RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Graphic Abstract:

Novel multifunctional alkoxysilanes were prepared by facile thiol-yne "click" chemistry, which were neatly ran in mild conditions without any heavy metallic catalyst or solvent. In addition, some of them showed blue light emission upon UV irradiation (365 nm). At last, obtained functionalized trialkoxysilanes are used to modify the Si (1, 0, 0) surface, which can then be used for further functionalization or the immobilization of polymers or biomolecules.

UV induced thiol-yne "click"reaction
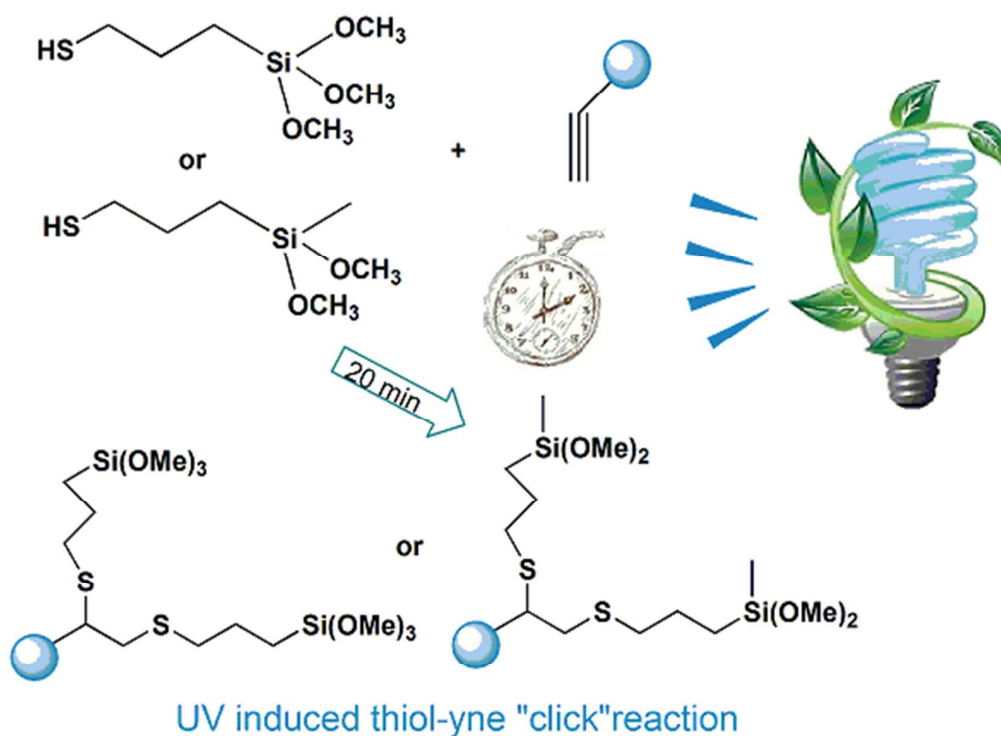
ARTICLE TYPE

Multifunctional Alkoxysilanes Prepared by Thiol-Yne "Click" Chemistry: Their Luminescent Properties and Modification on Silicon Surface

Yujing Zuo, Dengxu Wang, Jie Zhang, and Shengyu Feng*

The photoinitiated radical-based thiol-yne click reaction provides a simple and efficient method for the formulation of diverse alkoxysilanes. Seven alkoxysilanes, namely, 1,2-bis[3-(trimethoxysilyl)propylthio] hexane (**T1**), 1,2-bis[3-(trimethoxysilyl)propylthio]-3-chloropropane (**T2**), 1,2-bis[3-(trimethoxysilyl)
10 propylthio]-3-bromopropane (**T3**), trimethoxy[3-(styrylthio)propyl]silane (**T4**), 1,2-bis{3-[dimethoxy (methyl)silyl]propylthio}hexane (**D1**), 1,2-bis{3-[dimethoxy(methyl)silyl]propylthio}-3-chloropropane (**D2**), and1,2-bis{3-[dimethoxy(methyl)silyl]propylthio}-3-bromopropane (**D3**), were synthesized by reacting either alkynes with 3-mercaptopropylalkoxysilane in the presence of a photoinitiator. The thiol-yne reactions were neatly ran in standard glassware under 100 W UV irradiation. The functionalized
15 trialkoxysilanes were obtained in quantitative to near-quantitative yields with high purity. Results showed that the reaction of synthesized **T4** only remained in the first cycle, and vinyl sulfide adduct was formed with two configurations of Z and E. Moreover, the isomerization of **T4** was induced from Z to E configurations under UV irradiation. **T1** and **D1** showed excellent photoluminescence properties. Molecular calculations were also performed to confirm the experimental results. Computational results
20 revealed that all compounds exhibited relatively large HOMO-LUMO band gaps, making them promising candidates as host materials for emitters and hole/electron blocking materials in OLED display. In addition, **T1**, **T2**, and **T3** were selected to modify the surface properties of Si (1, 0, 0), which can then be used for further functionalization or the immobilization of polymers or biomolecules.

25 1. Introduction

Multifunctional alkoxysilanes, containing an alkoxysilane moiety as anchoring group to surfaces and a second functionality, are of great interest for numerous applications.[1, 2] These compounds also have important role in biotechnology, nanotechnology, and
30 molecular electronics.[3] The organic groups span from anionic to cationic groups and from nonpolar to polar groups as well as fluorescent dyes and electroactive moieties.[4] Given the numerous available and described silanes, the polarity and chemical reactivity of alkoxysilanes can be tailored over a wide
35 range. [5] However, the relative general hydrolytic fragility of alkoxysilanes, in particular, trialkoxysilanes, has considerably restricted the range of acceptable reaction types and experimental conditions that may be harnessed for their preparation. Therefore, access to alkoxysilanes depends on a relatively limited number of
40 approaches. Alkoxysilane with special functional groups are generally prepared via the hydrosilylation reactions in the presence of platinum or rhodium complexes. However, this reaction has suffered from several deficiencies; for example, the catalytic activity of the expensive heavy metal Pt catalyst is

45 always disturbed by the sensitive groups.[6] Furthermore, metallic catalysts should be avoided from the standpoint of green chemistry. Therefore, the establishment of a new general synthetic strategy to prepare functionalized alkoxysilane is necessary. Thiol chemistry has recently attracted significant
50 interest.[7] Thiol-ene reaction has been proposed as a new click reaction particularly for the reaction systems that can be triggered photochemically or thermally and without the oxygen inhibition associated with other radical-based systems. [8, 9]Thus, thiol-ene was used to synthesize small molecules and polymers such as
55 dendrimers and stars.[10, 11] Furthermore, the synthesis of functionalized trialkoxysilane under mild and neutral reaction conditions through the specific formation of robust sulfide bridges is also an attractive target because of the convenient features of the C–S bond. The divalent S atom largely dictates the
60 particular reactivity displayed by this class of compounds. [12, 13] Moreover, C–S bonds could also be activated by transition metal compounds.[14, 15]

Garrell et al. synthesized a range of trialkoxysilanes via facile thiol-ene click chemistry.[6] By contrast, the thiol-yne reaction
65 has not been extensively examined. Alkynes are relatively easy to

synthesize in a variety of structural formats and are typically stable until presented with an opportunity to react. [15, 16]Hence, alkynes have been considered as ideal substrates for a wide range of material applications *via* the Cu(I)-catalyzed Huisgen alkyne-azide reaction. [17, 18] Based on this premise, determining the mechanism by which yne chemistry can be readily extended to other types of highly efficient reactions is important. The thiol-yne reaction involves addition of a thiol to an alkyne followed by addition of another thiol to the resulting alkene, giving a fully saturated species.[19, 20] Thiol-yne reactions present a distinct opportunity to expand the chemistry of thiol-ene reactions providing access to a broad range of new materials and properties. [21] After considering these attributes, dual-functionalized alkoxysilane were fabricated by photo-induced thiol-yne reaction between mercaptopropylalkoxysilane and alkynyl molecules. The double-oxyalkylation of the alkynyl molecules can significantly affects their molecular structure and action activity more than mono-oxyalkylation. This paper reports on a new method for the synthesis of multifunctional alkoxysilanes by utilizing a thiol-yne reaction. Seven alkoxysilanes (**T1-T4**, and **D1-D3**) were synthesized by reacting either alkynes with 3-mercaptopropylalkoxysilane in the presence of photoinitiator without any solvent. Thiol-yne approach is versatile in reactions in terms of reaction conditions, and it tolerates chemical functionality to yield multifunctional alkoxysilanes. In addition, **T1** and **D1** showed blue light emission upon UV irradiation (365 nm). Contrary to traditional luminescent molecules containing typical luminescent groups, which may restrict their application, these novel luminophors only contain alkyl chains. They could be cured to films and used as blue-light-emitting materials and devices, which have attracted enormous interest because of their great potential for various lighting applications. Furthermore, engineering of the inorganic Si surface is the key in various applications such as in materials science and biotechnology. [22-24] Given that alkoxysilyl units bind to surface hydroxy groups, the second functionality, usually separated by an alkyl group from the anchoring group, determines the final properties of the surface. Organosilane chemistry can be applied to introduce carboxyl, amine, vinyl, or thiol groups onto the surface,[25, 26] which can then be used for further functionalization or the immobilization of polymers or biomolecules. Functionalized Si surface are traditionally readily prepared using 3-mercaptopropyltrimethoxysilane (**MPS**) and then usually submitted for further functionalization through thermal radical addition or other processes to conjugate other compounds.[27, 28] However, this post-functionalization method usually results in relatively low functionality.[29] In this article, obtained functionalized trialkoxysilanes (**T1**, **T2**, and **T3**) are used to modify the Si (1, 0, 0) surface to overcome this limitation and enhance functionality.

2. Experimental

2.1 Materials

1-hexyne, 3-chloro-1-propyn, 3-bromo-1-propyne, phenylacetylene and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were supplied by Aladdin Co. (China) and used without
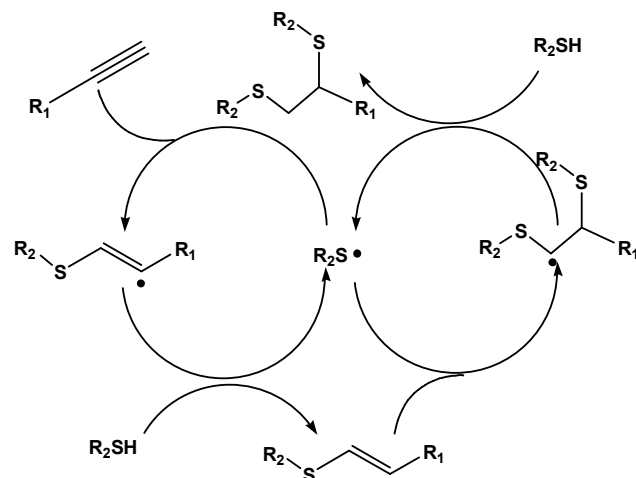
Scheme 1. Typical reaction mechanism of thiol-yne reactions.

further purification. 3-mercaptopropylmethyldimethoxysilane (MPDMS) and 3-mercaptopropyltrimethoxysilane (MPS) were purchased from Diamond Advanced Material of Chemical Inc. (China) and distilled before use.

2.2 Characterization and measurements

The thiol-yne reaction was irradiated by UV on a Spectroline Model SB–100P/FA lamp (365 nm, 100 w). UV intensity is $4500\mu W/cm^2$ at a distance of 38 cm. ^{1}H NMR spectra was recorded on a Bruker AVANCE 400 spectrometer at 25 °C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an interior label. Fourier transform infrared spectra (FT-IR) were recorded on a Bruker TENSOR27 infrared spectrophotometer with KBr pellet technique within the $4000\text{-}400cm^{-1}$ region. High-resolution mass spectra were obtained using positive mode on Agilent Technologies 6510 Q-TOF LC-MS. Luminescence (excitation and emission) spectra of the samples were determined with a Hitachi F-4500 fluorescence spectrophotometer using a monochromated Xe lamp as an excitation source; excitation and emission slits were 5 and 2.5 nm, respectively. XPS analyses were performed using a ThermoFisher Scientific Escalab 250 spectrometer with a monochromated Al Ka X-ray source at a residual pressure of 10^{-7} Pa. Survey and high resolution scans were performed at 100 eV pass energy with 1 eV step and 20 eV pass energy with 0.05 eV step, correspondingly. Contact angle was recorded on a Dataphysics OCA-20 contact angle analyzer with distilled water as the test liquid.

2.3 Synthesis of multifunctionalized alkoxysilanes

2.3.1 Synthesis of T1, T2, and T3

A cooled oven-dried 25 mL glass vessel was charged with 1-hexyne (0.82 g, 10 mmol), MPS (4.20 g, 22 mmol), and DMPA (1 wt%, 0.04 g), and then capped and purged briefly with Ar. The vessel was placed under a 100 W UV light (λ_{max} = 365 nm). The reaction mixture was irradiated for 20 min with gentle stirring to yield **T1** with high conversion (97%). After the thiol-yne reaction, the product was purified by precipitation in 1-hexane to eliminate unreacted mercaptans and photoinitiator.

Data of **T1**:
^{1}H NMR (300 MHz, CDCl$_3$):0.73-0.77(m, 4H, -*CH$_2$*Si(OCH$_3$)$_3$),

0.87-0.91(m, 3H, -CH_3), 1.69-1.73(t, 4H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 2.58–2.61 (m, 4H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 2.82 (dd, J=19.0, 5.8 Hz, 1H, S(CH$_2$)CH-C(H$_a$)H$_b$-S-), 2.75–2.60 (m, 2H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-), 3.50-3.60 (m, 18H, Si(OCH_3)$_3$), 1.53–1.11 (m, 4H, aliphatic CH_2), 1.75-1.85 (m, 2H, SCH(CH_2)CH$_2$S). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ = 8.43, (-CH_2Si(OCH$_3$)$_3$), 13.87, (-CH_3), 22.48, (CH$_3$CH_2CH$_2$CH$_2$CH(CH$_2$)S), 28.81, (CH$_3$CH$_2$CH_2CH$_2$CH(CH$_2$)S), 23.02, (SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 33.14, (CH$_3$CH$_2$CH$_2$CH_2CH(CH$_2$)S), 33.70, (CHSCH_2CH$_2$) 35.86, (CH$_2$SCH_2CH$_2$) 38.25, (-S-CH(CH_2-)-CH_2-S-), 45.63, (-S-CH(CH$_2$-)-CH$_2$-S-), 50.35, (Si(OCH_3)$_3$).HRMS (FAB) calcd for C$_{19}$H$_{44}$O$_6$S$_2$Si$_2$ (MNa$^+$): 497.2106, found 497.1989.

T2 was synthesized similar to that of **T1** and obtained as colorless liquid, yield: 96%.

Data of **T2**:

^{1}H NMR (400 MHz, CDCl$_3$):0.73-0.77(m, 4H, -CH_2Si(OCH$_3$)$_3$), 1.69-1.73(t, 4H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 2.58–2.61 (m, 4H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 2.83 (dd, J=19.0, 5.8 Hz, 1H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-)), 2.93–3.03 (m, 2H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-), 3.50-3.60 (m, 18H, Si(OCH_3)$_3$), 3.86 (dd, J=4.0 Hz, 1H, -SCH-(C(H$_a$)H$_b$Cl)-CH$_2$-S-), 3.89 (dd, J=4.1 Hz, 1H, -SCH-(C(H$_a$)H$_b$Cl)-CH$_2$-S-). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ =8.52, (-CH_2Si(OCH$_3$)$_3$), 22.87, (SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 34.46, (CHSCH_2CH$_2$), 35.95, (CH$_2$SCH_2CH$_2$), 38.38 (-S-CH(CH_2-)-CH_2-S-), 46.54, (-S-CH(CH$_2$-)-CH$_2$-S-), 47.42, (CHCH$_2$Cl), 50.36, (Si(OCH_3)$_3$). HRMS (FAB) calcd for C$_{15}$H$_{35}$ClO$_6$S$_2$Si$_2$ (MH$^+$): 466.1105, found 466.2548.

T3 was synthesized similar to that of **T1**. **T3** was obtained as light yellow liquid, yield: 94%.

Data of **T3**:

^{1}H NMR (400 MHz, CDCl$_3$):0.70-0.74 (m, 4H, -CH_2Si(OCH$_3$)$_3$), 1.66-1.70 (t, 4H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 2.57–2.60 (m, 4H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 2.83 (dd, J=19.0, 5.8 Hz, 1H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-)), 2.93–3.03 (m, 2H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-), 3.50-3.60 (m, 18H, Si(OCH_3)$_3$), 3.64 (dd, J=4.0 Hz, 1H, -SCH-(C(H$_a$)H$_b$Br)-CH$_2$-S-), 3.76 (dd, J=4.0 Hz, 1H, -SCH-(C(H$_a$)H$_b$Br)-CH$_2$-S-). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ =8.07, (-CH_2Si(OCH$_3$)$_3$), 22.26, (SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 34.46, (CHSCH_2CH$_2$), 35.95, (CH$_2$SCH_2CH$_2$), 38.38 (-S-CH(CH_2-)-CH_2-S-), 45.54, (-S-CH(CH$_2$-)-CH$_2$-S-), 49.14, (CHCH$_2$Br), 50.32, (Si(OCH_3)$_3$). HRMS (FAB) calcd for C$_{15}$H$_{35}$BrO$_6$S$_2$Si$_2$ (MH$^+$):512.0665, found 512.1742.

2.3.2 Synthesis of T4

A cooled oven-dried 25 mL glass vessel was charged with phenylacetylene(1.02 g, 10 mmol), MPS (2.10 g, 11 mmol), and DMPA (1 wt%, 0.02 g), and then capped and purged briefly with Ar. The reaction was neatly ran. The vessel was placed under a 100 W UV light (λ$_{max}$ = 365 nm). The reaction mixture was irradiated for 20 min with gentle stirring to yield **T4** with high conversion (97%).After the thiol-yne reaction, the resultant was purified by precipitation in 1-hexane to eliminate unreacted mercaptans and photoinitiator.

Data of **T4**:

^{1}H NMR (400 MHz, CDCl$_3$):0.73-0.76(m, 2H, -CH_2Si(OCH$_3$)$_3$), 1.80-1.84 (t, 2H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 2.78–2.85 (m, 2H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 3.47-3.57 (m, 9H, Si(OCH_3)$_3$), 6.22-6.46 (dd, J=14.8 Hz=C-H proton from the Z-vinylene unit),6.48-6.74 (m, J=15.6 Hz, =C-H proton from the E-vinylene units), 7.50-7.00 (m, 5H, Ar-H). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ =8.22 (-CH_2Si(OCH$_3$)$_3$), 22.42 (SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 38.59 (SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 50.32, (Si(OCH_3)$_3$), 125.21, 125.40, 126.54, 126.75, (C from the Z and E vinylene unit), 126.75, 126.85, 127.53, 128.19, 128.25, 128.31, (Ar-6C). HRMS (FAB) calcd for C$_{14}$H$_{33}$O$_3$SSi (MNa$^+$): 321.1030, found 321.0595.

2.3.3 Synthesis of D1, D2, and D3

A cooled oven-dried 25 mL glass vessel was charged with 1-hexyne (0.82 g, 10 mmol), MPDMS (3.78 g, 22 mmol), and DMPA (1 wt%, 0.04 g), and then capped and purged briefly with Ar. The reaction was neatly ran. The vessel was placed under a 100 W, λ$_{max}$ = 365 nm UV light. The reaction mixture was irradiated for 20 min with gentle stirring to yield **D1** with high conversion (95%). After the thiol-yne reaction, the product was purified by precipitation in 1-hexane to eliminate unreacted mercaptans and photoinitiator.

Data of **D1**:

^{1}H NMR (300 MHz, CDCl$_3$): 0.13-0.14(s, 3H, CH$_2$Si(CH_3)(OCH$_3$)$_2$), 0.65-0.73 (m, 4H, -CH_2Si(OCH$_3$)$_3$), 0.85-0.90(m, 3H, -CH$_3$), 1.53–1.11 (m, 4H, aliphatic CH_2), 1.69-1.73(t, 4H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 1.75-1.85 (m, 2H, SCH(CH_2)CH$_2$S), 2.58–2.61 (m, 4H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 2.82 (dd, J=19.0, 5.8 Hz, 1H, >CH-C(H$_a$)H$_b$-S-), 2.75–2.60 (m, 2H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-), 3.50-3.60 (m, 12H, Si(OCH_3)$_2$). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ =-5.80, (Si(CH_3), 8.43,(-CH_2Si(OCH$_3$)$_3$), 13.82, (-CH$_2$CH_3), 28.81, (CH$_3$CH$_2$CH_2CH$_2$CH(CH$_2$)S), 23.02, (SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 23.17, (CH$_3$CH_2CH$_2$CH$_2$CH(CH$_2$)S) 33.14, (CH$_3$CH$_2$CH$_2$CH_2CH(CH$_2$)S), 33.70, (CHSCH_2CH$_2$) 35.86, (CH$_2$SCH_2CH$_2$) 38.25, (-S-CH(CH$_2$-)-CH_2-S-), 45.63, (-S-CH(CH$_2$-)-CH$_2$-S-), 49.98, (Si(OCH_3)$_3$). HRMS (FAB) calcd for C$_{18}$H$_{42}$O$_4$S$_2$Si$_2$ (MH$^+$): 443.2206, found 443.2104.

D2 was synthesized similar to that of **D1**. **D2** was obtained as colorless liquid, yield: 94%.

Data of **D2**:

^{1}H NMR (400 MHz, CDCl$_3$):0.13-0.14 (s, 3H,CH$_2$Si(CH_3)(OCH$_3$)$_2$), 0.73-0.77 (m, 4H, -CH_2Si(OCH$_3$)$_3$), 1.69-1.73 (t, 4H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 2.58–2.61 (m, 4H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 2.83 (dd, J=19.0, 5.8 Hz, 1H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-)), 2.93–3.03 (m, 2H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-), 3.50-3.60 (m, 12H, Si(OCH_3)$_2$), 3.75 (dd, J=4.0 Hz, 1H, -SCH-(C(H$_a$)H$_b$Cl)-CH$_2$-S-), 3.86 (dd, J=4.1 Hz, 1H, -SCH-(C(H$_a$)H$_b$Cl)-CH$_2$-S-). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ = -5.80, (Si(CH_3), 8.60, (-CH_2Si(OCH$_3$)$_3$), 22.89, (SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 34.35, (CHSCH_2CH$_2$), 35.74, (CH$_2$SCH_2CH$_2$), 38.18, (-S-CH(CH$_2$-)-CH_2-S-), 46.58, (-S-CH(CH$_2$-)-CH$_2$-S-), 47.51, (CHCH_2Cl), 50.11, (Si(OCH_3)$_3$). HRMS (FAB) calcd for C$_{15}$H$_{35}$ClO$_4$S$_2$Si$_2$ (MH$^+$): 434.1217, found 434.5601.

D3 was synthesized similar to that of **D1**. **D3** was obtained as light yellow liquid, yield: 93%.

Data of **D3**:

^{1}H NMR (400 MHz, CDCl$_3$): 0.14-0.15 (s, 3H, CH$_2$Si(CH_3)(OCH$_3$)$_2$), 0.70-0.72 (m, 4H, -CH_2Si(OCH$_3$)$_3$), 1.67-1.71 (t, 4H, SCH$_2$CH_2CH$_2$Si(OCH$_3$)$_3$), 2.57–2.60 (m, 4H, SCH_2CH$_2$CH$_2$Si(OCH$_3$)$_3$), 2.83 (dd, J=19.0, 5.8 Hz, 1H, -S-CH(CH$_2$-)-C(H$_a$)H$_b$-S-)), 2.93–3.03 (m, 2H, -S-CH(CH$_2$-)-

C(H$_a$)H_b-S-), 3.50-3.60 (m, 18H, Si(OCH_3)$_3$), 3.66 (dd, J=4.0 Hz, 1H, -SCH-(C(H$_a$)H$_b$Br)-CH$_2$-S-), 3.77 (dd, J=4.0 Hz, 1H, -SCH-(C(H$_a$)H$_b$Br)-CH$_2$-S-). ^{13}C NMR (100.62 MHz, CDCl$_3$, ppm): δ = -5.89, (Si(CH_3), 8.07, (-CH$_2$Si(OCH$_3$)$_3$), 22.26, (SCH_2CH_2CH_2Si(OCH$_3$)$_3$), 34.46, (CHSCH$_2$CH_2), 35.95, (CH_2SCH$_2$CH_2), 38.38 (-S-CH(CH$_2$-)-CH$_2$-S-), 45.54, (-S-CH(CH$_2$-)-CH$_2$-S-), 49.14, (CHCH$_2$Br), 50.31, (Si(OCH$_3$)$_3$). HRMS (FAB) calcd for C$_{15}$H$_{35}$BrO$_4$S$_2$Si$_2$ (MH$^+$): 478.6454, found 478.2541.
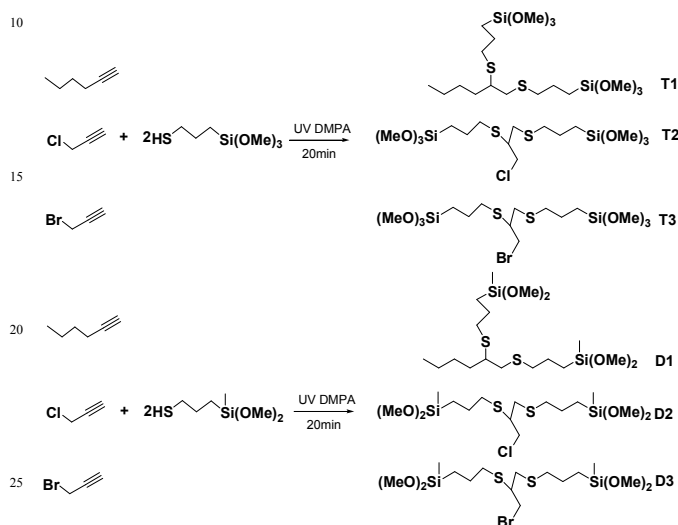
Scheme 2. Synthesis route of compounds T1, T2, T3, D1, D2, and D3.

2.4 Modification on Si (1, 0, 0) surface

Si wafers were cut into pieces, cleaned by sonication in chloroform, acetone, isopropanol, and deionized water, and then dried by Ar blowing. The clean Si (1, 0, 0) wafers were dipped in HF solution to remove the oxide layer and then treated with a freshly prepared Piranha solution (H$_2$O$_2$/H$_2$SO$_4$ = 1/3) for 30 min to obtain a hydroxy-terminated Si surface. The substrates were thoroughly washed with deionized water and again dried. A monolayer was formed by immersing the freshly prepared surfaces in a stirred solution of **T1**, **T2**, or **T3** in toluene (0.1 vol%) which was purged with Ar for 12 h. Unreacted silanes were removed from the surface by washing with ethanol and water. The modified Si wafers were reserved in distilled water and dried by Ar blowing before testing.

Results and Discussion

Synthesis of T1, T2, T3, D1, D2, and D3

For a widely used catalytic synthesis system, the catalytic efficiency, functional group tolerance, and structural tunability are of the primary concerns. Contrary to the low structural selectivity of the radical- and nucleophile-initiated alkyne hydrothiolations, the DMPA-catalyzed system is expected to work efficiently for a various functional monomers. In this study, the starting point was 3-mercaptopropylalkoxysilane, which was expected to produce a series of functionalized compounds via thiol-yne reaction, and the most important point is to develop a new synthetic method for diverse alkoxysilanes. 3-mercaptopropylalkoxysilane is versatile precursor to prepare other alkoxysilane derivatives. The thiol-yne reaction has been

proven to be a valid way to prepare new molecules and materials. For its' UV induced reaction process and free solvent reaction condition which are both friendly to the environment, this method meet the need of the concept of "green chemistry".
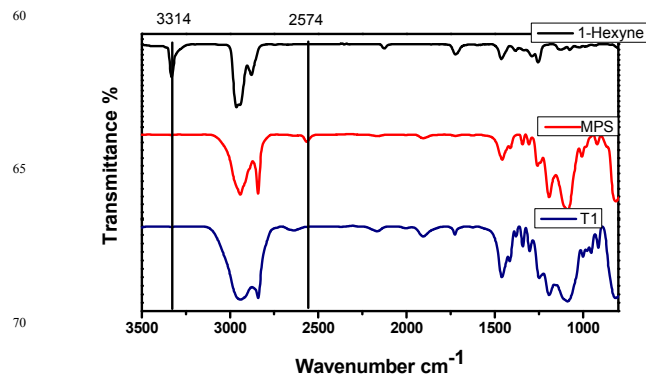
Figure 1. FTIR spectra of **1-Hexyne**, **MPS**, and **T1**.

A series of multifunctionalized alkoxysilane was synthesized via thiol-yne click reaction. Similar synthesis routes were applied to a number of alkyne monomers with different functional groups such as aliphatic chain and aliphatic chain with chlorine and bromine groups. Considering that two kinds of 3-mercaptopropylalkoxysilanes are used for these reactions, thiol-yne reaction should occur and products as depicted in Scheme 2 should be obtained. Typically, 3-mercaptopropylalkoxysilane and alkyne monomer are mixed together without any solvent. In this study, DMPA was chosen as the photoinitiator and irradiation was provided by 100 W UV-lamp (λ = 365 nm). Photoinitiation in thiol-yne systems was achieved through the generation of radical centers. In all cases, the reaction was completed within 20 min. The reaction was monitored by FTIR spectrophotometer, the results of which indicated by the disappearance of the characteristic absorption band of thiol group (2574 cm^{-1}) and the yne group (3314 and 2125 cm^{-1}) after reaction for 20 min (Figure 1).These compounds are generally obtained in high yield. To remove DMPA and impurity, the crude compounds need to be precipitated in n-hexane. Taking **T1** as an example, the ^{1}H-NMR spectrums of 1-hexyne, MPS and **T1** were shown in Figure 2. The appearance of a new *dd*-coupling peak at 2.82 ppm is attributed to hydrogen connected with chiral carbon that is adjacent to the S atom. The standard *dd* splitting is due to the effect of the chiral carbon. The signal that appeared at 2.82 ppm also suggests the completion of the thiol-yne reaction. The formation of compounds **T2**, **T3**, and **D1** to **D3** was also confirmed by ^{1}H-NMR and ^{13}C-NMR, and MS. The mechanism of a thiol-ene addition reaction also counts for thiol-yne additions, but an additional propagation cycle is operative. From the first cycle, a vinyl sulfide adduct is formed, which then undergoes a second thiol addition to yield the final product. Therefore, a full addition reaction consists of the consecutive addition of 2 eq thiol to an alkyne (Scheme 1). In most of the thiol-ene reactions, the internal double bond has relatively low reactivity. Given the unique two-step sequential radical addition mechanism of thiol-yne reaction, the defect of thiol-ene reaction was overcame. To further investigate the structural property of the compounds at the molecular level, molecular orbital calculations have been
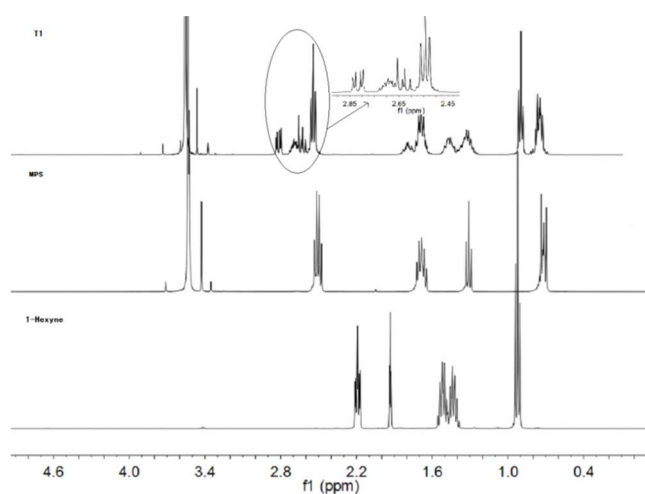
Figure 2. ^{1}H-NMR data of **T1, MPS, and 1-Hexyne**.

performed at the B3LYP/6-31G(d) level using the Gaussian 03
20 suite of programs. The HOMO and LUMO energies, as well as
the energy gap of these compounds, are shown in Table 1. All
compounds possess relatively large band gaps that range from
6.01 eV (**T1**) to 6.81 eV (**D2**), which can be attributed to the Si
atom which may endow large band gaps. This condition enables
25 the compounds as potential candidates as host materials for
emitters and hole/electron blocking layer in OLED displays.

Table 1. Physical data of compounds T1 to T4, D1 to D3, and T4 Z/E.

Compound	HOMO (eV)	LUMO (eV)	Band gap (eV)
T1	-5.65371	0.361095	6.01480
T2	-5.75494	0.321911	6.07685
T3	-5.71657	0.334972	6.05154
D1	-5.66324	1.108865	6.77210
D2	-5.76501	1.050632	6.81564
D3	-5.72963	0.593481	6.32311
T4 Z	-5.27357	-0.57879	4.69478
T4 E	-5.49589	-0.40246	5.09343

Synthesis of T4 and the isomerization phenomenon
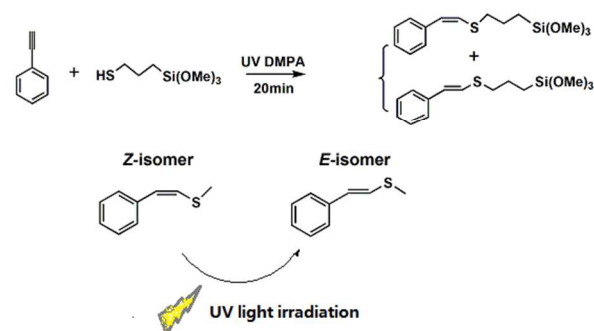
Scheme 3. Synthesis of **T4** and their isomerization under UV light.

Notably, the NMR spectrum of **T4** showed the presence of vinyl
proton signals at 6.3 and 5.6 ppm, which corresponded to the
50 unreacted vinylthioether intermediate. The thiol-yne reaction was
stopped in the first cycle of the completed addition process either
by increasing the reaction time or adding more thiol monomer
(Scheme 3). Moreover, the addition of thiol to 1-phenylalkyne
was found to be regio- and stereoselective, and this process leads
55 to the more stable aryl-substituted alkenyl radical intermediate.
UV light could induce the isomerization of **T4**. The isomerization
process was monitored by measuring the change in the ^{1}H NMR
spectrum with time using the crude products of **T4**. The E-Z
isomerization occurred upon UV irradiation (Figure 3). Z-isomer
60 was initially predominant. With an increase in the irradiation time,
the Z content of the molecule decreased. The isomerization
process proceeded quickly and achieved a state of equilibrium at
an E/Z ratio of 72/28 after irradiation for 50 min. The initially
formed Z-vinyl sulfide was probably isomerized into the E-
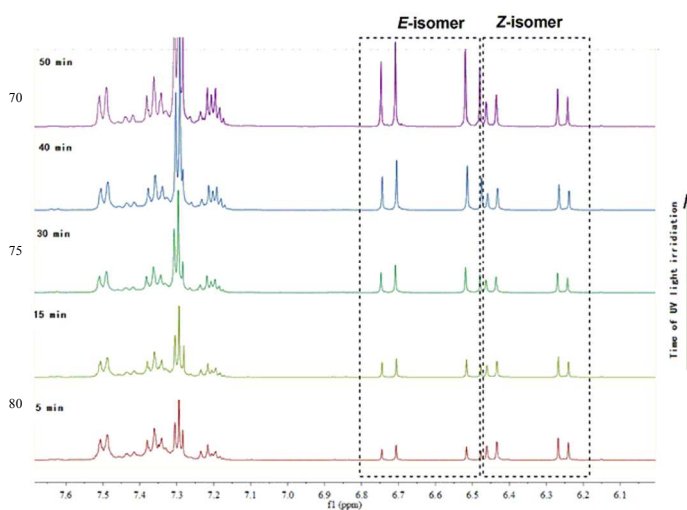65 product through reversible addition of the thiyl radical onto the
alkene.

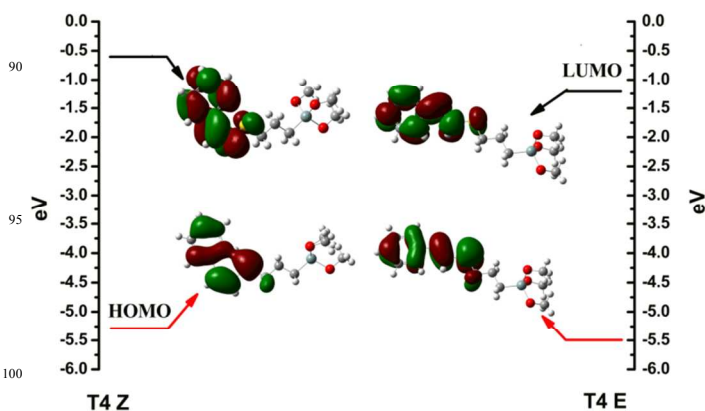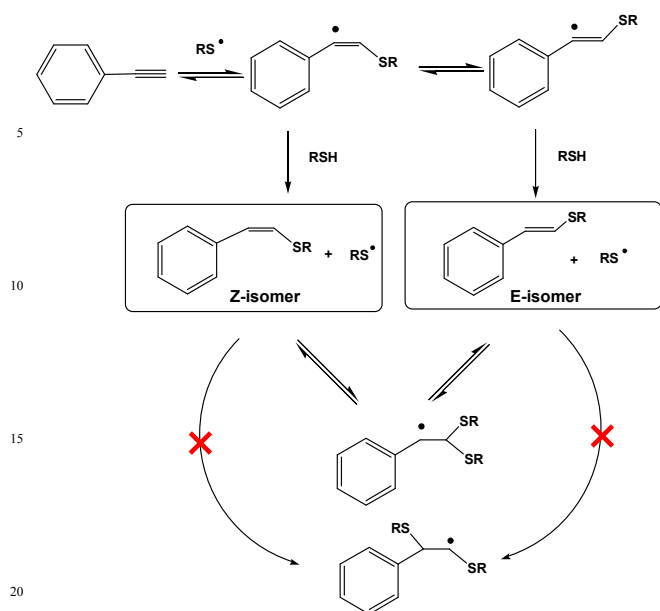85 **Figure 3**. Time course study on the isomerization of **T4** from 5 min to 50
min.

Figure 4. Calculated molecular orbital energy levels of **T4** Z and **T4** E
105 together with the molecular orbital maps of the HOMOs and LUMOs.

Scheme 4. Possible mechanism of UV-induced isomerization of T4.

To fully understand this phenomenon, density functional theory (DFT) was also used to calculate the molecular orbital at the B3LYP/6-31G(d) level using the Gaussian 03 suite of programs. Table 1 lists the corresponding HOMO and LUMO energies, as well as the energy gap, of T4 Z and T4 E. The calculated molecular orbital energy levels of T4 Z and T4 E together with the molecular orbital maps of the HOMOs and LUMOs are shown in Figure 4. The HOMO and LUMO energies of T4 E are lower than that of T4 Z. The results indicate that the product T4 E corresponds to thermodynamics, whereas the product T4 Z is a dynamic product. The speculated mechanism of the Z to E isomerization is shown in Scheme 4. At first, the addition of a thiyl radical to terminal alkynes occurs regioselectively at the less hindered position and gives a vinyl radical intermediate as a Z or E-mixture of isomers in equilibrium as expected. Then, hydrogen atom abstraction from the thiol by the resulting vinyl radical leads to the E- and Z- vinylsulfides. Eventually, the reversible addition of a thiyl radical to the vinyl sulfide may promote the isomerization of the kinetically favored Z-isomer into the thermodynamically more stable E-vinyl sulfide. Second step adducts will be unavailable because of the steric hindrance and the reversible isomerization. Steric hindrance probably prevents further addition of the thiyl radical thus the E-isomer being isolated as a dominate isomer. Subtle manipulation of the conformation may give rise to new molecule with different properties.

Luminescent properties of the compounds obtained

T1, D1, 3-mercaptopropylmethyldimethoxysilane (MPDMS) and 3-mercaptopropyltrimethoxysilane (MPS) emit a blue color in solution and without solvent when irradiated by UV light, whereas others do not. T1, T2, and T3 were chosen as examples

because T1 and D1, T2 and D2, and T3 and D3 have similar structures. Room temperature emission spectra of T1, T2, T3, and MPS excited by 365 nm are shown in Figure 5(a). MPS has an emission peak with a maximum emission wavelength (λ_{max}) of ~414 nm in pure substance state. Compound T1 also displays analogic fluorescence spectra with (λ_{max}) of ~414 nm. However, T1 showed an enhanced luminescent intensity and narrower half peak width compared with MPS after the reaction with 1-hexyne. By contrast, the fluorescence intensity of T2 or T3 was weak and could be neglected. The emission of T1 with different volume concentrations from 10% to 100% is shown in Figure 5(b). The luminescence intensity was enhanced with increasing volume concentration, which is consistent with most organic fluorescent molecules.[30-32] Besides, the emission of MPDMS and D1 was shown in Figure 5(c), which illustrated a similar luminescent intensity enhancement trend just like T1. We attributed this similar luminescent properties of T1 and D1 to the analogic structures.
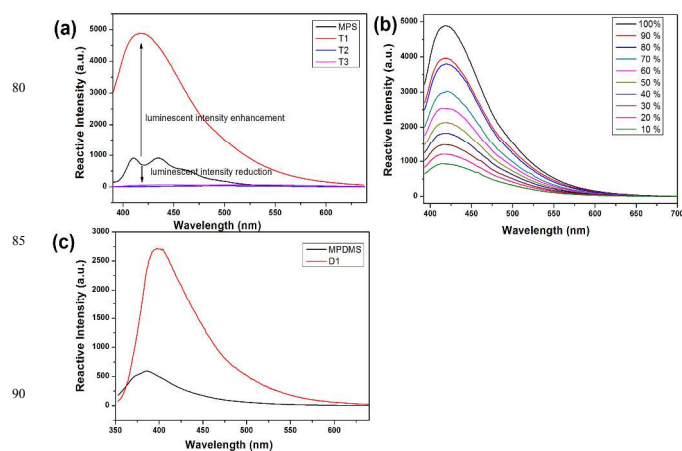

Figure 5. Emission spectra (λ_{ex} = 365 nm) of (a) MPS, T1, T2, and T3 , (b) T1 in CHCl$_3$ with different volume concentrations varying from 10% to 100% and (c) emission spectra of MPDMS and D1.

Compared with carbon, silicon has five empty 3d orbital that can be used as electron acceptor, facilitating the acceptance of electrons. Fluorescence was assumed to be generated by the lone pair electrons of S coordinated with Si atoms. The ligand field splitted the 3d orbital of Si atom, which was degenerated before coordination. The electrons rearranged in the split orbitals, and d-d transition occurred, which could be attributed to the luminescent properties of T1 and MPS.

Different substituent groups evidently affected the electronic orbital, which agrees with experimental results as mentioned previously. The pushing electron effect of alky caused the increasing electron density of S atom in T1, which may have strengthened the coordination effect between the S and Si atoms. Consequently, the fluorescence emission of T1 was considerably enhanced. Moreover, the electron density of S atom in T2 and T3 decreased because of the effect of the electron-withdrawal of the halogen atom. This phenomenon further hampered the coordination effect between S and Si atoms, which may account for the fluorescence emission that could be ignored by T2 or T3. XPS can effectively characterize the coordination condition via

detection of the binding energy between ligand and central atom.[33] The coordination conditions were more extensively
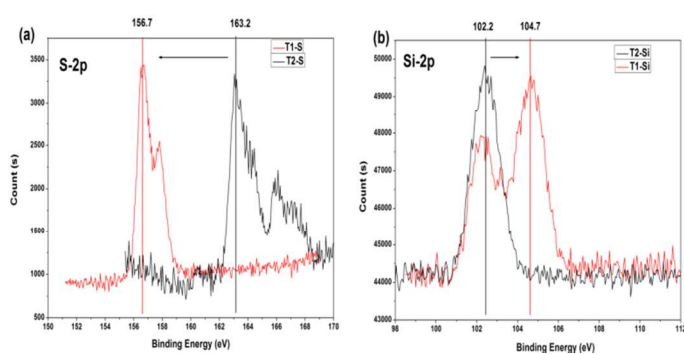

15 **Figure 6.** XPS of S 2p spectral regions in (a) **T1** and **T2**, and Si 2p spectral regions in (b)**T1** and **T2**.

examined by performing high-resolution XPS scans for S and Si atoms in **T1** and **T2**, respectively. The S 2p peak appeared at 20 163.2 eV in **T2**, but shifted to low binding energy at 156.7 eV (double–bond equivalent = 5.5 eV) in **T1** [Figure 6(a)]. Figure 6(b) displays the apparent shift of the peak of Si 2p. The Si 2p peak partly shifted from 102.2 eV to 104.7 eV in **T1**. The formation of coordination bonds is accompanied by electron 25 transfer between ligands and the central atoms. Thus, the shift of the binding energy peaks of S and Si atoms further confirmed the previous conjecture. Therefore, S atom coordinated with Si atom in **T1**, whereas **T2** and **T3** did not show any coordination between Si and S atoms. Such emission from structurally simple 30 organic molecules promises potential implementation in future applications. Of particular significance in this respect is the possibility to prepare blue-light-emitting polymeric films.[34]
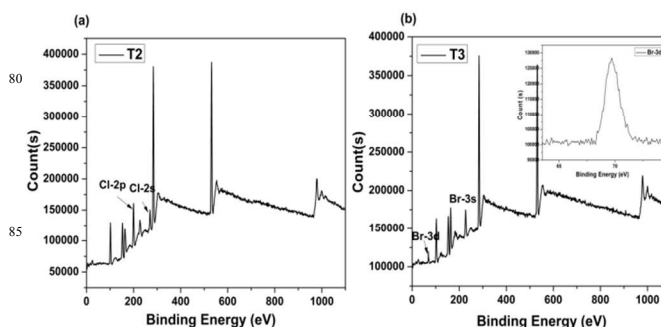
Surface modification on Si wafer

The monolayers prepared from organosilane compounds have 35 attracted increasing attention because of their technological applications such as in electronic devices and biomedical materials. A simple method was adopted to produce organosilane monolayers on Si (1, 0, 0). The general procedure for construction of monolayer structures on Si wafers is outlined in 40 Figure 7.
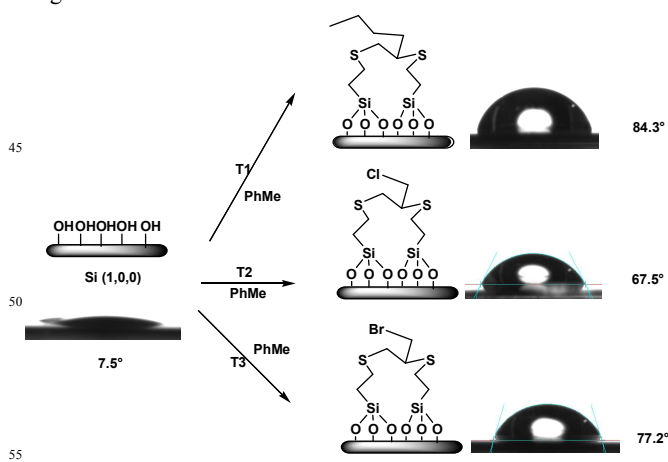
Figure 7. Modification on Si wafer [Si (1, 0, 0)] using **T1**, **T2**, and **T3** and the corresponding changesin contact angles.

60 Modified Si surfaces were prepared by a two-step method, that is, through acid wash and silanization. The effectiveness of cleaning step was confirmed by measuring the contact angle.[35] The contact angle of the cleaned slide was less than 8°. The exposure of Si-OH endows Si a hydrophilic surface, which was 65 consistent with the results from Cras et al. Three different alkoxysilanes **T1**, **T2**, and **T3** were grafted onto freshly prepared Si wafer. The contact angles measured by water confirmed the surface modification. **T2** exhibited the lowest contact angle (67.5°), which was attributed to the Cl group. Replacement of Cl 70 group by Br atom, that is, **T3**, increased the contact angle to 84.3°. **T3** showed the highest contact value (84.3°) because of its low affinity for water. The obvious change in the contact angles after reaction with different alkoxysilanes demonstrated that the proposed process achieved alkoxysilane coverage. The change of 75 contact angle is a result of the combination of the coverage content and the species of different alkoxysilanes.

90 **Figure 8.** XPS spectral of (a) **T2-** and (b) **T3-**modified Si wafer [Si (1, 0, 0)]

The existence of an organosilicon monolayer was supported by the elemental composition analysis via XPS. **T2-** and **T3-** 95 modified Si surfaces were selected to show the modification result. The peaks at 201 and 270 eV corresponded to 2p and 2s binding energies of Cl atom [Figure 8(a)]. A similar case happened to **T3-**modified Si, the peaks at 69 and 256 eV corresponded to 3d and 3s binding energies of Br atom, 100 respectively [Figure 8(b)]. The inserted figure displays the enlarged scale of 3*d* spectral region of Br atom in **T3-**modified Si wafer. The presence of the monolayers was further confirmed by XPS. Besides, the XPS element composition data of **T1**, **T2** and **T3-**modified Si wafer were listed in Table 2. The data related 105 were determined by integration of the peak areas. The C/Si ratio of the three modified Si wafer was almost same as the similarity of the three compounds used for modification process.

Table 2. XPS Composition Data of T1, T2, and T3
110 **Modified Silicon Wafer**

Compound%	Si%	C%	O%	S%	Si/C
T1	14.7	34.2	36.1	15.0	0.42
T2	12.2	32.0	39.7	13.1	0.38
T3	13.7	29.7	40.5	14.7	0.46

Conclusions

A flexible, atom-economical, and easily scalable approach for the synthesis of multi-functionalized alkoxysilanes is reported. Customization of generally inaccessible alkoxysilanes can now be readily tailor-made. Even more complex and sensitive function groups can also be incorporated into the products using a similar method. The isomerization property of **T4** is also expected to provide a gating tool in manipulating the functional properties of the functionalized trialkoxysilanes. In addition, the functionalized trialkoxysilanes may be applied in the production of Si (1, 0, 0) surfaces with organic coatings with different end groups under mild conditions. These Si surfaces can then be used for further functionalization or the immobilization of polymers or biomolecules.

Acknowledgments

Notes and references

Key Laboratory of Special Functional Aggregated Materials & Key Laboratory of Colloid and Interface Chemistry (Shandong University), Ministry of Education;School of Chemistry and Chemical Engineering, Shandong University,Jinan 250100,Shandong Province, P. R. China. Fax: 86-531-88564464; Tel: 86-531-88364866; E-mail:fsy@sdu.edu.cn

1. A. B. Descalzo, R. Martínez‑Máñez, F. Sancenon, K. Hoffmann and K. Rurack, *Angewandte Chemie International Edition*, 2006, **45**, 5924-5948.
2. W. Senaratne, L. Andruzzi and C. K. Ober, *Biomacromolecules*, 2005, **6**, 2427-2448.
3. S. Onclin, B. J. Ravoo and D. N. Reinhoudt, *Angewandte Chemie International Edition*, 2005, **44**, 6282-6304.
4. A. Lex, P. Pacher, O. Werzer, A. Track, Q. Shen, R. Schennach, G. Koller, G. Hlawacek, E. Zojer and R. Resel, *Chemistry of Materials*, 2008, **20**, 2009-2015.
5. B. Quiclet-Sire, Y. Yanagisawa and S. Z. Zard, *Chemical Communications*, 2014, **50**, 2324-2326.
6. A. K. Tucker-Schwartz, R. A. Farrell and R. L. Garrell, *Journal of the American Chemical Society*, 2011, **133**, 11026-11029.
7. C. E. Hoyle and C. N. Bowman, *Angewandte Chemie International Edition*, 2010, **49**, 1540-1573.
8. A. B. Lowe, *Polymer Chemistry*, 2010, **1**, 17-36.
9. Y. Zuo, H. Lu, L. Xue, X. Wang, L. Ning and S. Feng, *Journal of Materials Chemistry C*, 2014, **2**, 2724-2734.
10. C. Rissing and D. Y. Son, *Organometallics*, 2009, **28**, 3167-3172.
11. C. Rissing and D. Y. Son, *Organometallics*, 2008, **27**, 5394-5397.
12. S. G. Modha, V. P. Mehta and E. V. Van der Eycken, *Chemical Society Reviews*, 2013, **42**, 5042-5055.
13. M. Winkler, Y. S. Raupp, L. A. Köhl, H. E. Wagner and M. A. Meier, *Macromolecules*, 2014.
14. L. Wang, W. He and Z. Yu, *Chemical Society Reviews*, 2013, **42**, 599-621.
15. R. Tan and D. Song, *Organometallics*, 2011, **30**, 1637-1645.
16. Z. P. Demko and K. B. Sharpless, *Angewandte Chemie International Edition*, 2002, **41**, 2113-2116.
17. J. E. Hein and V. V. Fokin, *Chemical Society Reviews*, 2010, **39**, 1302-1315.
18. F. Gonzaga, G. Yu and M. A. Brook, *Macromolecules*, 2009, **42**, 9220-9224.
19. A. B. Lowe, C. E. Hoyle and C. N. Bowman, *Journal of Materials Chemistry*, 2010, **20**, 4745-4750.
20. M. Lo Conte, S. Pacifico, A. Chambery, A. Marra and A. Dondoni, *The Journal of organic chemistry*, 2010, **75**, 4644-4647.
21. R. Pötzsch, B. C. Stahl, H. Komber, C. J. Hawker and B. I. Voit, *Polymer Chemistry*, 2014, **5**, 2911-2921.
22. M. M. Stevens and J. H. George, *Science*, 2005, **310**, 1135-1138.
23. T. Horlacher and P. H. Seeberger, *Chemical Society Reviews*, 2008, **37**, 1414-1422.
24. N. S. Bhairamadgi, S. Gangarapu, M. A. Caipa Campos, J. M. J. Paulusse, C. J. M. van Rijn and H. Zuilhof, *Langmuir*, 2013, **29**, 4535-4542.
25. J. Zhao, M. Chen, Y. An, J. Liu and F. Yan, *Applied Surface Science*, 2008, **255**, 2295-2302.
26. A. Bertin and H. Schlaad, *Chemistry of Materials*, 2009, **21**, 5698-5700.
27. J.-J. Chen, K. N. Struk and A. B. Brennan, *Langmuir*, 2011, **27**, 13754-13761.
28. S. Park, M.-r. Lee, S.-J. Pyo and I. Shin, *Journal of the American Chemical Society*, 2004, **126**, 4812-4819.
29. J. Cras, C. Rowe-Taitt, D. Nivens and F. Ligler, *Biosensors and Bioelectronics*, 1999, **14**, 683-688.
30. M. Fujiki, J. R. Koe, K. Terao, T. Sato, A. Teramoto and J. Watanabe, *POLYM J*, 2003, **35**, 297-344.
31. Y. Chen, H. Cui, L. Li, Z. Tian and Z. Tang, *POLYM CHEM-UK*, 2014, **5**, 4441-4445.
32. Z. Zhaozhu, Z. Yunlong, L. Xinyu, L. Shaoqin and T. Zhiyong, *Biosens Bioelectron*, 2011, **26**, 3081-3085.
33. Y. Yue, Y. Liang, H. Wang, L. Feng, S. Feng and H. Lu, *Photochem Photobiol*, 2013, **89**, 5-13.
34. D. Ratchford, K. Dziatkowski, T. Hartsfield, X. Li, Y. Gao and Z. Tang, *J Appl Phys*, 2011, **109**, 103509.
35. Flinn, D. H.; Guzonas, D. A.; Yoon, R. H. Colloids Surf., A 1994, **87,** 163–176.