β-cyclodextrin's Orientation onto TiO_2 and Its Paradoxical Role in Guest's Photodegradation

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Experimental Section

Chemicals: Hombikat UV-100 is the TiO_2 used in this work, which has a 100% anatase phase, 8 nm diameter and 249 m^2/g BET specific surface area. Bisphenol A (97+%), bisphenol F (98%) and bisphenol AF (98%) were purchased from Alfa-Aesar and bisphenol E (99%) was obtained from Sigma-Aldrich. 2-O-methyl-β-CD (degree of substitution is 3.7) was a commercial product of the Shandong Binzhou Zhiyuan Bio-Technology Co. Ltd. (Jinan, China). β-Cyclodextrin and Heptakis(2,6-di-O-methyl)-β-cyclodextrin (2,6-di-O-methyl-β-CD, degree of substitution is 14) were obtained from Aladdin-reagent Corporation (Shanghai, China). All the chemicals were used as received.

Inclusion constants determination: The steady-state fluorescence spectra were recorded on a Hitachi FL-4500 fluorimeter at 20±1 ºC. The samples for the fluorescence measurements were placed in 10 mm×10 mm quartz cells. All samples were excited at 260 nm, and the fluorescence spectra were recorded between 290 nm and 400 nm. The fluorescence spectra were corrected for the baseline spectrum, which was a solution containing all compounds except guest. This procedure ensured that artifacts, such as Raman emission of the solvent, were subtracted from the fluorescence spectra. The bandpass for the excitation and emission monochromator was 5 nm.

After the 1:1 inclusion complex mode of bisphenols with cyclodextrins was confirmed by the

analysis of experimental data with Benesi-Hildebrand equation, the inclusion constants for the bisphenols with cyclodextrins (K_s, M^{-1}) were recovered from a nonlinear fit of the experimental data to Eq. (1).

$$F - F_0 = \frac{\kappa K_s[\mathrm{CD}]}{1 + K_s[\mathrm{CD}]} \quad (1)$$

where F and F_0 represent the fluorescence intensity at 305 nm in the presence and absence of cyclodextrins, respectively. κ is a constant.

Adsorption experiment: The adsorption studies were performed in the dark using aqueous suspensions containing 5–80 μM of cyclodextrins and 1.0 g L^{-1} of TiO_2 in continuously stirred 50 ml glass vessels for 12 h. The concentration of cyclodextrin was determined from the total organic carbon (TOC) data, which were recorded on an Anlytik Jena AG Multi N/C 2100 TOC/TN instrument. The effect of β-CD on the adsorption of bisphenols (BPA, BPE, BPF and BPAF) was performed in the same way. Langmuir isotherms were used to quantify the adsorption of cyclodextrins on the TiO_2 surface. K_L and q_{max} were determined from a nonlinear regression fit of the Langmuir equation (Eq. (2)):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e (μmol g^{-1}) is the amount of solute adsorbed per gram of TiO_2, K_L (M^{-1}) is the Langmuir equilibrium constant, q_{max} is the maximum adsorption capacity of the solute on the TiO_2 surface and C_e (μM) is equilibrium concentration of solute.

Photodegradation experiment: The photodegradation of bisphenols was performed in a self-made reactor.[1] The Philips Master Color lamp (CDM-T 150W/942) was used as the irradiation source, the

emission spectrum of the light was shown in Figure S5. The concentrations of bisphenols were determined using the HPLC method. The experiments were performed using a Waters 484 HPLC with an Agilent Zorbax SB-C18 column (5 μm, 4.6×150 mm). The mobile phase was a methanol aqueous solution (70/30, v/v) with a flow rate of 1.0 ml min^{-1}. The UV detection wavelength was set at 280 nm.

The observed pseudo-first order kinetic rate constant for the photocatalysis degradation was obtained from the linear fit of the experimental data to Eq. (3).

$$\ln(C_0 / C_t) = k_{obs} \times t + b \quad (3)$$

where C_0 represents the initial concentration of bisphenols and C_t represents the concentration of bisphenols at a different reaction time. k_{obs} (min^{-1}) represents the pseudo-first order reaction rate constant in the presence of cyclodextrins and k_{obs_0} was the degradation kinetic constant that was obtained in the absence of cyclodextrin.

As a control experiment, the degradation of bisphenols without TiO_2 was also investigated and the results were shown in Figure. S6. As all the bisphenols and β-CD have no absorption to the light with the wavelength longer than 300 nm, no photodegradation of bisphenols by β-CD occurred in the absence of TiO_2.

Preparation of the β-CD/bisphenol complex: β-CD/bisphenol complex was synthesized according to the method described in the previous work.[2] Typically, β-CD (0.4 mmol) and bisphenols (0.4 mmol) were dissolved in a little boiling water to make a supersaturated solution. And then, the solutions were slowly cooled to room temperature. The generated precipitates were filtered to obtain the transparent crystal suitable for the 2D ROESY experiments.

1. X. Zhang, F. Wu and N. Deng, *J. Hazard. Mater.*, 2011, **185**, 117-123.
2. Z.X. Yang, Y. Chen and Y. Liu, *Carbohyd. Res.*, 2008, **343**, 2439-2442.

Table S1. Complex stability constant K_s (M^{-1}) for bisphenols with β-CD and its derivatives in aqueous solutions at 25ºC.

Guests	lgK_s / lg M^{-1}		
	β-CD	2-O-methyl-β-CD	2,6-di-O-methyl-β-CD
BPA	4.9±0.3	4.7±0.1	4.8±0.4
BPE	4.6±0.4	4.4±0.2	4.6±0.1
BPF	4.2±0.2	4.0±0.4	4.4±0.2
BPAF	4.4±0.3	4.4±0.7	4.7±0.3

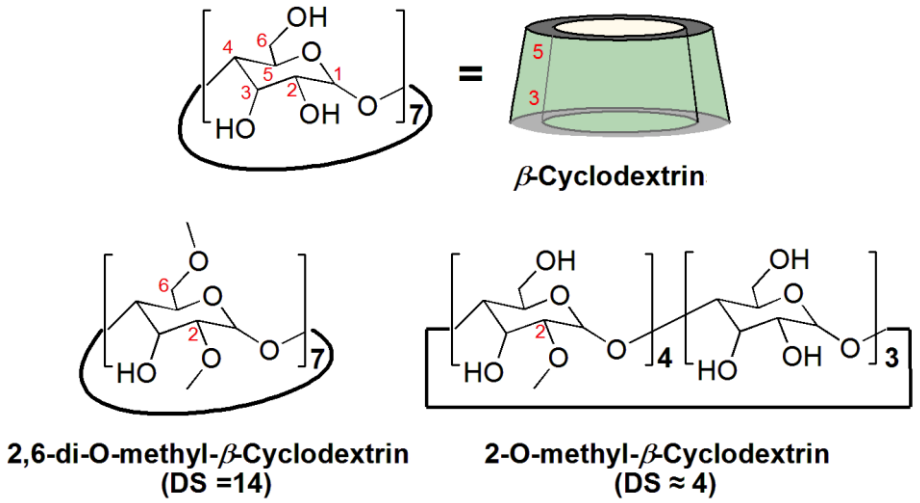

Figure S1 Chemical structures of β-CD, 2-O-methyl-β-CD and 2,6-di-O-methyl-β-CD (DS stands for the degree of substitution).

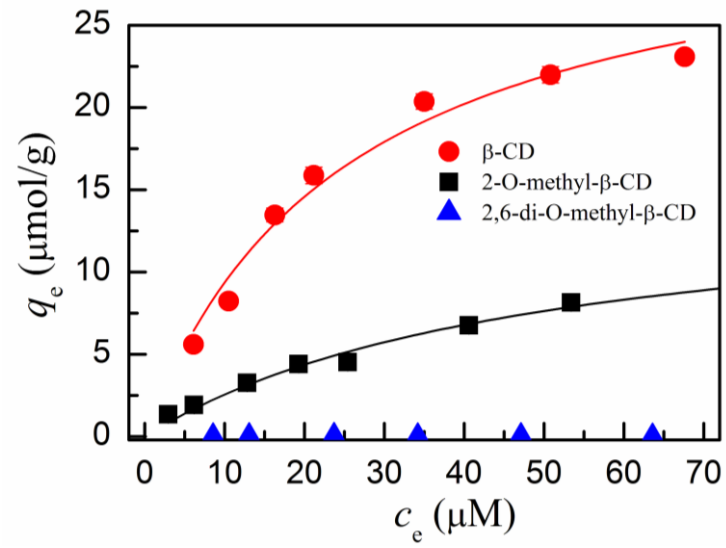

Figure S2. Adsorption of β-CD and its derivatives onto TiO_2 at 25ºC, the lines represent the fit of experimental data to Langmuir isotherm equation.

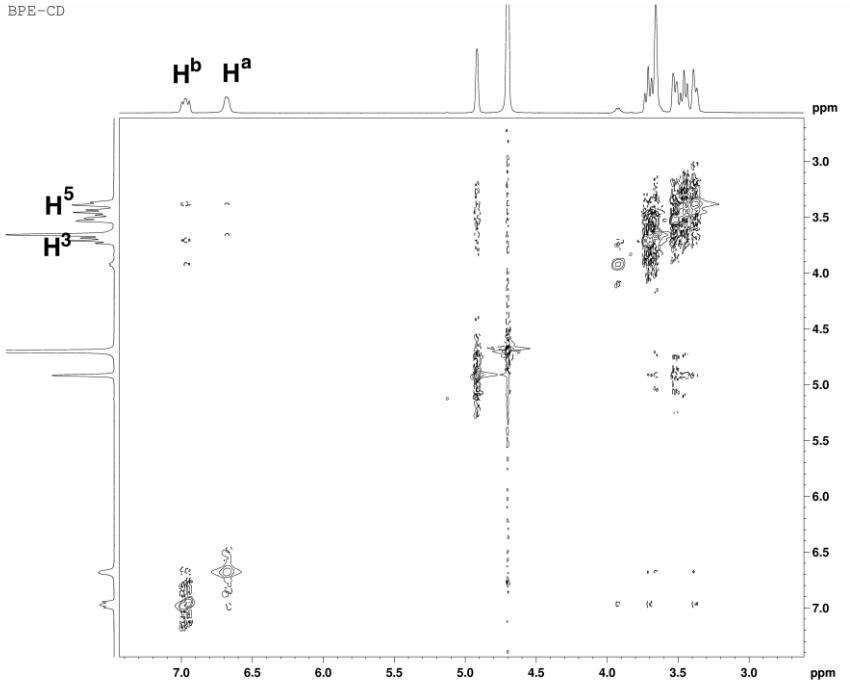

Figure S3. ^{1}H ROESY spectrum of the β-CD/BPE complex saturated in D_2O at 25 ºC.

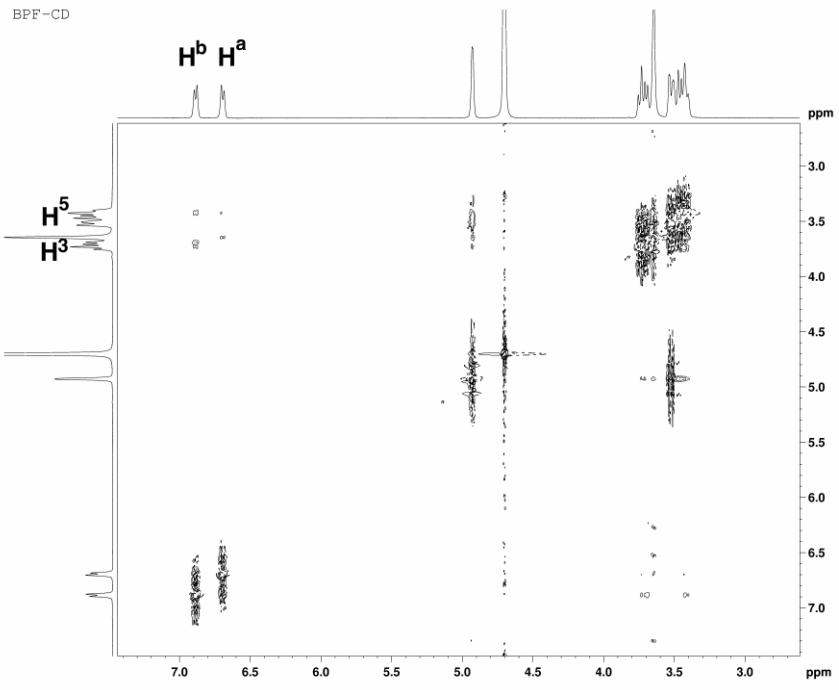

Figure S4. ^{1}H ROESY spectrum of the β-CD/BPF complex saturated in D_2O at 25 ºC.

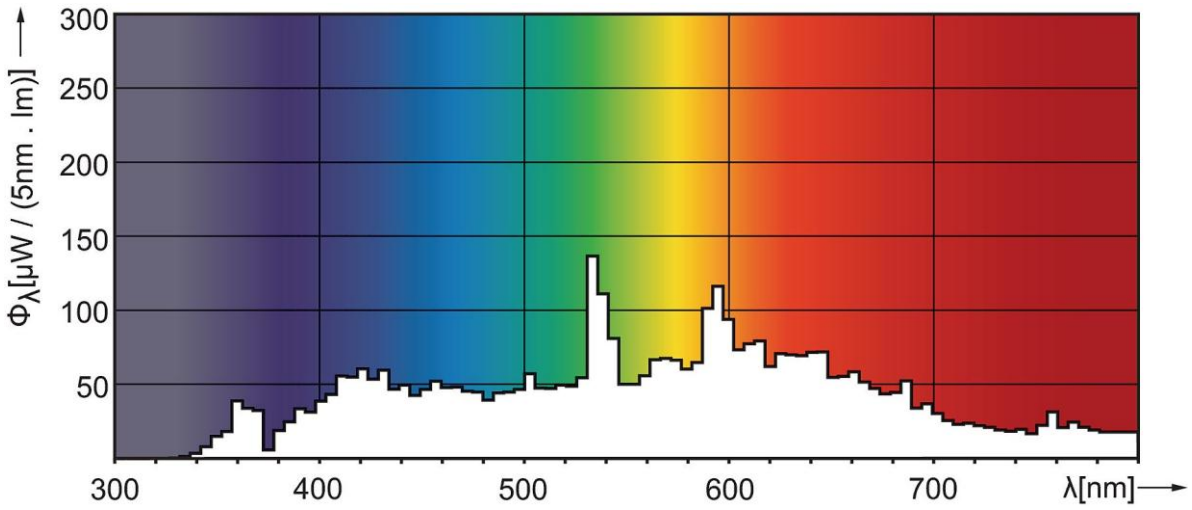

Figure S5. The emission spectrum of the Philips Master Color lamp (CDM-T 150W/942) (http://www.ecat.lighting.philips.com/l/lamps/compact-high-intensity-discharge/mastercolour-cdm/mastercolour-cdm-t/928084605175_eu/).

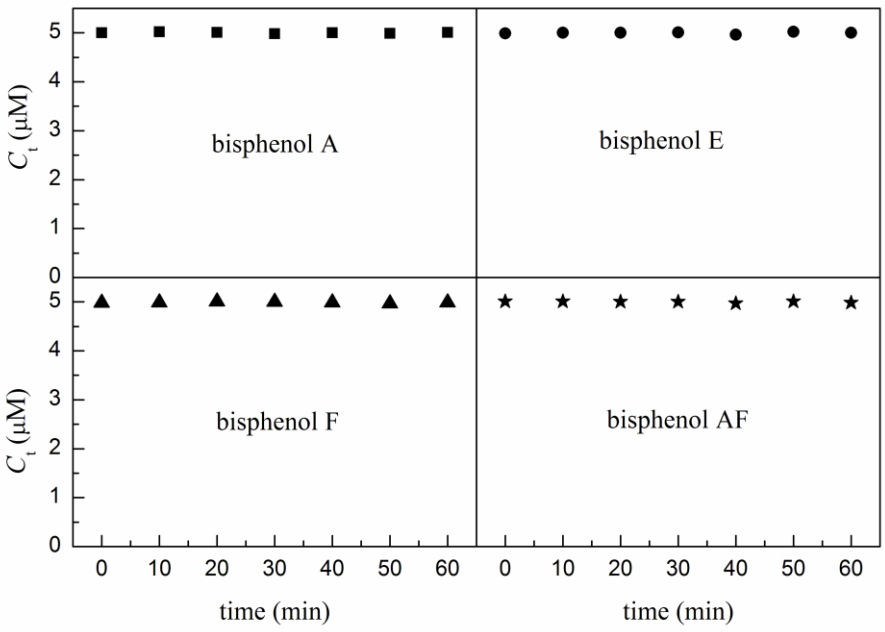

Figure S6. Effect of 20 μM β-CD on the photodegradation of 5 μM bisphenols (BPA, BPE, BPF, BPAF) without TiO_2 at 25 ºC.