Supporting Information
for

Dual Chiral, Dual Supramolecular Diastereodifferentiating Photocyclodimerization of 2-Anthracenecarboxylate Tethered to Amylose Scaffold

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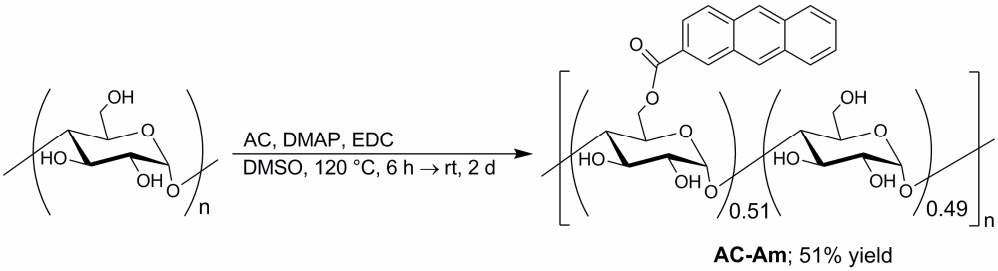
General

Instruments. ^{1}H NMR spectra at 600 MHz, ^{13}C NMR spectra at 150 MHz, and 2D-HSQC spectra at 600 MHz were recorded in DMSO-d_6 on a Varian INOVA-600 instrument. IR spectrum was recorded on a JASCO FT/IR-460 plus spectrometer. UV/vis and CD spectra were measured in a quartz cell (light path of 2 or 10 mm) on a JASCO V-550 or V-560 spectrometer and a J-720WI or J-820YH spectrometer, respectively, both equipped with an ETC-505T temperature controller. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorimeter. Fluorescence lifetimes were determined by the time-correlated single-photon-counting method on a Hamamatsu FL920S instrument equipped with a pulsed H_2 light source. HPLC analyses of the product distribution and ee of cyclodimers were performed at 35 °C on a tandem column of Cosmosil 5C18-AR-II (Nakalai) and Chiralcel OJ-RH (Daicel) eluted with a 64:36 (v/v) mixture of deionized water and acetonitrile containing 0.1% trifluoroacetic acid at a flow rate of 0.5 mL min^{-1}. Molecular weights of 6-*O*-(2-anthroyl)amylose (**AC-Am**) were determined relative to polystyrene standards by using analytical GPC with a TOSOH TSKgel α-4000 column at 40 °C eluted with DMF at a flow rate of 0.5 mL min^{-1} under isocratic conditions.

Materials. Amylose, purchased from TCI (M_w = ca. 15000), was dried at 80 °C under high vacuum prior to use. DMSO and water of fluorescence-free grade, purchased from Wako Chemicals, were used as solvents without further purification. Methyl 2-anthracenecarboxylate (**5**) was synthesized as reported previously and showed the satisfactory agreement with the literature values.[1]

Photolysis. A DMSO solution of **AC-Am** in a quartz cell (10 × 10 × 45 mm) was irradiated at 25 °C under a nitrogen atmosphere, by using a 300-W xenon lamp fitted with a band-pass filter (360 ± 10 nm). The irradiated DMSO solution was hydrolyzed for 24 h by adding an aqueous KOH solution (90 mM), and the resulting solution was ultrafiltrated with a membrane filter (>10 kDa) to give photocyclodimers **1**-**4**, which were subjected to chiral HPLC analysis.

Synthesis and Characterization of AC-Am. In a 50 mL three-necked flask, amylose (300 mg, 1.85 mmol based on the glucose units) was added to dry DMSO (30 mL) and the resulting highly viscous solution was heated to 120 °C and stirred for 6 h under a nitrogen atmosphere at that temperature. After cooling to room temperature, AC (230 mg, 1.03 mmol), DMAP (891 mg, 7.29 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (345 mg, 1.80 mmol) were added to the flask and the resulting mixture was stirred for additional 2 d at room temperature. The solution was slowly poured into methanol (550 mL) to give a precipitate. The precipitate was collected by filtration and washed with acetone and methanol to give **AC-Am** polymer as yellow solid (250 mg, 0.939 mmol in monomer unit) in 51% yield. The degree of substitution (DS) was determined as 0.51 by the UV/vis spectrometry described below. ^{1}H NMR (DMSO-d_6, 600 MHz, 25 °C) δ_H 9.09-7.15 (H_{Ar}), 6.21-4.17, 4.05-3.52 (sugar protons); ^{13}C NMR (DMSO-d_6, 150 MHz, 25 °C) δ_C 165.7 (C=O), 132.6, 132.0, 131.6, 129.7, 128.4, 128.1, 126.8, 126.1, 123.8 (C_{Ar}), 100.7, 100.2, 95.4, 78.8, 73.2, 72.0, 71.6, 64.1, 60.4 (sugar carbons); Anal. Calcd for $(C_{13.65}H_{16.08}O_{6.51}\bullet H_2O)_n$: C, 57.67; H, 5.66%; Found: C, 57.14; H, 5.17%; IR (KBr) ν 3398, 2928, 1705, 1633, 1414, 1315, 1280, 1237, 1185, 1153, 1082, 1024, 921, 874, 744 cm^{-1}; GPC (DMF) M_n = 10100 and PDI = 1.6 at 280 nm.



Determination of the DS of AC-Am. The DS of **AC-Am** was determined by the comparison of the absorbance of an authentic anionic AC solution with that of AC liberated upon hydrolysis of **AC-Am** in aqueous alkaline solution, using UV/vis spectroscopy. Thus, **AC-Am** (1.2 mg) was dissolved in DMSO (9.5 mL), to which 0.5 mL of aqueous KOH solution (300 mM) was added. The

[1] Takaguchi, Yutaka; US Patent 2004175568 A1 2004.

resulting mixture was hydrolyzed for 1, 2, 5, 24, and 28 h with UV/vis monitoring (Figure S1). Upon completion of the hydrolysis after 28 h (1 h seemed enough), the absorbance at 387 nm of AC anion obtained from **AC-Am** (0.12 mg mL^{-1}) was smaller by a factor of 1/1.56 than that of the authentic AC solution (0.27 mM), indicating that the AC concentration liberated from **AC-Am** was 0.17 mM (= 1/1.56 × 0.27). Since the concentration of liberated AC should be 0.33 mM if the DS of **AC-Am** was 1.0, the DS was calculated as 0.51 (= 0.17/0.33).

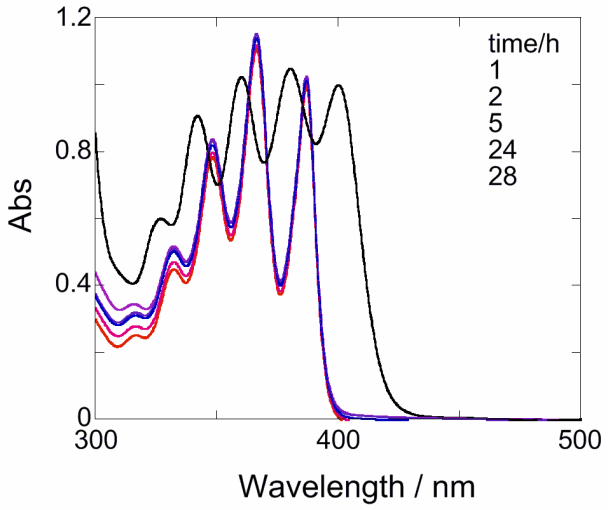


Figure S1. UV/vis spectra of **AC-Am** in 5:95 (v/v) H_2O-DMSO (black) and in 5:95 (v/v) 300 mM KOHaq-DMSO (measured after 1, 2, 5, 24, and 28 h of hydrolysis; from red to blue).

NMR Spectra of AC-Am

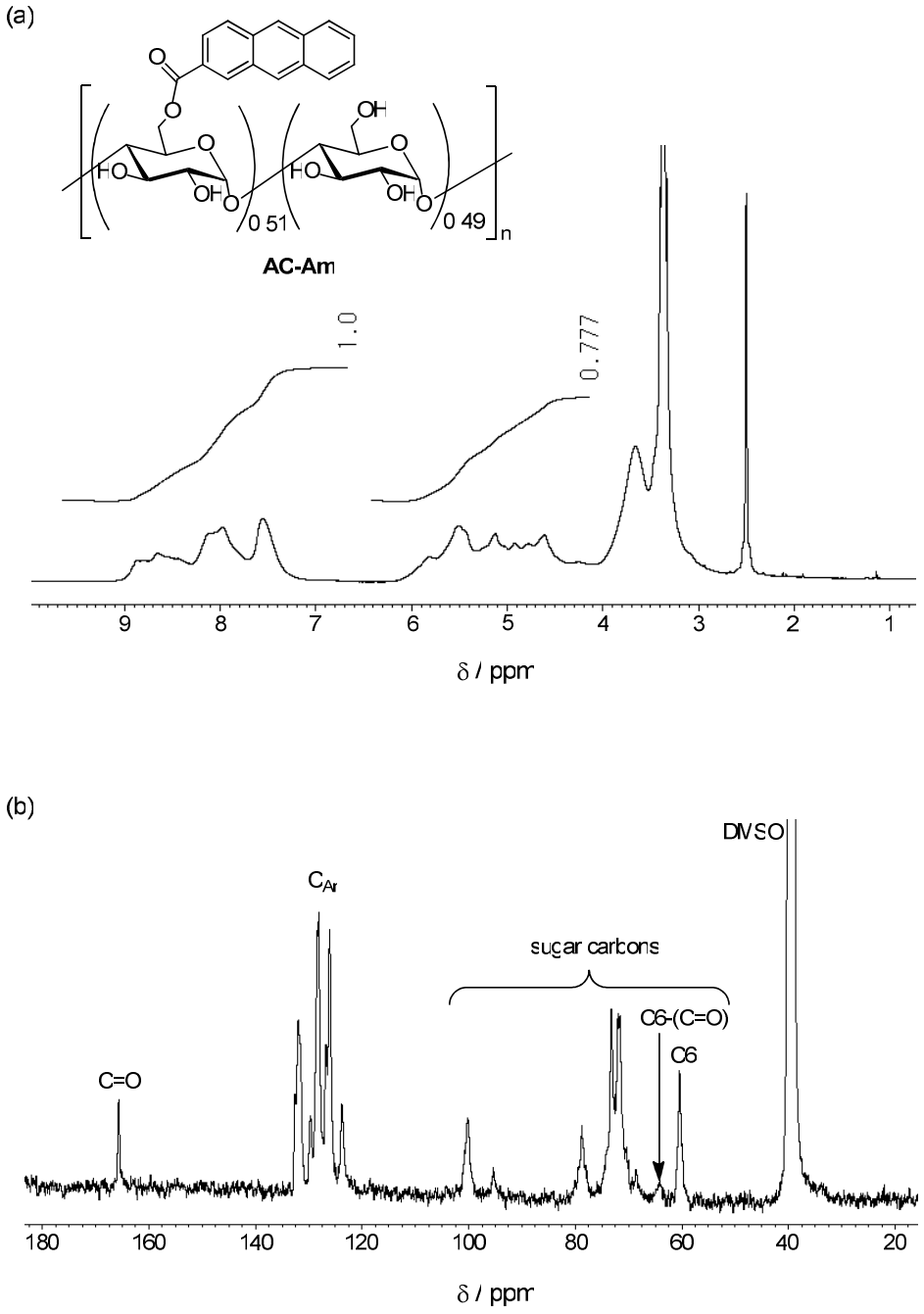


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectrum of **AC-Am** in DMSO-d_6 at room temperature.

HSQC spectrum of AC-Am

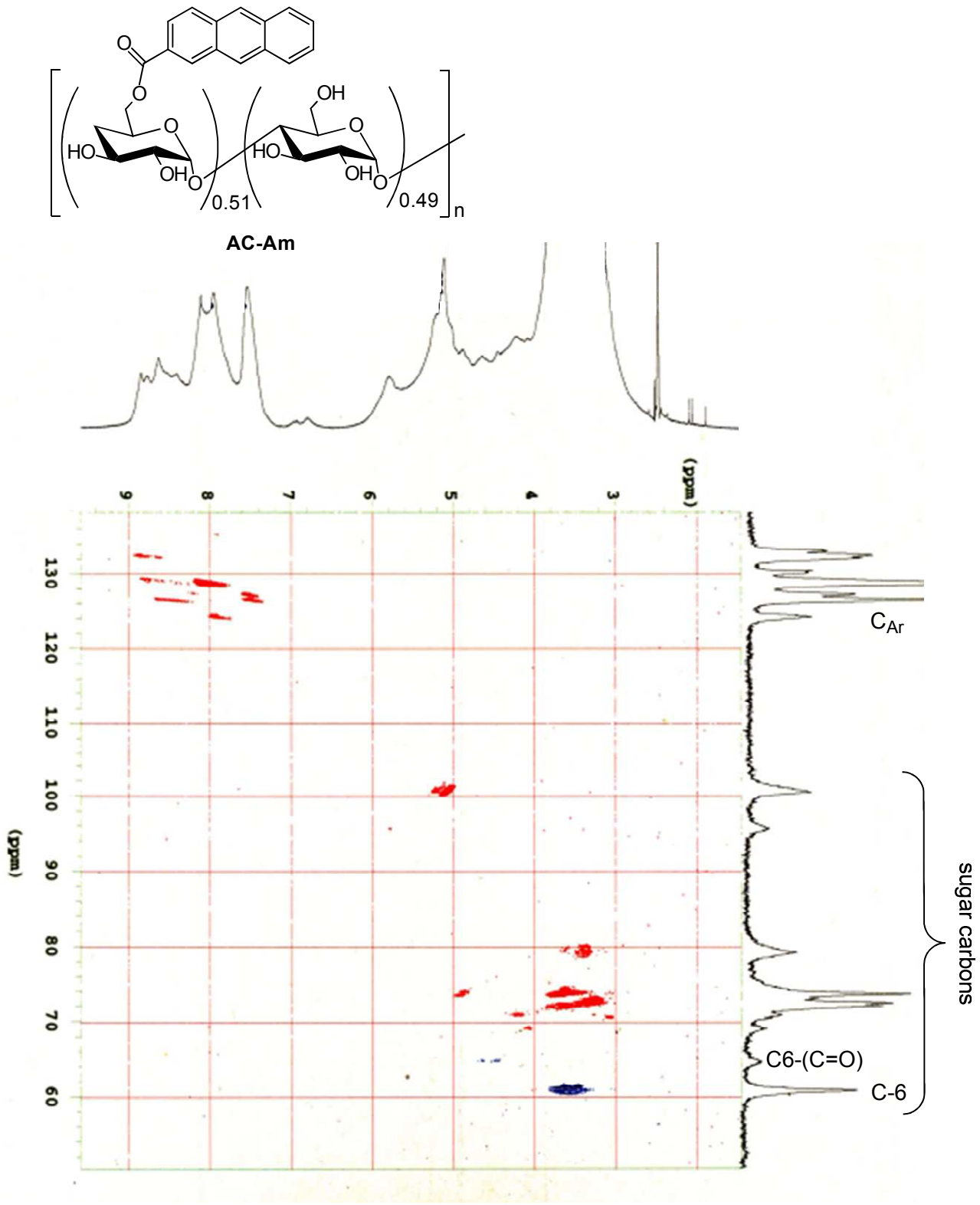


Figure S3. HSQC spectrum of **AC-Am** in DMSO-d_6 at 40 °C.

UV/vis Spectra of Reference Compound 5

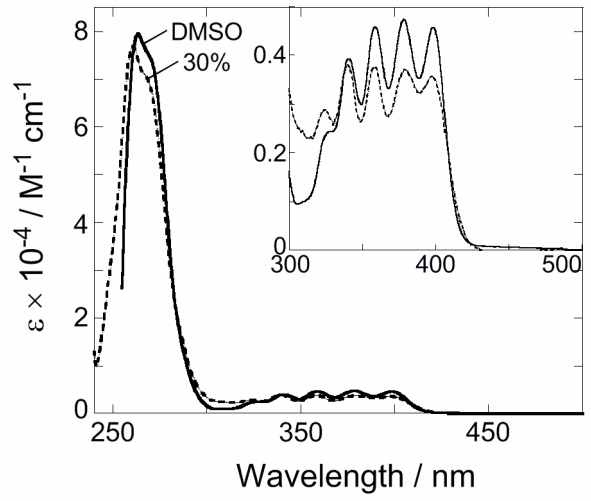


Figure S4. UV/vis spectra of a 24.5 μM solution in DMSO (solid line) and a 7.35 μM solution in 30% aqueous DMSO (dashed line) of **5** at room temperature, measured in a 1-cm cell; the inset shows the magnified spectra from 300 nm to 500 nm.

Eyring Plots Obtained for the Enantiomeric Excesses of Cyclodimers 2* and 3*

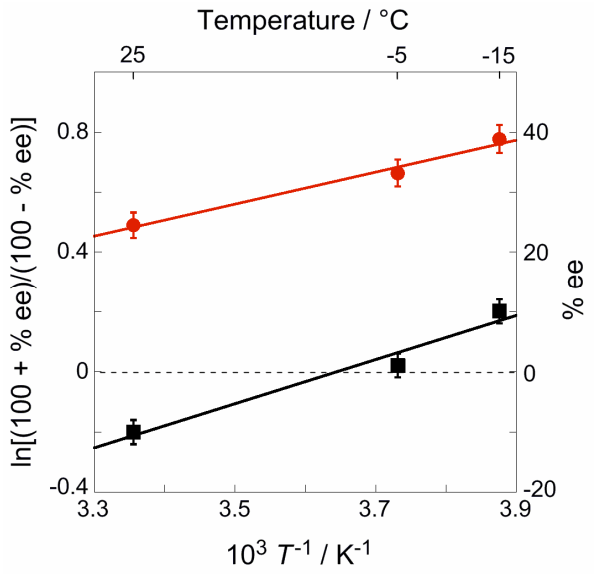


Figure S5. Eyring plots for the enantioselectivities of **2*** (red) and **3*** (black) obtained in the dual-supramolecular diastereodifferentiating photocyclodimerization of **AC-Am**.

Discussion. The product ee is thought to be controlled thermodynamically upon complexation and/or kinetically upon photocyclodimerization. Nevertheless, the ee values obtained at different temperatures were subjected to the Eyring analysis to give good straight lines for both of **2*** and **3*** (Figure S5), indicating operation of a single diastereodifferentiation mechanism over the entire temperature range employed. From the slope and intercept of the plot, the differential thermodynamic or activation parameters were calculated for **2*** as $\Delta\Delta H$ = –4.4 kJ mol^{-1} and $\Delta\Delta S$ = –10.8 J mol^{-1} K^{-1}, and for **3*** as $\Delta\Delta H$ = –6.1 kJ mol^{-1} and $\Delta\Delta S$ = –22 J mol^{-1} K^{-1}. However, further useful discussion is difficult without knowing the nature of these parameters.