Electronic Supplementary Information

Supramolecular photocyclodimerization of 2-hydroxyanthracene with chiral hydrogen-bonding template, cyclodextrin and serum albumin

Gaku Fukuhara, a Hiroaki Umehara, a Saki Higashino, a Masaki Nishijima, b Cheng Yang, a,c Tadashi Mori, a Takehiko Wada d and Yoshiisa Inoue a

a Department of Applied Chemistry and b Office for University-Industry Collaboration, Osaka University, 2-1 Yamada-oaka, Suita 565-0871, Japan
c College of Chemistry, Sichuan University, Chengdu 610064, P. R. China
d Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
E-mail: inoue@chem.eng.osaka-u.ac.jp

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UV-vis spectral changes of 2-hydroxyanthracene (HA) upon photoirradiation

Fig. S1 UV-vis spectral changes of a dichloromethane solution of HA (1.48 mM) upon photoirradiation at >320 nm for up to 6 h at 25 °C, measured in a 1 mm cell.

Preparative HPLC of the photolyzate of HA

Fig. S2 Preparative HPLC chart of the HA photolyzate (obtained in the preparative photoirradiation shown in Fig. S1) on a Sumipax ODS JP column (Sumika, 6 μm, 2 φ x 25 cm) at room temperature eluted with water/acetonitrile/TFA (54/46/0.1) at a flow rate of 5 mL min⁻¹, monitored by a UV detector at 254 nm.
Chiral HPLC analyses of fractions 1-4

Fig. S3 Chiral HPLC analyses of fractions (a) f1, (b) f2, (c) f3 and (d) f4 (separated by preparative HPLC (Fig. S2)) on a tandem column of Cosmosil 5C18-AR-II (Nakalai) and Chiralcel OJ-RH (Daicel) at 35 °C eluted with a 54:46 (v/v) mixture of deionized water and acetonitrile containing 0.1% trifluoroacetic acid at a rate of 0.5 mL min⁻¹, monitored by a CD detector at 230 nm (top) and a fluorescence detector at 434 nm (λ_ex 254 nm) (bottom).
HR-MS and NMR spectra and characterization of HA cyclodimers 1-4

Fig. S4 (a) $^1$H (600 MHz) and (b) $^{13}$C (150 MHz) NMR spectra of cyclodimer 1 (fraction 1) in acetone-$d_6$. 
Fig. S5 (a) COSY and (b) $^1$H NMR (top) and difference NOE (bottom) spectra of cyclodimer 1 (fraction 1) in acetone-$d_6$ at 600 MHz.
Fig. S6 HSQC spectrum of cyclodimer 1 (fraction 1) in acetone-$d_6$ at 600 MHz.
**Fig. S7** NOESY spectrum of cyclodimer 1 (fraction 1) at 600 MHz in acetone-$d_6$ at room temperature.

**Cyclodimer 1**

HR-MS (FAB): $m/z$ 386.1293 ([M – 2H]$^+$) (calcd. for C$_{28}$H$_{18}$O$_2$: 386.1301).

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.94 (m, 2H, H5), 6.92 (m, 2H, H8), 6.77 (m, 4H, H6,7), 6.72 (d, 2H, $J = 7.9$ Hz, H4), 6.48 (d, 2H, $J = 2.4$ Hz, H1), 6.21 (dd, 2H, $J = 7.9, 2.4$ Hz, H3), 4.53 (d, 2H, $J = 11.1$ Hz, H10), 4.50 (d, 2H, $J = 11.1$ Hz, H9).

$^{13}$C NMR (150 MHz, acetone-$d_6$) $\delta$ C 155.7, 146.5, 145.4, 145.2, 135.8 (C2, C4a, C8a, C9a, C10), 128.5 (C4), 127.7 (C5), 127.7 (C8), 125.9, 125.9 (C6, C7), 115.2 (C1), 112.1 (C3), 54.6 (C9), 53.5 (C10).

**Characterization of cyclodimers 2-4**

Since the quantities of fractions 2-4 (cyclodimers 2-4) obtained by the preparative HPLC (Fig. S2) were not enough for $^{13}$C NMR, the characterization was made by comparing their $^1$H NMR spectra (Figs. S9-11) with that of cyclodimer 1. Also, the whole photolyzate containing all cyclodimers was subjected to HR-MS analysis to show the M-2 and M/2 peaks of the cyclodimers as shown in Fig. S8.

HR-MS (EI): $m/z$ 386.1314 ([M – 2H]$^+$) (calcd. for C$_{28}$H$_{18}$O$_2$: 386.1301).
Fig. S8 Mass spectrum (EI) of the photolyzate of HA, displaying the M-2 peak at m/z 386 and the M/2 peak at m/z 194.
Fig. S9 $^1$H NMR spectrum of cyclodimer 2 (fraction 2) in acetone-$d_6$ at 600 MHz.

Cyclodimer 2

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$H 6.95 (m, 2H, H5), 6.92 (m, 2H, H8), 6.77 (m, 2H, H6,7), 6.72 (d, 2H, $J = 7.9$ Hz, H4), 6.48 (d, 2H, $J = 2.3$ Hz, H1), 6.22 (dd, 2H, $J = 7.9, 2.3$ Hz, H3), 4.52 (s, 2H, H10), 4.51 (s, 2H, H9).
**Fig. S10** $^1$H NMR spectrum of cyclodimer 3 (fraction 3) in acetone-$d_6$ at 600 MHz.

### Cyclodimer 3

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta_H$ 6.89 (m, 4H, H5,8), 6.77 (d, 2H, $J = 7.9$ Hz, H4), 6.73 (m, 4H, H6,7), 6.51 (d, 2H, $J = 2.4$ Hz, H1), 6.26 (dd, 2H, $J = 7.9$, 2.4 Hz, H3), 4.53 (d, 2H, $J = 11.1$ Hz, H10), 4.50 (d, 2H, $J = 11.1$ Hz, H9).
Fig. S11 $^1$H NMR spectrum of cyclodimer 4 (fraction 4) in acetone-$d_6$ at 600 MHz.

Cyclodimer 4

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$H 6.90 (m, 4H, H5,8), 6.74 (d, 2H, $J = 7.9$ Hz, H4), 6.73 (m, 2H, H6,7), 6.53 (d, 2H, $J = 2.3$ Hz, H1), 6.22 (dd, 2H, $J = 7.9$, 2.3 Hz, H3), 4.52 (s, 2H, H10), 4.51 (s, 2H, H9).