Electronic Supplementary Material (ESI) for RSC Advances.

**Supplementary Information (ESI)**

# Solid polymer substrates and smart fibres for the selective visual detection of TNT both in vapour and in aqueous media

Jesús L. Pablos,* Miriam Trigo-López, Felipe Serna, Félix C. García, José M. García*

Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza de Misael Bañuelos s/n, 09001 Burgos, Spain. Emails: jlpablos@ubu.es (J.L. Pablos), jmiguel@ubu.es (JM García); Tel: +34 947 258 085; Fax: +34 947 258 831.

## *Table of contents*

## S1. Experimental part

### Materials

All of the materials and solvents were commercially available and used as received, unless otherwise indicated. The materials included the following: 4-(chloromethyl)styrene (90%, Aldrich), triphenylphosphine (>95%, Aldrich), hydrochloric acid (37%, Scharlab), sodium hydroxide (97%, VWR-Prolabo), magnesium sulphate (> 99%, VWR-Prolabo), benzene (99.9%, Fluka), dichloromethane (99.99%, Fisher Chemical), *N,N*-dimethylformamide (DMF) (99.9%, Sigma-Aldrich), diethyl ether (99.9%, Fisher Chemical), 4-nitrotoluene (NT) (99%, Aldrich), 2,4-dinitrotoluene (DNT) (99%, Aldrich), acetone (99%, Aldrich), tetrahydrofuran (THF) (99%, Aldrich), ethylene glycol dimethacrylate (**EGDMMA**) (99%, Aldrich), 2-hydroxyethyl acrylate (**2HEA**) (99%, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (99%, Aldrich), 4-{*N*-(2-(methylamino)-ethyl)aminomethyl}styrene (**di-AMS**) (>90%, Aldrich). 2,4,6-trinitrotoluene (TNT) was prepared at a milligram scale from DNT and recrystallised from ethanol following a previously described procedure (CAUTION: this material is explosive, and although it is insensitive to shock and friction and can be milled and melted at 82 ºC, it must be handled with care. Only 500-mg quantities of TNT were prepared to avoid risk).[1]

### Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ as the solvent using a NMR Mercury 300-MHz spectrometer.

Infrared spectra (FTIR) were recorded with a Nicolet Impact spectrometer or with a JASCO FT/IR-4100 fitted with a PIKE TECH “Miracle” ATR.

---

[1] R. C. Dorey and W. R. Carper, *J. Chem. Eng. Data*, 1984, **29**, 93.

Thermogravimetric analysis (TGA) data were recorded using 4-5 mg of sample under a nitrogen atmosphere on a TA Instrument Q50 TGA analyser at a scan rate of 10 °C min$^{-1}$.

Ultraviolet–visible (UV-Vis) and fluorescence spectra were recorded using a Varian Cary3-Bio UV-Vis.

## Measurements

The solvent-swelling percentage (SSP) of the membrane was determined from the weights of a dry sample membrane ($\omega_d$) and a solvent-swelled sample membrane ($\omega_s$) (the membrane was immersed in the pure solvent at 20 ºC until the swelled equilibrium was achieved) using the following equation: $100 \times [(\omega_s-\omega_d)/\omega_d]$.

The UV/Vis TNT titration both of vapour and in aqueous solution was performed as follows. The detection and quantification experiments of TNT in solution with the sensory monomers **AMS** and **di-AMS** and the membranes $\mathbf{M_{AMS}}$ and $\mathbf{M_{di\text{-}AMS}}$ were performed under the following conditions: the 5-mm discs cut from the membranes were dipped into acetone:water (Millipore-Q) (80:20, v:v) in a measuring cuvette using a homemade support. The monomers were dissolved previously in acetone and were then added to achieve an 80:20 (v:v) mixture of acetone:water (Millipore-Q); the concentration of the sensory monomers was $1.2 \times 10^{-3}$ M. Next, the concentration of TNT was progressively increased by adding cumulative volumes of several stock acetone:water (Millipore-Q) (80:20, v:v) solutions of TNT from $9.9 \times 10^{-8}$ M to $5.5 \times 10^{-3}$ M. The UV-Vis or fluorescence spectra were acquired 10 min after each addition, a time adequate to allow the system to reach equilibrium. The TNT vapours detection experiments were performed using $\mathbf{M_{AMS}}$ and $\mathbf{M_{di\text{-}AMS}}$ membranes as sensory materials according to a previously described procedure.[2] The TNT vapour atmosphere

---

[2] Q. Fang, J. Geng., B. Liu, D. Gao, F. Li, Z. Wang, G. Guan and Z. Zhang, *Chem. Eur. J.*, 2009, **15**, 11507.

was created as follows: 50 mg of solid TNT was placed into a sealed UV/Vis quartz cuvette (1 x 1x3.5 cm) at 60 ºC for 24 hours to obtain a saturated TNT vapour atmosphere. Afterwards, the sensory membrane was introduced in the cuvette while maintaining the temperature at 60 ºC, and the UV/vis spectra were recorded every 30-60 min for 11 h or followed visually.

The naked eye qualitative concentration evaluation of the TNT acetone:water (80:20, v:v) solution was performed by dipping the colourless sensory discs of $\mathbf{M_{AMS}}$ and $\mathbf{M_{di\text{-}AMS}}$ into TNT solution (1 mL) at concentrations ranging from 1 x $10^{-6}$ to 5 x $10^{-2}$ M for 1 h and observing the colour development. The red colour development indicated the presence of TNT, and the intensity could be qualitatively correlated to its concentration. A digital photograph taken of the discs with a smartphone was used to quantitatively titrate the TNT concentration using the colour definition of each disc, i.e., the three RGB parameters (R= red, G = green, B = blue). These parameters were obtained for each disc directly after taking the photograph of the set of discs through analysis with a conventional Android smartphone using the app called ColourMeter, which was set to automatically average 11 × 11 (121) pixels.[3] The three parameters were reduced to one, called the principal component (PC1), using principal component analysis (PCA), which provided an account of >92% of the information on the three RGB parameters, thus permitting the simple elaboration of 2D titration curves ([TNT] vs. CP1) with concomitant noise reduction without a significant loss of information (the PCA data are presented in Tables S2–S9, SI). An in-depth description of the procedures can be found in recent publications by our research group.[4,5]

---

[3] The app from the software engineering company VisTech.Projects was downloaded and installed onto the smartphone from Google Play, App web page: http://www.vistechprojects.com/app/colourmeter.

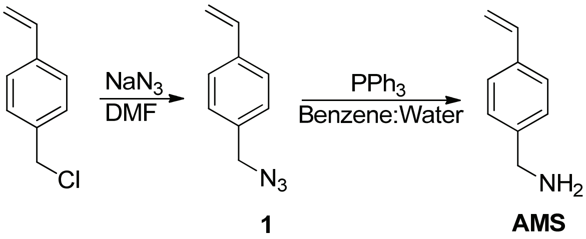
[4] H. El Kaoutit, P. Estevez, F. C. García, F. Serna and J. M. García, *Anal. Methods*, 2013, **5**, 54.

[5] S. Vallejos, A. Muñoz, S. Ibeas, F. Serna, F. C. García and J. M. García, *J. Mater. Chem. A*, 2013, **1**, 15435.

The visual detection and quantification experiments of TNT in solution with the sensory fabric **F<sub>AMS</sub>** and **F<sub>AEMA</sub>** were performed following the procedure described in the previous paragraph for the naked eye evaluation and TNT quantifications using the sensory membranes. The fabrics were dipped in TNT solutions in acetone for 5 min and then dried in air. The TNT concentration ranged from 1 x $10^{-6}$ to 5 x $10^{-2}$ M.

## Synthesis of the Sensory Monomer

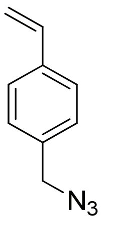
The styrenic monomer containing secondary amine groups 4-{*N*-(2-(methylamino)-ethyl)aminomethyl}styrene (**di-AMS**) is commercial and was purchased from the Sigma-Aldrich Corporation. The sensory monomer containing the primary amine 4-(aminomethyl)styrene (**AMS**) was prepared following the synthetic steps depicted in scheme S1. The spectra of the intermediate and of the monomers are presented in Figures S1-S3.



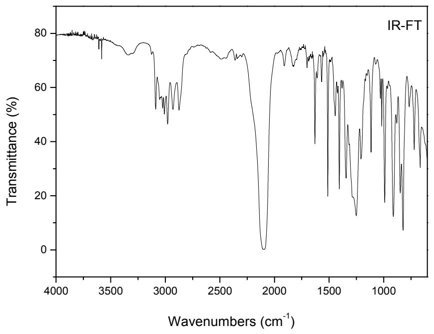
**Scheme S1**. Synthesis of monomer **AMS**.

*Synthesis of 4-(azidomethyl)styrene (**1**).* Five grams (32.9 mmol) of 4-(chloromethyl)styrene was dissolved in 40 mL of DMF and stirred overnight with 3 equivalents of $NaN_3$ (6.4 g, 98.7 mmol) at room temperature. Then, 100 mL of water was added, and the mixture was extracted with diethyl ether (3 x 100 mL). The organic phase was washed with brine (3 x 100 mL), dried with $MgSO_4$ and concentrated under reduced pressure. A yellow-orangish liquid was thus obtained. Yield: 5 g (6%). $^1$H

NMR $\delta_H$ (400 MHz, $CDCl_3$, $Me_4Si$): 7.44 (2H, d, *J* 8.1 Hz, Ph); 7.29 (2H, d, *J* 8.0 Hz, Ph); 6.76 (1H, dd, *J* 17.6 Hz, *J* 10.9 Hz, CH); 5.80 (1H, d, *J* 17.6 Hz, $=CH_2$); 5.30 (1H, d, *J* 10.9 Hz, $=CH_2$); 4.33 (2H, s, $CH_2$). $^{13}C$ NMR, $\delta_C$ (100.6 MHz, $CDCl_3$, $Me_4Si$): 137.79, 136.35, 134.92, 128.58, 126.77, 114.59, 54.68. EI-LRMS m/z: 159 ($M^+$, 5), 130 (7), 118 (11), 117 (100), 115 (12) 104 (5), 91 (12) 77 (5). FTIR [Wavenumbers ($cm^{-1}$)]: $\nu_{=CH_2}$: 3102-2860; $\nu_{N_3}$: 2099; $\nu_{C=C}$: 1631.



**1**



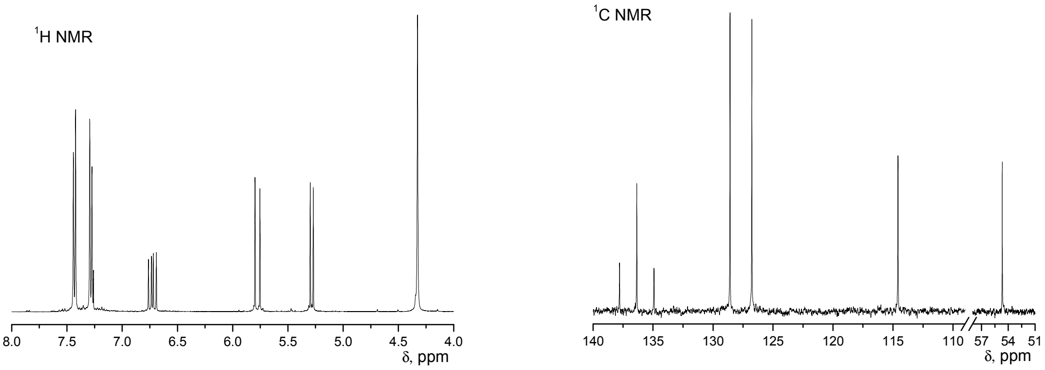


**Figure S1.** $^{1}$H and $^{13}$C NMR, and FTIR spectra of 4-(azidomethyl)styrene (**1**).

*4-(aminomethyl)styrene (**AMS**).* Five grams (31.3 mmol) of (**1**) was dissolved in 35 mL of benzene and stirred for 3 hours at 70 ºC with 1.5 equivalents of $PPh_3$ (12.4 g, 47.0 mmol) and 35 mL of water. The reaction mixture was extracted with 2N HCl (2 x 50 mL). The aqueous phase was washed with 70 mL of $CH_2Cl_2$, basified with NaOH and extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The yellowish product was purified by vacuum distillation (48 ºC, 0.1 mmHg), yielding a colourless liquid. Yield: 4.05 g (88%). $^{1}$H NMR $\delta_H$ (400 MHz, $CDCl_3$, $Me_4Si$): 7.39 (2H, d, *J* 8.1 Hz, Ph); 7.28 (2H, d, *J* 8.0 Hz, Ph); 6.75 (1H, dd, *J* 17.6 Hz, *J* 10.9 Hz, CH); 5.75 (1H, d, *J* 17.6 Hz, $=CH_2$); 5.24 (1H, d, *J* 10.9 Hz, $=CH_2$); 3.86 (2H, s, $CH_2$); 1.50 (2H, s, $NH_2$). $^{13}$C NMR, $\delta_C$ (100.6 MHz, $CDCl_3$, $Me_4Si$): 143.09, 136.65, 136.33, 127.36, 126.50, 113.56, 46.37. EI-LRMS m/z: 133 ($M^+$, 85), 134 (11), 132 (100), 117 (15), 116 (16), 115 (17) 106 (20), 105 (25), 103 (11), 79 (11) 73 (13). FTIR [Wavenumbers ($cm^{-1}$)]: $\nu_{NH2}$ (3384, 3288); $\nu_{=CH2}$: 3087-2850; $\nu_{C=C}$: 1623; $\delta_{N\text{-}H}$: 1504.

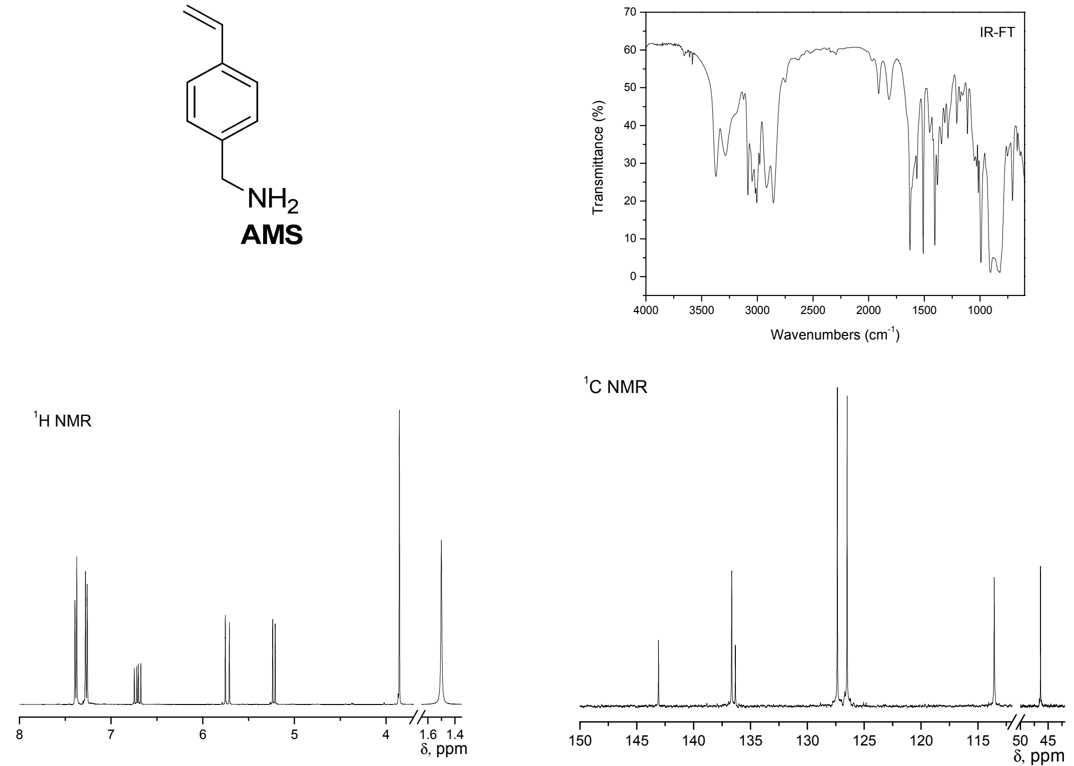


**Figure S2.** $^{1}$H and $^{13}$C NMR, and FTIR spectra of 4-(aminomethyl)styrene (**AMS**).

## Membrane preparation

The film-shaped sensory dense membranes were prepared by the radical polymerisation of the monomer 2-hydroxyethyl acrylate (**2HEA**) and the sensory monomers **di-AMS** and **AMS**, using ethylene glycol dimethacrylate (**EGDMMA**) as the cross-linking agent (5%), a co-monomer molar ratio **2HEA/AMS/EGDMMA** (membrane $\mathbf{M_{AMS}}$) or **2HEA/di-AMS/EGDMMA** (membrane $\mathbf{M_{di\text{-}AMS}}$) of 50/50/5, and 2,2-dimethoxy-2-phenylacetophenone (1.5 wt.%) as a radical photoinitiator. The homogenous solution comprised of **2HEA**, **AMS** or **di-AMS**, **EGDMMA** and the photoinitiator was transferred to an ampoule, degassed by nitrogen bubbling for 15 min and injected into an oxygen-free atmosphere 100-µm thick silanised glass hermetic mould, where the photoinitiated bulk polymerisations were performed upon irradiation with a UV mercury lamp (250 W, Philips HPL-N, emission band in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm) at 20 ºC for 2 h. Then, the membranes were demoulded and conditioned by standing 48 h at room temperature in air followed by drying in a vacuum oven at 20 ºC overnight. The thicknesses of the membranes were 118 µm ($\mathbf{M_{AMS}}$) and 112 µm ($\mathbf{M_{di\text{-}AMS}}$). The chemical structures are depicted in scheme 1. A reference membrane ($\mathbf{M_{Ref}}$), lacking the sensory monomer, was prepared following this procedure using a feed co-monomer molar ratio **2HEA/EGDMMA** of 100/5.

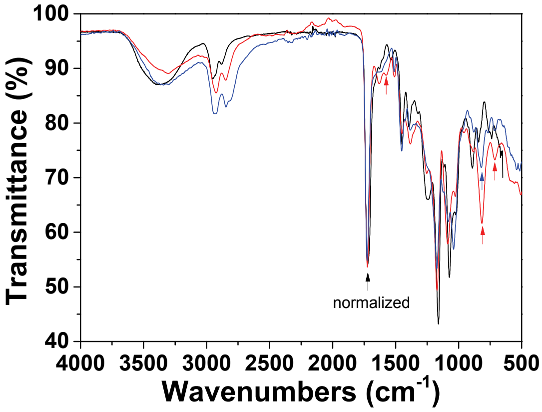


**Figure S3.** FT-IR spectra of $\mathbf{M_{Ref}}$ (black), $\mathbf{M_{AMS}}$ (red) and $\mathbf{M_{di\text{-}AMS}}$ (blue).

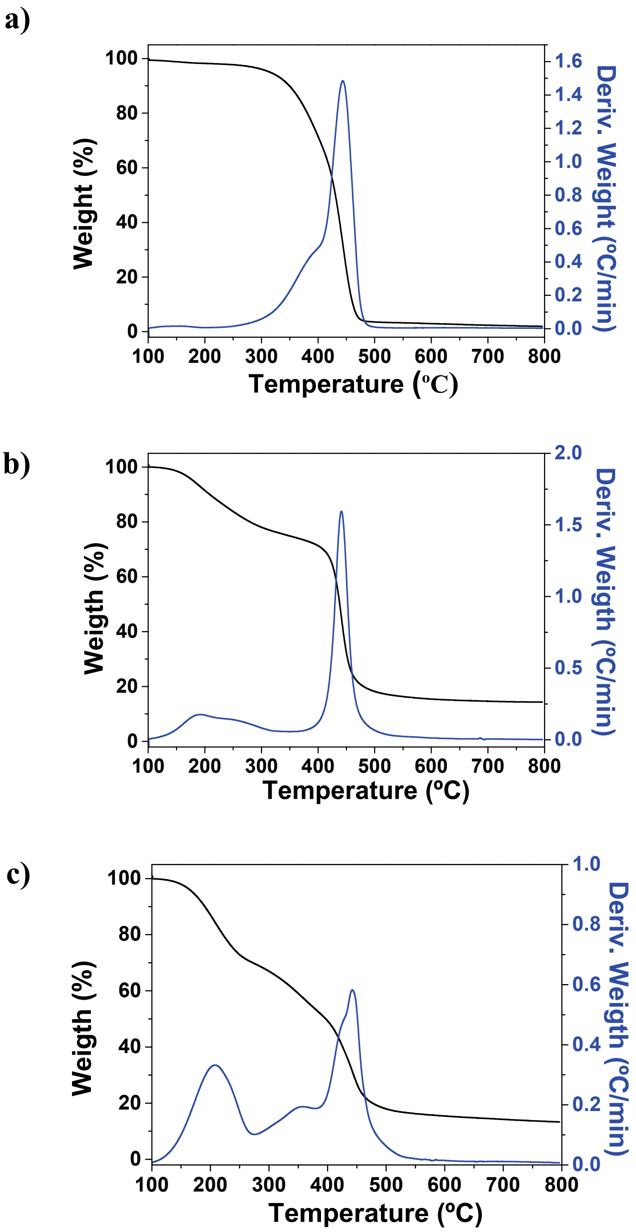


**Figure S4.** TGA of sensory membranes: a) $\mathbf{M_{Ref}}$, b) $\mathbf{M_{AMS}}$, and c) $\mathbf{M_{di\text{-}AMS}}$.

### Solid sensory substrates

The solid sensory substrates were manufactured from $\mathbf{M_{AMS}}$ and $\mathbf{M_{di\text{-}AMS}}$ films using a puncher to cut out sensory discs that were 5 mm in diameter and 118 μm (**AMS**) and 112 μm (**di-AMS**) thick.

### Coating of cotton fibres with sensory TNT polymers

Conventional cotton fabric cut from a new white lab coat was washed thoroughly with hot acetone and then cut into squares measuring approximately 1 cm x 1 cm, which were dried for 30 min at 60 ºC and weighed and stored under a nitrogen atmosphere. A homogeneous coating solution comprised of the sensory monomer **AMS** or **di-AMS**, **2HEA**, and **EGDMMA** as the cross-linking agent at a co-monomer molar ratio of **2HEA/AMS/EGDMMA** ($\mathbf{F_{AMS}}$) and **2HEA/di-AMS/EGDMMA** ($\mathbf{F_{di\text{-}AMS}}$) of 50/50/5 as well as 2,2-dimethoxy-2-phenylacetophenone (1.5 wt.%) as the radical photoinitiator was prepared. Then, the solution was degassed for 30 min by nitrogen bubbling, after which the fabrics were immersed into the solution, wrung, and irradiated, rendering the acrylic crosslink-coated cotton fibres $\mathbf{F_{AMS}}$ and $\mathbf{F_{di\text{-}AMS}}$; the entire procedure was performed under a nitrogen blanket. The irradiation was performed with a UV mercury lamp (250 W, Philips HPL-N, emission band in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm) at 20 ºC for 2 h. Then, the lab-coat square fabrics were dried at 60 ºC for 30 min and weighed again, yielding 77% and 79% by weight of cotton of polymer coating for $\mathbf{F_{AMS}}$ and $\mathbf{F_{di\text{-}AMS}}$, respectively, and the fabrics exhibited good tractability and tactile appearance.

## S2. Study of the interaction of the monomers with TNT by $^{1}$H-NMR

The $^{1}$H RMN spectra of the solution of **AMS** and **di-AMS** in $CDCl_3$ were recorded (Figures S5 and S6) at various concentrations of TNT (Table S1).

**Table S1.** Concentration data of **AMS** and TNT in an NMR tube using $CDCl_3$ as the solvent.

| | **AMS** | | | **di-AMS** | | |
|---|---|---|---|---|---|---|
| | **[TNT]** | **[AMS]** | **[TNT]/[AMS]** | **[TNT]** | **[AMS]** | **[TNT]/[AMS]** |
| **M1** | 0 | 0.120 | 0 | 0 | 0.120 | 0 |
| **M2** | 0.054 | 0.107 | 0.5 | 0.054 | 0.107 | 0.5 |
| **M3** | 0.097 | 0.097 | 1 | 0.162 | 0.081 | 2 |
| **M4** | 0.162 | 0.081 | 2 | 0.209 | 0.067 | 3 |
| **M5** | 0.209 | 0.067 | 3 | 0.245 | 0.061 | 4 |
| **M6** | 0.245 | 0.061 | 4 | | | |

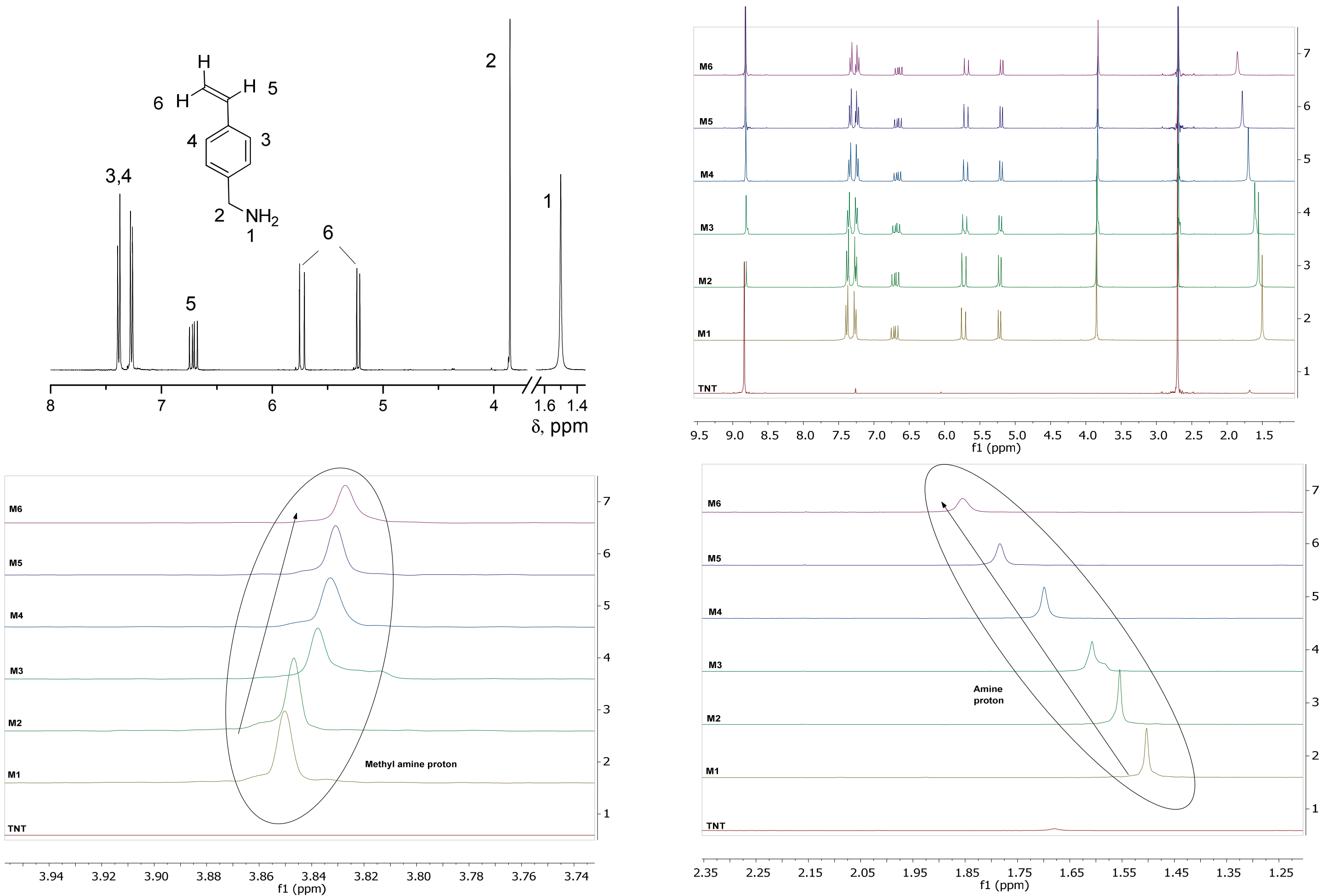


**Figure S5.** $^1$H RMN spectra of **AMS** with increasing concentration of TNT ($CDCl_3$).

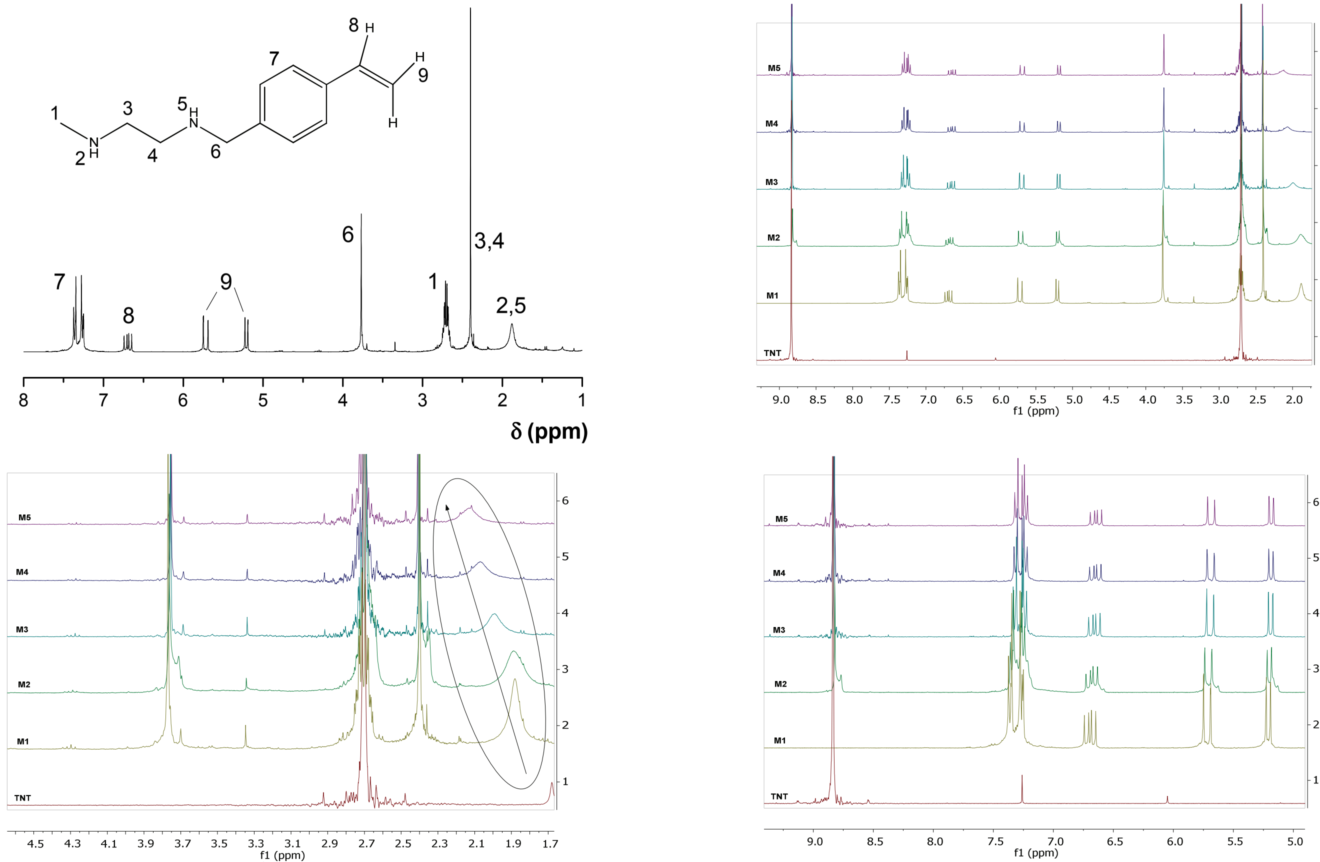


**Figure S6.** $^{1}$H RMN spectra of **di-AMS** with increasing concentration of TNT ($CDCl_3$).

## S3. UV/Vis titration study of solutions of TNT in acetone:water (80:20, v:v) with sensory monomers AMS, di-AMS and AEMA

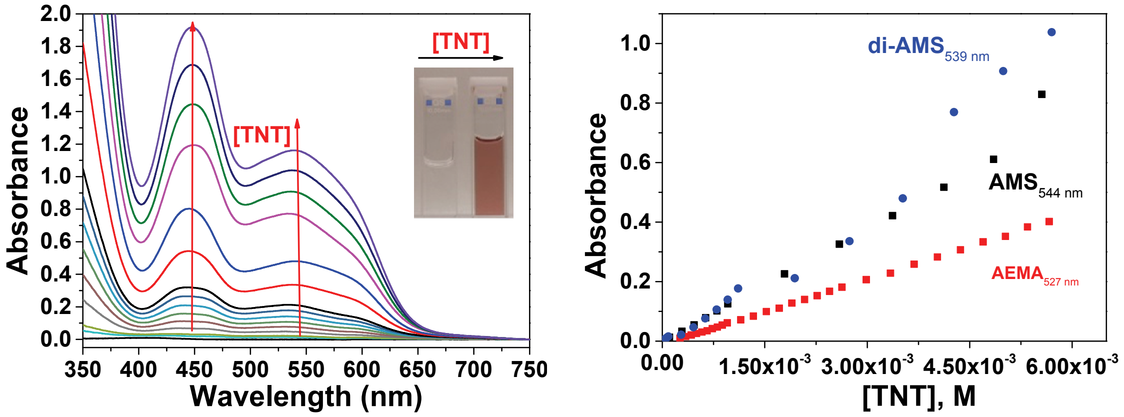


**Figure S7.** TNT titration with monomers containing amine groups as sensory motifs: a) selected UV/Vis titration curves for the monomer **di-AMS** (inset: image of UV/vis curves before and after the titration experiments); b) titration curves for monomers **AMS**, **di-AMS** and **AEMA** (absorbance second maxima *vs.* TNT concentration). Conditions: solvent acetone:water (80:20, v:v); monomer concentration 1.2 x 10$^{-3}$ M; TNT concentration ranged from 9.9 x 10$^{-8}$ to 5.5 x 10$^{-3}$ M.

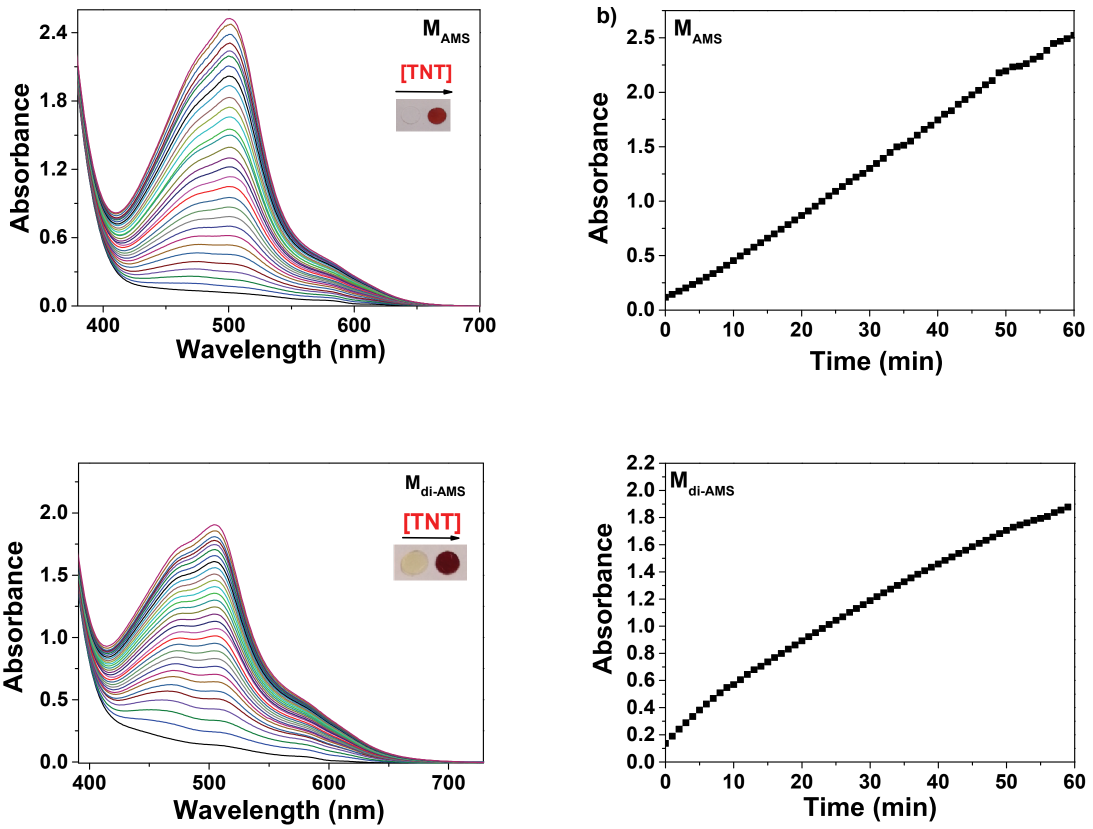


**Figure S8.** Detection kinetics of TNT (1 x $10^{-2}$ M) with sensory membranes $\mathbf{M_{AMS}}$ and $\mathbf{M_{di\text{-}AMS}}$: a) selected UV/Vis spectra as a function of time and b) absorbance maxima *vs.* time. The membranes were immersed in acetone:water (80:20, v:v) containing a TNT concentration of 1 x $10^{-2}$ M. The spectra were recorded every 1 min.

## S4. Principal component analysis (PCA) of sensory discs cut from $M_{AMS}$ and $M_{di\text{-}AMS}$ after immersing them in solutions of various concentrations of TNT in acetone:water (80:20, v:v)

**Table S2.** RGB parameters obtained from the digital images of the sensory discs cut from the sensory membranes.

| **[TNT], M** | **Membrane** | | | | | |
|---|---|---|---|---|---|---|
| | **$M_{AMS}$** | | | **$M_{di\text{-}AMS}$** | | |
| | **R** | **G** | **B** | **R** | **G** | **B** |
| 0 | 191 | 178 | 172 | 176 | 146 | 92 |
| 1 x 10$^{-6}$ | 190 | 177 | 171 | 175 | 143 | 88 |
| 1 x 10$^{-5}$ | 189 | 176 | 170 | 170 | 135 | 76 |
| 1 x 10$^{-4}$ | 189 | 171 | 167 | 169 | 121 | 58 |
| 1 x 10$^{-3}$ | 187 | 149 | 126 | 161 | 106 | 52 |
| 1 x 10$^{-2}$ | 156 | 50 | 36 | 74 | 21 | 23 |
| 5 x 10$^{-2}$ | 56 | 25 | 30 | 30 | 19 | 23 |

**Table S3.** Principal component analysis.

| **Component** | **Membrane** | | | | | |
|---|---|---|---|---|---|---|
| | **$M_{AMS}$** | | | **$M_{di\text{-}AMS}$** | | |
| | **Eigenvalue** | **Variance, %** | **Cumulative, %** | **Eigenvalue** | **Variance, %** | **Cumulative, %** |
| **PC1** | 2.78079 | 92.693 | 92.693 | 2.8658 | 95.527 | 95.527 |
| **PC2** | 0.216213 | 7.207 | 99.900 | 0.123831 | 4.128 | 99.654 |
| **PC3** | 0.00299916 | 0.100 | 100.000 | 0.0103727 | 0.346 | 100.000 |

Standardised data; number of extracted components: 1

**Table S4.** Component weights.

| **Variable** | **Membrane** | |
|---|---|---|
| | **$M_{AMS}$** | **$M_{di\text{-}AMS}$** |
| | **PC1** | **PC1** |
| **R** | 0.554282 | 0.572612 |
| **G** | 0.594296 | 0.588662 |
| **B** | 0.582738 | 0.570607 |

**Table S5.** Principal components (PC1).

| **[TNT], M** | **Membrane** | |
|---|---|---|
| | **$M_{AMS}$** | **$M_{di\text{-}AMS}$** |
| 0 | 1.12435 | 1.54866 |
| 1 x 10$^{-6}$ | 1.09519 | 1.42697 |
| 1 x 10$^{-5}$ | 1.06603 | 1.05318 |
| 1 x 10$^{-4}$ | 0.993891 | 0.534079 |
| 1 x 10$^{-3}$ | 0.403558 | 0.17729 |
| 1 x 10$^{-2}$ | -1.64556 | -2.1469 |
| 5 x 10$^{-2}$ | -3.03746 | -2.59329 |

## S5. Principal component analysis (PCA) of the sensory fibres $F_{AMS}$ and $F_{di\text{-}AMS}$ after immersion in solutions of various concentrations of TNT in acetone:water (80:20, v:v)

**Table S6.** RGB parameters obtained from the digital images of sensory fibres cut from the sensory membranes.

| [TNT], M | Coated fabric | | | | | |
|---|---|---|---|---|---|---|
| | $F_{AMS}$ | | | $F_{di\text{-}AMS}$ | | |
| | **R** | **G** | **B** | **R** | **G** | **B** |
| 0 | 203 | 186 | 179 | 192 | 172 | 127 |
| 1 x $10^{-6}$ | 200 | 185 | 180 | 191 | 172 | 120 |
| 1 x $10^{-5}$ | 198 | 184 | 176 | 190 | 172 | 119 |
| 1 x $10^{-4}$ | 190 | 166 | 154 | 189 | 170 | 119 |
| 1 x $10^{-3}$ | 184 | 110 | 77 | 187 | 165 | 117 |
| 1 x $10^{-2}$ | 134 | 54 | 45 | 152 | 85 | 67 |
| 5 x $10^{-2}$ | 76 | 31 | 26 | 86 | 33 | 29 |

**Table S7.** Principal component analysis.

| Component | Coated fabric | | | | | |
|---|---|---|---|---|---|---|
| | $F_{AMS}$ | | | $F_{di\text{-}AMS}$ | | |
| | Eigenvalue | Variance, % | Cumulative, % | Eigenvalue | Variance, % | Cumulative, % |
| **PC1** | 2.86278 | 95.426 | 95.426 | 2.96515 | 98.838 | 98.838 |
| **PC2** | 0.134307 | 4.477 | 99.903 | 0.0322709 | 1.076 | 99.914 |
| **PC3** | 0.0029133 | 0.097 | 100.000 | 0.00258275 | 0.086 | 100.000 |

Standardised data; number of extracted components: 1

**Table S8.** Component weights.

| Variable | Coated fabric | |
|---|---|---|
| | $F_{AMS}$ | $F_{di\text{-}AMS}$ |
| | **PC1** | **PC1** |
| **R** | 0.564996 | 0.574487 |
| **G** | 0.58857 | 0.578256 |
| **B** | 0.578242 | 0.579297 |

**Table S9.** Principal components (PC1).

| [TNT], M | Coated fabric | |
|---|---|---|
| | $F_{AMS}$ | $F_{di\text{-}AMS}$ |
| 0 | 1.39733 | 1.09659 |
| 1 x $10^{-6}$ | 1.36123 | 0.972816 |
| 1 x $10^{-5}$ | 1.29447 | 0.942662 |
| 1 x $10^{-4}$ | 0.851999 | 0.907589 |
| 1 x $10^{-3}$ | -0.372394 | 0.795974 |
| 1 x $10^{-2}$ | -1.73784 | -1.31439 |
| 5 x $10^{-2}$ | -2.7948 | -3.40124 |

## S6. Detection of TNT vapours with a sensory membrane using the UV/Vis technique

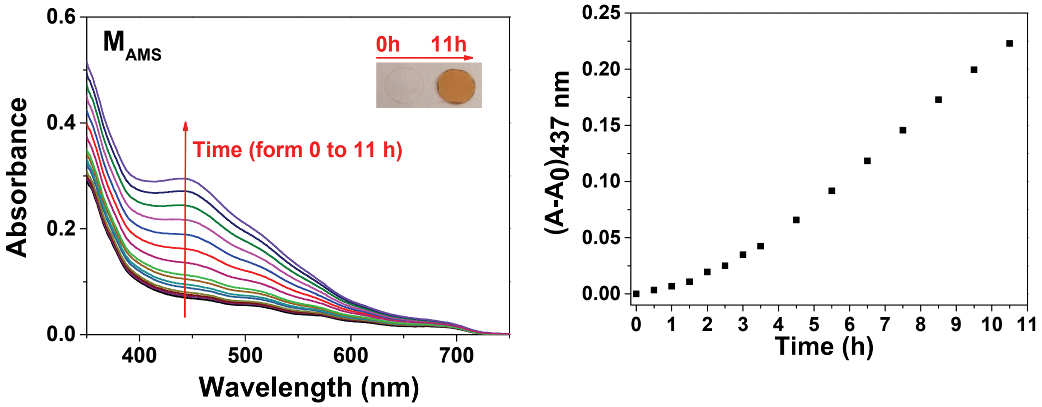


**Figure S9.** Detection of TNT with sensory membrane $M_{AMS}$ using the UV/Vis technique: a) UV/Vis spectra membrane $M_{AMS}$ in an atmosphere containing TNT vapour (inset: image of the sensory discs) and b) absorbance *vs.* time.