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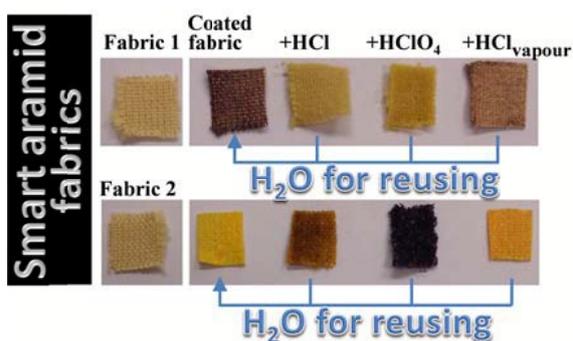
Polymer chemosensors as solid films and coated fibres for extreme acidity colourimetric sensing

Jesús Luis Pablos,^{1,*} Pedro Estévez,² Asunción Muñoz,¹ Saturnino Ibeas,¹ Felipe Serna,¹ Félix Clemente García¹ and José Miguel García^{1,*}

¹ Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza de Misael Bañuelos s/n, 09001 Burgos, Spain. Fax: (+) 34 947 258 831, Tel: (+) 34 947 258 085. E-mail: jlpablos@ubu.es; jmiguel@ubu.es

² Departamento de Ciencias de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

GRAPHICAL AND TEXTUAL ABSTRACT



Reusable smart films and textiles as colorimetric sensory materials for high acidity environments.

ABSTRACT

We have designed and successfully prepared polymer membranes as manageable films for colourimetric sensory materials for the visual detection of the acidity of water in the low *pH* range, below 4, and beyond the *pH* scale, up to a concentration of perchloric acid of 11.6 M. For this purpose, two monomers with weakly basic groups were synthesised, with these monomers containing up to four protonisable groups in the aforementioned acidic regions. The *pK_a*s were calculated for the membranes in water, which exhibited gel behaviour, and ranged between 2.7 to -6.5. Accordingly, visual colour changes qualitatively indicated the acidity of water containing perchloric acid,

and the quantification was performed inexpensively with UV/Vis spectroscopy. Titration with other acids is foreseen for practical applications. Moreover, polymer coatings of conventional cotton and high-tech *p*-aramid fibres, using the designed sensory monomers, yielded smart fabrics, which responded colourimetrically to the acidity of the water media. Furthermore, both membranes and smart fibres exhibited colour changes in air under acidic atmospheres, demonstrating the future development of fully sensory apparels and smart tags with envisaged health and safety applications. In addition, the sensory materials are reusable, because the protonations under acidic conditions are reverted by washing with water, and are highly stable under acidic conditions for long periods of time.

Introduction

Acidity or basicity are key parameters in industry, environmental control and remediation as well as in life science. Accordingly, the rapid, inexpensive and precise determination of *pH* is highly desirable. Currently, the practical determination of these values in aqueous environment in the medium-to-low acidity to basicity range, i.e., on the *pH* scale from 1 to 13,¹ is performed using *pH* test paper strips, potentiometric techniques employing *pH*-sensitive membranes such as glass membrane electrodes, and chemical *pH* sensors.^{2,3,4} Depending on the needs, and especially on the speed and accuracy of the measurements, these methods perform well and satisfy most of the requirements.

However, there is a lack of systems for the rapid, precise, and inexpensive measurement of acidity at very low *pH* and especially beyond the *pH* scale (i.e., for perchloric acid concentrations ranging from 1 to 11.6 M), and concomitantly, there is a strong need for the development of such a system for many applications, such as nuclear fuel reprocessing, the separation of rare-earth metals, and the recycling and reuse of strong acids in industrial processes.⁵⁻¹⁰ An approach to overcoming this challenge has been the development of *pH*-responsive polymeric materials,¹¹ and optical sensors among these materials, by immobilising *pH*-responsive organic molecules in polymer matrixes^{7-10,12} and, to a limited extent, the preparation of integral polymer chemosensors.^{6,13} The latter has been demonstrated to be a better approach in the design of *pH*-responsive materials^{14,15} than the immobilisation,¹⁶⁻²² because the design of a chemosensing monomer followed by its polymerisation renders sensory motifs chemically anchored to the polymer backbone, which is an advanced method of

avoiding the migration, leaching and hysteresis of sensory probes, and of achieving an unsurpassed long-term stability.

Thus, we have designed sensory acrylic monomers from which we have prepared colourimetric sensory materials that respond with a colour change in strong acid media, both in water solution and in the air. As a proof of concept for practical applications, the materials were prepared as manageable transparent membranes, films, and as coated fibres of cotton and *para*-aramid (Kevlar®) fabrics. Moreover, they were reusable by washing with water, and highly stable under acidic conditions for long periods of time.

EXPERIMENTAL PART

Materials

All materials and solvents were commercially available and used as received, unless otherwise indicated. The materials included: 2-amino-4,6-dimethyl pyrimidine (Aldrich, 95%), 4-methoxybenzaldehyde (Merck, >98%), 4-dimethylaminobenzaldehyde (Aldrich, 98%), sodium hydroxide (VWR chemicals, 98%), tetrabutylammonium hydrogensulphate (TBAHS, Sigma Aldrich, >99%), methacryloyl chloride (Fluka, 97%), triethylamine (TEA) (Fluka, >98%), dichloromethane (Fisher Scientific, >99.99%), 1-vinyl-2-pyrrolidone (VP) (Aldrich, >99%), ethylene glycol dimethacrylate (EGDMA) (Aldrich, 99%), methyl methacrylate (MMA) (Aldrich, 99%), 2-hydroxyethyl acrylate (2HEA) (Aldrich, 99%), perchloric acid (Panreac, 70%), hydrochloric acid (VWR Chemicals, 37%), D₂O (SDS, 99.9%), DCl (in D₂O, 1 M, 99 atom% D, Aldrich), CD₃CN (Aldrich, 99.8%), and CDCl₃ (Merck, 99.8 atom% D). Azo-bis-isobutyronitrile (AIBN) (Aldrich, 99%) was recrystallised twice from methanol.

Instrumentation

¹H and ¹³C-NMR spectra were recorded using a NMR Varian UNITY INOVA 400 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.

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

Ultraviolet-visible (Uv/Vis) and fluorescence spectra were recorded using a Varian Cary3-Bio Uv/Vis and a F-7000 Hitachi Fluorescence spectrophotometers, respectively.

The mechanical properties of the membranes were determined on a Shimadzu EZ Test Compact Table-Top Universal Tester at 20°C .

High-resolution electron-impact mass spectrometry (EI-HRMS) was performed on a Micromass AutoSpect Waters mass spectrometer (ionisation energy: 70 eV; mass resolving power: >10000).

The melting points were obtained in a Gallenkamp apparatus.

Measurements

The water-swelling percentage (WSP) of the membrane was determined from the weights of a dry sample membrane (ω_d) and a water-swelled (the membrane was immersed in pure water at 20°C until the swelled equilibrium was achieved) sample membrane (ω_s) as follows: $100 \times [(\omega_s - \omega_d) / \omega_d]$.

The sensing measurements acquired using dense membrane were performed using Millipore-Q water.

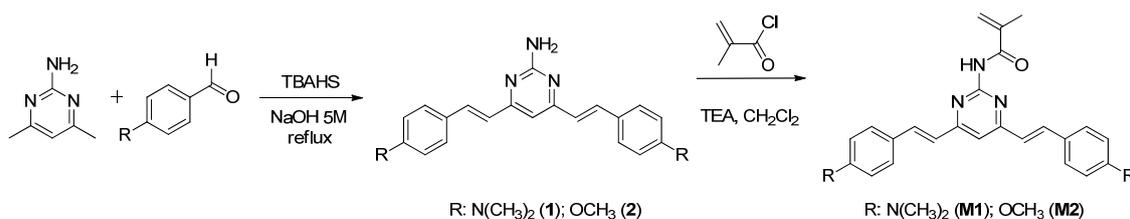
The acid titration of both vapours and aqueous solution by UV/Vis was performed as follows. The titration in solution with the sensory membranes was performed using perchloric acid as the acid source and under the following conditions: the 5-mm discs cut from the membranes were dipped into 200 mL of water (Millipore-Q) using a homemade support that also fits the UV/Vis cell holder. Next, the acidity of the solution was increased to a *pH* close to 1 by adding aliquots of the diluted perchloric acid. After each addition, the *pH* was measured with a *pH* meter with a glass electrode, the membranes were allowed to equilibrate for 10 min, and the UV/Vis spectra were recorded. For higher acidities, beyond the *pH* scale, vials containing 25 mL of perchloric acid of concentrations ranging from 0.1 to 11.6 M were prepared, and the membranes were successively immersed in these vials, starting from the vial with the lowest acid concentration. After equilibrating the four membranes in each vial for 10

min, the UV/Vis spectra were recorded. The measurements were performed at 24°C. The colourimetric detection of acidic vapours was performed qualitatively by exposing the membranes to HCl vapours from the headspace of a bottle of conc. hydrochloric acid for 5 min.

The tensile properties of the membranes were determined using strips (5 mm in width and 50 mm in length) cut from polymer films of 115-118 μm thickness. Mechanical clamps were used, and an extension rate of 5 mm/min was applied using a gauge length of 9.44 mm. At least six samples were tested for each polymer, and the data were averaged.

Synthesis of sensory monomers

The monomers were prepared according to the procedure schematically depicted in Scheme 1.



Scheme 1. Synthesis of monomers.

4,6-bis((E)-4-(N,N-dimethylamino)styryl)pyrimidin-2-amine (1). In a three-necked flask, 40.6 mmol (5.0 g) of 2-amino-4,6-dimethylpyrimidine, 88.0 mmol (13.1 g) of 4-dimethylaminobenzaldehyde and 3.9 mmol (1.3 g) of TBAHS were dissolved in a 5 M solution of NaOH (200 mL). The mixture was heated at reflux for 2 hours to obtain a dark orange solid. The solid was filtered off and washed with distilled water (3 x 200 mL) and recrystallised from ethanol: CHCl₃ (9:1). Yield: 69 % (10.8 g). M.p.: 189 \pm 1°C. ¹H-NMR (δ_{H} ppm) (400 MHz, DMSO-*d*₆, Me₄Si): 7.63 (2H, d, 15.9 Hz), 7.47 (4H, d, 8.5 Hz), 6.80 (1H, s), 6.74 (6H, dd, 6.2, 2.6 Hz), 6.31 (2H, s), 2.96 (12H, s). ¹³C-NMR (δ_{C} ppm) (100.6 MHz, DMSO-*d*₆, Me₄Si): 164.4, 151.6, 136, 129.5, 124.3, 122.8, 113.1, 106, 40.7. FTIR (wavenumbers, cm⁻¹): ν_{NH_2} : 3320-3174. EI-HRMS m/z: calcd for C₂₄H₂₇N₅ 385.2266, found 385.2275.

4,6-bis((E)-4-methoxystyryl)pyrimidin-2-amine (2). In a three-necked flask, 40.6 mmol (5.0 g) of 2-amino-4,6-dimethylpyrimidine, 88.0 mmol (12.0 g) of 4-methoxybenzaldehyde and 3.9 mmol (1.3 g) of TBAHS were dissolved in a 5 M

solution of sodium hydroxide (200 mL). The mixture was heated at reflux for 2 hours to obtain a yellow solid. The solid was filtered off and washed with distilled water (3 x 200 mL) and recrystallised from ethanol: CHCl_3 (9:1). Yield: 76 % (11.1 g). M.p.: $183 \pm 1^\circ\text{C}$. $^1\text{H-NMR}$ (δ_{H} ppm) (400 MHz, $\text{DMSO-}d_6$, Me_4Si): 7.69 (2H, d, 16.0 Hz), 7.61 (2H, d, 8.7 Hz), 7.00 (2H, d, 8.7 Hz), 6.95 (1H, s), 6.90 (2H, d, 16.0 Hz), 6.45 (1H, s), 3.80 (s, 6H). $^{13}\text{C-NMR}$ (δ_{C} ppm) (100.6 MHz, $\text{DMSO-}d_6$, Me_4Si): 162.57, 160.00, 134.32, 128.91, 128.43, 124.69, 114.37, 107.37, 106.32, 55.24, 23.50. FTIR (wavenumbers, cm^{-1}): ν_{NH_2} : 3315-3182. EI-HRMS m/z: calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2$ 359.1634, found 359.1631.

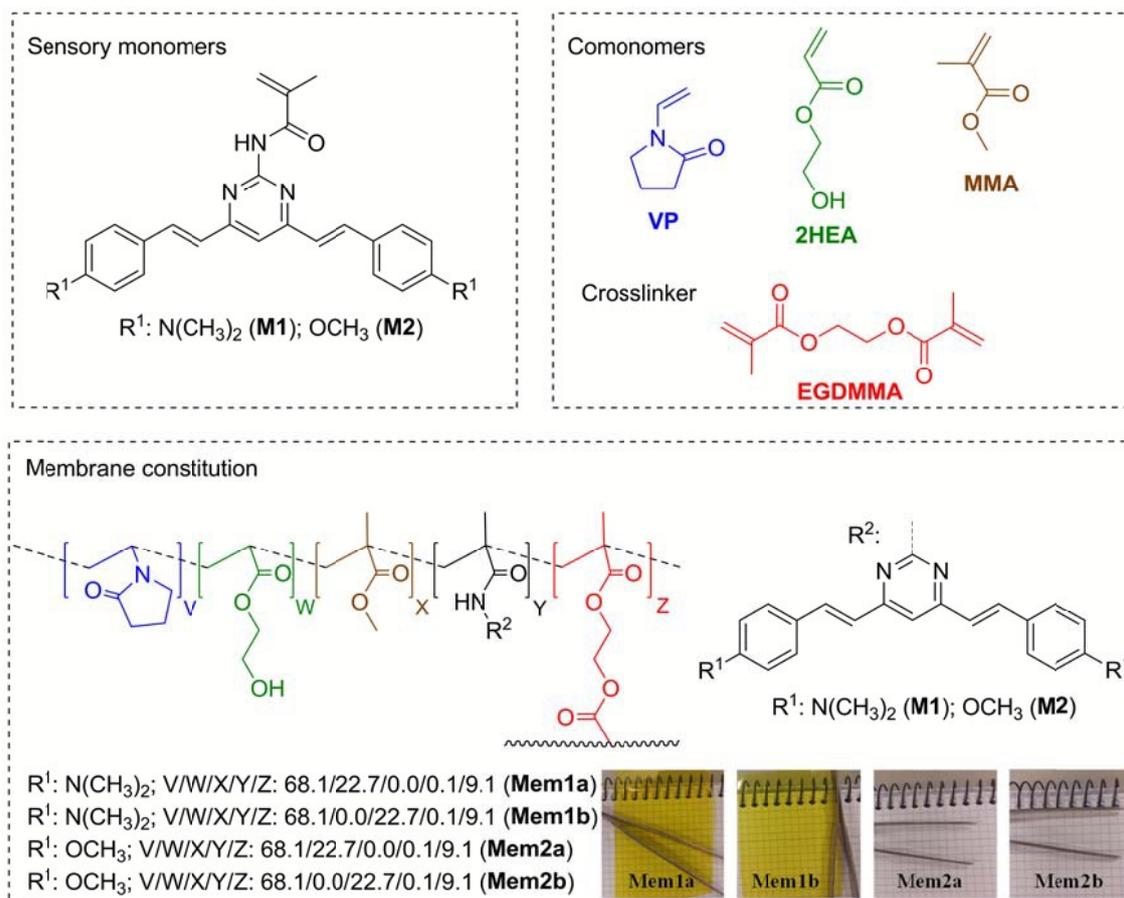
N-(4,6-bis((E)-4-(N,N-dimethylamino)styryl)pyrimidin-2-yl)methacrylamide (M1). In a round-bottomed flask, 13.0 mmol (5.0 g) of (1) was dissolved in 50 mL of dichloromethane at 0°C (ice bath) under nitrogen atmosphere. Afterwards, 19.0 mmol (2.7 mL) of TEA was added to the solution, and 17.0 mmol (1.7 mL) of methacryloyl chloride was added dropwise with stirring. After the addition, the system was stirred at rt for 8 h. The solution was filtered off and concentrated under reduced pressure. The solid obtained was washed with 2 x 250 mL of ethyl ether and afterwards with distilled water (500 mL). The solid product (M1) was collected and dried in a vacuum oven at 40°C overnight. Yield: 78 % (4.6 g). M.p.: $212 \pm 1^\circ\text{C}$. $^1\text{H-NMR}$ (δ_{H} ppm) (400 MHz, CDCl_3 , Me_4Si): 8.28 (1H, s), 7.80 (2H, d, 15.8 Hz), 7.50 (4H, dt, 8.8, 2.3 Hz), 6.94 (1H, s), 6.88 (2H, d, 8.5 Hz), 6.70 (4H, d, 8.9 Hz), 5.88 (1H, s), 5.59 (1H, s), 3.01 (12H, s), 2.11 (3H, s). $^{13}\text{C-NMR}$ (δ_{C} ppm) (100.6 MHz, CDCl_3 , Me_4Si): 165.97, 164.38, 157.12, 150.93, 141.03, 137.29, 129.03, 123.67, 120.78, 120.03, 111.84, 110.79, 40.04, 18.61. FTIR (wavenumbers, cm^{-1}): $\nu_{\text{N-H}}$: 3413, $\nu_{\text{C=O}}$ (amide I): 1701. EI-HRMS calcd for $\text{C}_{28}\text{H}_{31}\text{N}_5\text{O}$ 453.2529, found 453.2526.

N-(4,6-bis((E)-4-methoxystyryl)pyrimidin-2-yl)methacrylamide (M2). In a round-bottom flask, 13.9 mmol (5.0 g) of (2) was dissolved in 50 mL of dichloromethane at 0°C (ice bath) under nitrogen atmosphere. Afterwards, 20.1 mmol (2.8 mL) of TEA was added to the solution, and 18.2 mmol (1.8 mL) of methacryloyl chloride was added dropwise, and the solution was stirred at rt for 4 h. The solution was filtered and concentrated under reduced pressure. The solid obtained was washed with 2 x 250 mL of ethyl ether and afterwards with distilled water (500 mL). The solid product (M2) was collected and dried in a vacuum oven at 40°C overnight. Yield: 52% (3.1 g). M.p.: $208 \pm 1^\circ\text{C}$. $^1\text{H-NMR}$ (δ_{H} ppm) (400 MHz, CDCl_3 , Me_4Si): 8.25 (1H, s), 7.86 (2H, d, 15.9

Hz), 7.62 – 7.51 (4H, m), 6.98 (1H, s), 6.99 – 6.86 (6H, m), 5.90 (1H, s), 5.56 (1H, s), 3.84 (6H, s), 2.12 (3H, s). ^{13}C -NMR (δ_{C} ppm) (100.6 MHz, CDCl_3 , Me_4Si): 166.19, 164.56, 160.85, 157.50, 141.24, 137.22, 129.41, 128.67, 123.57, 120.61, 114.46, 111.90, 55.51, 18.90. FTIR (wavenumbers, cm^{-1}): $\nu_{\text{N-H}}$: 3438, $\nu_{\text{C=O}}$ (amide I): 1691. EI-HRMS calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_3$ 427.1896, found 427.1880.

Preparation of sensory materials

Preparation of membranes. The sensory dense membranes or films (**Mem1a**, **Mem1b**, **Mem2a** and **Mem2b**) were prepared by radical polymerisation of **VP**, **2HEA** or **MMA** and the sensory monomer **M1** or **M2**, using **EGDMMA** as the cross-linking agent. The co-monomer molar ratio **VP/2HEA/MMA/M1/M2/EGDMMA** was 68.1/22.7/0.0/0.1/0.0/9.1 (**Mem1a**), 68.1/0.0/22.7/0.1/0.0/9.1 (**Mem1b**), 68.1/22.7/0.0/0.0/0.1/9.1 (**Mem2a**), 68.1/0.0/22.7/0.0/0.1/9.1 (**Mem2b**). AIBN (1 wt.%) was used as thermal initiator. The homogenous solution comprised of **VP**, **2HEA** or **MMA**, **M1** or **M2**, **EGDMMA**, and the thermoinitiator was transferred to an ampoule, degassed by nitrogen bubbling for 15 min, and injected into an oxygen-free atmosphere in a 100- μm -thick silanised glass hermetic mould. The thermoinitiated bulk polymerisation was performed at 60°C overnight. Then, the membrane was demoulded and conditioned by standing for 48 h at room temperature in air, followed by drying in a vacuum oven at 20°C overnight. The structure of the comonomers and the constitution of the membranes are depicted in Scheme 2.



Scheme 2. Chemical structure of sensory dense membranes.

Solid sensory substrates. The solid sensory substrates were manufactured from **Mem1a**, **Mem1b**, **Mem2a**, and **Mem2b** films using a puncher to cut out sensory discs that were 5 mm in diameter and 114 μm (**Mem1a**), 116 μm (**Mem1b**), 113 μm (**Mem2a**) and 117 μm (**Mem2b**) thick.

Coating of cotton and *p*-aramid fibres with acidity sensory polymers. Conventional cotton fabric cut from a new white lab coat and *p*-aramid fabric (245 g/cm^3) were washed thoroughly with hot acetone and then cut into squares of 1 cm x 1 cm, approximately, which were dried for 30 min at 60°C and weighed and stored under a nitrogen atmosphere. A homogeneous coating solution comprised of the sensory monomers **M1** or **M2**, **2HEA**, and **EGDMA** as the cross-linking agent at a comonomer molar ratio of **2HEA/M1/EGDMA** (**F1**) and **2HEA/M2/EGDMA** (**F2**) of 95.1/0.1/4.8 as well as AIBN (1 wt.%) as the radical thermal initiator was prepared. Then, 30% by weight of acetone was added to the solutions to diminish the viscosity and to increase the wettability of the fibres. The fabrics were subsequently immersed into the solution, wrung, dried at rt to eliminate the acetone, introduced in a vial that was afterwards blanketed with nitrogen to remove oxygen, and then heated at 100°C for

10 min, rendering the acrylic crosslink-coated cotton fibres, **F1_{cot}** and **F2_{cot}**, and *p*-aramid coated fibres (Kevlar®), **F1_{ara}** and **F2_{ara}**. The lab-coated fabrics yielded ~100% by weight of polymer coating exhibiting good tractability and tactile appearance.

Results and discussion

Strategy for sensing high acidities in pure water and in gas phase

Our work aims to prepare solid systems for the easy determination of acidities in pure water media. The term *easy* means *in situ*, inexpensive, rapid, and for non-specialised personnel. For this purpose, we have designed organic probes that change their colour at different levels of acidity. Furthermore, the probes are acrylic monomers that allow for their polymerisation to render solid, handleable materials as films or membranes and coated fibres. In addition, regardless of the water insolubility of the probes, their copolymerisation with hydrophilic co-monomers renders materials with gel behaviour that can be used in water with excellent yield. The change of the colour of the materials is clearly visible at a given acid concentration, permitting the broad determination of the acidity by the naked eye; in parallel, the acidity can be quantified using the UV/Vis technique. Furthermore, the materials change their colour in air in presence of acid vapours, allowing for the preparation of smart fibres that could be used in personal protective equipment (EPP).

Designing the colourimetric chemosensory motifs

The electron-donating *N,N*-dimethylamino and methoxy groups of the pyrimidine derivatives **M1** and **M2** pump electrons to the poor pyrimidine ring through the conjugated double carbon-carbon bond providing an excellent colourimetric probe for protons, because protonation causes the former groups to behave as electron-withdrawing groups, with a concomitant variation in the optical properties of the molecules. Moreover, the weak basicity of these groups, i.e., low pK_{as} , from now on pKs , or even the pyrimidinic nitrogens, provide excellent binding points for protons only in high-acidity media, thus serving the designed purposes. Furthermore, the multiple slightly basic groups provide each probe with a different pK , allowing each probe to detect different acidities corresponding with the protonation of different groups as the concentration of the acid is increased.

Materials preparation and characterisation

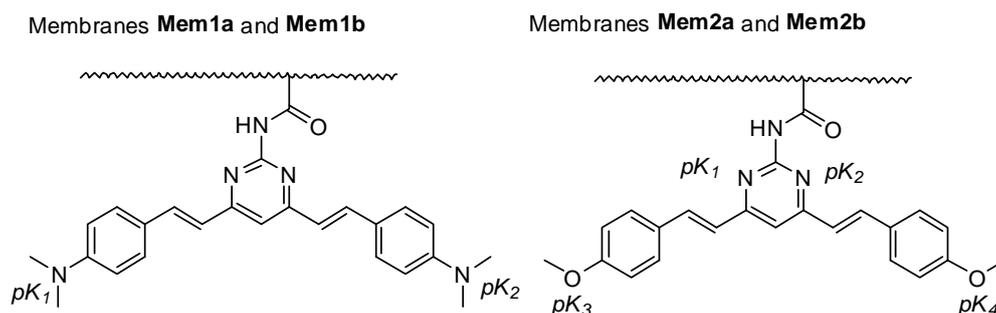
The sensory monomers **M1** and **M2** were prepared easily and inexpensively in two high-yield synthetic steps from widely available chemicals using proven organic reactions (Scheme 1). The ^1H and ^{13}C NMR and FTIR spectra of the intermediates and monomers are provided in the electronic supplementary information (ESI), Section S1. However, for a better understanding of the potential of the designed sensory systems, it is important to consider that 99.9 mol% of the materials are inexpensive commercial comonomers, and only 0.1% of the synthetic monomers **M1** and **M2** is needed to prepare the acid sensory materials, as will be described below.

The polymer dense membranes, or films, were characterised as materials from a mechanical and thermal viewpoint. Mechanically, the membranes were creasable and handleable, exhibiting a Young's modulus (GPa)/tensile strength (MPa) of 0.75/21.2 (**Mem1a**), 0.70/14.1 (**Mem1b**), 0.79/21.9 (**Mem2a**), and 0.72/15.4 (**Mem2b**). From the thermal resistance viewpoint, evaluated using TGA, the decomposition temperatures that resulted in 5% weight loss under a nitrogen atmosphere (T_5) were approximately 250-330°C, indicating that the materials exhibited reasonably good thermal stability. The TGA curves and full data are presented in ESI, Section S2. The chemical resistance will be discussed later and related to the stability and reusability of the materials as acid sensors in highly acidic water media.

The composition of the membranes was designed to provide high hydrophilicity, i.e., gel behaviour, to allow the solvated hydrated protons, hydronium ions, to enter the membranes by diffusion and to reach and interact with the hydrophobic sensory motifs evenly distributed all along the swelled membranes. The hydrophilic or hydrophobic character of the membranes was related to the water-swelling percentage (WSP); that is, it was related to the weight percentage of water uptake by the films upon soaking until equilibrium in pure water at rt. The membranes prepared have a WSP of 71%, 62%, 72% and 64% for **Mem1a**, **Mem1b**, **Mem2a** and **Mem2b**, respectively. WSP between 40 and 100% is good for both the rapid diffusion of chemicals into the membranes and for maintaining the tractability in terms of the mechanical properties of the water-swelled materials.

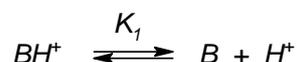
The chemosensing mechanism

The sensing phenomena towards acidity observed for membranes arise from the weak base characteristics provided for the organic monomers **M1** and **M2** and the different optical properties of their acidic (protonated) and basic (deprotonated) forms. Moreover, the different response observed at various acidities was originated from the presence of many protonisable groups in each monomer, with some of the groups protonated in the lab by increasing the concentration of perchloric acid to 11.6 M (Scheme 3).



Scheme 3. Protonation sites on sensory motif of membranes, marked with a pK label, upon increasing the acidity of the medium to a perchloric acid concentration of 11.6 M (the pK s are shown in Table 1).

The sensing mechanism was analysed in terms of the deprotonation/protonation equilibrium of weak basic species, which can be described by the equilibrium,



where the equilibrium constant is

$$K_1 = \frac{a_B a_{H^+}}{a_{BH^+}}, \quad (1)$$

and Eq. (1) can be rewritten as

$$pK_1 = pH + \log \frac{[BH^+]}{[B]} - \log \frac{f_B}{f_{BH^+}}, \quad (2)$$

where f represents the activity factors of the protonated specie, BH^+ , and free base, B . Considering the ionisation ratio, I , as the ratio between the concentrations of the protonated species and free base, and an ideal behaviour of the solutions, i.e., the activity coefficients are 1, Eq. (2) can be written as

$$\log I = -pH + pK_1. \quad (3)$$

However, Eq. (3) provides better results when expressed as^{23,24}

$$\log I = -n_1 pH + n_1 pK_1, \quad (4)$$

where n_1 gives an idea of the lack of ideality of the system. Eqs. (3) and (4) are the same for ideal systems where $n_1 = 1$. The ionisation ratio can be calculated from the absorbance of UV/Vis measurements using Eq. (5), obtained from a mass and absorbance balance, where A_B , A_{BH^+} and A represent the absorbances of the free base and protonated base and the absorbance at different pH at a given wavelength, λ , respectively. Substituting Eq. (5) into (4), Eq. (6) is obtained, which enables a nonlinear least squares fit of the sigmoid curve obtained from experimental measurements, known as the Chandler method.²⁵

$$I = \left(\frac{A - A_B}{A_{BH^+} - A} \right)_\lambda \quad (5)$$

$$A = \frac{A_B - A_{BH^+}}{1 + 10^{-n_1 pH + n_1 pK_1}} + A_{BH^+} \quad (6)$$

When working with weak bases, the acidity necessary to fully protonate the base is such that the concentration of protons in the medium is greater than 0.1 M, and the pH as a measure of the acidity of the medium is not useful. Moreover, when operating in increasingly acid medium, the ionic strength of the medium increases, making the approach used by Debye-Hückel increasingly unsatisfactory. It is therefore necessary to define a quantitative scale to express the acidity of the medium. Thus, Deyrup and Hammett proposed an acidity function,²⁶ H_0 , representative of the acidity of the medium and independent of the nature of the indicator used as a reference in its definition and calculation. From a series of reference bases, S , the H_0 function is defined as

$$H_0 = -\log \frac{a_{H^+} f_S}{f_{SH^+}}. \quad (7)$$

If the base objects of study, B , is fully or partially protonated in the acidic range in which the reference base is protonated, S , according to Hammett's hypothesis, the following relationship must be satisfied:

$$\frac{f_S}{f_{SH^+}} = \frac{f_B}{f_{BH^+}}. \quad (8)$$

H_0 in this case depends only on the activity of protons, being a measure of the acidity of the medium. Hammett and Deyrup calculated H_0 using a series of primary nitroanilines whose values are dependent only on the concentration of the mineral acid

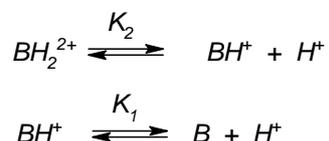
used. The correspondence of the calculated H_0 with the molar concentration of the acid used for this study, perchloric acid, is shown in Table S2 (ESI).²⁷

Following a similar reasoning to Eqs. (1) through (4), the corrected Hammett-Deyrup's equation is proposed:^{24,28}

$$\log I = -n_i H_0 + n_i pK_i. \quad (9)$$

Because the bases studied in this work are protonated in the high acidity region, in Eq. (6), pH is replaced by H_0 where needed, i.e., acid concentrations higher than 0.1 M.

For bases that exhibit two protonation equilibria, such as the membranes **Mem1a** and **Mem1b**, the membranes can be described with two equilibrium constants:



In this work, these two equilibria overlap, i.e., the difference between the pK s is less than or equal to three units, which indicates that both processes cannot be separated. To determine the values of the equilibrium constants by UV/Vis, different wavelengths characteristic of each one are required. In the event that it is not possible to satisfy this requirement, it is necessary to propose an alternative approach.

From the ratio of ionisation of the two equilibria obtained from Eq. (4), Eqs. (10) and (11) are obtained:

$$I_1 = \frac{[BH^+]}{[B]} = \left(\frac{a_{H^+}}{K_1}\right)^{n_1} \quad (10)$$

$$I_2 = \frac{[BH_2^{2+}]}{[BH^+]} = \left(\frac{a_{H^+}}{K_2}\right)^{n_2}. \quad (11)$$

For convenience, henceforth, the concentrations of B , BH^+ and BH_2^{2+} are represented by C_1 , C_2 , and C_3 , respectively. From a mass and absorbance balance, Eqs. (12) and (13) are obtained, where ε_1 , ε_2 y ε_3 are, respectively, the molar extinction coefficients of B , BH^+ and BH_2^{2+} . Considering Eqs. (10) to (12), Eqs. (14) to (16) are obtained.

$$C_T = C_1 + C_2 + C_3 \quad (12)$$

$$A = \varepsilon_1 C_1 + \varepsilon_2 C_2 + \varepsilon_3 C_3 \quad (13)$$

$$C_2 = C_1 K_1^{-n_1} a_{H^+}^{n_1} \quad (14)$$

$$C_3 = C_1 K_1^{-n_1} K_2^{-n_2} a_{H^+}^{n_1+n_2} \quad (15)$$

$$C_1 = \frac{C_T}{1 + K_1^{-n_1} a_{H^+}^{n_1} + K_1^{-n_1} K_2^{-n_2} a_{H^+}^{n_1+n_2}} \quad (16)$$

By substituting Eqs. (14) to (16) into (13), Eq. (17) is obtained, where A_1 , A_2 and A_3 represent the absorbance of species B , BH^+ y BH_2^{2+} , respectively. The activity of the proton can be replaced by 10^{-pH} or 10^{-H_0} , depending on the acidity of the experiment, while K_i can be replaced by 10^{-pK_i} in Eq. (17). Performing a nonlinear least squares fit, this equation allows values of the pK s, n_i and A_i to be obtained, as previously described.²⁹

$$A = \frac{A_1 + A_2 K_1^{-n_1} a_{H^+}^{n_1} + A_3 K_1^{-n_1} K_2^{-n_2} a_{H^+}^{n_1+n_2}}{1 + K_1^{-n_1} a_{H^+}^{n_1} + K_1^{-n_1} K_2^{-n_2} a_{H^+}^{n_1+n_2}} \quad (17)$$

Furthermore, **Mem2a** and **Mem 2b** exhibited protonation equilibria at extreme acid concentrations, from 4 to 11.6 M of perchloric acid. Three protonation equilibria were observed in this interval. Eq. (18) was obtained following similar approaches to those performed to obtain Eqs. (10) to (17), considering that the activity of the protons is replaced by 10^{-H_0} (working always in high acidity) and K_i is replaced by 10^{-pK_i} . Following a nonlinear least squares fit workup, Eq. (18) renders the pK s, n_i and A_i (Table 1):

$$A = \frac{A_1 + A_2 K_1^{-n_1} a_{H^+}^{n_1} + A_3 K_1^{-n_1} K_2^{-n_2} a_{H^+}^{n_1+n_2} + A_4 K_1^{-n_1} K_2^{-n_2} K_3^{-n_3} a_{H^+}^{n_1+n_2+n_3}}{1 + K_1^{-n_1} a_{H^+}^{n_1} + K_1^{-n_1} K_2^{-n_2} a_{H^+}^{n_1+n_2} + K_1^{-n_1} K_2^{-n_2} K_3^{-n_3} a_{H^+}^{n_1+n_2+n_3}} \quad (18)$$

Table 1. pK_s obtained from Eqs. (6), (17) and (18). The values between brackets are the pK_s calculated for the monomers **M1** and **M2** using the programme Marvin Suite.³⁰

Membrane	pK_s	Equation used
Mem1a	$pK_1 = 2.71 \pm 0.08$ (5.07)	(17)
	$pK_2 = 0.56 \pm 0.06$ (4.47)	(17)
Mem1b	$pK_1 = 2.9 \pm 0.1$ (5.07)	(17)
	$pK_2 = 0.16 \pm 0.07$ (4.77)	(17)
Mem2a	$pK_1 = 1.41 \pm 0.02$ (1.35)	(6)
	$pK_2 = -3.0 \pm 0.7$ (-3.69)	(18)
	$pK_3 = -4.5 \pm 0.2$ (-4.56)	(18)
	$pK_4 = -6.2 \pm 0.1$ (-5.12)	(18)
Mem2b	$pK_1 = 1.14 \pm 0.03$ (1.35)	(6)
	$pK_2 = -2.9 \pm 0.17$ (-3.69)	(18)
	$pK_3 = -4.74 \pm 0.05$ (-4.56)	(18)
	$pK_4 = -6.47 \pm 0.04$ (-5.12)	(18)

The behaviour of the materials as proton receptors, i.e., as sensory materials for high acidity media, is highly dependent on the nature of the receptor moiety, as shown in Table 1 and as discussed below. This dependency permits the design or tuning of the sensory materials for different applications and environments. Furthermore, the main composition of the materials plays an important role in their main properties as materials, and the use of the polar comonomer **2HEA** yielded membranes (**Mem1a** and **Mem2a**) with improved mechanical and thermal properties and greater hydrophilic character compared with the properties imparted by the comonomer **MMA** to membranes **Mem1b** and **Mem2b**. However, the effect of the membrane composition on the basic behaviour of the receptor groups of the sensory motifs is less evident.

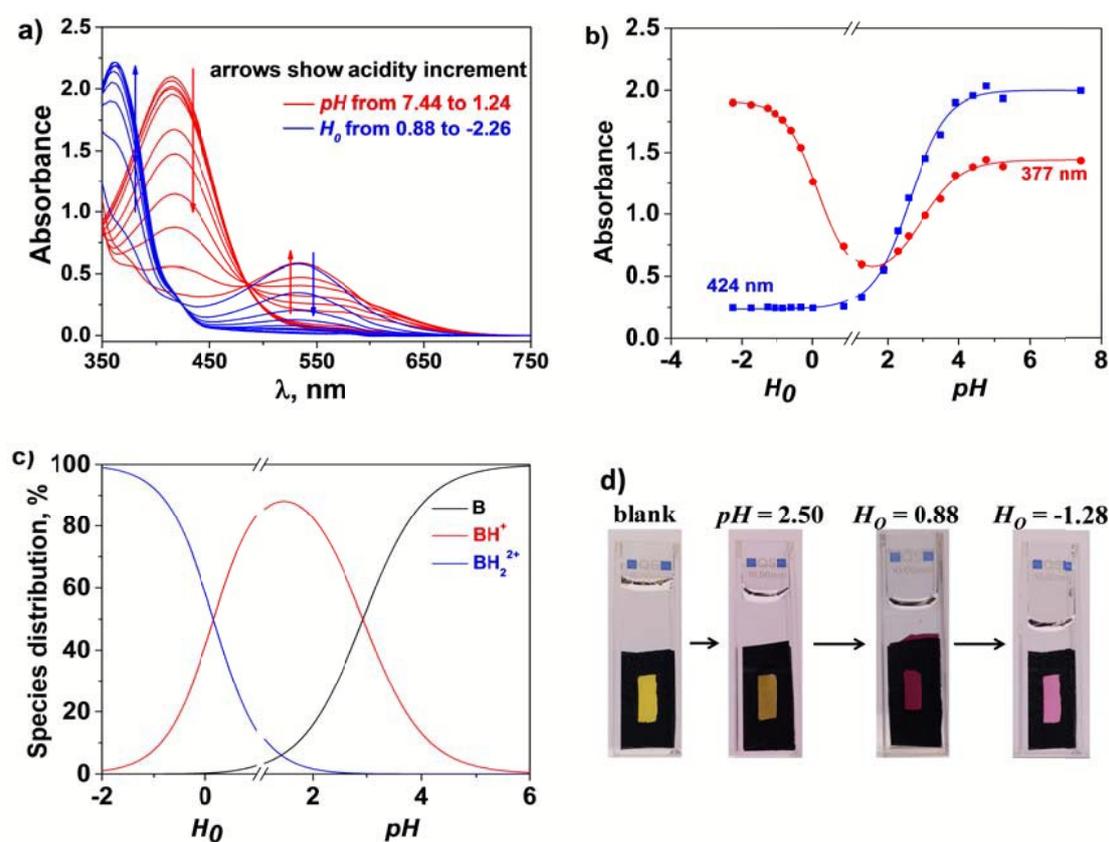


Figure 1. Titration of perchloric acid with **Mem1b** in MilliQ water with UV/Vis technique: a) UV/Vis spectra showing the two protonation processes (low and higher acidity in red and blue, respectively); b) the acidity absorbance relationship at 377 and 424 nm (the continuous lines correspond to the fitting using Eqs. 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.

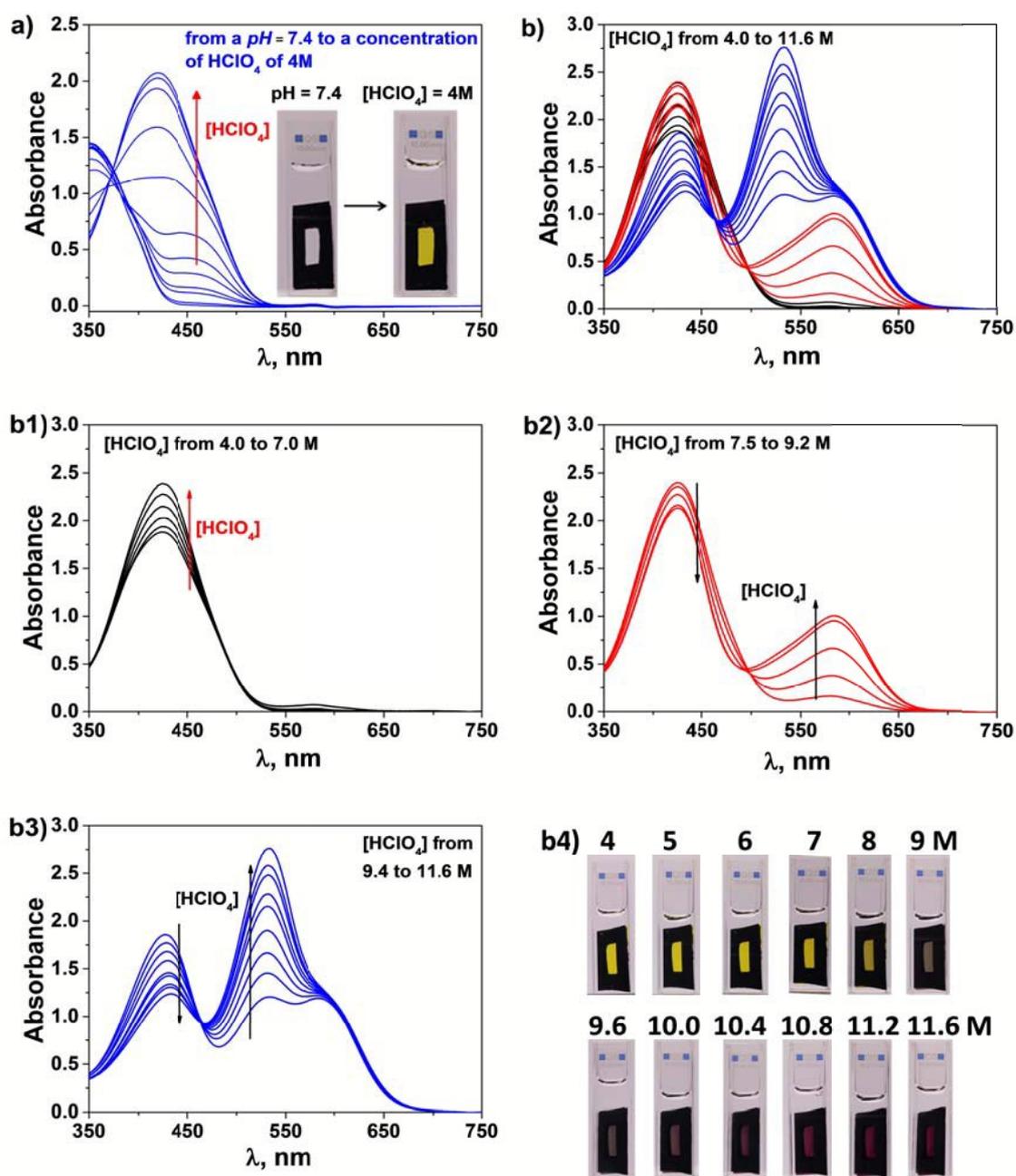


Figure 2. Titration of perchloric acid with Mem2a in MilliQ water using UV/Vis technique: a) UV/Vis spectra showing the first protonation process (inset: photograph of the sensory material inside the cuvette); b) UV/Vis spectra showing the second, third and fourth protonation processes. These processes are shown isolated as b1), b2) and b3), respectively, and photographs of the sensory materials along titration are presented in b4) together with the perchloric acid concentration.

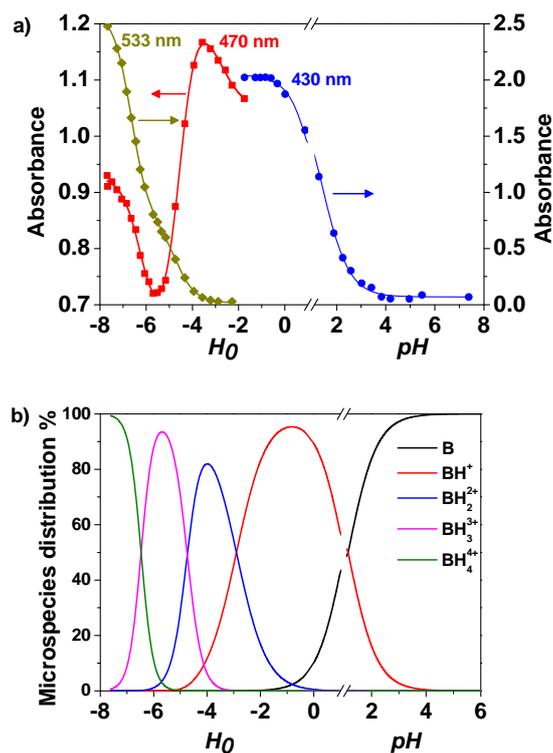


Figure 3. Titration of perchloric acid with **Mem2a** in MilliQ water using UV/Vis technique: a) acidity absorbance relationship. The process at 430 nm shows the first protonation process and at 470 nm the concomitant second, third and fourth protonation processed (continuous lines correspond to the fitting using Eqs. 6 and 18, respectively). The absorbance data at 533 nm are useful for determining the acidity of a system taking a single UV/Vis spectrum (continuous lines correspond to the fitting using Eq. 18); b) species distribution using Eqs. 10-11 assigning to C_T a value of 100.

The proposed protonation processes were also confirmed by ^1H NMR. Thus, solutions of 4 mg of **M1** or **M2** in 2 mL of $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (1.3/0.7 mL) in NMR tubes were gradually acidified to $pH = 2.2$ by adding deuterated hydrochloric acid (DCI), with the acidity determined with a pH meter fitted with a glass micro-electrode after each addition of acid. The pD was estimated according to the equation $pD = pH + 0.40$.³¹ The first protonation of the *N,N*-dimethyl amino group of **M1** was clear at pD of approximately 2.9, and it was observed at pD approximately 1.4 for **M2**, in accordance with the UV/Vis analysis for the membranes derived from these monomers. This result is significant because the studies of the monomers were performed in organic/aqueous solutions and the membranes were in a water-swelled solid state, i.e., the gel state. These facts can clearly be observed in the shift of different protons to lower and higher field (Figure S9, ESI). Unfortunately, it was not possible to increase the acidity in the NMR experiments to observe further protonation processes. The full assignment of the

NMR signals of protonated and unprotonated species was performed using ^1H , COSY 2D, and NOESY 2D experiments (Figures S10 and S11, ESI).

Interference study

The selectivity of the sensory materials as colourimetric acidity sensors was evaluated in presence of a broad set of salts (NaCl , KCl , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Pb}(\text{ClO}_4)_4$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, LiCl , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Thus, a solution of all these salt in a high concentration, 1×10^{-3} M of each one, in HClO_4 1 M in water was used in the study. The UV/Vis spectra of **Mem1a**, **Mem1b**, **Mem2a**, and **Mem2b** were recorded upon dipping the membranes in this solution and, in parallel, in a pure solution of 1 M HClO_4 in water (Figure S12, ESI). The spectra were fairly similar, and slight changes were ascribed to the change in the acidity caused by the acidic cations.

Reuse and stability of the sensory membranes in acidic media

The possibility of reusing a new material in any application is key for envisaging applications in terms of economy and sustainability. For chemosensory materials, three conditions are necessary: the reversible mechanism of the binding of the target molecule to the sensory motif, the chemical and mechanical stability during the cycles, and the maintenance of the selectivity and sensitivity during use.

Thus, the sensory materials **Mem1a**, **Mem1b**, **Mem2a**, and **Mem2b** were periodically subjected to 10 cycles of immersions in highly acidic water, 4 M HClO_4 , followed by washing in pure water, without loss of performance (Figures 4 and S14, manuscript and ESI). The known chemical stability of polymeric structures as solid materials, or even as swelled materials, compared with discrete molecules in solution provides the sensory membranes with an excellent acid stability, and hydrolysis reactions are not detected even in assays where the materials are dipped in acid water for longer periods, as depicted in Figures S13 (ESI).

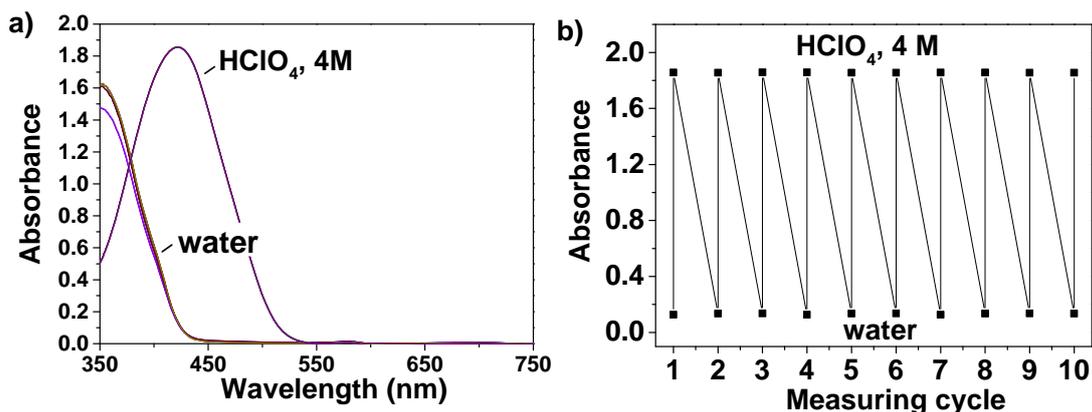


Figure 4. Reproducibility and reversibility of **Mem2a** as acidity sensor analysed by UV/Vis spectroscopy: a) UV/Vis spectra and b) absorbance at 422 nm vs. measuring cycle. The measurements were performed by successive cycles of dipping the material in highly acidic water, 4 M HClO₄, followed by washing with pure water. The cycle time was approximately 25 min, 5 min immersion in the acid medium and 20 min for washing.

Response time

The response time is a key parameter for sensors, where lower values are better for real life measurements. The response time was determined by UV/Vis spectroscopy as the time needed to achieve 99.8% of the absorbance variation (ESI, Figure S15). The results were lower than 5 min for all the sensory membranes, and colour changes were clearly appreciated by the naked eye in less than one minute.

Sensing acidic atmospheres

For health and safety at work and environmental and industrial control, the detection, control, and determination of acidic atmospheres is a topic of current interest. In this context, the visual signal indication of the presence of an acidic atmosphere is of the utmost importance.^{32,33} Within this frame, 5-min exposure to hydrogen chloride gases of the colourless membranes **Mem2a** and **Mem2b** turns the materials yellow. The yellow colour of membranes **Mem1a** and **Mem1b** does not allow for the visual detection of the acid atmosphere in 5 min; however, the membranes turn orange in 30 min and red in 12 h (Figure 5).

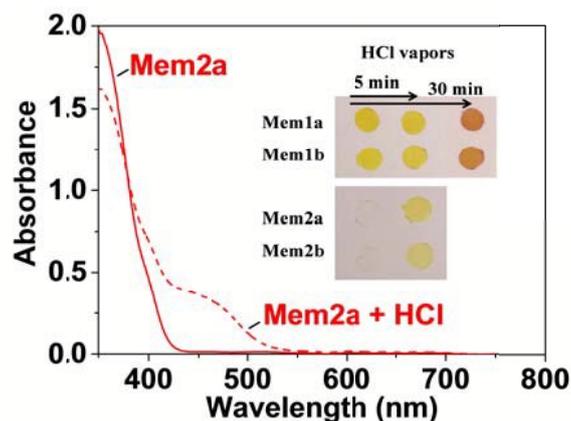


Figure 5. UV/Vis spectra of **Mem2a** before and after exposure for 5 min to the gas phase of a conc. hydrochloric acid in the neck of a freshly open bottle (inset: photographs of sensory discs cut from membranes with indication of the exposure time).

Smart fibres and fabrics as colourimetric acid sensors

Again, for health and safety reasons, there is a strong need for intelligent textiles made of smart fibres and yarns, i.e., stimuli responsive, to be used in apparels as stand-alone systems to be used as communications devices, energy-storage tools, actuators and sensors to name but a few applications.³⁴⁻³⁷

Within this context, intelligent fabrics capable of sensing acidic media with macroscopic colour changes are of especial interest. Thus, conventional cotton and high-tech *para*-aramid fabrics were prepared and subjected to acid environment, both in water solution and in the gas phase, exhibiting a clear colourimetric response, as depicted in Figure 6. These results are promising and envisage practical applications for this type of materials as smart apparel or tags.

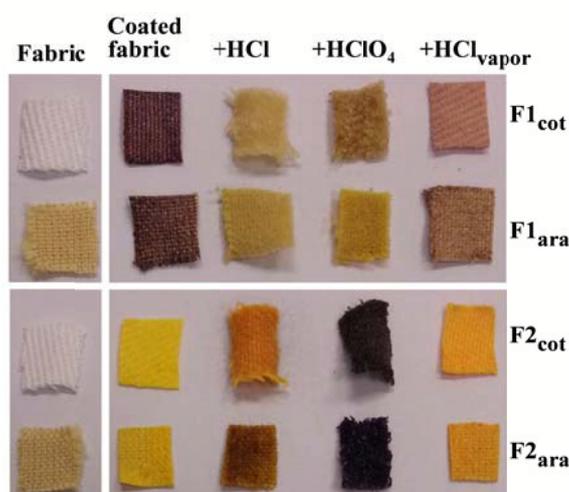


Figure 6. Coated fibres before and after immersion in aqueous acid media (37% HCl and 70% HClO₄) or exposure to hydrogen chloride (gas phase of a conc. hydrochloric acid in the neck of a freshly opened bottle). Exposure time = 5 min.

Conclusions

Reusable colourimetric sensory materials for visual sensing of highly acidic media have been successfully prepared by designing polymers containing conjugated moieties with feeble basic groups. Thus, monomers with as many as 4 protonisable groups were synthesised and copolymerised with other commercial comonomers to yield crosslinked membranes as handleable films and coated cotton and high-tech *p*-aramid fibres. These materials have *pK*s ranging from 2.7 to -6.5 in water solution and permitted the visual control of acidity below *pH* = 4 and beyond the *pH* scale up to a concentration of perchloric acid of 11.6 M and the quantification of the acidity using UV/Vis spectroscopy titration curves. These materials respond colourimetrically not only to acids in water media but also to acidic atmospheres, i.e., acids in the gas phase. Thus, applications including acidity control in industrial processes and laboratories and intelligent tags and textiles within the health and safety environment are envisaged.

Acknowledgments

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Supplementary Information

FTIR and NMR spectra of intermediates, monomers, and under neutral and acidic conditions; TGA curves and data of materials; correlation between the acidity function (H_0) and the concentration of perchloric acid; titration curves and species distribution of perchloric acid with sensory membranes; interference UV/Vis spectra and data; reusability, reproducibility and response time analyses by UV/Vis of sensory membranes.

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