Supplementary Information for

Supramolecular eantiodifferentiating photoisomerization of cyclooctene with modified β-cyclodextrins: A critical control by host structure

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Experimental

General

Mass spectra were obtained on a Bruker Biospins ToF IIIQ. ^{1}H and ^{13}C NMR spectra were recorded at 600 and 150 MHz in dimethyl sulfoxide-d_6 (DMSO-d_6) on a Bruker Avance 600 MHz instrument. Electronic absorption spectra were recorded on Shimadzu UV-240 and JASCO V-550 spectrophotometer. IR and circular dichroism spectra were obtained on Bruker IFS 120 HR FT-IR and JASCO J-820 spectropolarimeter in a conventional quartz cell (light path 1 cm), respectively. Elemental analysis was performed on a Vario El instrument.

Synthesis and characterization of 6-*O*-*m*-methoxybenzoyl-6-deoxy-β-CD (3) and 6-*O*-*p*-methoxybenzoyl-6-deoxy-β-CD (4)

β-CD (22.7 g, 20mmol) was dissolved with stirring in distilled dry pyridine (750 mL) in a round-bottomed flask in an ice bath, to which *m*- or *p*-methoxybenzoyl chloride (1.7 g, 10mmol) in dry pyridine (100 mL) was added dropwise in 20 min. The temperature was raised to room temperature after 4 h stirring and was kept at that temperature for another 10 h. Water was added to stop the reaction and the solvent was distilled under vacuum. The residue was dissolved in a small amount of DMF, and 800 mL of acetone-water (5:1) mixture was added，and the resultant was filtered and repeatedly recrystallized from water to give white solids (3.9 g, yield 31.5% for **3;** 4.2g, yield 32.3% for **4**).

3: TLC: R_f 0.47 (n-PrOH/ CH_3COOEt/H_2O=4:3:2, v/v); ESI-HRMS: *m/z* 657.1925 $[M+2Na]^+$; IR(KBr): ν 3391, 2927, 1723, 1608, 1288, 1157, 1080, 1029, 940, 855, 755, 705 cm^{-1}. ^{1}H-NMR (600MHz, DMSO-d_6, TMS, ppm): δ 7.57 (m,1H), 7.45 (m, 2H),

7.23(m, 1H), 5.69-5.84 (m, 14H), 4.82-4.89 (m,7H), 4.46-4.88 (m, 6H), 4.33-4.39 (m, 2H), 4.00 (m,1H), 3.29-3.78 (m, 39H), 3.99 (s, 3H); ^{13}C-NMR (150MHz, DMSO-d_6, TMS, ppm): δ 165.9, (C=O), 159.8, 131.4, 130.4, 122.0, 119.7, 114.5, 103.1, 102.5, 102.4, 102.10, 82.9, 82.1, 82.0, 82.0, 82.0, 81.8, 81.7, 73.6, 73.5, 73.4, 73.3, 72.9, 72.8, 72.7, 72.6, 72.5, 72.5, 69.4, 64.7, 60.4, 60.3, 60.1, 55.8; Elemental Analysis: Calcd for $C_{50}H_{76}O_{37}\cdot 3H_2O$: C: 45.35%; H: 6.11%, Found: C: 45.18%, H: 6.21%.

4: TLC: R_f 0.45 (n-PrOH/ CH_3COOEt/H_2O=4:3:2, v/v); HR-ESI-MS: *m/z* 657.1925 $[M+2Na]^{2+}$; IR(KBr): ν 3380, 2929, 1714, 1606, 1257, 1156, 1079, 1027, 945, 849, 757, 704 cm^{-1}; ^{1}H-NMR (600MHz, DMSO-d_6, TMS, ppm): δ 7.93 (d, 2H), 7.04 (d,2H), 5.68-5.86 (m,14H), 4.82-4.89 (br,7H), 4.46-4.56 (m,6H), 4.38 (m,1H), 4.38 (m,1H), 3.99 (m,1H), 3.28-3.69 (m,39H), 3.82 (s,3H); ^{13}C-NMR (150MHz, DMSO-d_6, TMS, ppm): δ 165.75 (C=O), 163.65, 131.88, 122.28, 114.45, 103.05, 102.46, 102.39, 102.03, 82.93, 82.09, 82.05, 81.95, 81.76, 81.71, 73.65, 73.55, 73.49, 73.42, 73.34, 72.90, 72.77, 72.70, 72.59, 72.54, 72.48, 69.49, 64.29, 60.43, 60.28, 60.10, 55.97; Elemental Analysis: Calcd for $C_{50}H_{76}O_{37}\cdot 3H_2O$: C: 45.35%; H: 6.11%, Found: C: 45.30%, H: 5.91%.