Vibronic Effects in the Ultrafast Interfacial Electron Transfer of Perylene Sensitized TiO$_2$ Surfaces

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This document is organized as follows:

Section S1: parameterization of the quantum method and electronic structure of the Pe-COOH/TiO$_2$ system;

Section S2: parametrization of molecular mechanics method.

S1 Electronic structure of the Pe-COOH/TiO$_2$ system

S1.1 Quantum Mechanical parameterization

The extended Hückel (EH) method is used to described the electronic properties of the system. The atomic basis set for the extended Hückel calculations is formed by Slater-type atomic orbitals:

$$\langle \mathbf{r}; \mathbf{R}_N | n \rangle \equiv f_\eta(\mathbf{r} - \mathbf{R_N}) = \sqrt{\frac{1}{(2n)!}} (2\zeta)^{n+1/2} (\mathbf{r} - \mathbf{R}_N)^{n-1} \exp\left[-\zeta(\mathbf{r} - \mathbf{R}_N)\right] Y_{lm}(\theta, \phi) \ , \ (1)$$

where the Y$_{lm}$ (θ , φ) are spherical harmonics; n, l, m are quantum numbers and ζ is a semiempirical parameter. The EH parameters were optimized by genetic algorithm and then by conjugate gradient procedures. The optimized parameters are: the radial part of the Slater-type orbitals (ζ), the elements h$_{ii}$ of the diagonal of the EH matrix and the Wolfsberg-Helmholz parameters k$_{HW}$. The parameters were optimized to reproduce the energy differences among frontier molecular orbitals and their wavefunctions, in comparison to their counterparts obtained at the DFT/B3LYP/6-31G(d,p) level of theory with the Gaussian 09 package.[1] The EH parameters used in this work for the (perylen-9-yl)carboxylic acid (Pe-COOH) dye molecule are presented in TableS1.

Table S1: Extended Hückel parameters used for the Pe-COOH molecule.

MM-Symbol	EHT-Symbol	N_{val}	n	spdf	IP (h_{ii})	ζ	k_{WH}
CA	CA	4	2	s	-21.98894	1.552166	1.197909
CA	CA	4	2	p	-11.32328	2.214218	4.099984
Ox	Ox	6	2	s	-31.52118	2.470926	0.807682
Ox	Ox	6	2	p	-15.18918	2.430855	3.181294

S1.2   Pe-COOH molecule

In this section we provide benchmarks of the parametrized Extended Hükel model versus DFT/B3LYP/6-31G(d,p) electronic structure calculations of frontier molecular orbitals {H-1, HOMO, LUMO, L+1} performed with the Gaussian-09 package. Figure S1 shows energy differences among such frontier MOs for the Pe-COOH molecule in the optimized geometry.

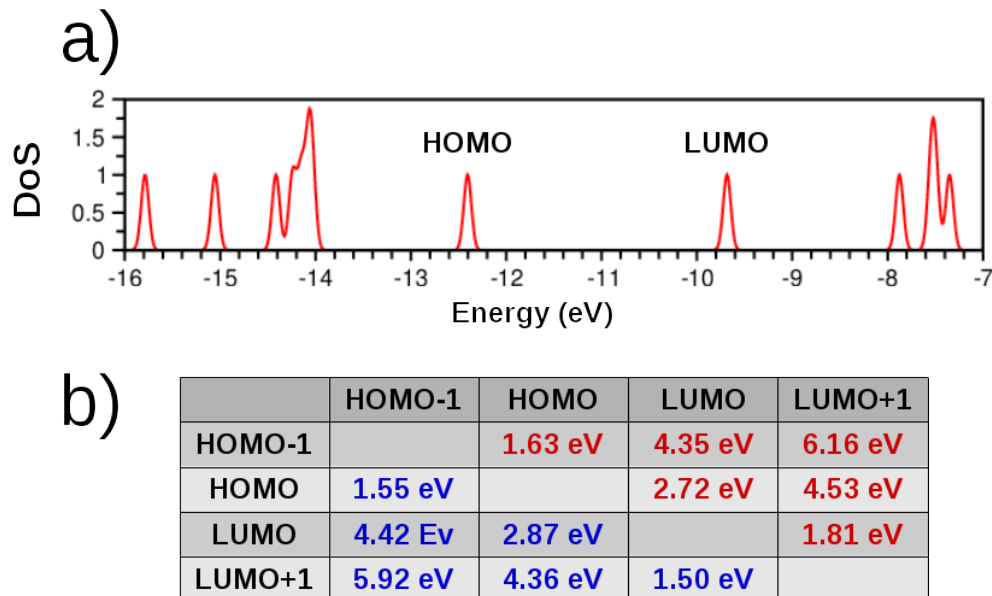|	HOMO-1	HOMO	LUMO	LUMO+1
HOMO-1		1.63 eV	4.35 eV	6.16 eV
HOMO	1.55 eV		2.72 eV	4.53 eV
LUMO	4.42 Ev	2.87 eV		1.81 eV
LUMO+1	5.92 eV	4.36 eV	1.50 eV	

Figure S1: a) Density of the states for the Pe-COOH molecule in the optimized geometry. b) Table shows the energy differences between frontier molecular orbitals, as obtained by the parametrized Extended Hückel method (red) and by the DFT/B3LYP/6-31G(d,p) level of theory (blue).

Figure S2 shows MO wavefunctions of the frontier orbitals {H-1, HOMO, LUMO, L+1} for the Pe-COOH molecule in the optimized geometry, as obtained by DFT (top) and Extended Hückel (bottom) methods.
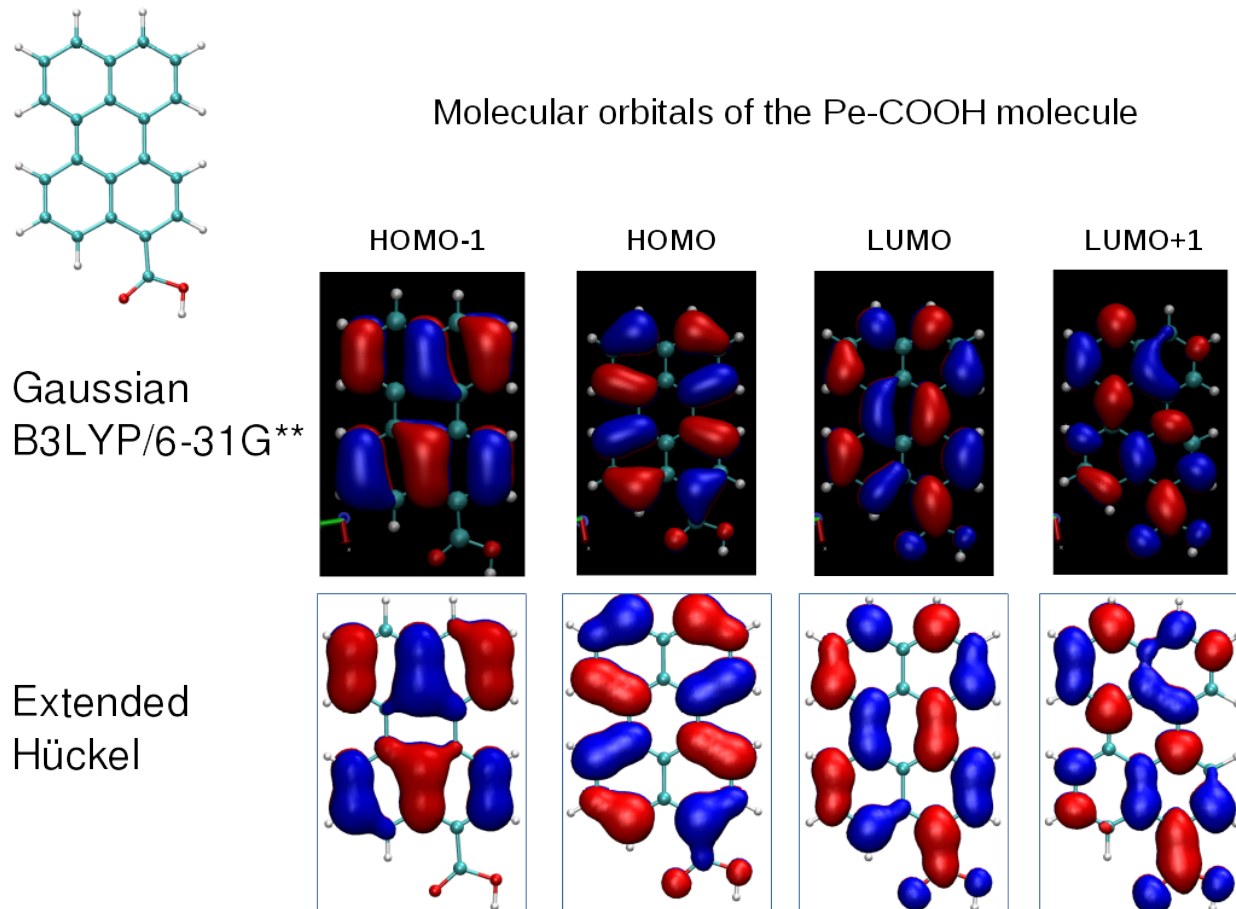

Figure S2: Molecular orbital wavefunctions for the frontier orbitals {H-1, HOMO, LUMO, L+1} of the Pe-COOH molecule in the optimized geometry. Upper panel orbitals calculated at the DFT/B3LYP/6-31G(d,p) level of theory. Lower panel orbitals obtained with the parametrized Extended Hückel method.

S1.3 Pe-COOH/TiO$_2$ system

For the Pe-COOH/TiO$_2$ system we use the same EHT parameters derived for the Pe-COOH molecule in gas phase, however, with a suitable adjustment of the energy offset between the Pe-COO's LUMO and the bottom of the TiO$_2$ conduction band. A systematic analysis of this offset was carried out. The results concerning electronic couplings and local density of states are presented in Figure S3. Experimental[2,3] and theoretical[4] studies report that such energy offset varies from 300 to 750 meV depending on the perylene derivative and the nature of the anchor. In this work, the energy offset between the Pe-COO's LUMO and the bottom of the TiO$_2$ conduction band was set to 300 meV, in qualitative accordance with *ab-initio* calculations that describe the LUMO π^* orbital as distributed among a mixture of molecule-semiconductor states 0.5 eV above the conduction band edge.[4] The offset does not affect the HOMO of the dye appreciably, but it modifies considerably the electronic couplings of the LUMO with the semiconductor CB states, thereby regulating the IET times.
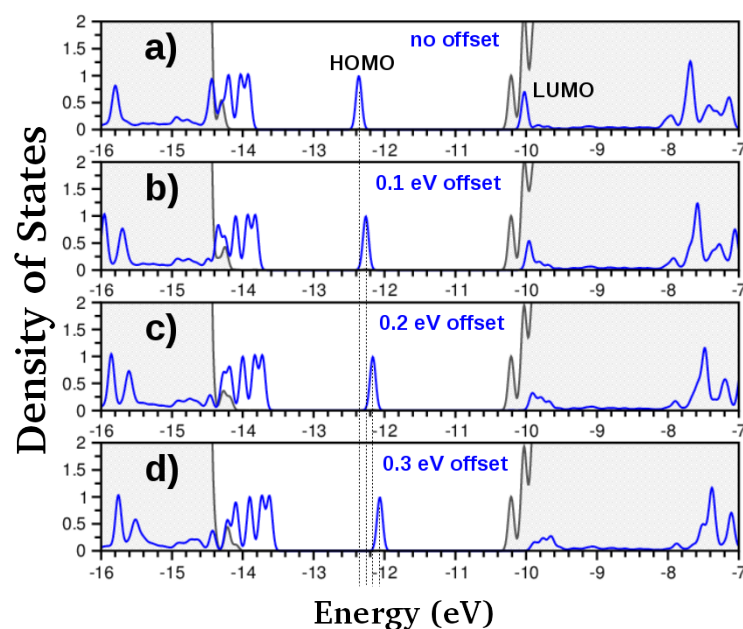
Figure S3: Local Density of states of the Pe-COOH/TiO$_2$ system as a function of the energy offset between the LUMO of the Pe-COO moiety and the bottom of the TiO$_2$ conduction band: a) no offset, b) 0.1 eV offset, c) 0.2 eV offset and d) 0.3 eV offset. The states localized on the Pe-COO moiety are shown by the blue line; the shaded area designates the valence and conduction bands of the TiO$_2$. The dashed lines are guides for the eyes. The HOMO and LUMO orbitals of the Pe-COO moiety are labeled.

S1.4 Self-Consistent Quantum/Classical Dynamics

Despite the large amplitude oscillations displayed by the frontier molecular orbitals during the mixed quantum/classical trajectories, the standard deviation of the total energy of the simulations ($E = \sum_{atoms} E_{MM} + E_{QM}^{EH}$) is around 6 meV, and its drift is approximately 25 meV after 150 fs. To be compared with Figure 5 of the paper.
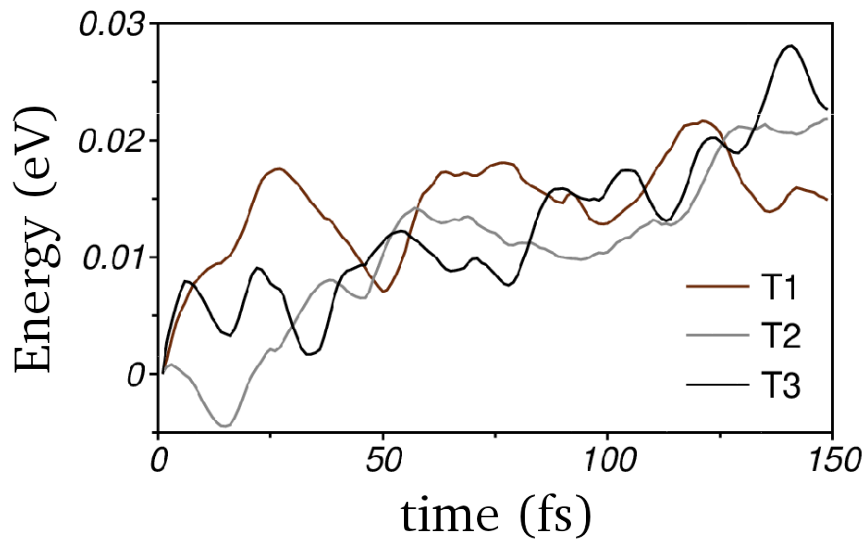

Figure S4: Total energy $E = E_{QM}^{EH} + \sum_{atoms} E_{MM}$ as a function of time during simulations {T1, T2, T3}. The energies were shifted as $E = E(t) - E(0)$.
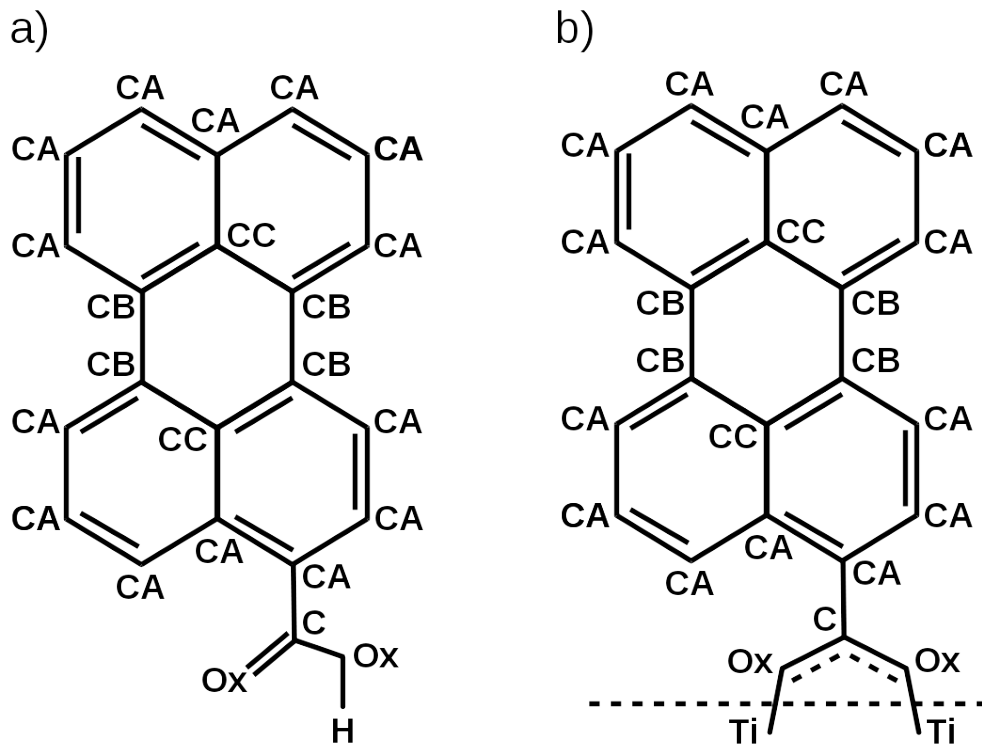
S2 Molecular Mechanics Parameters

Figure S5: Chemical structure of the a) Pe-COOH molecule and b) Pe-COO moiety adsorbed on the surface of TiO$_2$, showing the molecular mechanics (MM) atom types.

atom type	OPLS-AA name	type	σ (nm)	ε (kJ/mol)
CA, CB, CC	opls_145	CA	3.55000e-01	2.92880e-01
HA	opls_146	HA	2.42000e-01	1.25520e-01
C	opls_267	C	3.75000e-01	4.39320e-01
Ox	opls_269	O_3	2.96000e-01	8.78640e-01
Ti			1.95814e-01	2.5620881
O			2.88427e-01	1.4085130

Figure S6: Definition of molecular mechanics (MM) atom types.

atom type	d_0 (nm)	k (kJ/mol/nm)
CA CA	0.1400	196229.6
CA CB	0.1380	
CA CC	0.1410	
CB CB	0.1460	
CB CC	0.1410	
CA HA	0.1080	153552.8
C CA	0.1460	167360.0
C Ox	0.1229	238488.0
Ti Ox	0.1900	229701.6
atom type	angle (degree)	k (kJ/mol/rad^2))
Cx Cx Cx	120	450
Cx Cx HA		146.44
C CA CA		505.64
CA C Ox	122	334.72
Ox C Ox	121	

Figure S7: Molecular mechanics (MM) parameter for bond stretching and angle.

atom type	dihedral type	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol
X Cx Cx X CA CA C Ox	RB	30.354	0	-30.354	0	0	0	0
Ti Ox C Ox	RB	23.012	0	-23.012	0	0	0	0
CA C Ox Ti	RB	29.288	-8.368	-20.920	0	0	0	0
atom type	dihedral type							
C CA Ox Ox	periodic	180.0	43.932	2	improper_O_C_X_Y			
CA C CA CA	periodic	180.0	4.6024	2	improper_Z_CA_X_Y			

Figure S8: Molecular mechanics (MM) parameter for dihedrals and improper dihedrals. RB designates the Ryckaert-Bellemans function.

Figure S9a shows the bond lengths (in blue) of the dye in the Pe-COOH/TiO$_2$ system optimized with the force field. In red we present the bond lengths of the relaxed dye, after the interfacial electron transfer. The overall effect of electron transfer is schematically shown in Figure S9b, the molecule shrinks in the vertical direction and expands horizontally.
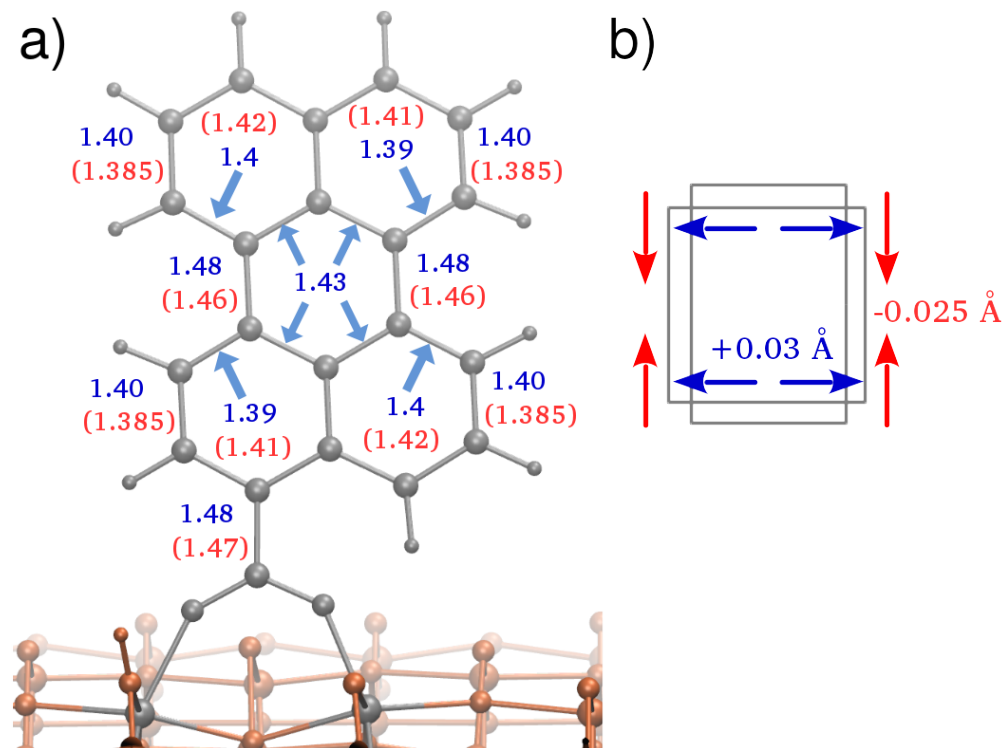

Figure S9: a) Pe-COOH/TiO$_2$ system with the geometry optimized in the force field; bond lengths in blue. In red we show bond lenghts of the relaxed dye, after the interfacial electron transfer. b) Schematic representation of the overall geometry relaxation effect, the molecule shrinks in the vertical direction and expands horizontally. Bond lengths are in Angstron.

The modes with frequencies within the range 1500 cm^{-1} and 1900 cm^{-1}, as calculated by the present force field, are shown in Figure S10. The higher activity detected for this modes on the VDOS, as well as in the Fourier spectrum of the time dependence of the frontier orbitals HOMO and LUMO indicate that they play an important role in the structural relaxation of the dye.
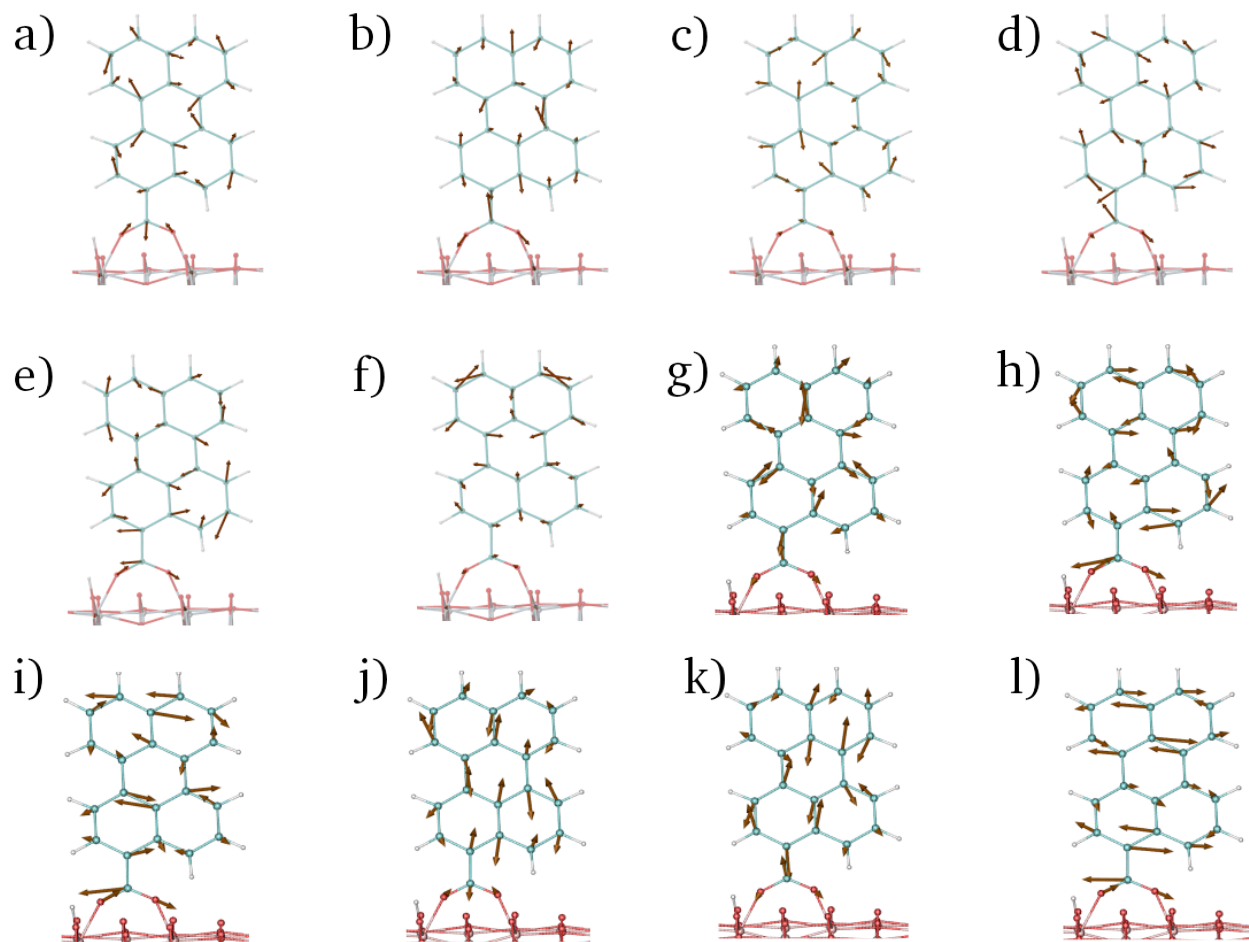
Figure S10: Vibrational normal modes of the Pe-COO dye moitety attached to the (101) TiO$_2$ anatase surface. Only the motion of C atoms are displayed. Normal mode frequencies are: a) $\nu = 1548$ cm^{-1}, b) $\nu = 1598$ cm^{-1}, c) $\nu = 1613$ cm^{-1}, d) $\nu = 1658$ cm^{-1}, e) $\nu = 1670$ cm^{-1} f) $\nu = 1685$ cm^{-1}, g) $\nu = 1760$ cm^{-1}, h) $\nu = 1780$ cm^{-1}, i) $\nu = 1835$ cm^{-1}, j) $\nu = 1848$ cm^{-1}, k) $\nu = 1867$ cm^{-1} and l) $\nu = 1909$ cm^{-1}.

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