Supporting Information for

Cavitand-Functionalized-SWCNTs for N-methylammonium Detection

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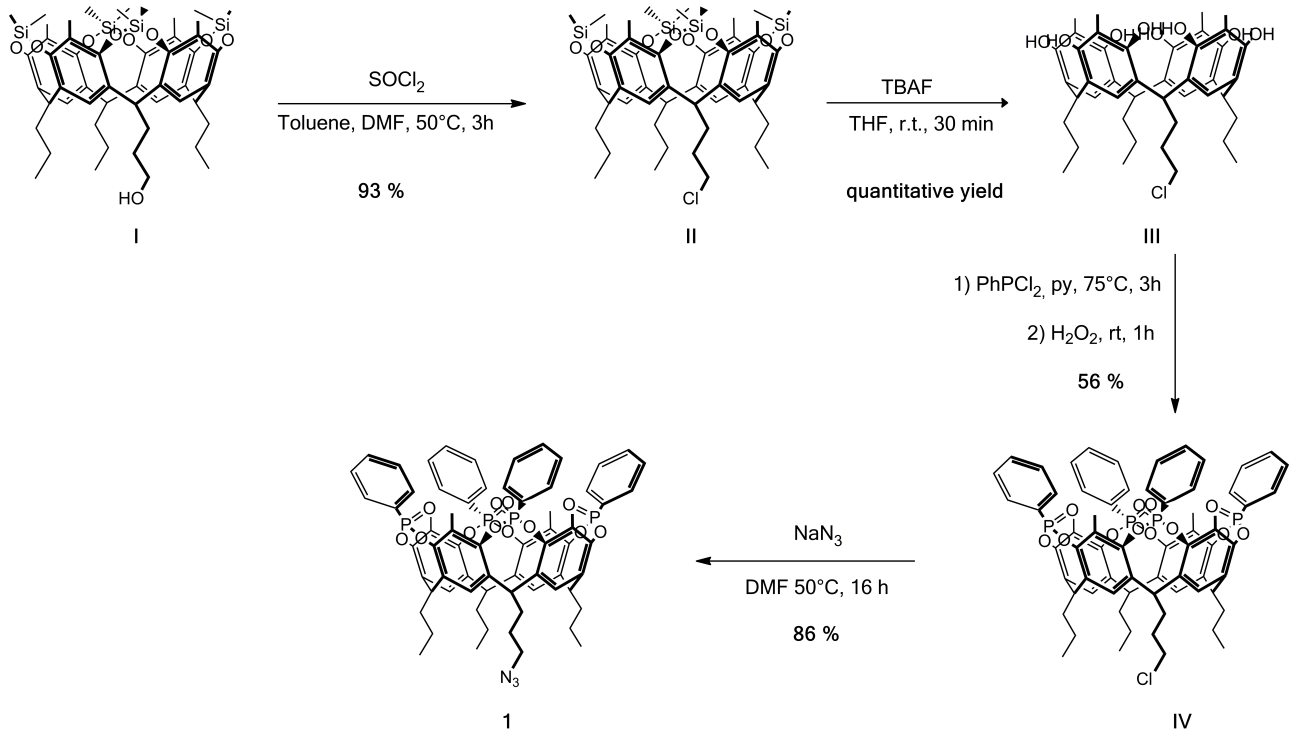
General Methods.

All reagents and chemicals were obtained from commercial sources and used without further purification. Single-walled carbon nanotubes were purchased from SouthWest Nano Technologies (SWeNT® CG100). Dry pyridine was distilled from KOH before use. Column chromatography was performed using silica gel 60 (MERCK 70-230 mesh). Electrospray ionization ESI-MS experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. Exact masses were determined using a LTQ ORBITRAP XL Thermo spectrometer equipped with an electrospray interface. ^{1}H NMR spectra were obtained using a Bruker AVANCE-300 (300 MHz) or a Bruker AVANCE 400 (400 MHz). All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. ^{31}P NMR spectra were obtained using a Bruker AVANCE-400 (162 MHz) spectrometer. All chemical shifts (δ) were recorded in ppm relative to external 85% H_3PO_4 at 0.00 ppm.
XPS spectra were recorded using a Kratos AXIS Ultra X-ray Photoelectron Spectrometer.
^{31}P MAS NMR: NMR experiments were conducted on a home-built 360 (B_o = 8.4T) spectrometer (courtesy of Dr. David Ruben) with a 4 mm triple-channel chemagnetics MAS probe. Samples were ground using a mortar and pestle, and placed within ZrO_2 rotors (60 µl volume). Spectral acquisition included Bloch and Hahn-echo experiments, using between 128 and 4096 co-added transients, spinning frequency (ω_r) between 0 and 12 kHz and high power ^{1}H decoupling (ν_{rf} = 83 kHz) when required. Recycle delays were optimized for each sample and were typically 35 seconds. All ^{31}P data were referenced using 85% H_3PO_4 (0.0 ppm).

Synthesis



Scheme S1 Synthesis of Monoazide footed tetraphosphonate cavitand **Tiiii[N_3, CH_3, Ph] 1**.

Monochloro silylcavitand (II). To a solution of monohydroxy footed silylcavitand[1] (0.76 g, 0.80 mmol) in dry toluene (15 ml), 5 drops of DMF were added. The suspension was cooled to 0°C and thyonil chloride was slowly added (2.40 mmol, 175 µl). The resulting suspension was stirred for 2h at 50°C. The solvent was evaporated; the residue was dissolved in chloroform and washed within water and dried over $MgSO_4$. The removal of the solvent gave **II** as a brownish solid (0.72g, 0.74 mmol, 93%). **^{1}H-NMR (CDCl$_3$, 400 MHz)**: δ = 7.21 (bs, 4H, Ar**H**); 4.65 (t, 4H, ^{3}J= 7.9 Hz, ArC**H**); 3.64 (t, 2H, ^{3}J= 6.4 Hz, $CH_2C\mathbf{H_2}Cl$); 2.39 (m, 2H, $C\mathbf{H_2}CH_2CH_2Cl$); 2.21 (m, 6H, $C\mathbf{H_2}CH_2CH_3$); 1.95 (s, 12H, ArC**H$_3$**); 1.82 (m, 2H, $C\mathbf{H_2}CH_2Cl$); 1.35 (m, 6H, $CH_2C\mathbf{H_2}CH_3$); 1.09 (t, 9H, ^{3}J=7.3 Hz, $CH_2CH_2C\mathbf{H_3}$); 0.55 (s, 12H, SiC**H$_{3,out}$**); -0.63 (s, 12H, SiC**H$_{3,in}$**). **ESI-MS**: *m\z* calcd. for $C_{52}H_{71}ClO_8Si_4$ (970.4), $[M+Na]^+$: 993.4. Found: 993.5 $[M-Na]^+$.

Monochloro resorcinarene (**III**). To a solution of **II** (0.59 g., 0.60 mmol) in THF (15ml), acetic acid (6 mmol, 350 µl) and 80% w,w TBAF (6 mmol, 1.90 ml) were added at 0°C. The solution was stirred for 30 min at room temperature, then $NH_4Cl_{(aq)}$ was added. The solution was diluted with ethyl acetate and the organic layer was separated, washed three times with $NH4Cl_{aq}$, then $NaCl_{aq}$ and dried over $MgSO_4$. The removal of the solvent afforded **III** as a brown solid (0.47 g, 0.60 mmol, quantitative yield). **^{1}H-NMR (Acetone-d$_6$, 300 MHz)**: δ = 8.37 (m, 8H, ArO**H**); 7.51 (s, 2H, Ar**H**); 7.50 (s, 2H, Ar**H**); 4.49 (t, 4H, ^{3}J=7.9 Hz, ArC**H**); 3.71 (t, 2H, ^{3}J= 6.7 Hz, $CH_2C\mathbf{H_2}Cl$); 2.53 (m, 2H, $CHC\mathbf{H_2}CH_2CH_2Cl$); 2.35 (m, 6H, $CHC\mathbf{H_2}CH_2CH_3$); 2.13 (s, 12H, ArC**H$_3$**); 1.83 (m, 2H, $CH_2C\mathbf{H_2}CH_3$); 1.38 (m, 6H, $CH_2C\mathbf{H_2}CH_3$); 1.02 (t, 9H, ^{3}J=7.3 Hz, $CH_2CH_2C\mathbf{H_3}$). **ESI-MS**: *m\z* calcd. for $C_{44}H_{55}ClO_8$ (746.4), $[M+Na]^+$ 769.6. Found: 769.50. $[M+Na]^+$.

Monochloro footed tetraphosphonate cavitand Tiiii[Cl, CH$_3$, Ph] (IV). To a solution of **III** (0.47g, 0.63 mmol) in freshly distilled pyridine (12 mL), dichlorophenylphosphine (380 µl, 2.84 mmol) was added slowly, at room temperature. After 3 hours of stirring under N_2 at 75 °C, the solution was cooled down to room temperature and 4.5 mL of aqueous 35% H_2O_2 was added. The resulting mixture was stirred for 1 h at room temperature, then the solvent was removed in vacuo. Addition of water resulted in the precipitation of a white powder. The crude was purified by chromatographic column (9:1 DCM:EtOH) affording **IV** as a brownish solid (0.44 g, 0.35 mmol, 56 %). **^{1}H-NMR (CDCl$_3$, 400 MHz)**: δ = 8.13 (m, 8H, P(O)Ar**H$_O$**); 7.68 (m, 4H, P(O)Ar**H$_P$**); 7.58 (m, 8H, P(O)Ar**H$_M$**); 7.40 (bs, 4H, Ar**H**); 4.84 (t, 4H, ^{3}J= 7.8 Hz, ArC**H**); 3.74 (t, 2H, ^{3}J= 7.2 Hz, $CH_2C\mathbf{H_2}Cl$); 2.63 (m, 2H, $C\mathbf{H_2}CH_2CH_2Cl$); 2.43 (m, 6H, $C\mathbf{H_2}CH_2CH_3$); 2.20 (s, 12H, ArC**H$_3$**); 1.92 (m, 2H, $CH_2C\mathbf{H_2}CH_2Cl$); 1.47 (m, 6H, $CH_2C\mathbf{H_2}CH_3$); 1.09 (t, 9H, ^{3}J= 7.3 Hz, $CH_2CH_2C\mathbf{H_3}$). **^{31}P{^{1}H} NMR (CDCl$_3$, 161.9 MHz)**: δ = 7.70 (bs,P(O)). **ESI-MS**: *m\z* calcd. for **Tiiii[Cl, CH$_3$, Ph]** $C_{68}H_{67}ClO_{12}P_4$ (1234.32); $[M+Na]^+$ 1257.75. Found:1257.78 $[M+Na]^+$.

Monoazide footed tetraphosphonate cavitand Tiiii[N$_3$, CH$_3$, Ph] (1) To a solution of **Tiiii[Cl, CH$_3$, Ph] (IV)** (0,44 g, 0.35 mmol) in DMF (15 ml), sodium azide was added (68 mg, 1.1 mmol). The solution was stirred overnight at 55°C. Then the solvent was evaporated and the crude was suspended in water and filtered affordin **1** as a brown solid (0,38 g., 0.31 mmol, 86%). **^{1}H-NMR (CDCl$_3$, 400 MHz)**: δ = 8.14 (m, 8H, P(O)Ar**H$_O$**); 7.65 (m, 4H, P(O)Ar**H$_P$**); 7.57 (m, 8H, P(O)Ar**H$_M$**); 7.19 (s, 4H, Ar**H**); 4.87 (m, 4H, ArC**H**); 3.48 (t, 2H, ^{3}J= 6.2 Hz $CH_2C\mathbf{H_2}N_3$); 2.38 (m, 20H, $C\mathbf{H_2}CH_2CH_2N_3$ + $C\mathbf{H_2}CH_2CH_3$ + ArC**H$_3$**); 1.73 (m, 2H, $CH_2C\mathbf{H_2}CH_2N_3$); 1.47 (m, 6H, $CH_2C\mathbf{H_2}CH_3$); 1.09 (t, 9H, ^{3}J= 7.2 Hz, $CH_2CH_2C\mathbf{H_3}$). **^{31}P{^{1}H} NMR (CDCl$_3$, 161.9 MHz)**: δ = 6.13 (bs P(O)). **HR ESI-MS**: calculated for the complex **Tiiii[N$_3$, CH$_3$, Ph]** $C_{68}H_{67}N_3O_{12}P_4$ (1241.36752) $[M+Na]^+$: 1264.35729. Found:1264.35674.

[1] a) Yebeutchou, R. M.; Tancini, F.; Demitri, N.; Geremia, S.; Mendichi, R.; Dalcanale,E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4504–4507; b) Hauke, F.; Myles, A.J.; Rebek, J. jr. Chem. Commun. 2005, 4164 – 4166.

General procedure for SWCNTs functionalization

10 mg of SWCNTs were placed in a schlenk and purged with argon for 10 minutes. **Tiii[N_3, CH_3, Ph] (1)** (200 mg, 0.16 mmol) was introduced with the addition of 1 ml of *o*-DCB. The suspension was sonicated for 10 minutes, then heated at 160°C for two days under argon. After evaporation of the solvent, the crude was dispersed in dichloromethane and sonicated for 10 min. Filtered on 2 µm millipore filter and washed with hexane, dichloromethane, acetone.

XPS spectra of functionalized SWCNTs

Si and F in the spectra originate from the substrate used. Cl signals were attributed to trace amounts of *o*-DCB.

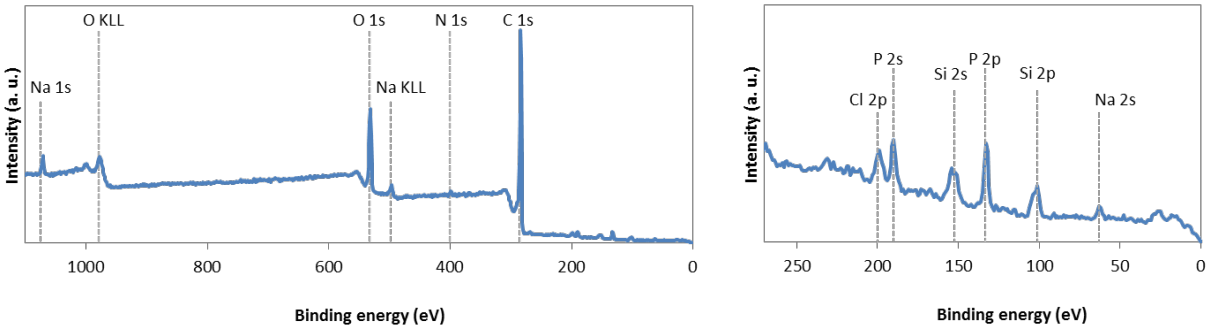


Figure S1 XPS spectrum of **Tiiii@SWCNTs**.

Attenuated total reflectance Fourier transform infrared spectra (ATR FTIR)

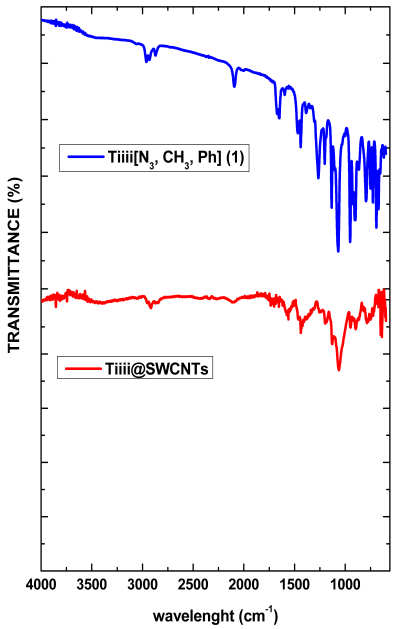


Figure S2 ATR-FTIR **Tiiii[N_3, CH_3, Ph] 1** (blue trace) and **Tiiii@SWCNTs** (red trace).

XPS complexation studies

To a dichloromethane (1 ml) suspension of **Tiiii@SWCNTs** (5 mg, 0.9 µM of cavitand) a guest solution (4-bromo-N-methylbutylammonium bromide, **2**) in dichloromethane was added (5 equivalent of 4.3 µM dichloromethane solution). After 12h the suspension was filtered and the solid washed with dichloromethane. The solid was collected, dried, redispersed in dichloromethane and dropcasted on silicon slide for XPS measurement. After the XPS measurement, the material was sonicated with DBU (9.2 equiv relative to initially used guest) in 5 mL DCM for 10 min and then stirred over night. Afterward, the Tiiii@SWCNTs were collected by filtration, washed with DCM, dried and drop-cast for an XPS measurement.

As a control experiment, pristine SWCNTs (5 mg) were treated with a similar guest solution for 12 h. The sample was washed and dried in a similar fashion and then analyzed by XPS.

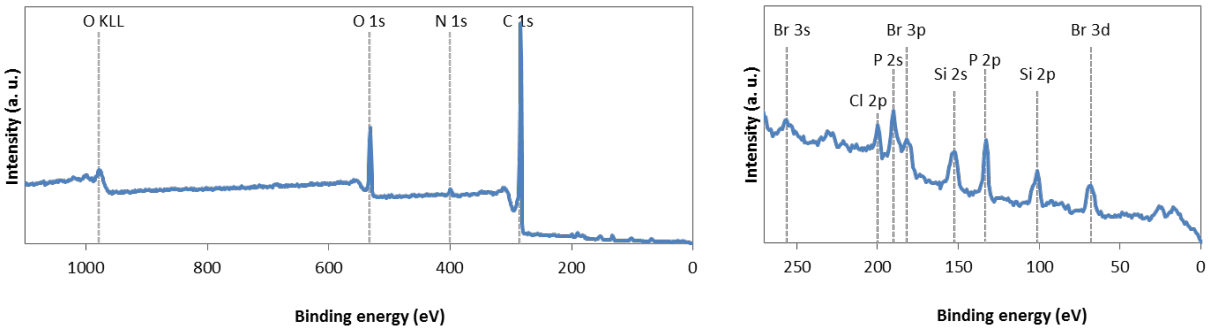


Figure S3 XPS spectrum of **Tiiii@SWCNTs** after treatment with guest **2**.

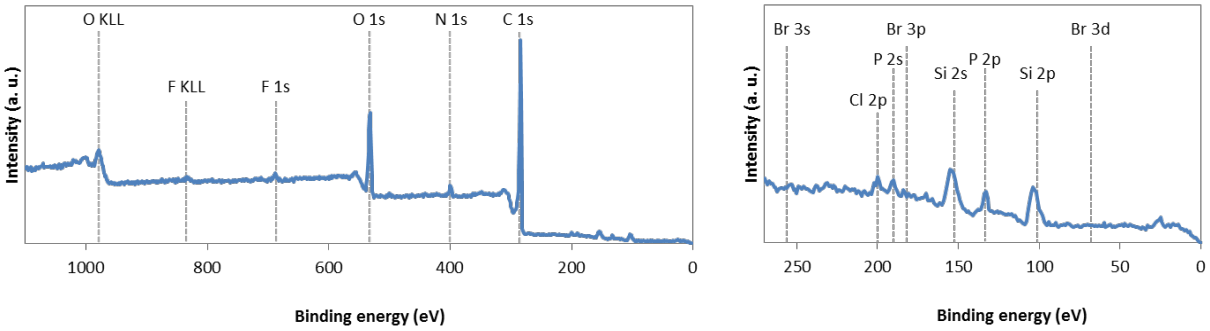


Figure S4 XPS spectrum of **Tiiii@SWCNTs•2** after washing with DBU. Positions of Br signals are labeled for better comparison to Figure S3.

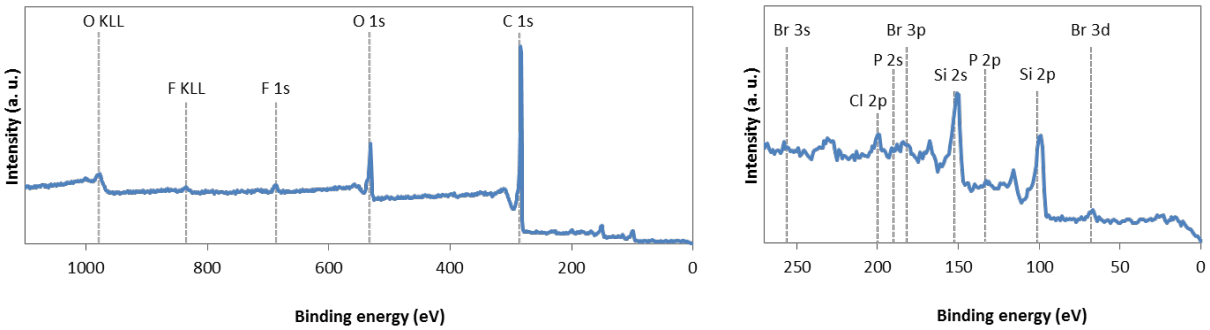


Figure S5 XPS spectrum of pristine SWCNTs after treatment with **2**. Positions of Br and P signals are labeled for better comparison to Figure S3.

Solid State-NMR complexation studies

Tiiii@SWCNTs (40 mg, 7.5 μM) were treated with 5 equivalents of N-methylbutyl ammonium chloride (4.29 mM solution in dichloromethane). After 12h the suspension was filtered and the solid washed with dichloromethane. The powder was collected, dried and submitted for MAS NMR experiments.

The **Tiiii@SWCNTs•2** complex was redispersed in dichloromethane and treated with an excess of DBU solution (4.29 mM solution in dichloromethane). After 12 h the suspension was filtered and the solid washed with dichloromethane. The powder was collected, dried and investigated by MAS NMR.

Scanning electron microscopy (SEM)

Devices of **Tiiii@SWCNT** were inspected by scanning electron microscopy (SEM) on a JEOL JSM 6700F SEM.

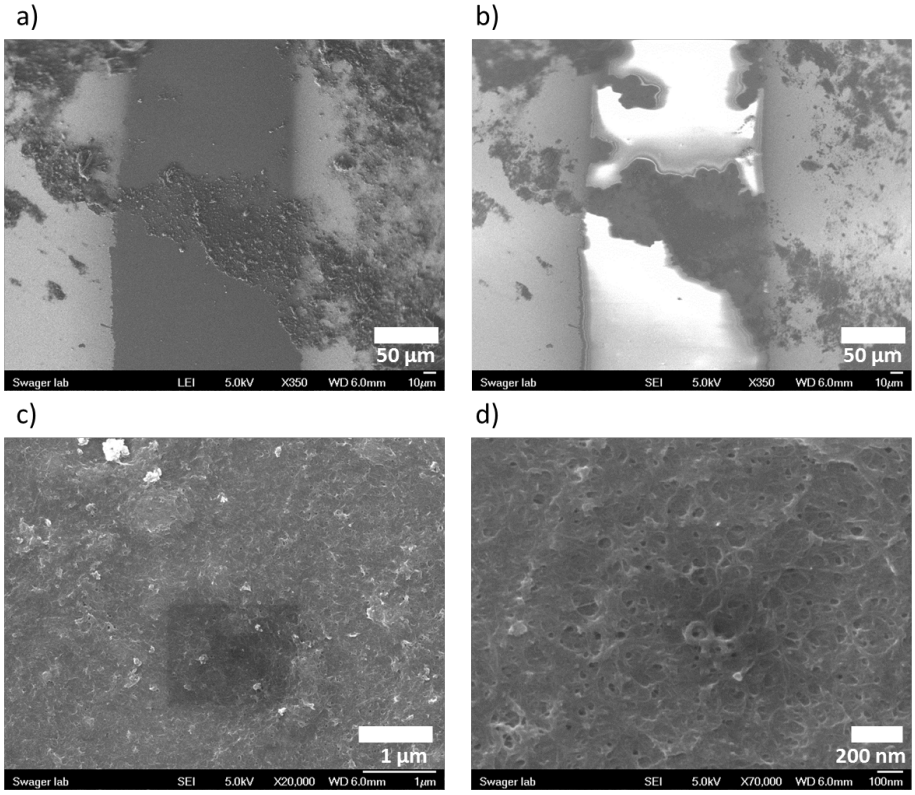


Figure S6 SEM images of Tiiii@SWCNT film used in sensing measurements. a) 350x LEI b) 350x SEI c) 20,000x SEI d) 70,000x SEI

Low resolution SEM images (Figure S6 a-b) of the devices show a rough film that covers part of the glass surface between the gold electrodes. At higher magnification, CNT bundles are visible (Figure S6 c-d).

Atomic force microscopy (AFM)

Devices of **Tiiii@SWCNT** were inspected by atomic force microscopy (AFM) using an Agilent 5100 AFM in tapping mode. AFM tips were obtained from App Nano (ACTA-20, <10 nm radius). A flattening procedure was applied to the data shown. AFM images of the devices confirm the morphology of the film as observed by SEM. Furthermore a high surface roughness was observed (RMS surface roughness of 285 nm with feature heights above 1 μm in Figure S7b).

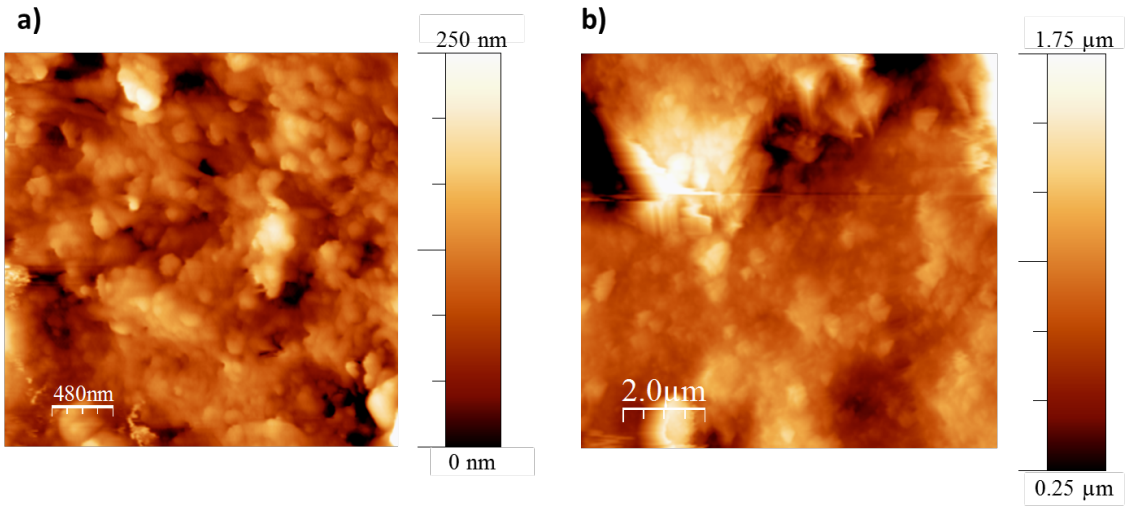


Figure S7 AFM images of **Tiiii@SWCNT** film used in sensing measurements

General procedure for sensing measurements

The devices were enclosed in a homemade Teflon liquid flow chamber for sensing measurement (see Figure S8). The gold electrodes of the device are contacted with connections to the outside of the chamber, and two ports on opposite sides of the chamber allow directing a continuous flow of liquid through the chamber.

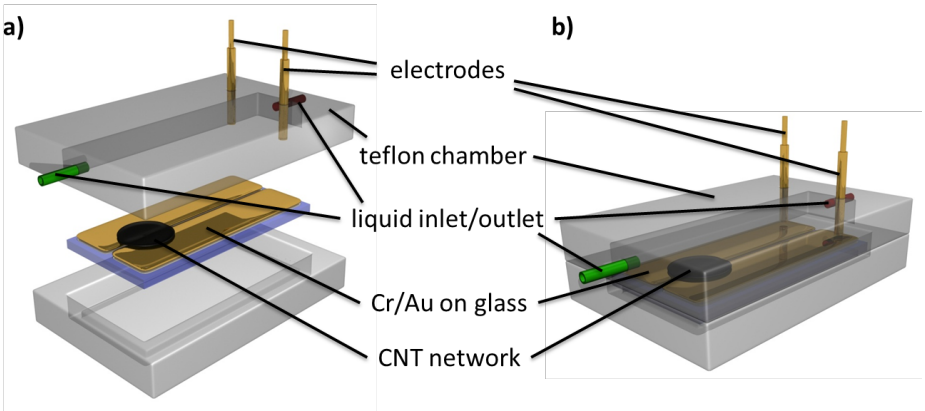


Figure S8 Liquid flow chamber for sensing measurements.

The inlet port of the flow chamber was connected to a tubing system with two 3-way valves that allowed directing a liquid from one of two syringes through the chamber (see Figure S9). By connecting both syringes to the same syringe pump, a constant flow rate of 0.5 mL/min was maintained for both syringes.

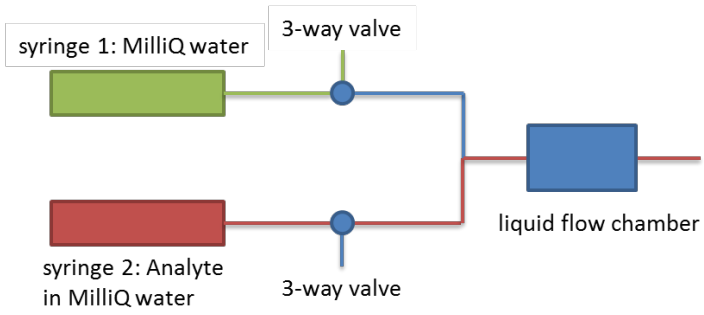
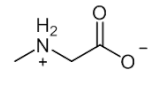


Figure S9 Setup for liquid flow sensing measurements. Using two 3-way valves, a liquid from one of two syringes could alternately be directed through the liquid flow chamber with the measurement device. Both syringes were connected to the same syringe pump ensuring the same flow rate for both liquids

Electrochemical measurements were performed using a PalmSens handheld potentiostat connected to a laptop computer. A constant bias voltage of 0.05 V was applied across the device, while current vs. time was measured.

In a typical measurement, the device was first exposed to MilliQ water. Subsequently, a 1 mM analyte solution in water was directed through the device for 100 s, followed by MilliQ water for 1000 s. In each measurement, the device was exposed to the analyte at least three times.

Sensing measurements



1 mM in H_2O
pH 7

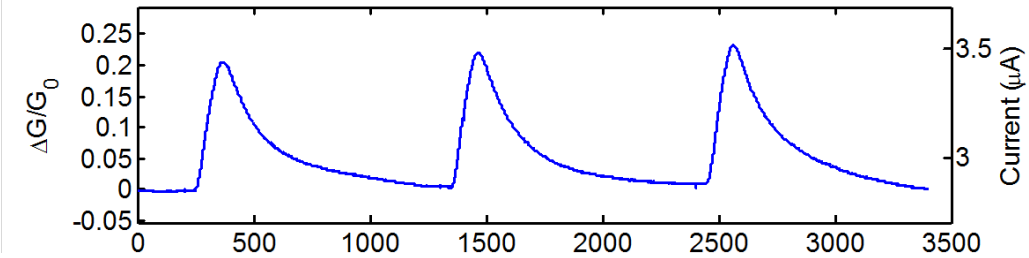
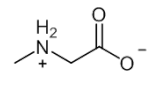


Figure S10 Sensing of sarcosine with **Tiiii@SWCNTs** at pH 7.



1 mM in H_2O
pH 5

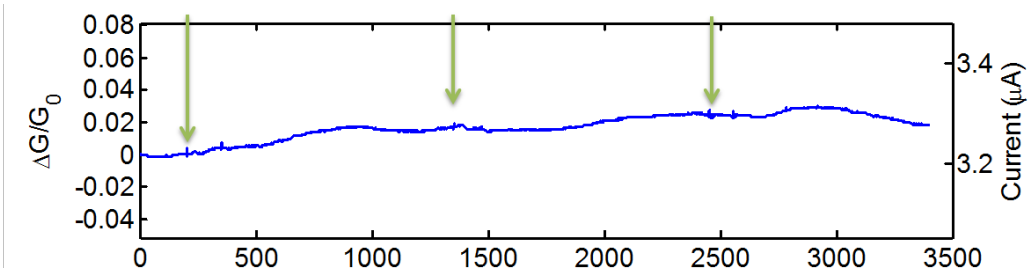


Figure S11 Sensing of sarcosine with **Tiiii@SWCNTs** at pH 5, arrows indicate exposure to analyte.

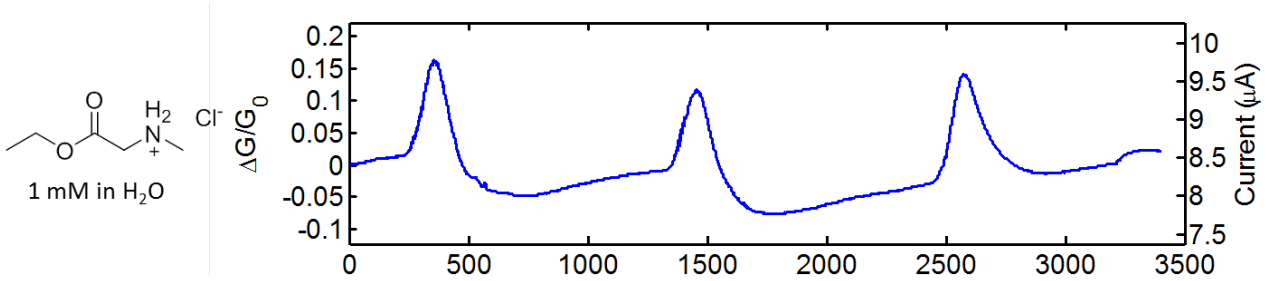


Figure S12 Sensing of **4** with **Tiiii@SWCNTs** at pH 5.

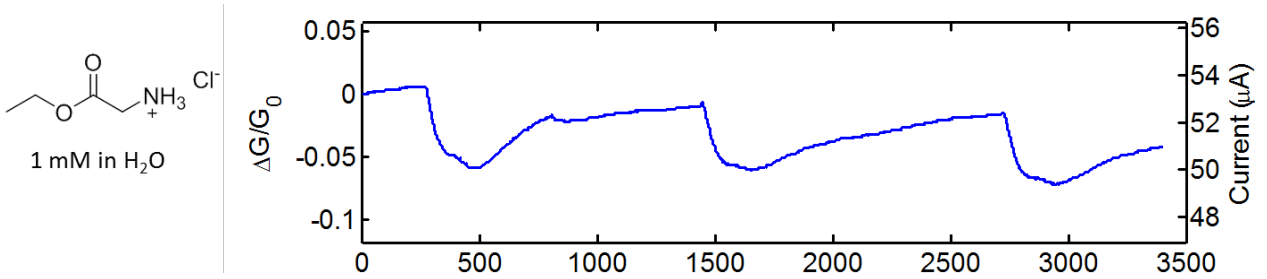


Figure S13 Sensing of **5** with **Tiiii@SWCNTs** at pH 5.

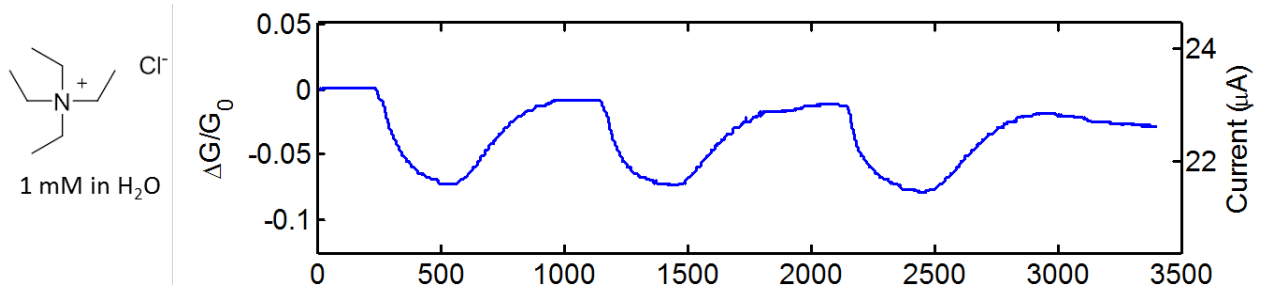


Figure S14 Sensing of **6** with **Tiiii@SWCNTs** at pH 5.

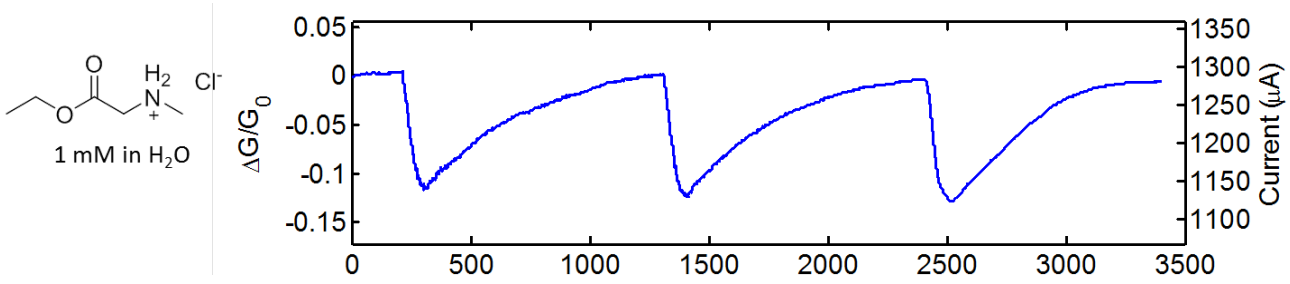


Figure S15 Sensing of **4** with pristine SWCNTs at pH 5.

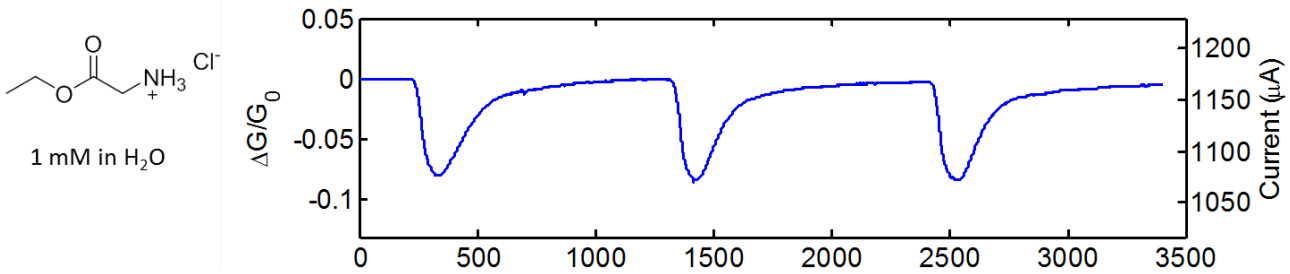


Figure S16 Sensing of **5** with pristine SWCNTs at pH 5.

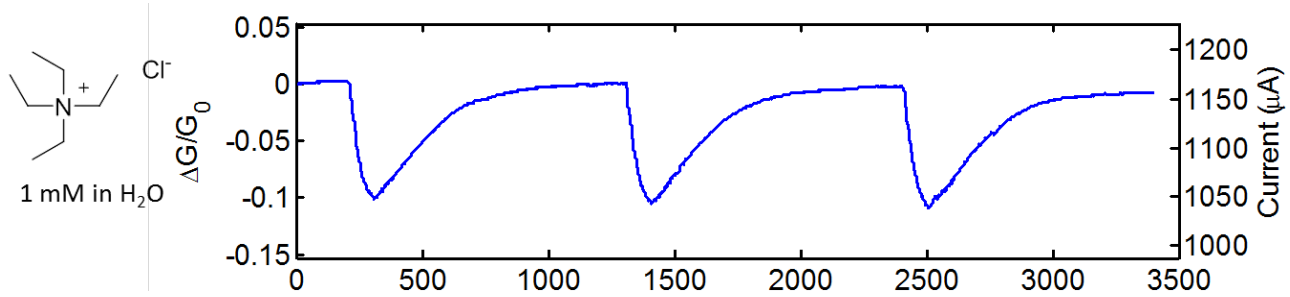


Figure S17 Sensing of **6** with pristine SWCNTs at pH 5.

To investigate the device to device reproducibility, the response of four different devices to **4** was compared (Figure S18-S21). Due to the device fabrication technique, the structure of the CNT network varies from device to device which results in different responses to **4** (Figure S22), while the error for measurements with the same device, is small compared to the device to device differences.

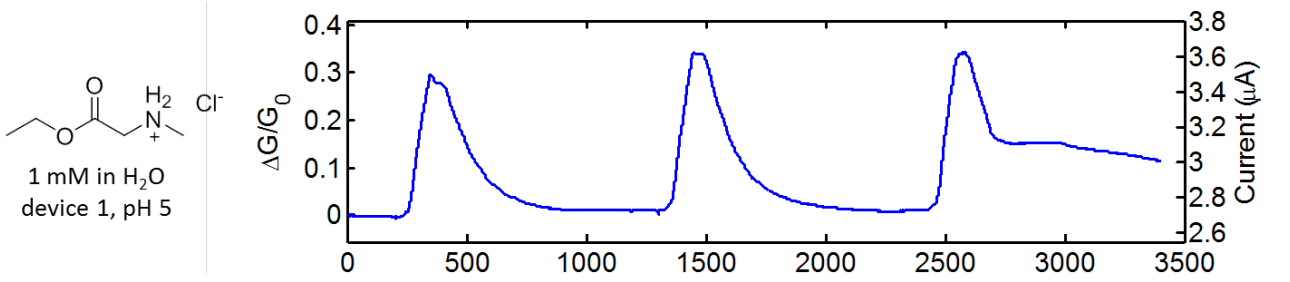


Figure S18 Sensing of **4** with **Tiiii@SWCNTs** at pH 5 using device 1.

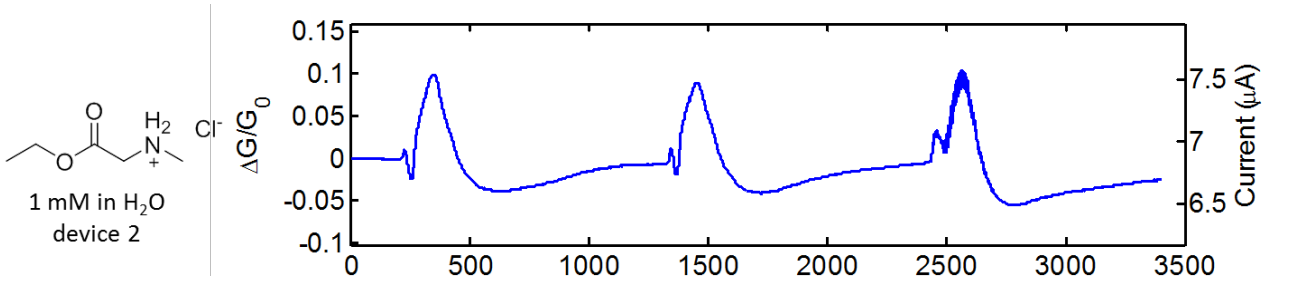


Figure S19 Sensing of **4** with **Tiiii@SWCNTs** at pH 5 using device 2.

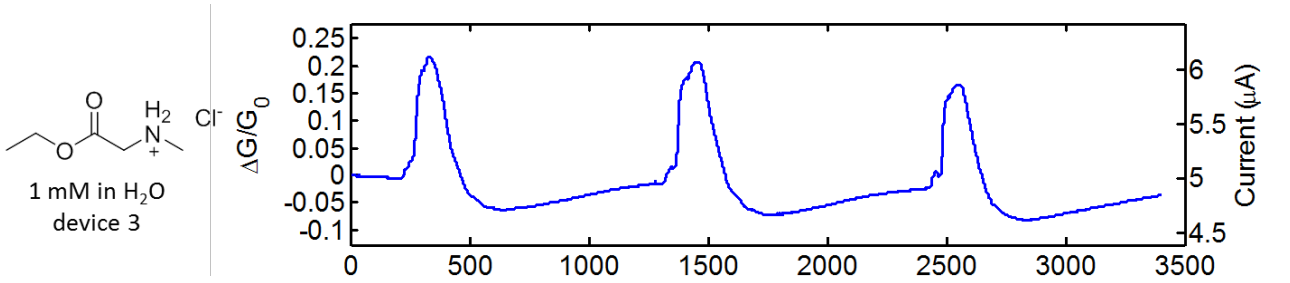


Figure S20 Sensing of **4** with **Tiiii@SWCNTs** at pH 5 using device 3.

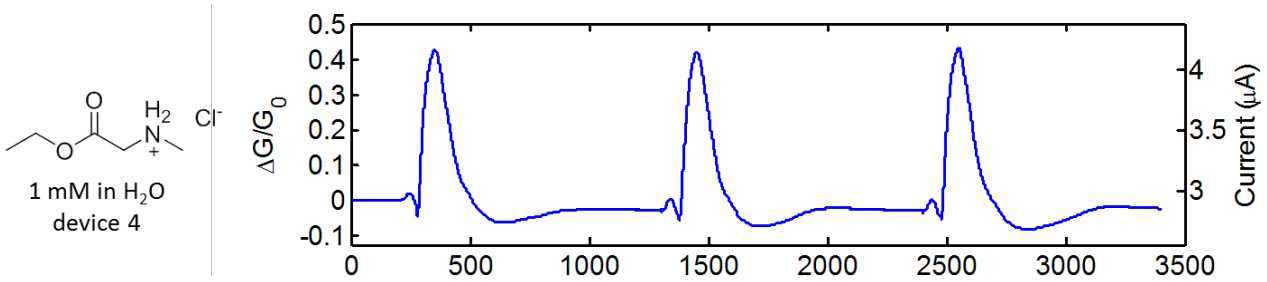


Figure S21 Sensing of **4** with **Tiiii@SWCNTs** at pH 5 using device 4.

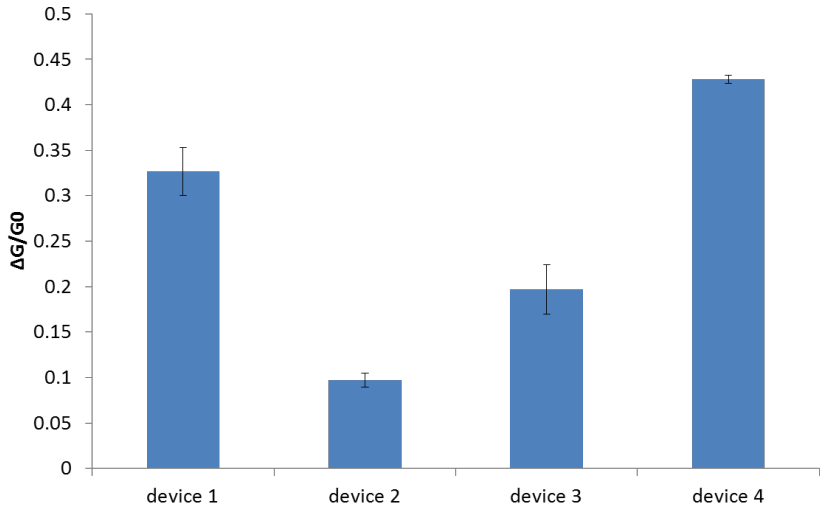


Figure S22 Sensing of **4** with **Tiiii@SWCNTs** using different devices, error bars are based on three consecutive measurements with the same device.

To investigate the pH dependence of sensing of **4** with **Tiiii@SWCNTs**, a measurement was performed at pH 7 showing a decrease in current when the device was exposed to the analyte. This can be attributed to the decreasing binding constant with increasing pH and as a result a response comparable to that of weaker binders (**5** or **6**) at pH 5.

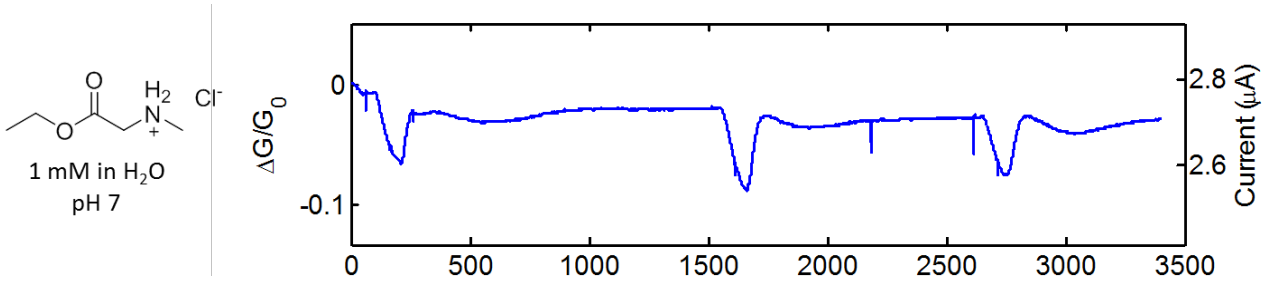


Figure S23 Sensing of **4** with **Tiiii@SWCNTs** at pH 7 (using device 1).