Supporting Information

1.0 Details of Vector network analyzer and sample holder for EMI shielding measurement:

Shielding effectiveness (SE) measurements were performed using vector network analyzer (VNA, E8263BAgilent Technologies) on the rectangular samples (15.8 mm x 7.9 mm) placed inside Ku-band (12.4-18.0 GHz frequency range) sample holder that was connected to coaxial-to-waveguide adopters as shown in Figure S1.



Figure S1: Picture of VNA showing different ports, coaxial connectors, coaxial-towaveguide adaptors, short and sample holder

The input power level was set at -5 dBm (10 mW) and a full two port calibration was performed prior to measurements using a perfectly reflecting termination (short) and quarter wavelength waveguide (also served as sample holder after calibration). Further, the incident and transmitted waves in a two port VNA can be mathematically represented by complex scattering parameters (or S-parameters) i.e. S_{11} (or S_{22}) and S_{12} (or S_{21}) respectively which inturn can be conveniently correlated with reflectance (R) and transmittance (T) i.e. $T = |E_T/E_I|^2 = |S_{12}|^2 = |S_{21}|^2$, $R = |E_R/E_I|^2 = |S_{12}|^2$, giving absorbance (A) as: A = (1-R-T). Here, it is

to be noted that A is given with respect to the power of the incident EM wave. In actual practice, the relative intensity of the effectively incident EM wave inside the shield after primary reflection (from the EM incident face) is based on quantity (1-R), which necessitates the normalization of absorbance (A) to yield effectives absorbance as $:A_{eff} = [(1-R-T)/(1-R)]$. Therefore, actual reflective and absorptive losses can expressed as:

$$SE_{R} = 10log_{10}(1-R)$$
 (S1)

$$SE_{A} = 10log_{10}(1 - A_{eff}) = 10log_{10}\left[\frac{T}{(1 - R)}\right]$$
 (S2)

2.0 Structural Details of Polyaniline

Polyaniline is composed of reduced (-B-NH-B-NH-) and oxidized (-B-N=Q=N-) repeated units where symbols 'B' and 'Q' denote benzenoid and quinoid forms of $-C_6H_4$ - ring. These units are distributed along the backbone so that the polyaniline can be represented by general structure [(-B-NH-B-NH-)_y-(-B-N=Q=N-)_{(1-y}], where '(1-y)' and 'n' are oxidation state (OS) and degree of polymerization (DP) respectively. Therefore, depending on the oxidation state, different forms of polyaniline can be realized viz. leucoemeraldine (fully reduced, y=1), pernigraniline (fully oxidized, y=0) and emeraldine base (EB, 50 % oxidized and 50 % reduced, y=0.5). The doping of EB with protonic acids covert it into emeraldine salt (ES) leading to formation of charge carriers i.e. polarons/bipolarons. However, even after doping, except ES all other forms are electrically insulating in nature which shows that both oxidation state as well as protonic acid doping plays a critical role in determining the electrical properties of the polyaniline

3.0 Polymerization mechanism of aniline via oxidative coupling route

The polymerization of aniline (AN) monomer in aqueous medium is initiated by water soluable oxidant like ammonium peroxydisulfate [APS i.e. $(NH_4)_2S_2O_8$] such that AN present

at the boundary of micelle-water surface gets oxidized and form anilinium radical cations as shown in Figure S2.



Figure S2: Representation of chemical oxidative polymerization of anilne

In the next step they rearrange and couple with another unit to form neutral dimer. Further oxidation and coupling of this dimer leads to the formation of a termer and reaction continued likewise (propagation) to form the oligomers (tetramer, octamer..... etc.) and finally a dark green color dispersion of highly conducting doped PANI particles is formed. The termination takes place by various chain transfer processes leading to formation of polymer.

4.0 FTIR spectroscopy and structural details

The FTIR spectra (Figure S3) of PDB, PCD, PLS and PCS display C=C stretching vibrations of quinoid diimine (N=Q=N) and benzenoid diamine (N-B-N) segments in the wavenumber range 1550-1570 cm⁻¹ and 1475-1495 cm⁻¹ respectively. The characteristic band around 870-885 cm⁻¹ corresponds to H-C-H out-of-plane (OOP) bending vibrations of para-coupled

benzene rings, which confirmed the head-to-tail-coupling of aniline monomer units. Further, 1002-1005 and 1020-1030 cm⁻¹ bands represent the symmetric (s) and asymmetric (as) stretching vibrations of the -S=O bonds of the dopant counter-anions confirming their presence in polymer matrix.



Figure S3: FTIR spectra of PANI samples doped with different bulky counter-ion organic sulfonic acids (a) PCD, (b) PDB, (c) PLS and (d) PCS

Furthermore, all samples give a band in the range 1146-1152 cm⁻¹ which is due to protonated imine nitrogens and can be correlated with the degree of doping and extent of charge delocalization (or conjugation) over polymer chain as its intensity gets significantly reduced in the respective undoped/base forms. A careful comparison of intensity of this band relative to 1475-1495 cm⁻¹ band (i.e. $I_{1146-1152}$ / $I_{1475-1496}$) gives a qualitative idea about the extent of doping, which in the present case also reflects the in-situ doping capability of used dopants (CDSA, LSA, DBSA or CSA).

5.0 UV-Visible analysis: optical band gap, oxidation satate and doping details

UV-visible absorption spectra of undoped forms of samples display two characteristic features. The first absorption in the range 320-330 nm can be ascribed to the $\pi_B \rightarrow \pi_B^*$ (or band

gap) transition of benzenoid units and its position is directly related to the extent of conjugation. On the other hand, the band near 630 nm (Peak-II) is due to the molecular exciton associated with the quinine–diimine structure i.e., transition of electrons from HOMO orbitals of benzenoid rings and LUMO orbitals of the quinoid rings ($\pi_B \rightarrow \pi_Q^*$ transition). Interestingly, comparison of absorbance (Abs.) of band-gap (~320 nm) and exciton transitions (~620 nm) can be used to get a qualitative estimate of oxidation state (OS) [i.e. quantity (1-y)] according to expression:

$$[O.S] = (1 - y) = \frac{[Abs_{620}]}{[Abs_{320} + Abs_{620}]}$$
(S3)



Figure 4: Tauc plot [i.e. $(\alpha hv)^2$ versus hv plot] and corresponding optical band gap $(Eg \sim 3.31 \text{ eV})$ & polaronic transition energy $(E \sim 1.64 \text{ eV})$ for PDBU.

The band gap energies of the conducting polymers are closely related to their OS and doping level and often lies in the UV-Visible region. Further, the band-gap of an amorphous semiconducting material can be expressed by following generalized Tauc relation:

$$\alpha h \nu = A (h \nu - E_g)^n \tag{S4}$$

Where α is the absorption coefficient (extinction coefficient), 'hv' is the energy of incident photons of frequency 'v', E_g is optical band gap and 'A' is a constant of proportionality which depends on temperature and can be related to degree of randomness. The exponent 'n' is related to the distribution of density of states within 'k-space' and assumes values of 1/2, 3/2, 2 and 3 direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. Therefore, for a direct band-gap semiconductor like undoped PANI (EB), the energy associated with the $\pi_B \rightarrow \pi_B^*$ optical absorption edge can be obtained using the expression:

$$\alpha h \nu = A(h \nu - E_g)^{1/2}$$
 (S5)

The intersection of the extrapolated tangent drawn on the linear portion of $(\alpha hv)^2$ versus hv plot, with the x-axis gives value of band-gap (E_g).

The redoping of undoped polymers convert them into electrically conducting emeraldine salt form which gives three characteristic transitions in the 200-1100 nm range. The first absorption around 330-360 nm was ascribed to combined effect of $\pi_B \rightarrow \pi_B^*$ (or band gap) transition of benzenoid units plus transition from low lying π_B levels to semiquinoid or polaron level (π_S), that are formed due to doping of imine (quinoid) nitrogen atoms. On the other hand, the absorptions around 420-440 nm ($\pi_S \rightarrow \pi_B^*$) and 700-800 nm ($\pi_B \rightarrow \pi_S$) are related to the polaronic states [60, 77]. The absorbance of these polaronic transitions with relative to band-gap transitions can be used for qualitative estimation of polaronic content and hence achieved doping level i.e. quantity (D.L) as:

$$D.L = \left\{ \frac{Abs.[(\pi_s \to \pi_B^*) + (\pi_B \to \pi_s)]}{Abs.[(\pi \to \pi^*)]} \right\}$$
(S6)

5.0 Electron paramagnetic resonance (EPR) analysis

The EPR spectra of conducting polymers can be analyzed using Gaussian/Lorentzian distribution function. A typical EPR spectrum in derivative signal form is shown in the Figure S5. The recorded spectra contains vital information about various parameters such as

 ΔH_{PP} , g-value, asymmetry parameter, spin concentration and T₂, which are further related to material structure/properties. The g-value (2.0023 for free electron) and asymmetry parameter (i.e. A/B ratio) gives information about the metallic character of composites and degree of freedom of charge carriers. The peak-to-peak width (Δ Hpp) and normalized area under peak carries information about spin-environment interaction (relaxation) and spin concentration respectively.



Figure S5: Typical electron paramagnetic resonance (EPR) spectra of conducting polymers showing line shape, peak-to-peak width and asymmetry parameters

The doping of polyaniline produces localized defects within the band leading to generation of charge carriers. In case of polyaniline, polaron (q=+e, s=1/2) and bipolaron (q=+2e, s=0) are thought to charge carriers, where symbols 'q' and 's' denote carrier's charge and spin respectively. The spin-less nature of bipolarons (dications) makes them undetectable during EPR measurement. However, polarons (radical cations) with associated unpaired electron can easily be identified as paramagnetic centers. Therefore, with bipolarons being EPR forbidden, the contribution to spin concentration comes exclusively from the spin bearing polarons. These polarons can move along (intra-chain) and across (inter-chain) the chains imparting electrical conductivity to material.

6.0 Microwave shielding and complex permittivity spectra

The term shielding is defined as attenuation of the propagating electromagnetic (EM) waves produced by the proposed shield can be expressed as⁸:

$$\operatorname{SE}_{\mathrm{T}}(\mathrm{dB}) = 10 \log_{10} \left(\frac{\mathrm{P}_{\mathrm{T}}}{\mathrm{P}_{\mathrm{I}}}\right) = 20 \log_{10} \left(\frac{\mathrm{E}_{\mathrm{T}}}{\mathrm{E}_{\mathrm{I}}}\right) = 20 \log_{10} \left(\frac{\mathrm{H}_{\mathrm{T}}}{\mathrm{H}_{\mathrm{I}}}\right) \tag{S7}$$

Where $P_I (E_I \text{ or } H_I)$ and $P_T (E_T \text{ or } H_T)$ are the power (electric or magnetic field intensity) of incident and transmitted EM waves respectively. As the ratio $P_T/P_I (E_T/E_I \text{ or } H_T/H_I)$ is always less than unity therefore, SE_T (total shielding effectiveness) is a negative quantity such that a shift towards more negative value means increase in magnitude of SE_T . In actual practice, three different phenomenon named reflection, absorption and multiple reflections contributes towards SE_T therefore, $SE_T = SE_R + SE_A + SE_M$. The re-reflection term (SE_M) which arises due to multiple reflections between both interfaces of the shield can be expressed as:

$$SE_{M} = 20 \log_{10} \left(1 - e^{-\frac{2t}{\delta}} \right) = 20 \log_{10} \left(1 - 10^{-\frac{SE_{A}}{10}} \right)$$
(S8)

Eqn. (S8) clarifies that when SE_A is greater than 10 dB, SE_M (~ -1.0 dB) can be safely neglected ^{9,10} and SE_T can be expressed as: SE_T = SE_R + SE_A.

Further, depending on the distance (r) between radiation source and detector and wavenumber (k), EM wave propagation mode can be classified as near filed (kr<<1) or far field (kr>>1). In far-filed regime, which is the case in our measurement range (i.e. in P-band), the EM radiation propagates with constant characteristic impedance (Z=E/H=(ϵ^*/μ^*)^{1/2}) and can be visualized as plane wave, where ϵ^* and μ^* are complex permittivity and permeability respectively. Another consideration, which has to be taken into account for transient (frequency dependent) fields, is the parameter skin depth (δ). It is defined as the depth of penetration of the incident EM radiation inside the shield at which its intensity is suppressed to ~37 % (1/eth) of its

original magnitude. Under good conductor approximation (i.e. $\sigma_T/\omega\epsilon_o >>0$), δ can be expressed as:

$$\delta = \left(\frac{2}{\sigma_{\tau}\omega\mu_{r}}\right)^{\frac{1}{2}}$$
(S9)

The term total conductivity (σ_T) which is composed of frequency dependent (ac) and independent (dc) components is presented in equation (6) as:

$$\sigma_{\rm T} = (\sigma_{\rm ac} + \sigma_{\rm dc}) = \omega \varepsilon_{\rm o} \varepsilon^{"} \tag{S10}$$

Here, parameters ω (2 π f), μ_r , ε'' and ε_o represents angular frequency (linear frequency), real permeability, imaginary permittivity and the free space permittivity respectively. Therefore, after careful comparison of δ with shield thickness (t) two situations can be visualized:

(a) When $(t \ll \delta)$: which occurs either at low frequencies (according to eqn. S9) or in case of electrically thin sample where actual shield thickness is much less than skin depth. In such a case the absorption which is a bulk (or thickness) related phenomenon can be neglected and attenuation occurs almost exclusively by reflection. The total shielding becomes frequency independent and can be expressed as:

$$SE (dB) = -20 \log_{10} \left[1 + \frac{Z_0}{2} t\sigma_T \right]$$
(S11)

where Z_0 is free space impedance (377 Ω)

(b) When $(t \gg \delta)$: which is valid in our case and generally occurs at higher frequencies where skin depth becomes much less as compared to actual shield thickness i.e. in case of electrically thick samples. Under such condition both reflective and absorptive attenuation are important and can be expressed as:

$$SE_{R}(dB) = -10\log_{10}\left(\frac{\sigma_{T}}{16\omega\varepsilon_{o}\mu_{r}}\right)$$
(S12)

$$\operatorname{SE}_{A}(\mathrm{dB}) = -20\frac{t}{\delta}\log_{10}e = -8.68\left(\frac{t}{\delta}\right) = -8.68t\left(\frac{\sigma_{\tau}\omega\mu_{r}}{2}\right)^{\frac{1}{2}}$$
(S13)