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ARTICLE

Method for Introducing Organic Functional Groups on Silica Surfaces Using a Functionalized Vinylsilane Containing Polymer

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A new method for introducing robustly bound organic functional groups on silica surfaces has been developed. Compared to conventional monomer immobilization procedures, the new vinylsilane-impregnated polymer based protocol can be employed for the preparation of various organic group functionalized silicas that are stable under both acidic and basic conditions. Organic functional group can be readily introduced by one-step Rh(I)-catalyzed hydroacylation reaction or appended by using Suzuki coupling reactions.
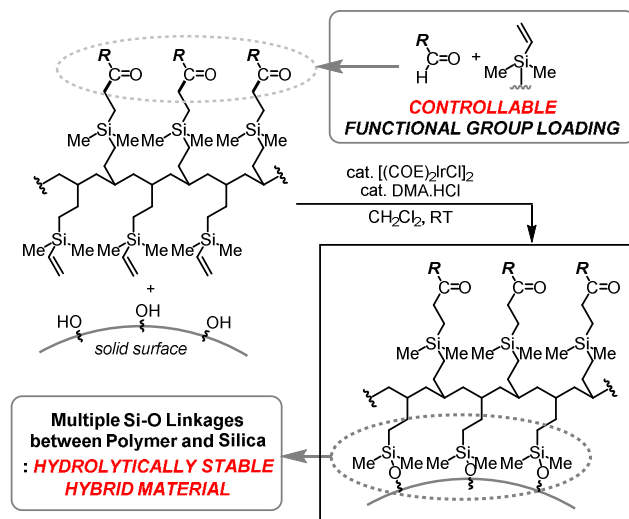
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Introduction

Studies aimed at the development of new methods for functionalizing surfaces of solids such as silica or glass have received considerable attention in the material science area.[1] Through efforts in this area, a wide variety of post-grafting methods have been devised for introducing organic functional groups onto inorganic solids through the use of monomeric silane precursors.[2-5] Recently we developed a new approach, which utilizes dimethyldivinylsilane as a coupling reagent for covalently linking aldehyde tethers to hydroxyl groups present on the surface of silica (Scheme 1a).[4] In this reagent, the vinylsilane groups are employed for two purposes, one being covalent Si-O bond formation to the surface and the other being introduction of aldehyde moieties utilizing a hydroacylation reaction. Use of the vinylsilane coupling reagent has two important meritorious features as compared to methods that rely on conventional coupling reagents such as alkoxysilanes and chlorosilanes. The first advantage is that the coupling reaction can be carried out under mild room temperature conditions owing to the fact that vinylsilanes readily react with hydroxyl groups on surfaces of solid supports when iridium(I)/HCl is utilized as a catalyst. The second feature is that the hydroacylated silane precursors generated prior to the coupling reaction can be readily purified using column chromatography. In spite of these merits, the functionalized solids prepared by using the divinylsilane approach are intrinsically unstable as a consequence of the presence of easily hydrolysable single Si-O bonds linking the functional group to the solids.[6] This fact limits applications of the functionalized silica when hydrolytic condition are employed.
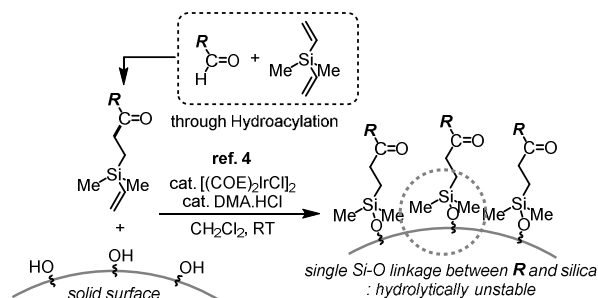

Scheme 1. Comparison of previous study and this work. (a) Previous approach using monomeric divinylsilane precursors. (b) Concept of this report: Immobilization of polymeric vinylsilane precursors to fabricate organic-group immobilized solid surface consisting of highly robust multiple Si-O bonds.

In the study described below, we developed a novel grafting method in which functionalized vinylsilyl group-linked polymers are covalently bonded to the surface of silica by using Ir-promoted multiple Si-O bond forming reactions (Scheme 1b). This new protocol allows unique fabrication of hydrolytically stable organic-inorganic hybrid silica materials with robust bonds between solid surface and multi-silyl groups on polymer side chain. The functionalized polymethylene polymers employed for this purpose are generated through facile hydroacylation reactions of vinylsilane-linked polymers derived from polybutadiene. Importantly, unlike their chloro- and alkoxy-silane analogs, the functionalized multiple vinylsilane-linked polymers used in this process are stable under chromatographic and hydrolytic conditions. Moreover, owing to the fact that they contain hydrophobic polymethylene layers that shield the underlying Si-O bonds, the functionalized surfaces are expected to be resistant to conditions that promote hydrolytic Si-O bond cleavage reactions.

Results and Discussion

Polybutadiene was selected as the polymer platform for the new method for functionalizing surfaces of inorganic materials because it is readily available in various molecular weight distributions and with different ratios of vinyl to internal olefin groups. The vinylsilane-linked polymer **3** is prepared by subjecting polybutadiene **1**[7] to Pt catalyzed hydrosilylation reaction to form the corresponding chlorosilane-linked polymer **2**, which is then subjected to reaction with vinyl magnesium chloride without isolation of **2** (Scheme 2a). The resulting vinylsilane-linked polymer **3** was purified by column chromatography. ^{1}H NMR analysis showed that polymer product **3** contains an 85:15 ratio of vinylsilane groups and internal olefins.
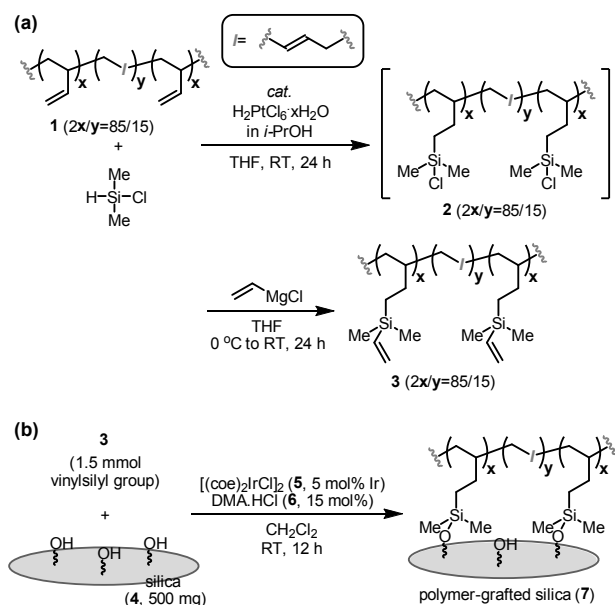
Scheme 2. (a) Preparation of immobilizable vinylsilyl group-impregnated polymer 3 and (b) catalytic grafting of 3 onto silica (4) in the presence of 5/6

The vinylsilane-linked polymer **3** can be covalently bonded to silica by using an Ir(I)/HCl catalyzed grafting reaction.[4] For example, treatment of silica (**4**, 500 mg, 1080 µmol/g available Si-OH groups)[8] with **3** (1.5 mmol vinylsilane groups) in the presence of [(COE)$_2$IrCl]$_2$ (**5**, 5 mol% Ir based on vinylsilane groups) and N,N-dimethylacetamide hydrochloride[9] (DMA·HCl, **6**, 15 mol%) at room temperature for 12 h leads to formation of the polymer-grafted silica **7** (Scheme 2b). Analysis of the solid-state cross polarization magic-angle-spinning (CP-MAS) ^{13}C NMR spectrum of **7** shows that resonances for the vinyl groups in **3** are substantially disappeared, showing that nearly all of the vinylsilane groups participate in creating Si-O bonds to the silica surface under the conditions used (Figure 1).[10]
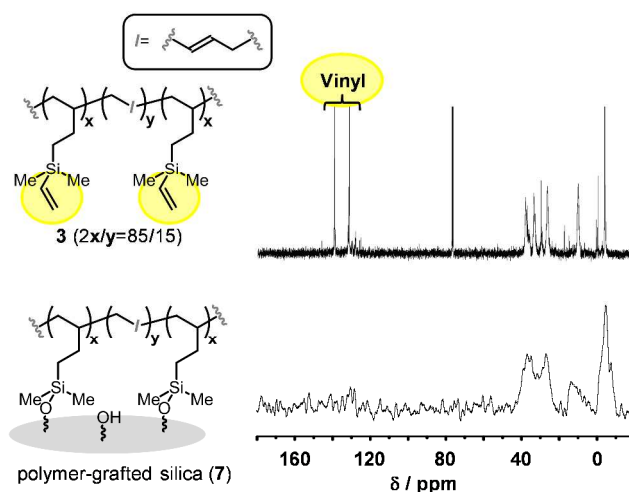

Figure 1. Characteristic ^{13}C NMR for **3** and **7** (solid state, CP-MAS).

The use of this protocol to prepare various organic group functionalized solid silicas was examined next. For this purpose, a portion of the vinylsilane groups in polymer **3** were functionalized by using chelation-assisted hydroacylation reactions with aldehydes.[11] For example, reaction of **3** with 1-pyrenebutyraldehyde (**8a**, 0.1, 0.25, 0.33, 0.5, 0.75 and 1.0 equiv. based on the vinylsilane groups) in the presence of a mixture of (Ph$_3$P)$_3$RhCl (**9**, 5 mol%), 2-amino-3-picoline (**10**, 50 mol%), and C$_6$H$_5$CO$_2$H (**11**, 20 mol%) at 130 ^{o}C for 12 h produced the 1-pyrenepropyl-ketone containing polymer **12a**. The ratio of remaining vinylsilane to introduced 1-pyrenepropyl-ketone groups [**x**/(**x**+**y**), Figure 2] in the polymers formed in this manner, determined by using ^{1}H NMR spectroscopy, was found to increase as the molar amount of aldehyde **8a** is increased from 0.1 to 1.0 equivalents (based on vinylsilane groups in **3**). The maximum percent incorporation of 1-pyrenepropyl-ketone groups was determined to be 47% with 0.75 equiv. of **8a** (Figure 2).

The multiple vinylsilane containing, 1-pyrenepropyl-ketone functionalized polymer **12a** (47% pyrenyl groups) can be catalytically grafted to silica (**4**). Accordingly, reaction of **12a** with **4** in the presence of **5** and **6** results in formation of

polymer grafted silica **13a**, in which the loading amount of pyrenyl groups is 264 µmol/g (Scheme 3).
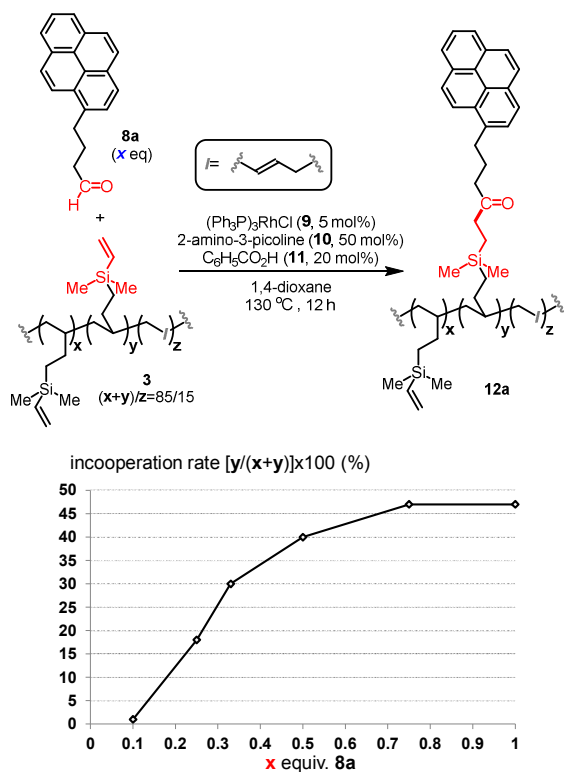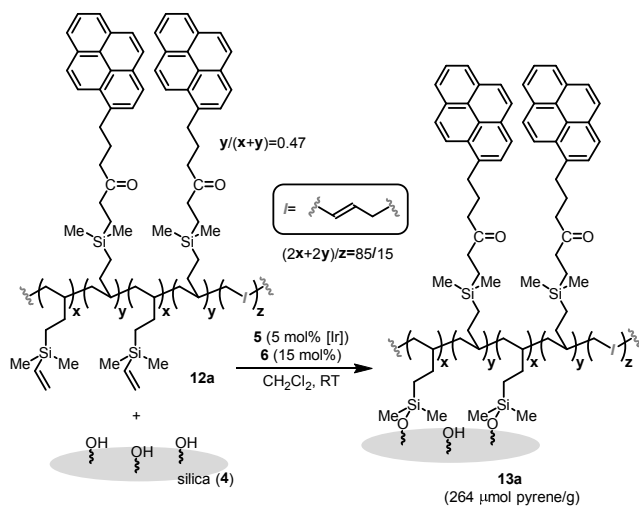

Figure 2. Conversion rate of vinylsilyl group in **12a** by hydroacylation of **3** with different molar amount of **8a**.
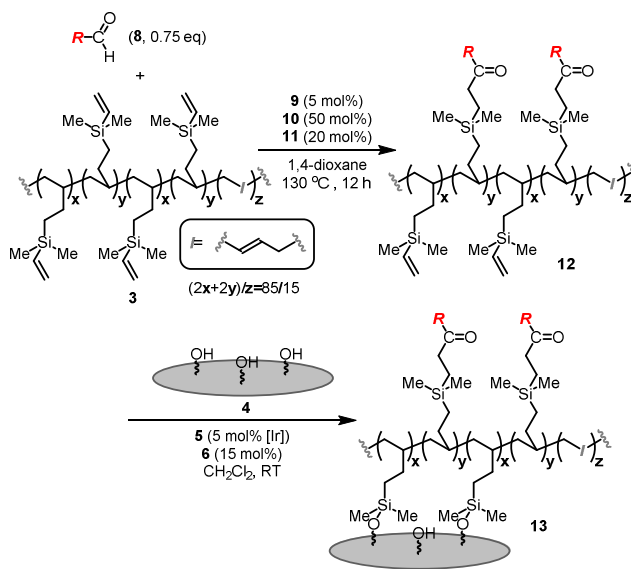

Scheme 3. Immobilization reaction of pyrene group-possessed polymer **13a** with silica in the presence of catalyst mixture **5** and **6**.

Chelation-assisted hydroacylation reactions of **3** using a variety of aliphatic (**8b-8d**), aromatic (**8e** and **8f**), and boron and ferrocene containing (**8g** and **8h**) aldehydes (0.75 equivalents based on vinylsilane groups in **3**) take place to generate the corresponding partially functionalized vinylsilane-linked polymers **12** with 29-59% incorporations (Table 1). Likewise, catalytic grafting reactions of the resulting polymers

12b-12i onto silica, performed in the presence of catalysts **5** and **6**, give the respective functional group grafted silicas **13b-13i** with incorporation amounts of 178-319 µmol/g.

Table 1. Controlled functionalization of polymer **2b** and grafting onto silica surface

$R-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}$ (8) $\left(R-\xi \right)$	$n\text{-}C_3H_7-\xi$ (**8b**)	$n\text{-}C_6H_{13}-\xi$ (**8c**)	$n\text{-}C_9H_{19}-\xi$ (**8d**)
Incorporation rate of **R** in **12**^{a} [%, **b**/(**a**+**b**)]	37 (**12b**)	40 (**12c**)	37 (**12d**)
loading amount of **R** in **13**^{b} (µmol/g)	319 (**13b**)	288 (**13c**)	246 (**13d**)

	(**8e**)	(**8f**)	(**8g**)	(**8h**)	(**8i**)^c
	42 (**12e**)	33 (**12f**)	59 (**12g**)	46 (**12h**)	29 (**12i**)
	317 (**13e**)	178 (**13f**)	262 (**13g**)	184 (**13h**)	187 (**13i**)

^{a} Determined by ^{1}H NMR. ^{b} Determined by elementary analysis. ^{c} 150 ºC, 12 h.

To gain insight into the robustness of the bond between organic component and silica, the stability of the polymer grafted silica **7** and monomeric dodecyldimethylsiloxy analog **14** were evaluated. Following immersion in aqueous 1 M solutions of HCl, K_2CO_3 and NaOH (Figure 3a and 3c), the organic carbon contents of the silicas were determined by using elemental analysis. The results show that the carbon wt-percentages of samples **7** and **14** do not change upon exposure to acidic solutions. This finding indicates that the Si-O bonds in hydrocarbon functionalized silicas are stable under acidic

conditions. However, under basic K_2CO_3 and NaOH conditions the carbon wt-percentage of the simple monomeric dodecyldimethylsilane group grafted silica **14** is significantly lowered while that of polymer grafted silica **7** is unchanged. The results of additional stability tests show that in 1 M K_2CO_3 at room temperature and 80 °C (Figure 3b and 3d) the carbon wt-percentage of **7** does not vary significantly even when the reaction time and temperature are increased (Figure 3d).[12] In contrast, carbon wt-percentage of **14** drastically decreases at longer times and higher temperatures (Figure 3b). Thus, these observations confirm our original expectation that Si-O bonds in the simple monomeric dodecyldimethylsilane group grafted silica **14** are labile under basic conditions and the polymeric components on **7** remain tightly bound under basic condition probably because of both the presence of multiple Si-O bonds between polymer and silica and effective shielding these bonds from the basic environment. Therefore, the new polymer grafting protocol serves as a unique method to prepare hydrolytically stable, surface functionalized silicas.
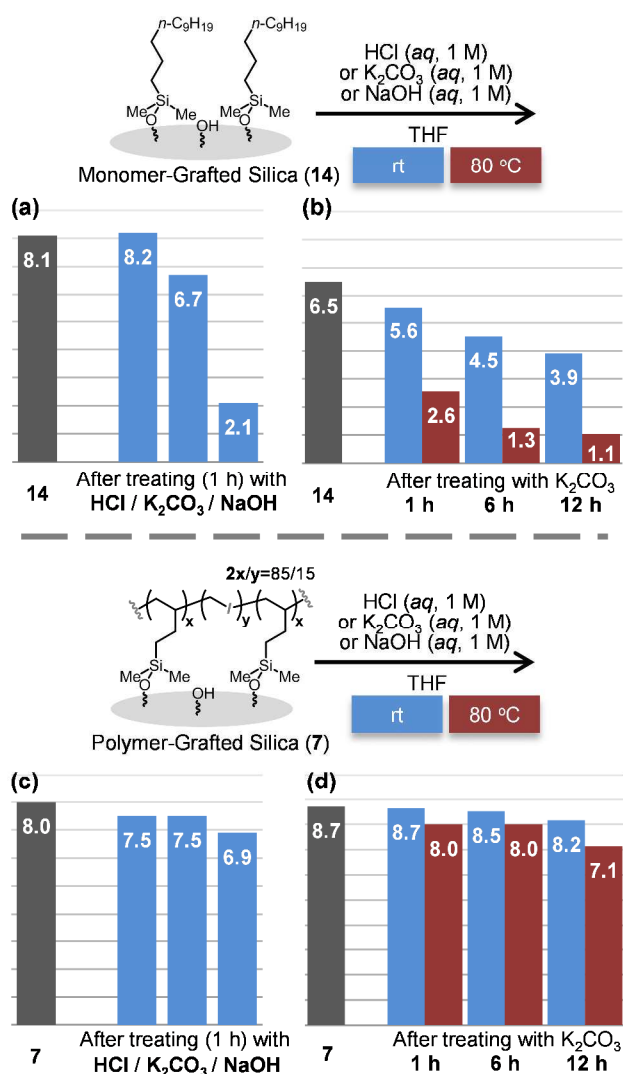
In the next phase of this investigation, we explored the use of Suzuki coupling reactions, taking place under K_2CO_3 base conditions, to introduce functional groups into polymeric backbone when it is already linked to silica. For this purpose, boronic acid (BA) group-linked silica **15** (carbon wt-percentage: 7.4, 301 μmol/g BA group incorporation amount) was prepared from the corresponding pinacol phenylboronic ester group covered silica **13g** (Table 1 andFigure 4a).[13] Suzuki coupling reaction of the BA moieties in **15** with 1-iodopyrene in the presence of $Pd(OAc)_2$ and K_2CO_3 at 80 °C for 6 h takes place to yield the pyrenyl group-functionalized polymer coated silica **16**.[14] Silica **16** shows a characteristic fluorescence peak at $\lambda_{em,max}$ = 470 nm (λ_{ex} = 345 nm, Figure 4c).

Figure 3. Comparison of bond robustness of silica-bound polymer (**7**) and monomer (**14**).
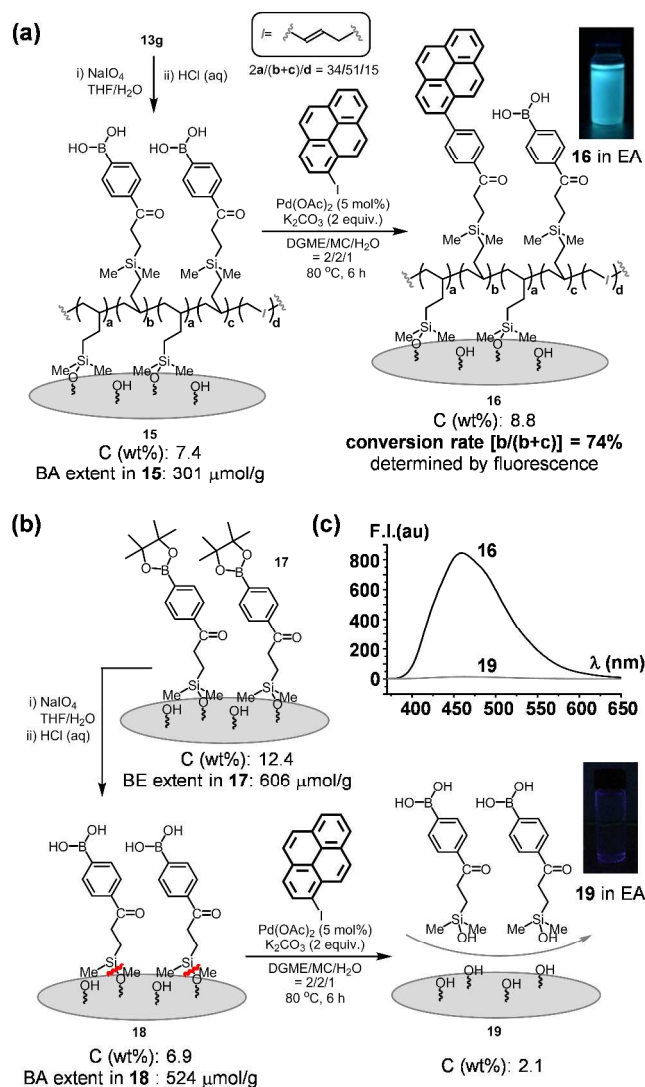
Figure 4. Comparsion of Suzuki coupling reaction of boronic acid (BA) group-covered silica surface (a) **15** and (b) **18** with 1-iodopyrene under basic condition (c) fluorescence spectra for **16** and **19** (1 mg each sample/1 ml EA). The pictures of **16** and **19** were taken under exposure of 365 nm UV. F.I.=fluorescence intensity, DGME=diglyme methyl ether.

To assess the extent of conversion of the boronic acid groups in **15** to 1-pyrenyl groups in **16**, quantitative

fluorescence analysis of pyrenyl group-bound silica **13i** (loading extent of 4-(1-pyrenyl)-phenyl groups: 187 μmol/g, Table 1), in which loading extent of desired functional group was precisely defined, was performed. After constructing a calibration curve for 4-(1-pyrenyl)-phenyl group (Figure 5a), the extent of 4-(1-pyrenyl)-phenyl group loading was determined by calculating the fluorescence intensity of **16** with the fluorescence calibration curve of **13i**. The analysis revealed that in **16**, 74% of the BA groups are converted to 1-pyrenyl groups (loading extent of 1-pyrenyl groups: 224 μmol/g). The results demonstrate that the functionality installed into organic-inorganic hybrid materials by using the new strategy will serve as reactive centers for post-modification of hybrid materials under Si-O bond hydrolytic condition.

In an exploratory effort, Suzuki coupling reaction of the boronic acid-grafted silica **18** derived from monomeric silane precursor was attempted (Figure 4b). Silica **18** (carbon wt-percentage: 6.9, loading extent of BA group: 524 μmol/g) was prepared by treatment of the pinacol-protected boronate **17**[4] with NaIO$_4$. Treatment of **18** with 1-iodopyrene using the standard Suzuki coupling conditions does not lead to incorporation of pyrenyl groups into the monomer linked silica. Elemental and fluorescence analysis of the material **19** generated in this process show that most of monomeric organic moieties linked to the surface are lost in the reaction, likely a result of the basic reaction condition employed.
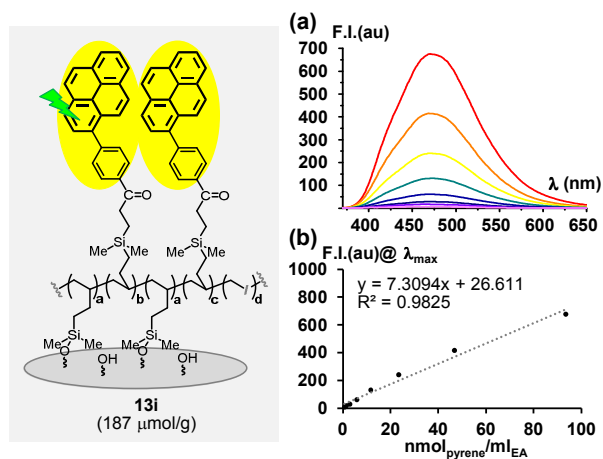

Figure 5. (a) Fluorescence spectra (λ_{ex} = 345 nm) and (b) calibration curve for F.I. at λ_{max} (470 nm) of well-defined 4-(1-pyrenyl)-phenyl group-bound silica 13i for quantitative analysis of Suzuki coupling reaction on silica surface. F.I.=fluorescence intensity.

Conclusions

We have described a new method for immobilization of organic functional groups on the silica surface that relies on the use of vinylsilane group-containing, polybutadiene derived polymers. Compared to conventional immobilization methods that utilize monomeric silane coupling reagents, the new protocol enables formation of organic functionalized silicas in which the functional groups are bonded to the surface through highly robust multiple Si-O bonds that tolerate acidic and basic

conditions. Moreover, the functional group are readily introduced by using one-step Rh(I)-catalyzed chelation-assisted hydroacylation reactions of vinylsilane group containing polymer. This new protocol enables post-modification of functionalized silica surface under hydrolytic conditions such as those employed in the Suzuki coupling reaction. Further applications of the new grafting protocol are being explored.

Experimental

Preparation of Vinylsilane-linked Polymer 3 (Scheme 2). A N$_2$-purged 100 mL two-necked RBF pre-equipped with reflux condenser was charged with chlorodimethylsilane (35.1 mL, 316 mmol (4.0 equiv. based on terminal vinyl groups in **1**)) and H$_2$PtCl$_6$•xH$_2$O (123 mg) in *i*-PrOH (0.1 mL). The mixture was stirred for 10 min. THF solution (10 mL) of polybutadiene **1** (5.0 g, 79 mmol terminal vinyl groups) was then added to the mixture, and the mixture was stirred for 24 hours at room temperature. After the reaction, unreacted chlorodimethylsilane was removed under reduced pressure. The resulting chlorodimethylsilyl group-containing polymer **2** was used in the next step without further purification. The polymer **2** was dissolved in distilled THF (20 ml), and the resulting solution was transferred to 250 ml RBF. Vinylmagnesium chloride (1.6 M solution in THF, 124 ml, 198.4 mmol) was added dropwise to the polymer-dissolved solution at 0 °C, and the resulting mixture was stirred for 24 hours at room temperature. The reaction was then quenched with saturated aq. NH$_4$Cl and extracted with diethyl ether. The extracts were dried over anhydrous MgSO$_4$, filtered through a celite pad and concentrated *in vacuo*, giving a residue that was subjected to column chromatography to give dimethylvinylsilyl group-impregnated polymer **3** (10.0 g, 98%). Polymer **3**: ¹H NMR (400 MHz, CDCl$_3$) δ 6.17-5.36 (m, 3H), 5.34 (br s, internal -CH=CH-), 1.94 (br m), 1.65 (br m), 1.33-0.97 (br, m), 0.47 (br s), 0.05 (s); ¹³C NMR (100 MHz, CDCl$_3$) δ 139.4, 131.6, 39.4-35.7, 34.7-32.3, 30.8-29.6, 28.2-25.9, 11.8-10.2, -3.15; IR spectrum (CDCl$_3$) 3046, 2923, 1899, 1592, 1452, 1249, 1178 cm⁻¹; M_w/M_n = 4.77.

Immobilization of Polymer 3 onto Silica 4 in the Presence of Catalyst Mixture of 5 and 6 (Scheme 2b). To a dichloromethane solution (2.5 mL) of polymer **3** (220 mg, 1.5 mmol vinylsilane moieties) in a 5 mL microreactor was added spherical shaped silica (**4**, 500 mg), [(COE)$_2$IrCl]$_2$ (**5**, 5 mol% [Ir] based on vinylsilanes, 33.6 mg) and DMA·HCl (**6**, 15 mol%, 27.7 mg). The mixture was stirred for 12 h at room temperature, filtered, washed thoroughly with dichloromethane, acetone and methanol, and dried under reduced pressure to give functionalized silica (**7**, 550 mg).

Representative Procedure for Hydroacylation of Polymer 3 with Aldehyde 8 (Table 1). A mixture of polymer **3** (500 mg, 3.34 mmol vinylsilane group), aldehyde (**8**, 0.75 mmol), (Ph$_3$P)$_3$RhCl (**9**, 5 mol%, 116 mg), 2-amino-3-picoline (**10**, 100 mol%, 270 mg), benzoic acid (**11**, 20 mol%, 61 mg), and 1,4-dioxane (3.0 mL) was stirred at 130 °C for 12 h in a 5 mL pressure vial. The mixture was concentrated *in vacuo*, and washed thoroughly with MeOH and dried to give the functionalized polymer **12**.

Representative Procedure for Immobilization of Functionalized Polymer 12 onto 4 in the Presence of the Catalyst Mixture of 5 and 6 (Table 1). A mixture of polymer **12** (0.3 mmol vinylsilane groups), spherical shaped silica (**4**, 100 mg), [(COE)$_2$IrCl]$_2$ (**5**, 5 mol% [Ir] based on vinylsilane

groups, 6.7 mg), DMA·HCl (**6**, 15 mol%, 5.5 mg) and dichloromethane (0.6 mL) in a 1 mL microreactor was stirred for 12 h at room temperature. The mixture was filtered, washed thoroughly with dichloromethane, acetone and methanol, and dried under reduced pressure to give functionalized silica **13**.

Acknowledgements

Notes and references

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Electronic Supplementary Information (ESI) available: Characterization data of compounds and detailed procedures. See DOI: 10.1039/b000000x/

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7 Polybutadiene **1** (predominantly 1,2-addition) was purchased from Sigma-Aldrich Co. The ratio of terminal over internal alkene group in **1** was determined to be 85:15 by ^{1}H NMR analysis.

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