Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplmentary Information (ESI)

Instant Detection of Picric Acid Vapour by Developing Layer by Layer Polymer Detectors and an Electronic Prototype

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Vapour pressure and vapour concentration of Picric acid (PA):

Vapour pressure of PA can be controlled by increasing the temperature and can be calculated with the help of standard Antonie equation [1, 2]

$$\mathrm{Log}(P/\mathrm{mmHg}) = (12.31+0.34)-(5175+105)/(T/K)$$
$$=12.65-5280/T$$

The vapour concentration can be calculated with the help of the following equation

$$\mathrm{Concentration} = (P/760).10^{6}\ \mathrm{ppm}$$

The vapour pressure of solid PA was controlled by increasing the operating temperature from 30 to 54°C.

Table S1: Vapour pressure and concentration of PA at different temperature

Temp(°C)	T (K)	5280/T	12.65-5280/T (K)	P (mmHg)	Conc (ppm)
30	303	17.42574	-4.77574	1.68E-05	0.022
36	309	17.08738	-4.43738	3.65E-05	0.048
42	315	16.7619	-4.1119	7.74E-05	0.102
48	321	16.4486	-3.7986	0.000159	0.209
54	325	16.24615	-3.59615	0.000253	0.335

Sensitivity of the LBL detectors:

Fig. S1-4 depicts the Z versus time plot of the detectors-2, 3, 4 and 5 with increasing concentration of PA.

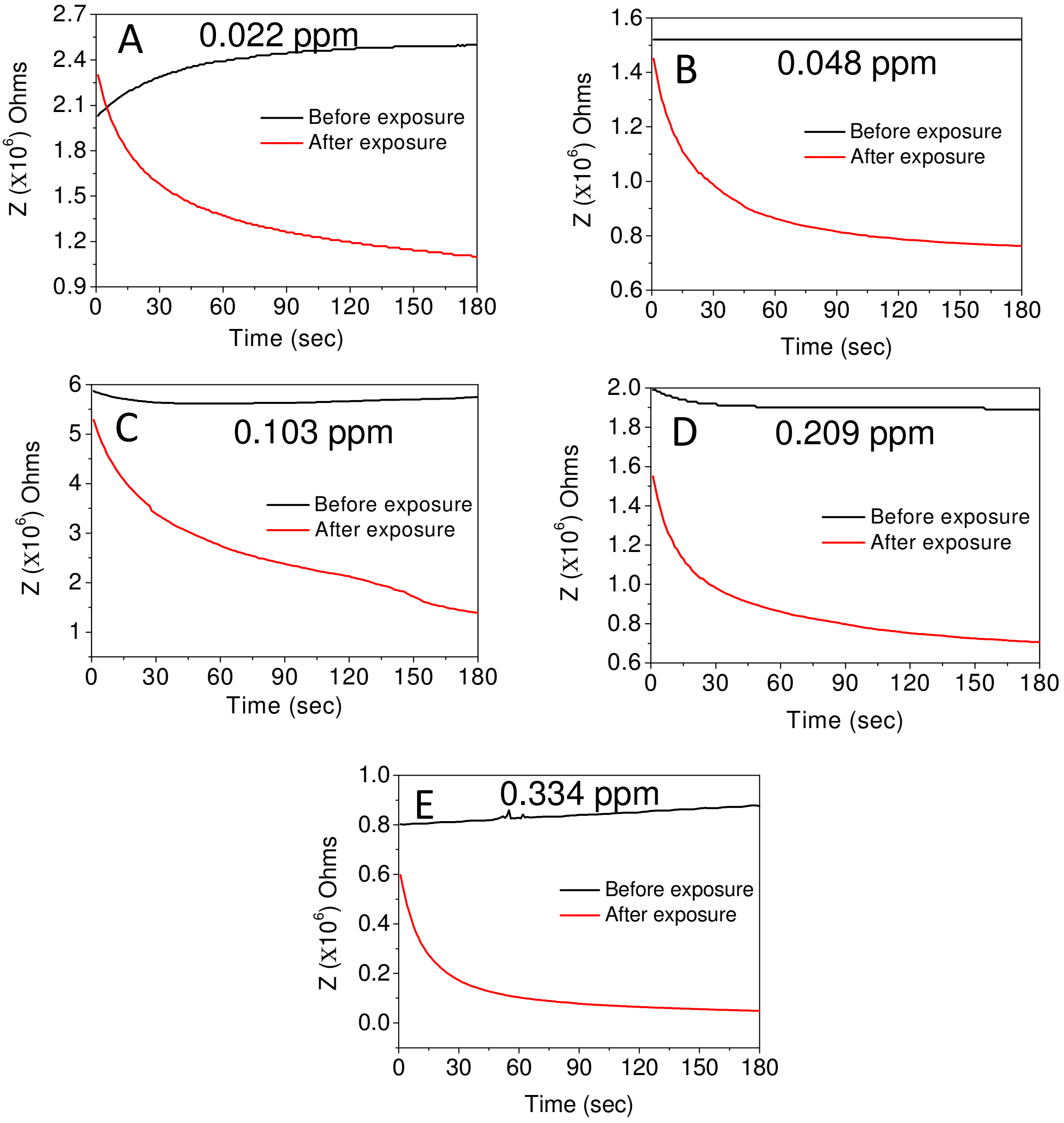

Fig. S1: Impedance (Z) versus time (sec) plot for the Detector-2 in presence of A. 0.022, B. 0.048, C. 0.103, D. 0.209, and D. 0.334 ppm of PA.

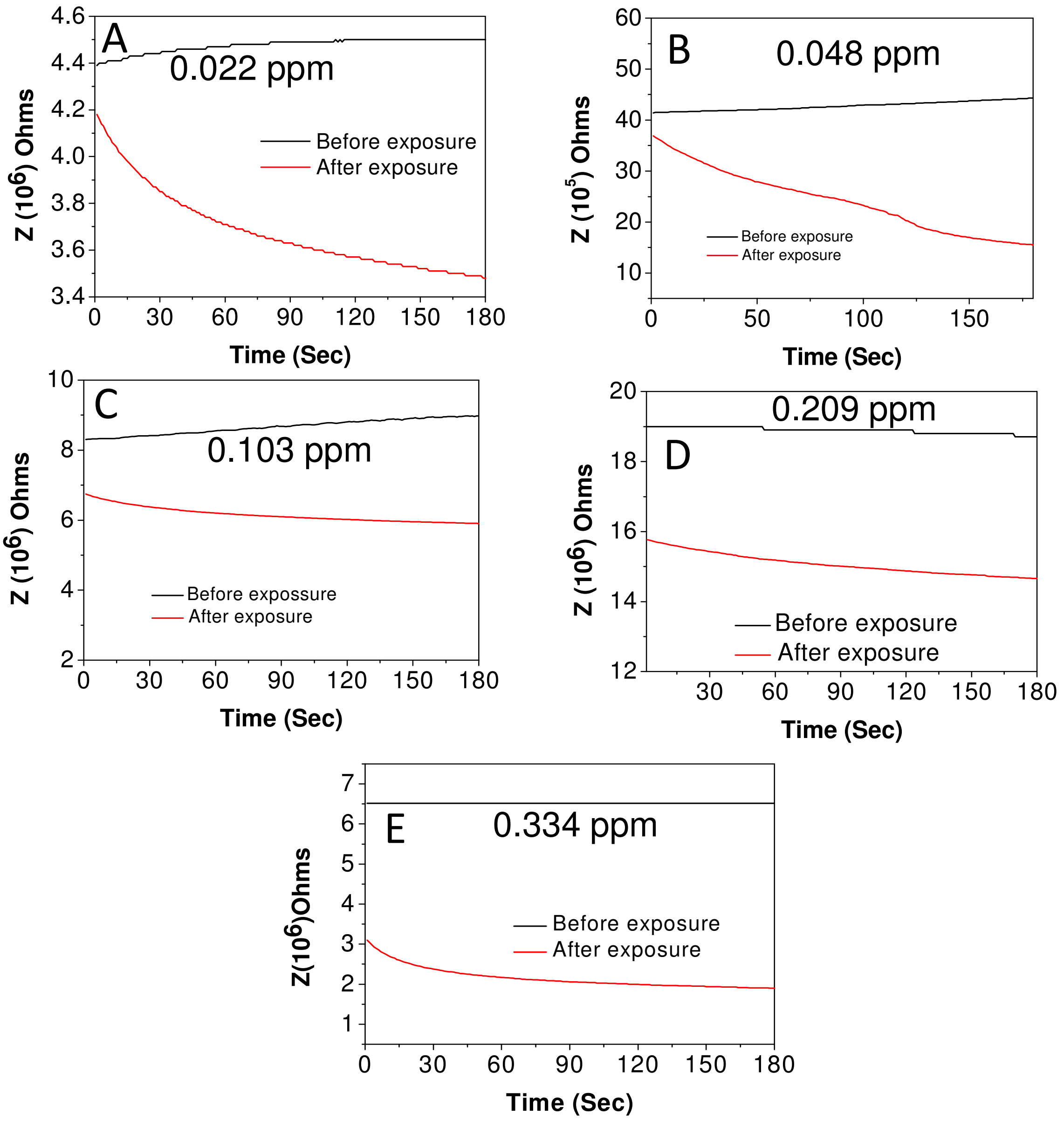

Fig. S2: Impedance (Z) versus time (sec) plot for the Detector-3 in presence of A. 0.022, B. 0.048, C. 0.103, D. 0.209, and D. 0.334 ppm of PA.

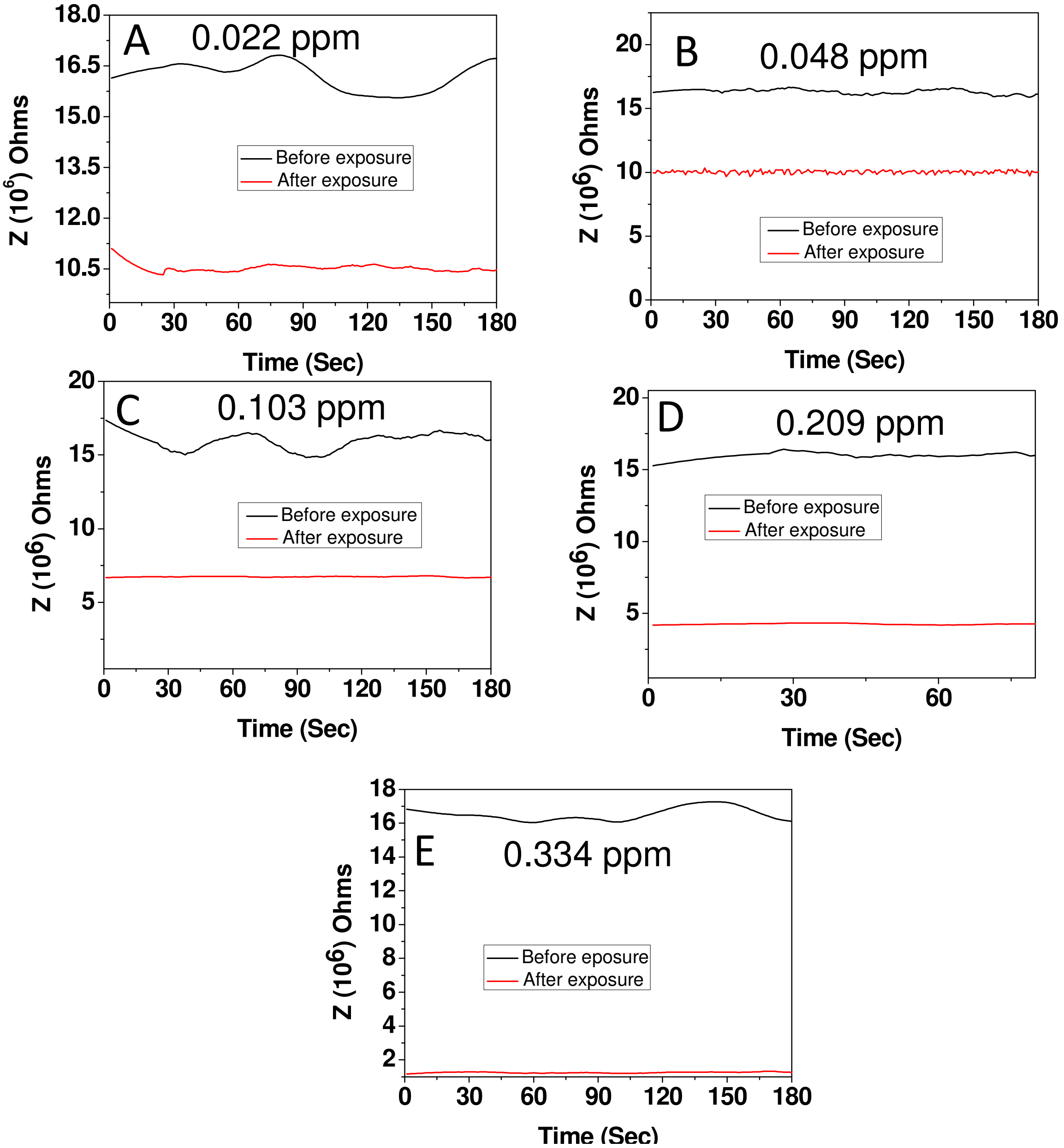

Fig. S3: Impedance (Z) versus time (sec) plot for the Detector-4 in presence of A. 0.022, B. 0.048, C. 0.103, D. 0.209, and D. 0.334 ppm of PA.

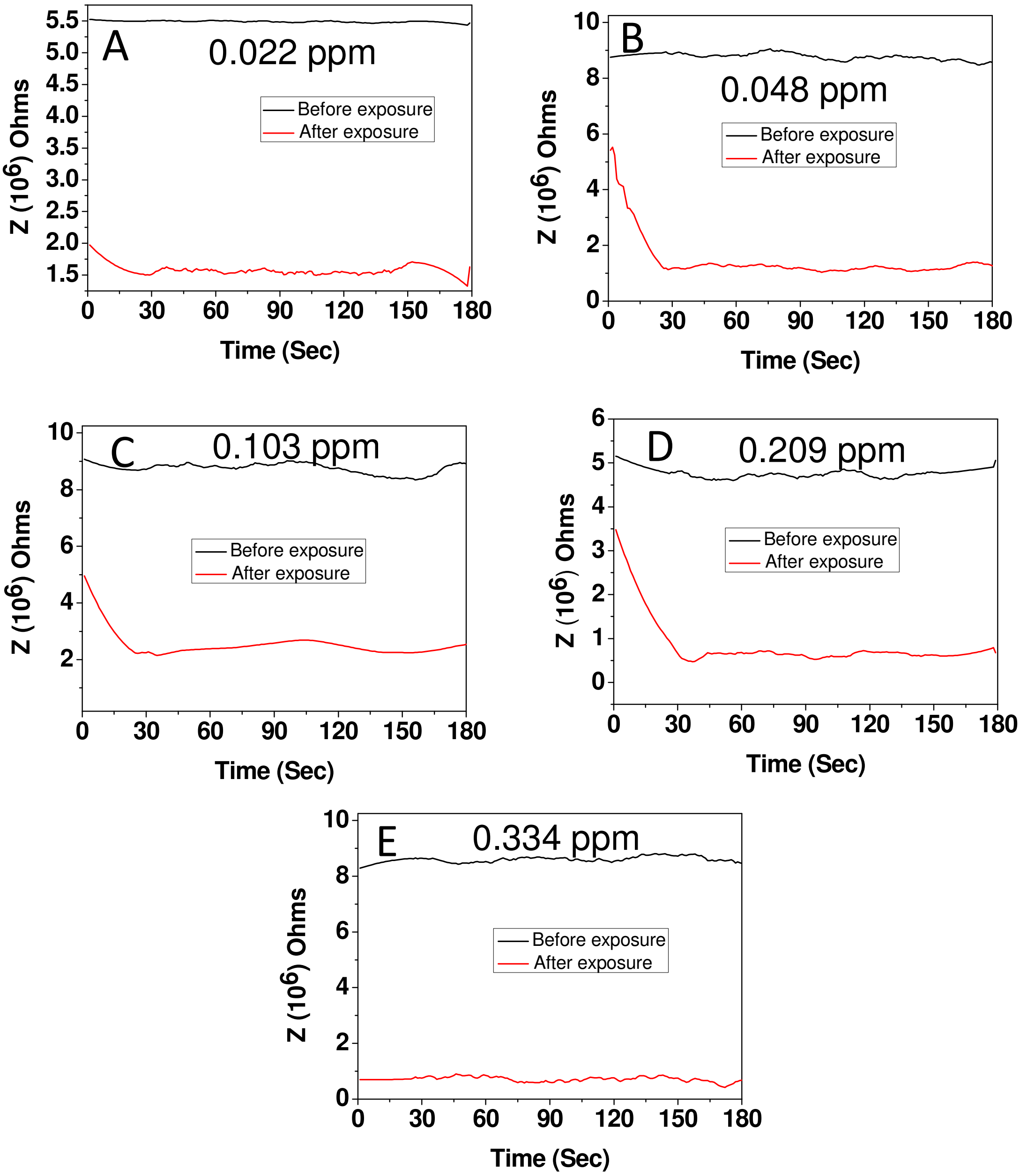

Fig. S4: Impedance (Z) versus time (sec) plot for the Detector-5 in presence of A. 0.022, B. 0.048, C. 0.103, D. 0.209, and D. 0.334 ppm of picric acid.

Sensing studies of the monolayer detectors:

Fig. S5 depicts the Z versus time plot for the monolayer polymers in presence of the vapour of PA at room temperature. It is evident that, P2VP-Co-AN (Fig. S5 A) undergoes an insignificant decrease in the Z values in presence of PA vapour and remains the same throughout the whole exposure time of 180 seconds. While, in case of PCHMASH (Fig. S5 B), a gradual decrease in the Z values were observed with respect to time although this decrease is not enough for efficient detection of picric acid vapour. PA do not effectively interact with the monolayer polymer detectors or it do not get adsorbed inside the polymer layer to cause notable change in the electrical properties of the detectors. The decrease in Z values for PCHMASH might be due to very weak interaction between this electron rich polymer (confirmed with the help of surface zeta potential determination) and electron withdrawing analyte. To increase the sensitivity for NAC vapour we have fabricated LBL detectors using these two polymers as described in the main manuscript.

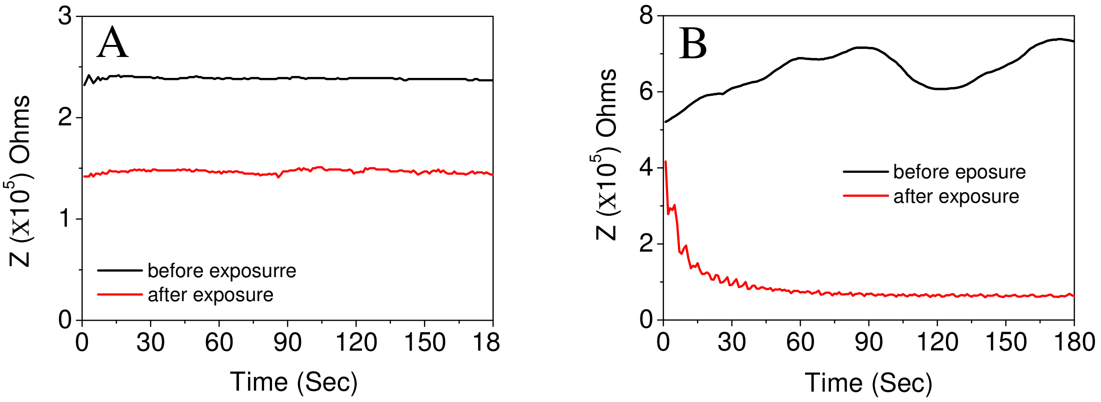

Fig. S5: Impedance (Z) versus time (sec) plot for A. P2VP-Co-AN and B. PCHMASH in presence of PA vapour at room temperature.

Sensing result of LBL detector with P2VP-Co-AN as outer layer:

Fig. S6 depicts the Z versus Time plot for LBL detector with P2VP-Co-AN as outer layers. It was observed that this LBL detector is inefficient in sensing PA vapour.

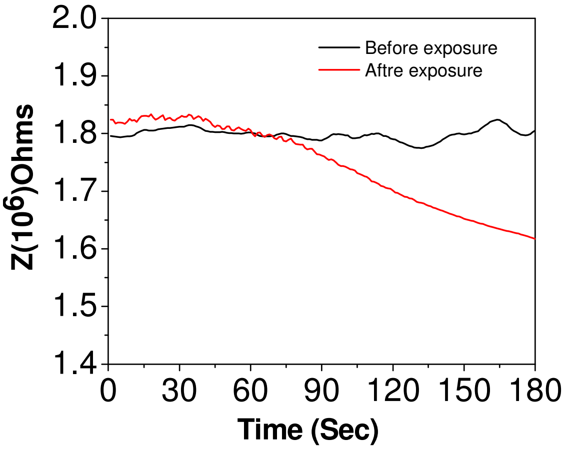

Fig. S6: Impedance (Z) versus time (sec) plot for LBL detector with P2VP-Co-AN as outer layers and PCHMASH ass middle layer.

Surface zeta potential (ζ):

The ζ plots of the polymers are shown in Figure S7. It was confirmed that the polymer PCHMASH is negatively charged with ζ value of about -37.9 mV. On the other hand, P2VP-Co-AN possesses a ζ value of about -2.42 mV.

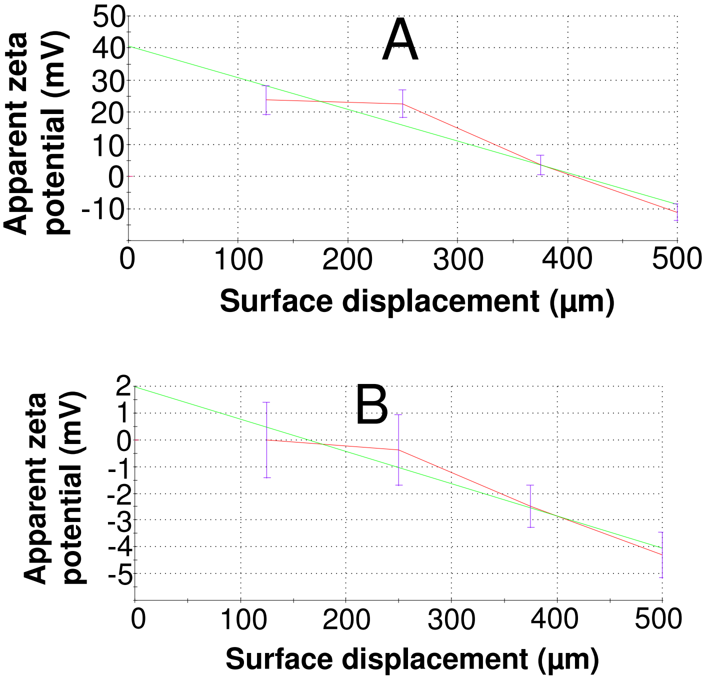

Fig S7: Apparent surface zeta potential of A. PCHMASH and B. P2VP-Co-AN.

FT-IR analysis: Table S2 and S3 depicts the FT-IR spectral analysis of PCHMASH and P2VP-Co-AN respectively after interaction with PA with different time scale. As mentioned in the main manuscript, there was no prominent peak shift of the polymers after sensing experiments.

Table S2: FT-IR spectral analysis of PCHMASH

Peak positions (cm^{-1})	Assignment
1720	Symmetric Stretching vibration of ester carbonyl group
1470	-CH$_3$ asymmetric deformation
1430	-CH$_2$, -CH$_3$ bending vibration
1394	In plane CH bending vibration
1166	-C-S stretching vibration
1068-1030	Ester C-O stretching vibration
856	Out of plane CH bending vibration

Table S3: FT-IR spectral analysis of P2VP-Co-AN

Peak positions (cm^{-1})	Assignment
2235	Stretching vibration of nitrile group
1600	C=C ring stretching vibration
1437	$-CH_2$ bending vibration
1150	Aromatic C-N stretching vibration
1050	=C-H bending vibration
800	Out of plane CH bending vibration

Cyclic voltammetry (CV): To perform CV, using three-electrode cell was used with glassy carbon electrode, platinum wire and the saturated Ag/Ag+ electrode as the working electrode, counter and reference electrode respectively. It was observed that the oxidation and reduction potential of PCHMASH remains unchanged as the plots are very similar to each other before and after interaction with PA as shown in Fig. S8.

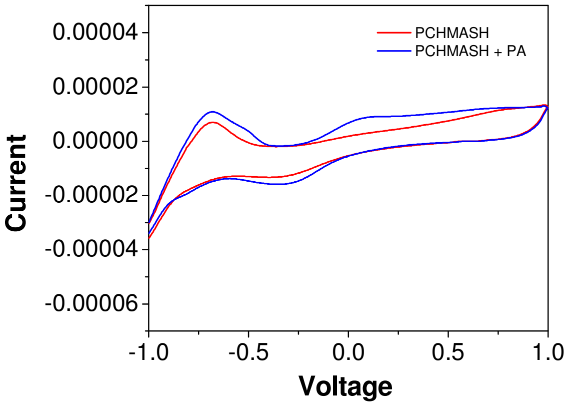

Fig. S8: Cyclic voltamogram of PCHMASH before and after sensing PA. Scan rate: 200 mV/sec.

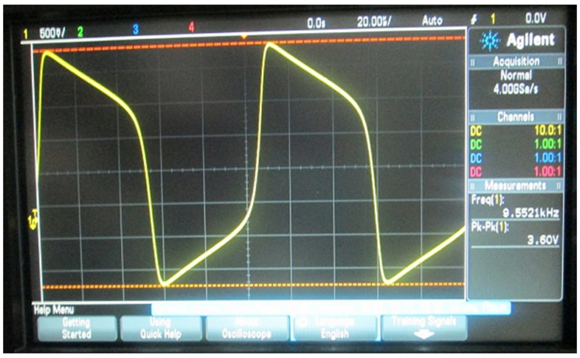

Fig. S9: Sinusoidal wave front used in the circuit as seen in the oscilloscope.

References:

1 S. J. Patil, N. Duragkar, V. R. Rao, *Sens. Actuators, B*, 2014, **192**, 444-451.

2 L. A. Pinnaduwage, T. Thundat, A. Gehl, S. D. Wilson, D. L. Hedden, R. T. Lareau, *Ultramicroscopy* 2004, **100**, 211-216.