## **SUPPLEMENTARY INFORMATION**

# Carbohydrate Recognition and Photodegradation by an Anthracene-Kemp's Acid Hybrid

Miyuki Nishibu, Daisuke Takahashi, and Kazunobu Toshima\*

Department of Applied Chemistry, Faculty of Science and Technology,

Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522 (Japan)

Fax: (+81)45-566-1576,

E-mail: toshima@applc.keio.ac.jp

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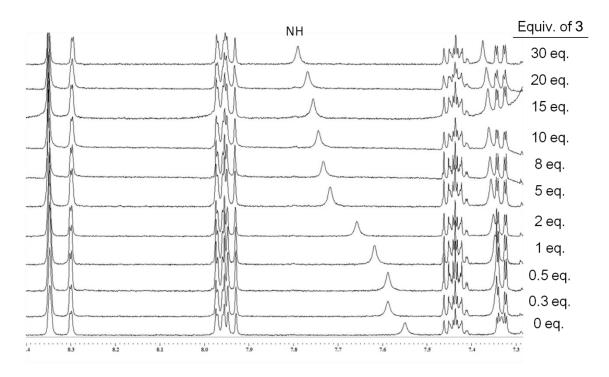
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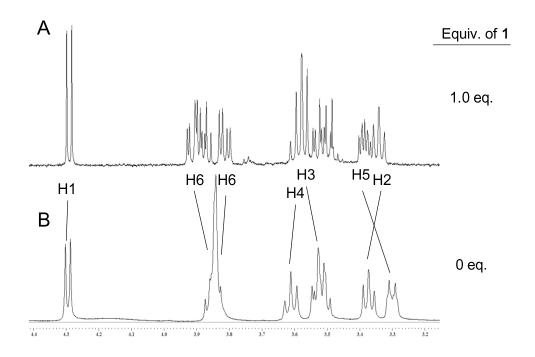
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# <sup>1</sup>H-NMR binding assay.

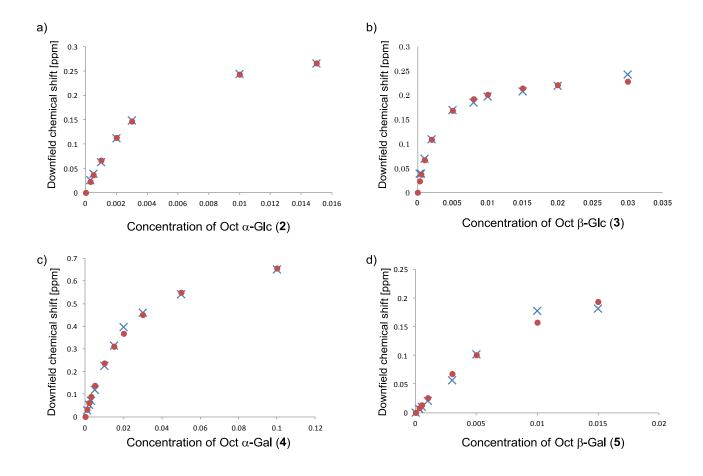
All <sup>1</sup>H-NMR measurements were performed on a JEOL ECA-500. The sample temperature was regulated at 298 K. For <sup>1</sup>H-NMR binding assay, a 2 mM solution of anthracene-Kemp's acid hybrid **1** in CDCl<sub>3</sub> (solution A) and 100 mM solution of each substrate in CDCl<sub>3</sub> (solution B) were prepared. And then, solution B was titrated into a solution A in order to make mixtures with a constant concentration of the hybrid and a range of concentration of each substrate (0.3 - 30 eq.). In general, ten different concentrations were made.  $\Delta\delta_{obs}$  was plotted against the concentration of a substrate, where  $\Delta\delta_{obs}$  is the difference between the observed <sup>1</sup>H-NMR chemical shift of the imide NH proton of **1** and the <sup>1</sup>H-NMR chemical shift of the free imide NH proton of **1**. The titration data were analyzed by nonlinear least-square method using Microsoft Excel 2010 software. <sup>1,2</sup>

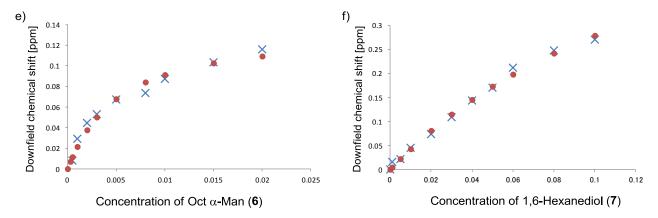


**Figure S1** Partial <sup>1</sup>H-NMR spectra (500 MHz, CDCl<sub>3</sub>, 298 K) of receptor **1** (1.0 mM) after addition of (from bottom to top) 0.0-30.0 equiv. of **3**.



**Figure S2** Partial <sup>1</sup>H-NMR spectra (500 MHz, CDCl<sub>3</sub>, 298 K) of **3** (B) and upon addition of 1 mM of **1** (A).





**Figure S3** Plot of the observed ( $\times$ ) and calculated ( $\bullet$ ) downfield chemical shifts of the imide NH signal of **1** as a function of added each monosaccharide in CDCl<sub>3</sub> at 500 MHz and T=298 K. (a) Oct α-Glc (**2**), (b) Oct β-Glc (**3**), (c) Oct α-Gal (**4**), (d) Oct β-Gal (**5**), (e) Oct α-Man (**6**), and (f) 1,6-Hexanediol (**7**).

## Photodegradation of $\beta$ -CD by anthracene derivative 8.

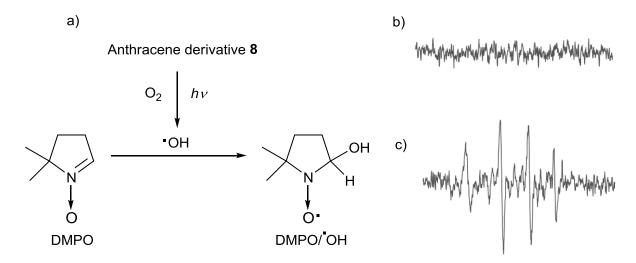
β-CD (30 μM) was incubated with an anthracene derivative **8** (0, 90 or 300 μM) in 1% DMSO/MeCN-H<sub>2</sub>O (9:1) at 25 °C for 2 h under irradiation with a UV lamp (365 nm, 100 W, Black-ray (B-100A), UVP Inc.,) placed 10 cm from the vessels, and analyzed by HPLC (TSK-GEL, Amide-80, 4.6×150 mm; 40 °C; detection by RI).

#### Photodegradation of monosaccharides 3 and 4 by anthracene-Kemp's acid hybrid 1.

Each monosacchaide (1.0 mM) was incubated with anthracene-Kemp's acid hybrid **1** (1.0 mM) in 1% DMSO/MeCN at 25 °C for 2 h under photo-irradiation (365 nm, 100 W) placed 10 cm from the mixture) and the mixture was dried *in vacuo*. The residue was acetylated using Ac<sub>2</sub>O in pyridine at 40 °C for 13 h, and then concentrated. The resulting residue was subjected to silica gel column chromatography and analyzed by HPLC (Mightysil RP-18 GP 5 mM, 4.6×150 mm; 40 °C; detection by UV (215 nm); 35:65 MeCN/H<sub>2</sub>O; flow rate 1.0 mL min<sup>-1</sup>).

## EPR spectrometry.

EPR experiments were carried out with a E-500 CW/EPR (Bruker) and recorded under the following conditions: microwave frequency 9.39 GHz, microwave power 16 mW, field modulation 0.1 mT at 100 kHz. DMPO was used as a spin-trapping agent. Anthracene derivative **8** (100 μM) and DMPO (500 mM) were incubated in 20% MeCN/H<sub>2</sub>O under irradiation with a UV lamp (365 nm, 100 W) placed 40 cm from a flat cell for 40 min.



**Figure S4** EPR spectra obtained during photo-irradiation of **8** in the presence of DMPO. **8** (100 μM) was incubated with DMPO (500 mM) in 20% MeCN/H<sub>2</sub>O under irradiation with a UV lamp (365 nm, 100 W) placed 40 cm from a flat cell for 40 min. a) Formation of DMPO/•OH from DMPO by reaction of photo-excited **8** and O<sub>2</sub>. b) Before irradiation; c) after 40 min irradiation.

#### References.

- B. Askew, P. Ballester, C. Buhr, K. S. Jeong, S. Jones, K. Parris, K. Williams and J. Rebek Jr., J. Am. Chem. Soc., 1989, 111, 1082; K. Williams, B. Askew, P. Ballester, C. Buhr, K. D. Jeong, S. Jones and J. Rebek Jr., J. Am. Chem. Soc., 1989, 111, 1090.
- 2 N. Hayashi, T. Ujihara and K. Kohata, *Biosci. Biotechnol. Biochem.*, 2004, **68**, 2512; K. Hirose, *J. Incl. Phenom. Macro.*, 2001, **39**, 193.