

Ion-pair separation *via* selective inclusion/segregation processes

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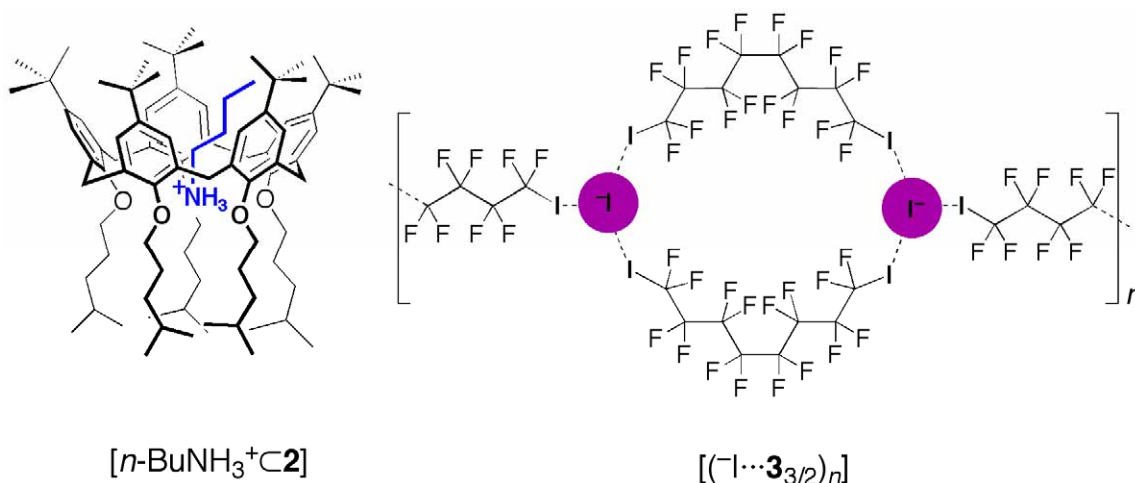
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Electronic Supplementary Information

Experimental

General. Melting points were determined on a Kofler melting point apparatus and are uncorrected. Unless otherwise stated, ^1H (300 MHz), ^{19}F (282 MHz), and ^{13}C (75 MHz) NMR spectra were obtained at 25 °C in CDCl_3 (using TMS and CFCl_3 as internal standards). ESI mass spectra were acquired on a Mariner ESI-TOF instrument using $\text{CHCl}_3/\text{MeOH}$ 2:1 v/v (positive ion mode). All solvents and chemicals were reagent grade and were used without further purification. Calix[5]arene **2** was prepared according to a literature procedure.¹ *n*-Butylammonium iodide was obtained by adding aqueous hydroiodic (57 wt. %, 1 eq.) to a methanolic solution of *n*-butylamine; subsequent evaporation of the solvents, and final precipitation of the residue formed from $\text{CH}_3\text{OH}/\text{Et}_2\text{O}$.



Formation and Characterization of “Supramolecular Salt” 1. Solid calix[5]arene **2** (37.0 mg; 0.030 mmol) was added to a solution of $n\text{-BuNH}_3^+\text{I}^-$ (6.0 mg, 0.030 mmol) and 1,8-diodoperfluorooctane **3** (29.4 mg, 0.045 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for a few minutes at r.t., and then evaporated to dryness. The solid residue was dissolved in toluene (5 mL) and the solution, placed into a vial, and left to slowly (*ca.* 60 days) evaporate inside a sealed chamber containing vaseline. **1** was isolated as off-white crystals, mp 235–236 °C (dec.). ^1H NMR^{2,3} δ –1.95 to –1.84 (m, $\beta\text{-CH}_2$, 2 H),* –1.19 to –1.06 (br m, $\alpha\text{-CH}_2$, 2 H),* –0.81 to –0.68 (m, $\gamma\text{-CH}_2$, 2H),* –0.38 (t, J = 7.2 Hz, CH_3 , 3H),* 0.95 (d, J = 6.7 Hz, $\text{CH}(\text{CH}_3)_2$, 30 H), 1.14 (s, $\text{C}(\text{CH}_3)_3$, 45 H), 1.20–1.36 (m, $\text{OCH}_2\text{CH}_2\text{CH}_2$, 10 H), 1.60 (sept, J = 6.7 Hz, $\text{CH}(\text{CH}_3)_2$, 5 H), 1.96–2.06 (m, $\text{OCH}_2\text{CH}_2\text{CH}_2$, 10 H),

¹ F. Arnaud-Neu, S. Fuangwasdi, A. Notti, S. Pappalardo and M. F. Parisi, *Angew. Chem. Int. Ed.*, 1998, **37**, 112.

² In addition to the peaks of the $n\text{-BuNH}_3^+\cdot\mathbf{2}$ complex, reported above, the spectrum shows a set of low intensity peaks consistent with the presence of about 5% of uncomplexed host and guest.

³ Resonances referring to the *endo*-cavity-included *n*-butylammonium ion guest are designated with an asterisk.

3.44 and 4.38 (AX, $J = 13.4$ Hz, ArCH₂Ar, 10 H), 4.00 (t, $J = 8.3$ Hz, OCH₂CH₂CH₂, 10 H), 5.57 (br s, NH₃⁺, 3H),* and 7.19 (s, ArH, 10 H) ppm; ¹³C NMR³ δ 13.5 (q),* 18.8 (t),* 22.6 (q), 27.2 (t),* 27.88 (d), 27.92 (t), 29.0 (t), 31.1 (q), 34.2 (s), 34.4 (t), 37.8 (t),* 76.4 (t), 94.4 (tt, $J = 320.8$, 42.0 Hz, CF₂I), 104.7–114.6 (m, CF₂), 126.8 (d), 133.0 (s), 133.0 (s), 148.0 (s) and 150.5 (s) ppm. ¹⁹F NMR –122.39 to –122.10 (m, CF₂CF₂CF₂CF₂I, 4F), –121.58 to –121.30 (m, CF₂CF₂CF₂CF₂I, 4F), –113.95 to –113.80 (m, CF₂CF₂CF₂CF₂I, 4F), and –62.26 (t, $J = 15.0$ Hz, CF₂CF₂CF₂CF₂I, 4F) ppm. ESI-MS m/z [2·NH₄]⁺ 1249.6, [2·K]⁺ 1270.6, and [2·*n*-BuNH₃]⁺ 1304.7.

¹⁹F NMR Studies. Upon addition of 1.5 equiv. of 1,8-diodoperfluorooctane **3** to a 50 mM CDCl₃ solution of [*n*-BuNH₃⁺·**2**]⁺I[–] (previously obtained, by solvent removal, from a solution (CDCl₃/CD₃OD, 9:1) of equimolar amounts of **2** and *n*-BuNH₃⁺I[–]) the resonance of the –CF₂I group of **3** undergoes an upfield induced shift $\Delta\delta = 2.76$ ppm ($\Delta\delta = \delta_3 - \delta_{\{3 + [n\text{-BuNH}_3^+\cdot\mathbf{2}]\}^-}$), fully consistent with halogen bonding formation.⁴

Crystal Structure Determination. Data were collected at 123(2) K on a Bruker APEX CCD area detector diffractometer, equipped with an OXFORD low temperature device, using MoK α radiation ($\lambda = 0.71073$ Å), graphite monochromator; ω and φ scans. Data collection and data reduction were performed by SMART and SAINT, absorption correction, based on multi-scan procedure, by SADABS.⁵ The structure was solved by SIR2002,⁶ and refined on all independent reflections by full-matrix least-squares based on F_o^2 by using SHELXL-97⁷. H atoms were riding in calculated positions, 1301 refined parameters. CCDC 698062 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

⁴ P. Metrangolo, W. Panzeri, F. Recupero and G. Resnati, *J. Fluorine Chem.*, 2002, **114**, 27.

⁵ Bruker, SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 1999.

⁶ M. C. Burla, M. Camalli, B. Carrozzini, G. L. Casciarano, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2003, **36**, 1103.

⁷ G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1997.

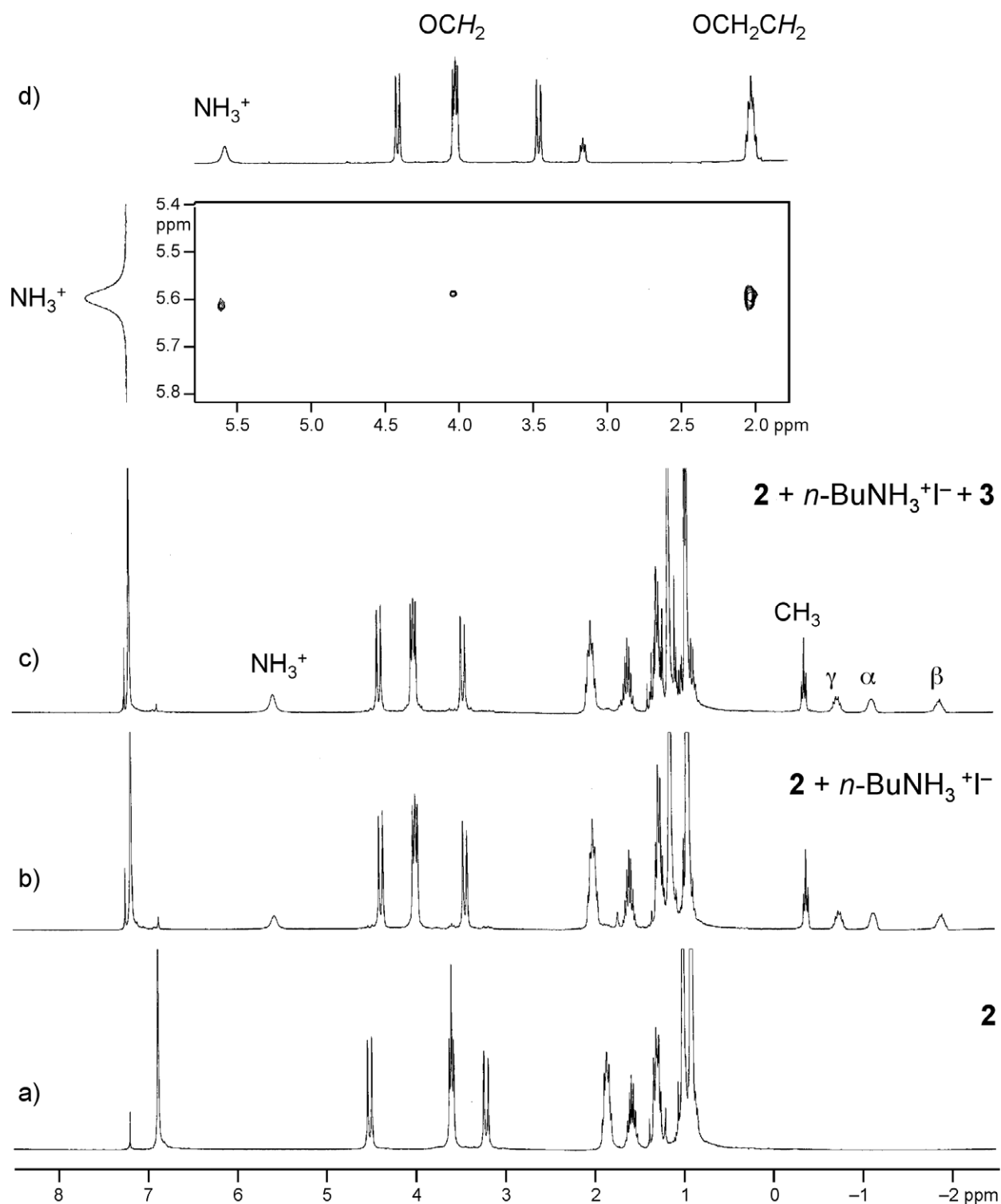


Fig. S1 ^1H NMR spectra (300 MHz, CDCl_3 , 295 K) of: a) **[2]** = 50 mM; b) **[2]** = $[n\text{-BuNH}_3^+\text{I}^-]$ = 50 mM; c) **[2]** = $[n\text{-BuNH}_3^+\text{I}^-]$ = 50 mM and **[3]** = 75 mM; and d) section of the TROESY (500 MHz, CDCl_3) spectrum of $n\text{-BuNH}_3^+\text{C}2$, obtained from **[2]** and $[n\text{-BuNH}_3^+\text{I}^-]$ 50 and 75 mM, respectively.

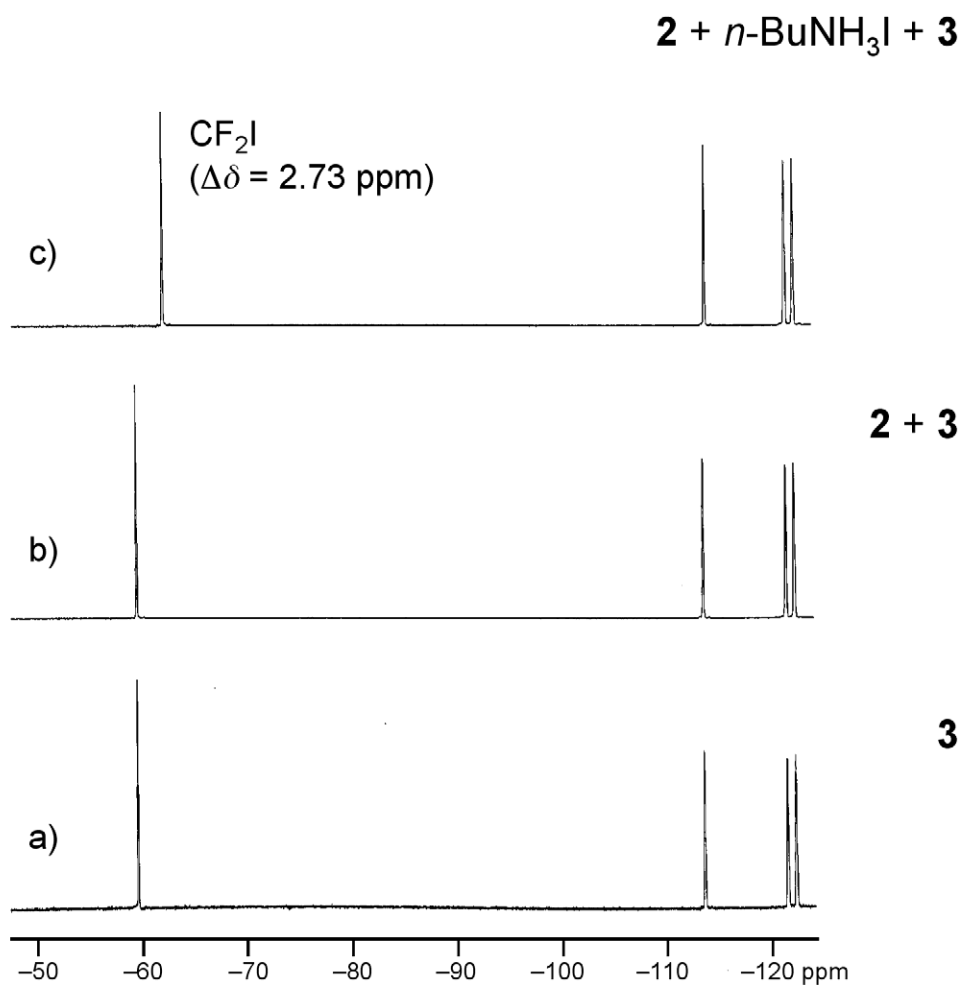


Fig. S2 ¹⁹F NMR spectra (282 MHz, CDCl₃, 295 K) of: a) [3] = 75 mM; b) [2] = 50 mM and [3] = 75 mM; c) [2] = [*n*-BuNH₃⁺I⁻] = 50 mM and [3] = 75 mM.

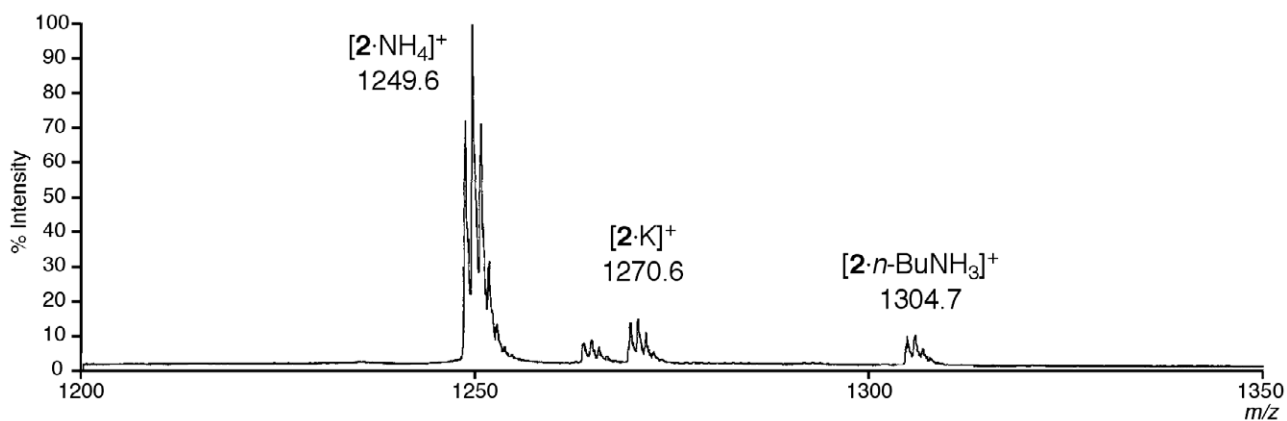


Fig. S3 ESI-MS spectrum (positive ion mode) of the 'supramolecular salt' **1**.