Supplementary Material for Chemical Communications
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Supplementary Information
for

The first supramolecular photosensitization of enantiodifferentiating bimolecular reaction: anti-Markovnikov photoaddition of methanol to 1,1-diphenylpropene sensitized by modified β-cyclodextrin

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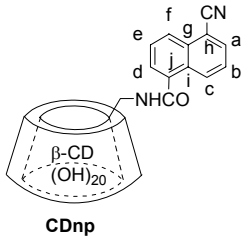
Experimental

General. Melting points were measured with a YANACO MP-21 apparatus. Mass spectra were obtained on a PerSeptive Biosystem MALDI-TOF. ^{1}H and ^{13}C NMR spectra were recorded at 600 and 150 MHz, respectively, in deuterated water (D_2O) on a Varian INOVA-600 instruments. Electronic absorption, fluorescence and circular dichroism spectra were measured in a quartz cell (light path 1 cm or 1 mm) on JASCO UV-550, FP-6500 and J-820 spectrometers equipped with a PTC-423L temperature controller. Fluorescence lifetimes were measured by the time-correlated single-photon-counting method on a Horiba NAES-1100 instrument equipped with a pulsed H_2 light source.

Synthesis and Characterization of CDnp



CDnp

6-Amino-6-deoxy-β-cyclodextrin[10] (766 mg, 0.675 mmol) and 5-cyanonaphthalene-1-carboxylic acid[11] (410 mg, 2.08 mmol) were dissolved in dehydrated DMF (20 mL) and cooled below 0 ºC in a 100 mL round-bottomed flask. To the mixture were added 1,3-dicyclohexylcarbodiimide (197 mg, 0.955 mmol) and

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1-hydroxybenzotriazole (150 mg, 1.11 mmol) dissolved in dehydrated DMF (2 mL). The reaction mixture was stirred for 2 h at 0 ºC and then at room temperature for additional 48 h. The solution was poured into acetone, and the resultant precipitates were collected and dried under high vacuum. This crude product was purified by reversed-phase column chromatography with Cosmosil 75C_{18}-OPN to give **CDnp** (276 mg, 0.210 mmol) as white solid in 31% yield; mp >200 °C; MALDI-TOF-MS: *m/z* 1336[M+Na]$^+$; ^{1}H NMR (D_2O, 25 ºC): δ 8.37 (d, *J* 10.3 Hz, 1H, c), 8.12 (d, *J* 7.68 Hz, 1H, f), 7.96 (d, *J* 7.68 Hz, 1H, a), 7.76 (d, *J* 5.94 Hz, 1H, d), 7.71 (t, *J* 7.68 Hz, 1H, e), 7.40 (t, *J* 8.58 Hz, 1H, b), 5.16–4.97 (m, 7H, CD's H_1), 4.40–3.22 (m, 49H, other CD protons); ^{13}C NMR (D_2O, 25 ºC): δ 172.24 (C=O), 135.90 (j), 135.70 (a), 134.18 (g), 132.72 (c), 131.41 (i), 130.12 (e), 129.56 (f), 129.34 (d), 127.59 (b), 120.06 (CN), 111.73 (h), 104.70, 104.48, 104.38, 104.36, 104.32, 104.16, 104.03 (C-1), 85.94, 83.31, 83.06, 83.01, 82.90, 82.84, 82.50 (C-4), 75.33-75.31 (overlapped), 75.23, 75.14, 75.07 (C-3), 74.53, 74.50, 74.41, 74.38, 74.36, 74.29, 74.23-74.19 (overlapped), 74.11, 73.98 (C-2, 5), 62.35, 62.24, 62.04, 61.99, 61.79, 61.64, 43.23 (C-6); Anal. Calcd for $C_{54}H_{76}O_{35}\cdot H_2O$: C, 48.72; H, 5.91; N, 2.10%; Found: C, 48.26; H, 5.84; N, 2.04%; TLC method: silica gel, eluent: 5:4:3 *n*-BuOH-EtOH-H_2O, R_f = 0.47.

Induced circular dichroism spectra

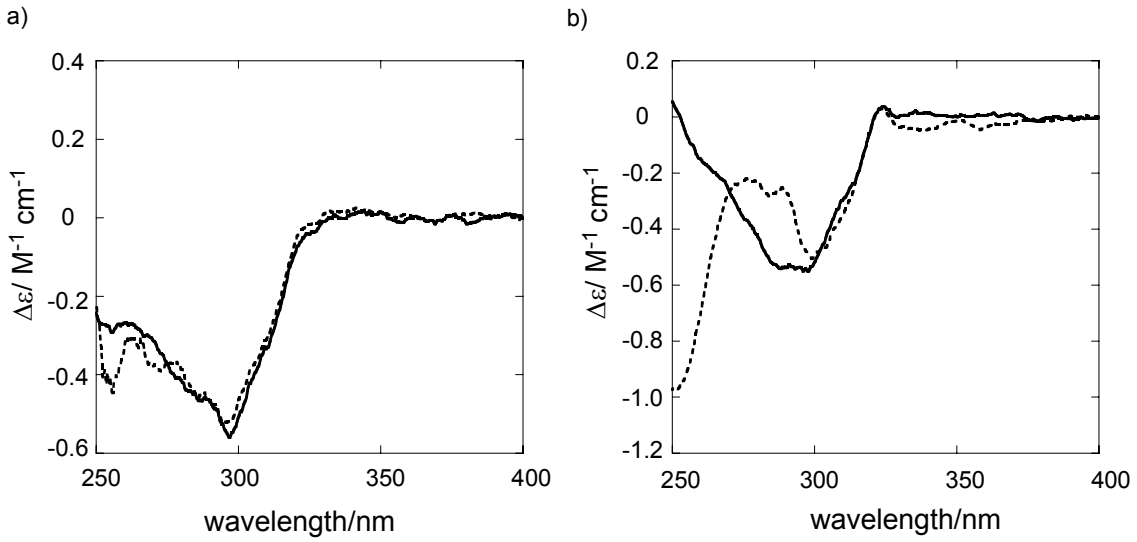

Figure S1. Circular dichroism spectra of **CDnp** in the absence (solid line) and presence (dashed line) of **DPP** at 25 ºC: a) [**CDnp**] = [**DPP**] = 1.0 mM in pure methanol (1 mm cell); b) [**CDnp**] = [**DPP**] = 0.1 mM in an aqueous solution containing 25% methanol (1 cm cell).