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Three-step pathway towards bis(1,2,3-triazolyl-γ-propylsilatranes) as Cu^{2+} fluorescent sensor, via 'Click Silylation'

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ABSTRACT

A series of substituted aniline derivatized bis(1,2,3-triazolyl-γ-propylsilatranes) **3a**–**3f** were designed in good yield from their triethoxysilane analogues via Cu(I) 'Click Silylation'. All the silatranes **3a**–**3f** were characterized by IR, NMR (^1H, ^{13}C) and HRMS studies. All these compounds were explored for their thermal stability by thermogravimetric analysis (TGA)/differential thermal analysis (DTA)/differential scanning calorimetry (DSC) study and electronic properties by UV–vis spectroscopy and fluorescence study. The binding of silatranes **3a**–**3f** to Cu^{2+} ion proves them to be good chemosensor. These silatranes were subjected to time dependent hydrolysis under normal atmospheric conditions. IR spectroscopic data support hydrolytic instability of **3a**, **3c** and **3e**.

Silatranes have always been of great interest due to the spatial arrangement of atoms,[1] particularly nitrogen lone pair donation generating hyper-coordination at silicon centre.[2] Silatranes are silicon caged cyclic ethers packed in trigonal bipyramidal geometry and synthesized by transetherification reaction of 'water-sensitive' organotriethoxysilanes.[1,3] The variation of axial substituents considerably affects the properties of silatranes and enhances their use in various bio-medical applications.[4] Silicon once embedded in this position becomes unavailable for 'water molecules' to disrupt the structure and hence finds more practical applications than their precursor organotriethoxysilanes.[5] The constant appreciation received by organosilatranes has attracted the interest of modern chemists to modify exocyclic fragment[6] with differently substituted aromatic and alkyl chain linkers. But so far to the best of our knowledge, no silatrane with 1,2,3-triazole bound aromatic linkage has been reported in the literature. So, we herein report first bis(1,2,3-triazolyl-γ-propylsilatranes) linked to primary aromatic functionalities via copper(I) catalysed alkyne–azide cycloaddition (CuAAC).

The modification of Huisgen 1,3-dipolar reaction by Sharpless[7] and Meldal[8] using Cu(I) salts has promoted its use in selective, efficient and versatile chemical reactions. The irreversible ligation[9] of two reactive molecular fragments to exceptionally stable 1,2,3-triazole[10] widens the scope of this methodology to medicine[11] and material chemistry.[12] The chemoselective coupling accompanied by the versatile functional group tolerance for alkyne–azide entities has made it a modular synthetic reaction. We have applied this approach for the synthesis of silatranes by cycloaddition reaction of substituted aromatic amine based terminal alkynes[13] with γ-azidopropyltriethoxysilane.[14,15] This combination of different synthetic moieties results into hybrid materials that can merge together the advantages of standard synthetic polymers to advanced biological applications; for example the ratiometric fluorescent sensing of Cu^{2+} by using the synthesized triazolyl silatranes.

Fluorescent chemosensors monitor electronic changes upon binding of the compound to a specific guest.[16] The essentiality of copper among heavy metals for organisms makes it a vital element to play a major role in biological processes.[17] However, prolonged exposure to high concentrations of copper has been known to cause major physiological disorders in organisms and increases toxicity in environment.[18] In the past few years, the approach to develop highly sensitive fluorescent probes towards different heavy metal ions has received considerable attention.[19] The general affinity of amine ligands[20] for transition metal ions encouraged us to synthesize aniline based 1,2,3-triazolyl silatranes as metal ion chemosensors. For this study, we used chloride salts of Cu^{2+}, Ni^{2+}, Ag^{+} and Ru^{+} to evaluate metal ion binding at concentration of 100 μM. The competitive studies indicate our system to be fit for Cu^{2+} sensing.

Silatranes **3a**–**3f** were synthesized by a three-step route involving 'Click Silylation'[14b] as azide–alkyne fragment linker. To begin

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with, the synthesis of terminal alkynes **1a–1f** was carried out by nucleophilic substitution reaction of substituted aromatic amines with 30% excess mole of 80% propargyl bromide solution, followed by the use of $[Cu(PPh_3)_3Br]$ in THF/TEA [1:1] reaction system to stitch alkynes **1a–1f** with γ-azidopropyltriethoxysilane (AzPTES) resulting into substituted 1,2,3-triazolyl triethoxysilanes **2a–2f**. The final step of atrane ring formation was proceeded by azeotropic refluxing of 1:2 solution of **2a–2f** and triethanolamine in toluene using catalytic amounts of KOH, yielding dull white powdered solid compounds **3a–3f**.[21] These silatranes **3a–3f** were found to be stable towards hydrolysis under atmospheric conditions with the exception of **3c** and **3e** which are highly moisture sensitive therefore requiring inert conditions for handling.

Vibrational spectroscopic data for silatranes **3a–3f** were recorded as neat spectra in the range 4000–400 cm^{-1}. The sharp absorption bands at 2960–2800 and 1650–1450 cm^{-1} were due to aromatic conjugation in the aniline ring and the 1,2,3-triazole ring. The flat region between 2300 and 2100 cm^{-1} proved complete conversion of triple bonded moieties to the 1,2,3-triazole ring, thereby proving high yield of the reaction. The transannular N → Si bond was marked by the presence of sharp peak for all silatranes **3a–3f** in the region 760–740 cm^{-1}. Upon examination of the effects of various positional isomers on silatrane cage, it was evident that asymmetric shifts corresponding to O—Si and N → Si bonds increase in case of p-isomeric substituents while the absorption frequency lowers down substantially for o-isomer to cope with the expected change.

NMR (^1H, ^{13}C) spectra recorded for compounds **3a–3f** in $CDCl_3$ and DMSO-d_6 at 25 °C were found to be well in agreement with the synthesized products. The successful azide–alkyne cycloaddition reaction in ^1H NMR was marked by the appearance of sharp singlet in the region $\delta \approx 7.6–7.2$ ppm and complete disappearance of peak that may arise from terminal alkyne moiety. Moreover, a major shift of $-N_3CH_2$ triplet from $\delta \approx 4.2–3.2$ ppm is attributed to 1,2,3-triazole formation. The close inspection of ^1H NMR spectra of silatranes reveals that protons on the carbon nearest to the silicon atom are displayed as a multiplet with upfield shift and methylene protons linked with nitrogen appeared as a triplet with relative downfield shift. The effect of different substituents having both o- and p-isomers was negligible on aliphatic protons while minimal shifting of triazole-H singlet was observed. In case of ^{13}C NMR spectra, the major shift was observed for C4 carbon of 1,2,3-triazole as it appeared in the region of $\delta \approx 130.9–128.4$ ppm. The methylene carbon of propyl chain attached to silicon atom appeared as the most shielded carbon atom, which was identified around $\delta \approx 7.0–6.0$ ppm for triethoxysilanes and $\delta \approx 13.0–12.0$ ppm for silatranes. This downfield shift of methylene carbon clearly indicates the hypervalency at silicon atom. Other peaks due to $-CH_2CH_2N_3$ were observed in the region $\delta \approx 25.1–24.7$ ppm and $\delta \approx 43.6–41.8$ ppm, respectively. No significant effect of positional isomers was evident.

Photophysical properties

Aromatic compounds are among the most absorbing chromophores due to low lying p-orbitals thus giving rise to rapid electronic transitions. The isomeric substituents strongly affect these transitions which were clearly observed upon irradiation of compounds **3a–3f** with electromagnetic radiations in UV–vis region and recording the absorption spectra in $CHCl_3$ as shown in Fig. 1. Considering **3a**, an unsubstituted aniline based 1,2,3-triazolylsilatranyl moiety, with λ_{max} at 298 nm, the absorption spectra for silatranes **3b–3f** were compared. The substitution of the aniline ring with various electronegative groups at p-position such as –F (**3c**), –Cl (**3d**) was found to have red shift of 20 nm with λ_{max} value at 308 nm; whereas –OMe at o-position (**3e**) absorbed at λ_{max} of 279 nm showing blue shift of 19 nm while its p-isomer (**3f**) absorbed at λ_{max} of 316 nm. The compound **3b** was absorbed at λ_{max} of 252 nm which was exceptionally lower in comparison to that for **3a**. This remarkable activating and deactivating properties of different groups regulate fundamental properties of silatranes at electronic level.

The photonic properties of newly synthesized silatranes were explored for fluorescence activity, as it is one of the most important properties of substituted aromatic functionalities. For a practical approach, the effect of concentration change in fluorescence emission spectra was recorded using MeOH as solvent media. There was substantial variation in emission maxima peak for

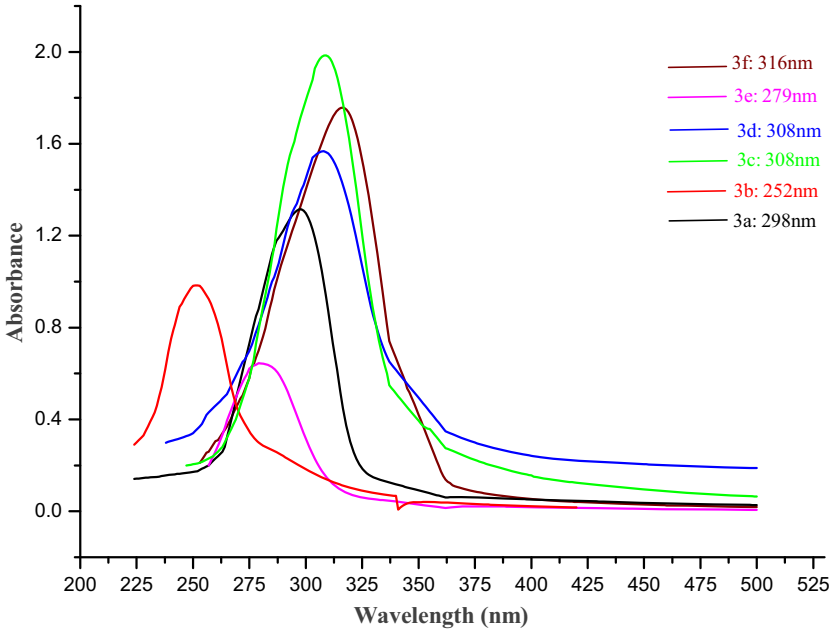


Figure 1. UV–vis spectra of synthesized silatranes **3a–3f**.

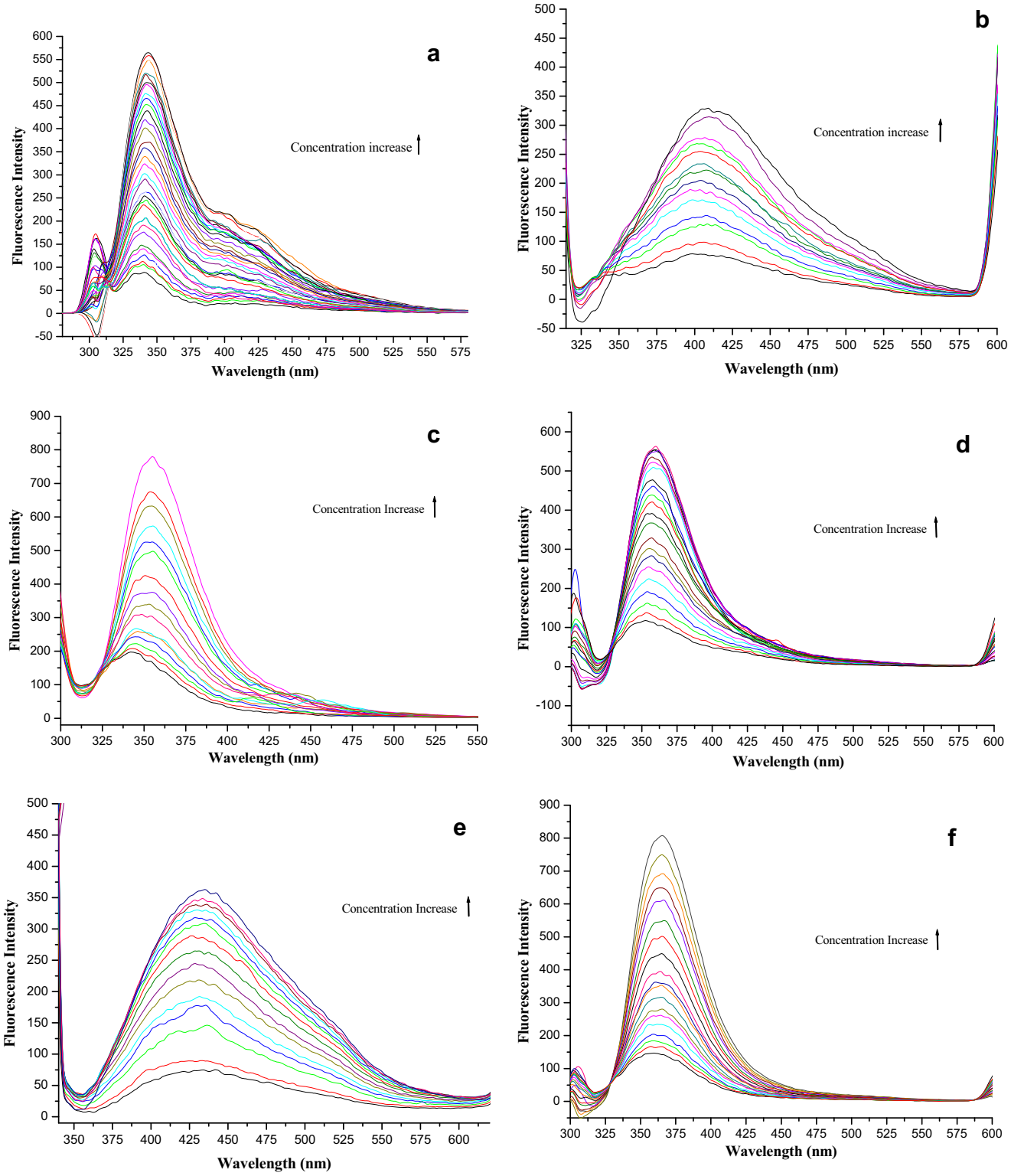


Figure 2. Fluorescence spectra of bis(1,2,3-triazolyl-γ-propylsilatranes) **3a**–**3f** carried out in MeOH at concentration of 100 μM with λ_{ex} = 310 nm for **3a**, **3b**, **3d** and **3f**, λ_{ex} = 300 nm for **3c** and λ_{ex} = 330 nm for **3e**.

different silatranes that resulted from the substituent's positional isomerization, that is **3a** at 343 nm, **3b** at 405 nm, **3c** and **3d** at 358 nm, **3e** at 435 nm and **3f** at 365 nm (Fig. 2). The increased intensity and red shift in wavelength were clearly evident on the substitution of **3a** with –F, –Cl, –OMe (-o and -p isomer), depending upon a decrease in electronic movement due to different electron withdrawing groups attached. The red shift of 15 nm both in case of **3c** (–F) and **3d** (–Cl) compared to **3a** was observed. The fluorescence yield increased with an increase in concentration till saturation, after which the intensity began to decrease

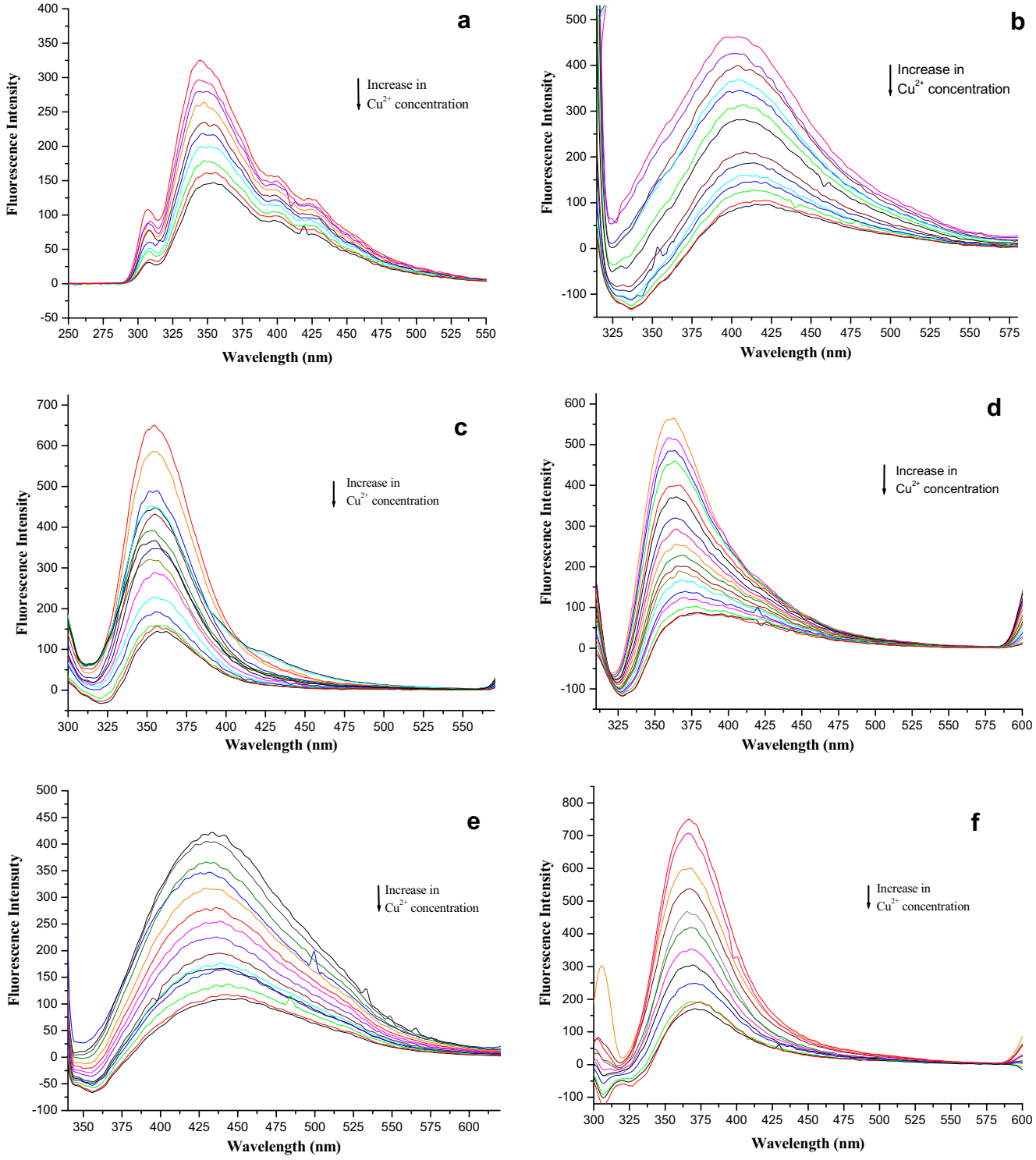


Figure 3. Quenching spectral response of silatranes **3a**–**3f** towards Cu^{2+} with red shift of 2–3 nm on addition of 5 equiv of CuCl soln. in MeOH.

gradually with a further increase in concentration. This decrease can be attributed to self quenching phenomenon in high concentrations of silatranes resulting from aggregation of the molecules. Further investigation of silatranes **3a**–**3f** to act as metal ion chemosensors was explored for Cu^{2+}, Ni^{2+}, Ag^{+} and Ru^{+} using their chloride salts and found to have remarkable sensing towards Cu^{2+}. The titration was performed using 100 μM solution of compounds **3a**–**3f** in MeOH with 5 equiv of Cu^{2+} (Fig. 3). On addition of $CuCl_2$, a strong and efficient quenching resulted into red shift of 2–3 nm for all silatranes **3a**–**3f**. The quenching in fluorescence spectra was due to the binding of Cu^{2+} with –N– of aniline and the triazole ring.[22] This unique behaviour of all silatranes **3a**–**3f** makes them different in the class of fluorescent Cu^{2+} chemosensors.

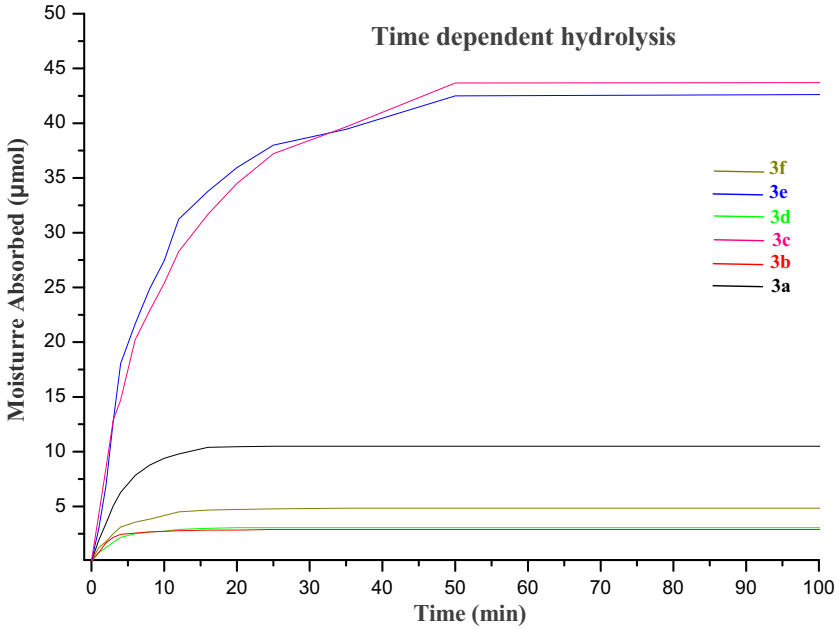


Figure 4. Rate of hydrolysis plotted as moisture absorbed in µmols for silatranes **3a**–**3f** against time; mols of water absorbed = (W2−W1)/18; where W1 is initial weight of sample at the beginning and W2 is final weight of sample.

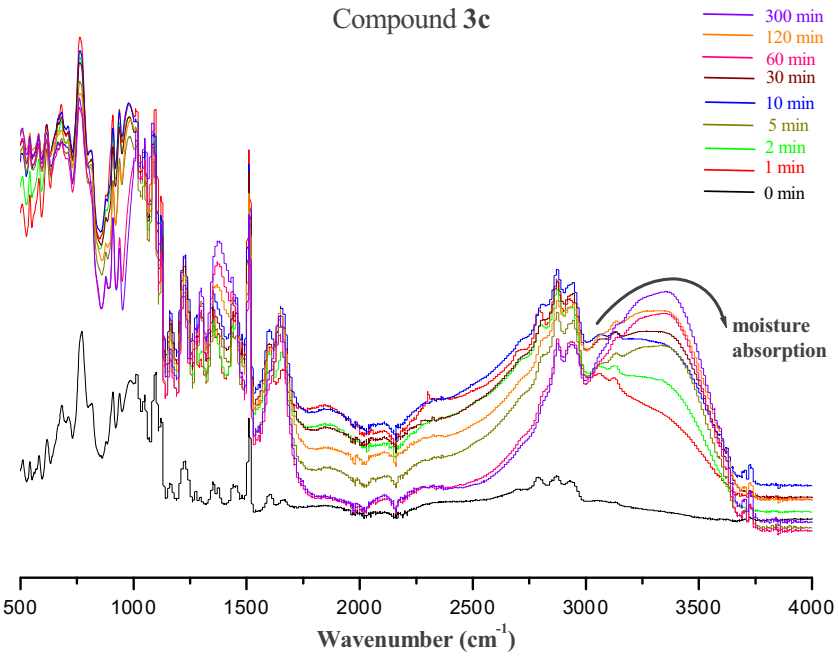


Figure 5. Hydrolysis behaviour of hydrolysed silatrane **3c** as monitored by IR spectroscopy with time.

Thermal behaviour

Compounds **3a**–**3f** were subjected to elevated temperature for response to thermal stability and investigation of temperature dependent decomposition pattern. TGA/DTA/DSC curves follow a vivid pattern for every different compound thereby indicating unique behaviour of silatranes at the molecular level of packing. TGA/DTA studies reveal a uniformity in pattern of decomposition in the temperature range of 320–400 °C for all the silatranes synthesized but the disintegration temperature varies for different silatranes. The thermal transformations for compounds **3a**–**3f** begins at lower temperature and show major decomposition at near 400 °C. DSC curves also followed the similar pathway for phase changes in all silatranes **3a**–**3f**. The onset for transition started at near 70–100 °C and then it varied randomly for different silatranes thereby proving distinguished behaviour of silatranes with change in aromatic substituent moiety.

Hydrolytic stability study

The hydrolytic stability of compounds **3a**–**3f** was studied under normal atmospheric conditions. It was found that **3c** and **3e** hydrolysed rapidly within few minutes on exposure to air, while **3a** gained moisture to a little extent and **3b**, **3d** and **3f** resisted moisture attack. This gain of water molecules from atmospheric air with time was studied and plotted to observe the amount of water ab-

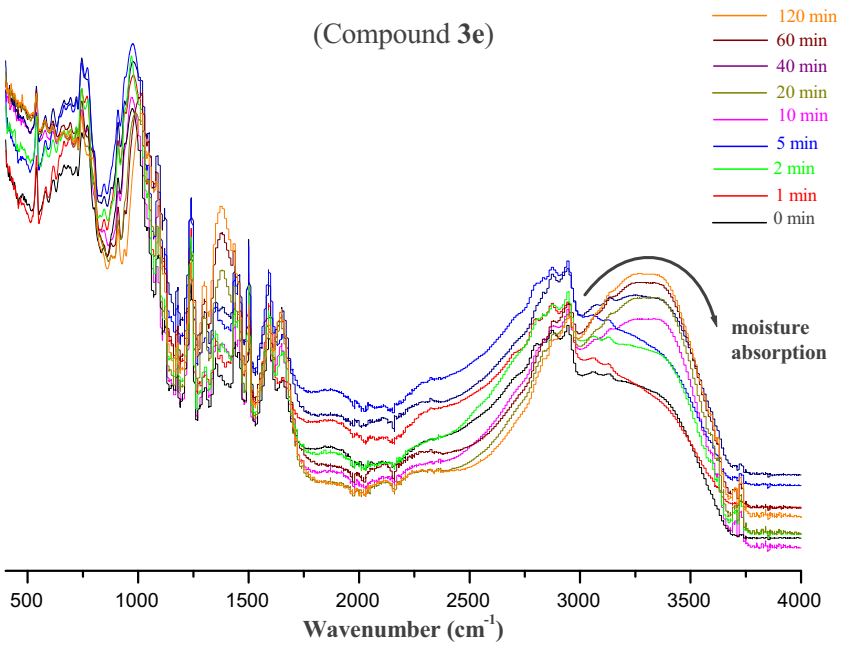
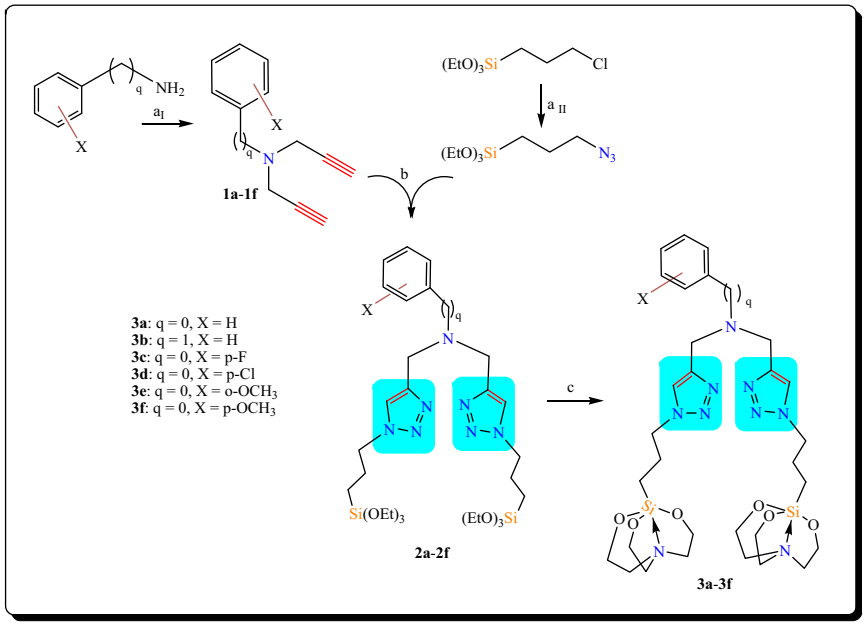


Figure 6. Hydrolysis behaviour of hydrolysed silatrane **3e** as monitored by IR spectroscopy with time.



Scheme 1. Synthesis of silatranes **3a**–**3f**. Schematic synthetic elaboration[a]: [a]Reagents and conditions: (**a$_I$**) propargyl bromide (1.3 equiv/aniline derivative), K_2CO_3 (5 equiv/aniline derivative), DMF, 16 h. (**a$_{II}$**) ClPTES (1.0 equiv), sodium azide (5 equiv/ClPTES), DMF, 4 h, 80 °C; (**b**) AzPTES (2 equiv/**1a**–**1f**), $Cu(PPh_3)_3Br$ (0.01 equiv), Et_3N (3 equiv/**1a**–**1f**), THF (3 equiv/**1a**–**1f**), 10 h, 60 °C; (**c**) triethanolamine (2 equiv/**2a**–**2f**), KOH (cat. amt.), toluene, 111 °C, 12 h.

sorbed. For this study, 2 mg of each compound **3a**–**3f** was taken on a dry aluminium lid under inert atmosphere, spread uniformly and exposed under atmospheric conditions. It was observed that silatranes **3a**, **3c** and **3e** gained 10, 44 and 43 μmols of water as moisture respectively. The plot of μmols of water absorbed versus time becomes a constant curve after 100 min (Fig. 4). Further, it was evident from these studies that the percentage moisture gain was dependent on surface area of sample exposed per given mass of sample and relative humidity of air under which experiment was carried out.

This fact was well proven and supported by the Infrared Spectroscopy technique which clearly indicated water gain with time. IR spectra of hydrolysed silatranes **3c** (Fig. 5) and **3e** (Fig. 6) with time provide additional information regarding stability of silatrane cage towards hydrolysis by the core existence of transannular N → Si bond which is clearly marked by the sharp and intense absorption bands in the region of 700–500 cm^{-1}. Moreover, to our surprise only **3c** and **3e** gained sufficient moisture to become jelly like material and insoluble in all organic solvents. The plausible explanation for this observation can be the tendency of compounds **3c** and **3e** to form extensive intermolecular hydrogen bonding with –F and *ortho* $-OCH_3$ on interaction with water molecules while others lack this ability and hence are inert to these conditions. Therefore, the presence of inert atmosphere was

mandatory to preserve the compounds **3a**, **3c** and **3e** to explore its further reactivity.[23]

We have successfully synthesized and characterized bis (1,2,3-triazolyl-γ-propylsilatranes) **3a**–**3f** via CuAAC reaction. The fluorescent activity and efficient ratiometric sensing of Cu^{2+} ions by these bis-silatranes are reported for the first time, to the best of our knowledge. On exploration for the sensitivity of silatranes **3a**–**3f** towards moisture, **3b**, **3d** and **3f** were found to be resistant towards hydrolysis whereas **3b** was moderately hydrolysed. The effects of positional isomers and electronegative atoms on fluorescence quenching and hydrolytic ability proved the variability of this reaction in diverse environments (Scheme 1).

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.03.043.

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21. *General procedure for the synthesis of bis(1,2,3-triazolyl-γ-propylsilatranyl) complexes (**3a**–**3f**)*: To a uniformly stirred solution of triethanolamine (2 equiv) and potassium hydroxide (cat. amt.) in toluene, was slowly added di-substituted triethoxysilanes **2a–2f** dropwise within 2 min. The mixture was refluxed at 111 °C for 12 h and allowed to cool at room temperature. The volume of solvent mixture was reduced to 2 ml by vacuum evaporation and on addition of 10 ml of *n*-pentane, dull white coloured solid separated out. The solid so obtained was stirred for 2 h, filtered and washed with 2 × 5 ml *n*-pentane to afford silatranes **3a**–**3f**.
3a: *N,N*-Bis((1-(3-(2,8,9-trioxa-5-aza-1-silatranyl)propyl)-1*H*-1,2,3-triazol-4-yl)methyl)benzenamine. A procedure as above was used. The quantities used were as follows: **2a** (1.0 g, 1.51 mmol), triethanolamine (0.45 g, 3.01 mmol) and toluene (50 ml). Yield: 85% (0.88 g, 1.28 mmol). Mp = 156 °C. IR (neat): 2928, 2872, 1667, 1597, 1505, 1453, 1350, 1275, 1211, 1171, 1121, 1085, 1047, 1013, 909, 750, 691, 615, 580 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35 (s, 2H), 7.10 (dd, *J* = 15.1, 7.8 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.62 (dd, *J* = 15.0, 7.8 Hz, 1H), 4.57 (s, 4H), 4.26–4.04 (m, 4H), 3.67 (t, *J* = 5.8 Hz, 12H), 2.74 (t, *J* = 5.8 Hz, 12H), 1.91–1.80 (m, 4H), 0.38–0.17 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 147.25, 143.64, 128.18, 127.34, 121.10, 116.30, 112.43, 56.28, 52.11, 49.69, 45.38, 25.33, 12.16. Empirical formula: $C_{30}H_{47}N_9O_6Si_2$: MS (EI) *m*/*z* 710 (16), 709 (46), 708 (100), 686 (47), 475 (16), 371 (18), 362 (33), 172 (14), 150 (26), 132 (11), 105 (17). HRMS (ES^+) Calcd for $[M+Na]^+$ 708.3086; Found 708.3068. Anal. Calcd: C, 52.5; H, 6.9; N, 18.4; Found: C, 52.5; H, 7.0; N, 18.5.
3b: *N,N*-Bis((1-(3-(2,8,9-trioxa-5-aza-1-silatranyl)propyl)-1*H*-1,2,3-triazol-4-yl)methyl)(phenyl)methanamine. A procedure as above was used. The quantities used were as follows: **2b** (1.0 g, 1.48 mmol), triethanolamine (0.44 g, 2.95 mmol) and toluene (50 ml). Yield: 82% (0.85 g, 1.21 mmol). Mp >200 °C. IR (neat): 2966, 2926, 2868, 1654, 1599, 1493, 1452, 1373, 1343, 1152, 1107, 1048, 963, 879, 741, 698, 544 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52 (s, 2H), 7.27 (dd, *J* = 15.9, 8.0 Hz, 4H), 7.17–7.12 (m, 1H), 4.29–4.15 (m, 4H), 3.72–3.64 (m, 12H), 3.63–3.47 (m, 6H), 2.74 (t, *J* = 5.8 Hz, 12H), 1.99–1.79 (m, 4H), 0.42–0.26 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 144.11, 139.21, 129.02, 128.23, 126.85, 122.93, 59.21, 57.43, 56.79, 53.14, 50.85, 47.52, 26.28, 13.05. Empirical formula: $C_{31}H_{49}N_9O_6Si_2$: MS (EI) *m*/*z* 722 (22), 701 (38), 700 (76), 475 (20), 443 (24), 442 (100), 301 (31), 279 (14), 102 (5). HRMS (ES^+) Calcd for $[M+H]^+$ 700.3422; Found 722.3404. Anal. Calcd: C, 53.2; H, 7.1; N, 18.0; Found: C, 53.3; H, 7.0; N, 18.1.
3c: *N,N*-Bis((1-(3-(2,8,9-trioxa-5-aza-1-silatranyl)propyl)-1*H*-1,2,3-triazol-4-yl)methyl)(4-fluorophenyl)methanamine. A procedure as above was used. The quantities used were as follows: **2c** (1.0 g, 1.47 mmol), triethanolamine (0.44 g, 2.94 mmol) and toluene (50 ml). Yield: 89% (0.92 g, 1.31 mmol). Mp = 182 °C. IR (neat): 2946, 2871, 2799, 1670, 1603, 1509, 1442, 1352, 1227, 1096, 983, 904, 766, 683, 542 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ = 7.26 (s, 2H), 6.85–6.71 (m, 4H), 4.50 (s, 4H), 4.18 (t, *J* = 7.5 Hz, 4H), 3.64 (t, *J* = 5.8 Hz, 12H), 2.71 (t, *J* = 7.7 Hz, 12H), 1.93–1.70 (m, 4H), 0.34–0.14 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 128.38, 122.03, 115.68, 115.59, 77.12, 57.55, 52.96, 51.13, 26.08, 12.61. Empirical formula: $C_{30}H_{46}N_9O_6Si_2F$: MS (EI) *m*/*z* 742 (22), 727 (45), 726 (100), 704 (37), 701 (16), 475 (31), 380 (12), 371 (22), 360 (10), 301 (17), 172 (9), 150 (76), 105 (29). HRMS (ES^+) Calcd for $[M+Na]^+$ 726.2991; Found 726.3004. Anal. Calcd: C, 51.2; H, 6.6; N, 17.9; Found: C, 51.1; H, 6.7; N, 18.0.
3d: *N,N*-Bis((1-(3-(2,8,9-trioxa-5-aza-1-silatranyl)propyl)-1*H*-1,2,3-triazol-4-yl)methyl)(4-chlorophenyl)methanamine. A procedure as above was used. The quantities used were as follows: **2d** (1.0 g, 1.43 mmol), triethanolamine (0.43 g, 2.87 mmol) and toluene (50 ml). Yield: 86% (0.89 g, 1.23 mmol). Mp >230 °C. IR (neat): 3130, 2923, 2873, 1596, 1498, 1453, 1352, 1276, 1213, 1121, 1095, 1048, 1014, 909, 876, 762, 681, 615, 580, 542 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 7.99 (s, 2H), 7.27–7.21 (m, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 4.75 (s, 4H), 4.33 (t, *J* = 7.3 Hz, 4H), 3.77 (t, *J* = 5.8 Hz, 12H), 2.95 (t, *J* = 5.7 Hz, 12H), 1.98–1.89 (m, 4H), 0.33–0.24 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C): δ = 147.18, 146.65, 143.65, 128.17, 122.55, 114.24, 113.57, 56.63, 52.64, 49.96, 45.69, 26.54, 18.07, 13.85. Empirical formula: $C_{30}H_{46}N_9O_6Si_2Cl$: MS (EI) *m*/*z* 745 (14), 743 (43), 742 (100), 731 (37), 720 (34), 709 (10), 462 (22), 446 (62), 444 (33), 424 (25), 379 (31), 360 (12), 301 (15), 192 (12), 174 (21), 172 (3), 105 (15). HRMS (ES^+) Calcd for $[M+Na]^+$ 742.2696; Found 742.2669. Anal. Calcd: C, 50.2; H, 6.4; N, 17.5; Found: C, 50.2; H, 6.4; N, 17.3.
3e: *N,N*-Bis((1-(3-(2,8,9-trioxa-5-aza-1-silatranyl)propyl)-1*H*-1,2,3-triazol-4-yl)methyl)-2-methoxybenzenamine. A procedure as above was used. The quantities used were as follows: **2e** (1.0 g, 1.44 mmol), triethanolamine (0.43 g, 2.88 mmol) and toluene (50 ml). Yield: 83% (0.86 g, 1.20 mmol). Mp = 163 °C. IR (neat): 2941, 2872, 2799, 1592, 1499, 1437, 1351, 1239, 1177, 1096, 984, 909, 745, 617, 583, 540 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.63–7.53 (m, 2H), 7.43–7.36 (m, 2H), 7.33 (s, 2H), 4.28 (s, 4H), 4.17 (t, *J* = 9.1 Hz, 4H), 3.82 (s, 3H), 3.66 (t, *J* = 5.8 Hz, 12H), 2.71 (t, *J* = 5.8 Hz, 12H), 1.92–1.75 (m, 4H), 0.39–0.15 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6, 25 °C): δ = 142.78, 130.81, 127.81, 122.40, 58.38, 56.45, 56.10, 51.90, 49.47, 38.97, 25.89, 12.93. Empirical formula: $C_{31}H_{49}N_9O_7Si_2$: MS (EI) *m*/*z* 754 (19), 739 (46), 738 (100), 716 (34),

701 (13), 496 (14), 480 (32), 458 (25), 386 (13), 301 (36), 279 (17), 172 (33), 150 (76), 132 (30), 105 (26). HRMS (ES^+) Calcd for $[M+Na]^+$ 738.3191; Found 738.3178. Anal. Calcd: C, 52.0; H, 6.9; N, 17.6; Found: C, 51.9; H, 7.0; N, 17.5. ***3f***: *N*,*N*-Bis((1-(3-(2,8,9-trioxa-5-aza-1-silatranyl)propyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-methoxybenzenamine. A procedure as above was used. The quantities used were as follows: **2f** (1.0 g, 1.44 mmol), triethanolamine (0.43 g, 2.88 mmol) and toluene (50 ml). Yield: 78% (0.80 g, 1.13 mmol). Mp = 109 °C. IR (neat): 2923, 2873, 1654, 1511, 1481, 1454, 1352, 1240, 1121, 1093, 1049, 1015, 937, 909, 877, 759, 616, 580 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.19 (s, 2H), 7.05 (d, J = 7.5 Hz, 2H), 6.74 (d, J = 9.0 Hz, 1H), 6.52 (d, J = 8.8 Hz, 1H), 4.56 (s, 4H), 4.25–4.13 (m, 4H), 3.70 (s, 3H), 3.67 (t, J = 5.8 Hz, 12H), 2.73 (t, J = 4.2 Hz, 12H), 1.92–1.80 (m, 4H), 0.38–0.17 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 142.78, 130.81, 127.81, 127.44, 122.27, 58.38, 56.45, 56.10, 49.47, 26.92, 17.68, 12.85. Empirical formula: $C_{31}H_{49}N_9O_7Si_2$: MS (EI) m/z 740 (16), 739 (44), 738 (100), 716 (61), 701 (13), 475 (24), 386 (20), 378 (25), 377 (51), 370 (36), 360 (11), 301 (7), 192 (8), 175 (13), 105 (28). HRMS (ES^+) Calcd for $[M+Na]^+$ 738.3191; Found 738.3207. Anal. Calcd: C, 52.0; H, 6.9; N, 17.6; Found: C, 52.0; H, 7.0; N, 17.7.

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