Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Aromatic Polyamides and Acrylic Polymers as Solid Sensory Materials and Smart Coated Fibres for High Acidity Colorimetric Sensing

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S1. Experimental part. Intermediate and monomer synthesis and characterisation

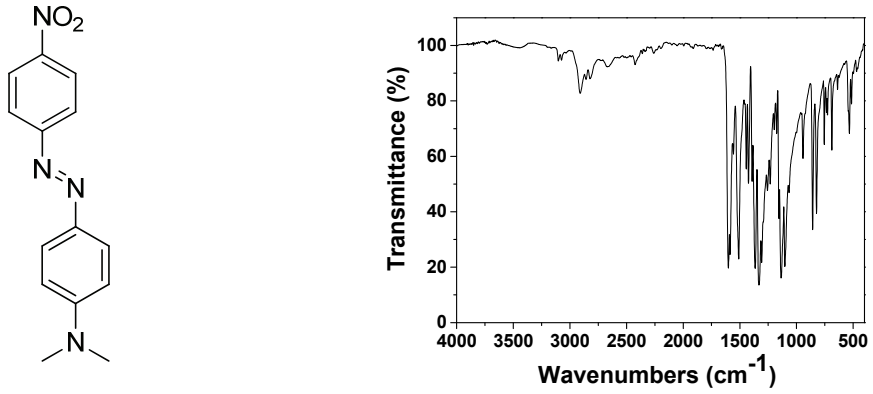
S1.1. Materials

All materials and solvents were commercially available and used as received, unless otherwise indicated: 4-nitroaniline (98%, Alfa Aesar), *N*,*N*-dimethylaniline (99%, Sigma-Aldrich), 5-aminoisophthalic acid (94% Sigma-Aldrich), hydrochloric acid (37%, Scharlau), sodium nitrite (≥ 98.5, AppliChem), potassium hydroxide (85%, Sigma-Aldrich), dioxane (99%, Probus), sodium sulphide nonahydrate (98%, Sigma-Aldrich), ethanol (99.97%, VWR-Prolabo), *N,N*-dimethylacetamide (DMA) (≥ 99%, Aldrich), aniline (99%, Sigma-Aldrich), 1-vinyl-2-pyrrolidone (VP) (≥ 99%, Sigma-Aldrich), 2-hydroxyethyl acrylate (2HEA) (96%, Sigma-Aldrich), ethylene glycol dimethacrylate (EGDMMA) (98%, Sigma-Aldrich), 2,2-dimethoxy-2-phenylacetophenone (99%, Sigma-Aldrich), and perchloric acid (70%, Panreac). Azo-bis-isobutyronitrile (AIBN, ≥ 98%, Aldrich) was recrystallised twice from methanol. *N*-Methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich) was vacuum-distilled twice over phosphorus pentoxide and then stored in the presence of 4 Å molecular sieves. Lithium chloride (≥ 99%, Sigma-Aldrich) was dried at 400ºC for 12 hours prior to use. Triphenylphosphite (TPP, ≥ 97%, Fluka) was vacuum-distilled twice, and then stored in the presence of 4 Å molecular sieves. Pyridine (≥ 99%, Probus) was dried under reflux over sodium hydroxide (≥ 98%, Prolabo) for 24 hours and distilled over 4 Å molecular sieves. *m*-Phenylenediamine (MPD) was purchased from Sigma-Aldrich (99%) and purified by double vacuum sublimation. Isophthalic acid was purchased from Fluka (99%) and was crystallised from water.

S1.2. Synthesis of sensory monomers

Synthesis of (E)-N,N-dimethyl-4-((4-nitrophenyl)diazenyl)aniline (1). A 1.38 g (10 mmol) sample of 4-nitroaniline was partially dissolved in a mixture of deionised water (4 mL) and concentrated aqueous HCl (4 mL) under heating in a water bath. After cooling in an ice bath, a solution of 0.69 g of sodium nitrite (10 mmol) in deionised water (2.5 mL) was added, and the mixture became homogeneous. After 1 h, an ice-cold solution of 1.21 g of *N*,*N*-dimethylaniline (10 mmol) in a mixture of deionised water (10 mL) and concentrated aqueous HCl (2 mL) were added dropwise for 30 min at 0–5 ºC. After stirring in an ice-water bath for 2 h, the mixture was neutralised with the proper amount of a 1 M KOH solution. The mixture was filtered and washed with deionised water. A red powder was obtained. Yield = 2.40 g (89%). M.p. = 240±1ºC. ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 8.40 (2H, d, *J* 9.1 Hz, Ph); 7.98 (2H, d, *J* 9.1 Hz, Ph); 7.90 (2H, d, *J* 9.2 Hz, Ph); 6.92 (2H, d, *J* 9.3 Hz, Ph); 3.15 (6H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 157.07, 154.36, 149.73, 143.73, 126.64, 125.73, 123.27, 112.52, 40.87. EI-LRMS m/z: 270.11 ($M^{+\bullet}$, 100), 148 (16), 121 (10), 120 (92), 105 (18), 104 (10), 79 (10), 77 (16), 42 (19). FTIR [Wavenumbers (cm^{-1})]: $\nu_{ar\ C\text{-}H}$: 2909; $\nu_{as\ NO2}$: 1509; $\nu_{s\ NO2}$: 1365; $\nu_{C\text{-}N}$: 1331.

a)



b)

c)

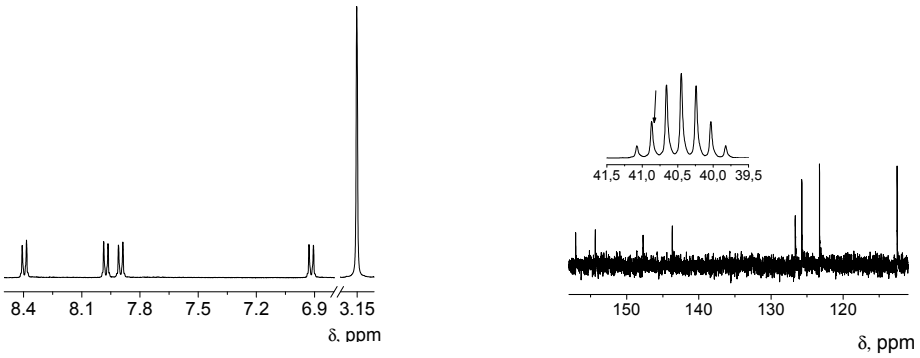


Figure S1. Characterisation of *N,N-dimethyl-4-((4-nitrophenyl)diazenyl)aniline* (**1**): a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6).

Synthesis of 4-((4-aminophenyl)diazenyl)-N,N-dimethylaniline (2). To a solution of 0.54 g (2.0 mmol) of (**1**) in 20 mL of dioxane, 1.58 g (6.6 mmol) of $Na_2S \cdot 9H_2O$ in 5 mL of H_2O at 75ºC was added portionwise. The mixture was heated at 80ºC and stirred under a nitrogen atmosphere for 45 minutes. Then, the mixture was diluted with 6 mL of water and stored at 4ºC for 16 hours. Afterward, the solid was filtered and washed with deionised water. The crude product was purified by recrystallisation from 50% ethanol to afford (**2**) as a brown solid. Yield = 0.37 g (77%). M.p. = 198±1ºC. ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 7.70 (2H, d, *J* 9.0 Hz, Ph); 7.60 (2H, d, *J* 8.7 Hz, Ph); 6.82 (2H, d, *J* 9.1 Hz, Ph); 6.68 (2H, d, *J* 8.7 Hz, Ph); 5.81 (2H, s, NH_2); 3.04 (6H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 152.17, 152.09, 144.08, 143.90, 124.86, 124.34, 114.36, 112.61. 40.85. EI-LRMS m/z: 240.14 ($M^{+\bullet}$, 100), 120 (45), 105 (8), 92 (27) 78 (35), 65 (8) 62 (34). FTIR [Wavenumbers (cm^{-1})]: ν_{NH2}: 3374-3206; δ_{NH2}: 1644.

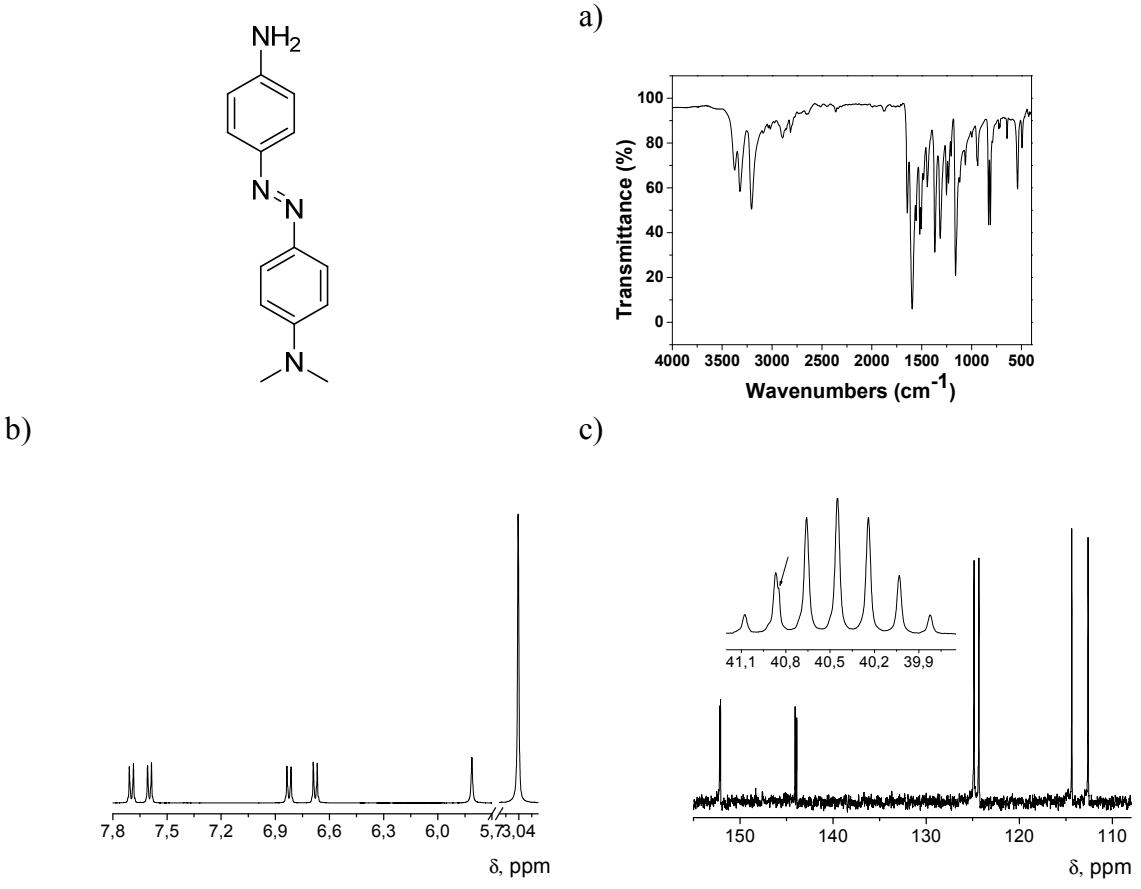


Figure S2. Characterisation of *4-((4-aminophenyl)diazenyl)-N,N-dimethylaniline* (**2**): a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6).

Synthesis of (E)-N-(4-((4-(dimethylamino)phenyl)diazenyl)phenyl)methacrylamide (3). A 1.43 g (5.95 mmol) sample of (**2**) was dissolved in 8 mL of NMP and stirred under a nitrogen atmosphere for 5 minutes. Then, 0.70 mL (7.14 mmol) of methacryloyl chloride was added dropwise The mixture was stirred at 50ºC for 12 hours and then precipitated in water. Finally, the precipitated brown solid formed was filtered. Yield = 1.25 g (68%). M.p. = 210±1ºC. ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 10.01 (1H, s, NH); 7.86 (2H, d, *J* 9.0 Hz, Ph); 7.76 (4H, dd, *J* 9.1 Hz, 2.0 Hz, Ph); 6.83 (2H, d, *J* 9.3 Hz, Ph); 5.84 (1H, s, $=CH_2$); 5.56 (1H, s, $=CH_2$); 3.05 (6H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 167.85, 153.14, 149.12, 143.55, 141.39, 141.20, 125.31, 123.30, 121.46, 121.18, 112.50, 40.77, 19.64. EI-LRMS m/z: 308.16 ($M^{+\bullet}$, 100), 239 (7), 160 (10), 148 (10), 121 (8) 120 (78), 105 (8) 40 (8). FTIR [Wavenumbers (cm^{-1})]: ν_{NH}: 3320; $\nu_{C=O}$: 1665; δ_{NH}: 1531.

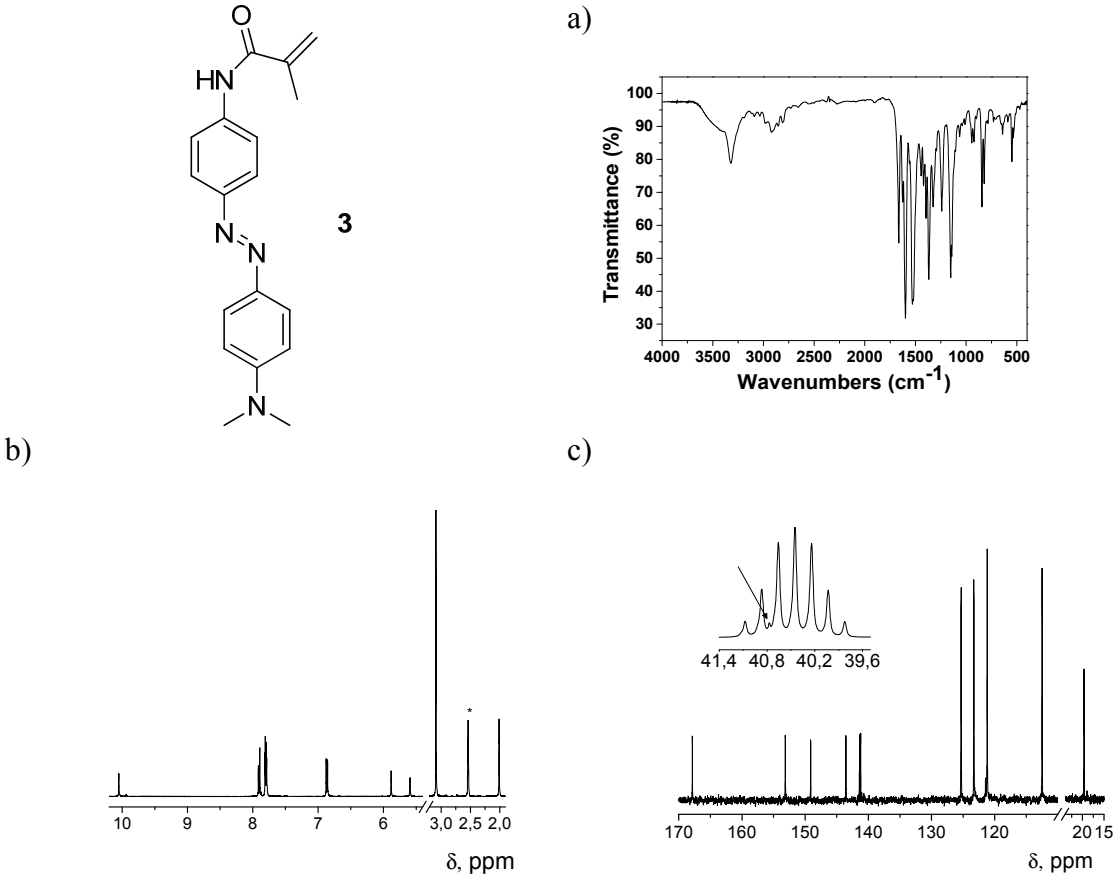


Figure S3. Characterisation of *N-(4-((4-(dimethylamino)phenyl)diazenyl)phenyl)methacrylamide* (**3**): a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6).

Synthesis of (E)-5-((4-dimethylamino)phenyl)diazenyl) isophthalic acid (4) 7.57 g (41.8 mmol) of 5-aminoisphthalic acid was dissolved in diluted hydrochloric acid (15% volume). A solution of 3.23 g (46.8 mmol) of sodium nitrite in 20 mL of water was then added. The mixture was stirred at 0ºC and 5.06 g (41.8 mmol) of *N*,*N*-dimethylaniline dissolved in an aqueous solution (30 mL) of 4.44 g of KOH (79.5 mmol) was added dropwise and the mixture was stirred for 3 hours. The red solid precipitate was filtered off and washed with water and acetone. Yield = 8.38 g (64%). M.p. = 237±1ºC. ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 13.51 (2H, s, COOH); 8.52 (1H, s, Ph); 8.50 (2H, s, Ph); 7.90 (2H, d, *J* 9.1 Hz, Ph); 6.89 (2H, d, *J* 9.1 Hz, Ph); 3.12 (6H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 167.18, 153.98, 153.61, 143.30, 133.39, 130.90, 126.89, 126.27, 112.2, 40.76. EI-LRMS m/z: 313.11 ($M^{+\bullet}$, 85), 181 (37), 148 (26), 136 (22), 122 (18) 120 (100), 106 (19) 69 (21). FTIR [Wavenumbers (cm^{-1})]: ν_{OH}: 3429-2553; $\nu_{C=O}$: 1694; ν_{C-N}: 1367.

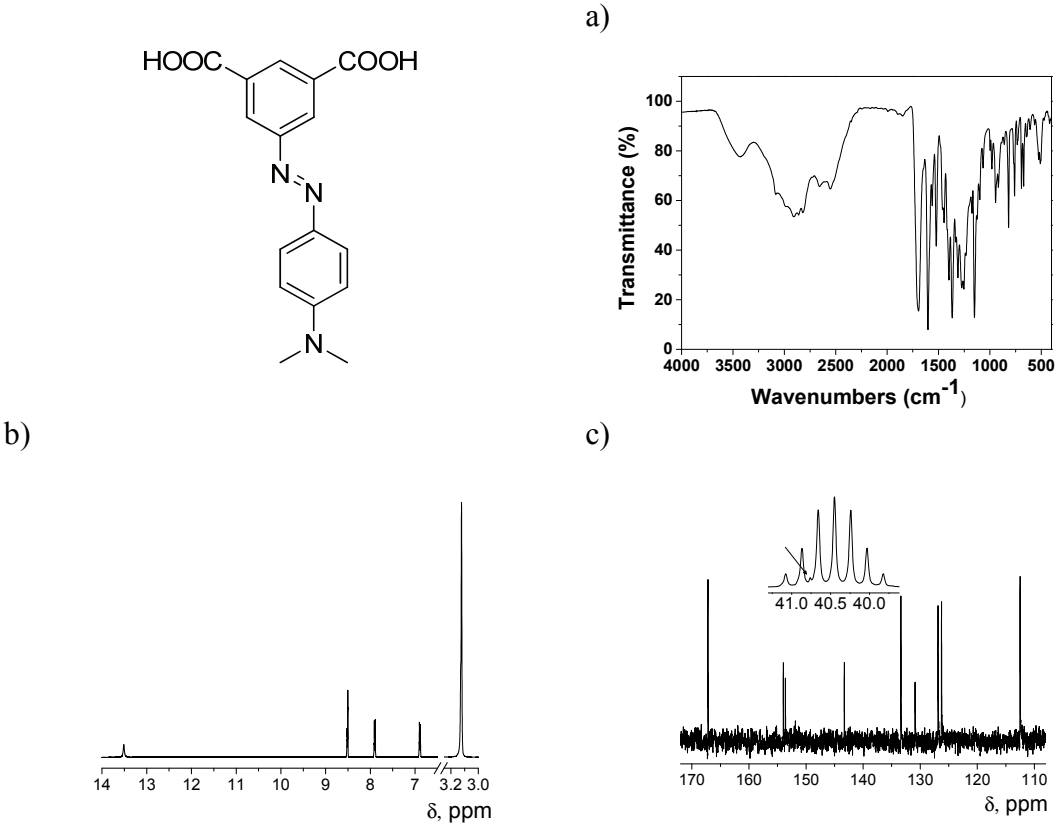


Figure S4. Characterisation of *(E)-5-((4-dimethylamino)phenyl)diazenyl) isophthalic acid* (**4**): a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6).

Synthesis of (E)-5-((4-(dimethylamino)phenyl)diazenyl)-N^1,N^3-diphenylisophthalamide (5). A 2.04-g (22 mmol) sample of aniline and 3.13 g (10 mmol) of **4** were dissolved in a mixture of 6 mL of pyridine, 5.81 mL (22 mmol) of TPP and 20 mL of NMP. The solution was stirred and heated at 110ºC under a dry nitrogen blanket for 4 hours. The system was then cooled at room temperature, and the solution precipitated in water. The dark brown oil formed was then stirred with methanol, filtered and washed with methanol to render a dark yellow solid. Yield = 2.64 g (57%). M.p. = 276±1ºC. ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 10.64 (2H, s, CONH); 8.63 (1H, s, Ph); 8.57 (2H, s, Ph); 7.94 (2H, d, *J* 8.6 Hz, Ph); 7.89 (4H, d, *J* 8.5 Hz, Ph); 7.43 (4H, t, *J* 7.7 Hz, Ph), 7.18 (2H, t, *J* 7.5 Hz, Ph), 6.91 (2H, d, *J* 8.8 Hz, Ph) 3.11 (6H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 165.56, 153.89, 153.37, 143.41, 139.93, 137.27, 129.62, 128.51, 126.17, 124.86, 124.45, 121.41, 112.57, 40.76. EI-LRMS m/z: 463.20 (M^+, 47), 331 (16), 239 (29), 148 (30), 121 (12) 120 (100), 78 (47) 69 (16) 63 (46). FTIR [Wavenumbers (cm^{-1})]: ν_{NH}: 3404-3284; $\nu_{C=O}$: 1647; δ_{N-H}: 1601.

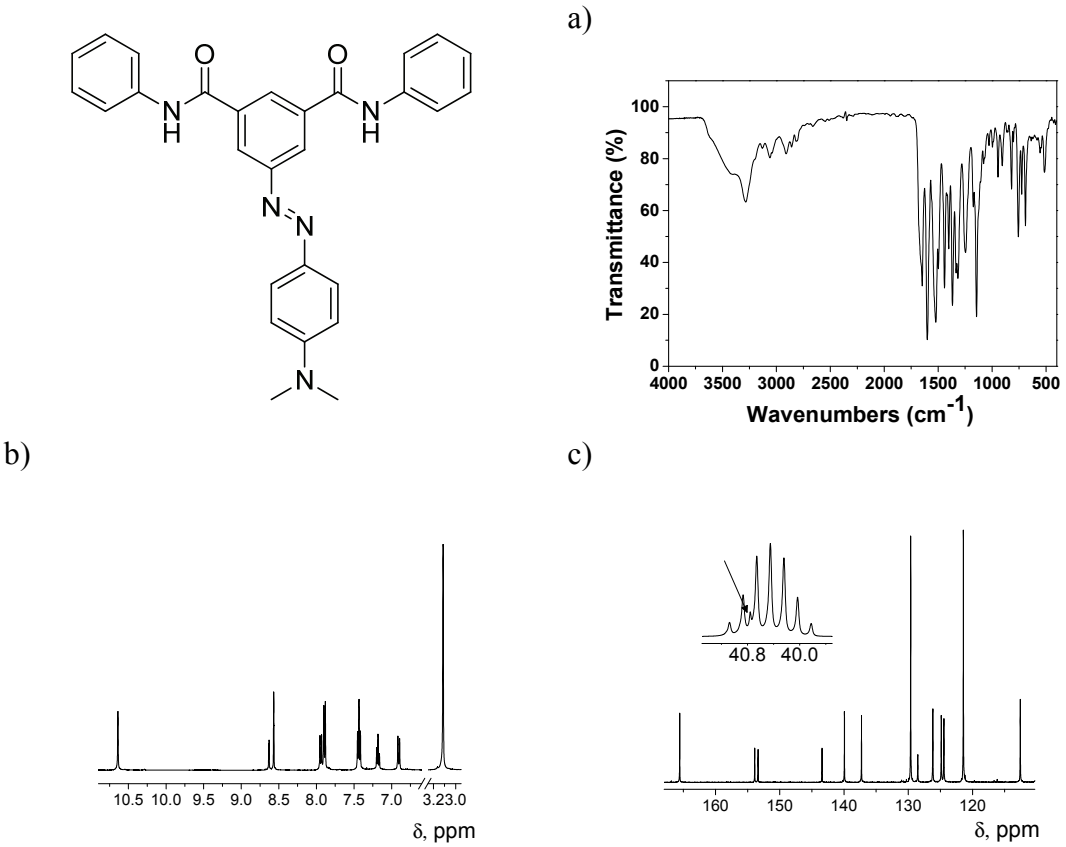


Figure S5. Characterisation of *5-((4-(dimethylamino)phenyl)diazenyl)-N1,N3-diphenylisophthalamide* (**5**): a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6).

S2. Experimental part. Preparation of sensory materials

S2.1. Linear aromatic polyamides (PA1 and PA2).

A typical polymerisation reaction is described as follows. In a three-necked flask fitted with a mechanical stirrer, 10 mmol of MPD, 10 mmol of diacid, and 1.4 g of lithium chloride were dissolved in a mixture of 6 mL of pyridine, 22 mmol of TPP, and 20 mL of NMP. The solution was then stirred and heated at 110ºC under a dry nitrogen atmosphere for 4 h. The system was then cooled to room temperature and the solution precipitated in 300 mL of methanol. The obtained polymer was filtered and washed with distilled water and acetone. It was then Soxhlet-extracted with acetone for 24 h and dried in a vacuum oven at 80ºC overnight. The homopolymer **PA1** was synthesised following this procedure using a 1:1 molar ratio of (5) and MPD, while the copolymer **PA2** was synthesised in a similar fashion using a 0.1:0.9:1.0 molar ratio of (5), isophthalic acid, and MPD.

S2.2. Crosslinked acrylic membrane (M1).

The sensory-dense membrane was prepared by the radical polymerisation of VP, 2HEA and the sensory monomer (3) using EGDMMA as the cross-linking agent (10%), and a co-monomer molar ratio VP/2HEA/(3)/EGDMMA of 74.9/25/0.1/10, respectively, as well as 2,2-dimethoxy-2-phenylacetatophenone (1 wt%) as photochemical initiator. The homogenous solution comprised of VP, 2HEA, (3), EGDMMA, and the photoinitiator were transferred to an ampoule, degassed by nitrogen bubbling for 15 min and injected into an oxygen-free atmosphere of a 100-μm thick silanised glass hermetic mould. In this mould, the photoinitiated bulk polymerisation was performed by irradiation with UV light at rt for 4 h (UV mercury lamp, 250w, Philips HPL-N, emission band in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm). The thickness of the membrane was 110 μm.

S2.3. Coating of cotton and aramid fibres with acidity sensory polymers.

Conventional cotton and high performance *p*-aramid (Kevlar®) and *m*-aramid (Nomex®) fabrics and yarns were coated with the aromatic polyamide PA1 and with a polyacrylic finishing polymer containing the sensory monomer (3). For coating with **PA1**, 1cm x 1cm squares of the fabrics and bundles of yarns were introduced in a solution of 5 mg of PA1 in 20 mL of DMA. Then, the fabrics and yarns were wrung out between two pieces of filter paper, air dried to remove the solvent, and then dried at 60ºC in a vacuum oven for 2h. For the polyacrylic coating, 1 cm x 1cm squares of the fabrics and yarns were immersed for 5 minutes in a solution comprised of 30% acetone, (3), and 2HEA (0.1:0.99 molar ratio) together with the crosslinking agent (5 mol%) and AIBN (1wt%) as the thermal radical initiator. They were then wrung out, air dried for 10 minutes, introduced into vials in which nitrogen was then bubbled for 5 minutes, and finally sealed and heated in an oven at 100ºC for 10 minutes. Both fabrics and yarns were previously cleaned with boiling acetone.

S3. Experimental part. Material characterisation

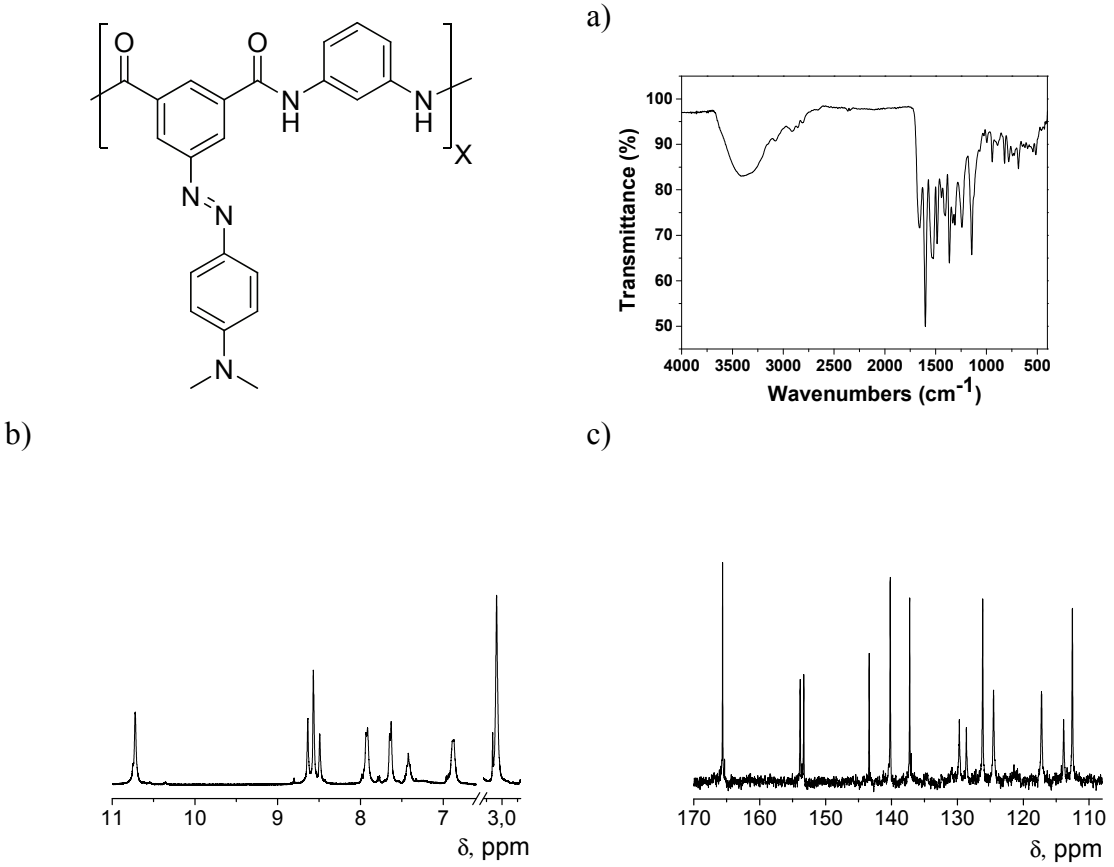


Figure S6. Characterisation of *homopolymer* **PA1**: a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6; the methyl region is not expanded because the carbon signal of the *N,N*-dimethyl amino group lay under the solvent peaks).

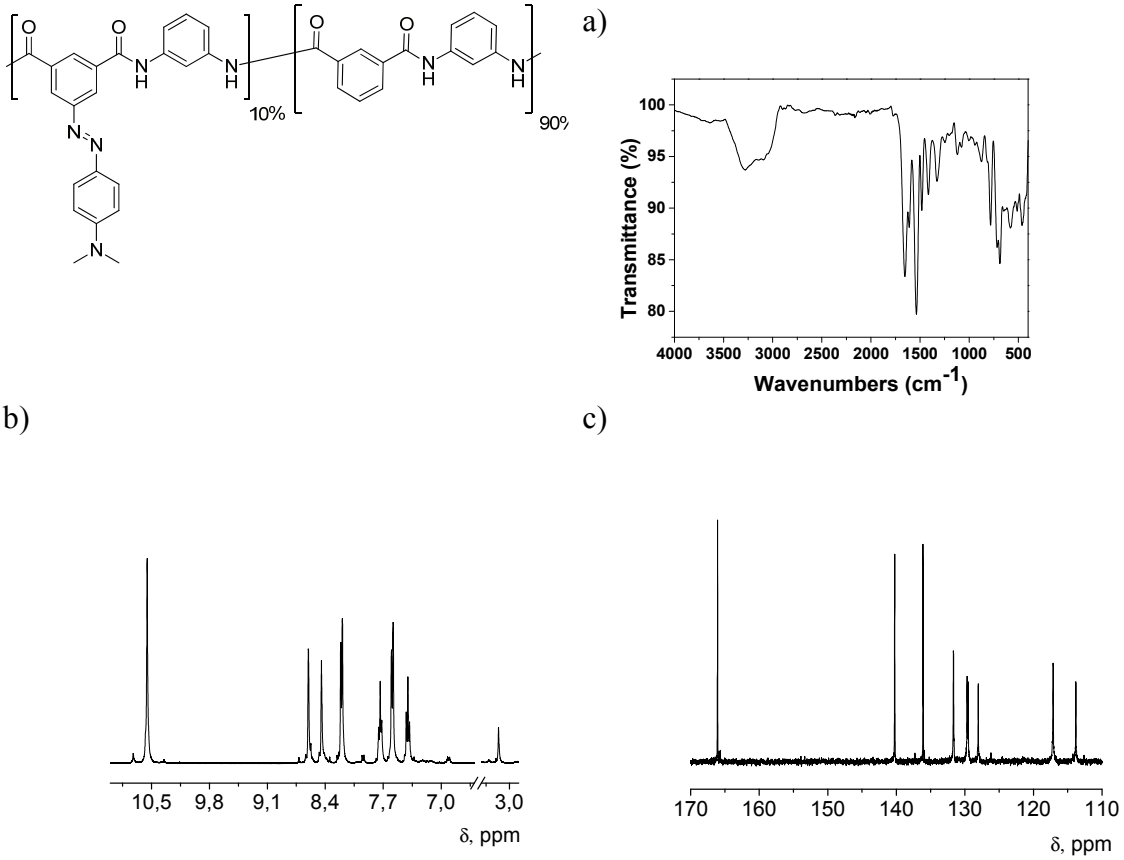


Figure S7. Characterisation of *copolymer* **PA2**: a) chemical structure; b) FT-IR; c) ^{1}H NMR; d) ^{13}C NMR (NMR solvent: DMSO-d_6; the methyl region is not expanded because the carbon signal of the *N,N*-dimethyl amino group lay under the solvent peaks).

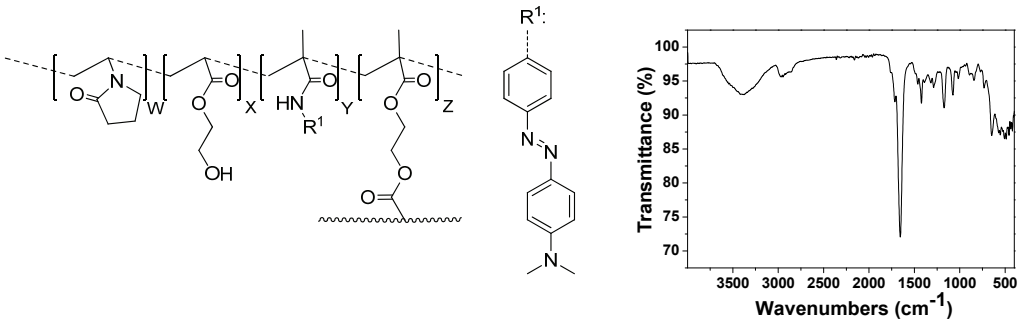


Figure S8. Characterisation of membrane **M1**: a) chemical structure; b) FT-IR.

S4. Correlation between the acidity function (H_0) and the concentration of perchloric and hydrochloric acids

Table S1. Correlation between the acidity function (H_0) and the perchloric acid concentration[1]

$[HClO_4]$, M	H_0	$[HClO_4]$, M	H_0
0.1	0.88	2.0	-0.84
0.5	0.02	2.5	-1.06
1.0	-0.32	3.0	-1.28
1.5	-0.60	3.5	-1.52

Table S2. Correlation between the acidity function (H_0) and the hydrochloric acid concentration[2]

[HCl], M	H_0	[HCl], M	H_0
0.1	0.980	5.5	-2.235
0.2	0.660	6.0	-2.434
0.3	0.463	6.5	-2.626
0.4	0.317	7.0	-2.821
0.5	0.199	8.0	-3.201
0.75	-0.031	8.5	-3.389
1.0	-0.213	9.0	-3.575
1.5	-0.509	9.5	-3.759
2.0	-0.762	10.0	-3.94
2.5	-0.993	10.5	-4.119
3.0	-1.212	11.0	-4.296
3.5	-1.424	11.5	-4.469
4.0	-1.631	12.0	-4.639
4.5	-1.835	12.5	-4.807
5.0	-2.035	13.0	-4.971

[1] K. Yates and H. Wai, *J. Am. Chem. Soc.*, 1964, **86**, 5408-5413.

[2] R. A. Cox, *Adv. Phys. Org. Chem.*, 2000, **35**, 1-66.

S5. Titration of perchloric acid

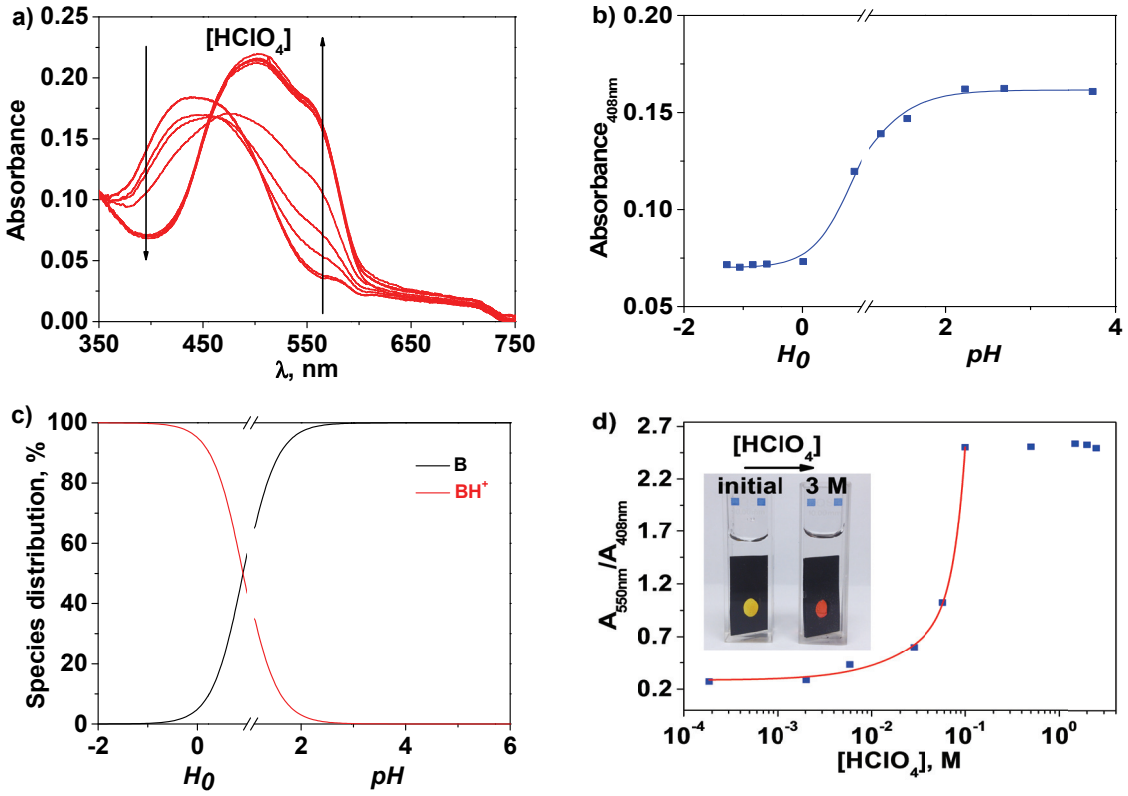


Figure S9. Titration of perchloric acid with a cast film of **PA1** in Millipore-Q water using the UV/Vis technique: a) UV/Vis spectra; b) acidity absorbance relationship at 408 nm (continuous lines correspond to the fitting using eqn 6); c) species distribution using eqn 10-11 assigning to C_T a value of 100; c) ratiometric titration curve of perchloric acid ([$HClO_4$] *vs.* absorbance at 550 and 408 nm ratio); inset: picture of the UV/vis cuvettes at the beginning and end of the experiment showing the colour change upon acidification of the medium.

S6. Titration of HCl vapours

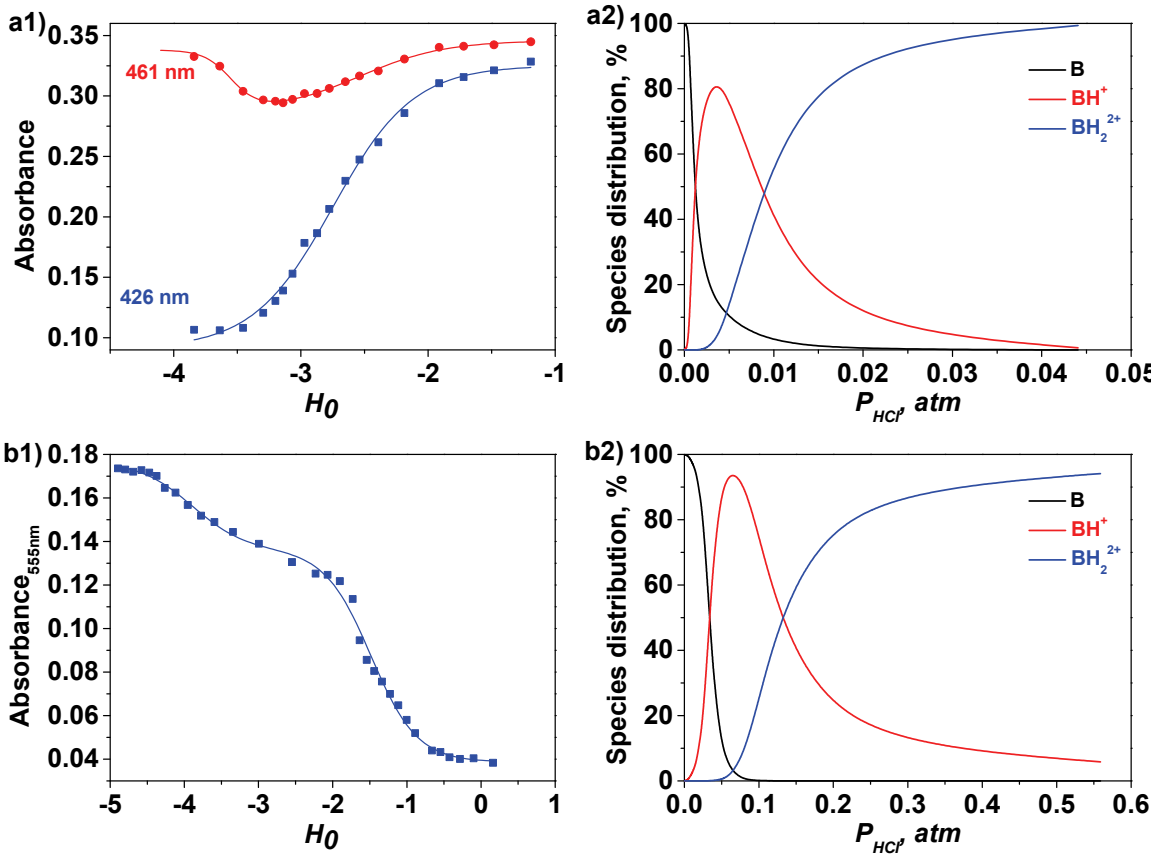


Figure S10. Titration of HCl vapours with the cast film of **PA1** and membrane **M1**: a1) **PA1**, UV/Vis acidity absorbance relationship at 461 and 426 nm (continuous lines correspond to the fitting using eqn 17 and 6, respectively). H_0 was calculated assuming a 10% hydration (10% by weight of water) of the film; a2) **PA1**, species distribution using eqn 10-11 assigning a value of 100 to C_T, assuming a 10% hydration of the film; b1) **M1**, UV/vis acidity absorbance relationship at 555 nm (continuous lines correspond to the fitting using eqn 17). H_0 was calculated assuming a 24% hydration (24% by weight of water) of the membrane; b2) **M1**, species distribution using eqn 10-11 assigning a value of 100 to C_T, assuming a 24% hydration of the membrane.

S7. pK_1 of monomer (3) and model (5) calculated by ^{1}H NMR

The pK_1 of monomer (**3**) and model (**5**) was studied by ^{1}H NMR in CD_3CN/D_2O (4mg in 1.3/0.7 mL) upon gradually increasing the acidity by adding deuterated hydrochloric acid. The acidity was determined after each addition of acid with a *pH* meter fitted with a glass micro-electrode. The *pD* was estimated using the equation $pD = pH + 0.40$.[3] The first protonation constants were calculated from the chemical shifts of different nuclei adapting the equation used in the UV/vis studies (eqn (6)). The second protonation processes were not observed because the acidity was not increased further due to experimental conditions.

$$\delta = \frac{\delta_B - \delta_{BH^+}}{1+10^{-n_1 pH + n_1 pK_1}} + \delta_{BH^+} \qquad \text{(S1)}$$

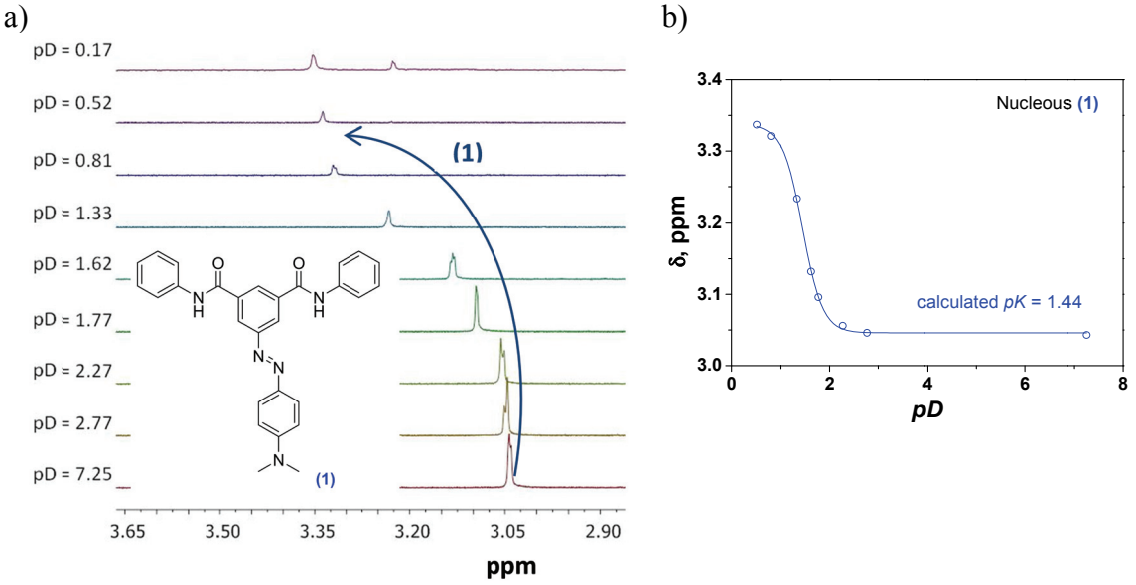


Figure S11. pK_1 of model **(5)**: a) expansion of the ^{1}H NMR spectra (methyl region) in CD_3CN/D_2O (1.3/0.7 mL) upon gradually increasing the acidity by adding deuterated hydrochloric acid; b) chemical shift of the methyl protons (the continuous line corresponds to the fitting using eqn S1 that yielded a pK_1 of 1.44).

[3] D.D. Perrin, B. Dempsey; Buffers for pH and Metal Ion Control; cap. 6.5 and 6.7; Chapman and Hall Ltd, 1974.

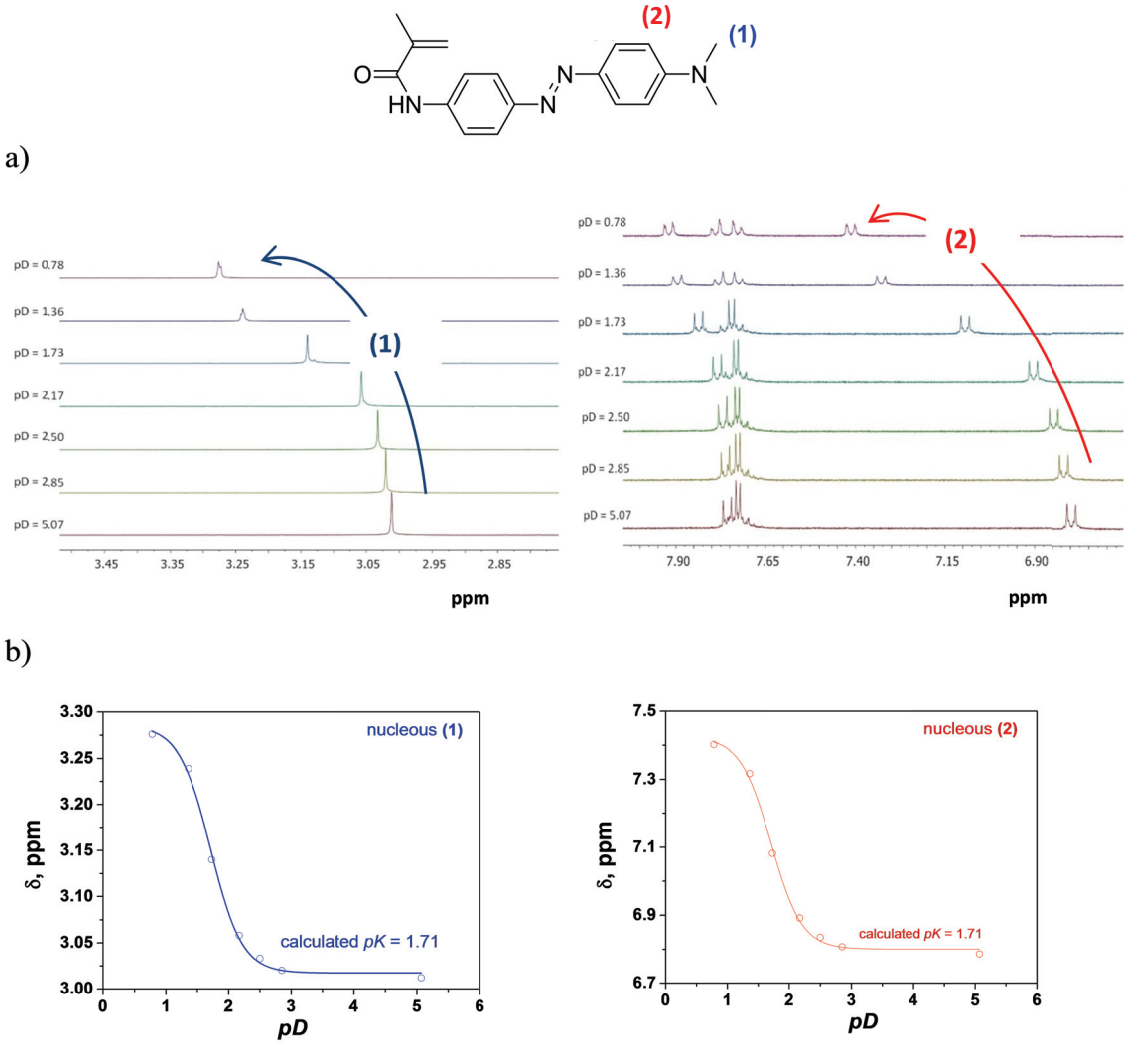


Figure S12. pK_1 of monomer **(3)**: a) expansion of the ^{1}H NMR spectra (aromatic-olephinic and methyl regions) in CD_3CN/D_2O (1.3/0.7 mL) upon gradually increasing the acidity by adding deuterated hydrochloric acid; b) chemical shift of the methyl and selected aromatic protons (the continuous lines correspond to the fitting using eqn S1 that yielded a pK_1 of 1.71).

S8. Response time

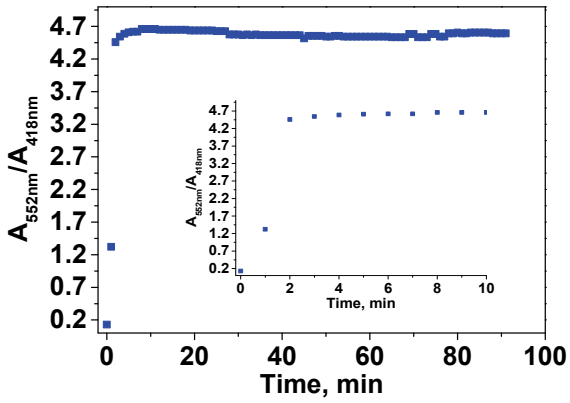


Figure S13. Response time (time *vs.* absorbance) of sensory membrane **M1** after immersion in acidic water (1M $HClO_4$).

S9. Interference study

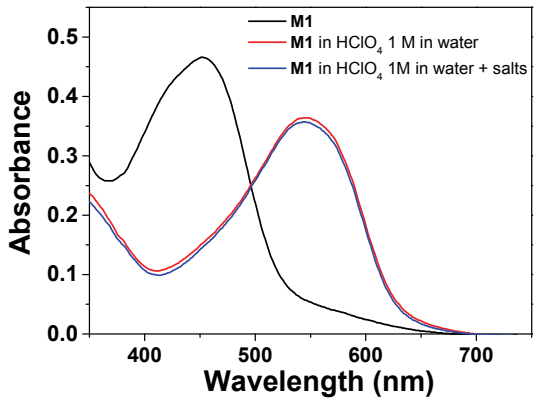


Figure S14. Interference study. UV/vis spectra of the membrane M1, after immersion in 1 M $HClO_4$ in water, and in a solution of salts (NaCl, KCl, $CuSO_4.5H_2O$, $Co(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, $Pb(ClO_4)_4$, $FeSO_4.7H_2O$, LiCl, $Zn(NO_3)_2.6H_2O$, $Hg(NO_3)_2.H_2O$, $Ni(NO_3)_2.6H_2O$) in 1 M $HClO_4$ in water (concentration of each salt = $1x10^{-3}$ M.