

## Supplementary Information

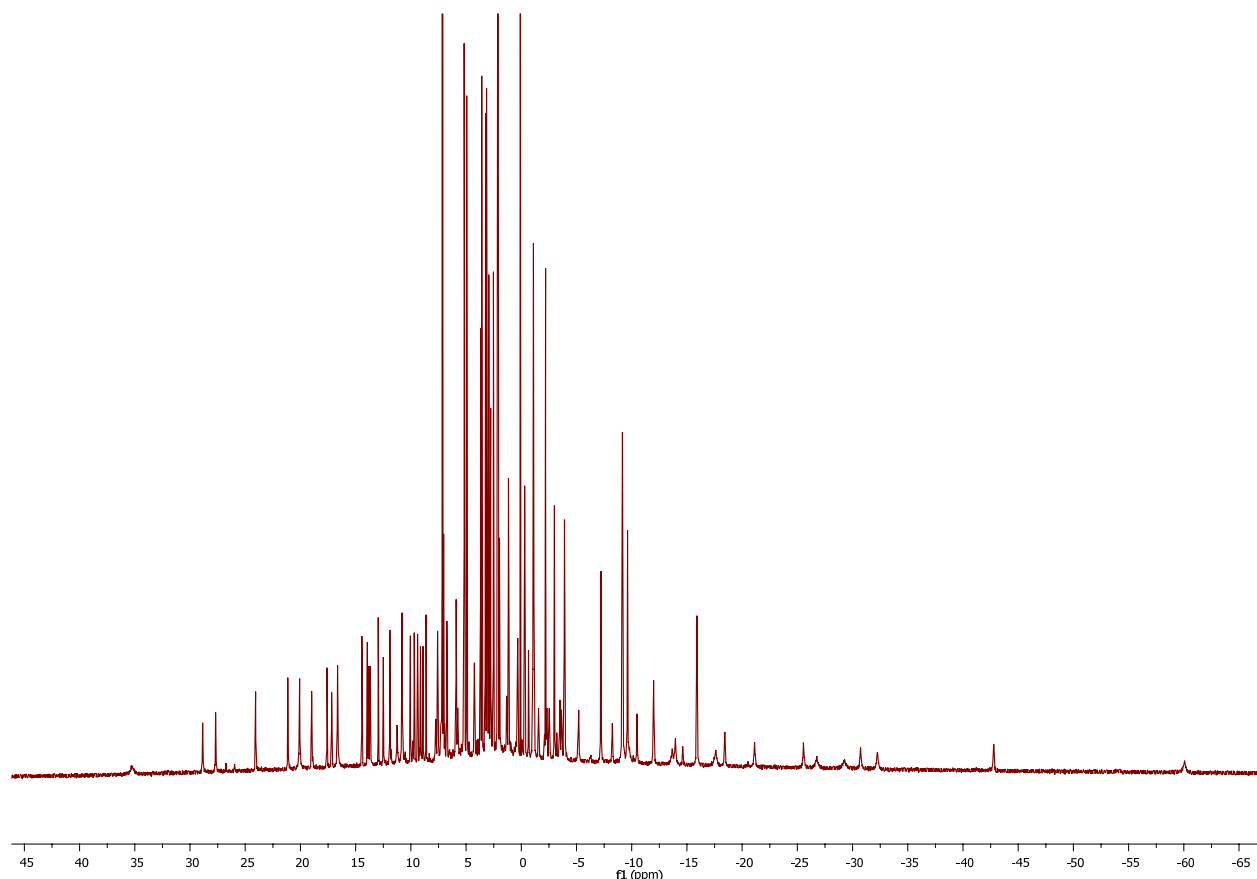
### Constructing cerium supramolecular wheels and encapsulating uranium with a Schiff-base calixpyrrole ligand

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#### Experimental:

Unless otherwise stated, all reactions were carried out using standard Schlenk techniques under an atmosphere of dinitrogen or in a dinitrogen filled glove-box. Solvents (hexanes, toluene, diethyl ether and THF) were dried by passage through Vacuum Atmospheres solvent towers and stored over 4 Å molecular sieves. Deuteriated benzene and tetrahydrofuran were dried over potassium and then distilled under reduced pressure. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-360 spectrometer operating at 360.75 MHz and resonances are reported relative to tetramethylsilane ( $\delta = 0$  ppm). Coupling constants are quoted in Hertz and chemical shifts in  $\delta$  (ppm) and at a temperature of 298 K. Elemental analyses were carried out by Mr. Stephen Boyer at the London Metropolitan University. IR spectra were recorded in the range 400-4000 cm<sup>-1</sup> on a Jasco 410 FT-IR spectrophotometer as Nujol mulls between KBr discs, unless otherwise stated. [U{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>]<sup>1</sup> (prepared from UI<sub>3</sub>)<sup>2</sup> was synthesised as reported in the literature. All other compounds were used as purchased without further purification.

**Synthesis of [{Ce(HL)}<sub>3</sub>]** - To a stirred solution of H<sub>4</sub>L ( 250mg, 0.349 mmol) in toluene (5 mL) was added dropwise a solution of [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] (217 mg, 0.349 mmol) in toluene (5 mL) at room temperature. The resulting orange mixture was stirred for 4 h, after which the solvent was removed under vacuum. The resulting orange solid was washed with cold hexanes (0 °C, 10 mL) and dried under vacuum to yield 208 mg, 70% of [Ce(HL)]<sub>3</sub>. Single crystals of [{Ce(HL)}<sub>3</sub>] were grown from a saturated C<sub>6</sub>D<sub>6</sub> solution.



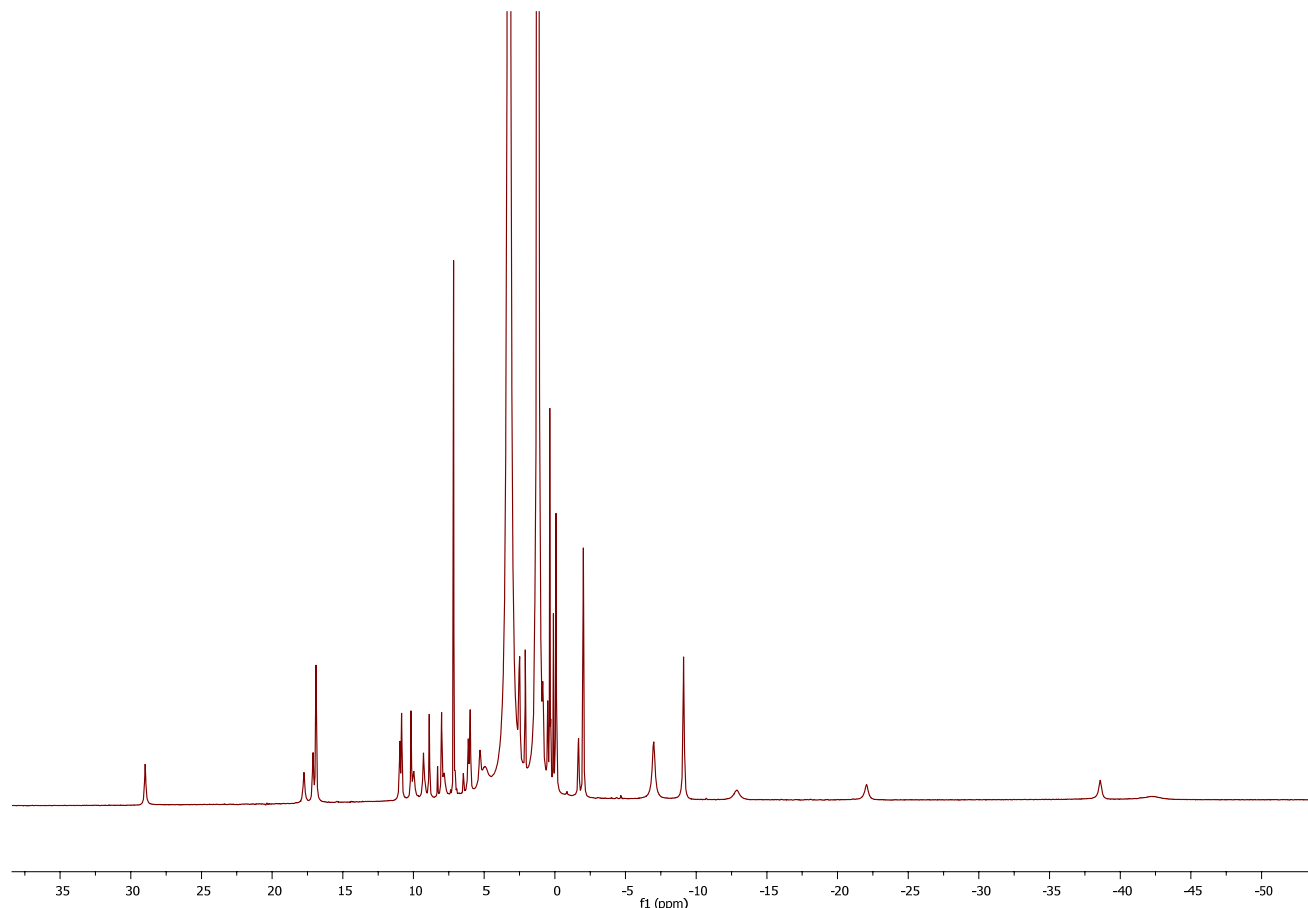
**Figure S1:**  $^1\text{H}$  NMR spectrum of  $[\{\text{Ce}(\text{HL})\}_3]$

$^1\text{H}$  NMR: ( $\text{C}_6\text{D}_6$ , 298 K, 360 MHz) :  $\delta$  H 35.00 (1H), 28.83 (1H), 27.67 (1H), 24.06 (1H), 21.13 (1H), 20.06 (2 x 1H), 18.97 (1H), 17.58 (1H), 17.17 (1H), 16.63 (2 x 1H), 14.43 (1H), 13.93 (1H), 13.80 (1H), 13.66 (1H), 12.95 (1H), 12.49 (1H), 11.90 (1H), 11.23 (1H), 10.79 (3 x 1H), 10.03 (1H), 9.68 (1H), 9.38 (1H), 9.11 (1H), 8.89 (1H), 8.62 (1H), 7.57 (1H), 7.52 (1H), 6.73 (1H), 5.89 (2 x 1H), 5.75 (1H), 5.16 (2 x 3H), 4.93 (3H), 4.24 (2H), 3.68 (3H), 3.56 (3H), 3.22 (3H), 3.13 (3H), 3.06 (3H), 2.93 (3H), 2.76 (3H), 2.51 (3H), 2.17 (3H), 1.96 (3H), 1.29 (2H), 1.15 (3H), 0.31 (2H), 0.09 (2 x 2H), -0.32 (3H), -0.67 (2H), -1.56 (2H), -2.20 (3H), -2.30 (1H), -3.00 (3H), -3.22 (1H), -3.52 (2H), -3.66 (2H), -3.92 (3H), -5.20 (2H), -7.22 (2 x 3H), -8.26 (2H), -9.18 (2 x 3H), -9.64 (3H), -10.50 (1H), -11.99 (2H), -13.69 (1H), -13.96 (1H), -14.64 (1H), -15.92 (3H), -17.64 (1H), -18.45 (1H), -21.14 (1H), -25.58 (1H), -26.78 (1H), -29.27 (1H), -30.73 (1H), -32.29 (1H), -42.79 (1H), -60.08 (1H).

Analysis. Calculated for  $\text{C}_{138}\text{H}_{147}\text{N}_{24}\text{Ce}_3$ : C, 64.69; H, 5.86; N, 13.12. Found: C, 64.77; H, 5.86; N, 13.02 %.

IR (Nujol): 3408.08 (N-H), 1602.80 (C=N), 1572.42 (C=N)  $\text{cm}^{-1}$ .

**Synthesis of [Ce(THF)<sub>2</sub>(HL)]** – A repeat of the reaction to form [ $\{Ce(HL)\}_3$ ] in THF instead of toluene afforded the solvated complex [Ce(THF)<sub>2</sub>(HL)] in 251 mg, 72 % yield after an identical work-up procedure. The THF adduct can also be synthesised by the addition of THF to a toluene solution of [ $\{Ce(HL)\}_3$ ]. Single crystals of [Ce(THF)<sub>2</sub>(HL)] were grown from a saturated THF solution at -20 °C.



**Figure S2: <sup>1</sup>H NMR of [Ce(THF)<sub>2</sub>(HL)]**

<sup>1</sup>H NMR: (C<sub>4</sub>D<sub>8</sub>O, 298 K, 360 MHz) : δ H 29.14 (1H), 16.99 (1H), 16.79 (1H), 16.71 (1H), 16.56 (1H), 11.11 (1H), 10.72 (1H), 9.93 (1H), 9.56 (1H), 8.83 (1H), 8.66 (1H), 8.12 (2H), 7.83 (1H), 5.89 (2H), 5.66 (1H), 5.09 (2H), 4.78 (2H), 2.76 (1H), 2.67 (1H), 1.33 (3H), 1.24 (3H), 0.96 (2H), 0.53 (3H), 0.05 (1H), -0.31 (3H), -1.68 (2H), -2.14 (3H), -7.22 (2 x 3H), -9.47 (3H), -12.25 (2H), -22.86 (2H).

Analysis. Calculated for C<sub>55</sub>H<sub>68</sub>N<sub>8</sub>O<sub>2</sub>Ce: C, 65.34; H, 7.05; N, 10.69. Found: C, 65.20; H, 6.94; N, 10.85 %.

IR (Nujol): 3411.94 (N-H), 1597.97 (C=N) 1572.66 (C=N) cm<sup>-1</sup>.

**Synthesis of [U(L)]** - To a high pressure ampoule charged with H<sub>4</sub>L (100 mg, 0.139 mmol) and [U{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] (100 mg, 0.139 mmol) was added THF (20 mL) and the resultant brown solution heated to 80 °C overnight, during which time a red solution formed. Removal of the solvents under vacuum afforded [U(L)] as a red solid which was washed with hexane (2 x 5 mL), in a yield of 105mg, 80 %. Two separate batches of crystals suitable for X-ray diffraction were grown: (i) from a C<sub>6</sub>D<sub>6</sub> solution of [(UI)<sub>2</sub>(L)], which had been heated to 80 °C, and (ii) from a C<sub>6</sub>D<sub>6</sub> solution of [(UN''')(H<sub>2</sub>L)], which had been heated to 80 °C.

Analysis. Calculated for C<sub>60</sub>H<sub>52</sub>N<sub>8</sub>U: C, 58.10; H, 5.09; N, 11.78. Found: C, 57.93; H, 4.94; N, 11.84 %.

IR (Nujol) – 1559.65 (C=N) cm<sup>-1</sup>.

#### References:

- <sup>1</sup> L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin, and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248.
- <sup>2</sup> C. D. Carmichael, N. A. Jones, and P. L. Arnold, *Inorg. Chem.*, 2008, **47**, 8577.