

Supplementary Information
for

Entropy-controlled supramolecular photochirogenesis: Enantiodifferentiating *Z-E* photoisomerization of cyclooctene included and sensitized by permethylated 6-*O*-benzoyl- β -cyclodextrin

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Experimental

General. Melting points were measured with a YANACO MP-21 apparatus. Mass spectra were obtained on a PerSeptive Biosystem MALDI-TOF. ¹H and ¹³C NMR spectra were recorded at 270 and 100 MHz in deuterated chloroform (CDCl₃) on a JEOL GSX-270 and EX400 instruments, respectively. Electronic absorption and circular dichroism spectra were measured in a quartz cell (light path 1 cm) on JASCO UV-550 and J-820 spectrometers equipped with a PTC-423L temperature controller.

Synthesis and Characterization of PMCDbz

To a 100 mL round-bottomed flask containing benzoic acid (347 mg, 2.84 mmol), permethylated 6-*O*-tosyl- β -cyclodextrin⁹ (854 mg, 0.544 mmol) and potassium carbonate (1.58 g, 11.4 mmol) dissolved in dehydrated DMF (10 mL) was added with stirring and the mixture was stirred overnight at 80 °C. After cooling down to the room temperature, the resulting solution was extracted with ethyl acetate, and the extract was washed with water and then with a saturated aqueous sodium hydrogen carbonate solution. The organic layer was dried over magnesium sulfate and concentrated, and the residue was dried under high vacuum to give **PMCDbz** (660 mg) as white foamy powder in 80% yield; mp 73-75 °C; MALDI-TOF-MS: *m/z* 1543[M+Na]⁺; ¹H NMR (CDCl₃, 23 °C): δ 8.05 (d, *J* 7.1 Hz, 2H), 7.58 (t, *J* 7.4 Hz, 1H), 7.45 (t, *J* 7.5 Hz, 2H), 5.21–5.11 (m, 7H, CD's H₁), 4.10–3.17 (m, 102H, other CD protons); ¹³C NMR (CDCl₃, 24.5 °C): δ 166.16 (C=O), 133.13 (*p*), 130.11 (*ipso*), 129.69, 128.44 (*o, m*), 99.70, 99.07, 99.04, 98.97, 98.93,

98.75 (C-1), 82.35, 82.11, 82.08, 82.05, 82.01, 81.98, 81.83, 81.79, 81.65, 81.60, 80.77, 80.54, 80.51, 80.23, 80.16, 80.11, 80.06, 71.51, 71.48, 71.47, 71.46, 71.44, 71.28, 71.23, 71.13, 71.08, 71.01, 70.98, 70.95, 70.91, 70.89, 70.84, 69.61 (other CD carbons), 61.67, 61.56, 61.53, 61.47, 61.41, 61.37, 59.17, 59.11, 59.04, 58.99, 58.96, 58.67, 58.60, 58.55, 58.54, 58.51, 58.33, 58.29 (OMe); Anal. Calcd for $C_{69}H_{114}O_{36} \cdot H_2O$: C, 53.90; H, 7.60%; Found: C, 53.91; H, 7.32%.