

SUPPLEMENTARY INFORMATION

Polymer chemosensors as solid films and coated fibres for extreme acidity colourimetric sensing

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S1. Experimental part. Intermediate and monomer characterisation

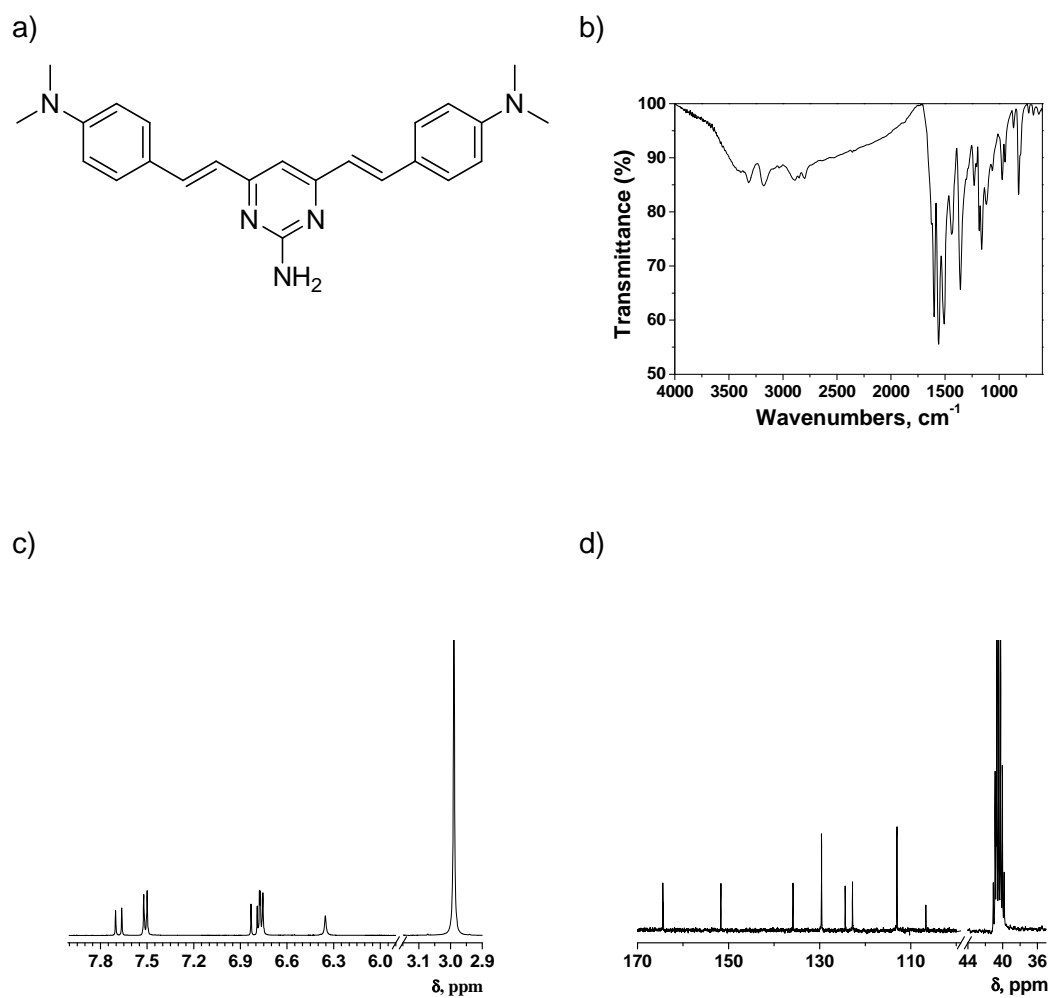


Figure S1. Characterisation of 4,4'-(2-aminopyrimidine-4,6-diyl)bis(ethene-2,1-diyl)bis(*N,N*-dimethylaniline) (**1**): a) chemical structure, b) FT-IR spectrum, c) ^1H NMR spectrum, d) ^{13}C NMR spectrum (NMR solvent: $\text{DMSO-}d_6$).

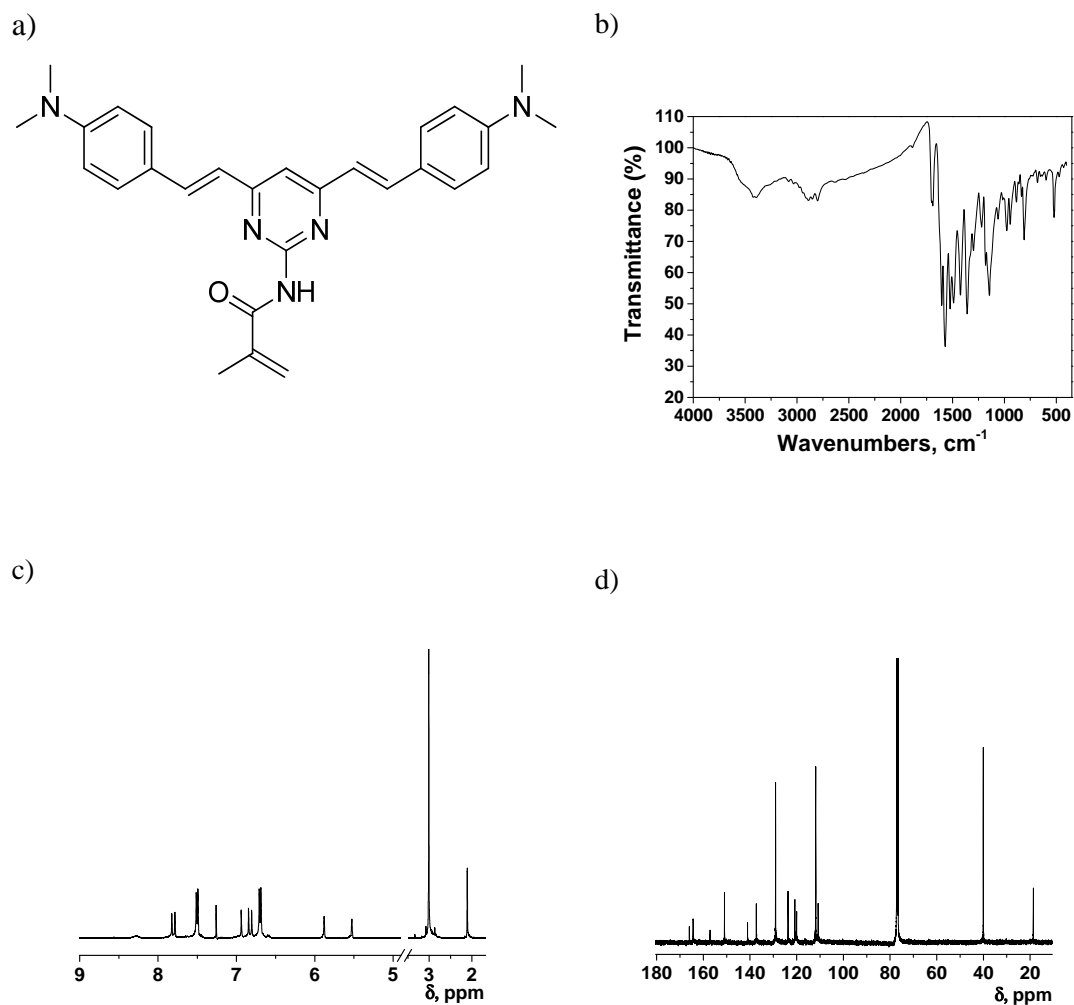


Figure S2. Characterisation of *N*-(4,6-bis(4-(dimethylamino)styryl)pyrimidin-2-yl)methacrylamide (**M1**): a) chemical structure, b) FT-IR spectrum, (c) ^1H NMR spectrum, d) ^{13}C NMR spectrum (NMR solvent: CDCl_3).

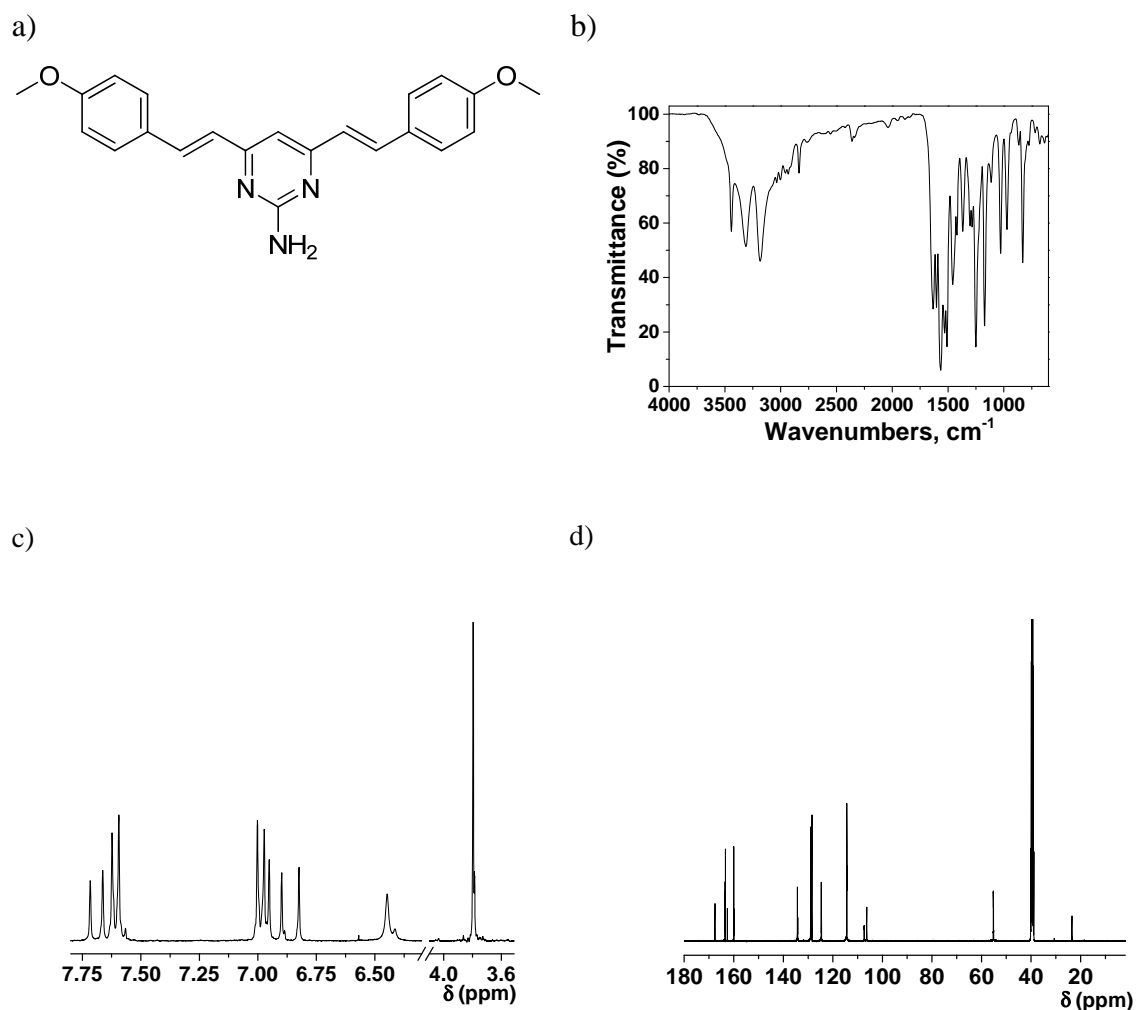


Figure S3. Characterisation of *4,6-bis(4-methoxystyryl)pyrimidin-2-amine* (**2**): a) chemical structure, b) FT-IR spectrum, c) ^1H NMR spectrum, d) ^{13}C NMR spectrum (NMR solvent: $\text{DMSO-}d_6$).

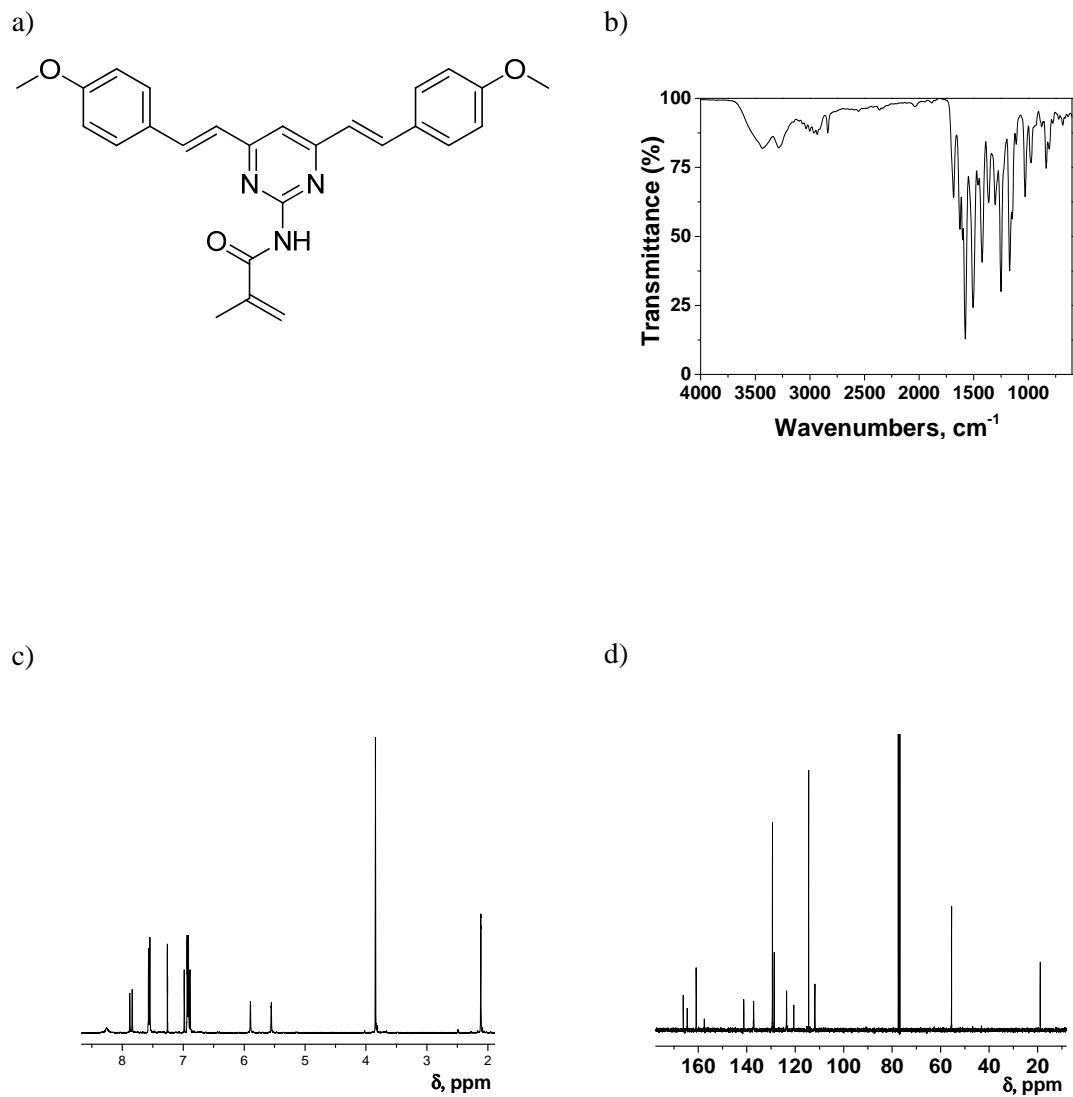


Figure S4. Characterisation of *N*-(4,6-bis((*E*)-4-methoxystyryl)pyrimidin-2-yl)methacrylamide (**M2**): a) chemical structure, b) FT-IR spectrum, c) ^1H NMR spectrum d) ^{13}C NMR spectrum (NMR solvent: CDCl_3).

S2. Experimental part. Material characterisation

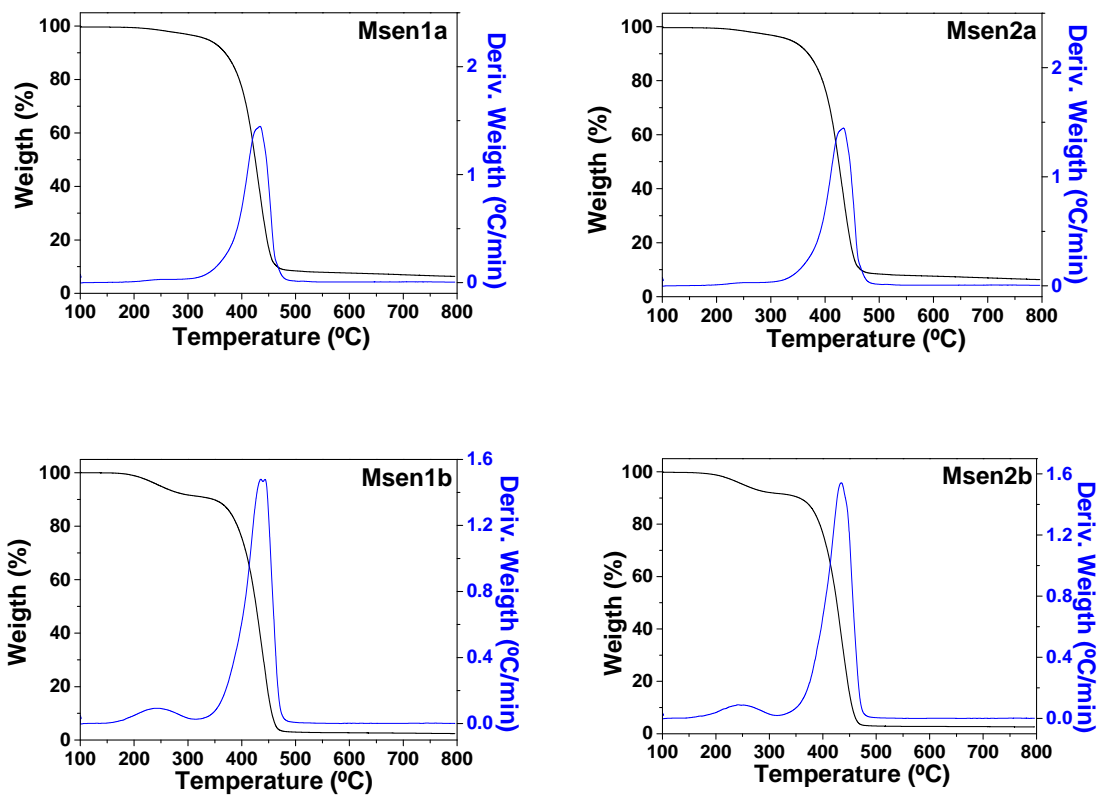


Figure S5. Thermogravimetric data for membranes. Measurements from 100°C to 800°C at a heating rate of 10°C/min in nitrogen atmosphere.

Table S1. Values obtained by TGA analysis, T_5 (°C), T_{10} (°C), T_{onset} (°C) and residue.

Membrane	T_5 (°C)	T_{10} (°C)	T_{ONSET} (°C)	Char yield (%)
M1	336	369	248	6
M2	250	348	197	3
M3	339	372	250	5
M4	253	356	202	3

S3. Correlation between the acidity function (H_0) and the concentration of perchloric acid

Table S2. Correlation between the acidity function (H_0) and the perchloric acid concentration¹

$[\text{HClO}_4], \text{M}$	H_0	$[\text{HClO}_4], \text{M}$	H_0
0.1	0.88	8.5	-4.74
0.5	0.02	9.0	-5.16
1.0	-0.32	9.2	-5.34
1.5	-0.60	9.4	-5.51
2.0	-0.84	9.6	-5.70
2.5	-1.06	9.8	-5.88
3.0	-1.28	10.0	-6.07
4.0	-1.74	10.2	-6.26
5.0	-2.26	10.4	-6.45
5.5	-2.58	10.6	-6.65
6.0	-2.89	10.8	-6.85
6.5	-3.22	11.0	-7.06
7.0	-3.57	11.2	-7.27
7.5	-3.94	11.4	-7.48
8.0	-4.33	11.6	-7.67

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

S4. Titration of perchloric acid

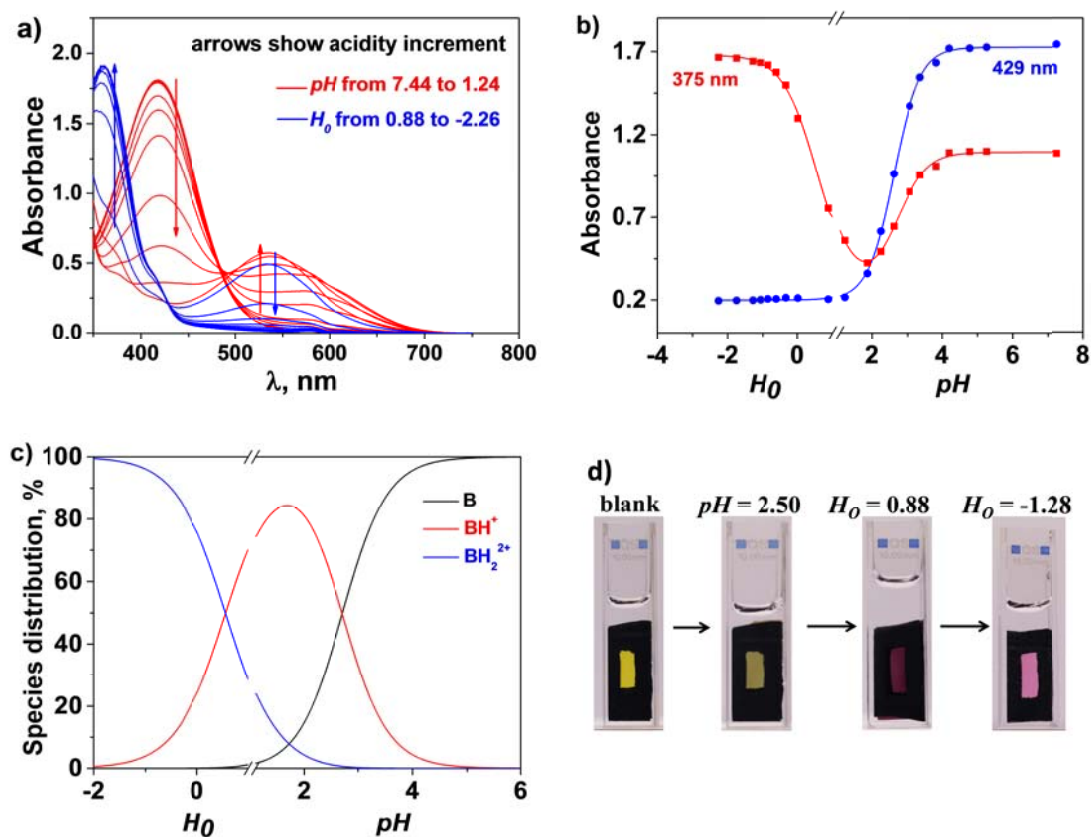


Figure S6. Titration of perchloric acid with Mem1a in MilliQ water using UV/Vis technique: a) UV/Vis spectra showing the two protonation processes (low and higher acidity in red and blue, respectively); b) acidity absorbance relationship at 375 and 429 nm (continuous lines correspond to the fitting using Eq. 17 and 6, respectively); c) species distribution using Eqs. 10-11 assigning to C_T a value of 100; d) photographs of the sensory material showing the colour during the titration experiment.

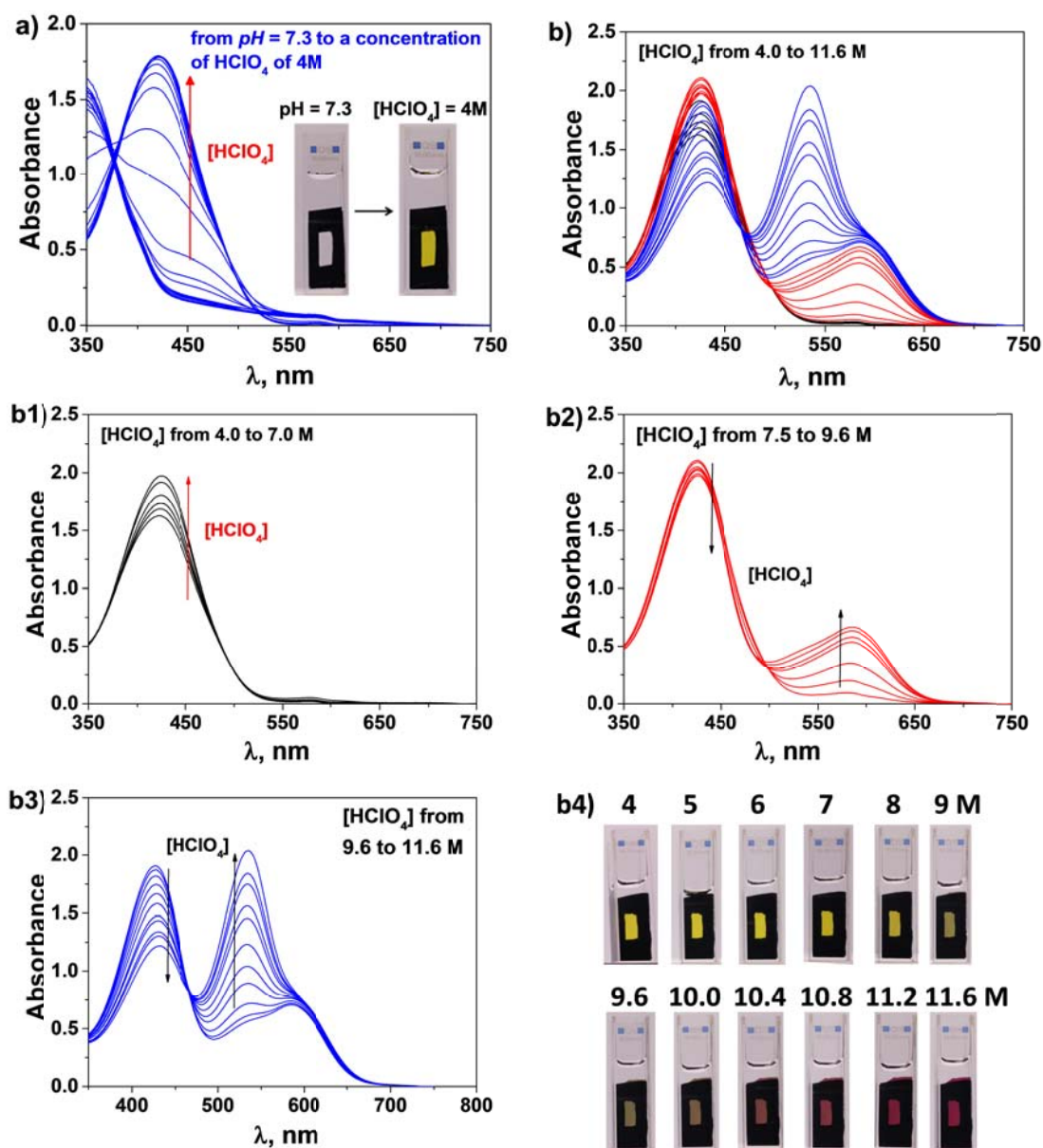


Figure S7. Titration of perchloric acid with **Mem2b** in MilliQ water using UV/Vis technique: a) UV/Vis spectra showing the first protonation process (inset: photograph of the sensory material inside the cuvette); b) UV/Vis spectra showing the second, third and fourth protonation processes. These processes are shown isolated as b1), b2) and b3), respectively, and photographs of the sensory materials during titration are depicted as b4) together with the perchloric acid concentration.

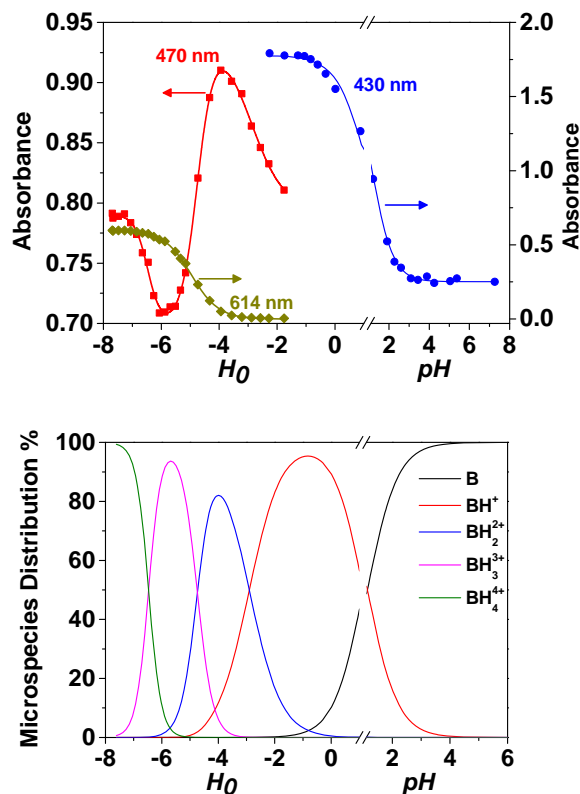


Figure S8. Titration of perchloric acid with **Mem2b** in MilliQ water using UV/Vis technique: a) acidity absorbance relationship. The process at 430 nm shows the first protonation process and that at 470 shows the concomitant second, third and fourth protonation processed (continuous lines correspond to the fitting using Eq. 18). The absorbance data at 614 nm are useful for determining the acidity of a system taking a single UV/Vis spectrum (the continuous lines correspond to the fitting using Eq. 6); b) species distribution using Eqs. 10-11 assigning to C_T a value of 100.

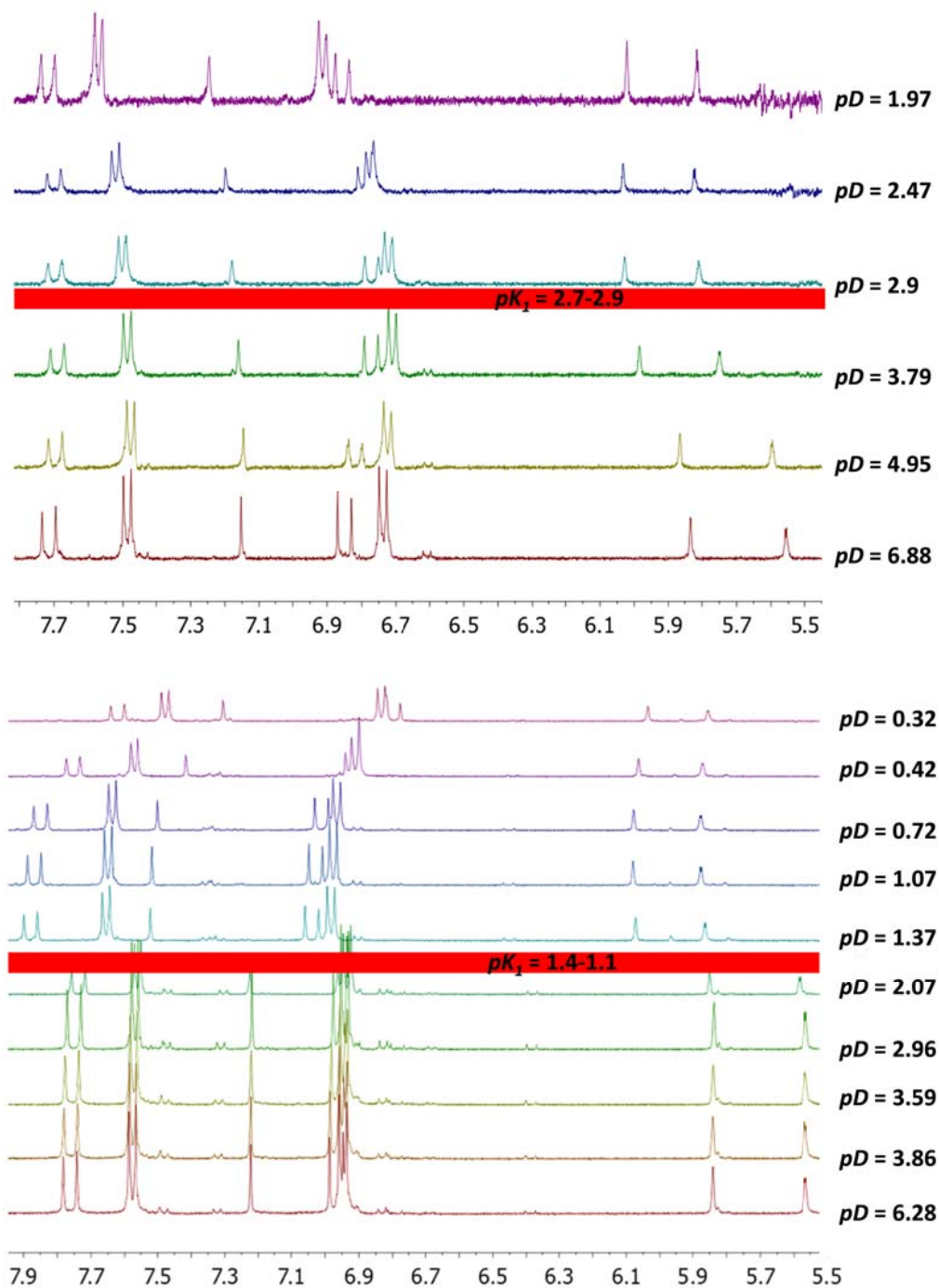


Figure S9. Expansion of the ^1H NMR spectra (aromatic and olefinic region) of **M1** (top) and **M2** (bottom) in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (1.3/0.7 mL) upon gradually increasing the acidity by adding deuterated hydrochloric acid. The horizontal red lines indicate the pK_1 calculated for the membranes prepared from **M1** and **M2** (see main manuscript, Table 1).

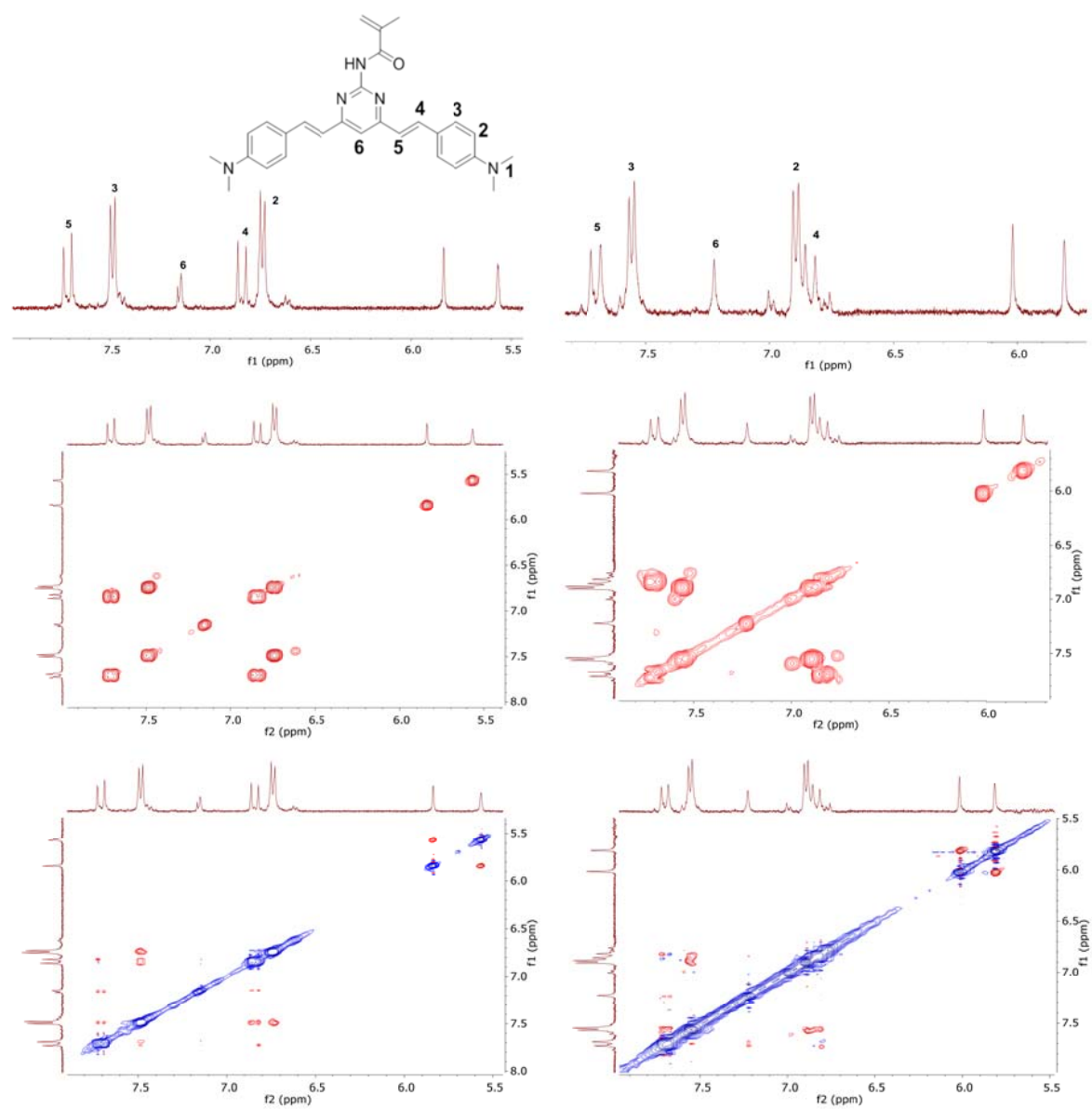


Figure S10. ^1H NMR, COSY 2D and NOESY 2D, from top to bottom, of monomer **M1** under neutral ($pD = 6.88$) and acidic ($pD = 1.97$) conditions, left and right, respectively. Solvent = $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (1.3/0.7 mL).

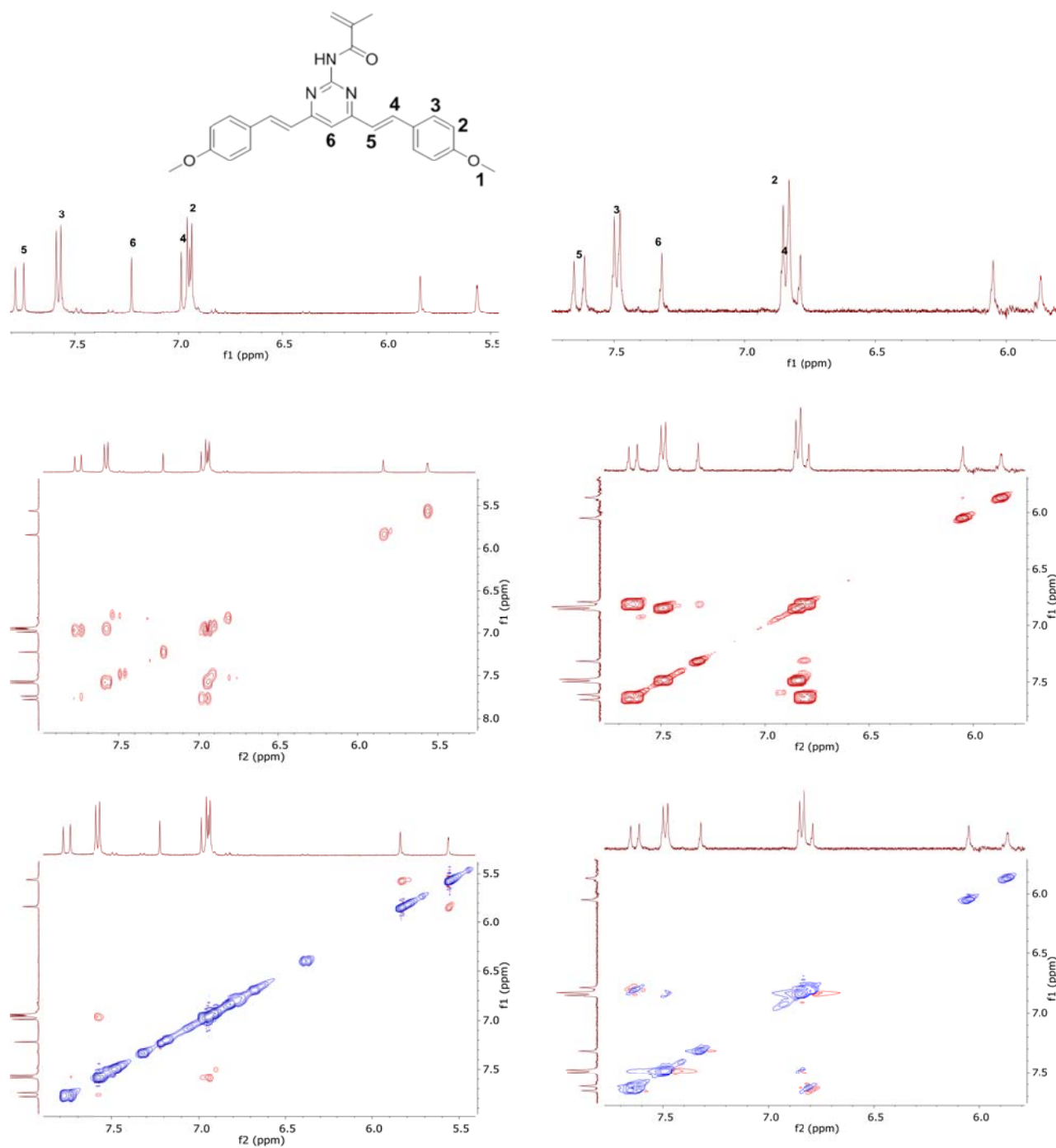


Figure S11. ^1H NMR, COSY 2D and NOESY 2D, from top to bottom, of monomer **M2** under neutral ($pD = 6.88$) and acidic ($pD = 1.97$) conditions, left and right, respectively. Solvent = $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (1.3/0.7 mL).

S5. Interference study.

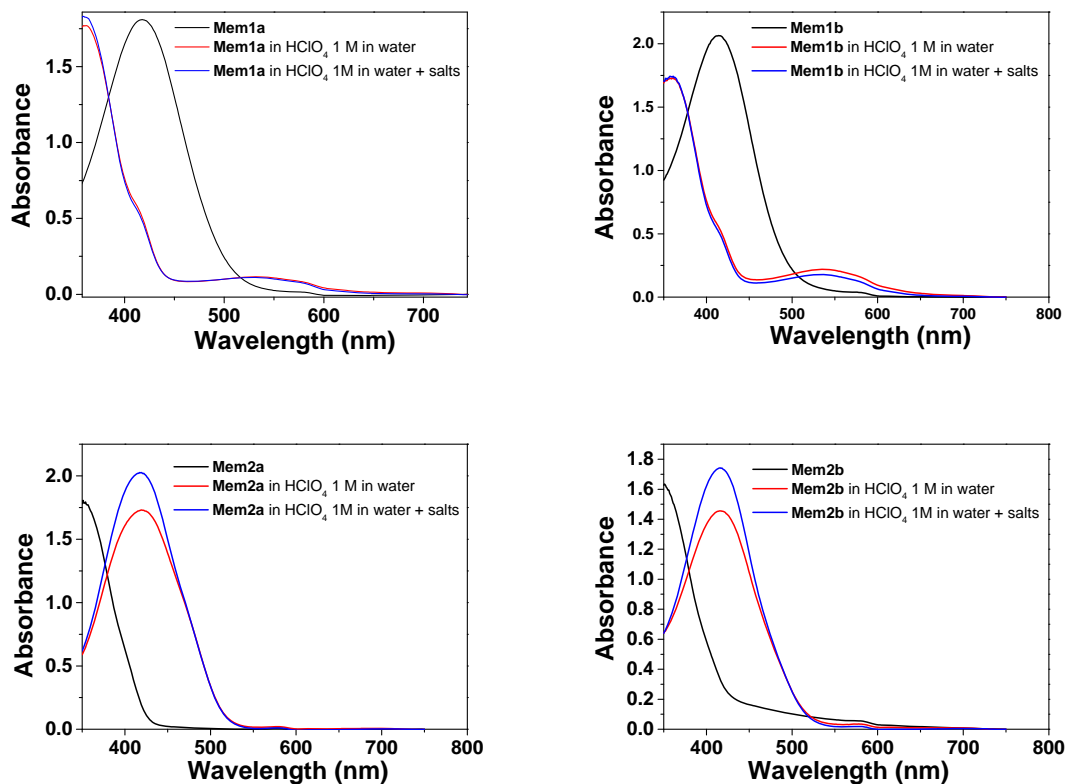


Figure S12. Interference study. UV/Vis spectra of the dry membranes and after immersion in 1 M HClO₄ in water and in a solution of salts (NaCl, KCl, CuSO₄·5H₂O, Co(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Pb(ClO₄)₄, FeSO₄·7H₂O, LiCl, Zn(NO₃)₂·6H₂O, Hg(NO₃)₂·H₂O, Ni(NO₃)₂·6H₂O) in 1 M HClO₄ in water. The concentration of each salt was 1 x 10⁻³ M.

S6. Reuse and stability of the sensory membranes

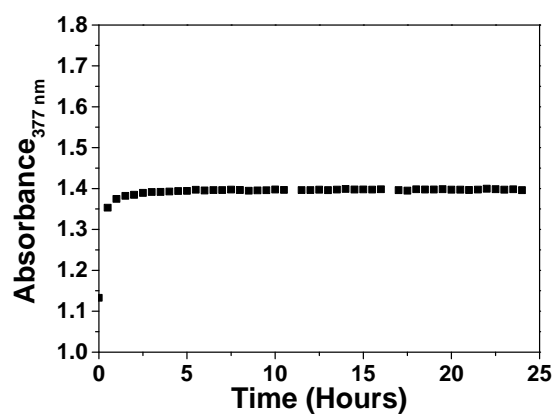


Figure S13. Stability study of **Mem1a** immersed in acidic water (HClO_4 1 M) with time analysed by UV/Vis.

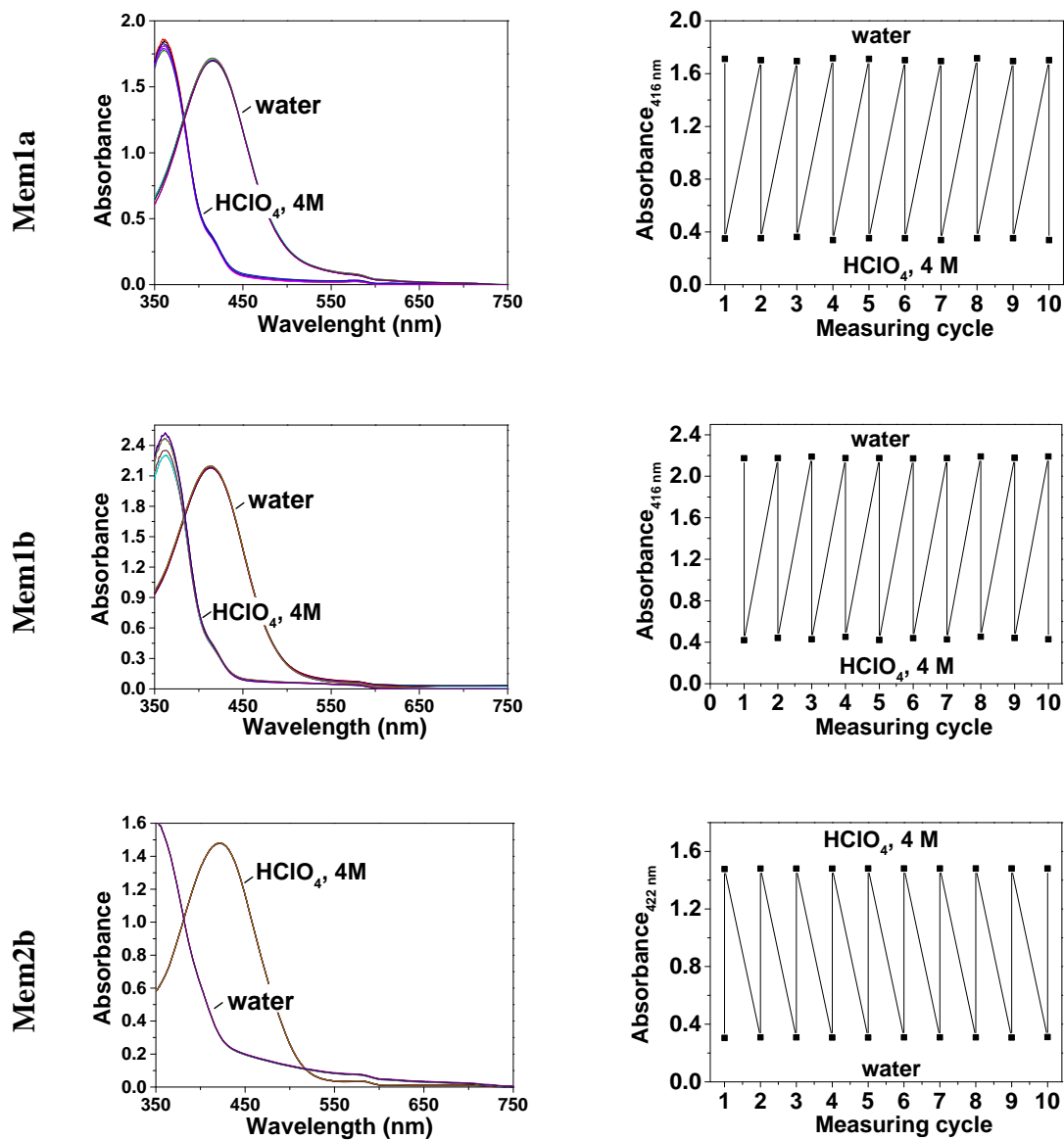


Figure S14. Reproducibility and reversibility of **Mem1a**, **Mem1b**, **Mem2b** as acidity sensors analysed by UV/Vis spectroscopy (left: UV/Vis spectra; right: absorbance vs. measuring cycle). The measurements were performed by successive cycles of dipping the material in highly acidic water, HClO₄ 4 M, followed by washing with pure water. The time of each cycle was approximately 30 min, 10 min in the acid medium and 20 min for washing.

S7. Response time

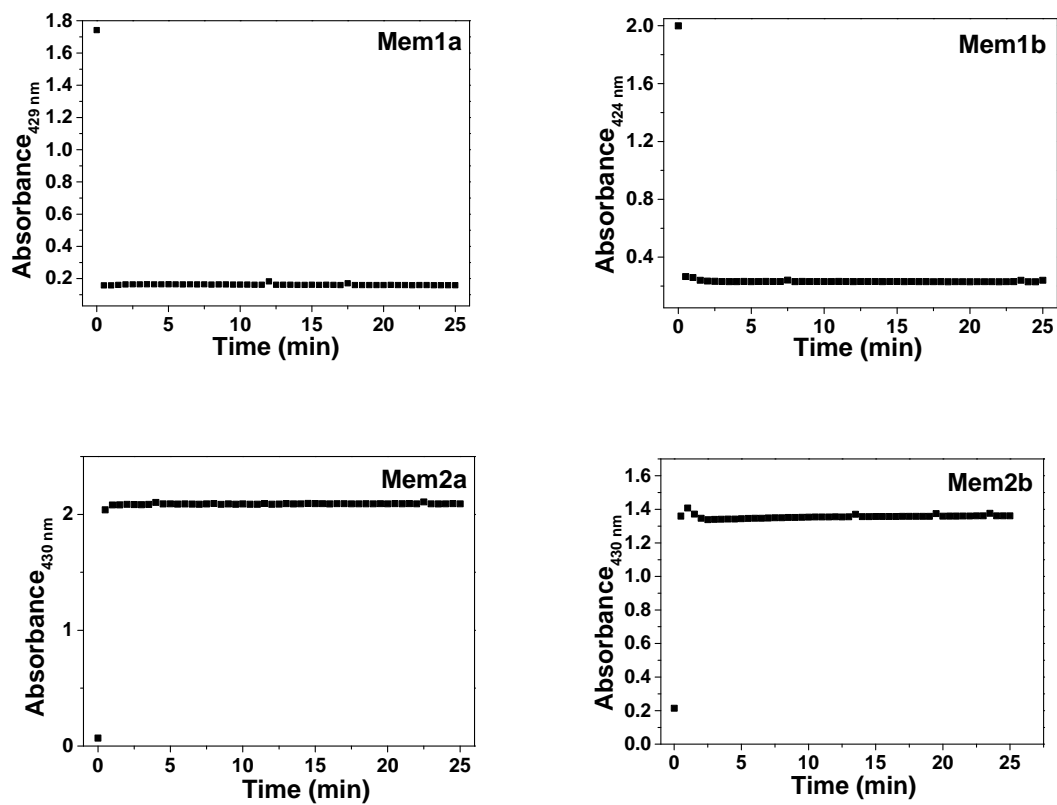


Figure S15. Response time (time vs. absorbance) of sensory membranes after immersion in acidic water (1 M HClO₄).