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# Supporting Information

# Nitroxide Radicals as Probes for Exploring the Binding Properties of the Cucurbit[7]uril Host

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Table 1S. $^1$H NMR chemical shifts of compounds **2** and **3** at 298 K in $D_2O$.

| Guest | | δ [ppm] | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_o$ | $H_m$ | $H_p$ | $C\boldsymbol{H_2}$–Ph | $CH_3$ | $CH_2$ |
| **2** | Free ($H_2O$) | 7.18 | 7.38 | 7.32 | 4.04 | 1.22 | – |
| | CB7@**2** | 7.48 | 7.39 | 7.27 | 3.28 | 0.43 | – |
| | CB7@**2**($K^+$)[a] | 7.61 | 7.53 | 7.42 | 3.39 | 0.48 | – |
| **3** | Free | 7.23 | 7.39 | 7.33 | 3.89 | 1.00 | 2.64 |
| | CB7@**3** | 6.40 | 6.58 | 6.71 | 3.16 | 0.66 | 1.96 |
| | CB7@**3**($K^+$)[a,b] | 6.53 | 6.81 | 6.84 | 3.20 | 0.57 | 2.13 |

[a] Spectra recorded in the presence of KCl 0.2 M.

[b] These values represent the concentration-weighted averaged signals for the free and complexed species (see text).

Figure 1S. EPR spectra (Field scan 73.3 G) of benzyl *tert*-butyl nitroxides at 298 K in the presence of CB7 6.0 mM and MCl 0.1 M (*a*: M=$Li^+$; *b*: M=$Na^+$; *c*: M=$K^+$; *d*: M=$Cs^+$ ). The dotted line correspond to the first EPR line of the spectra due to the free species.

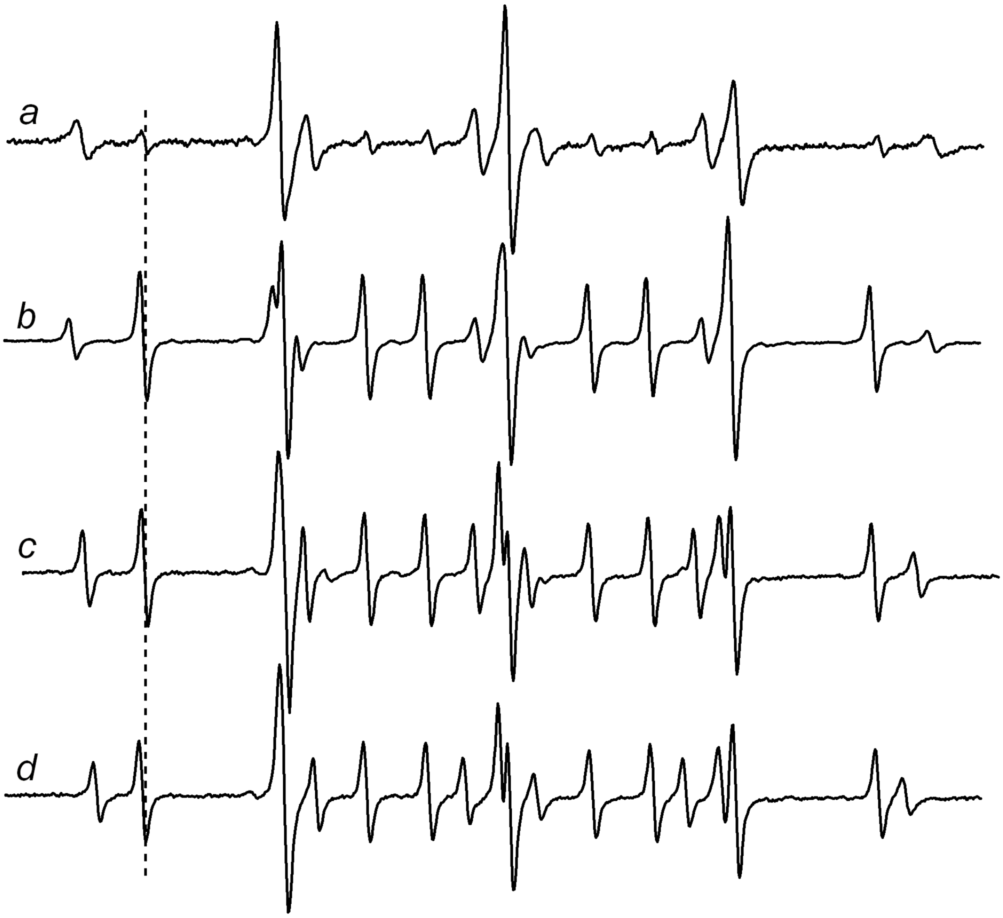
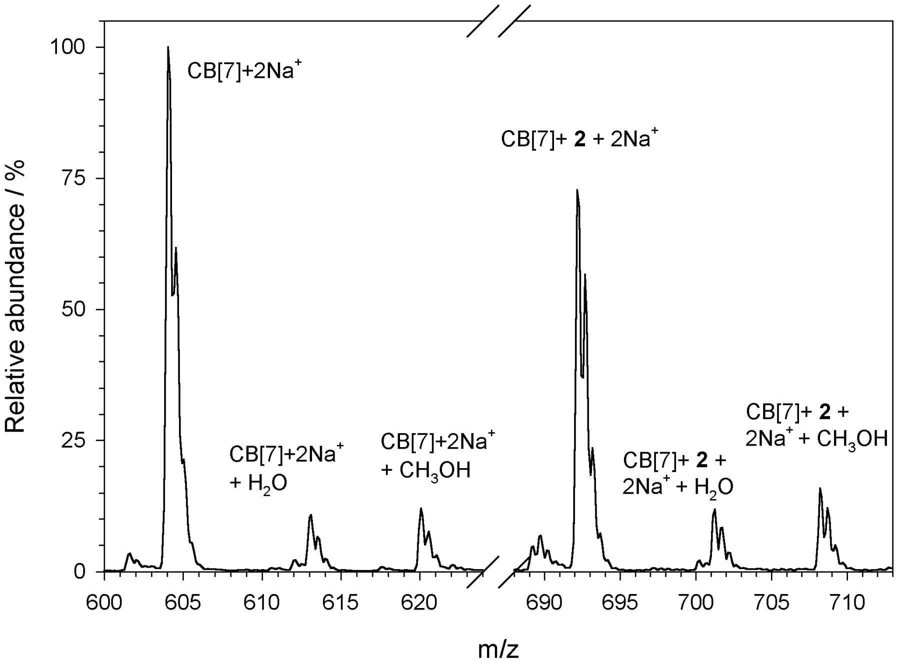

a
b
c
d

Figure 2S. Positive ESI-MS spectra of water/MeOH solution (1/1 v/v) containing CB7 (2 mM), ketone **2** (1 mM) and NaOAC 3 mM (a) or KOAc 3 mM (b). Mass spectra were recorded with Micromass ZMD ESI-MS spectrometer by using the following instrumental settings: desolvation gas ($N_2$) 240 L/h; cone gas (skimmer): 20 L/h; desolvation temp. 140° C; capillary voltage: 3.2 kV; cone voltage: 20-25 V; hexapole extractor: 3 V.

***a***



***b***

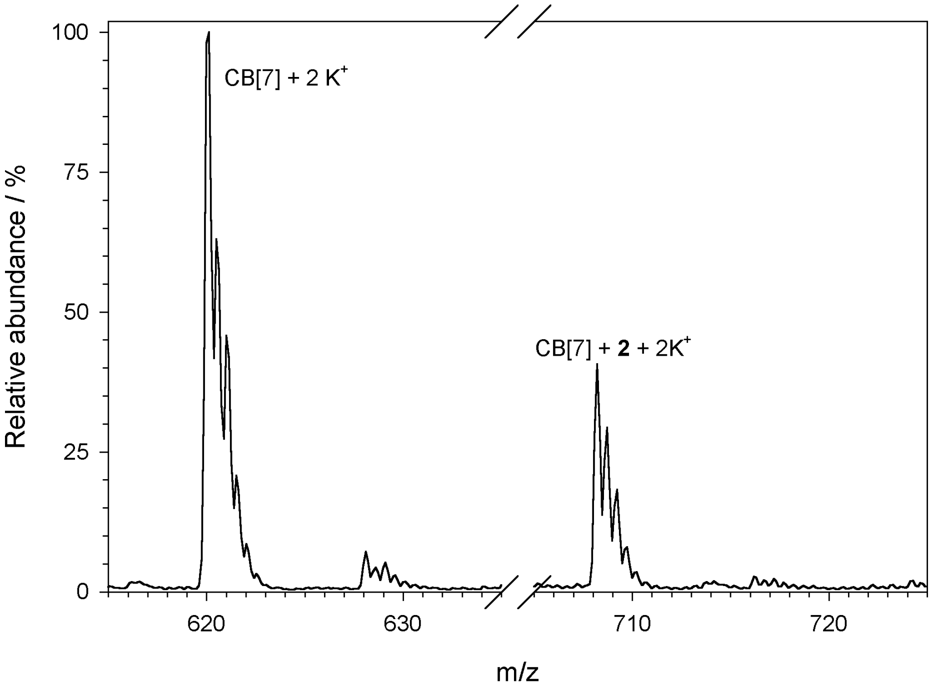


Figure 3S. Room temperature (298 K) benzyl region of $^1$H NMR spectra in $D_2O$ of ethyl benzyl ketone (2.0 mM) recorded in the presence of different amount of CB7.

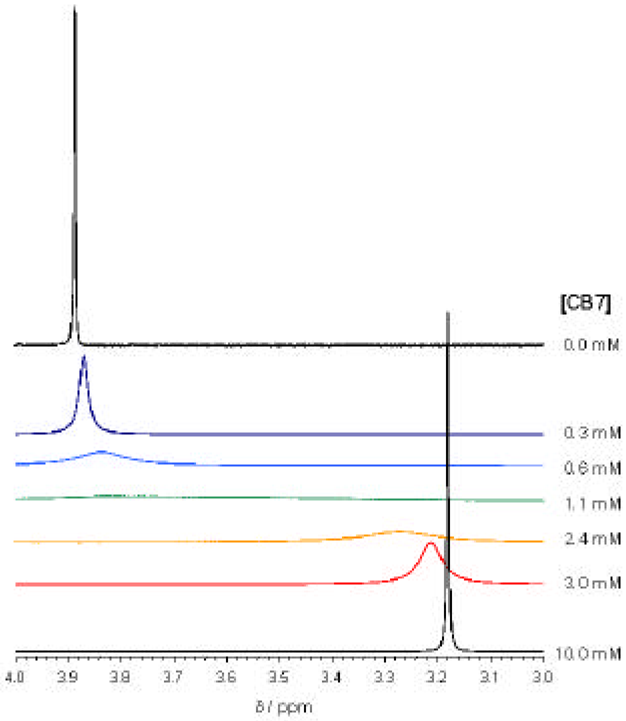


Figure 4S. $^1$H NMR spectra of CB7 2mM in $D_2O$ solution in recorded in the absence (a) and in the presence of 0.8 mM benzyl *tert*-butyl ketone (b); 0.8 mM benzyl *tert*-butyl ketone and KCl 0.24 M (c); 0.8 mM benzyl *tert*-butyl ketone and KCl 0.24 M (d). Red and blue circles refer to the free and to the complexed host signals, respectively.

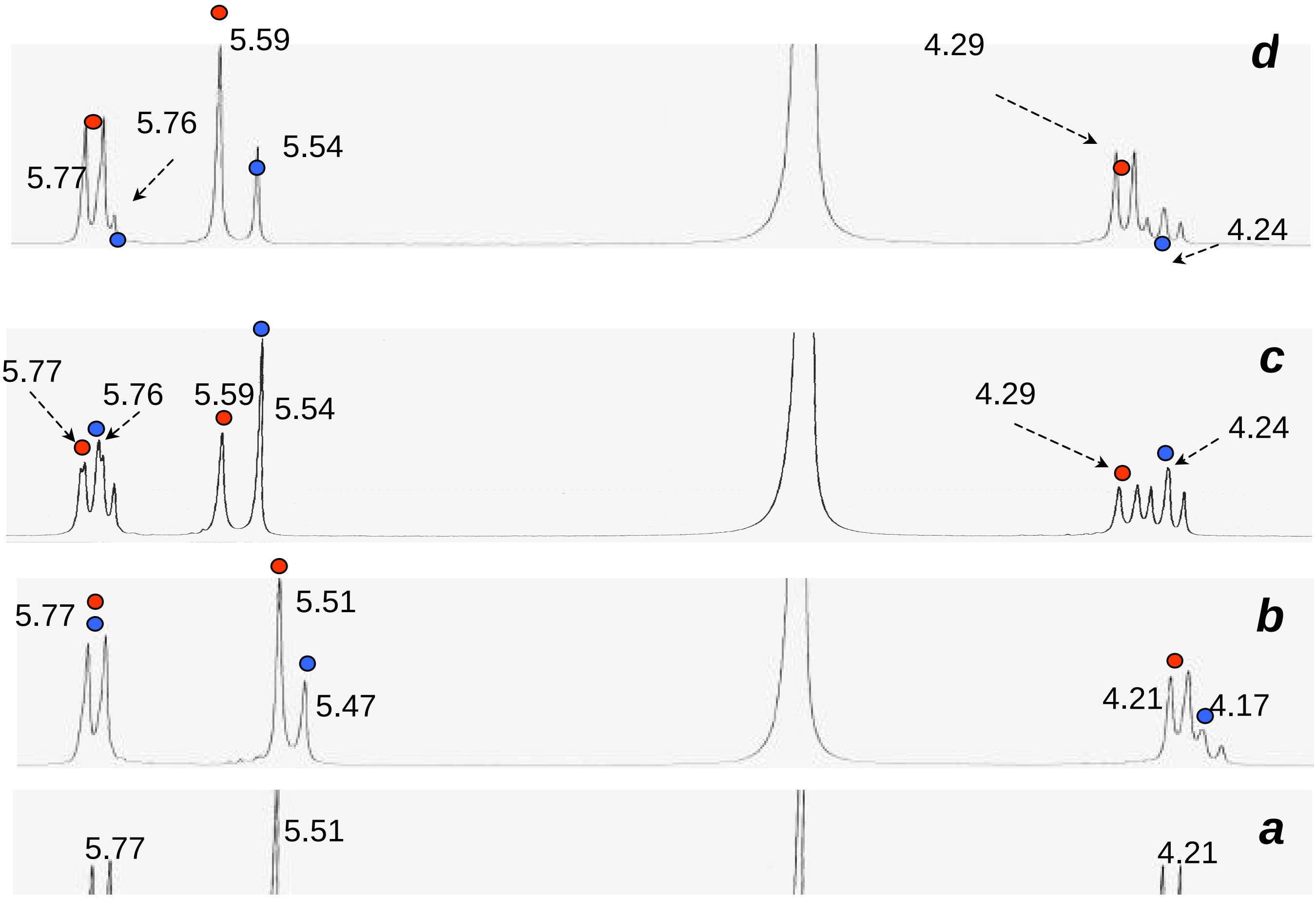


Figure 5S. 2D ROESY region (600 MHz, $D_2O$, 298 K) of CB7 1.4 mM recorded in the presence of an equimolar amount of di-*tert*-butyl ketone (**5**). The contour plots reflect the intermolecular cross peaks connecting NOE interaction of the methyl protons of the *tert*-butyl groups of the guest molecule with the methylene hydrogen of the macrocyclic host pointing toward the carbonyl portals and resonating at 5.77 ppm.