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Novel optical sensors for detection of nitroaromatics based on supported thin flexible poly(methylhydrosiloxane) permeable films functionalised with silole groups

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ABSTRACT

A new silole bearing an allyl group at silicon has been incorporated into previously-reported novel reactive polysiloxane coatings made from polymethylhydrosiloxane (PMHS) polymers crosslinked by the sol–gel process allowing subsequent functionalization by hydrosilylation of the SiH reactive groups. The thin films of crosslinked resin are covalently bonded to the glass substrate and contain a very low concentration of silole groups. They exhibit the aggregation-induced emission effect owing to restricted intramolecular rotation, and show enhanced sensitivity to nitroaromatic analytes because of the very low concentration of silole groups. The films can be used to test for nitroaromatics present not only in the vapour phase but also in many types of solvent because of the robust nature of the crosslinked network and covalent bonding to the substrate. They can be made in thicknesses ranging from 20 nm up to 1 μm. The silole groups are readily accessible, and the sensors can be regenerated by washing with solvents such as chloroform.

Keywords: sensor, silole, polymethylhydrosiloxane, film, nitroaromatic, explosive, hydrosilylation

1. INTRODUCTION

Chemical sensors for detection of traces of explosives, in particular nitroaromatic compounds, are of great current interest for purposes of public security and environmental protection.[1-3] A variety of conjugated polymers have been used as sensors for nitroaromatics explosives detection[4] including metallole-containing polymers.[5, 6] The first metallole to be used was a polysilole,[7] polymers[8, 9] and nanoparticles[10] containing silole groups being of particular interest. Silole molecules and polymers exhibit aggregation-induced emission (AIE) caused by the restricted intramolecular rotations of the peripheral aromatic rings about the axes of the single bonds linked to the central silole cores.[11, 12] The emission is quenched by nitroaromatic compounds, the effect being enhanced by Lewis acid-base interactions between the silacycle and the nitroaromatic compound.[13]

However, polymer-based sensors made from linear uncrosslinked polymers usually suffer from the drawback of polymer leakage into the medium and ensuing shortened lifetime and inefficient analyses. We report here the development of a new family of fluorescent film sensors for which these disadvantages have been overcome, made from thin films of crosslinked resin covalently bonded to the substrate and containing a very low concentration of silole groups. They exhibit the AIE effect owing to restricted intramolecular rotation,[12] and show enhanced sensitivity to nitroaromatic analytes because of the very low concentration of silole groups. Thus, a new silole bearing an allyl group at silicon has been incorporated into previously-reported novel reactive polysiloxane coatings made from polymethylhydrosiloxane (PMHS) polymers crosslinked by the sol–gel process allowing subsequent functionalization by hydrosilylation of the SiH reactive groups.[14-17] The films can be used to test for nitroaromatics present not only in the vapour phase but also in many types of solvent because of the robust nature of the crosslinked network and covalent bonding to the substrate. They can be made in thicknesses ranging from 20 nm up to 1 μm. The silole groups are readily accessible, and the sensors can be regenerated by washing with solvents such as chloroform.

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2. RESULTS AND DISCUSSION

2.1 Preparation of 1-allyl-1-methyl-2,3,4,5-tetraphenylsilole (1)

The new pale yellow fluorophore 1-allyl-1-methyl-2,3,4,5-tetraphenylsilole (**1**) was synthesized in 55% yield by using Curtis's method[18] in two steps; (a) lithiation of tolane, followed by (b) reaction of the intermediate dilithiotetraphenylbutadiene with allylmethyldichorosilane (Scheme 1).
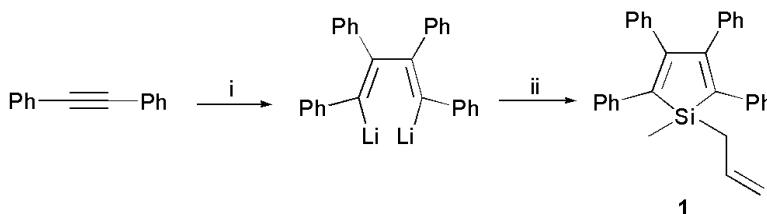
Scheme 1. Synthesis of 1-allyl-1-methyl-2,3,4,5-tetraphenylsilole (**1**). *Reagents and conditions*: i, Li shavings, THF, 12 h, room temp.; ii, allylmethyldichlorosilane, THF, 2 h at room temp., 5 h under reflux.

2.2 Preparation of crosslinked polymethylhydrosiloxane (PMHS) thin films

Crosslinked polymethylhydrosiloxane (PMHS) thin films of 5% crosslinking density were prepared by room temperature sol–gel polymerization of methyldiethoxysilane/triethoxysilane 95:5 (mol %) sol mixtures deposited by spin-coating on silicon wafer Si(100) or microscope glass slide substrates freshly activated with "piranha" solution. The substrates bearing PMHS thin films were then cured at 100 °C in an oven for 10 min. The thickness of the virgin PMHS films was found to be *ca*. 1 μm as measured by infrared spectroscopy from the absorbance of the Si–H peak at *ca*. 2167 cm^{-1} and the calibrated absorption coefficient.

2.3 Hydrosilylation of 1 by PMHS thin films and characterization of resulting silole-containing films

The hydrosilylation reaction between the allyl group of **1** and the PMHS Si-H function was performed in air by placing the virgin PMHS thin film/substrate samples in a toluene solution of **1** in the presence of Karstedt's catalyst for 18 h at 60°C with stirring. The samples were then removed from the reaction mixture, rinsed with toluene and chloroform to remove any physisorbed material, and dried in a stream of dinitrogen. Dioxygen acts as a co-catalyst in hydrosilylation reactions catalyzed by Karstedt's catalyst.[19] Hydrosilylation of **1** with triethoxysilane showed that the reaction is regiospecific at the allyl group.

Previous studies on hydrosilylation by PMHS have shown that the reaction goes essentially to completion.[14, 15] Indeed, in this case too, no IR spectral evidence for any remaining unreacted silole allyl groups present in the thin films was observed. The degree of silole incorporation into the thin films was found to be 7-8% from the normalized IR absorbance ratio of the methylene group $\nu_{as}(CH_2)$ antisymmetric stretch at *ca*. 2922 cm^{-1} (Fig. 1) and the $\nu(SiH)$ band at *ca*. 2167 cm^{-1} for the unreacted sample (virgin PMHS), all the methylene groups originating from the silole allyl groups. As expected, the total intensity of the methylene absorbance corresponded to three methylene groups per silole following complete hydrosilylation of **1** and covalent bonding into the PMHS network. The residual SiH function was determined to be *ca*. 15-17% from the IR spectra by measuring the total integrated absorbances of the $\nu(SiH)$ bands in the 2100–2300 cm^{-1} region for the reacted and unreacted samples (Fig. 1).
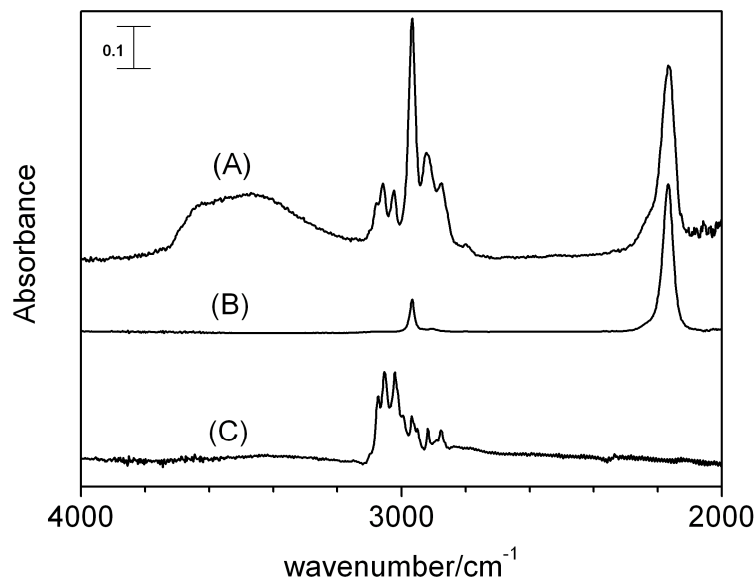
Figure 1. IR absorption spectra: PMHS film on glass slide (A) after (magnified x 10), and (B) before incorporation of **1** by hydrosilylation; (C) **1** in KBr.

To summarize, 15-17% of the SiH groups remained unreacted, 7-8% underwent hydrosilylation, and the remainder (*ca.* 75%) underwent reaction with water (present from air moisture) catalyzed by Karstedt's catalyst[19] (Scheme 2) as confirmed by the increase in the IR Si-O-Si stretch band at *ca.* 1100 cm^{-1} and the Si-OH band at *ca.* 3500 cm^{-1} observed after hydrosilylation of **1** with the PMHS films. The formation of additional Si-O-Si crosslinks serves to strengthen the film resistance.
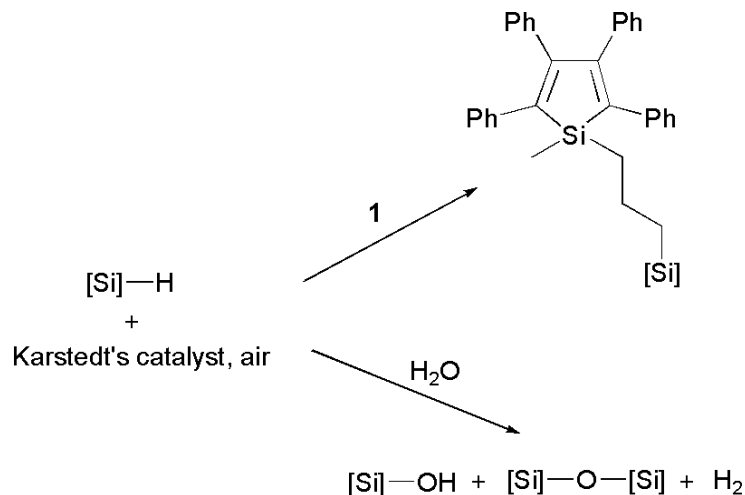
Scheme 2. Reactions of PMHS (represented by [Si]-H) in the presence of Karstedt's catalyst and air: hydrosilylation of **1** and reaction with H$_2$O.

The UV/visible absorption and emission spectra of the thin films confirm the presence of silole groups showing a characteristic absorption band at *ca.* 370 nm assigned to the silole π-π* transition (Fig. 2(a)) and an intense emission band at 485 nm (Fig. 2(b)). The spectra remain unchanged after repeated washing of the samples with chloroform, thus confirming the covalent bonding of the silole groups to the PMHS matrix and ruling out physisorption. The silole-containing PMHS films retain their fluorescent properties for at least 3 months in air, and the Si-H groups in PMHS gels are stable.[16]
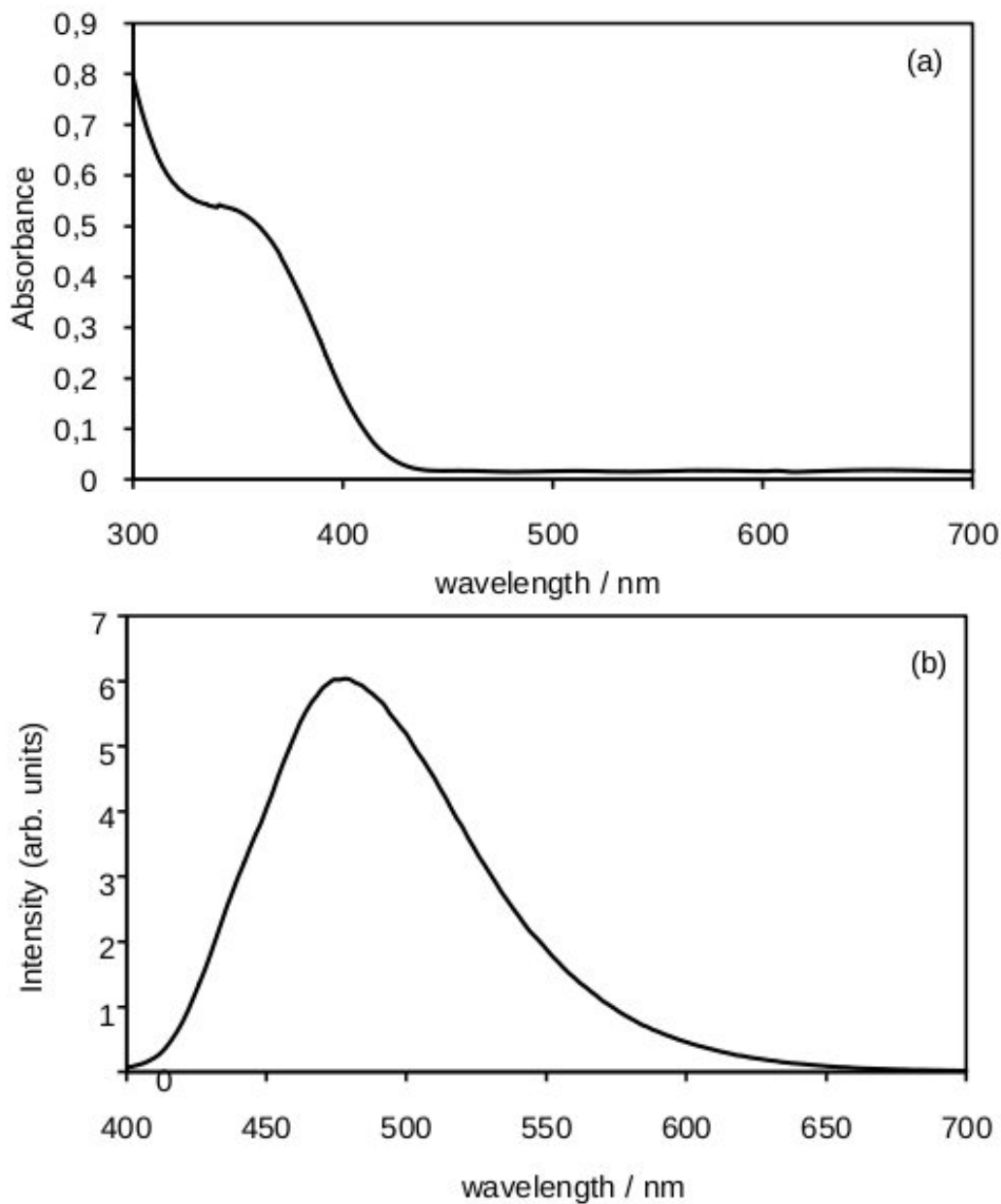
Figure 2. (a) UV/visible absorption, and (b) emission spectra ($\lambda_{excit.}$ = 375 nm) of PMHS film containing **1**.

2.4 Nitroaromatic sensor properties of silole 1 in chloroform solution

The ability of the new silole to act as a nitroaromatic sensor was first studied in solution. Fluorimetric analysis of a solution of **1** in chloroform (10^{-5}M) containing increasing amounts of *m*-dinitrobenzene (Fig. 3(a)) and picric acid (Fig. 3(b)) showed the expected fluorescence quenching attributed to Lewis acid-base interactions between the silole silicon centres and the lone pairs of the nitro groups of the nitroaromatic analyte, providing a bridging bond through which electron transfer occurs from the excited state of the silole to the analyte.[13]
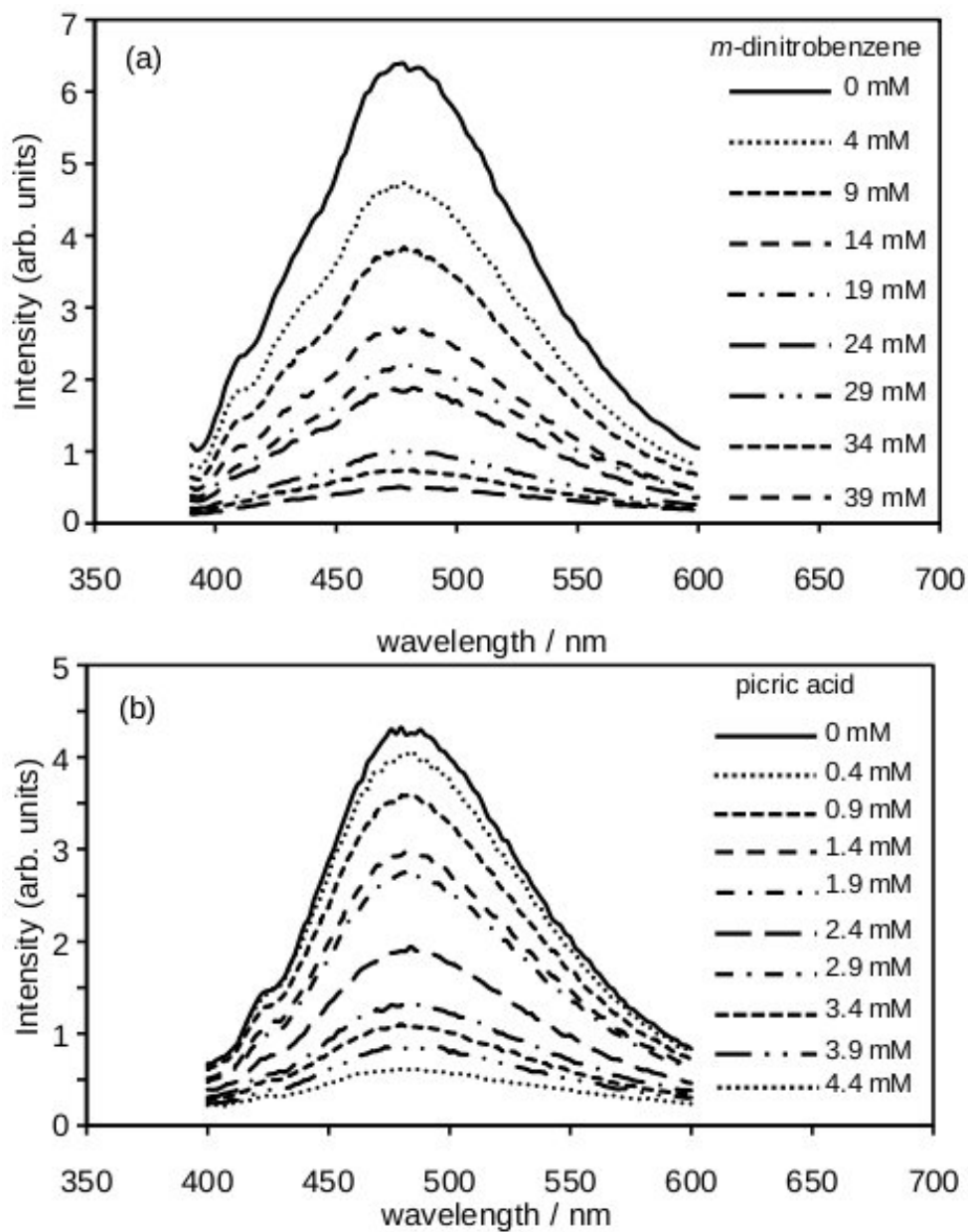
Figure 3. Decrease in emission intensity ($\lambda_{excit.}$ = 375 nm) of chloroform solution of **1** (10^{-5}M) with increasing concentration of (a) *m*-dinitrobenzene, and (b) picric acid.

2.5 Nitroaromatic sensor properties in solution of PMHS thin films containing silole 1

Similar results were observed for a thin film of PMHS containing **1**. The sample was immersed in a chloroform solution and increasing amounts of *m*-dinitrobenzene (Fig. 4) and picric acid (Fig. 5) were added. The emission spectra show that the quenching effect increases with the concentration of *m*-dinitrobenzene (Fig. 4) or picric acid (Fig. 5).

No corrections for inner filter effects or analyte absorption in the emission spectra were made since, firstly, re-absorption of emitted photons in the ultra-thin PMHS films can be neglected and, secondly, a front-face setup with an optical path of *ca*. 1 cm and extremely low analyte concentrations were used.
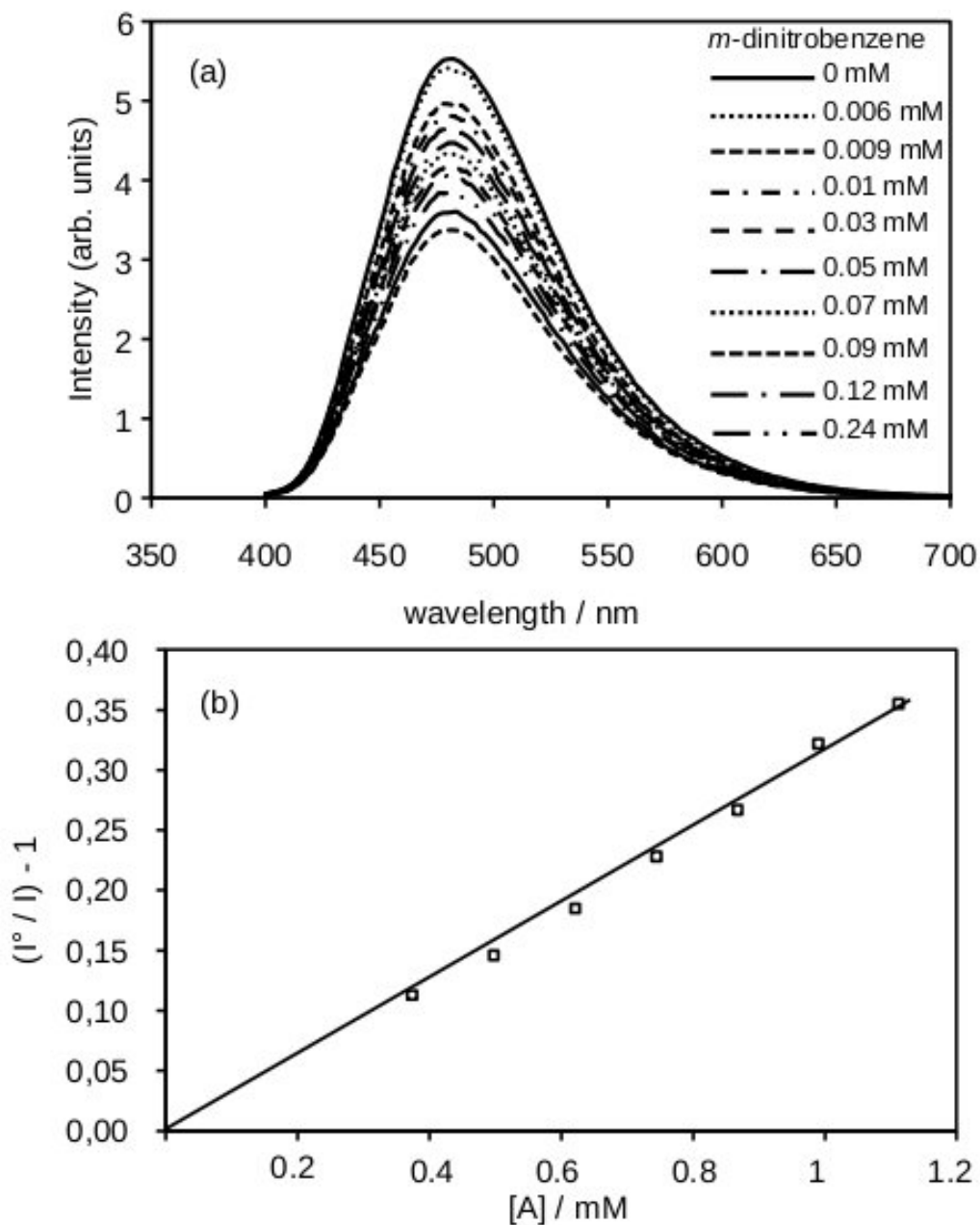
Figure 4. (a) Emission spectra ($\lambda_{excit.}$ = 375 nm) and (b) Stern-Volmer plot for sample of PMHS containing **1** immersed in chloroform solution with increasing concentration of *m*-dinitrobenzene.

In the case of the *m*-dinitrobenzene solution, the emission spectra did not change with time of immersion. However, after the sample had been immersed for 1 h in the picric acid solution, the emission intensity decreased markedly (*cf.* Fig. 5(a), the two measurements in the presence of 0.025 mM picric acid) consistent with some secondary reaction occurring between the silole groups and picric acid. This is reflected in the break exhibited by the Stern-Volmer plot (Fig. 5(b)).
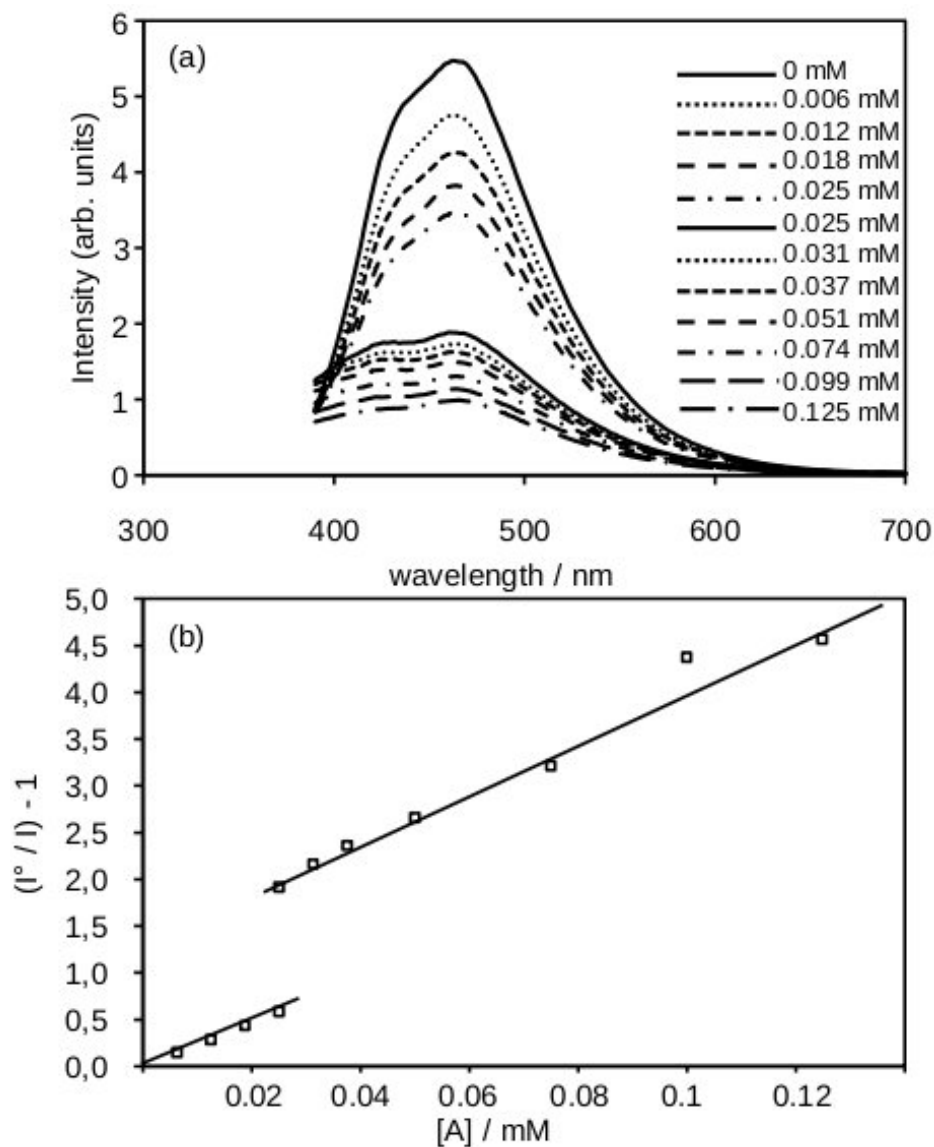
Figure 5. (a) Emission spectra ($\lambda_{excit.}$= 375 nm) and (b) Stern-Volmer plot for sample of PMHS containing **1** immersed in chloroform solution with increasing concentration of picric acid (a period of 1 h passed between the two measurements in the presence of 0.025 mM picric acid).

In the case of the *m*-dinitrobenzene analyte the quenching effect is found to be reversible. Simple washing of the detector film with chloroform regenerates the initial fluorescence peak with the same intensity and form (Fig. 6 (B)) as for the pristine film (Fig. 6 (A)). The same procedure of washing with chloroform the sensor film treated with picric acid gives rise to an emission spectrum of lower intensity and showing two peaks at 408 and 455 nm (Fig. 6 (C)). This behaviour is consistent with the formation of a new fluorescent product by reaction of the silole groups and picric acid. Indeed, with picric acid the quenching effect has been found previously to be partly irreversible in some cases.[7, 20]
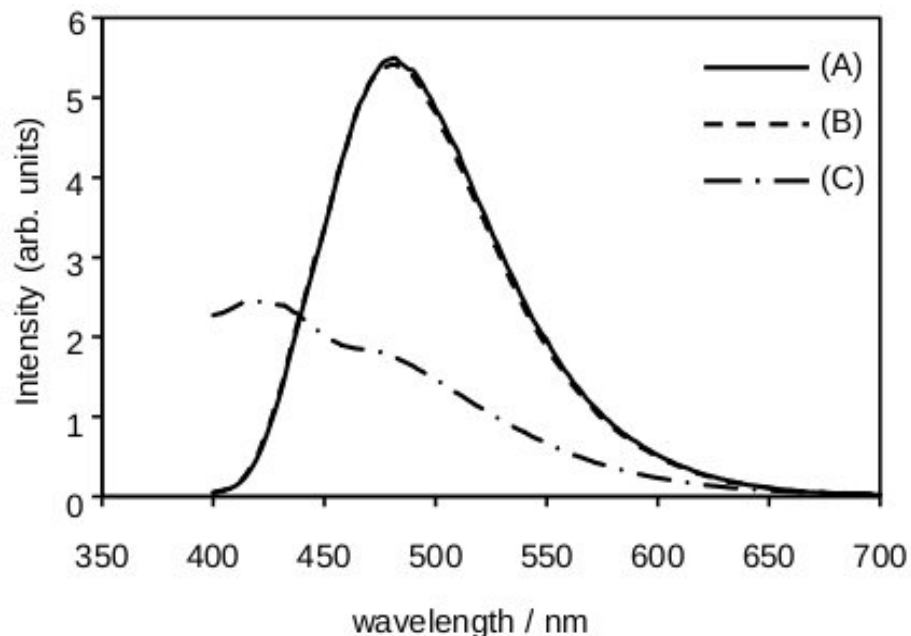
Figure 6. Emission spectra ($\lambda_{excit.}$= 375 nm) of sample of PMHS containing **1**: (A) pristine film, (B) after immersion in chloroform solution containing *m*-dinitrobenzene followed by rinsing with chloroform, and (C) after immersion in chloroform solution containing picric acid followed by rinsing with chloroform.

2.6 Nitroaromatic sensor properties in the vapour phase of PMHS thin films containing silole 1

The sample of the PMHS thin film containing silole **1** was placed in a closed container and the emission spectrum was measured (Fig. 7 (A)). Crystals of *m*-dinitrobenzene were then added and the container re-closed. The emission spectrum was measured after 1 min (Fig. 7 (B)). Almost instantaneous visible quenching was observed, the effect being reversible after *ca*. 1 h in ambient air.
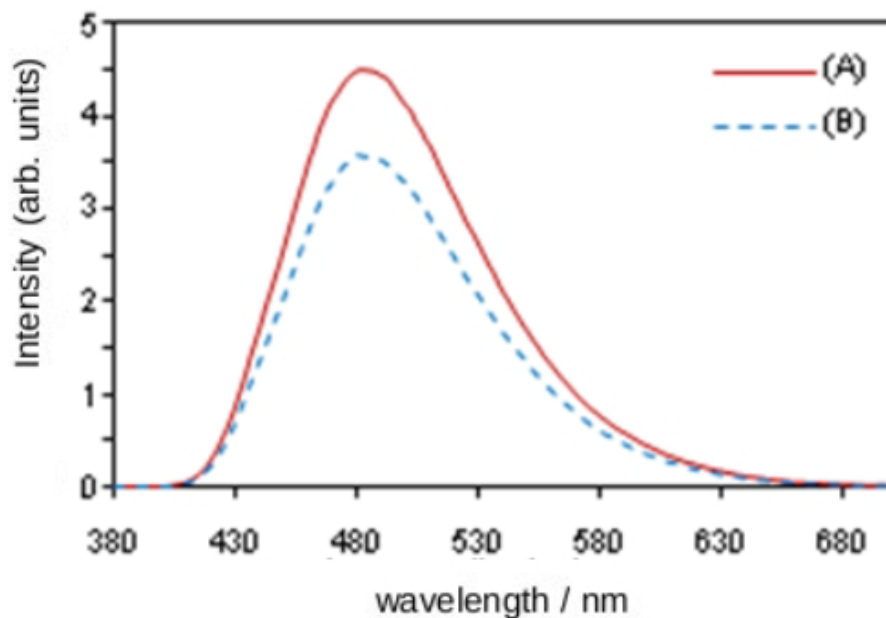

Figure 7. Emission spectra ($\lambda_{excit.}$= 375 nm) of sample of PMHS containing **1**: (A) pristine film, (B) 1 min after immersion in *m*-dinitrobenzene vapour at ambient temperature.

3. EXPERIMENTAL

3.1 Preparation of PMHS thin films

Both precursors methyldiethoxysilane $HSi(CH_3)(OCH_2CH_3)_2$ (DH) and triethoxysilane $HSi(OCH_2CH_3)_3$ (TH) were purchased from ABCR (Karlsruhe, Germany) and used as received. Water used for cleaning the substrates was obtained from a Milli-Q water purification apparatus (Millipore). Absolute ethanol for sol−gel synthesis was of synthesis grade purity. The catalyst trifluoromethanesulfonic acid CF_3SO_3H (Aldrich) was dissolved in absolute ethanol (1 M). Toluene used for thin film hydrosilylation was distilled before use. The platinum-divinyltetramethyldisiloxane complex in xylene (PC072) (platinum concentration *ca.* 0.1 M assuming 2.4% Pt in xylene), also known as Karstedt's catalyst, was purchased from ABCR.

Silicon wafers Si(100) or microscope glass slides cut into rectangular square strips of 2×2 cm^2 were used as substrates. To bond covalently the PMHS thin films to native oxide silica wafers (thickness ∼2 nm), or to silica glass slides, the substrates were first cleaned and activated using the previously described procedure.[16] The substrates were placed for 30 min in a hot (90°C) H_2SO_4/H_2O_2 (70/30 v/v) solution ("piranha" solution) and then allowed to cool to room temperature. *Caution! Piranha solution should be handled with extreme care.* The clean substrates were then rinsed thoroughly with high-purity water, dried in a stream of dinitrogen and heated at 110°C in an oven for 20 min.

PMHS thin films of 5% crosslinking density were prepared by room temperature sol−gel polymerization of DH/TH 95:5 (mol %) sol mixtures deposited by spin-coating on freshly activated substrates using the previously described procedure[14, 15] which is summarized as follows. Trifluoromethanesulfonic acid CF_3SO_3H (1M in absolute ethanol) was used as sol−gel catalyst (0.5 mmol/mol of monomers). The mixture of monomers DH/TH was polymerized at *ca.* 4 M concentration in EtOH (molar ratio [EtOH]/[Si] = 1), with 0.5 equiv. water (hydrolysis ratio $h = [H_2O]/[SiOEt] = 0.5$). The resulting clear sol was allowed to age for 30 minutes with magnetic stirring before deposition by spin-coating. Subsequently, a fully crosslinked film was obtained by spin-coating the mixture under dinitrogen at 4000 rpm (spin acceleration 2000 rpm/s) the time of rotation being 30 s. The substrates with PMHS thin films were then cured at 100 °C in an oven for 10 min. The thickness of the PMHS film was about 1 μm as measured by infrared spectroscopy (see 3.4).[14]

3.2 Synthesis of 1-allyl-1-methyl-2,3,4,5-tetraphenylsilole (1)

All the reagents were purchased from Acros. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately before use. The ^1H, ^{13}C and ^{29}Si NMR spectra were obtained on a Bruker Advance 200 DPX spectrometer, the FT-IR spectra on a Thermo Nicolet Avatar 320 spectrometer, the UV-visible absorption spectra on a Secomam Anthelie spectrometer and the mass spectra were determined on a Waters Q-tof instrument. Elemental analyses were determined with a Thermofinigane Flash EA 1112 apparatus. Photoluminescence (PL) studies were made with a SPEX Fluorolog 1681 0.22 m spectrometer.

Under dry argon, freshly cut lithium (177 mg, 25.3 mmol) shavings were added to a solution of diphenylacetylene (5 g, 28.0 mmol) in THF (25 cm^3). The mixture was stirred for 12 h at room temperature and the resulting THF solution of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was added dropwise to a solution of allylmethyldichlorosilane (1.55 cm^3, 10.7 mmol) in THF (120 cm^3). The mixture was stirred for 2 h at room temperature and refluxed for 5 h. After being allowed to cool to room temperature, the mixture was filtered and the crude product was purified on a silica gel column using pentane/dichloromethane (8:2 by volume) as eluent. Product **1** (2.6 g) was isolated in 55% yield (based on allylmethyltrichlorosilane) as a yellow-white solid: mp 120-121 °C. ^1H-NMR (200MHz, CDCl$_3$) δ [ppm] 7.07 (m, 6H), 6.95 (m, 10H), 6.79 (m, 4H), 5.72 (m, 1H), 4.85 (m, 2H, $J = 8$ Hz, $J = 17$ Hz), 1.99 (d, 2H, $J = 8$ Hz, SiCH$_2$), 0.55 (s, 3H, SiCH$_3$); ^{13}C-NMR (200MHz, CDCl$_3$) δ [ppm] 155.5, 140.7, 140.2, 139.2, 133.6, 130.5, 129.5, 128.4, 127.9, 126.7, 126.0, 114.5, 21.3, -5.4; ^{29}Si NMR (200MHz, CDCl$_3$) δ [ppm] 7.0; IR (KBr), $\overline{v}$ (cm^{-1}): 3047, 2872, 1621, 698. UV (CH$_2$Cl$_2$) λ_{max} 365 nm; ε_{max} 5394 dm^3 mol^{-1} cm^{-1}. m/z 441 [(M+1)]. Anal. Calcd for C$_{32}$H$_{28}$Si: 87.22 %C, 6.51 %H; found: 87.33 %C, 6.51 %H.

3.3 Incorporation of silole 1 into PMHS thin films by hydrosilylation

In a typical preparation, two samples grafted with a PMHS thin film (~1 μm) were placed in the presence of air in a 10 mM solution of the silole **1** (24 mg; 0.055 mmol) and Karstedt's catalyst (4 μL) in toluene (25 cm³). After the reaction mixture had been stirred for 18h at 60°C, the samples were removed, rinsed with toluene (twice) and chloroform (once) to remove any physisorbed material, and dried under a stream of dinitrogen.

3.4 Characterization of PMHS thin films

Infrared spectra of the PMHS layer were recorded on a Nexus FTIR spectrometer with the use of unmodified silicon wafer substrates as the background in the 400–4000 cm⁻¹ range. The thickness (*e*) of the virgin PMHS thin films deposited on the glass or wafer substrate by spin-coating was measured by infrared spectroscopy from the absorbance of the Si–H peaks at *ca.* 2167 cm⁻¹ : $A_{2167} = \alpha_{SiH} e$ where α_{SiH} (0.27 μm⁻¹) is the calibrated absorption coefficient.[14] A mean thickness of 1.23 ± 0.05 μm was found for four spin-coated samples.

To quantify the *SiH* conversion after hydrosilylation of the PMHS thin films, the disappearance of the strong Si–H stretching bands *v*(SiH) of both DH and TH subunits was studied by measuring the total integrated absorbances in the 2100–2300 cm⁻¹ region of the reacted and unreacted samples. The SiH residual percentage (% *SiH*) of *ca.* 15-17 % is calculated by dividing the integrated absorbance of the reacted samples with that measured before reaction (same sample).

Following PMHS hydrosilylation with the silole compound **1**, the percentage of PMHS functionalization (% *SiC*) of *ca.* 7-8 % can be measured with good sensitivity from the strong absorption of the methylene group, $v_{as}(CH_2)$ antisymmetric stretching, in the 2935–2915 cm⁻¹ region for alkanes.[21] For this calculation, the $v_{as}(CH_2)$ absorption was previously calibrated for alkyl-functionalized PMHS thin films (~1 μm) prepared by hydrosilylation with 1-akenes $CH_2=CH(CH_2)_{n-2}CH_3$ of various lengths (*n* = 5 to 17).[14, 15] Following reaction of the SiH groups, the normalized absorbance ratio A_{CH_2}/A_{SiH} increases with the number of methylene groups (*n*) in the hydrocarbon chain $Si(CH_2)_nCH_3$ as follows:

$$\frac{A_{CH_2}}{A_{SiH}} = 0.284 n \times SiC$$

where *SiC* = 100% for complete addition of the alkene molecules to the SiH bonds as well as for the functionalization of the PMHS network with short alkyl sides chains.

In the case of the silole fonctionnalized PMHS, the above equations were applied assuming the number of methylene groups is *n* = 3 ; A_{CH_2} of the reacted silole samples was measured from the peak at *ca.* 2922 cm⁻¹; A_{SiH} was measured before the hydrosilylation reaction at *ca.* 2167 in the corresponding unreacted samples (virgin PMHS).

4. CONCLUSIONS

A new family of fluorescent highly sensitive crosslinked film sensors has been developed which does not suffer from commonly observed polymer leakage into the medium with ensuing shortened lifetime and inefficient analyses. The thin film sensors made from crosslinked PMHS polymers covalently bonded to the glass substrate contain a very low concentration of covalently bonded silole groups. They exhibit the AIE effect owing to restricted intramolecular rotation, and show enhanced sensitivity to nitroaromatic analytes because of the very low concentration of silole groups. The films can be used to test for nitroaromatics present not only in the vapour phase but also in many types of solvent because of the robust nature of the crosslinked network and covalent bonding to the substrate. They can be made in thicknesses ranging from 20 nm up to 1 μm. The silole groups are readily accessible, and the sensors can be regenerated by washing with solvents such as chloroform.

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