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A one-step co-condensation method for the synthesis of well-defined functionalized mesoporous SBA-15 using trimethallylsilanes as organosilane sources†

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A new method for the preparation of well-defined functionalized mesoporous SBA-15 has been developed by a one-step co-condensation method using trimethallylsilanes as organosilane sources. This new method enables the incorporation of various bulky organic functional groups with long alkyl chain tethers into the mesoporous silica network.

Fabrication of high performance, organo-functionalized mesoporous silicas has received considerable attention owing to the high recyclabilities and enhanced stabilities of these materials.[1–4] Among many approaches devised for this purpose, co-condensation methods employing alkoxysilanes have been most often used to introduce organic functional groups into silica networks. Advantageous features of the functionalized silicas generated in this manner include high loading efficiencies and homogeneous surface coverage.[5] However, alkoxysilanes, commonly used in this technique, are difficult to functionalize and purify.[1–6] As a consequence, applicable substrates employed in this approach are limited to distillable short chain alkoxysilanes containing a small range of functionalities.[2–4] And often inefficient, multistep functional group transformations must be performed on the mesoporous materials to generate desired functional mesoporous silica materials. Another formidable challenge when alkoxysilane-based protocols are utilized is the difficulty in preparing materials that contain functional groups attached to the silica surface through long tethers. This is an important feature because long tethers enable ideal interactions to take place between the immobilized catalytic moieties with substrates, a requirement for high catalytic performance.[7]

In earlier studies, we developed an efficient grafting method, which utilizes methallylsilanes as alkoxysilane surrogates, for installation of organic functional groups on the silica surface.[7b,8] Considering their unique properties, including high stability in functional group transformation reactions and purification processes, and their intrinsic lability under acidic conditions, trimethallylsilanes (**1**) serve as ideal precursors of functionalized mesoporous silicas (SBA-15s).[9,10] In the studies described below, we developed a new co-condensation method using trimethallylsilanes containing bulky organic functional groups linked through long tethers (Fig. 1). A notable feature of this approach is its ability to produce high performance functionalized SBA-15s through a direct, one-pot co-condensation protocol. Specifically, we observed that the reaction of properly structured trimethallylsilanes with TEOS under acidic conditions generates long alkyl chain-tethered functionalized mesoporous silicas that are otherwise difficult to prepare. Finally, in this effort we employed the functionalized, organic and organometallic group-impregnated SBA-15s as recyclable catalysts to promote highly efficient reactions.

The first phase of this investigation was designed to demonstrate the practical utility of a new, one step method for synthesizing functionalized SBA-15s. As a model trimethallylsilane substrate

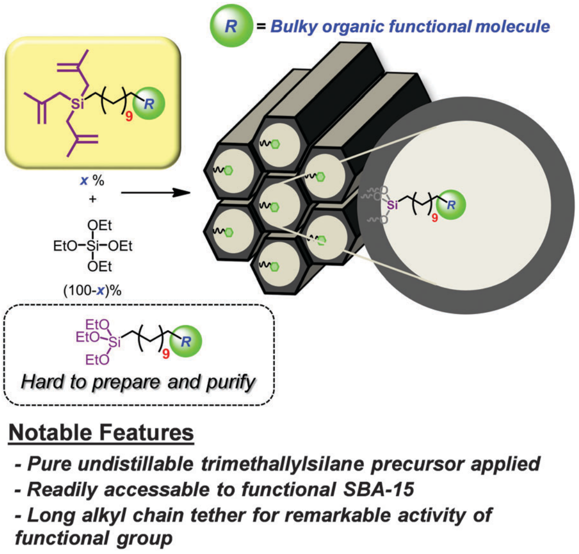

Fig. 1 Advantage of one-step synthesis of functionalized SBA-15 using functional organotrimethallylsilanes with an undecyl tether.

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for this process, we selected 4-(pyren-1-yl)-1-(11-(tris(2-methylallyl)-silyl)undecyl)-1*H*-1,2,3-triazole (**1a**), which contains pyrenyl groups tethered through a long alkyl chain to the methallylsilane moiety. We reasoned that successful incorporation of pyrenyl groups on the silica surface would be easily demonstrated by using fluorescence techniques. The desired silane **1a** was prepared by using the Cu(I)-promoted [3+2]-cycloaddition reaction[11] of 1-ethynylpyrene with 11-azidoundecyltrimethallylsilane, and purified by using silica-gel chromatography. The modified procedure described by Gupta and coworkers was applied in this co-condensation method.[5c] The reaction of TEOS (tetraethyl orthosilicate) with **1a** (TEOS/**1a**) in the presence of aqueous HCl and P123 followed by solvent extraction gave the pyrene functionalized SBA-15, **Pyr@Si**s. Under the reaction conditions, the trimethallylsilane moiety is completely consumed, as determined by using ^{1}H NMR spectroscopy.[12] The one-pot co-condensation process was carried out using different ratios (99/1, 95/5, 90/10 and 85/15) of TEOS and **1a** (Fig. 2a). The loading of pyrene triazolyl groups on the surfaces of the resulting materials, determined by using elemental analysis, was found to increase linearly as the amount of **1a** used in the reaction increases up to 15% (0.12 mmol g^{-1} for 1% **1a**; 0.40 mmol g^{-1} for 5% **1a**; 0.77 mmol g^{-1} for 10% **1a**; 1.0 mmol g^{-1} for 15% **1a**, Fig. 2b).

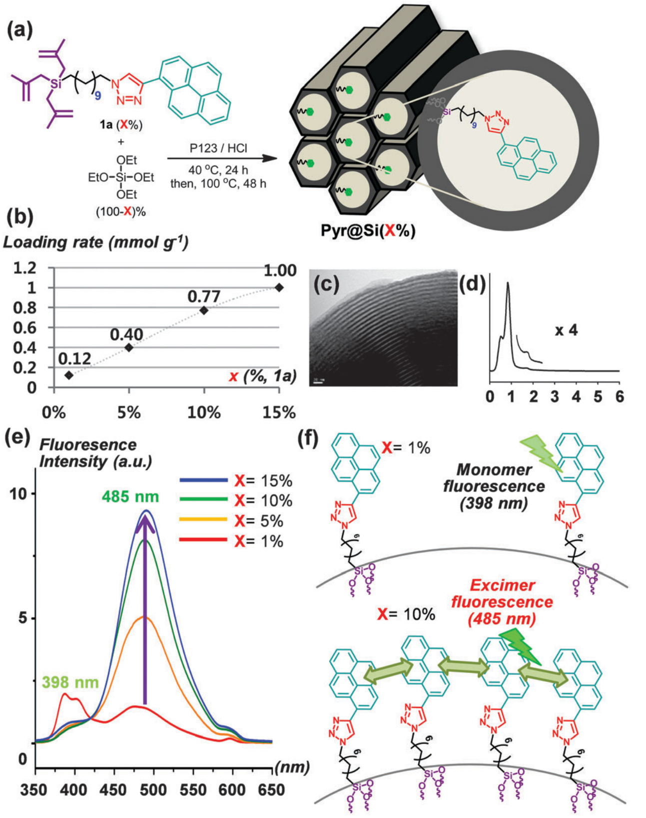


Fig. 2 (a) Pyrenetriazolyl functionalized SBA-15s (**Pyr@Si**s) prepared using different ratios of TEOS and **1a** (99/1, 95/5, 90/10, and 85/15) using the one-step co-condensation method. (b) Loading of pyrene triazolyl groups in each **Pyr@Si**. (c) TEM image of **Pyr@Si(15%)**, (d) SAXS of **Pyr@Si(15%)**, (e) fluorescence spectra of **Pyr@Si(1%)**, **Pyr@Si(5%)**, **Pyr@Si(10%)** and **Pyr@Si(15%)** (normalized at 414 nm). (f) Illustrational rationale for the excimer peak of 485 nm.

Thus, the amount of pyrenyl groups on the functionalized mesoporous SBA-15 can be controlled by simply regulating the ratio of TEOS and **1a**. TEM (Fig. 2c) and SAXS (Fig. 2d) of the **Pyr@Si(15%)** gave data that correspond directly to those of the original SBA-15.[5b] The ^{13}C CP-MAS solid-state NMR spectrum of **Pyr@Si(15%)** clearly displays peaks that are representative of the pyrene-triazolylundecyl group (see ESI,† Fig. S2).

We also determined the fluorescence properties of the **Pyr@Si**s containing different pyrene loading levels (Fig. 2e). The emission spectrum of the low pyrene group-embedded **Pyr@Si(1%)** contains maxima at 398 nm with a weak peak at 485 nm. In contrast, **Pyr@Si**s containing greater than 5% loading have fluorescence spectra in which the band at 485 nm becomes more intense relative to the 398 nm band in a manner that is dependent on the %-loading. These observations are consistent with the assignment of the maximum at 485 nm to emission from excimers which become more dominant as the surface is more populated by pyrene fluorophores (Fig. 2f). This phenomenon was also observed earlier by Stack *et al.*[5a,b] Therefore, the results of this analysis show clearly that the extent of pyrene group loading on the surface of mesoporous silica can be readily determined by using fluorescence spectroscopy.

The one-step co-condensation reaction was performed using the 4-(dimethylamino)azobenzene-4′-sulfonyl (dabsyl) group containing trimethallylsilane **1b** (Fig. 3a). Reactions utilizing various ratios of TEOS and **1b** lead to the formation of the dabsyl group linked SBA-15s with loading levels in the range of 0.11–0.78 mmol g^{-1}. The loading amount on SBA-15 was readily determined by using elemental analysis and measuring the intensity of the red color associated with the dabsyl group (Fig. 3b and c). Noteworthily, the analysis of TEM images shows that the mesoporous structures of **Dabsyl@Si** are retained up to 15% loading of dabsyl group (see ESI†).

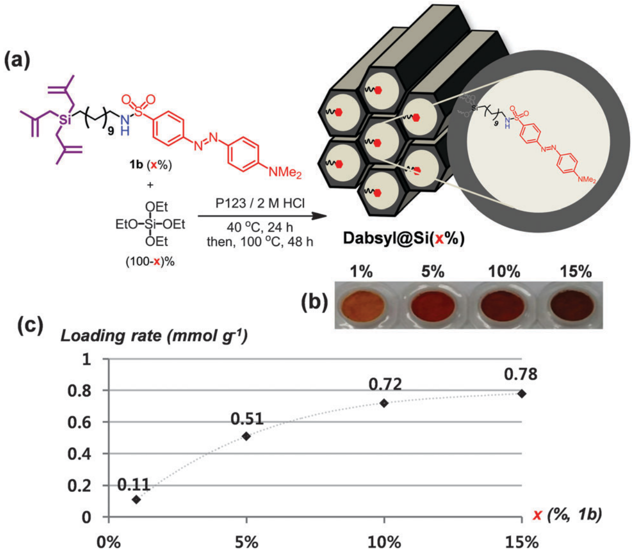


Fig. 3 (a) Preparation of **Dabsyl@Si**s by using different ratios of TEOS and **1b** (99/1, 95/5, 90/10, 85/15) utilizing the co-condensation method. (b) Intensity change of the red color and (c) loading rate of the dabsyl group in **Dabsyl@Si(1%)**, **Dabsyl@Si(5%)**, **Dabsyl@Si(10%)** and **Dabsyl@Si(15%)**.

The SBA-15s, prepared by using the approach described above, contain functional groups that are tethered to the silica surface through long alkyl chains. Consequently, it is anticipated that these functionalized mesoporous silicas will display much higher catalytic activities than conventional functionalized SBA-15 with short tethers owing to the fact that the pendant functional groups can better interact with substrates.[7] To evaluate this hypothesis, a study was conducted to probe the use of an amine containing catalyst of this type to promote a Knoevenagel reaction.

For this purpose, we prepared primary amine-functionalized SBA-15s from the corresponding azide-functionalized silicas, **Pr-N_3@Si** and **Und-N_3@Si**, which were synthesized by using one-pot co-condensation reactions of the respective 3-azidopropyltrimethallylsilane (**1c**) and 11-azidoundecyltrimethallylsilane (**1d**) with TEOS (TEOS/**1c**, TEOS/**1d** = 90/10) (Fig. 4a). The amine functionalized SBA-15s, **Pr-NH_2@Si** and **Und-NH_2@Si** were then generated from the corresponding azides through Staudinger reactions,[13] involving treatment with a mixture of PPh_3 and water. The success of these processes was demonstrated by analysis of the IR spectra of the products, which showed that peaks at 2110 cm^{-1} corresponding to the azide moiety were absent (see ESI,† Fig. S3).

The amine-functionalized silicas, **Pr-NH_2@Si** and **Und-NH_2@Si**, were tested as catalysts for the Knoevenagel reaction of malononitrile (**2**) with benzaldehyde (**3**) (Fig. 4b).[14] Reaction between **2** and **3** carried out using **Und-NH_2@Si** as a catalyst at ambient temperature for 2 h resulted in the formation of 2-benzylidenemalononitrile (**4**) in a quantitative yield. Under identical conditions, the condensation reaction promoted by **Pr-NH_2@Si** required 8 h to complete (Fig. 4c). The results show that **Und-NH_2@Si**, in which the amine group is tethered to the silica surface by a longer alkyl chain, is a superior catalyst for the Knoevenagel reaction.

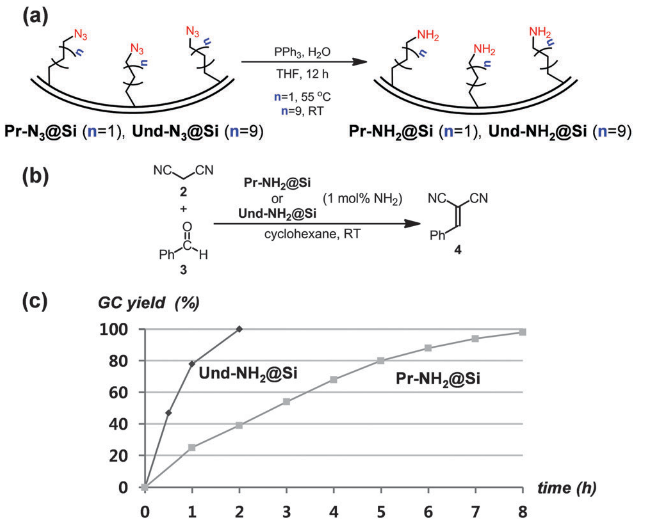
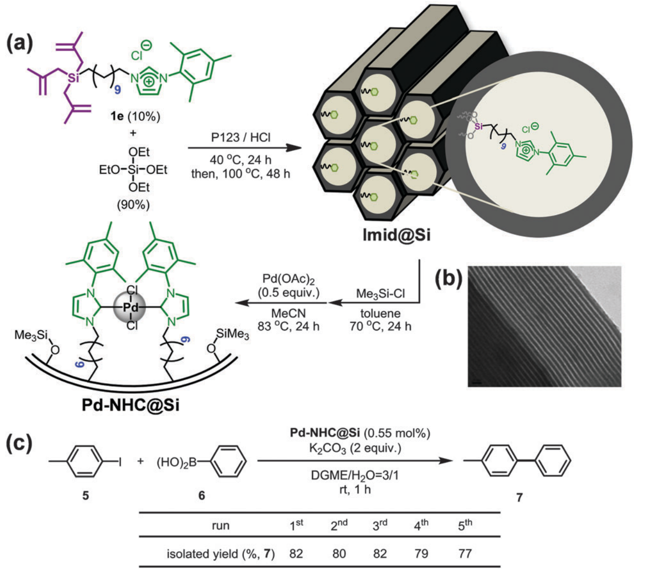


Fig. 4 (a) Synthesis of amine functionalized SBA-15s (**Pr-NH_2@Si** and **Und-NH_2@Si**) through the Staudinger reaction of **Pr-N_3@Si** and **Und-N_3@Si** with PPh_3 and H_2O. (b) Knoevenagel reactions of malononitrile and benzaldehyde using **Pr-NH_2@Si** and **Und-NH_2@Si** as catalysts. (c) GC yield (%) of products **4** *versus* reaction time.



run	1st	2nd	3rd	4th	5th
isolated yield (%, 7)	82	80	82	79	77

Fig. 5 (a) One-step synthesis of imidazolium salt functionalized SBA-15 (**Imid@Si**) and preparation of **Pd-NHC@Si**. (b) TEM image of **Imid@Si**. (c) Suzuki reaction using **Pd-NHC@Si** as a catalyst and isolated yields of recycled catalytic reactions.

This finding suggests that interactions between the catalytic groups in **Und-NH_2@Si** and substrates are superior to those occurring with **Pr-NH_2@Si**.

A new approach was also employed to prepare a silica based catalytic system containing a supported transition metal.[15] Because imidazolium groups are readily transformed into 4-imidazoline (NHC) ligands for Pd when treated with $Pd(OAc)_2$,[16] an imidazolium group containing trimethallylsilane **1e** was selected as the reagent for the preparation of the modified mesoporous silica. Trimethallylsilane derivative **1e** was prepared by the reaction of 11-chloroundecyltrimethallylsilane with 1-mesityl-1*H*-imidazole at 120 °C for 24 h.[17] Co-condensation of TEOS with **1e** (TEOS/**1e** = 90/10) then generated the imidazolium-bound SBA-15, **Imid@Si** (1.13 mmol g^{-1} loading, Fig. 5a). A TEM image of the modified silica shows that it contains a uniform distribution of mesopores (Fig. 5b, pore size: 6.7 nm), and inspection of its ^{13}C CP-MAS NMR spectrum shows that it contains surface imidazolium groups (see ESI,† Fig. S4). In addition, the solid state ^{29}Si NMR spectra of **Imid@Si** shows Q_3 (single silanol), Q_4 (silicate) and T_3 $[R(SiO)_3Si]$ signals, which are consistent with previously reported data of functionalized SBA-15 prepared by the classical alkoxysilane protocol (see Fig. S5 in ESI†).[5c]

The Pd–NHC complex-tethered SBA-15, **Pd-NHC@Si**, was prepared by first blocking residual surface silanol groups in **Imid@Si** by treatment with trimethylchlorosilane (TMCS) and then carrying out the reaction with $Pd(OAc)_2$ in toluene at reflux.[18] The loading of Pd in the resulting **Pd-NHC@Si** was determined to be 2.9% by using ICP-MS. In addition, the presence of the transition metal in its Pd^{2+} state was demonstrated by analysis of the XPS spectrum (see ESI†), which contains a Pd(3d) peak at 337 eV that is identical to the previously reported value for the Pd^{2+} state.[18]

The catalytic activity of **Pd-NHC@Si** was demonstrated by its use to promote a Suzuki coupling reaction of 4-iodotoluene (**5**) with phenylboronic acid (**6**). Reaction of **5** with **6** in the presence of **Pd-NHC@Si** (0.55 mol%) at room temperature gave 4-methyl-1,1′-biphenyl (**7**) in 82% isolated yield (Fig. 5c).[19] The insoluble catalyst **Pd-NHC@Si**, recovered from the reaction mixture by using centrifugation, was reused for a second Suzuki cross coupling reaction between **5** and **6**, which produced **7** in 80% yield.[20] The results of experiments in which recovered **Pd-NHC@Si** was employed repeatedly showed that its catalytic efficiency is retained even after five cycles and that the transition metal remains in the Pd^{2+} state.

In the study described above, we have devised a new method for the preparation of functionalized mesoporous silicas that take advantage of the characteristic properties of methallylsilanes, notably their high stabilities during functional group transformations and purification, and their labilities under acidic conditions. These unique properties have been used to develop a method for the one-step synthesis of high-performance, functionalized mesoporous silicas from appropriately modified organo-trimethallylsilanes that contain functional groups tethered through long alkyl chains. Employing this method, a variety of bulky functional groups such as a fluorophore, chromophore, and even an ionic imidazolium moiety for recycling transition metal catalysts can be incorporated into mesoporous silica networks with loading extents of up to 15% of the organosilane (*ca.* 1.0 mmol g^{-1}). The new method developed in this effort overcomes the limitations of the conventional alkoxysilane approach and the accompanying requirement for inefficient multistep, solid-phase transformations.

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