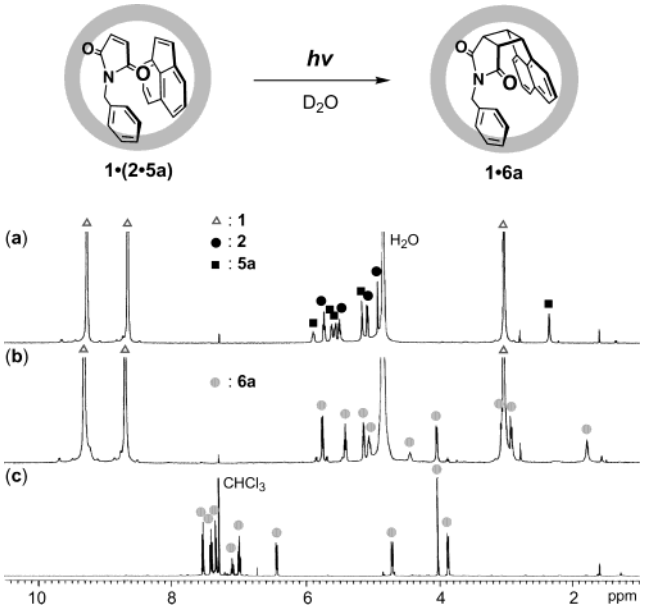
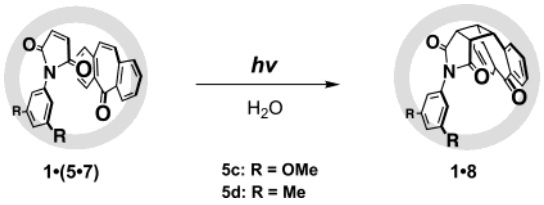


Figure 2. Monitoring the photodimerization of **2** and **5a** within cage **1** by ^{1}H NMR (500 MHz, D_2O, 27 °C). (a) Before irradiation: **1**•(**2**•**5a**) complex in D_2O. (b) After irradiation (400 W) for 3 h. (c) After irradiation and extraction with $CDCl_3$. Triangles, black circles, squares, and gray circles indicate the signals of **1**, **2**, **5a**, and **6a**, respectively.

chemical shifts of the guests were immediately changed, suggesting the formation of the ternary complex (Figure 2a). From this solution, indeed **6a** was exclusively formed upon irradiation. When **3a** was replaced by sterically less demanding *N*-methylmaleimide (**5b**), the size compatibility was poor, and the irradiation gave a mixture of two products: a hetero-dimer **6b** and a homo-dimer of **2** in 51 and 49% yields (based on **2**), respectively.[14]

We have also found that the maleimide derivative (**5c** and **5d**) and dibenzosuberenon (**7**) undergo the [2 + 2] cross-photodimerization in an efficient fashion to give cross-dimer **8** in quantitative yield (based on **7**) with syn stereochemistry (eq 3). In a manner similar to that above, the bulkiness of substrate **7** prohibited the formation of the **1**•(**7**)$_2$ complex, and equilibration among the components was pushed toward the **1**•(**5**•**7**) ternary complex formation.



(3)

Absorption Studies. UV−vis spectroscopic measurement provided some interesting aspects of the cavity-directed photodimerization. Highly π-conjugated cage **1** has a strong absorption band at λ_{max} = 285 nm, and, for as long as we

(14) The equilibration of eq 4 should be rapid on the NMR time scale because averaged signals for guest **2** were observed when excess **2** was added. Thus, the selective formation of the cross-dimer may be interpreted by the rapid consumption of the hetero pair from an equilibrium mixture of eq 4. However, because of the remarkable steric effect on the substrate, we consider the selective formation of the hetero pair rather than the rapid consumption.

$$\mathbf{1}\cdot(\mathbf{2})_2 + \mathbf{1}\cdot(\mathbf{5a})_2 \underset{H_2O}{\rightleftharpoons} 2\ \mathbf{1}\cdot(\mathbf{2}\cdot\mathbf{5a}) \qquad (4)$$

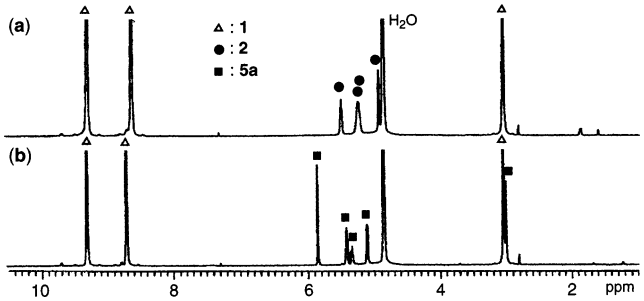


Figure 3. ^{1}H NMR spectra (500 MHz, D_2O, 27 °C). Enclathtration complex of (a) **1**•(**2**)$_2$ and (b) **1**•(**5a**)$_2$ in D_2O. Triangles, black circles, and squares indicate the signals of **1**, **2**, and **5a**, respectively.

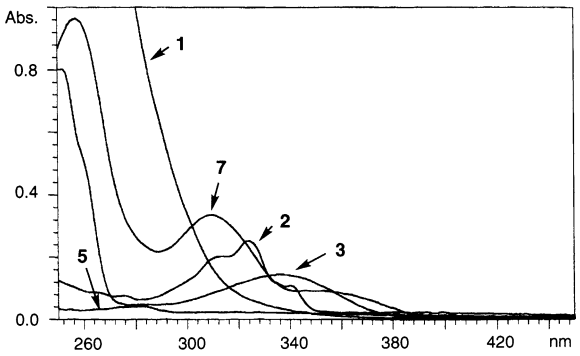


Figure 4. UV−vis spectra of cage **1** in H_2O and substrates in CH_2Cl_2 (room temperature, 1.0×10^{-5} M). The numbers indicate the compounds.

examined, the dimerization of olefins whose absorption bands are <300 nm (e.g., styrenes and quinones) is suppressed within the cage. On the other hand, the cage is transparent above ca. 310 nm wavelength, allowing the photodimerization of highly conjugated olefins such as **2**, **3**, and **7**, whose absorption bands are >310 nm (Figure 4).

The absorption of maleimide **5** is centered at 280 nm. Therefore, in the photoaddition of **2** and **5**, the reaction should occur between excited **2** and the ground state of **5**. Because λ_{max} of **2** and **3** are both >310 nm, two possibilities are considered for the cross addition of **2** and **3**: **2*** + **3** or **2** + **3*** (the asterisks refer to the excited state).

The reverse reaction (photodissociation) should be strongly suppressed because the absorption of the [2 + 2] adducts is below 310 nm. This "filter effect" of the cage, in addition to the preorganization effect, is supposed to lead to the rapid, quantitative formation of the photoadduct.[8]

These are two possible pathways to the excited state of the substrate: (i) direct absorption of UV light by the substrate around its λ_{max}, and (ii) the absorption of UV light by the cage followed by energy transfer into the substrate. To clarify the reaction pathway, the **1**•(**2**)$_2$ complex was irradiated by UV light at 290 nm where the absorption band of **2** is completely covered by that of the cage. The adduct was formed much less efficiently. From these results, we suggest that substrate **2** is directly excited by irradiation, not via the excitation of the cage followed by energy transfer.

Conclusions

In summary, we have revealed a new aspect of the self-assembled coordination nanocage **1** that facilitates [2 + 2] cross-photodimerization of large olefins, leading to cross syn-dimers in high yields. These results are in sharp contrast to those of common photodimerization in organic media with respect to the yield and pairwise selectivity. Our strategy is referred to as *cavity-directed synthesis*, where confined space strictly controls the enclathration by steric nature, and the subsequent chemical transformation can be strictly controlled as desired.

Experimental Section

Materials and Instrumentation. ^{1}H, ^{13}C NMR, and other 2D NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. TMS ($CDCl_3$ solution) in a capillary served as external standard (δ 0 ppm). IR measurements were carried out as KBr pellets using a SHIMADZU FTIR-8300 instrument. HR-MS (EI) measurements were recorded on a JEOL JNM-700 instrument. Melting points were determined on a Yanaco (MP-500 V) melting point apparatus. Photoirradiation was carried out with a SEN LIGHTS CORP. HB400X-15 400-W high-pressure mercury lamp. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich chemical., Ltd. All of the chemicals were of reagent grades and used after simple purification. Dueterated solvents were acquired from Cambridge Isotope Laboratories, Inc., and used as such for the complexation reactions and NMR measurements. Self-assembled compound **1** was prepared following the procedure as reported earlier.[12] *N*-Alkyl and *N*-arylmaleimide were prepared according to the literature from maleic anhydride and amines.[15]

Cross-Photodimerization of Acenaphthylene (2) with 5-Ethoxynaphthoquinone (3a) within the Cage. Typical procedure: Acenaphthylene (**2**) (2.3 mg; 0.015 mmol) and 5-ethoxynaphthoquinone (**3a**) (3.0 mg; 0.015 mmol) were suspended in a D_2O solution of **1** (30.0 mg; 15.0 μmol, 5.0 mM), and the mixture was stirred for 10 min at 80 °C. After being filtered, the clear filtrate was irradiated (400 W, high-pressure mercury lamp) for 3 h at room temperature. The aqueous solution was extracted with $CDCl_3$, and then the product was identified as hetero syn-dimer **4a**, and the yield was determined to be 92% (based on **2**) by ^{1}H NMR. The crude product was purified by GPC to give **4a** (4.5 mg; 0.013 mmol, 86% isolated yield).

Physical Data of 1•(2•3a). ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ 9.26 (d, J = 5.6 Hz, 24H, PyH_α), 8.63 (d, J = 5.6 Hz, 24H, PyH_β), 5.77 (br, 2H, **2**), 5.63 (br, 2H, **3a**), 5.55 (br, 2H, **3a**), 5.42 (br, 4H, **2**), 5.22 (br, 1H, **3a**), 5.00 (s, 2H, **2**), 2.98 (s, 24H, $-CH_2-$), 2.51 (br, 2H, **3a**), 0.41 (br, 3H, **3a**).

Physical Data of 4a. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.30 (m, 3H, Ar*H*), 7.25 (m, 2H, Ar*H*), 7.14 (d, J = 6.1 Hz, 1H, Ar*H*), 6.96 (dd, J = 7.7, 8.2 Hz, 1H), 6.62 (d, J = 7.7 Hz, 1H), 6.57 (d, J = 8.2 Hz, 1H), 4.79 (d, J = 10.5 Hz, 2H), 4.18 (m, 2H), 3.93 (dq, J = 7.1, 8.5 Hz, 1H), 3.55 (dq, J = 7.1, 8.5 Hz, 1H), 1.443 (s, J = 7.0 Hz, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 196.6 (*C*O), 195.0 (*C*O), 156.3 (C_q), 142.8 (C_q), 142.5 (C_q), 141.6 (C_q), 137.2 (C_q), 132.9 (*C*H), 131.0 (C_q), 127.9 (*C*H), 127.3 (*C*H), 124.8 (C_q), 123.2 (*C*H), 123.0 (*C*H), 121.5 (*C*H), 120.8 (*C*H), 117.6 (C_q), 116.6 (*C*H), 64.6 (CH_2), 47.8 (*C*H), 47.7 (*C*H), 46.2 (*C*H), 45.5 (*C*H), 14.7 (CH_3). IR (KBr, cm^{-1}): 2919, 2853, 1680 (CO), 1584, 1462, 1296, 1215, 1054, 786. mp: 182−186 °C. MS (FAB, *m*/*z*) calcd. for $C_{24}H_{18}O_3$ (M^+) 354.1256, found 354.1268.

Cross-Photodimerization of Acenaphthylene with 5-Methoxynaphthoquinone (3b) within the Cage. The products were identified as hetero syn-dimer **4b**, and homo-dimers of **2** and **3b** (44, 6, and 22% yield based on **2**, respectively) by ^{1}H NMR and MS analyses.[8]

Physical Data of 4b. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.31 (m, 3H, Ar*H*), 7.25 (m, 4H, Ar*H*), 7.14 (d, J = 5.4 Hz, 1H, Ar*H*), 7.00 (dd, J = 7.6, 10.4 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H, H_p), 6.60 (d, J = 10.4 Hz, 1H), 4.79 (d, J = 10.9 Hz, 2H), 4.18 (m, 2H), 3.63 (s, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 196.6 (*C*O), 195.2 (*C*O), 156.9 (C_q), 142.7 (C_q), 142.5 (C_q), 141.5 (C_q), 137.3 (*C*H), 133.1 (*C*H), 131.0 (C_q), 127.9 (*C*H), 127.3 (*C*H), 123.2 (*C*H), 122.9 (*C*H),

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121.5 (*C*H), 121.0 (*C*H), 119.2 (Cq), 117.9 (*C*H), 115.7 (*C*H), 56.1 (CH_3), 47.8 (*C*H), 47.7 (*C*H), 46.2 (*C*H), 45.6 (*C*H). IR (KBr, cm^{-1}): 2923, 2853, 1684 (CO), 1580, 1458, 1284, 786. mp: 180−185 °C. HRMS (EI, *m*/*z*) calcd. for $C_{23}H_{16}O_3$ (M^+) 340.1099, found 340.1093.

Cross-Photodimerization of Acenaphthylene with Naphthoquinone (3c) within the Cage. The extracted products were identified as hetero syn-dimer **4c**, and homo-dimers of **2** and **3c** (35, 21, and 14% yield based on **2**, respectively) by ^{1}H NMR and MS analyses.

Physical Data of 4c. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.37 (dd, J = 3.2, 5.8 Hz, 2H), 7.33 (br, 2H), 7.32 (d, J = 5.8 Hz, 2H), 7.24 (dd, J = 3.2, 5.8 Hz, 2H), 7.18 (d, J = 6.2 Hz, 2H), 4.86 (d, J = 11.5 Hz, 2H), 4.29 (d, J = 11.5 Hz, 2H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 195.7 (*C*O), 142.2 (C_q), 140.9 (C_q), 135.2 (C_q), 133.2 (*C*H), 131.1 (C_q), 127.9 (*C*H), 125.8 (*C*H), 123.3 (*C*H), 121.6 (*C*H), 47.2 (*C*H), 46.9 (*C*H). IR (KBr, cm^{-1}): 2919, 2849, 1676 (CO), 1592, 1296, 1257, 965, 785, 735. mp: 178−183 °C. HRMS (EI, *m*/*z*) calcd. for $C_{22}H_{14}O_2$ (M^+) 310.0994, found 310.0974.

Cross-Photodimerization of Acenaphthylene (2) with *N*-Benzylmaleimide (5a) within the Cage. Typical procedure: Acenaphthylene (**2**) (2.3 mg; 0.015 mmol) and *N*-benzylmaleimide (**5a**) (2.8 mg; 0.015 mmol) were suspended in a D_2O solution (3.0 mL) of **1** (45.0 mg; 15.0 μmol, 5.0 mM), and the mixture was stirred for 10 min at 80 °C. The mixture was filtered to remove the nonencapsulated guest, and then the clear filtrate was irradiated for 3 h at room temperature. After being extracted with $CDCl_3$, the product was identified as cross syn-dimer **6a** by ^{1}H NMR and MS analyses, and the yield was determined by ^{1}H NMR (97% yield based on **2**). The crude product was purified by GPC to give **6a** (4.5 mg; 0.014 mmol, 90% isolated yield).

Physical Data of 1•(2•5a). ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ 9.24 (d, J = 6.0 Hz, 24H, PyH_α), 8.62 (d, J = 6.0 Hz, 24H, PyH_β), 5.86 (br, 1H, **5a**), 5.72 (t, J = 7.4 Hz, 2H, **2**), 5.60 (br, 2H, **5a**), 5.54 (br, 2H, **5a**), 5.47 (d, J = 7.4 Hz, 2H, **2**), 5.14 (s, 2H, **5a**), 5.06 (d, J = 7.4 Hz, 2H, **2**), 4.91 (s, 2H, **2**), 2.99 (s, 24H, −CH_2−), 2.31 (s, 2H, **5a**).

Physical Data of 1•6a. ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ 9.26 (d, J = 5.8 Hz, 24H, PyH_α), 8.64 (d, J = 5.8 Hz, 24H, PyH_β), 5.72 (d, J = 8.2 Hz, 2H, **6a**), 5.38 (t, J = 7.5 Hz, 2H, **6a**), 5.11 (d, J = 6.7 Hz, 2H, **6a**), 5.03 (br, 2H, **6a**), 4.41 (br, 1H, **6a**), 4.01 (d, J = 7.5 Hz, 2H, **6a**), 3.03 (d, J = 10.3 Hz, 2H, **6a**), 2.99 (s, 24H, −CH_2−), 2.89 (d, J = 10.3 Hz, 2H, **6a**), 1.74 (br, 2H, **6a**).

Physical Data of 6a. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.51 (d, J = 8.2 Hz, 2H), 7.38 (dd, J = 6.9, 8.2 Hz, 2H), 7.31 (d, J = 6.9 Hz, 2H), 7.07 (dd, J = 7.5 Hz, 1H), 6.97 (dd, J = 7.5, 7.5 Hz, 2H), 6.42 (d, J = 7.5 Hz, 2H), 4.69 (d, J = 10.3 Hz, 2H), 4.01 (s, 2H), 3.86 (d, J = 10.3 Hz, 2H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 176.1 (*C*O), 141.2 (C_q), 140.5 (C_q), 134.9 (C_q), 131.4 (C_q), 128.2 (*C*H), 127.8 (*C*H), 127.7 (*C*H), 127.1 (*C*H), 124.2 (*C*H), 121.4 (*C*H), 44.2 (*C*H), 42.2 (*C*H), 41.9 (CH_2). IR (KBr, cm^{-1}): 3042, 2957, 2919, 1700 (CO), 1391, 1361, 1338, 1176, 1138, 823, 786, 711. mp: 180−183 °C. HRMS (EI, *m*/*z*) calcd. for $C_{23}H_{17}NO_2$ (M^+) 339.1259, found 339.1239.

Physical Data of 1•(2)$_2$. ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ 9.28 (d, J = 5.9 Hz, 24H, PyH_α), 8.52 (d, J = 5.9 Hz, 24H, PyH_β), 5.43 (dd, J = 7.2, 7.5 Hz, 4H, **2**), 5.12 (m, 8H, **2**), 4.86 (s, 4H, **2**), 2.99 (s, 24H, −CH_2−).

Physical Data of 1•(5a)$_2$. ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ 9.30 (d, J = 4.6 Hz, 24H, PyH_α), 8.67 (d, J = 4.6 Hz, 24H, PyH_β), 5.87 (s, 4H, **5a**), 5.25 (br, 4H, **5a**), 5.09 (br, 2H, **5a**), 5.02 (br, 4H, **5a**), 3.02 (s, 24H, −CH_2−), 2.99 (s, 4H, **5a**).

Cross-Photodimerization of Acenaphthylene with *N*-Methylmaleimide (5b) within the Cage. The products were identified as hetero syn-dimer **6b** and homo syn-dimer of **2**. The yields were estimated to be 51 and 49% (based on **2**), respectively, by ^{1}H NMR.

Physical Data of 6b. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.64 (d, J = 8.2 Hz, 2H), 7.49 (dd, J = 6.9, 8.2 Hz, 2H), 7.35 (d, J = 6.9 Hz, 2H), 4.71 (d, J = 10.2 Hz, 2H), 3.85 (d, J = 10.2 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 176.3 (*C*O), 141.2 (C_q), 141.0 (C_q), 131.5 (C_q), 128.0 (*C*H), 123.9 (*C*H), 121.5 (*C*H), 44.3 (*C*H), 42.6 (*C*H), 23.9 (CH_3). IR (KBr, cm^{-1}): 3050, 2926, 2849, 1688 (CO), 1431, 1377, 1300, 1273, 1112, 1086, 969, 785, 773, 638. mp: 198−202 °C. HRMS (EI, *m*/*z*) calcd. for $C_{17}H_{13}NO_2$ (M^+) 263.0946, found 263.0933.

Cross-Photodimerization of *N*-(3,5-Dimethoxyphenyl)maleimide (5c) with Dibenzosuberenon (7) within the Cage. The product was identified as cross syn-dimer **8c**, and the yield was determined to be 99% based on **7** by ^{1}H NMR.

Physical Data of 8c. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.77 (d, J = 7.8 Hz, 2H), 7.49 (dd, J = 7.2, 7.4 Hz, 2H), 7.35 (dd, J = 7.4, 7.8 Hz, 2H), 7.26 (d, J = 7.2 Hz, 2H), 6.42 (s, 1H), 6.25 (s, 2H), 4.85 (d, J = 10.6 Hz, 2H), 3.87 (d, J = 10.6 Hz, 2H), 3.78 (s, 6H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 196.7 (*C*O), 174.5 (*C*O), 160.7 (C_q), 140.6 (C_q), 134.5 (C_q), 133.0 (C_q), 132.8 (*C*H), 131.2 (*C*H), 130.7 (*C*H), 128.4 (*C*H), 104.4 (*C*H), 101.6 (*C*H), 55.5 (CH_3), 45.6 (*C*H), 45.0 (*C*H). IR (KBr, cm^{-1}): 2921, 2852, 1707 (CO), 1646, 1596, 1474, 1290, 1204, 1158, 1057, 1019, 830, 766, 631. mp: 252−256 °C. HRMS (EI, *m*/*z*) calcd. for $C_{27}H_{21}NO_5$ (M^+) 439.1420, found 439.1406.

Cross-Photodimerization of *N*-(3,5-Dimethylphenyl)maleimide (5d) with Dibenzosuberenon within the Cage. After being extracted with $CDCl_3$, the product was identified as cross syn-dimer **8d** (97% yield based on **7**) by ^{1}H NMR and MS analyses.

Physical Data of 8d. ^{1}H NMR (500.13 MHz, $CDCl_3$, 27 °C): δ 7.77 (d, J = 7.7 Hz, 2H), 7.49 (dd, J = 7.4 Hz, 2H), 7.36 (dd, J = 7.4, 7.7 Hz, 2H), 7.26 (d, J = 7.4 Hz, 2H), 6.94 (s, 1H), 6.64 (s, 2H), 4.87 (d, J = 10.9 Hz, 2H), 3.86 (d, J = 10.9 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (125.77 MHz, $CDCl_3$, 27 °C): δ 196.5, 174.9, 140.7, 138.3, 134.4, 132.7, 131.1, 130.7, 128.4, 126.1, 123.5, 104.4, 45.6, 45.0, 21.3. IR (KBr, cm^{-1}): 2919, 2850, 1710 (CO), 1650, 1596, 1373, 1292, 1192, 1154, 830, 766, 631. mp: 238−242 °C. HRMS (EI, *m*/*z*) calcd. for $C_{27}H_{21}NO_3$ (M^+) 407.1521, found 407.1512.

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