SUPPORTING INFORMATION

Water soluble polymers, solid polymer membranes, and coated fibres as smart sensory materials for the naked eye detection and quantification of TNT in aqueous media.

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S1. Characterisation of the sensory membranes

Table S1. TGA results analysis of films M_{100} , M_{50} , and M_{ref} (T_5 and T_{10} are the temperatures at which 5 and 10% weight loss are observed, T_{max} is the temperature at which the maximum or maxima weight loss rate takes place, and R is the char yield at 800°C).

Membrane	<i>T</i> ₅ , °C	<i>T</i> ₁₀ , °C	T _{max} °C	<i>R</i> , %			
M_{100}	288	311	334, 434	6			
M_{50}	250	267	271, 432	3			
M _{ref}	315	349	443	2			



Figure S1. TGA of sensory membranes: a) M_{100} , b) M_{50} , and c) M_{ref} .



Figure S2. FT-IR of films M₁₀₀, M₅₀, and M_{ref}.



S2. Characterisation of the sensory linear polymers

Figure S3. FTIR spectra of linear copolymers L_{100} , and L_{50} .



Figure S4. ¹H NMR spectra (CDCl₃) of linear copolymers L₁₀₀, and L₅₀.



Figure S5. TGA curves of linear copolymers L₁₀₀, and L₅₀.

Table S2. TGA results analysis of homo- and copolymer L_{100} , and L_{50} (T_5 and T_{10} are the temperatures at which 5 and 10% weight loss are observed, T_{max} is the temperature at which the maximum or maxima weight loss rate takes place, and R is the char yield at 800°C).

Linear polymer	<i>T</i> ₅ , °C	<i>T</i> ₁₀ , °C	T _{max} °C	<i>R</i> , %
L_{100}	280	301	326, 432	5
L_{50}	232	251	272, 421	0

S3. Colorimetric sensing of TNT with the monomer DMAEMA



Figure S6. Visual colorimetric detection of TNT by the monomer **DMAEMA** ($1x10^{-3}$ M). From left to right: blank, TNT, 2,4-DNT, 4-NT. The concentration of each nitroaromatic compound is $5x10^{-3}$ M.



Figure S7. ¹H NMR spectra of the monomer **DMAEMA** upon adding increasing concentrations of TNT: a) **DMAEMA** spectrum, b) experimental conditions and concentrations of the different NMR tubes, and c) expansion of the spectra.



Continuation of Figure S7. c) Expansion of the ¹H NMR spectra and d) TNT to **DMAEMA** molar ratio, [TNT]/[**DMAEMA**], *vs*. chemical shift of the dimethylamino group protons of the DMAEMA monomer.



Figure S8. UV/Vis spectra of solutions of the monomer **DMAEMA** $(1x10^{-3} \text{ M})$ and TNT $(5x10^{-3} \text{ M})$ in acetone and acetone:water (80:20). The pictures show the colour development upon adding 1 ml of TNT solution $(1x10^{-2} \text{ M})$ to 1 ml of a solution of the monomer **DMAEMA** $(2x10^{-3} \text{ M})$ in acetone and acetone:water (80:20).



Figure S9. TNT titration with **DMAEMA** $(1.2x10^{-3} \text{ M})$ upon increasing the concentration of TNT. The solvent used is acetone:water (80:20): a) selected UV/Vis spectra and b) titration curves (TNT concentration *vs.* absorbance at 437 nm; inset shows a digital picture of the **DMAEMA** solutions before and after finishing the TNT addition). The concentration of TNT ranges from $1x10^{-6}$ to $1x10^{-2}$ M.



S4. Colorimetric sensing of TNT with the sensory linear polymers L_{100} , and L_{50}

Figure S10. Titration of TNT with acetone:water (80:20, v:v) solutions of L_{100} : a) UV/vis spectra (inset: digital picture of the cuvettes before and after the TNT detection experiment) and b) titration curves (concentration of TNT *vs.* absorbance). The concentration of sensory dimethylamino motifs is 1.2 mEq/L and the concentration of TNT ranges from 8.0×10^{-6} to 1×10^{-2} M.



Figure S11. Titration of TNT with acetone:water (80:20, v:v) solutions of L_{50} : a) UV/vis spectra (inset: digital picture of the cuvettes before and after the TNT detection experiment) and b) titration curves (concentration of TNT *vs.* absorbance). The concentration of sensory dimethylamino motifs is 1.2 mEq/L and the concentration of TNT ranges from 8.0x10⁻⁶ to $1x10^{-2}$ M.

S5. Colorimetric sensing of TNT with the linear sensory membranes M_{100} and M_{50}



Figure S12. Digital picture of sensory discs cut from M_{ref} , M_{100} and M_{50} after dipping in a solution of nitroaromatic compounds (TNT, 2,4-DNT, 4-NT) in acetone:water (80:20, v/v) for 5 min. The concentration of each nitroaromatic compound is 1×10^{-2} M.



Figure S13. Detection kinetics of TNT ($1x10^{-2}$ M) with sensory membranes M_{100} and M_{50} : a) selected UV/Vis spectra along time and b) absorbance *vs.* time curves. The membranes have been immersed in acetone:water (80:20, v:v) containing a TNT concentration of $1x10^{-2}$ M.

S6. Principal component analysis (PCA) of the sensory discs





	Niembrane									
[TNT], M		M_{100}			M_{50}					
	R	G	В	R	G	В				
0	168	165	156	172	169	157				
1×10^{-6}	167	163	152	170	168	156				
1×10^{-5}	161	158	151	168	164	155				
1×10^{-4}	156	156	148	165	164	155				
1×10^{-3}	150	146	134	163	160	151				
1×10^{-2}	154	121	80	158	124	96				
5 x 10 ⁻²	119	24	4	98	10	1				

Table S3. RGB parameters obtained from the digital pictures of sensory discs cut from the sensory membranes.

Table S4. Principal component analysis.

		Membrane							
Component		M_{100}		\mathbf{M}_{50}					
	Figenvelue	Variance, Cumulative,		Figenvolue	Variance,	Cumulative,			
	Eigenvalue	%	%	Eigenvalue	%	%			
PC1	2.90552	96.851	96.851	2.96619	98.873	98.873			
PC2	0.0843368	2.811	99.662	0.0334387	1.115	99.988			
PC3	0.0101471	0.338	100.000	0.00036765	0.012	100.000			

Standardised data; number of extracted components: 1

Table S5. Component weights.

	Mem	brane
Variable	M ₁₀₀	M_{50}
	PC1	PC1
R	0.571505	0.575413
G	0.584248	0.580538
В	0.576226	0.576086

Table S6. Principal components (PC1).

	Membrane					
[11\1], 1\1	M_{100}	M_{50}				
0	1.25105	0.985446				
1×10^{-6}	1.15285	0.921585				
1×10^{-5}	0.878483	0.82776				
1×10^{-4}	0.652916	0.76167				
1×10^{-3}	0.188519	0.638403				
1x10 ⁻²	-0.512317	-0.371068				
5 x 10 ⁻²	-3.61149	-3.7638				

S7. Principal component analysis (PCA) of the sensory fibres

Table S7. RGB parameters obtained from the digital pictures of sensory fibres cut from the sensory membranes.

	Coated fabric								
LINIJ,	F ₆₁				\mathbf{F}_{47}		F ₂₇		
IVI	R	G	В	R	G	В	R	G	В
1×10^{-5}	168	154	153	164	151	150	165	151	148
1×10^{-4}	162	151	149	160	148	148	160	148	146
1×10^{-3}	159	145	144	159	144	139	158	144	141
1×10^{-2}	155	129	114	149	116	99	139	111	100
5 x 10 ⁻²	81	49	36	126	79	69	136	107	98

Table S8. RGB parameters obtained from the digital pictures of sensory discs cut from the sensory membranes.

	Coated fabric								
LINIJ,		F ₁₂			\mathbf{F}_{6}				
111	R	G	В	R	G	В			
1×10^{-5}	165	155	154	170	160	159			
1×10^{-4}	163	153	154	164	154	155			
1×10^{-3}	157	145	145	161	151	152			
1×10^{-2}	155	140	137	152	137	134			
5 x 10 ⁻²	148	118	107	145	126	119			

Table S9. Principal component analysis.

		Coated fabric							
Component	F ₆₁				\mathbf{F}_{47}				
	Eigenvalue	Variance,	Cumulative,		Eigenvalue	Variance,	Cumulative,		
	2-9	%	%		2-9	%	%		
PC1	2.97618	99.206	99.206	2.9	96306	98.769	98.769		
PC2	0.02355	0.785	99.991	0.0	0361794	1.206	99.975		
PC3	0.00027	0.009	100.000	0.0	000756642	0.025	100.000		

Standardised data; number of extracted components: 1

Table S10. Principal component analysis.

		Coated fabric							
Component		F ₂₇			F ₁₂				
Component	Figonwoluo	Variance, Cumulative,			Figenvelue	Variance,	Cumulative,		
	Eigenvalue	%	%		Eigenvalue	%	%		
PC1	2.99101	99.700	99.700	2.9	4582	98.194	98.194		
PC2	0.00860	0.286	99.995	0.0	535905	1.786	99.980		
PC3	0.00040	0.013	100.000	0.0	0059026	0.020	100.000		

	Coated fabric					
Component		\mathbf{F}_{6}				
Component	Figonyoluo	Variance,	Cumulative,			
	Eigenvalue	%	%			
PC1	2.9811	99.370	99.370			
PC2	0.0188424	0.628	99.998			
PC3	0.00005340	0.002	100.000			

Table S11. Principal component analysis.

Table S12. Component weights.

[TNT],	F ₆₁	F ₄₇	F ₂₇	F ₁₂	F ₆
Μ	PC1	PC1	PC1	PC1	PC1
R	0.57607	0.57582	0.575827	0.572549	0.576401
G	0.579598	0.580785	0.578467	0.581613	0.579166
В	0.576376	0.575431	0.577754	0.577853	0.576479

Table S13. Principal components (PC1).

[TNT],	Coated fabric						
Μ	F ₆₁	\mathbf{F}_{47}	\mathbf{F}_{27}	F ₁₂	\mathbf{F}_{6}		
1x10 ⁻⁵	1.13989	1.37874	1.58320	1.56208	1.79760		
1×10^{-4}	0.957436	1.13924	1.23744	1.31439	1.06064		
1×10^{-3}	0.771484	0.88032	0.92769	0.22548	0.65793		
1×10^{-2}	0.143318	-0.67341	-1.73157	-0.37759	-1.06760		
5 x 10 ⁻²	-3.01213	-2.72489	-2.01676	-2.72436	-2.44856		

S8. Experimental section

Materials

All materials and solvents were commercially available and used as received, unless otherwise indicated, and included the following: 2-(dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 98%), ethylene glycol dimethacrylate (EGDMMA, Aldrich, 99%), 2-hydroxyethyl acrylate (2HEA, Aldrich, 99%), 4-nitrotoluene (4-NT, Aldrich, 99%), 2,4-dinitrotoluene (2,4-DNT, Aldrich, 99%), DMSO (Merck, 99%), acetone (Aldrich, 99%), tetrahydrofuran (THF, Aldrich, 99%), and hexane (Aldrich, 99%). Azo-bis-isobutyronitrile (AIBN, Aldrich, 99%) was recrystallised twice from methanol. 2,4,6-trinitrotoluene (TNT) was prepared at a milligram scale from 2,4-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°C, it must be handled with care. Only 500-mg quantities of TNT were prepared to avoid risk).

Instrumentation

¹H and ¹³C-NMR spectra were recorded with deuterated dimethyl sulphoxide (DMSO- d_6) as the solvent using a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively.

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

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

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

Measurements

The solvent-swelling percentage (SSP) of the membrane was obtained from the weights of a dry sample membrane (ω_d) and a solvent-swelled sample membrane (ω_s) (the membrane was immersed in pure solvent at 20 °C until the swelling equilibrium was achieved) as follows: SSP = 100 x [(ω_s - ω_d)/ ω_d].

The TNT titration experiments with the sensory polymers L_{100} and L_{50} and the membranes M_{100} and M_{50} were carried out as follows. The membranes were dipped into acetone:water (Millipore-Q) (80:20, v:v) in a measuring cuvette. The linear polymers had been dissolved previously in water (Millipore-Q) and were then added to achieve an 80:20 (v:v) mixture of acetone:water (Millipore-Q); the concentration of sensory dimethylamino motif was 1.2×10^{-3} mEq/L. 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 (1x10⁻⁶ M, 1x10⁻⁵ M, 1x10⁻⁴ M, 1x10⁻² M, and 5x10⁻² M). The UV-Vis or fluorescence spectra were taken 10 min after each addition, a time adequate to allow the system to reach equilibrium.

Linear copolymer synthesis

The linear copolymers L_{100} and L_{50} were prepared by thermally initiated radical polymerisation according to the following experimental procedure. A nitrogen gas inlet and a reflux condenser, 6.36 mmol (1000 mg) of the sensory monomer (**DMAEMA**) for L_{100} or 3.18 mmol (500 mg) of the sensory monomer (**DMAEMA**) and 3.18 mmol (370 mg) of **2HEA** for L_{50} were dissolved in THF (6.4 mL) in a 50-mL three-necked flask equipped with a magnetic stirrer. Next, 0.64 mmol (105 mg,) of AIBN was added and the solution was heated to 55 °C. After stirring for 12 h under a nitrogen atmosphere, the solution was allowed to cool and added dropwise to hexane (150 mL) under vigorous stirring, yielding a white-pale yellow viscous precipitate. The polymers were purified by solving them in acetone twice and subsequently precipitating them in hexane. The final products were dried overnight at rt. The yields for both polymers ranged from 80-83% (0.8 g).

Membrane preparation

The film-shaped dense sensory membrane M_5 was prepared by the radical polymerisation of **2HEA**, the sensory monomer **DMAEMA**, and **EGDMMA** as a cross-linking agent. The co-monomer molar ratio **2HEA/DMAEMA/EGDMMA** was 50/50/10, and AIBN (1 wt.%) was used as a thermal initiator. The homogenous solution comprised of the comonomers and thermoinitiator were transferred to an ampoule, degassed by nitrogen bubbling for 15 min and injected into an oxygen-free atmosphere, a 100-µm-thick silanised glass hermetic mould. The thermoinitiated bulk polymerisation

was performed overnight in this mould at 60 °C. Next, the membrane was demoulded and conditioned by standing at room temperature in air for 48 h, followed by drying in a vacuum oven overnight at 20 °C. The final thickness of the membrane was 108 μ m.

The dense sensory membrane M_{100} was prepared in a similar manner, with a comonomer molar ratio **DMAEMA/EGDMMA** of 100/10.

A reference or blank membrane (**Mref**), lacking the sensory monomer **DMAEMA**, was prepared according to this procedure and using a feed co-monomer molar ratio **2HEA/EGDMMA** of 100/10.

The chemical structures are depicted in scheme 2.

Coating of cotton fibres with sensory TNT polymer

A conventional cotton fabric was cut into squares measuring 1 cm x 1 cm. The cut and weighed squares were immersed in an acetone solution comprised of the sensory monomer **DMAEMA**, with **EGDMMA** as a cross-linking agent, at a co-monomer molar ratio **DMAEMA** /**EGDMMA** of 100/10, along with the thermal radical initiator AIBN (1 wt.%). The squares were slightly wringed out between filter paper and dried at 60°C for 60 min. Next, they were introduced into vials and nitrogen was then gently bubbled. The vials were sealed and heated to 60°C overnight, during which polymerisation occurred on the surface of the fibres. The coated fibres of the sensory fabric squares were then dried at 60°C for 30 minutes and weighed again.

Following this procedure, and depending on the comonomer concentration of in the acetone solution, fabric containing 61% (\mathbf{F}_{61}), 47% (\mathbf{F}_{47}), 27% (\mathbf{F}_{27}), 12% (\mathbf{F}_{12}), and 6% (\mathbf{F}_{6}) by weight of polymer coating were obtained (Figure S14). The comonomer weight concentrations in the acetone solution that rendered these coatings were 100% (i.e., without solvent), 50%, 25%, 10%, and 5%, respectively.



Figure S15. Lab-coated cotton fabric. From left to right: F₆₁, F₄₇, F₂₇, F₁₂, and F₆.