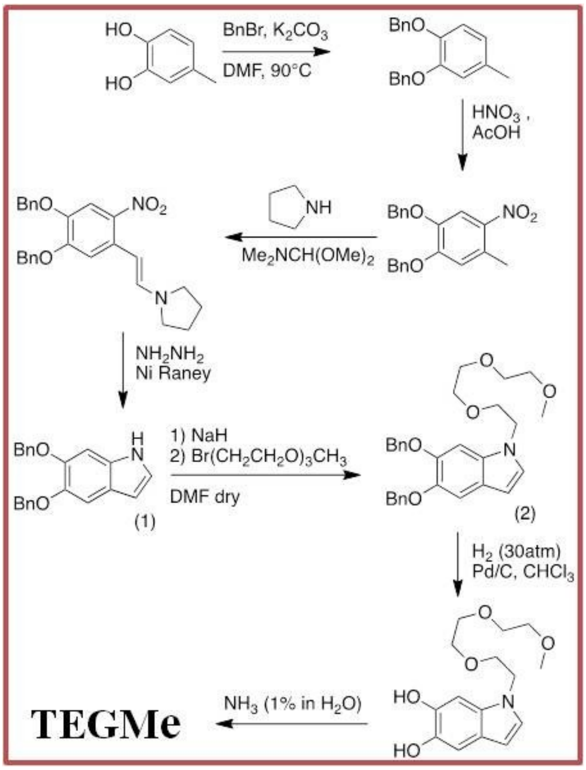
## Supporting Information




**Scheme 1.** Scheme of the Synthesis of N-functionalized 5,6-dibenzyloxyindole (1) and its conversion to TEGMe by aerial polymerization following debenzylation.(from. Ref. 17)

### The adsorption isotherms

When a solid is exposed in a closed space to a gas or vapor at some definite pressure, the solid adsorbs the gas by increasing the weight and decreasing the pressure of the gas. When the equilibrium is attained the pressure becomes constant and the weight ceases to increase. The amount of gas taken up by a solid at a fixed temperature is proportional to the mass of a sample and depends on the pressure p of the vapor and on the nature of both the solid and the gas.

$$n = f(p/p^o)_{T,\text{gas, solid}}$$

where

n = quantity of gas adsorbed (mol/g)

$p^o$ = Saturation vapor pressure

Because of the hydrogen bonding propensity of the water molecules, the adsorption isotherms of water vapor are especially sensitive to the degree of polarity of the adsorbent surface. The water contained in a solid shows different forms in dependence on the interactions between the solid chemical structure and water molecules. The sorption isotherms describe the thermodynamic relationship between water activity ($a_w$ = p/p°) and the moisture content of the solid at a constant temperature. The shape of an isotherm reflects the way in which water binds the system. Brunauer et al (1940) classified sorption isotherms according to their shape and processes, establishing five different types. Sorption isotherms can be classified according to their shape and processes, establishing six different types. Among these, type III, known as Flory-Huggins isotherm, accounts for sorption isotherms characteristic of weak gas-solid interactions promoting cooperative adsorption processes and type VI is the stepped one. Sorption isotherms can be generated by an adsorption process or a desorption one: the difference between the curves is defined as a hysteresis.

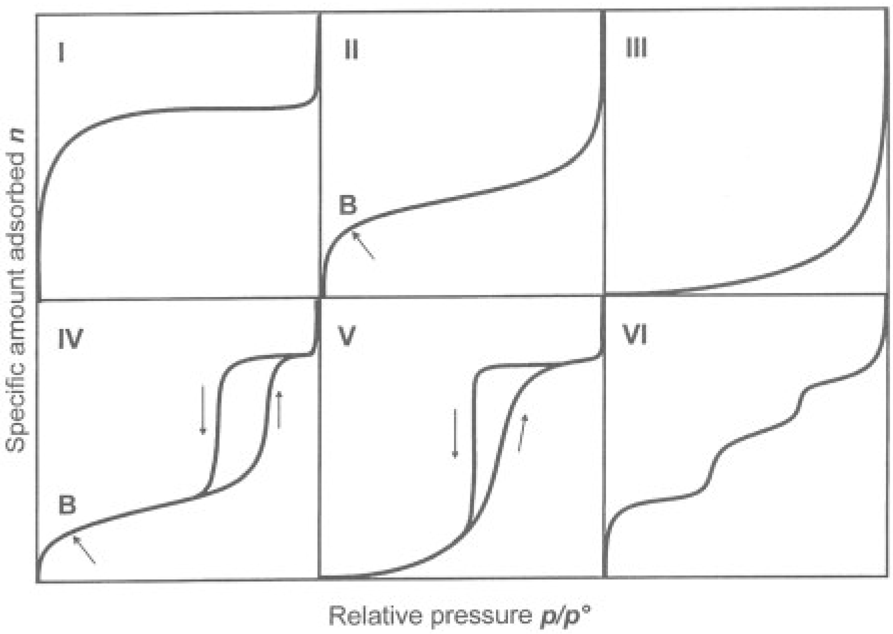



**Figure S1** The IUPAC classification for adsorption isotherms (reprint from. F. Rouquerol, J. Rouquerol and K. Sing, "Adsorption by Powder & Porous Solid", Academic Press, London, (1999))

## AC measurements brief theoretical support

*Permittivity and conductivity calculations from impedance data.*

The measurement of the impedance, Z, allowed to determine the permittivity ε, and the actual real, ε', and imaginary, ε", parts, provide that the geometrical parameters of the items under study are well defined known. Defining as Z' the real part and –Z" the imaginary part of the impedance Z, ω = 2πf, (ω the angular frequency and f are the AC signal frequency), the permittivity and the AC term of the conductivity are expressed by ε = ε'+j ε"

□with

$$\varepsilon' \equiv \frac{-Z''}{\omega C_0\left(Z'^2 + Z''^2\right)} \; and \; \varepsilon'' \equiv \frac{Z'}{\omega C_0\left(Z'^2 + Z''^2\right)} \tag{1}$$

With $C_0 = \varepsilon_0 \Sigma / d$ ($\varepsilon_0 = 8.85\ 10^{-14}$ F/cm$^2$) the equivalent vacuum capacitance of the electrode embedding the dielectric Sample under test with d the electrode distance and S the cross-sectional area of the electrode. The permittivity relates also to the AC conductivity via the expression $\sigma_{AC} = \omega\varepsilon' \tan\delta$ where $\tan\delta = \varepsilon''/\varepsilon'$ is the loss factor.

**Table S.1** Summary of the best fit parameters of AC conductivities following expr.3 (main text) for the (a) Dev.1(⊥) (b) Dev.2 (∥) configurations embedding TEGMe and AMe . The frequency ranges are labeled as I, II, III corresponding to the frequency regions where the AC conductivity were fitted by the expr.3 returning the displayed $\sigma_{0,}$ A and s as the best fit parameters.

1.a

| Eumelanin | TEGMe (⊥) | | | AMe (⊥) | | |
|---|---|---|---|---|---|---|
| Parameters / ω regions | $\sigma_0$ | A | s | $\sigma_0$ | A | s |
| I (low freq) | | | | $1.0\ 10^{--12}$ | $9.8\ 10^{-13}$ | 0.8 |
| II (med. freq.) | - | | | | $2.9\ 10^{-13}$ | 1.3 |
| III (high freq.) | $2.2\ 10^{-9}$ | $3.2\ 10^{-12}$ | 0.7 | | $1.4\ 10^{-6}$ | 0.6 |

TEGMe (⊥) : I e II → ω = 0.1 Hz÷10 MHz; III → ω = 100 Hz÷1MHz

AMe (⊥) : I → ω = 0.1 Hz÷100 Hz; II→ ω = 100 Hz÷10 kHz; III→ ω = 10 kHz ÷ 1 MHz

1.b

| Eumelanin | TEGMe (∥) | | | AMe (∥) | | |
|---|---|---|---|---|---|---|
| Parameters / ω regions | $\sigma_0$ | A | s | $\sigma_0$ | A | s |
| I (low freq) | $2.0\ 10^{-6}$ | $3.1\ 10^{-7}$ | 0.6 | $1.0\ 10^{-6}$ | $4.6\ 10^{-7}$ | 0.1 |
| II (med. freq.) | - | $1.6\ 10^{-7}$ | 0.8 | | $1.1\ 10^{-9}$ | 1.1 |
| III (high freq.) | | $1.2\ 10^{-7}$ | 1.7 | | $2.3\ 10^{-13}$ | 1.9 |

TEGMe (∥) : I → ω = 0.1 Hz÷100 Hz; II→ ω = 100 Hz÷10 kHz; III→ ω = 10 kHz ÷ 1 MHz

AMe (∥) : I → ω = 0.1 Hz÷1.0 kHz; II→ ω = 1.0 kHz÷10 kHz; III→ ω = 10 kHz ÷ 1 MHz

## NPs electrical circuit representation.

Electrical Impedance Spectroscopy data can be represented via Nyquist Plots (NPs) i.e. *ReZ vs –ImZ*. The ReZ is an index of the carrier response under a continuous electric field while the -ImZ refers to the carrier response to the AC field. NPs are generally examined by fitting the experimental data with the NP returned by a properly designed electrical equivalent circuits.

The equivalent circuit is generally constitute by a combination of a resistive R, a pure capacitive C, and peculiar like the constant phase ($Z_{CPE}$) and diffusion ( $Z_W$) elements that are properly assembled in order to represent the overall AC electrical carrier transport mechanisms.. Moreover, each circuital element combination can be assigned to a specific interaction in specific AC frequency signal range.

The constant phase element $Z_{CPE}$ is expressed by

$$Z_{CPE} = \frac{1}{Q_0\,(j\omega)^n} \tag{1}$$

and is a phenomenological element introduced in order to simulate a non-perfect capacitive element. The n – parameter plays the main role since if it is close to zero the impedance element behaves more like a resistor, while when it is close to 1 it acts like a pure capacitor.

The diffusion element ($Z_W$) is given by:

$$Zw = \frac{A_W}{\omega^{1/2}} - j\frac{A_W}{\omega^{1/2}} \tag{2}$$

and is generally represented in NPs through a straight line whose slope is equals to 0.5. If the diffusion element is represented in the NPs by a straight line with slope different (higher /lower) than 0, the circuital element is substitute by a constant phase element and we refer it to an anomalous diffusion or CPE-limited diffusion mechanisms[36]

A commonly adopted circuit for representing carrier transport mechanisms occurring when a electronic/ionic material is placed in between two metallic electrode is the Randles circuit (**Figure S.2**) generally made up of a resistor (the contact resistance) in series with the parallel of a constant phase element or a capacitor (representing the charge double layer) with the series of a resistance (defined as the charge transfer resistance) and the diffusion element.

Finally it is possible to extract the true capacitance value from a Randles circuit by using the $R_{ct}$- $Z_{CPE}$,dl terms representing the NPs. The expression suitable for electronic-ionic conductor used is: [35]

$$C = R_{ct}^{(1-n)/n} Z_{CPE,dl}^{1/n} \sin(n\cdot\pi/2) \quad .(3)$$

**Figure S.2** Randles circuit used for the representation of the impedance via NPs of electronic/ionic material in between metallic electrodes; the constant phase element is represented both in the case of a normal ($Z_W$) and anomalous ($Z_{CPE}$, constant phase restricted diffusion, see text). The $R_{HF}$ is the contact resistance while at the catode (+) charge transfer mechanisms take place.

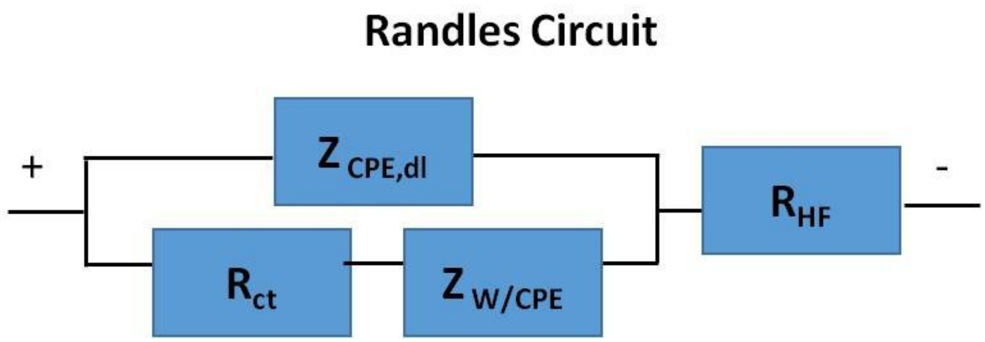


**Table S.2**. EIS best fit parameters as extracted by using the EIS analyser program that best fitt the NP data with those of the equivalent circuit in Figure S.3 on TEGMe (a) and AMe(b) - based devices in Dev.1(⊥) configuration.

2.a

| Eumelanin | TEGMe (⊥) | | | AMe (⊥) | | |
|---|---|---|---|---|---|---|
| Voltage (V) / Fit | 0.0mV | 400 mV | 800 mV | 0.0 mV | 400 mV | 800 mV |
| $R1_{,HF}$(kΩ) | 3600 | 3800 | 3800 | 81 | 80 | 79 |
| $R_{2,ct}$(kΩ) | 1040 | 940 | 890 | 0.8 | 1.1 | 1.1 |
| $Z_{CPE,1}$(dl) | 86 | 91 | 93 | 198 | 387 | 710 |
| $n_1$ | 0.9 | 0.9 | 0.9 | 0.4 | 0.4 | 0.4 |
| $Z_{CPE,2}$ | 7400 | 7900 | 8700 | 1400 | 1400 | 1400 |
| $n_2$ | 0.8 | 0.8 | 0.8 | 0.9 | 0.9 | 0.9 |
| $Z_{CPE,3}$ | 0.15 | 0.13 | 0.12 | 2.7 | 2.8 | 2.6 |
| $n_3$ | 0.9 | 0.9 | 0.9 | 0.8 | 0.8 | 0.8 |

$Z_{CPE}$ (pF·$s^{(n-1)}$/$cm^2$): 1: Double layer; 2: CPE-limited Diffusion; 3: HF capacitance

**Figure S.3** Equivalent circuit representing the NPs data in TEGMe (a) and AMe (b) –based devices in Dev.1(⊥) configuration.

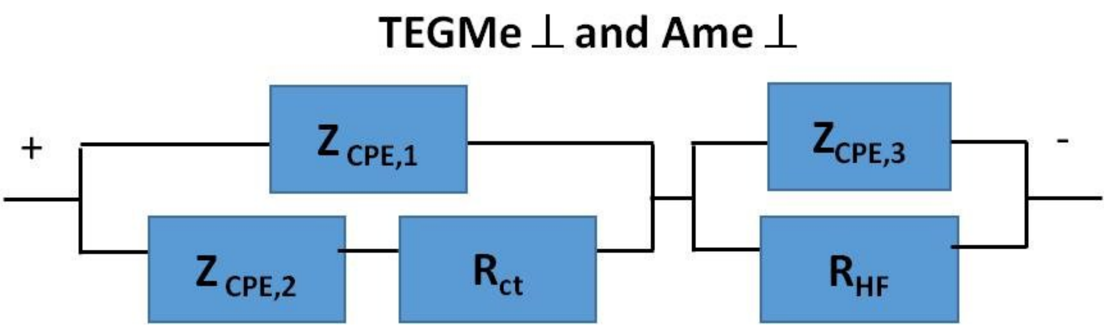


**Table S.3**. EIS best fit parameters extracted as in Table S.2 by fitting the NP data with those of the equivalent circuit in Figure S.4 on TEGMe (S.4a) and AMe (S.4b) - based devices in Dev.2(‖) configuration.

| Eumelanin | TEGMe (‖) | | | AMe (‖) | | |
|---|---|---|---|---|---|---|
| Voltage (V) / Fit | 0.0mV | 400 mV | 800 mV | 0.0 mV | 400 mV | 800 mV |
| $R_{1,LF,ct}$(MΩ) | 556 | 544 | 670 | 205 | 44 | 9.4 |
| $R_{2,HF}$(Ω) | 1063 | 1078 | 1050 | 306 | 264 | 262 |
| $Z_{CPE,1(dl)}$ | 1.25 | 1.25 | 1.26 | 0.4 | 0.4 | 0.4 |
| $n_1$ | 0.99 | 0.99 | 0.99 | 0.99 | 1 | 1 |
| $Z_{CPE,2(HF)}$ | 39 | 42 | 42 | - | - | - |
| $n_2$ | 0.74 | 0.73 | 0.73 | - | - | - |

$Z_{CPE}$ (nF·s(n−1)/cm$^2$) 1: Double layer capacitance; 2:HF capacitance

**Figure S.4** Equivalent circuits representing the NPs data in TEGMe (a) and AMe (b) –based device in Dev.2(‖) configuration.