

# Organic–inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts as recyclable organocatalysts for Knoevenagel condensations

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Organic–inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts prepared from monosilylated and disilylated monomers by sol–gel methodologies are active and reusable organocatalysts for the Knoevenagel condensation of aromatic aldehydes with malononitrile and ethyl cyanoacetate under solvent-free conditions. Our immobilized systems present higher activities than related homogeneous bis-imidazolium salts, showing the cooperative effect of the matrix surface and the additional advantage of easy recycling. The best performances were obtained with the material derived from polycondensation of a disilylated dihydroimidazolium salt in the absence of tetraethoxysilane (TEOS).

## Introduction

Among the carbon–carbon bond forming reactions, the Knoevenagel condensation of aldehydes with active methylene compounds constitute one of the most important synthetic methods for the preparation of electrophilic trisubstituted alkenes, which involves a simple operation process and mild conditions. Traditional homogeneous catalysts include primary or secondary amines or buffer systems containing ammonia or amines and the corresponding conjugated acid.<sup>1</sup> Some reports about the use of *gem*-diamines<sup>2</sup> and guanidines<sup>3</sup> as organocatalysts of this reaction can be found. Other common catalysts are alkali alkoxides, alkali hydroxides and Lewis acids in liquid phase systems.<sup>1</sup> Solid inorganic bases (zeolites, hydroxyapatite, sepiolites, hydrotalcites, basic oxides *etc.*) or solid acids (sulfation promoted zirconia) have also been employed as heterogeneous catalysts.<sup>4</sup> Recently, alkylammonium,<sup>5</sup> imidazolium<sup>6</sup> and guanidium-type<sup>7</sup> ionic liquids or other task-specific ionic liquids<sup>8</sup> have been described as promoters of this condensation. Lewis acidic ionic liquids based on imidazolium and pyridinium chloroaluminates have been used as both solvent and Lewis acid-type catalysts.<sup>9</sup> In other cases, the imidazolium-based ionic liquids act only as reaction media which allows easy recycling and other catalysts are required, such as glycine, KOH or hydrotalcite.<sup>10</sup>

Organocatalysis has experienced a renewed and growing interest in the last decade.<sup>11</sup> The relatively high catalyst loading required in many of the organocatalytic processes has led a number of groups to investigate the possibility of the catalyst recycling,

which would provide some advantages from both the economical and environmental points of view. Immobilization of the organocatalysts<sup>12</sup> to an insoluble polymer matrix allows an easy separation by filtration, simplifying the work-up procedure and facilitating the catalyst recovery and reuse. In this sense, some few reports exist about heterogeneous reusable organocatalysts for Knoevenagel condensations, such as polystyrene-supported poly(amidoamine) dendrimers,<sup>13</sup> purely organic mesoporous poly(benzimidazole),<sup>14</sup> mesoporous silicas (MCM-41, MCM-48 and SBA-15) with grafted aminopropyl groups, dihydroimidazole groups or other organic bases,<sup>15</sup> and silica gel or mesoporous SBA-15 functionalized with imidazolium or pyridinium based ionic liquids.<sup>16</sup>

Very recently, we have described the preparation of organic–inorganic hybrid silica materials containing imidazolium and bis-dihydroimidazolium salts and their use, together with a palladium source, as recoverable palladium catalysts for cross-coupling reactions.<sup>17</sup> These reactions were performed in a mixture of solvents, namely DMF and H<sub>2</sub>O. Herein we present the catalytic activity and recyclability of these materials towards Knoevenagel condensation of aromatic aldehydes with active methylene compounds under solvent-free conditions. Moreover we studied the influence of the amount of the organic salt loading in the materials toward the efficiency of the studied reaction.

## Results and discussion

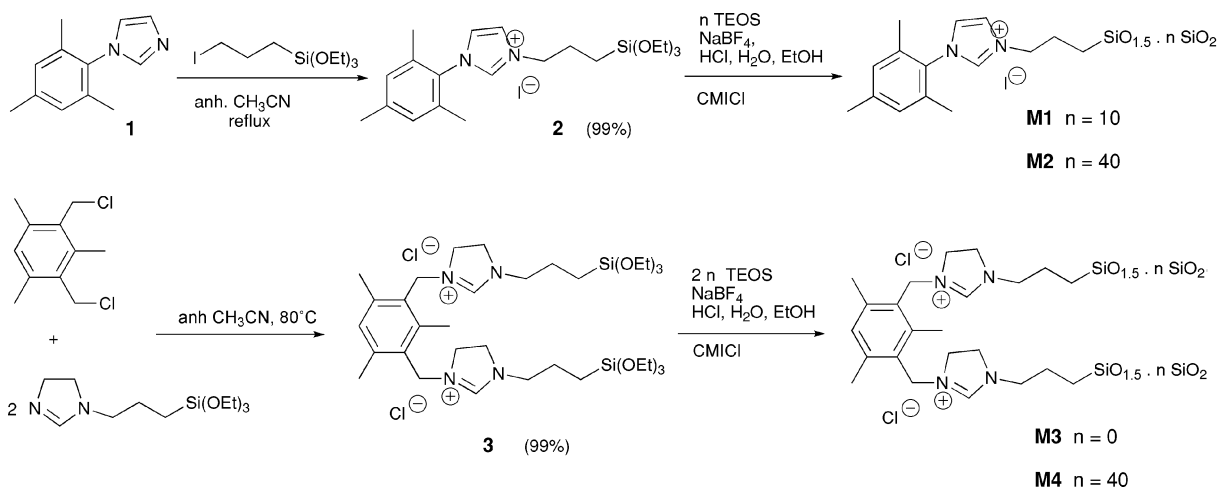
### Preparation of the hybrid materials M1–M4

We summarize in Scheme 1 the synthesis of the monosilylated and disilylated monomers **2** and **3** and the preparation of hybrid materials **M1–M2** and **M3–M4** derived thereof. In both types of materials, two hybrids with different amounts of organic loading were prepared. We already reported the synthesis of **M2–M4**.<sup>17</sup> Material **M1** was prepared similarly to **M2** but with different molar ratio of **2**: TEOS. The following reactant molar ratios were used in the

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**Scheme 1** Synthesis of the silylated monomers and hybrid silica materials **M1–M4**.

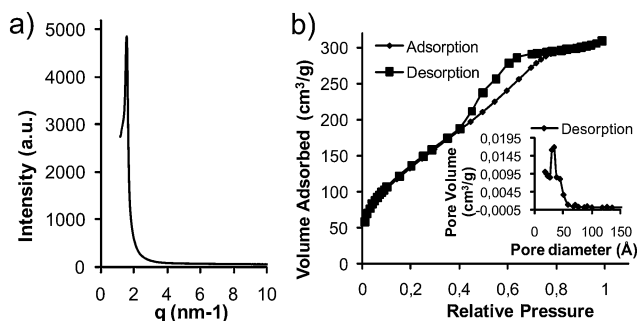
**Table 1** Physicochemical data of materials **M1–M4**

Material	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_p$ (nm)	mmol N $\text{g}^{-1}$
<b>M1</b>	477	0.381–0.388	3.6–3.4	1.706
<b>M2</b>	506	0.308–0.364	3.1–2.7	0.585
<b>M3</b>	2	—	—	7.430
<b>M4</b>	266	0.262–0.253	4.3–4.2	0.828

case of **M1**:  $[\text{CMCl}]_0/[\text{NaBF}_4]_0/[\text{TEOS}]_0/[\mathbf{2}]_0/[\text{H}_2\text{O}]_0/[\text{HCl}]_0/[\text{EtOH}]_0 = 1.0:0.6:4.5:0.45:771:38:25$ .

The materials were characterized by solid state CP-MAS  $^{29}\text{Si}$  spectroscopy (and  $^{13}\text{C}$  NMR for **M1** and **M3**), surface area BET measurements, IR and elemental analysis. Some relevant physicochemical data are given in Table 1. Material **M3** prepared from disilylated **3** without TEOS shows a low surface area as a result of the voluminous organic fragment in the material as already observed before.<sup>18</sup> The other materials prepared in the presence of TEOS are mesoporous and present higher  $S_{\text{BET}}$  values.

**M1** presents a nitrogen sorption isotherm of type IV according to IUPAC (Fig. 1(b)) and its powder X-ray diffraction (PXRD) exhibits a sharp diffraction peak indicating an organised mesoporous structure but with less defined periodicity as in **M2** as expected (Fig. 1(a)).<sup>19</sup> PXRD of the more diluted material **M2** (ratio 1:40)<sup>17</sup> exhibits a 2D hexagonal mesopore structure (MCM-41 type) as expected.<sup>20</sup> This fact indicates that higher dilution of the organic monosilylated moiety favors a more

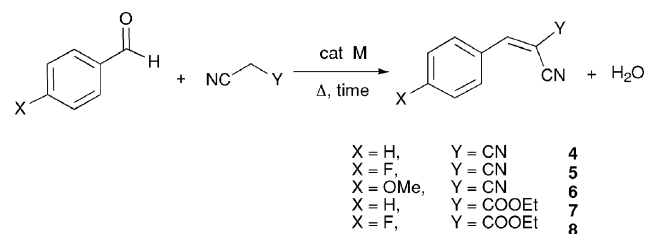


**Fig. 1** (a) PXRD of **M1**; (b)  $\text{N}_2$  sorption isotherm of **M1** and plot of the pore size distribution.

ordered structure in the hybrid silica. Contrarily, **M4** exhibits a worm-like mesoporous organization, while **M3** is even less organized with no mesoporosity at all.<sup>17</sup> The solid state  $^{29}\text{Si}$  NMR spectra of **M1**, **M2** and **M4** show two groups of chemical shifts:  $\text{T}^2$  and  $\text{T}^3$  units at around  $-61$  to  $-66$  ppm, resulting from the hydrolysis–condensation of the corresponding monomers **2** and **3**, and Q units ( $\text{Q}^3$  and  $\text{Q}^4$ ) ranging from  $-96$  to  $-110$  ppm formed from TEOS. **M3** spectrum shows only  $\text{T}^2$  and  $\text{T}^3$  units at  $-57.3$  and  $-65.6$  ppm showing that no Si–C bond cleavage occurred during the hydrolysis process.

### Catalytic activity and recyclability of the hybrid materials **M1–M4** in the Knoevenagel condensation

The catalytic activity of our materials was tested in the Knoevenagel condensation of malononitrile and ethyl cyanoacetate with aromatic aldehydes under solvent-free conditions (Scheme 2). Benzaldehyde, 4-fluorobenzaldehyde and 4-methoxybenzaldehyde were chosen as electrophilic substrates. The stirred mixture of reagents (1.1 eq. of the active methylene compound) and catalyst (0.4–1.2% mol of organic ligand) was heated at  $100$  °C or  $130$  °C for the required time. The products were obtained after addition of dichloromethane to the cold reaction mixtures, filtration of the solid material, drying and evaporation of the filtrate. A more environmentally friendly solvent could be used based on product solubility. Thus, analogous results can be achieved using ethanol as green organic<sup>21</sup> extracting solvent. The recovered catalytic materials were washed and dried prior to their reuse in subsequent runs. The same reaction conditions and the same reaction times were



**Scheme 2** Knoevenagel condensations catalyzed by hybrid materials **M1–M4**.

**Table 2** Knoevenagel condensations catalyzed by **M1–M4**, and blank experiments

Entry	X	Y	M (% mol)	T (°C)	t (h)	Product	% in consecutive cycles
1	H	CN	<b>M3</b> (0.4)	100	6	<b>4</b>	93/95/97/96/99 <sup>a</sup>
2	H	CN	<b>M3</b> (1.2)	100	2	<b>4</b>	96/94/94/92/95 <sup>a</sup>
3	F	CN	<b>M3</b> (1.2)	100	4	<b>5</b>	97/100/97/95/100 <sup>a</sup>
4	OMe	CN	<b>M3</b> (1.2)	100	4	<b>6</b>	99/81/77/66/75 <sup>b</sup>
5	H	COOEt	<b>M3</b> (1.2)	130	2	<b>7</b>	100/81/94/79/42 <sup>b</sup>
6	F	COOEt	<b>M3</b> (1.2)	130	2	<b>8</b>	97/100/57/38/31 <sup>b</sup>
7	H	CN	<b>M1</b> (0.8)	100	6	<b>4</b>	98/97/100/97/96 <sup>a</sup>
8	F	CN	<b>M1</b> (0.8)	100	15	<b>5</b>	73/74/72/72/71 <sup>a</sup>
9	OMe	CN	<b>M1</b> (0.8)	100	16	<b>6</b>	100/96/98/93/97 <sup>a</sup>
10	F	COOEt	<b>M1</b> (0.8)	130	16	<b>8</b>	98/97/76/53/42 <sup>b</sup>
11	H	CN	<b>M2</b> (0.8)	100	6	<b>4</b>	80/76/75/72/84 <sup>a</sup>
12	F	CN	<b>M2</b> (0.8)	100	16	<b>5</b>	60/59/66/58/71 <sup>a</sup>
13	H	CN	<b>M4</b> (0.4)	100	6	<b>4</b>	76/68/67/64/61 <sup>a</sup>
14	H	CN	—	100	6	<b>4</b>	8 <sup>b</sup>
15	F	CN	—	100	16	<b>5</b>	5 <sup>b</sup>
16	OMe	CN	—	100	16	<b>6</b>	11 <sup>b</sup>
17	H	COOEt	—	130	4	<b>7</b>	2 <sup>b</sup>
18	H	CN	MCM-41	100	6	<b>4</b>	32 <sup>b</sup>
19	H	CN	<b>9</b> (1.2)	100	22	<b>4</b>	98 <sup>a</sup>
20	H	COOEt	<b>9</b> (1.2)	130	4	<b>7</b>	66 <sup>b</sup>

<sup>a</sup> Isolated yields. <sup>b</sup> Calculated yields based on NMR integration.

maintained in five consecutive cycles with the same batch of catalyst to assess its recyclability.

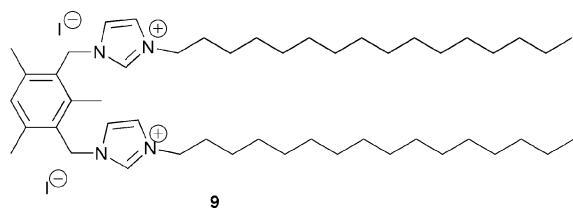
The first essays were performed with catalytic material **M3** (Table 2, entries 1–6). As it was prepared without the addition of TEOS, it has a much higher content of organic moiety per gram of material and less amount of this solid has to be added. In practice, this is quite advantageous for a solvent-free procedure. The reactions of aromatic aldehydes with malononitrile were performed at 100 °C (entries 1–4), requiring between 2 and 6 h to be completed, depending on the amount of catalyst (compare entries 1 and 2) and the aldehyde used. The electronic character of the substituent on the aldehyde does not seem to have a significant influence on the first cycle, reactions with benzaldehyde proceeding faster than those with substituted ones (compare entries 2, 3 and 4). However, with 4-methoxybenzaldehyde as the electrophile, this catalyst was found less effective in the recycling (entry 4), whereas no decrease in activity was observed in the other cases in five consecutive cycles (entries 1–3). Less reactive ethyl cyanoacetate required higher temperatures (130 °C) when treated with benzaldehyde and 4-fluorobenzaldehyde (entries 5–6), the yields of product decreasing after the third or fourth cycle for the same reaction time.

Next, the material **M1** was tested (Table 2, entries 7–10). An amount of 0.8% mol of this monocationic organic ligand would be equivalent to the 0.4% mol used for the biscationic organic ligand present in **M3** (compare entries 7 and 1). Again, the reaction was slower with substituted benzaldehydes (compare entries 8 and 9 with entry 7), although good to excellent activity and recyclability upon five runs was found. Treatment of ethyl cyanoacetate with 4-fluorobenzaldehyde at 130 °C for 16 h gave nearly complete conversion, although the yields decreased upon recycling (entry 10) as observed before (entry 6).

Material **M2** (1:40) was inferior to **M1** (1:10) (compare entries 11 and 12 with entries 7 and 8 for the same reactions performed under analogous conditions). In the same way, **M4** (with TEOS) performed less than **M3** (without TEOS) (compare

entries 13 and 1). Thus, higher dilution of the organic moiety into the inorganic matrix is detrimental, probably due, in part, to the need of high amounts of solid for the diluted material. The number of catalytic centers can be estimated from the elemental analysis and BET surface area (see Table 1). Material **M3** prepared without TEOS gives an elemental analysis of 7.43 mmol of N/g, which corresponds to a 3.715 mmol of dihydroimidazolium sites per g of solid material. Material **M4** prepared with 80 molar equivalent of TEOS has almost 10 times less sites per g (0.828 mmol N/g; 0.414 mmol of dihydroimidazolium sites per g of solid material). Although we are using similar molar amount of organic ligand (compare, for instance, entry 1 with entry 13 of Table 2), **M3** has a higher density of active sites on a smaller surface area and hence has the organic ligands quite close, whereas in **M4** the organic ligands are spread (or diluted) in the silica matrix formed by the added TEOS. The fact that **M3** provides the best results is probably due, in part, to a cooperative effect between neighboring centers.

Blank experiments were also performed. Compounds **4**, **5**, **6** and **7** were obtained in very low yields (2 to 11%) upon prolonged heating in the absence of any catalyst (entries 14–17). Mesoporous silica MCM-41 containing no organic moiety gave a 32% NMR yield of compound **4** under the same conditions used for catalysts **M1–M4** (compare entry 18 with entries 1, 7, 11 and 13). This makes clear that, although the surface of the silica support can itself play a role on the catalytic activity, the imidazolium and dihydroimidazolium salts anchored to the silica matrix display a crucial catalytic effect. Cooperativity between the surface and active site in hybrid organic–inorganic heterogeneous catalysts has been previously reported.<sup>22</sup> Finally, we compared the activity of our immobilized systems with that of a related homogeneous bis-imidazolium salt **9** (Fig. 2) which we recently described.<sup>23</sup> Compound **4** was prepared in 98% isolated yield after 22 h at 100 °C in the presence of 1.2% mol of **9** (Table 2, entry 19) and the acrylate derivative **7** in 66% NMR yield after 4 h at 130 °C (Table 2,



**Fig. 2** Homogeneous catalyst **9** for Knoevenagel condensation.

entry 20). These results are inferior to those obtained with materials **M1–M4** (compare entry 19 with entries 2, 7, and entry 20 with entry 5), which have the additional advantage of easy recovery and recycling. This fact would be in accordance with the above mentioned cooperativity effect.

Compounds **7** and **8** were each obtained as a single stereoisomer (GLC) and their  $^1\text{H}$  NMR spectra were coincident with those described for the isomers with (*E*) configuration.<sup>24,25</sup> Moreover, observed experimental values show good accordance with the estimated values<sup>26</sup> for the olefinic protons of (*E*) isomers **7** and **8**; the (*Z*) isomers should present these protons at higher fields.

The mechanism of the condensation under our conditions is presently unknown as no classic basic catalysis can be claimed with no basic centers being present here as in common catalysts such as amines, imidazole or dihydroimidazole, and as no external base was added. Speculations may be drawn from the relatively high acidity of the proton at the C-2 position of the imidazolium and dihydroimidazolium salts (these salts are precursors of *N*-heterocyclic carbenes), which could be the origin of the catalysis through activation of both the electrophile and the active methylene compound by hydrogen bond formation with the carbonyl group of the aldehyde and the cyano and/or ester group of the pre-nucleophile. Like in classic acid-catalyzed aldol-type reactions the process probably takes place through an “enol-type” intermediate. Inferior results obtained with ethyl cyanoacetate when compared with malononitrile (entry 4 vs. entry 2 of Table 2) can be related to the lower nucleophilic activity of the ethyl cyanoacetate compared with malononitrile. Attempts to detect some adducts resulting from the interaction of the aldehydes, ethyl cyanoacetate and malononitrile with the bis-imidazolium iodide **9** by ESI-MS (electrospray ionization mass spectrometry) at different temperatures were, however, unsuccessful (binary mixtures of catalyst/electrophile, catalyst/nucleophile and ternary mixtures catalyst/nucleophile/electrophile were tested on ESI-MS). A very recent work<sup>27</sup> postulates that chloride anions associated with soft cations (like tetraalkyl ammoniums, alkyl imidazoliums and alkylpyridiniums) act as catalysts for the Knoevenagel condensations through an alternative nucleophilic pathway. The authors attribute the enhanced nucleophilicity of the chloride anion to a softness/hardness mismatch between the anion and cation. Under the conditions used by the authors, using acetonitrile as solvent at 80 °C, ammonium salts with bromide anion and imidazolium salts with tetrafluoroborate anion did not catalyze the reaction. Most of this work deals, however, with tetraalkylammonium salts. In sharp contrast with these results, in our hands, bis-imidazolium iodide **9** effectively catalyzed the reaction in solvent-free conditions (entries 19 and 20 of Table 2) and [bmim][BF<sub>4</sub>] has been reported<sup>6</sup> to act as solvent and pro-

motor in Knoevenagel condensations; however no mechanistic details were mentioned by the authors. From these facts, it is clear that although the chloride-based nucleophilic mechanism can not be excluded in our chloride dihydroimidazolium salts, another alternative reaction pathway is required to account for the results with other anions. We think that the catalytic activity is more likely related to the relative acidity of C-2 hydrogens of the imidazolium and dihydroimidazolium salts. The better catalytic performance of **M3** which has been associated before to its higher density of active sites and to a cooperative effect between neighboring centers would be in accordance with our mechanistic proposal of concomitant activation of both nucleophilic and electrophilic reagents through their interaction with proximal dihydroimidazolium moieties.

## Conclusions

In summary, several hybrid silica materials containing imidazolium and dihydroimidazolium salts in different dilutions have been easily and efficiently prepared in a few steps from commercial sources using template-based sol–gel methodologies from the corresponding mono- and disilylated monomers. These materials are good recyclable catalysts for the Knoevenagel condensation between active methylene compounds and aromatic aldehydes in solvent-free conditions, providing a green and sustainable route to electrophilic trisubstituted alkenes. The immobilized catalysts show higher activities for this transformation than other related homogeneous bis-imidazolium salts and are also much more active than non-functionalized mesostructured MCM-41, which presents some residual activity. This suggests a certain degree of cooperativity between the surface of the inorganic matrix and the active sites and underlines the crucial role of the organic moiety. Moreover, better performance was observed from the hybrid catalysts with higher organic loading, showing that the predominant factor is the concentration of the organics rather than the porosity in the materials, at least from these trials in neat conditions. The material obtained from polycondensation of a disilylated dihydroimidazolium salt in the absence of TEOS gave the best results, no precedents being available for this type of organocatalyst for Knoevenagel reaction.

## Experimental

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX250 and the *J* values are given in Hz. ESI-MS analyses were recorded at the *Universitat de Girona* on an Esquire 6000 Ion Trap Mass Spectrometer (Bruker) equipped with an electrospray ion source. The instrument was operated either in the positive ESI(+) or in the negative ESI(−) ion mode. The samples (5 μL) were introduced into the mass spectrometer ion source through an Agilent HPLC with a mobile phase flow of 100 μL/min (80/20 v/v CH<sub>3</sub>CN/H<sub>2</sub>O). Nitrogen was employed as both a drying and nebulizing gas. IR data were obtained with a Perkin-Elmer (System 2000 FT-IR) spectrophotometer. The CP-MAS  $^{13}\text{C}$  and  $^{29}\text{Si}$  solid state NMR spectra were recorded on a Bruker AV-400-WB and on a Bruker FT-AM 400. Surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics Tristar 3000

analyzer, and the average pore diameter was calculated by the BJH method. Elemental analyses have been performed at the *Serveis Científicotècnics* of the *Universitat de Barcelona*. X-Ray diffraction experiments were carried out on solid powders in 1 mm diameter glass capillaries, in the *Laboratoire des Colloïdes, Verres et Nanomatériaux* (UMR5587), *Université de Montpellier II*, France, working in a transmission configuration. A copper rotating anode X-ray source (functioning at 4 kW) with a multilayer focusing "Osmic" monochromator giving high flux ( $10^8$  photons  $\text{sec}^{-1}$ ) and punctual collimation was employed. An "Image plate" 2D detector was used. Diffraction curves were obtained giving diffracted intensity as a function of the wave vector  $q$ . Diffracted intensity was corrected by exposition time, transmission and intensity background coming from diffusion by an empty capillary. Compounds **1**, **2** and **3** and materials **M2–M4** were prepared as described.<sup>17</sup>

### Preparation of material M1

1-Cetyl-3-methylimidazolium chloride (1.635 g, 4.767 mmol), sodium tetrafluoroborate (0.333 g, 2.972 mmol), hydrochloric acid (15 mL of conc. HCl, 0.181 mol HCl, 0.624 mol of water) and distilled and deionized water (55 mL, 3.053 mol) were mixed and stirred together at 40 °C. In a few minutes an emulsion was formed. A solution of the silylated monomer **2** (1.113 g, 2.147 mmol) and TEOS (4.583 g, 0.0216 mol) in absolute ethanol (7 mL, 0.120 mol) was added over the emulsion and stirred together at 40 °C for one day. The resulting white powder was filtered, washed twice with water and three times with ethanol. The solid **M1** was obtained after template removal by soxhlet extraction with acetone for one day, powdering and drying under vacuum at 70 °C during 6 h (1.786 g).  $S_{\text{BET}}$ : 477  $\text{m}^2 \text{g}^{-1}$ ; pore diameter: 3.65–3.37 nm; pore volume: 0.381–0.388  $\text{cm}^3 \text{g}^{-1}$ ; IR  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3316 (s and br), 1611, 1564, 1549, 1486, 1455, 1082 ( $\nu_{\text{S}}$  and br), 957, 803, 577, 469;  $^{29}\text{Si}$  CP-MAS NMR (79.5 MHz):  $\delta$  -66.2 ( $\text{T}^3$ ), -100.3 ( $\text{Q}^3$ ), -109.7 ( $\text{Q}^4$ ).  $^{13}\text{C}$  CP-MAS NMR (100.62 MHz):  $\delta$  10.3, 17.7, 26.2, 41.2, 51.4, 127.0, 131.9, 135.8, 141.5. Anal. (%) calculated for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{Si}_{11}\text{O}_{21.5}\text{I}$  (assuming total condensation and no halide anion exchange) N 2.78, C 17.87, H 2.00; found: N 2.39, C 16.51. The hydrolysis and condensation is never complete in these hybrid materials (see, for instance, the presence of  $\text{Q}^3$  signals in  $^{29}\text{Si}$  CP-MAS NMR).

### Preparation of 2-benzylidenemalononitrile (4). Typical procedure

A mixture of freshly distilled benzaldehyde (470  $\mu\text{L}$ , 1.04  $\text{g mL}^{-1}$ , 4.61 mmol), malononitrile (330  $\mu\text{L}$ , 1.049  $\text{g mL}^{-1}$ , 5.24 mmol) and **M3** (0.0297 g, 7.430 mmol  $\text{N g}^{-1}$ , 0.0552 mmol of bis-dihydroimidazolium ligand) was stirred at 100 °C for 2 h (GLC monitoring). Dichloromethane was added to the cold mixture, the catalyst **M3** was filtered, the filtrate was dried with anhydrous sodium sulfate and the solvent was evaporated to give pure **4** (0.684 g, 96%). Mp 80–82 °C (lit.,<sup>7</sup> 80–81 °C); IR  $\nu_{\text{max}}$  (ATR)/ $\text{cm}^{-1}$  3032, 2222 (CN), 1588, 1565, 1449, 1215, 754, 677, 615;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.55 (2 H, t,  $J$  7.4), 7.64 (1 H, t,  $J$  7.4), 7.79 (1 H, s, =CH-), 7.91 (2 H, d,  $J$  7.0). The catalytic material **M3** was washed with water, ethanol and diethyl ether, and dried under vacuum (2 mm Hg) to be reused in the next run.

The following compounds were obtained by an analogous procedure (see Scheme 2 and Table 2 for modifications in the reagents, reaction temperature, reaction time, catalyst and yields).

### 2-(4-Fluorobenzylidene)malononitrile (5)

Mp 125–126 °C (lit.,<sup>28</sup> 125–126 °C); IR  $\nu_{\text{max}}$  (ATR)/ $\text{cm}^{-1}$  3036, 2229 (CN), 1594, 1574, 1505, 1415, 1304, 1238, 1161, 1107, 836, 615;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.22 (2 H, d,  $J$  8.7), 7.73 (1 H, s, =CH-), 7.96 (2 H, m).

### 2-(4-Methoxybenzylidene)malononitrile (6)

Mp 113–114 °C (lit.,<sup>28</sup> 113–114 °C); IR  $\nu_{\text{max}}$  (ATR)/ $\text{cm}^{-1}$  3028, 2219 (CN), 1603, 1568, 1556, 1509, 1367, 1317, 1276, 1179, 1019, 832, 609;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 3.91 (3 H, s,  $\text{OCH}_3$ ), 7.01 (2 H, d,  $J$  9.0), 7.65 (1 H, s, =CH-), 7.91 (2 H, d,  $J$  9.0);  $\delta_{\text{C}}$  (62.5 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 56.1, 113.6, 114.7, 115.4, 124.4, 133.8, 159.2, 165.1.

### (E)-Ethyl-2-cyano-3-phenylacrylate (7)

Mp 45–46 °C (lit.,<sup>7</sup> 46–47 °C); IR  $\nu_{\text{max}}$  (ATR)/ $\text{cm}^{-1}$  3029, 2981, 2223 (CN), 1722 (CO), 1605, 1444, 1296, 1253, 1200, 1088, 1009, 766, 683;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.41 (3 H, t,  $J$  7.0, - $\text{OCH}_2\text{-CH}_3$ ), 4.40 (2 H, q,  $J$  7.0, - $\text{OCH}_2\text{-CH}_3$ ), 7.54 (3 H, m), 7.99 (2 H, m), 8.26 (1 H, s, =CH-);  $\delta_{\text{C}}$  (62.5 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.4, 63.0, 103.3, 115.8, 129.6, 131.4, 131.8, 133.6, 155.3, 162.8.

### (E)-Ethyl 2-cyano-3-(4-fluorophenyl)acrylate (8)

Mp 94–95 °C (lit.,<sup>24</sup> 96–97 °C); IR  $\nu_{\text{max}}$  (ATR)/ $\text{cm}^{-1}$  3035, 2297, 2226 (CN), 1714 (CO), 1594, 1262, 1226, 1162, 1087, 837, 763;  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.42 (3 H, t,  $J$  7.0, - $\text{OCH}_2\text{-CH}_3$ ), 4.40 (2 H, q,  $J$  7.0, - $\text{OCH}_2\text{-CH}_3$ ), 7.21 (2 H, dd,  $J$  8.6 and 8.4), 8.05 (2 H, dd,  $J$  8.5 and 5.3), 8.23 (1 H, s, =CH-);  $\delta_{\text{C}}$  (62.5 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.4, 63.1, 102.8, 115.7, 117.0 (d,  $^2J_{\text{CF}}$  22.0), 128.1 (d,  $^4J_{\text{CF}}$  3.2), 133.9 (d,  $^3J_{\text{CF}}$  9.1), 153.8, 162.7, 165.7 (d,  $^1J_{\text{CF}}$  255.7).

When some amount of starting reagent was detected in the NMR spectrum of the crude mixture, together with the final product, the yield was calculated from the molar ratio of the compounds in the mixture (derived from NMR integration), the weight of the crude mixture and the molecular weight of the compounds present in the mixture. We do not use the NMR conversion because starting reagents can be partially evaporated under reduced pressure.

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