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Development of new precursors for immobilizing dyes onto silica surfaces Ruchi Mutneja^a, Raghubir Singh^{b*}, Varinder Kaur^{a*}, Jörg Wagler^c and Edwin Kroke^c

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Abstract

A series of new precursors for immobilization of dyes onto silica surface have been synthesized and characterized. Diazobenzene-derived dyes were synthesized by coupling salicylaldehyde and a diazotized aniline derivative. Condensation of the resultant carbaldehyde functionalized dyes with 3-aminopropylsilatrane afforded diazo-azomethine functionalized compounds containing silatranyl moiety, which were characterized using spectroscopic techniques, elemental analysis and single-crystal X-ray diffraction. Substituent dependent variation in electronic properties of silatranyl dyes was studied and the capability of immobilization of silatranyl substituted dyes was tested by synthesizing silica nanoparticles coated with immobilized dye. The derivatization of silica was confirmed by spectrophotometric, thermogravimetric and microscopic studies. The functionalized silica exhibit uniformly dispersed spherical particles of 170 nm diameter with an estimated approximate 8 nm coating of dye. As the silatranyl substituted dyes can be isolated in crystalline forms, they proved to be better precursors for immobilization in terms of purity and uniform distribution onto silica surfaces. The modified silica surfaces possess binding sites for capturing copper ions.

Key words

Diazobenzene-derived dyes, silica nanoparticles, 3-aminopropylsilatrane, silatranyl, silatranes

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Introduction

Azo dyes have received much attention because of their wide application in the field of dyeing textile fibre, biomedical studies, advanced application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devices and ink-jet printers etc. [1-4]. Silica supported dyes have been utilized for catalytic purposes, dye sensitized solar cells [5,6] and biomedical purposes [7]. Dyes immobilized on silica surface enhance the stability of pigments and reduce their toxicity in printer's ink [8,9]. In addition, dye functionalized silanes have been proved better linkers for dye sensitized solar cells [10,11]. Keeping in mind the importance of dye immobilized on silica surfaces, an attempt is made to develop some new precursors for immobilization of dyes on silica surfaces.

The primary requirement for immobilization of a desired functionality onto silica surface is an adequate precursor with capability of controlled hydrolysis and condensation. Generally, alkyltrialkoxysilanes with suitable functionality had been utilized as precursors for the modification of silica surfaces [12-22]. In the previous reports, two main strategies have been described for the functionalization of silica: 1) derivatization of precursor to introduce the desired functionality followed by immobilization onto silica surface, or 2) by immobilizing precursor onto silica surface followed by derivatization to link the desired functionality with the precursor [23,24]. An illustration for the modification of silica via strategies 1) and 2) is given in Scheme 1. Functionalization via both strategies may lead to heterogeneous distribution of functional sites on silica surface. In the first strategy, this problem may be associated with difficulties to isolate the derivatized alkyltrialkoxysilanes (which contain bulky groups) in pure form. These compounds are generally oils and can be purified by vacuum distillation at higher temperature, which may lead to partial decomposition of attached functionalities. Hence, use of precursors without purification may lead to non-uniform distribution of functionalities due to the presence of impurities. In the second strategy, when precursors are immobilized in pure form followed by derivatization with suitable reagent, silica with mixed functionalities is achieved due to incomplete derivatization of the parent functional group immobilized on silica. Generally, 3aminopropyltriethoxysilane is used as a precursor for developing functionalized silica surfaces and allows for wide applications in the field of catalysis and metal ion sensing [25-27].

Moreover, polymerization of alkyltrialkoxysilanes is relatively fast as they are very susceptible to hydrolysis, so it is difficult to get desired thickness and morphology of coatings. Thus, it is interesting to use silatranyl group as an organosilicate precursor, because silatrane Si–O bonds are more stable towards hydrolysis as compared to those in related triethoxysilanes [28]. Therefore, silatranyl derivatives may be useful synthons to generate dye functionalized silica surfaces. Previously we reported some silatranyl derivatives with useful functionalities [29-32]. In the present work, silatranyl moiety is introduced into different dyes to develop new precursors for the development of dye functionalized silica. Syntheses of the silatranyl derivatives of the dyes were explored via azomethine bond formation between dye and 3-aminopropylsilatrane. One of the silatranyl derivatives of dyes was further tested for the development of dye functionalized silica nanoparticles.

2. Experimental

2.1. Materials

All the solvents were purchased commercially, dried before use and stored under nitrogen atmosphere. Salicylaldehyde (Acros), p-anisidine (Acros), 2-methylaniline (Sd-fine), aniline (Merck), 4-methylaniline (Sd-fine), 4-ethylaniline (Acros), sodium carbonate (Merck), sodium nitrite (Qualigens), 3-aminopropyl(triethoxy)silane (Aldrich) and triethanolamine (Merck) were used as suc h without any purification. 3-aminopropylsilatrane was synthesized from 3-aminopropyltriethoxysilane and triethanolamine as reported in literature [29].

2.2 Physical measurements

Infrared spectra were routinely obtained on Thermo scientific NICOLET IS50 FT-IR and Perkin Elmer RX-I FT IR Spectrophotometer. Mass spectral measurements (ESI source with capillary voltage 2500 V) were carried out on a VG Analytical (70-S) spectrometer. C, H, N elemental microanalyses were obtained on a FLASH-2000 organic elemental analyzer. The solution NMR spectra were recorded at 25°C on a Bruker Avance II FT NMR (AL 400 MHz) spectrometer (¹H, ¹³C). Chemical shifts in ppm are reported relative to tetramethylsilane (TMS). Single-crystal X-ray structure analyses were carried out on a Stoe IPDS-2T diffractometer using Mo K α -radiation (λ = 0.71073 Å). The structures were solved

by direct methods (SHELXS-97) and refined with full-matrix least-squares method (refinement of F^2 against all reflections with SHELXL-97). Electronic spectral measurements were carried out using JASCO V-530 double beam spectrophotometer in the range 250-600 nm. The morphology and size of silica nanoparticles was investigated by using transmission electron microscopy (TEM) at 80 kV (Hitachi H-7500).

2.3 Synthesis of Azo dyes

Azo dyes were synthesized according to a well known method reported in literature [33]. That is, aniline or its derivatives (25.0 mmol) were dissolved in conc. hydrochloric acid (6.0 mL) and heated to form a clear solution. Upon cooling the solution in an ice/NaCl bath a solution of sodium nitrite (28.0 mmol) in water (10 mL) was added drop-wise keeping the temperature of the reaction mixture in the range 0-5 °C. The contents were stirred for 30 min at 0 °C followed by the drop-wise addition of salicylaldehyde (25.0 mmol). Sodium carbonate (9.0 g) dissolved in water (75 mL) was added to the resulting mixture and stirred for 2 h at 0-5 °C. The orange precipitate thus formed was filtered and recrystallized from ethanol.

2.3.1 2-Hydroxy-5-phenylazobenzaldehyde (1a)

Yield: 73%. M.p.: 120-125 °C. IR (cm⁻¹): 1568 v (-N=N-), 1637 v (C=O), 3186 v (O-H). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.05 (d, 1H¹¹), 7.40 (t, 2H^{3,5}), 7.46 (tt, 1H⁴), 7.81 (dd, 2H^{2,6}), 8.08 (dd, 1H¹²), 8.11(d, 1H⁸), 9.97 (s, 1H, CHO), 11.21 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 118.5 (C³), 120.3 (C^{8,12}), 122.7 (C¹), 122.8 (C⁴), 129.0 (C⁶), 129.2 (C^{9,11}), 130.6 (C¹⁰), 145.8 (C⁵), 152.3 (C⁷), 162.3 (C²), 196.5 (CHO).

2.3.2 2-Hydroxy-5-p-tolylazobenzaldehyde (1b)

Yield: 71%. M.p.: 155-160 °C. IR (cm⁻¹): 1567 v (-N=N-), 1646 v (C=O), 3325 v (O-H). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 2.09 (s, 3H, Ar–CH₃), 6.81 (d, 1H¹¹), 7.28 (d, 2H^{3,5}), 7.69 (dd, 2H^{2,6}), 7.72 (dd, 1H¹²), 8.06 (d, 1H⁸), 9.95 (s, 1H, CHO), 11.07 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 120.5 (C³), 122.3 (C^{8,12}), 126.7 (C¹), 128.3 (C⁶), 129.55 (C^{9,11}), 129.63 (C⁴), 140.2 (C¹⁰), 143.5 (C⁵), 150.8 (C⁷), 164.1(C²), 195.6 (CHO).

2.3.3 5-(4-Ethylphenylazo)-2-hydroxybenzaldehyde (1c)

Yield: 75%. M.p.: 120-122 °C. IR (cm⁻¹): 1578 v (-N=N-), 1656 v (C=O), 3182 v (O-H). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 1.25 (t, 3H, Ar–CCH₃), 2.67 (q, 2H, Ar–CH₂C), 7.01 (d, 1H¹¹), 7.23 (d, 2H^{3,5}), 7.72 (d, 2H^{2,6}), 8.0 (dd, 1H¹²), 8.11 (d, 1H⁸), 9.96 (s, 1H, CHO), 11.19 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 120.5 (C³), 122.3 (C^{8,12}), 122.9 (C¹), 128.6 (C⁶), 129.0 (C^{9,11}), 129.1 (C⁴), 146.0 (C¹⁰), 147.9 (C⁵), 150.6 (C⁷), 164.8 (C²), 196.6 (CHO).

2.3.4 2-Hydroxy-5-(4-methoxyphenylazo)benzaldehyde (1d)

Yield: 71%. M.p.: 125-128 °C. IR (cm⁻¹): 1597 v (-N=N-), 1655 v (C=O), 3785 v (O-H), ¹H NMR (CDCl₃, 300 MHz, ppm): δ 3.83 (s, 3H, OCH₃), 6.91(d, 1H¹¹), 7.00 (d, 2H^{3,5}), 7.79 (d, 2H^{2,6}), 7.77 (dd, 1H¹²), 8.06 (d, 1H⁸), 9.96 (s, 1H, CHO), 11.15 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 114.5 (C^{8,12}), 118.4 (C³), 120.3 (C¹), 124.7 (C^{9,11}), 128.7 (C⁶), 130.5 (C⁴), 145.9 (C⁵), 146.6 (C⁷), 162.1 (C¹⁰), 163.2 (C²), 196.60 (CHO).

2.3.5 2-Hydroxy-5-o-tolylazobenzaldehyde (1e)

Yield: 76%. M.p.: 120-123 °C. IR (cm⁻¹): 1580 v (-N=N-), 1651 v (C=O), 3300 v (O-H). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 2.66 (s, 3H, Ar-CH₃), 7.01 (d, 1H¹¹), 7.18 - 7.24 (m, 3H^{3,4,5}), 7.79 (d, 1H⁶), 8.05 (dd, 1H¹²), 8.08 (d, 1H⁸), 9.97 (s, 1H, CHO), 11.20 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 119.8 (C³), 136.0 (C^{8,12}), 125.6 (C¹), 128.46 (C⁶), 130.8 (C^{9,11}), 129.5 (C⁴), 137.8 (C¹⁰), 144.7 (C⁵), 151.3 (C⁷), 168.1 (C²), 195.3 (CHO).

2.4 Linking silatranyl moiety with dyes

3-Aminopropylsilatrane (2.15 mmol, 0.50 g) in toluene (15 mL) was added to a single-neck round bottom flask fitted with Dean-Stark trap. Azo dye (2.01 mmol) dissolved in toluene was added to 3-aminopropylsilatrane drop-wise using a syringe. The contents were refluxed and water produced during the reaction was removed by azeotropic distillation with toluene. The contents were cooled to room temperature and toluene was removed under vacuum to obtain a solid product. The orange solid was washed with diethyl ether, filtered and dried. Crystals for X-ray crystallography were obtained at room temperature in DCM/hexane mixture by slow evaporation method.

2.4.1 4-Phenylazo-2-{[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)propylimino]me thyl}-phenol (**2a**)

Yield 74%. M.p.:150-155 °C. Anal. Calcd for $C_{22}H_{32}N_4O_4Si$: C, 61.51; H, 6.88; N, 11.96; Found: C, 59.83; H, 6.63; N, 12.00. IR (cm⁻¹): 580 m (υ Si \leftarrow N), 717 s, 762 s (υ_s Si-O), 844 m, 877 w (υ C-N), 903 m (υ_s NC₃), 934 m (υ C-C), 986 w, 1021 s, (υ_{as} NC₃), 1098 vs (υ_{as} Si-O), 1128 vs (υ C-O), 1179 m (τ CH₂O), 1279 m (ω CH₂O), 1372 m, 1413 w (δ CH₃C), 1476 (υ C=C), 1568 (-N=N-), 1658 vs (υ C=N), 2876 s, 3039 (υ_s CH₂), 3186 b (N-H--O). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.36 (m, 2H, SiCH₂), 1.75 (m, 2H, CCH₂C), 2.71 (t, 6H, NCH₂C, J = 5.8 Hz), 3.54 (t, 2H, CCH₂N), 3.66 (t, 6H, OCH₂, J = 5.8 Hz), 6.48 (d, H¹¹), 7.00-7.38 (m, 3H^{3.4,5}), 7.40 (dd, 2H^{2.6}), 7.51 (dd, 1H¹²), 7.52 (d, 1H⁸), 7.91 (s, 1H, N=CH), 13.90 (s, 1H, OH), ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 13.32 (SiCH₂), 26.48 (CCH₂C), 51.36 (CCH₂N), 57.84 (NCH₂), 60.73 (OCH₂), 120.5 (C³), 122.4 (C¹), 122.8 (C⁸), 128.2 (C¹²), 129.0 (C⁶), 129.1 (C⁴), 130.1 (C⁹) 130.2 (C¹¹), 131.1 (C¹⁰), 143.8 (C⁵), 152.7 (C⁷), 164.7 (C=N), 165.9 (C²). MS (\vee relative abundance of m/z assignment): 174 (16.8, N(CH₂CH₂O)₃Si)⁺, 233.2 {8.07, N(OCH₂CH₂)₃Si(CH₂)₃NH₃⁺}, 441.2 (100, M + H)⁺, 463.4 (6.60, M + Na)⁺, 464.2 (8.81, M + H + Na)⁺.

2.4.2 4-p-Tolylazo-2-{[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)propylimino]met hyl}phenol (**2b**)

Yield: 77%. M.p.:125-128°C. Anal. Calcd for C₂₃H₃₀N₄O₄Si: C, 60.77; H, 6.65; N, 12.32; Found: C, 58.67; H, 6.43; N, 12.49. IR (cm⁻¹): 582 m (v Si←N), 710 s, 768 s (v_s Si–O), 794 m, 866 w (v C–N), 910 m (v_s NC₃), 940 m (v C–C), 986 w, 1021 s, (v_{as} NC₃), 1088 vs (v_{as} Si– O), 1124 vs (υ C–O), 1176 m (τ CH₂O), 1225 m (ω CH₂O), 1352 m, 1413 w (δ CH₃C), 1481 (v C=C), 1580 (-N=N-), 1630 vs (v C=N), 2876 s, 2962 (v_s CH₂), 3325 b (N-H---O). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.36 (m, 2H, SiCH₂), 1.74 (m, 2H, CCH₂C), 2.35 (s, 3H, Ar-CH₃), 2.69 (t, 6H, NCH₂C, J = 5.7), 3.53 (t, 2H, CCH₂N), 3.65 (t, 6H, OCH₂, J = 5.7 Hz), 6.98 (d, 1H¹¹), 7.30 (d, 2H^{3,5}), 7.72 (dd, 2H^{2,6}), 7.92 (dd, 1H¹²), 7.98 (d, 1H⁸), 8.27 (s, 1H, N=CH), 14.45 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 13.30 (SiCH₂), 21.60 (Ar-CH₃), 26.48 (CCH₂C), 51.32 (CCH₂N), 57.79 (NCH₂), 60.99 (OCH₂), 116.1 (C³), 119.3 (C¹), 122.6 (C⁸, C¹²), 126.7 (C⁶), 128.3 (C⁴), 129.6 (C^{9,11}), 139.9 (C¹⁰), 144.2 (C⁵), 150.9 (C⁷), 163.9 (N=CH), 168.04 (C²). MS (% relative abundance of m/z assignment): 174 (15.5, $N(CH_2CH_2O)_3Si)^+),$ 192 {3.75, $N(CH_2CH_2O)_3Si)^+$ + NH_3 233 {4.89, $N(CH_2CH_2O)_3Si(CH_2)_3NH_3^+$, 455.1 (100, M + H)⁺, 478.1 (5.83, M + Na)⁺.

2.4.3 *4-(4-Ethylphenylazo)-2-{[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)propyl imino]methyl}phenol(2c)*

Yield: 73%. M.p.:135-138°C. Anal. Calcd for $C_{24}H_{32}N_4O_4Si$: C, 61.51; H, 6.88; N, 11.96; Found: C, 62.70; H, 6.76; N, 10.92. IR (cm⁻¹): 585 m (υ Si \leftarrow N), 710 s, 762 s (υ_s Si \leftarrow O), 783 m, 866 w (υ C-N), 910 m (υ_s NC₃), 940 m (υ C-C), 986 w, 1021 s, (υ_{as} NC₃), 1088 vs (υ_{as} Si \leftarrow O), 1124 vs (υ C-O), 1176 m (τ CH₂O), 1225 m (ω CH₂O), 1352 m, 1413 w (δ CH₃C), 1439 (υ C=C), 1598 (-N=N-), 1634 vs (υ C=N), 2864 s, 2974 (υ_s CH₂), 3392 b (N-H--O). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.47 (m, 2H, SiCH₂), 1.27 (t, 3H, Ar–C=CH₃) 1.84 (m, 2H, CCH₂C), 2.71 (q, 2H, Ar–CH₂–C), 2.78 (t, 6H, NCH₂C, J = 4.35 Hz), 3.59 (t, 2H, CCH₂N), 3.75 (t, 6H, OCH₂, J = 4.35 Hz), 6.91 (d, 1H¹¹), 7.26 (d, 2H^{3.5}), 7.76 (d, 2H^{2.6}), 7.80 (dd, 1H¹²), 7.94 (d, 1H⁸), 8.25 (1H, N=CH), 14.60 (s, 1H, OH). ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 13.26 (SiCH₂), 15.73 (Ar–CH₂CH₃), 26.51 (CCH₂C), 28.9 (Ar-CH₂CH₃), 51.45 (CCH₂N), 57.90 (NCH₂), 61.39 (OCH₂), 116.3 (C³), 120.3 (C^{8,12}), 122.4 (C¹), 128.3 (C⁶), 128.4 (C⁴), 129.4 (C^{9,11}), 143.8 (C¹⁰), 146.7 (C⁷), 151.0 (C⁵), 163.2 (N=CH), 164.7 (C²), MS (% relative abundance of m/z assignment): 174 (17.22, N(CH₂CH₂O)₃Si)⁺), 233 {15.1, N(CH₂CH₂O)₃Si(CH₂)₃NH₃⁺}, 266.3 {4.59, Si(OCH₂CH₂)N(CH₂)₃N=CH + Na}, 469.4 (100, M + H)⁺, 491.5 (1.59, M + Na)⁺, 492.5 (0.49, M + H + Na)⁺.

2.4.4 4-(4-Methoxyphenylazo)-2-{[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)pro pyimino]methyl}phenol (**2d**)

Yield: 78%. M.p.:160-163°C. Anal. Calcd for $C_{23}H_{30}N_4O_5Si$: C, 58.70; H, 6.43; N, 11.91; Found: C, 56.25; H, 6.07; N, 10.55. IR (cm⁻¹): 586 m (υ Si \leftarrow N), 721 s, 771 s (υ _s Si-O), 840 m, 877 w (υ C-N), 908 m (υ _s NC₃), 937 m (υ C-C), 987 w, 1028 s, (υ _{as} NC₃), 1089 vs (υ _{as} Si-O), 1129.42 vs (υ C-O), 1181 m (τ CH₂O), 1225 m (ω CH₂O), 1352 m, 1413 w (δ CH₃C), 1461 (υ C=C), 1595 (-N=N-), 1628 vs (υ C=N), 2866 s, 2929 (υ _s CH₂), 3342 b (N-H---O). ¹H NMR (300 MHz, CDCl₃): δ (ppm); δ 0.35 (m, 2H, SiCH₂), 1.74 (m, 2H, CCH₂C), 2.69 (t, 6H, NCH₂C, J = 5.7 Hz), 3.53 (t, 2H, CCH₂N), 3.65 (t, 6H, OCH₂, J = 5.7 Hz), 3.80 (s, 3H, OCH₃), 6.84 (d, 1H¹¹), 7.23 (d, 2H^{3.5}), 7.75 (d, 2H^{2.6}), 7.79 (dd, 1H¹²), 7.82 (d, 1H⁸), 8.28 (N=CH), 11.15 (s, 1H, OH), ¹³C NMR (75.57 MHz, CDCl₃): δ (ppm) 13.34 (SiCH₂), 26.52 (CCH₂C), 51.32 (CCH₂N), 57.79 (NCH₂), 55.37 (Ar–OCH₃), 61.21 (OCH₂), 114.1 (C^{9,11}), 117.7 (C³), 119.1 (C¹), 124.3 (C^{8.12}), 126.5 (C⁴), 127.8 (C⁶), 163.9 (C¹⁰), 147.7 (C⁷), 144.8 (C⁵), 163.9 (N=CH), 167.41 (C²). MS (% relative abundance of m/z assignment):

150{3.47, NH(CH₂CH₂OH)₃}, 174 (10.68, N(CH₂CH₂O)₃Si)⁺), 233 {12.02, N(CH₂CH₂O)₃Si(CH₂)₃NH₃⁺}, 471.2 (100, M + H)⁺, 493.2 (3.83, M + Na)⁺.

2.4.5 4-o-Tolylazo-2-{[3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-yl)-propyliminome thyl}phenol (2e)

Yield: 80%. M.p.:125-128°C. Anal. Calcd for $C_{23}H_{30}N_4O_4Si: C, 60.77; H, 6.65; N, 12.32;$ Found: C, 59.12; H, 6.28; N, 11.77. IR (cm⁻¹): 583 m (υ Si \leftarrow N), 717 s, 762 s (υ_s Si-O), 835 m, 877 w (υ C-N), 904 m (υ_s NC₃), 934 m (υ C-C), 1013 w, 1052 s, (υ_as NC₃), 1098 vs (υ_as Si-O), 1128 vs (υ C-O), 1179 m (τ CH₂O), 1274 m (ω CH₂O), 1372 m, 1479 w (δ CH₃C), 1479 (υ C=C), 1590 (-N=N-), 1633 vs (υ C=N), 2863 s, 2925 (υ_s CH₂), 3300 b (N-H--O). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.37 (m, 2H, SiCH₂), 1.75 (m, 2H, CCH₂C), 2.63 (s, 3H, Ar–CH₃), 2.70 (t, 6H, NCH₂C, J = 5.7 Hz), 3.59 (t, 2H, CCH₂N), 3.75 (t, 6H, OCH₂, J = 5.7 Hz), 6.84 (d, 1H¹¹), 7.11 - 7.47 (m, 3H^{3,4,5}), 7.52 (d, 1H⁶), 7.83 (dd, 1H¹²), 7.86 (d, 1H⁸), 8.28 (N=CH), 14.20 (s, 1H, OH), ¹³C NMR (75.57 MHz, CDCl₃) δ (ppm) 13.36 (SiCH₂), 17.72 (Ar-CH₃), 26.51 (CCH₂C), 51.32 (CCH₂N), 57.83 (NCH₂), 60.68 (OCH₂), 115.5 (C³), 116.1 (C⁸), 117.3 (C¹), 119.7 (C⁶), 126.35 (C⁹), 126.4 (C¹¹), 126.5 (C⁴), 129.2 (C¹⁰), 129.9 (C¹²), 137.2 (C⁷), 131.1 (C⁵), 163.9 (N=CH), 168.75 (C²). MS (% relative abundance of m/z assignment): 174 {13.08, Si(OCH₂CH₂)₃N⁺}, 233.2 {61.95, N(CH₂CH₂O)₃Si(CH₂)₃NH₃⁺}, 455.2 (100, M + H)⁺, 477.2 (28.49, M + Na)⁺, 478.3 (7.62, M + H + Na)⁺.

2.5 Synthesis of dye coated silica nanoparticles (D-SNP)

Silatranyl functionalized dye compound **2d** was used to test immobilization onto silica surface using a modified Stöber method [34]. Dye functionalized silica nanoparticles (D-SNP) were prepared by stirring 1.5 mL of tetraethylorthosilicate and 3 mL of aqueous 25% ammonia solution in 45 mL of ethanol at room temperature. When the solution turned milky (after ca. 1 h), silatranyl functionalized dye (**2d**, 0.25 g, 5.3 mmol) was added to the above solution and stirred overnight. The particles formed were centrifuged and washed 4-5 times with anhydrous ethanol followed by washing with dichloromethane to remove physically adsorbed dye. In addition, silica nanoparticles (SNPs) without the addition of dye were prepared following same procedure but without adding dye compound (**2d**). The obtained silica particles (SNPs and D-SNPs) were characterized by IR, TEM and TGA analysis to confirm immobilization of dye onto silica surface.

2.6 Metal binding studies

Binding capability of D-SNPs for coordinating metal ions was studied by UV-Vis spectrophotometry. Two solutions containing 5 mL of copper(II) chloride solution (0.5 mmol L^{-1}) in methanol were stirred with 0.1 g of SNPs and D-SNPs in separate flasks for 30 min. The solutions were filtered and the absorbance of filtrate was recorded spectrophotometrically. It was compared with absorbance of 0.5 mmol L^{-1} copper(II) chloride solution.

3. Results and Discussion

3.1 Synthesis

Substituted anilines were diazotized with sodium nitrite in the presence of hydrochloric acid followed by coupling with salicylaldehyde to yield azo dyes (**1a-1e**). To introduce the active moiety for immobilization, azo dyes were reacted with 3-aminopropylsilatrane to form their silatranyl derivatives (**2a-2e**), which are diazo-azomethine dyes (Scheme 2). Compounds **2a-2e** were stable at room temperature and were isolated as solids, which were purified by recrystallization from a mixture of dichloromethane (DCM) and hexane. As a representative example, compound **2d** was utilized further for the development of dye functionalized silica nanoparticles using Stöber's method, which involves addition of silatranyl derivative of dye during the nucleation of silica nanoparticles.

Silatranyl derivatives of dyes offer advantages in the purification of dyes as well as immobilization via formation of Si-O bonds. Silatranyl moiety also acts as hydrolysis retarding agent, which regulates the hydrolysis and condensation processes very efficiently due to steric and chelate effects of the tricyclic cage. It also results in the formation of uniform coating onto silica surface. Apart from this, steric effects are observed when dyes are directly reacted with active silanol groups on silica surface, which retards the immobilization due to restriction of incoming molecules. Therefore, insertion of the propyl chain as a linking group between silica surface and dyes facilitates tethering of bulky dye molecules by reducing steric hindrance at the silica surface. The distribution of functionalities on the silica surface is also uniform as the precursor is modified before immobilization and isolated in pure form. In addition, Schiff base linkage in the modified surface extends the coordination sites and may act as active centre for extracting metal ions.

Azo-dye immobilization using precursor 2d is illustrated in Scheme 3. Herein, two types of silica nanoparticles were developed in the absence of 2d and in the presence of dye precursor using the same method to correlate the parameters. Dye functionalized silica nanoparticles were obtained by one pot synthesis following the Stöber Method. It involves the formation of silica nanoparticles with the simultaneous addition of 2d on the appearance of turbidity after nucleation of silica obtained by hydrolysis/condensation of TEOS. The –OH groups formed on the surface of silica nanoparticles react with silatranyl moiety to release ethanolamine, which also helps in the dispersion of particles. The modifier binds with silica surface through covalent bonding.

3.2 Characterization of silatranyl dyes

Both dyes **1a-1e** and their Schiff bases **2a-2e** exhibited broad bands in the IR region 3200-3400 cm⁻¹ and 1434-1495 cm⁻¹ due to OH stretching and N=N stretching vibration, respectively. Absence of C=O absorption and appearance of absorption band in the region of 1600-1620 cm⁻¹ indicates the formation of diazo-azomethine derivatives of dyes. NMR (¹H and ¹³C) spectra of silatranyl derivatives of dyes support the formulation of synthesized compounds. The characteristic peaks of silatranyl moieties appeared in the range of 2.69-2.78 and 3.65-3.75 ppm due to NCH₂ and OCH₂ groups, respectively. The mass spectra of diazo-azomethine compounds exhibited corresponding molecular ion peaks. Besides these peaks, all compounds show peaks at m/e 493.2, 478.1, 491.5, 477.2, 463.4 due to (M+Na)⁺. A most common fragmentation of silatranyl ring by the cleavage of Si-CH₂ bond caused a peak at m/e 174 and cleavage of azomethine linkage forms aminopropylsilatranyl cation observed at m/e 233 in all compounds.

3.2.1 X-Ray Crystallography

Molecular structures of compounds **2a-2e** are shown in Fig. **1-5** along with the atomic numbering scheme. X-ray crystallographic parameters, selected bond angles, and bond distances are given in Tables 1-2. In case of **2b-2d**, molecules are packed in such a way that long axial chains of two molecules approach towards each other but their dye scaffolds turned away producing antenna like projections. Packing in **2e** is found to be different as the molecules form a V-shaped structure in which dye part approach towards each other to form a cone while silatranyl rings form terminal ends of cone. These cones are further arranged antiparallel to each other in a lattice (Fig. S1- S4).

3.2.2 Thermogravimetric analysis

Thermogravimetric (TGA) curves of compounds **2a-2e** were recorded to study their thermal stability (Fig. 6). All the complexes were heated from 25 to 1000 °C. The compounds showed a similar pattern on heating due to loss of complete skeleton in the form of ethanol, methanol, nitrogen dioxide, carbon dioxide and water. The thermogravimetric curve for SNP and D-SNP are also shown, which revealed the immmobalization of dye on SNPs.

The tricyclic cage of silatranyl moiety may be lost as ethanol up to 250° C, which is clearly indicated on the TGA graph of each compound. The rest of the molecule is decomposed after crossing 300 °C with the evolution of common gases leaving only silica at the end. Silica nano particles with immobilized dye showed only 22% loss, which revealed the rest part of silica nanoparticles is composed of siloxane and remained unaffected even at 1000° C.

3.2.3 Electronic absorption Spectra

The electronic spectra of azo dyes (**1a-1e**) and their diazo-azomethine derivatives (**2a-2e**) were recorded in acetonitrile at room temperature (Fig. S5). Spectra of compounds **2a-2e** show absorption bands in the region 270-300 nm and 344-385 nm with a shoulder in the region 420-440 nm. The bands are broad, which is quite common in the systems having –OH group opposite to N=N and C=N in aromatic skeletons. Broadness of bands and appearance of shoulders in the spectra may be attributed to the formation of azo-hydrazone-enaminone tautomers, which exist in equilibrium in solution phase (Fig. S6). The UV-Visible spectra of diazo-azomethine derivatives show slight bathochromic shift in lower energy transition relative to corresponding azo dyes, which may be explained on the basis of extended conjugation system and intramolecular hydrogen bonding of C=N and OH group. Solvatochromism behavior of all dyes after the introduction of silatranyl moiety was studied, which revealed slight change in the electronic transitions with the variation in polarity of solvent used.

This indicates shifts in transitions are independent upon the polarity of solvent and variation in band is due to change in the equilibrium between three tautomers. All solvents except THF show high capability to accept the proton of OH-group and results in the formation of imino-hydrazone and azo-enaminone tautomers. Therefore, assignment of bands into π - π ^{*} transition in benzenoid system and π - π ^{*} transition in conjugated system (azo, azomethine and aryl rings) is difficult.

3.3 Characterization of silica nanoparticles functionalized with dyes

The FT-IR spectra of precipitated silica nanoparticles and dye coated silica nanoparticles are shown in **Fig. 7** Absorption peaks at 469, 801, 954 and 1099 cm⁻¹ correspond to the bending vibration, symmetric stretching vibration, asymmetric stretching vibration of Si-O-Si and bending vibration of Si-OH, respectively. The absorption bands at 1638 and 3428 cm⁻¹ correspond to bending and stretching vibration of OH. At the same time, the absorption bands at 1400 and 1501 cm⁻¹ correspond to the stretching vibration of diazo group, which demonstrates coating of dye onto silica surface.

TEM images of spherical and uniformly coated silica nanoparticles (SNPs) are shown in **Fig. 8**. The size of the silica nanoparticles prepared without the addition of modifier lies in the range of 160-170 nm. The average size of dye functionalized silica nanoparticles is calculated around 180 nm indicating the coating of modifier on the silica surface without affecting the size of particles to much extent. The images revealed smooth surface of silica after immobilization of dyes, which may be due to uniform distribution of modifier on silica surface. TEM images of SNPs after immobilization of diazo-azomethine dyes clearly indicate increased particle size, which is interpreted to be due to a uniform layer with an estimated thickness of ~8 nm coated on the surface of SNPs. The smoothness in coating is obtained due to silatranyl group as modifier because triethanolamine anions released during the hydrolysis prevents the formation of aggregates on silica surfaces. This particular advantage of silatranes for developing smooth surfaces has also been reported in AFM applications [35].

4. Metal binding studies

Dye coated silica nanoparticles (D-SNPs) carrying binding sites for metal ions may act as metal capturing surfaces. These binding sites are found to be capable of coordinating copper ions from the solution more efficiently relative to uncoated silica nanoparticles (SNPs). Both the SNPs and D-SNPs were stirred with copper(II) chloride solution to study the sorption of copper ions. After filtration, UV-Vis spectra of filtrates obtained from both solutions were recorded. The band with absorption maximum at 270 nm for copper chloride solution diminishes as it is stirred with D-SNPs whereas absorption remains same after stirring with SNPs. It clearly indicates high affinity of D-SNP for the sorption of copper due to the presence of diazo and azomethine moieties (**Fig. 9**).

5. Conclusion

Silatranyl moieties are introduced in azo dye structures by a simple and efficient method via azomethine linkage. The derivatization of dyes makes them immobilizable on silica surfaces directly through Si-O covalent bonding. Monodispersed, spherical silica nanoparticles can be isolated by one pot synthesis as suggested by Stöber. The method is highly efficient and results in the formation of smoothly coated silica nanoparticles. It may be attributed to direct interaction of dyes with silanol groups during the formation of silica nanoparticles. The long propyl chain in the modifier also helps in reducing the steric hindrance at silica surface, which may result from direct interaction with bulky dye substituents. The surfaces can be used for analytical and catalytic application due the presence of metal coordination sites.

Appendix A. Supplementary material

CCDC 968725-968729 contain the supplementary crystallographic data for **2a-2e**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

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References

[1] Catino SC, Farris E. Concise encyclopedia of chemical technology. New York: John Wiley & Sons; 1985.

[2] Venkataraman K. The chemistry of synthetic dyes. New York and London: Academic Press; 1970. [Chapter VI)].

[3] Egli R, Peter AP, Freeman HS. Colour chemistry: the design and synthesis of organic dyes and pigments. London: Elsevier; 1991. [Chapter VII)].

[4] Dincalp H, Yavuz S, Haklı O, Zafer C, Ozsoy C, Durucasu I, Icli S. Optical and photovoltaic properties of salicylaldimine-based azo ligands. J Photochem Photobiol A 2010;210:8-16.

[5] Serhan U, Mustafa D, Mehmet T. Synthesis and catalytic activities of silica-supported multifunctional azo-containing schiff base complexes with Cu(II), Co(II), Ni(II) and Mn(II). J Inorg Organomet Polym 2010;20:706-13.

[6] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells Chem Rev 2010;110:6595-663.

[7] Haynes CL, Lin YS. Hydrothermal process for enhanced stability of mesoporous silica nanoparticles. PCT Int Appl (2012), WO 2012051341 A1 20120419.

[8] Jesinowski T. Synthesis of organic–inorganic hybrids via adsorption of dye on an aminosilane-functionalised silica surface. Dyes pigm 2002;55:133-41.

[9] Cui Y, Qian G, Chen L, Wang Z, Gao J, Wang M. Enhanced thermal stability of dipole alignment in inorganic–organic hybrid films containing benzothiazole chromophore. J Phys Chem B 2006;110:4105-10.

[10] Brennan BJ, Keirstead AE, Liddell PA, Vail SA, Moore TA, Moore AL, Gust D. 1-(3-amino)propylsilatrane derivatives as covalent surface linkers to nanoparticulate metal oxide films for use in photoelectrochemical cells. Nanotechnology 2009;20:505203-13.

[11] Szpakolski K, Latham K, Rix C, Rani, RA, Zadeh KK. Silane: A new linker for chromophores in dye-sensitised solar cells. Polyhedron 2013;52:719-32.

[12] Bhunia S, Sen R, Koner S. Anchoring of palladium(II) in chemically modified mesoporous silica: An efficient heterogeneous catalyst for Suzuki cross-coupling reaction. Inorg Chim Acta 2010;363:3993-9.

[13] Baleizao C, Garcia H. Chiral salen complexes: An overview to recoverable and reuseable homogeneous and heterogeneous catalyst. Chem Rev 2006;106:3987-4043.

[14] Singha GU, Williams RT, Hallam KR, Allen GC. Exploring the distribution of copper– Schiff base complex covalently anchored onto the surface of mesoporous MCM 41 silica. J Solid State Chem 2005;178:3405-13.

[15] Binkowski S, Jesionowski T, Krysztafkiewicz A. Preparation of pigments on modified precipitated silicas. Dyes Pigm 2000;47:247-57.

[16] Seçkin T, Gültek A, Kartaca S. The grafting of Rhodamine B onto sol-gel derived mesoporous silicas. Dyes Pigm 2004;56:51-7.

[17] Jesionowski T, Pokora M, Tylus W, Dec A, Krysztafkiewicz A. Effect of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane surface modification and C.I. Acid Red 18 dye adsorption on physicochemical properties of silicas precipitated in an emulsion route, used as a pigment and filler in acrylic paints. Dyes Pigm 2003;57:29-41.

[18] Jesionowski T, Binkowski S, Krysztafkiewicz A. Adsorption of the selected organic dyes on the functionalized surface of precipitated silica via emulsion route. Dyes Pigm 2005;65:267-79.

[19] Jesionowski T, Przybylska A, Kurc B, Ciesielczyk F. The preparation of pigment composites by adsorption of C.I. Mordant Red 11 and 9-aminoacridine on both unmodified and aminosilane-grafted silica supports. Dyes Pigm 2011;88:116-24.

[20] Jesionowski T, Przybylska A, Kurc B, Ciesielczyk F. Hybrid pigments preparation via adsorption of C.I. Mordant Red 3 on both unmodified and aminosilane-functionalised silica supports. Dyes Pigm 2011;89:127-36.

[21] Piers AS, Rochester CH. Part 3. - Adsorption and coupling agents of bifunctional silanes on silica at solid/liquid interface. J Chem Soc Faraday Trans. 1995;91:1253-1260.

[22] Matsumoto A, Tsutsumi K, Schumacher K, Unger KK. Surface functionalization and stabilization of mesoporous silica spheres by silanization and their adsorption characteristics. Langmuir 2002;18:4014-19.

[23] Titinchi SJJ, Abbo HS. Salicylaldiminato chromium complex supported on chemically modified silica as highly active catalysts for the oxidation of cyclohexene. Catal Today 2013;204:114-24.

[24] Tang D, Zhang W, Zhang Y, Qiao ZA, Liu Y, Huo Q. Transition metal complexes on mesoporous silica nanoparticles as highly efficient catalyst for epoxidation of styrene. J Colloid and Interface Sci 2011;356:262-6.

[25] Modak A, Nandi M, Bhaumik A. Titanium containing periodic mesoporous organosilica as an efficient catalyst for the epoxidation of alkenes. Catal Today 2012; 198:45-51.

[26] Chena X, Yamaguchic A, Namekawaa M, Kamijoa T, Teramaea N, Tong A. Functionalization of mesoporous silica membrane with a Schiff base fluorophore for Cu(II) ion sensing. Anal Chim Acta 2011;696:94-100.

[27] Peng Y, Li Z, Zeng Y, Xie X, Wang H, Li L, Liu X. Solid phase extractors derived by functionalising sub-micro silica gel with chelating agents and their pH-tunable adsorbing capability towards Pb(II) and Ag(I). Michrochim Acta 2010;170:17-26.

[28] Puri J, Singh R, Chahal VK. Silatranes: a review on their synthesis, structure, reactivity and applications. Chem Soc Rev 2011;40:1791-840.

[29] Singh R, Puri JK, Sharma RP, Chahal VK, Sharma, RP, Venugopalan P. Synthesis and reactivity of novel 3-isothiocyanatopropylsilatrane derived from aminopropylsilatrane: X-ray crystal structure and theoretical studies. J Organomet Chem 2010;695:183-8.

[30] Singh R, Puri JK, Sharma RP, Malik AK, Ferretti V. Synthesis, characterization and structural aspects of 3-azidopropylsilatrane. J Mol Struct 2010;982:107-12

[31] Puri JK, Singh R, Chahal VK, Sharma RP, Wagler J, Kroke E. New silatranes possessing urea functionality: Synthesis, characterization and their structural aspects. J Organomet Chem 2011;696:1341-8.

[32] Singh R, Mutneja R, Chahal VK, Wagler J, Kroke E. Derivatization of 3aminopropylsilatrane to introduce azomethine linkage in the axial chain: Synthesis, characterization and structural studies. J Organomet Chem 2013;724:186-91.

[33] Odabasoglu M, Albayrak C, Ozkanca R, Aykan FZ, Lonecke P. Some polyhydroxy azoazomethine derivatives of salicylaldehyde: Synthesis, characterization, spectroscopic, molecular structure and antimicrobial activity studies. J Mol Struct 2007;840:71-89.

[34] Ibrahim IAM, Zikry AAF, Sharaf AM. Preparation of spherical silica nanoparticles: Stober silica. J Am Sci 2010;6:985-9.

[35] Shlyakhtenkoa LS, Gallc AA, Filonovd A, Cerovaca Z, Lushnikova A, Lyubchenko YL. Silatrane-based surface chemistry for immobilization of DNA, protein-DNA complexes and other biological materials. Ultramicroscopy 2003;97:279-87.

Scheme and Figure Captions

- Scheme 1 Modification of silica
- Scheme 2: General procedure for the introduction of silatranyl group in diazo azomethine dyes
- Scheme 3: Immobilization of silica nanoparticles with diazo-azomethine dyes
- Fig. 1 Molecular structure of 2a in the crystal structure of its DCM solvate. Ellipsoids are shown at the 40% probability level. Most of the C-bound H atoms were omitted and selected atoms are labelled for clarity.
- Fig. 2 Molecular structure of 2b in the crystal. Ellipsoids are shown at the 40% probability level. C-bound H atoms were omitted and selected atoms are labelled for clarity.
- Fig. 3 Molecular structure of 2c in the crystal. Ellipsoids are shown at the 40% probability level. C-bound H atoms were omitted and selected atoms are labelled for clarity.
- Fig. 4 Molecular structure of 2d in the crystal. Ellipsoids are shown at the 40% probability level. C-bound H atoms were omitted and selected atoms are labelled for clarity.
- Fig. 5 Molecular structure of 2e in the crystal. Ellipsoids are shown at the 40% probability level. C-bound H atoms were omitted and selected atoms are labelled for clarity.
- Fig.6 Thermogravimetric curves for 2a-2e as well as for SNP and D-SNP
- Fig. 7 IR spectra of (A) Silica nanoparticles (B) Dye modified silica nanoparticles
- Fig. 8 Transmission Electron Micrograph of Silica nanoparticles at different magnification (A-C). Dye modified silica nanoparticles showing coating of dye at different magnifications (D-F)
- Fig. 9 UV-Vis absorbance spectra of 0.5 mmol L⁻¹ copper(II) chloride solution in methanol (a) before binding (b) after stirring with 0.10 g of D-SNP in 5 mL of this solution (c) after stirring with 0.10 g of SNP in 5 mL of this solution

	$(2a)_2(CH_2Cl_2)_{0.7}$	2b	2c	2d	2e
Empirical formula	C _{44.7} H _{57.4} Cl _{1.4} N ₈ O ₈ S	$C_{23}H_{30}N_4O_4Si$	C ₂₄ H ₃₂ N ₄ O ₄ Si	C ₂₃ H ₃₀ N ₄ O ₅ Si	$C_{23}H_{30}N_4O_4Si$
Formula weight	¹ 2 940.60	454.60	468.63	470.60	454.60
Т (Қ)	150(2)	180(2)	200(2)	180(2)	180(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions					
a (Å)	11.2221(8)	18.3768(10)	18.8325(11)	16.1912(8)	7.2149(4)
b (Á)	12.9533(11)	7.7832(3)	7.9000(2)	7.8419(6)	29.7236(15)
c (Å)	17.2325(14)	18.1366(11)	18.2846(10)	18.2830(10)	10.9266(6)
α (°)	70.994(6)	90	90	90	90
β(°)	77.271(6)	115.992(4)	117.352(4)	92.036(4)	101.510(4)
γ (°)	86.757(6)	90	90	90	90
$V(A^3)$	2309.9(3)	2331.7(2)	2416.2(2)	2319.9(2)	2296.1(2)
Z	2	4	4	4	4
$\rho_{calc}(Mg/m^3)$	1.352	1.295	1.288	1.347	1.315
$\mu_{\text{Moku}\alpha}(\text{mm}^{-1})$	0.220	0.138	0.135	0.144	0.140
F (000)	994.7	968	1000	1000	968
Crystal size (mm)	0.15 x 0.10 x 0.02	0.45 x 0.40 x 0.08	0.60 x 0.55 x 0.18	0.30 x 0.15 x 0.07	0.35 x 0.20 x 0.15
Theta range for data collection	2.4 to 25.0 deg.	2.5 to 27.0 deg.	2.4 to 28.0 deg.	2.5 to 25.0 deg.	2.3 to 27.0 deg.
Limiting indices	-13≤h≤13,	$-23 \le h \le 23$,	$-24 \le h \le 24$	-19≤h≤19	$-9 \le h \le 8$,
-	$-15 \le k \le 15$,	$-9 \le k \le 9$,	-8≤ k≤ 10	$-9 \le k \le 9$	$-37 \le k \le 37$,
	$-20 \le 1 \le 20$	$-23 \le 1 \le 23$	$-24 \le 1 \le 22$	$-21 \le 1 \le 20$	-13≤l≤13
Reflections collected	15879	20574	19107	17859	20906

Table 1 X-ray crystal data and structure refinement of 2a-2e.

000 [R(IIIt) = 0330] 7.0/ 99.9
0330] 7.0/ 99.9
7.0/99.9
tegration
9894 and 0.9139
Ill-matrix least-
uares on F ²
00/3/324
022
-0.0367 wR ₂
0.0891
-0.0402D
$= 0.0492, WK_2$
0.0951
.328 and -0.226
te 98 111 00 1 = 0.1 1 = 0.1

¹ This crystal structure was determined from a twin. Refinement was carried out with a HKLF5 data set with merged equivalents. Thus, no R(int) is reported. The batch scale factor for the twin populations refined to 0.471(1).

A C

Parameter	X-ray crystal data					
	2a	2b	2c	2d	2e	
N(1)-Si	2.163(3)	2.1930(12)	2.1729(10)	2.192(2)	2.177(8)	
C(7)-Si	1.881(4)	1.8831(14)	1.8870(12)	1.884(2)	1.8778(15)	
C(9)-N(2)	1.470(5)	1.4566(18)	1.4593(16)	1.464(3)	1.4645(19)	
O(1)-Si	1.677(3)	1.6644(10)	1.6656(9)	1.664(2)	1.6598(11)	
O(2)-Si	1.654(3)	1.6651(10)	1.6656(9)	1.673(2)	1.6629(11)	
O(3)-Si	1.667(2)	1.6716(11)	1.6769(9)	1.663(2)	1.6670(11)	
C(7)-C(8)	1.524(5)	1.531(2)	1.5295(17)	1.527(3)	1.526(2)	
C(8)-C(9)	1.515(5)	1.5285(19)	1.5272(17)	1.524(3)	1.513(2)	
O(1)-Si-O(2)	117.51(14)	119.06(6)	118.78(5)	117.21(10)	118.74(6)	
O(1)-Si-O(3)	119.16(14)	118.59(6)	118.78(5)	119.11(11)	117.97(6)	
O(2)-Si-O(3)	119.27(14)	117.42(6)	117.91(5)	118.64(10)	118.35(6)	
C(7)-Si-O(1)	97.11(14)	97.67(5)	97.40(5)	97.67(10)	98.09(6)	
C(7)-Si-O(2)	96.80(15)	96.99(6)	96.96(5)	96.97(10)	97.17(7)	
C(7)-Si-O(3)	96.29(15)	97.63(6)	96.98(5)	97.88(9)	97.03(6)	
N(1)-Si-O(1)	83.19(13)	82.71(5)	83.32(4)	82.68(8)	83.21(7)	
N(1)-Si-O(2)	83.23(12)	82.61(5)	82.82(4)	82.18(8)	81.88(7)	
N(1)-Si-O(3)	83.38(12)	82.40(5)	96.98(5)	82.61(8)	82.62(7)	
N(1)-Si(1)-C(7)	179.64(15)	179.55(6)	179.26(5)	179.15(11)	178.66(8)	

Table 2 Selected bond length (Å) and angles (°) of 2a-2e $\,$





















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Research Highlights

- Silatranes as precursors for immobilization of useful functionalities on to silica surface
- ▶ Linkage of different azo dyes with immobilizable precursor
- > 3-aminopropylsilatrane is used as immobilizable precursor due to silatranyl ring
- Synthesis of D-SNP using Stober's method
- > D-SNP are capable of capturing copper ions

Cter the Mark

Development of new precursors for immobilizing dyes onto silica surfaces

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Supplementary Information







2d

Fig. S3. Packing Diagram of 2d







Fig. S5. Electronic spectra of 2a-2e in different solvents. (0.004×10⁻³ mmol, Cuvette Path length: 10 mm, Cuvette material: Quartz)



Fig. S6. Azo-hydraozone - enaminone tautomers of 2a-2e