Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Host-guest interaction between corannulene and γ-cyclodextrin: Mass spectrometric evidence of a 1:1 inclusion complex formation

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Experimental Section

Materials

Dimethyl sulphoxide (DMSO), deuterated DMSO (DMSO-d^6), deuterated water (D_2O), gamma cyclodextrin (γ-cd), 2,5 dihydroxybenzoic acid (DHB), and sodium trifluroacetate (CF_3COONa) were purchased from Sigma Aldrich and used without further purification.

Characterization

NMR spectra were recorded at room temperature on Bruker 500-AV NMR instrument. Variable temperature NMR measurements were recorded on JEOL ECA400 instrument. OMNICAL SuperCRC Reaction micro calorimeter was used to study the thermodynamic and kinetic parameters of the reaction. The raw data from the ITC was processed using Origin and MATLAB software. MALDI-TOF analysis was conducted using JMS-S3000 Spiral TOF and the MS-MS analysis was conducted by helium (He) gas bombardment.

NMR studies

NMR samples were prepared in DMSO-d^6 with the required mole ratio of γ-cd and corannulene/methylcorannulene. Subsequently, *ca.* 40 μl aliquots of D_2O were added during NMR titration experiments. 500 MHz NMR machine was used to conduct the ^{1}H-NMR and 2D (ROESY) experiments. Variable temperature measurements were conducted on the 400 MHz instrument.

MALDI-TOF sample preparation

1mL of 1 mM (1:1) cor-γ-cd was prepared in 30% water-DMSO solvent system without any visible precipitation. To a 500 μL of aliquot of the above solution, few drops of methanol were added. A very slow and careful addition was required to prevent precipitation. This solution was allowed to rest for 30 min. Subsequently, 20 μL of the solution with methanol was thoroughly mixed with 30 μL of DHB (20 mg/mL in MeOH). While preparing the MALDI plate, CF_3COONa was first deposited on the plate and subsequently the mixture of matrix and sample was spotted. The spot was allowed to dry for 24hrs until all the solvent was evaporated.

ITC sample preparation and measurements

A typical experiment was setup by taking 2 mL of analyte with the required concentration in the sample chamber. The machine was stabilized with the sample and reference for approximately 30-45 min. After this the titrant with the specific concentration was added in aliquots of 50 μL to the analyte. Subsequent additions of titrant were made only after stabilization of reaction mixture. Around 15-20 additions were obtained in each study, which were then used to analyze the data. Data analysis was conducted with Origin, MATLAB, and Microsoft Excel.

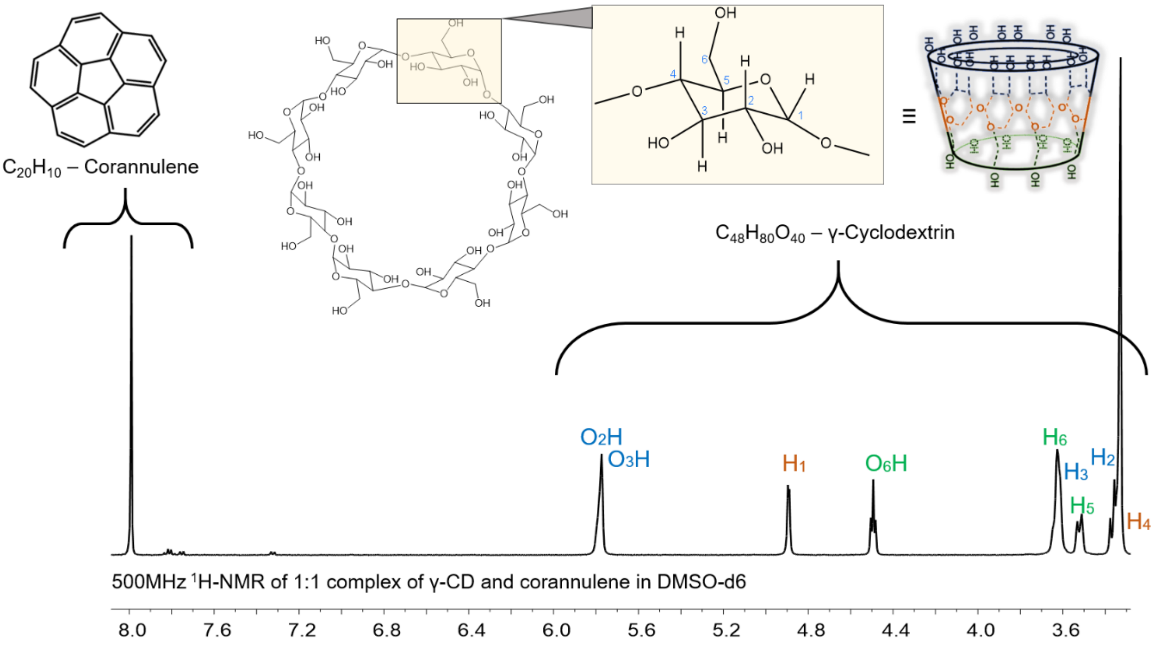

Figure S1. 500 MHz ^{1}H-NMR of cor-γ-cd in DMSO-d^6 showing the various regions in the spectrum for monitoring the changes during titration experiments.

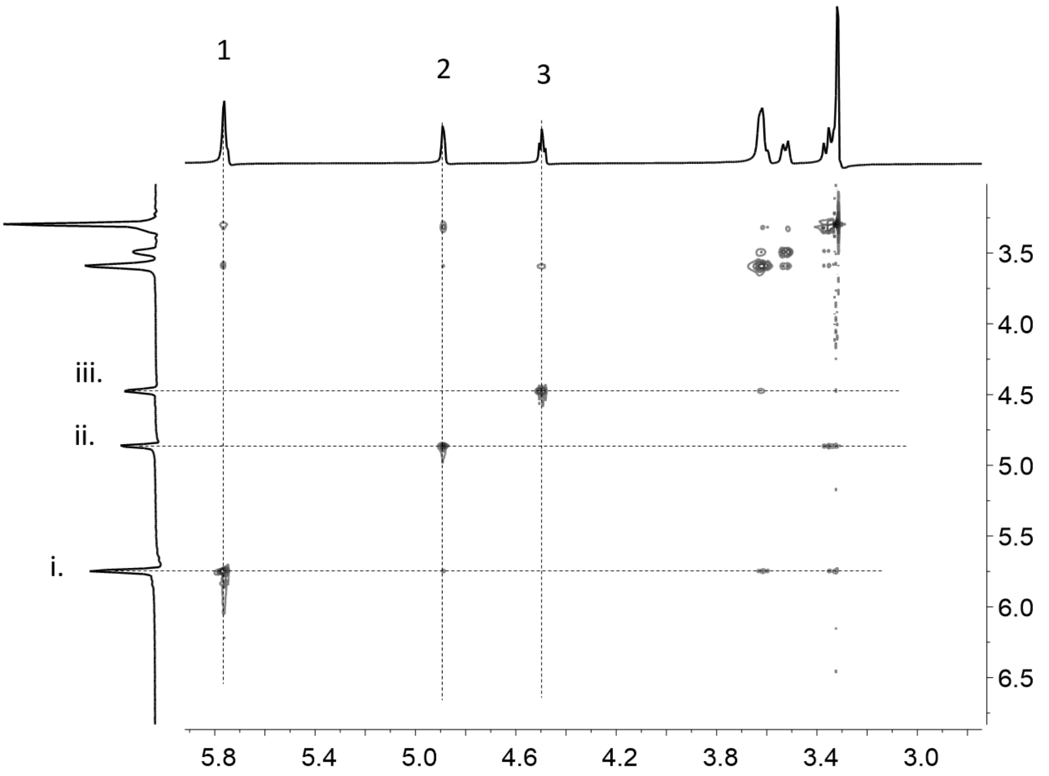

Figure S2. Two-dimensional NOESY spectrum of γ-cd showing the bonded interactions. (1-i) O^3H and O^2H regions, (2-ii) H^1 proton and (3-iii) O^6H proton.

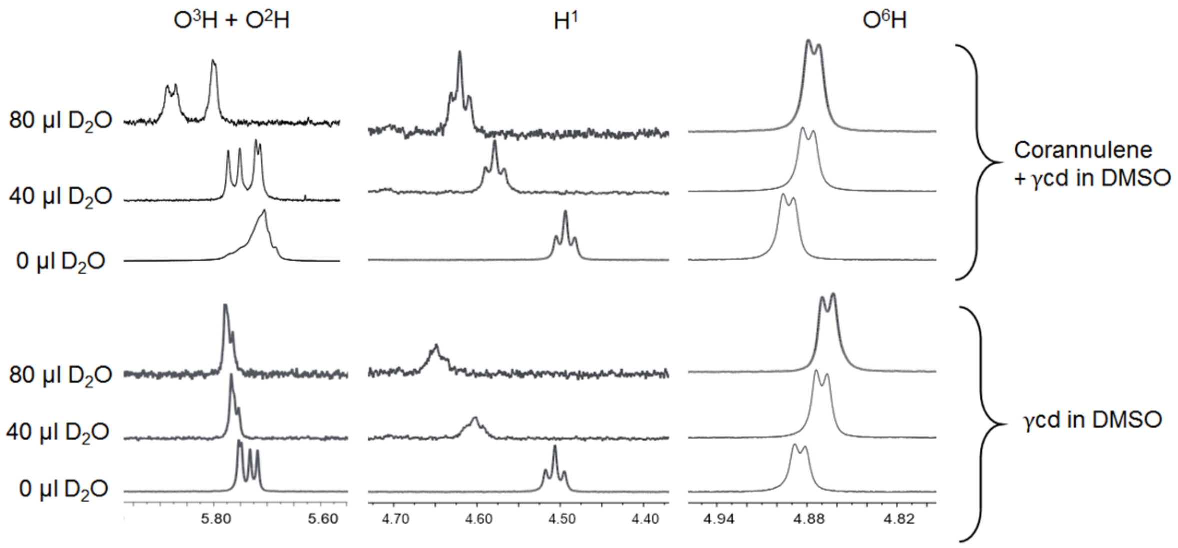

Figure S3. 500 MHz ^{1}H-NMR titration study of corannulene + γ-cd in DMSO-d^6 showing changes in the OH and H^1 region on addition of D_2O (0 µL to 80 µL).

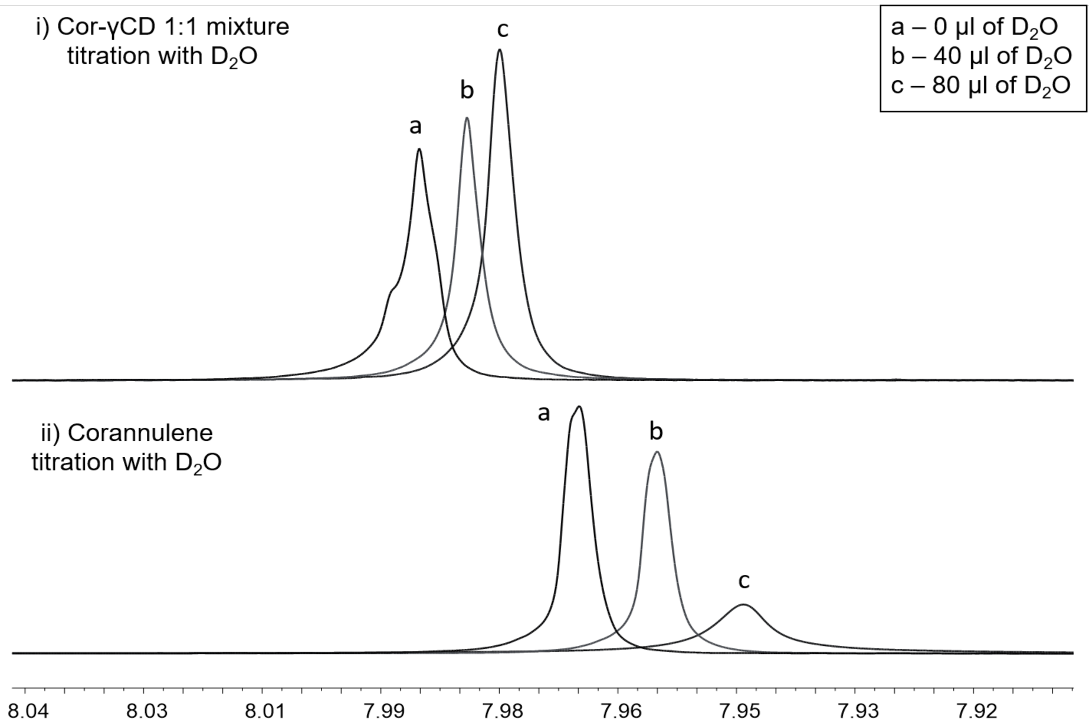

Figure S4. 500 MHz ^{1}H-NMR titration study showing changes in the corannulene region on addition of D_2O (0 μL to 80 μL) with and without γ-cd.

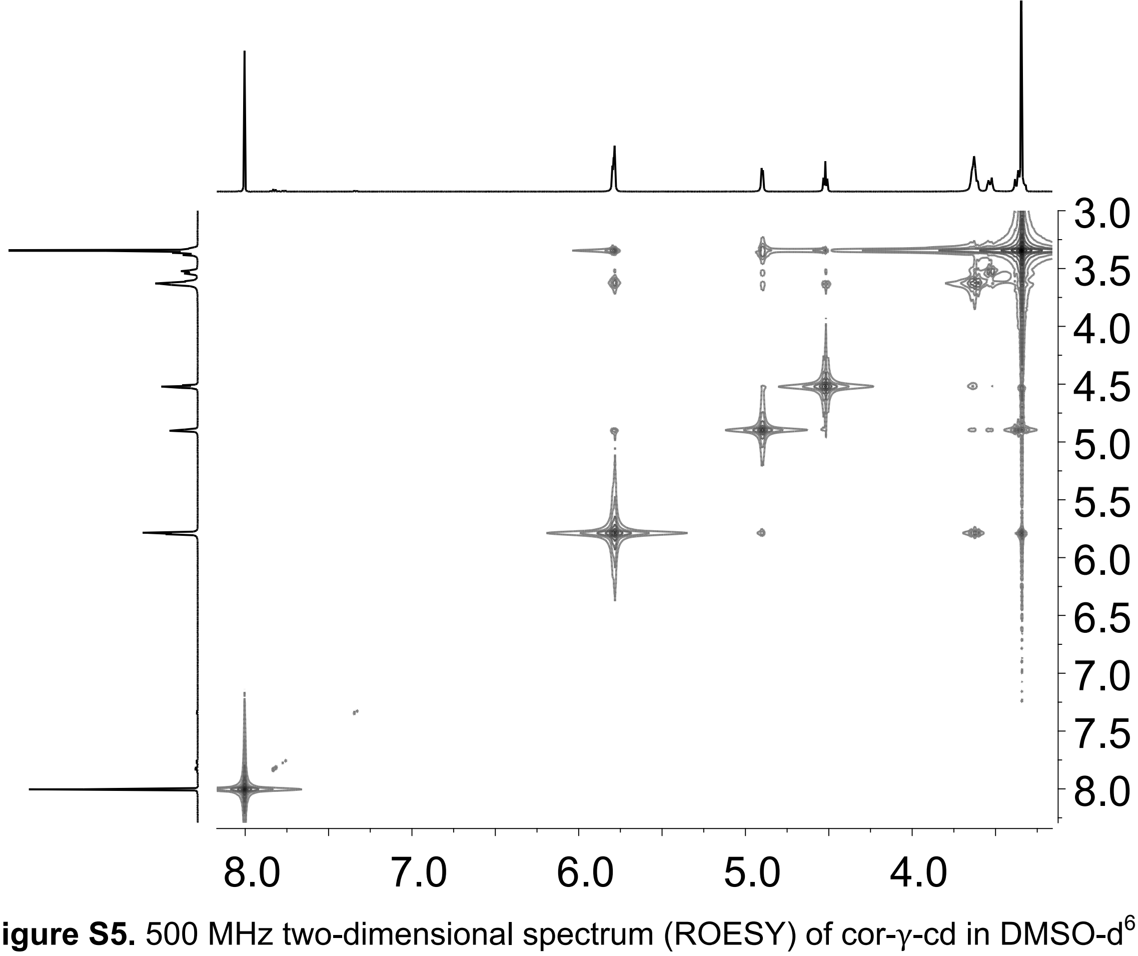

Figure S5. 500 MHz two-dimensional spectrum (ROESY) of cor-γ-cd in DMSO-d^6 without addition of D_2O.

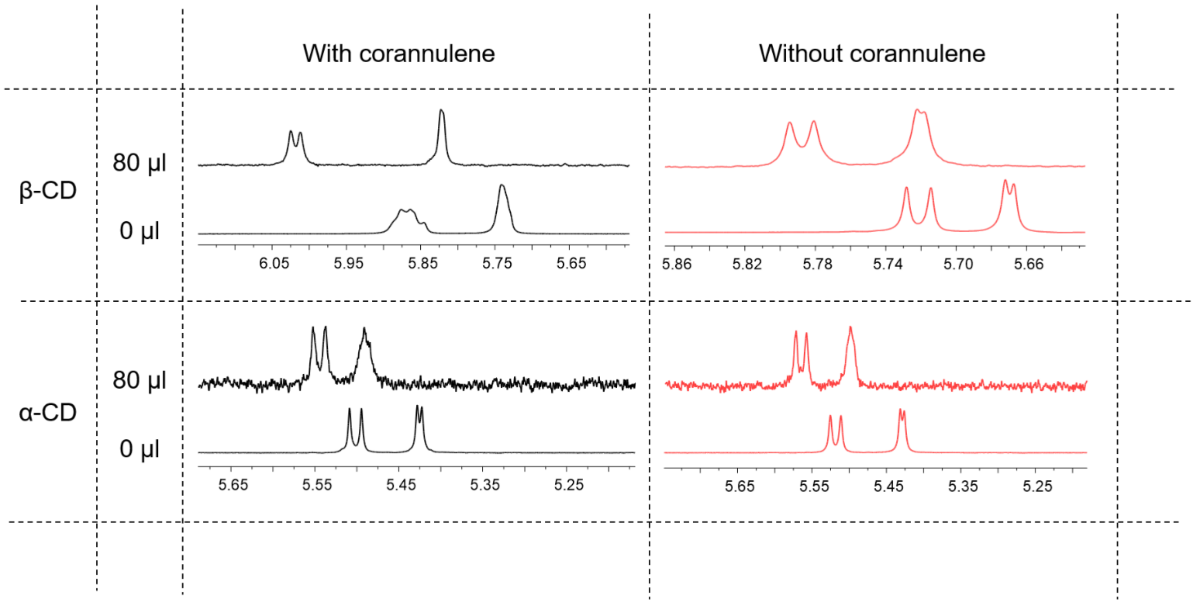

Figure S6. 500 MHz ^{1}H-NMR titration spectra of 1:1 mixture of α-cd and β-cd, with and without corannulene.

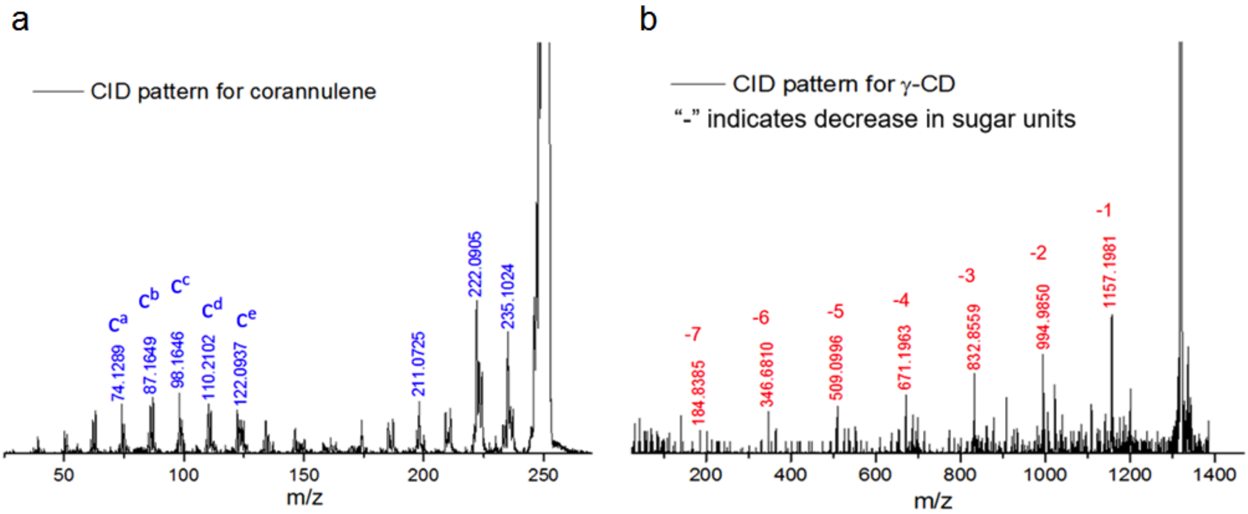

Figure S7. MS-MS analysis via collision induced disintegration (CID) spectra of (a) corannulene and (b) γ-cd by bombardment of helium gas.

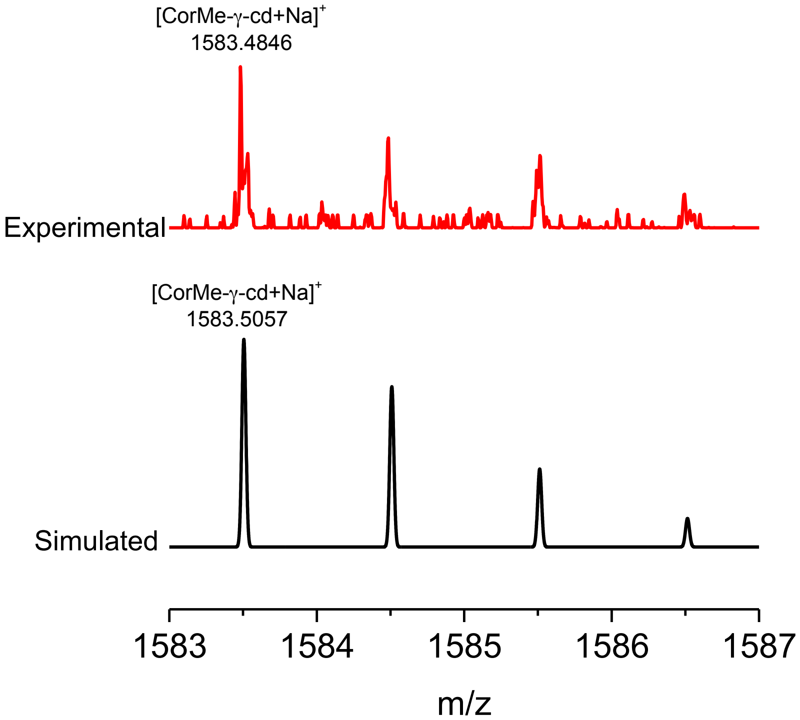

Figure S8. MALDI-TOF spectrum of sodium adduct of methyl corannulene and γ-cd. The experimental is indexed to the simulated spectrum to 4 isotopic peaks.

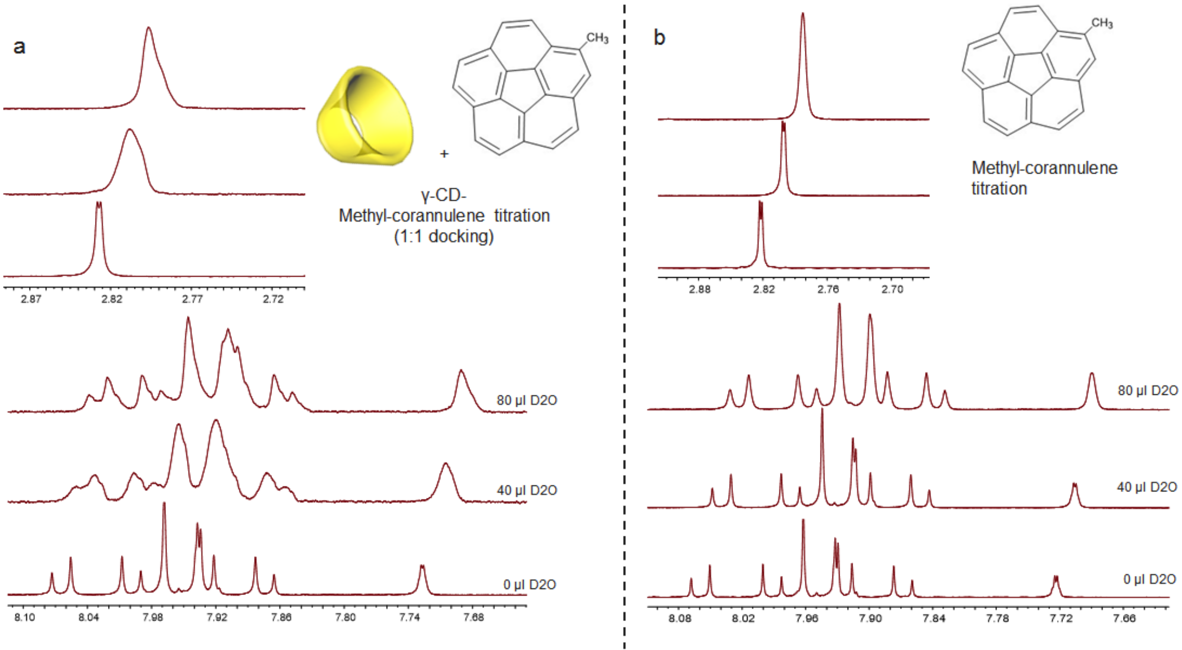

Figure S9. 500 MHz ^{1}H-NMR titration of methyl corannulene with D_2O (a) with γ-cd and (b) without γ-cd.

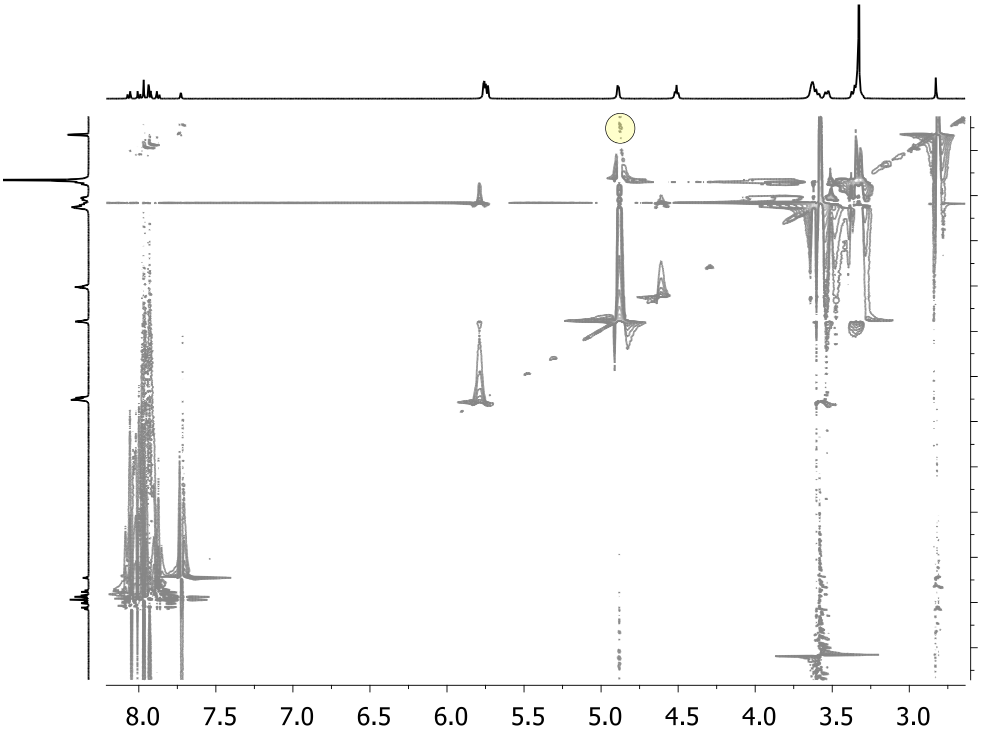

Figure S10. 500 MHz two-dimensional spectrum (ROESY) of methylcorannulene-γ-cd in DMSO-d^6 with 40 µL of D_2O.

Table S1. Thermodynamic and kinetic parameters of the docking reaction calculated from the ITC studies.

	Units	$T_{25\ °C}$	$T_{40\ °C}$	$T_{60\ °C}$
$\Delta G_{docking}$	kJ mol^{-1}	-20.53	-20.21 (-)	-20.43 (-)
$\Delta S_{docking}$	J mol-1 K-1	-20.73	-19.32 (↑)	-18.84 (↑)
K_{eq}	mol L^{-1}	3.99 x 10^3	2.41 x 10^3 (↓)	1.04 X 10^3 (↓)
$\Delta H_{docking}$	kJ mol^{-1}	-26.31	-27.12 (-)	-26.42 (-)

(↑) indicates increase in value, (↓) indicates decrease in value and (-) indicates no change in the value compared to previous lower temperature. A detailed discussion of the results presented herein will be described in a full paper in the near future.