Eumelanin Adsorption on Silicon: Optical Properties of Si(001)-adsorbed Eumelanin Tetrameric Protomolecules: Supporting Information

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Figure S1 shows photoabsorption cross-section spectra of the gas phase IMIM tetramer in its Si(001)-adsorbed geometries, for chosen light polarization directions. In particular, with "IMIM-only-0deg-adsgeom" ("IMIM-only-45deg-adsgeom", respectively) we indicate gas phase IMIM in the geometry it assumes in the Si(001):IMIM-0° (Si(001):IMIM-45°) system. For the IMIM-only-0deg-adsgeom we chose the "standard" par1 and par2 polarization directions used throughout this work, while for IMIM-only-45deg-adsgeom we chose two polarization directions, Y and Z, that are rotated by 45° with respect to par1 and par2 respectively, so that they would coincide with the par1 and par2 directions of the IMIM-only-0deg-adsgeom, if the two gas phase systems had an identical geometry. This is, however, not the case, since the gas phase IMIM models extracted from the Si(001):IMIM systems display geometric rearrangements due to adsorption, which are dependent on the adsorption orientation. Despite these differences, we can indeed observe a similarity between "corresponding" absorption components of the two analyzed systems, *i.e.* the par1 (par2) component of the IMIM-only-0deg-adsgeom model and the Y (Z) component of the IMIM-only-45deg-adsgeom one. This suggests that also some features of the molecule-molecule contribution to absorption in Si(001):tetramer systems (such as a peculiar low energy anisotropy between the two chosen in-plane polarization directions, par1 and par2, for the Si(001):IMIM-45° system) may be at least partially explained by simple geometric considerations on the molecule only, namely the relative orientation of the chosen polarization directions with respect to the symmetry axes of the molecule.

Figure S2 shows selected details of the Si(001):X systems for X = PNZ (two top panels) and IMIM (two bottom panels), both in the 0° configuration, allowing a close view of some possible tetramer- silicon chemical bonds and/or molecule atoms significantly close to the silicon surface in these systems. From a visual inspection of these configurations (Figure S2) and of the 22.5° and 45° ones both for PNZ and for IMIM (data not shown) we can conclude that in all these systems at most eight tetramer atoms can form bonds to the Si surface, so that 24 silicon atoms per (8×4) cell are not bonded to any molecule atom. Therefore, as

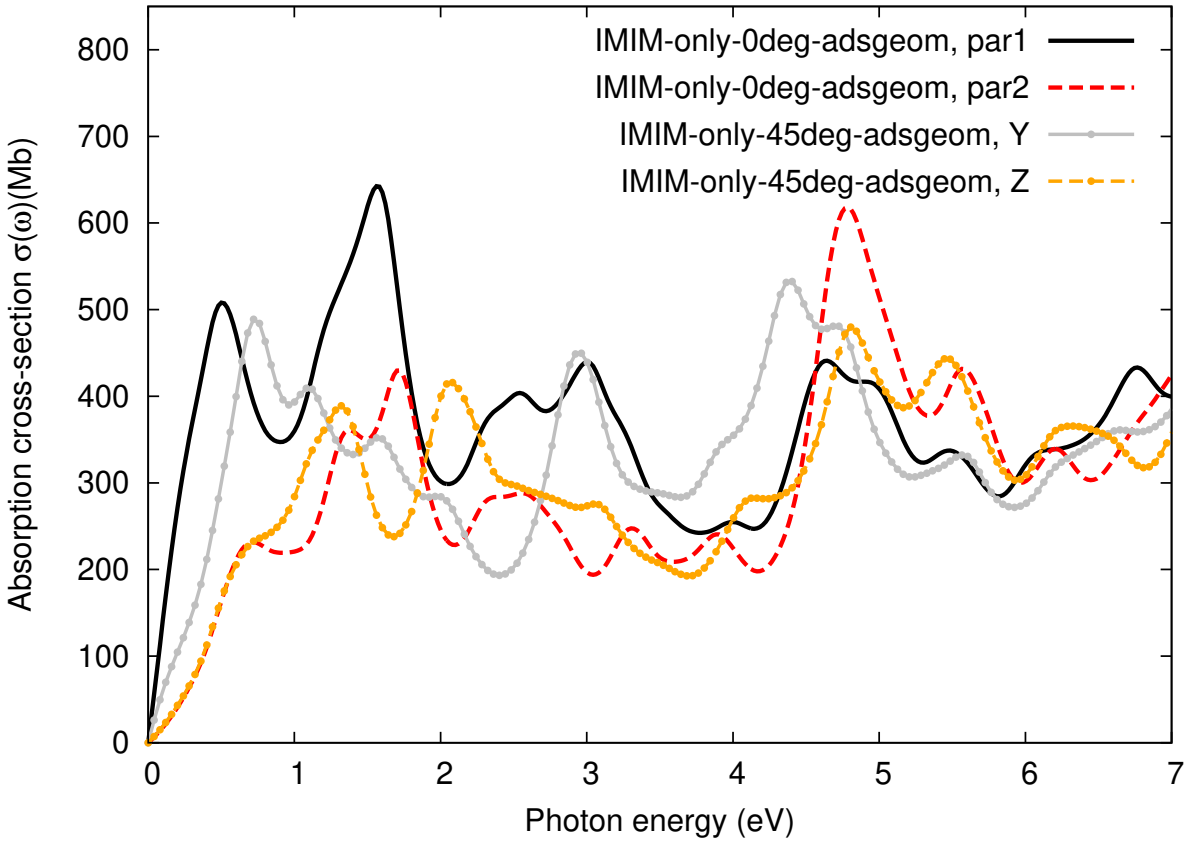

Figure S1: Photoabsorption cross-section for the gas phase IMIM-only-0deg-adsgeom and IMIM-only-45deg-adsgeom models (see text for their description) for light polarization along chosen directions.

already mentioned in the comment to Figure 2 in the Results and Discussion section of the manuscript, the PNZ and IMIM tetramers in the chosen adsorption configurations do not fully saturate the silicon surface. On the contrary, as discussed here, they leave a significantly higher density of unsaturated silicon dangling bonds per unit surface area with respect to the case of uracil-like nucleobases on Si(001) (see references in the main text). This may explain the less pronounced quenching of the two characteristic clean Si(001) negative RAS peaks in the here investigated Si(001):PNZ and Si(001):IMIM systems with respect to the Si(001):nucleobase case, where these two peaks are almost completely quenched.

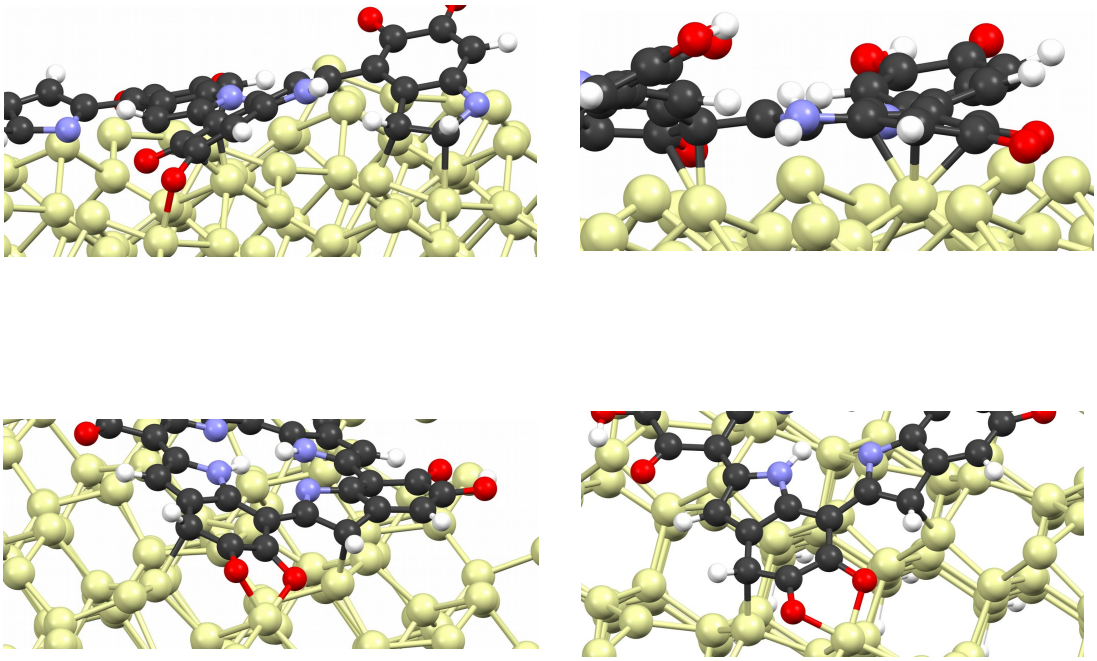

Figure S2: Details of the Si(001):PNZ-0° (two top panels) and Si(001):IMIM-0° (two bottom panels) systems, highlighting the regions where the tetramer molecule can potentially form bonds to the silicon surface.