Supporting information


Jiecheng Ji, a Wanhua Wu,*, a Xueqin Wei, b Ming Rao, a Dayang Zhou, c Guo Cheng, a Qiyong Gong, a Kui Luo,*, a and Cheng Yang*, a

*a Huaxi MR Research Center (HMRRC), Department of Radiology, West China Hospital, Healthy Food Evaluation Research Center and College of Chemistry, Sichuan University, Chengdu 610041, China
b School of Pharmacy, Guangxi Medical University, Nanning 530021, China
c Comprehensive Analysis Center, ISIR, Osaka University, Mihogaoka, Ibaraki 5670047, Japan

E-mails: wuwanhua@scu.edu.cn; luo@scu.edu.cn; yangchengyc@scu.edu.cn

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1. General

Materials and Instruments

All reagents were commercially available and used without further purification. Doubly distilled water and HPLC-grade solvents were used for photoreactions and spectral measurements. NMR spectra were recorded on a Bruker AMX-400 at 400 MHz for $^1$H and 101 MHz for $^{13}$C, where the residual proton of solvent, TMS or DMF were used as the internal standard. MALDI-TOF HRMS spectra were obtained with a Waters-Q-TOF Premiers (ESI). UV-vis and circular dichroism spectra were recorded on JASCO V-650 and J-1500 spectrometer, respectively. The diastereoisomers of hosts were resolved by HPLC, using a column of 5C$_{18}$-PAQ eluted with a 67:33 (v/v) mixture of water and acetonitrile at 35 °C. Chiral HPLC analyses were performed on a Shimadzu UFLC system equipped with SPD-20A and RF-20A detectors, using a tandem column of Inertsil ODS-2 and Daicel Chiralcel OJ-R eluted with a 64:36:0.1 (v/v) mixture of water, acetonitrile, and trifluoroacetic acid at 35 °C.

Preparation of Sample Solutions

Borate buffer solutions (BBS) at pH = 9.0 were prepared by dissolving appropriate amounts of Na$_2$B$_4$O$_7$·10H$_2$O in distilled water ([buffer] = 25 mM, at 25 °C). Both UV-vis and circular dichroism spectra were measured in 1 cm cell unless stated otherwise. All photoreactions were carried out in a buffer solution under Ar irradiated with a 200-mW LED (365 nm).

Scheme S1. Representation for the $S_P$ and $R_P$ conformational interconversion of the enantiomeric P5 pair.
2. Synthesis and Characterization of Hosts

Compound 10, 14, 15, and 16 were prepared by the reported procedures.

Scheme S2. Synthetic routes for trimers.

Synthesis

10. An acetone solution (60.0 mL) containing hydroquinone (2.2 g, 20.0 mmol) and Na$_2$CO$_3$ (6.9 g, 49.9 mmol) was stirred at 25°C for 10 min, propargyl bromide (8.5 g, 71.2 mmol) was then added dropwise within 3 minutes. The reaction mixture was stirred and refluxed under nitrogen for an additional 16 hours. The reaction was monitored by TLC (petroleum ether: ethyl acetate = 3:1) to confirm the reaction was completed. Then, the reaction mixture was cooled down and filtered. The crude product was purified by column chromatography (petroleum ether: ethyl acetate = 3:1) to give 10 as faint yellow solid in 78.0% yield (2.9 g).$^1$H NMR (400 MHz, acetone-$_d_6$) δ: 6.98 (s, 4H), 4.74 (s, 4H), 3.04 (t, $J = 2.4$ Hz, 2H).$^{13}$C NMR (101 MHz, acetone-$_d_6$) δ: 205.50, 152.44, 116.20, 115.88, 115.52, 79.18, 75.93, 55.99.

11. Compound 10 (2.5 g, 13.4 mmol), 1,4-dimethoxybenzene (7.5 g, 54.1 mmol) and polyoxymethylene (4.8 g) was dissolved in 250 mL dichloroethane, the mixture was stirred at 25°C for 10 min, and then BF$_3$·Et$_2$O (8.5 g, 71.2 mmol) was added dropwise within 30 seconds. The reaction mixture was stirred at 25°C for an additional 16 minutes, then water (10.0 mL) was added to quench the reaction. The solvent was removed under reduced pressure, and then the residue was dissolved in dichloromethane, washed 3 times with water and dried over Na$_2$SO$_4$. The solvent was then removed under reduced pressure. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 10:1) to give 11 as white solid in 75.93, 55.99.
9.3% yield (1.0 g). ¹H NMR (400 MHz, CDCl₃) δ 6.83 (s, 2H), 6.81 (s, 2H), 6.80 (s, 2H), 6.78 (s, 2H), 6.75 (s, 2H), 4.49 (d, J = 2.4 Hz, 4H), 3.79 – 3.76 (m, 10H), 3.69 (d, J = 5.1 Hz, 12H), 3.65 (s, 12H), 2.08 (t, J = 2.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 150.65, 150.60, 150.54, 149.36, 129.10, 128.43, 128.34, 128.13, 127.89, 115.48, 114.05, 113.83, 113.75, 113.62, 78.99, 74.73, 56.37, 55.79, 55.70, 55.67, 55.58, 29.62, 29.54. MALDI-HRMS: m/z calcd. for [M]+: 798.3404, found: 798.3896.

12. A pyridine solution (200.0 mL) containing β-CD (20.0 g, 17.6 mmol) and tosyl chloride (24.0 g, 125.8 mmol) was stirred at 25°C for 6 hours, after the fully consumption of the raw materials monitored by TLC, a pyridine solution (2.0 L) was used to give pure 12 as white powder in 23.8% yield (5.4 g) after freeze drying. ¹H NMR (400 MHz, DMSO-d₆+D₂O (1:1, v/v)) δ 7.65 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 4.87 – 4.75 (m, 7H), 4.31 (d, J = 4.33 Hz, 1H), 4.22 – 4.17 (m, 1H), 3.70 – 3.16 (m, 40H), 2.38 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆+D₂O (1:1, v/v)) δ 146.28, 132.44, 130.21, 127.68, 101.98, 101.73, 100.91, 81.41, 81.06, 80.76, 80.61, 73.32, 72.90, 72.22, 71.98, 71.66, 71.53, 70.47, 69.48, 59.84, 21.43. ¹³C NMR (101 MHz, D₂O). MALDI-HRMS: m/z calcd. for [M+Na]+: 1311.3678, found: 1311.3816.

13. Compound 12 (3.0 g, 2.3 mmol) and NaN₃ (2.5 g, 38.4 mmol) was dissolved in a mixed solution of 30 mL DMF and 3.0 mL water, the mixture was stirred at 80°C for 5.5 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from water to 40% aqueous EtOH (2.0 L) was used to give pure 13 as white powder in 70.0% yield (1.87 g) after freeze-drying. ¹H NMR (400 MHz, D₂O) δ 4.99 (d, J = 3.1 Hz, 7H), 3.91 – 3.70 (m, 28H), 3.61 – 3.48 (m, 14H). ¹³C NMR (101 MHz, D₂O) δ 101.89, 101.68, 82.08, 81.13, 73.13, 72.88, 72.01, 71.87, 70.60, 60.21. MALDI-HRMS: m/z calcd. for [M+H]+: 1160.3835, found: 1160.3735.

15 and 16. Compound 14 (1.0 g, 0.7 mmol) and NaN₃ (0.8 g, 12.8 mmol) was dissolved in a mixed solution of 10.0 mL DMF and 1.0 mL water, the mixture was stirred at 80°C for 5.5 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from water to 15% aqueous EtOH (2.0 L) was used to give pure 15 (2A-N3) and 16 (3G-N3) after freeze-drying.

15 (2A-N3) (white powder, 89.0 mg, yield: 11.4%): ¹H NMR (400 MHz, D₂O) δ 5.10 (d, J = 4.0 Hz, 2H), 5.01 – 4.94 (m, 4H), 4.81 (d, J = 7.3 Hz, 1H), 4.28 – 4.24 (m, 1H), 3.98 – 3.63 (m, 31H), 3.61 – 3.50 (m, 10H). ¹³C NMR (101 MHz, D₂O) δ 101.93, 101.82, 101.14, 80.92, 80.67, 80.32, 78.78, 78.69, 75.93, 73.32, 73.14, 72.92, 72.59, 72.38, 72.08, 72.04, 71.84, 71.68, 71.63, 71.51, 71.08, 69.01, 63.61, 60.29, 60.04, 59.97, 59.44. MALDI-HRMS: m/z calcd. for [M+H]+: 1160.3835, found: 1160.3797.

16 (3G-N3) (white powder, 303.0 mg, yield: 38.8%): ¹H NMR (400 MHz, D₂O) δ 4.99 (d, J = 3.6 Hz, 7H), 3.91 – 3.76 (m, 28H), 3.65 – 3.41 (m, 14H). ¹³C NMR (101 MHz, D₂O) δ 101.78, 101.72, 101.54, 101.41, 100.68, 81.05, 80.77, 80.64, 77.98, 73.02, 72.44, 71.97, 71.78, 71.51, 71.37, 65.70, 60.21. MALDI-HRMS: m/z calcd. for [M+H]+: 1160.3835, found, 1160.3921. MALDI-HRMS: m/z calcd. for [M+H]+: 1160.3835, found: 1160.3921.

7 (6G-P5-6G). Compound 11 (73.0 mg, 97.7 µmol), 13 (244.0 mg, 210.5 µmol) and CuI (80.0 mg, 420.0 µmol) was dissolved in 5.0 mL DMF, the mixture heated to 50°C and was stirred under nitrogen for 16 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from 50% to 70% aqueous EtOH (2.0 L) was used to give pure 7 (6G-P5-6G) as white powder in 39.4% yield (120.0 mg)
after freeze-drying. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.17 (s, 2H), 7.01 (s, 2H), 6.79 – 6.72 (m, 8H), 5.87 – 5.71 (m, 7H), 5.07 – 4.97 (m, 4H), 4.84 – 4.82 (m, 10H), 4.65 – 4.55 (m, 4H), 4.00 – 3.95 (m, 2H), 3.68 – 3.55 (m, 80H), 3.37 – 3.33 (m, 30H), 3.21 – 3.12 (m, 2H), 2.97 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 162.91, 150.37, 149.68, 143.51, 143.51, 127.91, 127.83, 126.10, 113.66, 102.41, 81.90, 73.35, 72.70, 72.53, 60.26, 55.96, 55.84, 55.75, 31.25. MALDI-HRMS: m/z calcd. for [M+Na]$^+$: 3141.0855, found: 3141.0844.

8 (2A-P5-2A). Compound 11 (25.4 mg, 34.0 μmol), 15 (85.0, 73.3 μmol) and CuI (27.8 mg, 146.0 μmol) was dissolved in 1.5 mL DMF, the mixture heated to 50°C and was stirred under nitrogen for 16 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from 50% to 70% aqueous EtOH (2.0 L) was used to give pure 8 (2A-P5-2A) as white powder in 34.0 % yield (36.0 mg) after freeze-drying. $^1$H NMR (400 MHz, CDCl₃) δ 8.35 (d, $J = 7.8$ Hz, 2H), 7.01 (s, 2H), 6.82 – 6.74 (m, 7H), 6.57 (d, $J = 2.9$ Hz, 1H), 5.98 – 5.50 (m, 5H), 5.37 (s, 2H), 5.03 – 4.86 (m, 14H), 4.57 – 4.54 (d, $J = 5.8$ Hz, 4H), 4.18 (d, $J = 11.6$ Hz, 2H), 3.99 (s, 4H), 3.68 – 3.53 (m, 84H), 3.37 – 3.26 (d, $J = 9.8$ Hz, 20H), 3.10 – 3.09 (s, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 155.10, 132.69, 107.31, 87.00, 87.00, 78.11, 77.30, 65.10, 60.80. MALDI-HRMS: m/z calcd. for [M+Na]$^+$: 3141.0855, found: 3141.0888.

9 (3G-P5-3G). Compound 11 (73 mg, 97.7 μmol), 16 (400.0, 343.0 μmol) and CuI (80.0 mg, 420.0 μmol) was dissolved in 5.0 mL DMF, the mixture heated to 50°C and was stirred under nitrogen for 16 hours. After the reaction mixture was cooled, the solvent was removed in vacuo, and the crude product was purified by reverse-phase column chromatography, a gradient elution from 50% to 70% aqueous EtOH (2.0 L) was used to give pure 9 (3G-P5-3G) as white powder in 55.8 % yield (170.0 mg) after freeze-drying. $^1$H NMR (400 MHz, CDCl₃) $^1$H NMR (400 MHz, CDCl₃) δ 8.20 (d, $J = 8.5$ Hz, 2H), 7.00 (d, $J = 11.4$ Hz, 2H), 6.83 – 6.71 (m, 8H), 6.00 – 5.52 (m, 4H), 5.01 (s, 4H), 4.86 – 4.80 (m, 10H), 4.63 (s, 2H), 4.37 – 4.27 (m, 4H), 3.89 – 3.68 (m, 36H), 3.63 – 3.40 (m, 56H), 3.34 – 3.27 (m, 20H), 2.92 (d, $J = 9.6$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 155.10, 155.09, 154.54, 133.34, 132.83, 132.71, 131.41, 118.50, 107.15, 86.84, 78.06, 77.25, 65.06, 60.79, 60.70. MALDI-HRMS: m/z calcd. for [M+Na]$^+$: 3141.0855, found: 3141.0875.
3. NMR and HR-MS Spectra

**Figure S1.** $^1$H NMR spectrum of 10 (400 MHz, acetone-$d_6$).

**Figure S2.** $^{13}$C NMR spectrum of 10 (101 MHz, acetone-$d_6$).
Figure S3. $^1$H NMR spectrum of 11 (400 MHz, CDCl$_3$). The signal with the symbol * is due to trace amount of water.

Figure S4. $^{13}$C NMR spectrum of 11 (101 MHz, CDCl$_3$).
**Figure S5.** MALDI-HRMS spectrum of 11.

**Figure S6.** $^1$H NMR spectrum of 12 (400 MHz, DMSO-$d_6$: D$_2$O = 1:1, v/v).
**Figure S7.** $^{13}$C NMR spectrum of 12 (101 MHz, DMSO-$d_6$; D$_2$O = 1:1, v/v).

**Figure S8.** MALDI-HRMS spectrum of 12.
Figure S9. $^1$H NMR spectrum of 13 (400 MHz, D$_2$O).

Figure S10. $^{13}$C NMR spectrum of 13 (101 MHz, D$_2$O).
**Figure S11.** MALDI-HRMS spectrum of 13.

**Figure S12.** $^1$H NMR spectrum of 15 (400 MHz, D$_2$O).
Figure S13. $^{13}$C NMR spectrum of 15 (101 MHz, D$_2$O).

Figure S14. MALDI-HRMS spectrum of 15.
Figure S15. $^1$H NMR spectrum of 16 (400 MHz, D$_2$O).

Figure S16. $^{13}$C NMR spectrum of 16 (101 MHz, D$_2$O).
Figure S17. MALDI-HRMS spectrum of 16.

Figure S18 $^1$H NMR spectrum of 7 (400 MHz, DMSO-<sub>d6</sub>). *DMF.
Figure S19. $^{13}$C NMR spectrum of 7 (101 MHz, DMSO-$d_6$). *DMF

Figure S20. MALDI-HR-MS spectrum of 7.
Figure S21. $^1$H NMR spectrum of 8 (400 MHz, DMSO-$d_6$). *DMF.

Figure S22. $^{13}$C NMR spectrum of 8 (101 MHz, DMSO-$d_6$).
Figure S23. MALDI-HR-MS spectrum of 8.

Figure S24. $^1$H NMR spectrum of 9 (400 MHz, DMSO-$d_6$). *DMF.
**Figure S25.** $^{13}$C NMR spectrum of 9 (101 MHz, DMSO-$d_6$).

**Figure S26.** MALDI-HR-MS spectrum of 9.
Figure S27. $^1$H NMR spectra of $7S$ (dark red) and $7R$ (dark cyan) (400 MHz, DMSO-$d_6$: D$_2$O = 5:2, v/v) at room temperature.

Figure S28. $^1$H NMR spectra of $8S$ (dark red) and $8R$ (dark cyan) (400 MHz, D$_2$O) at room temperature.
Figure S29. $^1$H NMR spectra of 9s (dark blue) and 9r (dark cyan) (400 MHz, D$_2$O), and 9s in a mixed solvent (dark red, 400 MHz, DMSO-d$_6$: D$_2$O = 5:1, v/v) at room temperature.

4. Binding Behavior

Figure S30. a) UV-vis spectra of AC and 7r in different fractions (pH = 9.0, [buffer] = 25 mM) at 25 °C, where the total concentration ([AC] + [7r] = 0.1 mM) as kept constant at 0.1 mM. b) The Job plots of the absorbance changes at 386.5 nm).
Figure S31. a) UV-vis spectra of AC and 8R in different fractions (pH = 9.0, [buffer] = 25 mM) at 25 °C, where the total concentration ([AC] + [8R] = 0.1 mM) as kept constant at 0.1 mM. b) The Job plots of the absorbance changes at 386.5 nm).

Figure S32. a) UV-vis spectra of AC and 9R in different fractions (pH = 9.0, [buffer] = 25 mM) at 25 °C, where the total concentration ([AC] + [9R] = 0.1 mM) as kept constant at 0.1 mM. b) The Job plots of the absorbance changes at 368.5 nm).

Figure S33. MM2-optimized structures 2:2 complexes of AC with trimer CD host 7υ: (a) front view, (b) left view, (c) top view. Color code: white for hydrogen, grey for carbon, red for oxygen, blue for nitrogen, blue and white dotted line for hydrogen bond.
**Figure S34.** $^1$H NMR spectra (400 MHz, D$_2$O) of $9_R$ (2.0 mM), $9_R + AC$ ([AC] = 2[$9_R$] = 4.0 mM), AC (4.0 mM) in D$_2$O contain 10 mM NaOH.

**Figure S35.** $^1$H-$^1$H COSY NMR spectra of $9_R + AC$ ([AC] = 2[$9_R$] = 4.0 mM) in D$_2$O contain 10 mM NaOH (400 MHz, D$_2$O).
Figure S36. a) UV-vis spectra of AC (0.05 mM) with increasing the concentration of 9R in buffer (pH = 9.0, 25 mM) at 25 °C. b) A least-mean-squares fit of the absorption changes at 389 nm gave the 1:1 association constant ($K_1$) and the 1:2 association constant ($K_2$), $K_1 = 43200 \pm 3000$ M$^{-1}$, $K_2 = 520 \pm 40$ M$^{-1}$.

Figure S37. a) NMR spectra of 9R (0.05 mM) with increasing the concentration of AC in buffer ([NaOH] = 10 mM) at 25 °C. b) A least-mean-squares fit of the peak changes at 7.83 ppm (Ha) gave the 1:1 association constant ($K_1$) and the 1:2 association constant ($K_2$), $K_1 = 46000 \pm 2800$ M$^{-1}$, $K_2 = 480 \pm 50$ M$^{-1}$.
Figure S38. MM2-optimized structures 1:2 complexes of AC with trimer CD host 9₉. (a) front view, (b) left view, (c) top view. Color code: white for hydrogen, grey for carbon, red for oxygen, blue for nitrogen, blue and white dotted line for hydrogen bond.
5. Photoreaction Studies

![Graphs](image)

**Figure S39.** (a) UV-vis spectral changes upon photolysis (irradiation by 200 mW LED at 365 nm) of AC (0.1 mM) in buffer (pH = 9.0) at 25 °C. (b) Absorbance changes at 386.5 nm upon photolysis of AC. (c) Second-order kinetics plot, affording $k_2 = 290.2 \pm 17.1$ M$^{-1}$ s$^{-1}$. Thus, if [AC] = 0.1 mM, then $k_2[AC] = 0.029$ s$^{-1}$. (d) UV-vis spectral change upon photolysis (irradiation by 200 mW LED at 365 nm) of AC (0.1 mM) in the presence of 0.2 mM 9R in buffer (pH = 9.0) at 25 °C. (e) Absorbance changes at 388 nm upon photolysis of AC in the presence of 9R. (f) First-order kinetics plot, affording $k_1 = 0.0115 \pm 0.00007$ s$^{-1}$. The real acceleration as 14-fold by 9R when concentration of AC is 0.1 mM.
Table S1. Supramolecular Photocyclodimerization of 2-Anthracenecarboxylate (AC) Mediated by Native and Chiral Hosts in Borate Buffer (pH 9.0) at Different Temperature

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</table>

a [AC] = 0.1 mM, pH = 9.0; irradiated at 365 nm for 30 min with a 200-mW LED, unless stated otherwise.

b Determined by HPLC. c Nonclassical cyclodimer content: [(5 + 6)/(1 + 2 + 3 + 4 + 5 + 6)] × 100. d Not determined due to the extremely low yield (<0.1%) or affected by high and broad peak of AC.

Figure S40. Circular dichroism (top) and UV (bottom) spectra of 9S, 9R in presence and absence of AC in buffer ([buffer] = 25 mM, [host] = 0.2 mM = 2[AC], pH = 9.0) at different conditions. a) 0.5 °C. b) Containing CsCl (6 M) at 0.5 °C. All measured in 2 mm cell.

Figure S41. a) Fluorescence spectra of AC (0.02 mM) with increasing the concentration of 9R in buffer ([CsCl] = 500 mM) at 25 °C. b) A least-mean-squares fit of the peak changes at 425.5 nm gave the 1:1 association constant (K1) and the 1:2 association constant (K2), K1 = 75000 ± 14000 M⁻¹, K2 = 1100 ± 200 M⁻¹.
6. Reference

