Supplementary Material (ESI) for Chemical Communications

Self-Assembled Microspheres From f-Block Elements and Nucleoamphiphiles

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Supporting data
Materials:

TEM microscopy experiments were performed on a Philips CM 10 and a Jeol JEM-3010 (CRMC2, Luminy, Marseille, France) for High Resolution pictures (Cu/Pd carbon coated grids). SEM secondary electron microscopy experiments were conducted at the University of Montpellier II, Service commun de Microscopie Electronique, on a JSM-6300 F. SEM samples were deposed on carbon coated support and platin shadowed. X-ray diffraction: samples were prepared by placing a small amount of microspheres in a sealed quartz capillary (diameter 1 mm), and then placing the capillary in a sample holder. SAXS measurements were conducted at the University of Montpellier II, Laboratoire GDPC on a diffraction system equipped with a two-dimensional position-sensitive area detector. The sample to-detector distance was 30 cm, source: “Rigaku” Copper rotating anode working at 40 KV, 100 mA, monochromator confocal Max Flux Osmic optic. Diffraction patterns were obtained using an image plate 2 D detector. The low angle reflections were in accordance with Bragg’s law $2d \sin\theta = h\lambda$, where λ is the wavelength (1.54Å), d is the repeat period, h is the number of the diffraction order, and θ is the Bragg angle. Conductivities measurements were carried out with a Mettler Toledo MC 226 conductivity meter. The solid-state 31P MAS NMR spectra were obtained on a Bruker Avance-400 MHz NMR spectrometer (magnetic field 9.4T) operating at a 31P resonance frequency of 162.1 MHz and using a commercial Bruker 2.5 mm double-bearing probe. About 12 mg of samples were placed in a zirconium dioxide rotors of 2.5-mm outer diameter and spin at a Magic Angle Spinning rate of 20 kHz. The experiments were performed at room temperature, 256 scans were accumulated using a delay of 10 s. The 31P chemical shifts were referenced to 85% aqueous phosphoric acid (H3PO4).

General procedure for microspheres preparation:

To prepare hybrides microspheres, 25 mg of freeze dried DSUPC are hydrated 2 minutes at 75 °C by 500 µl of a 0.16 M aqueous solution of Thorium IV nitrate (or Cerium III nitrate), at their natural acidic pH. The precipitate is washed twice with 200 µl of deionized water and then freeze dried.

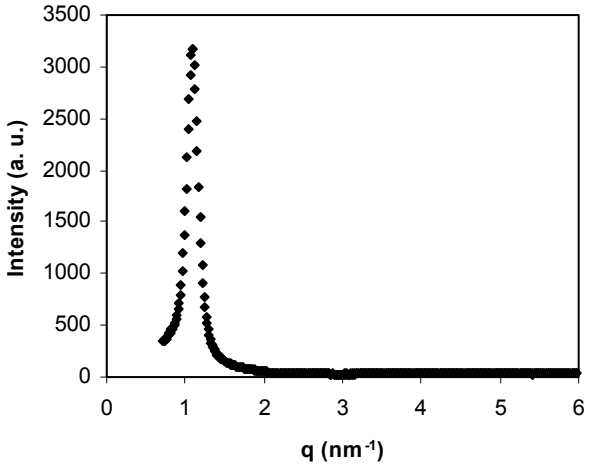

Figure 1. SAXS profile of DSUPC-Thorium based microspheres.

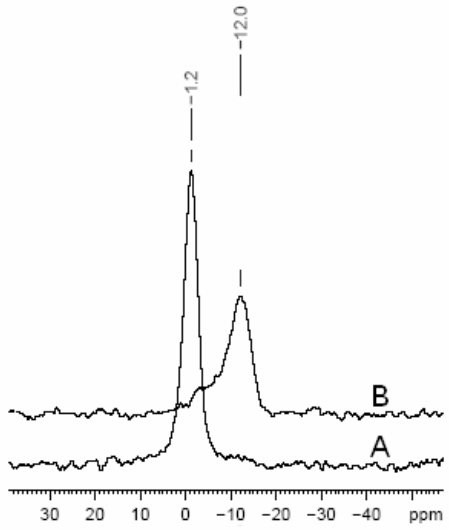

Figure 2. ^{31}P HRMAS NMR spectra of (A) DSUPC and (B) DSUPC-Thorium based microspheres.

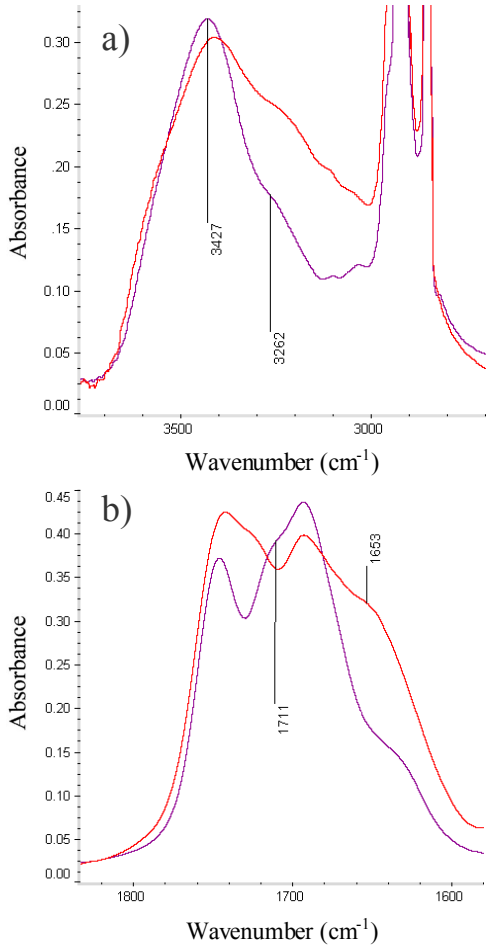

Figure 3. FTIR spectra of DSUPC (Blue line) and DSUPC-Thorium based microspheres (Red line).

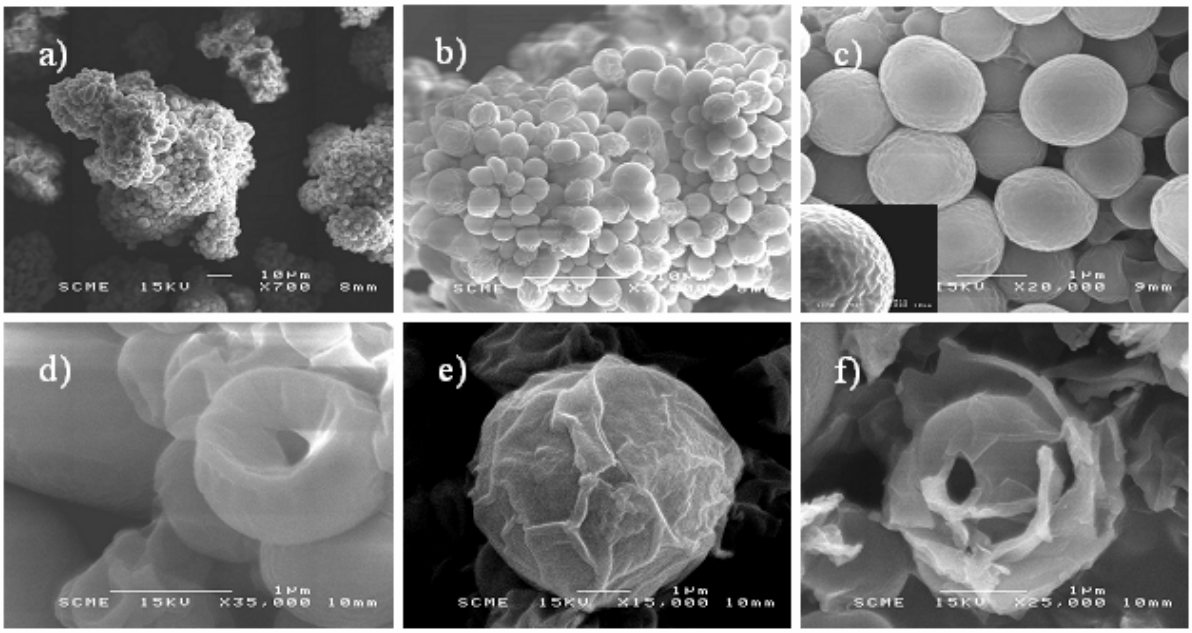

Figure 4. Typical SEM images of thorium (a), (b), (c), and Cerium (e) microspheres at different magnification. Inset (c): magnification of a thorium microsphere surface. (d) and (f) are images of respectively thorium and cerium destroyed microspheres showing their hollow stucture.

Conductivity measurements

The composition of the shells was determined as following: In a typical experiment (realized in triplicate), 25.0 mg of DSUPC (2.65 x 10^{-5} moles) are hydrated at 75 °C by 500 µL of a thorium IV nitrate solution (8.00 x 10^{-5} moles). After 2 minutes the precipitate obtained is vigorously triturated. The volume of the suspension is extended to 10 mL with milli Q water and an average conductance of G = 2.80 mS/cm is measured at 300 °K. This value gives a concentration of 6.80 x 10^{-3} M (6.80 x 10^{-5} moles). The amount of thorium nitrate incorporated in the microsphere shells corresponds to the difference of soluble thorium nitrate before and after the formation of microspheres; 8.00 x 10^{-5} - 6.80 x 10^{-5} = 1.20 x 10^{-5} moles. The ratio R = Th^{4+}/DSUPC in the shells is R = 1.20 x 10^{-5}/2.65 x 10^{-5} = 0.45.

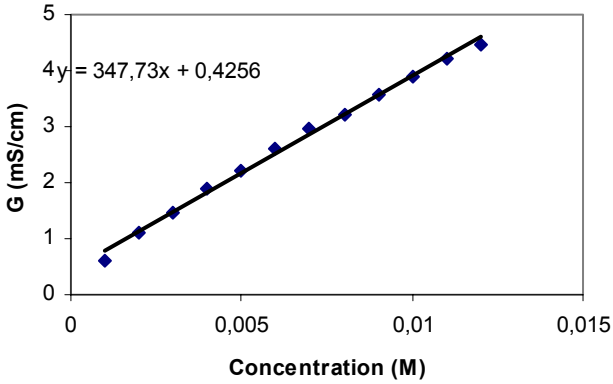

Figure 5. Standard curve of thorium IV nitrate in milli Q water conductance G at 22 °C versus concentration C.

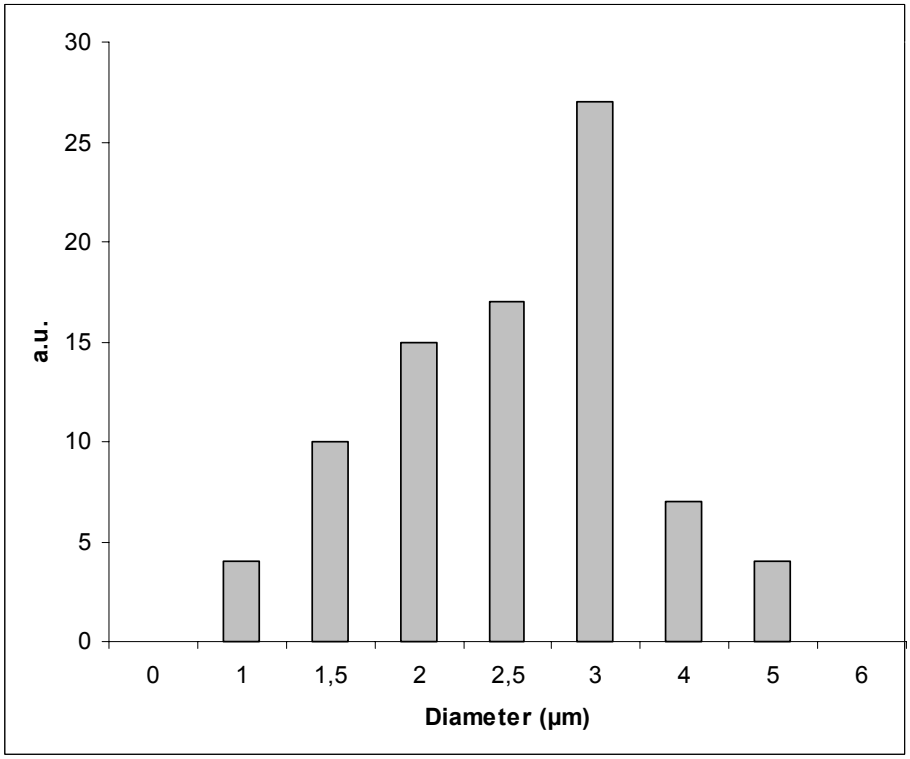

Figure 6. Size distribution of the microspheres (objects versus size) obtained from the electron microscopic images (SEM).