Highly efficient latent fingerprint detection by eight-dansyl-functionalized octasilsesquioxane nanohybrids

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The largely demand in continued 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 methodologies. 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 with excellence legibility.

1. Introduction

Fluorescent labeled materials (FLMs) are already being applied in 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 routine use. Thus, validation of 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 fingerprint components) and, iii) to have optical properties that facilitate fingerprint 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 poly (allylamine) (PAA). Due to this appropriate structural design, the nanohybrid was capable of both fingerprint staining and drug/explosive visualization. Cui and co-workers [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 e.g. 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 LF detection (Fig. 1A). [8] We demonstrated that these cubic octameric frameworks (TB) with an adequate cage size (0.5–0.7 nm), exhibited high stability, excellent biocompatibility in the biological environment [9,10] and effectiveness for LF detection. Fingermark ridges and the interstitial space between them are narrow (ca. 435.5 ± 57.4 μm in width). [11] In theory, the use of nanoparticles could result in greater ridge pattern clarity than using the micron-sized particles in traditional powders that normally contain particles in the submicron to micrometer range. [12] The ability to
deposit a greater number of luminescent nanoparticles along a ridge may also provide enhanced contrast between the ridge and substrate [5]. From a mechanistic point of view, recent studies have shown that hydrophobicity is a major yardstick to fingerprinting development mechanism. [13,14] 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 sensitivity) 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 unprecedented characteristics in terms of photophysical properties, photostability and great effectiveness on LF detection. In this study, two novel eight-dansyl-functionalized POSS nano-hybrids have been successfully synthesized (POSS-D8 and POSS-S-D8) following a three-step procedure (Fig. 1B). Both nanohybrids fulfill the three prime requisites: i) they are smaller 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.

2. Experimental section

2.1. 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 $\delta$ scale relative to residual CDCl$_3$ (7.26 ppm) for $^1$H 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 Cary 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-Chloropropyltrimethoxysilane, trichlorovinylsilane, amberlite-R120, 3-chloro-1-propanethiol and N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma-Aldrich. All other solvents were purchased from Sigma-Aldrich.

Fig. 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]octaisesquioxane (POSS-D8) and its analogue with thioether bridges (POSS-S-D8). C) Synthetic routes for POSS-D8 and POSS-S-D8. D) Normalized emission spectra ($\lambda_{exc} = 340$ nm) of POSS-D8 (top) and POSS-S-D8 (bottom) in different solvents (DMF = dimethylformamide; ACN = acetonitrile; THF = tetrahydrofuran; DCM = dichloromethane) under aerobic conditions. Concentrations were fixed at [POSS-D8] = 0.004 mM and [POSS-S-D8] = 0.04 mM. Insets: Photographs of both nanohybrids in solution before and after light exposure.
commercially available reagents and solvents were used without further purification.

2.2. Synthesis and characterization of compounds

Synthesis of alkylnyl dansyl derivative: 5-(dimethylamino)-N-(2-propynyl)-1-naphthalenesulfonamide (2.2. Synthesis and characterization of compounds

- Elemental analysis: calculated for C_{38}H_{38}N_{10}O_{9}S_{4}S_{6}Si (384.56). 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 NaSO_{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%).

- FT-IR (cm^{-1}): v (CH) 2932.6; (CN) 1646; (NCO) 1644.7 v (C–Ar) 1741.9; v (Si–O–Si) 1305 cm^{-1}; FT-IR (cm^{-1}) v (CH) 2932.6; (CN) 1646; (NCO) 1644.7 v (C–Ar) 1741.9; v (Si–O–Si) 1305 cm^{-1}; MS (API-ESI) m/z: 397.40 [M+H]+. Elemental analysis: calculated for Cu_4H_4N_2O_2S_2Si_6 (MW 3976.40) C 45.12, H 5.80, N 18.47; found C 45.16, H 5.88, N 18.51.

- Synthesis of octakis(3-dansylpropyl)octasilsesquioxane (POSS-vinyl): Formation of POSS-vinyl was realized based on literature data. [18] Thus, acidic amberliter 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 30 °C. 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.

- Synthesis of POSS-NPOSS-SCl: POSS-vinyl (2.0 g, 3.16 × 10^{-3} mol) was dissolved in anhydrous toluene (15 mL) under N_{2} atmosphere. The radical initiator AIBN (0.2 g, 1.22 × 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 × 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 × 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%).

- Synthesis of POSS-NPOSS-SCl (1.5 g, 9.9 × 10^{-4} mol) and excess of Na_{2}S (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_{2}Cl_{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. Spectra results were in accordance with previously reported data.

- Synthesis of octakis(3-dansylpropyl)octasilsesquioxane (POSS-vinyl): Formation of POSS-vinyl was realized based on literature data. [18] Thus, acidic amberliter 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 30 °C. 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.
2.3. Calculation of molecular dimension

The optimized geometries of POSS-D₈ and POSS-S-D₈ were obtained using the MM2 calculation using the CHEMDFRAW 3D software (Job type: Minimize energy to Minimum; RMS Gradient of 0.010; iterations = 10,000).

2.4. 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:

\[ \text{Abs} = C \cdot \varepsilon \cdot L \]

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 spectrophotometer 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 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 optimized geometries of nano-hybrids were synthesized following a three-step procedure (Fig. 1C). In the case of POSS-D₈, catalytic treatment of 3-chloropropytrimethoxysilane by di-n-butyltin dilaurate in acidic methanol gave the desired octakis (3-chloropropyl)octasilsequioxane (POSS-CI). Then, typical reaction of POSS-CI with sodium azide in dimethylformamide afforded the corresponding azide-substituted material octakis (3-azidopropyl)octasilsequioxane (POSS-N₃). Last step involved the copper “click” reaction between the resultant POSS-N₃ 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-D₈ was obtained in high yield (78%) as a light yellow solid. Regarding POSS-S-D₈, the protocol commenced with the octavinylsilsequioxane (POSS-vinyl) which was fabricated as described in the experimental section. [14] Thus, treatment of POSS-vinyl with a radical initiator (azoisobutyronitrile, AIBN) in the presence of 3-chloro-1-propanethiol afforded quantitatively the octakis (2-(3-chloropropyl)thio)ethyl)octasilsequioxane (POSS-S-CI). Following the same synthetic sequence as above-mentioned, POSS-S-CI was converted into octakis (2-(3-azidopropyl)thio)ethyl)octasilsequioxane (POSS-S-N₃) by azidation in high yield (82%) and, subsequently formation of the final product, POSS-S-D₈ was obtained in excellent yield (91%) by the CuBr/PMDETA catalyzed “click” reaction of POSS-S-N₃ with N-dansyl propynyl D. The chemical structures of POSS-D₈ and POSS-S-D₈ were fully characterized by NMR spectroscopy (Figs. S1-S6). For POSS-D₈, characteristic hydrogen resonances of -SiCH₂CH₂CH₂-N, dansyl- N(CH₃)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, ²⁹Si NMR spectrum of POSS-D₈ (Fig. 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-CI → POSS-S-N₃ → POSS-D₈ was displayed (Fig. 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-D₈, protons due to -SiCH₂CH₂CH₂-S-(CH₂)₂N, dansyl- N(CH₃)₂, -CH₂NH- and dansyl aromatics were clearly assigned in the ¹H NMR spectrum, confirming the chemical structure (Figs. S9-S10). Again, the integrity of the nanocage was confirmed by the presence of one signal in the ²⁹Si NMR spectrum (Fig. S11), which is typical of T8R8 structure corresponding to the T₃ silicon units. [19, 20] Finally, on the basis of the FTIR spectra (Fig. S12), structural evolution POSS-S-CI → POSS-S-N₃ → POSS-S-D₈ was also observed. Energy-minimized structure of nano-hybrids POSS-D₈ and POSS-S-D₈ showed a molecular dimension of ca. 3.2 nm and 4 nm, respectively (Fig. S13). Optical properties of POSS-D₈ and POSS-S-D₈ were detailed studied in several solvents (Fig. 1D and Table 1).

Similar absorption spectra of both nano-hybrids were found in which the absorption band in the UVA region was clearly dominated by the dansyl-type chromophore (Fig.s S14, S15). They presented very high values of Stokes shifts as typically found for dansylated derivatives. [21] The most important difference was attributed to the corresponding molar absorption coefficients (ε), being remarkably higher in the case of POSS-D₈ than those for POSS-S-D₈. On the contrary, fluorescence quantum yields (ΦF) POSS-S-D₈ were found to be in general 2 times higher than the values observed for nanohybrid POSS-D₈, 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 ΦF were detected in moderately polar solvents. It was noteworthy that the ΦF of POSS-S-D₈ was found to be unity in DCM, indicating no energetic losses. A satisfactory fitting was obtained by considering a biexponential decay function for the emission decay of POSS-D₈ and POSS-S-D₈ (Table 2 and Figs. S16, S17). This was in full agreement with previously reported data [8] for similar POSS nano-hybrid 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

3. Results and discussion

The 3D POSS nano-hybrids were synthesized following a three-step procedure (Fig. 1C). In the case of POSS-D₈, catalytic treatment of 3-chloropropytrimethoxysilane by di-n-butyltin dilaurate in acidic methanol gave the desired octakis (3-chloropropyl)octasilsequioxane (POSS-CI). Then, typical reaction of POSS-CI with sodium azide in dimethylformamide afforded the corresponding azide-substituted...
aggregates. As a premise, it could evidence for enhancing the fluorescence intensity.

A judicious balance of hydrophobic and π-π interactions have been recognized in previous reports for the application of FLMs in LF detection \cite{8,9,10}. Accordingly, our FLMs were designed based on the combination of a Si-O-Si skeleton and multiple dansyl scaffolds. Fig. 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-D₈ and POSS-S-D₈ 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. $S=O \times \times \times \times H-N$ (amino acid)). \cite{8,22,23} Moreover, enlarged areas showed whorl, bifurcation, and ridge ending (Fig. 3, right side), which fulfill the requirements for fingerprint identification.

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.

Author statement

Enock O. Dare: Conceptualization, Methodology, preparation of materials and characterization, Writing - original draft. Victoria Vendraal-Criado: Photophysical characterization. M. Consuelo Jiménez: Supervision photophysical characterization, proof-reading manuscript. Raúl Pérez-Ruiz: Supervision, Formal analysis, photophysical characterization, photophysical data analysis, writing manuscript. David Díaz Díaz: Conceptualization, Methodology, Supervision, Writing - original draft.
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

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References


