**Figure S1.** Image of a printing model that includes a supporting structure and proper model orientation.

**Table S1.** Hue values given by BG, BP, PR, and Ph sensors for pH values from 2 to 12. Error bars correspond to mean values ± SD (n = 3).

| pH | BG | BP | PR | Ph |
|---|---|---|---|---|
| 2 | 103 ± 21 | 55 ± 1 | 36 ± 10 | 89 ± 24 |
| 3 | 143 ± 9 | 53 ± 8 | 36 ± 16 | 73 ± 8 |
| 4 | 173 ± 22 | 61 ± 4 | 40 ± 6 | 74 ± 14 |
| 5 | 189 ± 14 | 69 ± 4 | 37 ± 6 | 86 ± 15 |
| 6 | 195 ± 11 | 90 ± 7 | 28 ± 17 | 83 ± 14 |
| 7 | 199 ± 10 | 131 ± 25 | 29 ± 11 | 90 ± 16 |
| 8 | 202 ± 7 | 158 ± 12 | 20 ± 13 | 92 ± 15 |
| 9 | 207 ± 9 | 177 ± 16 | 11 ± 13 | 96 ± 21 |
| 10 | 212 ± 10 | 222 ± 31 | 319 ± 18 | 124 ± 20 |
| 11 | 227 ± 8 | 249 ± 5 | 294 ± 22 | 269 ± 17 |
| 12 | 229 ± 10 | 249 ± 2 | 281 ± 6 | 284 ± 16 |

**Ionogel pH sensor performance**

The barcode pH sensor is used to obtain the pH of unknown solutions passing though the microchannel. The pH of the solution is given by a sigmoid function following the Henderson–Hasselbach Equation (1) as an approximation [1], assuming that a particular species can exist in two forms, $HI \rightleftharpoons H^+ + I^-$ with a given $pK_a$.

Accordingly, the performance of the pH indicators inside the ionogel matrix can be described with the Equation (2), where the coefficient $A$, $B$, $C$ and $D$ can be derived by fitting the calibration curves to sigmoidal equations, as shown in Figure 3b.

$$pH = pK_a + log\left(\frac{[I^-]}{[HI]}\right) \tag{1}$$

$$Hue = A + \frac{(B-A)}{(1 + 10^{(C-pH)\cdot D})} \tag{2}$$

For Figure 4b, the main text and SI Table 1 show the fittings for BG, BP, PR, and Ph. The $pK_a$ values were obtained by calculating the inflexion point of the sigmoidal fittings

in MATLAB. Finally, Excel's Solver tool was used to find the pH values that met with the Hue values observed in the measurements for the acid/base reaction.

**Table S2.** Fitting data for the calibration curves of BG, BP, and PR**.**

| Fitting Coefficient | BG | BP | PR | Ph |
|---|---|---|---|---|
| $A$ | -303402.4 | 59.9 | 10.7 | 86.99 |
| $B$ | 222.6 | 238.5 | 319.0 | 284.7 |
| $C$ | -19.3 | 5.9 | 9.5 | 10.4 |
| $D$ | 0.16 | 0.50 | 0.50 | 1.66 |
| $R^2$ | 0.9615 | 0.9902 | - | 0.9887 |
| $pK_a$ | 2 | 5.9 | 9.5 | 10.4 |
| Hue value from acid/base reaction | 211 | 206 | 25 | 87 |
| Derived pH of the reaction (Solver) | 7.5 | 7.2 | 6.9 | 6.8 |

This manuscript does not intend to elucidate the complex mechanism that occurs during the pH analysis of the different ionogels/ pH indicators, where other considerations such as hydrophobicity and ion extraction capability of the IL [2,3] and the effect of the continous flow regime—enabling a dynamic interactions within the sensors—,among others, could have an effect in the behaviour of ionogels. The ion co-extraction capability of ILs plays an essential role in sensing when the IL takes active part in the sensing reaction, e.g., when the pH dye is part of the IL [2,4]; however, in our polymeric sensors, the pH responsive dye is independent from the IL, and it is the one giving the colour response to pH. In this work, the IL does not take active part in sensing, but it provides chemical stability to the polymeric sensors. Moreover, this study does not consider possible colour interferences coming form the matrix when using real samples; for that, modifications to lightening conditions should be considered.

**MATLAB CODE**

The MATLAB code used for the calculations of the $pK_a$ values and to plot the fitted curves is as follows, for the example of BG:

```
% *****BG****
    A=-303402.39329;
    B=222.62426;
    C=-19.27771;
    D=0.16056;
    %%%% Fitting equation of the characterization results (sigmoidal) %%%%
    x_BG = 2:0.001:12; %pH
    fx_BG = A+(B-A)./(1+10.^((C-x_BG)*D)); % Hue value

% **** Plot the fitted sigmoidal equation for the ionogels characterization ***
figure('Name','3D pH sensor characterization curves','NumberTitle','off');
plot(x_BG,fx_BG,'-');grid;hold;
legend('BG','Location','northwest'); hold off lgd=legend;
xlabel('pH')
ylabel('Hue')

% ********   Now calculate the gradient   ******
[nt,N] = size (fx_Ph);
h=(12-0)/(N-1);

%calculate the pKa value%
    BG  %%
DR = gradient(fx_BG,h);
IP_BG_i = round(median(find(DR == max(DR)))); % IP means inflection point
IP_BG_x = x_BG (IP_BG_i);
IP_BG_y = fx_BG (IP_BG_i);
```

```matlab
IP1 = msgbox (sprintf('pKa_BG = %0.4f',IP_BG_x));
    Plot the pKa values in the graph
plot(IP_BG_x,IP_BG_y,'X');

% Save the data in .txt files
    % The fitting curves
x_fx_BG = [x_BG(:), fx_BG(:)];
dlmwrite('Fitting_BG.txt', x_fx_BG, 'delimiter', '\t','newline', 'pc');
    % The pKa values
pKa_BG = [IP_BG_x,IP_BG_y];
dlmwrite('pKa_BG.txt', pKa_BG, 'delimiter', '\t','newline', 'pc');
```
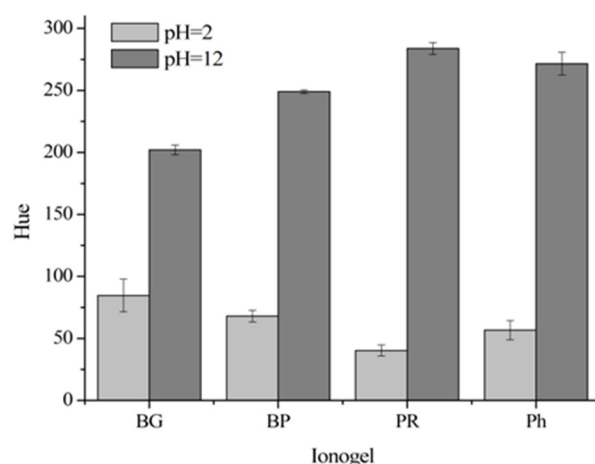


**Figure S2.** Reproducibility tests for the sensors over 14 cycles (from pH 2 to 12). The columns indicate the average hue values and the error bars represent the repetitiveness for each sensor at the two pH values.

# Reference

1.  Curto, V.F.; Fay, C.; Coyle, S.; Byrne, R.; O'Toole, C.; Barry, C.; Hughes, S.; Moyna, N.; Diamond, D.; Benito-Lopez, F. Real-time sweat pH monitoring based on a wearable chemical barcode micro-fluidic platform incorporating ionic liquids. *Sens. Actuators B Chem.* **2012**, *171–172*, 1327–1334. https://doi.org/10.1016/j.snb.2012.06.048.
2.  Mizuta, T.; Sueyoshi, K.; Endo, T.; Hisamoto, H. Ionic liquid-based dye: A "Dyed plasticizer" for rapid and highly sensitive anion optodes based on a plasticized PVC membrane. *Sens. Actuator B* **2018**, *258*, 1125–1130.
3.  Gourishetty, R.; Crabtree, A.M.; Sanderson, W.M.; Johnson, R.D. Anion-selective electrodes based on ionic liquid membranes: Effect of ionic liquid anion on observed response. *Anal. Bioanal. Chem.* **2011**, *400*, 3025–3033.
4.  Gao, L.; Lin, X.; Zheng, A.; Shuang, E.; Wang, J.; Chen, X. Real-time monitoring of intracellular pH in live cells with fluorescent ionic liquid. *Anal. Chim. Acta* **2020**, *1111*, 132–138.