Supporting Information for

Assessing the Charge Transfer at the Cytochrome c_{553}/Graphene Interface: A Multiscale Investigation

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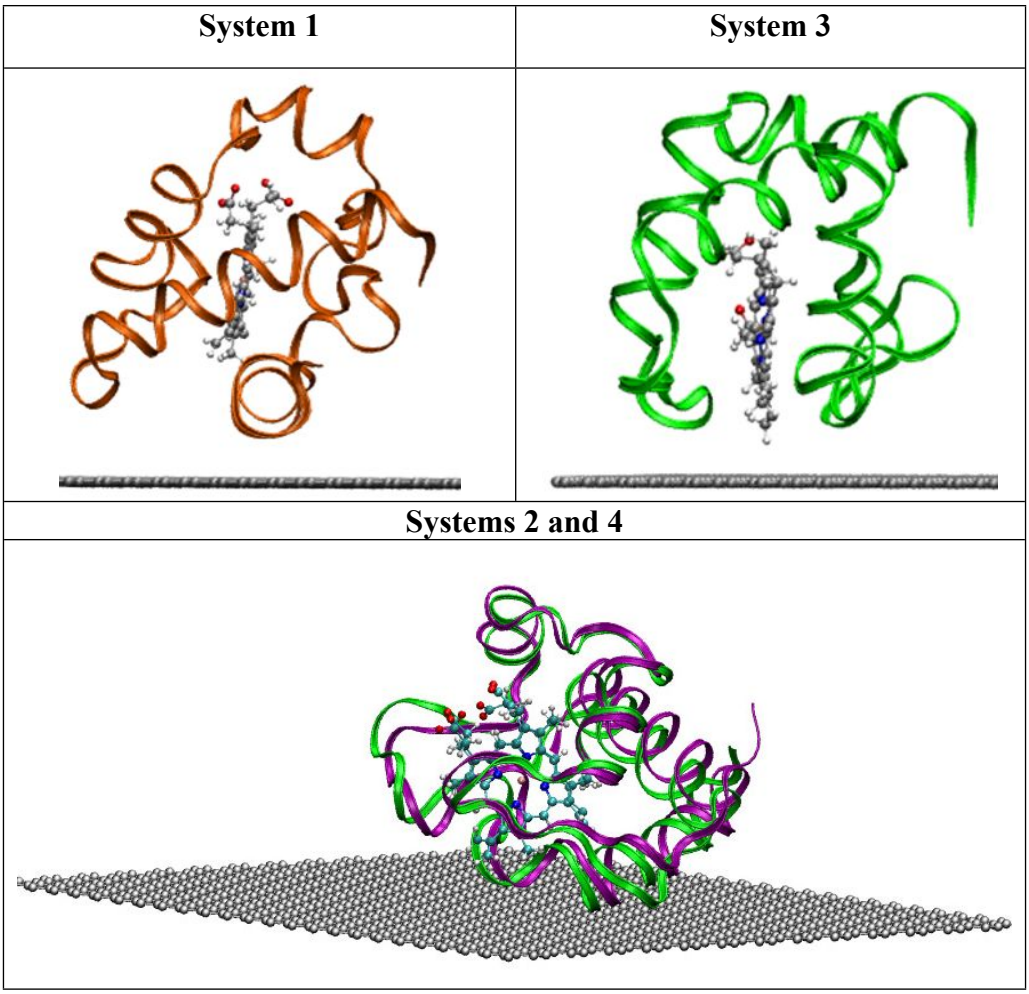


Figure S1. Comparison of structures after 100 ns of MD simulations. For the sake of comparison, System 2 and 4 are overlapped to better present their similarity in structure.

Parameters for graphene monolayer

Forcefield: CHARMM27

Since an infinite sheet of graphene has no charges, all CJ atom type has been set with neutral charge.

Atomtype CJ has been derived from the CA atomtype present in the CHARMM27 forcefield as implemented in GROMACS2016.3 software.

Bonds

Atom	**Atom**	**Function**	**b0**	**Kb**
CJ	CJ	1	0.1375	255224.00

Angles

Atom	**Atom**	**Atom**	**Function**	**theta0**	**ktheta**	**ub0**	**kub**
CJ	CJ	CJ	5	120.000	334.72	0.24162	29288.00

Dihedral

Atom	**Atom**	**Atom**	**Atom**	**Function**	**Phi0**	**kphi**	**mult**
CJ	CJ	CJ	CJ	9	180.00	12.9704	2

Non-Bonding interactions

Atom	**Sigma**	**Epsilon**
CJ	0.356359487256	0.46024

Benchmark analysis

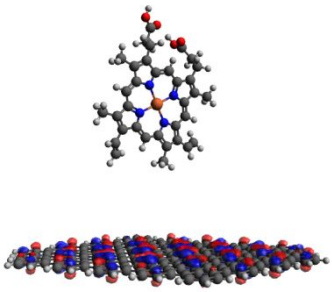
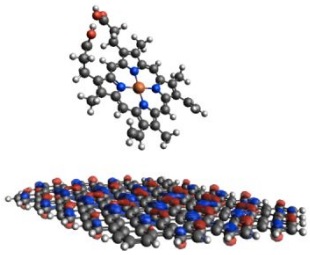
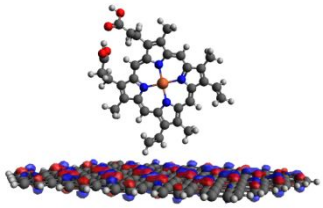
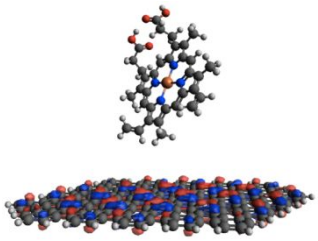
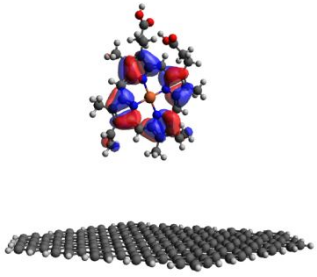
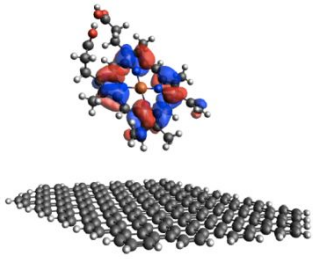
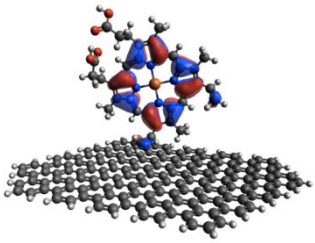
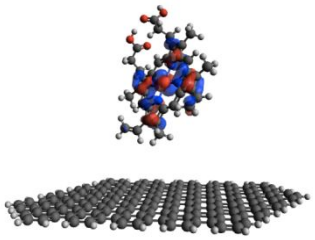
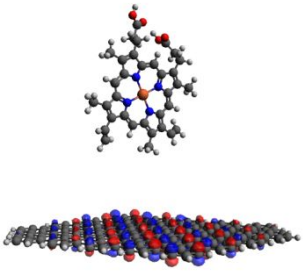
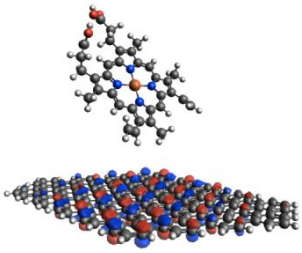
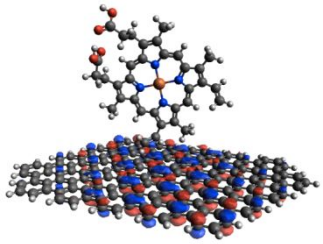
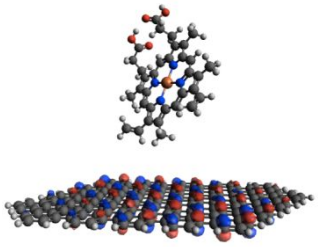
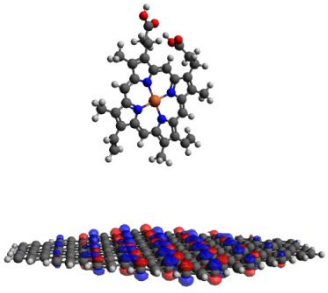
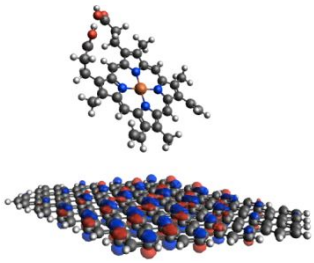
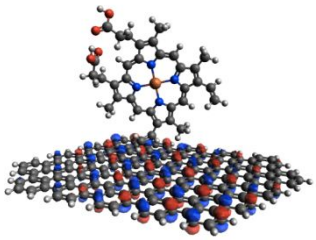
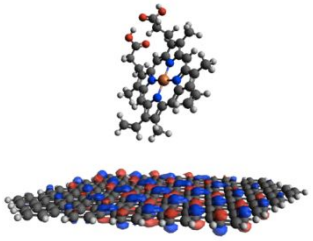
Considering the size of the system studied, around 280 atoms, the benchmark was performed only on the closest Heme / GNF interface found, namely System 3, and only a single point was performed on the geometry extracted form MD simulation.

Four different functionals, CAM-B3LYP, M062X, wB97xD and HSE were considered for the analysis, and the the frontier orbital energy, energy gap and the charge distribution were considered. All calculations were performed with the 6-31G(d,p) Pople's basis set and a posteriori dispersion term was added considering the Grimme D3 correction for CAM-B3LYP and M062X. Electrostatic potential (ESP) charge analysis was considered for the benchmark.

	wB97xD	**CAM-B3LYP**	**M06-2X**	**HSE**
HOMO (eV)	-5.67	-5.18	-5.27	-4.41
LUMO (eV)	-1.74	-2.08	-2.45	-3.03
Energy Gap (eV)	3.94	3.10	2.82	1.38
ESP Fe (II)	1.08	1.07	1.76	1.07
ESP Heme	0.06	0.06	0.06	0.05

All the parameters considered for the benchmarking are similar for the four functional, with the exception of the Fe (II) charge described with the M06-2X functional, and the energy gap.

Considering the energy gap value as a main factor to choose the proper functional, we selected the HSE since it gives the most reasonable band gap in the semiconductor range. Moreover, since all the other important values for the analysis and the localization of the molecular orbital have very similar values, we choose the HSE functional since it is reported to well describe solid state interfaces and has been extensively used to describe graphene and its derivatives.

	System 1	System 2	System 3	System 4
HOMO -2				
HOMO -1				
HOMO				
LUMO				

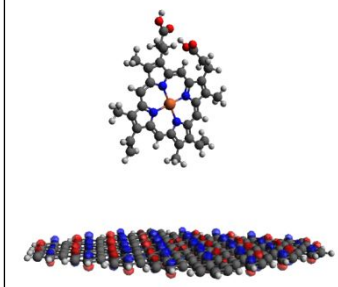
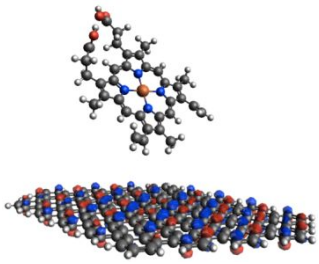
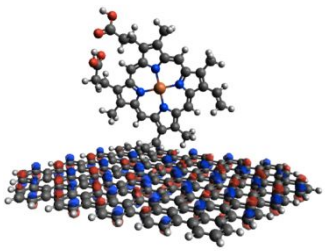
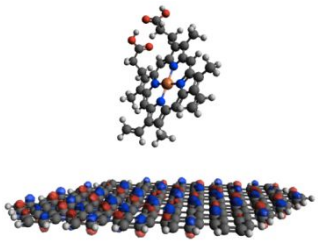
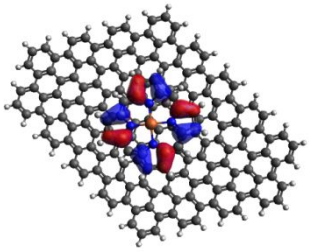
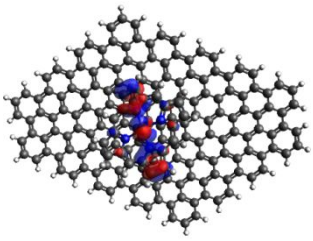
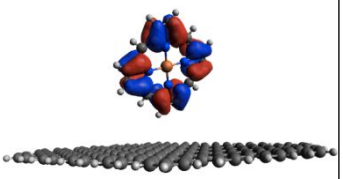
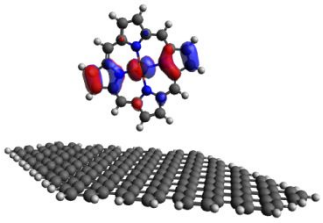
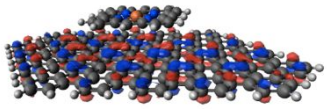
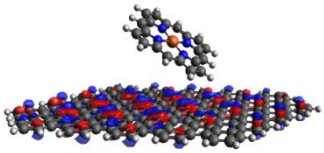
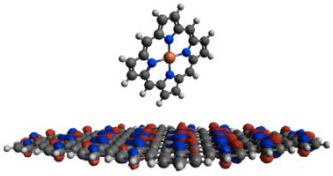
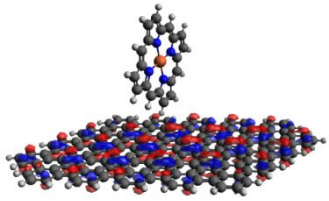
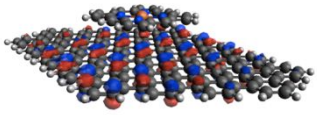
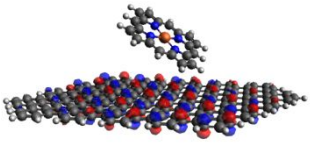
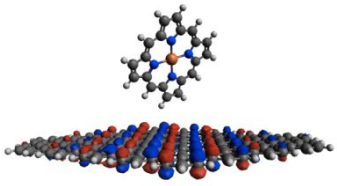
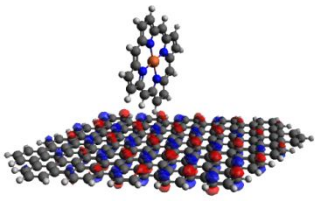
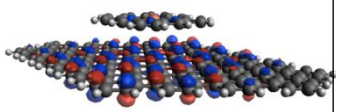
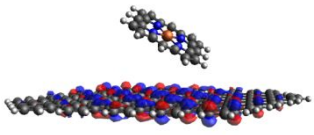
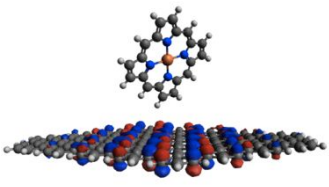
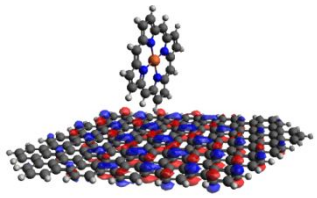
LUMO +1				

Figure S2. Frontier molecular orbitals for the four different interfaces obtained after single point calculations at the HSE/6-31G(d,p) level of theory.

	0	30	60	90
HOMO -2				
HOMO -1				
HOMO				
LUMO				

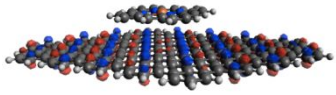
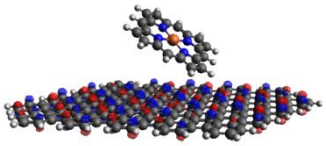
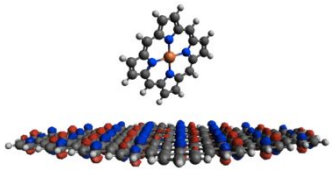
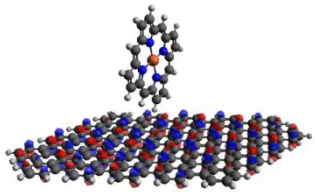
LUMO +1				

Figure S3. Frontier molecular orbitals of the model of porphyrin-SLG interfaces, with porphyrin tilted every 30 degrees.