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Template effects of metal ions on photodimerization of bis-1-anthracenecarboxamide linked by the oxyethylene chain

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Abstract—A bis-fluorophore linked by an oxyethylene chain, *N*,*N'*-(4,7,10-trioxatridecane-1,13-diyl)bis(1-anthracenecarboxamide) **1**, was synthesized, and intramolecular photodimerization of the anthracene units in acetonitrile was carried out. The photoproduct ratio of intramolecular regioisomers in the absence and presence of metal ions in acetonitrile was evaluated. Upon photoirradiation of **1**, three photodimers formed, *trans* head-to-head dimer **D1**, *cis* head-to-head **D2**, *cis* head-to-tail **D3**, and the product ratio was **D1**:**D2**:**D3** = 32:57:11. On the other hand, photodimerization of $\mathbf{1}\cdot Ba^{2+}$ gave the product ratio as 46:54:0.1, respectively. In the case of $\mathbf{1}\cdot Mg^{2+}$, the regioisomer ratio was determined as 17:81:2. These isomer ratios strongly depended on the structure of the complex induced by metal ions. © 2002 Elsevier Science Ltd. All rights reserved.

The photodimerization of anthracene and its derivatives has been extensively investigated as photochromic materials and for preservation of photoenergy.[1,2] In the case of the photodimerization of 1-substituted anthracene derivatives, four regioisomers are expected as shown in Fig. 1. The regioselectivity in photoreaction products has been rationalized in terms of steric and electrostatic effects between the substituents.[3–5] To achieve controlled stereochemistry on photodimerization of anthracene derivatives, a variety of approaches have been employed.[6–13]

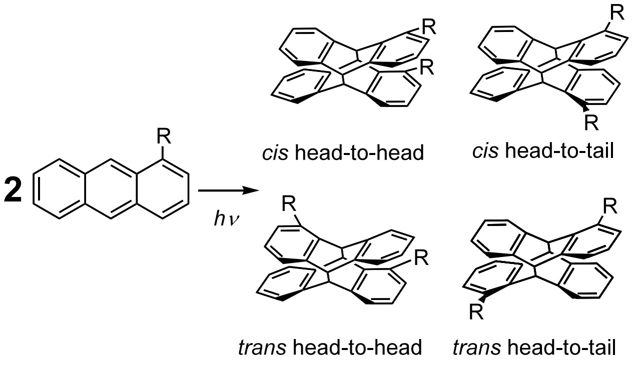

Figure 1. Photodimerization of anthracene derivatives.

Recently, we have been studying the photochemical behavior of a series of bis-fluorophores linked by an oxyethylene chain in the presence and absence of various metal ions.[14,15] It was found that the complexation with a metal ion induced a large change in the electronic interaction between two fluorophores indicating a drastic change in the fluorescence spectra. Thus, the photochemical behavior can be controlled upon complexation with metal ions. To extend these investigations, bis-anthracene linked at position 1 by the oxyethylene chain was employed for controlling the stereochemistry of the photodimerization.

The bis-anthracenecarboxamide **1**[16] was synthesized by a coupling of oxyethylene diamine and 1-anthracenecarbonyl chloride in the presence of triethylamine in THF at room temperature. The crude product was purified on HPLC through ODS column and characterized by ^{1}H NMR and elemental analysis. The irradiation of degassed acetonitrile solution of **1** (1×10^{-4} M) was carried out with a 500-W xenon lamp with a bandpass filter for isolating UV light near 350 nm. In all cases, the irradiation was continued until the absorbance at 365 nm decreased to steady values. Three photoproducts (**D1**, **D2**, and **D3**) were separated using HPLC, and their structures were confirmed by H–H COSY and NOESY spectra (Fig. 2).

Table 1 shows the isomer ratios of **D1**–**D3**. In all cases of irradiation of **1**, the formation of *trans* head-to-tail isomer **D4** was not detected. This suggested that **1** did not have enough chain length for the formation of **D4**.

Keywords: 1-substituted-anthracene derivative; photodimerization.

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Table 1. Isomer ratio (%) of photodimers of **1** before and after complexation with metal ions[a]

	NON	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
D1	31.9	16.5	24.7	40.9	45.7
D2	57.0	81.3	74.1	59.0	54.2
D3	11.1	2.2	1.2	0.1	0.1
D4	–[b]	–[b]	–[b]	–[b]	–[b]

[a] In case of Mg^{2+}, $[Mg^{2+}]/[\mathbf{1}]=20$, and in case of the other metal ions, M^{2+}, $[M^{2+}]/[\mathbf{1}]=10$.

[b] Isomer **D4** was not formed.

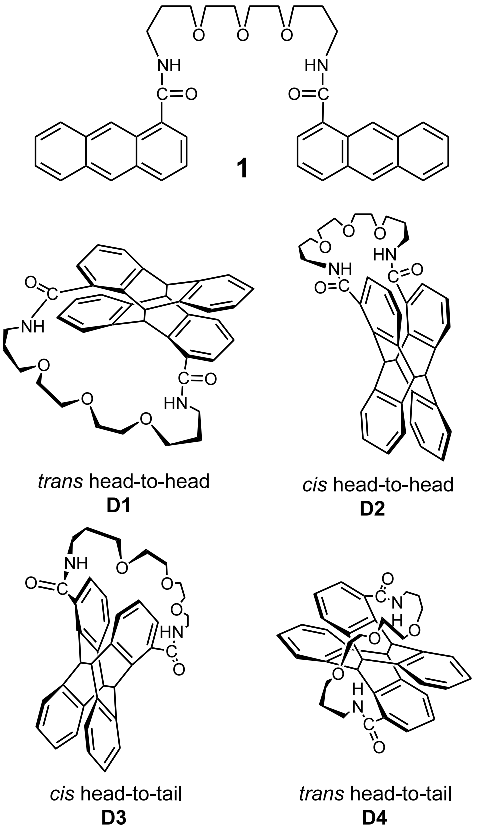

Figure 2. Structures of **1** and its photodimerized isomers.

Upon irradiation of **1** in the absence of metal ions, the ratio of the regioisomers was evaluated as **D1**:**D2**:**D3** = 32:57:11. This suggested that **1** preferred to stack modes of anthracene in *cis* head-to-head and *trans* head-to-head conformer on the ground state by linking with the oxyethylene chain. These conformers can be also considered to have little steric strain around the oxyethylene moiety in **D1** and **D2** molecules. When Mg^{2+} was added as a guest for **1**, the formation of **D2** was predominantly enhanced, and the isomer ratio was changed to **D1**:**D2**:**D3** = 17:81:2. From our previous results, it was found that Mg^{2+} bound strongly at only the carbonyl oxygen in the amide group.[15] This shortened the distance between amide groups in $\mathbf{1}\cdot Mg^{2+}$. Thus, the structure of $\mathbf{1}\cdot Mg^{2+}$ corresponded to *cis* head-to-head conformer as shown in Fig. 3(a). A similar trend was obtained in the case of $\mathbf{1}\cdot Ca^{2+}$. After the addition of $\mathbf{1}\cdot Ba^{2+}$, the formation of **D1** was slightly enhanced, and the isomer ratio was changed to **D1**:**D2**:**D3** = 46:54:0.1. This result can be interpreted to imply that the distance between the amide groups in $\mathbf{1}\cdot Ba^{2+}$ was longer in comparison with that in $\mathbf{1}\cdot Mg^{2+}$ since the ionic radius of Ba^{2+} is larger than that of Mg^{2+}. This induced preferential formation of the *trans* head-to-head conformer in $\mathbf{1}\cdot Ba^{2+}$ as shown in Fig. 3(b). A similar result was observed when Sr^{2+} was present as a guest for **1**.

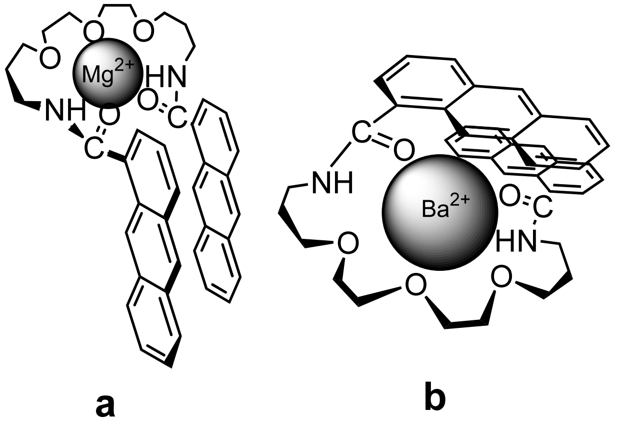

Figure 3. Schematic representation of expected structures of (a) $\mathbf{1}\cdot Mg^{2+}$ and (b) $\mathbf{1}\cdot Ba^{2+}$ complexes.

The quantum yields Φ for photodimerization of **1** were determined to clarify the effect of metal ions quantitatively for preparation of the regioisomers, as depicted in Table 2. Total quantum yields Φ were almost the same ($\Phi \approx 0.3$) in all experiments. The acceleration effect of metal ions for photodimerization of **1** was not observed. However, the value of Φ_{D1} for $\mathbf{1}\cdot Ba^{2+}$ was increased 1.5 times compared with that for free **1** whereas the Φ_{D2} was almost the same as that for free **1**. It can be pointed out that Ba^{2+} enhanced the generation of **D1**, but did not give any perturbation for Φ_{D2}. Thus, the total value of Φ was slightly increased. After the addition of Mg^{2+}, the Φ_{D1} became 0.38 times smaller than that of free **1** whereas the Φ_{D2} was not changed. Hence, the total value of Φ was slightly decreased. It is noteworthy that high selectivity for **D2** in $\mathbf{1}\cdot Mg^{2+}$ was originated from the suppression for the formation of **D1** and **D3**.

We conclude that use of a metal template method allowed us to demonstrate a simplified controllable photodimerization system for stereochemistry of 1-anthracenecaboxamide. This approach would be feasible for controlling the stereochemistry.

Table 2. The quantum yields of dimerization of **1**

Cation	ε	Φ	Φ_{D1}[a]	Φ_{D2}[a]	Φ_{D3}[a]
NON	8252	0.301	0.096	0.172	0.033
Mg^{2+}	8397	0.226	0.037	0.184	0.005
Ca^{2+}	7682	0.305	0.075	0.226	0.004
Ba^{2+}	8304	0.327	0.149	0.177	0.001

[a] $\Phi_{D1,\ D2,\ D3} = \Phi \times$isomer ratio (**D1**, **D2**, **D3**)

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16. Physical data for compound **1**: pale yellow solid, mp 158–160°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (4H, m, C-CH_2-C), 3.14 (4H, m, O-CH_2-), 3.17 (4H, m, O-CH_2-), 3.42 (4H, t, $J=6.0$ Hz, O-CH_2-), 3.61 (4H, t, $J=6.0$ Hz, N-CH_2-), 6.83 (4H, t, N-H), 7.33 (2H, dd, $J=6.8$ Hz, aromatic H-3), 7.45 (4H, m, aromatic H-6,7), 7.52 (2H, d, $J=6.8$ Hz, aromatic H-2), 7.94 (2H, d, $J=9.2$ Hz, aromatic H-8), 7.97 (2H, d, $J=8.4$ Hz, aromatic H-4), 7.98 (2H, m, aromatic H-5), 8.37 (2H, s, aromatic H-10), 8.91 (2H, s, aromatic H-9). Anal. calcd for $C_{40}H_{40}N_2O_5$: C, 76.41; H, 6.41; N, 4.46. Found: C, 76.31; H, 6.56; N, 4.41%.