A Versatile Route to Bifunctionalized Silsesquioxane (POSS): Synthesis and Characterization of Ti-containing aminopropylisobutyl-POSS.

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Contents:

1.  Experimental Section
2.  Figures

Experimental Section

Materials:

- Completely condensed aminopropyl heptaisobutyl-POSS (1):

Commercial completely condensed aminopropyl heptaisobutyl-POSS (1) from Hybrid Plastics Company has been used as reactant for the preparation of partially condensed trisilanol aminopropyl hexaisobutyl-POSS via cleavage reaction. The preparation has been performed under inert conditions using a nitrogen atmosphere. All solvents, freshly opened, have been used without further purification.

- Partially condensed trisilanol aminopropyl hexaisobutyl-POSS (2):

An equimolar solution of aqueous tetraethylammonium hydroxide (TEAOH 35% from Sigma Aldrich) and completely condensed aminopropyl heptaisobutyl-POSS (1) was prepared adding a 0.5mL of TEAOH (35 wt.%) (mol 5.71·10^{-4}) to a solution of (1) (1 g, mol 5.7·10^{-4}) in 25mL of THF under vigorous stirring. After addition, the temperature was raised to reflux and stirred for 4 h to complete the reaction. The base excess was neutralized by few mL of 2N HCl. During this phase, tetraethylammonium chloride salt (C_{2}H_{5})_{4}N(Cl) was isolated and removed by the solution. Filtration of the solution through a fine sintered glass funnel, and solvent removal in vacuum, led to the formation of 600 mg of partially condensed trisilanol aminopropyl hexaisobutyl-POSS (2) product as white amorphous foam which was dissolved in Et_{2}O and dried over anhydrous MgSO_{4}.

- Ti-NH_{2}POSS (3):

160 µL (mol. 5.37·10^{-4}) of Ti(i-PrO)_{4} (97%, Sigma Aldrich) were added with vigorous stirring to a solution made of 400 mg (mol. 5.05·10^{-4}) of (2) in 30 ml of chloroform. The reaction solution was previously carefully purged with nitrogen to prevent the rapid
hydrolysis of Ti(i-PrO)₄. After addition, the temperature was raised to 60 °C and stirred for 4h30min under nitrogen flow. Subsequently, the solvent was evaporated until a white powder (300 mg) was obtained.

Description of equipment:

- NMR spectra of the samples dissolved in CDCl₃ (concentration M 0.1) at room temperature have been recorded on a Jeol Eclipse Plus spectrometer with a 8 T magnet.

- Infrared (IR) spectra of solid samples in KBr pellets have been recorded in the range 4000 - 400 cm⁻¹ at 4 cm⁻¹ resolution using a Bruker Equinox 55 spectrometer.

- XPS spectrum has been collected using a Physical Electronics 5602 CI Mulhettechnique equipped with Al Kα X-Ray source with a X-Ray anodic power of 400W and a pass energy from 5.85 to 50 eV. The sample (powder) was diluted in metallic Indium matrix. The analysis surface was 800µm (diameter).

- UV-Visible spectra were recorded in the range 190 - 750 nm using a Perkin Elmer Lambda 900 spectrometer equipped with a diffuse reflectance sphere accessory (DR-UV-Vis). The samples were dispersed in anhydrous BaSO₄ (10 wt %).

Figures

²⁹Si NMR spectrum of Ti-NH₂POSS (3) in CDCl₃:
DR-UV-Visible spectrum of Ti-NH$_2$POSS (3) diluted in BaSO$_4$ matrix (10 wt%).