Supplementary Information

Synergistic radical concentration increase in eumelanin-PEDOT:PSS blends: mammalian pigment-based doping for thermopower improvement.

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Materials and Methods:

All commercially available reagents were used as received and all the solvents were analytical grade quality.

5,6- Dihydroxindole (DHI) was prepared according to a reported procedure.[1]

The film thicknesses were measured by KLA Tencor P-10 surface profiler. Film thickness was estimated by scratching the film down to the substrate with a needle and measuring by surface profiler the height of the resulting trench. Film roughness was estimated as Root Mean Square (RMS) from several scans on the same sample.

UV–vis optical transmittance analysis of layers deposited on glass substrates was carried out by using Perkin-Elmer Lambda 900 spectrophotometer.

Thermogravimetric analysis were run in nitrogen atmosphere at 10 °C/min.

Electrical characterization

The measurements have been effectuated using Linseis specific sample holders, which consist of integrated PCB boards equipped with primary and secondary heaters, thermocouples and metallic points as shown in FIG1.

The films were deposited on 2cmx2cm glass or PE substrate to align with the dimensions of the sample holders. To address low conductivity in organic material films, a masking technique was employed to create aluminum pads with dimensions of 2mmx2mm, as sketched in Figure S1. This approach was implemented to improve the contact between the thermo-couple wires (metalic points) for the Seebeck (conductivity) measurements.
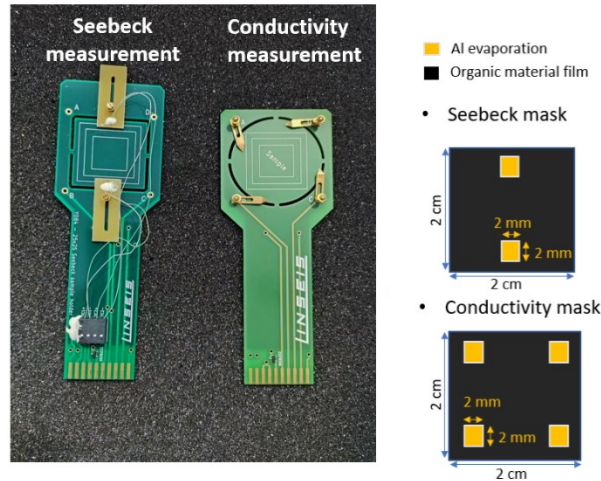
Figure S1

The sample holder employed for Seebeck measurements enables precise control over both sample temperature and temperature gradient. This is achieved through the strategic positioning of Thermo-Couple (TC) wires, which make direct contact with the sample surface, and heaters positioned precisely on the back. While the gradient heater power undergoes a linear increase, the Seebeck voltage along with the temperature gradient are recorde
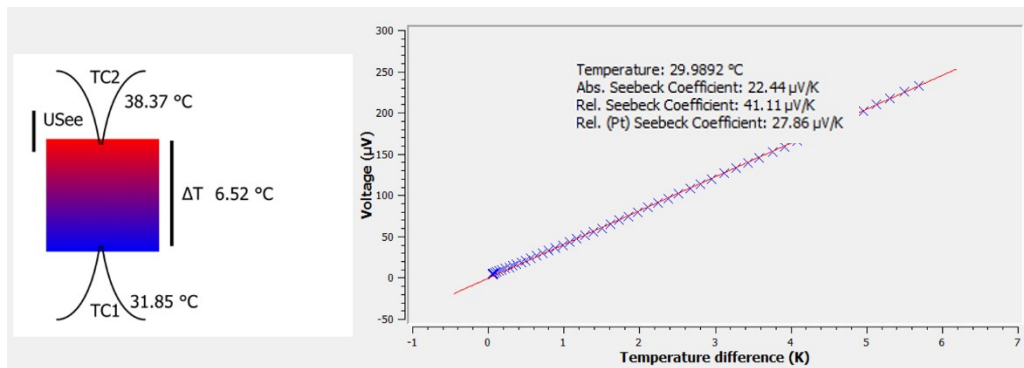

Figure S2

The Seebeck coefficient is obtained from the linear fit of the Seebeck Voltage over the temperature difference (ΔT), as shown in Figure S2 as an example for the sample Ped-Mel 1:1. This approach effectively mitigates offsets in temperature gradient measurements, contributing to an enhanced level of measurement accuracy.

The Linseis software measures the Seebeck coefficient relative to Alumel and automates the calculation of the Seebeck coefficient relative to platinum, commonly utilized as a reference in the literature, enabling the determination of the absolute Seebeck coefficient.

For conductivity measurements, the second sample holder, in Fig1 on the right, consents to determine the electrical conductivity of the sample using the Van der Pauw technique. This methodology suppresses parasitic influences such as contact or wire resistances increasing the measurement accuracy.

The sample is connected with four metal points directly on the edge. A current is induced along two contacts at one edge of the sample and the voltage across the other two contacts on the opposite edge

is measured, deriving the resistance value using Ohm's law. In this way, the software measures the horizontal and vertical resistance and directly calculates the sheet resistance solving the Van der Pauw formula[2]:

$$e^{-R_{(=)}\frac{\pi d}{\rho}} + e^{-R_{(||)}\frac{\pi d}{\rho}} = 1$$

Finally, inserting the thickness of the thin film "d", the resistivity and the conductivity are obtained.

Atomic Force Microscopy

The topography of the samples was obtained by means of an Atomic Force Microscope (AFM – Witec Alpha 300 RAS) working in tapping mode with non-contact cantilevers at resonance frequency of 280 kHz and spring constants of k = 42N/m. All the analyzed AFM images have dimensions of 1x1μm with 256 points per scan line and with 256 scan lines and at a 1 Hz scan rate (i.e. at a corresponding tip to sample velocity of 1 μm/s). The resulting pixel size is 4nm which is equal or less than the tip dimensions (nominal radius of curvature R ≤ 10nm). The AFM parameters (non-contact operation mode, gain values, set-point value, scan rate, driving amplitude) were kept constant during the scans in order to ensure the roughness comparison among the samples. The samples were analyzed in random order to eliminate nuisance factors resulting from the tip degradation or laboratory temperature and humidity variation.
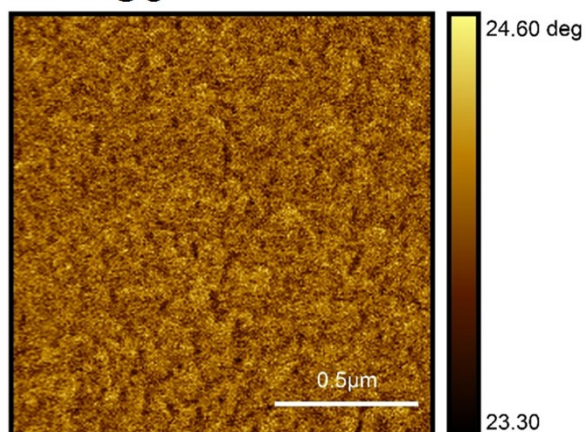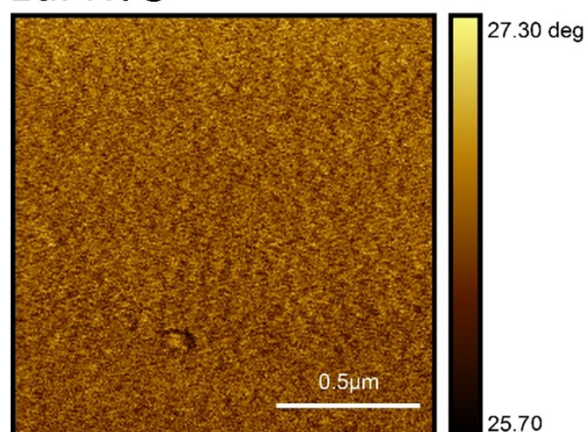
PEDOT:PSS
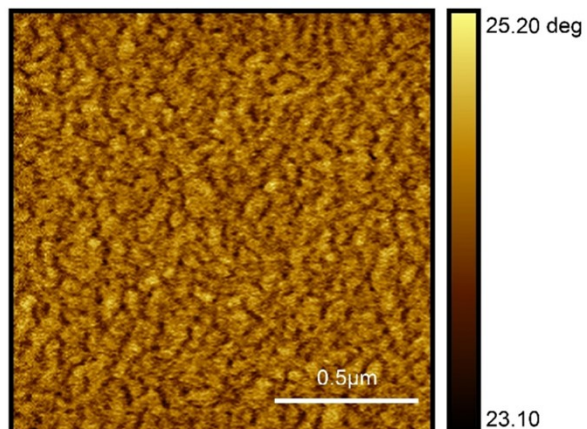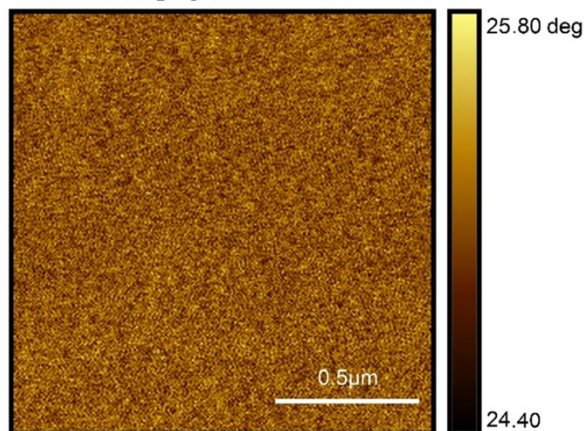

EuPH25
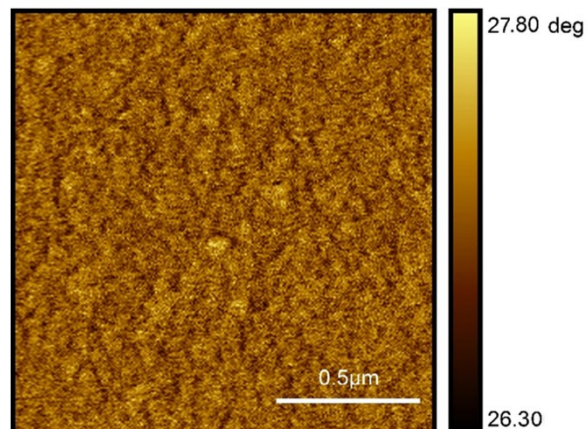
EuPH50

EuPH75

DHI-melanin

Figure S3. Topography phase images of PEDOT:PSS and Eu-PH blends obtained using tapping-mode AFM.

PEDOT:PSS
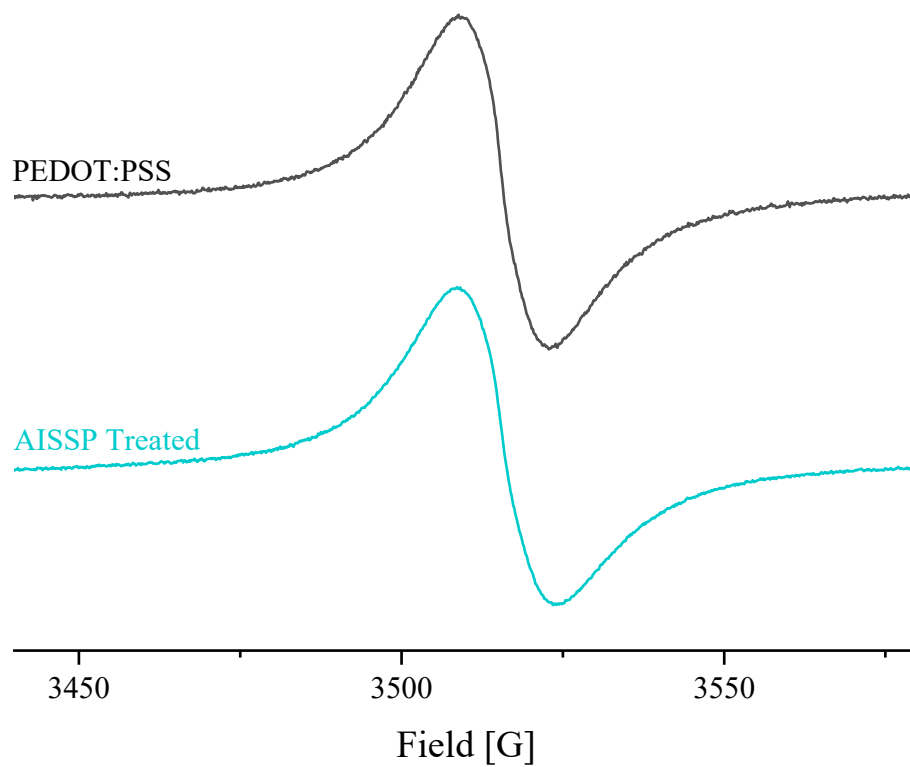
AISSP Treated

3450   3500   3550

Field [G]

Figure S4. PEDOT:PSS spectra before and after the AISSP treatment. The analysis reveals that there are hardly any discernible variations between the two spectra, indicating that the treatment has limited effect on the sample.
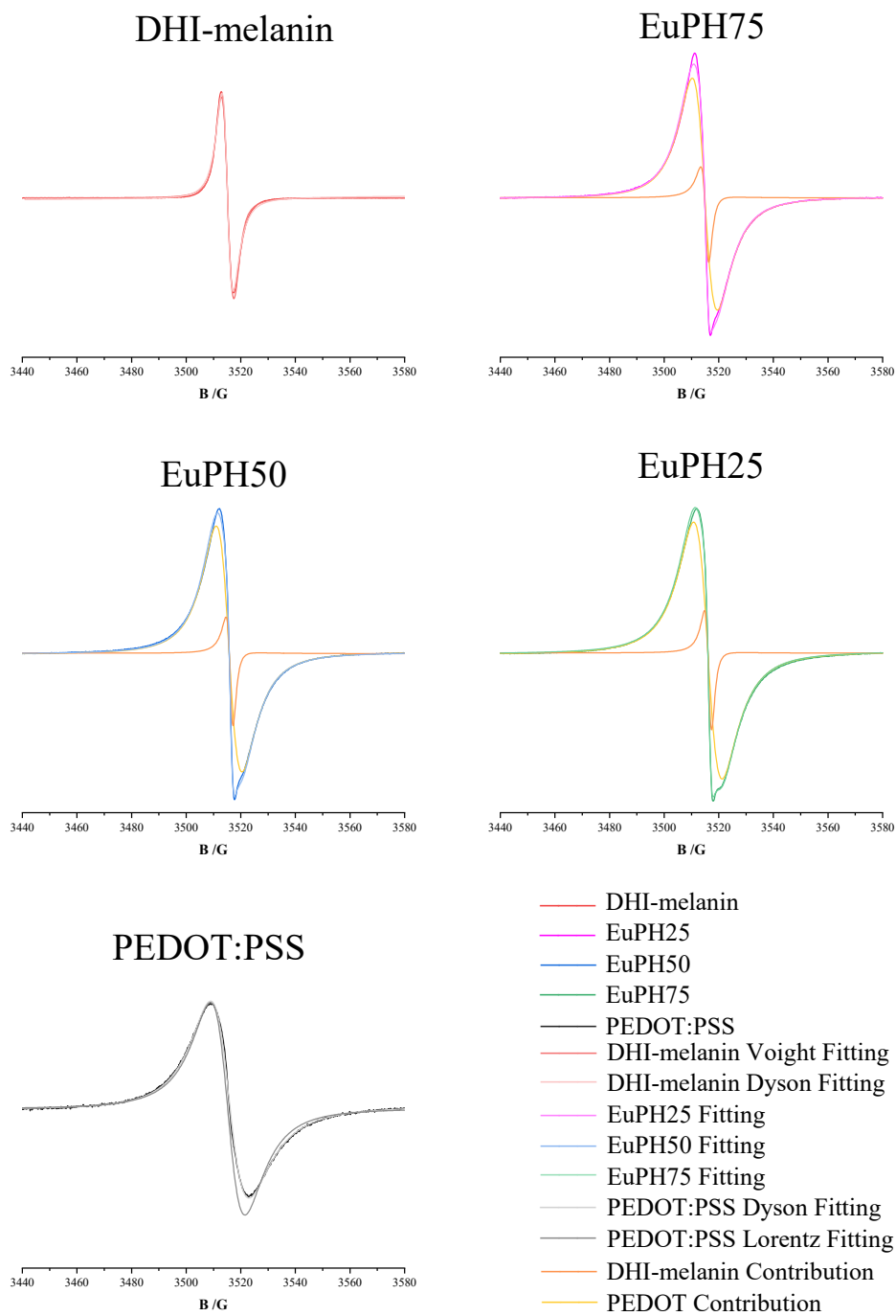
Figure S5. Analysis of the EPR spectra. In all cases, darker lines represent the experimental signal, lighter lines represent the best fit. For the blends (EuPH75, EuPH50, EuPH25), an orange line represents the DHI-melanin contribution and a yellow line represents the PEDOT contribution to the signal. For DHI-melanin, Voight and Dyson fits are compared. For PEDOT:PSS, the Lorentz and Dyson fits are compared.
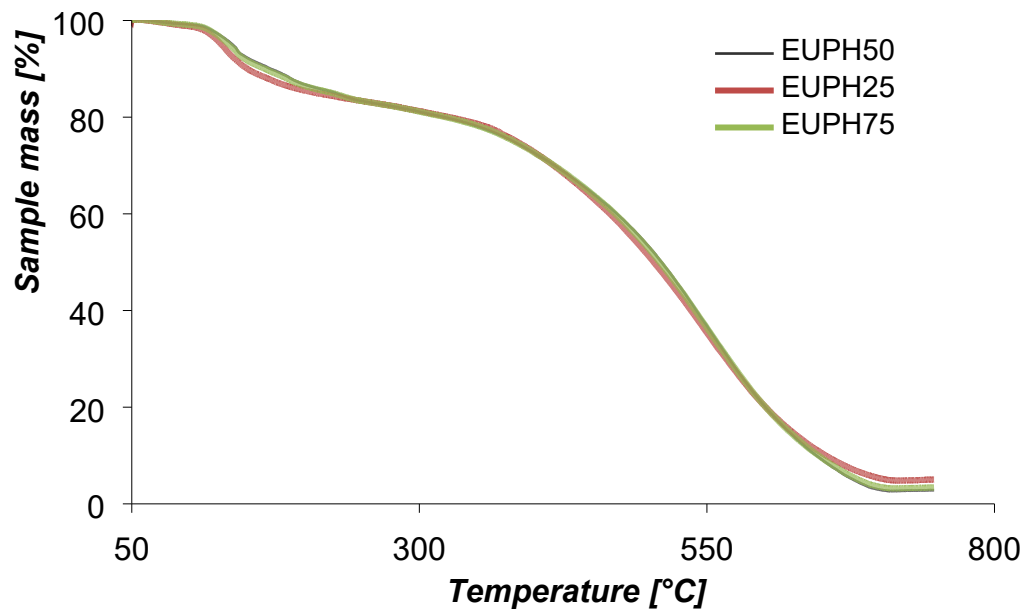
Figure S6. Thermogravimetric analysis profiles of the blends EuPH 25, EuPH 50, and EuPH 75.

1. R. Edge, M. D'Ischia, E. J. Land, A. Napolitano, S. Navaratnam, L. Panzella, A. Pezzella, C. A. Ramsden and P. A. Riley, *Pigment Cell Research*, 2006, **19**, 443-450.
2. F. S. Oliveira, R. B. Cipriano, F. T. da Silva, E. C. Romão and C. A. M. dos Santos, *Scientific Reports*, 2020, **10**, 16379.