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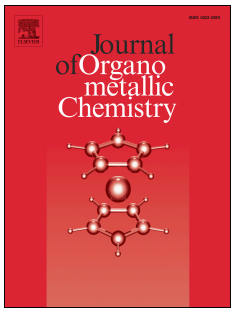

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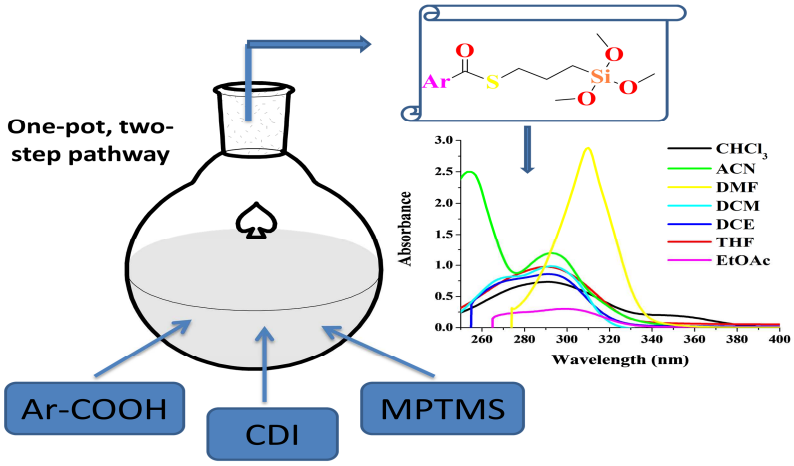
Graphical abstract



Organo-functionalized trimethoxysilanes featuring thioester linkage: Synthetic and UV-Vis spectral investigations

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Abstract

The current work reveals a series of new organo-functionalized trimethoxysilanes (OfTMS) linked *via* a 3 C tether to the thioester group along with the inclusion of versatile aromatic and heteroaromatic sequences. The synthetic procedure implicates the one-pot thioesterification reaction of the precursor carboxylic acids (**1a-r**) with 3-mercaptopropyltrimethoxysilane (MPTMS), stimulated by 1,1'-carbonyldiimidazole (CDI). The OfTMS have been attentively characterized by elemental analysis, infrared and [^{1}H, ^{13}C] NMR spectroscopic techniques. The UV-Vis absorption behaviour demonstrates that the alkoxysilanes possess high sensitivity to the changes caused in the environment on account of different substitutions. Furthermore, the solvent effect on the absorption spectra has been scrutinized and quantified using the Kamlet-Taft approach. Importantly, the fabricated stable alkoxysilanes can be aspired for advance applications in the field of material science.

Key words: Organosilanes, Thioester, Solvatochromism, Kamlet-Taft equation

1. Introduction

Organically modified silanes, Y-$(CH_2)_3$-SiX_3 consist of the hydrolysable silyl bonds with alkoxy, amine, acyloxy, glycidyloxy or halogen units (X) and a substituent Y which provides structural malleability for the explicit functioning.[1,2] The organosilanes represent a fiercely developing branch of synthetic chemistry having the utmost importance in organic synthesis, metal complexes, catalysis, drug designing, polymers, analyte sensing and HPLC packing.[3] The assimilation of fascinating organic fragments with the trialkoxysilyl moiety is grabbing even more attention. This is because of their potential to react with both inorganic and organic substrates, adhesives, as well as other alkoxysilane derivatives to form multifarious organic-inorganic hybrids, dominant in nanomaterial and polymer science.[4] So far in the field of siliceous materials, alkoxysilanes have been the most common platform for the

functionalization of metal oxide surface by siloxane bonding, along with an ease of handling and smooth reaction governance abilities.[5]

The exploitation of smaller organic transformations that employ simple synthetic steps to provide maximum structural diversity within a single molecular framework is a deep-rooted area in the organosilicon chemistry.[6] However, more discreet measurements are required during the synthesis of organosilanes so that the organic moiety cannot interfere with the susceptible silyl part.[7] Conventional approaches to synthesize alkoxysilanes involve cross-coupling, hydrosilylation, transmetalation and replacement reactions.[8] The expensive metals involved, limited functional group tolerance, lower product yields, tedious isolation and purification techniques were the major shortcomings of these methodologies.

On the other hand, carboxylic acids are ubiquitous in the form of natural products, transition metal complexes, pharmaceutics and polymers etc.[9] The carboxyl group and its derivatized forms, for instance amide, ester, anhydride, carbamate etc. have been incorporated as an organic linker to the trialkoxysilyl moiety.[7,10] To-date, the blending of thioester unit with the silyl fragment is rarely reported and that too has been achieved by the complicated synthetic pathways.[11] The thioesters are biologically important motifs having vital roles in living cells, explicitly as intermediate for acyl group transfer reaction in metabolic processes and in the biosynthesis of polyketides and nonribosomal polypeptides.[12] Not only pharmacologically, these mono S-analogues of oxyesters are actively involved in organic synthesis such as asymmetric addition, aldol and Michael reactions etc.[13] Keeping the above perspectives in mind and extending our research interest on the alkoxysilanes[14], we have now designed an efficacious synthetic route in which atmospheric reaction conditions are employed. The rationale behind the synthesis of an array of compounds is to have a better visualization of the effect of incorporating different aromatic rings (**3a**-**i**) as well

as the electronic nature of the substituent attached at the phenyl ring (**3j-r**) on the UV-Vis absorption profiles and solvatochromic properties.

The paper is organized as follows: Firstly, the synthetic procedure and characterization of new OfTMS bearing thioester linkage are described. Secondly, we have discussed the UV-Vis spectra of the silanes and then continued with the investigation on the solvatochromic behaviour of these compounds where substitution effect is clearly observed. Finally in the end, an appropriate conclusion is presented to summarize the paper.

2. Experimental

2.1. Materials and equipments

All carboxylic acids (Aldrich), MPTMS (Avra) and CDI (Avra) were used directly as received. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL (AL 300 MHz) spectrometer using $CDCl_3$ as an internal reference and chemical shifts were reported relative to tetramethylsilane. Electronic spectral measurements were carried out using a JASCO V-530 UV-Vis spectrophotometer. The infrared spectra were recorded as neat spectra on a Thermo Scientific NICOLET IS50 spectrophotometer. Elemental analysis was obtained on Perkin Elmer Model 2400 CHNS elemental analyzer and Thermo Scientific Flash 2000 organic elemental analyzer.

2.2. General procedure for the synthesis of OfTMS (3a-r)

1 equiv. of the respective carboxylic acid (**1a-r**) and 1.20 equiv. of CDI were mixed in THF (20 ml) at room temperature in a round bottomed flask. The reaction mixture was heated to reflux for 1 h while evolution of the by-product carbon dioxide gas started within 10-15 min. After cooling to room temperature, the addition of MPTMS (1 equiv.) was carried out and heating was continued for 8 h. The reaction mixture was diluted with water and the aqueous layer was extracted with dichloromethane (15 ml). The combined organic layer was washed

with brine (25%) and dried over anhydrous Na_2SO_4. The mixture was concentrated in *vacuo* to furnish highly viscous oil as the desired product.

2.2.1. *S-3-(trimethoxysilyl)propyl benzothioate* (**3a**)

The quantities used were as follows: **1a** (0.50 g, 4.09 mmol), CDI (0.80 g, 4.91 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{13}H_{20}O_4SSi$: C, 51.97; H, 6.71; S, 10.67. Found: C, 51.91; H, 6.67; S, 10.59. IR (neat, cm^{-1}): 1648 (ν C═O), 1075 (ν Si–O), 684 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.67 (m, 2H, $SiCH_2$), 1.69 (m, 2H, CCH_2C), 2.99 (t, 2H, CH_2S, J = 7.3 Hz), 3.47 (s, 3H, OCH_3), 7.33 (t, 2H, $H^{3,5}$, J = 8.1 Hz), 7.43 (d, 1H, H^4, J = 8.3 Hz), 7.86 (d, 2H, $H^{2,6}$, J = 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.64 ($SiCH_2$), 20.33 (C**C**H_2C), 31.44 (CH_2S), 50.09 (OCH_3), 127.03 ($C^{2,6}$), 128.27 ($C^{3,5}$), 132.87 (C^4), 137.19 (C^1), 191.02 (C═O).

2.2.2. *S-3-(trimethoxysilyl)propyl pyridine-2-carbothioate* (**3b**)

The quantities used were as follows: **1b** (0.50 g, 4.06 mmol), CDI (0.79 g, 4.88 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{12}H_{19}NO_4SSi$: C, 47.81; H, 6.35; N, 4.65; S, 10.64. Found: C, 47.78; H, 6.33; N, 4.60; S, 10.59. IR (neat, cm^{-1}): 1653 (ν C═O), 1088 (ν Si–O), 688 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.56 (m, 2H, $SiCH_2$), 1.62 (m, 2H, CCH_2C), 3.06 (t, 2H, CH_2S, J = 7.3 Hz), 3.49 (s, 9H, OCH_3), 7.22 (m, 1H, H^4), 8.04-8.11 (m, 1H, H^3), 8.52 (d, 1H, H^2, J = 4.7 Hz), 8.92 (s, 1H, H^5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.37 ($SiCH_2$), 18.48 (CCH_2C), 37.98 (CH_2S), 57.66 (OCH_3), 123.29 (C^2), 131.43 (C^4), 135.42 (C^3), 147.88 (C^5), 151.49 (C^1), 190.69 (C═O).

2.2.3. *S-3-(trimethoxysilyl)propyl pyridine-3-carbothioate* (**3c**)

The quantities used were as follows: **1c** (0.50 g, 4.06 mmol), CDI (0.79 g, 4.88 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{12}H_{19}NO_4SSi$: C, 47.81; H, 6.35; N, 4.65;

S, 10.64. Found: C, 47.72; H, 6.28; N, 4.60; S, 10.59. IR (neat, cm^{-1}): 1655 (*v* C═O), 1084 (*v* Si–O), 680 (*v* C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.58 (m, 2H, $SiCH_2$), 1.64 (m, 2H, CCH_2C), 2.97 (t, 2H, CH_2S, J = 7.3 Hz), 3.56 (s, 9H, OCH_3), 7.24 (t, 1H, H^4, J = 5.5 Hz), 8.09 (t, 1H, H^3, J = 5.7 Hz), 8.54 (d, 1H, H^5, J = 4.7 Hz), 8.94 (s, 1H, H^1). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.84 ($SiCH_2$), 17.63 (C**C**H_2C), 31.26 (CH_2S), 50.25 (OCH_3), 120.24 (C^4), 127.32 (C^2), 136.82 (C^3), 149.04 (C^5), 152.32 (C^1), 193.07 (C═O).

2.2.4. *S-3-(trimethoxysilyl)propyl pyridine-4-carbothioate* (**3d**)

The quantities used were as follows: **1d** (0.50 g, 4.06 mmol), CDI (0.79 g, 4.88 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{12}H_{19}NO_4SSi$: C, 47.81; H, 6.35; N, 4.65; S, 10.64. Found: C, 47.78; H, 6.39; N, 4.60; S, 10.59. IR (neat, cm^{-1}): 1657 (*v* C═O), 1090 (*v* Si–O), 683 (*v* C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.59 (m, 2H, $SiCH_2$), 1.65 (m, 2H, CCH_2C), 2.86 (t, 2H, CH_2S, J = 7.3 Hz), 3.51 (s, 9H, OCH_3), 7.61 (d, 2H, $H^{2,5}$, J = 5.8 Hz), 8.56 (d, 2H, $H^{3,4}$, J = 5.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.35 ($SiCH_2$), 15.30 (C**C**H_2C), 37.20 (CH_2S), 60.94 (OCH_3), 150.44 (C^1), 165.64 ($C^{3,4}$), 191.59 (C═O).

2.2.5. *S-3-(trimethoxysilyl)propyl pyrazine-2-carbothioate* (**3e**)

The quantities used were as follows: **1e** (0.50 g, 4.03 mmol), CDI (0.78 g, 4.83 mmol), MPTMS (0.79 ml, 4.03 mmol). Anal. Calcd. for $C_{11}H_{18}N_2O_4SSi$: C, 43.69; H, 6.00; N, 9.26; S, 10.60. Found: C, 43.62; H, 5.96; N, 9.29; S, 10.53. IR (neat, cm^{-1}): 1659 (*v* C═O), 1087 (*v* Si–O), 680 (*v* C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.69 (m, 2H, $SiCH_2$), 1.74 (m, 2H, CCH_2C), 2.99 (t, 2H, CH_2S, J = 7.2 Hz), 3.48 (s, 9H, OCH_3), 8.56 (m, 1H, H^4), 8.71 (m, 1H, H^3), 9.06 (m, 1H, H^2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.63 ($SiCH_2$), 20.92 (CCH_2C), 32.31 (CH_2S), 51.26 (OCH_3), 141.94 ($C^{2,3}$), 143.65 (C^4), 148.32 (C^1), 192.62 (C═O).

2.2.6. *S,S-bis(3-(trimethoxysilyl)propyl) pyridine-2,3-bis(carbothioate)* (**3f**)

The quantities used were as follows: **1f** (0.50 g, 2.99 mmol), CDI (1.16 g, 7.18 mmol), MPTMS (1.17 ml, 5.97 mmol). Anal. Calcd. for $C_{19}H_{33}NO_8S_2Si_2$: C, 43.57; H, 6.35; N, 2.67; S, 12.24. Found: C, 43.51; H, 6.19; N, 2.62; S, 12.20. IR (neat, cm^{-1}): 1665 (ν C═O), 1075 (ν Si–O), 689 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.63 (m, 4H, $SiCH_2$), 1.62 (m, 4H, CCH_2C), 2.85 (t, 2H, CH_2S, J = 7.3 Hz), 3.05 (t, 2H, CH_2S, J = 7.3 Hz), 3.43 (s, 9H, OCH_3), 3.47 (s, 9H, OCH_3), 7.57 (t, 1H, H^4, J = 8.1 Hz), 7.77 (d, 1H, H^5, J = 9.1 Hz), 8.79 (d, 1H, H^3, J = 9.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.90 ($SiCH_2$), 15.98 (CCH_2C), 33.35 (CH_2S), 50.51 (OCH_3), 122.28 (C^2), 126.96 (C^4), 151.55 (C^3), 155.16 ($C^{1,5}$), 190.74 (C═O), 191.91 (C═O).

2.2.7. *S,S-bis(3-(trimethoxysilyl)propyl) pyridine-2,6-bis(carbothioate)* (**3g**)

The quantities used were as follows: **1g** (0.50 g, 2.99 mmol), CDI (1.16 g, 7.18 mmol), MPTMS (1.17 ml, 5.97 mmol). Anal. Calcd. for $C_{19}H_{33}NO_8S_2Si_2$: C, 43.57; H, 6.35; N, 2.67; S, 12.24. Found: C, 43.49; H, 6.30; N, 2.63; S, 12.18. IR (neat, cm^{-1}): 1650 (ν C═O), 1070 (ν Si–O), 678 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.59 (m, 4H, $SiCH_2$), 1.77 (m, 4H, CCH_2C), 3.03 (t, 4H, CH_2S, J = 7.4 Hz), 3.46 (s, 18H, OCH_3), 7.96 (t, 1H, H^3, J = 9.1 Hz), 8.26 (d, 2H, $H^{2,4}$, J = 7.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.27 ($SiCH_2$), 16.85 (CCH_2C), 38.10 (CH_2S), 50.77 (OCH_3), 125.21 (C^3), 139.21 ($C^{2,4}$), 149.57 ($C^{1,5}$), 192.32 (C═O).

2.2.8. *S-3-(trimethoxysilyl)propyl furan-2-carbothioate* (**3h**)

The quantities used were as follows: **1h** (0.50 g, 4.46 mmol), CDI (0.87 g, 5.37 mmol), MPTMS (0.87 ml, 4.44 mmol). Anal. Calcd. for $C_{11}H_{18}O_5SSi$: C, 45.49; H, 6.25; S, 11.04. Found: C, 45.42; H, 6.16; S, 11.00. IR (neat, cm^{-1}): 1667 (ν C═O), 1085 (ν Si–O), 689 (ν

C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.59 (m, 2H, $SiCH_2$), 1.61 (m, 2H, CCH_2C), 2.90 (t, 2H, CH_2S, J = 7.2 Hz), 3.38 (s, 9H, OCH_3), 7.38 (t, 1H, H^3, J = 4.5 Hz), 7.47 (d, 1H, H^2, J = 4.6 Hz), 7.71 (d, 1H, H^4, J = 4.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.16 ($SiCH_2$), 15.92 (CCH_2C), 37.43 (CH_2S), 59.78 (OCH_3), 113.48 (C^3), 129.22 (C^2), 146.18 (C^4), 152.12 (C^1), 176.72 (C═O).

2.2.9. *S-3-(trimethoxysilyl)propyl thiophene-2-carbothioate* (**3i**)

The quantities used were as follows: **1i** (0.50 g, 3.91 mmol), CDI (0.76 g, 4.69 mmol), MPTMS (0.76 ml, 3.90 mmol). Anal. Calcd. for $C_{11}H_{18}O_4S_2Si$: C, 43.11; H, 5.92; S, 20.93. Found: C, 43.02; H, 5.84; S, 20.88. IR (neat, cm^{-1}): 1675 (ν C═O), 1078 (ν Si–O), 670 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.68 (m, 2H, $SiCH_2$), 1.73 (m, 2H, CCH_2C), 3.00 (t, 2H, CH_2S, J = 7.3 Hz), 3.49 (s, 9H, OCH_3), 7.02 (t, 1H, H^3, J = 4.5 Hz), 7.51 (d, 1H, H^2, J = 5.0 Hz), 7.69 (d, 1H, H^4, J = 3.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 9.08 ($SiCH_2$), 16.75 (CCH_2C), 36.28 (CH_2S), 56.79 (OCH_3), 127.69 (C^3), 128.52 (C^2), 130.03 (C^4), 140.33 (C^1), 181.34 (C═O).

2.2.10. *S-(3-(trimethoxysilyl)propyl) 2-(phenylthio)ethanethioate* (**3j**)

The quantities used were as follows: **1j** (0.50 g, 2.98 mmol), CDI (0.58 g, 3.57 mmol), MPTMS (0.58 ml, 2.98 mmol). Anal. Calcd. for $C_{14}H_{22}O_4S_2Si$: C, 48.52; H, 6.40; S, 18.51. Found: C, 48.24; H, 6.19; N, S, 18.31. IR (neat, cm^{-1}): 1645 (ν C═O), 1099 (ν Si–O), 689 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.60 (m, 2H, $SiCH_2$), 1.57 (m, 2H, CCH_2C), 2.80 (t, 2H, CH_2S, J = 7.3 Hz), 3.45 (s, 9H, OCH_3), 3.70 (s, 2H, SCH_2), 7.11-7.29 (m, 5H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.44 ($SiCH_2$), 15.88 (CCH_2C), 35.93 (CH_2S), 51.63 (SCH_2), 58.26 (OCH_3), 123.89 (C^4), 125.84 ($C^{2,6}$), 128.93 ($C^{3,5}$), 136.02 (C^1), 190.12 (C═O).

2.2.11. *S-3-(trimethoxysilyl)propyl 2-methylbenzothioate* (**3k**)

The quantities used were as follows: **1k** (0.50 g, 3.67 mmol), CDI (0.71 g, 4.40 mmol), MPTMS (0.72 ml, 3.67 mmol). Anal. Calcd. for $C_{14}H_{22}O_4SSi$: C, 53.47; H, 7.05; S, 10.20. Found: C, 53.39; H, 5.87; S, 10.70. IR (neat, cm^{-1}): 1655 (*v* C═O), 1078 (*v* Si–O), 684 (*v* C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.47 (m, 2H, $SiCH_2$), 1.68 (m, 2H, CCH_2C), 2.39 (s, 3H, CH_3), 3.02 (t, 2H, CH_2S, *J* = 7.3 Hz), 3.45 (s, 3H, OCH_3), 7.25-8.67 (m, 4H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.53 ($SiCH_2$), 15.52 ($C\mathbf{C}H_2C$), 17.04 (CH_3), 36.88 (CH_2S), 58.19 (OCH_3), 126.87 (C^5), 127.61 (C^6), 129.82 (C^3), 133.36 ($C^{2,4}$), 135.46 (C^1), 191.19 (C═O).

2.2.12. *S-3-(trimethoxysilyl)propyl 4-methoxybenzothioate* (**3l**)

The quantities used were as follows: **1l** (0.50 g, 3.28 mmol), CDI (0.64 g, 3.95 mmol), MPTMS (0.64 ml, 3.28 mmol). Anal. Calcd. for $C_{14}H_{22}O_5SSi$: C, 50.88; H, 6.71; S, 9.70. Found: C, 50.77; H, 6.65; S, 9.63. IR (neat, cm^{-1}): 1665 (*v* C═O), 1078 (*v* Si–O), 676 (*v* C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.70 (m, 2H, $SiCH_2$), 1.70 (m, 2H, CCH_2C), 2.98 (t, 2H, CH_2S, *J* = 7.3 Hz), 3.49 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.82 (d, 2H, $H^{3,5}$, *J* = 8.6 Hz), 7.85 (d, 2H, $H^{2,6}$, *J* = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.86 ($SiCH_2$), 16.88 ($C\mathbf{C}H_2C$), 31.60 (CH_2S), 50.45 (OCH_3), 55.27 (OCH_3), 113.72 ($C^{3,5}$), 129.49 ($C^{2,6}$), 134.88 (C^1), 163.74 (C^4), 189.89 (C═O).

2.2.13. *S-3-(trimethoxysilyl)propyl 2-hydroxybenzothioate* (**3m**)

The quantities used were as follows: **1m** (0.50 g, 3.62 mmol), CDI (0.70 g, 4.32 mmol), MPTMS (0.71 ml, 3.62 mmol). Anal. Calcd. for $C_{13}H_{20}O_5SSi$: C, 49.34; H, 6.37; S, 10.13. Found: C, 49.29; H, 6.33; S, 10.06. IR (neat, cm^{-1}): 1657 (*v* C═O), 1075 (*v* Si–O), 680 (*v* C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.73 (m, 2H, $SiCH_2$), 1.78 (m, 2H, CCH_2C),

3.06 (t, 2H, CH_2S, J = 7.3 Hz), 3.54 (s, 3H, OCH_3), 6.91 (d, 1H, H^3, J = 5.6 Hz), 7.40 (t, 1H, H^5, J = 5.8 Hz), 7.81 (d, 1H, H^4, J = 5.9 Hz), 8.13 (s, 1H, H^6). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.93 ($SiCH_2$), 16.67 (C**C**H_2C), 31.43 (CH_2S), 50.43 (OCH_3), 118.36 (C^3), 119.06 (C^1), 128.96 (C^5), 131.02 (C^6), 135.68 (C^4), 159.91 (C^2), 191.82 (C═O).

2.2.14. *S-(3-(trimethoxysilyl)propyl) 2-mercaptobenzothioate* (**3n**)

The quantities used were as follows: **1n** (0.50 g, 3.25 mmol), CDI (0.63 g, 3.89 mmol), MPTMS (0.64 ml, 3.26 mmol). Anal. Calcd. for $C_{13}H_{20}O_4S_2Si$: C, 46.96; H, 6.06; S, 19.29. Found: C, 46.29; H, 6.33; S, 10.06. IR (neat, cm^{-1}): 1653 (ν C═O), 1078 (ν Si–O), 667 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.37 (m, 2H, $SiCH_2$), 1.64 (m, 2H, CCH_2C), 2.99 (t, 2H, CH_2S, J = 7.3 Hz), 3.58 (s, 3H, OCH_3), 7.05 (s, 1H, H^5), 7.46 (s, 2H, $H^{3,4}$), 8.18 (s, 1H, H^6). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.45 ($SiCH_2$), 15.74 (C**C**H_2C), 35.36 (CH_2S), 51.36 (OCH_3), 127.40 (C^5), 127.94 (C^2), 128.15 (C^4), 129.01 (C^6), 132.19 (C^3), 136.71 (C^1), 191.57 (C═O).

2.2.15. *S-3-(trimethoxysilyl)propyl 2-aminobenzothioate* (**3o**)

The quantities used were as follows: **1o** (0.50 g, 3.64 mmol), CDI (0.71 g, 4.37 mmol), MPTMS (0.71 ml, 3.62 mmol). Anal. Calcd. for $C_{13}H_{21}NO_4SSi$: C, 49.50; H, 6.71; N, 4.44; S, 10.16. Found: C, 49.39; H, 6.66; N, 4.40; S, 10.09. IR (neat, cm^{-1}): 1658 (ν C═O), 1078 (ν Si–O), 684 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.66 (m, 2H, $SiCH_2$), 1.68 (m, 2H, CCH_2C), 3.11 (t, 2H, CH_2S, J = 7.3 Hz), 3.60 (s, 3H, OCH_3), 6.58 (d, 1H, H^3, J = 5.6 Hz), 6.93 (s, 1H, H^5), 7.42 (t, 1H, H^4, J = 5.8 Hz), 7.90 (d, 1H, H^6, J = 5.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.37 ($SiCH_2$), 15.94 (C**C**H_2C), 36.74 (CH_2S), 51.03 (OCH_3), 113.69 (C^3), 119.78 (C^1), 123.29 (C^5), 131.52 (C^6), 135.42 (C^4), 147.88 (C^2), 191.88 (C═O).

2.2.16. *S-3-(trimethoxysilyl)propyl 2-nitrobenzothioate* (**3p**)

The quantities used were as follows: **1p** (0.50 g, 2.99 mmol), CDI (0.58 g, 3.48 mmol), MPTMS (0.59 ml, 3.00 mmol). Anal. Calcd. for $C_{13}H_{19}NO_6SSi$: C, 45.20; H, 5.54; N, 4.05; S, 9.28. Found: C, 45.14; H, 5.45; N, 4.01; S, 9.24. IR (neat, cm^{-1}): 1660 (ν C═O), 1078 (ν Si–O), 685 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.26 (m, 2H, $SiCH_2$), 1.55 (m, 2H, CCH_2C), 2.86 (t, 2H, CH_2S, J = 7.3 Hz), 3.51 (s, 3H, OCH_3), 7.10-7.43 (m, 4H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.25 ($SiCH_2$), 16.23 (C**C**H_2C), 33.83 (CH_2S), 57.74 (OCH_3), 124.51 (C^3), 128.96 (C^6), 131.31 ($C^{1,4}$), 135.33 ($C^{2,5}$), 191.98 (C═O).

2.2.17. *S-3-(trimethoxysilyl)propyl 2-chlorobenzothioate* (**3q**)

The quantities used were as follows: **1q** (0.50 g, 3.19 mmol), CDI (0.62 g, 3.83 mmol), MPTMS (0.63 ml, 3.20 mmol). Anal. Calcd. for $C_{13}H_{19}ClO_4SSi$: C, 46.62; H, 5.72; S, 9.57. Found: C, 46.25; H, 5.57; S, 9.36. IR (neat, cm^{-1}): 1655 (ν C═O), 1086 (ν Si–O), 678 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.68 (m, 2H, $SiCH_2$), 1.71 (m, 2H, CCH_2C), 2.99 (t, 2H, CH_2S, J = 7.3 Hz), 3.47 (s, 3H, OCH_3), 7.20 (t, 1H, H^5, J = 5.9), 7.31 (m, 2H, $H^{3,4}$), 7.52 (d, 1H, H^6, J = 5.8). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.49 ($SiCH_2$), 17.45 (C**C**H_2C), 32.31 (CH_2S), 50.14 (OCH_3), 126.42 (C^5), 128.91 (C^6), 130.61 (C^3), 131.81 (C^1), 137.73 (C^4), 191.17 (C═O).

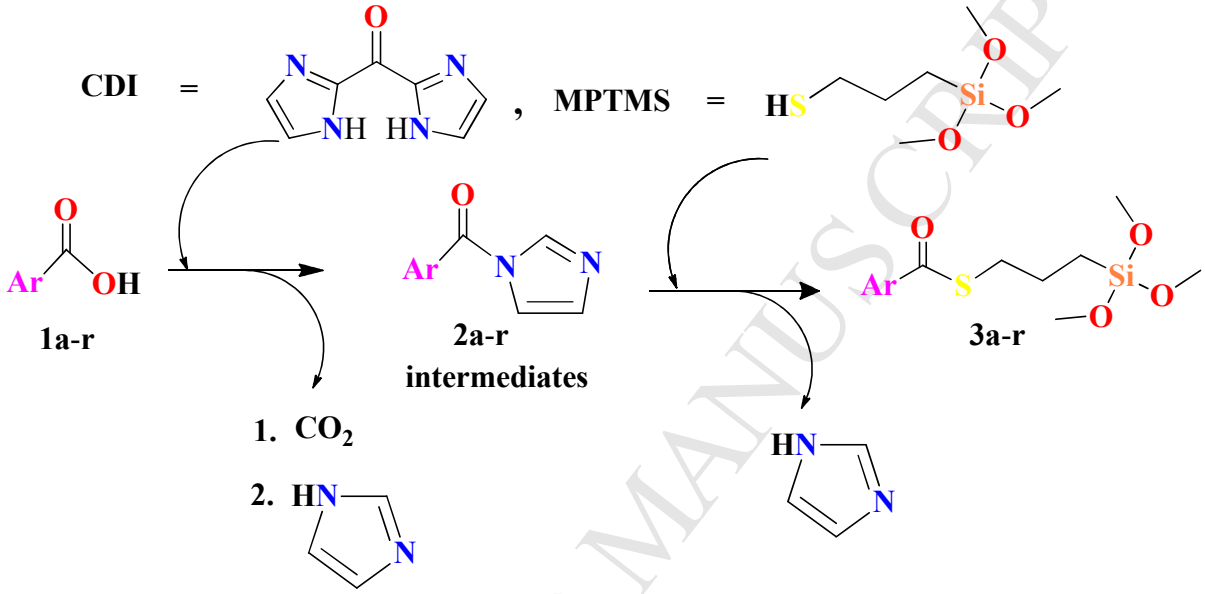
2.2.18. *S-3-(trimethoxysilyl)propyl biphenyl-4-carbothioate* (**3r**)

The quantities used were as follows: **1r** (0.50 g, 2.52 mmol), CDI (0.49 g, 3.03 mmol), MPTMS (0.49 ml, 2.50 mmol). Anal. Calcd. for $C_{19}H_{24}O_4SSi$: C, 60.61; H, 6.42; S, 7.46. Found: C, 60.56; H, 6.38; S, 7.43. IR (neat, cm^{-1}): 1651 (ν C═O), 1083 (ν Si–O), 684 (ν C–S). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.68 (m, 2H, $SiCH_2$), 1.72 (m, 2H, CCH_2C), 3.00 (t, 2H, CH_2S, J = 7.3 Hz), 3.45 (s, 3H, OCH_3), 7.22-7.31 (m, 3H, $H^{9,10,11}$), 7.45-7.53 (m, 4H, $H^{3,5,8,12}$), 7.91 (d, 2H, $H^{2,6}$, J = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 9.41 ($SiCH_2$),

15.53 (C**C**H$_2$C), 36.35 (CH$_2$S), 57.49 (OCH$_3$), 126.95 (C^{10}), 127.10 (C^{8}), 127.57 (C^{12}), 127.78 (C^{3,5}), 128.79 (C^{2,6}), 133.59 (C^{9,11}), 140.16 (C^{1,7}), 143.92 (C^{4}), 190.79 (C=O).

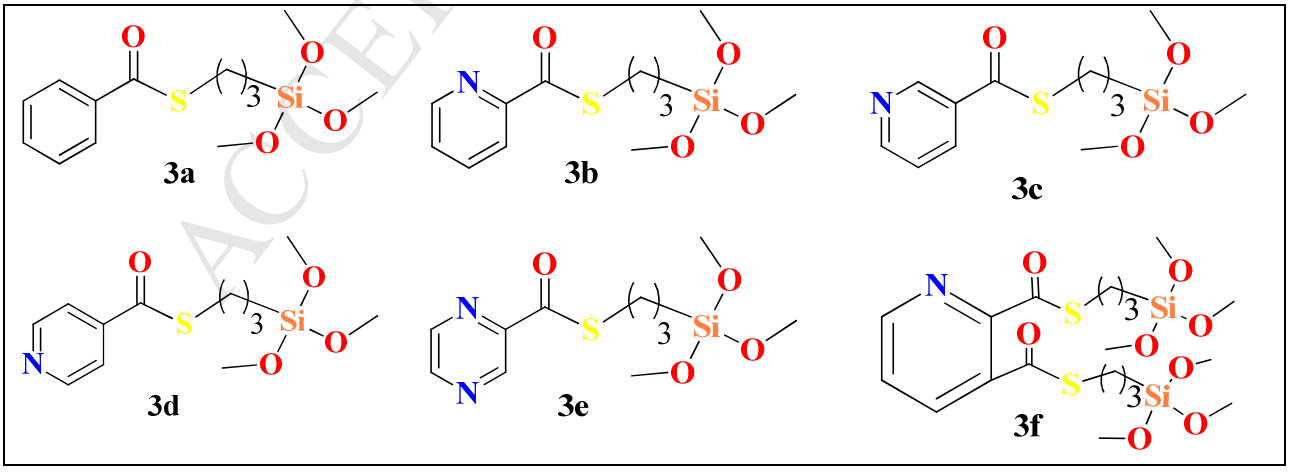
3. Results and discussion

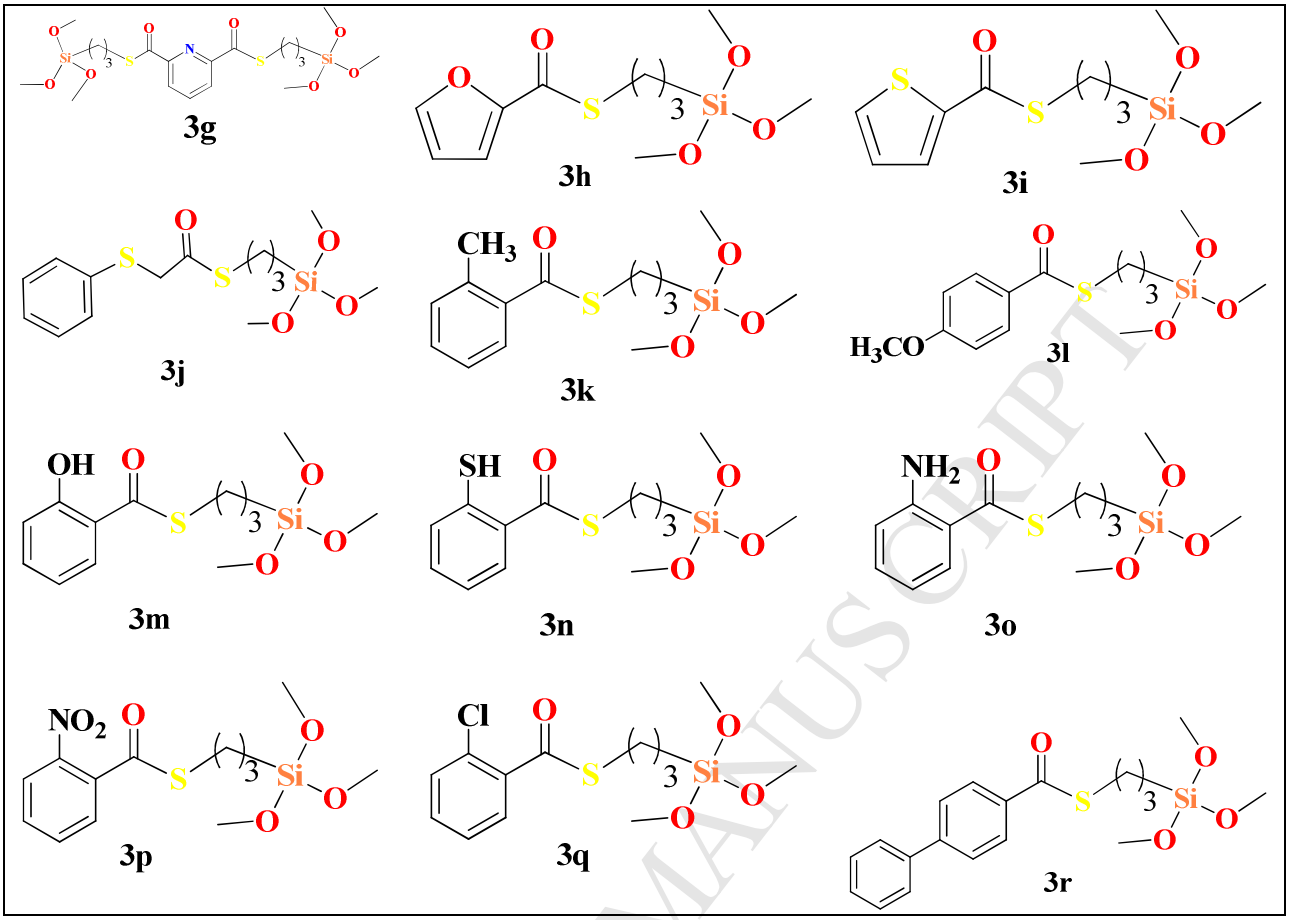
The synthetic route to access alkoxysilanes is outlined in Scheme 1.



Scheme 1: Synthesis of thioester allied organosilanes (**3a-r**)

Table 1 Thioester allied organosilanes (**3a-r**)





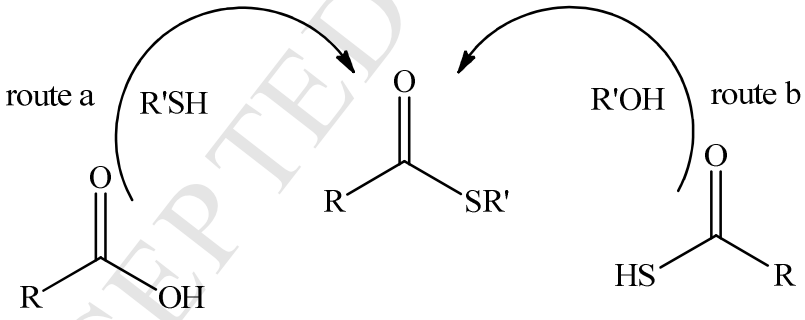
3.1 Synthesis

As the organosilanes turned out to be moisture sensitive; it was preferred traditionally to functionalize the organic fragment with silyl group in the later step of synthesis. For this reason, it is highly enviable to apply those reactions which can afford the alkoxysilane with an easy pathway that can be performed under normal atmospheric conditions without any chromatographic separation or distillation approach. Recently we have reported an adept methodology for the preparation of heteroaromatic thioester based organosilatranes.[15] The same synthetic formula is found to be pertinent for the generation of the present silanes. A one-pot, three-component protocol involving the CDI mediated thioesterification of carboxylic acid with MPTMS has been employed as a synthetic guideline here (Scheme 1). The acyl carboxy substituted imidazole is first formed during the reaction of carboxylic acid with CDI, which combines rapidly with the imidazole unit to form respective acyl imidazole

(**2a-r**). The in-situ coupling of these acyl imidazole units with MPTMS imparts OfTMS derivatives (Table 1). The merit of this protocol was tested by varying the substrate and all reactions were executed using optimized reaction conditions (Table 2, entry 10). The highlight of this route is that all silanes are easily generated without utilizing inert atmosphere and the trimethoxysilyl group can be successfully integrated with each challenging substrate.

3.1.1. Optimization of reaction conditions

To optimize the best suitable path for stitching of silyl moiety with various aromatic units *via* thioester linkage, different reaction conditions were attempted. Out of the numerous protocols for preparing thioester, the one involving carboxylic acid and alcohol condensation have emerged as the smartest and simplest method (Scheme 2). Subsequently, the thioesters can be prepared *via* acylation of thiol [15] with carboxylic acid (route a), or by the reaction of thiocarboxylic acid with alcohol [16] (route b). However, in our case due to the non-availability of both the ingredients required for route b, this could not be attempted.



Scheme 2: Possible routes of synthesis of thioester from carboxylic acid

Following route a, we initiated our work using benzoic acid (**1a**) and MPTMS as substrates to optimize the reaction conditions. In the first place, the blank reaction i.e. without any coupling reagent or catalyst was tried. The reaction did not proceed at all even after keeping for a long duration, implying that some additional driving force has to be applied as a high energy barrier exists between the two components. Following this, a well known bronsted acid catalyst for the esterification reaction *viz*. conc. H_2SO_4 was added to the

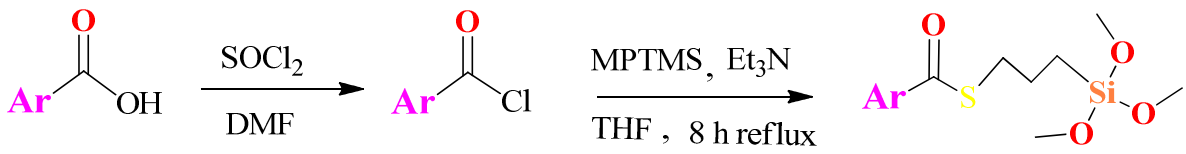
reaction mixture.[17] This time the reaction commenced but with a very low yield of the expected product. The possible explanation for this can be the hydrolysis of the product silane under acidic condition.[18] In the next case, **1a** was pre-activated with thionyl chloride forming its highly reactive derivatized form i.e. acid chloride[19] (Scheme 3), which was then coupled with MPTMS. Though we were successful in the generation of the desired product, but there were some serious and unavoidable shortcomings of this methodology, which include handling of fuming and moisture sensitive thionyl chloride, acyl chloride and the liberation of toxic HCl gas. Besides, an additional base had to be used in this reaction to absorb the by-product HCl gas (Scheme 3). To overcome these limitations, another reagent was sought out. Out of the commercially available coupling reagents[19] like DCC, CDI, DEAD etc, we have opted for the CDI mediated coupling of acid with MPTMS since CDI is economically viable and generates cleaner reaction with easily removable innocuous by-products (Scheme 1). When started with carboxylic acid:CDI in 1:1 ratio, only 40% product yield was achieved. Although thiol can also be activated with CDI but thiolysis *via* this method required prolonged heating along with an extra nucleophile such as sodium ethoxide to catalyse the reaction on account of its weaker acidic character.[20] Consequently, this path was eradicated and the reaction was further attempted with acid and CDI in different ratios (Table 2, entries 5-10). The thiol source was added only after the complete activation of the acid (ca 1 h, monitored by TLC). Using acid and CDI in 1:1.2 ratios, a significant increment in the product yield was observed.

Table 2 Optimization of reaction conditions for the synthesis of compound **3a**

Entry	Catalyst/ coupling agent	Amount employed[a]	Solvent	Reaction conditions	Reaction duration (h)	Yield (%)[b]
1	None	-	Toluene	110 °C, st	10	0
2	H_2SO_4	0.1 equiv.	Toluene	110 °C, st	8	20
3	$SOCl_2$	10 equiv.	DCM	40 °C, st	5	72
4	CDI	1 equiv.	Toluene	110 °C, st	12	40
5	CDI	1.1 equiv.	Toluene	110 °C, st	12	56
6	CDI	1.2 equiv.	Toluene	110 °C, st	8	79
7	CDI	1.3 equiv.	Toluene	110 °C, st	8	78
8	CDI	1.4 equiv.	Toluene	110 °C, st	8	79
9	CDI	1.5 equiv.	Toluene	110 °C, st	8	79
10	**CDI**	**1.2 equiv.**	**THF**	**65 °C, st**	**8**	**85**
11	CDI	1.2 equiv.	DCM	40 °C, st	8	75
12	CDI	1.2 equiv.	$CHCl_3$	60 °C, st	8	72

a: the amount used is w.r.t. carboxylic acid (**1a**), b: determined by ^{1}H NMR analysis of the sample. The bold values specify the best optimized condition for the reaction.

By changing the ratios further, any augment in the yield was not obtained (entries 6-8). The solvent medium inspection revealed that THF is a better choice amongst the tested solvents (entries 9-11). On the whole, we can state that the coupling of carboxylic acid with MPTMS *via* CDI mediation is an attractive route to assemble silyl unit with the aromatic thioester.



Scheme 3: Synthesis of OfTMS derivatives *via* acid chloride

3.2. Characterization of OfTMS (3a-r)

The structures and purity of all the products were inferred from their infrared, NMR (^{1}H and ^{13}C), and elemental analysis data. In the FT-IR spectra, absence of S-H (MPTMS), O-H (carboxylic acids) absorption bands and the occurrence of strong bands at 1648-1675 cm^{-1} due to C=O stretching vibrations verify the coupling of carboxylic acid with MPTMS. The bands at 1070-1099 cm^{-1}, typical of the Si-O asymmetric vibrations confirm the product formation.

^{1}H NMR spectra have demonstrated the symbolic peaks of the silyl fragment corresponding to the Si-OCH_3 group in the range of 3.43-3.79 ppm. In the spectra of all compounds, signal due to CH_2S protons shifts its position from δ = 2.55 ppm (MPTMS) to δ = 2.80-3.11 ppm (**3a-r**). This shift confirms the acylation of thiol group to form thioesters. In ^{13}C NMR spectra, the peak belonging to C=O group of thioester linkage in the region 176.72-193.07 ppm validate the product formation. Even though we have employed non-inert conditions for the synthesis and used water for the work up, the spectroscopic studies have revealed that only non-hydrolysed species are present in the product, corroborating the stability of trimethoxysilanes modified with aromatic thioester.

3.3. UV-Vis spectral study

The molecular frameworks with various substitutions possess atypical properties when exposed to UV-Vis radiations.[21] Therefore, we intend to undertake the tailoring of different aromatic moieties with the organosilicon derivatives. The chemical structure, electronic character and the position of the aromatic ring with respect to the thioester group are expected to alter the absorption band definitely, if not largely for the different alkoxysilanes. The UV-Vis absorption analyses of the compounds (**3a-r)** were carried out at a

molar concentration $3x10^{-5}$ M in chloroform (Fig. 1). The OfTMS derivatives acquire major absorption bands in the region of 249-349 nm with very high values of extinction coefficients (ε_{max}), which are ascribed to the π-π^* electronic transitions in these conjugate systems and the salient features of the absorption peaks are presented in Table 3.

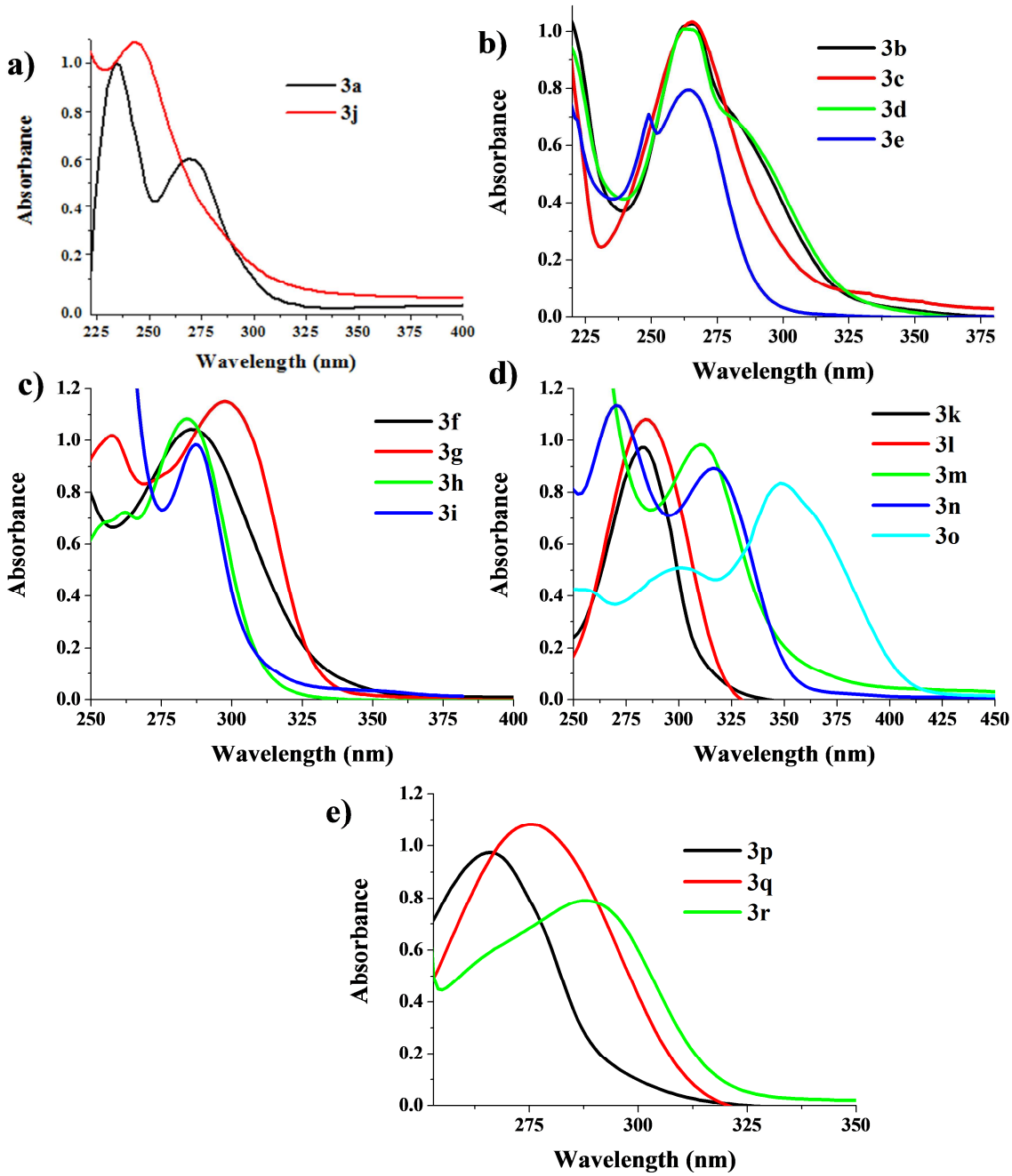


Fig. 1. UV-Vis spectra of compounds (**3a-r**) in chloroform

Table 3 Observed yields, UV-Vis absorption parameters for compounds (**3a-r)** and the % contribution of the solvatochromic parameters

Compound ID	Substrate	Synthetic yield (%)	λ_{max} (nm)	$\varepsilon_{max} \times 10^4$ ($Lmol^{-1}cm^{-1}$)	% contribution of solvatochromic parameters		
					P_π	P_α	P_β
3a	Ph	85	272	11.49	25.38	30.08	44.53
3b	*o*-Py	83	265	12.33	13.99	55.47	30.54
3c	*m*-Py	80	265	12.30	33.88	62.99	3.13
3d	*p*-Py	81	265	12.29	21.53	45.57	32.89
3e	pyza	82	263	10.88	23.24	48.36	28.40
3f	2,3-py	86	284	11.15	17.52	50.66	31.82
3g	2,6-py	84	296	13.40	30.94	37.95	31.11
3h	furan	84	283	9.27	35.68	59.62	4.66
3i	thiophene	87	287	9.58	23.31	14.55	62.13
3j	Ph-SCH_2	84	249	10.15		-	
3k	Ph-Me	81	280	10.55	59.69	3.28	37.03
3l	Ph-OMe	79	282	10.78	38.27	22.99	38.73
3m	Ph-OH	85	309	11.95	10.75	41.67	47.58
3n	Ph-SH	72	315	12.35	24.50	30.54	44.96
3o	Ph-NH_2	82	348	13.98	55.67	36.74	7.58
3p	Ph-NO_2	80	265	11.17		-	
3q	Ph-Cl	84	274	11.67	32.40	37.54	30.06
3r	Ph-Ph	83	290	12.35	18.13	49.48	32.39

The spectral characteristics of any chromophore depend on the electronic environment and degree of conjugation existing in it. Now considering the carbonyl group in our system, its one side is occupied by the silyl substituted thiopropyl chain, which imposes only weak electron releasing effect and can be surmised to have a little effect on the π-π* transition of carbonyl bond. It is only the delocalized aromatic rings attached to the carbonyl group due to which the λ_{max} values are observed at higher values than the unsubstituted derivative.[22] For instance compound **3j**, where the carbonyl group is not directly bonded to the aromatic ring but connected alternatively *via* CH_2S linker, shows the absorption band at a low λ_{max} value i.e. 249 nm (Fig. 1a). While unsubstituted benzene ring allied silane **3a** absorbs at 272 nm, this accentuates the conjugation influence on the UV-Vis absorption profile. The π_1-conjugation corresponding to C=O group combines synergistically with π_2-conjugation arising from the attached aromatic moiety, leading to the higher λ_{max} values (Fig. 2a). For a better vision about the substituent effect on the absorption behaviour, it seems necessary to categorize the silanes into two series: first one enclosing various heterocyclic rings as the binding unit, while the second series is integrated with differently substituted phenyl ring analogues. Further, the silane **3a** carrying unsubstituted phenyl ring has been chosen as the reference compound for comparative analysis.

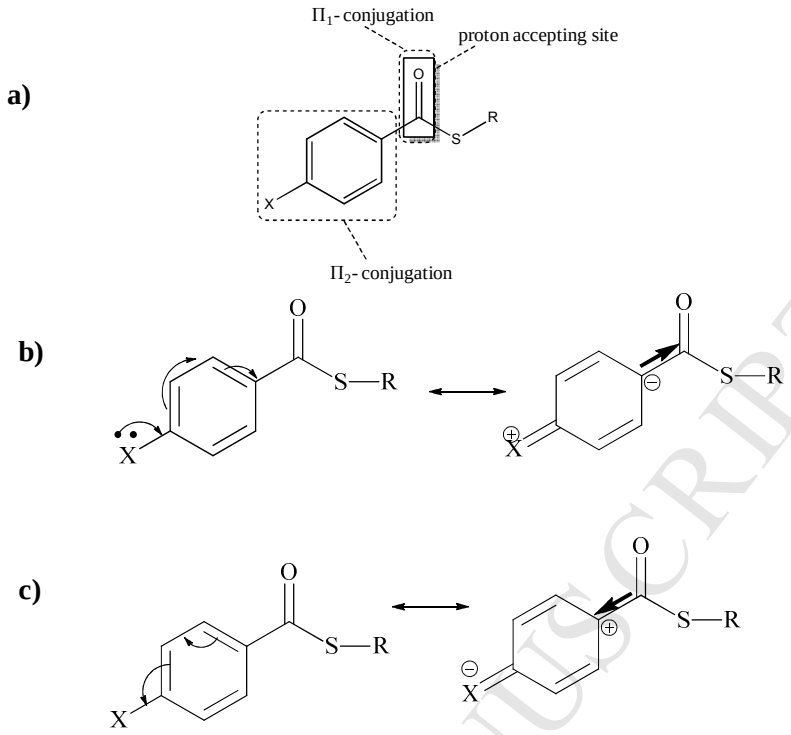


Fig. 2. (a) Defined π-electronic units present in the aromatic thioesters; (b) mesomeric structures of substituted thioesters with electron-donating; (c) with electron-accepting substituent

The replacement of CH group with the N atom at the aromatic ring (**3b-d**), instigates a blue shift in the absorption spectra owing to the electron withdrawing effect of the ring N atom. The electron density reduction leads to more energy gap between HOMO and LUMO, which result in lower λ_{max} values.[23] The absorption profiles of the pyridine ring derivatized silanes (**3b-d**) have the same features (Fig. 1b) and it is worth mentioning here that the positional isomeric effect on the λ_{max} value is not observed in these compounds. The incorporation of the 2nd N atom into the ring in compound **3e** further decreases λ_{max} values as depicted in Fig. 1b. The disubstituted pyridine ring derivatives **3f** and **3g** possess higher λ_{max} values than the corresponding mono derivatives (**3b-d**) owing to the bonus conjugation imposed by the 2nd thioester group (Fig. 1c). However, the five-membered ring systems behaved differently than we expected. On the basis of conjugation length, both **3h** and **3i** should absorb UV radiations at lower λ_{max} values than previously discussed six-membered

derivatives, while these compounds have shown much higher absorptions (Fig. 1c). We infer that this phenomenon is caused by the difference in the overall electronic influence of the aromatic ring on the carbonyl group. Both furan and thiophene rings are electron releasing heterocycles[24] whereas pyridine and pyrazine are electron withdrawing in nature, which is responsible for the higher λ_{max} values in **3h** and **3i**.

Moving over to the second series of silanes, where the core phenyl ring featuring electron donor and acceptor unit of varying electron density allow a systematic fine tuning with the UV-Vis absorptions. The electron releasing power of the affixed substituents is in the order: Me < OMe < OH < SH < NH_2. Exactly same increasing order has been observed in the λ_{max} values as shown in Fig. 1d. Here the non-bonding electrons of the substituent also contribute towards the mobility of π-electrons into the aromatic ring through resonance and consequently shifting of absorption maxima towards higher wavelength region occurs.

Switching over to the electron withdrawing substituent, the effect of NO_2 group (**3p**) is coherent with the theoretical consideration and an expected blue shift of 7 nm is observed (Table 3). An assessment of the absorption profile of **3q** (Fig. 1e) reveals that the results are contradictory here. This can be explicated on the basis of electron releasing mesomeric effect of Cl atom which induces higher λ_{max} value than could be proposed for an electronegative substituent, though still lower than the electron releasing substituents.[14c] The extended conjugation bestowed by the additional phenyl ring in the aromatic sequence (**3r**) leads to 18 nm red-shifted absorption profile as compared to **3a**. Briefly we can say that the π-electron density shift from the aromatic unit (resulting from the ring itself, its position or the substituent attached to it) influences the π-delocalization around C=O group. For instance, in the resonance structures (Fig. 2b), the additional electrons at the ring generate an increased charge density at the carbonyl group, while with electro withdrawing substituents, a decrease

in electron density occurs (Fig. 2c), which is responsible for the variation of absorption maxima values in these compounds.

3.4. Solvatochromism

Solvent-dependent absorption or solvatochromism, a term coined by Hantzsch, explores the local polarity and solvent interactions with a chromophore.[25] Owing to the solute-solvent interactions, an influence on the electronic absorption can be observed in terms of changes in the shape, spectral maxima position and intensity as well. Solvatochromism is generated by the differential solvation of the ground and the first excited states of the solute molecules which further depend upon the solute structure, solvent nature and solute-solvent interactions. The general trend observed with changing solvent polarity is as follows: if with increasing solvent polarity, the ground state of the solute is better stabilized than the electronically excited state, the negative solvatochromism persists leading to a blue shift in the absorption maxima. Conversely, if stabilization of the excited state is better than the ground state, the positive solvatochromism will prevail i.e. a red shifted profile will be observed with an increase in solvent polarity. The system which undergoes π-π^* transitions on the absorption of UV light generally has more polar electronically excited state compared to the ground state and hence the energy of the excited state is more affected by the dipole-dipole interactions with the solvent molecules.[26] A legitimate corollary of these interactions leads to the conclusion that the energy gap for π-π^* transitions falls causing the red shifting in absorption maxima. The specific chemical interactions, for instance, the possible H-bonding with the solvent molecule also affect the absorption behaviour since H-bonding leads to an overall alteration in the electronic density distribution.[27]

Herein we have embarked on a comprehensive study of solute-solvent interactions with a series of solvents of different polarity and H-bonding attributes. To the best of our

knowledge such a study on the organosilicon derivatives has not been conducted so far. To start with, the concentration-dependent UV-Vis spectroscopic study of all the compounds was carried out which showed no apparent shift in the UV-Vis absorption maxima wavelength. This implies that these compounds do not self-aggregate and hence can be investigated with regard to their solvatochromic properties.[28] For achieving a correlation of the solvent effect on the solute molecules, a large number of scales have been meticulously developed and utilized.[29] In the present work, we have explored the empirical solvatochromic scale developed by Kamlet and Taft.[30] The linear regression approach articulated by Kamlet and Taft is one of the most ambitious and successful quantitative treatment for the estimation of diverse intermolecular solute-solvent interactions by means of a multi parameter equation:

$$\bar{\nu}_{max} = \bar{\nu}_{max,0} + s\pi^* + a\alpha + b\beta$$

where $\bar{\nu}_{max}$ is the UV-Vis absorption maximum wavelength of a solute in a particular solvent; $\bar{\nu}_{max,0}$ is the value of this property for the same solute in a hypothetical solvent for which $\pi^* = \alpha = \beta = 0$. π^* is an index of the solvent dipolarity/polarizability, α is a measure of the solvent hydrogen-bond donor (HBD) capacity and β is a measure of the solvent hydrogen-bond acceptor (HBA) capacity. The regression coefficients s, a and b are the respective susceptibility constants. These analytical parameters are important as their magnitude and sign are the direct measurement of the type of solvatochromism the solute molecules exhibit.

We have used seven aprotic solvents tetrahydrofuran (THF), acetonitrile (ACN), N,N-dimethylformamide (DMF), ethylacetate (EtOAc), chloroform ($CHCl_3$), dichloromethane (DCM), dichloroethane (DCE) and six protic solvents *viz.* methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), n-butanol (BuOH), iso-propanol (^{i}PrOH), iso-butanol (^{i}BuOH) of varying polaritiy (Table 4) for studying the solvatochromic properties of the silanes by observing their absorption spectral changes.

Table 4 Physical properties and Kamlet-Taft parameters of the employed solvents[31]

Solvent	ε	n	α	β	π*
MeOH	32.7	1.33	0.98	0.66	0.68
EtOH	24.5	1.36	0.86	0.75	0.54
PrOH	20.5	1.38	0.84	0.90	0.52
BuOH	17.6	1.39	0.84	0.84	0.47
^{i}PrOH	17.9	1.38	0.76	0.84	0.48
^{i}BuOH	22.0	1.39	0.82	0.80	0.69
$CHCl_3$	4.81	1.44	0.20	0.10	0.69
ACN	37.5	1.34	0.19	0.40	0.75
DMF	36.7	1.43	0.00	0.69	0.88
DCM	8.93	1.42	0.13	0.10	0.82
DCE	10.36	1.44	0	0.10	0.81
THF	7.58	1.41	0	0.11	0.54
EtOAc	6.02	1.37	0	0.45	0.55

ε: relative permittivity; n: refractive index; α: the solvent's HBD acidity; β: the solvent's HBA basicity; π*: the solvent's dipolarity/polarizability.

The absorption studies of the non-conjugated derivative (**3j**) could not be observed in all solvents because of its lower λ_{max} value as compared to the cut-off values of most of the solvents, whereas compound **3p** was partly soluble or insoluble in the majority of them. Therefore, these compounds could not be analysed for their solvatochromic behaviour. The absorption pattern of compound **3r** has been represented in Fig. 3a for protic solvents and in Fig. 3b for aprotic solvents, while the absorption data of all compounds in different solvents has been depicted in Table 5.

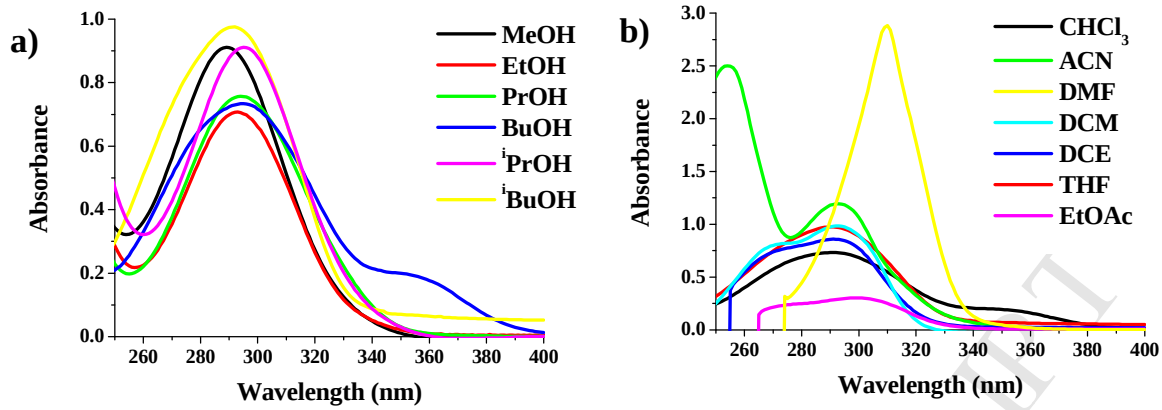


Fig. 3. UV-Vis spectra of compound **3r** in (a) protic solvents; (b) aprotic solvents

Table 5 UV spectral data ν_{max} (10^3 cm^{-1}) of aromatic thioester substituted silanes

ID	MeOH	EtOH	PrOH	BuOH	^{i}PrOH	^{i}BuOH	$CHCl_3$	ACN	DMF	DCM	DCE	THF	EtOAc
3a	36.81	36.84	36.80	36.87	36.87	36.87	36.76	36.93	b	36.86	36.82	36.72	37.09
3b	37.98	37.88	37.84	37.88	37.84	37.84	37.73	37.59	b	37.59	37.59	37.59	37.88
3c	38.17	38.17	36.80	38.17	38.17	38.17	37.77	37.95	b	37.73	37.73	37.95	37.73
3d	37.30	36.90	36.90	36.90	36.90	36.90	37.78	36.76	b	37.48	37.48	36.48	36.28
3e	37.31	37.31	37.31	37.31	37.31	37.31	37.95	38.96	b	38.4	38.4	38.95	38.90
3f	35.99	35.75	35.75	35.75	35.84	35.99	35.09	35.21	35.21	35.15	35.15	35.15	35.21
3g	34.48	34.90	34.90	34.90	34.90	34.90	33.80	34.16	34.16	33.60	33.60	33.69	34.08
3h	36.17	35.95	35.40	35.49	35.49	35.33	35.25	34.83	34.35	35.28	34.67	34.78	34.33
3i	35.59	35.59	a	35.27	35.46	35.46	34.83	33.59	33.05	34.78	34.78	34.45	34.35
3k	36.36	36.06	35.94	35.94	36.06	35.99	35.65	36.23	36.87	35.95	35.88	35.44	35.88
3l	35.59	35.46	35.46	35.46	35.46	35.46	35.59	35.59	37.04	35.59	35.33	35.20	35.97
3m	31.65	32.05	32.80	32.89	32.89	32.55	32.36	32.80	34.49	32.35	32.47	32.75	34.15
3n	31.54	32.05	31.85	31.85	31.85	31.78	31.74	32.26	34.13	31.95	31.73	31.38	31.95
3o	30.12	29.95	29.70	29.85	29.85	29.65	28.67	28.83	28.16	28.43	28.76	28.72	29.35
3q	37.17	36.76	a	36.49	36.49	a	37.03	36.63	35.21	35.08	35.08	a	36.63

3r	34.56	34.01	34.01	34.01	34.01	34.24	34.45	34.08	32.45	34.16	34.26	34.46	33.29

a: insoluble in the given solvent; b: solvent has higher cut off value

The data in Table 6 shows that a few of the derivatives with Ph, pyrazine, Ph-Me, Ph-OMe and Ph-SH substituent have +ve s values hinting that they have more polar ground state than the corresponding excited state and thereby these compounds possess negative solvatochromism. It is worth pointing out that in these compounds the increased polarity of the solvents leads to a hypsochromic shift in the absorption profiles, while all other derivatives have shown the positive solvatochromism, usual of π-π* transitions.

Table 6 ν_o, s, a and b (in cm^{-1}) and correlation coefficients (R^2) obtained from the Kamlet-Taft fitting of the absorption data

Compound ID	**Substituent**	ν_o **(10^3 cm^{-1})**	**s (10^3 cm^{-1})**	**a (10^3 cm^{-1})**	**b (10^3 cm^{-1})**	R^2
3a	Ph	36.45	0.485	-0.575	0.851	0.910
3b	*o*-Py	37.71	-0.147	0.583	-0.321	0.981
3c	*m*-Py	37.94	-0.227	0.422	-0.021	0.870
3d	*p*-Py	38.04	-0.521	1.719	-1.088	0.938
3e	pyrazine	37.76	1.143	2.379	1.397	0.921
3f	2,3-py	34.51	-0.685	1.981	-1.244	0.943
3g	2,6-py	35.91	-1.781	2.185	-1.791	0.905
3h	furan	35.38	-0.468	0.781	0.061	0.945
3i	thiophene	33.83	-0.495	0.309	1.319	0.966
3k	Ph-Me	34.19	2.021	-0.111	1.254	0.950
3l	Ph-OMe	34.23	1.668	-1.002	1.688	0.893
3m	Ph-OH	32.85	-0.748	-2.898	3.309	0.922
3n	Ph-SH	30.48	1.668	-2.079	3.060	0.932

3o	Ph-NH_2	29.70	-1.689	1.114	0.230	0.948
3q	Ph-Cl	35.15	-1.498	1.735	-1.389	0.825
3r	Ph-Ph	34.97	-0.749	-1.766	-2.574	0.932

Meanwhile, if the coefficients a and b have negative signs, the bathochromic shifts are expected with increasing solvent HBD and HBA capabilities, respectively. In the silanes belonging to series 2 i.e. with substituted phenyl ring derivatives, the parameter a has -ve sign, suggestive of the bathochromic shift with increase in solvent hydrogen-bond donor acidity. Such a shift arises on account of H-bonding interactions of the HBD solvents with O of C=O group. Whereas in silanes of series 1 which is composed of heterocyclic analogues, the already existing C=O interaction competes with the additional interaction of heteroatom with HBD solvent. This is illustrated by the +ve sign of parameter a which means that the interaction of heteroatom with the HBD solvent is so strong that it outweighs the interaction with the C=O group and therefore these silanes have shown hypsochromic shift with increasing solvent hydrogen-bond donor acidity.[24] Moreover, the largest value of coefficient a is observed in silane **3e** containing pyrazine ring which is in accord with its structure as this molecule has the maximum tendency to form H-bonds with the HBD solvent owing to the presence of two N atoms in the aromatic ring.

Additionally, some of the silanes with Ar-OH, Ar-SH, Ar-NH_2 substituents contain H-bond donor sites and hence can interact with the H-bond acceptor solvents. The maximum value of parameter b is found in case of silane with OH substituent on the phenyl ring which is attributed to its capability of forming strong H-bonding with the HBA solvent.[32] An exceptional behaviour is shown by the Ar-NH_2 substituent as it is having the least value of the coefficient b. This anomaly might be due to the involvement of NH_2 group in the intra-molecular H-bonding with the O atom of the thioester group.[33]

Overall the percentage contributions of the three solvatochromic parameters (Table 3) for the investigated silyl derivatives with different substituent show that the solvent effect on UV absorption spectra is very complex and strongly dependable on the nature of the aromatic unit, its electronic behaviour as well as degree of conjugation imposed by it on the carbonyl group. Therefore, a simple generalization cannot be made. The present set of compounds has depicted different results depending on the substituent attached to the carbonyl group indicating that the C=O bond stretching is very sensitive. In a nut-shell, we can say that the exploration of degree of solvation is helpful to identify the chemical and physical properties of the solute molecules.

4. Conclusions

We have elaborated the facile and proficient methodology for the stitching of silyl moiety with the versatile aromatic thioesters. The synthesis allows an easy access for modifying carboxyl group virtually of any substrate with MPTMS, leading to high purity, easy work up and minimal by-products. The assembled system quotes an amazing example of organic-inorganic hybrids and can be put forth for applications in the field of advanced siliceous chemistry. The photoelectronic spectral analysis in the UV-Vis region has shown that the alteration in the structural profile by varying the aromatic core or imposing substitutions at the phenyl ring significantly affects the λ_{max} values. The nature and extent of interactions of these organo-silicon derivatives with various solvents are characterized and quantified using Kamlet-Taft scale. The results demonstrate that the solvent effect on the prepared silanes is of complex nature which involves polarity, H-bond donor and acceptor features depending upon the kind of substituent attached.

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Research Highlights

- A new pathway for the synthesis of alkoxysilanes is developed.
- The silanes are meticulously characterized by IR and NMR spectroscopic techniques.
- The substituent effect on the absorption behaviour is analysed.
- The solvatochromic behaviour is studied by utilizing Kamlet Taft approach.