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Supplementary Material

(Benzene-1,2,4,5-tetrayl)tetrakis(3-(1-carboxylatomethylpyridinium)), a novel uranyl-complexing tetrazwitterion

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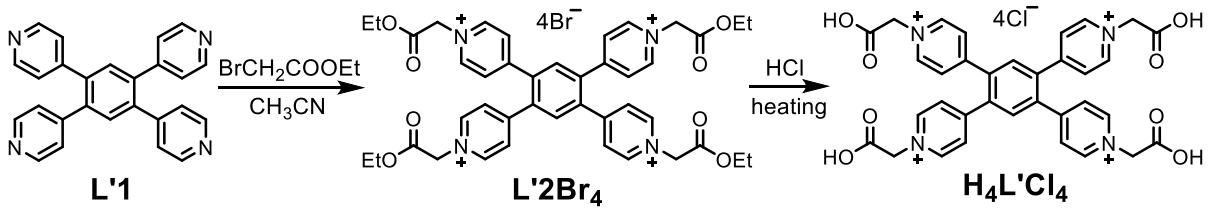
Reagents and procedures

All chemicals were purchased from Aldrich Chemical Co. and used without further purification. Deuterated solvents from Eurisotop were used. Proton NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer at ambient temperature. Chemical shifts are given in parts per million, and are referenced against external Me_4Si. ^1H NMR spectra were measured on a JEOL400 MHz spectrometer.

Synthesis of Ligand L'

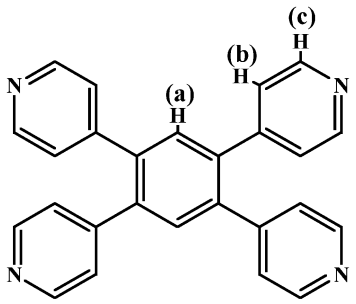


1,2,4,5-Tetra(pyridin-4-yl)benzene, L'1
This compound was prepared in the same manner as the method applied to **L1**, except that pyridine-4-ylboronic acid was used instead of pyridine-3-ylboronic acid. (Yield: 1.57 g, 79%). ^1H NMR (400 MHz) in CD_2Cl_2: δ 8.55 (m, br, $8H_c$), 7.59 (s, $2H_a$), 7.19–7.17 (d, J = 4.0 Hz, $8H_b$).

4,4',4'',4'''-(Benzene-1,2,4,5-tetrayl)tetrakis(1-(carboxymethyl)pyridin-1-ium) tetrabromide, L'2Br4
This compound was prepared in a manner analogous to the synthesis of **L2Br4** using **L'1** (1.0 g, 2.59 mmol), bromoacetate (2.5 mL, 13.52 mmol) in dry acetonitrile (50 mL) to afford **L'2Br4** as a yellow powder (2.5 g, 92%). ^1H NMR (400 MHz) in D_2O: δ 8.77 (d, J = 6.5 Hz, $8H_c$), 8.11 (s, $2H_a$), 8.05 (d, J = 6.5 Hz, $8H_b$), 5.48 (s, 8H, NCH_2), 4.21 (q, J = 7.1 Hz, 8H, OCH_2), 1.18 (t, J = 7.1 Hz, 12H, CH_3).

4,4',4'',4'''-(Benzene-1,2,4,5-tetrayl)tetrakis(1-(carboxymethyl)pyridin-1-ium) tetrachloride, H4L'Cl4
This compound was prepared in a manner analogous to the synthesis of **H4LCl4** using **L'2Br4** (2.5 g, 2.37 mmol) in 2 M HCl (50 mL) to afford **H4L'Cl4** as a white powder (1.5 g, 83%). ^1H NMR (400 MHz) in D_2O: δ 8.72 (d, J = 6.7 Hz, $8H_c$), 8.07 (s, $2H_a$), 8.00 (d, J = 6.7 Hz, $8H_b$). 5.34 (s, 8H, NCH_2).

Inequivalent aromatic proton designations:



NMR spectra

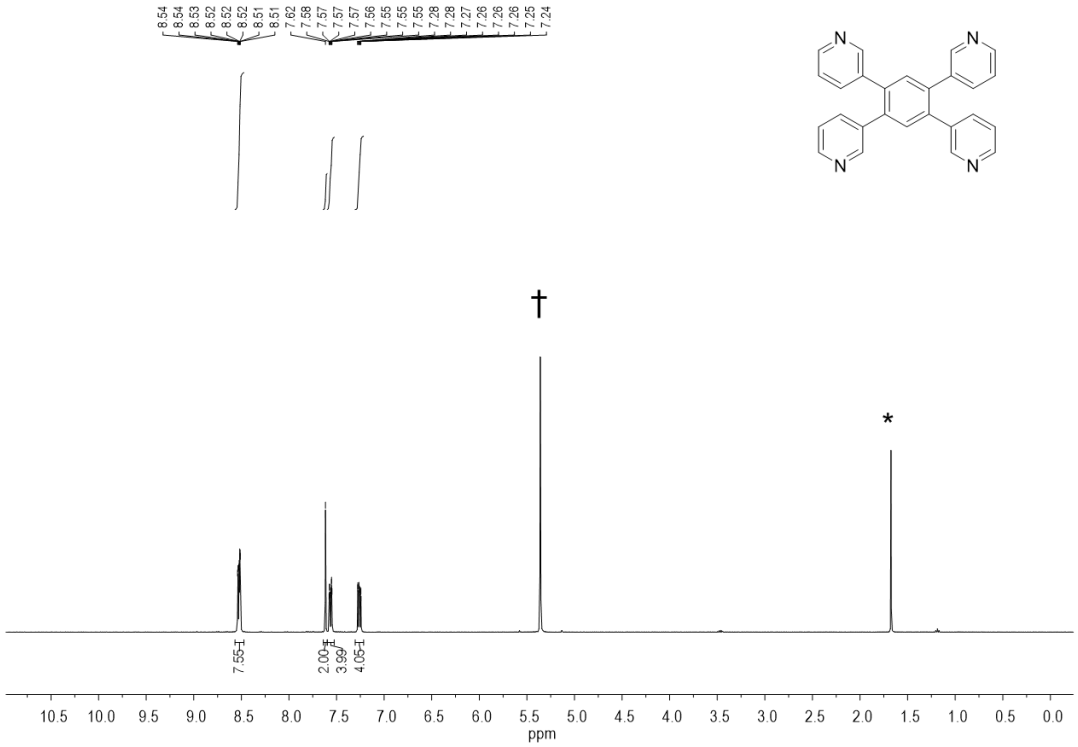


Fig. S1. ^{1}H NMR spectrum of **L1** in CD_2Cl_2 († from $CDHCl_2$ and * from water).

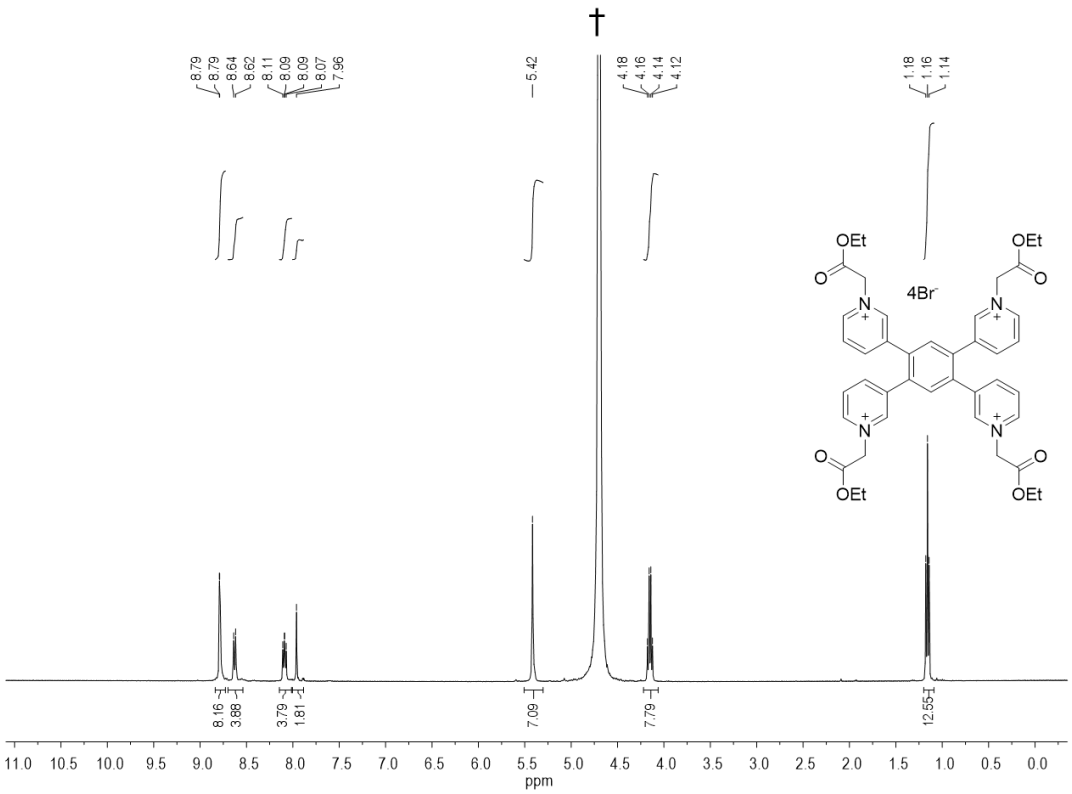


Fig. S2. ^{1}H NMR spectrum of **L2Br$_4$** in D_2O († from HOD).

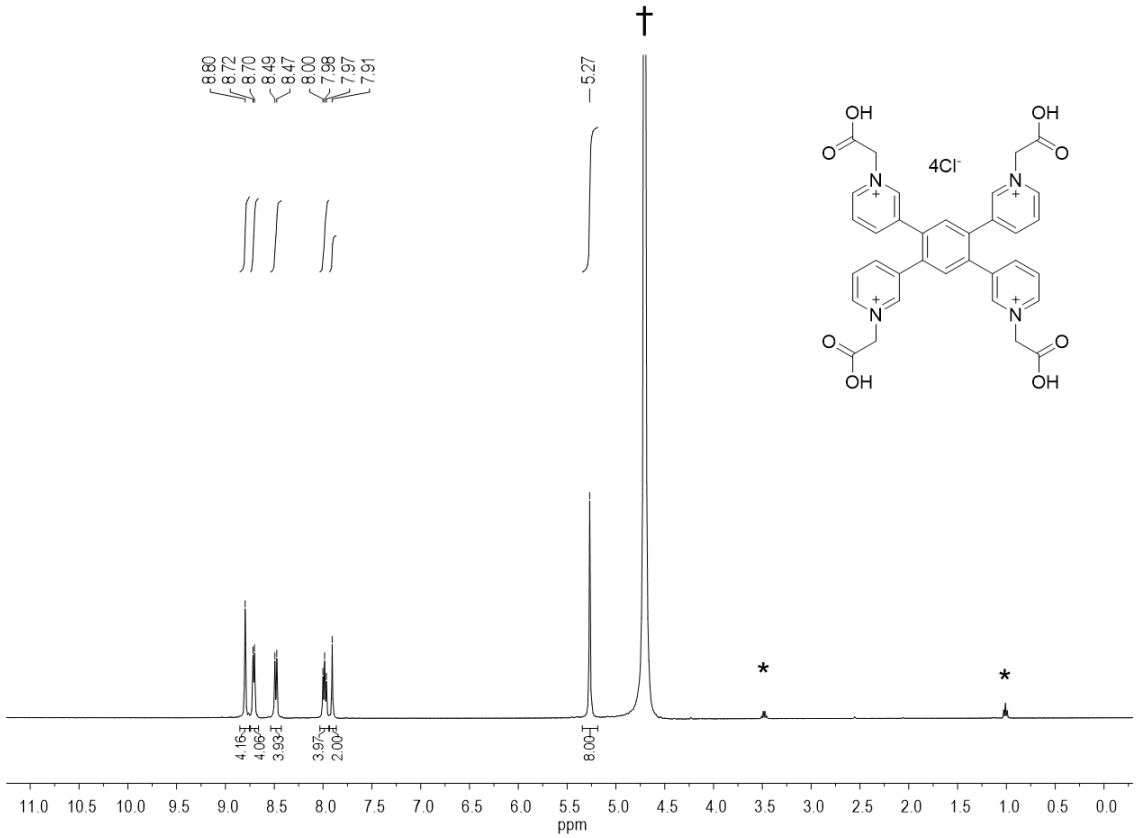


Fig. S3. ^{1}H NMR spectrum of **H_4LCl_4** in D_2O († from HOD and * from ethanol).

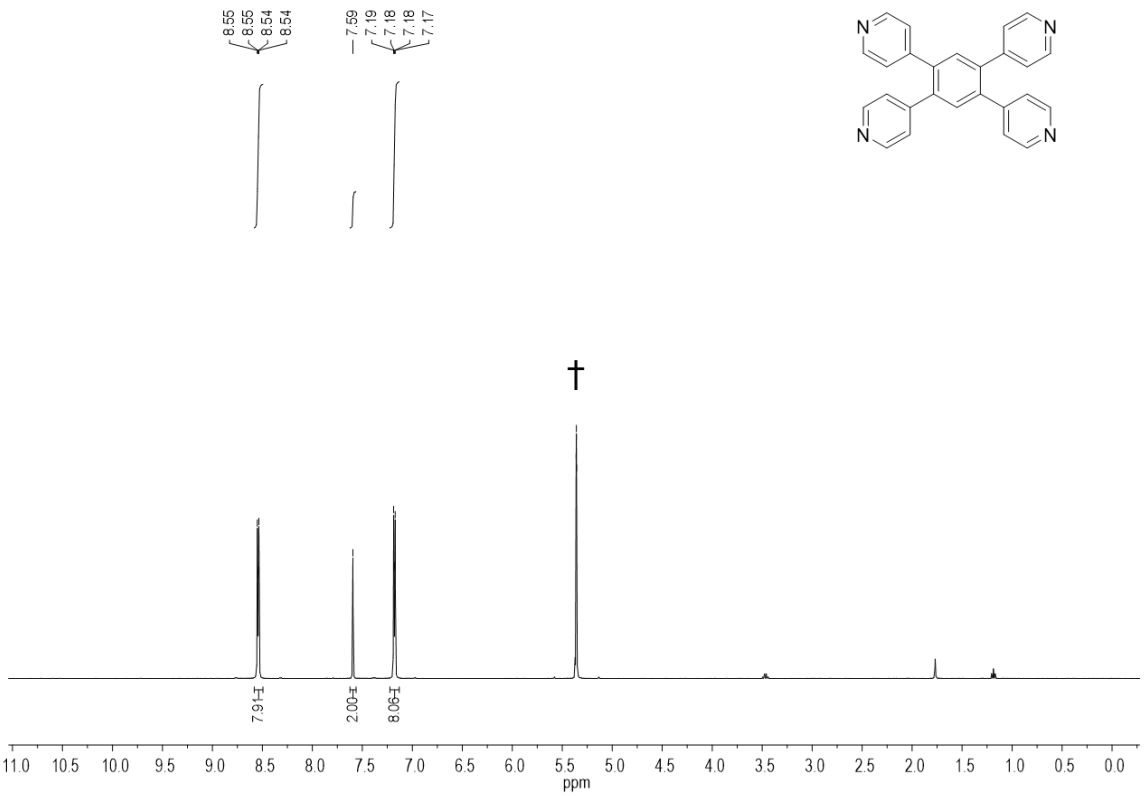


Fig. S4. ^{1}H NMR spectrum of **L'1** in CD_2Cl_2. († from $CDHCl_2$).

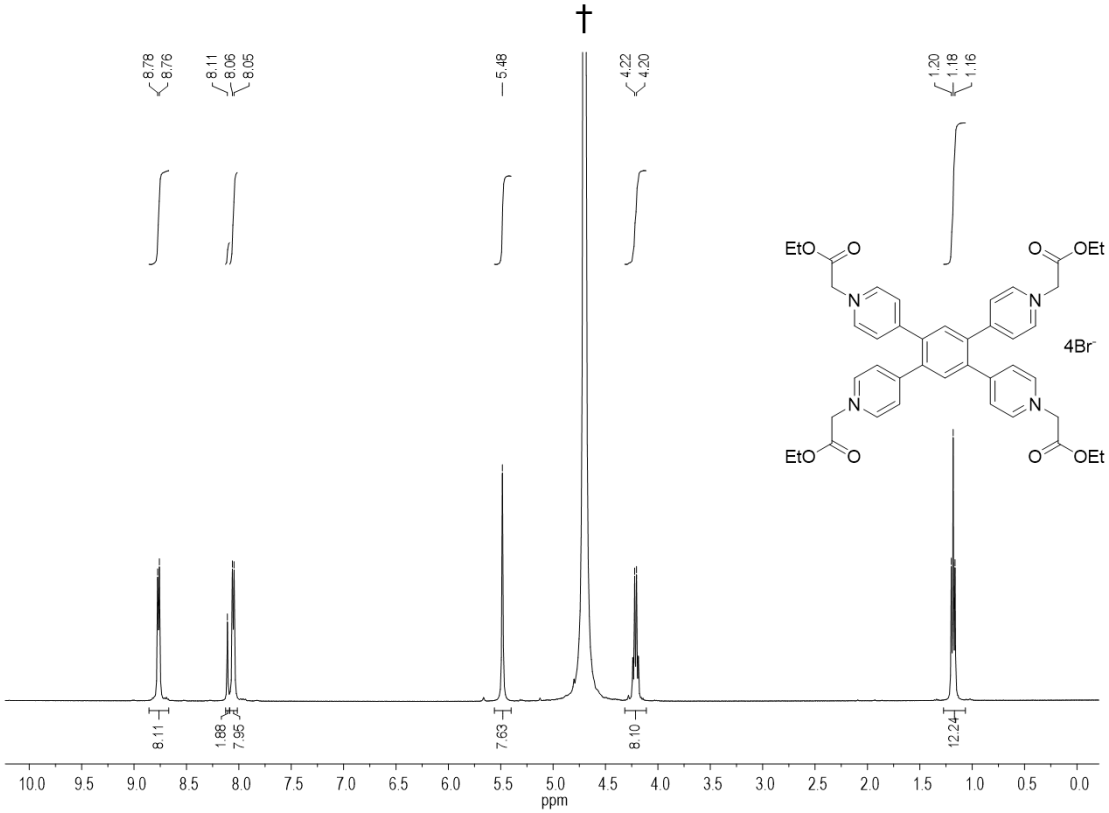


Fig. S5. ^{1}H NMR spectrum of **L'2Br$_4$** in D_2O († from HOD).

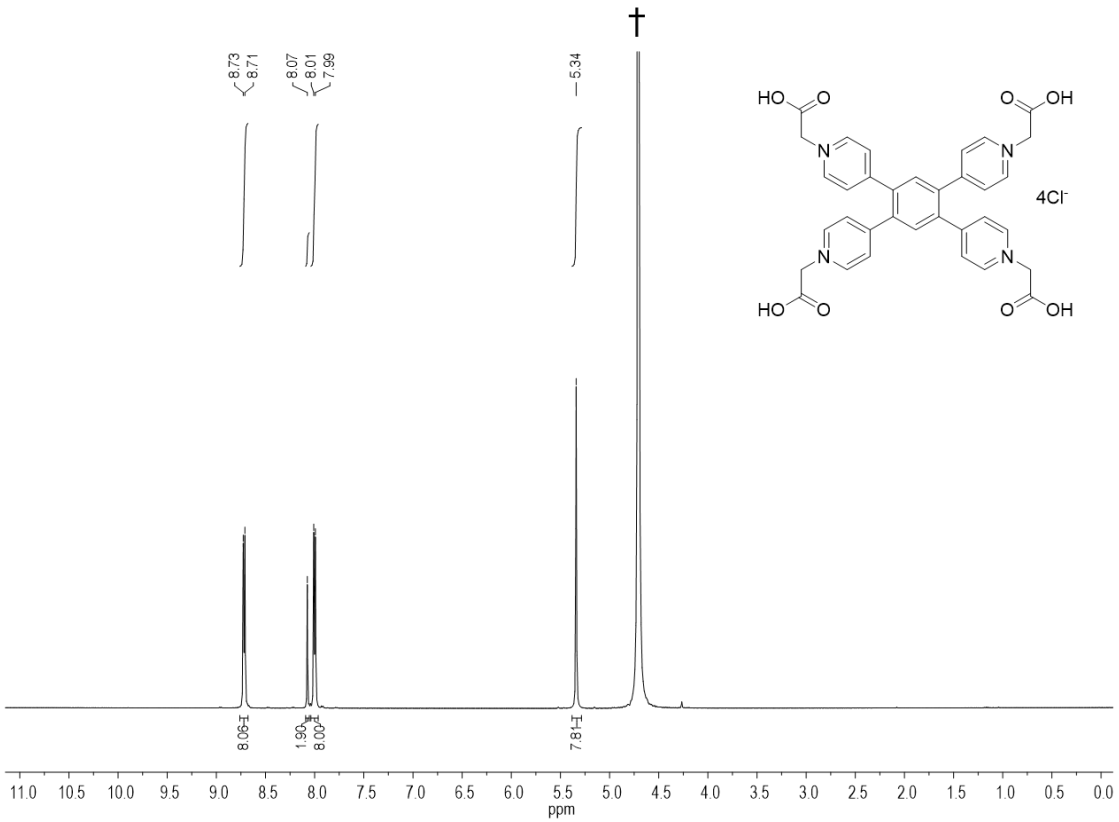


Fig. S6. ^{1}H NMR spectrum of **H$_4$L'Cl$_4$** in D_2O († from HOD).