Wavelength-Controlled Supramolecular Photocyclodimerization of Anthracenearboxylate Mediated by γ-Cyclodextrins

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Table of Contents

Experimental .................................................................................................................................................... S2
Materials ...................................................................................................................................................... S2
Instruments .................................................................................................................................................. S2
Photolyses ..................................................................................................................................................... S2
Synthesis of 6 ................................................................................................................................................ S2

Figure S1. 1H NMR spectra of 6....................................................................................................................... S3

Figure S2. 13C NMR spectra of 6 ................................................................................................................... S4

Figure S3. HR FAB mass spectra of 6 ............................................................................................................ S5

Figure S4. UV-vis spectral titration of AC with 6 in pH 9 phosphate buffer solution at 25 °C. .................... S6

Figure S5. Circular dichroism spectral titration of AC with 6 in pH 9 phosphate buffer at 25 °C ................. S6

Figure S6. The changes of enantiomeric excess (ee) and excitational excess (xx) of 2 and 3 as a function of
genewavelength with 6 ................................................................................................................................ S7

Table S1. Product distribution, ee and xx values in photocyclodimerization of 2-AC with native and modified
genew-CDs at various wavelengths. ........................................................................................................ S8
Experimental

Materials. 2-Anthracenecarboxylic acid was purchased from Tokyo Chemical Industry, and γ-cyclodextrin and other chemicals from Wako Pure Chemicals Industries. These were used as received. Host 5 was synthesized as reported previously.1

Instruments. UV-vis and circular dichroism spectra were recorded on JASCO V-560 spectrophotometer and JASCO J-810 spectropolarimeter, respectively. FAB mass spectra were measured on a JEOL JMS-DX303 mass spectrometer. 1H and 13C NMR spectra were recorded on JEOL GSX-400 and Bruker DRX-600 spectrometer, respectively.

Photolyses. Sample solutions in quartz cells were deoxygenated with N2 bubbling, and then irradiated at different wavelengths using a xenon lamp equipped with appropriate band-pass filters of fwhm = 10 nm. The irradiated samples were analyzed by chiral HPLC as reported previously.2

Synthesis of 6. 6-TsO-γ-CD (300 mg) was dissolved in 1,6-diaminohexane (5 mL) under Ar atmosphere. After heating the mixture at 80 °C for 12 h, the resulting solution was added dropwise to acetone (100 mL) to give a white precipitate. The precipitate was collected by centrifugation, washed three times with 30 mL acetone, and then dissolved in water and freeze-dried to give 6-(6-aminohexyl)amino-6-deoxy-γ-CD in 83 % yield as a white powder. The white powder (200 mg) was dissolved in 20 mL DMF, to which was added iodomethane (2 mL) under N2. After stirred for 15 h at 60 °C, the solution was cooled down to room temperature and added dropwise with stirring to acetone (300 mL) to give a precipitate. The precipitate was collected by filtration, washed three times with acetone, and then dissolved in water and freeze-dried to give 6 in 75 % yield as a white solid.

1H NMR (400 MHz, D2O): δ 5.06-4.93 (m, 8H), 3.87-3.56 (m, 32H), 3.53-3.37 (m, 16H), 3.33-3.22 (m, 4H), 3.05 (s, 3H), 3.04 (s, 3H), 3.01 (s, 9H), 1.72 (m, 4H), 1.33 (m, 4H). 13C NMR (150 MHz, D2O): δ 101.72, 101.65, 101.32, 99.45, 81.92, 81.04, 80.57, 80.41, 80.24, 80.16, 79.94, 77.96, 77.56, 73.08, 72.95, 72.87, 72.75, 72.64, 72.50, 72.36, 72.29, 72.25, 72.18, 72.01, 71.98, 71.91, 71.76, 71.71, 71.63, 71.49, 71.43, 71.35, 66.66, 66.27, 65.87, 64.50, 60.74, 60.27, 60.05, 59.95, 52.85, 52.08, 51.95, 25.15, 25.08, 22.20, 22.10. HR FAB-MS: calcd. for [6 - I]+ (C59H106IN2O39) 1593.54; found, 1593.54.

**Figure S1.** $^1$H NMR spectrum of 6 in D$_2$O.
Figure S2. $^{13}$C NMR spectrum of 6 in D$_2$O.
Figure S3. HR FAB-MS spectrum of 6.
Figure S4. UV-vis spectra of 0.20 mM AC in a pH 9 phosphate buffer solution upon addition of 0, 0.040, 0.080, 0.119, 0.197, 0.275, 0.388, 0.573 and 0.753 mM 6 at 25 °C measured in a 0.1 cm-path length cell.

Figure S5. Circular dichroism spectra of 0.20 mM AC upon addition of 0, 0.040, 0.080, 0.119, 0.197, 0.275, 0.388, 0.573, 0.753 and 1.095 mM 6 in a pH 9 phosphate buffer solution at 25 °C measured in a quartz cell of 0.1 cm light-pass length. Inset: a plot of Δθ at 276 nm as a function of 6/AC ratio.
Figure S6. Enantiomeric excess (ee) (blue) and excitational excess (xx) (black) of (a) 2 and (b) 3 as a function of wavelength in photocyclodimerization of AC with 6 in aqueous phosphate buffer solution (pH 9) at 0.5 °C.
Table S1. Product distribution, enantiomeric excess (ee) and excitational excess (xx) in photocyclodimerization of 2-AC with native and modified γ-CDs at various wavelengths

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a Irradiated at different wavelengths by using a xenon lamp fitted with appropriate band-pass filters of fwhm = 10 nm. Relative yield and % ee were determined by the peak area on the HPLC chromatogram. The positive/negative signs of ee correspond to the dominant formation of the first/second-eluted enantiomer, respectively. Xx values were calculated supposing the precursor complexes have the same extinction coefficient at the pseudo-isosbestic point (380 nm). c Solvent B: aqueous phosphate buffer (pH 9). cBM1: a 1:1 (v/v) mixture of phosphate buffer (pH 5) and methanol. cBM2: a 5:2 (v/v) mixture of phosphate buffer (pH 5) and methanol.