Supporting information for

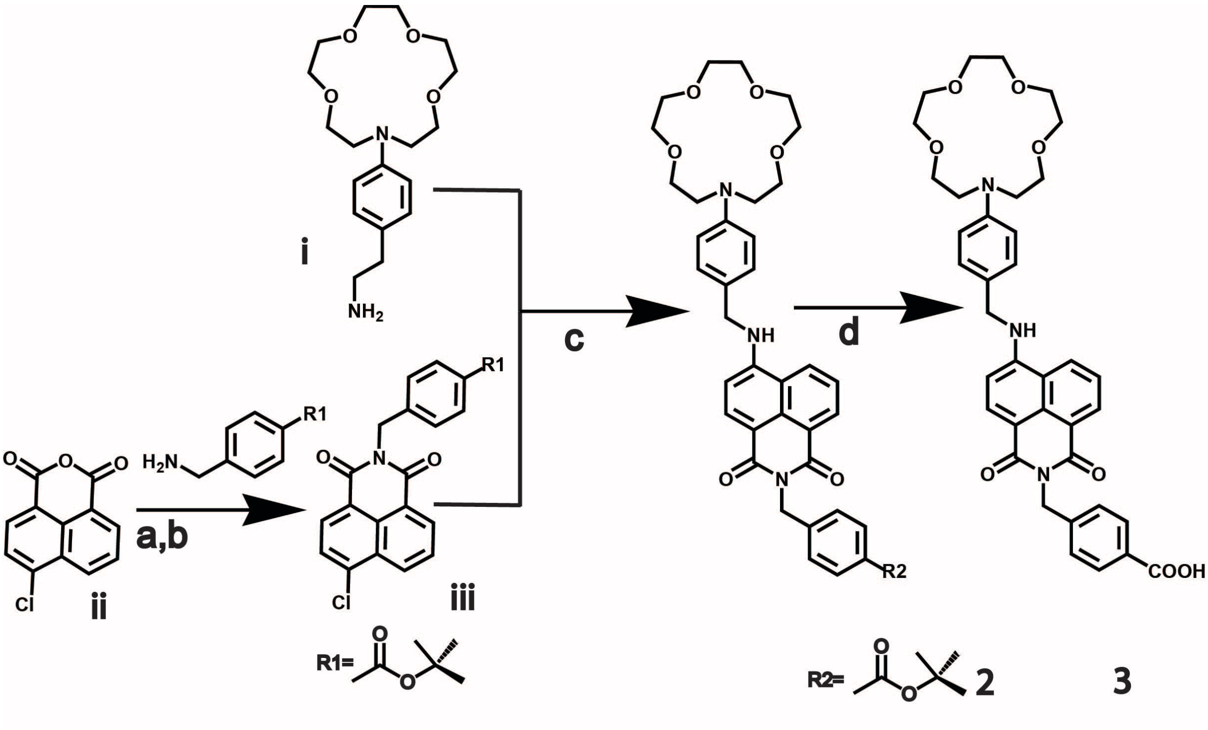
Towards Microstructured Optical Fibre Sensors: Surface Analysis of Silanised Lead Silicate Glass

Herbert T. C. Foo,[a] Heike Ebendorff-Heidepriem,[a] Christopher J. Sumby,[a] Tanya M. Monro[a]*

[a] *Institute of Photonics & Advanced Sensing (IPAS) and School of Chemistry & Physics, The University of Adelaide, South Australia, Australia, SA 5005. Tel. +61 8 8313 7406. Fax. +61 8 8313 4358. Email:* christopher.sumby@adelaide.edu.au

1. Synthesis

Scheme 1 shows the approach for the synthesis of compounds **2** and **3.** The synthesis of compound **i** was previously described.[1]



Scheme 1. Synthesis of PET fluoroionophore derivatives. (a) DMF, 60°C, 82% (b) CDI, DBU, DMF, 60°C, 38% (c) NMP, DIPEA, microwave 100°C, 37%; (d) TFA, dichloromethane, room temperature, 50%.

General procedures

All commercially available reagents were used without further purification. Thin layer chromatograms were run on MERCK aluminium-backed silica gel 60 F_{254} plates (20 x 20 cm, 0.25 mm thickness) and viewed with 254 nm UV light. Flash column chromatography was performed using Davisil silica gel 60 (particle size 0.040 - 0.063 mm) from Grace Gmbh and Co. KG following the guidelines outlined in literature.[2] Microwave synthesis was performed in the CEM focused microwave^{TM} synthesis system, (Discover@ SP) using a reaction tubes and seals provided by CEM. Microwave irradiation started after 30 seconds pre-mixing. The microwave power was variable but the set point temperature was fixed.

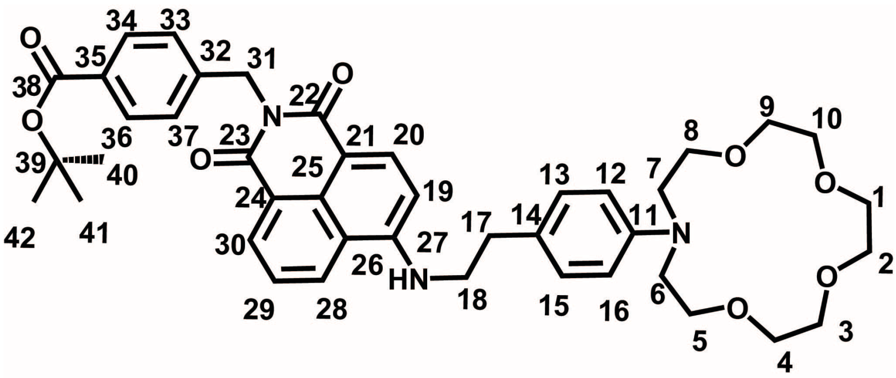
^{1}H and ^{13}C NMR spectra were obtained using either a Varian Gemini 2000 Spectrometer (^{1}H: 300.13 MHz, ^{13}C: 75.48) or a Varian Inova Spectrometer (^{1}H: 599.842, ^{13}C: 150.842 MHz). The chemical values are given on δ scale quoted in parts per million (ppm), followed by the integration, multiplicity, coupling constant J and assignment. All spectra were recorded either in chloroform-D ($CDCl_3$) from Cambridge Isotope Laboratories or dimethoxyl sulfoxide-d6 (DMSO-*d6*) from Sigma Aldrich. ^{1}H NMR spectra recorded in $CDCl_3$ were referenced relative to the internal standard Me_4Si, $\delta_H = 0.0$, while for ^{13}C NMR spectra using $CDCl_3$ used $\delta_C = 77.23$ as an internal standard. ^1H NMR spectra recorded in DMSO-d_6 were referenced to DMSO, $\delta_H = 2.5$, while for ^{13}C NMR spectra in DMSO-d_6 used $\delta_C = 39.51$ as an internal standard. The following abbreviations for proton multiplicities are used: s, singlet; d, doublet; t, triplet; br, broad singlet; m, multiplet; indicates a broadened signal due to unresolved J value(s). ^1H and ^{13}C NMR signals for compound **5** and **6** were assigned by the combination of information from Correlation spectroscopy (COSY), Nuclear Overhauser effect spectroscopy (NOESY), Heteronuclear Single Quantum Coherence (HSQC) and Heteronuclear Multiple Bond Correlation (HMBC) performed on the Varian Inova Spectrometer (^1H: 599.842, ^{13}C: 150.842 MHz). All infrared spectra were obtained using a Perkin Elmer Spectrum 100 UATR FT-IR spectrometer mounted with a diamond coated zinc selenide crystal. All electrospray ionization (ESI) mass spectra, except for compound **3**, were obtained using a Finnigan LCQ mass spectrometer. Samples are all diluted with HPLC grade methanol. High resolution mass spectrometry (HRMS) was performed by the Adelaide Proteomics Centre, The University of Adelaide, using LTQ Orbitrap XL mass spectrometer from Thermo Fisher Scientific. All melting points were determined by Gallenkamp variable heat melting point apparatus.

***t*-Butyl-4-chloro-1,8-naphthalimidylmethyl benzoate (iii)**

Step a: 4-Chloro-1,8-naphthalic anhydride **(ii)** (10 g, 0.043mol),4-(aminomethyl)benzoic acid (6.498 g, 0.043 mol) and potassium carbonate (2.972 g, 0.0215 mol) were suspended in DMF (350 mL) and stirred at room temperature for 19 hrs and then stirred at 60°C for 7 hrs. The reaction mixture was poured into water and adjusted to pH 2 to 4 by 1 M HCl solution. The precipitate was collected via filtration and dry under high vacuum at room temperature to remove solvent. The resulting off-white solid (12.91 g, 0.0353 mol, 82 %) was used in the next step without purification. m.p. over 300°C; ^1H NMR (300 MHz, DMSO-d_6) δ 8.56 - 8.63 (m, 2H), 8.43 (d, *J* = 7.69 Hz, 1H), 7.96 - 8.07 (m, 2H), 7.83 - 7.91 (m, 2H), 7.41 - 7.52 (m, 2H), 5.24 - 5.32 (m, 2H).

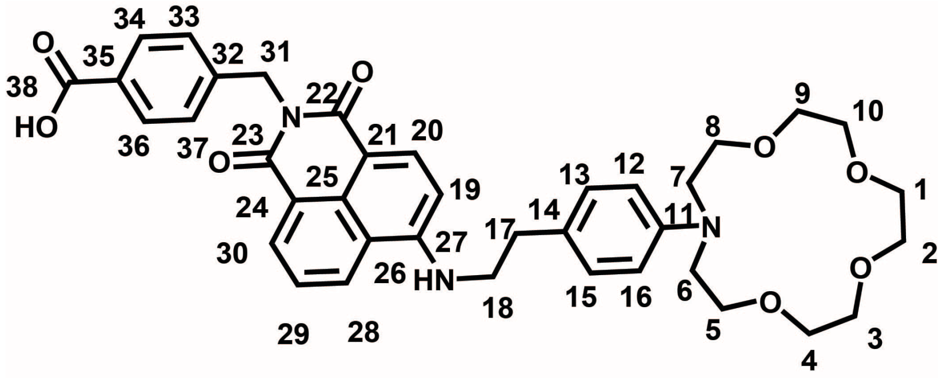
Step b: Product of step a (4-Chloro-*N*-(4-carboxyphenylmethyl)-1,8-naphthalimide) (5.49 g, 150 mmol) was stirred in DMF (150 mL) under nitrogen and then 1,1-carbonyldiimidazole (CDI) (9.75 g, 60.13mmol) was added into the reaction mixture and stirred for 15 mins. t-butyl alcohol (29 ml, 303.2 mmol) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (9 ml, 60.18 mmol) were added into the mixture. The mixture was stirred at 60°C for 16 hrs. The reaction mixture was poured into ice-cold 1 M HCl solution (250 mL) and filter of the precipitate. The precipitate was washed with 1 M HCl (2 x 50 mL) and dry under high vacuum at room temperature for at least 24 hrs to yield brown solid. The crude product was purified by silica gel column with chloroform to yield white powder (**iii**) (2.41 g, 5.71 mmol, 38%). m.p. 193 – 195°C;^1H NMR (300 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 1.24, 7.28 Hz, 1H), 8.62 (dd, *J* = 1.10, 8.52 Hz, 1H), 8.52 (d, *J* = 7.97 Hz, 1H), 7.81 - 7.96 (m, 3H), 7.55 (d, *J* = 8.52 Hz, 2H), 5.41 (s, 2H), 1.54 - 1.57 (m, 9H).

N-(*t*-Butyl-benzonate)-[4-(aza-15-crown-5)-phenylethylamino]-1,8-naphthalimide (2)



Compounds **iii** (429 mg, 1.016 mmol), **i** (683 mg, 2.018 mmol) and *N*,*N*-diisopropylethylamine (DIPEA) (445 µL, 2.55 mmol) were dissolved in *N*-methyl-2-pyrrolidone (NMP) (20 mL) in a CEM ^{TM} reaction tube. The tube was sealed and heated at 100°C under microwave irradiation for 5 hours. NMP was removed by distillation under reduced pressure at 50 - 60°C and the crude product was dried at ~50°C under high vacuum. Purification on silica gel with 1:1 ethyl acetate: chloroform eluent afforded an orange yellow crude product which was triturated with ethyl acetate/ hexane to yield (203 mg, 0.281 mmol, 28%) of **2** as orange-yellow crystals. m.p. 132 – 134°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.02 Hz, 1H,H30), 8.48 (d, *J* = 8.19 Hz, 1H, H20), 7.93 (d, *J* = 8.19 Hz, 1H, H28), 7.90 (d, *J* = 8.19 Hz, 2H, H34 and H36), 7.56 - 7.61 (m, 1H, H29), 7.54 (d, *J* = 8.19 Hz, 2H, H33 and H37), 7.10 (d, *J* = 8.19 Hz, 2H, H13 and H15), 6.77 (d, *J* = 8.78 Hz, 1H, H19), 6.65 (d, *J* = 8.78 Hz, 2H, H12 and H16), 5.39 (s, 2H, H31), 5.33 (br. s., 1H, NH), 3.55 - 3.79 (m, 23H, aza-15-crown-5 and H18), 2.99 (t, *J* = 6.73 Hz, 2H, H15), 1.55 (s, 9H, t-butyl ester). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7 (C35), 164.6 (C22), 164.0 (C23), 149.5 (C11), 146.7 (C27), 142.5 (C32), 134.8 (C20), 131.4 (C30), 130.9 (C35) , 129.9 (C25), 129.6 (C13 and C15, C34 and C36), 128.3 (C33 and C37), 126.1 (C28), 124.7, 124.6 (C14), 123.0 (C24), 120.3 (C26), 111.8 (C12 and C16), 110.1 (C21), 104.6 (C27), 80.7 (C38), 71.3(aza-15-crown-5), 70.2(aza-15-crown-5), 70.1(aza-15-crown-5), 68.6(aza-15-crown-5), 52.5 (C18), 44.7 (aza-15-crown-5), 43.1 (C31), 33.7 (C17), 28.2 (C40-C42). UATR FTIR (Diamond/ZnSe) υ/cm^{-1} 3360, 2862, 1715, 1683, 1632, 1616, 1589, 1573, 1537, 1523. MS (ESI, +ve mode) *m/z* 724.2 ($[M + H]^+$, 100 %), 725.2 (43 %), 746.2 ($[M + Na]^+$, 28 %), 747.2 (11 %). HRMS (ESI) *m/z* found 724.35913, $[C_{42}H_{49}N_3O_8 + H]^+$ required 724.35924.

4-[4’-[4’’-(aza-15-crown-5)-phenylethylamino]-1’, 8’ naphthalimidylmethyl] Benzoic Acid (3)



Trifluoroacetic acid (TFA) (2 mL) was added to **2** (80 mg, 0.111 mmol) dissolved in dichloromethane (8 mL). The mixture was stirred at room temperature for 1 hr. The solution was diluted with chloroform and the solvent was evaporated. The residue was redissolved in methanol/chloroform mixture (1:9, 50 mL) and the solvent evaporated. The process was performed three times. The residue was dissolved in methanol/chloroform mixture (1: 9) again and washed with 5% TFA solution (50 mL x 2). The organic phase was dried with MgSO$_4$ and the solvent was removed. The crude product was triturated with ethyl acetate/hexane to yield **3** as yellow crystals (64 mg, 0.0959 mmol, 90%). m.p. 180 – 183°C. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 8.70 (d, *J* = 8.20 Hz, 1H, H28), 8.44 (d, *J* = 7.03 Hz, 1H, H20), 8.28 (d, *J* = 8.20 Hz, 1H, H30), 7.92 (s, 1H, NH), 7.85 (d, *J* = 8.79 Hz, 2H, H34/36), 7.68 (t, 1H, *J* = 8.2 Hz, 1H, H29), 7.40 (d, *J* = 8.20 Hz, 2H, H33/H37), 7.08 (d, *J* = 8.20 Hz, 2H, H13/H15), 6.85 (d, *J* = 8.79 Hz, 1H, H19), 6.56 (d, *J* = 8.79 Hz, 2H, H12/H16), 5.26 (s, 2H, H31), 3.40 - 3.66 (m, 23H, Aza-crown and H18), 2.86 (t, *J* = 7.62 Hz, 2H, H17). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 167.5 (C35), 164.3 (C21), 163.3 (C24), 151.2 (C25), 146.4 (C11), 143.4 (C32), 135.1 (C30), 131.5 (C20), 130.1, 130.0, 129.9, 129.3 (C28), 127.8 (C33/C37), 125.9 (C14), 124.8 (C29), 122.1 (C24), 120.7 (C26), 111.7 (C13/C15), 107.7, 104.6 (C19), 70.8 (aza-crown and C18), 69.9 (aza-crown and C18), 69.5 (aza-crown and C18), 68.4 (aza-crown and C18), 52.3 (C18), 45.4 (C31), 33.4 (C17). UATR FTIR (Diamond/ZnSe) υ/cm^{-1} 3359, 2971, 2948, 2885, 2646, 1737, 1718, 1682, 1635, 1616, 1570, 1544, 1521. MS (ESI, +ve mode) *m/z* 668.3 ([M + H]$^+$, 100 %), 669.3 (36 %).HRMS (ESI) *m/z* found 668.29662, [C$_{38}$H$_{41}$N$_3$O$_8$ + H]$^+$ required 668.29664.

2. Results of time-dependent coating experiments

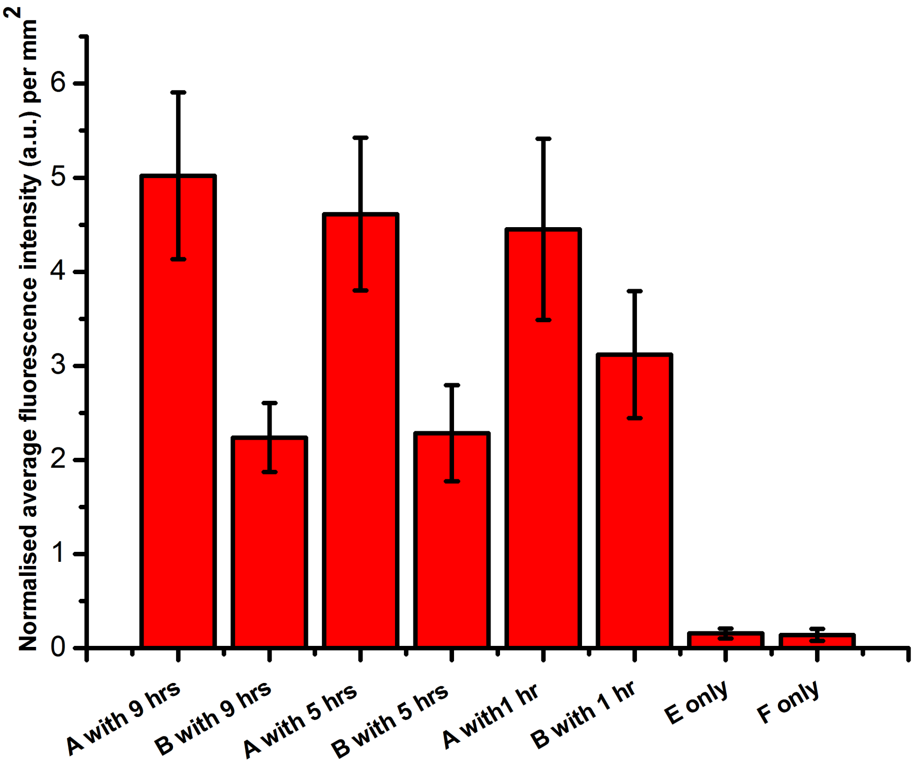


Figure S1. Normalised averaged fluorescence intensity per mm^2 for slides grafted with APTES and **3** after 1, 5 and 9 hours incubation and their respective negative controls. A= **3**/EDC/NHS/base, B1 = **3** only, E = APTES only and F = F2 glass only.

3. Additional XPS data

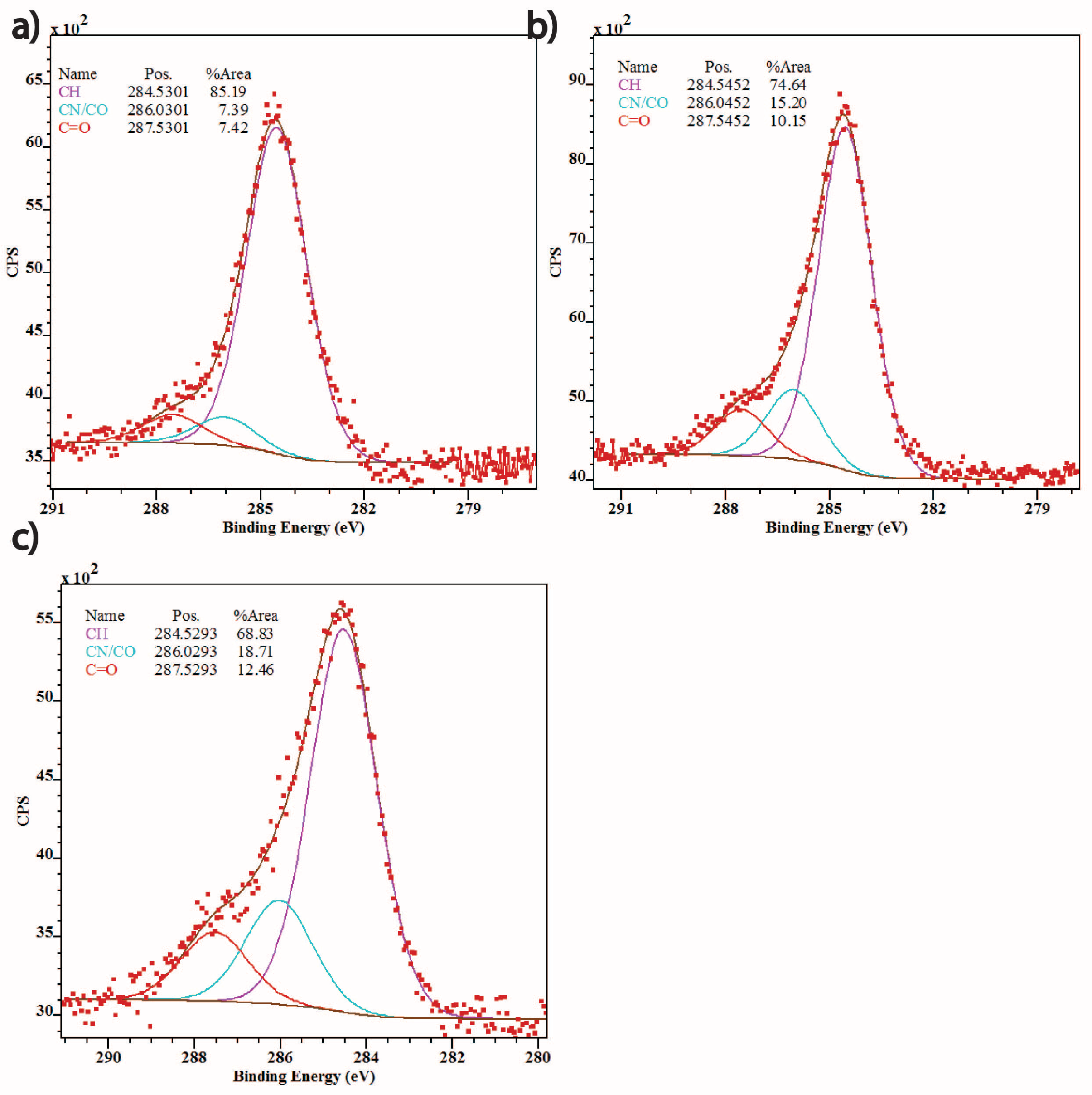


Figure S2. Deconvolution of the HR carbon XPS spectra at the first sampling position of (a) an APTES-grafted glass, (b) the negative control (no coupling agents) and (c) APTES-grafted F2 glass coupled with **3**.

4. Loading plot of PC1 and PC2 for the PCA analysis of the ToF-SIMS data

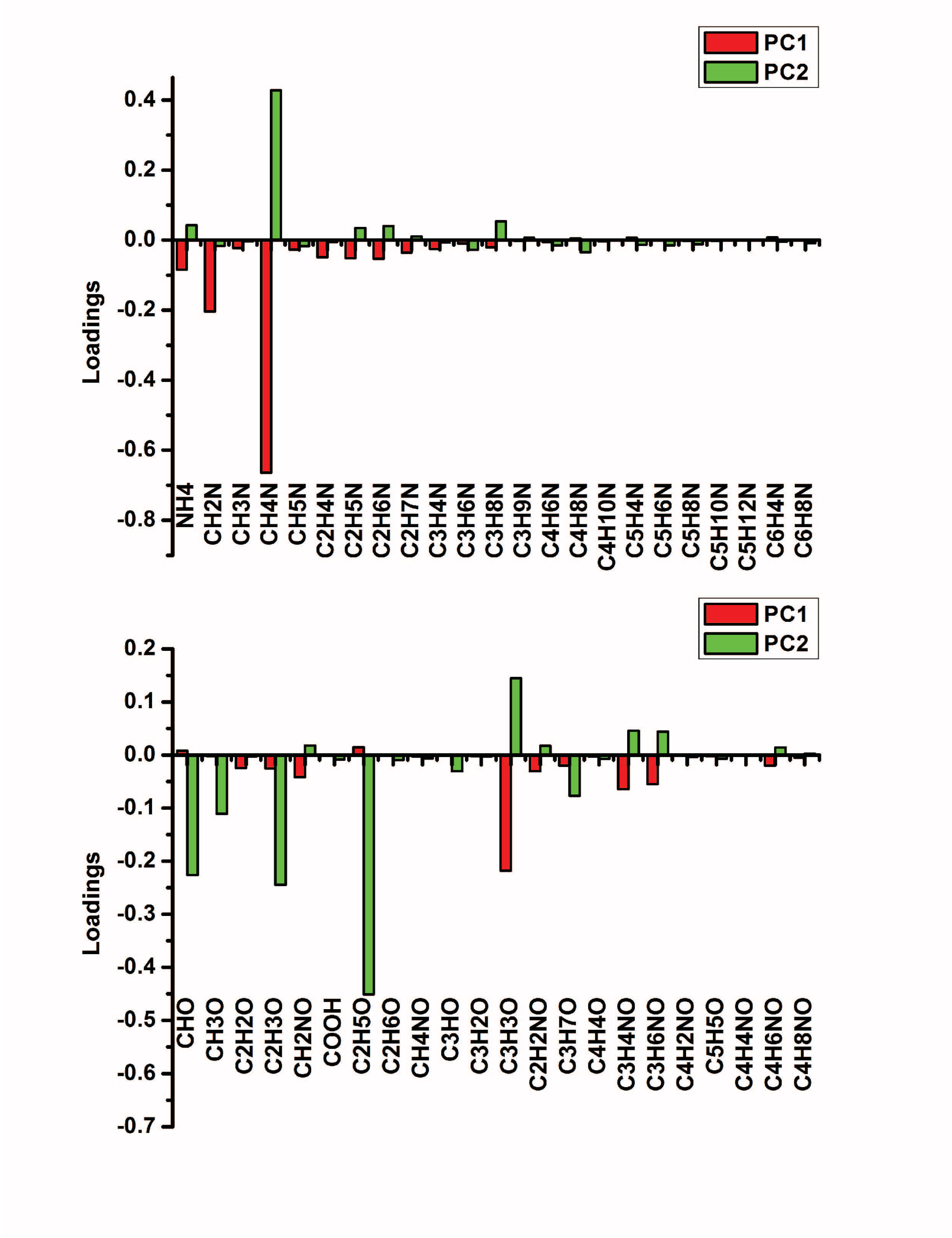
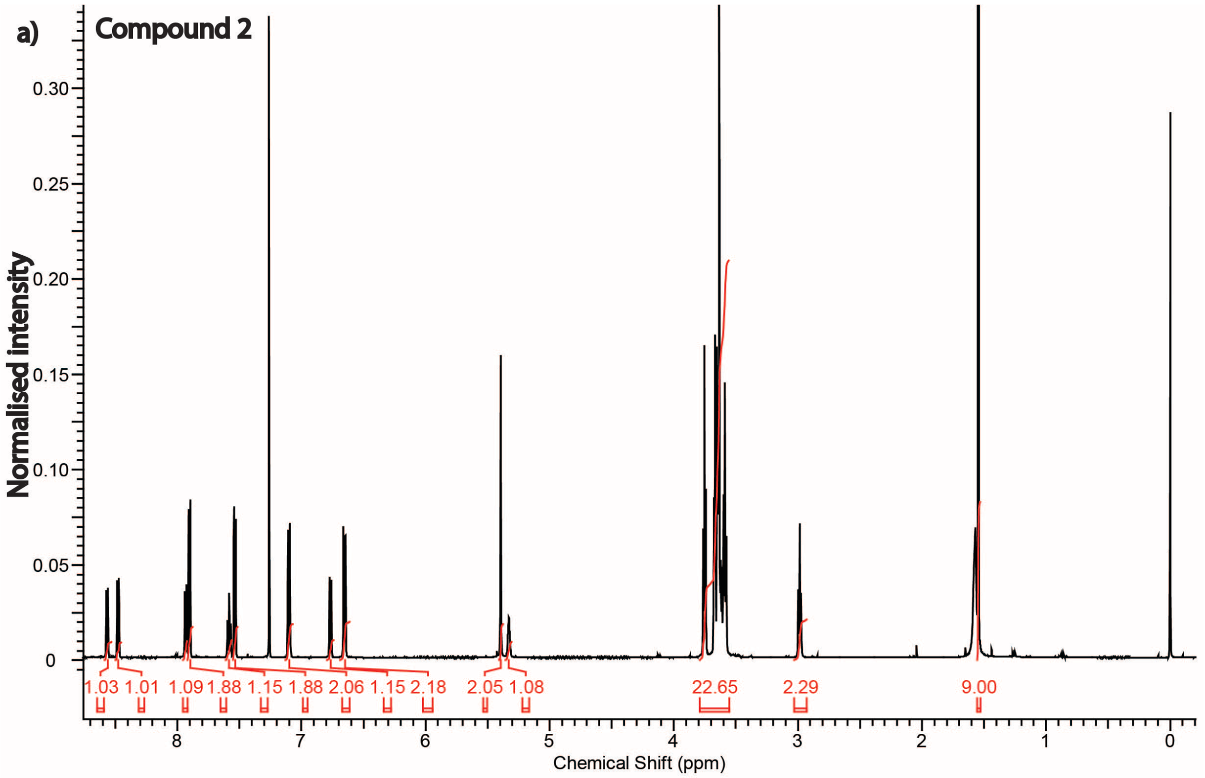
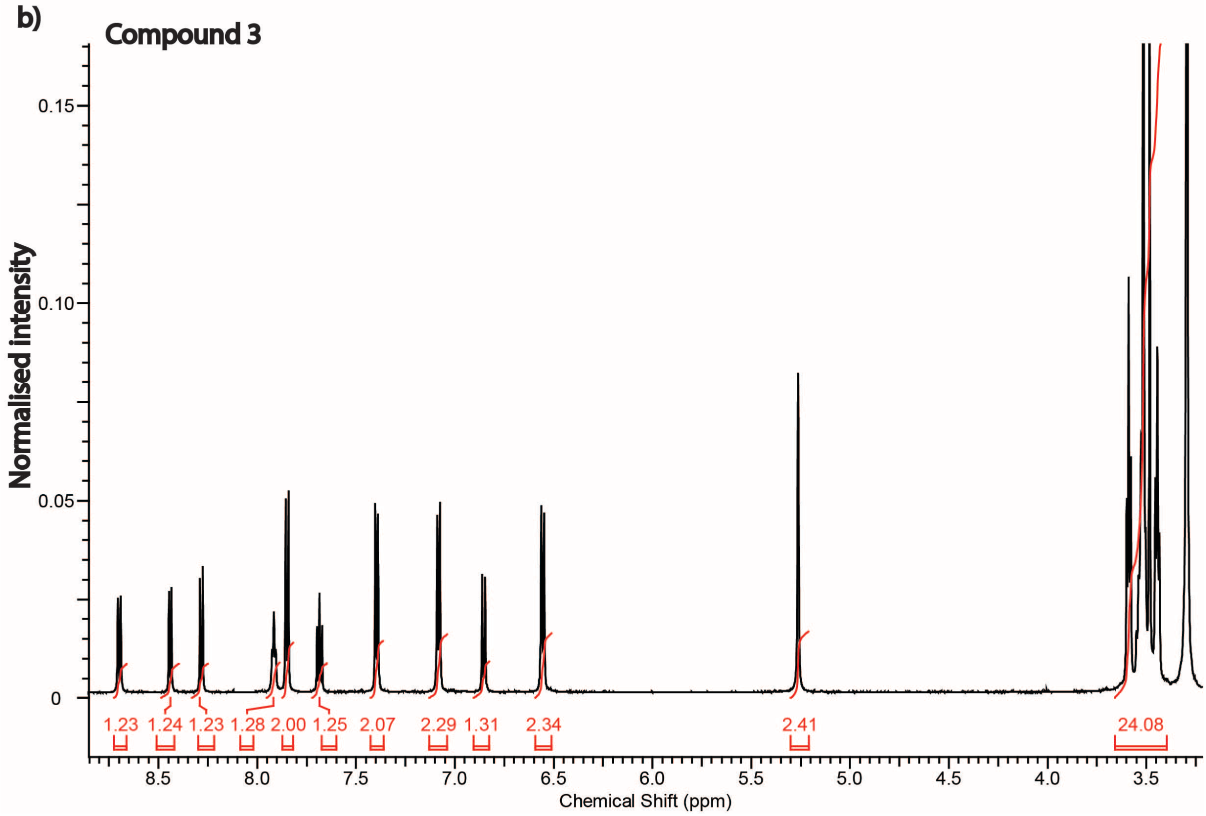


Figure S3. The loading plots of (a) $C_xH_yN_z$ and (b) $C_xH_yN_zO$ for the PCA analysis of the ToF-SIMS data.

5. ^{1}H NMR spectra of compounds 2 and 3





6. Excitation and emission spectrum of fluoroionophore 3

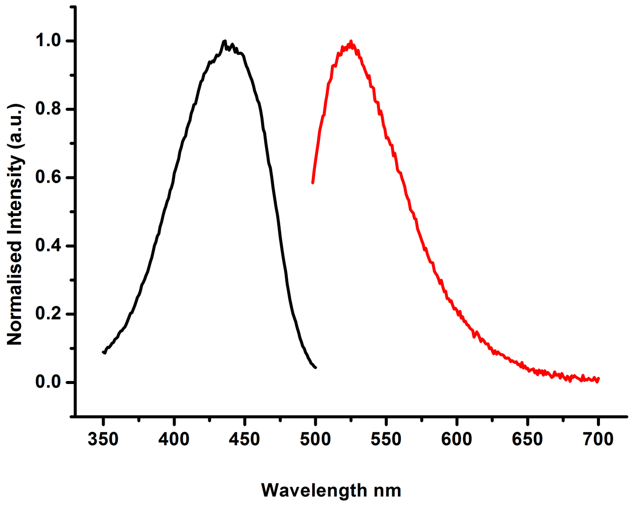


Figure S4. The left (black) spectrum is the normalized excitation spectrum of **3** with emission fixed at 520 nm, and the right (red) spectrum is the normalised emission spectrum of **3** with excitation fixed at 488 nm in CH_3CN (I = 0.1 M).

7. References

1. Englich, F. V.; Foo, T. C.; Richardson, A. C.; Ebendorff-Heidepriem, H.; Sumby, C. J.; Monro, T. M., Photoinduced Electron Transfer Based Ion Sensing within an Optical Fiber. *Sensors* **2011,** *11*, 9560-9572.
2. J. Leonard, N. L., G. Procter, *Advanced practical organic chemistry*. 2nd ed.; CRC Press Taylor & Francis group: 1998.