Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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Reversible Photochemically Gated Transformation of a Hemicarcerand to a Carcerand**

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Supporting Information – Table of Contents

Experimental Section

Host **3**. Diol **2** (192 mg, 0.10 mmol) was dissolved in dry DMF (10 ml), anhydrous Cs_2CO_3 (326 mg, 1 mmol) was added and stirred under Ar for 15 min. 9-chloromethylanthrancene (68 mg, 0.30 mmol) was then added and the mixture was stirred at 50 ^oC overnight. The mixture was washed with 1N HCl and extracted with $CHCl_3$. The organic solvent was concentrated and the crude product was purified by column chromatography using hexane/EtOAc = 10/1 as the eluent to afford **3** (182 mg, 79%) as a yellow powder. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, J = 5.4 Hz, CH_3, 24H), 1.30-1.53 (m, $CH_2CH_2CH_2$, 48H), 1.90-2.21 (m, $CHCH_2$, OCH_2CH_2, 28H), 3.82-3.93 (m, OCH_2CH_2, 12H), 4.08-4.20 (m, OCH_2O (inner H), 8H), 4.55 (t, J = 7.8 Hz, $CHCH_2$, 4H), 4.68 (t, J = 7.8 Hz, $CHCH_2$, 4H), 4.79 (s, OCH_2Ar, 4H), 5.50-5.79 (m, OCH_2O (outer H), 8H), 6.65 (s, ArH, 2H), 6.73 (s, ArH, 6H), 7.20-7.33 (m, ArH, 8H), 7.52 (d, J = 8.1 Hz, ArH, 4H), 7.91 (s, ArH, 2H), 8.16 (d, J = 8.1 Hz, ArH, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.9, 148.7, 148.4, 144.5, 144.0, 139.1, 138.7, 138.4, 131.5, 131.1, 129.1, 128.4, 127.5, 125.5, 124.6, 124.2, 113.8, 99.6, 73.0, 72.3, 36.9, 32.1, 29.9, 29.7, 27.7, 22.7, 14.1. MALDI HRMS calcd for $C_{146}H_{166}O_{24}Na$ 2327.12, found 2326.94 $[M+Na]^+$.

Complexation and decomplexation studies:

4Θ1,4-$(MeO)_2C_6H_4$. To a 10^{-4} M solution of **3** in 5 ml degassed Ph_2O was added 1.4 g 1,4-$(MeO)_2C_6H_4$. The mixture was irradiated at 350 nm for 1 h and then poured into 10 ml of methanol. The precipitate was collected on a fine-mesh sintered glass funnel and dried under vacuum (25 ^oC) overnight to give the carceplex as a light yellow solid. ^1H NMR ($CDCl_3$, 400 MHz) δ -0.37 (s, OCH_3, 6H), 0.92 (t, J = 5.4 Hz, CH_3, 24H), 1.28-1.55 (m, $CH_2CH_2CH_2$, 48H), 1.90-2.25 (m, $CHCH_2$, OCH_2CH_2, 28H), 3.78-3.96 (m, OCH_2CH_2, 12H), 4.25-4.35 (m, OCH_2O (inner H), 8H), 4.45 (s, 2H, CH), 4.70-4.80 (m, $CHCH_2$, OCH_2Ar, 12H), 5.80-5.92 (m, OCH_2O (outer H), 8H), 5.95 (s,

ArH, 4H), 6.60 (s, ArH, 2H), 6.75-6.92 (m, ArH, 22H). MALDI HRMS calcd for $C_{154}H_{176}O_{26}Na$ 2465.28, found 2465.40 $[M+Na]^+$.

Stability of **4**Θ1,4-$(MeO)_2C_6H_4$. A solution of 3 mg carceplex **4**Θ1,4-$(MeO)_2C_6H_4$ in 1 ml of $CDCl_3$ at 25 ^oC was monitored by ^1H NMR for 4 weeks, and no change was observed in the spectrum.

Decomplexation of **4**Θ1,4-$(MeO)_2C_6H_4$. A solution of 3 mg carceplex **4**Θ1,4-$(MeO)_2C_6H$ in 1 ml of $CDCl_3$ at 25 ^oC was irradiated at 254 nm for 1 h. The decomplexation was monitored by following the decrease of the intensity of the singlet at -0.37 ppm and the reappearance of the anthracene peaks from 7.20-8.20 ppm in the ^1H NMR spectrum.

Other guest molecules:

The complexation and decomplexation studies for the other guest molecules (Table S1, Supporting Information) were similar to that of 1,4-dimethoxybenzene.

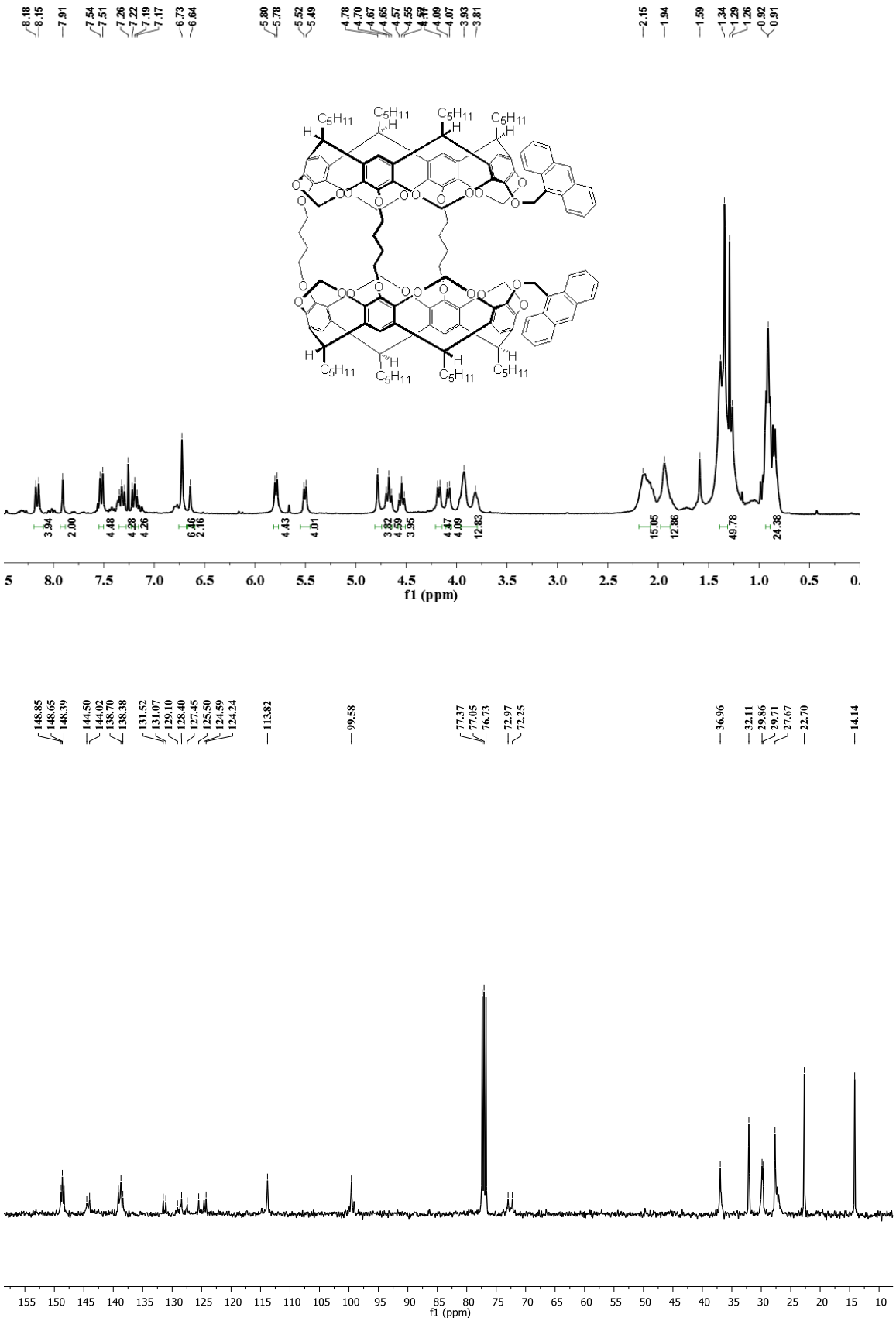


Figure S1: ^{1}H NMR and ^{13}C NMR spectra of **3**.

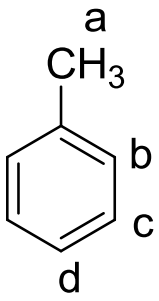
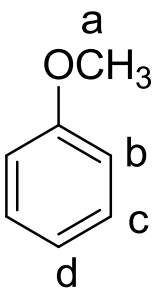
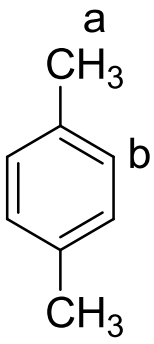
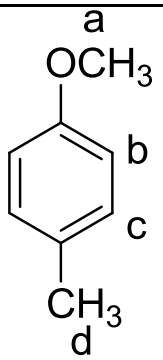
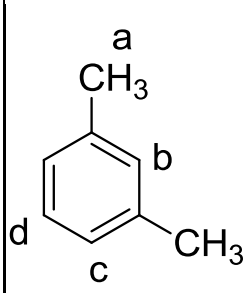
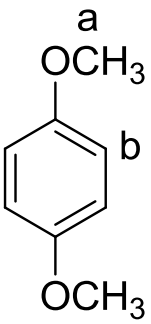
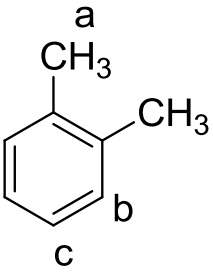
Guest	H	Δδ (ppm)	Guest	H	Δδ (ppm)
	H_a H_b H_c H_d	3.96 1.53 1.85 3.35		H_a H_b H_c H_d	3.87 1.60 1.95 3.30
	H_a H_b	4.17 1.06		H_a H_b H_c H_d	4.01 0.84 0.98 4.21
	H_a H_b H_c H_d	3.17 hidden 1.86 hidden		H_a H_b	4.15 0.85
	H_a H_b H_c	2.34 1.54 1.95	$CH_aCl_2—CHCl_2$	H_a	0.95
			$CH_aBr_2—CHBr_2$	H_a	1.02

Table S1: Complexation of **4** with various guest molecules and the chemical shift changes of corresponding Hs (before and after complexations) on the guests.

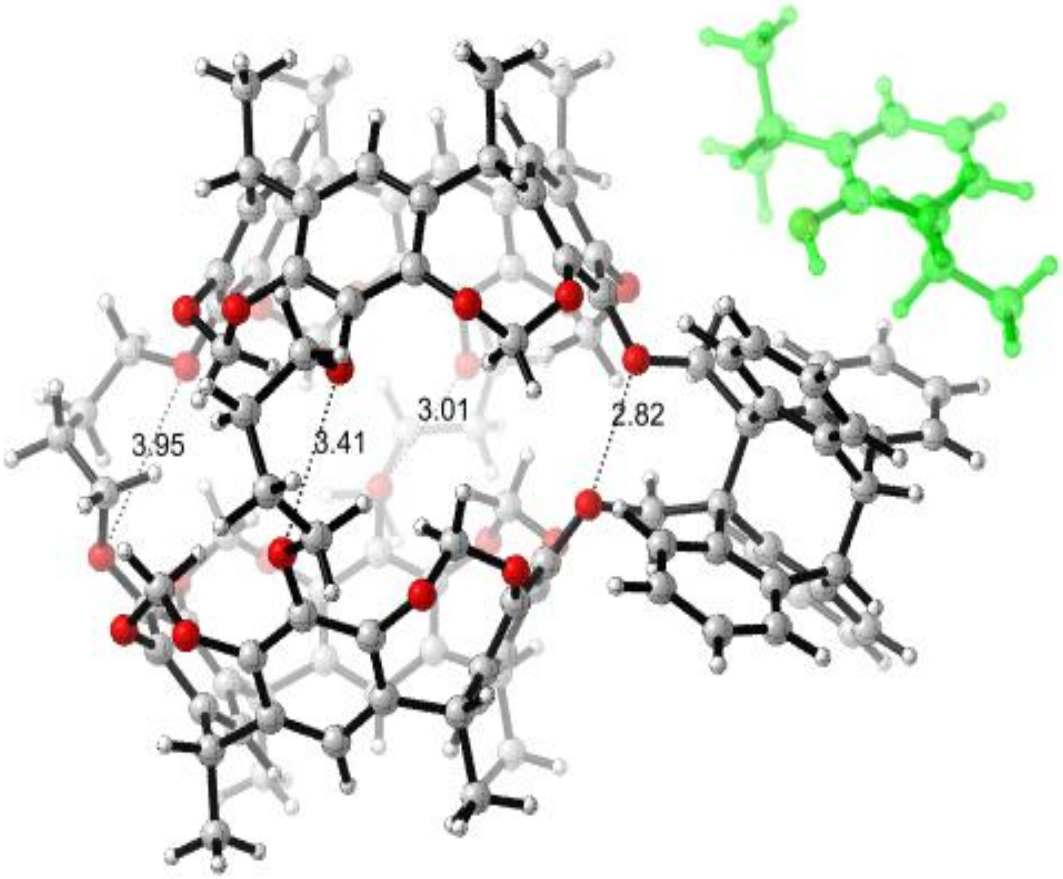


Figure S2: Molecular modelling of complexation of **4** with propofol (2,6-diisopropylphenol) using Schrödinger Macromodel (OPLS_2005, GB/SA $CHCl_3$). (The geometry began with the guest inside the host; the guest came out of the host after the minimization)