Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Sensor Arrays Made by Self-Organized Nanoreceptors for Detection and Discrimination of Carboxylate Drugs

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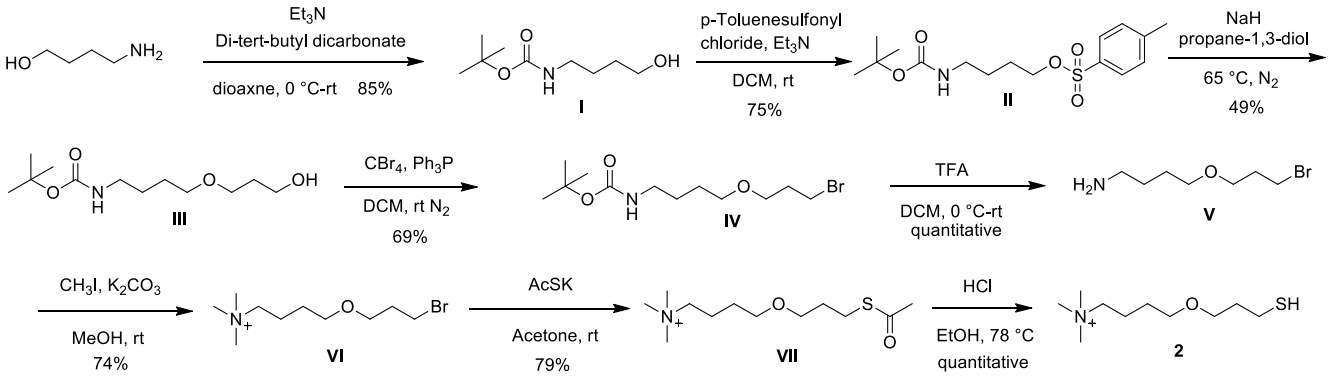
1. Synthesis of thiol 1, 2 and 3

1.1 Synthesis of thiol 1

Thiol 1 were prepared according to the literature.[1]

1.2 Synthesis of thiol 2.

Thiol **2** was prepared according to the following scheme:



Scheme S1. Synthesis of thiol 2.

1.2.1 Synthesis of tert-butyl (4-hydroxybutyl)carbamate (I)

4-Amino-1-butanol (1.0 g, 11.218 mmol, 1 equiv) was dissolved in dioxane (2.0 mL), then Di-tert-butyl dicarbonate (2.94 g, 13.462 mmol, 1.2 equiv) and trimethylamine (1.36 g, 13.462 mmol, 1.2 equiv) were added at 0 °C. The mixture was stirred for 6 hours at room temperature. After solvent evaporation, the crude product was purified by flash chromatography (silica gel, eluent: PE/ EtOAc 3:7). 1.82 g (85%) of tert-butyl (4-hydroxybutyl)carbamate (**I**) were obtained.

^{1}H NMR (500 MHz, MeOD) δ 3.62 – 3.53 (t, 2H, CH_2O), 3.10-3.04 (t, 2H, CH_2N), 1.55 (m, J = 6.3, 2.9 Hz, 4H, CH_2), 1.45 (s, 9H, CH_3).

^{13}C NMR (126 MHz, MeOD) δ 157.08 (1C, COO), 61.23 (1C, CH_2O), 78.41 (1C, $C(CH_3)_3$), 39.79 (1C, CH_2NH), 29.42 (1C, CH_2), 27.41 (3C, CH_3), 26.05 (1C, CH_2).

ESI-MS (m/z): 212.0 [M+Na^+].

1.2.2 Synthesis of 4-((tert-butoxycarbonyl)amino)butyl 4-methylbenzenesulfonate (II)

I (600 mg, 3.170 mmol, 1 equiv) and p-toluenesulfonyl chloride (1.209 g, 6.341 mmol, 2 equiv) were dissolved in aqueous CH_2Cl_2 (10 mL) and triethylamine (641.7 mg, 6.341 mmol, 2 equiv) was added. The mixture was stirred for 12 hours under nitrogen at room temperature. After solvent evaporation, the crude product was purified by flash chromatography (silica gel, eluent: PE/EtOAc 7:3). 820 mg (75%) of **II** were obtained.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.73 (d, 2H, CH), 7.38-7.33 (d, 2H, CH), 4.07-4.01 (t, 2H, CH_2O), 3.12-3.04 (t, 2H, CH_2N), 2.46 (s, 3H, CH_3), 1.72-1.65 (m, 2H, CH_2), 1.57 – 1.48 (m, 2H, CH_2), 1.43 (s, 9H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.94 (1C, COO), 144.78 (1C, CS), 133.02 (1C, C), 129.86 (2C, CH), 127.86 (2C, CH), 79.24 (1C, C), 70.12 (1C, CH_2O), 39.78 (1C, CH_2NH), 28.38 (3C, CH_3), 26.19 (2C, CH_2) , 21.64 (1C, CH_3).

ESI-MS (m/z): 366.1 [M+Na^+], 382.0 [M+K^+]

1.2.3 Synthesis of tert-butyl (4-(3-hydroxypropoxy)butyl)carbamate (III)

Sodium hydride (605 mg, 15.414 mmol) was added to propane-1,3-diol (8 mL). The solution was stirred for 30 minutes and then **II** (1.30 g, 3.785 mmol) was added. The mixture was refluxed at 65 °C for 14 hours. After the completion of the reaction, the mixture was washed with H_2O and extracted with DCM. The combined organic layer was dried with $MgSO_4$ and filtered. After solvent evaporation,

the crude product was purified by flash chromatography (silica gel, eluent: PE/EtOAc 3:7). 461 mg (49%) of **III** were obtained.

^{1}H NMR (500 MHz, MeOD) δ 3.68-3.62 (t, 2H, CH_2O), 3.56-3.51 (t, 2H, CH_2O), 3.49-3.44 (t, 2H, CH_2O), 3.09-3.04 (t, 2H, CH_2N), 1.83-1.76 (qn, 2H, CH_2), 1.64 – 1.50 (m, 4H, CH_2), 1.45 (s, 9H, CH_3).

^{13}C NMR (126 MHz, MeOD) δ 157.14 (1C, CO), 78.44 (1C, C), 70.17 (1C, CH_2O), 67.28 (1C, CH_2O), 58.61 (1C, CH_2OH), 39.78 (1C, CH_2N), 32.27 (1C, CH_2), 27.35 (3C, CH_3), 26.60 (1C, CH_2), 26.34 (1C, CH_2).

TOF ES+ HRMS: [M+Na+] calcd. for $C_{12}H_{25}NNaO_4$ = 270.1681. Found = 270.1700.

1.2.4 Synthesis of tert-butyl (4-(3-bromopropoxy)butyl)carbamate (IV)

III (435.0 mg, 1.759 mmol), tetrabromomethane (1.166 g, 3.516 mmol) and triphenylphosphine (922.7 mg, 3.516 mmol) were dissolved in DCM. The mixture was stirred for 12 hours at room temperature. Then the solvent was evaporated and the crude product was purified by flash chromatography (silica gel, eluent: PE/EtOAc 1:9). 375 mg (69%) of **IV** were obtained.

^{1}H NMR (500 MHz, MeOD) δ 3.57-3.49 (m, 4H, CH_2), 3.48-3.44 (t, 2H, CH_2O), 3.18-3.11 (t, 2H, CH_2N), 2.16 – 2.07 (q, 2H, CH_2), 1.67 – 1.52 (m, 4H, CH_2), 1.46 (s, 9H, CH_3).

^{13}C NMR (126 MHz, MeOD) δ 157.15 (1C, CO), 78.33 (1C, C), 70.18 (1C, CH_2O), 67.76 (1C, CH_2O), 39.72 (1C, CH_2N), 32.65 (1C, CH_2Br), 29.65 (1C, CH_2), 27.38 (3C, CH_3), 26.60 (1C, CH_2), 26.34 (1C, CH_2).

TOF ES+ HRMS: [M+Na^+] calcd. for $C_{12}H_{24}BrNNaO_3$ = 332.0837. Found = 332.0847.

1.2.5 Synthesis of 4-(3-bromopropoxy)butan-1-amine (V)

IV (375 mg, 1.209 mmol) was dissolved in DCM and trifluoroacetic acid (2 mL) was added at 0 °C. The mixture was stirred for 4 hours at room temperature. Then the solvent was evaporated and the product (250 mg, quantitative) was obtained.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66-3.61 (t, 2H, CH_2Br), 3.56-3.52 (t, 2H, CH_2O), 3.50-3.46 (t, 2H, CH_2O), 3.11-3.03 (m, 2H, CH_2N), 2.15-2.08 (q, 2H, CH_2), 1.89-1.82 (q, 2H, CH_2), 1.79-1.72 (q, 2H, CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ 70.43 (1C, CH_2O), 68.79 (1C, CH_2O), 40.22 (1C, CH_2N), 32.09 (1C, CH_2Br), 30.05 (1C, CH_2), 26.93 (1C, CH_2), 25.19 (1C, CH_2).

TOF ES+ HRMS: [M+H$^+$] calcd. for $C_7H_{17}BrNO$ = 210.0494. Found = 210.0502.

1.2.6 Synthesis of 4-(3-bromopropoxy)-N,N,N-trimethylbutan-1-aminium (VI)

V (123.0 mg, 0.585 mmol) and iodomethane (332.4 mg, 2.342 mmol) was dissolved in methanol and potassium carbonate (323.6 mg, 2.342 mmol) was added. The flask used for this reaction was covered with aluminum paper. The mixture was stirred for 12 hours at room temperature. Then the solvent was evaporated and the crude product was purified by flash chromatography (silica gel, eluent: DCM/MeOH 8.5:1.5). 110 mg (74%) of **VI** were obtained.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58-3.52 (t, 4H, CH_2), 3.49-3.43 (t, 2H, CH_2O), 3.37--3.32 (t, 2H, CH_2NH), 2.08-2.01 (m, 2H, CH_2), 1.97-1.87 (q, 2H, CH_2), 1.73-1.64 (q, 2H, CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ 69.44 (1C, CH_2O), 67.82 (1C, CH_2O), 66.23 (1C, CH_2N), 52.42 (3C, CH_3), 33.17 (1C, CH_2Br), 29.97 (1C, CH_2), 25.89 (1C, CH_2), 19.7 (1C, CH_2).

ESI-MS (m/z): 253.2 [M+H$^+$].

1.2.7 Synthesis of 4-(3-(acetylthio)propoxy)-N,N,N-trimethylbutan-1-aminium (VII)

VI (0.263 g, 0.716 mmol, 1 equiv) was dissolved in acetone (4 mL) and potassium thioacetate (0.0981 g, 0.859 mmol, 1.2 equiv) was added. The mixture was stirred for 12 hours at room temperature. After solvent evaporation, the crude product was purified by flash chromatography (silica gel, eluent: DCM/ MeOH 8.5:1.5). 81 mg (79%) of **VII** were obtained.

^{1}H NMR (500 MHz, MeOD) δ 3.56 – 3.44 (m, 6H, CH_2), 3.24 – 3.17 (s, 9H, CH_3), 3.02-2.96 (t, 2H, CH_2N), 2.34 (s, 3H), 1.98–1.90 (q, 2H, CH_2), 1.87-1.80 (q, 2H, CH_2), 1.73-1.65 (q, 2H, CH_2).

^{13}C NMR (126 MHz, MeOD) δ 196.28 (1C, COS), 69.32 (1C, CH_2O), 68.68 (1C, CH_2O), 66.29 (1C, CH_2N), 52.32 (3C, CH_3), 33.45 (1C, CH_2S), 29.38 (1C, CH_2), 25.77 (1C, CH_2), 19.52 (1C, CH_2).

ESI-MS (m/z): 248.2 [$M+H^+$].

1.2.8 Synthesis of 4-(3-mercaptopropoxy)-N,N,N-trimethylbutan-1-aminium (2)

VII (24.6 mg, 0.0987 mmol) was dissolved in ethanol (2.0 mL). A 6 M HCl solution in water (2.0 mL) was added and the mixture was stirred at 78 °C for 2 hours. The reaction mixture was allowed to cool and the solvent was evaporated to obtain 20.37 mg (quantitative) of **2**.

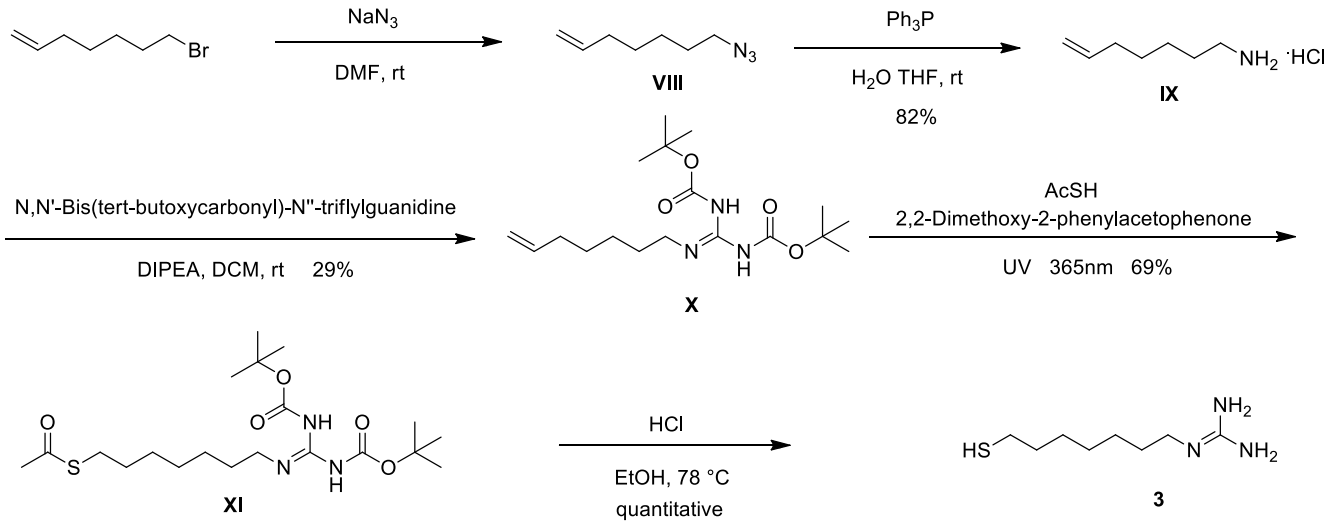
^{1}H NMR (500 MHz, MeOD) δ 3.59-3.56 (t, 2H, CH_2O), 3.55-3.52 (t, 2H, CH_2O), 3.46–3.40 (t, 2H, CH_2N), 3.18 (S, 9H, CH_3), 2.63-2.58 (t, 2H, CH_2S), 1.96–1.82 (m, 4H, CH_2), 1.71-1.64 (q, 2H, CH_2).

^{13}C NMR (126 MHz, MeOD) δ 69.32 (1C, CH_2O), 68.39 (1C, CH_2O), 66.25 (1C, CH_2N), 52.18 (1C, CH_3), 33.46 (1C, CH_2S), 25.92 (1C, CH_2), 20.32 (1C, CH_2), 19.67 (1C, CH_2).

TOF ES+ HRMS: [$M+H^+$] calcd. for $C_{10}H_{25}NOS$ = 207.1651. Found = 207.1599.

1.3 Synthesis of thiol 3.

Thiol **3** was prepared according to the following scheme:



Scheme S2. Synthesis of thiol 3.

1.3.1 Synthesis of 7-azidohept-1-ene (VIII)

7-bromohept-1-ene (0.516 g, 3.140 mmol) and sodium azide (0.220 g, 9.157 mmol) were dissolved in aqueous DMF (10 mL). After 10 hour stirring, the mixture was washed with H_2O and extracted with DCM. The combined organic layer was concentrated in vacuo and used in the next step without any purification.

1.3.2 Synthesis of hept-6-en-1-amine hydrochloride (IX)

VIII (1.179 g, 8.47 mmol) was dissolved in H_2O (5 mL) and THF (13 mL). Triphenylphosphine (4.400 g, 33.88 mmol) was then added to the mixture. The solution was stirred for 12 hours at room temperature. After the completion of the reaction, the mixture was washed with DCM and extracted

with HCl solution (1 M). the combined aqueous solution was evaporated to dryness in vacuo. 785 mg (82%) of I**X** were obtained as white solid.

^{1}H NMR (500 MHz, D_2O) δ 5.89 – 5.73 (m, 1H, CH), 5.02–4.86 (dd, 2H, CH_2), 2.94-2.87 (t, 2H, CH_2N), 2.05–1.94 (q, 2H, CH_2), 1.63 – 1.50 (q, 2H, CH_2), 1.40–1.24 (m, 4H, CH_2).

^{13}C NMR (126 MHz, D_2O) δ 139.67 (1C, CH), 114.32 (1C, CH_2), 39.42 (1C, CH_2N), 32.69 (1C, CH_2), 27.41 (1C, CH_2), 26.47 (1C, CH_2), 25.00 (1C, CH_2).

ESI-MS (m/z): 114.1 [$M+H^+$].

1.3.3 Synthesis of X

IX (215.7 mg, 1.4411 mmol) and N,N'-Bis(tert-butoxycarbonyl)-N''-triflylguanidine (470.0 mg, 1.201 mmol) were dissolved in DCM. Then N,N-Diisopropylethylamine (465.6 mg, 3.603 mmol) was added to the solution. The mixture was stirred for 25 hours at room temperature. After the solvent evaporation, the crude product was purified by flash chromatography (silica gel, eluent: PE/ EtOAc 9.5:0.5). 150 mg (29%) of **X** were obtained.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86-8-5.75 (m, 1H, CH), 5.06–4.91 (m, 2H, CH_2), 3.46-3.39 (q, 2H, CH_2), 2.11-2.04 (q, 2H, CH_2N), 1.63 – 1.56 (m, 2H, CH_2), 1.55-1.49 (d, 18H, CH_3), 1.48 – 1.35 (m, 4H, CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.09 (1C, C), 153.33 (2C, CH_2O), 138.71 (1C, CH), 114.39 (1C, CH_2), 83.04 (1C, C), 79.23 (1C, C), 40.93 (1C, CH_2N), 33.54 (1C, CH_2), 28.83 (1C, CH_2), 28.47 (1C, CH_2), 28.32 (3C, CH_3), 28.08 (3C, CH_3), 26.30 (1C, CH_2).

TOF ES+ HRMS: [$M+H^+$] calcd. for $C_{18}H_{34}N_3O_4$ = 356.2549. Found = 356.2561.

1.3.4 Synthesis of XI

X (130 mg, 0.366 mmol) was dissolved in methanol (3 mL). Nitrogen was injected into the solution for 20 min to remove oxygen. Afterwards, 2, 2-Dimethoxy-2-phenylacetophenone (4.741 mg, 0.0183 mmol) and ethanethioic S-acid (111.4 mg, 1.463 mmol) were added. The mixture was left under irradiation (UV, 365 nm) for 2 hours. After solvent evaporation, the crude product was purified by flash chromatography (silica gel, eluent: PE/ EtOAc 9.5:0.5). 108 mg (69%) of **XI** were obtained.

^{1}H NMR (500 MHz, MeOD) δ 3.39-3.34 (t, 2H, CH_2S), 2.91-2.86 (t, 2H, CH_2), 2.32-2.30 (s, 3H, CH_3), 1.63-1.56 (m, 4H, CH_2), 1.55 (s, 9H, CH_3), 1.49 (s, 9H, CH_3), 1.44-1.35 (m, 6H, CH_2).

^{13}C NMR (126 MHz, MeOD) δ 196.15 (1C, COS), 163.17 (1C, CN) , 156.17 (1C, CO), 152.85 (1C, CO), 83.04 (1C, C), 78.93 (1C, C), 40.31 (1C, CH_2N), 29.24 (1C, CH_3), 29.09 (1C, CH_2) , 28.55 (1C, CH_2), 28.39 (1C, CH_2), 28.31 (1C, CH_2), 28.22 (1C, CH_2) , 27.17 (1C, CH_3), 26.82 (1C, CH_3), 26.23 (1C, CH_2).

1.3.5 Synthesis of 2-(7-mercaptoheptyl)guanidine (3)

XI (42.6 mg, 0.0987 mmol) was dissolved in ethanol (2.0 mL). A 6 M HCl solution in water (2.0 mL) was added and the mixture was stirred at 78 °C for 2 hours. The reaction mixture was allowed to cool and the solvent was evaporated to obtain 18.7 mg (quantitative) of **3**.

^{1}H NMR (500 MHz, MeOD) δ 3.23-3.17 (t, 2H, CH_2N), 2.54-2.48 (t, 2H, CH_2S), 1.65-1.56 (m, 4H, CH_2), 1.48 – 1.33 (m, 6H, CH_2).

^{13}C NMR (126 MHz, MeOD) δ 157.23 (1C, CN), 41.12 (1C, CH_2N), 33.68 (1C, CH_2S), 30.05 (1C, CH_2), 28.42 (1C, CH_2), 28.36 (1C, CH_2), 27.84 (1C, CH_2), 26.2 (1C, CH_2).

TOF ES+ HRMS: [$M+H^+$] calcd. for $C_8H_{19}NS$ = 190.1378. Found = 190.1398.

2. Characterization of monolayer protected gold nanoparticles (MPGN-1,2 and 3)

TEM analysis (Figures S1, S2 and S3) of the different samples of nanoparticles yields an average diameter for MPGN-1 of 1.6 ± 0.3nm, for MPGN-2 and 3 of 1.6 ± 0.3 nm and 1.4± 0.2 nm. This data, together with the loss of organic weight obtained by TGA analysis (Figures S4, S5 and S6), were used to calculate average formulas for the MPGN using the spherical approximation.[2] Average nanoparticles composition resulted to be $Au_{120}SR_{60}$ for MPGN-1, $Au_{131}SR_{46}$ for MPGN-2, $Au_{90}SR_{47}$ for MPGN-3. NMR analysis (Figure S7, S8, S9) indicates monolayer formation (broadening of all signals and absence of the SCH2CH2 protons' signals). UV-vis spectra (Figure S10, S11, S12) recorded also showed no or small plasmonic band at 520 nm, which suggests the size of the MPGNs is smaller than 3 nm.

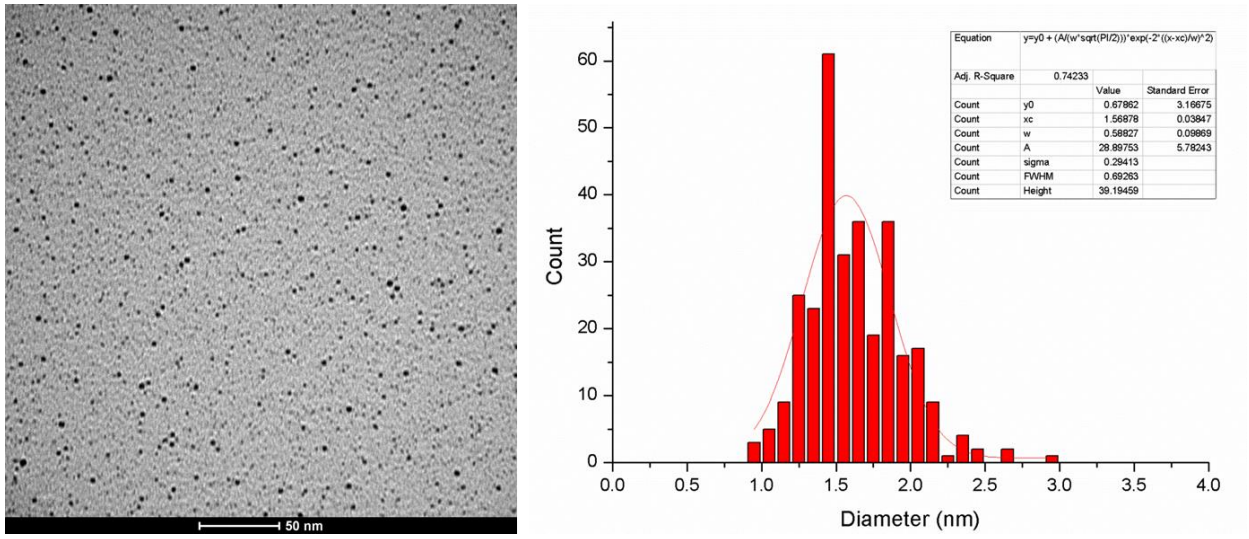


Figure S1. TEM image of MPGN-1 and its size distribution: average diameter=1.6 nm (σ= 0.3 nm).

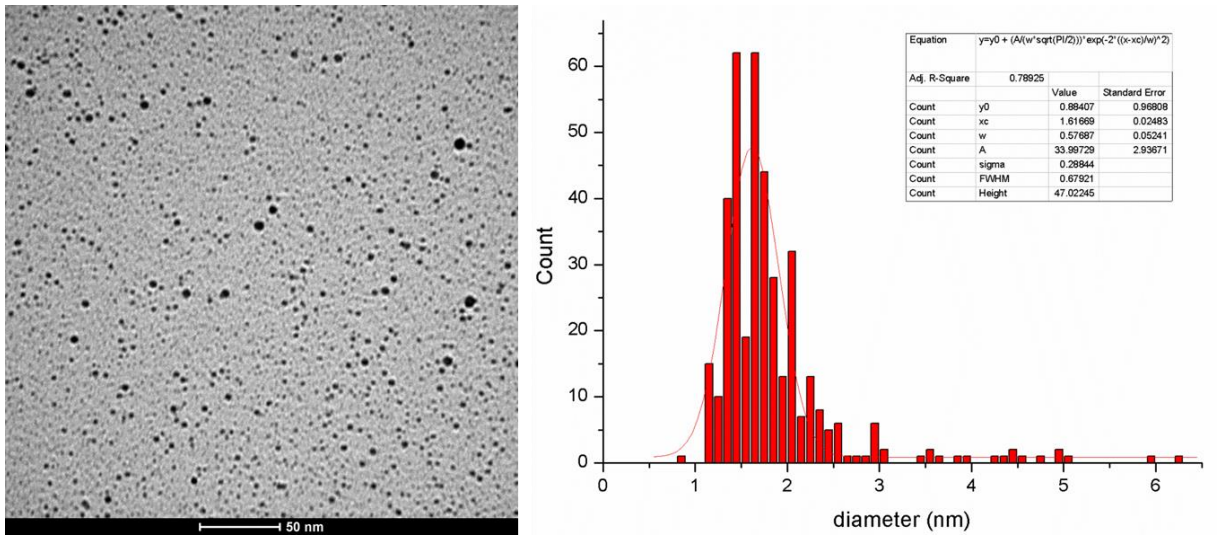


Figure S2. TEM image of MPGN-2 and its size distribution: average diameter=1.6 nm (σ= 0.3 nm).

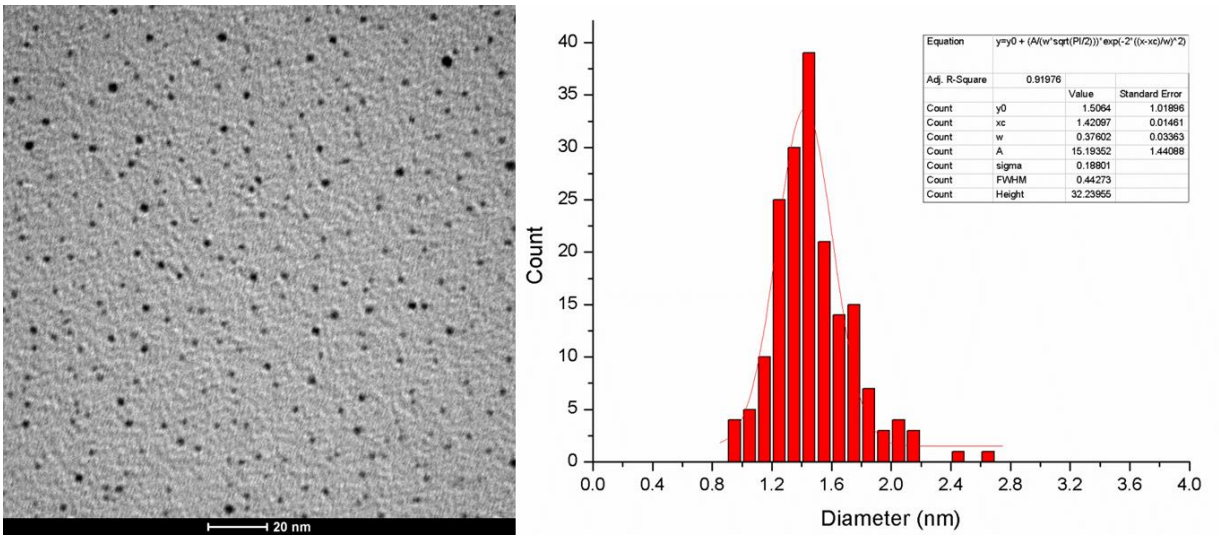


Figure S3. TEM image of MPGN-3 and its size distribution: average diameter=1.4 nm (σ= 0.2 nm).

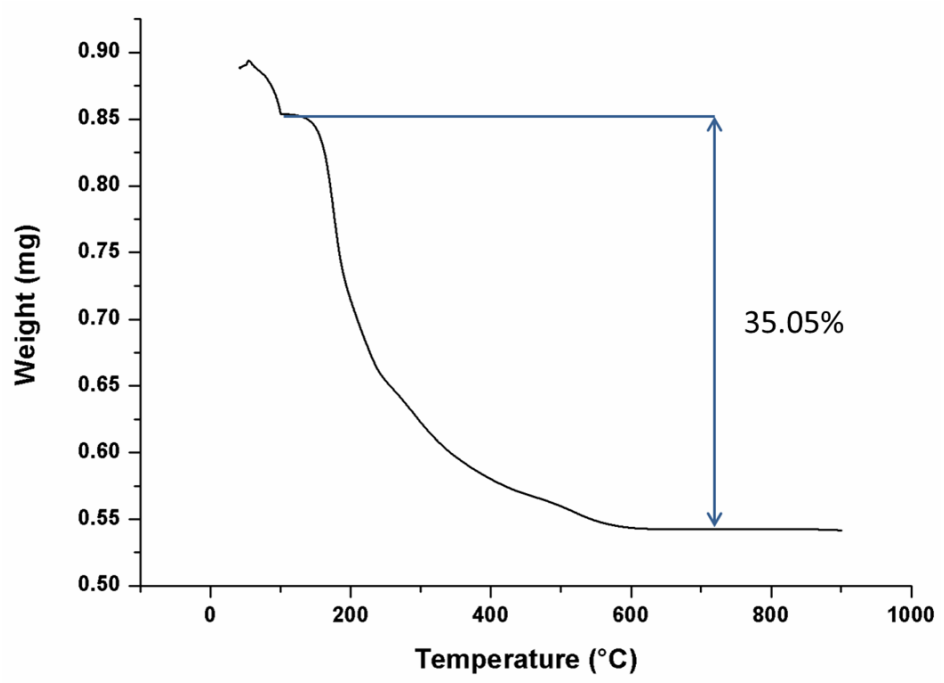


Figure S4. TGA analysis of MPGN-1 under air atmosphere.

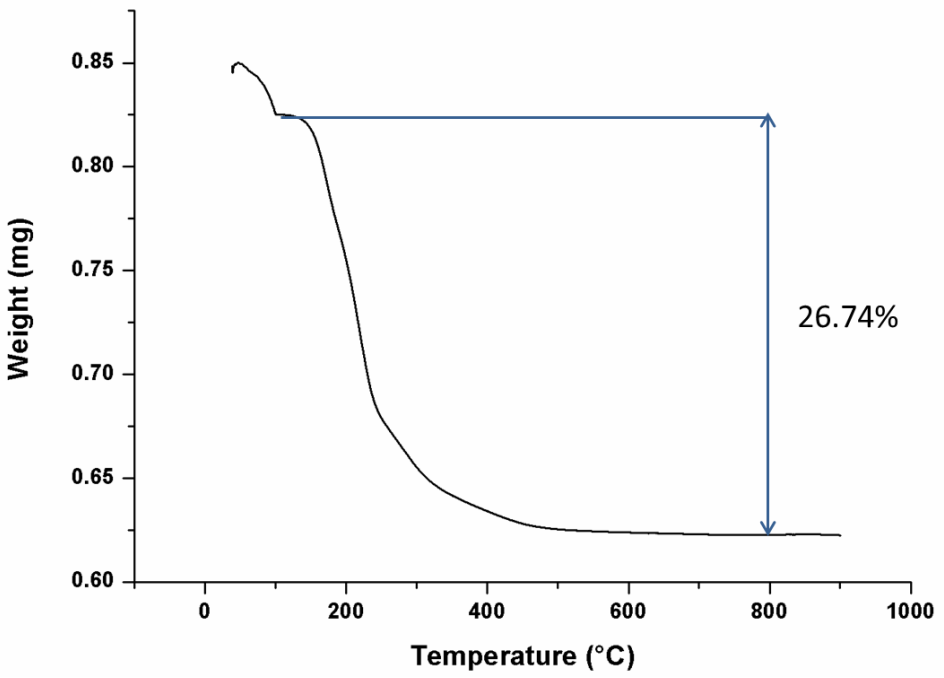


Figure S5. TGA analysis of MPGN-2 under air atmosphere.

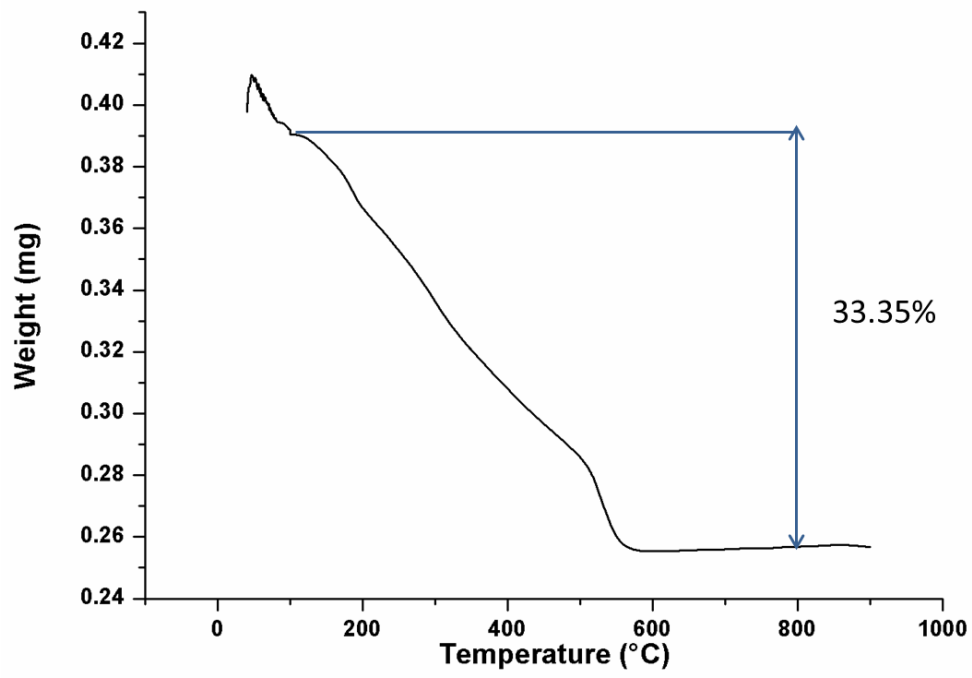


Figure S6. TGA analysis of MPGN-3 under air atmosphere.

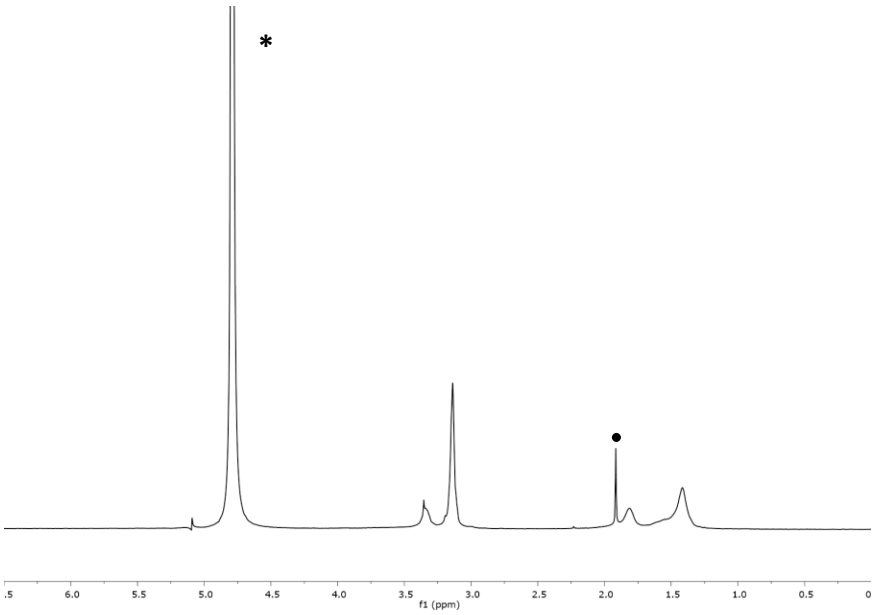


Figure S7. ^{1}H NMR spectrum of MPGN-1 in H_2O (* indicates the residual solvents, • indicates CH_3COO^-).

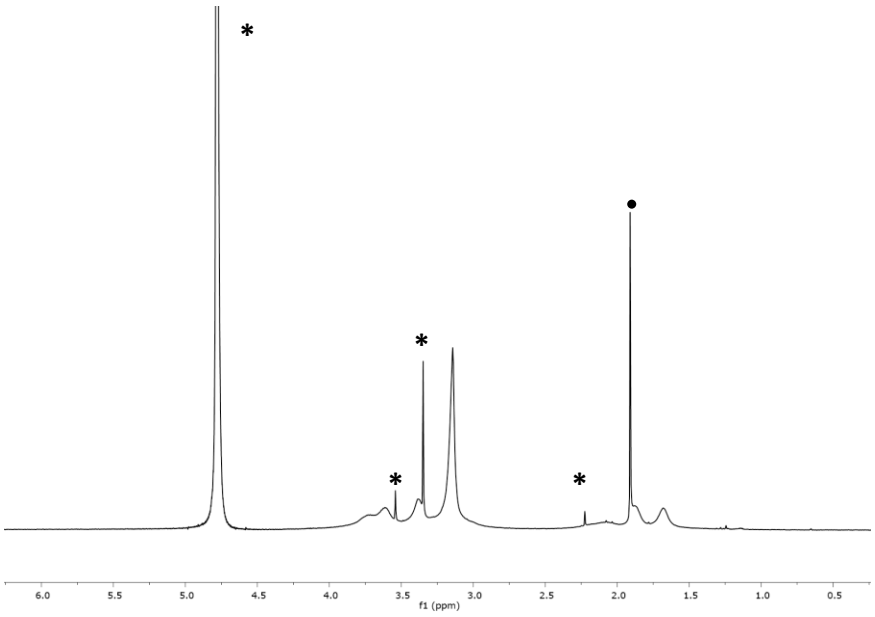


Figure S8. ^{1}H NMR spectrum of MPGN-2 in H_2O (* indicates the residual solvents , • indicates CH_3COO^-).

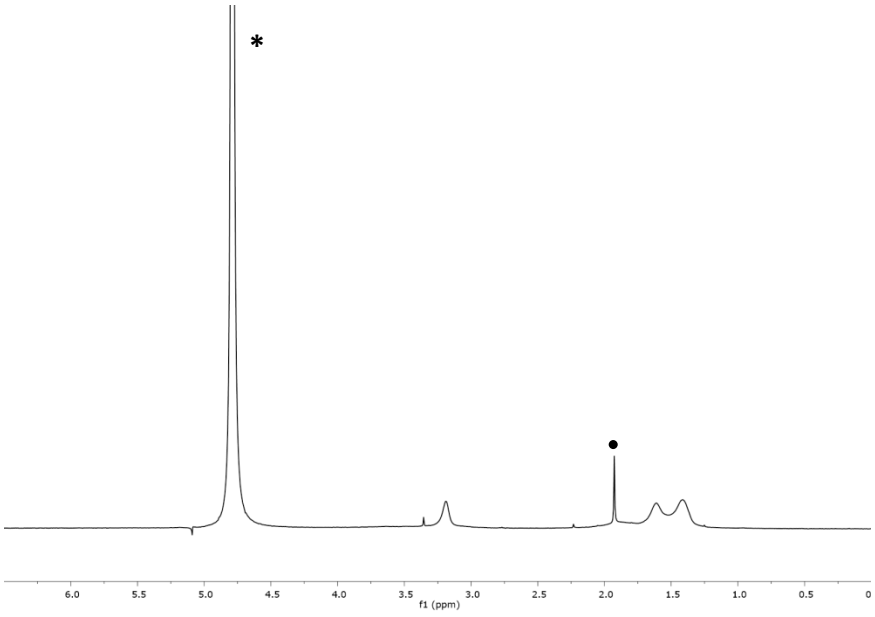


Figure S9. ^{1}H NMR spectrum of MPGN-3 in H_2O (* indicates the residual solvents, • indicates CH_3COO^-).

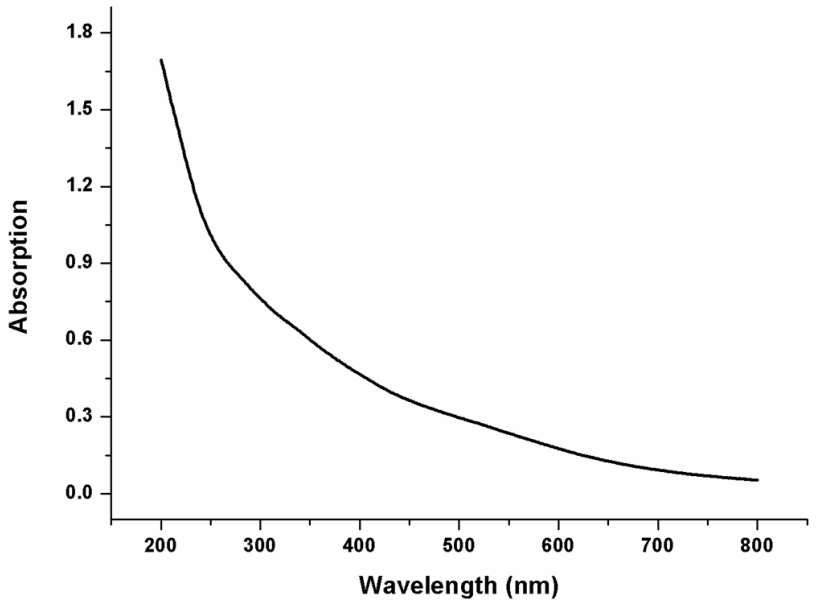


Figure S10. UV-Vis spectrum of MPGN-1 (0.1 mg/mL) at 25 ℃ in H_2O.

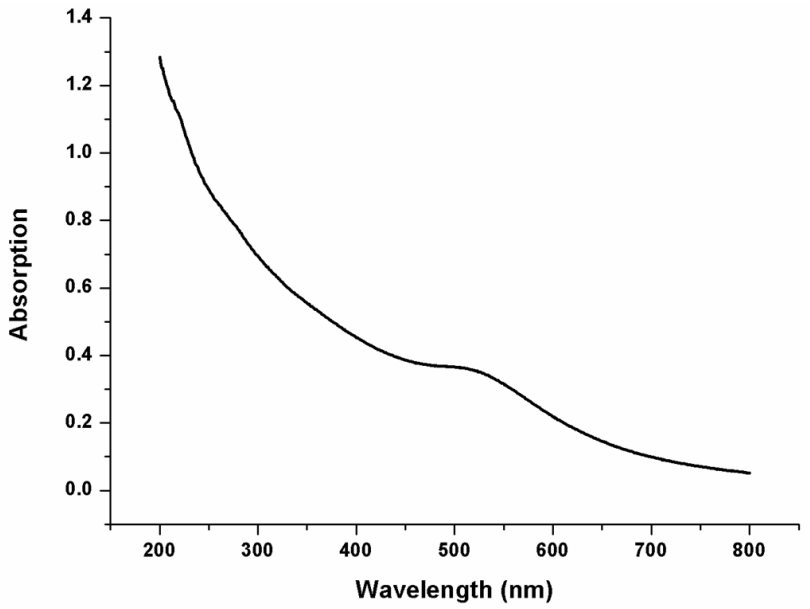


Figure S11. UV-Vis spectrum of MPGN-2 (0.1 mg/mL) at 25 ℃ in H_2O.

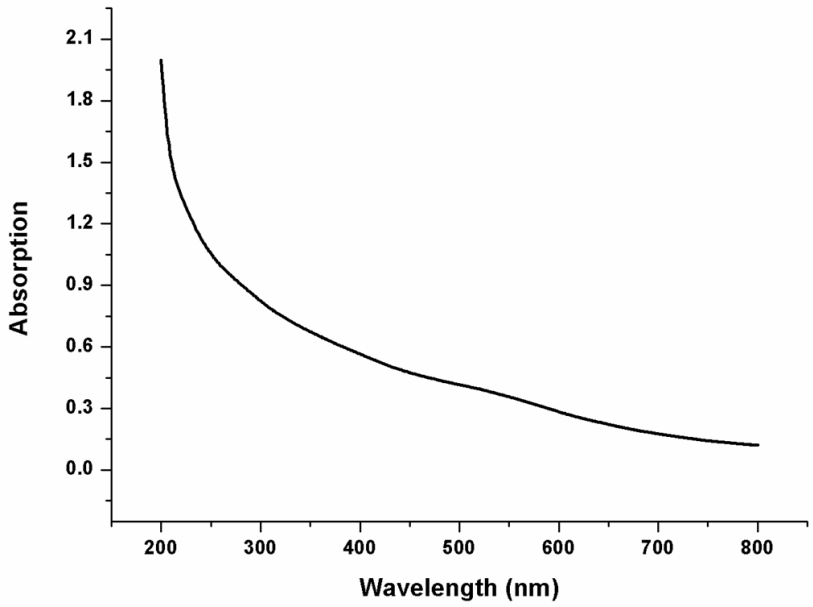


Figure S12. UV-Vis spectrum of MPGN-3 (0.1 mg/mL) at 25 °C in H_2O.

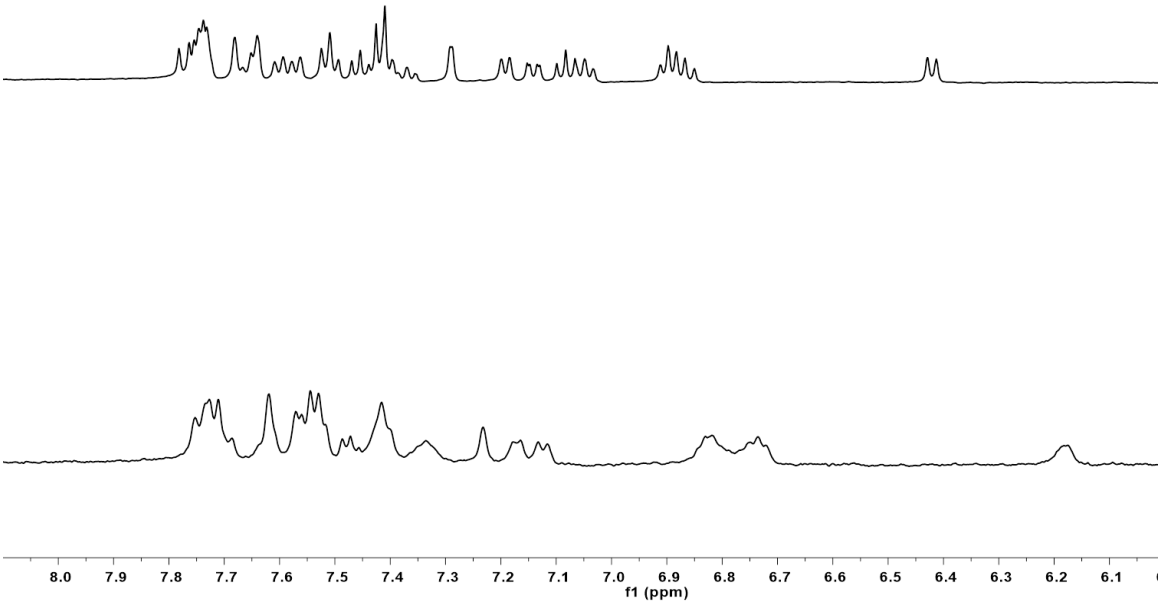


Figure S13. 1 H NMR spectrum of a mixture of sodium diclofenac, naproxen, sodium salicylate and ketoprofen in D_2O (250 μM each). Upper: in the presence of HEPES buffer (10 mM). Lower: in the presence of MPGN-1 (2 mM in thiol) and HEPES buffer (10 mM).

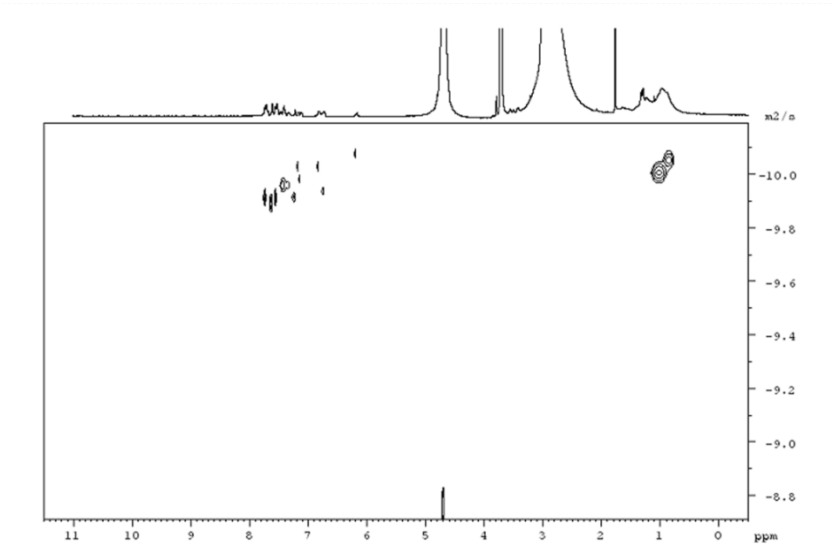


Figure S14. The DOSY spectrum of MPGN-1 in the presence of sodium diclofenac, naproxen, sodium salicylate and ketoprofen. Experimental conditions: Solvent, D_2O. MPGN-1, 2 mM in thiols. Analytes, 250 μM each.

3. Fluorescence experiments

3.1 Fluorescence titration

The fluorescence titrations were performed using a Perkin Elmer LS50B instrument. Intensities generated upon subsequent additions of the fluorescent indicators to a solution of the MPGNs (100 μM in thiol) in buffered H_2O (HEPES 10 mM, pH=7) were recorded after the signal had stabilized. The fluorescence intensities were plotted against the concentration of the fluorescent indicators added. The titrations were fitted according to the following 1:1 binding model using DynaFit for Windows.

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[mechanism]
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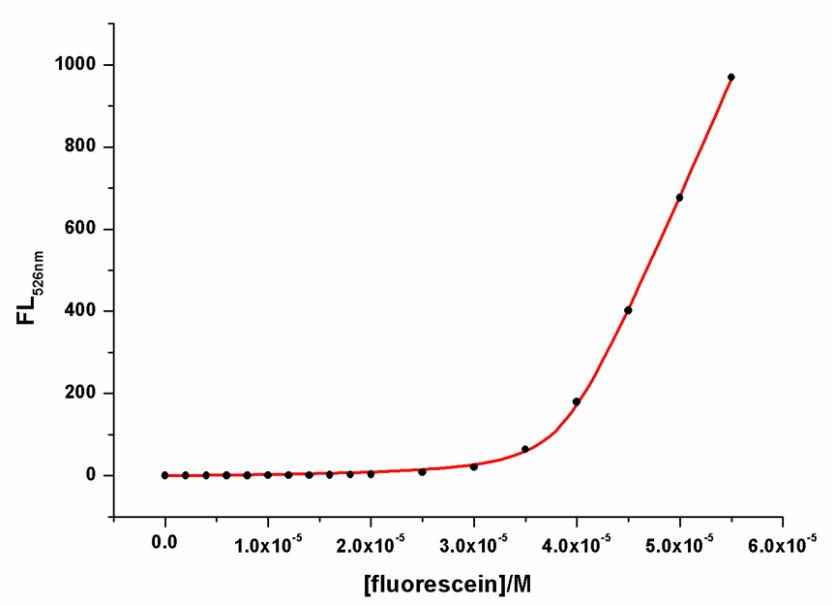

Figure S15. The fluorescence emission of the solution of MPGN-1 as a function of the concentration of added fluorescein (black sphere). The fitting curve obtained from Dynafit (red line). Experimental conditions: MPGN-1, 100 μM in thiol. HEPES, pH=7, 10 mM.

3.2 Fluorescent displacement experiments

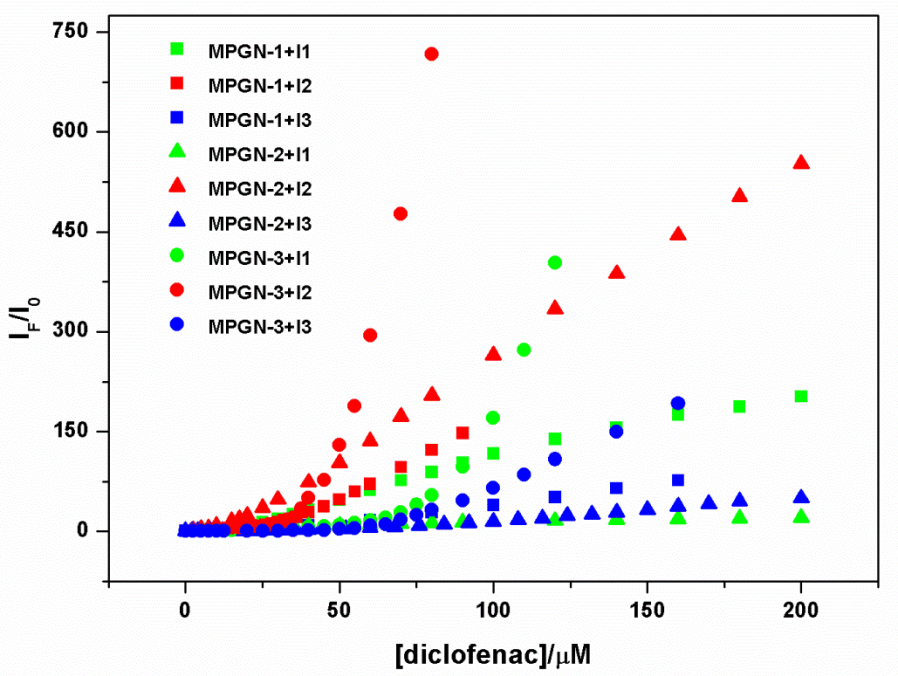

Figure S16. The normalized fluorescence intensity of the sensing systems as a function of the concentration of diclofenac. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

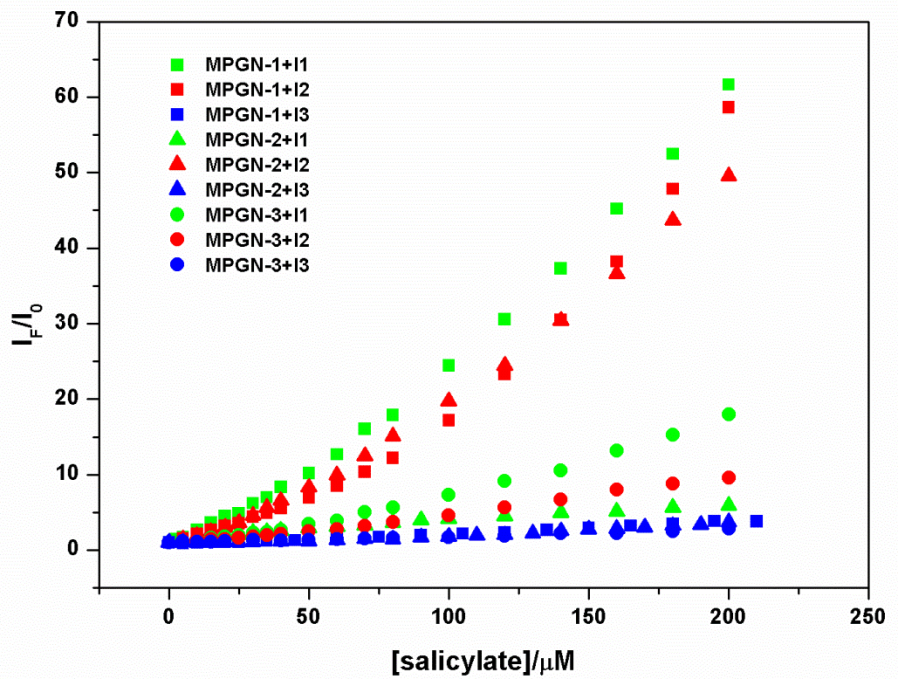

Figure S17. The normalized fluorescence intensity of the sensing systems as a function of the concentration of salicylate. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

3.3 Multivariate measurement

The multivariate studies were conducted on a multimode microwell plate reader for rapid data acquisition in an array format, with 8 repetitions for each sample.

To obtain rich signals, the information from both fluorescence (8 channels) and UV-vis absorption (4 channels) at different wavelength were recorded for sensor array A. For S1, S4 and S7, the fluorescence intensity was recorded at the wavelengths of 530, 550, 570 and 590 nm upon excitation at 460 nm and 480 nm. The absorption intensity was recorded at the wavelength of 450, 470, 490 and 510 nm. For S2, S5 and S8, the fluorescence intensity was recorded at the wavelengths of 530, 550, 570 and 590 nm upon excitation at 492 nm and 512 nm. The absorption intensity was recorded at the wavelength of 450, 470, 490 and 510 nm. For S3, S6 and S9, the fluorescence intensity was recorded at the wavelengths of 510, 530, 550 and 570 nm upon excitation at 452 nm and 472 nm. The absorption intensity was recorded at the wavelength of 440, 456, 470 and 486 nm. All the emission and intensity data obtained were used, without manipulation, for the PCA and LDA analyses.

To better visualize the array behavior, since the raw values from different channels have different ranges, the fluorescence emission and the absorption recorded from the same fluorescent indicator were rescaled (0 to 1) by dividing them for the maximum intensity value obtained and the rescaled values are reported as the color gradient map in Figure 3.

For sensor array B, the fluorescence of all the six sensors was recorded at the wavelength of 530, 550, 570 and 590 nm upon excitation at 460 nm and 480 nm. The absorption intensity was recorded at the wavelength of 450, 470, 490 and 510 nm. All the emission and intensity data obtained were used, without manipulation, for the PCA and LDA analyses.

3.4 Multivariate analysis

The PCA and LDA analysis were performed as implemented in the SPSS software package (IBM SPSS Statistics 20).

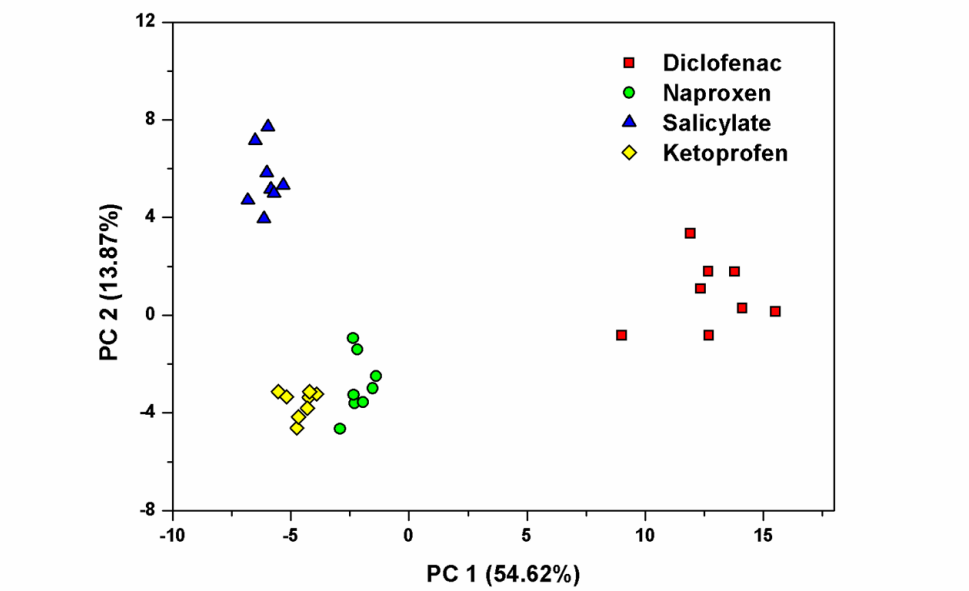

Figure S18. The PCA plot for the analysis of the four analytes at the concentration of 30 μM using sensor array A. Experimental conditions MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

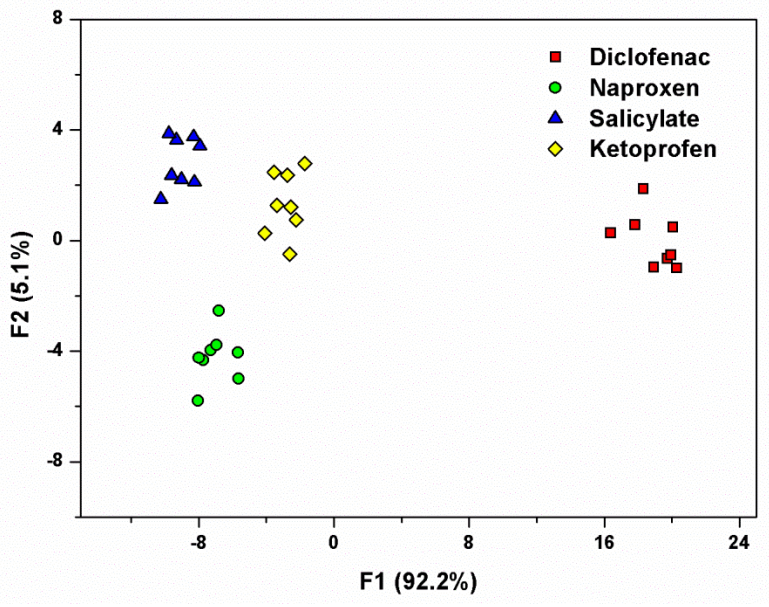

Figure S19. The LDA plot for the analysis of the four analytes at the concentration of 30 μM using S1-S9. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

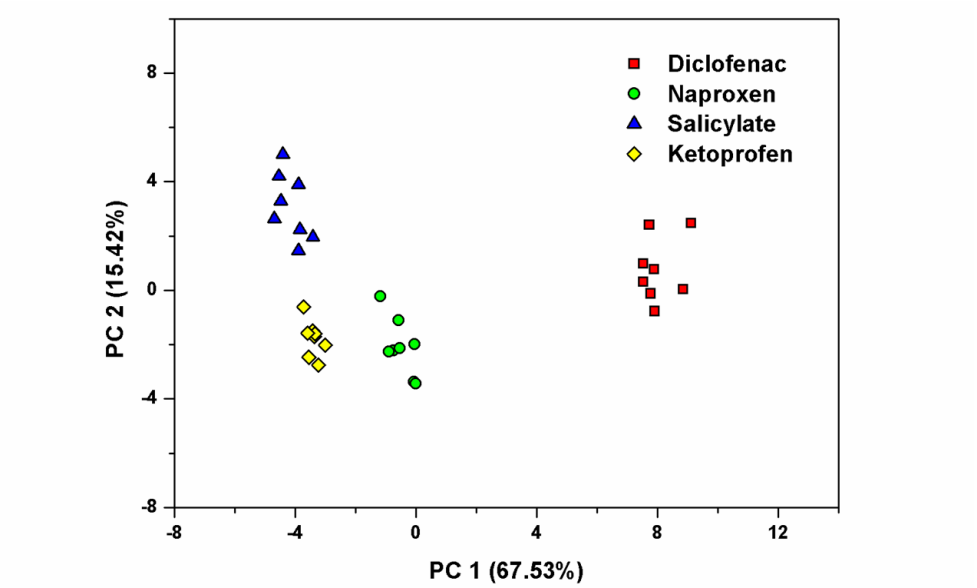

Figure S20. The PCA plot for the analysis of the four analytes at the concentration of 50 μM using S1, S4 and S7. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

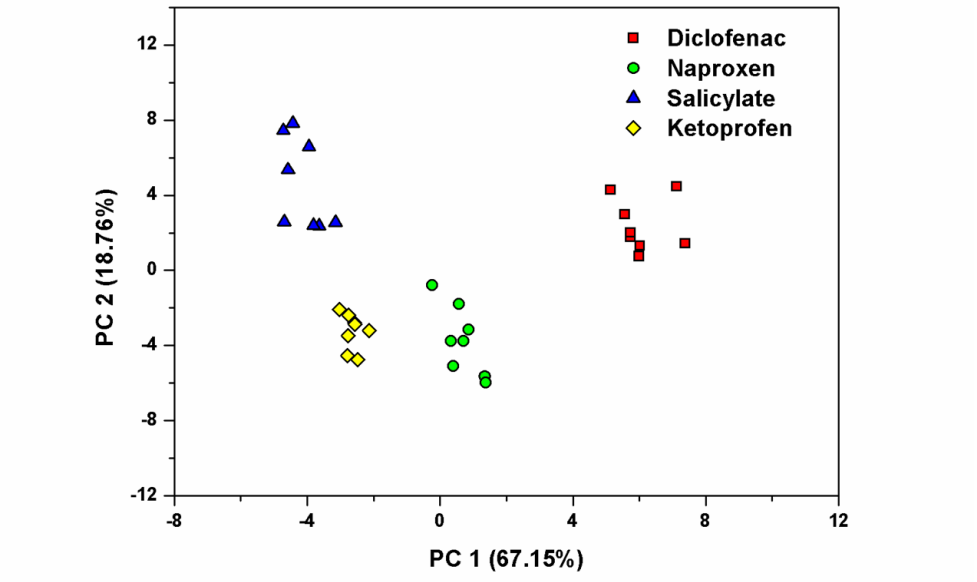

Figure S21. The PCA plot for the analysis of the four analytes at the concentration of 50 μM using S4 and S7. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

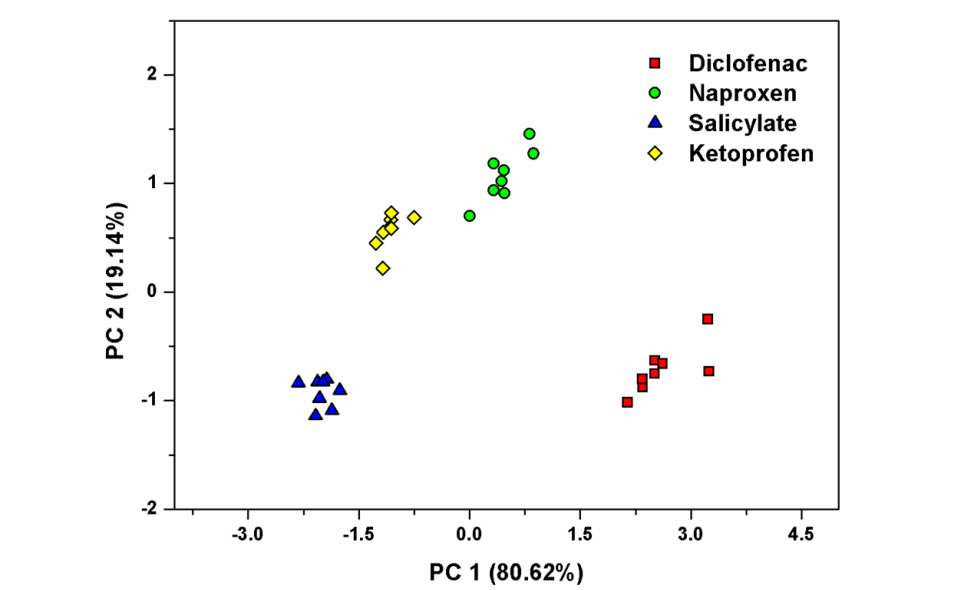

Figure S22. The PCA plot for the analysis of the four analytes at the concentration of 50 μM using S4 and S7. For each sensor, only two channels, emission at 570 nm (Ex=480 nm) and absorbance at 450 nm, were used. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

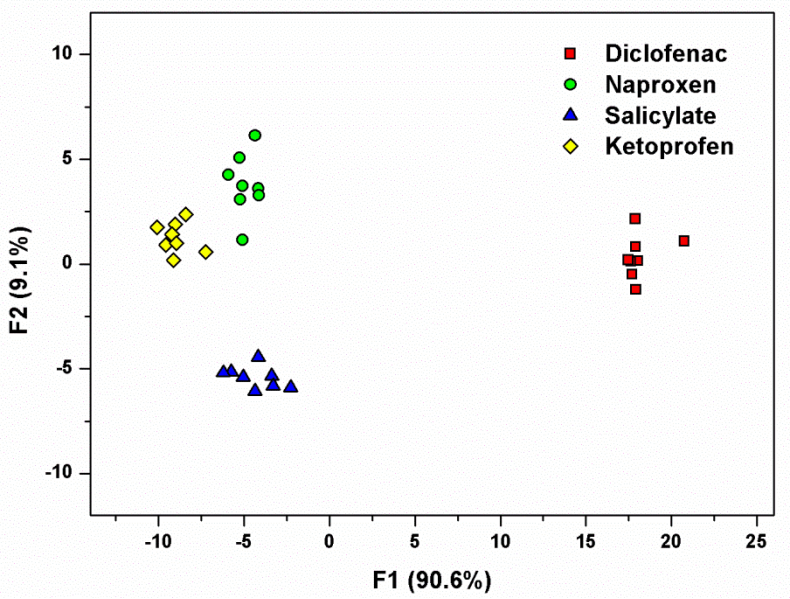

Figure S23. The LDA plot for the analysis of the four analytes at the concentration of 50 μM using S4 and S7. For each sensor, only two channels, emission at 570 nm (Ex=480 nm) and absorbance at 450 nm, were used. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

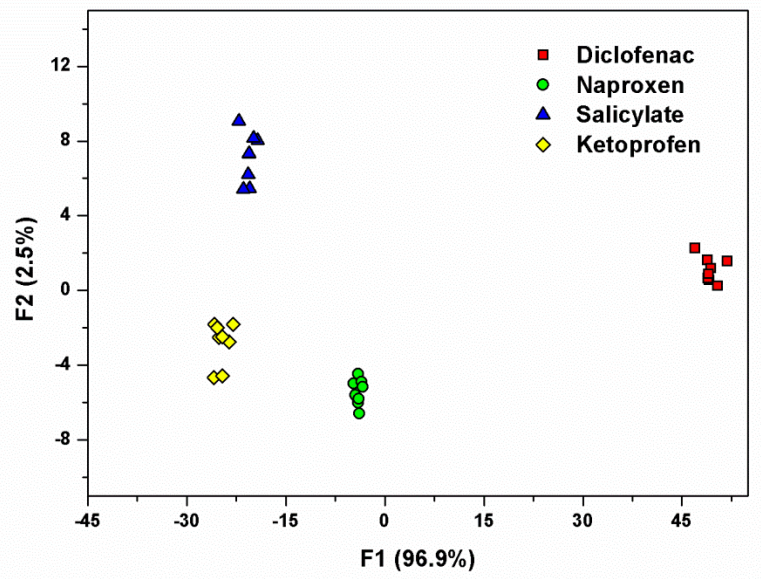

Figure S24. The LDA score plot for the analysis of the four carboxylate anions at the concentration of 50 μM using sensor array B. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

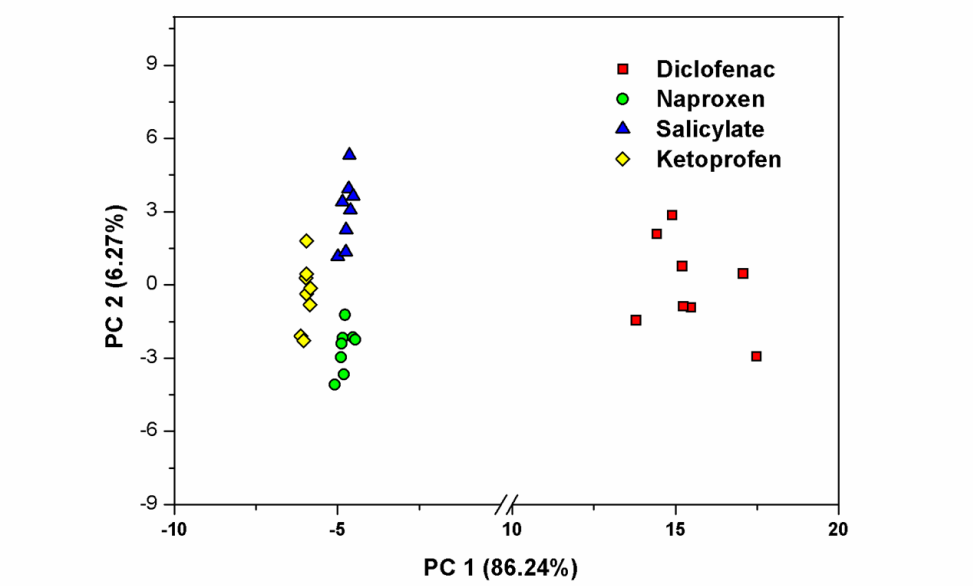

Figure S25. The PCA score plot for the analysis of the four carboxylate anions at the concentration of 100 μM using sensor array B. Experimental conditions: MPGNs, 100 μM in thiol. HEPES, pH=7, 10 mM.

4. ^{1}H, ^{13}C-NMR spectra of the synthesized compounds

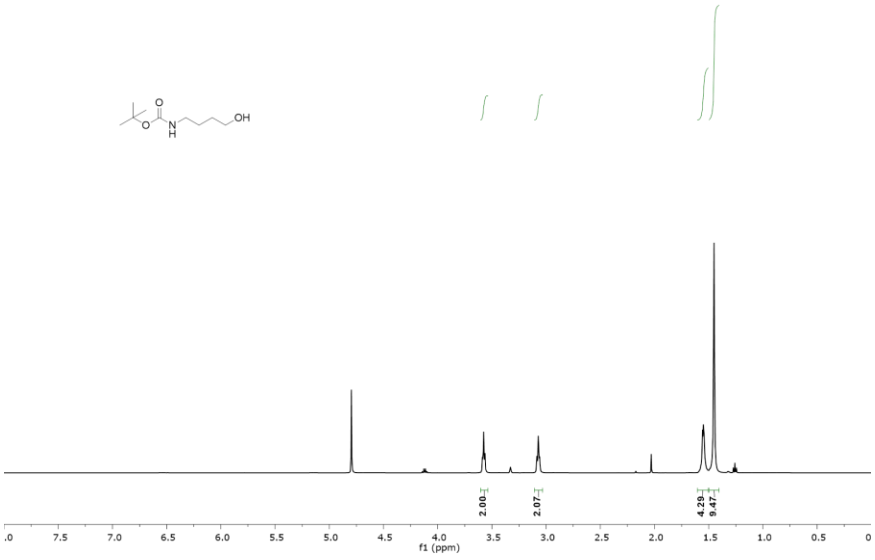

Figure S26: ^{1}HNMR spectrum of compound I.

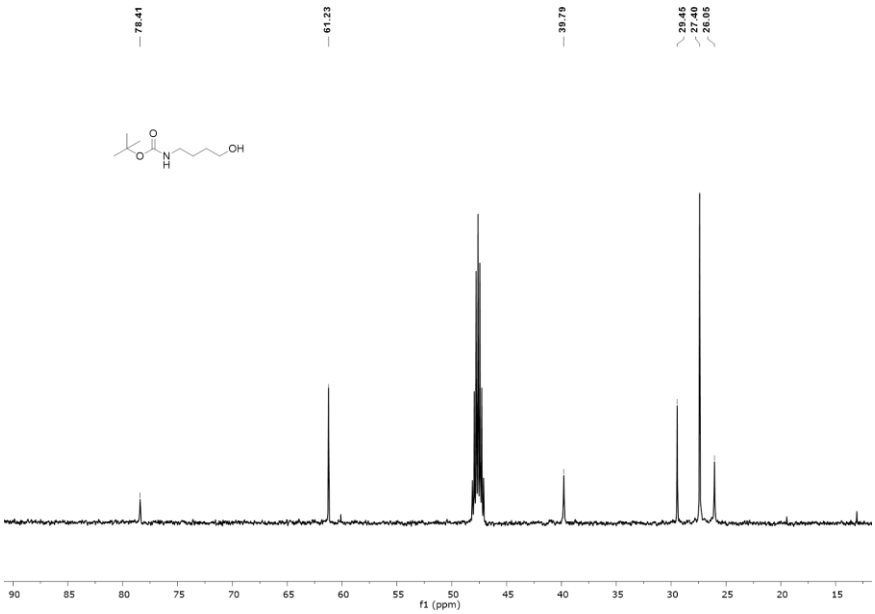

Figure S27: ^{13}C NMR spectrum of compound I.

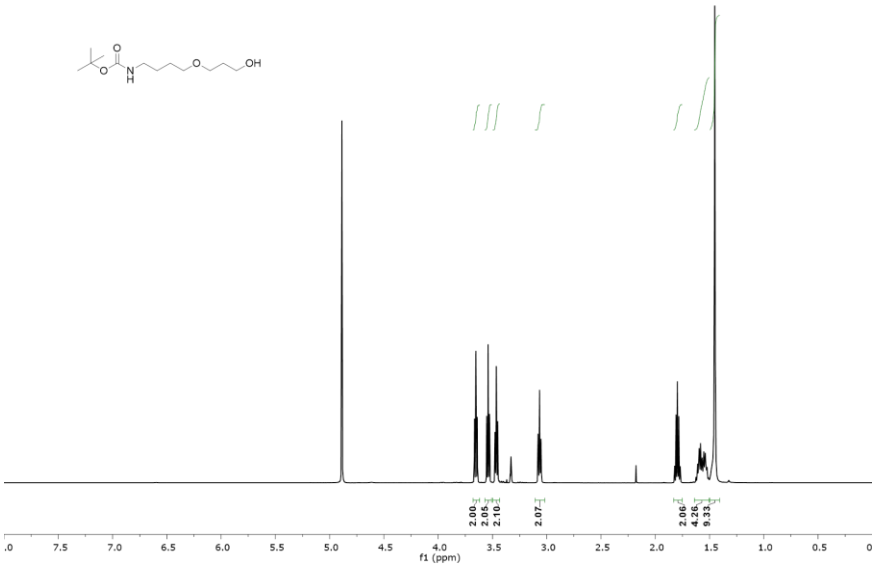

Figure S28: ^{1}HNMR spectrum of compound III.

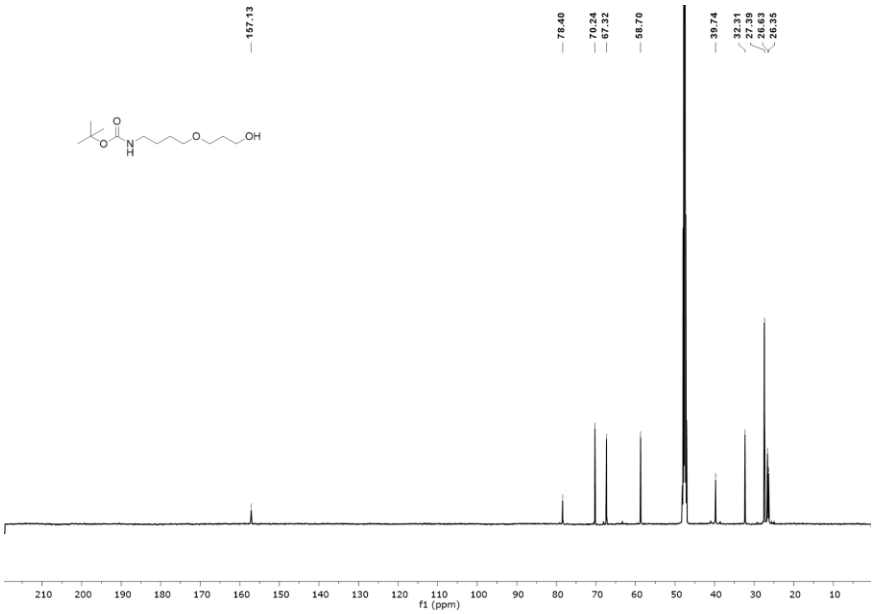

Figure S29: ^{13}C NMR spectrum of compound III.

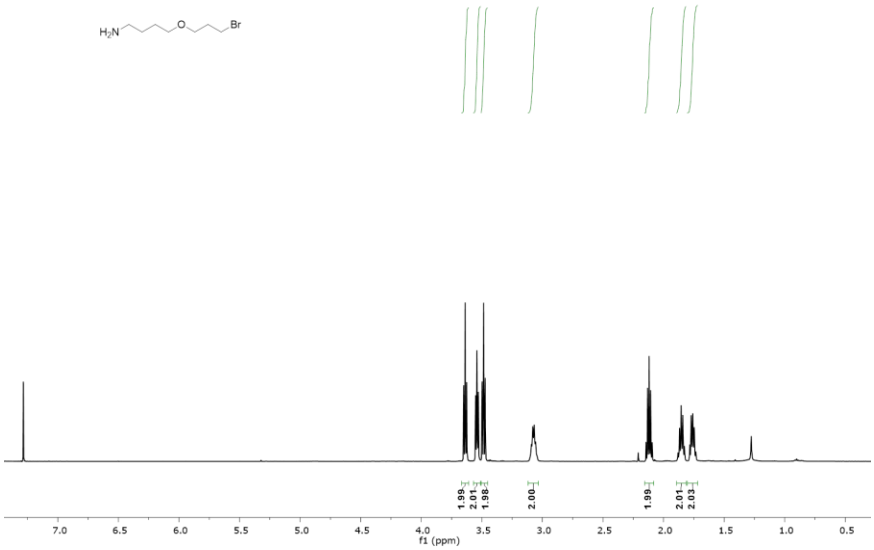

Figure S30: ^{1}HNMR spectrum of compound V.

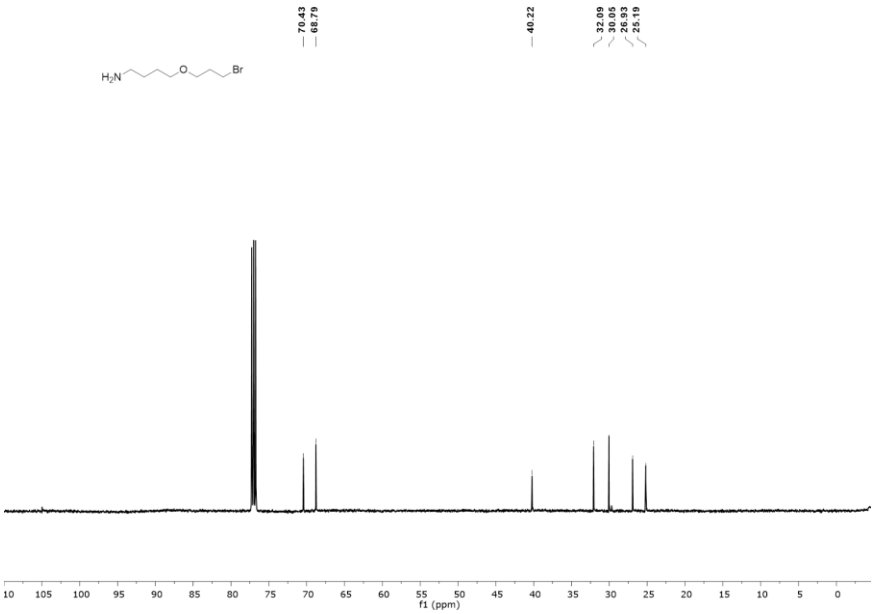

Figure S31: ^{13}C NMR spectrum of compound V.

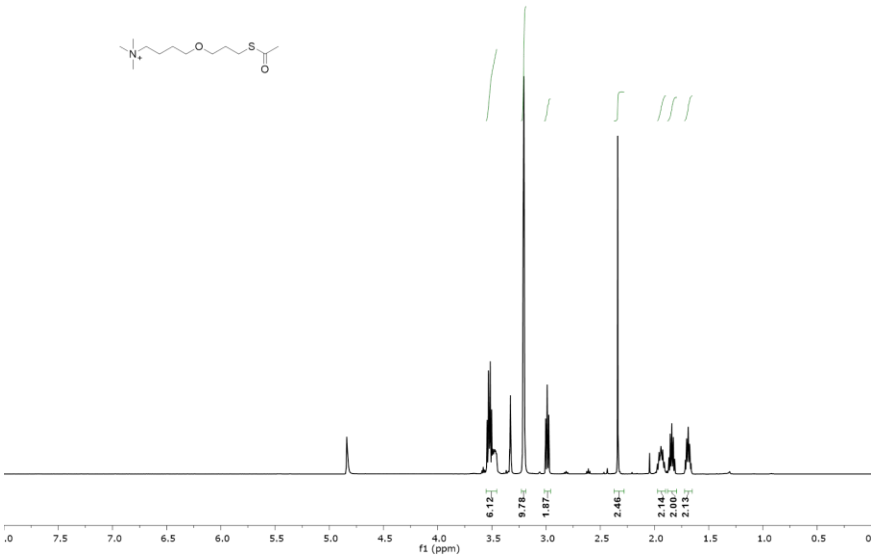

Figure S32: ^{1}HNMR spectrum of compound VII

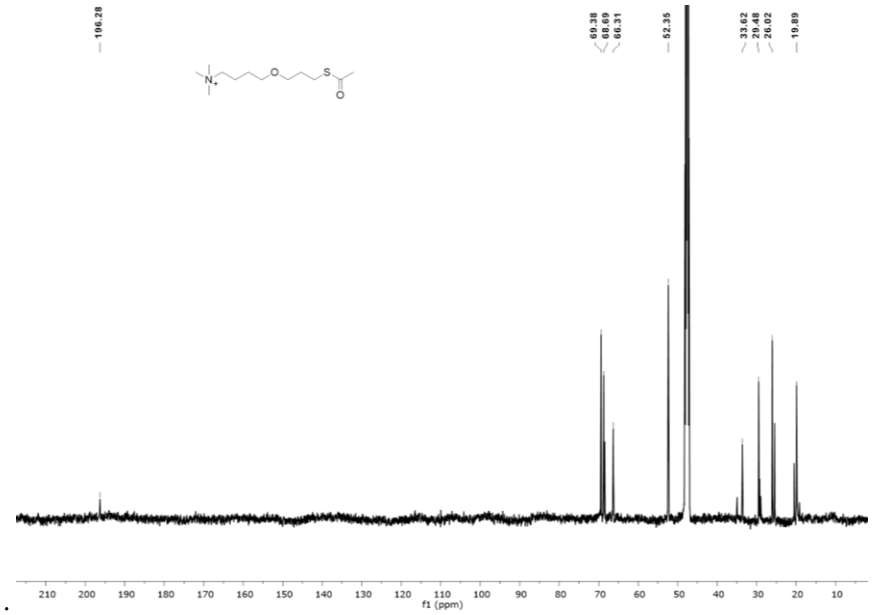

Figure S33: ^{13}C NMR spectrum of compound VII.

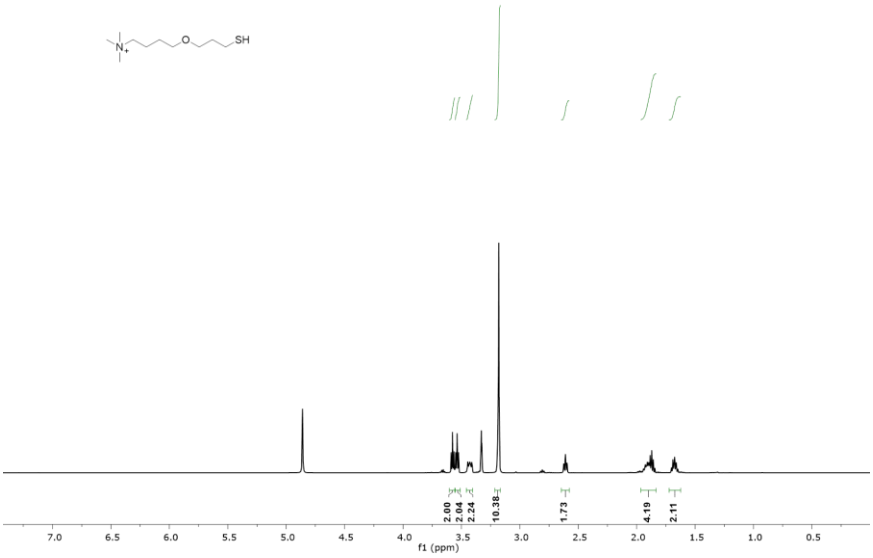

Figure S34: ^{1}HNMR spectrum of thiol 2.

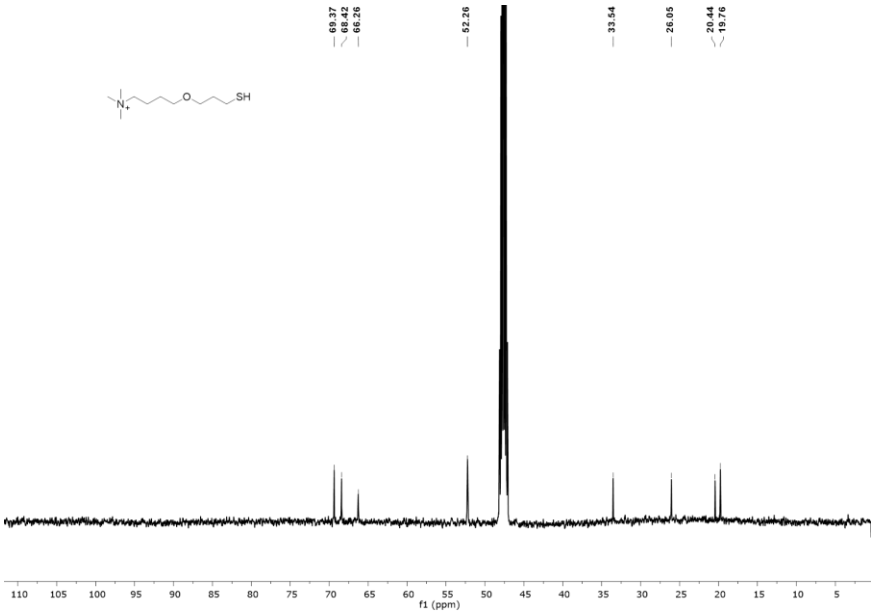

Figure S35: ^{13}C NMR spectrum of thiol 2.

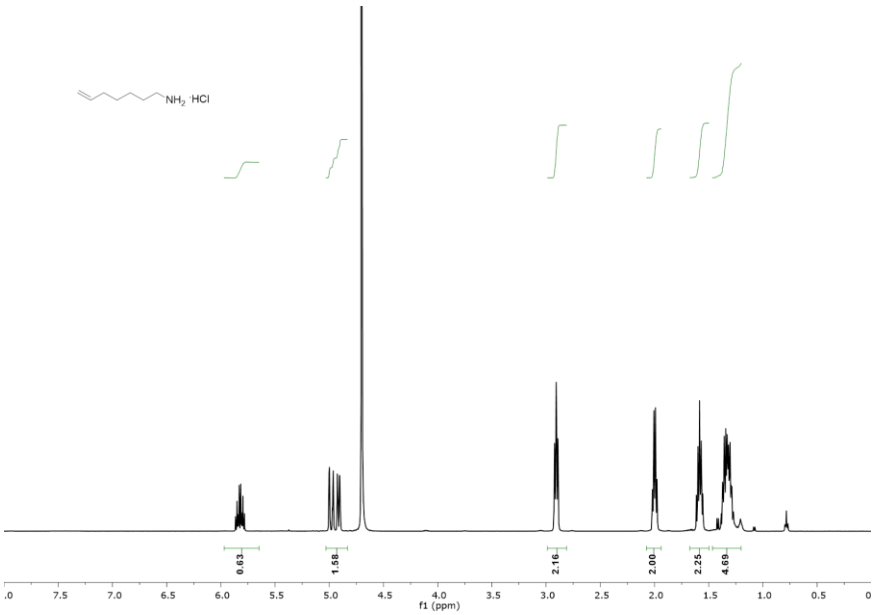

Figure S36: [1]HNMR spectrum of compound IX.

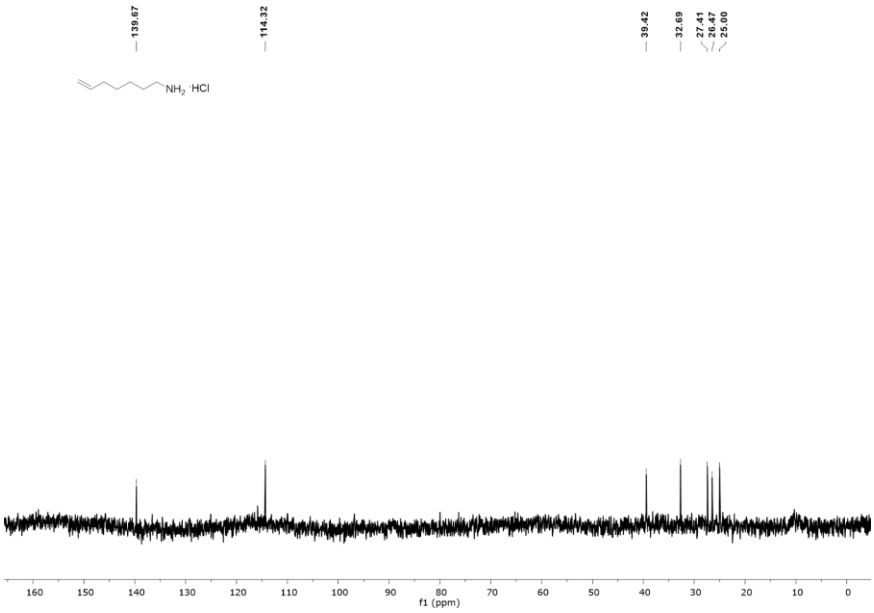

Figure S37: [13]C NMR spectrum of compound IX.

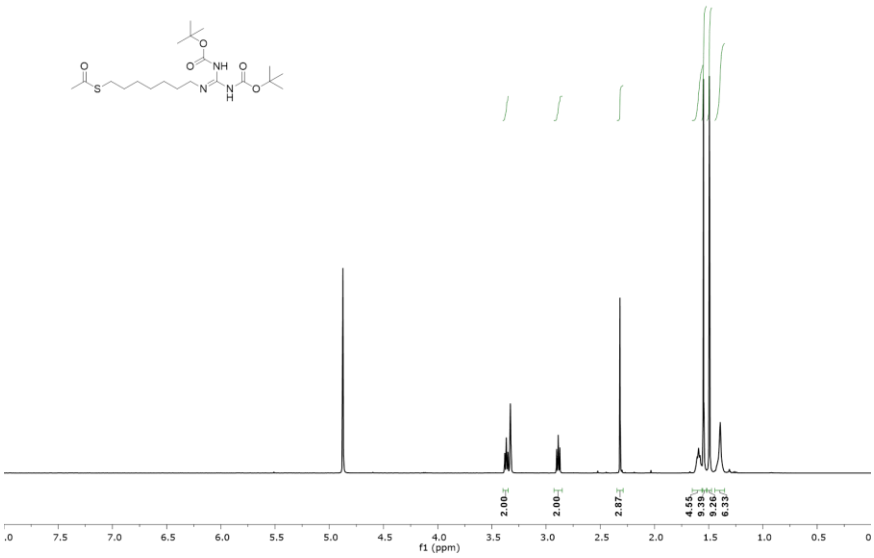

Figure S38: [1]HNMR spectrum of compound XI.

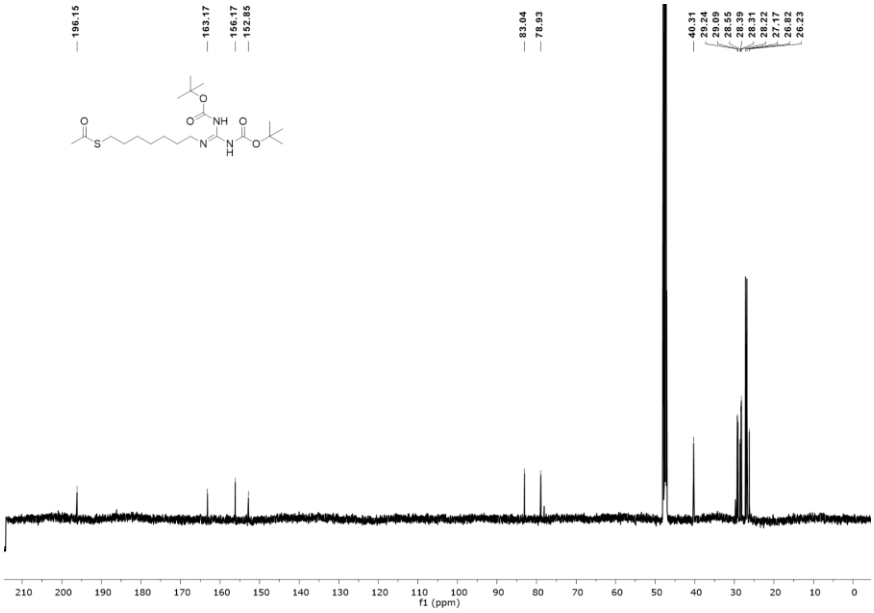

Figure S39: [13]C NMR spectrum of compound XI.

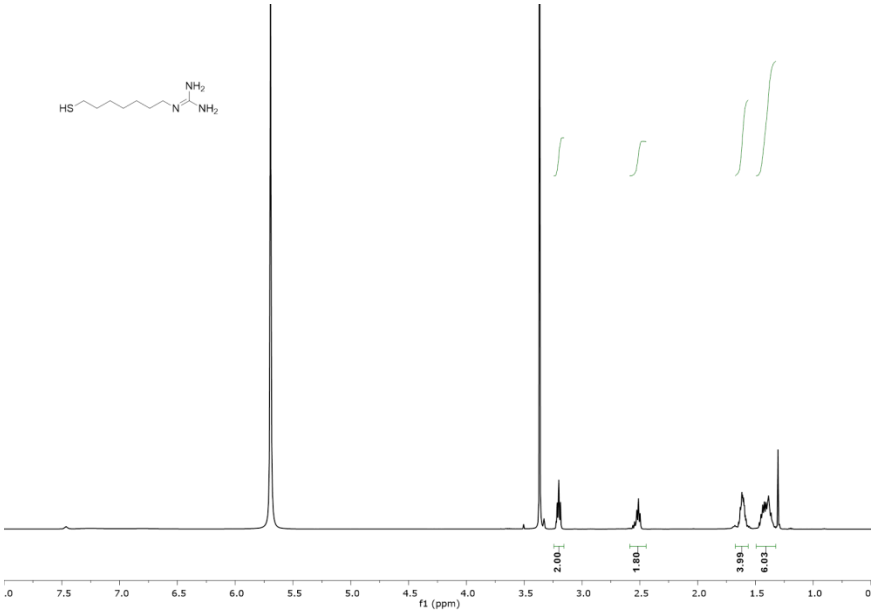

Figure S40: [1]HNMR spectrum of thiol 3.

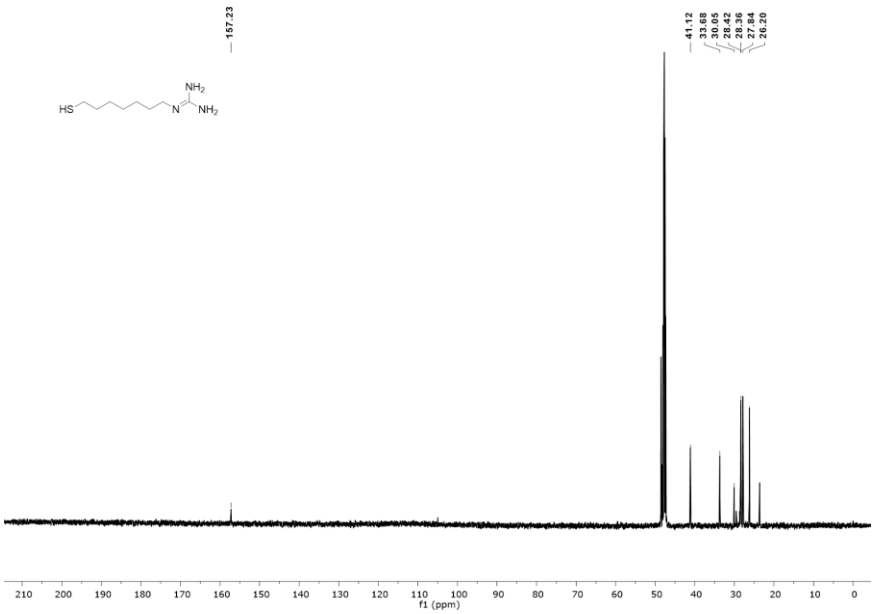

Figure S41: ^{13}C NMR spectrum of thiol 3.

References

(1) Salvia, M. V.; Ramadori, F.; Sprighetti, S.; Diez-Castellnou, M.; Perrone, B.; Rastrelli, F.; Mancin, F.; J. Am. Chem. Soc. **2015**, *137*, 886-892.

(2) Rio-Echevarria , I. M.; Tavano, R.; Causin, V.; Papini, E.; Mancin, F.; Moretto, A.; *J. Am. Chem. Soc.* **2011**, *133*, 8-11.