Supplementary Material (ESI) for Chemical Communications

Chemical Functionalization of Electrodes for Detection of Gaseous Nerve Agents with Carbon Nanotube Field-Effect Transistors

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1. Synthesis of compound 3

General Experimental Details

All reactions were performed using standard Schlenk techniques under inert atmosphere of dry argon. Dichloromethane, THF, pyridine, ethyl acetate, pentane and hexanes were purchased anhydrous analytical-grade from Sigma-Aldrich. Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C) spectra were recorded in deuterated solvents on Bruker Avance DMX 200 (200 MHz) or Bruker Avance-300 (300 MHz) spectrometers at 298 K (20 °C). Chemical shifts are reported in ppm, relative to residual $CHCl_3$ (δ 7.26). Infrared spectra were recorded on a Vertex 70 FT-IR spectrometer from Bruker on attenuated total reflection mode, wavenumbers are reported in cm^{-1} with the corresponding intensities s (strong), m (medium), w (weak), l (large). Column chromatography was performed on silica gel Geduran® 60 (0.063-0.200 mm) from Merck; thin layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} from Merck. The mass spectra were acquired in positive mode on a LXQ- linear ion trap (THERMO SCIENTIFIC) equipped with an electrospray source.

3-(4-ethynylbenzyl)-1,5,7-trimethyl-3-azabicyclo[3.3.1]nonane-7-methanol (1)

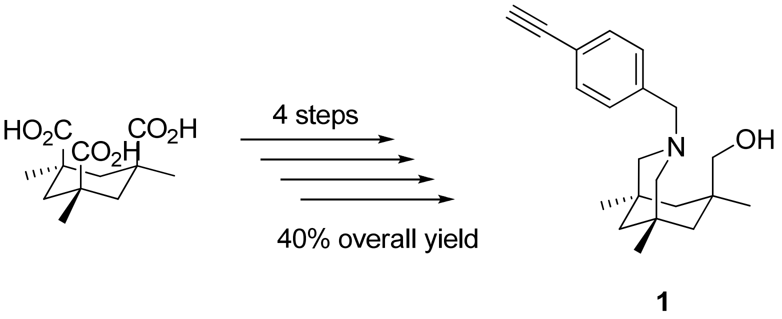

Figure S1. Synthesis of compound **1**

Compound **1** was synthesized in four steps starting from the Kemp's triacid with an overall yield of 40% accordingly to the synthetic procedure published elsewhere.[1]

FTIR, ^{1}H and ^{13}C NMR, and mass spectrometry spectra were in agreement with literature data.

4-iodophenylthioacetate (4)

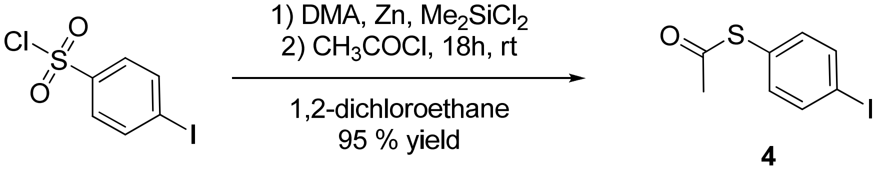

Figure S2. Synthesis of intermediate **4**

4-iodobenzenesulfonyl chloride (1 g, 3.3 mmol, 1 eq) and dimethylacetamide (0.9 mL, 9.9 mmol, 3 eq) were solubilised in 1,2-dichloroethane (25 mL) and poured dropwise to a solution of 1,2-dichloroethane (25 mL), Zn (0.75 g, 11.5 mol, 3.5 eq) and Me_2SiCl_2 (1.5 g, 11.5 mmol, 3.5 eq). The reaction mixture was refluxed for 1.5h. Acetyl chloride (1.14 mL) was added and the reaction mixture stirred overnight at room temperature. The solvent was removed in vacuo and the solid residue solubilised in CH_2Cl_2, washed with deionised water, dried with $MgSO_4$ and filtered. The

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[1] S. Clavaguera, A. Carella, L. Caillier, C. Celle, J. Pecaut, S. Lenfant, D. Vuillaume and J. P. Simonato, Angew. Chem. Int. Ed., 2010, 49, 4063-4066.

volatiles were removed in vacuo and the crude product purified by column chromatography on silica gel using pentane/CH_2Cl_2 (1:1) as eluent to give 850 mg (3.06 mmol, 93%) of white solid after drying in vacuo. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.4 (s, 3H), 7.1 (d, 2H, *J*=8.4 Hz), 7.7 (d, 2H, *J*=8.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 30.3, 96.1, 127.6, 135.8, 138.7, 192.9; FT-IR (ATR) ν (cm^{-1}) 1693.5 (s), 1557.7 (w), 1466.0 (m), 1382.5 (w), 1354.4 (w), 1261.4 (w), 1122.0 (m), 1092.0 (w), 1051.8 (w), 1005.4 (s), 967.3 (m), 811.6 (s), 722.7 (m), 623.3 (s).

S-(4-((4-((-7-(hydroxymethyl)-1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-3-yl)methyl)phenyl)ethynyl)phenyl) thioacetate (2)

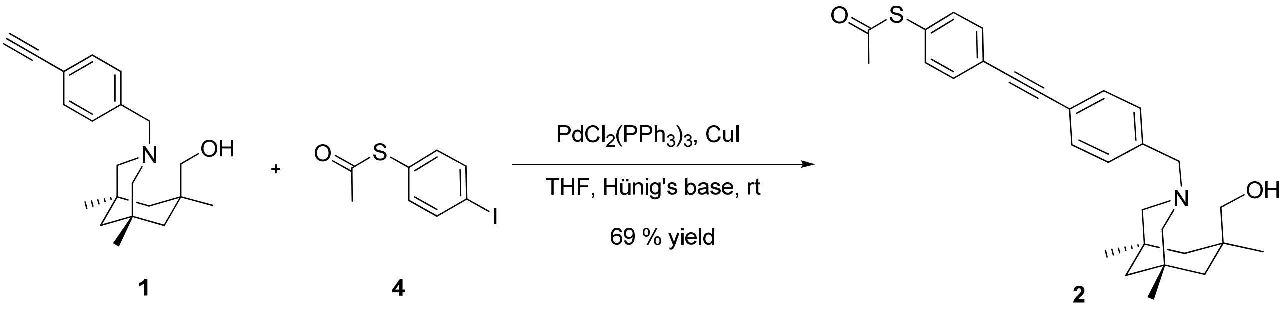

Figure S3. Synthesis of compound **2**

3-(4-ethynylbenzyl)-1,5,7-trimethyl-3-azabicyclo[3.3.1]nonane-7-methanol (**1**) (282.6 mg, 0.77 mmol, 1.1 eq), 4-iodophenylthioacetate (**4**) (200 mg, 0.7 mmol, 1 eq), $PdCl_2(PPh_3)_2$ (13 mg) and CuI (4.3 mg) were added in THF (2 mL) and Hünig’s base (1 mL) and stirred 18 hours at room temperature under Ar. The volatiles were removed in vacuo and the crude product was purified by column chromatography on silica gel using ethyl acetate / pentane (40:60) as eluent to give 223 mg (0.48 mmol, 69%) of pure product after drying in vacuo. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.84 (s, 6H), 0.86 (s, 3H), 0.90 (s, 1H), 1.25 (m, 4H), 1.63 (m, 4H), 2.49 (s, 3H), 2.53 (d, 2H), 3.38 (s, 2H), 3.50 (s, 2H), 7.30-7.45 (m, 4H), 7.52-7.60 (m, 4H); ^{13}C NMR (50 MHz, Acetone-d6) δ (ppm)

29.60, 31.85, 33.49, 34.39, 45.34, 46.65, 63.04, 66.61, 74.30, 88.56, 91.10, 121.86, 129.21, 130.41, 131.76, 132.35, 133.02, 135.06, 139.41, 192.97 ; FT-IR (ATR) ν (cm^{-1}) 2925 (m), 2854 (m), 2200 (w), 1742 (s), 1459 (w), 1377 (w), 1239 (w), 1163 (m), 1098 (w), 973 (w), 724 (w); ESI MS (CH_2Cl_2) m/z (a.m.u) calcd for $[C_{29}H_{36}NO_2S]+$: 462.25; found: 462.5.

Bis[S-(4-((4-((-7-(hydroxymethyl)-1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-3-yl)methyl)phenyl)ethynyl)phenyl)] disulfide (3)

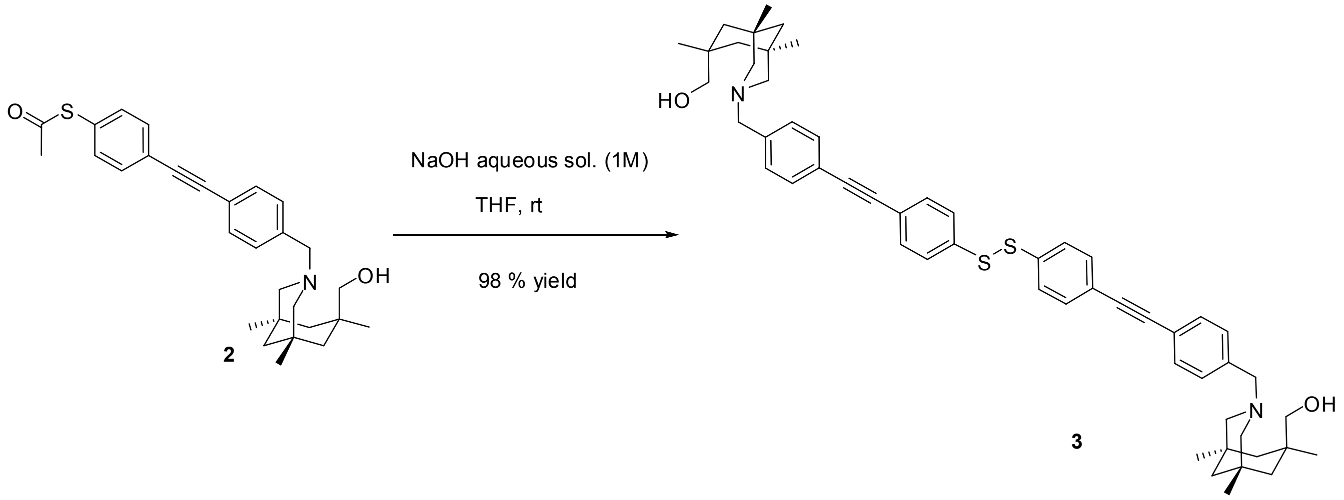

Figure S4. Synthesis of compound **3**

S-(4-((4-((-7-(hydroxymethyl)-1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-3-yl)methyl)phenyl)-ethynyl)phenyl) thioacetate (**2**) (169.6 mg, 0.36 mmol, 1 eq) was dissolved in THF (2 mL). To the resulting solution was added dropwise a solution of NaOH (1M, 0.73 mL, 2 eq). The reaction mixture was stirred at room temperature under argon for 3 hours. The mixture was poured in water (10 mL), the organic layer was separated, and the aqueous was extracted twice with ethyl acetate (10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate as eluent. The desired fractions were concentrated under vacuum to give 152 mg (0.18 mmol, 98%) of **3** as a pale yellow solid. ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.86 (s, 9H), 0.90 (s, 1H), 1.26 (m, 4H), 1.63 (m, 4H), 2.61 (s, 2H), 3.35 (s, 2H), 3.50 (s, 2H), 7.29-7.45 (m, 4H), 7.48-7.60 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 30.85, 32.18, 34.08, 36.36, 45.23, 47.20, 63.31, 66.07, 76.74, 89.37, 90.73, 122.61, 122.69, 127.65, 130.86, 131.96, 132.61, 136.32, 137.33 ; FT-IR (ATR) ν (cm^{-1}) 2949 (m), 2901 (m), 2200 (w), 1511 (m), 1459 (m), 1396 (w), 1376 (m), 1264 (w), 1171 (w), 1095 (m), 1059 (m), 1017 (m), 883 (m), 820 (s), 737 (s). ESI MS (CH_2Cl_2) m/z (a.m.u) calcd for $[C_{54}H_{65}N_2O_2S_2]^+$: 837.23; found: 837.8.

2. Preparation of a monolayer of 3 *on gold surface*

A freshly prepared 0.7 mM solution of compound **3** in acetone (2 mL) was degassed with argon. The chip was carefully placed in the flask with a chip holder so that the chip surface was completely immersed and without any contact with the walls of the flask in order to avoid shocks while agitating. The substrate was left in solution under argon overnight at room temperature. Then the chip was taken out of the solution and rinsed extensively with acetone. Finally, the substrate bearing a monolayer of **3** was dried in a stream of argon and used thereafter for tests and characterizations.

3. Analysis of a monolayer of 3 *on gold surface (contact angle, XPS)*

Silicon single-side-polished Si (1 0 0) wafers were purchased from Siltronix. A gold layer (100 nm) was deposited on a silicon wafer with a titanium layer (20 nm) as an adhesion promoter using an e-beam evaporator in high vacuum. Gold-coated silicon wafers were cleaned by placing them in a "piranha" solution (*i.e.* H_2SO_4/H_2O_2 (3:1) mixture) for 5 minutes. Thereafter, the samples were rinsed three times thoroughly with deionised water and argon-blow dried before being functionalized with **3**.

Static water contact angles were obtained using a Krüss Drop-shape-analysis-DSA-10-MK2 (drop volume of ultrapure water = 1.5 μL). Contact angles of four or five independent drops were measured.

SAMs with ***3***

The water contact angle of the sample (*i.e.* 86.6 ± 3.70 °) is in accordance with the literature data for aromatic SAMs on gold.[2]

SAMs with ***3*** *after reaction with DPCP*

The reaction of the surface functionalized with a SAM of compound 3 with vapours of DPCP induces a significant variation of the contact angle which is in agreement with a higher hydrophilic quaternary ammonium (*i.e.* 86.6 ± 3.7 before exposure and 72.8 ± 4.4° after 1h exposure to vapours of DPCP).

The XPS spectra of **3** were recorded with a NOVA-KRATOS spectrometer using a monochromatic Al Kα X-ray source (*225W*). XPS spectra were measured with a takeoff angle of 20°. The binding-energy scale was calibrated with the Au $4f_{7/2}$ peak position at 84.00 eV.

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[2] Barkschat, C. S.; Stoycheva, S.; Himmelhaus, M.; Müller, T. J. J. Chem. Mater. 2010, 22, 52-63.

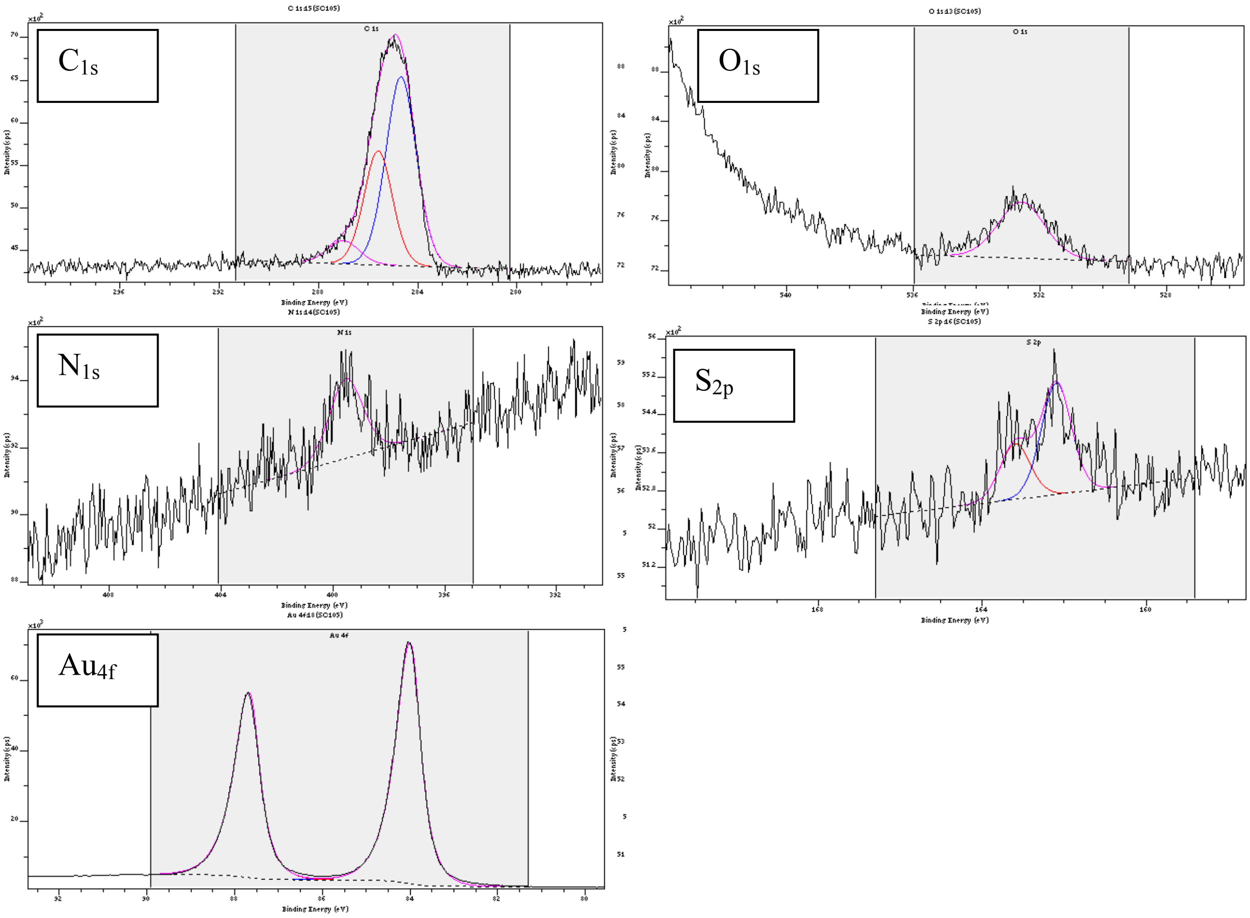

Figure S5. XPS spectra of C_{1s}, O_{1s}, N_{1s}, Au_{4f} and S_{2p}

Table 1: Elementary composition (% at.) of the SAM

	O	N	C	S	Au		N/C	O/C	S/C
							x 100	x 100	x 100
Calculated	8.7	2.2	84.8	2.2	-		2.2	8.7	2.2
Measured									
90°	2.8	1.9	53.5	1.3	40.5		3.6	5.3	2.4
55°	3.3	1.7	60.8	1.1	33.2		2.7	5.4	1.8
20°	5.0	2.9	77.5	1.3	13.3		3.8	6.4	1.7

Interestingly, after reaction with DPCP, a new peak appears for N1s with binding energy of 402.0 eV, which is due to the quaternization of the nitrogen atom upon reaction with DPCP.

4. Gas sensor fabrication

4.1. Linear electrodes devices

Devices with bottom gate/bottom contact geometry were fabricated on a heavily doped (100) silicon wafer (n^{++}, 2–5 mΩ cm) covered by a thermally grown silicon dioxide layer (100 nm). The source and drain electrodes of the device were patterned by optical photolithography, followed by Ti (5 nm) and Au (30 nm) evaporation and lift-off (see figure 1). The lengh and width of the CNTFETs channel are 10 µm and 1000 µm.

4.2. Dispersion of carbon nanotubes

Commercial SWCNTs from SouthWestNanoTechnologies, CoMoCat SG65 (90% of semiconducting SWCNTs) were used in this study. Dispersions of SWCNTs were prepared by sonication in N-methylpyrrolidone (NMP) followed by centrifugations steps. SWCNT powder (10 mg) was dispersed in filtrated N-methylpyrrolidone (NMP) (200 mL) and sonicated for 1 hour at room temperature with a 53 kHz frequency (180 W). The SWCNTs bundles were separated from the solution by two consecutive centrifugations steps at 14,500 rpm where 80% of the supernatant were collected each time. The dispersions were used without any further treatment and were found to be stable for weeks.

4.3. Spreading of SWCNTs

SWCNTs were spread on devices using the spray coating technique. We used a commercial airbrush (Aztek A4709 with large flow nozzle 0.7 mm) and the SWCNTs NMP solution described hereinbefore. In a typical experiment, chips with electrodes were placed on a hot plate at 250°C. The solution was sprayed with the airbrush at a distance of 20 cm from the substrate at 2 bar air pressure. After spreading, the devices were cured at 100°C for two hours and cooled down to room temperature under nitrogen atmosphere.

Chips were then functionalized following the procedure described hereinbefore (section 2).

5. KPFM experiments

The control samples for KPFM experiments were made by grafting **3** on a large area evaporated gold surface (100 nm thick, on a native oxidized silicon wafer, SiO_2 thickness ca. 1.5 nm). We prepared two samples, one with a monolayer of **3**, and a second one with a monolayer of **3** reacted with DPCP in the same conditions as the CNTFET sensors used for I-V measurements. Then, we evaporated, simultaneously on the two samples, clean gold dots through a shadow mask (Fig. S6), and both samples were immediately transferred to the KPFM set-up and measured together.

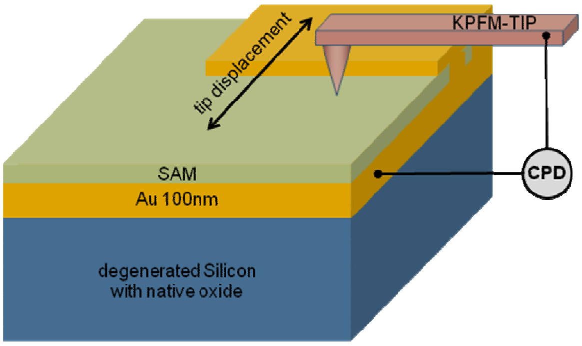

Figure S6. Schematic description of the KPFM experiment.

This protocol insures that the WF of the two organic monolayer modified Au surfaces are referenced to the same reference electrode (bare Au dots). Since it is well known that gold atoms easily diffuse through organic monolayers and form many short-circuits, the WF of the upper Au dots is thus a correct reference for the underlying Au films. KPFM measurements were carried out at room temperature with a Dimension 3100 placed under dry nitrogen atmosphere. We used Pt/ Ir (0.95/0.05) metal-plated cantilevers with spring constant of ca. 3 N/m and a resonance frequency of ca. 70 kHz. Topography and KFM data were recorded using a standard two-pass procedure, in which each topography line acquired in tapping mode is followed by the acquisition of KPFM data in a lift mode, with the tip scanned at a distance z ~ 80 nm above the sample so as to discard short-range surface forces and be only sensitive to electrostatic forces. A dc and ac biases ($V_{dc} + V_{ac} \sin(\omega t)$) are applied to the cantilever, and the gold dot is electrically grounded. Experimentally, the contact potential difference (CPD) is measured using a feedback loop which sets to zero the cantilever oscillation amplitude at ω by adjusting the tip dc bias V_{dc}. This potential is simply equal to the CPD, in absence of side capacitances (for more details see REF-S1) .

Figure S7-a shows the CPD versus the lateral position of the tip for the two samples (**3** alone and **3**+DPCP) taken at 3-4 different places on each samples.

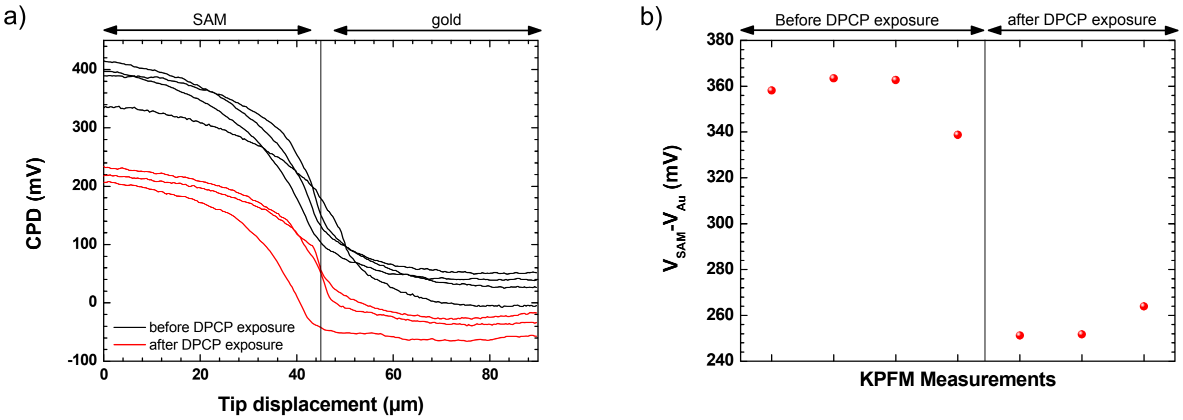

Fig. S7. (a) CPD measured along a line as shown in Fig. S6 for the Au functionalized with 3 before (black curves) and after (red curves) reaction with DPCP. 3 to 4 measurements were done at different places for each sample. (b) Potential difference calculated between V_{SAM} at x=0 on Fig. S7a and V_{Au} at x = 90 µm.

When the tip is over the Au dots, the measured CDP is around zero (the Pt/It tip and Au dots have almost the same WF), although with sample-to-sample variations of ca. ± 50 mV. These variations are likely due to some contaminations of the cantilever tip with the time. Nevertheless, when the tip moves over the organic monolayer, we clearly observe a significant increase of the measured CPD, corresponding to a reduction of the WF of the functionalized Au surface. Fig. S7-b shows the calculated WF difference, W_{Au}-W_{SAM} = e(V_{SAM}-V_{Au}) , where V_{SAM} is the potential at x = 0 (Fig. S7-a) and V_{Au} is the one at x =90 µm (Fig. S7-a). Results in Fig. S7-b clearly indicates that the WF of Au functionalized with **3** is reduced by ca. 360 meV compared to the bare Au, while the WF of Au with **3** reacted with DPCP is reduced by ca. 250 meV. It means that reacting **3** with DPCP increases the WF by ca. 110 meV, probably due to some change of the molecule dipole in the monolayer upon the chemical reaction and the formation of a quaternary ammonium in the monolayer.

REF-S1. Determination of the electrostatic lever arm of carbon nanotube field effect transistors using Kelvin force microscopy, D. Brunel, D. Deresmes, T. Mélin, *Appl. Phys. Lett.*, 2009, **94**, 223508.