Supplementary Information for

Synthesis engineering and development of emergent conducting pi-conjugated materials: applications in energy harvesting and storage devices

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SI – 1. Raman Spectroscopy

The Raman spectra exhibited the characteristic peaks of PEDOT, see Figure SI – 1a, corresponding to specific vibrational modes: the symmetric C–S–C deformation observed at ~700 cm⁻¹, deformation of the oxyethylene ring at ~985 cm⁻¹, and the C_{α}–C_{α} inter-ring stretching located around 1250 cm⁻¹. Additionally, the band detected around 1360 cm⁻¹ is attributed to the C_{β}–C_{β} stretching vibration.^{1–3} The symmetric stretching of the aromatic C_{α}=C_{β} bonds within the thiophene ring is found between 1350 and 1500 cm⁻¹, see Figure SI – 1b. A shift of this peak towards lower wavenumbers (red shift) is indicative of the transition of PEDOT segments from the neutral benzenoid form to the doped quinoid configuration, reflecting changes in the polymer doping state.



Figure SI – 1. (a) Raman spectra of PEDOT:PSS ink films. (b) Close view of the Raman spectra for the $C_{\alpha} = C_{\beta}$ symmetrical stretching intramolecular vibration of PEDOT between 1500 and 1350 cm⁻¹.



Figure SI – 2. Electrical conductivity and 1SI-1: Electrical conductivity and power factor of PEDOT:PSS inks

SI – 2. Conductivity and Power Factor.



Figure SI – 3. UV-Vis-NIR spectra of PEDOT:PSS films in the wavelength range from 250 to 2500 nm. The films have a thickness of ~ 120 nm. The dashed lines indicate the absorptions of polarons and bipolarons.

SI – 3. UV – Vis – NIR spectroscopy.

SI – 4. Fourier-transform infrared (FTIR) spectroscopy.

In Figure SI-4, several bands characteristic of PEDOT:PSS can be observed: the peak at 1520 cm⁻¹ corresponds to C=C asymmetric stretching; the band at 1300 cm⁻¹ is attributed to C–C inter-ring stretching; and the signals at 1180, 1139, 1083, and 1051 cm⁻¹ arise from angular deformations of C–O–C linkages. Additionally, peaks appearing at 974, 930, 831, and 685 cm⁻¹ are related to thiophene C–S–C stretching vibrations.^{1,4,5} The absorption bands at 685 cm⁻¹ and 831 cm⁻¹ are linked to CH vibrations of mono- and bi-substituted EDOT units, respectively, and can be employed as markers to assess the degree of PEDOT polymerization, as detailed



Figure SI – 4. FTIR spectra of PEDOT:PSS inks. The dashed lines indicate the absorptions band centered at 835 cm⁻¹ and 685 cm⁻¹.

in Table SI – 1.

Table SI – 1. FTIR absorption intensity of PEDOT:PSS inks in 835 cm ⁻¹ and 64	85 cm ⁻¹ , respectively and FTIR
intensity ratios	between 835

cm⁻¹ and 685

cm⁻¹.

Ink	835 cm ⁻¹	685 cm ⁻¹	FTIR ratio (835 cm ⁻¹ /685 cm ⁻¹)
1P	0.78	0.55	1.42
Tupane	0.95	0.72	1.32
Fluxel	1.08	0.87	1.24



Figure SI – 5. AFM topography images (Height Sensor mode) of six different PEDOT:PSS formulations, acquired in retrace mode over a $1 \times 1 \mu m^2$ scan area with a resolution of 256 × 256 pixels and a scan rate of 1 Hz. The Root Mean Square roughness values obtained for each sample were: Tupane (1.32 ± 0.21 nm), Polaraci (0.68 ± 0.06 nm), Fluxel (2.99 ± 0.31 nm), Clevios P (0.25 ± 0.01 nm), Al4083 (0.75 ± 0.01 nm) and PH1000 (0.87 ± 0.07 nm).

SI – 5. Atomic Force Microscopy (AFM).

SI – 6. Organic Solar Cell's (OSCs)

PEDOT:PSS	*VOC (V)	*JSC(mA/cm2)	*FF (%)	*Rs (Ω·cm2)	*Rsh (Ω·cm2)	*PCE (%)
0.5P	0.75	34.03	51.50	2.51	111.58	11.61
	(0.721 ± 0.022)	(30.18 ± 1.7)	(48.50 ± 4.23)	(1.95 ± 0.40)	(90.79 ± 22.58)	(10.53 ± 1.0)
Polaraci	0.83	25.65	70.06	3.48	899.60	14.57
	(0.828 ± 0.004)	(23.70 ± 1.0)	(69.15 ± 0.83)	(2.05 ± 0.62)	(741.16 ± 112.35)	(13.56 ± 0.5)
AI 4083	0.84	24.87	71.25	2.91	734.32	14.49
	(0.838 ± 0.004)	(23.51 ± 0.7)	(69.34 ± 1.51)	(1.87 ± 0.66)	(678.59 ± 35.17)	(13.65 ± 0.5)
Clevios P	0.83	34.05	59.68	1.13	96.17	15.50
	(0.828 ± 0.004)	(31.76 ± 1.3)	(55.73 ± 1.85)	(0.65 ± 0.38)	(79.97 ± 7.25)	(14.64 ± 0.8)
HTL solar	0.82	35.90	54.83	0.23	69.92	15.25
	(0.814 ± 0.005)	(33.39 ± 1.9)	(52.58 ± 1.36)	(0.19 ± 0.01)	(55.89 ± 7.96)	(14.29 ± 0.7)

Table SI – 2. Photovoltaic Parameters of glass/ITO/PEDOT:PSS/PBDB-T-2F:Y6/PFN-Br/Ag OSC's, varying the HTL of PEDOT:PSS.

*Calculated from the mean curve of 12 cells; maximun value (a ± b) (mean ± standard deviation).



Figure SI - 6. Photocurrent density versus effective voltage (Jph - Veff).

References

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