Electronic Supplementary Information

Encapsulation of charge-diffuse peralkylated onium cations in the cavity of cucurbit[7]uril

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General experimental details

The cucurbit[7]uril was prepared and characterized by Day's method,[1] while the cationic guests and competitive guests were used as received (Sigma-Aldrich, Alfa Aesar). The ^{1}H and ^{31}P NMR chemical shift titrations and competitive NMR binding experiments (Bruker Avance 400 MHz instrument) were carried out at 25 ˚C in D_2O using a 0.050 dm^3 mol^{-1} NaOAc/HOAc buffer (pD 4.75) with 1.0 mmol dm^{-3} guest and, in the case of the competition experiments (with 1,2-phenylenediammonium ($K_{CB[7]}$ = (8.04 ± 1.28) x 10^4 dm^3 mol^{-1}), 1,4-phenylenediammonium ((2.07 ± 0.33) x 10^6 dm^3 mol^{-1}), or 3-trimethylsilylpropionic acid-2,2,3,3-d_4 ((1.82 ± 0.22) x 10^7 dm^3 mol^{-1})),[2] 1.0 mmol dm^{-3} competitor in the presence of a slight deficiency of CB[7] using Isaac's methods for stability constant and error calculations (Table S1).[2] The gas-phase energy-minimization calculations (Fig. S1-S9) were perfomed using Chem3D Pro 11.0 software (CambridgeSoft).

1. A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.* 2001, **66**, 8094.
2. S. Liu, C. Ruspic, P. Mukhopadhyay, S. Chakrabarti, P. Y. Zavalij and L. Isaacs, *J. Am. Chem. Soc.* 2005, **127**, 15959.

Table S1. Host-guest stability constants ($K_{CB[7]}$) for the inclusion of peralkylated onium cations in CB[7] by competitive ^{1}H NMR experiments in D_2O.

Guest	Competitor Guest	$K_{CB[7]}$, $dm^3\ mol^{-1}$
$N(CH_3)_3^+$	1,2-phenylenediamine	$(1.2 \pm 0.4) \times 10^5$
	$P(CH_3)_4^+$	$(1.3 \pm 0.2) \times 10^5$
$N(CH_2CH_3)_4^+$	1,4-phenylenediamine	$(1.0 \pm 0.2) \times 10^6$
	$P(CH_3)_4^+$	$(1.3 \pm 0.3) \times 10^6$
	$N(CH_3)_4^+$	$(8.8 \pm 1.6) \times 10^5$
$N(CH_2CH_2CH_3)_4^+$	1,2-phenylenediamine	$(9.0 \pm 2.4) \times 10^3$
$N(CH_2CH_2CH_2CH_3)_4^+$	chemical shift titration	$(2.8 \pm 0.7) \times 10^3$
$P(CH_3)_4^+$	1,4-phenylenediamine	$(2.2 \pm 0.4) \times 10^6$
$P(CH_2CH_3)_4^+$	1,4-phenylendiamine	$(1.3 \pm 0.3) \times 10^5$
	$N(CH_2CH_3)_4^+$	$(8.3 \pm 1.5) \times 10^4$
	$P(CH_3)_4^+$	$(1.1 \pm 0.2) \times 10^5$
$S(CH_3)_3^+$	1,2-phenylenediamine	$(3.4 \pm 0.6) \times 10^4$
	$P(CH_3)_4^+$	$(2.9 \pm 0.5) \times 10^4$
$S(CH_2CH_3)_4^+$	1,4-phenylenediamine	$(5.2 \pm 0.9) \times 10^6$
	$P(CH_2CH_3)_4^+$	$(1.3 \pm 0.2) \times 10^7$
	$S(CH_3)_3^+$	$(1.2 \pm 0.2) \times 10^7$
$N(CH_3)_3(CH_2Ph)^+$	1,4-phenylenediamine	$(2.0 \pm 0.3) \times 10^8$
	3-trimethylsilylpropionic acid	$(3.0 \pm 0.4) \times 10^8$
	$N(CH_2CH_3)_4^+$	$(2.7 \pm 0.9) \times 10^8$
	$P(CH_3)_4^+$	$(1.2 \pm 0.2) \times 10^8$

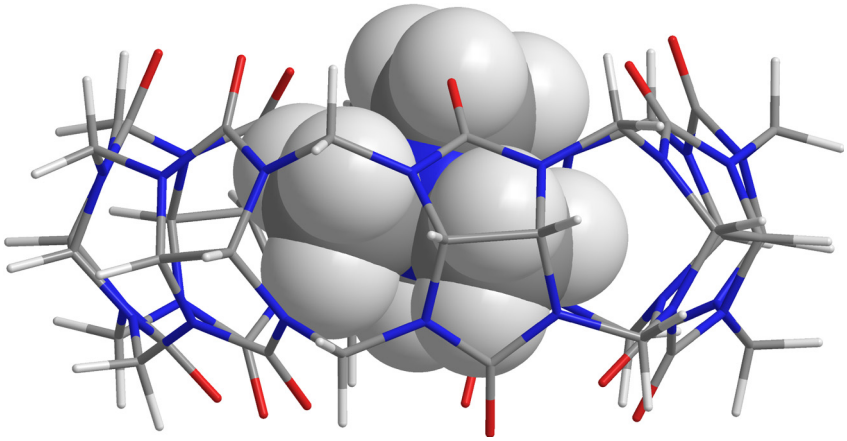

Figure S1 Energy-minimized structure of $\{NMe_4 \bullet CB[7]\}^+$ with the CB[7] shown as sticks and the guest as space-filling atoms.

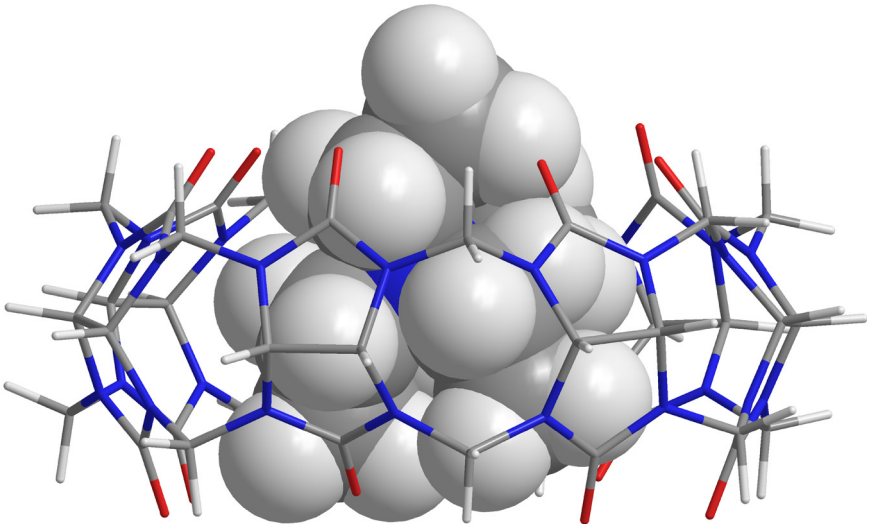

Figure S2 Energy-minimized structure of $\{NEt_4 \bullet CB[7]\}^+$ with the CB[7] shown as sticks and the guest as space-filling atoms.

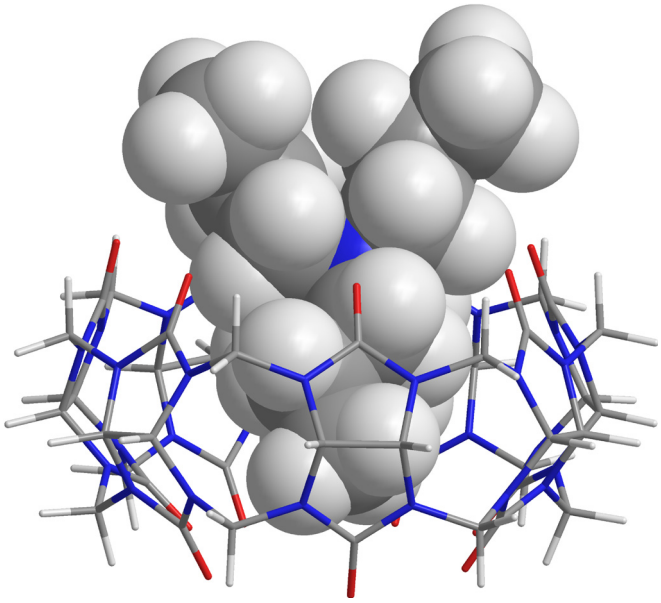

Figure S3 Energy-minimized structure of $\{N^nPr_4 \bullet CB[7]\}^+$ with the CB[7] shown as sticks and the guest as space-filling atoms.

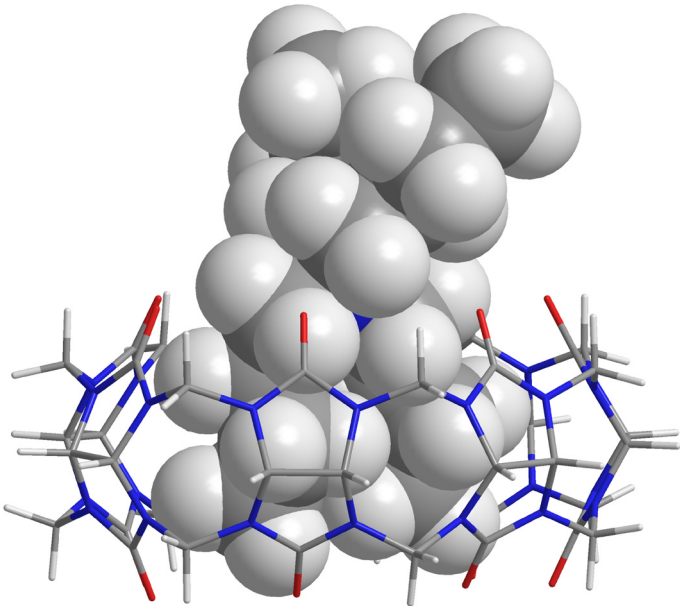

Figure S4 Energy-minimized structure of $\{N^nBu_4 \bullet CB[7]\}^+$ with the CB[7] shown as sticks and the guest as space-filling atoms.