Electronic Supplementary Information

Strictly Diastereocontrolled Photocyclodimerization of 2-Anthracenecarboxylates Tethered to Cyclic Tetrasaccharide

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General

Instruments. Melting point was measured with a BÜCHI B-545 apparatus. Mass spectrum was obtained on a Bruker Autoflex III MALDI-TOF. ^{1}H NMR spectra at 600 MHz, ^{13}C NMR spectra at 150 MHz, and 2D-HSQC and COSY spectra at 600 MHz were recorded in DMSO-d_6 on a Varian INOVA-600 instrument. UV/vis and CD spectra were measured in a quartz cell (light path of 1 cm) on JASCO V-550 or V-560 and J-720WI or J-820YH instrument, 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}.

Materials. Cyclic nigerosylnigerose (CNN) was supplied by Hayashibara Co., Ltd. Acetonitrile and water of fluorescence-free grade were used without further purification. Methyl 2-anthracenecarboxylate (**5**) was synthesized as reported previously.[1]

Spectroscopic Analyses and Photolysis Procedures. A given amount of 2^{B},3^{B}-di(2-anthroyl)-CNN (**AC_2-CNN**) and **5** were dissolved in 45:55 CH_3CN-H_2O to subject to the UV/vis, CD, fluorescence, excitation spectroscopies and fluorescence lifetimes at room temperature, measured in a 1 cm cell. An aqueous acetonitrile solution of **AC_2-CNN** in a quartz cell (10 x 10 x 45 mm) was irradiated at 25 and -5 °C under a nitrogen atmosphere, by using a 300-W xenon lamp fitted with a band-pass filter (360 ± 10 nm). The irradiated aqueous acetonitrile solution was hydrolyzed for 24 h by adding KOH powder; the total KOH concentration was 300 mM, and the resulting solution was subjected to chiral HPLC analysis.

Synthesis and Characterization of 2^{B},3^{B}-Di(2-anthroyl)-CNN (AC_2-CNN).

CNN (1.0 g, 1.5 mmol) was dissolved in dry DMF (50 mL), to which were added *N*,*N'*-dicyclohexylcarbodiimide (DCC) (700 mg, 3.4 mmol) and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (415 mg, 3.4 mmol) under nitrogen. After the complete dissolution of the reagents, 2-anthracenecarboxylic acid (1.0 g, 4.5 mmol) was added and the mixture was stirred under nitrogen for 24 h at room temperature. After removing byproduct urea by filtration, the clear filtrate obtained was slowly poured onto diethyl ether (450 mL) and stirred for 2 h to give a precipitate, which was collected by filtration, washed with diethyl ether, and dried in vacuo to give a crude product as yellow solid (720 mg). The crude product was a mixture of CNN and

[1] Takaguchi, Y. US Patent 2004175568 A1 2004.

mono-, di-, and tri-AC-esters in ca. 1:2:1:0.1 (estimated from the MALDI-TOF-MS spectrum, without taking into account the difference in ionization efficiency). Although the HPLC analysis of the crude product on a Cosmosil 5C_{18}-AR-II column (4.6 mm ϕ x 150 mm; Nacalai Tesque) eluted by H_2O-CH_3CN (55:45) at a flow rate of 0.5 mL min^{-1} revealed several isomer peaks in the diester region (retention time = 8-32 min), the desired diester eluted as the last peak well spaced apart from the other diester peaks, and was readily isolated by preparative HPLC on a Sumipax ODS (20 mm ϕ x 250 mm; SCAS) eluted by H_2O-CH_3CN (58:42) at 5 mL min^{-1} under an isocratic condition. Thus, 25 mg of the crude product was dissolved in 25 mL of H_2O-CH_3CN (55:45) with sonication. After removing a small amount of undissolved residue by filtration, the clear sample solution was injected into the preparative HPLC in five portions, and the fraction containing the desired product was collected. The combined fraction was evaporated and then freeze-dried to give pure 2^B,3^B-di(2-anthroyl)-CNN (**AC_2-CNN**) as pale yellow solid (0.25 mg; 1% yield). **AC_2-CNN**: dp >250 °C; ^{1}H NMR (DMSO-d_6, 600 MHz, 25 °C): δ_H 8.78 (1H, s), 8.68 (1H, s), 8.63 (1H, s), 8.59 (1H, s), 8.48 (2H, s), 8.07 (1H, d, J = 7.0 Hz), 8.01-7.98 (5H, m), 7.84 (1H, d, J = 8.6 Hz), 7.71 (1H, d, J = 8.8 Hz), 7.51-7.46 (4H, m), 5.84 (1H, d, J = 3.2 Hz, B_1), 5.76 (1H, t, J = 9.6 Hz, B_3), 5.33 (1H, d, J = 3.1 Hz, D_1), 5.15 (1H, dd, J = 10.3 Hz, 3.4 Hz, B_2), 4.89 (1H, t, J = 9.7 Hz, B_5), 4.65 (1H, d, J = 2.3 Hz, A_1), 4.62 (1H, d, J = 2.5 Hz, C_1), 4.50 (1H, t, J = 8.1 Hz, D_5), 3.92 (1H, t, J = 9.1 Hz, C_3), 3.83 (1H, t, J = 9.1 Hz, A_3), 3.70 (1H, t, J = 9.9 Hz, B_6), 3.62-3.59 (3H, m), 3.47-3.15 (13H, m), 2.83 (1H, t, J = 9.4 Hz, D_4); ^{13}C NMR (DMSO-d_6, 150 MHz, 25 °C): δ_C 166.2 (C=O), 165.7 (C=O), 133.0, 133.0, 132.4, 132.0, 131.9, 130.1, 123.0, 129.0, 128.8, 128.7, 128.5, 127.3, 127.3, 126.9, 126.5, 124.1, 123.9, 100.5 (A_1), 100.3 (C_1), 97.9 (D_1), 95.3 (B_1), 76.7 (C_3), 76.2 (A_3), 74.2 (B_3), 73.9 (C_2), 73.0 (A_2), 72.9 (D_2), 72.7 (B_2), 71.7, 71.5 (D_3, D_4), 70.9, 70.7, 70.6 (B_5), 70.1 (D_5), 69.3 (D_6), 69.1 (B_4), 68.8 (B_6), 61.0, 60.6; HR-MS (MALDI-TOF): [M+Na^+] m/z 1079.3169 (calcd. for $C_{54}H_{56}O_{22}Na$: 1079.3161).

NMR Spectra of AC_2-CNN

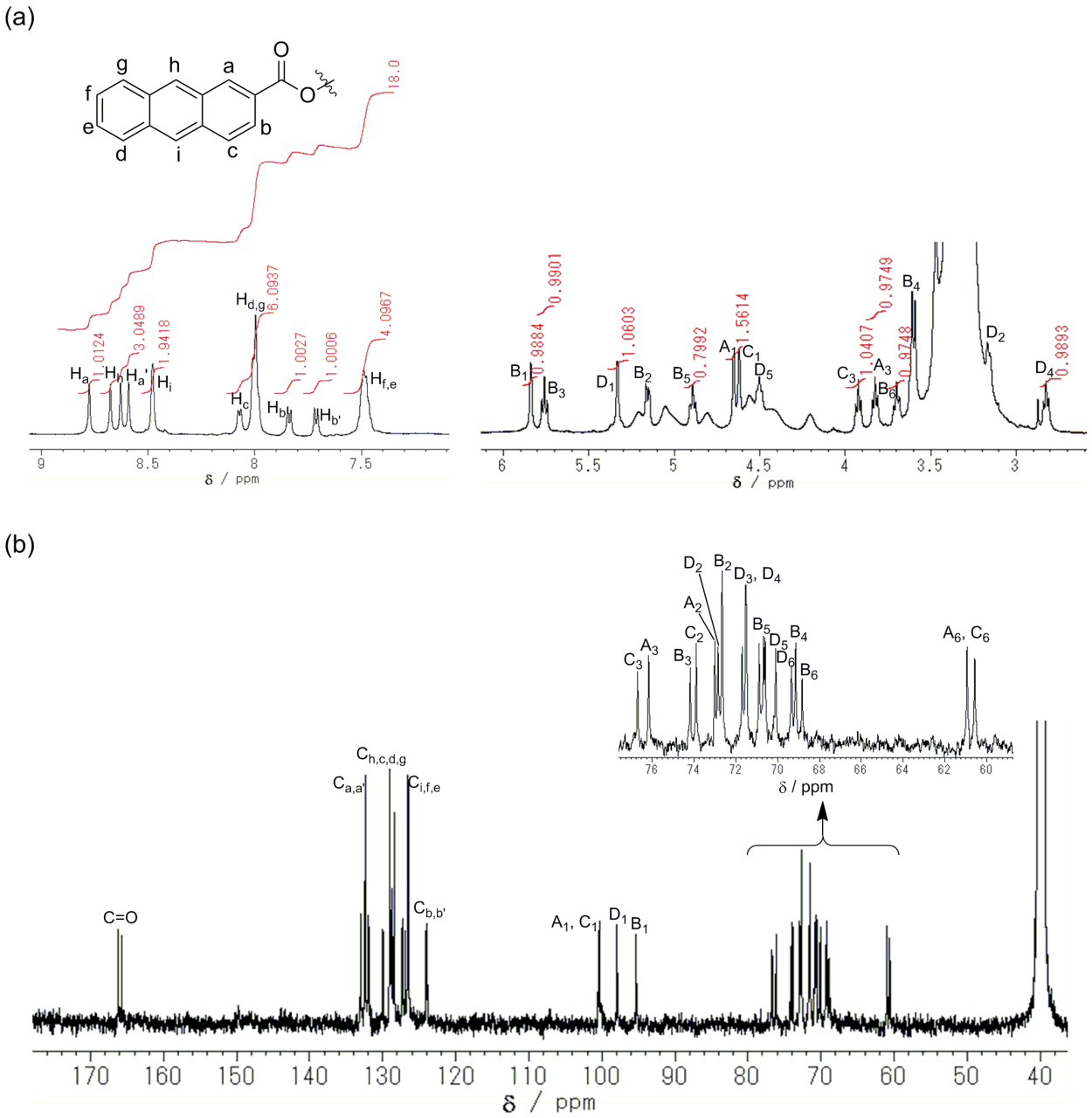

Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of **AC_2-CNN** in DMSO-d_6 at room temperature.

HSQC Spectra of AC_2-CNN

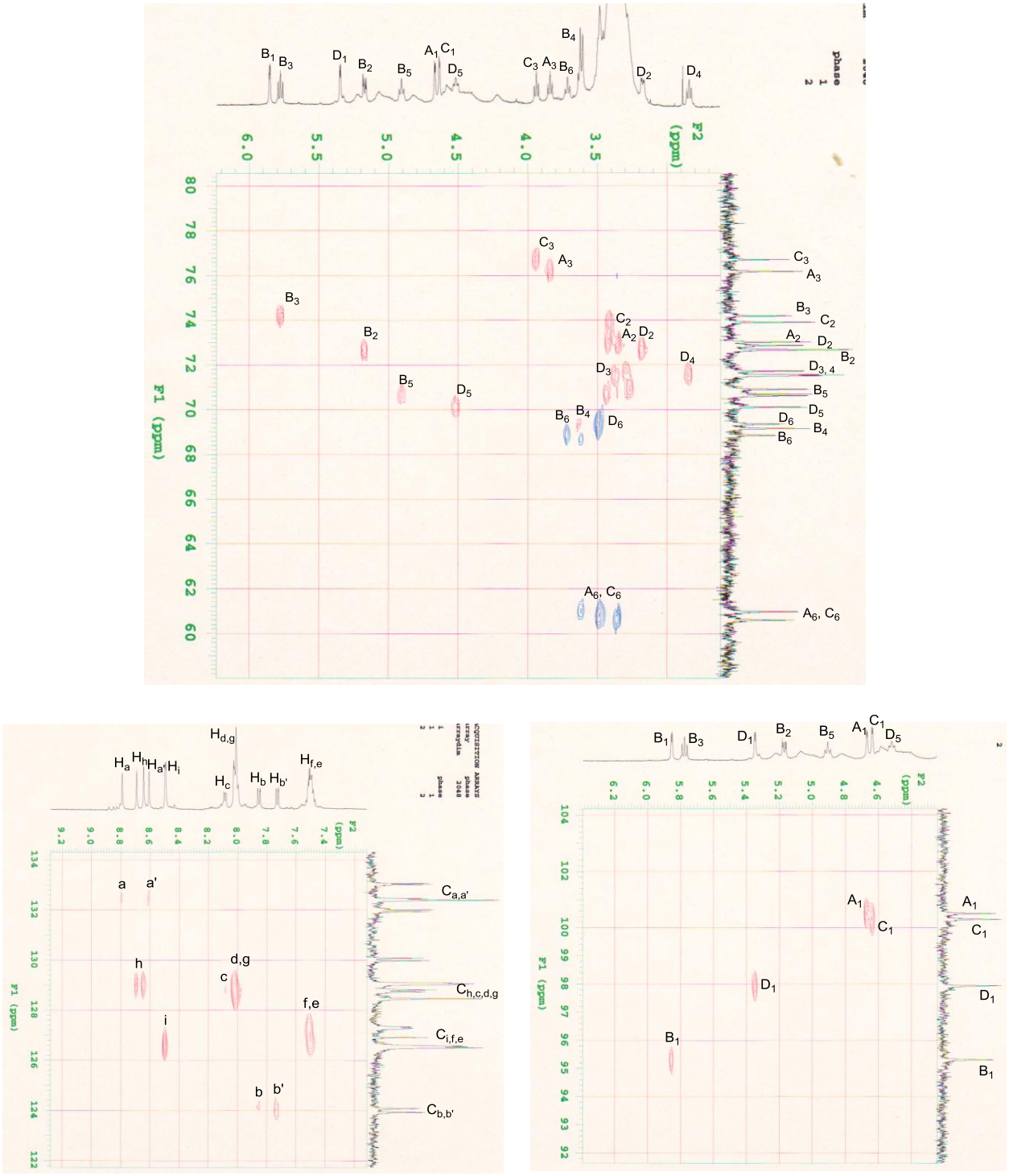

Figure S2. HSQC spectra of **AC_2-CNN** in DMSO-d_6 at room temperature.

COSY Spectra of AC_2-CNN

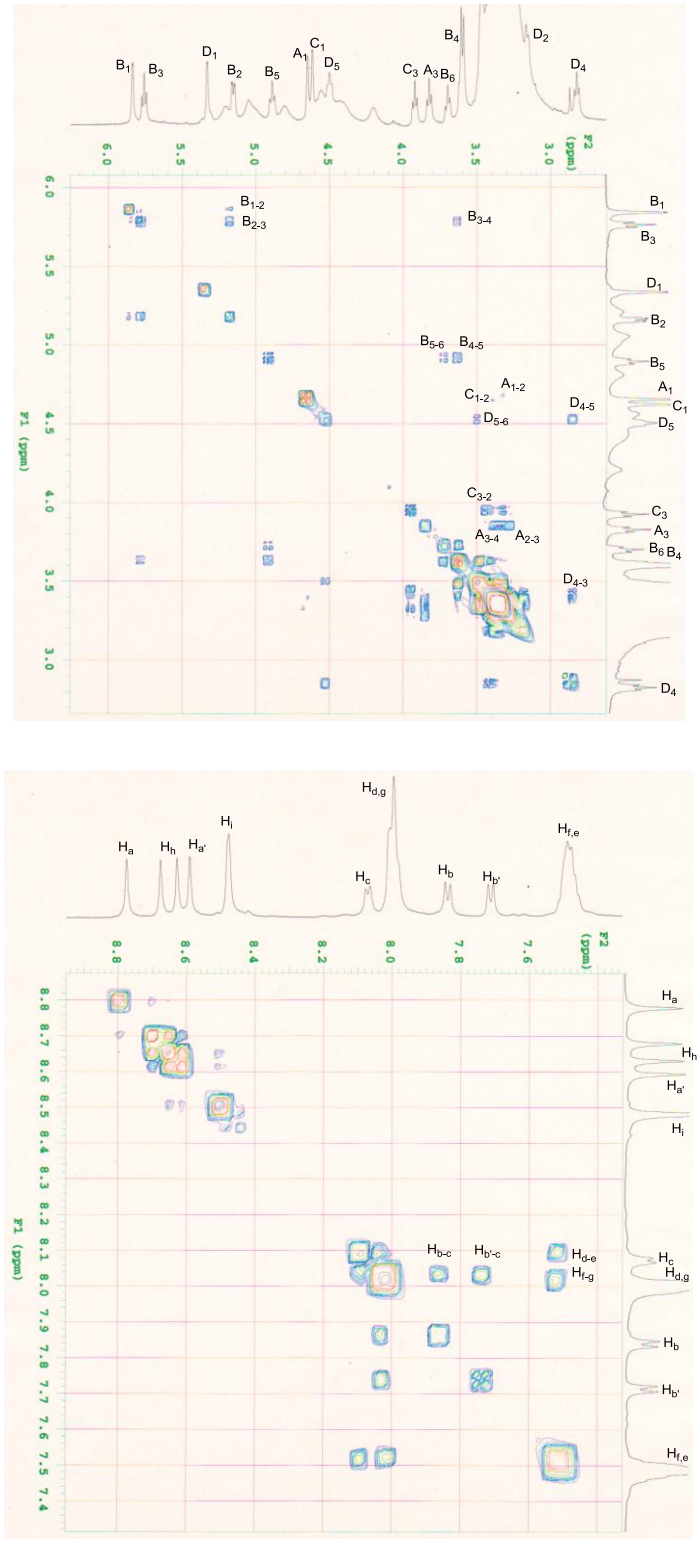

Figure S3. COSY spectra of **AC_2-CNN** in DMSO-d_6 at room temperature.

UV/vis and Excitation Spectra of AC_2-CNN

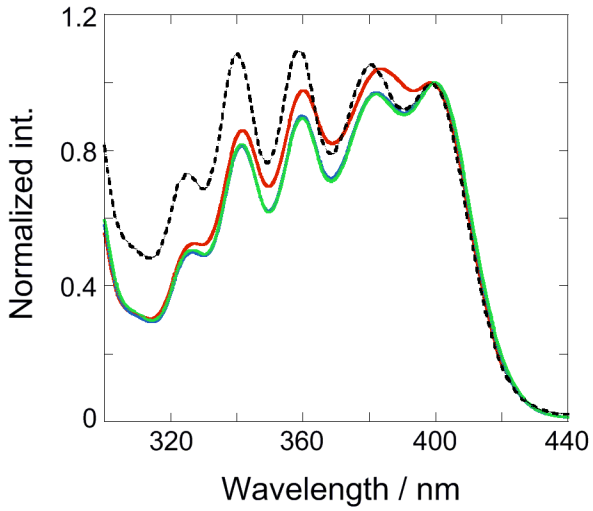

Figure S4. Normalized UV/vis (dotted black) and fluorescence excitation spectra (monitored at 450 nm (red), 500 nm (blue), and 525 nm (green)) of a CH_3CN-H_2O (45:55) solution of **AC_2-CNN** (25 μM).

Analytical Chiral HPLC

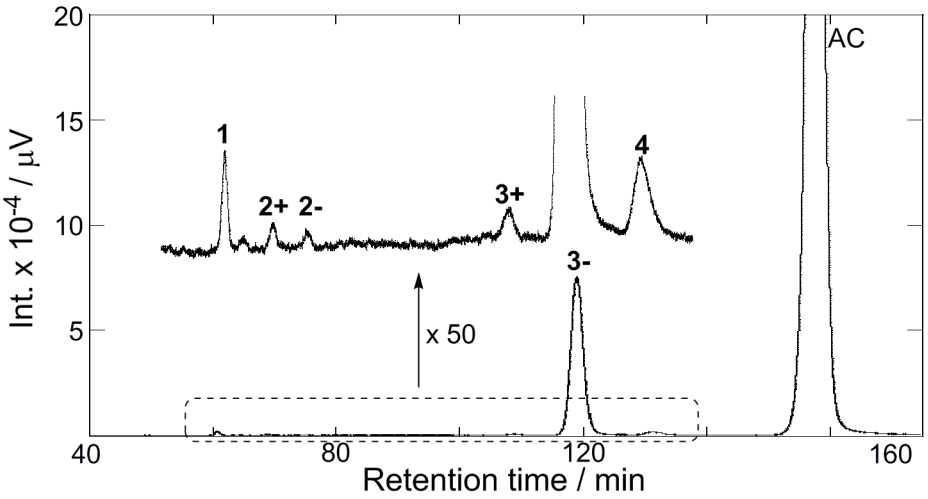

Figure S5. Analytical chiral HPLC chromatogram of the cyclodimers obtained by photoirradiation of **AC_2-CNN** (29 μM) in CH_3CN-H_2O (45:55) at 25 °C and the subsequent saponification.

In-in, *in-out*, *out-in*, and *out-out* Conformers of AC_2-CNN•H_2O

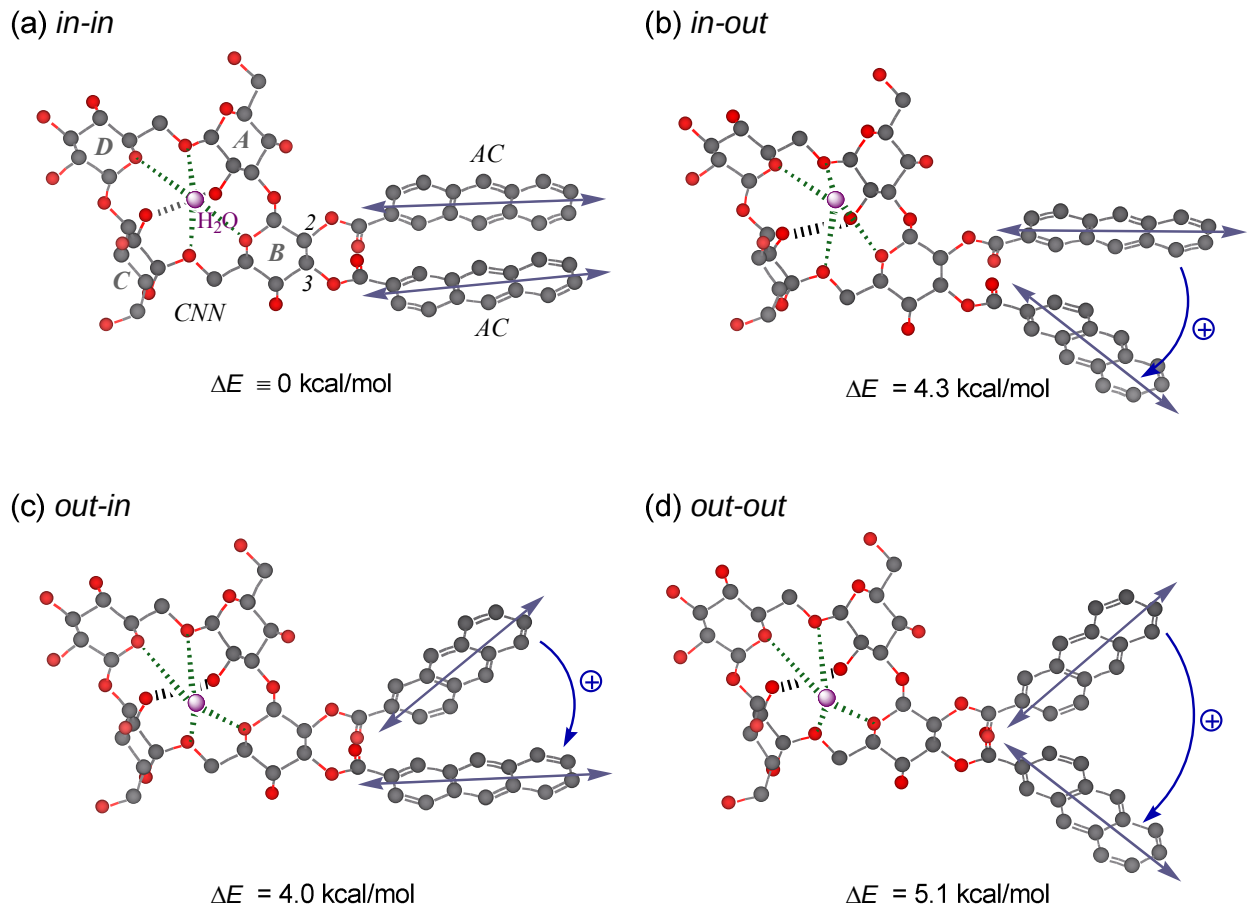

Figure S6. Schematic illustrations of representative *in-in*, *in-out*, *out-in*, and *out-out* conformers of **AC_2-CNN**•H_2O optimized by MM2 (no full structure search was made); hydrogens are omitted for clarity purpose.

Discussion. In the optimized structures a-d, the 2-OH of glucose residue C is hydrogen-bonded to the 2-OH of residue A (a black hashed broad line in the back) and the water molecule (shown as a shaded magenta sphere in the center of the CNN ring) forms four hydrogen bonds (hashed green wedges) bridging all of the A-D glucose residues of CNN (as was the case in the X-ray crystallographic structure; see refs 10 and 11 in the main text). These hydrogen-bonds jointly maintain the rigid saucer-shaped structure of CNN.

The double-headed arrow indicates the direction of transition moment of AC's ^1B_b band, while the curved arrow shows the right/left-handed helical arrangement of the two transition moments, leading respectively to the positive/negative exciton coupling in CD spectrum, according to the exciton chirality rule. Exciton coupling amplitude is known to critically depend on the angle and

distance of the coupling transitions (see ref. 12 in the main text) and hence the positive exciton couplet experimentally observed (Figure 1b) should reflect the weighted average of all the conformers, including many others that are not shown in Figure S6.

Fluorescence Decay Profiles of AC_2-CNN and Methyl 2-Anthracenecarboxylate 5

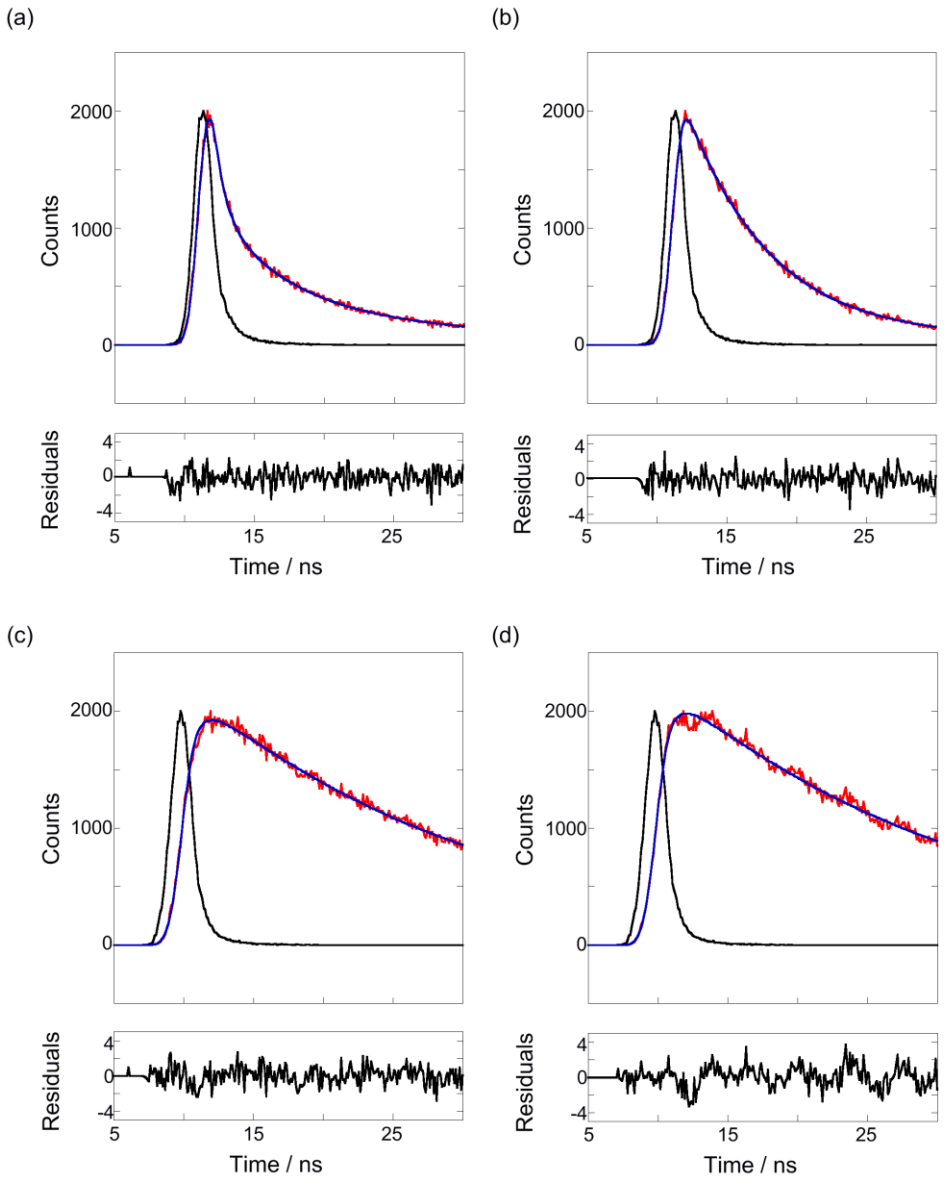

Figure S7. Time-resolved fluorescence decays of 31 μM **AC_2-CNN** (a, b) and of 25 μM **5** (c, d), both monitored at 450 nm (a, c) and 515 nm (b, d) in 45:55 CH_3CN-H_2O at room temperature; excitation at 300 nm; black (IRF), red (decay profile), blue (fitting result). The residuals correspond to the fit of the decay to a sum of three exponential functions for **AC_2-CNN** and to a single exponential function for **5**.