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Synthesis, Structures and Properties of Self-Assembling Quaternary Ammonium Dansyl Fluorescent Tags for Porous and Non-Porous Surfaces

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A series of H_2O and/or EtOH soluble, self-assembling quaternary ammonium salts containing a dansyl (DNS) fluorescent moiety suitable for attachment to both porous ([DNS-NH-$(CH_2)_3$-NMe_2-R^+][X^-] (**2**; R = -Si$(OMe)_3$, X^- = Cl^-) and non-porous (**3a**; R = -PO$(OEt)_2$, **3b**; -PO(*Oi*-Pr)$_2$, **3c**; -$(PO(OH)_2$, X^- = Br^-), **4**; ([DNS-NH-$(CH_2)_3$-NMe_2-$(CH_2)_3$-NH$(CH_2PO(OEt)_2)_2^+$][Br^-], **5**; R = -$((CH_2)_3SCOCH_3$, X^- = Cl^-), **6a**; (R = -$(CH_2)_nO(C_6H_4)CO(C_6H_5)$, n = 3, X^- = Br^-, **6b**; n = 3, X^- = Cl^-, **6c**; n = 3, X^- = I^-, **6d**; n = 4, X^- = Br^-, **6e**; n = 4, X^- = I^-, **6f**; n = 6, X^- = Br^-, **6g**; n = 6, X^- = Cl^-, **6h**; n = 6, X^- = I^-), **7**; (R = -CH_2-CH=CH_2, X^- = Br^-) surfaces were prepared from the precursor dansyl amine (**1**; DNS-NH-$(CH_2)_3$-NMe_2). Compounds **1**-**7** were characterized by NMR (^1H, ^{13}C, ^{29}Si (**2**), ^{31}P (**3a**-**c**, **4**)) spectroscopy, HRMS, UV-vis and Fluorescence spectroscopy. Additional characterization of compounds **1** and **7** were carried out by X-ray structure determinations. Physical attachment of compound **2** to cotton surfaces after immersion in solutions containing fluorescent dyes was verified by exposure to UV light and by complexation with bromo-phenol blue that rendered the surfaces visibly blue in colour. Phosphorus containing dansyl fluorescent dye, **3c**, was attached to a stainless steel surface by exposure to an aqueous solution containing this dye, resulting in the formation of a self-assembled fluorescent monolayer. UV cure of plastic surfaces (polypropylene, silicon medical tubing) coated with compound **6a** resulted in the covalent attachment of the dyes.

Introduction

Infection control and reduction of the spread of microorganisms such as fungi and bacteria is a key challenge facing health care providers. Many microorganisms have the ability to attach to surfaces and proliferate, forming colonies called biofilms.[1] The use of antibiotics to treat infectious diseases, including those caused by biofilms, is one of the most significant medical developments over the last century. However, after widespread use of these antibiotics, as well as other chemicals used for the purpose of disinfection, several strains of microorganisms (e.g. bacteria), have developed resistance.[2-4] For the growing number of microorganisms with clinical importance (pathogens), there is either no efficacious therapy or only one or two effective antibiotics that are difficult to administer, expensive and/or have increasingly toxic side effects. Furthermore, when growing on surfaces as biofilms, microorganisms are generally more persistent, and it is now estimated that the majority of infections (65-80%) involve these biofilms in some form.[4] Biofilms also pose a notable threat of contamination in food processing facilities and spoilage of other products susceptible to microbial attack.[5] One approach in preventing pathogenic biofilm formation, and thus the potential to cause spoilage or infection, is the use of antimicrobial coatings on surfaces that are not susceptible to the development of resistance by the target microorganisms.[1,6,7] These coatings have bacteriostatic (inhibiting) or bactericidal (killing)[8-12] properties and thus afford a preventative strategy compared to disinfection, which is reactive, often after some damage or infection has occurred. In contrast to conventional antibiotics, bacteria do not readily develop resistance to antimicrobial coatings that inhibit microorganisms in a mechanical, as opposed to a chemical, fashion. This important distinction, and the related alarming

rate at which the number of effective antibiotics has declined, is a primary reason for the rapidly growing interest in antimicrobial coatings in recent years.[13-20]

Fig. 1 Examples of absorbed (left) and surface functionalized (right) QAC's.

Quaternary ammonium compounds ("QAC's") including benzylalkonium salts (Figure 1), are well established as surfactants, possess antimicrobial activity and are used as disinfectants.[21,22] QAC's consist of an irreversibly positively charged quaternary nitrogen atom where at least one substituent is often a long aliphatic chain. The synthesis of these compounds involves the quaternization of a tertiary amine following a Menshutkin reaction (i.e. a reaction of a tertiary amine with an alkyl halide).[23-25] Surface bound antimicrobial QAC surface coatings, such as dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride, were first described by Isquith *et al.* who bound dimethyloctadecyl ammonium chloride via a silane anchor onto a variety of polyhydroxy surfaces.[8,26-28] Research into developing alternative ways of grafting QAC's to a multitude of surfaces is hampered by the lack of simple, rapid and non-destructive detection methods for these coatings after they are applied. Traditionally, detection of surface silane bound QAC's on textiles has been achieved by visible staining of treated surfaces with a dilute aqueous solution of the bromophenol blue dye, (4,4'-(1,1-dioxido-3*H*-2,1-benzoxathiole-3,3-diyl)bis(2,6-dibromophenol).[29] Bromophenol blue is a water soluble anionic dye that readily binds to QAC's and is characterized by a strong blue coloured ion pair that is visible to the naked eye. However, this dye often irreversibly binds to the textile, visibly staining the surface and destroying the material for future use. One solution that we envisioned was the use of surface anchored, water soluble QAC's functionalized with a fluorescent dansyl tag as an inexpensive, rapid and simple alternative to bromophenol blue for the facile detection of product surface coverage and coating uniformity. Thus, treated surfaces would glow fluorescent under exposure to a low power UV lamp, identifying areas of poor adhesion as well as missed areas during application. Additionally, it can also act as a unique product identifier and security feature for treated surfaces when added in trace amounts to functional antimicrobial solutions.

The dansyl fluorophore, capable of intermolecular charge-transfer, possesses high emission quantum yields and displays solvatochromism in the excited state giving rise to interesting and useful fluorescence properties.[30,31] Along with the chemical flexibility of the sulfonic acid group, the dansyl amide has been utilized in various applications ranging from chemical sensing materials for the detection of explosives, biological weapons, metal ions, pH and as a probe/label for amino acids in the study of various diseases and metabolic pathways. For example, dansyl-functionalized organosilane self-assembled monolayers (SAM's) on glass surfaces were used to sense explosives (e.g. nitroarenes),[32] whereas SAM's on silicon were used to sense pH, Hg^{2+}, Cl^-, and Br^- ions.[33] Other functionalized dansyl probes have been used to study various diseases. In a study of the effect of copper on Alzheimer's and Wilson's diseases, Pitchumani designed dansyl-thiol silver nanoparticles for sensing Cu^{2+} ions.[31] Meanwhile, Viirre and his group utilized Pd catalysis chemistry to incorporate a dansyl probe for the study of protein-protein interactions in cystic fibrosis research.[34] Dansyl phosphonic acid was also recently used to help elucidate organophosphonate metabolism in bacteria.[35]

Experiments and Methods

Materials

The reagents, 3-(dimethylamino)propylamine, 3-(chloropropyl)trimethoxysilane, diethyl(3-bromopropyl)phosphonate, *N*,*N*'-dimethylethylenediamine, 3-chlorpropylthioacetate, allyl bromide, ACN, EtOH, were used as received (Sigma Aldrich). Anhydrous DCM and Et_2O were obtained by passage through a bed of activated molecular sieves under an atmosphere of dry $N_{2(g)}$. Dansyl chloride (> 97%) was used as received (Alfa Aesar). All fluorescent compounds were stored in glass vials in the absence of light.

Nuclear magnetic resonance (NMR) experiments were recorded on a 400 MHz Bruker Avance II Spectrometer using deuterated chloroform ($CDCl_3$) as the solvent unless otherwise indicated. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual $CHCl_3$ (δ_H = 7.26 ppm) and the central peak of $CDCl_3$ (δ_C = 77.0 ppm) solvent signal respectively. The $^{31}P\{^1H\}$ spectra were referenced externally to 85% phosphoric acid (δ_P = 0.00 ppm). Proton chemical shift assignments given in δ (ppm) were interpreted with the aid of 2-D COSY spectra, while carbon chemical shift assignments given in δ (ppm) were interpreted with the aid of 2-D HSQC spectra. Microwave reactions were performed in sealed glass reaction tubes utilizing the Biotage® Initiator Microwave Synthesizer (2.45 GHz). UV-VIS and fluorescence measurements were recorded on a Perkin Elmer Spectrophotometer (Lambda 20) and a Perkin Elmer Luminescence Spectrophotometer (LS 50B) respectively at the Ryerson University Analytical Centre (RUAC). High resolution mass spectra (HRMS) were recorded by direct analysis in real time by DART-TOF or by electrospray time-of-flight (ESI-TOF) at the Advanced Instrumentation for Molecular Structure (AIMS) laboratory at the University of Toronto. X-ray crystal structure analysis was performed with a Bruker-Nonius Kappa-CCD diffractometer at the University of Toronto X-ray diffraction facilities. Thin Layer Chromatography (TLC) was carried out on Silica gel 60 aluminium backed plates and visualized with a UV lamp or staining with ($KMnO_4$ or Ninhydrin). Melting points were measured using a Fischer Scientific melting point apparatus. UV curing of samples was achieved with a Novocure UV curing system from EFOS. UV curing of samples was initiated by UV curing at UV(A) (320-390 nm) and UV(V) (395-445 nm) wavelengths by exposing 1

× 1 cm^2 samples for 2.5 mins at distance of 5 cm from the light source. Samples were subjected to an average UV dosage of 3.80 ± 0.369 J/cm^2 UV(A) and 2.32 ± 0.242 J/cm^2 UV(V) and irradiance of 3.05 × 10^{-2} ± 1.90 × 10^{-3} W/cm^2 UV(A) and 1.90 × 10^{-2} ± 1.90 × 10^{-3} W/cm^2 UV(V). Dose and irradiance measurements were measured with an EIT Power Puck.

Synthesis of Precursors for the Dansyl Quaternization Reaction

Tetraethyl(((3-iodopropyl)azanediyl)bis(methylene)) bis(phosphonate)

A mixture of 3-(bis((diethoxyphosphoryl)methyl)amino)propyl methanesulfonate (1.0 g: 2.21 mmol) and NaI (0.69 g: 4.6 mmol) in acetone (3 mL) were placed, with a magnetic stirring bar, into a 5 mL μW glass reaction tube and sealed. The reaction mixture was placed in microwave and, with constant stirring, run at 100°C for 5 min. The yellow solid was transferred to a 100 mL round bottom flask and washed with acetone (50 mL). Volatiles were removed with the aid of rotary evaporation and the crude material diluted with brine (10 mL) and then extracted with $CHCl_3$ (10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, and dried on a vacuum line and recovered as a yellow oil. Yield: 0.80 g (75%). TLC (10% w/w NH_4OH/acetone): R_f = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.20-4.09 (m, 8H: H6), 3.24 (t, 2H, *J* = 7.0 Hz: H5), 3.15 (d, 4H, *J* = 8.7 Hz: H4), 2.89 (t, 2H, *J* = 6.6 Hz: H3), 2.03-1.94 (m, 2H: H2), 1.33 (t, 12H, *J* = 7.0 Hz: H1); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 61.92 (t, $^2J_{C\text{-}P}$ = 3.4 Hz, C6), 55.08 (C3), 49.46 (C4), 31.09 (C5), 30.96 (C2), 16.49 (t, $^3J_{C\text{-}P}$ = 2.9 Hz: C1); ^{31}P{^{1}H} NMR (121.45 MHz, $CDCl_3$, δ): 24.79 ppm.

4-(3-bromopropyoxy)benzophenone[36,37]

1,3-dibromopropane (6.14 mL: 60.5 mmol), K_2CO_3 (4.18 g: 30.2 mmol) and 4-hydroxybenzophenone (3.0 g: 15.1 mmol) were stirred in ACN (20 mL) under reflux for 24 h. The crude product was recrystallized in toluene/hexanes to give an off white coloured powder. Yield: 3.22 g (66.7%). Mp = 52-53°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.83 (d, 2H, *J* = 8.7 Hz: H1), 7.77 (d, 2H, *J* = 8.3 Hz: H7), 7.58 (t, 1H, *J* = 7.4 Hz: H3), 7.48 (t, 2H, *J* = 7.7 Hz: H2), 6.98 (d, 2H, *J* = 8.7 Hz: H8), 4.20 (t, 2H, *J* = 5.8 Hz: H10), 3.63 (t, 2H, *J* = 6.3 Hz: H12), 2.37 (q, 2H, *J* = 6.0 Hz: H11) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.51 (C5), 162.30 (C9), 138.23 (C4), 132.58 (C3), 131.94 (C7), 130.36 (C6), 129.74 (C1), 128.21 (C2), 114.04 (C8), 65.53 (C10), 32.13 (C12), 29.74 (C11) ppm. This compound was previously prepared by Krichelodorf *et al.*, but not characterized by NMR.[38] HRMS-DART (m/z): [MH^+] calculated for $C_{16}H_{15}BrO_2$, 319.0334; found, 319.0329.

4-(3-chloropropoxy)benzophenone[37,38]

1-bromo-3-chloropropane (5.00 mL: 50.4 mmol), K_2CO_3 (3.49 g: 25.3 mmol) and 4-hydroxybenzophenone (2.50 g: 12.6 mmol) were stirred in ACN (20 mL) under reflux for 24 h. The crude product was filtered off and recrystallized in toluene/hexanes to yield an off white coloured powder. Yield: 1.21 g (34.9%). Mp = 60-61°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.83 (d, 2H, *J* = 8.4 Hz: H1), 7.76 (d, 2H, *J* = 7.2 Hz: H7), 7.56 (t, 1H, *J* = 7.3 Hz: H3), 7.48 (t, 2H, *J* = 7.5 Hz: H2), 6.96 (d, 2H, *J* = 8.4 Hz: H8), 4.23-4.16 (m, 2H: H10), 3.76 (t, 2H, *J* = 5.9 Hz: H12), 2.28 (t, 2H, *J* = 11.4 Hz: H11) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.53 (C5), 162.34 (C9), 138.25 (C4), 132.58 (C3), 131.93 (C7), 130.37 (C6), 129.74 (C1), 128.21 (C2), 114.04 (C8), 64.50 (C10), 41.30 (C12), 32.07 (C11) ppm. HRMS-DART (m/z): [MH^+] calculated for $C_{16}H_{15}ClO_2$, 275.0838; found, 275.0841. (This compound was previously reported by Saettone *et al.*, but not fully characterized).[40]

4-(3-iodopropoxy)benzophenone[37]

4-(3-bromopropyoxy)benzophenone (1.00 g: 3.13 mmol) and NaI (1.41 g: 9.40 mmol) were mixed in acetone (10 mL) under reflux for 24 h. The crude product was filtered off and recrystallized in toluene/hexanes (1:2) to afford a yellow coloured powder. Yield: 0.59 g (51%). Mp = 72-74°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.85-7.80 (m, 2H: H1), 7.77-7.73 (m, 2H: H7), 7.56 (ddt, 1H, *J* = 8.6 Hz, *J* = 6.6 Hz, *J* = 1.3 Hz: H3), 7.50-7.43 (m, 2H: H2), 6.99-6.89 (m, 2H: H8), 4.13 (t, 2H, *J* = 5.8 Hz: H10), 3.38 (t, 2H, *J* = 6.7 Hz: H12), 2.35-2.27 (m, 2H: H11) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.54 (C5), 162.30 (C9), 138.24 (C4), 132.59 (C3), 131.94 (C7), 130.39 (C6), 129.75 (C1), 128.21 (C2), 114.06 (C8), 67.52 (C10), 32.72 (C11), 2.13 (C12) ppm. HRMS-DART (m/z): [MH^+] calculated for $C_{16}H_{15}IO_2$, 367.0195 found, 367.0202.

4-(4-bromobutoxy)benzophenone[37]

1,4-dibromobutane (6.02 mL: 50.4 mmol), K_2CO_3 (3.49 g: 25.3 mmol) and 4-hydroxybenzophenone (2.50 g: 12.6 mmol) were stirred in ACN (20 mL) under reflux for 24 h to give a crude product of 4-(4-bromobutoxy)benzophenone which was recrystallized in toluene/hexanes to yield a pale yellow powder. Yield: 3.84 g (91.6%). Mp = 50-51°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.81 (d, 2H, *J* = 8.8: H1), 7.74 (d, 2H, *J* = 7.2: H7), 7.55 (t, 1H, *J* = 7.4: H3), 7.46 (t, 2H, *J* = 7.7: H2), 6.94 (d, 2H, *J* = 8.8 Hz: H8), 4.07 (t, 2H, *J* = 5.9 Hz: H10), 3.50 (t, 2H, *J* = 6.5 Hz: H13), 2.14-2.05 (m, 2H: H11), 2.04-1.95 (m, 2H: H12) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.53 (C5), 162.52 (C9), 138.29 (C4), 132.59 (C3), 131.90 (C7), 130.20 (C6), 129.73 (C1), 128.20 (2), 113.99 (C8), 67.13 (C10), 33.29 (C13), 29.36 (C12), 27.77 (C11) ppm. HRMS-DART (m/z): [MH^+] calculated for $C_{17}H_{17}BrO_2$, 333.0490 found, 333.0486.

4-(4-iodobutoxy)benzophenone[39]

4-(4-bromobutoxy)benzophenone (1.00 g : 3.00 mmol) and NaI (0.900 g: 6.00 mmol) were mixed in acetone (10 mL) under reflux for 24 h to give crude product of 4-(4-iodobutoxy)benzophenone which was recrystallized in toluene/hexanes (1:2) to afford a pale yellow powder. Yield: 1.03 g (90.2%). Mp = 84-86°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.80 (d, 2H, *J* = 8.7: H1), 7.74 (d, 2H, *J* = 7.3: H7), 7.54 (t, 1H, *J* = 7.3: H3), 7.47 (t, 2H, *J* = 7.6: H2), 6.93 (d, 2H, *J* = 8.8 Hz: H8), 4.06 (t, 2H, *J* = 5.9 Hz: H10), 3.26 (t, 2H, *J* = 6.7 Hz: H13), 2.10-2.02 (m, 2H: H11), 2.00-1.90 (m, 2H: H12) ppm;

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 195.54 (C5), 162.52 (C9), 138.29 (C4), 132.59 (C3), 131.90 (C7), 130.20 (C6), 129.73 (C1), 128.20 (C2), 113.99 (C8), 66.93 (C10), 30.06 (C12), 30.02 (C11), 6.15 (C13) ppm. HRMS-DART (m/z): $[MH^+]$ calculated for $C_{17}H_{17}IO_2$, 381.0351 found, 381.0339. (This data is in good agreement with previously reported values).[39]

4-(6-bromohexoxy)benzophenone[38,39]

1,6-dibromohexane (6.21 mL: 40.4 mmol), K_2CO_3 (2.79 g: 20.2 mmol) and 4-hydroxybenzophenone (2.00 g: 10.1 mmol) were stirred in ACN (20 mL) under reflux for 24 h to give a crude product of 4-(6-bromohexoxy)benzophenone which was recrystallized in toluene/hexanes to yield a white coloured powder. Yield: 1.50 g (42.7%). Mp = 62-64˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.84-7.80 (m, 2H: H1), 7.77-7.41 (m, 2H: H7), 7.59-7.54 (m, 1H: H3), 7.50-7.44 (m, 2H: H2), 6.97-6.93 (m, 2H: H8), 4.05 (t, 2H, *J* = 6.4 Hz: H10), 3.43 (t, 2H, *J* = 6.8 Hz: H15), 1.95-1.81 (m, 4H: (H11, H12)), 1.55-1.52 (m, 4H: (H13, H14)) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 195.64 (C5), 162.96 (C9), 138.22 (C4), 132.57 (C3), 131.07 (C7), 129.98 (C6), 129.78 (C1), 128.21 (C2), 113.98 (C8), 67.99 (C10), 34.02 (C15), 32.74 (C14), 29.15 (C13), 27.87 (C11), 25.59 (C12) ppm. HRMS-DART (m/z): $[MH^+]$ calculated for $C_{19}H_{21}BrO_2$, 361.0803; found, 361.0796. (This data is in good agreement with previously reported values).[39]

4-(6-chlorohexoxy)benzophenone[37]

1-bromo-6-chlorohexane (2.77 mL: 13.9 mmol), K_2CO_3 (3.49 g: 25.2 mmol) and 4-hydroxybenzophenone (2.50 g: 12.6 mmol) were stirred in ACN (20.0 mL) under reflux for 24 h to give a crude product of 4-(6-chlorohexoxy)benzophenone which was recrystallized in toluene/hexanes to yield an off white coloured powder. Yield: 3.07 g (76.8%). Mp = 65-66˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.81 (d, 2H, *J* = 8.7 Hz: H1), 7.75 (d, 1H, *J* = 7.4 Hz: H7), 7.55 (t, 2H, *J* = 7.4 Hz: H3), 7.47 (t, 2H, *J* = 7.6 Hz: H2), 6.94 (d, 2H, *J* = 8.7 Hz: H8), 4.04 (t, 2H, *J* = 6.4 Hz: H10), 3.55 (t, 2H, *J* = 6.6 Hz: H15), 1.85-1.80 (m, 4H: H11, H12), 1.55-1.51 (m, 4H: H13, H14) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 195.55 (C5), 162.77 (C9), 138.35 (C4), 132.58 (C3), 131.86 (C7), 130.01 (C6), 129.72 (C1), 130.01 (C2), 114.01 (C8), 68.01 (C10), 44.98 (C15), 32.48 (C14), 28.98 (C13), 26.61 (C11), 25.38 (C12) ppm. HRMS-DART (m/z): $[MH^+]$ calculated for $C_{19}H_{21}ClO_2$, 317.1308; found, 317.1311.

4-(6-iodohexoxy)benzophenone[39]

4-((3-bromohexoxy)benzophenone (0.500 g: 1.38 mmol) and NaI (0.622 g: 4.15 mmol) were mixed in acetone (10.0 mL) under reflux for 24 h to give crude product of 4-(6-iodohexoxy)benzophenone which was recrystallized in toluene/hexanes (1:2) to afford an off white coloured powder. Yield: 0.480 g (85.0%). Mp = 55-57˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (m, 4H: H1, H7), 7.51 (m, 3H: H2, H3), 6.95 (m, 2H: H8), 4.05 (m, 2H: H10), 3.21 (m, 2H: H15), 1.85 (m, 4H: H11, H12), 1.55 (m, 4H: H13, H14) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 195.61 (C5), 162.62 (C9), 138.35 (C4), 132.57 (C3), 131.85 (C7), 130.00 (C6), 129.72 (C1), 128.17 (C2), 113.89 (C8), 68.13 (C10), 33.12 (C14), 30.17 (C11), 29.04 (C13), 25.02 (C12), 6.85 (C15) ppm. (This data is in good agreement with previously reported values).[39]

5-(dimethylamino)-*N*-(3-(dimethylamino)propyl)naphthalene-1-sulfonamide **1**[40,41]

To a flame dried 500 mL round bottom flask with a reflux condenser connected to an inert atmosphere manifold, anhydrous DCM (300 mL) was added followed by dansyl chloride (10.0 g: 37.07 mmol), Et_3N (8 mL: 55.6 mmol). While the solution was stirring at room temperature (23 ± 2˚C), 3-(dimethylamino)propylamine (7.0 mL: 55.6 mmol) was added drop wise via an inert syringe resulting in a colour change from orange to lime-green. After stirring for 1 h, HCl (g) was bubbled through the solution until a pH of 2 was achieved. The resulting mixture was evaporated to dryness, re-dissolved in saturated brine H_2O (100 mL) and brought to pH 11 with 6N NaOH (15 mL) at 0˚C until a white-yellow coloured precipitate was observed. The mixture was refrigerated overnight enhancing further precipitation of product. The precipitate was filtered and washed (2 × 30 mL) with H_2O and the filtrate extracted with DCM (500 mL) and evaporated to dryness to afford a white coloured solid, **1**. The crude sample was recrystallized using a minimum volume (25 mL) of 80% EtOH/H_2O. Yield: 12.1 g (97%). Mp = 122-124˚C. TLC (5% w/w NH_4OH:Acetone), R_f = 0.72. UV-Vis (MeOH, 1×10^{-3} M), $\lambda_{Abs\ max}$ = 516 nm, ε = 447 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.52 (d, 1H, *J* = 8.5 Hz: H8), 8.31 (d, 1H, *J* = 8.6 Hz: H5), 8.23 (dd, 1H, ^{1}J = 1.2 Hz, ^{2}J = 7.3 Hz: H10), 7.58 – 7.50 (m, 2H: H4, H9), 7.17 (d, 1H, *J* = 7.5: H3), 2.94 (t, 2H, *J* = 5.5 Hz: H13), 2.88 (s, 6H: H1), 2.21 (t, 2H, *J* = 5.5 Hz: H15), 2.12 (s, 6H: H16), 1.58-1.52 (m, 2H: H14) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 151.90 (C2), 134.77 (C11), 129.98 (C6), 128.89 (C8), 129.71 (C4), 129.65 (C9), 128.07 (C10), 123.17 (C5), 119.03 (C7), 115.00 (C3), 59.58 (C15), 45.42 (C1, C16), 44.54 (C13), 24.61 (C14) ppm. HRMS-DART (m/z): $[M^+]$ calculated for $C_{17}H_{26}N_3O_2S_1$, 336.1736; found, 336.1745. (This compound has also been prepared on a 25 g, 92.6 mmol scale).

General Procedure for the Synthesis of Dansyl Quaternary Ammonium salts

In a glass screw cap vial 5-(dimethylamino)-*N*-(3-(dimethylamino)propyl)naphthalene-1-sulfonamide **1** (1.0 equiv.) and the appropriate alkyl halide (1.0-2.0 equiv.) were dissolved in ACN or EtOH (0.5-1.0 M). The resultant solution was stirred at reflux (4-24 h) until TLC analysis showed the disappearance of the starting materials (EtOAc/hexanes 1:4). The residue was then precipitated from the resultant solution by the addition of cold Et_2O (5 × 5 mL) followed by decanting the solvent and placing the vial under high vacuum (~ 1 h) to afford the desired product.

3-(5-(dimethylamino)naphthalene-1-sulfonamido)-*N*,*N*-dimethyl-*N*-(3-(trimethoxysilyl)propyl)propan-1-aminium chloride **2**

To a flame dried 25 mL round bottom flask with a reflux condenser connected to an inert atmosphere manifold, ACN (20 mL) was added followed by 5-(dimethylamino)-*N*-(3-(dimethylamino)propyl)naphthalene-1-sulfonamide (3.35 g: 10 mmol). While stirring, (3-chloropropyl)trimethoxysilane (5 mL: 25 mmol) was added via syringe. The solution was stirred for 48 h at 110°C, with the solution turning to yellow-brownish coloured oil. The oil was then precipitated in cold (1:1) DCM:Et_2O mixture, forming two layers; a gummy layer and a white liquid layer. The white liquid layer was separated inside a 10 mL syringe and collected in a second 25 mL round bottom flask; the gummy layer was dissolved using DCM and collected in a 25 mL round bottom flask. Excess DCM was evaporated using rotary evaporator resulting in the recovery of a yellow coloured solid, **2**. Yield: 3.85 g (72.0%). Mp = 85-87°C. UV-Vis (MeOH, 1×10^{-3} M), $\lambda_{Abs\ max}$ = 340 nm, ε = 413 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.48 (d, 2H, *J* = 8.6 Hz: H8, H5), 8.37 (s, 1H, H12), 8.19 (d, 1H, *J* = 7.3 Hz: H10), 7.59 (t, 1H, *J* = 7.9 Hz: H4), 7.49 (t, 1H, *J* = 8.2 Hz: H9), 7.13 (d, 1H, *J* = 7.6 Hz: H3), 3.57-3.52 (m, 2H: H17), 3.49 (s, 9H: H20), 3.27-3.20 (m, 2H: H15), 3.10 (s, 6H: H16), 3.08–3.03 (m, 2H: H13), 2.84 (s, 6H: H1), 2.01-1.90 (m, 2H: H14), 1.71–1.60 (m, 2H: H18), 0.54 (t, 2H, *J* = 7.8 Hz: H19) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 151.70 (C2), 135.06 (C11), 130.18 (C4), 129.75 (C6), 129.58 (C8), 128.93 (C9), 128.53 (C10), 123.35 (C5), 119.45 (C7), 115.14 (C3), 65.62 (C15), 62.27 (C17), 50.79 (C16), 50.68 (C20), 45.40 (C1), 39.81 (C13), 26.00 (C14), 16.16 (C18), 5.35 (C19) ppm; ^{29}Si{^{1}H} NMR (79.4 MHz, CD_3OD, δ): -68.86 ppm. HRMS-DART (m/z): [M^+ - Cl^-, - CH_3], calculated for $C_{23}H_{40}ClN_3O_5SSi$, 484.2314; found 484.2315.

3-(diethoxyphosphoryl)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-aminium bromide **3a**

To a stirred solution of **1** (2.06 g: 6.13 mmol) in refluxing ACN (15 mL) was added diethyl(3-bromopropyl)phosphonate (2.40 g: 9.2 mmol) via syringe, and the vial was capped and refluxed for 20 h. To purify, the mixture was first triturated, washed with Et_2O (2 × 40 mL) to remove any unreacted starting material followed by drying under high vacuum overnight to afford **3a** as a yellow coloured solid. Yield: (3.64 g: 90%). Mp = 37-39°C. UV-Vis (MeOH, 1×10^{-3} M), $\lambda_{Abs\ max}$ = 334 nm, ε = 505 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.51 (d, 1H, *J* = 8.3 Hz: H8), 8.43 (d, 1H, *J* = 8.6 Hz: H5), 8.20 (dd, 1H, ^1J = 1.0 Hz, ^2J = 7.3 Hz: H10), 7.71 (s, 1H: H12), 7.59 (t, 1H, *J* = 8.4 Hz: H9), 7.50 (t, 1H, *J* = 7.3 Hz: H4), 7.16 (d, 1H, *J* = 7.4 Hz: H3), 4.11–4.02 (m, 4H: H20), 3.67–3.56 (m, 4H: H15, H17), 3.17 (s, 6H: H16), 3.10–2.99 (m, 2H: H13), 2.86 (s, 6H: H1), 2.10-1.95 (m, 4H: H14, H18), 1.89–1.77 (m, 2H: H19), 1.28 (t, 6H, *J* = 7.1 Hz: H21) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 151.79 (C2), 134.62 (C11), 130.29 (C4), 129.79 (C6), 129.47 (C8), 129.34 (C9), 128.60 (C10), 123.28 (C5), 119.28 (C7), 115.30 (C3), 62.23–62.16 (overlap, C15, C17, C20), 51.31 (C16), 45.43 (C1), 39.73 (C13), 24.75–22.83 (C14, C18, C19), 16.45 (d, ^2J = 6.0 Hz: C21) ppm; ^{31}P{^{1}H} NMR (121.45 MHz, $CDCl_3$, δ): 29.29 ppm. HRMS-DART (m/z): [M^+ - Br^-] calculated for $C_{24}H_{41}BrN_3O_5P_1S_1$, 514.2504; found, 514.2519.

3-(diisopropoxyphosphoryl)-*N*-(3-(5-(dimethylamino) naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-aminium bromide **3b**

To a stirred solution of **1** (0.5 g: 1.5 mmol) in refluxing ACN (3 mL) was added diisopropyl(3-bromopropyl)phosphonate (0.46 g: 1.6 mmol) via syringe, and the vial was capped and refluxed for 7 h. To purify, the mixture was first triturated, washed with Et_2O (2 × 15 mL) to remove any unreacted starting material, followed by drying under high vacuum overnight to afford **3b** as a yellow coloured solid. Yield: 0.653 g: (70%). Mp = 36-38°C; UV-Vis (MeOH, 1×10^{-3} M), $\lambda_{Abs\ max}$ = 340 nm, ε = 519 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.50 (d, 1H, *J* = 8.3 Hz: H8), 8.43 (d, 1H, *J* = 8.6 Hz: H5), 8.22 (dd, 1H, ^1J = 1.0 Hz, ^2J = 7.3 Hz: H10), 7.75 (s, 1H: H12), 7.59 (t, 1H, *J* = 8.4 Hz: H9), 7.49 (t, 1H, *J* = 7.3 Hz: H4), 7.15 (d, 1H, *J* = 7.4 Hz: H3), 4.68–4.56 (m, 2H: H20), 3.66–3.49 (m, 4H: H15, H17), 3.16 (s, 6H: H16), 3.09–2.97 (m, 2H: H13), 2.85 (s, 6H: H1), 2.05-1.90 (m, 4H: H14, H18), 1.80–1.69 (m, 2H: H19), 1.26 (t, 12H, *J* = 7.1 Hz: H21) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 151.79 (C2), 134.62 (C11), 130.31 (C4), 129.87 (C6), 129.49 (C8), 129.31 (C9), 128.64 (C10), 123.28 (C5), 119.28 (C7), 115.30 (C3), 70.69 (C20), 62.23–62.16 (overlap, C15, C17), 51.19 (C16), 45.42 (C1), 41.80 (C13), 39.60 (C21), 33.76 (C19), 24.08 (C14, C18) ppm; ^{31}P{^{1}H} NMR (121.45 MHz, $CDCl_3$, δ): 27.32 ppm. HRMS-ESI-TOF (m/z): [M^+ - Br^-] calculated for $C_{26}H_{45}BrN_3O_5P_1S_1$, 542.2813; found, 542.2815.

3-(5-(dimethylamino)naphthalene-1-sulfonamido)-*N*,*N*-dimethyl-*N*-(3-phosphonopropyl)propan-1-aminium bromide **3c**

Inside a flame dried and evacuated 20 mL screw cap vial *N*-(3-(diethoxyphosphoryl)propyl)-*N*,*N*-dimethyloctadecan-1-ammonium bromide (0.35 g: 0.58 mmol) was dissolved in anhydrous DCM (5 mL). To the clear solution, with stirring, was added trimethylsilyl bromide (0.23 mL: 1.76 mmol) through a rubber septum via syringe and the reaction was then stirred at room temperature overnight. Completion of the reaction was monitored by ^{31}P NMR, after which the reaction was quenched with EtOH (10 mL) and stirred for 1 h followed by the addition of H_2O (1 mL). Volatiles were removed under high vacuum and the crude product was first triturated then washed with Et_2O (2 × 10 mL) to remove brown colored impurities. Further purification entailed extraction with NH_4OH:H_2O (1:10, 10 mL) and washed with Et_2O (1 × 5 mL). The aqueous fluorescent layer was evaporated from ACN (50 mL) to give **3c** as a light yellow coloured solid. Yield: 0.25 g: (79%). Mp = 166-168°C; UV-Vis (MeOH, 1×10^{-3} M), $\lambda_{Abs\ max}$ = 342 nm, ε = 449 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, D_2O, δ): 8.58 (d, 1H, *J* = 8.5 Hz: H8), 8.35 (d, 1H, *J* = 8.5 Hz: H5), 8.23 (d, 1H, *J* = 7.0 Hz: H10), 7.70–7.58 (m, 2H: H4, H9), 7.31 (d, 1H, *J* = 7.5 Hz: H3), 3.32 (s, 6H: H16), 3.30-3.22 (m, 2H: H17 overlap), 3.19-3.11 (m, 2H: H15), 2.97 (t, 2H, *J* = 6.0 Hz: H13), 2.89 (s, 6H: H1), 1.93-1.86 (m, 4H: H14, H18), 1.57-1.49 (m, 2H, H19) ppm; ^{13}C{^{1}H} NMR (100 MHz, D_2O, δ): 133.80

(C2), 131.15 (C11), 130.15 (C6), 129.76 (C8), 128.99 (C4), 128.61 (C9), 128.40 (C10), 124.54 (C5), 119.81 (C7), 116.59 (C3), 64.32 (d, $^{3}J_{C\text{-}P}$ = 18.8 Hz, C17), 61.33 (C15), 53.99 (C16), 45.08 (C1), 39.04 (C13), 24.77 (d, $^{1}J_{C\text{-}P}$ = 136.1 Hz, C19), 21.96 (C14), 16.85 (d, $^{2}J_{C\text{-}P}$ = 3.2, C18) ppm; $^{31}P\{^{1}H\}$ NMR (121.45 MHz, D_2O, δ): 20.99 ppm. HRMS-ESI-TOF (m/z): [M^+ - Br^-] calculated for $C_{20}H_{33}BrN_3O_5P_1S_1$, 458.1873; found, 458.1868.

3-(bis((diethoxyphosphoryl)methyl)amino)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-aminium iodide **4**

To a stirred solution of **1** (0.658 g: 1.35 mmol) in refluxing ACN (3 mL) was added tetraethyl (((3-iodopropyl)azanediyl)bis(methylene))bis(phosphonate) (0.658 g: 1.35 mmol), and the vial was capped and refluxed for 7 h. To purify, the mixture was triturated, washed with Et_2O (2 × 15 mL) to remove any unreacted starting material followed by drying under high vacuum overnight to afford **4** as a yellow solid. Yield: 0.626 g: (60%). Mp = 40-42˚C; UV-Vis (MeOH, 1 × 10^{-3} M), $\lambda_{Abs\ max}$ = 340 nm, ε = 526 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.48-8.38 (m, 2H: H8), 8.37-8.29 (m, 1H: H5), 8.19-8.12 (m, 1H: H10), 7.72 (s, 1H: H12), 7.56-7.38 (m, 2H: H4, H9), 7.15 (m, 1H: H2), 4.16-3.97 (m, 8H: H21), 3.62-3.25 (m, 4H: H15, H17), 3.05-2.85 (s, 6H: H16), 3.10-2.91 (m, 8H: H19, H20, H13), 2.81 (s, 6H, H1), 1.99-1.75 (m, 4H: H14, H18), 1.25 (t, 12H, *J* = 7.0 Hz: H22) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 151.85 (C2), 135.16 (C11), 130.18 (C6), 129.76 (C8), 129.47 (C4), 129.12 (C9), 128.38 (C10), 123.34 (C5), 119.34 (C7), 115.19 (C3), 62.74 (C15), 62.24 (t, $^{2}J_{C\text{-}P}$ = 3.5 Hz: C21), 61.84 (C17), 53.78 (C19), 51.65 (C16), 50.49 (C20), 45.38 (C1), 39.61 (C13), 22.79 (C14), 21.22 (C18), 16.51 (d, $^{2}J_{C\text{-}P}$ = 2.5 Hz: C22) ppm; $^{31}P\{^{1}H\}$ NMR (121.45 MHz, $CDCl_3$, δ): 24.42 ppm. HRMS-ESI-TOF (m/z): [MH^+ - I^-] calculated for $C_{30}H_{55}IN_4O_8P_2S_1$, 693.3210; found, 693.3213.

3-(acetylthio)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-aminium chloride **5**

To a stirred solution of **1** (1.0 g: 2.98 mmol) in refluxing EtOH (4 mL) was added 3-chloropropylthioacetate (90%) (0.65 mL: 4.9 mmol) via syringe, and the vial capped and refluxed for 24 h. To purify, the mixture was first triturated, washed with Et_2O (2 × 15 mL) to remove any unreacted starting material followed by drying under high vacuum overnight to afford **5** as a yellow coloured solid. Yield: 1.1 g (63%). Mp = 35-36˚C. UV-VIS (MeOH, 1 × 10^{-3} M), $\lambda_{Abs\ max}$ = 334 nm, ε = 439 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49 (d, 1H, *J* = 8.4 Hz: H8), 8.43 (d, 1H, *J* = 8.5 Hz: H5), 8.18 (d, 1H, *J* = 7.3 Hz: H10), 7.57 (t, 1H, *J* = 8.0 Hz: H4), 7.49 (t, 1H, *J* = 8.2 Hz: H9), 7.15 (d, 1H, *J* = 7.5 Hz: H3), 3.57-3.48 (m, 2H: H15), 3.40-3.32 (m, 2H: H17), 3.10 (s, 6H: H16), 3.05-2.98 (m, 2H: H13), 2.86 (s, 6H, H1), 2.83-2.77 (m, 2H: H19), 2.28 (s, 3H: H21), 2.03-1.85 (m, 4H: H14, H18) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 195.80 (C21), 149.79 (C2), 134.73 (C11), 130.34 (C4), 129.67 (C6), 129.43 (C8), 128.32 (C9), 128.71 (C10),124.64 (C5), 123.52 (C7), 115.45 (C3), 62.92 (C15), 62.73 (C17), 55.14 (C16), 45.32 (C1), 42.90 (C13), 30.77 (C21), 25.57 (C19), 23.16 (C18), 23.00 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - Cl^-] calculated for $C_{22}H_{34}ClN_3O_3S_2$, 452.2036; found, 452.2037.

3-(4-benzoylphenoxy)-*N*-(3-((5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-aminium bromide **6a**[37]

To a stirred solution of compound **1** (0.5 g: 1.5 mmol) in refluxing ACN (4 mL) was added (4-(3-bromopropoxy)benzophenone (0.72 g: 2.25 mmol) via syringe, and the vial was capped and refluxed for 24 h. To purify, the mixture was first triturated and washed with Et_2O (2 × 15 mL) to remove any unreacted starting material followed by drying under high vacuum overnight and recovered **6a** as a yellow coloured powder. Yield: 0.91 g (93%). Mp = 75-76˚C; UV-VIS (MeOH, 1 × 10^{-3} M), $\lambda_{Abs\ max}$ = 335 nm, ε_1 = 524 M^{-1} cm^{-1}, $\lambda_{Abs\ max}$ = 288 nm, ε_2 = 327 M^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49-8.43 (m, 2H: H5, H10), 8.18 (d, 1H, *J* = 7.3 Hz: H8), 7.76-7.68 (m, 5H: H28, H22, H12, H9), 7.59-7.52 (m, 2H: H27), 7.47-7.42 (m, 3H: H26, H4), 7.07 (d, 1H, *J* = 7.6 Hz: H3), 6.82 (d, 2H, *J* = 8.8 Hz: H21), 4.00 (t, 2H, *J* = 5.4 Hz: H19), 3.73-3.69 (m, 2H: H15), 3.62-3.59 (m, 2H: H17), 3.22 (s, 6H: H16), 3.11-3.03 (m, 2H: H13), 2.81 (s, 6H: H1), 2.29-2.09 (m, 2H: H14), 2.05-1.95 (m, 2H: H18) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 195.47 (C24), 161.69 (C20), 151.86 (C2), 137.99 (C11), 134.86 (C25), 132.42 (C6), 132.06 (C28), 130.51 (C23), 130.37 (C8), 129.71 (C22), 129.44 (C26), 129.23 (C4), 129.20 (C9), 128.71 (C10), 128.25 (C27), 123.36 (C5), 119.39 (C7), 115.30 (C3), 114.15 (C21), 65.82 (C17), 64.50 (C15), 62.50 (C19), 51.37 (C16), 45.34 (C1), 39.87 (C13), 22.90 (C18), 15.26 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - Br^-] calculated for $C_{33}H_{40}BrN_3O_4S$, 574.2749; found, 574.2734.

3-(4-benzoylphenoxy)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-ammonium chloride **6b**[37]

To a stirred solution of compound **1** (0.870 mmol: 0.291 g) and (4-(3-chloropropoxy)benzophenone (0.790 mmol: 0.250 g) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath for 24 h. The resultant residue was precipitated using cold Et_2O (4 mL) to afford the desired product 6b as a yellow coloured powder. Yield: 0.25 g (51.9%). Mp = 73-75˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.54-8.48 (m, 2H: H5, H10), 8.29 (d, 1H, J = 7.3 Hz: H8), 7.77-7.67 (m, 5H: H28, H9, H22), 7.60-7.42 (m, 5H: H27, H26, H4), 7.19-7.12 (m, 1H: H3), 7.00-6.92 (m, 2H: H21), 4.23-4.16 (m, 2H: H19), 3.79-3.72 (m, 2H: H15), 3.63-3.59 (m, 2H: H17), 3.23 (s, 6H: H16), 2.81-2.79 (m, 2H: H13), 2.20 (s, 6H: H1), 2.32-2.28 (m, 2H: H14), 2.15-1.92 (m, 2H: H18) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ): 195.53 (C24), 162.33 (C20), 151.90 (C2), 138.16 (C11), 134.75 (C25), 132.57 (C6), 131.93 (C28), 130.00 (C23), 129.87 (C8), 129.72 (C22), 129.68 (C26), 129.62 (C4), 128.23 (C9), 128.20 (C10), 128.10 (C27), 123.17 (C5), 118.99 (C7), 115.01 (C3), 114.02 (C21), 64.48 (C17), 64.45 (C15), 59.49 (C19), 45.41

(C16), 44.47 (C1), 41.29 (C13), 32.04 (C18), 24.63 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - Cl^-] calculated for $C_{33}H_{40}ClN_3O_4S$, 574.2751; found, 574.2734.

3-(4-benzoylphenoxy)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylpropan-1-ammonium iodide **6c**[37]

To a stirred solution of compound **1** (0.252 g: 0.750 mmol) and (4-(3-iodopropoxy)benzophenone (0.250 g: 0.680 mmol) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath for 24 h. The resultant residue was precipitated using cold Et_2O (4 mL) to afford the desired product **6c** as a yellow coloured powder. Yield: 0.267 g: (56%) Mp = 73-75˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49-8.39 (m, 2H: H5, H10), 8.18 (d, 1H, *J* = 7.7 Hz: H8), 7.75-7.65 (m, 5H: H28, H22, H12, H9), 7.59-7.49 (m, 2H: H27), 7.48-7.38 (m, 3H: H26, H4), 7.09 (d, 1H, *J* = 7.6 Hz: 1H, H3), 6.85 (d, 2H, *J* = 7.4 Hz: H21), 4.05-3.95 (m, 2H: H19), 3.65-3.56 (m, 4H: H15, H17), 3.15 (s, 6H: H16), 3.11-3.04 (m, 2H: H13), 2.80 (s, 6H: H1), 2.23-2.10 (m, 2H: H14), 2.05-1.93 (m, 2H: H18) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.45 (C24), 161.68 (C20), 151.88 (C2), 137.75 (C11), 134.33 (C25), 132.53 (C6), 132.45 (C28), 132.04 (C23), 130.55 (C8), 129.74 (C22), 129.29 (C26), 129.27 (C4), 128.91 (C9), 128.26 (C10), 128.10 (C27), 123.03 (C5), 118.94 (C7), 115.30 (C3), 113.80 (C21), 68.72 (C17), 64.00 (C15), 58.43 (C19), 51.42 (C16), 45.37 (C1), 39.03 (C13), 22.99 (C18), 18.42 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - I^-] calculated for $C_{33}H_{40}IN_3O_4S$, 574.2734; found, 574.2753.

4-(4-benzoylphenoxy)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylbutan-1-ammonium bromide **6d**[37]

To a stirred solution of compound **1** (0.240 g: 0.717 mmol) and (4-(4-bromobutoxy)benzophenone (0.721 mmol, 0.240 g) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath for 24 h. The resultant residue was precipitated using cold Et_2O (4 mL) to afford the desired product **6d**. Yield: 0.168 g (35.0%). Mp = 73-75˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.51-8.44 (m, 2H: H5, H10), 8.19 (d, 1H, *J* = 7.3 Hz: H8), 7.77-7.67 (m, 5H: H29, H23, H9), 7.60-7.51 (m, 2H: H28), 7.48-7.42 (m, 3H: H27, H4), 7.12 (d, 1H, *J* = 7.6 Hz: H3), 6.90 (d, 2H, *J* = 8.9 Hz: H22), 4.06-3.97 (m, 2H: H20), 3.71-3.60 (m, 2H: H15), 3.56-3.43 (m, 2H: H17), 3.16 (s, 6H: H16), 3.14-3.00 (m, 2H: H13), 2.82 (s, 6H: H1), 2.08-1.96 (m, 2H: H19), 1.94-1.65 (m, 4H: H18, H14) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.56 (C25), 162.22 (C21), 151.63 (C2), 138.09 (C11), 134.73 (C26), 132.51 (C6), 132.00 (C29), 130.35 (C24), 130.18 (C8), 129.73 (C23), 129.46 (C27), 129.26 (C4), 128.90 (C9), 128.74 (C28), 128.23 (C10), 123.44 (C5), 119.12 (C7), 114.87 (C3), 114.11 (C22), 67.23 (C17), 64.00 (C15), 61.66 (C20), 51.18 (C16), 45.39 (C1), 39.87 (C13), 25.74 (C19), 23.00 (C14), 19.75 (C18) ppm. HRMS-ESI-TOF (m/z): [M^+ - Br^-] calculated for $C_{34}H_{42}BrN_3O_4S$, 588.2908; found, 588.2890.

4-(4-benzoylphenoxy)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylbutan-1-ammonium iodide **6e**[37]

To a stirred solution of compound **1** (0.201 g: 0.598 mmol) and (4-(4-iodobutoxy)benzophenone (0.250 g: 0.658 mmol) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath for 24 h. The resultant residue was precipitated using cold diethyl ether (4 mL) to afford the desired product **6e** as a yellow coloured powder. Yield: 0.244 g (56.9%). Mp = 73-75˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49 (d, 1H, *J* = 8.20 Hz: H5), 8.40 (d, 1H, *J* = 8.6 Hz: H10), 8.18 (d, 1H, *J* = 7.3 Hz: H8), 7.77-7.70 (m, 5H: H29, H23, H9), 7.61-7.53 (m, 2H: H28), 7.50-7.42 (m, 3H: H27, H4), 7.12 (d, 1H, *J* = 7.4 Hz: H3), 6.91 (d, 2H, *J* = 8.6 Hz: H22), 4.10-3.99 (m, 2H: H20), 3.86-3.54 (m, 2H: H15), 3.53-3.43 (m, 2H: H17), 3.14 (s, 6H: H16), 3.10-3.01 (m, 2H: H13), 2.84 (s, 6H: H1), 2.09-1.78 (m, 6H: H19, H18, H14) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.45 (C25), 162.22 (C21), 151.92 (C2), 138.05 (C11), 134.37 (C26), 132.58 (C6), 132.51 (C29), 132.04 (C24), 130.55 (C8), 130.19 (C24), 129.74 (C27), 129.32 (C24), 128.91 (C9), 128.25 (C28), 128.20 (C10), 123.62 (C5), 119.37 (C7), 115.53 (C3), 114.20 (C22), 66.99 (C17), 64.41 (C15), 62.73 (C20), 51.39 (C16), 45.40 (C1), 39.62 (C13), 29.81 (C19), 25.74 (C14), 19.77 (C18) ppm. HRMS-ESI-TOF (m/z): [M^+ - I^-] calculated for $C_{34}H_{42}IN_3O_4S$, 588.2890; found, 588.2904.

6-(4-benzoylphenoxy)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylhexan-1-ammonium bromide **6f**[37]

To a stirred solution of compound **1** (0.211 g: 0.629 mmol) and (4-((6-bromohexoxy)benzophenone (0.250 g: 0.692 mmol) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath for 24 h. The resultant residue was precipitated using cold Et_2O (4 mL) to afford the desired product **6f** as a yellow coloured powder. Yield: 0.385 g (87.8%). Mp = 70-71˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49 (d, 1H, *J* = 8.8 Hz: H5), 8.46 (d, 1H, *J* = 8.7 Hz: H10), 8.21-8.19 (m, 1H: H8), 7.78-7.71 (m, 5H: H31, H25, H12, H9), 7.60-7.53 (m, 2H: H30), 7.50-7.42 (m, 3H: H29, H4), 7.13 (d, 1H, *J* = 7.4 Hz: H3), 6.89 (d, 2H, *J* = 8.4 Hz: H24), 3.90 (t, 2H, *J* = 6.4 Hz: H21), 3.70-3.58 (m, 2H: H15), 3.39-3.28 (m, 2H: H17), 3.15 (s, 6H: H16), 3.13-3.00 (m, 2H: H13), 2.87 (s, 6H: H1), 1.79-1.62 (m, 6H: H21, H18, H14), 1.57-1.41 (m, 2H: H20), 1.40-1.28 (m, 2H: H19) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.58 (C27), 162.68 (C23), 151.21 (C2), 138.20 (C11), 134.94 (C28), 132.56 (C6), 132.50 (C31), 131.92 (C26), 129.86 (C8), 129.68 (C25), 129.45 (C30), 129.17 (C4), 128.69 (C9), 128.20 (C29), 128.17 (C10), 123.17 (C5), 119.13 (C7), 115.30 (C3), 114.06 (C24), 67.81 (C17), 64.65 (C15), 55.01 (C22), 50.77 (C16), 45.38 (C1), 39.20 (C13), 33.76 (C21), 32.59 (C19), 28.70 (C20), 27.78 (C18), 25.42 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - Br^-] calculated for $C_{36}H_{46}BrN_3O_4S$, 616.3224; found, 616.3203.

6-(4-benzoylphenoxy)-N-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-N,N-dimethylhexan-1-ammonium chloride **6g**[37]

To a stirred solution of compound **1** (0.291 g: 0.870 mmol) and (4-(6-chlorohexoxy)benzophenone (0.250 g: 0.790 mmol) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath

for 24 h. The resultant residue was precipitated using cold Et_2O (4 mL) to afford the desired product **6g** as a yellow coloured powder. Yield: 0.435 g (84.5%). Mp = 65-67˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.50 (d, 1H, *J* = 8.5 Hz: H5), 8.28 (d, 1H, *J* = 8.7 Hz: H10), 8.22-8.20 (m, 1H: H8), 7.80-7.71 (m, 5H: H31, H25, H12, H9), 7.60-7.42 (m, 5H: H30, H29, H4), 7.15 (d, 1H, *J* = 7.5 Hz: H3), 6.93 (d, 2H, *J* = 8.8 Hz: H24), 4.03 (t, 2H, *J* = 6.4 Hz: H22), 3.54 (t, 2H, *J* = 6.6 Hz: H15), 3.30-3.26 (m, 2H: H17), 3.10 (s, 6H: H16), 3.08-3.06 (m, 2H: H13), 2.87 (s, 6H: H1), 1.84-1.78 (m, 6H: H21, H18, H14), 1.55-1.25 (m, 4H: H20, H19) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.58 (C27), 162.76 (C23), 151.89 (C2), 138.31 (C11), 134.74 (C28), 132.57 (C6), 132.53 (C31), 131.96 (C26), 130.01 (C8), 129.91 (C25), 129.70 (C30), 129.68 (C4), 128.62 (C9), 128.20 (C29), 128.17 (C10), 123.17 (C5), 118.98 (C7), 115.02 (C3), 113.99 (C24), 67.99 (C17), 67.77 (C15), 59.44 (C22), 50.93 (C16), 45.41 (C1), 44.41 (C13), 32.46 (C21), 28.95 (C19), 26.59 (C20), 25.46 (C18), 24.64 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - Cl^-] calculated for $C_{36}H_{46}ClN_3O_4S$, 616.3221; found, 616.3203.

6-(4-benzoylphenoxy)-*N*-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylhexan-1-ammonium iodide **6h**[37]

To a stirred solution of compound **1** (0.272 g: 0.366 mmol) and (4-((6-iodohexoxy)benzophenone (0.136 g: 0.333 mmol) were dissolved in ACN (2 mL) and left to stir in a 100˚C sand bath for 24 h. The resultant residue was precipitated using cold Et_2O (4 mL) to afford the desired product as a yellow coloured powder **6h**. Yield: (0232 g (93.5%). Mp = 67-68˚C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.48 (d, 1H, *J* = 8.5 Hz: H5), 8.41 (d, 1H, *J* = 8.7 Hz: H10), 8.20-8.17 (m, 1H: H8), 7.78-7.70 (m, 5H: H31, H25, H12, H9), 7.61-7.42 (m, 5H: H30, H29, H4), 7.13 (d, 1H, *J* = 7.2 Hz: H3), 6.90 (d, 2H, *J* = 8.9 Hz: H24), 3.95 (t, 2H, *J* = 6.3 Hz: H22), 3.56-3.49 (m, 2H: H15), 3.33-3.29 (m, 2H: H17), 3.10 (s, 6H: H16), 3.08-3.06 (m, 2H: H13), 2.83 (s, 6H: H1), 1.76-1.59 (m, 6H: H21, H18, H14), 1.49-1.40 (m, 2H: H20), 1.36-1.24 (m, 2H: H19) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 195.63 (C27), 162.69 (C23), 151.87 (C2), 138.21 (C11), 132.53 (C28), 131.94 (C6), 131.76 (C31), 130.55 (C26), 129.92 (C8), 129.72 (C25), 129.45 (C30), 129.33 (C4), 128.89 (C9), 128.22 (C29), 128.18 (C10), 123.62 (C5), 119.36 (C7), 115.54 (C3), 114.11 (C24), 67.23 (C17), 64.65 (C15), 59.09 (C22), 51.42 (C16), 45.42 (C1), 39.22 (C13), 28.71 (C21), 25.69 (C19), 25.47 (C20), 22.96 (C18), 22.59 (C14) ppm. HRMS-ESI-TOF (m/z): [M^+ - I^-] calculated for $C_{36}H_{46}IN_3O_4S$, 616.3217; found, 616.3203.

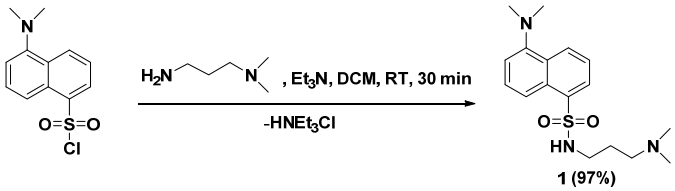
N-(3-(5-(dimethylamino)naphthalene-1-sulfonamido)propyl)-*N*,*N*-dimethylprop-2-en-1-aminium bromide **7**[42]

In a 5 mL microwave vial equipped with a magnetic stir bar, compound **1** (0.355 g: 1.06 mmol) was dissolved in ACN (1 mL). Allylbromide (0.09 mL, 1 mmol) was carefully added to the solution with a syringe and the reaction vessel was slightly heated, using a heat gun, to allow the reactants to fully dissolve. The capped vial was then placed in the microwave and, with constant stirring, run at 150˚C for 2 min. To the resulting yellow mixture was added Et_2O (~10 mL) and the vial placed in the refrigerator overnight. The excess solvent was decanted out of the vial and a yellow precipitate layer attached to the bottom of the vial remained. The vial was then attached to a high-vacuum pump for 1 h to remove any remaining solvent. A yellow coloured oil was recovered and the crude product recrystallized in minimal amount of MeOH (2 mL). After 48 h, yellow solid crystals suitable for X-ray crystallography were obtained. Yield: 0.36 g (75%). Mp = 164-166˚C; R_f = 0.38 (5%, NH_4OH:Acetone). UV-Vis (MeOH, 1×10^{-3} M), $\lambda_{Abs\ max}$ = 339 nm, ε = 413 M^{-1} cm^{-1}.ε = 560 M^{-1} cm^{-1}. ^{1}H NMR (CD_3OD, 400 MHz) δ 8.58 (d, 1H, *J* = 8.5 Hz: H9), 8.35 (d, 1H, *J* = 8.4 Hz: H6), 8.23 (d, 1H, *J* = 8.5 Hz: H11), 7.66-7.59 (m, 4H: H5, H10), 7.30 (d, 1H, *J* = 7.4 Hz: H4), 5.96-5.86 (m, 1H: H18), 5.67-5.63 (m, 2H: H19), 3.83 (d, 2H, *J* = 7.35 Hz: H17), 3.21-3.17 (m, 2H: H15), 2.97 (t, 2H, *J* = 6.09 Hz: H13), 2.90 (s, 6H: H16), 2.88 (s, 6H: H1), 1.89-1.84 (m, 2H: H14) ppm; ^{13}C{^{1}H} NMR (CD_3OD, 100.6 MHz) δ 151.94 (C2), 135.17 (C11), 130.08 (C8), 129.76 (C7), 129.37 (C9), 129.17 (C10), 128.31 (C6), 128.15 (C19), 124.54 (C18), 123.20 (C4), 118.94 (C5), 115.25 (C3), 66.23 (C17), 61.50 (C15), 47.42 (C16), 44.44 13 (C1), 39.26 (C13), 22.66 (C14) ppm. HRMS (ESI-TOF) (m/z): [M^+ - Br^-] calculated for $C_{20}H_{30}BrN_3O_2S$: 376.2057; found 376.2053.

Results and Discussion

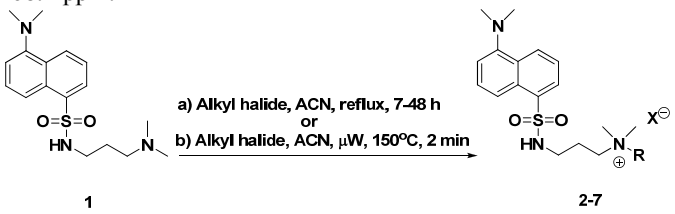
Synthesis and Characterization

Quaternary ammonium dansyl fluorescent tags were synthesized by a Menshutkin reaction between the dansyl amine precursor **1** (Scheme 1) and various linkers (Scheme 2). Compound **1** was obtained in high yield (97%) by a modified procedure from literature and purified by avoiding both a problematic acid/base extraction and column chromatography.[41] Previous preparations of 1 had called for quenching of the reaction with phosphate buffer and or sequential acidifying/basifying steps followed by extraction into DCM, which in our hands lead to inseparable emulsions and low yields. A more direct work up included the initial acidification of the reaction, removal of the DCM, followed by the addition of base (6N KOH in brine at -20℃, O/N) and finally precipitation of the desired compound. Precursor 1 was isolated by vacuum filtration, washed (4 × 50 mL) with cold H_2O and recrystallized from 20% (v/v) EtOH/H_2O to afford X-ray quality crystals. Compound **1** can be readily scaled up (25 g) and used in the preparation of new dansyl QAC's (Scheme 2) displaying a variety of functional linkers for grafting onto porous and non-porous surfaces.

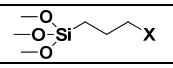
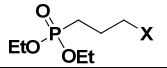
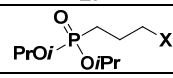
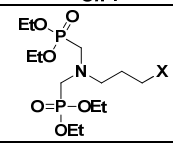
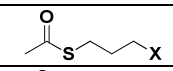
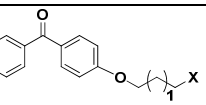
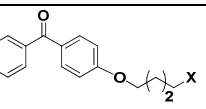
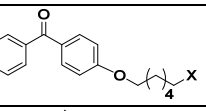
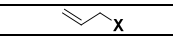


Scheme 1: Preparation of the precursor dansyl amine **1**.

All quaternization reactions were performed in sealed glass vials with refluxing acetonitrile (ACN) for 7-48 h depending on the alkyl halide. Reaction completion, monitored by NMR (^{1}H: $CDCl_3$) for products **2-7**, revealed the characteristic disappearance of the dimethylamino protons at ~ 2.2 ppm of **1** and the appearance of two new upfield resonances at ~ 3.5 ppm [(-CH_2-N$^+$(Me$_2$)-CH_2-)] and at ~ 3.3 ppm [(-N$^+$-(CH_3)$_2$] (Figure 2). The phosphorus containing compounds, **3a-b**, prepared from precursors possessing a bromo leaving group formed within 7 h, while the chloro-containing silane (**2**) and thioacetate (**5**) compounds prepared from precursors with chloro leaving groups required substantially longer reaction times (24-48 h). A simple and convenient purification method was developed based on the insolubility in Et_2O of the newly formed QACs. Compounds **2-7** precipitated directly from solutions using cold Et_2O. They are initially isolated as viscous oils attached to the walls of the vial after several cycles of rinsing and decantation. Further drying under reduced pressure resulted in the isolation of light yellow fluorescent powders in modest to good yield (35-94%) and high purity. The quaternization reaction for the silane derivative **2** showed, along with the two new upfield proton resonances, a ^{29}Si{^{1}H} NMR (CD_3OD) resonance at δ = -68.4 ppm.



1 2-7

R	X$^-$	Product	Yield %
	Cl$^-$	**2**	72
	Br$^-$	**3a**	90
	Br$^-$	**3b**	70
	I$^-$	**4**	60
	Cl$^-$	**5**	69
	Br$^-$ Cl$^-$ I$^-$	**6a** **6b** **6c**	93 52 56
	Br$^-$ I$^-$	**6d** **6e**	35 57
	Br$^-$ Cl$^-$ I$^-$	**6f** **6g** **6h**	88 85 94
	Br$^-$	**7**	75

Scheme 2: Preparation of fluorescent anchors for binding to porous and non-porous surfaces.

The dansyl phosphonate QAC's, **3a** and **3b**, were twice de-alkylated to the corresponding phosphonic acid **3c** by refluxing in mineral acids (Scheme 3). As expected, faster de-alkylation was accomplished with HBr when compared to HCl, and with the *i*-PrO leaving group versus that of the EtO group. It was also necessary to use aqueous HBr as anhydrous HBr (20% in EtOH) was significantly slower at cleaving the phosphonate ester and could not be forced to reach completion even after prolonged heating. In aqueous HBr, the reaction with **3a** or **3b** was complete after 1-2 h, whereas after 48 h of heating **3a** in ethanolic HBr, the reaction was only 71% complete by NMR. The NMR (^{1}H, ^{31}P{^{1}H}: $CDCl_3$) spectrum for the diphosphonate esters **3a** and **3b** (^{31}P NMR, δ_P = 29.29 and δ_P = 27.32 ppm respectively) showed a slight upfield shift in ^{31}P resonance to 20.99 ppm (D_2O) and the disappearance of the hydrogen resonances of the Et (δ_H = 4.06, 1.28 ppm) and i-Pr groups (δ_H = 4.69, 1.26 ppm) after ester hydrolysis to the free phosphonic acid **3c** (Figure 2). Dansyl α-bisphosphonate, **4**, was also synthesized from **1** and 3-iodopropyl-α-bisphosphonate with NMR ($CDCl_3$) analysis showing the expected hydrogen (δ_H = 3.06 ppm), carbon (δ_C = 50.49 ppm) and phosphorus (δ_P = 24.42 ppm) resonances characteristic of the aminophosphonate group. However, no dealkylation of **4** to the free phosphonic acid was investigated.

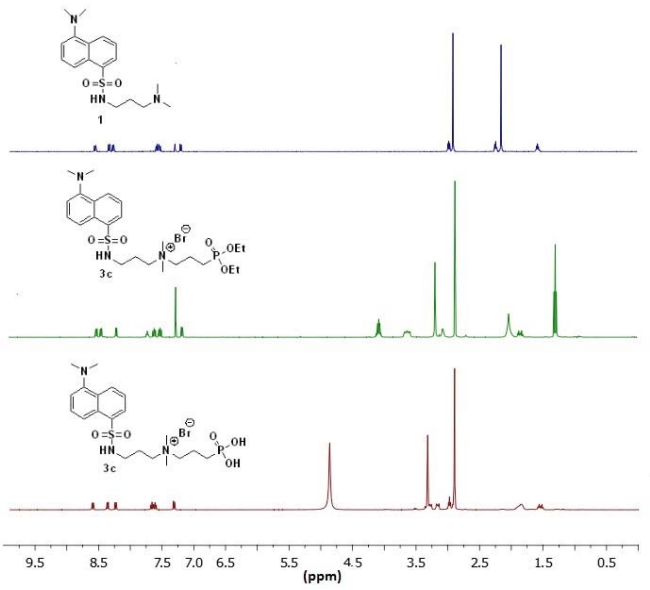
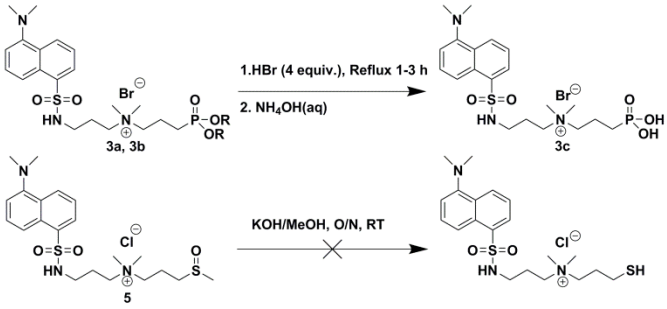


Fig. 2 ^{1}H NMR spectra overlay of compounds **1** ($CDCl_3$), **3a** ($CDCl_3$) and **3c** (D_2O).

The thioacetate protected dansyl derivative, **5**, selected for potential binding onto noble metals, was also successfully prepared from **1** and commercially available 3-chloropropylthioacetate. NMR analysis (^{1}H, ^{13}C: $CDCl_3$) of **5** revealed characteristic acetate hydrogen (δ_H = 2.28 ppm) and carbon resonances (δ_C = 195.80 and δ_C = 30.77 ppm). However, an attempted deprotection of **5** to the free thiol (MeOH/KOH) was unsuccessful with the reaction mixture changing colour from a light yellow to green and finally to a deep purple colour. This is likely due to decomposition of the free thiol. No further attempts to make the free thiol derivative were carried out.



Scheme 3: Cleavage of dansyl phosphonate and attempted cleavage of the dansyl thioacetate.

A series of benzophenone terminated quaternary ammonium materials, with different counter ions and alkyl chains, were prepared from the reaction of **1** with the appropriate (n-haloalkoxy)benzophenone derivative (100°C for 24 h). NMR analysis (^{1}H, ^{13}C{^{1}H}: $CDCl_3$) of compounds **6a-h** confirmed their expected structures; with the ^{13}C NMR spectra revealing the expected ketone carbon resonance at $\delta_C \approx 195$ ppm with the aromatic carbon bound to oxygen shifted slightly upfield at $\delta_C \approx$ 162 and 152 ppm. Compound **1**, allyl bromide, and ACN were combined in a reaction vessel and stirred with microwave heating at 150°C for 2 min. The reaction was cooled, filtered and compound **7** recovered as an oily, yellow coloured semi-solid. Recrystallization in a minimal amount of MeOH provided yellow crystals in good yield (75%). Analysis of **7** by NMR (CD_3OD) revealed characteristic vinyl hydrogen (δ_H = 5.89 and δ_H = 5.64 ppm) and carbon (δ_C = 128.15 and δ_C = 124.54 ppm) resonances. With the exception of **6** and **7**, all dansyl QAC derivatives with an electronegative atom present in the linker (i.e. **2**, **3a**, **3b**, **3c**, **4**, **5**) are H_2O soluble. Compounds **6a-h** and **7**, bearing the hydrophobic benzophenone and/or allyl group are only slightly soluble in H_2O, but readily dissolved in EtOH.

X-ray Crystallography of 1 and 7

Schematic representations of a unit cell molecule of precursor dansyl compound **1** and the ammonium dansyl allyl salt **7** are depicted in Figure 3. Crude **1** was re-crystallized using a 20 % (v/v) EtOH/H_2O mixture, resulting in the isolation of fine, clear prismatic crystals. Crystal structure analysis of **7** reveals C-N bond lengths typical for an ammonium salt (~ 1.50Å).[43]

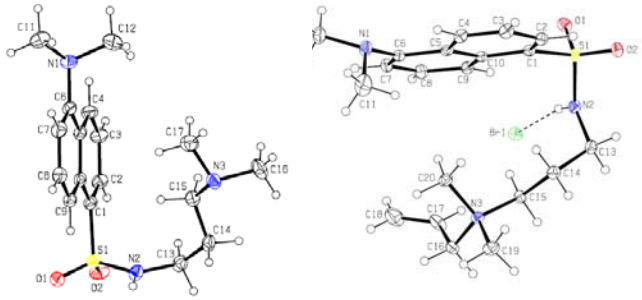


Figure 3: ORTEP representations of the unit cell components of **1** and **7**.

UV-Vis and Fluorescence Spectroscopy

As expected, all dansyl QAC derivatives analysed in MeOH exhibit nearly identical absorption spectra ($\lambda_{Abs\ max}$ = 340 nm, Figure 4) and fluorescence emission spectra ($\lambda_{Em\ max}$ = 516 nm, Figure 5) characteristic of the green-yellow dansyl tag.[35] Only compound **6a** exhibited a major absorption wavelength outside typical values with $\lambda_{Abs\ max}$ centered closer to ~ 300 nm. This is likely the result of strong π-π* absorption of the benzophenone group. In aqueous environments at low pH (0.1 N HCl), fluorescence quenching of the dansyl fluorophore **2** was observed likely due to protonation of the aromatic *N*,*N*-dimethylamine moiety (see ESI≠, Figure S84). At pH 7 (phosphate buffer), no quenching was observed and a characteristic dansyl fluorescence spectra, similar to the fluorescence in MeOH solutions, was observed. At high pH (0.1 N NaOH), the absorption was shifted to ~ 310 nm resulting in a lower intensity emission at 516 nm when excited at 340 nm (see ESI≠, Figures S83 and S84).

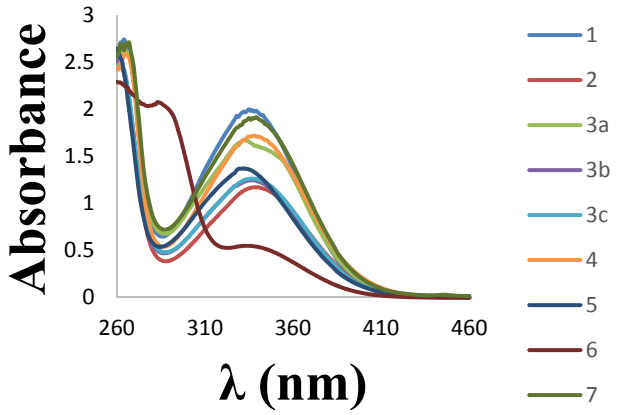


Fig. 4 Absorption spectra of compounds **1**-**7** in MeOH (λ_{Abs} max = 340 nm).

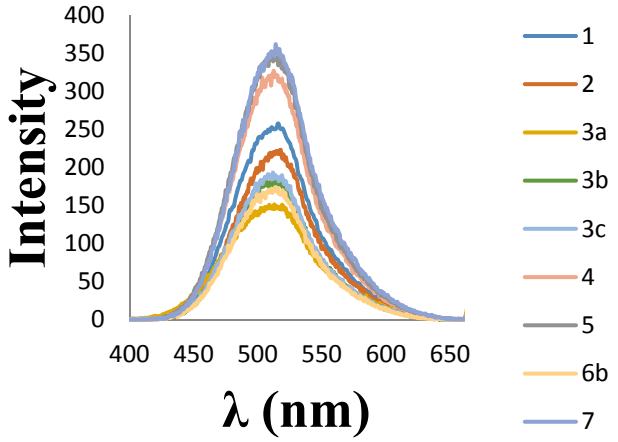


Fig. 5 Fluorescence spectra of compounds **1**-**7** in MeOH (λ_{Em} max = 516 nm).

Coating Experiments and the Grafting Mechanism

Functional quaternary ammonium dansyl fluorescent tags attach to selective porous and non-porous surfaces via a self-assembly process. Upon application, either by dip or spray coating, anchors from the reactive dansyl molecule presumably form bonds with complementary functional groups on the substrate surface, thereby immobilizing an assumed monolayer of the compound on the surface. Both silane, **2**, and phosphonic acid, **3c**, dansyl compounds can form monolayers on –OH and metal oxides surfaces respectively after a thermal curing step. In the process, H_2O is eliminated as the by-product resulting in M-O-Si or M-O-P (where M = Titanium, Stainless steel) to the surface. If improperly cured, the monolayer may easily become displaced with a rinsing step because it is non-covalently bound to the surface. The benzophenone **6a-h** and vinyl **7** dansyl compounds require UV light to initiate binding (Figure 6 c-d). Excitation by UV can create radicals within the compounds and/or at the substrate surface that facilitate grafting (Figure 6c-d).

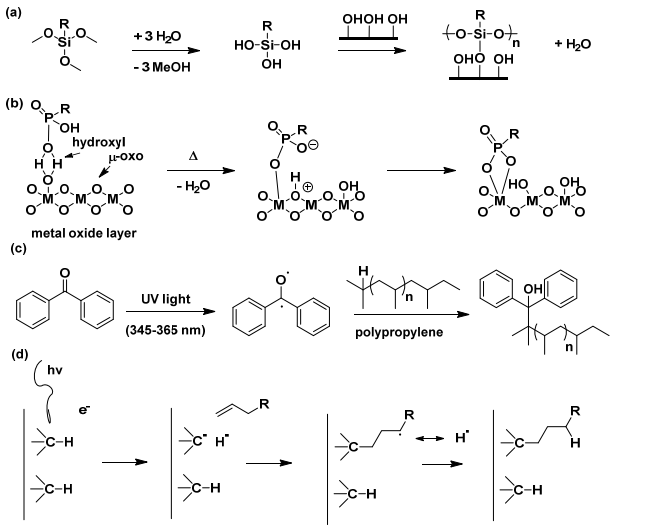


Fig. 6 Mechanism of grafting (a) silanes on polyhydroxy surfaces; (b) phosphonic acids on metal oxide surfaces; (c) benzophenone and (d) allyl groups onto plastic (C-H) surfaces

Fluorescent coatings (Figure 7) of **2** on to cotton and silica nanoparticles (NP's) and **3c** on to stainless steel were prepared by dip coating or immersion of pre-cleaned samples in 0.01% (w/v) H_2O or MeOH solution of **2** or **3c** followed by heating (80°C, 5 min) and drying. Grafting of **6a** or **7** onto polypropylene (PP) and silicone was performed by first pre-cleaning of all plastic samples (3.5 × 2.5 cm rectangles) by rinsing in distilled H_2O, followed by immersion in a MeOH bath and finally air drying prior to use. The clean substrates were then dipped into a 0.01% (w/v) EtOH solution of **6** or **7** and irradiated with UV for 2.5 min. Any unbound material was then rinsed off from substrates using distilled H_2O prior to visualization with UV light.

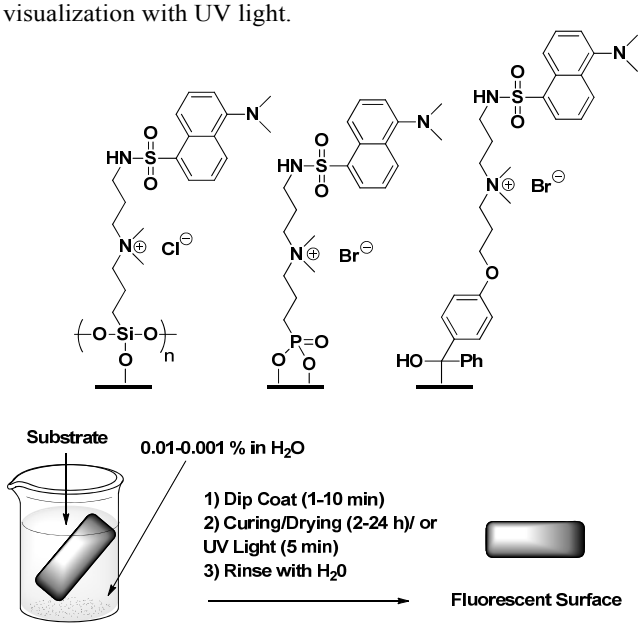


Fig.7 Coating procedure of dansyl QAC tags onto porous and non-porous surfaces.

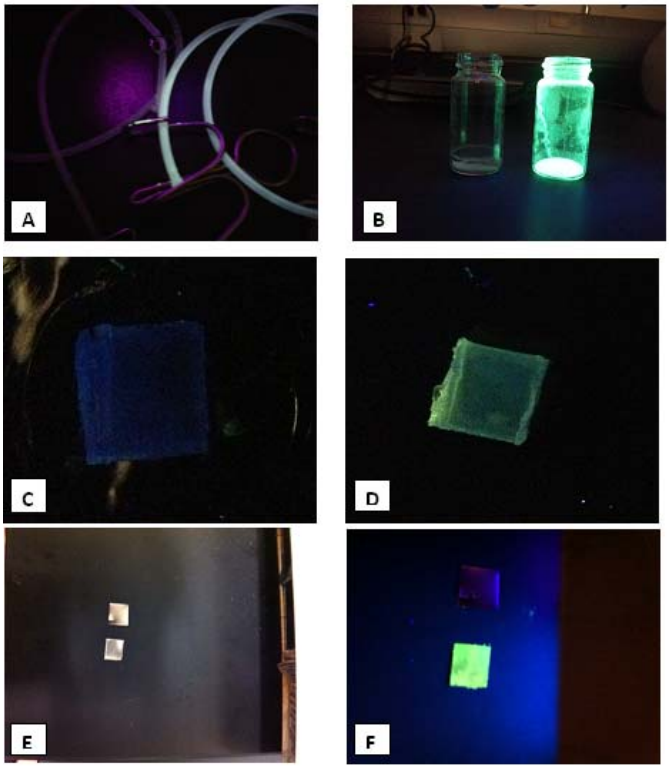


Fig.8 Images of A) medical grade silicone tubing coated with **6a** under UV light (control to the left), B) silica NP's with control left and treated with **2** right, C) polypropylene sample UV coated with **6a** and stained with bromophenol blue, D) polypropylene UV coated with **6a** under UV light, E) Stainless steel control top and a **3c** coated sample bottom under visible light and F) under UV light.

The dansyl fluorescent coatings **2**, **3c**, and **6a** were evaluated on a number of porous and non-porous surfaces (Figure 8). All fluorescent coatings adhered to the surfaces without leaching, as evident by the evaluation of the washings for fluorescence active residue.

Conclusions

Novel dansyl-functionalized QAC's bearing various chemical anchors specific for grafting onto porous and non-porous surfaces were successfully prepared via a Menschutkin reaction with the dansyl amine, **1**. Compounds **2-7** were readily purified by trituration with Et_2O without resorting to column chromatography and fully characterized by NMR (^1H, ^{13}C, ^{29}Si (**2**), ^{31}P (**3a-3c**, **4**)), HRMS, UV-VIS and fluorescence spectroscopy. X-ray crystal structures were obtained for fluorophores (**1**, **7**). The dansyl-silane **2** was prepared on a large scale and grafted onto textiles and silica NP's. Dansyl phosphonic acid **3c** was successfully grafted to stainless steel coupons, while the dansyl QAC **6a** containing the benzophenone photoactive crosslinker was used to coat plastic surfaces (PP, silicone). The inclusion of a trace amount of covalently bound dansyl molecules to surfaces treated with an antimicrobial QAC coating is expected to provide a simple and useful way of determining product identity and coverage quality.

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Notes and references
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Electronic Supplementary Information (ESI) available: This ESI contains the (a) NMR (^1H, ^{13}C, and where identified, ^{29}Si, ^{31}P NMR data) for all synthesized compounds, (b) DART or ESI-TOF MS spectra for new compounds (c) X-ray crystallographic data for compounds **1** and **7**. Structure data was also deposited with the Cambridge Crystallographic Data Centre for compounds **1** (CCDC 971464) and **7** (CCDC 971465). See DOI: 10.1039/b000000x/

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