

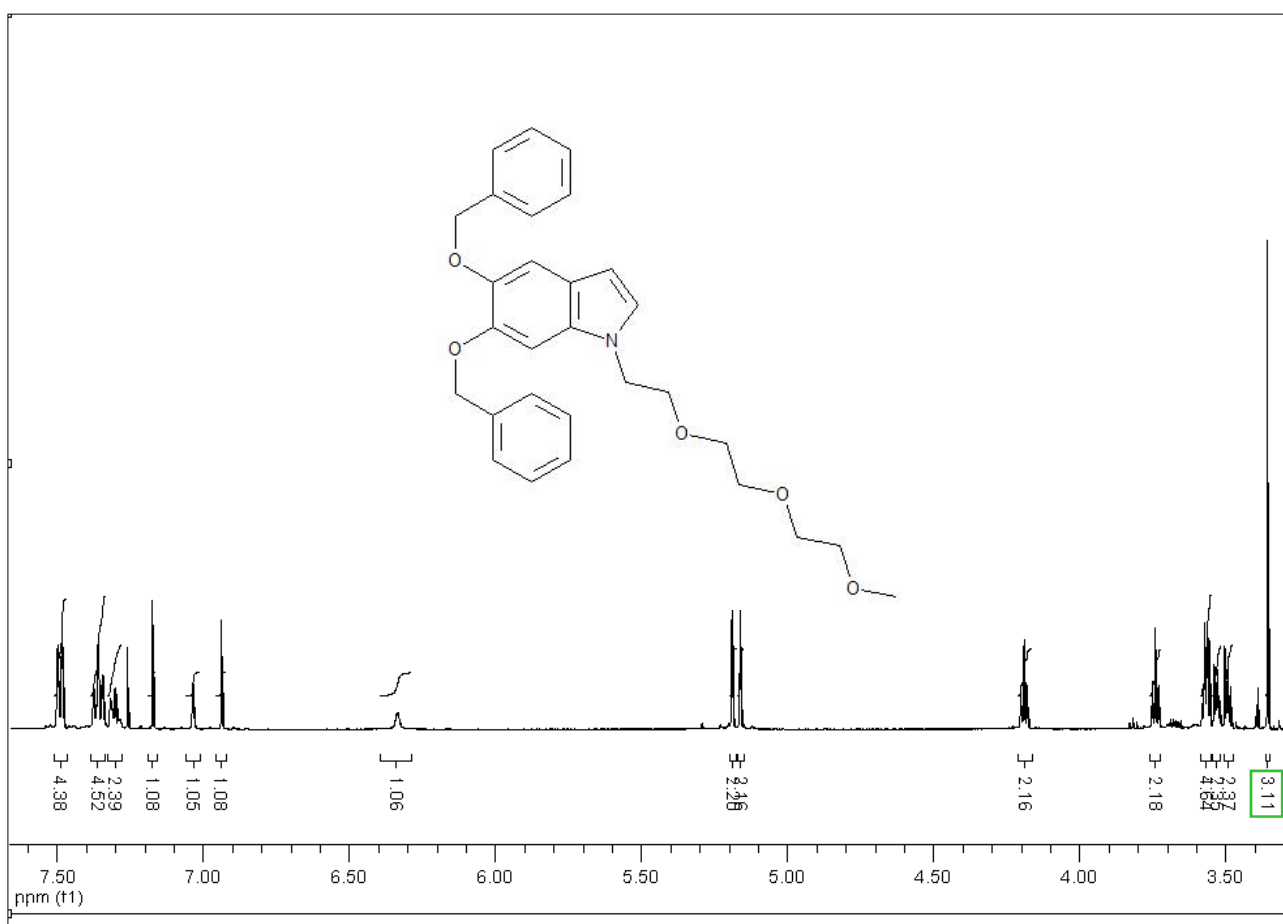
## ELECTRONIC SUPPLEMENTARY INFORMATION

### A water-soluble eumelanin polymer with atypical polyelectrolyte behaviour by triethyleneglycol *N*-functionalization

Stefania R. Cicco, Marianna Ambrico Paolo F. Ambrico, Maurizio Mastropasqua Talamo, Antonio Cardone, Teresa Ligonzo, Rosa Di Mundo, Cinzia Giannini, Teresa Sibilano and Gianluca M. Farinola\*

Paola Manini, Alessandra Napolitano Valeria Criscuolo<sup>§</sup> and Marco d'Ischia\*

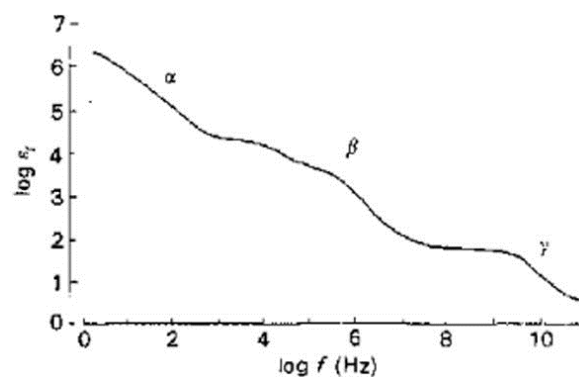
**Figure S1**-<sup>1</sup>H NMR spectra of the 5,6-bis(benzyloxy)-1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1H-indole



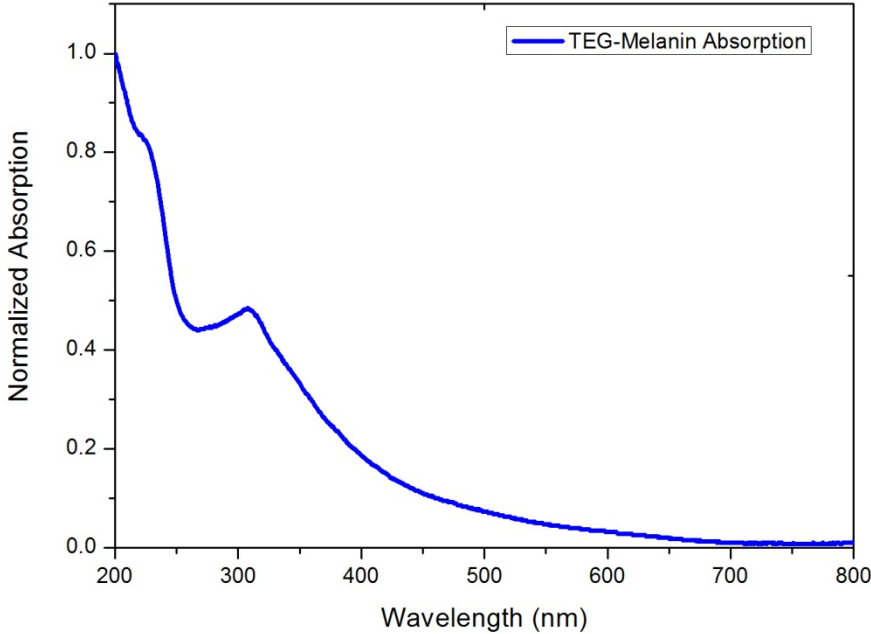
## S.2 Impedance spectra of biological materials

It is recognized that the permittivity spectra of a biological item shows some specific features represented by three relaxation regions, termed as  $\alpha$ ,  $\beta$  and  $\gamma$ . Each of them is linked to a process able to follow the AC signal up to the relaxation frequency. The  $\alpha$  relaxation region is ascribed to the formation of the electrical double layer and is present up to few kHz. This is a typical interfacial phenomena generally occurring when a metallic object (for example a metallic electrode) is contacted by an electrolyte. A double layer consists of two surface charge distributions, one facing the metallic electrode and the other of opposite sign at the electrolyte surface. A capacitance value is generally attributed to this layer. The  $\beta$  relaxation region is between 10 Hz up to 1 MHz and is due to ions mediated interfacial polarization; such ions are accumulated or blocked at the surfaces under the external electric field. The charging effect is called Maxwell-Wagner effect and occurs at frequencies from tens of kHz to tens of MHz, depending on the layer structure and composition. Moreover, in biological items, dependence of such a component on the water content is expected i.e. the higher the water content the higher the permittivity. In the higher frequency region, i.e. from tens of MHz all phenomena are relaxed except that due to water molecule polarization ( $\gamma$  region) that switches off in the GHz region.

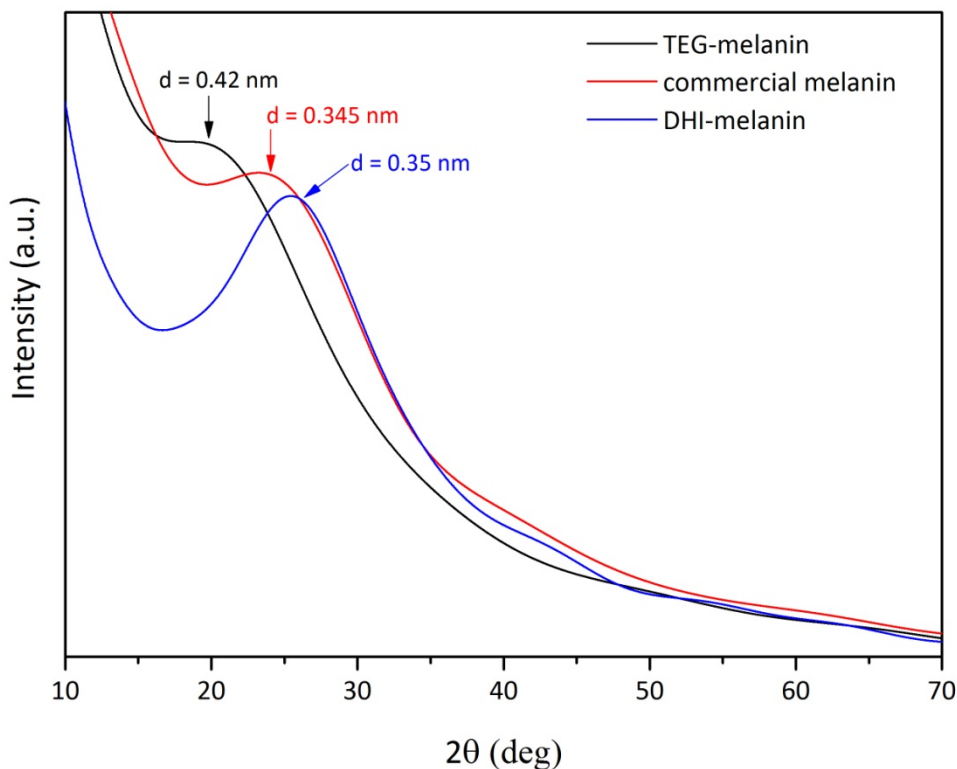
**Figure S2.** Ideal plot for impedance dispersion of biological items (tissue, membranes etc..) [aft. Schwan et al. (see ref.[25] main text)



**Figure S.3** Normalized broadband Optical Absorption spectra of drop casted TEG-Melanin layer on quartz



**Figure S.4** Powder X-ray diffraction spectra of TEG-melanin (black curve), commercial melanin SM (red curve) and DHI-Mel (blue-curve).



The effect of the TEG chains on eumelanin solid state packing was investigated by X-ray diffraction analysis of TEGM in comparison with a commercial synthetic melanin (SM) powder and a 5,6-dihydroxy-indole-melanin (DHI-Mel) samples as references. DHI-Mel was ad-hoc synthesized for this comparison and experimental details of its preparation will be reported in due course. This is a melanin-like material equivalent to TEGM, without the TEG chains. Typically, melanin-like amorphous compounds produce broad peaks in the diffraction spectrum.<sup>24</sup> In the case of TEGM powder, the position of the first amorphous peak was found at around  $2\theta \sim 21.5^\circ$ , suggesting a correlation distance  $d = 0.42$  nm, whereas in the case of SM and DHI powders the same peak was registered at around  $2\theta \sim 25^\circ$  indicating a distance  $d = 0.35$  nm, the latter being 20% smaller compared to the TEG-melanin.