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From phosphate rocks to uranium raw materials: hybrid materials designed for selective separation of uranium from phosphoric acid.

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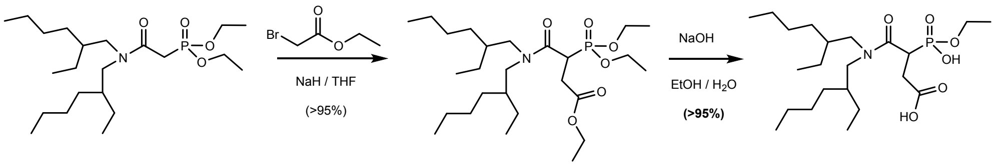
SUPPLEMENTARY MATERIALS

Precursor synthesis



1 **2** **TR**

Diethyl N,N di(2-ethylhexyl)carbamoylmethylphosphonate (**1**) was synthesized according to the procedure describe in the literature.[1]

3-(N,N-di(2-éthylhexyl)carbamoyl)-3-(diéthoxy)phosphono)-ethylpropanoate (**2**):

A solution of **1** (1 eq.) in anhydrous THF (1 mol/L) was added dropwise to a suspension of sodium hydride (1.5 eq.) in anhydrous THF (2 mol/L). The mixture was stirred for 1 hour at room temperature before cooling at 0°C. Ethyl bromoacetate (1.5 eq.) was slowly added to the cold mixture, after return to room temperature the mixture was stirred for 1h.

The mixture was acidified with HCl (1 mol/L) until the solution reached to pH 1, and then extracted with dichloromethane. The combined extracts were dried over sodium sulphate, filtered and evaporated under *vacuum*. The excess of ethyl bromoacetate was removed by distillation under *vacuum* to give the desired compound **2** (yield >95%).

^{1}H NMR *(400 MHz, $CDCl_3$) δ (ppm):* 0.77 – 0.89 (m, 12H) ; 1.16 – 1.28 (m, 27H) ; 1.63 – 1.70 (m, 1H) ; 1.74 – 1.83 (m, 1H) ; 2.68 – 2.76 (m, 1H) ; 2.70 – 2.90 (m, 1H) ; 3.01 – 3.18 (m, 2H) ; 3.50 – 3.75 (m, 3H) ; 4.01 – 4.13 (m, 6H).

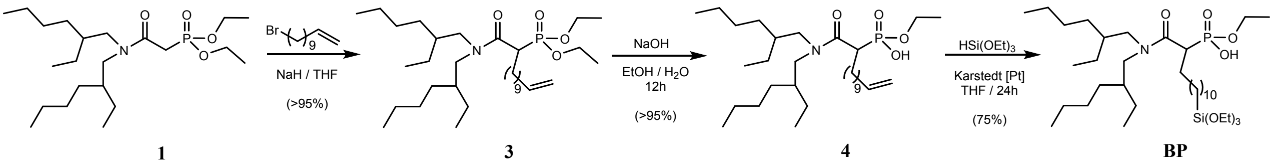
^{13}C NMR *(100 MHz, $CDCl_3$) δ (ppm):* 10.3 ; 10.5 ; 10.6 ; 10.9 ; 14.0 ; 14.1; 16.3 ; 16.4 ; 23.1 ; 23.5 ; 23.7 ; 24.0 ; 28.6 ; 28.7 ; 28.8 ; 28.9 ; 30.2 ; 30.3 ; 30.6 ; 30.7 ; 32.7 ; 37.0 ; 37.1 ; 37.2 ; 37.3 ; 37.7 – 39.1 (d, J = 132.0 Hz) ; 38.6 ; 38.7 ; 38.9 ; 50.2 ; 50.6 ; 50.9 ; 51.2 ; 51.9 ; 52.4 ; 60.8 ; 62.4 ; 62.5 ; 63.1 ; 63.2 ; 63.3 ; 167.4 ; 168.5 ; 171.3 – 171,5 (dd, J = 18.5 Hz, d = 4.5 Hz).
^{31}P NMR *(160 MHz, $CDCl_3$) δ (ppm):* 23.1.

3-(N,N-di(2-ethylhexyl)carbamoyl)-3-(ethoxy)hydroxyphosphoryl)-propanoic acid (**TR**):

To a solution of **2** in ethanol (0.4 mol/L) was added an aqueous solution of potassium hydroxide (20%, 6 eq). The solution was then heated under reflux for 3 h. After return to room temperature, the mixture was acidified with HCl (1 mol/L) until the solution reached to pH 1, and then extracted with dichloromethane. The combined extracts were dried over sodium sulphate, filtered and evaporated under *vacuum* to give the desired compound **TR** (yield >95%).

^{1}H NMR *(400 MHz, $CDCl_3$) δ (ppm):* 0.82 – 0.92 (m, 12H) ; 1.22 – 1.38 (m, 19H) ; 1.66 – 1.73 (m, 1H) ; 1.74 – 1.82 (m, 1H) ; 2.88 – 3.0 (m, 2H) ; 3.01 – 3.23 (m, 2H) ; 3.46 – 3.80 (m, 3H) ; 4.07 – 4.17 (m, 2H) ; 8.96 (bs, 2H).

^{13}C NMR *(100 MHz, $CDCl_3$) δ (ppm):* 10.3 ; 10.5 ; 10.7 ; 10.8 ; 14.0 ; 16.2 ; 16.3 ; 23.0 ; 23.4 ; 23.6 ; 23.8 ; 28.5 ; 28.6 ; 28.7 ; 30.2 ; 30.3 ; 30.4 ; 32.9 ; 37.1 ; 37.7 – 39.0 (d, J = 132.0 Hz) ; 38.5 ; 38.6 ; 50.4 ; 50.6 ; 52.3 ; 52.8 ; 62.4 168.8 ; 174.2 (d, J = 9.0 Hz) ; 174.4 (d, J = 9.0 Hz).
^{31}P NMR *(160 MHz, $CDCl_3$) δ (ppm):* 24.0.



Compound **3** and **4** were synthesized using 11-Bromo-1-undecene and according to the previous protocol.

Diethyl-1-(N, N- di(2-ethylhexyl)carbamoyl)-1-undecenyl phosphonate (**3**) (yield >95%)

^{1}H NMR *(400 MHz, $CDCl_3$): δ (ppm)* = 0.74-0.80 (m, 12H) ; 1.15-1.31 (m, 38H) ; 1.51-1.61 (m, 1H) ; 1.64-1.71 (m, 1H) ; 1.89-1.93 (m, 1H) ; 1.97-2.02 (m, 1H) ; 2.76-2.81 (m, 1H) ; 2.82-2.86 (m, 1H) ; 3.06-3.13 (m, 1H) ; 3.42-3.61 (m, 1H) ; 3.61-3.63 (m, 1H) ; 3.98-4.06 (m, 4H) ; 4.78-4.88 (m, 2H) ; 5.64-5.71 (m, 1H).

^{13}C NMR *(100 MHz, $CDCl_3$): δ (ppm)* = 13.8 ; 13.9 ; 22.4 ; 26.3 ; 26.4 ; 27.1 ; 28.9 ; 31.3 ; 31.4 ; 41.2 ; 46.0 ; 48.1 ; 165.8.

^{31}P NMR *(160 MHz, $CDCl_3$): δ (ppm)* = 24.7

Ethyl-1-(N, N- di(2-ethylhexyl)carbamoyl)-1-undecenyl phosphonate (**4**) (yield >95%)

^{1}H NMR *(400 MHz, $CDCl_3$): δ (ppm)* = 0.73-0.80 (m, 12H) ; 1.22-1.30 (m, 35H) ; 1.51-1.71 (m, 2H) ; 1.90-1.94 (m, 1H) ; 1.97-2.02 (m, 1H) ; 3.06-3.23 (m, 1H) ; 3.40-3.62 (m, 1H) ; 3.62-3.63 (m, 1H) ; 3.88-3.95 (m, 2H) ; 4.55-4.70 (m, 2H) ; 4.84-5.02 (m,1H)

^{31}P NMR *(160 MHz, $CDCl_3$): δ (ppm)* = 26.8

Ethyl-1-(N, N- di(2-ethylhexyl)carbamoyl)-1-(triethoxysilylundecyl) phosphonate (**BP**)

To a stirred solution of **4** (1 eq.) in anhydrous THF (0.1 mol/L) heated to reflux was added triethoxysilane (10 eq.) under nitrogen atmosphere, followed by the Karstedt catalyst solution (0.01 eq. ; Pt(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 3% Pt). The reflux was pursued for 24h, then the solvent was evaporated and the residue obtained was washed several times with pentane to give the desired compound **BP** (yield 75%).

^{1}H NMR *(400 MHz, $CDCl_3$): δ (ppm)* = 0.6 (m, 2H) ; 0.8-0.87 (m, 12H) ; 1.12-1.34 (m, 41H) ; 1.51-1.71 (m, 2H) ; 1,91-2.02 (m, 2H) ; 3.1-3.22 (m, 1H) ; 3.40-3.65 (m, 2H) ; 3.77-3.98 (m, 6H)

^{31}P NMR *(160 MHz, $CDCl_3$): δ (ppm)* = 26,1

^{29}Si NMR *(80 MHz, $CDCl_3$): δ (ppm)* = -44.47

Materials synthesis

Ordered mesoporous silica (SBA15) was synthesized as previously reported in the literature.[2]

Ordered nanoporous carbon material (CMK-3) was prepared following synthesis procedure reported in the literature.[3]

The modification of the surface of SBA[4] (silanisation with APTES or **BP**) or CMK[5] (Diels Adler cycloaddition with propargylamine) was performed according to the procedure reported in the literature.

The introduction of **TR** ligand (2 eq.) onto the modified supports NH2@SBA and NH2@CMK (1eq. of functional group) was performed using the coupling reagent system N,N'-Dicyclohexylcarbodimide (DCC, 2 eq.) / 1-Hydroxybenzotriazole (HOBt, 2 eq.) / N, N- diisopropylethylamine (DIPEA, 1.5 eq) in anhydrous THF. The mixture was stirred for 48h under argon at room temperature; the solid was filtered off, washed several times with methanol and dichloromethane then dried under *vacuum*.

Each step of TR@SBA and BP@SBA synthesis were followed by CP-MAS NMR (^{29}Si, ^{13}C, ^{31}P) and by XRD and Raman spectroscopy for the CMK based materials. The characterization of the TR@SBA and TR@CMK materials are given hereafter (Figure S3 & S4).

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Figures and Table

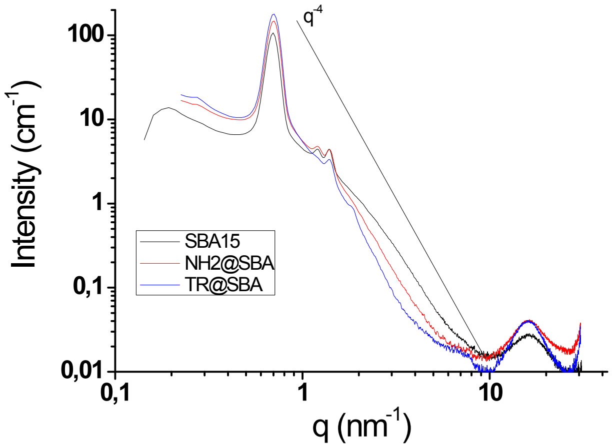

Figure S1: SAXS experiments for SBA15; NH2@SBA15 and TR@SBA15 materials.

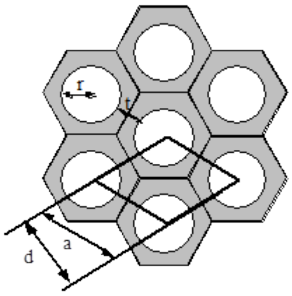

Figure S2 : 2D hexagonal structure of SBA15.

Sample	q_{10} *(nm⁻¹)*	S_{BET} *(m²g⁻¹)*	S_{μ} *(m²g⁻¹)*	D_p *(nm)*	a(nm)	t(nm)
SBA15	0.697	760	117	6.7	10.41	3.71
NH2@SBA15	0.702	497	61	5.8	10.33	4.53
TR@SBA15	0.707	286	6	4.7	10.26	5.56
CMK3		1400	-	3.5		
NH2@CMK		600	-	3.2		
TR@CMK		300	-	2.8		

Table S1: pores structure and meso-structure of SBA15, NH2@SBA, TR@SBA15 and CMK3, NH2@CMK and TR@CMK samples. q_{10} is the SAXS diffraction peak characteristics of a 2D-hexagonal structure S_{BET} is the specific surface area calculated by the BET model; S_{μ} is the microporosity surface area obtained by the t-plot model; D_p is the pore size diameter form BJH model, a is the distance between two pores (calculating from q10 and as according to Figure S2); t is the wall thickness (see Figure S2).

Characterization of TR materials:

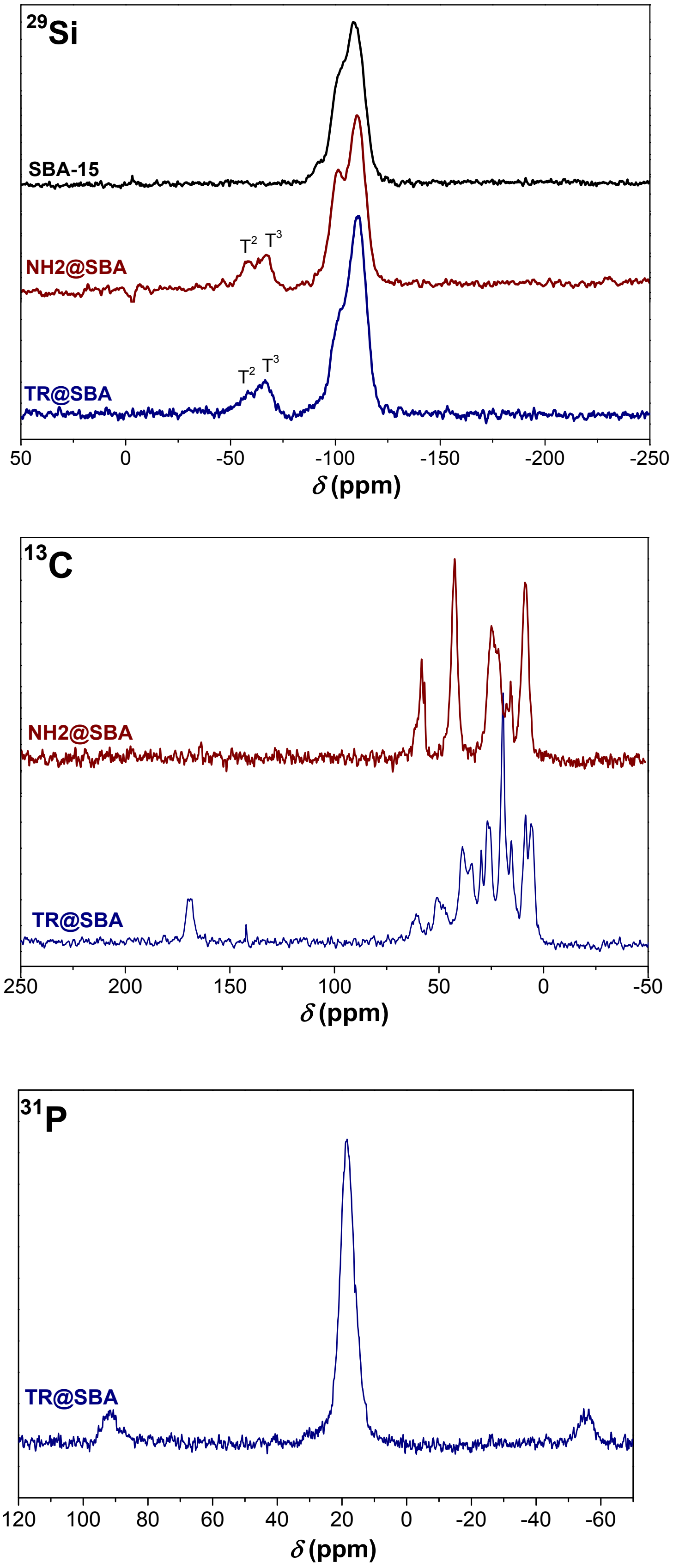

Figure S3 : ^{29}Si, ^{13}C and ^{31}P CP-MAS spectra

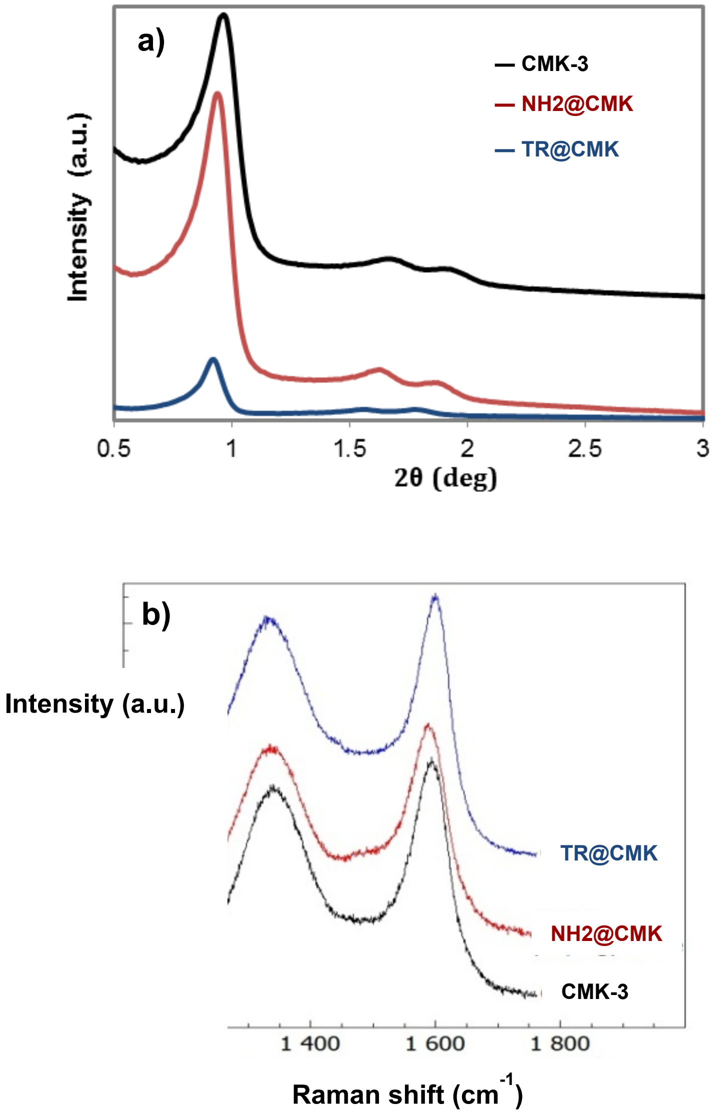

Figure S4: a) X-ray diffraction spectra and b) Raman spectroscopy