

Electronic Supplementary Information

N-Alkyl calix[4]azacrowns for the selective extraction of uranium

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Table SI-1 : ¹H-NMR signals of NOCAC and NOCAC-UO₂²⁺.

	Ar-CH ₂ -Ar	Ar-H	O-CH ₂ -C(O)	Ar-OH	NH-CH ₂ -CH ₂ -N	NH-CO	[NRH] ⁺
NOCAC	AB	2 singlets	1 singlet	1 singlet	2 triplets	1 singlet	-
δppm	4.15 & 3.38	7.19 & 6.79	4.51	6.42	3.52 & 2.75	8.19	-
Complex NOCAC-UO₂²⁺	2 AB	4 singlets	AB	2 singlets	4 multiplets	Broad singlet	Broad singlet
δppm	4.32 & 3.46 4.13 & 3.43	7.13, 7.09, 6.90 & 6.87	4.88 & 4.66	7.61 & 7.30	4.37, 3.8, 3.7, & 3.59	9.42	10.19

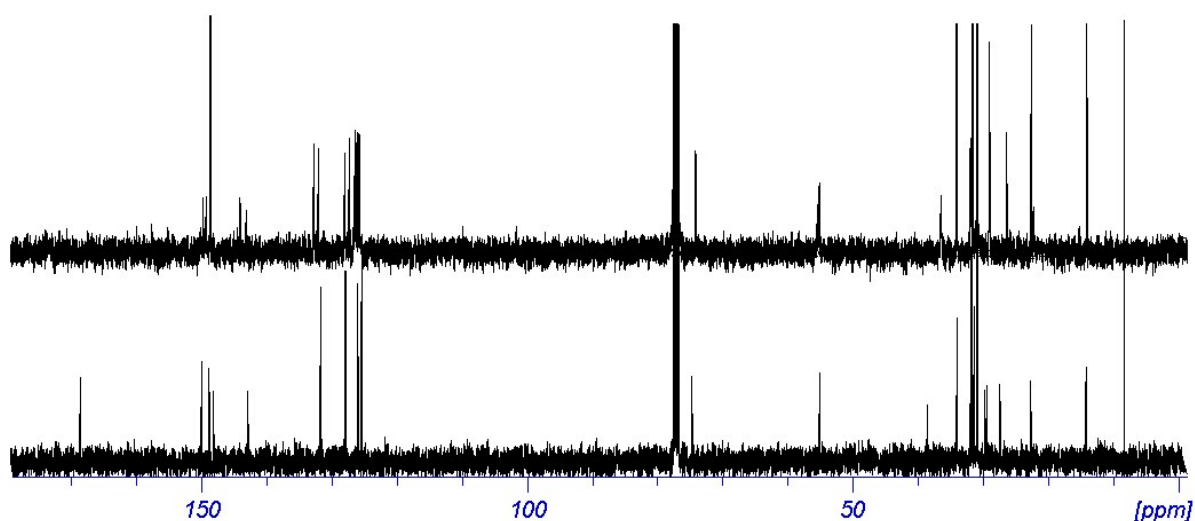


Figure SI-1: ¹³C-NMR spectra of the free ligand (bottom) and the complex (top) at [NOCAC]/[UO₂²⁺] = 1:2.

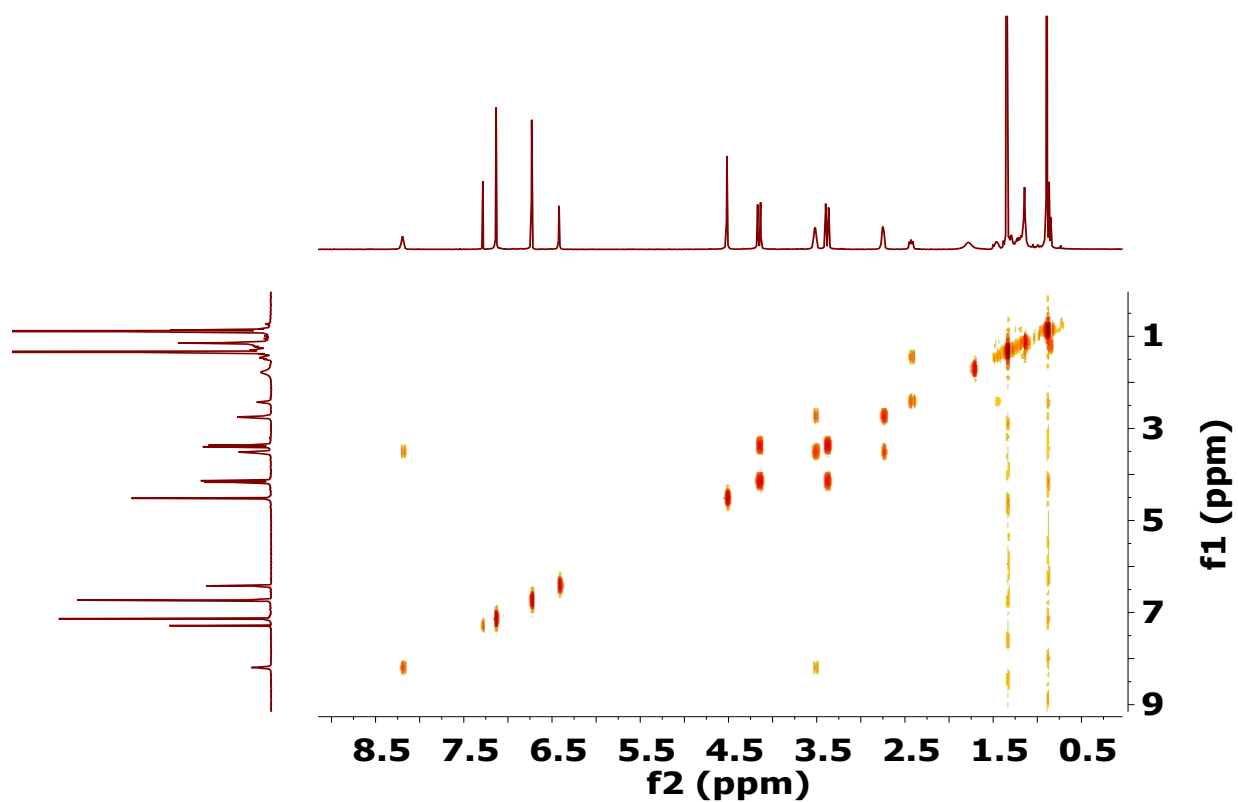


Figure SI-2: COSY-NMR spectrum of free LI : NOCAC.

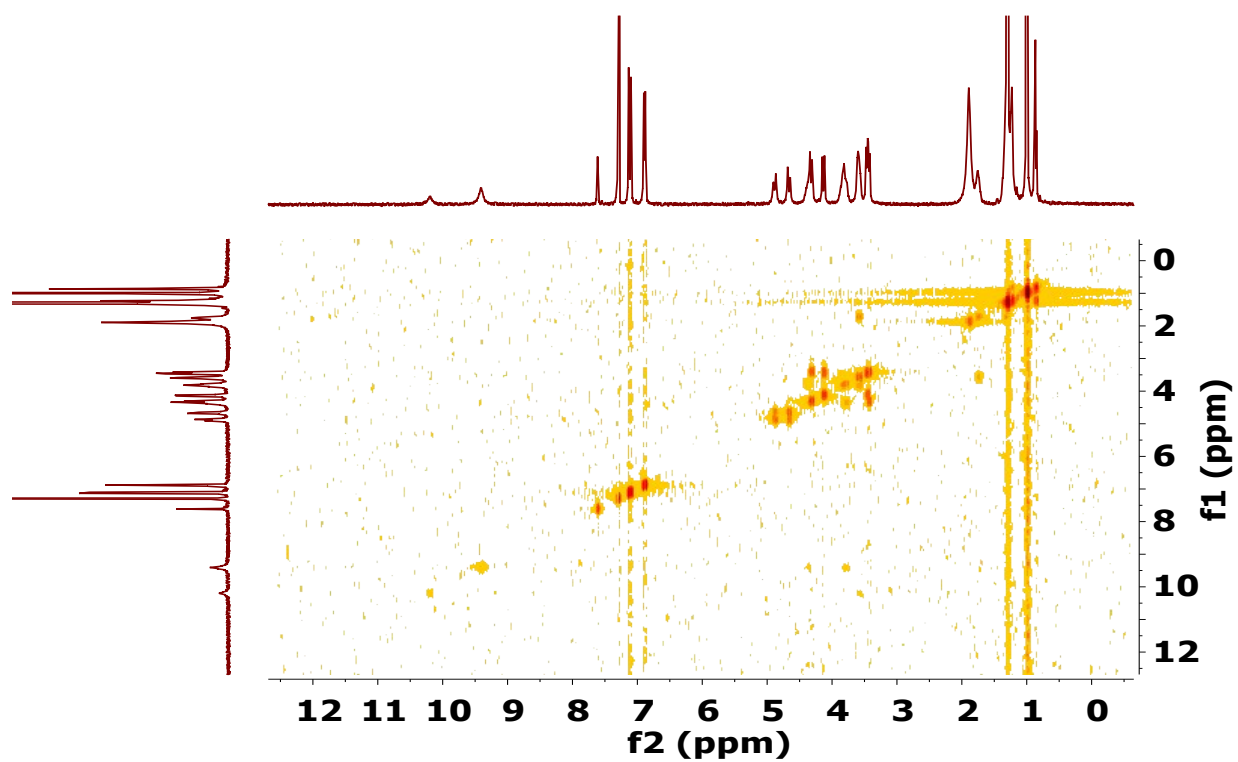


Figure SI-3: COSY-NMR spectrum of the LI-U complex, $[\text{NOCAC}]/[\text{UO}_2^{2+}] = 1:2$.

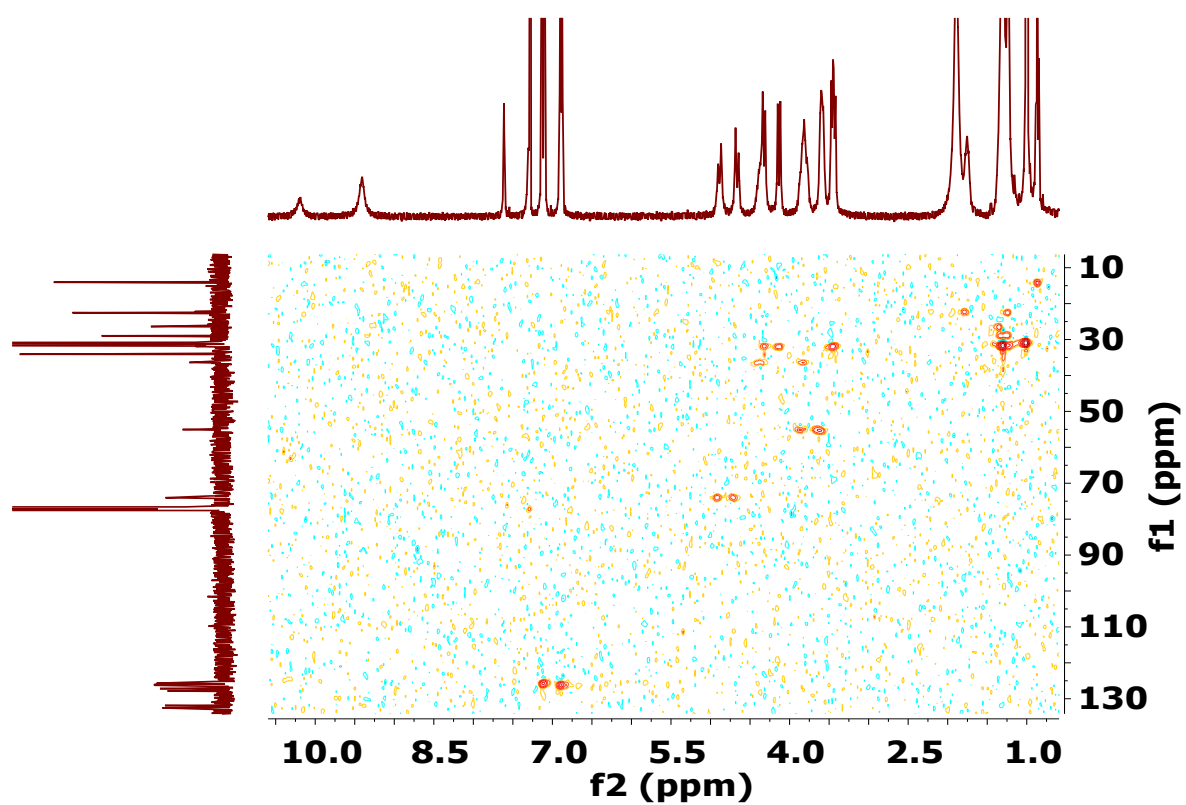


Figure SI-4: HSQC spectrum of the LI-U complex, $[\text{NOCAC}]/[\text{UO}_2^{2+}] = 1:2$.

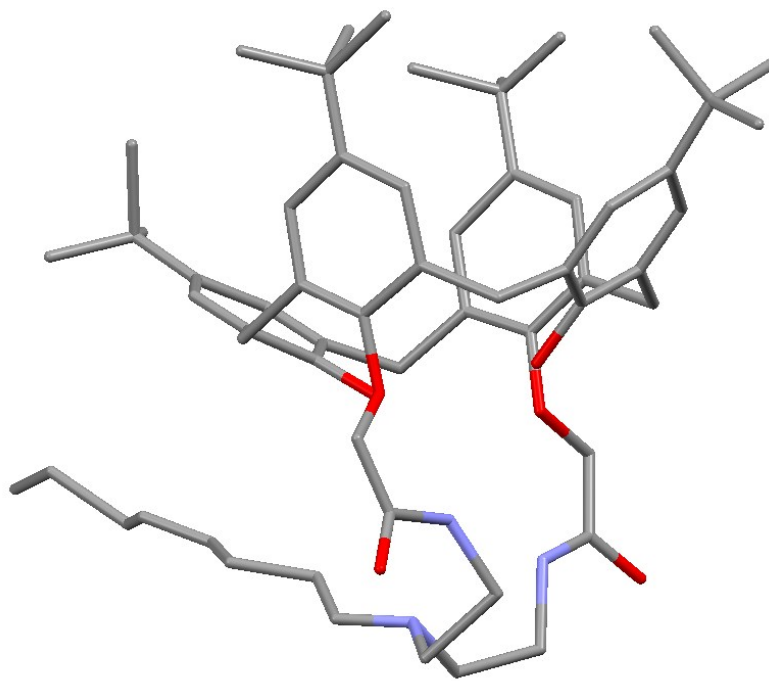


Figure SI-5: Solid state structure of NOCAC determined by single-crystal X-ray diffraction

Space group: **C 2/c**

Cell Lengths: **a** 14.964(1) **b** 32.328(1) **c** 25.693(1)

Cell angles **α** 90 **β** 90.102 **γ** 90

Cell volume : 12429.1

Theta max : 21°

Completion : 99,6%

R(int) : 7,7%

Affinement : Isotrope / without hydrogen atoms

R1 : 29,5%

wR2 : 66,4%

Table SI-2: Individual extraction of uranium by NOCAC and NEHCAC.

Ligand	[L] mM	[H ₂ SO ₄]	Diluent	D_U	Extraction %	Stoichiometry L:M
NOCAC	50	0.1 M	Dodecane / 15% Octanol	23.0	95.8	1:1
NEHCAC	50	0.1 M	Dodecane / 15% Octanol	56.9	98.3	-

Table SI-3: Selective extraction of uranium by NOCAC and NEHCAC from a leaching solution containing seven metals.

Ligand	[L] mM	[H ₂ SO ₄] M	Diluent	D_U	Extraction %	$S_{(U/Mo)}$
NOCAC	20	0.1 M	Dodecane / 15% Octanol	6.8	87.2	2.4
NEHCAC	20	0.1 M	Dodecane / 15% Octanol	16.59	94.3	3.1