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# Electronic Supplementary Information

## Evaluation of the supramolecular interaction of Congo Red with cucurbiturils using mass spectrometry and spectroscopic methods

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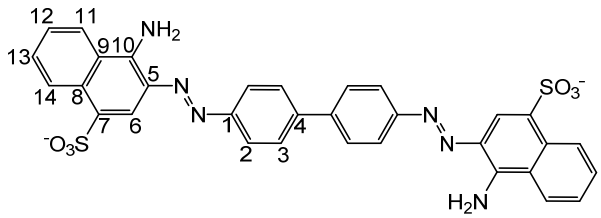
### General instrumentation

Microanalyses (CHNS) were performed with a Truspec Micro CHNS 630-200-200 instrument. Powder X-ray diffraction (PXRD) was performed with automatic data acquisition (X'Pert Data Collector v4.2 software) and monochromated Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å) using a Philips Analytical Empyrean ($\theta/2\theta$) diffractometer equipped with a PIXcel1D detector. Samples were step-scanned with 0.02° 2$\theta$ steps and a counting time of 50 s per step. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 system at a heating rate of 5 °C min$^{-1}$ under air. FT-IR spectra were obtained as KBr pellets in the range of 300 to 4000 cm$^{-1}$ using a Mattson-7000 spectrophotometer. Raman spectra were recorded on a Bruker RFS100/S FT instrument (Nd:YAG laser, 1064 nm excitation, InGaAs detector). $^1$H NMR spectra were obtained with a 500 MHz Jeol spectrometer equipped with a Royal HFX probe. Solid-state $^{13}$C{$^1$H} cross-polarisation (CP) magic-angle spinning (MAS) NMR spectra were recorded at 100.62 MHz on a Bruker Avance 400 spectrometer, using 3.5 μs $^1$H 90° pulses, a 2 ms contact time, a spinning rate of 10 kHz, and 5 s recycle delays. Chemicals shifts are quoted in ppm relative to TMS.

**Spectroscopic data for purified CR**

FT-IR ($cm^{-1}$): $\nu$ = 3456 (s, br), 2924 (w), 1610 (m), 1448 (w), 1421 (s), 1373 (m), 1227 (vs), 1176 (s, $\nu_{as}(SO_3^-)$), 1118 (m), 1045 (s, $\nu_s(SO_3^-)$), 1000 (w), 947 (w), 917 (w), 860 (w), 829 (m), 784 (w), 755 (m), 720 (w), 696 (w), 663 (w), 628 (w), 596 (w), 538 (w), 496 (w), 464 (w). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ = 8.77 (d, $J_{H\text{-}H}$ = 8.6 Hz, $H^{14}$), 8.43 (d, $J_{H\text{-}H}$ = 8.2 Hz, $H^{11}$), 8.31 (s, $H^6$), 8.10 (d, $J_{H\text{-}H}$ = 8.6 Hz, $H^2$), 7.96 (d, $J_{H\text{-}H}$ = 8.7 Hz, $H^3$), 7.74 (s, $NH_2$), 7.60 (t, $J_{H\text{-}H}$ = 7.7 Hz, $H^{13}$), 7.50 (t, $J_{H\text{-}H}$ = 8 Hz, $H^{12}$). The $^1$H NMR spectrum is in agreement with that reported previously and has been assigned similarly (see below for atom numbering).[1] $^{13}C\{^1H\}$ CP MAS NMR: $\delta$ = 149.9 ($C^1$), 138.8 ($C^{10}$), 137.4 ($C^4$), 126.7 ($C^{3,5,7,8,12,14}$), 124.8 ($C^{2,9,11,13}$), 114.4 ($C^6$). Assignments for the solid-state $^{13}$C NMR spectrum are based on those made previously for the solution spectrum in DMSO-$d_6$.[1]




**Preparation and spectroscopic data for PrCR**

Addition of 1 M HCl to an aqueous solution of CR (0.07 g, 0.1 mmol) resulted in a blue precipitate which was isolated by filtration, washed with water and air-dried. FT-IR ($cm^{-1}$): $\nu$ = 3432 (s, br), 1611 (m), 1598 (s), 1543 (m), 1504 (m), 1475 (w), 1457 (w), 1421 (vs), 1360 (vs), 1280 (vs), 1172 (vs, $\nu_{as}(SO_3^-)$), 1043 (s, $\nu_s(SO_3^-)$), 998 (s), 1000 (w), 947 (w), 917 (w), 829 (m), 784 (w), 755 (m), 720 (w), 696 (w), 663 (w), 628 (w), 596 (w), 538 (w), 496 (w), 464 (w). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ = 8.74 (d, $J_{H\text{-}H}$ = 8.4 Hz, $H^{14}$), 8.44 (d, $J_{H\text{-}H}$ = 7.8 Hz, $H^{11}$), 8.31 (s, $H^6$), 8.11 (d, $J_{H\text{-}H}$ = 8.6 Hz, $H^2$), 7.97 (d, $J_{H\text{-}H}$ = 8.7 Hz, $H^3$), 7.60 (t, $J_{H\text{-}H}$ = 7.6 Hz, $H^{13}$), 7.50 (t, $J_{H\text{-}H}$ = 6 Hz, $H^{12}$). $^{13}C\{^1H\}$ CP MAS NMR: $\delta$ = 158.6 ($C^1$), 139.5 ($C^{10}$), 136.3 ($C^4$), 132.4 ($C^5$), 127.5 ($C^{3,7,8,12,14}$), 124.4 ($C^{2,9,11,13}$), 116.4 ($C^6$) ppm. Assignments for the solid-state $^{13}$C NMR spectrum are based on those made previously for the solution spectrum in DMSO-$d_6$.[1]

1. E. Pigorsch, A. Elhaddaoui, S. Turrell, Spectrochim. Acta 50A (1994) 2145-2152.

## ESI-MS, $^1$H NMR, PXRD and TGA data

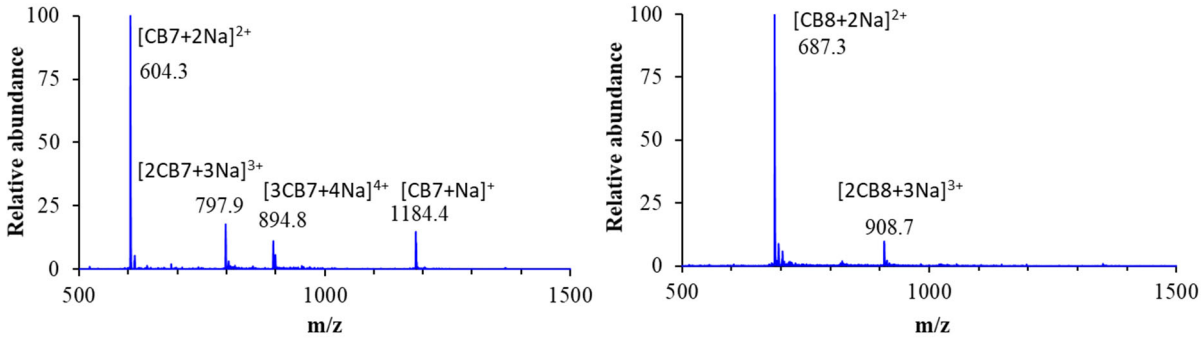



**Fig. S1** Full scan spectra of aqueous solutions of CB[7] and CB[8] with CR (50 μM : 50 μM) under positive ESI. The m/z values are of the first peak of the isotope series.

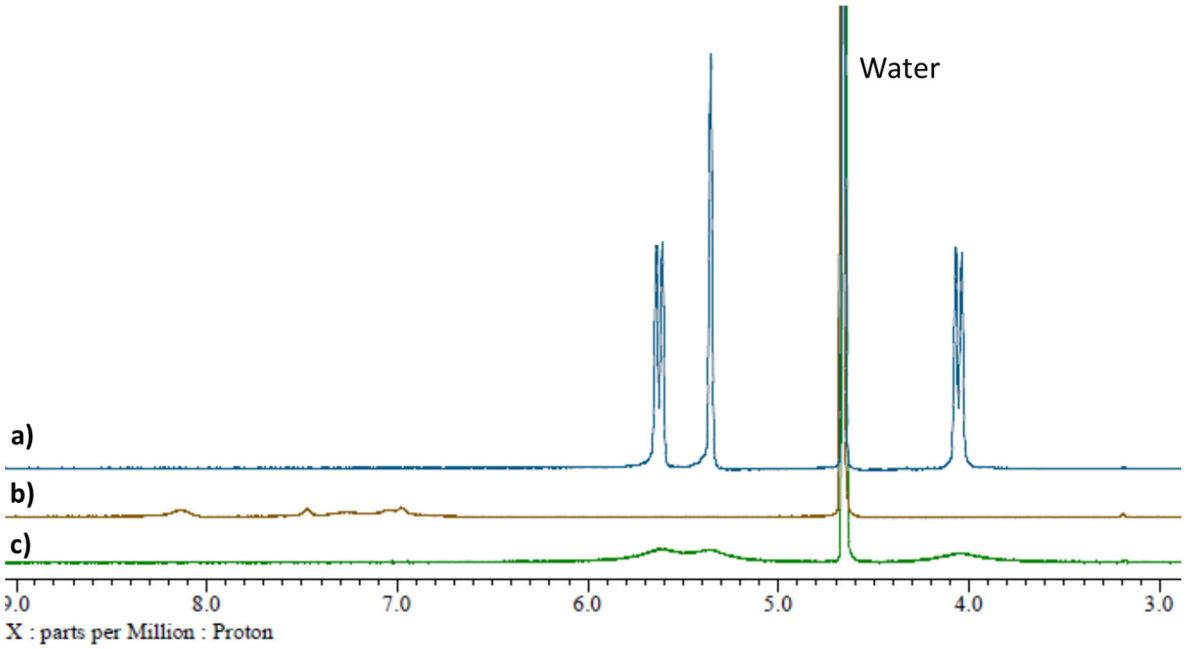



**Fig. S2** $^1$H NMR spectra of a) CB[7], b) CR, and c) mixture of CB[7] (1 mM) + CR (1 mM).

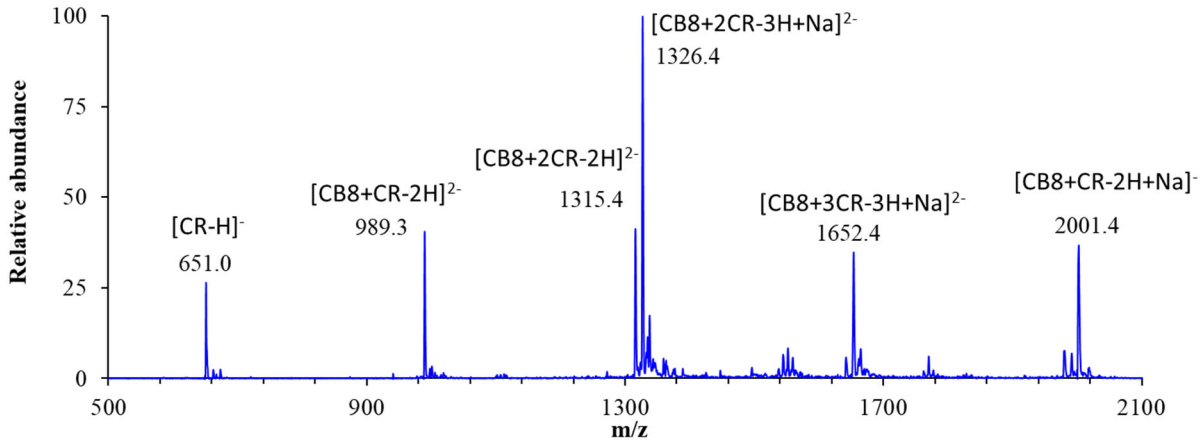



**Fig. S3** Full scan spectrum of aqueous solutions of CR@CB[8] (50 μM : 50 μM) under negative ESI. The m/z values are of the first peak of the isotope series.

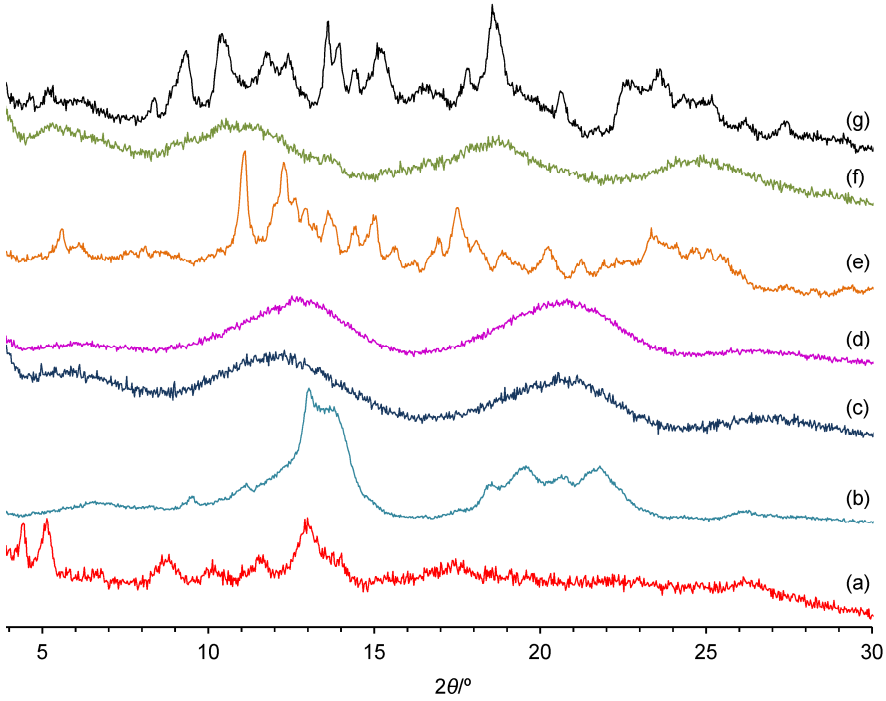



**Fig. S4** PXRD patterns in the range of 4-30° 2$\theta$ of (a) CR, (b) CB[7], (c) CR@CB[7](RT), (d) CR@CB[7](100), (e) CB[8], (f) CR@CB[8](RT), and (g) CR@CB[8](100).

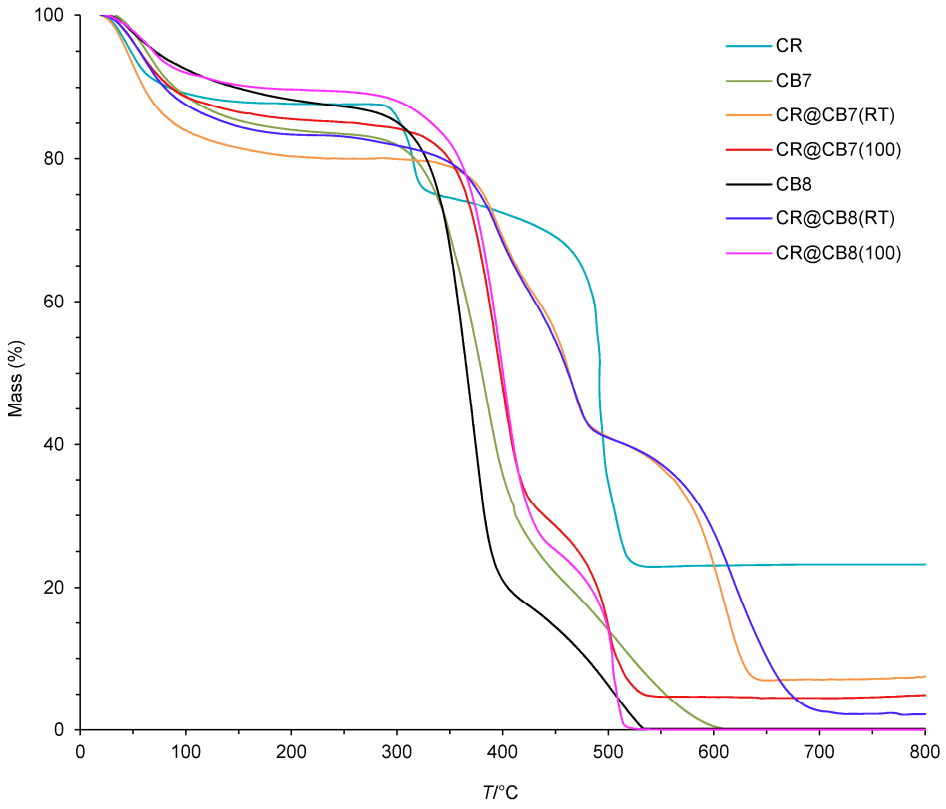



**Fig. S5** TGA curves for CR, CB[$n$] and the CR@CB[$n$] adducts.

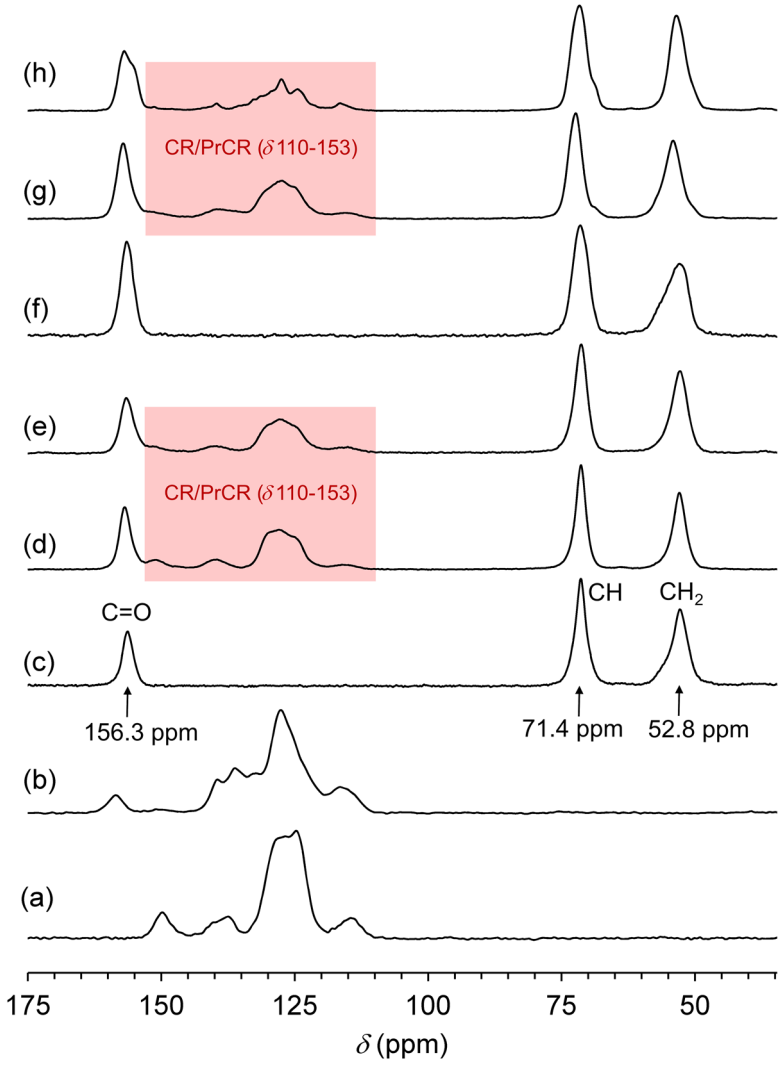



**Fig. S6** $^{13}C\{^{1}H\}$ CP MAS NMR spectra of (a) CR, (b) PrCR, (c) CB[7], (d) CR@CB[7](RT), (e) CR@CB[7](100), (f) CB[8], (g) CR@CB[8](RT), and (h) CR@CB[8](100).

The $^{13}C\{^{1}H\}$ CP MAS NMR spectra of CB[7] and CB[8] display broad and featureless signals centred at 156.3 ppm for the C=O groups, 71.4 ppm for the CH groups, and 52.8 ppm for the bridging $CH_2$ groups (Fig. S6). A similar set of peaks is present in the spectra of the CR@CB[*n*] adducts. In addition, several weak, overlapping resonances are observed in the 110-153 ppm range that can be attributed to unprotonated and/or protonated forms of CR. For CR@CB[7](RT), CR@CB[7](100) and CR@CB[8](RT), the spectral profiles in this chemical shift range are similar and resemble that observed for CR (Fig. S6(a)). On the other hand, the profile for CR@CB[8](100) (Fig. S6(h)) is different and more closely matches that for PrCR (Fig. S6(b)). The spectra are consistent with other measurements in indicating that on going from CR@CB[*n*](RT) to CR@CB[*n*](100) the CR content in the adducts decreases as does the relative proportion of the unprotonated form of CR.