# Encapsulation of the uranyl dication

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## Electronic Supplementary Information

# 1. General Information

$^{1}$H NMR spectra were recorded on a Bruker DRX-600 spectrometer with a 5mm QNP probe. Proton chemical shifts are reported in parts per million with respect to tetramethylsilane (TMS $\delta$ = 0, $^{1}$H and $^{13}$C NMR). Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. All chemicals were purchased from commercial suppliers and used without further purification.

# 2. Synthesis of 2,6-terphenylcarboxylates 1-3 and their corresponding uranyl complexes

## 2.1 Ligand synthesis

**Synthesis of 2,6-terphenylcarboxylic acid 1[i]**

To a vigourously stirred mixture of magnesium turnings (1.50 g, 61.72 mmol) in 200 ml of dry THF was slowly added phenyl bromide (9.60 g, 61.70 mmol) and this mixture was refluxed for 2.5h. Seperately, the 2,6-dichloroiodobenzene (8.18 g, 30.0 mmol) was activated with vinylmagnesium bromide (1 eq.; 0.7 M in cyclohexane) by keeping the solution at -18 °C for 2h. The cold solution was transferred to the refluxing Grignard solution and was stirred for 2.5h. After cooling to room temperature $CO_2$ was bubbled over night through the yellow solution, whereby a jelly yellow mass was formed. The reaction was quenched with 150 ml of 6N HCl and extracted with $Et_2O$ (3×150 ml). Washing ($H_2O$ and sat. $NaHCO_3$) and evaporation of the solvent afforded the crude product **1**, which was purified by flash chromatography (silica gel; hexane : $CH_2Cl_2$ 1:4). The pure product **1** was isolated in 58% (4.77 g) as white powder. $^{1}$H NMR ($CDCl_3$): $\delta$ 7.38-7.42 (12 H, m), 7.52 (1 H, dd); ($CD_2Cl_2$): $\delta$ 7.39-7.41 (12 H, m), 7.55 (1 H, dd); $^{13}$C NMR ($CDCl_3$): $\delta$ 127.75, 128.49, 128.55, 129.10, 129.74, 131.83, 140.40, 174.44.

**Synthesis of 2,6-terphenylcarboxylic acid 2**

The methoxy derivative **2** was prepared as described above with the following reagent quantities;

2,6-dichloroiodobenzene (6.818 g, 25.0 mmol)

vinylmagnesium bromide (32.5 ml, 1 eq.) in 80 ml THF

magnesium turnings (1.25 g, 50.5 mmol)

bromoanisole (9.43 g, 50.5 mmol) in 180 ml THF

Yield: 3.56 g (42.6%) of a white powder

$^{1}$H NMR ($CDCl_3$): δ 3.83 (6 H, s), 6.90 (4 H, d), 7.30-7.35 (6 H, m), 7.46 (1 H, t);

$^{13}$C NMR ($CDCl_3$): δ 55.47, 114.02, 128.90, 129.75, 129.79, 131.74, 132.95, 140.11, 159.43, 174.23. MS: [$MH^+$] 335.1278.

**Synthesis of 2,6-terphenylcarboxylic acid 3**

To a 100-mL flask were added 2,6-terphenylcarboxylic acid **2** (1.2 g, 3.6 mmol) and 30 mL of dry dichloromethane. This mixture was cooled in a dry ice/2-propanol bath and boron tribromide (0.38 mL, 4.0 mmol) was added through a septum with use of a syringe. The cold bath was removed and the mixture was stirred for 30 min, poured into ice water, stirred for 30 min, saturated with salt, and extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated. The solvent was removed under reduced pressure and the crude material was purified by flash chromatography over silica gel eluting with 1:2 hexanes:ethyl acetate to afford 690 mg of pure product as a white solid. (62%).

$^{1}$H NMR (acetone-$d_6$): δ 6.87 (4 H, m), 7.29-7.32 (6 H, m), 7.48 (1 H, t, J = 7.48 Hz);

$^{13}$C NMR (acetone-$d_6$): δ 116.23, 129.49, 129.93, 131.00, 133.25, 140.79, 158.30, 171.18.

## 2.2 Synthesis of Uranyl Complexes

**$[Et_3NH]^+[UO_2(1)_3]^-$**

$Et_3N$ (101.7 mg, 1.00 mmol) was added to a methanol solution (15 ml) of 2,6-terphenylcarboxylic acid **1 (**100 mg, 0.37 mmol). [The clean formation of the salt was analyzed by $^1H$ NMR] The addition of 61.2 mg (0.122 mmol) $UO_2(NO_3)_2$•$6H_2O$ in MeOH (10 ml) afforded an instant precipitation of a light yellow solid which was isolated by filtration. The pale yellow solid was washed with MeOH and $H_2O$ and dried in vacuo to afford 74 mg of the product. Additional product could be obtained by filtering the filtrate again (21 mg, 66.1% total yield). Single crystals, which were suitable for single crystal X-ray diffraction, could be obtained from a saturated solution in $CH_2Cl_2$.
$^1H$ NMR ($CD_2Cl_2$): δ 0.48 (C*H*3, 9 H, t), 2.53 (C*H*2, 6 H, q), 6.95 (Ar*H*, 12 H, t), 7.10 (Ar*H*, 6 H, t), 7.50-7.60 (Ar*H*, 21 H, m), 8.62 (N*H*, 1 H, s); $^{13}C$ NMR ($CD_2Cl_2$): δ 8.25, 46.32, 105.21, 127.54, 128.78, 129.36, 129.54, 129.59, 139.81, 140.93, 186.37. +MS: [$MSH^+$] 1293.56804, exp. For $Et_3NH^+$•**1**$_3UO_2^-$+$Et_3NH$: 1293.57128. $[Et_3NH]^+[UO_2(\mathbf{1})_3]^-$•MeOH: Anal. For $C_{64}H_{59}NO_9U$. Calc.: C, 62.79; H, 4.86; N, 1.14. Found: C, 62.88; H, 5.09; N 1.27%

A similar reaction (1.00 mmol of ligand) with $UO_2OAc_2$•$2H_2O$ afforded the identical product in analogous yield.

**$[Et_3NH]^+[UO_2(2)_3]^-$**

$Et_3N$ (38.0 mg, 0.368 mmol) was added to a methanol solution (5 ml) of 2,6-terphenylcarboxylic acid **2 (**123.0 mg, 0.368 mmol). The addition of $UO_2(NO_3)_2$•$6H_2O$ (60.4 mg, 0.120 mmol) in MeOH afforded an instant precipitation of a light yellow solid which was isolated by filtration after stirring for 15 minutes. The pale yellow solid was washed with MeOH and $H_2O$ and dried in vacuo to afford 116 mg of the compound $[Et_3NH]^+[UO_2(\mathbf{2})_3]^-$. Additional compound could be obtained by again filtering the filtrate after the washes (20 mg) 80% total yield. Single crystals, which were suitable for single crystal X-ray diffraction, could be obtained from a saturated solution in $CH_2Cl_2$.
$^1H$ NMR ($CD_2Cl_2$): δ 0.51 (C*H*3, 9 H, t), 2.54 (C*H*2, 6 H, q), 3.61 (OC*H*3, 18 H, s), 6.50 (Ar*H*, 12 H, d), 7.46 (Ar*H*, 6 H, d), 7.51-7.56 (Ar*H*, 15 H, m), 8.76 (N*H*, 1 H, s); $^{13}C$

NMR ($CD_2Cl_2$): δ 8.15, 46.11, 54.36, 114.20, 128.91, 129.41, 130.52, 133.38, 138.15, 139.28, 159.52, 186.90. MS (ESI: $[M^+Cl^-]$ 1405.4104, exp. 1405.4679. $[Et_3NH]^+[UO_2(\mathbf{2})_3]^-$•MeOH: Anal. For $C_{70}H_{71}NO_{15}U$. Calc.: C, 59.87; H, 5.10; N, 1.00. Found: C, 59.88; H, 5.30; N 1.13%

**$[^i Pr_2EtNH]^+[UO_2(\mathbf{3})_3]^-$**

$^i Pr_2EtN$ (38 mg, 0.30 mmol) was added to a methanol solution of **3** (86.6 mg, 0.283 mmol) and $UO_2(NO_3)_2$•$6H_2O$ (45.0 mg, 0.090 mmol) whereby an instant color change was observed. Evaporation of the solvent and extraction with $CHCl_3$ afforded $^i Pr_2EtNH^+$•$\mathbf{3}_3UO_2^-$ as single crystals upon cooling to 0 °C. $^1$H NMR (MeOD) at 330K: δ 1.33 ($CH_3$, 3H, t), 1.34 ($CH_3$, 24H, d), 3.18 ($CH_2Me$, 4H, q), 3.69 (CH*i*$Pr_2$, 4H, sept), 6.64 (ArH, 12H, d), 7.33 (ArH, 6H, d), 7.44 (ArH, 15H, m); MS (FTICR: [M+2C.I.] 1445.58380, exp. 1445.60388.

## 3. Extraction Studies

ICP analysis was performed on a Varian Vista AX CCD simultaneous ICP-AES spectrometer. Uranium and yittrium standard solutions were purchased from Inorganic Ventures and were used without further modification. Calibration curves were obtained by preparing 5 standard uranium solutions (100 ppb, 400 ppb, 600 ppb, 800 ppb and 1200 ppb each containing 10 ppm yittrium as an internal standard) were prepared by dilution of a standard 10 ppm uranium solution after addition of the appropriate amount of the yittrium standard. The wavelength of analysis was 307.278.

Using volumetric glassware 2,6-terphenyl carboxylic acid (**2**) (0.0871 g, 0.260 mmol) was diluted to 5 ml with $CDCl_3$. Separately, $UO_2(NO_3)_2$•$6H_2O$ (0.0873 g, 0.174) was weighed out and diluted to 10 ml with acetate buffer adjusted to pH 5. Another uranium stock solution was prepared with the addition of NaCl [$UO_2(NO_3)_2$•$6H_2O$ (0.0857 g, 0.171 mmol), NaCl (0.1034 g, 1.77 mmol) diluted to 10 ml with acetate buffer adjusted to pH 5]. 2 ml of the 2,6-terphenyl carboxylic acid (**2**) stock was added to two separate 25 ml scintillation vials containing magnetic stir bars. To one vial was added 2 ml of the

uranium stock solution and to the other 2 ml of the uranium stock containing NaCl. Each vial was capped and wrapped in parafilm and vigorously stirred for 16 hours. The following day it was noted that the aqueous layer was no longer yellow and the $CDCl_3$ layer contained a milky yellow suspension. $^1$H NMR analysis confirmed the presence of $[Et_3NH]^+[UO_2(\mathbf{2})_3]^-$ in the organic layer. ICP analysis of the aqueous layer was performed to assess the uranium content left in the aqueous phase. Using gas tight Hamilton syringes 10 μL was removed from the aqueous layer and diluted to 50 ml with 2% $HNO_3$ after adding 0.5 ml of a 10 ppm yittrium standard.

Blank samples were also prepared analogously with the omission of 2,6-terphenyl carboxylic acid (**2**).

ICP analysis was performed on the resulting solutions as well as the uranium stock solutions:

| | |
|---|---|
| **2** + $UO_2$ = 27.2003 ppb | (sample 1) |
| **2** + $UO_2$ + NaCl = 20.9741 ppb | (sample 2) |
| $CDCl_3$ + $UO_2$ = 897.326 ppb | (blank) |
| $CDCl_3$ + $UO_2$ + NaCl = 794.519 ppb | (blank) |
| $UO_2$ stock = 799.764 ppb | (calculated concentration = 820.62 ppb) |
| $UO_2$ + NaCl stock = 795.779 ppb | (calculated concentration = 805.58 ppb) |

The uranium could be released from the complex by vigorously stirring the organic layer with an equal portion of 0.5 M $HNO_3$ for 3 hours. $^1$H NMR analysis confirmed the disappearance of the complex.

## 4. X-ray Experimental

Data was collected with a Bruker SMART APEX diffractometer equipped with a molybdenum sealed tube and a highly oriented graphite monochromator. The frame data are acquired with SMART software using a three axis stage. The chi-axis on this stage is fixed at 54.74°, and the CCD detector is maintained at -40 °C. Cell constants are determined from 600 30s frames. A complete hemisphere of data is scanned on ω (0.3°) with a run time of 30s per frame at the detector resolution of 512x512 pixels. A total of 1800 frames are collectd in three sets. The frames are then processed on a IBM

compatible PC by using SAINT+ software to give the hkl file corrected for Lp/decay and absorption.

For $[Et_3NH]^+[UO_2(\mathbf{1})_3]^-\bullet 1.5CH_2Cl_2$, the structure was solved by direct methods and refined based on $|F|2$. Atoms in the investigated structure was found from the residual density maps and refined with isotropic thermal parameters except one of the 2,6-terphenyl carboxylate ligands which was disordered. The disorder of the ligand could not be modeled and the aromatic rings were constained with AFIX. Besides the uranyl anion and triethylamine cation the crystal lattice includes two solvent dichloromethane molecules. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the ideal positions with fixed isotropic U values.

For $[^iPr_2EtNH]^+\bullet[UO_2(\mathbf{3}_3)]^-\bullet 4H_2O$ the systematic absences (hkl, h+k=2n+1; hol, 1=2n+1) indicated a choice between the space groups Cc and C2/c. The former space group was chosen based on the fact that X=4 and the compound cannot exhibit a two-fold or center of inversion local symmetry. The structure was solved by direct methods using SHELXTL-PC. Besides Uranyl anion and amine cation, the crystal lattice contains 4 water molecules and one molecule of bis-(isopropyl) ethyl amine ligand. All non-hydrogen atoms were refined anisotropically by the full matrix least-squares method. The function minimized was $\sum w(\|Fo\|-\|Fc\|)^2$. Hydrogen atoms were included in the ideal positions with fixed isotropic U values equal to 1.2 times that of the atom they are attached to. A weighting scheme of the form $w=1/[\sigma^2(Fo^2)+(ap)^2)+bp]$ with a=0.08 and b=0.00 was used. (P is defined as $Max(Fo^2,0)+2F_c^2)/3$). There was no evidence of secondary extinction; therefore it was not applied. The refinement converged to the R indices given in the Table which also includes the largest difference peak and the hole in the last cycles of refinement. The final difference map was devoid of significant features.

All calculations were done on an IBM compatible PC using windows-NT operating system. The programs used were SMART (data collection), SAINT+ (data reduction), SADABS (absorption correction), SHELXTL-PC (XS for solution, XL for refinement, XP for plotting and XCIF for tables).

## 5. Titration study:

$[Et_3NH]^+[UO_2(\mathbf{1})_3]^-$ (3.5 mg; 0.00294 mmol) was dissolved in $CD_2Cl_2$ (0.6 ml). Separately, 2,6-terphenyl carboxylic acid **1** (0.083 mg, 0.302 mmol) was dissolved in $CD_2Cl_2$ (4 ml) and triethyl amine was added (0.042 ml, 0.302 mmol) and the solution mixed. $^1$H NMR spectra were acquired of just the complex and following the addition of the deprotonated ligand stock solution 0.040 ml (1 eq.), 0.160 ml (4 eq.), 0.200ml (5 eq.) and 0.400 ml (10 eq.). The full NMR spectra are illustrated below in Fig. S1.

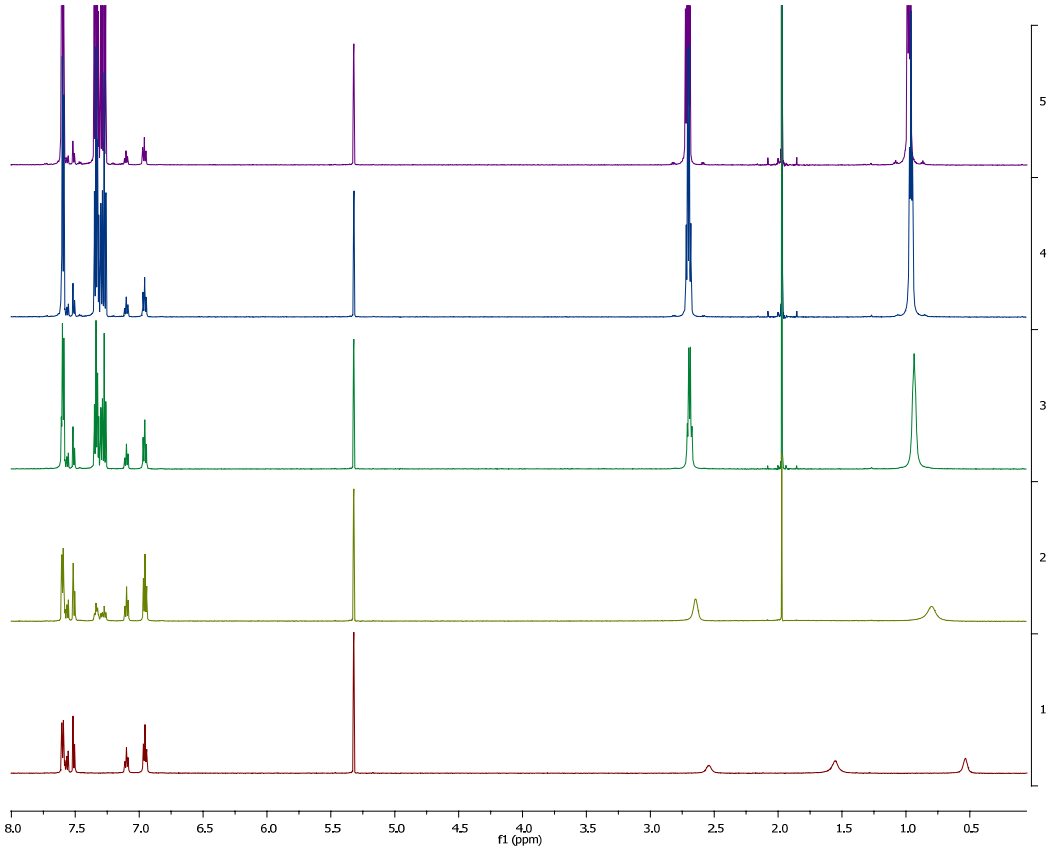


**Fig. S1**. Full spectra from titration experiment illustrating slow exchange of ligands on the 1D $^1$H NMR time scale. $^1$H NMR spectra were acquired of just the complex $[Et_3NH]^+[UO_2(\mathbf{1})_3]^-$ (bottom, red) and following the addition of 0.040 ml (yellow, 1 eq.), 0.160 ml (green, 4 eq.), 0.200ml (blue, 5 eq.) and 0.400 ml (purple, 10 eq.) of the deprotonated ligand stock solution (ascending respectively).

## 6. Ligand exchange NMR experiments

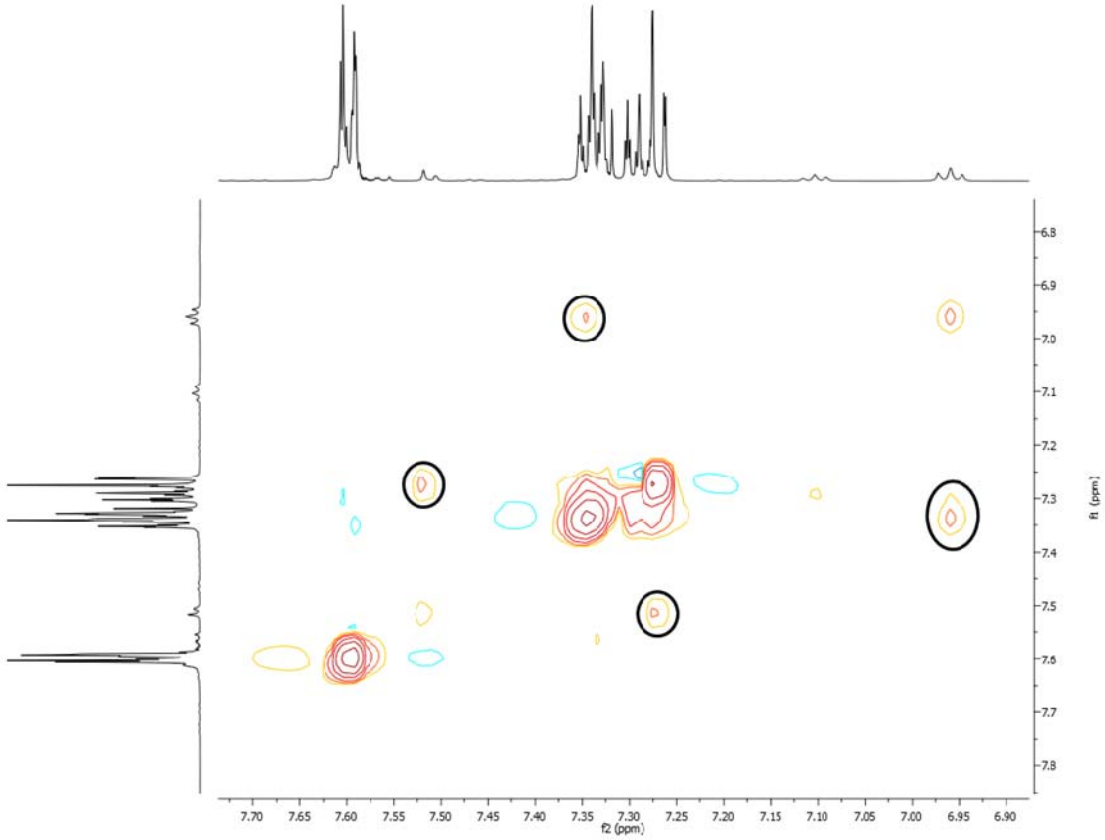


**Fig. S2.** Aromatic region of the ROESY spectrum of $[Et_3NH]^+[UO_2(\mathbf{1})_3]^-$ with 10 eq. of the triethyl amine salt of 2,6-terphenyl carboxylic acid **1**. Exchange peaks have been circled in black. Experimental details are from the titration study above.

**EXSY experiment of $[Et_3NH]^+[UO_2(2)_3]^-$ with 2.5 eq. of the triethyl amine salt of 2,6-terphenyl carboxylic acid 2.**

$[Et_3NH]^+[UO_2(\mathbf{2})_3]^-$ (3.5 mg; 0.00255 mmol) was dissolved in $CD_2Cl_2$ (0.6 ml). Separately, 2,6-terphenyl carboxylic acid **2** (0.0363 mg, 0.108 mmol) was dissolved in $CD_2Cl_2$ (2 ml) and triethyl amine was added (0.015 ml, 0.108 mmol) and the solution mixed. The 1D $^1$H NMR spectrum is shown in Fig. S3. $^1$H NMR NOESY spectra were acquired after the addition of the deprotonated ligand stock solution (0.120 ml, 2.5 eq.). Two NOESY spectra were acquired, one with 0.40000001 mixing time and the second with 0 mixing time. The diagonal and off-diagonal methoxy signals were integrated

respectively and the activation barrier for the exchange process was calculated using the Eyring equation ($k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$) and the rate constant obtained from the program EXSYCalc.[ii] $\Delta G^{\ddagger}$ = 17.1 kcal mol$^{-1}$.

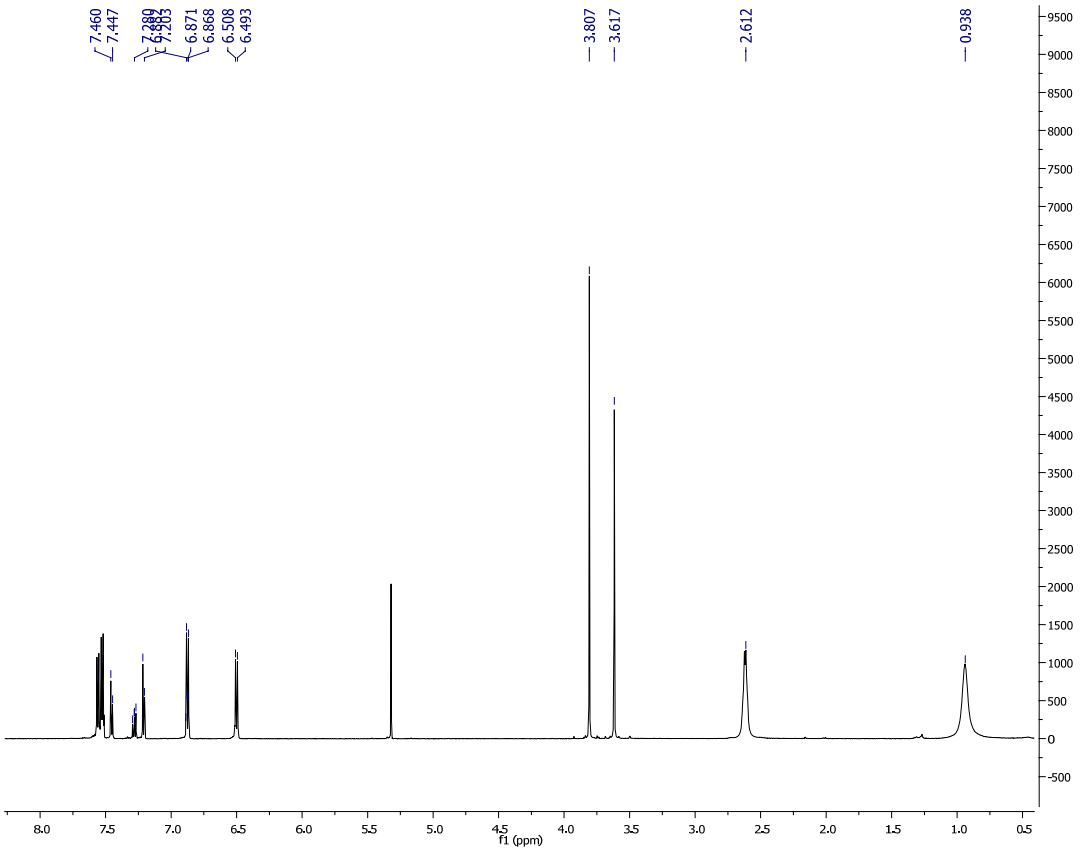


**Fig. S3**. 1D $^1$H NMR spectrum of the EXSY experiment $[Et_3NH]^+[UO_2(\mathbf{2})_3]^-$ with the triethyl amine salt of 2,6-terphenyl carboxylic acid **2**.

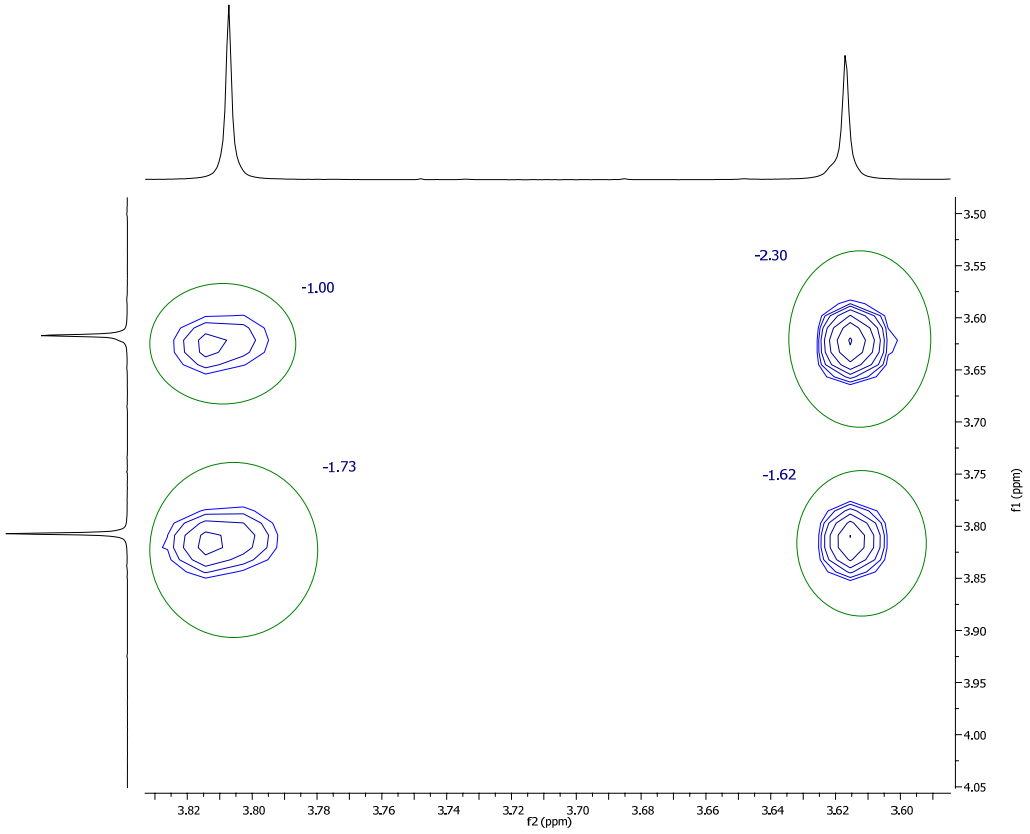


**Fig. S4**. Zoom of the methoxy signals from the EXSY experiment illustrating the off-diagonal exchange signals.

## 7. References

[i] C. J. F. Du, H. Hart, K. K. D. Ng, *J. Org. Chem.* 1986, **51**, 3162-3165.
[ii] ExsyCalc Version 1.0, Juan Carlos Cobas, M. Martin-Pastor, ©Mestrelab Research