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Highly Efficient Latent Fingerprint Detection by Eight-Dansyl-Functionalized Octasilsesquioxane Nanohybrids

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Abstract

The largely demand in security issues makes necessary the development of novel materials with outstanding properties to improve the current detection techniques. In this context, latent fingerprint (LF) by fluorescent labeled materials (FLM) is one of the most attractive personnel identification methodology. Here, two FLM based on polyhedral oligomeric silsesquioxane (POSS) nanohybrids labeled with dansyl chromophores have been synthesized and fully characterized. Their photophysical properties have confirmed that these materials clearly possess the prime qualifications as suitable LF sensing platforms. In fact, they adequately detect LFs on glassy surface in excellence legibility.

Keywords

fingerprint detection • silsesquioxanes • dansyl • click chemistry • photostability

1. Introduction

Fluorescent labeled materials (FLMs) are already applying to forensic science such as encoding information for anti-counterfeiting,[1] encryption of confidential data[2] or latent fingerprint (LF).[3] The latter appears to be the best option for personal identification due to their uniqueness and complexity of ridge patterns.[4] Despite the fact that nanoparticles are found to be a potential tool for LF detection,[5] development of novel systems is still required in order to finally take them into account for routine use. Thus, validate nanoparticles should fulfill three desirable properties at the same time: i) particles with nanometric range (up to 100 nm), ii) to be facilely functionalized onto the surface (to permit the selective targeting of fingermark components) and, iii) to have optical properties that facilitate fingermark visualization post development. In this context, some nanohybrids have appeared to suit these characteristics and can be found in the literature.[6,7] For instance, Chen and co-workers[6] developed a nanohybrid which exhibited traffic light-type fluorescence color change when exposed to TNT. Thus, red-emitting Cu-doped ZnCdS (Cu–ZnCdS) quantum dots were embedded into silica nanoparticles and the green-emitting ZnCdS quantum dots were anchored onto the surface of the silica nanoparticles and further functionalized with polyallylamine (PAA). Due to this proper structural design, the nanohybrid was capable of both fingerprint staining and drug/explosive visualization. Cui and coworkers[7] synthesized fluorescent carbon and silica nanohybrids in one simple step which resulted in effective FLMs for the image of LFs on a variety of surfaces including i.e. single background color materials (marbles, transparent tape, white ceramic tiles, black plastic pages, stainless steel sheets, and painted wood) and multicolored surfaces (drink bottle foils and fresh fruits); in this particular case a comparative study with benchmark techniques was however missed. Very recently, we have explored the feasibility of a rigid 3D hetero-structural material based on polyhedral oligomeric silsesquioxane (**POSS**) mono-doped with different chromophores for LFs detection (Figure 1A).[88] We demonstrated that these cubic octameric frameworks (T8) with an adequate cage size (0.5-0.7 nm), exhibited high stability, excellent biocompatibility in biological

environment and effectiveness for LF detection. From a mechanistic point of view, recent studies have shown that hydrophobicity is a major yardstick to fingerprinting development mechanism.[9,10] In this line, the Si–O–Si skeleton clearly provided hydrophobic properties. In addition, labelling with a dansyl fluorophore was carefully chosen considering not only its photophysical properties (very large Stoke's shift and environment-sensibly) but also hydrophobicity of the 3D nanohybrid remained unaltered. The mechanism of detection implied hydrogen-bonding with the residual amino acids in the fingerprints. In view of the necessity of progressing in the forensic science area and the non-stop evolution on constructing new materials for LF application, we have made a step forward into these promising 3D materials which are barely known. The strategy is now based on anchoring to the Si–O–Si skeleton with eight fluorescent chromophores in order to provide it with unprecedent characteristics in terms of photophysical properties, photostability and great effectiveness on LF detection, pointing to favor hydrogen-bonding interactions (Figure 1A).

In this study, two novel eight-dansyl-functionalized POSS nanohybrids have been successfully synthesized (**POSS-D8** and **POSS-S-D$_8$**) following a three-step procedure (Figure 1B). Both nanohybrids fulfil the three prime requisites: i) they fall less than 100 nm, ii) they can be easily functionalized by simple synthetic routes and, iii) they present excellent optical properties for a successful real LF detection.

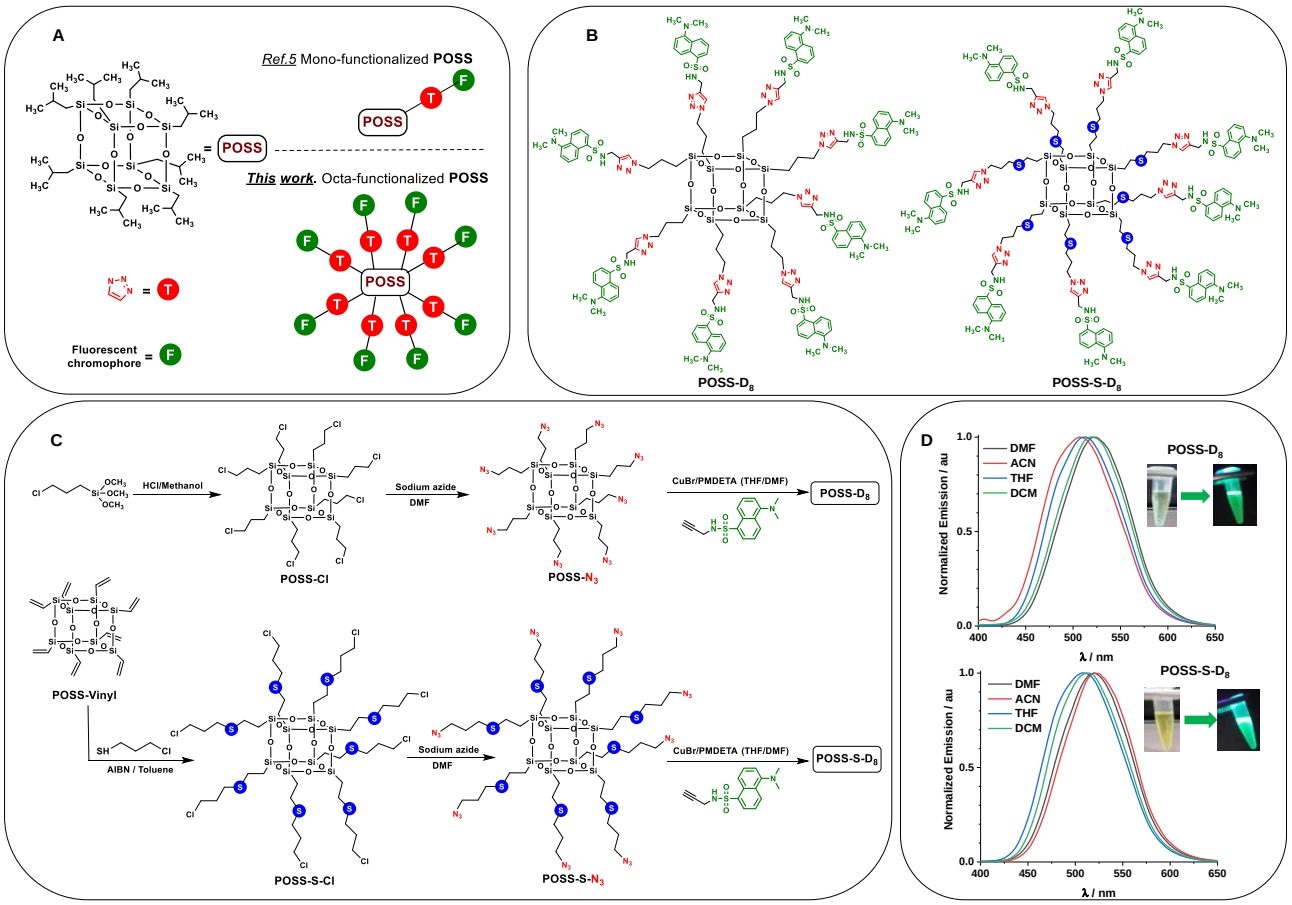

Figure 1. A) Schematic illustration of the mono- (see ref. 8) and octa-functionalization (this work) of 3D POSS. **B**) Chemical structures of octakis(N-dansyl-((1-propyl-1H-1,2,3-triazol-4-yl)methyl))octasilsesquioxane (**POSS-D$_8$**) and its analogue with thioether bridges (**POSS-S-D$_8$**). **C**) Synthetic routes for **POSS-D$_8$** and **POSS-S-D$_8$**. **D**) Normalized emission spectra (λ_{exc} = 340 nm) of **POSS-D$_8$** (top) and **POSS-S-D$_8$** (bottom) in different solvents (DMF = dimethylformamide; ACN = acetonitrile; THF = tetrahydrofuran; DCM = dichloromethane) under aerobic conditions. Concentrations were fixed at [**POSS-D$_8$**] = 0.004 mM and [**POSS-S-D$_8$**] = 0.04 mM. Insets: Photographs of both nanohybrids in solution before and after light exposure.

2. Experimental Section

Materials

^{1}H NMR spectra were recorded on a Bruker Avance 300 or 400 MHz spectrometer in $CDCl_3$ or DMSO-d^6. The residual undeuterated solvent signal was used as reference, relative to the

tetramethylsilane signal. ^{13}C NMR were recorded on a Bruker Avance 300 or 400 MHz (respective resonance frequency: 75 and 101 MHz) under broadband ^{1}H decoupling in $CDCl_3$ or DMSO-d^6. ^{29}Si NMR were recorded in the same vein. The residual undeuterated solvent signal was used as reference, relative to the tetramethylsilane signal. ^{1}H NMR and ^{13}C NMR data were reported as follows: Chemical shifts were reported in the δ scale relative to residual $CDCl_3$ (7.26 ppm) for 1H NMR and to the central line of $CDCl_3$ (77.16 ppm) for ^{13}C NMR. FT-IR spectra were obtained with an Agilent Technologies Cary 630 FT-IR spectrometer equipped with Golden Gate Diamond ATR (attenuated total reflection. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F254; visualization was accomplished with short-wavelength UV light (254 nm) and/or staining with appropriate stains (anisaldehyde, orthophosphomolybdic acid). Standard flash chromatography was performed using Macherey-Nagel silica gel of a particle size 40−63 μm. 3-chloropropyltrimethoxylsilane, trichlorovinylsilane, amberlite-R120, 3-chloro-1-propanethiol and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma-Aldrich. All other commercially available reagents and solvents were used without further purification.

Synthesis and characterization of compounds

Synthesis of alkynyl dansyl derivative: 5-(dimethylamino)-*N*-(2- propynyl)-1-naphthalenesulfonamide (*N*-dansyl propynyl, **D**) was prepared according to previous procedure.[11] ^{1}H and ^{13}C NMR spectral data for **D** were found to be similar to those found in literature.

Synthesis of octakis(3-chloropropyl)octasilsesquioxane (**POSS-Cl**):[12] A solution of 150 mL of dry methanol and 5 mL of concentrated hydrochloric acid was placed in a two-necked, round-bottomed flask equipped with a condenser, an addition funnel, and a magnetic stir bar. To this solution was added dropwise a portion of (3-chloropropyl)trimethoxysilane (15 g, 0.075 mol) through the addition funnel over a period of 10 min with vigorous stirring. The stirring was continued for 2 h until the solution had cooled to room temperature. The reaction mixture was kept at room temperature for another 48 h without stirring. After 2 days, di-*n*-butyltin dilaurate (0.15 g, 0.24 mmol), as a

condensation catalyst, was added with stirring. The reaction mixture was maintained at room temperature for 2 days until a white crystalline precipitate appeared. The solution was filtered, and the crystals were collected, washed several times with methanol, and dried under vacuum.

^{1}H NMR ($CDCl_3$, 298 K, 300 MHz; ppm): 0.78 (t, 16H, $SiCH_2$); 1.84 (q, 16H, CH_2); 3.53 (t, 16H, CH_2Cl). ^{13}C NMR ($CDCl_3$, 298 K, 75.5 MHz; ppm): 9.9 ($SiCH_2$-); 26.4 (-CH_2-); 47.1 (-CH_2Cl). ^{29}Si NMR (CDCl3, 298 K, 59.6 MHz; ppm): -67.28.

Synthesis of octakis(3-azidopropyl)octasilsesquioxane (**POSS-N_3**):[13] **POSS-Cl** (0.935 mmol, 0.98 g) and NaN_3 (2.13 g) were added to a flask equipped with a magnetic stirrer along with 17 mL of anhydrous N,N-dimethylformamide (DMF). The reaction was carried out at 120 °C for 48 h. After completion of the reaction, distilled water was added, and the mixture was extracted with CH_2Cl_2. Organic layers were dried over anhydrous sodium carbonate, filtered, and concentrated under reduced pressure to obtain the desired product as a yellow viscose liquid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 0.71-0.74 (t, 16H, $SiCH_2$), 1.66-1.73 (q, 16H, CH2), 3.25-3.28 (t, 16H, CH_2N_3). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 8.95 ($SiCH_2$-), 22.42 (-CH_2), 53.36 (-CH_2N_3). ^{29}Si NMR (CDCl3, 99 MHz) δ (ppm) -67.04.

Synthesis of octakis(3-dansylpropyl)octasilsesquioxane (**POSS-D_8**): Under nitrogen atmosphere, to a 10 mL DMF/THF (1:1) solution of **POSS-N_3** (0.1 g, 9.2 x 10-5 mol) was added *N*-dansyl propynyl, **D** (0.24 g, 8.3 x 10-4). CuBr (50% mol equivalent) and PMDETA (50% mol equivalent) were successively added. The reaction mixture was stirred at RT overnight. 0.02 M EDTA was added and extracted with DCM. Organic phase was further washed with deionized water and Na_2SO_4 added. After filtration and concentration in a rotary evaporator, further purification was achieved in a column chromatography (Hexane: Ethyl acetate, 30%) to afford the desired product as a light yellow solid (0.078 g, yield 78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.61 (t, 16H, -$SiCH_2$-), 1.81 (m, 16H, Si-CH_2CH_2-), 2.8 (s, 48H, -$N(CH_3)_2$), 4.24 (overlapped 16H, -CH_2N-), 4.25 (overlapped 16H, triazole-CH_2NH-), 7.15 (s,

8H, -CH_2NH-) 7.7 (s, 8H, in 1,2,3-triazole), 7.3-7.5, 8.25-8.3, 8.5 (all d, 6H, CH in dansyl aromatic); ^{13}C NMR (125 MHz, CDCl3) δ (ppm): 102.5, 107, 116, 118, 123, 128, 131. ^{29}Si NMR (59.6 MHz, CDCl3) δ (ppm): -67.93 (Si-O-Si); FT-IR (cm^{-1}): ν(CH) 2932.6; (CN) 1646; (NCO) 1644.7 ν(C=C-Ar) 1741.9; ν(Si-O-Si) 1161-1020; MS (API-ESI) m/z: 3397.40 [M+H]+. Elemental analysis: calculated for $C_{144}H_{176}N_{40}O_{28}S_8Si_8$ (MW 3396.40) C 45.12, H 5.80, N 18.47; found C 45.16, H 5.88, N 18.51%.

Synthesis of octavinylsilsesquioxane (**POSS-vinyl**): Formation of **POSS-vinyl** was realized based on literature data.[14] Thus, acid Amberlite of medium porosity (40 g) was washed with concentrated hydrochloric acid, water and methanol before charging it into a 500 mL flask, which was equipped with a magnetic stirrer. Methanol (150 mL) was added and stirred at 30ºC. Vinyltrichlorosilane (4.0 mL, 0.04 mol) was added slowly with stirring to the Amberlite methanolic solution. The stirring continued at room temperature for 10 h during which white microcrystals were deposited on the wall of the flask. Methanol was decanted into a pre-prepared 500 mL flask (to be reused in the next experiment). Dichloromethane was added to dissolve the microcrystals and the Amberlite was filtered out for reuse in subsequent experiments. The solvent was evaporated and the vinyl-T8 microcrystals washed several times with methanol.

^{1}H NMR (CDCl3) δ (ppm): 5.69–6.15 (m, H_2C=CH–, 24H); ^{13}C NMR ($CDCl_3$) δ (ppm): 128.70 (C1), 136.95 (C2); ^{29}Si NMR ($CDCl_3$) δ (ppm): −79.8, −80.6 (–SiCH=CH_2).

Synthesis of **POSS-S-Cl**: **POSS-Vinyl** (2.0 g, 3.16 x10^{-3} mol) was dissolved in anhydrous toluene (15 mL) under N_2 atmosphere. The radical initiator AIBN (0.2 g, 1.22 x 10^{-3} mol) was added to **POSS-Vinyl** solution and the reaction mixture was heated to 40 °C. Then the linker 3-chloropropanethiol (2.64 mL, 27 x 10^{-3} mol) was slowly added to the mixture and the reaction was stirred for 13 h at 60°C. After cooling the reaction at room temperature, the supernatant was removed, and the gel was solubilized in dichloromethane (5.0 mL) and precipitated with hexane (5 x 50 mL) at 0°C. Finally,

the gel was dried under reduced pressure to give the desired product as transparent viscous gel (1.97 g, yield 99%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.08 (t, 16H, -$SiCH_2$-); 2.1 (m, 16H, -SCH_2CH_2-); 2.63 (overlapped, 16H, -SCH_2-); 2.65 (overlapped, 16H, $SiCH_2CH_2$-S-); 3.71 (t, 16H, -CH_2Cl). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 42.5, 32.6, 29.8, 26.3, 14.1. ^{29}Si NMR (99 MHz) δ (ppm): -68. Elemental analysis (%) for $C_{40}H_{80}Cl_8O_{12}S_8Si_8$, calculated: C = 31.64, H = 5.30 S = 16.91; found: C = 31.89, H = 5.28, S = 16.55.

Synthesis of **POSS-S-N$_3$**. **POSS-S-Cl** (1.5 g, 9.9 x 10^{-4} mol) and excess of NaN_3 (2.0 g) were added to a flask equipped with a magnetic stirrer along with 15 mL of anhydrous *N*,*N*-dimethylformamide (DMF). The reaction was carried out at 70°C for 2 days. After completion of the reaction, distilled water was added, and the mixture was extracted with CH_2Cl_2. Organic layers were dried over anhydrous sodium carbonate, filtered, and concentrated under reduced pressure to obtain the desired product as a yellow viscose liquid (1.23 g, Yield 82%)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.01 (t, 16H, -$SiCH_2$-); 1.90 (m, 16H, -SCH_2CH_2-); 2.58 (overlapped, 16H, -SCH_2-); 2.61 (overlapped, 16H, $SiCH_2CH_2$-S-); 3.60 (t, 16H, -CH_2Cl). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 41.9, 32.9, 28.8, 25.7, 13.6. ^{29}Si NMR (99 MHz) δ (ppm): -68. Elemental analysis (%) for $C_{40}H_{80}N_{24}O_{12}S_8Si_8$, calculated: C = 30.59, H = 5.13, N = 21.41; found: C = 30.41, H = 5.11, N = 21.44.

Synthesis of **POSS-S-D$_8$**: Under nitrogen atmosphere, *N*-dansyl propynyl, **D** (2.25 g, 7.8 x 10^{-3} mol) was added to 10 mL THF/DMF (1:1) solution of **POSS-S-N$_3$** (1.23 g, 7.8 x 10^{-4} mol). CuBr (50% mol equivalent) and PMDETA (50% mol equivalent) were successively added. The reaction mixture was stirred at RT overnight. 0.02 M EDTA was added and extracted with DCM. Organic phase was further washed with deionized water and Na_2SO_4 added. After filtration and concentration in a rotary evaporator, the solid was recrystallized in chloroform/methanol (1:3) to give the desired product as a light yellow solid (1.12 g, Yield 91%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.09 (t, 16H, -$SiCH_2$-); 2.14 (m, 16H, -SCH_2CH_2-); 2.49 (t, 16H, -SCH_2-); 2.61 (t, 16H, $SiCH_2CH_2$-S-); 2.85 (s, 48H, Ar-$N(CH_3)_2$); 4.15 (t, 16H, -$SCH_2CH_2CH_2$-N-); 4.30 (s, 16H, -CH_2NH); 7.1 (s, 8H, sulfonamide proton NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 15.1, 25, 38, 45.1, 52, 53.3, 66.2, 116.0, 118.6, 121, 128.4, 135.8, 151. ^{29}Si NMR (99 MHz) δ (ppm): - 67. FT-IR (cm^{-1}): v(CH) 2966.6; (CN) 1678; (NCO) 1644.7 v(C=C-Ar) 1741.9; v(Si-O-Si) 1161-1020; MS (API-ESI) m/z: 3875.98 [M+H]+; Elemental analysis (%) for $C_{160}H_{208}N_{40}O_{28}S_{16}Si_8$; ; calculated: C = 48.56, H = 5.41 N = 13.98; found: C = 48.39, H = 5.52, N = 13.79.

Photophysical characterization

Absorption measurements: Steady state absorption spectra were recorded in a JASCO V-630 spectrophotometer. Quartz cells with 1 cm optical path length and 3 mL of capacity were employed. Molar coefficient extinction, ε, was determined according to the Lambert-Beer law:

$Abs = C \cdot \varepsilon \cdot L$

Where, Abs is the absorbance of sample, C concentration, and L the optical path length of the cuvette. Fluorescence experiments: Emission spectra were recorded on a JASCO FP-8500 spectrofluorometer system, provided with a monochromator in the wavelength range of 200-850 nm. From the intersection between normalized excitation and emission spectra the singlet energy was determined. Fluorescence quantum yields were determined using 9,10-dimethylantracene as standard (0.95, ETOH). Experiments were performed at 22 °C.

$$\phi_F = \frac{A_i}{A_{std}} \cdot \frac{Abs_{std}}{Abs_i} \cdot \frac{n}{n_{std}} \phi_{F(std)}$$

Where, A_i is the fluorescence area of the sample, A_{std} is the fluorescence area of standard, Abs and Abs_{std} correspond to the absorbance intensity at excitation wavelength of the sample and standard, respectively, and n is the refraction index of the solvent employed. Fluorescence lifetimes were recorded on a PTI (Photon Technology International) fluorometer which includes a pulsed LED excitation source, a sample holder, and a lifetime detector. For lifetime analysis, EasyLife X software

was used. The employed LEDs source was 340 nm. The excitation conditions are expressed in the supplementary information.

Photostability studies

The two FLMs (**POSS-D$_8$** and **POSS-S-D$_8$**) and alkynyl dansyl precursor in THF, were irradiated with a monochromatic light for 60 hours and photostability was monitored by absorption and emission at interval of time. A conservative monochromatic light irradiation of the samples was equally employed in our laboratory and the absorption profiles were monitored. For this, samples (1.0 x 10^{-5} M) were irradiated with Xenon arc lamp at irradiances of 0.039 W/cm^2 and 0.052 W/cm^2.

Fingerprint development and imaging

As far as this study is concerned, fingermarks were collected from 2 voluntary donors (27 years old and 14 years old) and deposited on phone glassy surface. The donor rubbed his thumb on forehead/nose tip and then it was press-stamped on selected substrate, immersed in FLM solution, and rinsed with water or some organic solvents. The developed fingerprint in **POSS-D$_8$** or **POSS-S-D$_8$** was illuminated with UV lamp (365 nm) and image taken with Samsung smartphone camera.

3. Results and Discussion

The 3D **POSS** nanohybrids were synthesized following a three-step procedure (Figure 1C). In the case of **POSS-D$_8$**, catalytic treatment of 3-chloropropyltrimethoxylsilane by di-*n*-butyltin dilaurate in acidic methanol gave the desired octakis(3-chloropropyl)octasilsesquioxane (**POSS-Cl**). Then, typical reaction of **POSS-Cl** with sodium azide in dimethylformamide afforded the corresponding azide-substituted material octakis(3-azidopropyl)octasilsesquioxane (**POSS-N$_3$**). Last step involved the copper "click" reaction between the resultant **POSS-N$_3$** and 5-(dimethylamino)-*N*-(2- propynyl)-1-naphthalenesulfonamide (*N*-dansyl propynyl, **D**) which had been previously synthesized according to literature.[11] Our desired product, **POSS-D$_8$**, was obtained in high yield (78%) as a light yellow solid. Regarding **POSS-S-D$_8$**, the protocol commenced with the octavinylsilsesquioxane (**POSS-**

Vinyl) which was fabricated as described in the experimental section.[14] Thus, treatment of **POSS-Vinyl** with a radical initiator (azobisisobutyronitrile, AIBN) in the presence of 3-chloro-1-propanethiol afforded quantitatively the octakis(2-((3-chloropropyl) thio)ethyl)octasilsesquioxane (**POSS-S-Cl**). Following the same synthetic sequence as abovementioned, **POSS-S-Cl** was converted into octakis(2-((3-azidopropyl)thio)ethyl)octasilsesquioxane (**POSS-S-N_3**) by azidation in high yield (82%) and, subsequently formation of the final product, **POSS-S-D_8**, was obtained in excellent yield (91%) by the CuBr/PMDETA catalyzed "click" reaction of **POSS-S-N_3** with *N*-dansyl propynyl **D**. The chemical structures of **POSS-D_8** and **POSS-S-D_8** were fully characterized by NMR spectroscopy (Figures S1-S6). For **POSS-D_8**, characteristic hydrogen resonances of -$SiCH_2CH_2CH_2$-N, dansyl-$N(CH_3)_2$, downfield sulfonamide singlet proton (δ 7.15) and dansyl aromatic protons were clearly identified. Additionally, the presence of the triazole singlet proton (δ 7.7) evidenced that the "click" reaction was succeeded. Furthermore, ^{29}Si NMR spectrum of **POSS-D_8** (Figure S7) showed a strong single peak, confirming that the Si–O–Si skeleton was not affected during the different synthetic steps. As a matter of fact, FTIR spectra reflected this fact where the structural evolution **POSS-Cl** → **POSS-N_3** → **POSS-D_8** was displayed (Figure S8). To highlight the disappearance of the azide group after the "click" reaction together with the appearance of carbon-carbon double bond which corresponded to the aromatic dansyl chromophore anchored to the Si–O–Si skeleton. In the case of **POSS-S-D_8**, protons due to –$SiCH_2CH_2$-S-$(CH_2)_3$- arms of **POSS**, sulfonamide, triazole, -$N(CH_3)_2$, -CH_2NH- and dansyl aromatics were clearly assigned in the ^{1}H NMR spectrum, confirming the chemical structure (Figures S9-S10). Again, the integrity of the nanocage was confirmed by the presence of one signal in the ^{29}Si NMR spectrum (Figure S11), which is typical of T8R8 structure corresponding to the T3 silicon units.[15,16] Finally, on the basis of the FTIR spectra (Figure S12), structural evolution **POSS-S-Cl** → **POSS-S-N_3** → **POSS-S-D_8** was also observed. Energy-minimized structure of nanohybrids **POSS-D_8** and **POSS-S-D_8** showed a molecular dimension of ca.

3.2 nm and 4 nm, respectively (Figure S13). Optical properties of **POSS-D$_8$** and **POSS-S-D$_8$** were detailed studied in several solvents (Figure 1D and Table 1).

Table 1. Photophysical properties of **POSS-D$_8$** and **POSS-S-D$_8$**

	POSS-D$_8$							**POSS-S-D$_8$**						
solvent	$^a\lambda_{abs,max}$	$^a\lambda_{em,max}$	$^b\varepsilon$	^{c}Stokes	$^d E_S$	ϕ_F	ϕ_{nrad}	$^a\lambda_{abs,max}$	$^a\lambda_{em,max}$	$^b\varepsilon$	^{c}Stokes	$^d E_S$	ϕ_F	ϕ_{nrad}
DMF	338	519	54510	10328	67.4	0.33	0.67	335	519	2998	10582	67.3	0.91	0.09
ACN	338	522	40350	10429	66.5	0.31	0.69	339	522	2456	10341	66.6	0.64	0.26
THF	341	506	62019	9562	70.2	0.50	0.50	340	509	5469	9765	68.5	0.70	0.30
DCM	341	512	57848	9794	67.0	0.46	0.54	340	514	3675	9956	66.9	1	0

^{a}in nm; ^{b}in $M^{-1}cm^{-1}$; ^{c}*in* cm^{-1}; ^{d}in kcal mol^{-1}

Similar absorption spectra of both nanohybrids were found in which the absorption band at UVA region was clearly dominated by the dansyl-type chromophore (Figures S14-S15). They presented very high values of Stoke's shifts as typically found for dansylated derivatives.[17] The most important difference was attributed to the corresponding molar absorption coefficients (ε), being remarkably higher in the case of **POSS-D$_8$** than those for **POSS-S-D$_8$**. On the contrary, fluorescence quantum yields (ϕ_F) **POSS-S-D$_8$** were found to be in general 2 times higher than the values observed for nanohybrid **POSS-D$_8$**, with the occurrence that the sulfur bridge may influence in the radiative and non-radiative pathways of the material. As a general trend, higher values of ϕ_F were detected in moderately polar solvents. To noteworthy that the ϕ_F of **POSS-S-D$_8$** was found to be the unity in DCM, indicating no energetic losses. A satisfactory fitting was obtained by considering a biexponential function for the emission decay traces of **POSS-D$_8$** and **POSS-S-D$_8$** (Table 2 and Figures S16-S17). This was in fully agreement with previously reported data[8] for similar **POSS** nanohybrid containing only one dansyl chromophore. Thus, an intramolecular charge transfer (ICT) state (shorter lifetimes) and possible aggregates (longer lifetimes) could be the responsible of these two emissive lifetimes. However, contribution of the longer lifetime component was actually in the same extend or even higher, especially in moderately polar solvents, indicating unambiguously

formation of aggregates. As a premise, it could evidence for enhancing the fluorescence quantum yield and stability of the nanohybrids.

Table 2. Fluorescence lifetimes[a] of **POSS-D$_8$** and **POSS-S-D$_8$**

	POSS-D$_8$	**POSS-S-D$_8$**
solvent	τ_F (τ_1;τ_2)	τ_F (τ_1;τ_2)
DMF	11.7 (53%); 25.4 (47%)	13.1 (62%); 31.1 (38%)
ACN	11.7 (77%); 27.5 (23%)	13.2 (81%); 36.6 (19%)
THF	10.1 (53%); 23.8 (47%)	11.1 (60%); 29.4 (40%)
DCM	11.6 (40%); 26.2 (60%)	12.3 (48%); 29.8 (52%)

[a]in ns; in brackets the contribution of each lifetime.

Photostability of **POSS-D$_8$** and **POSS-S-D$_8$** was evaluated by monitoring their absorption spectra before and after (60 min) monochromatic light irradiation (λ_{irr} = 340 nm) in THF as solvent (Figure 2). Hence, the absorption spectra of both materials were completely similar even after 60 min of continuous photolysis, showing a magnificent photostable properties. In order to use more sensitive analytical technique, emission spectra were also recorded before and after irradiation (Figure S18). Here, **POSS-D$_8$** and **POSS-S-D$_8$** retained the 90% and 86%, respectively, of the fluorescence intensity.

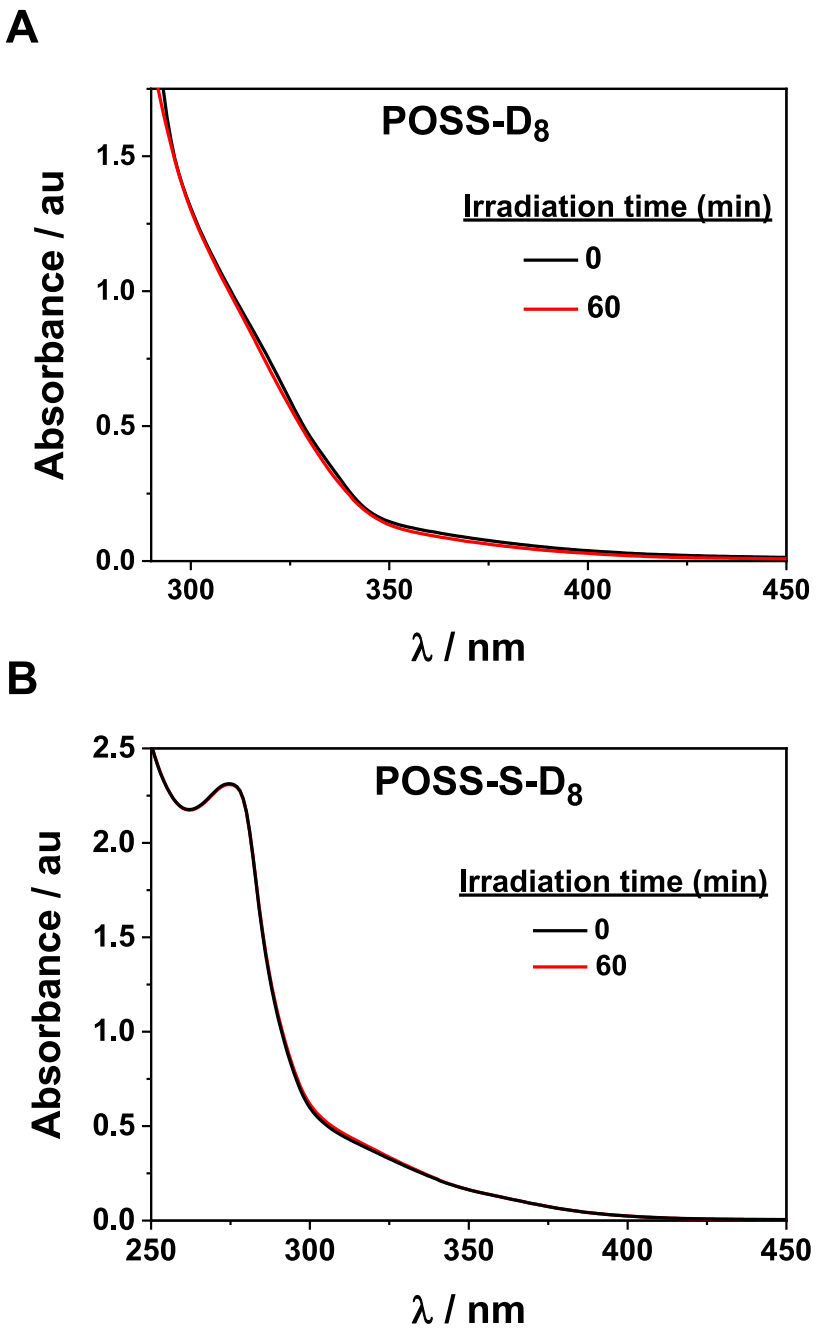

Figure 2. Absorption spectra of **A**) **POSS-D8** (0.004 mM) and **B**) **POSS-S-D8** (0.04 mM) in aerated THF before and after monochromatic light irradiation (λ_{irr} = 340 nm).

A judicious balance of hydrophobic and π-π interactions have been recognized in previous reports for the application of FLMs in LF detection.[8,9,10] Accordingly, our FLMs were designed based on the combination of a Si-O-Si skeleton and multiple dansyl scaffolds. Figure 3 shows images

corresponding to fresh (0 day) and aged fingerprints (i.e. stored at RT for 60 days) (see ESI for details). While undeveloped fingerprint patterns were hardly visible under UV (365 nm) or visible light, those developed under diluted solution of **POSS-D$_8$** or **POSS-S-D$_8$** apparently exhibited enhanced legibility due to greater contrast between the fluorescent ridge and non-fluorescent furrow. Importantly, the brightness, contrast and general visual legibility remained intact for at least 60 days, indicating a very good photostability of both FLMs. This is ascribed to the structural hydrophobic features of the nanohybrids, which provide an optimal affinity to the amino acid-based oily compounds present in the fingerprints through hydrogen bonding (e.g. S=O××××H-N (amino acid)).[18,19] Moreover, enlarged areas showed whorl, bifurcation, and ridge ending (Figure 3, right side), which fulfill the requirements for fingerprint identification.

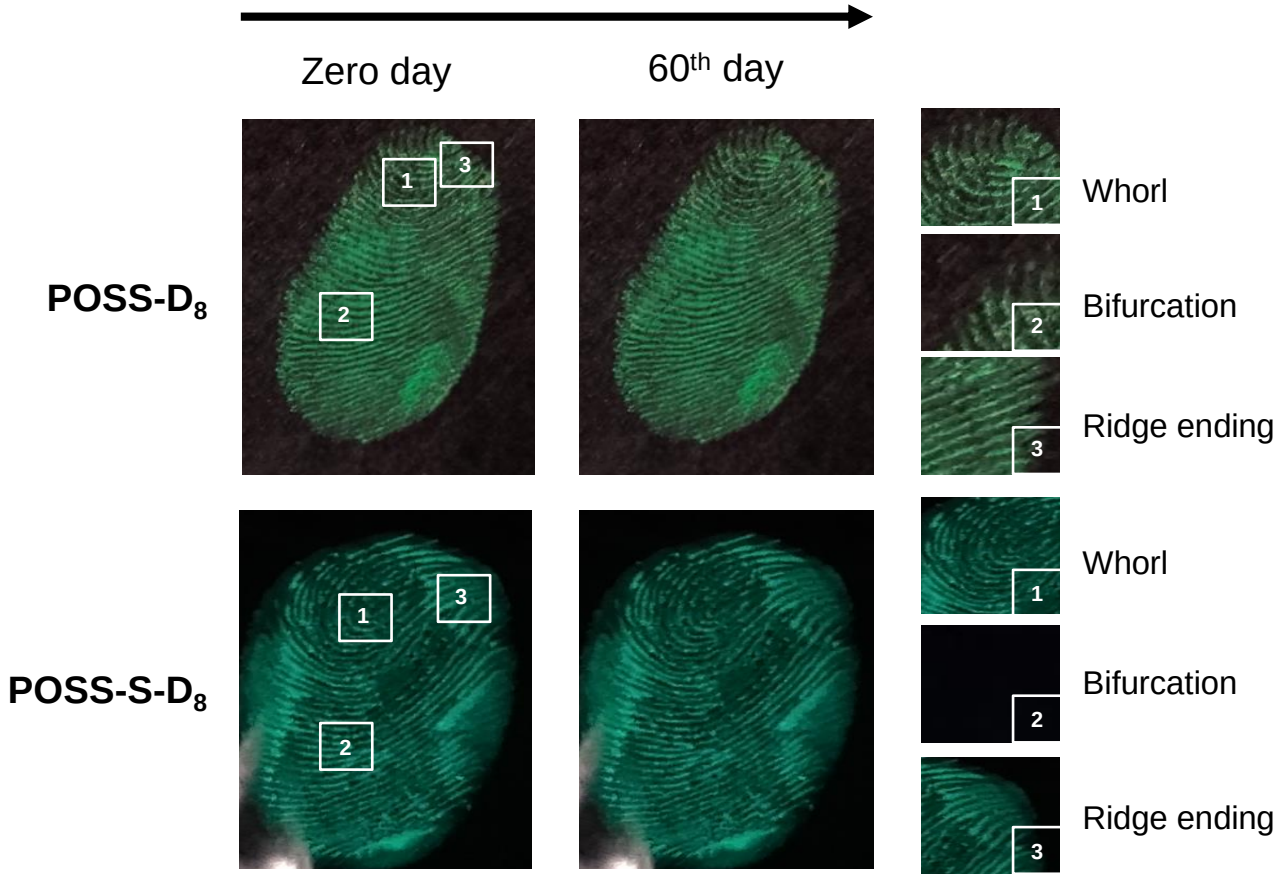

Figure 3. Representative digital photos of fingerprints on smooth phone-glass surfaces detected by means of **POSS-D$_8$** and **POSS-S-D$_8$**. Enlarged zones identified with numbers are given on the right.

4. Conclusions

In summary, two novel octa-dansyl fluorescently labeled POSS (POSS-D8 and POSS-S-D8) have been easily synthesized via “click” chemistry. These nanohybrids were fully characterized and the photophysical study revealed significantly higher molar absorption coefficient for POSS-D8, while the fluorescence quantum yield was 2 times higher in the case of POSS-S-D8. Both FLMs displayed exceptionally distinguished photostability well above that of the N-dansyl propynyl precursor. The two photoresponsive octadansyl labeled POSS enabled the detection of latent fingerprints on phone glassy surfaces with very good legibility according to the requirements for forensic applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

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