**Supporting Information
for**

**Entropy-controlled Supramolecular Photochirogenesis: Enantiodifferentiating *Z-E*
Photoisomerization of Cyclooctene Included and Sensitized by Permethylated
6-*O*-Modified- β -cyclodextrins**

Gaku Fukuhara,[†] Tadashi Mori,[†] Takehiko Wada,^{†,‡} and Yoshihisa Inoue^{*,†,§}

[†] Department of Applied Chemistry and [‡] PRESTO (JST), Osaka University, 2-1
Yamada-oka, Suita 565-0871, Japan. Fax: 81 6 6879 7923; Tel: 81 6 6879 7921;

[§] Entropy Control Project, ICORP, JST, 4-6-3 Kamishinden, Toyonaka 560-0085, Japan

E-mail: inoue@chem.eng.osaka-u.ac.jp

List of Contents

1) Supplement 1	p.2
2) Supplement 2	p.3
3) Supplement 3	p.4
4) Supplement 4	p.5
5) Supplement 5	p.6
6) Supplement 6	p.7
7) Supplement 7	p.8
8) Supplement 8	p.9
9) Supplement 9	p.10
10) Supplement 10	p.11
11) General Experimental Methods	p.12
12) Synthesis and Characterization of Compounds 2a-2d	p.12-18

Supplement 1

Possibility of exciton couplet for 2a. The elucidation of the conformation of **2a** by the expanded sector rule was not straightforward. As illustrated in Figure 2, while the benzoate's 1L_b band showed a negative Cotton effect peak, the major 1L_a band exhibited an apparent exciton couplet. Exciton coupling interactions seem unlikely for monomeric **2a**, possessing a single chromophore, and hence we suspected the formation of self-assembled cyclic or acyclic supramolecular complexes,^{21,22} in which the benzoate moiety is successively included in the cavity of other **2a** host. To test this possibility, we measured the CD spectra of **2a** at different concentrations ranging from 5.3×10^{-5} M to 1.48×10^{-3} M in 50% aqueous methanol solution, but essentially no concentration dependence was observed in the CD spectra (data not shown). Closer examinations of the CD spectra and the g factor profile in different solvents (Figure 2a) and at different temperatures (Figure 2b) also do not support the assignment of the apparent couplet to the exciton coupling interactions, since the shape of the CD spectrum in methylcyclohexane and in particular those of the g factor profiles in all the solvents are quite difficult to be accepted as a regular couplet.

Supplement 2

S2. ROESY spectrum of a 11.5 mM solution of **2a** in 1:1 CD₃OD-D₂O at 25 °C (mixing time: 0.5 s).

Supplement 3

(a) at 25 °C

S3. ^1H NMR spectra of a 1:1 mixture of **2a** and **1Z** in 1:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ (a) at 25 °C and (b) at -40 °C.

Supplement 4

S4. (a) CD and (b) differential CD spectra and (c) g factor profiles of **2a** (0.191 mM) in the presence of **1Z** (0–6.71 mM) in 50% aqueous methanol at 45 °C. (d) Plot of the differential CD intensity at 245 nm against **1Z** concentration. Assuming the 1:1 stoichiometry, the complex stability constant was determined as $1100 \pm 120 \text{ M}^{-1}$ by the non-linear least-squares fitting technique.

Supplement 5

S5. (a) CD and (b) differential CD spectra and (c) g factor profiles of **2a** (0.148 mM) in the presence of **1Z** (0–5.75 mM) in 50% aqueous methanol at 25 °C. (d) Plot of the differential CD intensity at 245 nm against **1Z** concentration. Assuming the 1:1 stoichiometry, the complex stability constant was determined as $1180 \pm 100 \text{ M}^{-1}$ by the non-linear least-squares fitting technique

Supplement 6

S6. (a) CD and (b) differential CD spectra and (c) *g* factor profiles of **2a** (0.198 mM) in the presence of **1Z** (0–0.984 mM) in 25% aqueous methanol at 45 °C. (d) Plot of the differential CD intensity at 245 nm against **1Z** concentration. Assuming the 1:1 stoichiometry, the complex stability constant was determined as $4070 \pm 440 \text{ M}^{-1}$ by the non-linear least-squares fitting technique

Supplement 7

S7. (a) CD and (b) differential CD spectra and (c) g factor profiles of **2a** (0.198 mM) in the presence of **1Z** (0-0.646 mM) in 25% aqueous methanol at 25 °C. (d) Plot of the differential CD intensity at 245 nm against **1Z** concentration. Assuming the 1:1 stoichiometry, the complex stability constant was determined as $4890 \pm 640 \text{ M}^{-1}$ by the non-linear least-squares fitting technique.

Supplemental 8

S8. (a) CD and (b) differential CD spectra and (c) g factor profiles of **2a** (0.198 mM) in the presence of **1Z** (0–0.369 mM) in 25% aqueous methanol at 5 °C. (d) Plot of the differential CD intensity at 245 nm against **1Z** concentration. Assuming the 1:1 stoichiometry, the complex stability constant was determined as $5420 \pm 4010 \text{ M}^{-1}$ by the non-linear least-squares fitting technique.

Supplement 9

S9. (a) CD and (b) differential CD spectra and (c) g factor profiles of **2a** (0.189 mM) in the presence of **1E** (0–3.07 mM) in 50% aqueous methanol at 25 °C. (d) Plot of the differential CD intensity at 245 nm against **1E** concentration. Assuming the 1:1 stoichiometry, the complex stability constant was determined as $1580 \pm 130 \text{ M}^{-1}$ by the non-linear least-squares fitting technique.

Supplement 10

S10. (a) CD spectra changes of a 0.192 mM solution of **2a** in the presence of **1Z** (0-61.3 mM) in methanol at 5 °C. (b) Plot of the modified Benesi-Hildebrand at 245 nm ($[\mathbf{1Z}]_0 \gg [\mathbf{2a}]$; correlation coefficient r 0.998.). The 1:1 complex stability constant was determined as 4.58 M^{-1} .

General Experimental Methods

^1H NMR for 270 and 400 MHz, ^{13}C NMR for 100 MHz spectra, 2D-COSY and ROESY for 600 MHz were recorded in deuterated chloroform (CDCl_3), in deuterated water containing 0.01 M deuterated chloride ($\text{DCl-D}_2\text{O}$) or in deuterated water and methanol mixture ($\text{D}_2\text{O-CD}_3\text{OD}$). Deionized and distilled water, non-fluorescent grade methanol and methylcyclohexane were used as solvents. **1Z** was purified by fractional distillation. **1E** was prepared by the sensitized photoisomerization of **1Z** as reported previously.²⁶ β -cyclodextrin was dried overnight at 60 °C *in vacuo* prior to use. Permethylated β -cyclodextrin was prepared from β -cyclodextrin with methyl iodide and sodium hydrogen in dehydrated *N,N*-dimethylformamide (DMF) in a thermostated bath.

Synthesis and Characterization of Compounds 2a-2d.

Permethylated 6-*O*-modified β -cyclodextrins **2a-2d** were synthesized in good-high yields by esterification of permethylated 6-*O*-tosyl β -cyclodextrin²⁷ with the corresponding benzoate derivatives, according to the procedures similar to those reported previously.^{11j} **2a** is a known compound and showed the spectra identical to the literature data.^{11j}

2b; yield 82%; mp 73-75 °C; Anal. Calcd for $\text{C}_{71}\text{H}_{116}\text{O}_{38}$: C, 54.05; H, 7.41%; Found: C, 53.62; H, 7.15%; FAB-MS(NaI) m/z 1600 $[\text{M}+\text{Na}]^+$; ^1H NMR (CDCl_3 , 20 °C) δ_{H} 7.77-7.69 (m, 2H), 7.59-7.52 (m, 2H), 5.16-5.09 (m, 7H, CD- H_1), 3.89-3.17 (m, CD-H); ^{13}C NMR (CDCl_3 , 25.3 °C) δ_{C} 167.9, 167.0, 132.4, 131.7, 131.3, 131.0, 129.0, 128.8, 99.7, 99.13, 99.07, 99.0, 98.8, 82.3, 82.1, 82.0, 81.8, 81.7, 81.6, 80.7, 80.5, 80.4, 80.3, 80.1, 77.4, 77.0, 76.7, 71.5, 71.3, 71.2, 71.0, 70.9, 69.5, 64.7, 61.6, 61.5, 61.4, 61.3, 59.04, 58.98, 58.7, 58.6, 58.5, 58.4, 52.6.

^1H NMR spectrum of **2b** in CDCl_3 .

^{13}C NMR spectrum of **2b** in CDCl_3 .

2c; yield 93%; mp 73-75 °C; Anal. Calcd for $\text{C}_{71}\text{H}_{116}\text{O}_{38}$: C, 54.05; H, 7.41%; Found: C, 53.55; H, 7.21%; FAB-MS(NaI) m/z 1600 $[\text{M}+\text{Na}]^+$; ^1H NMR (CDCl_3 , 21 °C) δ_{H} 8.68 (s, 1H), 8.23 (t, J 8.1 Hz, 2H), 7.54 (t, J 8.1 Hz, 1H), 5.20-5.12 (m, 7H, CD- H_{I}), 3.94-3.17 (m, CD-H); ^{13}C NMR (CDCl_3 , 25.3 °C) δ_{C} 166.1, 165.4, 134.0, 133.8, 130.79, 130.76, 130.6, 128.7, 99.8, 99.1, 99.00, 98.95, 98.8, 82.3, 82.1, 82.0, 81.84, 81.77, 81.68, 81.65, 80.7, 80.6, 80.5, 80.4, 80.3, 80.2, 80.1, 77.7, 77.4, 77.2, 77.0, 76.7, 71.5, 71.34, 71.29, 71.1, 71.02, 70.95, 69.5, 64.2, 61.6, 61.52, 61.47, 61.40, 61.36, 59.1, 59.04, 58.98, 58.62, 58.57, 58.54, 58.4, 52.4.

^1H NMR spectrum of **2c** in CDCl_3 .

16

^1H NMR spectrum of **2d** in CDCl_3 .

^{13}C NMR spectrum of **2d** in CDCl_3 .