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Preparation of A Novel Functionated POSS Nano-particle Bearing the Perfluoro Aryl Ether Dendron

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Abstract. In this paper, the perfluoro aryl ether dendrons were synthesized by mesylate reaction, and using the dendron as a modifier to prepare a novel fluorinated polyhedral oligomeric silsesquioxane (F-POSS) nano-particle bearing this fluorine-containing dendron. In this approach, the Williamson ether synthesis technique was used as the generation enhancement step. Second generation perfluorobenzyl alcohol dendron was obtained from active mesylated precursors. This mesylate actiation technology has the advantage of short reaction times in the subsequent steps and avoids chromatographic purifiction. Second genenriation dendron was then built by repitition of Williamson ether synthesis reaction of mesylate derivative. It is possible for this new nano-particle to be used in the modification of polymer materials to make the durable superhydrophobic and oilphobic surface functional materials with excellent self-cleaning properties.

Introduction

Self-cleaning surfaces have potential applications in many fields. However, the self-cleaning surfaces are easy to be damaged during the practical usage and thus lose their structures and properties. Therefore, scientists pay increasing attention to improve the durability of the self-cleaning surface. Because of their low surface tension, fluoro radicals have been widely used in the study of self-cleaning coatings to decrease the surface energy of polymers [1]. At the same time, the hyperbranched polymers have attracted extensive attention due to their unique structures and properties [2,3]. Among these, fluoro hyperbranched structures with preferable thermodynamic stability [4], hydrophobicity, lipophobicity and chemical resistance have been widely used in low surface energy materials. Polyhedral oligomeric silsesquioxane (POSS) is a new class of organic-inorganic hybrid material with stable stuctures and high thermal endurance. The functional and hybrid materials based on POSS have drawn much attention of researchers [5-8] owing to their new properties, such as heat resistance, pressure-proof, fire resistance and high solidness [9].

This article reported the functionated POSS nano-particle bearing perfluoro aryl ether dendron, which was prepared with amino-POSS and (3,5-bis (3,5-bis (perfluorobenzyloxy) benzyloxy)phenyl) methanol by mesylate reaction. And the (3,5-bis(3,5-bis(perfluorobenzyloxy) benzyloxy) phenyl)methanol was prepared with 3,5-dihydrobenzyl alcohol and 2,3,4,5,6-pentafluoro benzyl bromide by mesylate reaction. The structure was characterized with IR spectra and ^{1}HNMR. This new nano-partical is probably used in preparation of organic-inorganic hybrid functional surfaces and composite coatings.

Experimental section

3,5-dihydrobenzyl alcohol, Shanghai Jiachen chemical company, China, was used as received. PSS-(3-(2-Aminoethyl)-amino)propyl-Heptaisobutyl substituted, sigma-aldrich company, America. 2,3,4,5,6-pentafluoro benzyl bromide, EHSY Lab, Shanghai, China. Acetone was dried with anhydrous K_2CO_3 and distilled, dichloromethane was dried with anhydrous $CaCl_2$ and distilled.

Column chromatography was carried out with Merck silica gel-60 (70-230 mesh). Preparative TLC plates were Merck aluminum sheets covered with silica gel-60 F_{254}. Structure characterizations were performed at Hubei University, Hubei, China.

Synthesis of [3,5-bis(perfluorobenzyloxy)phenyl]methanol (3)

A mixture of 2,3,4,5,6-pentafluoro benzyl bromide (1.52g, 0.83ml), 3,5-dihydrobenzylalcohol (0.39g), K_2CO_3 (0.85g), and 18-Crown-6 (0.0741g) in dry acetone (60ml) was reflexed for three days under a nitrogen atmosphere at 40℃ .The reaction mixture was poured into water (100ml) and extracted with dichloromethane (3*100ml). The combined extracts were dried with $MgSO_4$ and evaporated. The residue was chromatographed on silica gel with dichloromethane / hexane (1:1) as the eluent to give the product(yield: 78%), mp:98-99℃; IR: ν = 3361, 2924, 2854, 1658, 1597, 1523, 1507, 1456, 1434,1382 , 1311, 1290, 1164, 1059, 976, 941, 834, 773, 689, 624cm^{-1}. ^{1}H-NMR (400MHz-$CDCl_3$): δ=4.68(S, 2H $ArCH_2OH$), 5.11(S, 4H $C_6F_5CH_2O$), 6.50 (d, 1H J=2Hz), 6.67(d, 2H J=2Hz)

Synthesis of [3,5-bis(perfluorobenzyloxy) phenyl] methanesulfonate(4)

To a mixture of [3,5-bis(perfluorobenzyloxy)phenyl]methanol (0.148g), and NEt_3 (0.148g) in dry dichloromethane (50ml) was added methanesulfonyl chloride (0.136g, 0.92ml) diluted by dichloromethane (10ml) over 15min at -10℃ under a nitrogen atmosphere. After stirring for 80min at -10℃, the reaction mixture was poured into a mixture of crushed ice (50ml) and concentrated HCl (5ml). The dichloromethane layer was separated and washed with saturated $NaHCO_3$ and dried with $MgSO_4$. After evaporation of the solvent, the crude product was crystallized from diethyl ether to give the product. (yield: 85%), mp: 80.5-81.5℃; IR: ν= 2920, 1659, 1524, 1508, 1463, 1356, 1174, 1059, 975, 941, 842, 529cm-1. 1H-NMR (400MHz-CDCl3)： δ= 3.00(S, 3H CH3), 5.12(S, 4H C6F5CH2O), 5.19(S, 2H ArCH2OSO2CH3), 6.59(d, 1H J=2.2Hz), 6.69(d, 2H J=2.2Hz)

Synthesis of (3,5-bis(3,5-bis(perfluorobenzyloxy)benzyloxy)-phenyl)methanol (5)

A mixture of [3,5-bis(perfluorobenzyloxy) phenyl] methanesulfonate (1.14g), 3,5-dihydrobenzyl alcohol (0.129g), K_2CO_3 (0.19g), and 18-Crown-6 (0.066g) in dry acetone (80ml) was reflexed for four days under a nitrogen atmosphere at 40℃ .The reaction mixture was poured into water (100ml) and extracted with dichloromethane (3*100ml). The combined extracts were dried with $MgSO_4$ and evaporated. The residue was chromatographed on silica gel with dichloromethane / diethyl ether (20:1) as the eluent to give the product. (yield: 62%), mp:96-97℃; IR: ν= 3424, 3025, 2926, 2855, 1725, 1659, 1598, 1524, 1509, 1454, 1380, 1310, 1290, 1163, 1059, 975, 942, 832, 799, 757, 699, 624 cm^{-1}. ^{1}H-NMR (400MHz-$CDCl_3$): δ= 4.51(S, 2H $ArCH_2OH$), 5.08(S, 8H $ArCH_2O$), 5.28(S, 4H $C_6F_5CH_2O$), 6.50-6.65(m 9H Ar)

Synthesis of (3,5-bis(3,5-bis(perfluorobenzyloxy)benzyloxy)phenyl) methanesulfonate (6)

To a mixture of (3,5-bis(3,5-bis(perfluorobenzyloxy)benzyloxy)phenyl)methanol(0.105g), and NEt_3 (0.105g) in dry dichloromethane (20ml) was added methanesulfonyl chloride (0.029g,0.02ml) diluted by dichloromethane (10ml) over 15min at -10℃ under a nitrogen atmosphere. After stirring for 100min at -10℃, the reaction mixture was poured into a mixture of crushed ice (50ml) and concentrated HCl (5ml). The dichloromethane layer was separated and washed with saturated $NaHCO_3$ and dried with $MgSO_4$. After evaporation of the solvent, the crude product was crystallized from diethyl ether to give the product. (yield: 79%), mp:84-85℃; ^{1}H-NMR (400MHz-$CDCl_3$)： δ=3.58(3H SO_3CH_3), 4.5(S, 2H $ArCH_2O$), 5.11(S, 12H $C_6F_5CH_2O$), 6.50-6.65(m 9H Ar)

Synthesis of the functionated POSS nano-particle wearing perfluoro aryl ether dendron (8)

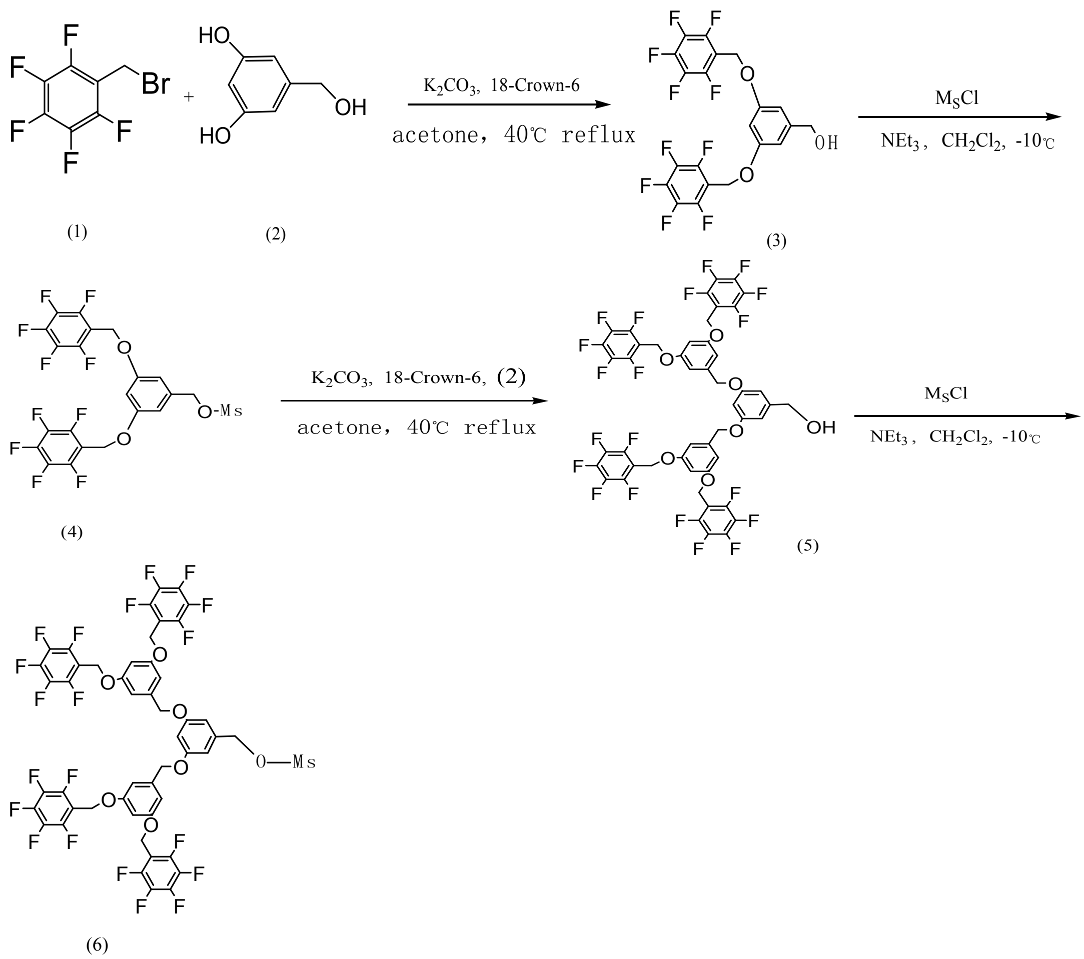
A mixture of (3,5-bis(3,5-bis(perfluorobenzyloxy)benzyloxy)phenyl)methanesulfonate (0.151g), POSS-(3-(2-Aminoethyl)-amino)propyl-Heptaisobutyl substituted (0.198g), K_2CO_3 (0.085g), and moderate18-Crown-6 in dry dichloromethane (50ml) was reflexed for four days under a nitrogen atmosphere at 40℃ .The reaction mixture was poured into water (100ml) and extracted with dichloromethane (3*100ml). The combined extracts were dried with $MgSO_4$ and evaporated to give the crude product. (yield: 62%), IR: ν= 2957, 2927, 1741, 1595, 1508, 1431, 1367, 1262, 1229, 1101, 802, 742, 699, 485cm^{-1}. ^{1}H-NMR (400MHz-$CDCl_3$):δ=0.57(S, 16H $SiCH_2$), 0.93(S, 42H $SiCH_2CH(CH_3)_2$), 1.27(S,2H $POSSCH_2CH_2CH_2NH$), 1.65(S, 7H $SiCH_2CH$), 1.94(S, 2H NH), 2.35(S, 2H $POSSCH_2CH_2CH_2NH$), 2.61(S, 4H $NH(CH_2)_2NH$), 3.64（S, 2H $ArCH_2NH$）, 5.27(S, 12H $C_6F_5CH_2O$), 6.77-6.95(m 9H Ar)

Results and Discussion

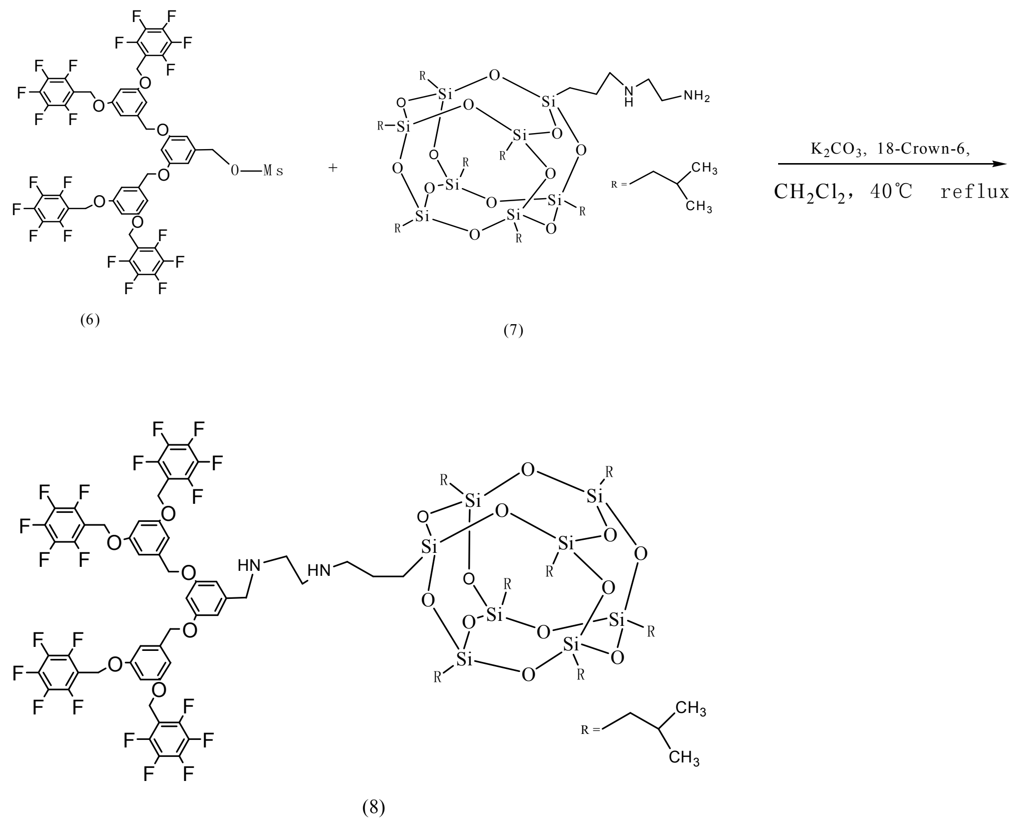
Mesylate reaction overcomes the disadvantage of high cost of the procedure regarded PPh_3/CBr_4 as catalyst; The reaction was carried out at -10℃ to prevent chloride by-product-forming side reactions; it is time-saving (in this experiment, mesylate reactions only cost about 1.5h); The crude products by mesylate reaction can be purified by crystallization, therefore, chromatographic separations can be avoided.

The synthesis of the first generation perfluorinated dendron (3) starts from the reaction of two equivalents of perfluorobenzyl bromide (1) with one equivalent of 3,5-dihydrobenzyl alcohol (2) in dry acetone in the presence of K_2CO_3 and 18-Crown-6 at 40℃ for three days in 78% yield after purification by silica gel column chromatography. This product was then activited for further generation enhancement with methanesulfonyl chloride in the presence of an excess of NEt_3 in dichloromethane at -10℃ for 80min. The product (4) was purified by crystallization from diethyl ether in 85% yield. The second generation perfluorinated poly(aryl ether) dendron (5) was obtained in 62% yield by the reaction of two equivalents of the first generation perfluorinated mesylate with one equivalent of 3,5-dihydrobenzyl alcohol (2) at 40℃ in the presence of K_2CO_3 and 18-Crown-6, following purification by silica gel column chromatography. The corresponding mesylate (6) was obtained in 79% yield with methanesulfonyl chloride in the presence of an excess of NEt_3 in dichloromethane at -10℃ for 100min (scheme 1). At last, a functionated POSS nano-particle wearing perfluoro aryl ether dendron (8) was prepared with POSS-(3-(2-aminoethyl)-amino) propyl-Heptaisobutyl substituted (7) and (3,5-bis (3,5-bis (perfluorobenzyloxy)benzyloxy)- phenyl) methanol (6) in dry dichloromethane in the presence of K_2CO_3 and 18-Crown-6 at 40℃ for three days in 62% yield (scheme 2).

In order to seperate the first generation perfluorinated dendron (3) from other impurities, the mixed solution of dichloromethane / hexane (1:1), which can confer a preferable R_f (R_f=0.4) for the product, has been definited as the eluent after attempting solvent composites repeatedly. Following many times of failures, the second generation perfluorinated poly(aryl ether) dendron (5) was seperated successfully by dichloromethane / diethyl ether (20:1) providing the product with a suitable R_f (R_f=0.6). The corresponding mesylates (4 and 6) for these two perfluorinated dendrons were simply purified by crystallization from diethyl ether.



Scheme 1



Scheme 2

Conclusion

1. The mesylate reaction route was applied to synthesis a perfluoro aryl ether dendron-(3,5-bis(3,5-bis (perfluorobenzyloxy)benzyloxy)phenyl)methanol.
2. Functionated POSS nano-particle bearing perfluoro aryl ether dendron was prepared successfully with (3,5-bis (3,5-bis (perfluorobenzyloxy) benzyloxy) phenyl) methanol and PSS-(3-(2-Amino ethyl)-amino)propyl Heptaisobutyl substituted by further mesylate reaction. This new nano-partical filler has the potential value for the relative foundational and applied research. Numerous of documents have demonstated that the properties of composite polymers can be improved greatly by using POSS nano-particles to modify polymers. Therefore, functionated POSS nano-particle bearing perfluoro aryl ether dendron will have positive effects on preparing superhydrophobic and oilphobic functional materials with outstanding mechanical property and chemical durability.

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