

Electronic Supplementary Information

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

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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, 77.56, 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.

1. A. Nakamura and Y. Inoue, *J. Am. Chem. Soc.*, 2003, **125**, 966.

2. C. Ke, C. Yang, T. Mori, T. Wada, Y. Liu and Y. Inoue, *Angew. Chem. Int. Ed.*, 2009, **48**, 6675.

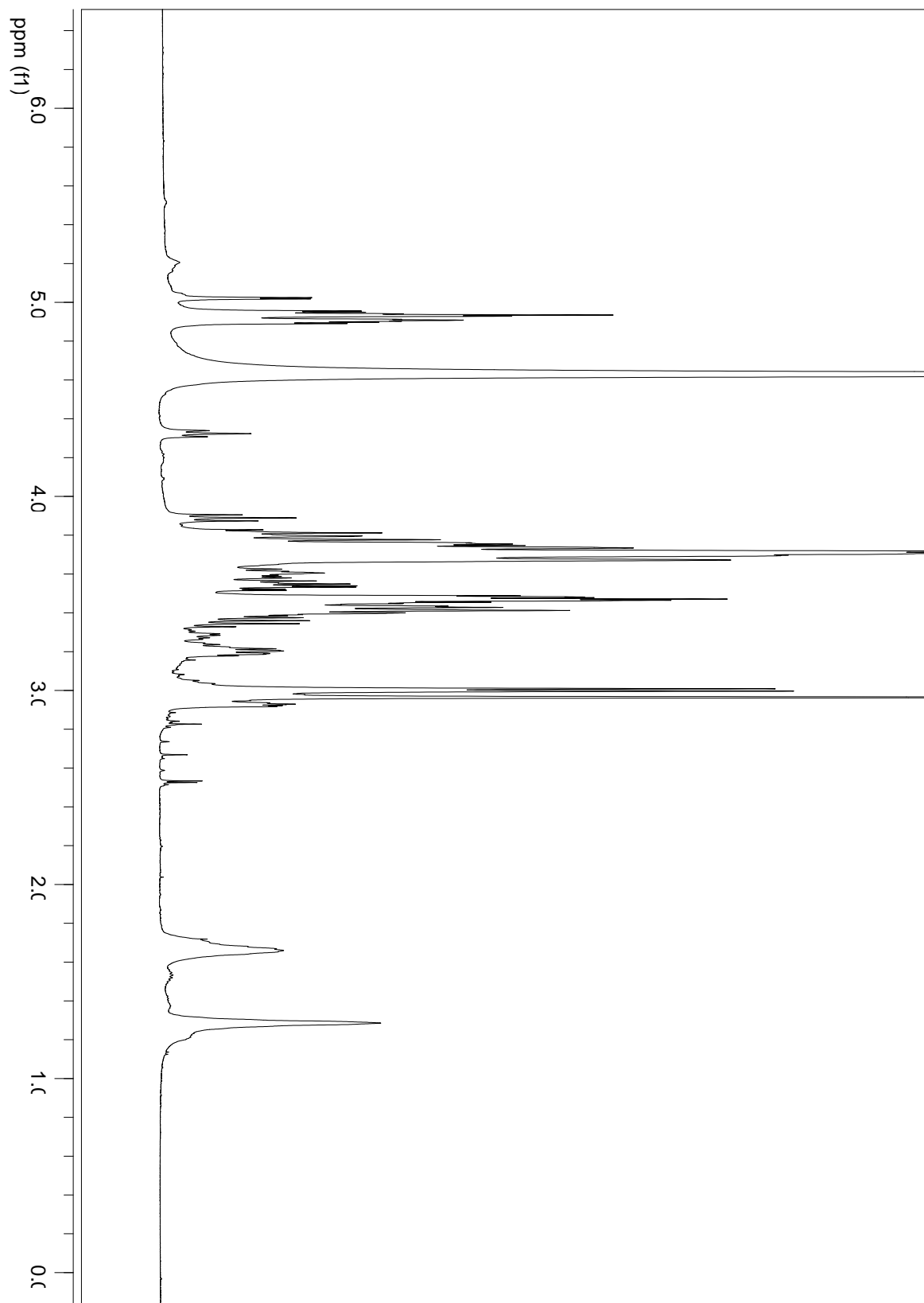


Figure S1. ^1H NMR spectrum of **6** in D_2O .

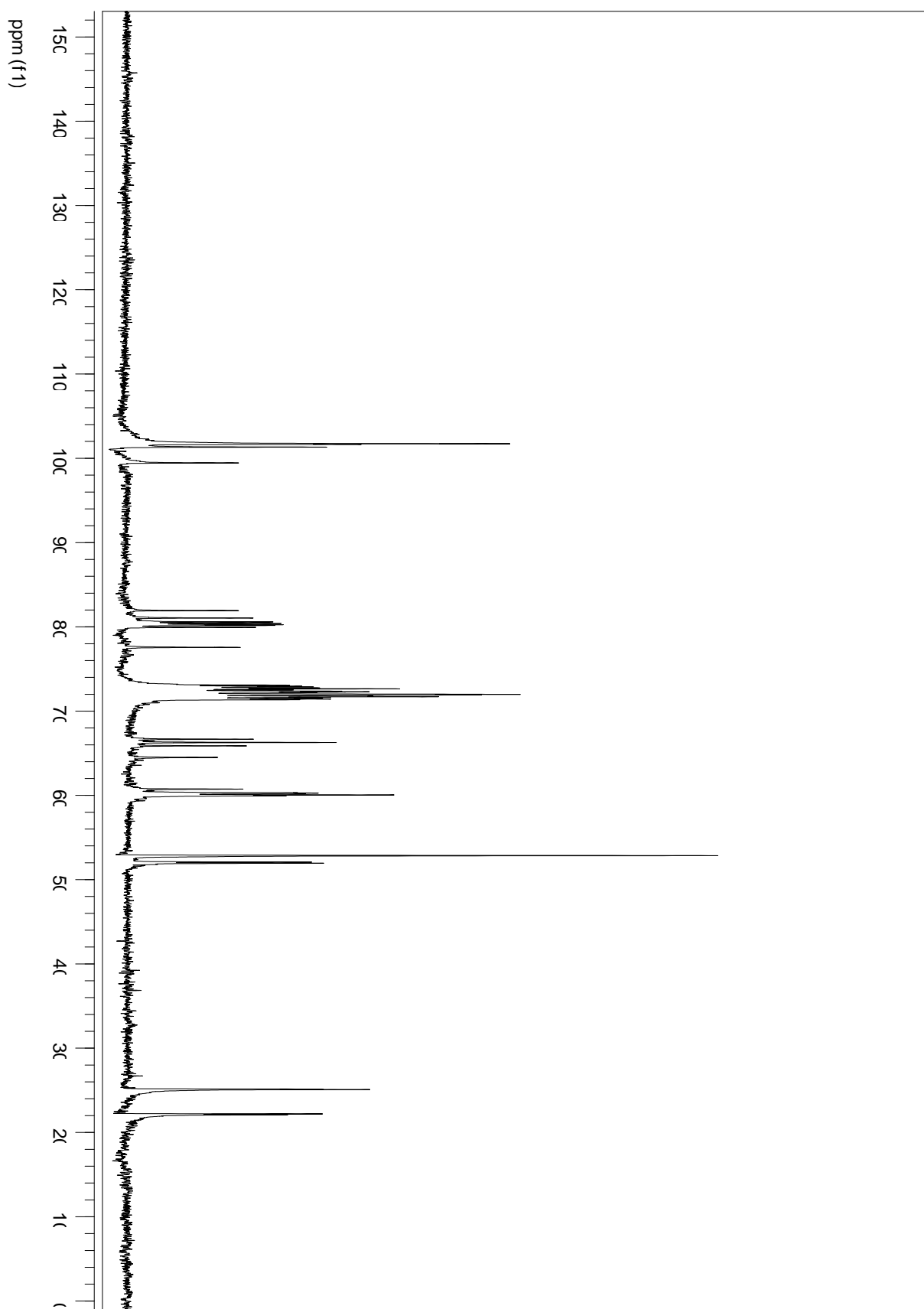


Figure S2. ^{13}C NMR spectrum of **6** in D_2O .

[Elemental Composition]
Data : HRO03023 Date : 18-Jan-2011 16:33
Sample: 1/12
Note : Magic Bullet DTT:DTE=3:1
Inlet : Direct Ion Mode : FAB+
RT : 0.92 min Scan#: (11,13)
Elements : C 100/0, H 120/0, N 2/0, O 39/0, I 1/0
Mass Tolerance : 10mmu
Unsaturation (U.S.) : -1.0 - 20.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
1593.5436	100.0	-3.1 / -4.9	16.0 C 67 H 104 N 0 34 I
		+4.8 / +7.7	16.5 C 66 H 102 N 2 O 34 I
		-1.4 / -2.2	11.5 C 64 H 106 O 37 I
		+1.1 / +1.8	7.5 C 59 H 106 N 2 O 39 I

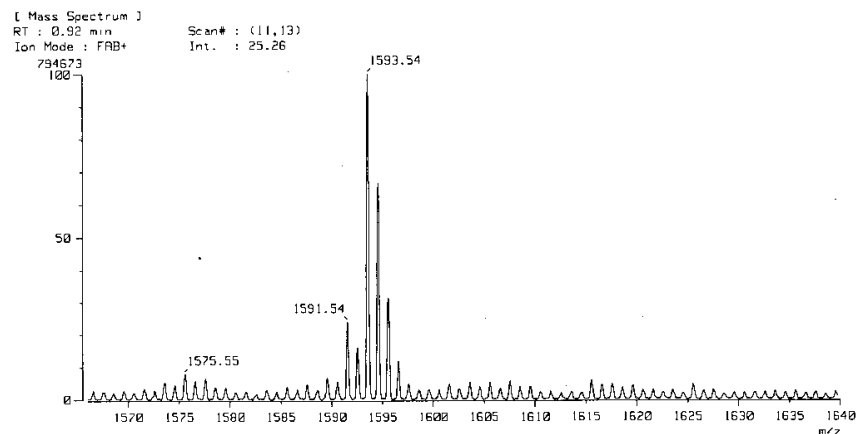
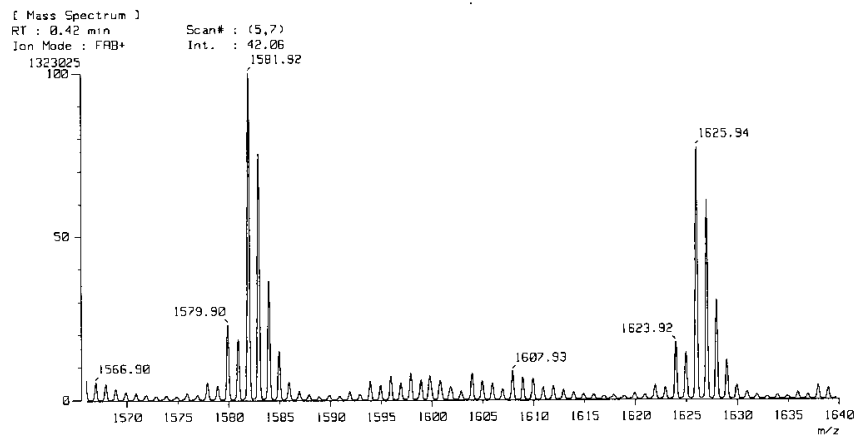
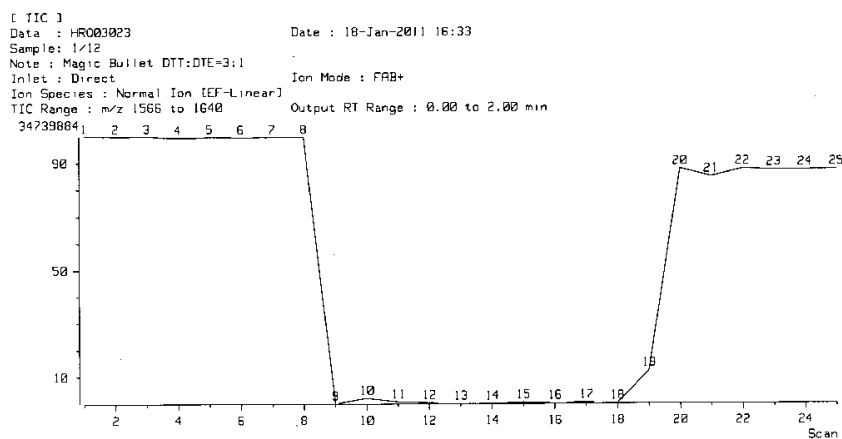


Figure S3. HR FAB-MS spectrum of 6.

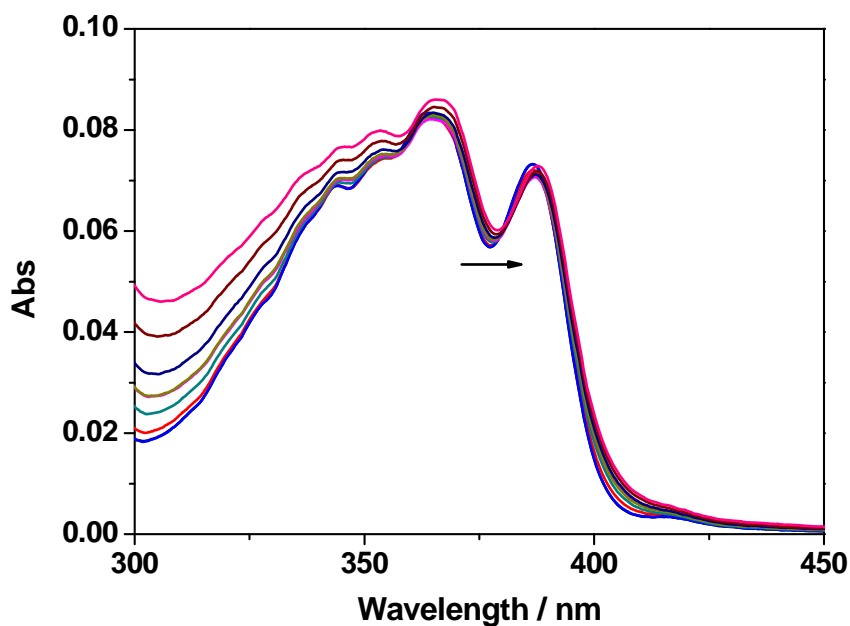


Figure S4. UV-vis spectra of 0.20 mM AC in a pH 9 phosphate buffer solution upon addition of 0, 0.040, 0.080, 0.119, 0.197, 0.275, 0.388, 0.573 and 0.753 mM **6** at 25 °C measured in a 0.1 cm-path length cell.

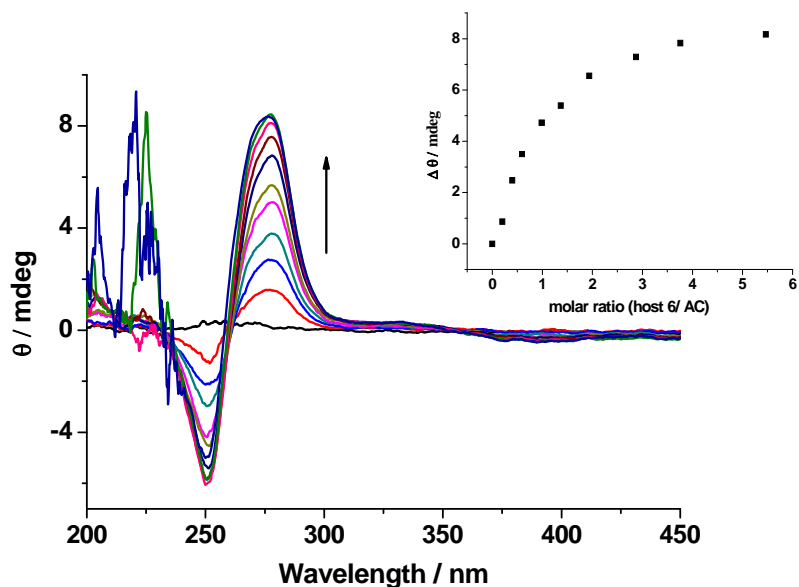


Figure S5. Circular dichroism spectra of 0.20 mM AC upon addition of 0, 0.040, 0.080, 0.119, 0.197, 0.275, 0.388, 0.573, 0.753 and 1.095 mM **6** in a pH 9 phosphate buffer solution at 25 °C measured in a quartz cell of 0.1 cm light-pass length. Inset: a plot of $\Delta\theta$ at 276 nm as a function of **6**/AC ratio.

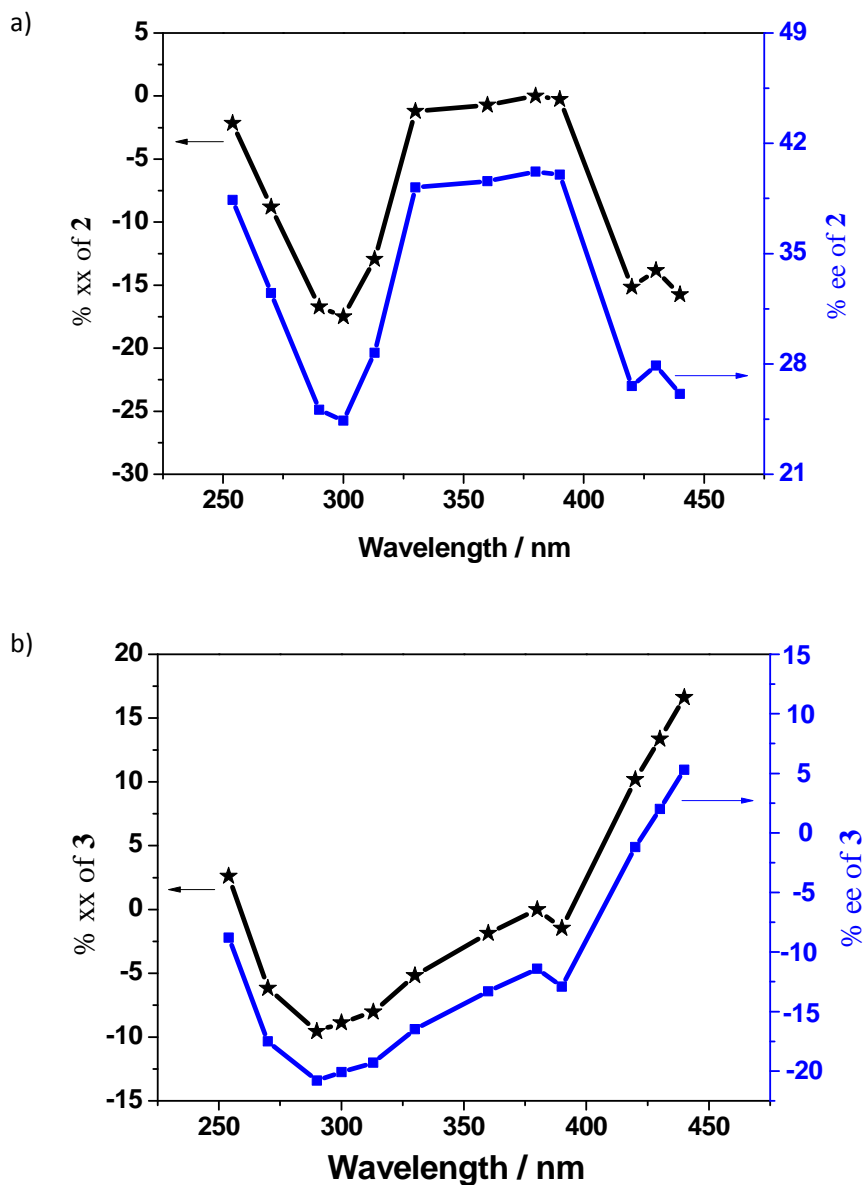


Figure S6. Enantiomeric excess (ee) (blue) and excitational excess (xx) (black) of (a) **2** and (b) **3** as a function of wavelength in photocyclodimerization of AC with **6** in aqueous phosphate buffer solution (pH 9) at 0.5 °C.

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

Host	Sol-vent	Temp/ °C	λ^a /nm	Relative yield ^b /%				HT/HH	ee ^{b,c} /%		xx ^d /%		
				1	2	3	4		2	3	2	3	
γ -CD	B ^e	0.5	254	33.3	52.7	7.4	6.6	6.14	39.9	3.6	-0.1	0.2	
			270	45.5	38.8	8.8	6.9	5.37	34.8	-5.4	-6.1	-8.9	
			280	47.7	35.9	10.1	6.3	5.10	32.4	-8.3	-8.8	-11.7	
			290	47.7	35.3	10.2	6.8	4.88	26.2	-8.8	-15.6	-12.2	
			300	54.5	33.3	6.1	6.1	7.20	26.7	-4.4	-15.0	-11.8	
			313	43.6	43.0	7.8	5.6	6.46	29.5	-5.7	-12.0	-9.1	
			360	41.2	46.2	7.1	5.5	6.94	40.8	0.7	0.8	-2.7	
			380	41.2	47.0	7.0	4.8	7.47	40.1	3.5	0.0	0.0	
			390	40.0	47.6	7.1	5.3	7.06	40.7	1.0	0.7	-2.5	
			420	39.7	49.7	7.2	3.4	8.43	24.7	4.7	-17.0	1.2	
			430	34.3	56.2	7.0	2.5	9.53	24.7	9.4	-17.1	5.9	
			440	30.7	60.9	6.6	1.8	10.90	24.1	11.9	-17.7	8.5	
			5	B ^e	0.5	290	46.3	33.3	12.2	8.2	3.90	25.7	-10.8
300	52.4	32.1				7.9	7.6	5.45	24.2	-10.5	-15.6	-9.1	
360	39.6	44.8				8.9	6.7	5.41	38.5	-2.6	2.3	-1.2	
380	38.9	45.4				9.2	6.4	5.40	38.3	-1.4	0.0	0.0	
440	29.3	59.4				8.8	2.5	7.85	22.1	12.6	-17.7	14.0	
BM1 ^f	-40	290		31.5	13.3	19.7	35.5	0.99	-16.5	-35.1	-14.3	8.4	
		300		34.0	12.7	15.3	38.0	0.88	-18.3	-38.3	-16.1	4.7	
		360		29.7	19.7	19.3	31.3	0.98	-0.7	-35.5	1.5	7.9	
		380		29.6	19.2	20.3	30.9	0.95	-2.2	-42.2	0.0	0.0	
		390		29.9	20.6	19.7	29.8	1.02	1.8	-37.8	4.1	5.3	
		440		30.7	29.3	25.8	14.2	1.50	-1.5	-37.1	0.8	6.1	
BM2 ^g	-70	290		32.3	8.4	27.4	31.9	0.69	-7.4	-54.6	-17.1	-3.9	
		300		37.1	9.9	22.0	31.0	0.89	-4.0	-55.8	-13.8	-5.6	
		360		30.6	16.0	26.9	26.5	0.87	7.3	-52.0	-2.6	-0.2	
		380		33.0	13.2	28.8	25.0	0.86	9.8	-51.8	0.0	0.0	
		440		29.6	28.3	29.2	12.9	1.38	-1.4	-48.7	-11.3	4.2	
6	B ^e	0.5		254	31.6	49.8	9.8	8.8	4.38	38.4	-8.8	-2.2	2.6
				270	44.0	36.7	11.0	8.3	4.18	32.5	-17.5	-8.8	-6.2
			290	46.7	32.6	12.1	8.6	3.83	25.1	-20.8	-16.7	-9.6	
			300	51.7	31.7	8.8	7.8	5.02	24.4	-20.1	-17.5	-8.9	
			313	41.3	43.5	8.7	6.5	5.58	28.7	-19.3	-12.9	-8.0	
			330	40.6	43.9	9.1	6.4	5.45	39.2	-16.5	-1.2	-5.2	
			360	40.6	44.2	8.8	6.4	5.58	39.6	-13.3	-0.7	-1.9	
			380	38.6	45.2	9.5	6.8	5.16	40.2	-11.4	0.0	0.0	
			390	39.5	45.1	9.0	6.4	5.49	40.0	-12.9	-0.3	-1.5	
			420	39.0	46.7	10.0	4.3	5.99	26.6	-1.2	-15.1	10.2	
			430	34.3	52.6	9.7	3.4	6.63	27.9	2.0	-13.8	13.4	
			440	30.2	58.7	8.6	2.5	8.01	26.1	5.3	-15.7	16.6	

^a Irradiated at different wavelengths by using a xenon lamp fitted with appropriate band-pass filters of fwhm = 10 nm. ^b Relative yield and % ee were determined by the peak area on the HPLC chromatogram. ^c The positive/negative signs of ee correspond to the dominant formation of the first/second-eluted enantiomer, respectively. ^d Xx values were calculated supposing the precursor complexes have the same extinction coefficient at the pseudo-isosbestic point (380 nm). ^e Solvent B: aqueous phosphate buffer (pH 9). ^f BM1: a 1:1 (v/v) mixture of phosphate buffer (pH 5) and methanol. ^g BM2: a 5:2 (v/v) mixture of phosphate buffer (pH 5) and methanol.