An Anion-Binding Zwitterionic Capsule Based on Electrostatic Interactions Between Self-Complementary Hemispheres

Ammie L. Cresswell, Marc-Oliver M. Piepenbrock, and Jonathan W. Steed

Supplementary Material

Fig. S1 ¹H NMR spectroscopic titration data for 2-HPF₆·2H₂O with NBu₄⁺Cl⁻ in DMSO solution.
Fig. S2 $^1$H NMR spectroscopic titration data for 2·HPF$_6$·2H$_2$O with NBu$_4^+$Br$^-$ in DMSO solution.
Fig. S3: $^1$H NMR spectra of 1 before (green) and after (red) treatment with AgPF$_6$.

**Synthesis**
All chemicals were purchased from commercial sources. $^1$H NMR spectra were performed on Bruker Avance 400MHz, Mercury 400MHz and Inova 500MHz instruments. $^{13}$C HMR spectroscopy were performed on a Inova-500MHz, operating at 125 MHz. Mass spectrometry was performed using MALDI+ on a Voyager Spectrometer. IR spectroscopy was performed on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

**Synthesis of 2**

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\begin{align*}
\text{H}_{2}\text{O}, \text{NaOH} & \quad \rightarrow \\
\text{3} & \quad + \quad 3\text{NaBr}
\end{align*}
\]
Tris-ethylnicotinium tripod bromide salt (3) was dissolved in 20ml water. Sodium hydroxide (0.138 g, 3.45 mmol) was dissolved in 20ml water and the solution added dropwise. The mixture was then stirred for an hour and evaporated to dryness to a yellow-orange sticky solid. The solid was washed with tetrahydrofuran (20 ml) and then recrystallised from a minimum volume of ethanol to yield white crystals. Yield: 0.580g, 1.02mmol, 94%. 1H NMR (400 MHz, D2O) δ 8.97 (s, 1H, Hd), 8.80 (d, 1H, Hg), 8.67 (d, 1H, He), 8.03 (t, 1H, Hf), 6.04 (s, 2H, Hc), 2.59 (q, 2H, Hb), 0.81 (t, 3H, Ha). Anal. (after drying) calc. for C33H33N3O6⋅5H2O: C, 53.00; H, 5.79; N, 5.62; Br, 0.0 %. Found: C, 52.89; H, 5.89; N, 5.48; Br, 0.00%.

Synthesis of 2·HPF6·2H2O

Compound 2 (200mg) was dissolved in 20ml water. 20 equivalents of hexafluorophosphoric acid was added to the solution and stirred for an hour. The white product precipitated out of solution and was washed with water. Yield: 0.1526g, 0.213mmol, 61%. 1H NMR (400 MHz, DMSO) δ 9.51 (s, 1H, Hd), 8.96 (d, 1H, Hg), 8.68 (d, 1H, He), 8.16 (t, 1H, Hf), 6.13 (s, 1H, Hc), 2.67 (q-broad, 2H, Hb), 0.77 (t, 3H, Ha). IR ν(PF6) 832 cm⁻¹. Anal. (hygroscopic material) calc. for C33H34N3O6PF6⋅5.5H2O: C, 43.47; H, 4.97; N, 4.61 %. Found: C, 43.45; H, 4.26; N, 4.57 %.

Synthesis of 1
A similar procedure to the literature method was employed to prepare the tris(isonicotinium) tripod al ester precursor. Yield (based on 3.00g tri-1,3,5-bromomethyl-2,4,6-triethyl benzene): 5.64g, 6.30 mmol, 82 % 1H NMR (400 MHz, D2O) δ 8.90 (d, J = 6.7, 6H, Hd), 8.47 (d, J = 6.9, 6H, He), 6.07 (s, 6H, Hc), 4.40 (q, J = 7.1, 6H, Hf), 2.57 (q, J = 7.6, 6H, Hb), 1.31 (t, J = 7.2, 9H, Hg), 0.81 (t, J = 7.3, 9H, Hh). 13C NMR (126 MHz, D2O) δ 163.20, 151.27, 145.99, 144.95, 128.28, 127.73, 64.44, 58.57, 24.17, 14.32, 13.31. Anal. (hygroscopic material) calc. for C39H48N3O6Br3 ⋅ 1.25H2O: C, 49.85; H, 5.69; N, 4.47 %. Found: C, 49.85; H, 5.36; N, 4.47 %.

To make the carboxylate a similar procedure was employed to that described for 2. Yield: 0.5408g, 0.437 mmol, 81 %. 1H NMR (400 MHz, D2O) δ 8.70 (d, J = 6.6, 6H, Hd), 8.18 (d, J = 6.6, 6H, He), 5.99 (s, 6H, Hc), 2.56 (q, J = 7.4, 6H, Hb), 0.79 (t, J = 7.4, 9H, Hg). 13C NMR (126 MHz, D2O) δ 168.83, 153.38, 150.90, 144.17, 127.92, 127.46, 57.88, 24.04, 14.27. –ve ion ESI-MS 1213 (M –). Anal. (partially dehydrated, hygroscopic material) calc. for C66H66N6O12NaBr ⋅ 4.5H2O: C, 56.61; H, 6.05; N, 6.00 %. Found: C, 56.94; H, 5.99; N, 6.00 %.

**Crystallographic Notes**

Hydrogen atoms attached to carbon were placed in idealised positions and allowed to ride. Water hydrogen atoms were located by difference Fourier synthesis and set to ride on the parent atoms. For Na[(I)2Br] the disorder (mixed Na / H2O site) meant that no water hydrogen atoms could be reliably located and they were not included within the model. In the structure of 2⋅9H2O some evidence of water disorder was apparent which was modelled in terms of 50 % occupancy for affected water oxygen atoms. Hydrogen atoms were not located for these disordered water molecules. In the case of 2⋅9H2O relatively weak diffraction resulting in data only to 23.3° in θ. For 2⋅9H2O the largest residual peak is associated with a minor disordered component of C72 that is was not possible to model. For 2⋅HPF6⋅2H2O six least squares restraints were applied to idealise the geometry of the water molecules.

**References**