

**One-pot synthesis of hierarchical porous layered hybrid materials based on  
aluminosilicate sheets and organic functional pillars**

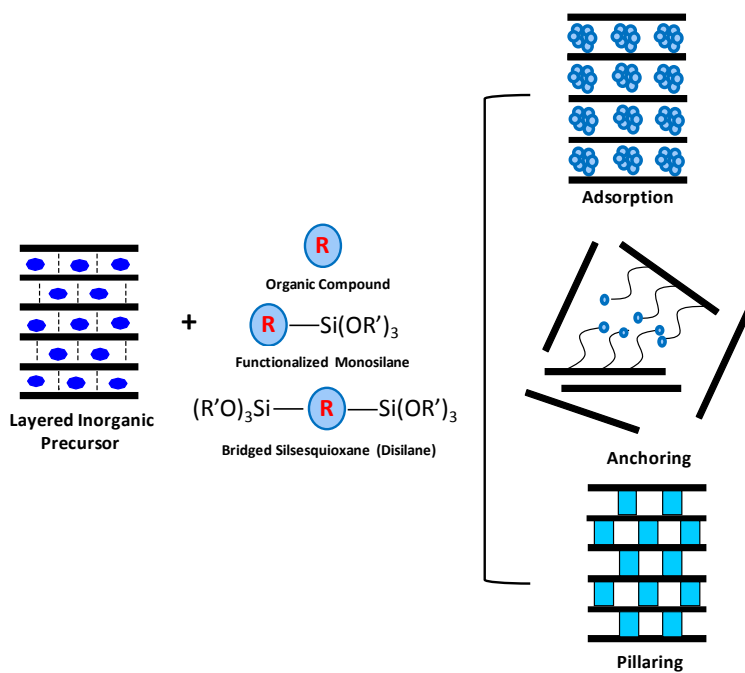
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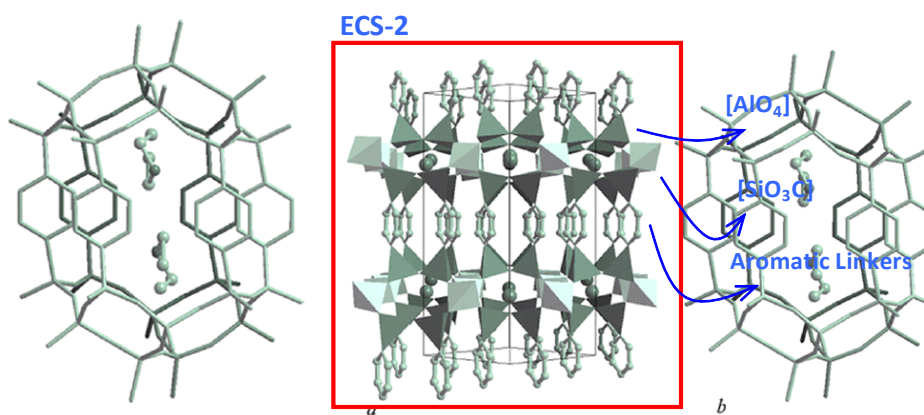
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**Supplementary Information**

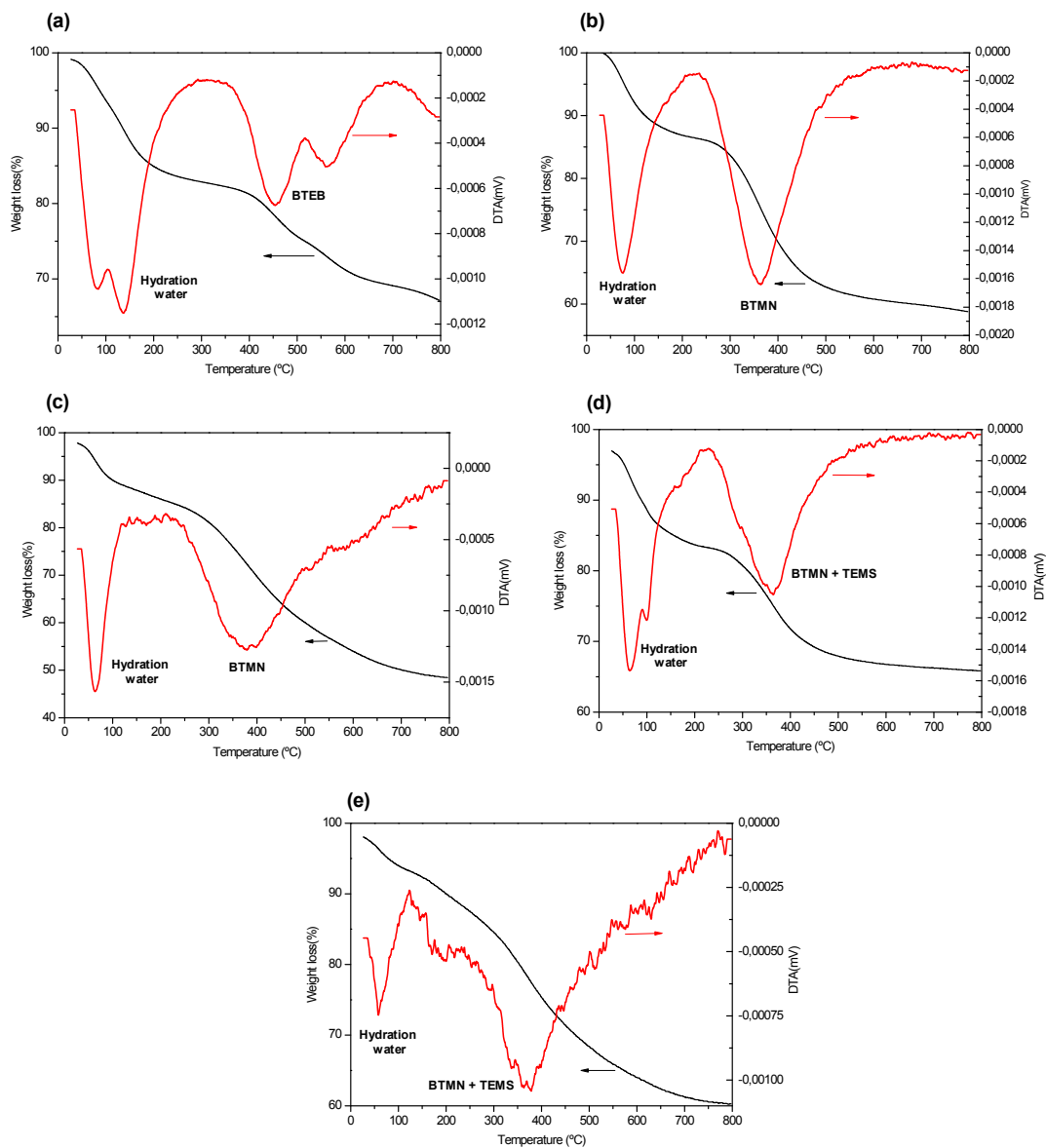
**Figure S1.** Different hybrid layered materials obtained from organic and inorganic precursors.



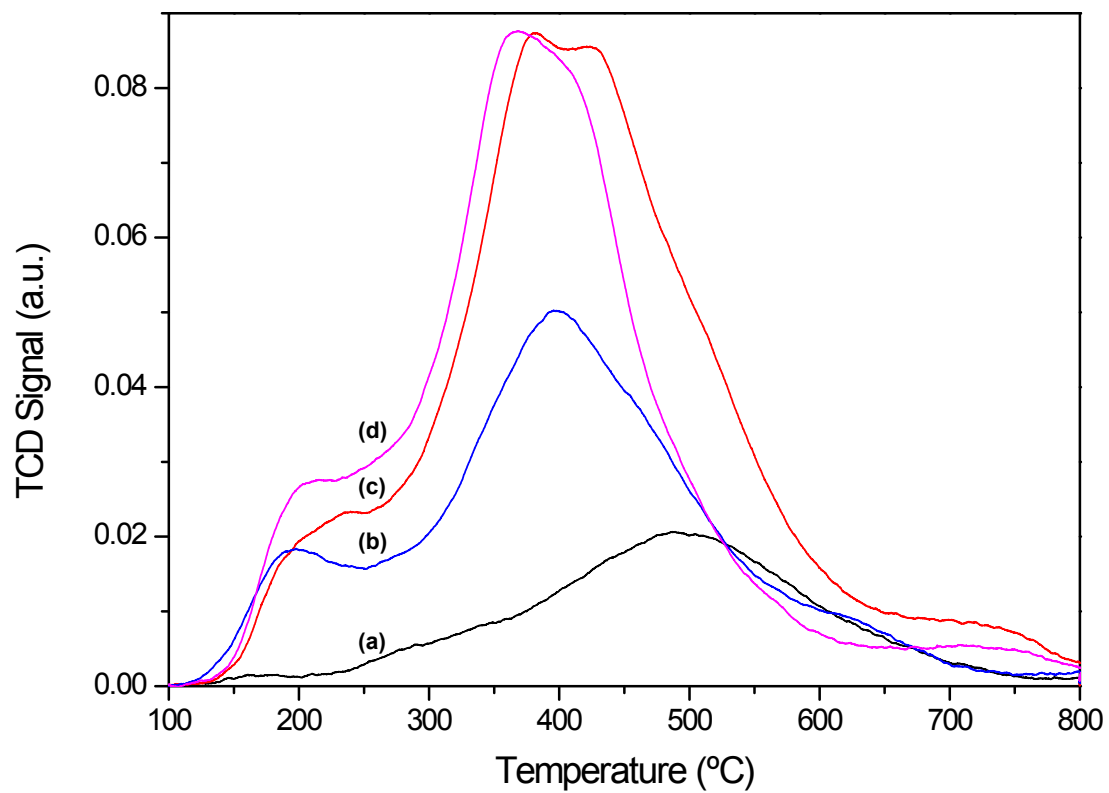
**Figure S2.** Representation of ECS layered hybrid materials (according to references 36 and 39).



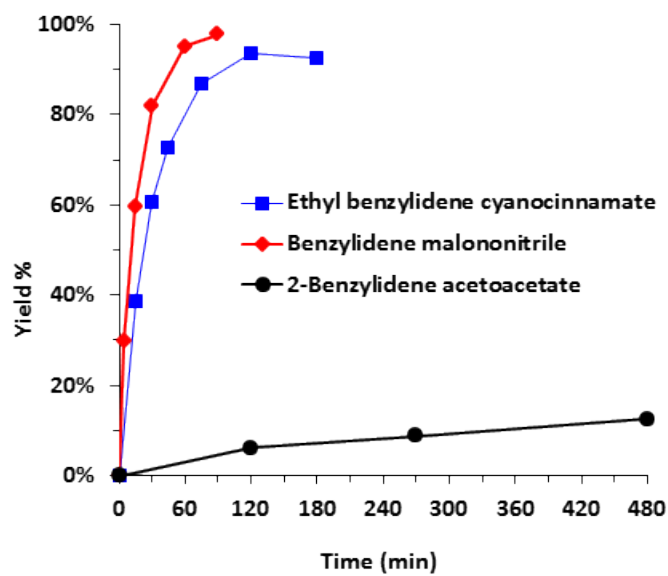
**Figure S3.** Thermogravimetical curves (TGA) and their corresponding derivatives (DTA) of hybrid layered materials: (a) ECS-1, (b) LHM-BTMN, (c) LHM-BTMN-H, (d) LHM-TEMS and (e) LHM-TEMS-H.



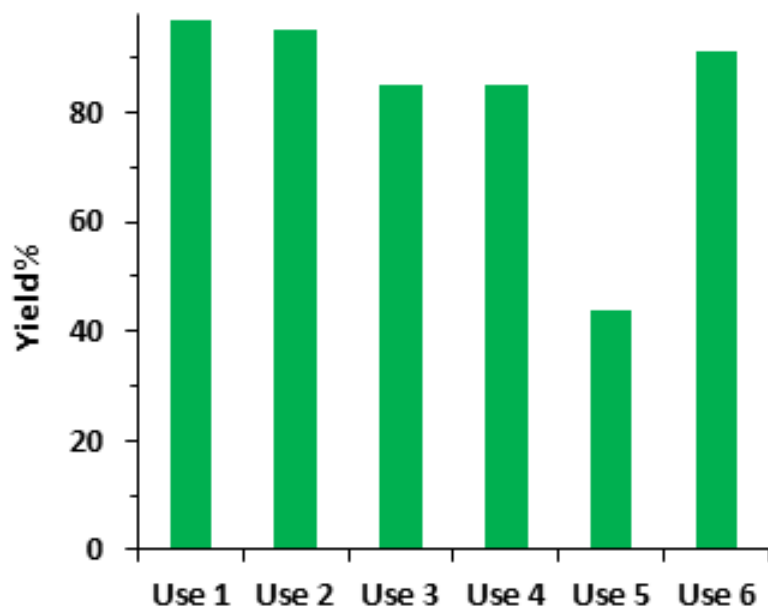
**Figure S4.** NH<sub>3</sub> thermoprogammed desorption curves of layered hybrid materials: (a) LHM-BTMN, (b) LHM-TEMS, (c) LHM-BTMN-H and (d) LHM-TEMS-H.



**Figure S5.** Benzylidene malononitrile (◆), ethyl benzylidene cyanocinnamate (■) and ethyl 2-benzylidene acetoacetate (●) yields versus time when the Knoevenagel reactions were carried out in presence of LHM-TEMS-H material. Reaction conditions: benzaldehyde (2.67 mmol) and methylenic substrates (2.87 mmol) at 60 °C, under inert atmosphere (N<sub>2</sub>), 25 mg of catalyst, 5 mol% of N and 1 mL of acetonitrile.



**Figure S6.** Ethylcyanoacrylate yield was plotted when the Knoevenagel reaction was carried out in presence of LHM-TEMS-H for six successive uses. Conditions of reaction: benzaldehyde (8.8 mmol), ethyl cyanoacetate (9.5 mmol) at 60 °C, under an inert atmosphere (N<sub>2</sub>), 100 mg of catalyst, and 5 mL of acetonitrile were used as solvent.



**Acid-base titration to evaluate interlayered ethylenediamino groups (LHM-BTMN-H and LHM-TESM-H samples)**

In typical experiment, 50 mg (0.25 mmol of N) of LHM-BTMN-H sample was added to 10 mL of HCl solution (0.02 M). After 5 h of stirring at room temperature, the mixture was filtrated and the solid was washed with water (4x25 mL). The obtained filtrate was titrated by a solution of NaOH (0.02 M). The titration was repeated three times. The same procedure was performed using 50 mg (0.14 mmol of N) of LHM-TEMS-H sample.