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Synthesis of novel stilbene-alkoxysilane fluorescent brighteners, and their performance on cotton fiber as fluorescent brightening and ultraviolet absorbing agents

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ABSTRACT

Two novel fluorescent brightening agents (compounds 3a–b shown in Figure 1) were synthesized, using a facile three-step synthetic route, from 4,4′-diamino-2,2′-disulfonic-stilbene, cyanuric chloride, and a readily cross-linkable 3-aminopropyltrimethoxy silane. The products contain hydrolytically active trimethoxysilyl, ($-Si(OCH_3)_3$), functional groups that readily hydrolyze in the presence of water, and subsequently generate a water insoluble silicon cross-linked-network (Si–O–Si) via a condensation process. The cross-linked product hydrolyzes on treatment with hot aqueous sodium hydroxide to silanols ($-Si(OH)_3$) to form compounds 4a–b which are readily water soluble and produce a clear fluorescent solution. The silanol forms of compounds 4a–b were used for further characterization and performance evaluation. The structures of compounds 4a–b were characterized by ^{1}H-NMR, Fourier-Transform infrared (FT-IR) spectroscopy and negative electrospray ionization mass ($^-$ESI-MS) spectroscopy. Compounds were applied to cotton fiber as fluorescent brightening agents and their performance was evaluated by measuring the degree of whiteness, ultraviolet protection factor (UPF), fluorescence and acid fastness. Results showed that application of 0.25% (o.w.f) of compounds 4a–b impart a high degree of whiteness (CIE WI = 144, 139) as well as good ultraviolet protection factor (UPF = 29, 27) on cotton fiber exhibiting a significant increase in whiteness and UV blocking properties compared to untreated substrate (CIE WI = 81, UPF = 5). Acid fastness tests of both compounds showed a slight change in fluorescence emission intensities as a function of pH. In acidic solutions, a shift in emission maximum occurs at pH 3 from 434 to 453 nm and from 435 to 457 nm, due to the protonation of amino and sulfonic groups of stilbene fluorophore which substantially reduces the quenching process.

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1. Introduction

Fluorescent brightening agents (FBAs) are primarily applied to textiles to enhance their whiteness and brightness; they also significantly increase the UV-blocking properties of the medium to which they are applied [1–3]. A greater awareness of the adverse effects of the UV- radiation on human health has prompted a number of manufactures to incorporate UV protective agents in various media. For instance, FBAs are commonly added to textile substrates at various manufacturing steps in order to increase their apparent whiteness and to provide an additional layer of protection against UV-A and UV-B radiation [4,5]. They increase whiteness by absorbing UV light around 360 nm and re-emitting at a longer wavelength in the blue region, via fluorescence, with a typical maximum at 430–440 nm [6,7]. One important class of FBAs is based on triazine-stilbene derivatives, which are widely used to create intense and bright white shades when incorporated in plastics, textiles, pulp and paper or when applied to textiles through washing with laundry detergents [8]. In addition by incorporating new chemical functionalities to the fluorophore, the FBAs are used in diverse fields including for biological staining [9], light emitting diodes [10], photoinduced electron transfer sensors [11], fluorescent switchers [12] chemosensors [13], pH chemosensing materials [14] and polyurethane fluorescent brightener dispersions [15].

Trimethoxysilyl containing compounds (Fig. 1) are a unique class of organosilanes with increasing applications in a range of diverse fields and are a dynamically developing branch of the chemical industry [16]. The unique ability of alkoxysilanes containing inorganic and organic reactive groups, and their potential to

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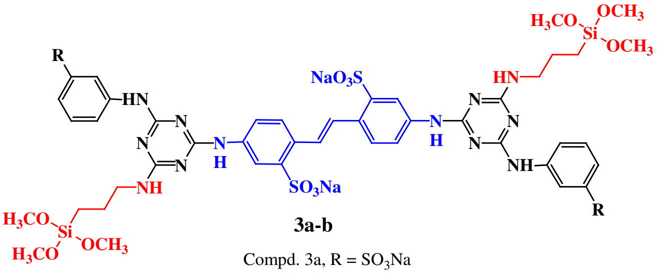

3a-b

Compd. 3a, R = SO_3Na
Compd. 3b, R = H

Fig. 1. Trimethoxysilyl containing compounds.

react with inorganic substrates, such as glass, metal/minerals, and organic materials, such as polymers, coatings or adhesives, as well as themselves and other silanes to form hybrid organic-inorganic complexes makes alkoxysilane compounds a key component in high-performance paints and coatings [17–19]. These compounds are well known for improving the adhesion of coatings to metal or siliceous substrates by forming covalent bonds via dual organic–inorganic reactivity [20]. The use of silanes in coatings can provide improvements in adhesion; resistance to moisture, chemicals, ultraviolet (UV) rays and abrasion; and improved dispersion of fillers [21]. They are also used in both thermoset and thermoplastic systems. Mineral-filled systems include reinforced polypropylene, silica-filled molding compounds, silicon-carbide grinding wheels, aggregate-filled polymer concrete, fiberglass, sand-filled foundry resins, sealants and other moisture-sensitive formulations as water scavengers. Alkoxysilanes that contain trialkoxysilyl reactive groups can bond well to the metal hydroxyl groups on most inorganic substrates, especially if the substrate contains silicon, aluminum or heavy metals in its structure [22]. The silanols coordinate with metal hydroxyl groups on the inorganic surface to form an oxane bond and eliminate water [23].

In this paper, we are reporting a novel synthetic method for the preparation of hydrolytically active silicone based triazine-stilbene fluorescent brightening agents, a mechanism of formation of water insoluble silicon cross-linked-network (Si–O–Si), its hydrolysis to water soluble silanol form ($-Si(OH)_3$), and their performance evaluation on cotton fiber as fluorescent brightening and UV absorbing agents.

2. Experimental

2.1. Materials and equipment

The mass spectra were obtained using negative electrospray ionization mass spectrometry ($^-$ESI-MS) on an Agilent Technologies (Santa Clara, California) 6210 LC-TOF mass spectrometer. ^{1}H NMR spectra were recorded in a Bruker 700 MHz spectrometer. FT-IR spectra (KBr) were recorded on a Nicolet Nexus 470 FT-IR spectrometer (Thermo Scientific, USA). Fluorescence was measured in aqueous solution with a concentration of 5 ppm in a quartz cell (1.0 cm). The spectrum was recorded at room temperature on a Fluorolog spectrofluorometer (HORIBA Jobin Yvon Inc. USA). CIE Whiteness was recorded on a SF600X Datacolor reflectance spectrophotometer. UPF was measured using a Cary 300 UV–Visible spectrophotometer fitted with an integrating sphere and a fabric holder accessory. The progress of all reactions was monitored by the thin layer chromatography (TLC) technique, which was performed on 2.0 × 5.0 cm, PET sheets pre-coated with silica gel to a thickness of 0.25 mm with a 254 nm fluorescent indicator, and the developed TLC plates were viewed under ultraviolet light (254–366 nm). The starting materials, 4,4′-diaminostilbene-2,2′-disulfonic acid (96%; Acros Organics) and 2,4,6-trichloro-1,3,5-triazine (99%; Acros Organics) were available in house, all other chemicals were of chemical grade (Fisher Scientific and Sigma Aldrich).

2.2. Synthesis

Novel fluorescent brightening agents (compounds 3a–b) were synthesized in a three-step synthetic route as summarized in Fig. 2 by reacting 4,4′-diaminostilbene-2,2′-disulfonic acid (DAS) with cyanuric chloride to give the 4,4′-bis(4,6-dichloro-1,3,5-triazin-2-yl)-aminostilbene-2,2′-disulphonic intermediate. This intermediate was further condensed with aromatic amines via nucleophilic substitution reactions at the electron deficient carbons of the triazine ring. Compounds 2a–b were isolated by salting out and then collected through vacuum filtration, and dried under vacuum overnight at 40 °C. The compounds 2a–b were isolated and analyzed by FT-IR and $^-$ESI-MS. Compounds 2a–b were further reacted with $H_2N-(CH_2)_3-Si(OCH_3)_3$ in DMF under argon gas in the presence of N,N-diisopropylethylamine (a proton scavenger), and the product of this reaction was precipitated by adding toluene, and the reaction mixture was filtered by vacuum to isolate the precipitate. The precipitate was washed with toluene to remove excess 3-aminopropyltrimethoxy silane and dried overnight under vacuum at 40 °C. The product was kept in a desiccator.

2.2.1. Synthesis of compound 3a: Sodium 2-[(E)-2-{2-[(sodiooxy)sulfonyl]-4-{[4-({3-[(sodiooxy)sulfonyl]phenyl}amino)-6-{[3-(trimethoxysilyl)propyl]amino}-1,3,5-triazin-2-yl]amino}phenyl}ethenyl]-5-{[4-({3-[(sodiooxy)sulfonyl]phenyl}amino)-6-{[3-(trimethoxy silyl) propyl]amino}-1,3,5-triazin-2-yl]amino}benzene-1-sulfonate

To a 250 mL round-bottom flask, equipped with a stirring bar, pH meter, thermometer and a reflux condenser, 25 mL acetone and 20 g of ice were added. To this stirred mixture, 20 mmol cyanuric chloride (3.688 g) was added. The pH was then increased from about 3 to 4–5 by drop-wise addition of aqueous 10% (w/v) sodium carbonate solution. Then 10 mmol disodium salt of 4,4′-diaminostilbene-2,2′-disulfonic acid solution (3.704 g) was gradually added to the slurry of cyanuric chloride while maintaining temperature at 0–5 °C with external cooling. The reaction vessel was kept in an ice bath with continuous stirring for 2 h while testing for the disappearance of disodium salt of 4,4′-diaminostilbene-2,2′-disulfonic acid by TLC analysis and iodine spot test. To the reaction mixture, 20 mmol aqueous sodium salt of *m*-amino sulfonic acid (2.744 g, 50 mL) was added. The mixture was heated to 40 °C and stirred for 3 h while maintaining pH at 6. Compound 2a was isolated by adding 20% sodium chloride and collected through vacuum filtration, and dried under vacuum overnight at 40 °C. A 250 ml reaction flask equipped with a condenser and a stirring bar was purged with argon for 5 min. Then the flask was charged with 5 mmol (5.138 g) compound 2a, 150 mL anhydrous DMF and stirred for 5 min. To the vigorously stirred mixture, 10 mmol 3-aminopropyltrimethoxy silane (1.793 g) and 10 mmol N,N-diisopropylethylamine (1.292 g) were added; 5% excess of the 3-aminopropyltrimethoxy silane was employed to drive the reaction to completion. The reaction vessel was confined, and argon gas was allowed to gradually flow into the vessel. The reaction mixture was stirred at room temperature for 24 h. The disappearance of compound 2a was confirmed by TLC analysis. After 24 h the product was isolated by adding 100 mL of toluene to the reaction mixture. The product was precipitated out and filtered by vacuum, and the precipitate was washed with toluene three times (25 mL each time) to remove unreacted 3-aminopropyltrimethoxy silane and then washed with acetone (50 mL). The product was dried under vacuum overnight at 40 °C and stored in a desiccator. The yield was 94% with respect to compound 2a. The isolated

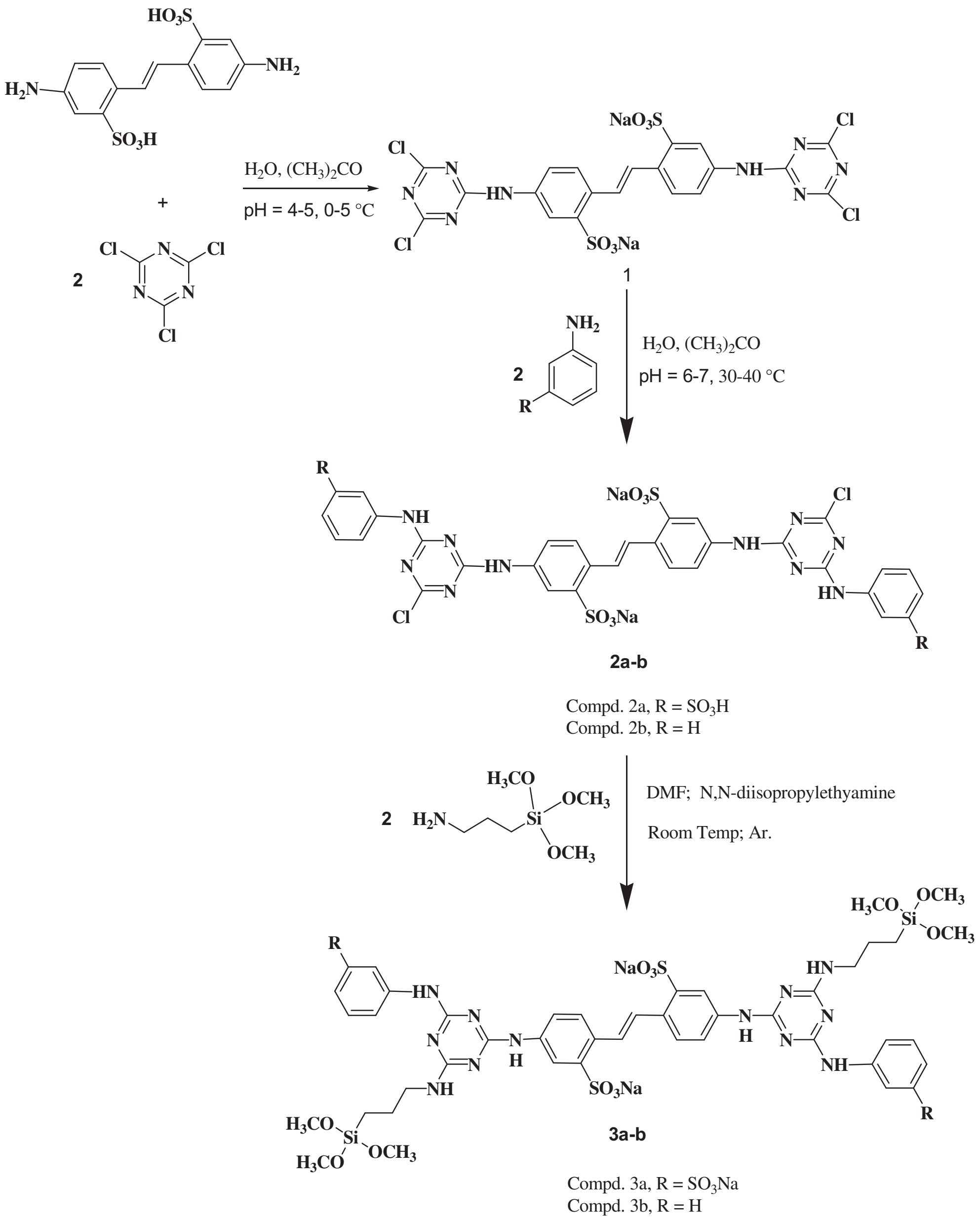

Fig. 2. Synthetic scheme proposed for the formation of compounds 3a–b.

compound **3a** was hydrolyzed by treatment in hot sodium hydroxide to form compound **4a** which was further characterized.

2.2.1.1. –ESI-MS, compound 2a. $C_{32}H_{20}Cl_2N_{10}Na_4O_{12}S_4$, mass 1027.69, $[M-4Na+3H]^{-1}$, theoretical $m/z = 936.97652$, measured $m/z = 936.97620$, error = 0.3 ppm; $[M-4Na+2H]^{-2}$, theoretical $m/z = 467.9845$, measured $m/z = 467.9397$, error = −1.1 ppm.

2.2.1.2. –ESI-MS, compound 4a. $C_{38}H_{40}N_{12}Na_4O_{18}S_4Si_2$, Mass 1228.06, $[M-Na]^{-1}$, theoretical $m/z = 1205.0704$, measured $m/z = 1205.07173$, error = 1.1 ppm); $[M-3Na+H]^{-2}$, theoretical $m/z = 580.0496$, measured $m/z = 580.05169$, error = 3.6 ppm; $[M-4Na+H]^{-3}$, theoretical $m/z = 379.0367$, measured $m/z = 379.03805$, error = 3.6 ppm; $[M-4Na]^{-4}$, theoretical $m/z = 284.0257$, measured $m/z = 284.02612$, error = 1.5 ppm). **^{1}H-NMR** (700 MHz, D_2O, 40 °C): δ/ppm 1.44 (t, 4H, $J = 7.7$ Hz, CH_2), 1.79 (p, 4H, $J = 8.2$ Hz, CH_2), 2.71 (t, 4H, $J = 7.0$ Hz, CH_2), 7.45 (d, 2H, $J = 13.6$ Hz, $\underline{CH}{=}\underline{CH}$, corresponding to *trans*-coupling of vicinal protons), 7.53–7.60 (m, 6H, ArH), 7.67 (d, 2H, $J = 7.5$ Hz, ArH), 7.79 (s, 2H, ArH), 7.86 (d, 2H, $J = 8.0$ Hz, ArH), 7.95 (s, 2H, ArH). **I.R. (KBr):** 1614–1573.1 (triazine C=N); 1363.7–1303.7 (C–N, stretch); 1186.6–1025 (Si–O–Si, asymmetric stretch); 994.3 (=C–H, alkenes, out-of-plane C–H bend), 808.1 (Si–O–Si, symmetric stretch) cm^{-1}.

2.2.2. Synthesis of compound 3b:Sodium 5-{[4-(phenylamino)-6-{[3-(trimethoxysilyl) propyl]amino}-1,3,5-triazin-2-yl]amino}-2-[(E)-2-(4-{[4-(phenylamino)-6-{[3-(trimethoxy silyl)propyl] amino}-1,3,5-triazin-2-yl]amino}-2-[(sodiooxy)sulfonyl]phenyl) ethenyl] benzene-1-sulfonate

The first step of reaction was carried out as described in Section 2.2.1. After 2h, 20 mmol aniline (1.862 g) in 10 mL acetone was added gradually to the reaction mixture while maintaining pH 6–7 by drop-wise addition of aqueous 10% (w/v) sodium carbonate solution. The mixture was heated to 30–40 °C and stirring continued for 2h. The reaction was monitored by checking the disappearance of aniline using TLC. Compound 2b was isolated by adding sodium chloride (10%) and collected through vacuum filtration and dried overnight under vacuum at 40 °C. A 250 ml reaction flask equipped with a condenser and stirring bar was charged with 5 mmol compound 2b (4.120 g), 150 mL anhydrous DMF, 10 mmol 3-aminopropyltrimethoxy silane (1.793 g) and 10 mmol N,N-diisopropylethylamine (1.292 g). Argon was purged and reaction mixture was stirred at room temperature for 24 h. The disappearance of compound 2b was confirmed by TLC. After 24 h the product was precipitated by adding 100 mL of toluene to the reaction mixture, and the precipitate was isolated by vacuum filtration, and washed three times with 25 mL of toluene to remove the unreacted 3-aminopropyltrimethoxy silane and then washed with acetone (50 mL). The product was dried overnight under vacuum at 40 °C and stored in a desiccator. The yield was 92% with respect to compound 2b. The isolated compound **3b** was hydrolyzed by treatment in hot sodium hydroxide to form compound **4b** which was also further characterized.

2.2.2.1. −ESI-MS, compound ***2b****.* $C_{32}H_{22}Cl_2N_{10}Na_2O_6S_2$, mass 822.03, $[M - Na]^{-1}$, theoretical $m/z = 799.0445$, measured $m/z = 799.04580$, error = 1.6 ppm), $[M - 2Na]^{-2}$, theoretical $m/z = 388.02770$, measured $m/z = 388.02770$, error = 0.0 ppm.

2.2.2.2. −ESI-MS, compound ***4b****.* $C_{38}H_{42}N_{12}Na_2O_{12}S_2Si_2$, mass 1024.18, $[M - Na]^{-1}$, theoretical $m/z = 1001.1928$, measured $m/z = 1001.19421$, error = 1.4 ppm); $[M - 2Na]^{-2}$, theoretical $m/z = 489.1018$, measured $m/z = 489.10224$, error = 0.9 ppm). ^{1}**H-NMR** (700 MHz, D_2O, 40 °C): δ/ppm 1.62 (t, 4H, $J = 8.4$ Hz, CH_2), 1.63 (p, 4H, $J = 8.0$ Hz, CH_2), 2.53 (t, 4H, $J = 7.0$ Hz, CH_2), 6.95 (d, 2H, $J = 13.2$, Hz, $C\underline{H}{=}C\underline{H}$, corresponding to *trans*-coupling of vicinal protons), 7.10 (t, 4H, $J = 7.3$ Hz, ArH), 7.35 (t, 4H, $J = 7.7$ Hz, ArH), 7.49 (d, 4H, $J = 7.5$ Hz, ArH), 7.77 (d, 2H, $J = 8.0$ Hz, ArH), 7.85 (d, 2H, $J = 8.2$ Hz, ArH). **I.R. (KBr)**: 1612.5–1569.5 (triazine C═N); 1363.6–1305.7 (C–N Stretch); 1180.3–1023 (Si–O–Si; asymmetric stretch); 901.1 (═C–H, alkenes, out-of-plane C–H bend), and 807.9 cm^{-1} (Si–O–Si, symmetric stretch).

2.3. Mass spectrometry

Mass spectra, shown in Figs. 3 and 4 were obtained at high resolution (≥10,000 R FWHM) using negative electrospray ionization ($^-$ESI) on an Agilent Technologies (Santa Clara, USA) 6210 LC-TOF mass spectrometer. Sample concentration was 5000 mg L^{-1}, and the analysis used 30 μL min^{-1} infusions via a syringe pump. The mass spectrometer was operated in negative-ion mode with a capillary voltage of 3.5 kV, nebulizer pressure of 30 psi, and a drying gas flow rate of 10 L min^{-1} at 350 °C. The fragmentor and skimmer voltages were 110 and 65 V respectively. Reference ions of m/z 112.9856 and m/z 966.0007 were simultaneously introduced via a second orthogonal sprayer, and used as internal calibranes.

2.4. ^{1}H NMR spectra

^{1}H NMR spectra were recorded in D_2O at 40 °C using a Bruker 700 MHz spectrometer. Splitting patterns reported here are: s (singlet), d (doublet), dd (double-of-doublet), t (triplet), p (pentet), and m (multiplet). Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hertz (Hz), respectively.

2.5. FT-IR spectra

FT-IR spectra were recorded on a Nicolet Nexus 470 FT-IR Spectrometer, Thermo Scientific, USA. About 600 mg of KBr was ground in a mortar with a pestle, and sufficient amounts of synthesized compounds were ground with KBr to make a 0.6 wt% mixture. After each sample was loaded, the sample chamber was purged with nitrogen for a minimum of 10 min before data collection. A minimum of 64 scans were collected for each sample at a resolution of 4 cm^{-1}.

2.6. Measurement of fluorescence

Fluorescence measurement of compounds 4a–b was carried out using a concentration of 5 ppm in deionized water in a quartz cell (1.0 cm), and an increment of 1 nm was used for recording of all spectra. The spectra were recorded at room temperature on a Fluorolog spectrofluorometer. The excitation and emission spectra of compounds 4a–b are shown in Figs. 5–6, respectively. The excitation spectra were collected by fixing the emission wavelength and by running the excitation monochromator at a wavelength range of 250 nm–425 nm, using a slit width of 2 nm with an increment of 1 nm and a scan integration time of 0.10 s whereas emission spectra were collected by running the emission monochromator at a range of 360 nm–650 nm, using a slit width of 1 nm with an increment of 1 nm and a scan integration time of 0.10 s at the fixed excitation wavelength. In order to measure the acid fastness properties of compounds 4a–b, fluorescence emission spectra were measured at six different pH values, shown in Figs. 7–8. The pH was adjusted by using 0.1 mol aqueous solution of HCl and NaOH. Data obtained are presented in Table 1.

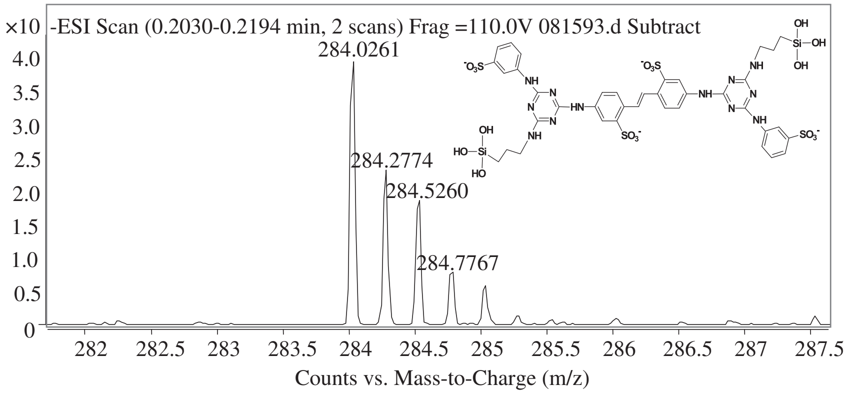

Fig. 3. $^-$ESI mass spectrum of compound 4a; $[M - 4Na]^{-4}$; Theoretical. M/4 = 284.0257; measured M/z = 284.02612; Error = 1.5 ppm.

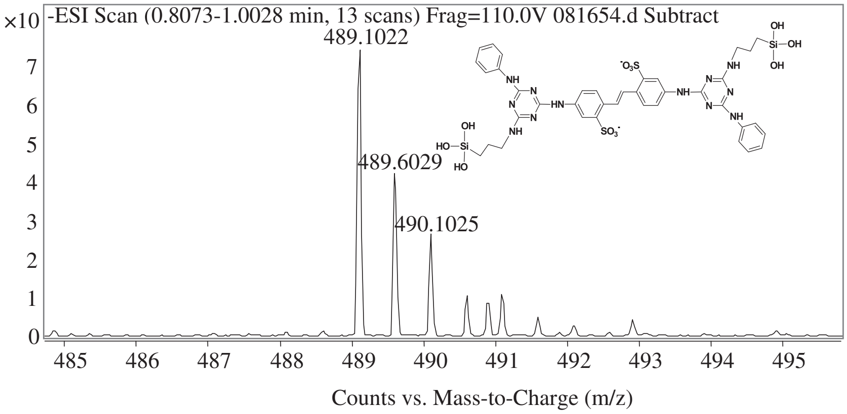

Fig. 4. $^{-}$ESI mass spectrum of compound 4b; $[M - 2Na]^{-2}$; Theoretical. M/2 = 489.1018; measured M/z = 489.10224; error = 0.9 ppm.

2.7. *Optical whitening*

Whitening of scoured and bleached cotton fabric that contained no FBA was carried out at 50 °C for 30 min using different concentrations of a paste of finely ground compounds 4a–b (FBAs) at 0.03, 0.05, 0.15, 0.25, 0.35 and 0.5% (o.w.f). Crystalline Glauber's salt (5 gL^{-1}) was used as an auxiliary in the treatment bath to improve exhaustion of FBAs by cotton substrate. The liquor to goods ratio was adjusted to 20:1; temperature was increased at a rate of 2 °C min^{-1} over 15 min from 20 to 50 °C; and the bath was maintained at 50 °C for a further 15 min. Treated samples were removed from the treatment bath, rinsed in cold water and air dried at room temperature.

2.8. *Whiteness measurements*

The CIE Whiteness Index (WI) values were obtained for optically brightened substrates using the AATCC test method 110–2000 [24]. The values were measured using a Datacolor SF600X spectrophotometer with the following setting: illuminant D65, large area view (30 mm), specular included, UV calibrated and CIE 1964 standard colorimetric observer (10°). Four measurements were obtained from each sample at different locations and the average whiteness value was recorded. Results are presented in Table 2.

2.9. *Measurement of UV protection factor (UPF)*

The UV transmission of fabric samples containing 0.03, 0.05, 0.15, 0.25, 0.35 and 0.5% (o.w.f) of compounds 4a–b at was measured. Results are summarized in Table 2. In order to measure the total transmitted index of the optically brightened fabrics, a non-fluorescent filter was used which transmitted UV radiation below 400 nm but allowed no radiation within the visible range from 400 nm to 700 nm. The calculations were performed over the spectral region of 280–380 nm using a Cary 300 UV–Visible spectrophotometer fitted with an integrating sphere and a fabric holder accessory. A 2 nm wavelength interval was used, and a scan speed of 300 nm min^{-1} was employed and six scans were recorded. The UPF indices were calculated according to the AATCC test method 183–2000 [25]. According to this method a fabric rated as UPF 30 would allow 1 out of 30 units of incident UV light to pass through, thus blocking 96.7% of UV radiation.

3. Results and discussion

Cyanuric chloride is a trifunctional compound in which the three reactive chlorine atoms can be replaced in a stepwise fashion. In an aqueous-organic medium, the DAS reacts with cyanuric chloride ideally at 0–5 °C at pH 4.5–5.5. In the second step, amines react at 30–40 °C under neutral conditions. The third chlorine atom can be replaced at 70–90 °C in aqueous medium under slightly alkaline conditions; the second and third step conditions depend on the nature of the attacking nucleophile, reaction medium and the substituent already present on triazine moiety.

Generally the reactivity of chlorine groups on triazine moiety decreases after each substitution due to a decrease in electropositive character of the triazine moiety, however, we observed that the

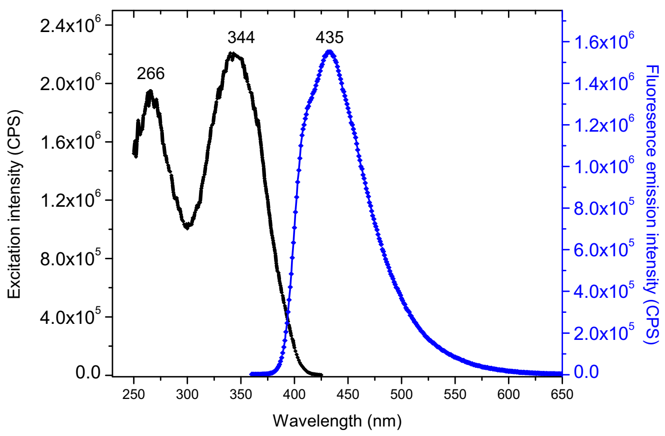

Fig. 5. The fluorescence spectra of 5 ppm of compound 4a in water, excited at 344 nm.

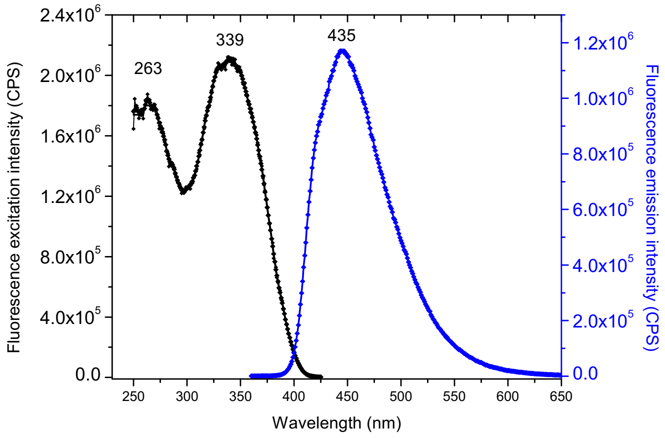

Fig. 6. The fluorescence spectra of 5 ppm of compound 4b in water, excited at 339 nm.

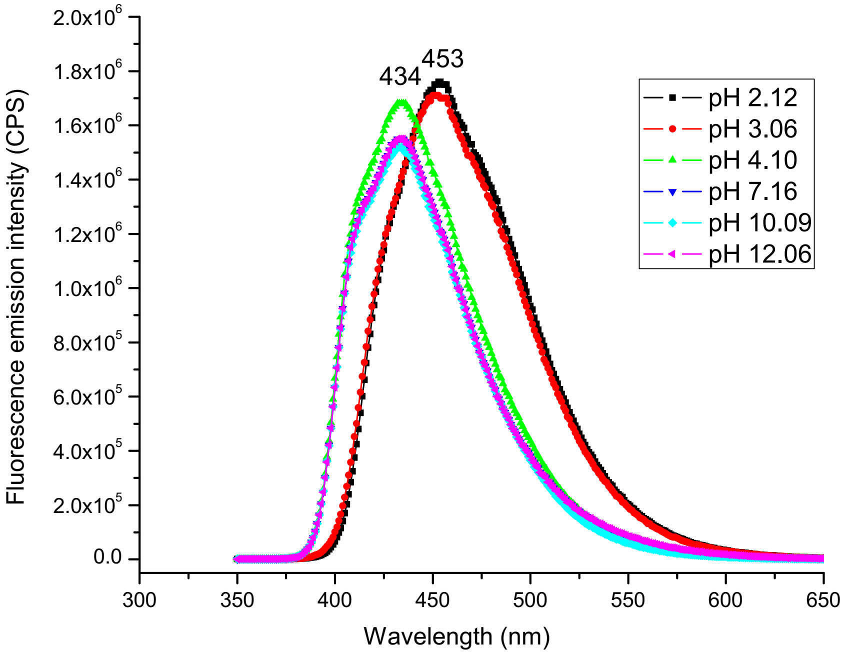

Fig. 7. Effect of pH on fluorescence properties of compound 4a, in water at 5 ppm.

third chlorine reacts with amines at room temperature in an organic medium (anhydrous DMF). Similar observations in different solvents have been previously reported [26,27]. To initiate the reaction course, N,N-diisopropylethylamine was used as an acid scavenger because N,N-diisopropylethylamine is a base with poor nucleophilicity due to the shielding effect of isopropyl groups as well as the ethyl group on nitrogen atom hence a proton is small enough to easily fit. It is important to avoid moisture during the third step of the reaction because 3-aminopropyltrimethoxy silane is very sensitive to moisture and readily self condenses. Undesirable hydrolyzed byproducts may be formed during the synthesis of diamino-stilbene-triazine (DAST) type brighteners. A very careful control of the reaction conditions, especially at steps 1 and 2, is therefore necessary to avoid the formation of hydrolyzed impurities which are hard to remove and are likely to reduce the performance of the product. The newly synthesized brighteners contain cross-linkable trimethoxysilyl groups, which are effectively free from undesirable impurities. Since trimethoxysilyl groups readily crosslink in the presence of moisture and form essentially an insoluble compound, the impurities can be removed easily by washing the product with different solvents. After purification, the cross-linked network can be broken into silanols by treatment with

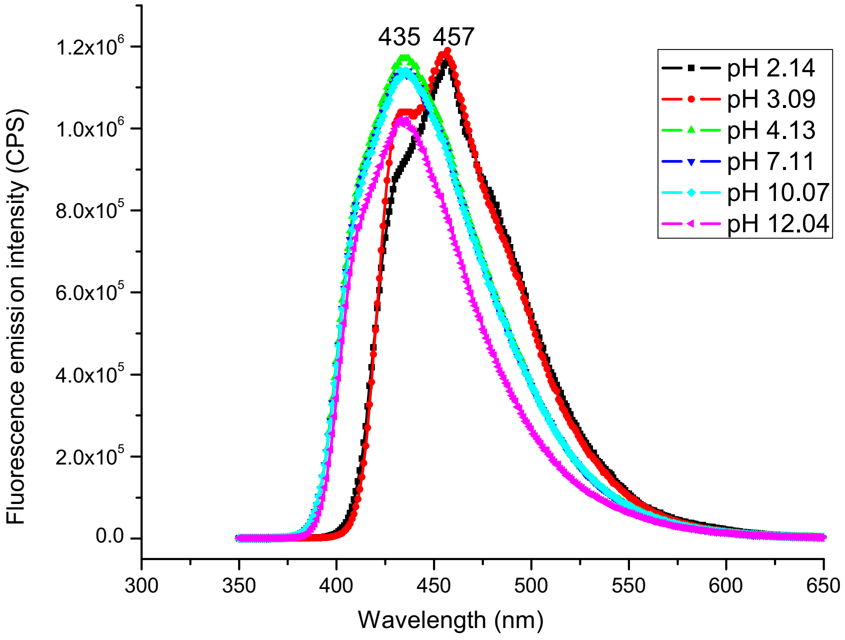

Fig. 8. Effect of pH on fluorescence properties of compound 4b, in water at 5 ppm.

Table 1
Excitation and fluorescence characteristics of cis and trans-isomers of compounds 4a–b in deionized water at 5ppm.

Compounds	Excitation			Fluorescence emission		Stoke's shift (δλ)
	Cis-isomer	Trans-isomer		λ_{em} (nm)	Intensity (CPS)	(nm)
	λ_{ex} (nm)	λ_{ex} (nm)	Intensity (CPS)			
4a	266	344	2.20×10^6	435	1.56×10^6	91
4b	263	339	2.10×10^5	435	1.58×10^5	96

aqueous sodium hydroxide, which gives a clear solution. By adjusting pH to neutral using HCl and evaporating water by heating, the remaining compound exhibits insolubility in water and other solvents indicating reassembly of the cross-linked network. The silicon network can be effectively disrupted and re-assembled based on the proposed mechanism given in Fig. 9. During the flouting and restoration of the cross-linked network, the sodium hydroxide breaks the (Si–O–Si) bonds to silanols, as verified by FT-IR and $^{-}$ESI-MS. The $^{-}$ESI-MS analysis of compounds 4a–b confirms the presence of $RSi(OH)_3$ groups which provide a strong evidence in favor of the proposed mechanism shown in Fig. 9.

The FT-IR spectra of both compounds 2a–b showed intense peaks at 793 cm^{-1} and 797 cm^{-1} corresponding to C–Cl (stretch), whereas these peaks were not observed in the final compounds 3a–b. This confirms a complete nucleophilic substitution of the three chlorine atoms. A strong peak at 1658 cm^{-1} ($SiO–CH_3$) was observed for both compounds 3a–b, however, this peak was not observed in compounds 2a–b or in hydrolyzed compounds 4a–b. We suggest that the trimethoxysilyl groups were hydrolyzed into silanols which spontaneously crosslink and thus are not observed individually. Silicone Cross-linked products showed peaks at 1186–1025 cm^{-1} (Si–O–Si, asymmetric stretch); and 808 cm^{-1} (Si–O–Si, symmetric stretch), which confirm the presence of silicon cross-linked network.

In order to measure the $^{-}$ESI spectra the cross-linked products were hydrolyzed to silanols ($–Si(OH)_3$) and used for the mass analysis. Samples containing compounds 4a–b showed signals for ions that correspond to the exact theoretical molecular ions. The standard error difference (between theoretical mass and measured mass) in $^{-}$ESI spectra of both compounds 4a–b was blow 5 ppm, as shown in Figs. 3 and 4 respectively. The molecular mass of compound 4a, based on the molecular formula $C_{38}H_{40}N_{12}Na_4O_{18}S_4Si_2$, is 1228.06. With the loss of four sodium ions, the signal corresponding to $[M - 4Na]^{-4}$ would be M/4 = 284.026 as shown in the $^{-}$ESI spectrum in Fig. 3. The molecular mass of compound 4b, based on the molecular formula $C_{38}H_{42}N_{12}Na_2O_{12}S_2Si_2$, is 1024.18. In absence of two sodium ions the signal corresponding to $[M - 2Na]^{-2}$ would be calculated as M/2 = 489.102 and this was obtained in the $^{-}$ESI spectrum shown in Fig. 4.

Table 2
CIE Whiteness and UPF index values of cotton fabric treated with compounds 4a–b.

Compounds	Amount applied o.w.f (%)	CIE whiteness index	UV-Protection Factor (UPF)
Untreated cotton fabric	–	80.63	5.281
Compound 4a	0.03	129.51	9.600
	0.05	136.36	11.992
	0.15	145.52	21.186
	0.25	144.10	29.054
	0.35	142.97	34.059
	0.50	139.99	40.610
Compound 4b	0.03	116.89	8.832
	0.05	128.78	10.299
	0.15	139.49	23.298
	0.25	139.73	27.236
	0.35	137.55	35.609
	0.50	134.37	43.996

Emission of light due to fluorescence is the result of formation of excited states; however, the emission lifetime is in the picot-to-nanoseconds time frame. Hence, the fluorophore must remain excited to enable the observation of the rapid fluorescence emission spectrum. The fluorescence spectra are technically perturbed by two problems: the intensity of the light incident upon the substance and the intensity of light detected. In order to obtain an accurate measure of fluorescence and the excitation spectrum of a given fluorophore, the excitation scan is corrected for the wavelength characteristics of the xenon lamp. After acquiring the fluorescence spectra, correction was made to compensate for the wavelength-dependent components of the system (inner filter effect) by multiplying the data by an appropriate correction factor determined by the software [28]. While the corrections of fluorescence excitation and emission spectra resulted in a minor increase in the intensities, they did not induce a shift in the spectral maxima. The excitation and emission spectra of compounds 4a–b are shown in Figs. 5–6, respectively.

The fluorescence spectra of both compounds have similar profiles although they have different intensities. The Stoke's shift of these compounds was calculated using Eq. (1) [29].

$$\textit{Stoke's shift} = \delta\lambda = \lambda_{em} - \lambda_{ex} \qquad (1)$$

The wavelengths of absorbed versus emitted light by the FBAs should preferably be within the range of approximately 100 nm. A large Stoke's shift increases the chance of significant fluorescence in the green-yellowish region of the spectrum which causes a reduction in total whiteness [30]. The Stoke's shifts obtained for compounds 4a and 4b are 91 nm and 96 nm respectively which are appropriate for the end use intended.

Triazine-stilbene FBAs are well known for their photochemical process of trans-cis isomerization. They undergo partial conversion from the strongly fluorescent trans-isomer to the non-fluorescent cis-isomer upon exposure to light. In aqueous solutions the cis-isomer state is favored resulting in a reduction in overall fluorescence. A rotation occurs in the stilbene moiety around the central ethylene bond as a result of exposure to light until equilibrium is attained. The cis-isomer gradually converts to trans-form after short exposures to light resulting in a strong fluorescence. This rearrangement, however, can take place in either direction depending on the nature of solvent or substrate used [31]. The excitation and emission spectra of compounds 4a–b in aqueous solution exhibit similar profiles, with a maximum emission at 435 nm, though fluorescence intensity of compound 4a is slightly greater than that of compound 4b. However, they show different absorption maximum in the UV region for the trans-isomer around 339–344 nm and for the cis-isomer around 263–266 nm. Results are also shown in Table 1.

In alkaline solution both compounds show slightly diminished emission intensity compared to acidic solutions. The emission intensity increases as the pH is reduced because of the protonation of amino and sulfonic groups on stilbene fluorophore which substantially minimizes the quenching process and thus increases overall intensity. A decrease in solution pH to 3 results in a shift of the maximum emission from 434 to 453 nm and from 435 to 447 nm for compounds 4a and 4b respectively. The shift in emission might be due to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied

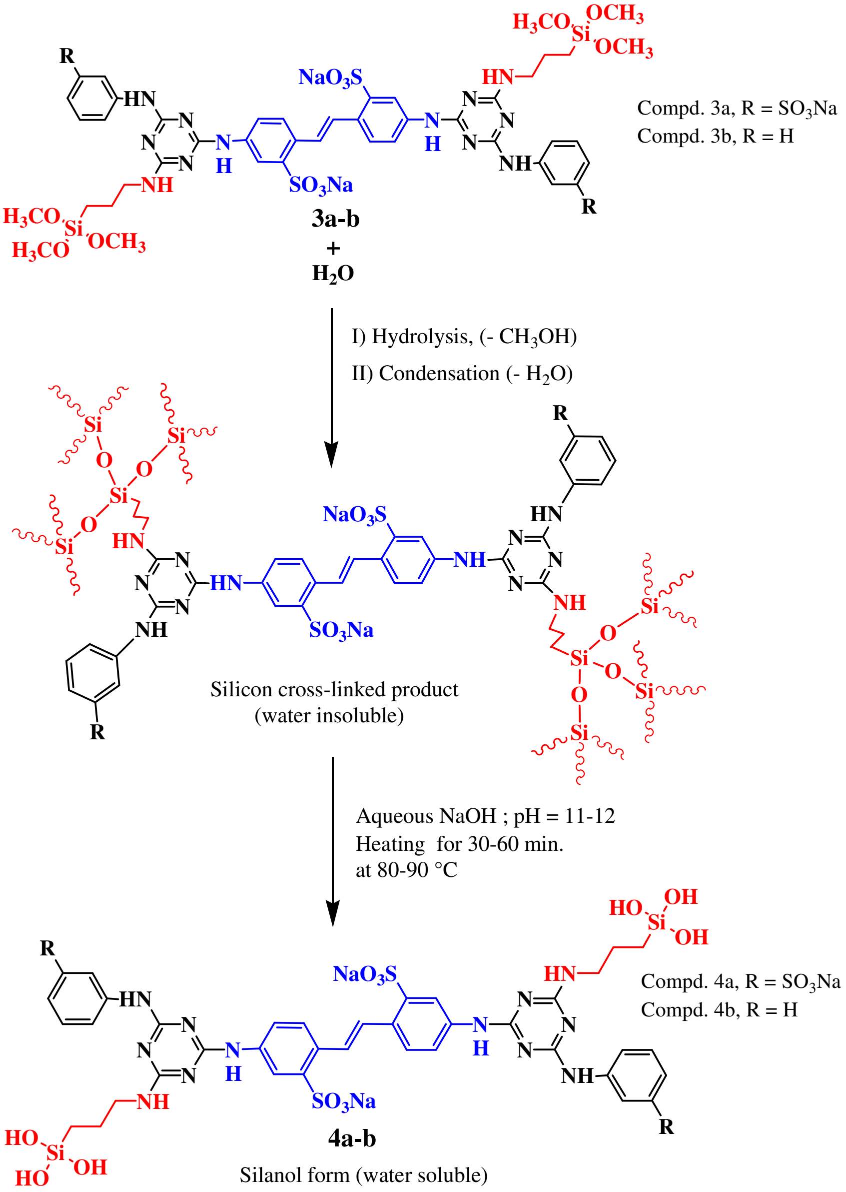

Fig. 9. The proposed mechanism for the formation and hydrolysis of silicon network using an aqueous hot NaOH.

molecular orbital (LOMO) of acidic form ($-SO_3H$) and salt form ($-SO_3Na$) of stilbene fluorophore. The acidic form might have a larger gap between HOMO and LOMO thus resulting in a shift in emission characteristics.

The CIE WI of treated cotton substrates were measured and are shown in Table 2. The application of both compounds resulted in imparting a high degree of whiteness to treated substrates with WI values of 140–145. The WI of untreated fabric was 81. An examination of results showed that as the amount of brightener on the substrate increased, the WI also increased until a maximum value was reached. A further increase in the concentration of FBA beyond this point (0.15–0.2%) resulted in an absorption shift from violet to green, which in turn reduced the overall WI value. Total fluorescence, because of the aggregation of the FBAs on the substrate, was also reduced when the concentration of FBAs on the fabric was increased beyond 0.2%.

UV protective properties of textile substrates are influenced by various parameters which include fabric construction, density of weave as well as the type and amount of dye applied, especially in dark shades. A reliable estimation of the degree of protection provided by the fabric requires the measurement of UV transmittance in fabrics between 280 and 390 nm, which includes UV-B (290–315 nm) and UV-A (315–380 nm) radiation. The UV transmission in fabric samples treated with compounds 4a–b at various concentrations was measured, and the results are summarized in Table 2. The UPF of cotton fabric prior to treatment was 5 indicating essentially no protection against UV radiation. Fabric samples treated with compounds 4a–b, however, showed UPF values between 9 and 44, indicating an adequate to good protection against harmful UV rays. Fig. 10 (a–b) shows the UV-A and UV-B blocking properties of the treated fabric in presence of compounds 4a–b and Fig. 10c shows the UV transmission behavior of the substrate that does not contain any fluorescent brightener.

The transmittance spectra show that both compounds exhibit a maximum UV absorption between 290 nm and 330 nm and hence are effective in blocking the UV-B radiation which is more harmful to human health compared to UV-A radiation.

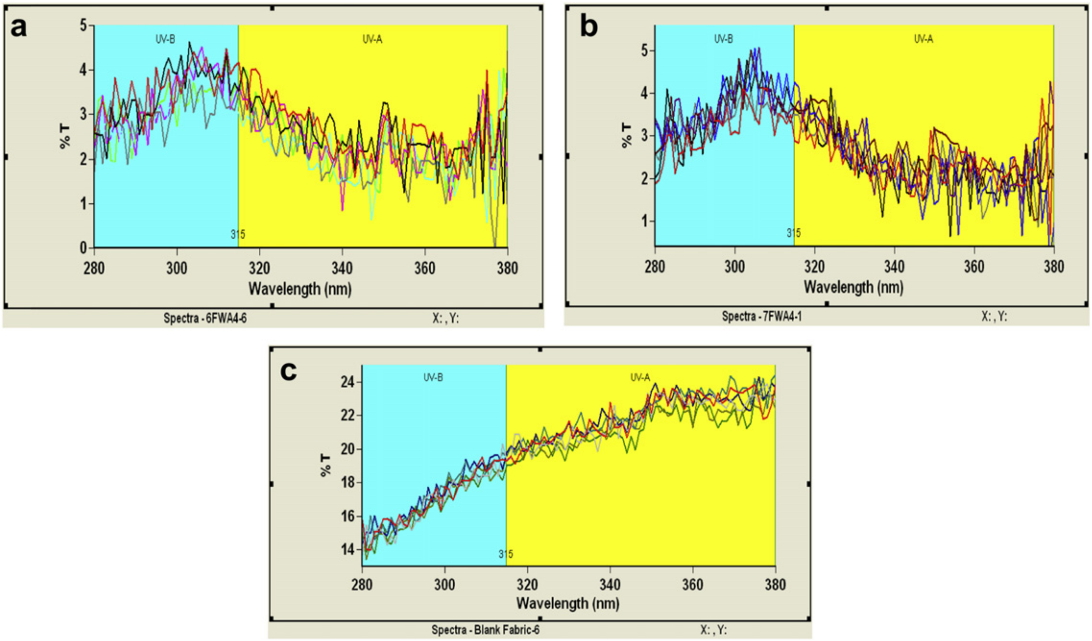

Fig. 10. a) UV-transmittance spectra of cotton fabric treated with 0.25% (o.w.f) compound 4a (UPF = 29), b) UV-transmittance spectra of cotton fabric treated with 0.25% (o.w.f) compound 4b (UPF = 27) and c) UV-transmittance spectrum of cotton fabric before optical whitening (UPF = 5).

4. Conclusion

A three-step synthetic route involving a stilbene-triazine moiety and a readily cross-linkable trimethoxysilyl functional group was used to synthesize novel fluorescent brightening agents. The trimethoxysilyl groups hydrolyze upon reaction with water or moisture and generate silanols that undergo a cross-linking reaction with adjacent molecules to produce a stable silicone based cross-linked network. The cross-linked product is insoluble in a wide range of solvents from non-polar hexane to polar DMF as well as strong mineral acids. However, treatment with strong aqueous sodium hydroxide at ~80 °C hydrolyzes the (Si—O—Si) cross-linked bonds and gives a clear strongly fluorescent solution. The evaporation of water from the solution at neutral conditions results in the formation of an insoluble compound in water and other solvents and reformation of the cross-linked network. An examination of the structures of synthesized intermediates as well as the final compounds by FT-IR and $^{-}$ESI-MS techniques confirmed the formation of silanols. The photo-physical characteristics of the molecules were also investigated by measuring the fluorescence spectra in aqueous solution. The fluorescence spectra of final compounds were very similar although they exhibited slightly different intensities (1.56×10^6 and 1.58×10^5, CPS). The maximum CIE WI values of fabrics treated with 0.25% (o.w.f) compounds 4a–b were found to be 144 and 140 which is in the range of commercially available brightening agents. The UPF of cotton fabric prior to whitening was 5 effectively providing no protection against UV radiation. The incorporation of the synthesized FBAs into the fiber resulted in a significant increase in the UV blocking properties of the treated fabric (UPF = 27–29) thus demonstrating their ability to absorb harmful UV radiation. Acid fastness results showed that a decrease in pH values causes a slight increase in emission intensities. The protonation of amino and sulfonic groups of stilbene fluorophore reduces the quenching processes and as a result increases the overall emission intensity. Due to their unique characteristics these novel products could be employed in a number of potential applications from surface coating, plastics, pulp and paper, textile industries as well as detergents to increase the whiteness of various products and absorb UV light.

References

[1] Cuesta F, Mertzger G, Naef R, Rohringer P, Traber RH. Triazinylaminostilbene disulphonic acid mixtures. US20060030707A1; 2006.
[2] Reinher D, Luther H, Mertzger G. Use of fluorescent whitening agents. US20030103924A1; 2003.
[3] Farrar JM, Jackson AJ. Optical brighteners compositions their production and their use. US6890454 B2; 2005.
[4] Wang X, Li W, Zhang XH, Liu DZ, Zhou XQ. Dyes Pigm 2005;64:141–6.
[5] Czajkowski W, Paluszkiewicz J, Stolarski R, Kazmierska M, Grzesiak E. Dyes Pigm 2006;71:222–30.
[6] Zollinger H. Color chemistry. 3rd ed. 2003. p. 365–367.
[7] Lee JK, Um SI, Kang Y, Baek DJ. Dyes Pigm 2005;64:93–9.
[8] Shore J. Colorants and auxiliaries. Soc Dyers Colourists 1990;2:470–509.
[9] Harrington BJ. LabMedicine 2009;40:219–23.
[10] Zhu W, Hu C, Chen K, Tian H. Synth Met 1998;96:151–4.
[11] Tian H, Gan J, Chen K, He J, Liang Song Q, Yuan Hou X. J Mater Chem 2002;12: 1262–7.
[12] Gunnlaugsson T, McCoy CP, Morrow RJ, Phelan C, Stomeo F. Arkivoc 2003;7: 216–28.
[13] Bojinov VB, Konstantinova TN. Sensors Actuators B 2007;123:869–76.
[14] Georgiev NI, Bojinov VB, Marinova N. Sensors Actuators B 2010;150:655–66.
[15] Xian HH, Xing YZ, Jia BD. Chin Chem Letters 2011;22(8):997–1000.
[16] Witucki GL. J Coating Technol 1993;65(822):57–60.
[17] Tesoro G, Wu Y. J Adhes Sci Technol 1991;5(10):771–84.
[18] Campbell DH, Echols JE, Ohrbom WH, BASF Corporation. Scratch resistant clearcoats containing surface reactive microparticles and method therefore, U.S. Patent 5853809, 1998.
[19] Pape PG, Plueddemann EP. History of silane coupling agents in polymer composites, History of polymer composites. VNU Science Press; 1987. 105–139.
[20] Witucki GL. Proceedings of the 57th Annual Meeting of the Federation of the Societies for Coating Technology, Chicago, 1992.
[21] de Buyl F. Int J Adhes Adhesives 2001;5(21):411–22.
[22] Plueddemann EP, Pape PG, Collogue Les Mineraux Industrials Materiaux Des Annees 90 Quebec, Proceedings,1989; 269.
[23] Pape PG, Plueddemann EP. Methods of improving the performance of silane coupling agents silanes and other coupling agents; 1992.
[24] AATCC. Test Method 110–2000, CIE whiteness of textiles. AATCC Technical Manual; 2004. p. 165–166.
[25] AATCC. Test Method 183–2000, Transmittance or blocking of erythemally weighted ultraviolet radiation through fabrics. AATCC Technical Manual; 2004. p. 341–343.

[26] Kumar A, Srivastava K, Raja Kumar S, Puri SK, Chauhan PMS. Bioorg Med Chem Lett 2008;18:6530–3.
[27] Hayashi M, Yamasaki T, Kobayashi Y, Imai Y, Watanabe Y. Eur J Org Chem; 2009:4956–62.
[28] Fluorlog-3 (HORIBA Jobin Yvon). Operation manual, V. 2.2; 2002. 4–18.
[29] Grabchev I. J Photochem Photobiol A Chem 2000;135:41–4.
[30] Shore J. Colorants and auxiliaries. Soc Dyers Colourists 1990;2:763–5.
[31] Lanter J. J Soc Dyers Colourists 1966;82(4):125–32.