"CLICK" CHEMISTRY AS A NOVEL ROUTE FOR THE INTRODUCTION OF FUNCTIONAL GROUPS TO OCTAPHENYLSILSESQUIOXANE

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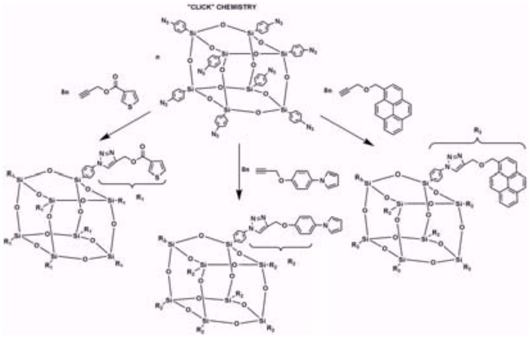
Introduction

The development of materials with enhanced properties at the molecular level is the premier challenge of the 21st century. In an effort to meet this challenge, "click" chemistry, the recent advanced of Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes to form the five-membered (1,2,3)-triazole heterocycle, has been proposed by Sharpless *et al*.[1,2] This approach brings an enormous potential in material science. The key features in "click" chemistry is represented by quantitative yields, high tolerans of functional groups, simple product isolations, lack of by-product, superior regioselectivity, and mild and simple reaction conditions. The development and the application of click chemistry in polymer and material science are extensively reviewed in recent articles.[3]

Polyhedral oligomeric silsesquioxane (POSS), $(RSiO_{1.5})_n$ or T_n with n=6, 8,10 is a cage-like silsesquioxane with an inner inorganic framework made up of silicone and oxygen $(SiO_{1.5})_n$ and external organic substituents. Depending on the structure, these organic substituents can be reactivite or inertial functional group. Recent efforts have focused on stoichiometrically well-defined cubic silsesquioxane frameworks with synthetically useful functional group.

In the scope of this study, our main goal was to report the synthesis of azide functionalized octaphenylsilsesquioxane (O*N₃*PS) and subsequent use of "click" chemistry as a facile route toward functionalization of silsesquioxanes (Scheme 1).



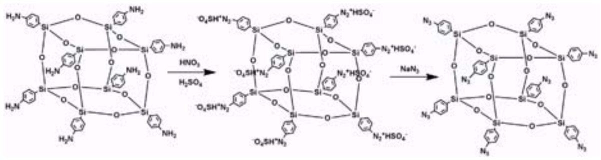
Scheme 1

Results and Discussion

Our initial desire was to synthesize octa(azidophenyl) silsesquioxane (ON_3PS) cube. For this purpose, the octa(nitrophenyl) silsesquioxane (ONO_2PS) was synthesized by a modified literature procedure reported by Laine *et al*.[4,5] This improved procedure provides octa(nitrophenyl) silsesquioxane (ONO_2PS) with one nitro group per phenyl unit. ONO_2PS is easily transformed to ONH_2PS by hydrogen-transfer reduction in the presence of formic acid, triethylamine and Pd/C catalyst with a quantitative conversion.[4,5]

For the synthesis of parent ON_3PS cube, a simple synthetic strategy was used (Scheme 2). The corresponding diazonium salt was obtained by using aqueous solution of sodium nitrite in concentrated sulfuric acid at about 0 °C. The resulting diazonium salt was used to obtain azido functional OPS (ON_3PS) with a quantitative conversion (99–100).

The structures of the intermediates and final product were confirmed by ^{1}H NMR spectra (d_6-DMSO) (**Figure 1**). The aromatic protons of phenyl groups emerge at around 8 ppm, due to the electron withdrawing effect of the $-NO_2$. The reduction process leads to two changes in the spectra. While N–H protons appeared at 5.50–4.40 as new peaks, the aromatic peaks appear at higher magnetic fields in the range of 7.9-6.1 ppm.



Scheme 2

Moreover, the integrals of N–H protons and aromatic C–H protons are in the ratio of 1:2, indicating the quantitative reduction. The efficient transformation of ONH_2PS to ON_3PS was evidenced also from ^{1}H NMR spectrum wherein the resonance due to N–H protons disappeared completely.

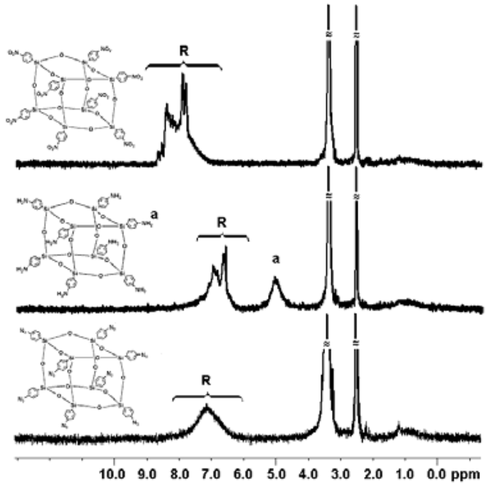


Figure 1. ^{1}H NMR spectra of ONO_2PS, ONH_2PS and ON_3PS (**R**: Aromatic Protons).

Additionally, FT-IR spectra of the related compounds confirm the NMR data. The spectra of ONO_2PS exhibit strong symmetric and asymmetric *v*N=O peaks at 1348 and 1527 cm^{-1} (Figure 2). These peaks disappear completely after the reduction and new broad symmetric and asymmetric *v*N–H peaks appear at 3368 cm^{-1} and 3456 cm^{-1}. After the transformation of amine groups to azide groups, a strong and new vibration centered at 2104 cm^{-1}appeared in the spectrum. Notably, all functionalized OPS, discloses characteristic of *v*Si-O-Si stretching signals between 1304-990 cm^{-1} with relatively high intensity.

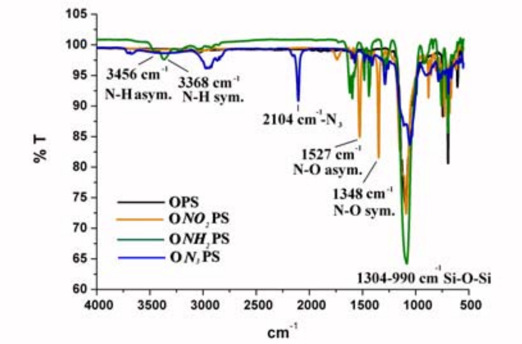
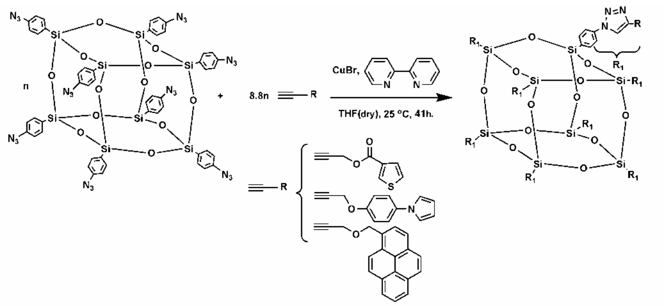


Figure 2. FT-IR spectra of ONO_2PS, ONH_2PS and ON_3PS.

Then a standard "click" protocol has been established. Experimantally, the ON_3PS was dissolved in THF and reacted with *propargyl* containing electroactive- and photo-active molecules (*propargyl*thiophene, *propargyl*pyrrole or *propargyl*pyrene) in the precence of a catalytic system including CuBr as the copper source, bipyridine as the ligand at room temperature. The reaction afforded the desired products (O*(thiophene)*PS, O*(pyrrole)*PS or O*(pyrene)*PS) (**Scheme 3**). After removing the catalyst, the polymers were precipitated and dried under vacuum.



Scheme 3

The successful transformation of azide moieties into each functional triazoles was confirmed ^{1}H NMR. Typically, in the case of O*(thiophene)*PS, the appearance of the new methylene protons adjacent to the triazole ring at 5.3 ppm (triazole-CH_2Ph) and new triazole proton at 7.8 ppm were observed (**Figure 3**). Additional peaks corresponding thiophene moiety overlapped with those of aromatic protons of OPS.

FT-IR spectrum of the O*(thiophene)*PS, reveals characteristic of *v*Si-O-Si stretching signals between 1304-990 cm^{-1}. Moreover, the FT-IR spectra of O*(thiophene)*PS show the disappearance of the acetylene peak at ~3293 cm^{-1} and the azide peak at ~2104 cm^{-1} while a strong carbonyl band at 1716 cm^{-1} Thus, click reaction was efficient and near-quantitative as evidenced by spectral methods.

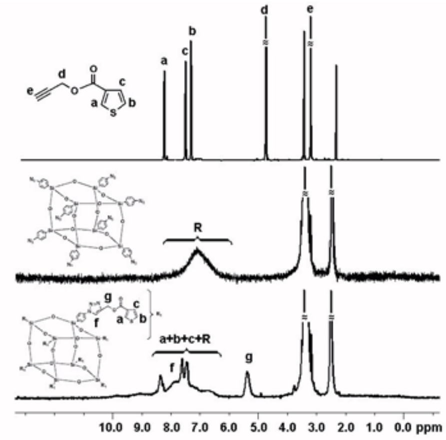


Figure 3. ^{1}H NMR spectra of *propargyl*thiophene, O*N_3*PS and O*(thiophene)*PS (**R**: Aromatic protons).

Conclusion

We have demonstrated a novel route, for the introduction of functional groups to octaphenylsilsesquioxanes [OPS] via click [3+2] chemistry. The process involves the synthesis of azide functionalized OPS and reaction of these functional groups with electro- and photoactive molecules also possessing propargyl groups as the components of the click reaction. The strategy adopted in this study appears to be entirely satisfactory in terms of efficiency and simplicity. Further wok is in progress to expand this approach to other functionalities.

References

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