ELECTRONIC SUPPLEMENTARY INFORMATION

Paper : "Uranium adsorption from sulfuric acid media using silica materials functionalised with amide and phosphorous ligands

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Ligand synthesis

APO

Apo(OEt)$_2$

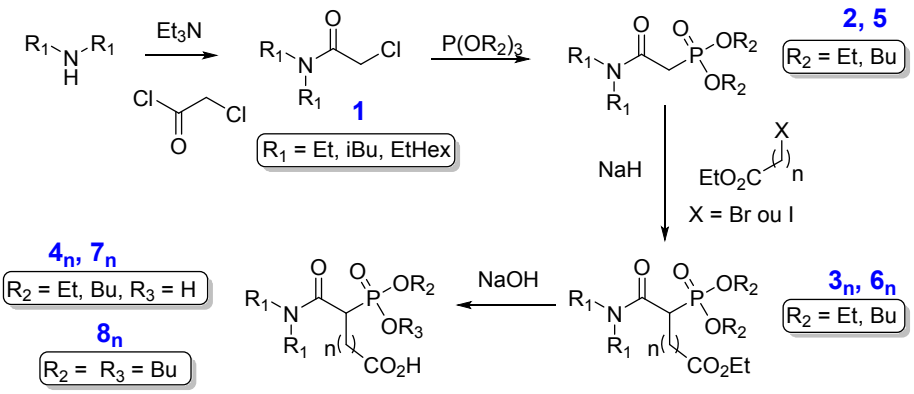
In a round-bottomed flask was charged Triethyl 2-phosphonopropionate (10g), NaOH in excess (4g) with EtOH (200ml) and H_2O (50ml). The reaction mixture was stirred overnight, concentrated, acidified with 50ml HCl 1M, extracted twice with ethyl acetates, dried over $MgSO_4$, filtered. Solvent removal yielded 5.7g of pure diethyl 2-phosphonopropionic acid as green oil.

Apo(OEt)

In a round-bottomed flask was charged Triethyl 2-phosphonopropionate (4,5g), NaOH in excess (3,6g) with EtOH (200ml) and H_2O (50ml). The reaction mixture was refluxed for 48h, concentrated, acidified with 50ml HCl 1M, extracted twice with ethyl acetates, dried over $MgSO_4$, filtered. Solvent removal yielded 2.8g of pure ethyl 2-phosphonopropionic acid as brown viscous oil.

diAPo

Coumpounds **4a1**, **4c1** and **7c1** were directly purchased from SpecificPolymers and used without further purification:

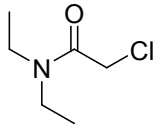


DiAPo@silica precursor synthesis

General procedure for the synthesis of compounds 1

2-choloroacethyl chloride (8.25g, 70 mmol, 1éq.) is introduced in a 1L round bottom flask with 200 mL Et_2O. Di-alkyl-amine $(R1)_2NH$ (70 mmol, 1 éq) and triethylamine (8.03, 80 mmol, 1.12 eq) are diluted into 30 mL of diethyl ether and then added dropwise under heavy stirring. The mixture is allowed to stir overnight, filtered, evaporated to dryness. The residue was purified by flash chromatography (SiO_2) (Cyclohexane, Et_2O).

Compound 1a

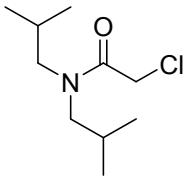


^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ (ppm): 4.0 (s, 2H, OC-C*H*$_2$-Cl), 3.4-3.3 (m, 4H, N-C*H*$_2$-CH$_3$), 1.2-1.0 (m, 6H, N-CH$_2$-C*H*$_3$)

^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 165.4 (O-*C*-CH$_2$), 42.2 (CH$_2$), 41.0 (CH$_2$), 40.3 (CH$_2$), 14.0 (CH$_3$), 12.4 (CH$_3$)

Yield: 70%

Compound 1b



^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.1 (s, 2H, OC-C*H*$_2$-Cl), 3.19-3.17 (d, 2H, N-C*H*$_2$-CH), 3.13-3.11 (d, 2H, N-C*H*$_2$-CH), 2.03-1.86 (m, 2H, (CH$_3$)$_2$-C*H*-CH$_2$), 1.93-1.86), 0.92-0.86 (m, C*H*$_3$-CH)

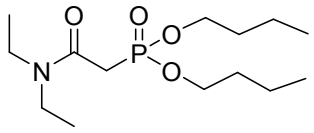
^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 167.6 (O-*C*-CH$_2$), 56.2 (CH$_2$), 53.5 (CH$_2$), 41.9 (CH$_2$), 28.3 (CH), 26.8 (CH), 20.5 (CH$_3$)

Yield: 86%

General procedure for the synthesis of compounds 2 and 5

Coumpound 1 (10 mmol, 1 Eq) and trialkyl phosphite (120 mmol, 12 Eq) are introduced a 250 mL round bottom flask, flushed 15 min with N_2. The mixture refluexed overnight under stirring. The mixture is distillated around (110°C for triethyl phosphate, 160°C for tributyl lphosphite) to remove the excess of Phosphite. The residue was purified by flash chromatography (SiO_2) (Cyclohexane, EtOAC). and yield the targeted product.

Compound 5a



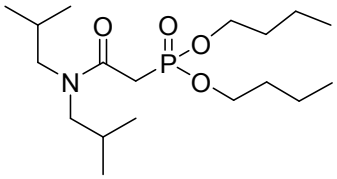
^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 21.4

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.01-3.96 (m, 4H, O-C*H*$_2$-CH$_2$), 3.33-3.25 (m, 4H, N-C*H*$_2$-CH$_3$), 2.93-2.87 (d, 2H, J_{H-P}=22 Hz, P-C*H*$_2$-CON), 1.73-1.58(m, 4H, O-CH$_2$-C*H*$_2$), 1.48-1.34 (m, 4H, O-(CH$_2$)$_2$-C*H*$_2$), 1.23-1.10 (td, 6 H, C*H*$_3$-CH$_2$-N), 0.96-0.91 (t, 6H, O-(CH$_2$)$_3$-C*H*$_3$).

^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 164.2 (CH$_2$-*C*-ON), 67.6 (CH$_2$), 66.5 (CH$_2$), 43.3 (CH$_2$), 40.8 (P-*C*H$_2$-CON), 34.26 (CH$_2$), 32.8 (CH$_2$), 14.5 (CH$_3$), 13.9 (CH$_3$), 13.2 (CH$_3$)

Yield: 81%

Compound 5b



^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 21.8

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.05-3.99 (q, 4H, O-C*H*$_2$-CH$_2$), 3.01-2.96 (d, 2H, J_{H-P}=22 Hz, P-C*H*$_2$-CON), 3.14-3.11 (q, 4H, N-C*H*$_2$-CH), 1.96 (m, 1H, (CH$_3$)$_2$-C*H*-CH$_2$), 1.84 (m, 1H, (CH$_3$)$_2$-C*H*-CH$_2$), 1.62-1.55 (m, 5H), 1.37-1.30 (m, 5H), 0.80-0.81 (m, 18H)

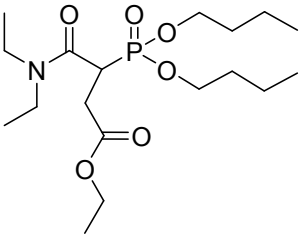
^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 164.7 (s, CH$_2$-*C*-ON), 65.9 (CH$_2$), 56.1 (CH$_2$), 53.1 (CH$_2$), 33.8 (CH$_2$), 32.2 (CH$_2$), 27.6 (CH), 26.3 (CH), 19.8 (*C*H$_3$-CH-*C*H$_3$), 18.4 (CH$_2$), 13.3 (*C*H$_3$-CH$_2$)

Yield: 85%

General procedure for the synthesis of compounds 3n and 6n

Coumpound 2 or 5 (6.5 mmol, 1 Eq) and 40 mL of dry DMF are introduced into a 100 mL three-neck round bottom flask dried under N_2. Sodium hydride (7.2 mmol, 1.1 Eq) 60% in grease and the appropriate halogenated reagent RX: X-$(CH_2)_n CO_2Et$ (11 mmol, 1.7 Eq) are added. The mixture is allowed to stir overnight under N_2 for 24h. The residue was concentrated under reduced pressure, resolved into dichloromethane, centrifuged, filtered, then purified by flash chromatography (SiO_2) (Cyclohexane/EtOAc) to yield the desired compound.

Compound 6a1



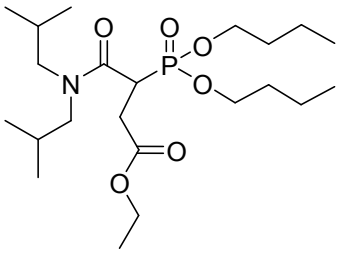
RX: n= 1, X = Br, Ethyl bromocaetate

^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 23.3

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.18-4.07 (m, 6H, OC*H*$_2$), 3.81-3.33 (m, 6H, C*H*$_2$-CO & N-C*H*$_2$), 2.77-2.72 (m, 1H, P-C*H*(CH$_2$)-CO), 1.66-1.54 (m, 4H, N-CH$_2$-C*H*$_2$), 1.41-1.34 (m, 4H, CH$_2$-C*H*$_2$-CH$_3$), 1.33-1.24 (m, 6H, N-CH$_2$-C*H*$_3$), 1.11 (t, 3H, CO-O-CH$_2$-C*H*$_3$), 0.92 (m, 6H, CH$_2$-CH$_2$-C*H*$_3$)

Yield: 66%

Compound 6b1



RX: n= 1, X = Br, Ethyl bromocaetate

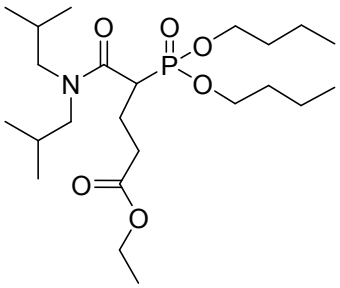
^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 23.0

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.11-4.00 (m, 6H, OC*H*$_2$), 3.65-3.57 (m, 1H, N-C*H*$_2$), 3.23-3.14 (m, 1H, N-C*H*$_2$), 3.06-3.00 (m, 1H, N-C*H*$_2$), 2.79-2.69 (m, 1H, CH-C*H*$_2$), 2.15-2.00 (m, 2H, CH-C*H*$_2$-C), 1.66-1.54 (m, 5H, N-CH$_2$-C*H*), 1.41-1.34 (m, 4H, C*H*$_2$-CH$_3$), 1.25-1.96 (t, 3H, O-CH$_2$-C*H*$_3$), 0.96-0.84 (m, 18H, C*H*$_3$)

^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 171.9 (N-*C*O), 167.5 (O-*C*O), 67.1 (O-*C*H$_2$), 66.2 (O-*C*H$_2$), 61.7 (CO-O-*C*H$_2$), 56.9 (N-*C*H$_2$), 55.5 (N-*C*H$_2$), 37.9 (CO-*C*HPCH$_2$), 32.9-32.7 (O-CH$_2$-*C*H$_2$), 28.4 (CH$_3$), 26.9 (CH$_3$), 20.8 (CH$_3$), 20.4 (CH$_3$), 20.3 (CH$_3$), 18.9 (CH$_2$), 14.4 (CH$_3$), 13.8 (CH$_3$)

Yield: 52%

Compound 6b2



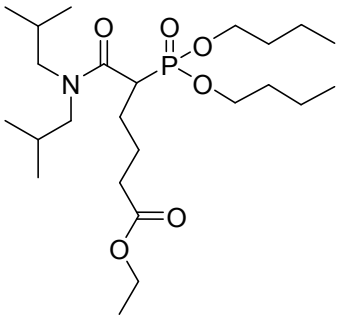
RX: n= 2, X = I, Ethyl 2-iodopropionate

^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 23.56

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.08 (m, 4H, O-C*H*$_2$), 3.55 (m, 1H, OC-C*H*PCH$_2$), 3.42-3.37 (m, 2H), 2.95 (m, 1H), 2.77 (m, 1H), 2.26-2.02 (m, 6H), 1.62-1.57 (m, 6H), 1.37-1.36 (m, 3H), 1.24-1.20 (m, 3H), 0.93-0.85 (m, 16H)

Yield: 40%

Compound 6b3



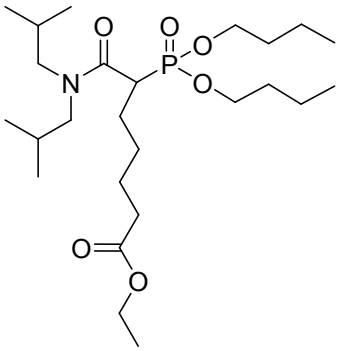
RX: n= 3, X = I, Ethyl 4-iodobutyrate

^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 23.86

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.09-4.00 (m, 6H, O-C*H*$_2$), 3.61-3.56 (q, 1H), 3.47-3.41 (q, 1H), 3.20 (m, 1H), 2.98-2.92 (q, 1H), 2.82-2.77 (q, 1H), 2.29-2.25 (m, 2H), 2.06-2.02 (m, 2H), 1.91-1.89 (m, 2H), 1.65-1.53 (m, 9H), 1.40-1.32 (m, 6H, CH$_2$-CH$_2$-C*H*$_3$), 1.24-1.19 (t, 3H, O-CH2-C*H*3), 0.94-0.83 (m, 18H)

Yield: 23%

Compound 6b4



RX: n= 4, X = I, Ethyl 5-iodovalerate

^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 24.13

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.09-4.01 (m, 6H, O-CH_2), 3.57-3.54 (m, 1H), 3.43-3.38 (m, 1H), 3.20-3.12 (m, 1H), 2.95-2.90 (m, 1H), 2.94-2.90 (m, 1H), 2.81-2.76 (m, 1H), 2.26-2.23 (m, 2H), 2.07-1.73 (m, 5H), 1.72-1.61 (m, 6H), 1.36-1.35 (m, 6H), 1.23-1.19 (m, 4H), 0.91-0.85 (m, 18H, C*H*$_3$)

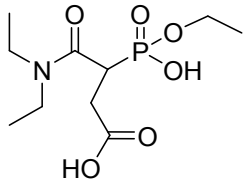
^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 173.7 (*C*O-N), 168.4 (*C*O-O), 66.7 (CH_2), 66.2 (CH_2), 64.4 (CH_2), 60.4 (CH_2), 56.2 (CH_2), 55.1 (CH_2), 43.1 (CH), 41.8 (CH), 34.2 (CH_2), 32.8 (CH_2), 30.9 (CH_2), 28.7 (CH), 28.2 (CH_2), 26.9 (CH), 25.2 (CH_2), 20.6 (CH_3), 20.3 (CH_2), 18.9 (CH_2), 14.5 (CH_3), 13.9 (CH_3)

Yield: 69%

General procedure for the synthesis of compounds 4n and 7n

Coumpound 3n or 6n (2.5 mmol, 1 Eq) is introduced into a 50 mL round bottom flask dried under N_2, with 10 mL of ethanol, 2ml H_2O and sodium hydroxide (22.5 mmol, 9 Eq). The mixture is refluxed overnight. The mixture is allowed to room temperature, diluted with 10 mL of ethanol and acidified with 14M HCl to reach pH=1. The residue was concentrated under reduced pressure, resolved into dichloromethane, dried with MgSO4, filtered and re-evaporated to yield the desired compound.

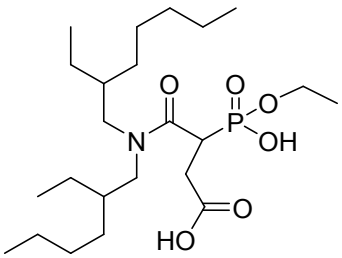
Compound 4a1



^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 22.4

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.11 (m, 2H, POC*H*$_2$), 3.62-3.30 (m, 6H, C*H*$_2$-CO & N-C*H*$_2$), 2.85 (m, 1H, P-C*H*(CH_2)-CO), 1.28 (m, 6H, N-CH_2-C*H*$_3$), 1.10 (m, 3H, PO-CH_2--C*H*$_3$), 0.89 (m, 6H,

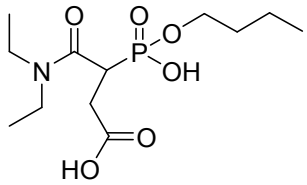
Compound 4c1



^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 23.7

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4,07 – 4,00 (m, 2H, O-C*H*$_2$-CH$_3$), 3,72 – 3,65 (m, 1H, C*H*$_2$-N) ; 3,48 – 3,09 (m, 5H, C*H*$_2$-N & CO-C*H*$_2$), 2.90-2.86(m, 1H, , CO-C*H*-P) ; 1,78 – 1,66 (m, 2H, C*H*-CH$_2$-N) ;. 1,37 – 1,17 (m, 15H, C*H*$_2$,& O-CH$_2$-C*H*$_3$) ; 0,81 – 0,86 (m, 12H, C*H*$_3$).

Compound 7a1

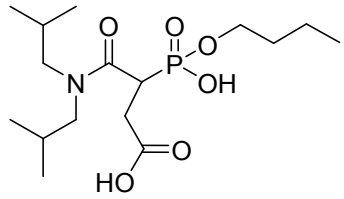


^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 22.9

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 3.90 (m, 2H, POC*H*$_2$), 3.52-3.01 (m, 6H, C*H*$_2$-CO & N-C*H*$_2$), 2.77 (broad s, 1H, P-C*H*(CH$_2$)-CO), 1.54 (m, 2H, PO-CH$_2$-C*H*$_2$), 1.34 (m, 2H, PO-CH$_2$-CH$_2$-C*H*$_2$-CH$_3$), 1.24 (m, 3H, N-CH$_2$-C*H*$_3$), 1.05 (m, 3H, N-CH$_2$-C*H*$_3$), 0.89 (m, 3H, PO-CH$_2$-CH$_2$-CH$_2$-C*H*$_3$)

Yield: 82%

Compound 7b1

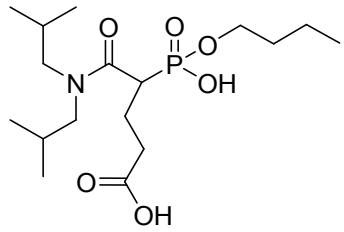


^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 24.5

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.11-4.03 (m, 2H, OC*H*$_2$), 3.65-3.12 (m, 5H, N-C*H*$_2$& C*H*-P), 2.99-2.81 (m, 2H), 2.15-2.00 (m, 2H), 1.61-1.59 (m, 2H), 1.36-1.34 (m, 2H), 0.96-0.84 (m, 15H, C*H*$_3$)

Yield: 75%

Compound 7b2



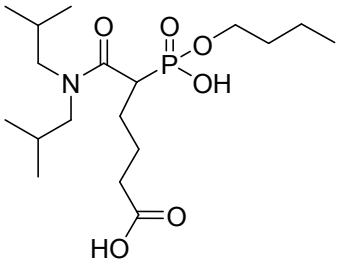
^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 25.25

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.12-4.07 (q, 2H, O-C*H*$_2$-CH$_2$-CH$_2$), 4.02-4.01 (m, 2H), 3.23-3.15 (m, 4H, N-C*H*$_2$), 2.64 (m, 1H), 2.38 (m, 1H), 2.22 (m, 2H, C*H*-(CH$_3$)$_2$), 1.97 (m, 2H, CH-CH$_2$), 1.62-1.58 (m, 2H), 1.38-1.32 (m, 2H), 1.24-1.21 (t, 2H,), 0.92-0.85 (m, 15H, C*H*3)

^{13}C NMR (CDCl3, 100 MHz, 25°C) δ (ppm): 173.1 (C=O), 65.6 (CH$_2$), 60.7 (CH$_2$), 56.6 (CH$_2$), 55.3 (CH$_2$), 40.9 (CH), 32.7 (CH$_2$), 31.9 (CH$_2$), 28.6 (CH), 26.9 (CH$_3$), 23.8 (CH$_2$), 20.3 (CH$_3$), 18.9 (CH$_2$), 14.4 (CH$_3$), 13.8 (CH$_3$)

Yield: 87%

Compound 7b3

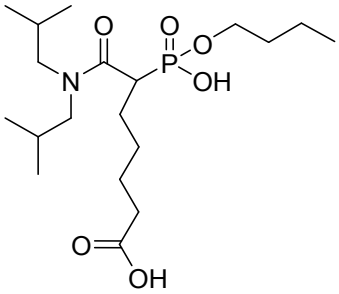


^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 25.4

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.09-4.03 (m, 3H), 3.23-3.04 (m, 10H), 2.29 (m, 2H), 1.97 (m, 4H, N-CH_2-C*H* et CO-CH_2), 1.62-1.58 (m, 4H, CH-CH_2 et O-CH_2-CH_2), 1.38-1.34 (m, 3H), 1.23 (t, 2H), 0.93-0.88 (m, 15H, C*H*3)

Yield: 99%

Compound 7b4

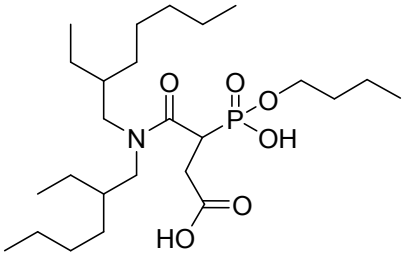


^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 26.1

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 6.36 (s, O*H*), 4.11-4.05 (m, 2H, O-CH_2), 3.69 (m, 1H, CO-C*H*), 3.27-3.07 (m, 4H, N-CH_2), 2.28-1.89 (m, 4H), 1.65-1.57 (m, 3H), 1.39-1.30 (m, 4H), 1.24-1.19 (m, 3H, O-$(CH_2)_2$-CH_3), 0.92-0.86 (m, 12H, $(CH_3)_2$-N)

Yield: 99%

Compound 7c1



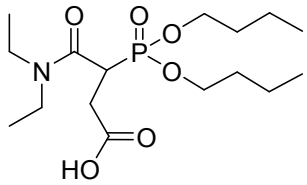
^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 23.8

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4,04-3.98 (m, 2H, O-CH_2-CH_3), 3,71 – 3,18 (m, 6H, CH_2-N & CO-CH_2), 2.97-2.76 (m, 1H, , CO-C*H*-P) ; 1,81 – 1,63 (m, 4H, C*H*-CH_2-N& PO-CH_2-Cl-) ;. 1,44 – 1,15 (m, 15H, CH_2,& O-CH_2-CH_3) ; 0,98 – 0,75 (m, 12H, CH_3).

General procedure for the synthesis of compounds 8n

Coumpound 6n (2.5 mmol, 1 Eq) is introduced into a 50 mL round bottom flask dried under N_2, with 10 mL of ethanol, 10ml H_2O and potassium carbonate (5 mmol, 2 Eq). The mixture is stirred overnight. The mixture is diluted with 10 mL of ethanol and acidified with 14M HCl to reach pH=1. The residue was concentrated under reduced pressure, dissolved into dichloromethane, dried with MgSO4, filtered and re-evaporated to yield the desired compound.

Compound 8c1



^{31}P NMR (CDCl3, 162 MHz) δ (ppm): 24.7

^{1}H NMR (CDCl3, 400 MHz, 25°C) δ (ppm): 4.07 (m, 4H, POC*H*$_2$), 3.78-3.57 (m, 3H, N-C*H*$_2$)3.52-3.01 (m, 3H, C*H*$_2$-CO & N-C*H*$_2$), 2.80-2.76 (m, 1H, P-C*H*(CH_2)-CO), 1.65 (m, 4H, PO-CH_2-C*H*$_2$), 1.38 (m, 4H, PO-CH_2-CH_2-C*H*$_2$-CH_3), 1.25 (m, 3H, N-CH_2-C*H*$_3$), 1.11 (m, 3H, N-CH_2-C*H*$_3$), 0.92 (m, 6H, PO-CH_2-CH_2-CH_2-C*H*$_3$)

Yield: 92%

Hybrid materials

Direct silanisation

Following a classical procedure, a round-bottomed flask was charged with silica powder (6 g), toluene (80 mL) and siloxane. To calculate the quantity of APTES needed, an overestimate was made that the silica materials held five silanols per square nanometre; then, accounting for the specific surface areas of the different materials, 1.2 equivalents of siloxane grafted in T3 mode (viz. with three linked silanols per molecule) were then added. The mixture was stirred vigorously and refluxed at 90 1C for 24 h under nitrogen. The resulting materials were washed overnight by Soxhlet extraction with ethanol, and dried at 80°C.

NH_2@silica	siloxane used:	APTES (Aldrich)
PO@silica	siloxane used	(2-diethylphosphatoethyl)triethoxysilane (SpecificPolymers)

Peptide coupling

In a classical approach, a roundbottomed flask was charged under nitrogen with NH_2@Silica (3 g, 1 eq.), dicyclohexylcarbodiimide (2 eq.), N-hydroxybenzotriazole (2 eq.), diisopropylethylamine (2.5 eq.), Ligand (1,5 eq.) and anhydrous tetrahydrofuran (60 mL), provided that one equivalent represents the amount of primary amine groups previously determined by TGA. The solution was stirred at room temperature for 48 h and then filtered. The resulting material was washed overnight by Soxhlet extraction with a tetrahydrofuran–dichloromethane mixture, and dried overnight.

Amd@silica	ligand used:	AcOH (Fluka)
APo@silica	ligand used:	$APo(OEt)_2$ – APo(OEt-1H)
DiaPO@silica)	ligand used	DiAPo (see below)

Grafted DiAPo	Precursor used
A	4c
B	7c
C	4a
D or (OBu-1H)	7a n
E	7b n
OBu_2	8
2H	8 + post grafting hydrolysis

Post grafting hydrolysis

In a round-bottomed flask was charged under nitrogen starting material (2g), TriMethylSilaneBromure in excess (TMSBr from Aldrich, 1,4 ml) and acetonitrile 20 mL). The mixture was heated under stirring (50°C, 18h, under Nitrogen or Argon). The resulting material was washed with water, refluxed for 12 hours and then dried under vacuum at 100°C to give the desired material.

Po-2H@Davisil60	starting material:	Po@silica
DiAPo-2H@silica	starting material:	DiAPo-OBu_2@silica

Kinetics

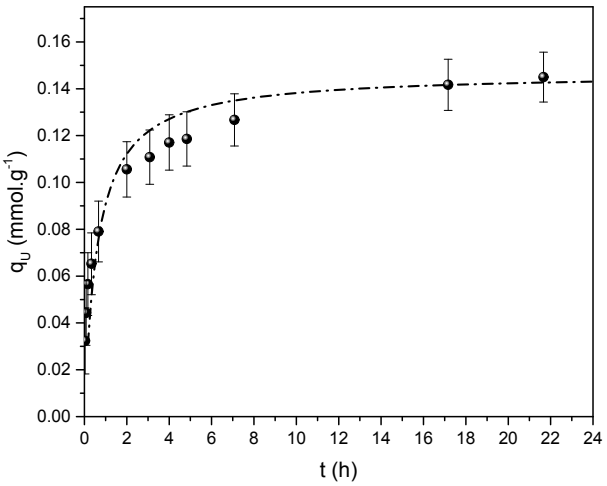


Fig. S1: kinetics of extraction for DiAPo(D)@Davisil60 : experimental points and pseudo-second order fit (dotted line)

NMR specta

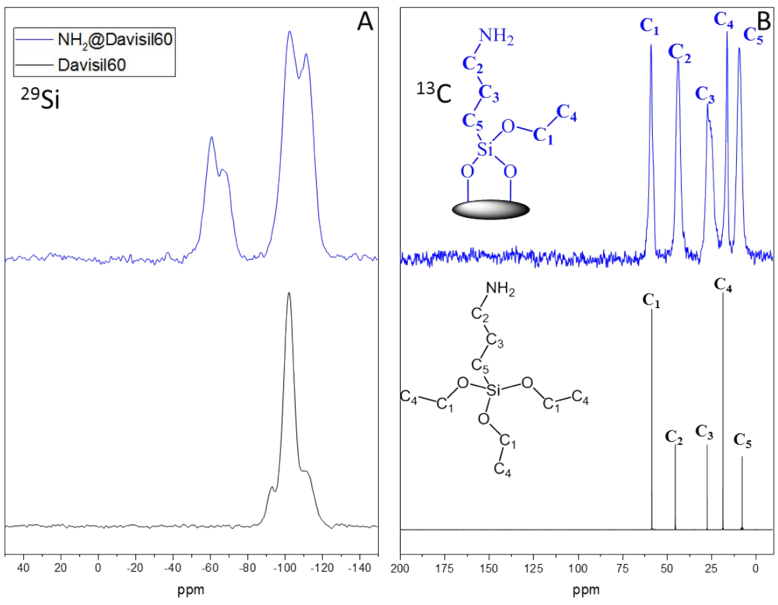


Figure S2 : ^{13}C and ^{29}Si solid state NMR of functionalization of Davisil with amino groups (APTES)

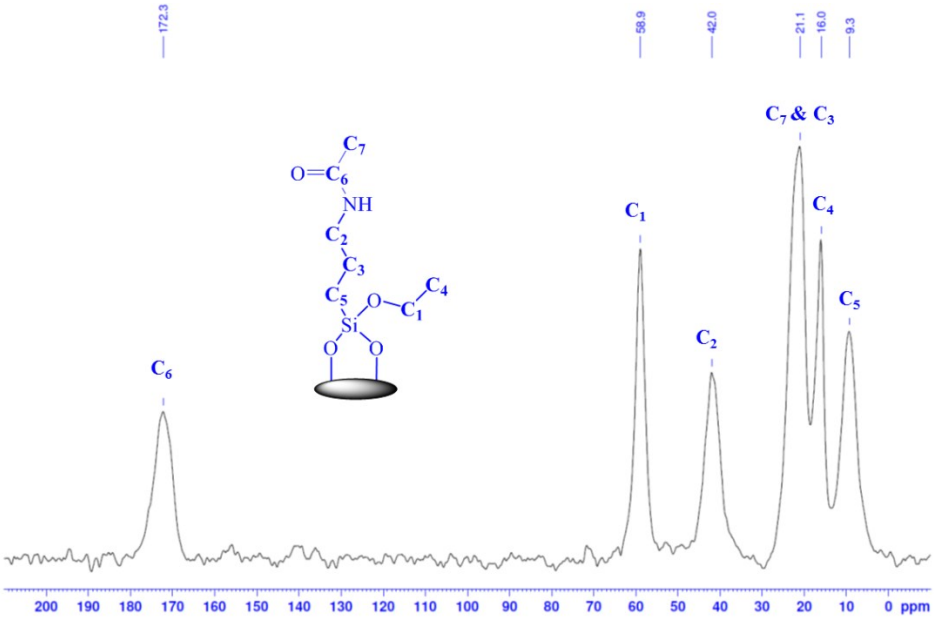


Figure S3 : functionalization of Davisil with amido groups (Amd)

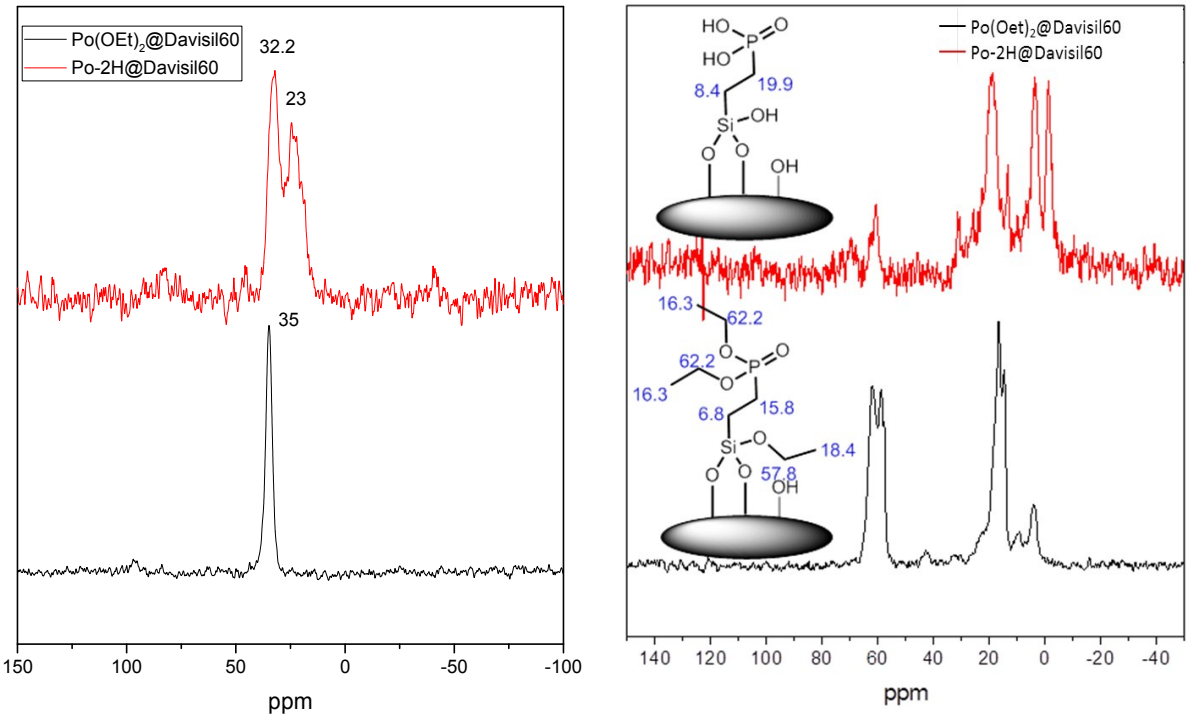


Figure S4 : functionalization of Davisil with mono-phosphonate based functions (Po)

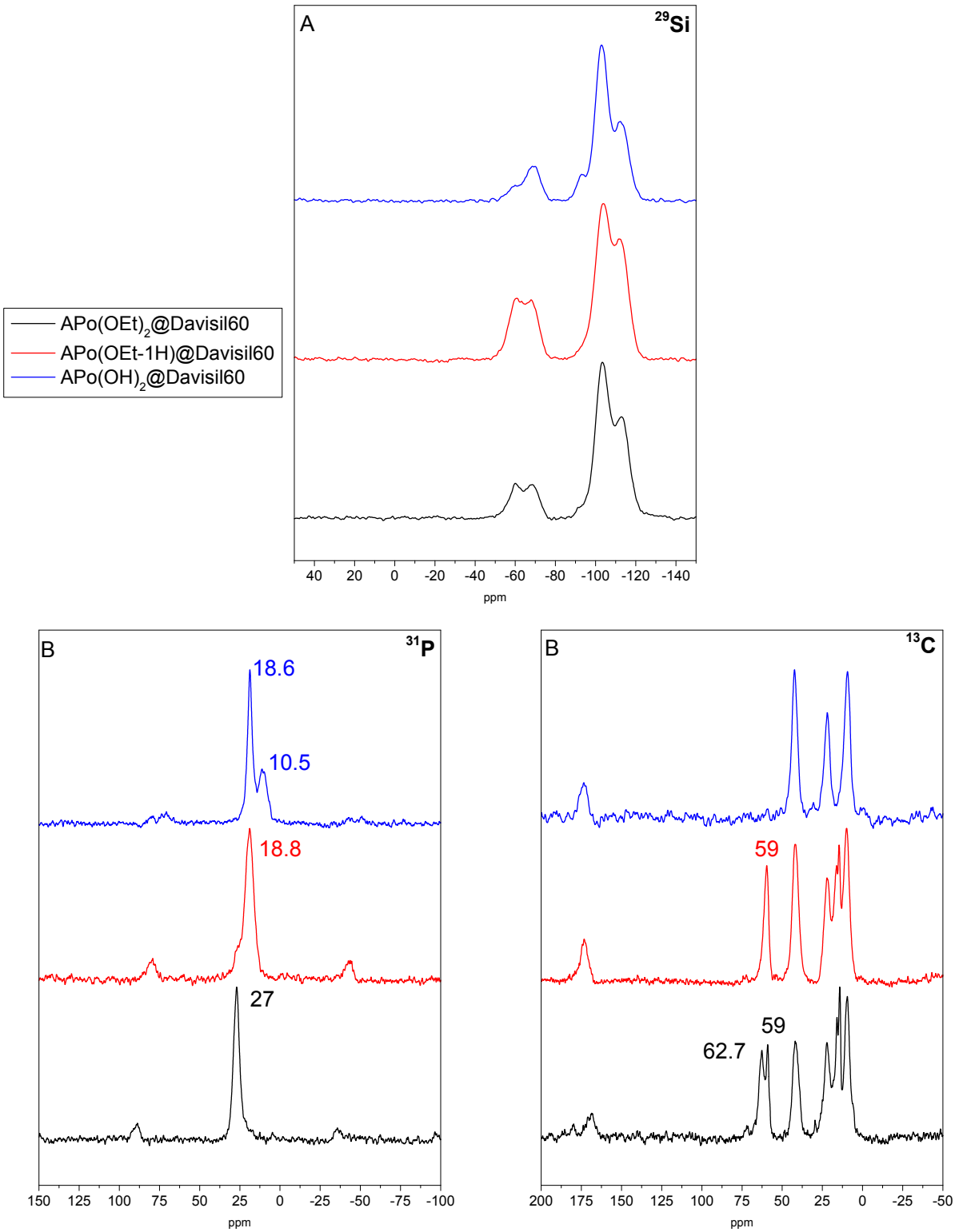


Figure S5 : functionalization of Davisil with amidophosphonates groups (APo)

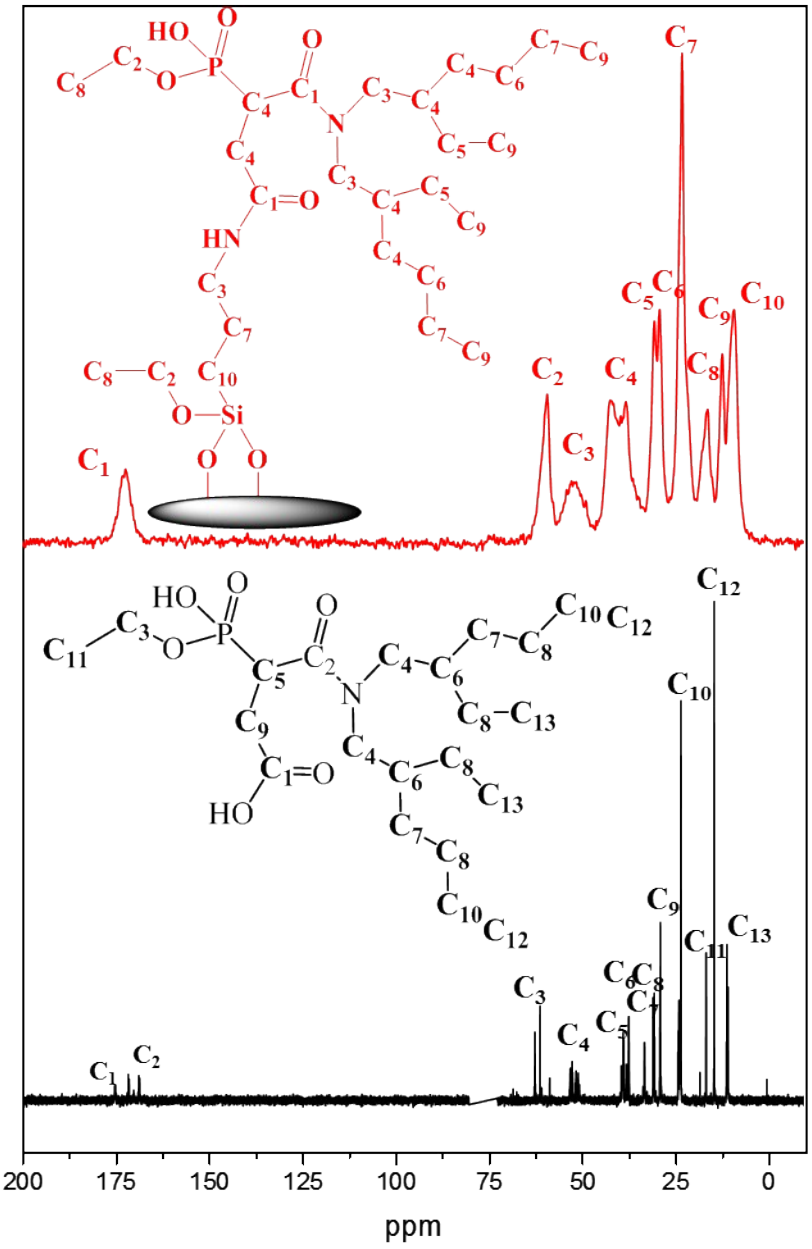


Figure S6 : functionalization of Davisil with di amido phosphonates groups (DiAPo)

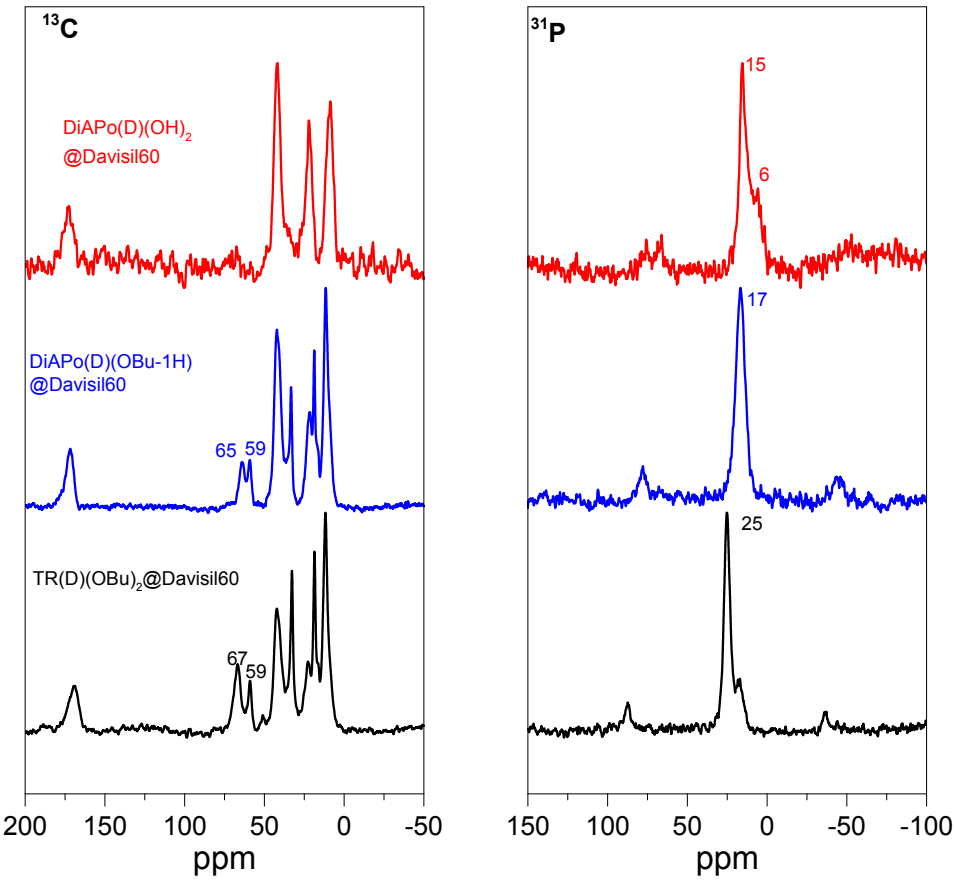


Figure S7 : functionalization of Davisil with di amido phosphonates groups (DiAPo (D))

IR specta

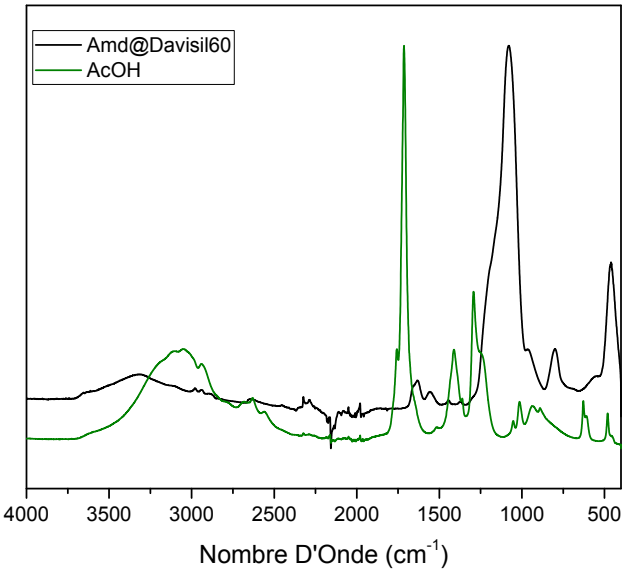


Figure S8 : IR spectra of Amd@Davisil60 (black) and acetic acid (green).

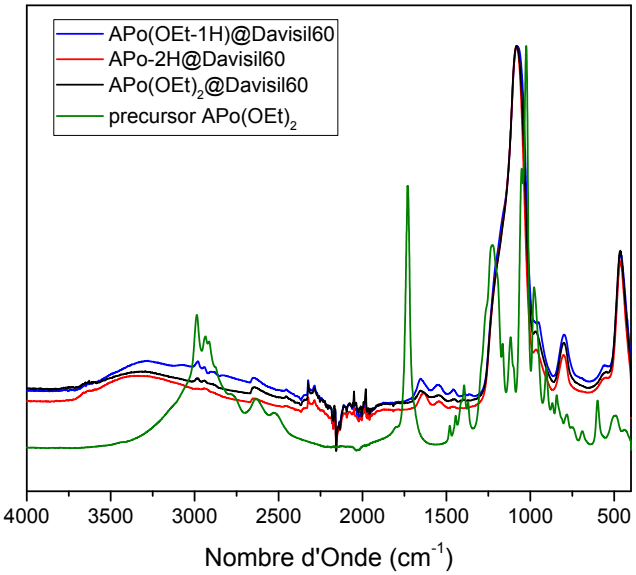


Figure S9 : IR spectra of precursor $APo(OEt)_2$ (green); $APo(OEt)_2$@Davisil60 (black); APo-2H@Davisil60 (red); APo(OEt-1H)@Davisil60 (blue)