

Electronic Supplementary Information for

Miniaturisation and simplification of solid-state proton activity sensor for non-aqueous media and ionic liquids

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Schematic for ΔE_{half} measuring principle

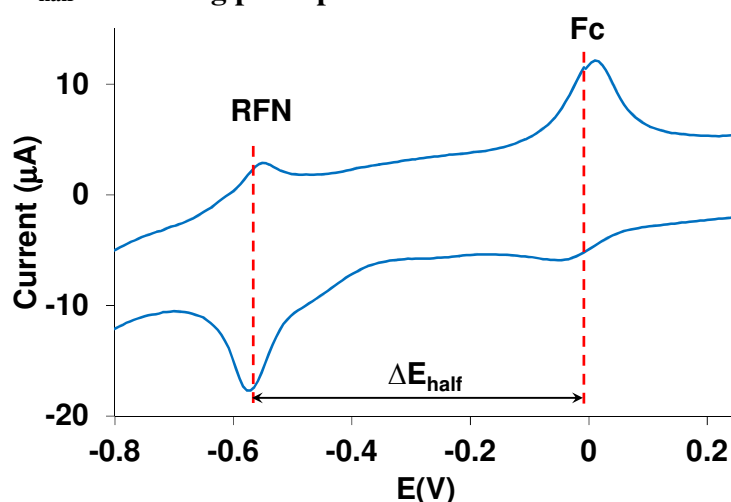


Figure S1 A sample CV showing the measuring principle of PEDOT:RFN-Fc electrodes. E_{ox} and E_{red} of RFN and Fc give E_{half} of each redox couple. ΔE_{half} defines the potential between E_{half} of the Fc reference redox couple and E_{half} of the RFN redox couple. ΔE_{half} will vary with the change in pH as the E_{half} of RFN change according to the pH. Consequently, a calibration curve from ΔE_{half} and pH changes can be constructed.

Full Raman spectra and assignments

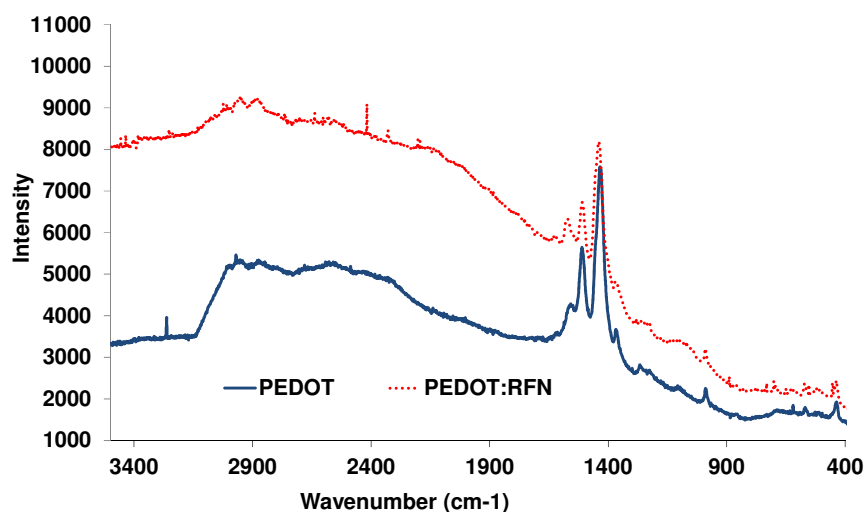


Figure S2 Raman spectra of PEDOT and PEDOT:RFN.

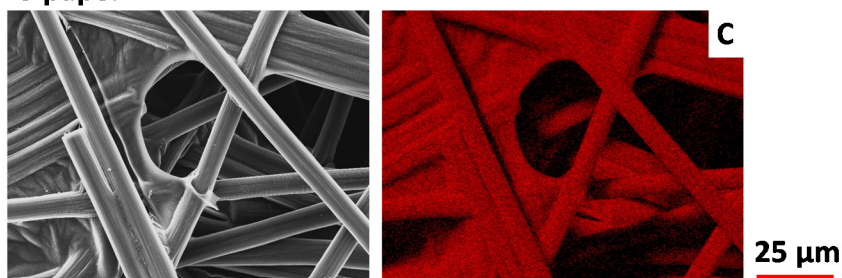
The intense peak at around 1433 cm^{-1} (for PEDOT) and 1444 cm^{-1} (for PEDOT:RFN) is attributed to the symmetric $C_{\alpha}=C_{\beta}$ stretching [1]. The bands at around 1511 cm^{-1} , 1368 cm^{-1} , 1267 cm^{-1} are assigned to the antisymmetric $C_{\alpha}=C_{\beta}$ stretching, $C_{\beta}-C_{\beta}$ stretching and inter-ring $C_{\alpha}-C_{\alpha'}$ stretching respectively [1]. Deformation of the oxyethylene ring appeared as the peak at 990 cm^{-1} [1].

FTIR assignments for RFN and Fc

Main characteristic peaks of RFN have some intense characteristic peaks which are 1732 (assigned for $C=O$ stretching), 1646 (assigned for $C=C$ stretching), 1580 and 1540 cm^{-1} (assigned for $C=N$ and $C=C$ stretching) [2], and 1072 and 1014 cm^{-1} which could be due to $C-O$ stretching from alcohol groups. Fc peaks 1104 , 999 , and 813 cm^{-1} have been assigned as $C-Fe$ stretching, $C-H$ out of plane bending (ring breathing), $C-H$ ring metal stretching, respectively [3].

C-paper and PEDOT coated C-paper characterisation

C-paper



PEDOT coated C-paper



Figure S3 SEM and EDX images of C-paper and PEDOT coated C-paper at 15 kV. For PEDOT coated C-paper, PEDOT coating is not blocking the C-paper pores and sulfur from PEDOT appeared as a thin layer coating on the C fibres (bottom right image).

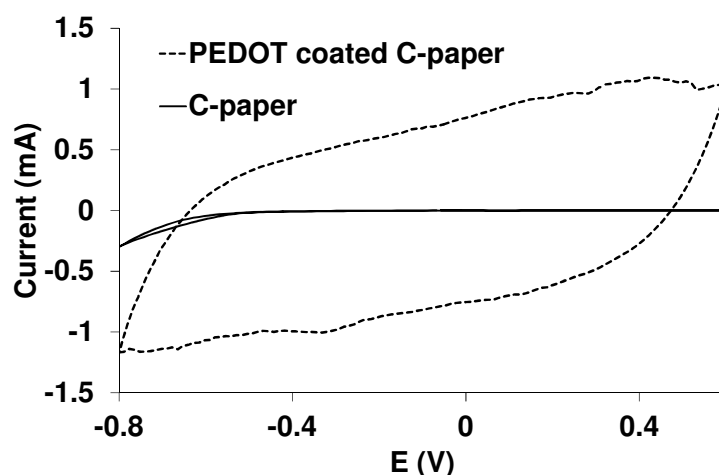


Figure S3 CVs of PEDOT coated C-paper (dotted trace) and C-paper (solid trace) in 0.1 M PB pH 5 at 10 mV/s. Ag/AgCl (3 M NaCl) and large Ti mesh ($\sim 2.5 \times 4 \text{ cm}^2$) was used as reference and counter electrodes, respectively.

Stability of RFN and Fc peaks over repetitive CV scans

Table S1 % RSD of peak current upon three repetitive CV scans of PEDOT:RFN-Fc in various ILs

ILs	RFN		Fc	
	E _{ox}	E _{red}	E _{ox}	E _{red}
P _{1,3} NTf ₂	22	2	11	23
EMIm(CN) ₄ B	16	10	5	8
EMImSCN	10	14	17	16
67% P _{1,4,4,4} TOS in PC	4	31	54	43
EAN	19	9	7	15

Reference

- [1] S. Garreau, G. Louarn, J.P. Buisson, G. Froyer, S. Lefrant, *Macromolecules*, 32 (1999) 6807-6812.
- [2] S. Ye, F. Wei, *Analyst*, 136 (2011) 2489-2494.
- [3] J.O. Enlow, H. Jiang, J.T. Grant, K. Eyink, W. Su, T.J. Bunning, *Polymer*, 49 (2008) 4042-4045.