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Supporting Information

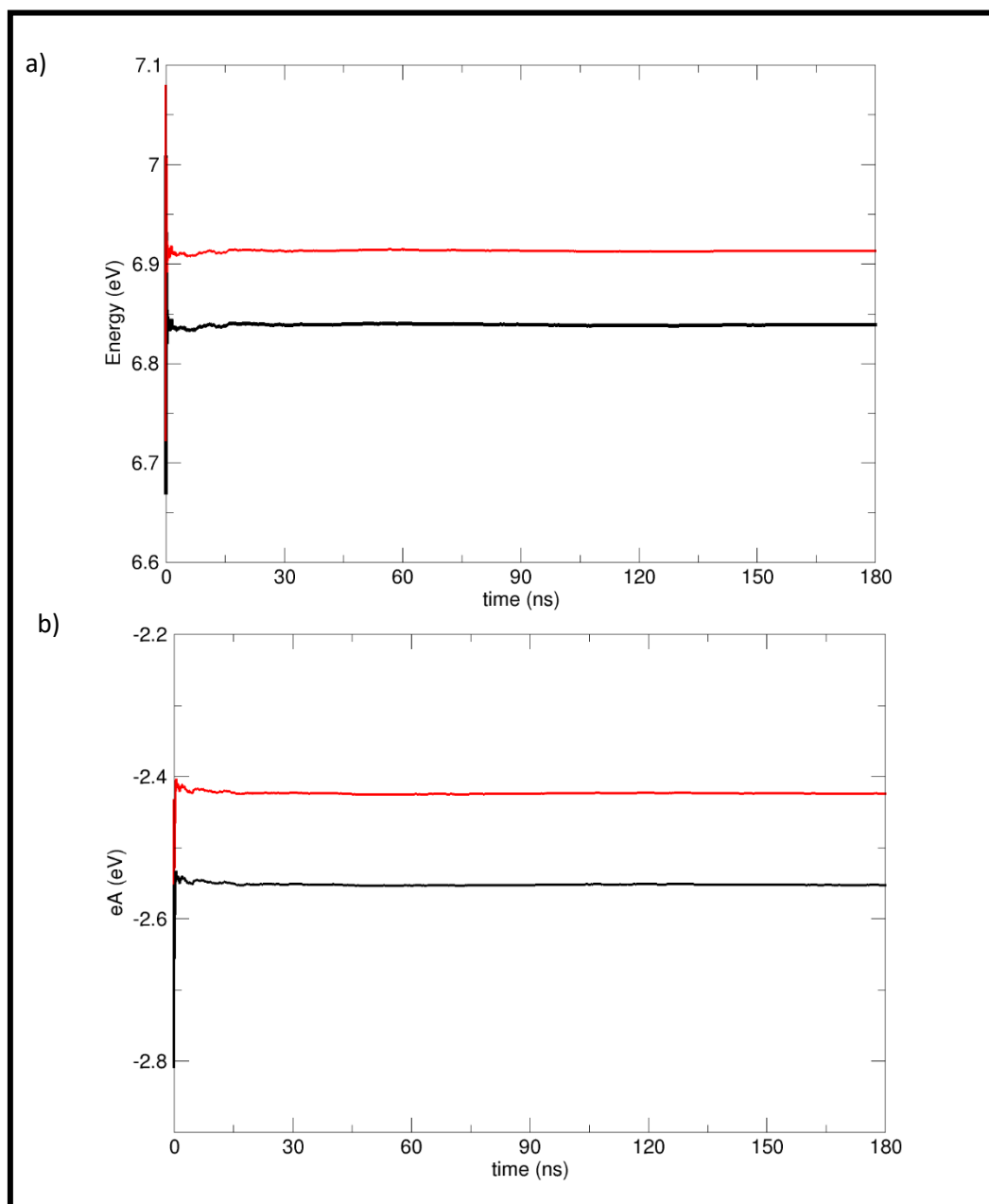
P1 Push-Pull Dye as a Case Study in QM/MM Theoretical Characterization for Dye-sensitized Solar Cell Organic Chromophores**

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SUPPORTING INFORMATION

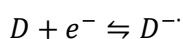
1. Convergence of the Energy

In **Panel S1 a)**, the convergence of the Adiabatic Ionization Energy (AIE) and the Vertical Ionization Energy (VIE) are shown. As expected, the estimated AIE (6.84 eV) is lower than VIE (6.91 eV), due to the stabilization given by the optimized first excited state relaxed geometry of the Quantum Center (QC), using mPW1PW91/6-31+G(d,p) as level of theory. For the calculation of VIE, the same optimized ground state geometry was used for the first excited state QC.



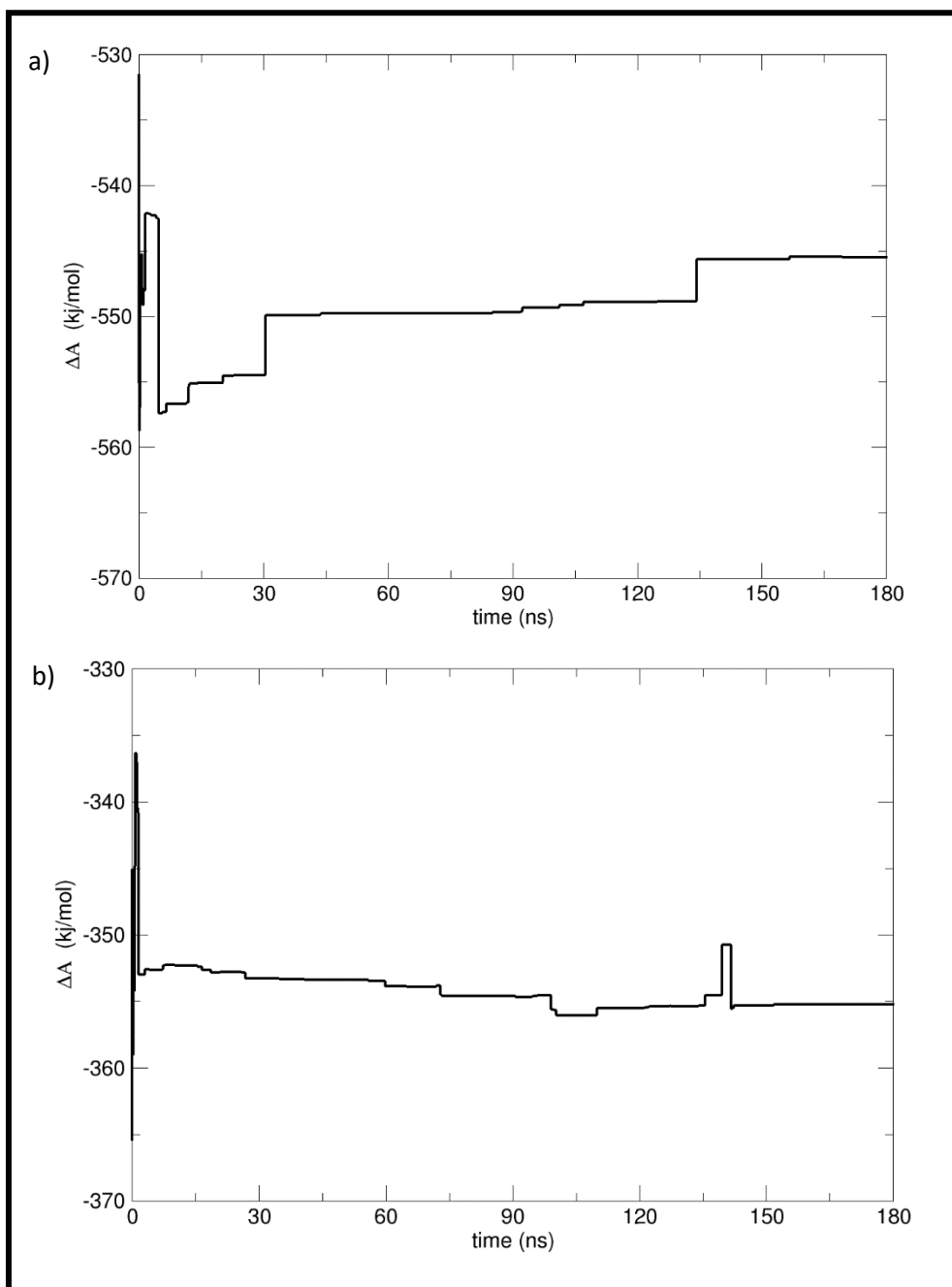
Panel S1: Convergence of Adiabatic (**black line**) and Vertical (**red line**) a) Ionization Energy and b) Electron Affinity.

Similarly, we estimate the Adiabatic and Vertical Electron Affinity (eA), for the process:



The convergence of eA is shown in **Panel S1 b)**.

In **Panel S2**, the convergence of Helmholtz free energy change is presented for the reduction and oxidation processes. In both cases, the reported data are the mean value of the Helmholtz free energy for the neutral and radical cation/anion ensemble:

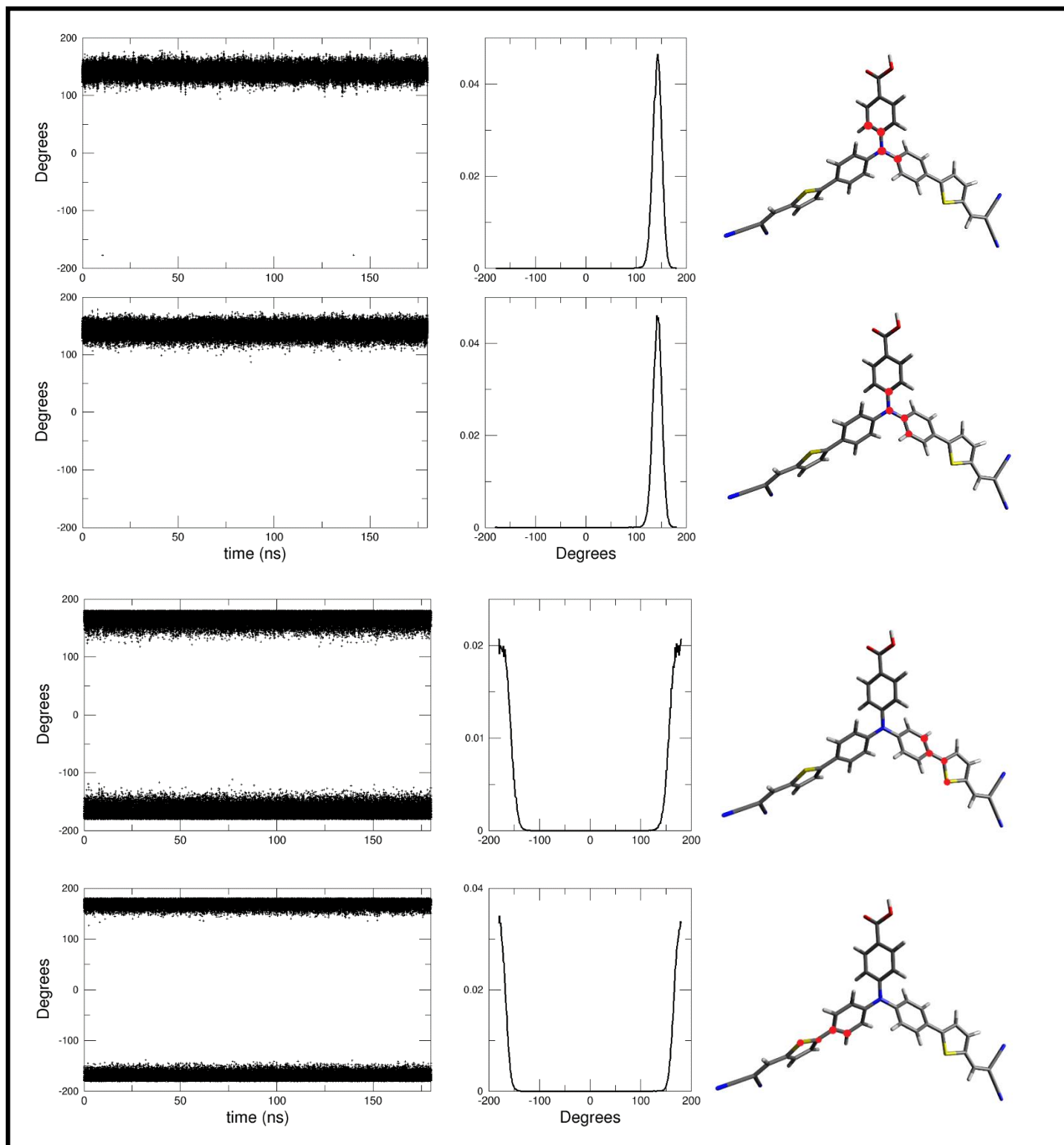


Panel S2: Convergence of Helmholtz free energy change for the a) oxidation and b) reduction processes.

2. Dihedral angles analysis

The choice of considering the entire molecule as a unique QC, was supported by dihedral angles analysis. The conjugated structure of the dye, constituted by aromatic rings, along the Molecular Dynamics (MD) simulations is essentially rigid and explores a low variability of conformations.

The most relevant dihedral angles of the molecules were selected and shown in **Panel S3**. A relatively limited interval of dihedral angle values was explored, allowing us to use a single QC geometry.



Panel S3: Dihedral angles range explored by the dye molecule along the MD trajectory.

3. Uv-Vis spectrum transitions

The first six electronic transitions, as obtained by the PMM-MD procedure, are reported in **Figure S1**.

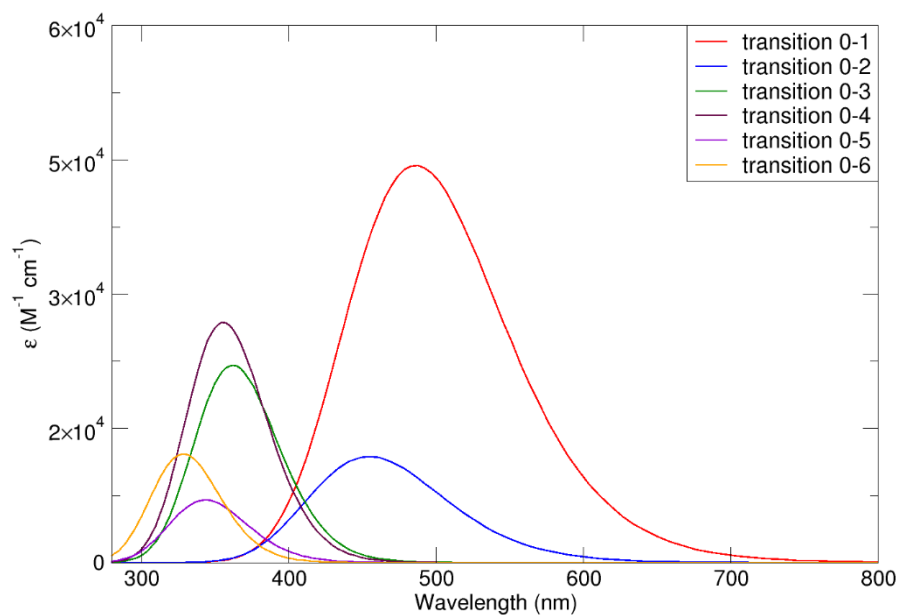


Figure S1: First six calculated electronic transitions for P1 dye.

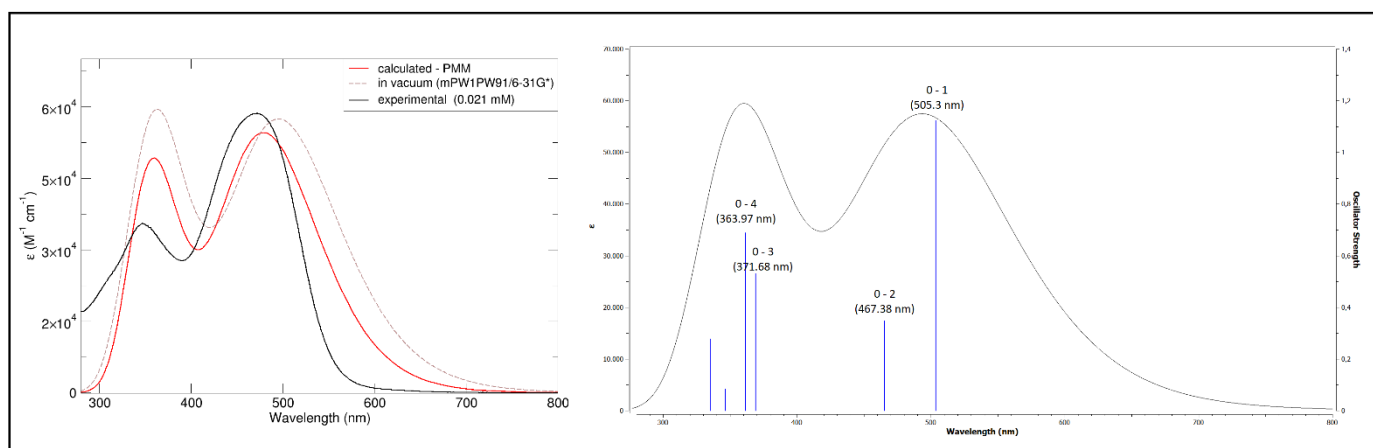


Figure S2: Comparison between calculated spectrum with PMM hybrid method (red line); experimental spectrum (black line) and in vacuum simulated spectrum at mPW1PW91/6-31G* level of theory (light brown dotted line).

Table S2: Comparison between the (calculated) wavelengths of the first four $0 \rightarrow n$ transitions in vacuum and in solution (in the latter, the values of the maximum are reported).

TRANSITION $0 \rightarrow n$	mPW1PW91/6-31+G*	PMM
$0 \rightarrow 1$	505 nm	479 nm
$0 \rightarrow 2$	467 nm	453 nm
$0 \rightarrow 3$	372 nm	363 nm
$0 \rightarrow 4$	364 nm	355 nm

4. Excitation Energies in vacuum

The comparison between excitation energies for P1 in the neutral, radical cation, and radical anion form are reported in the following tables:

Table S3: P1 neutral excitation energies

EXCITED STATE	EXCITATION ENERGY (eV)	
	B3LYP/6-31+G(d,p)	mPW1PW91/6-31+G(d,p)
1 st	2.29	2.45
2 nd	2.47	2.65
3 rd	3.14	3.34
4 th	3.19	3.41
5 th	3.36	3.55
6 th	3.44	3.67

Table S4: P1 radical cation excitation energies

EXCITED STATE	EXCITATION ENERGY (eV)	
	B3LYP/6-31+G(d,p)	mPW1PW91/6-31+G(d,p)
1 st	0.91	0.95
2 nd	1.29	1.34
3 rd	1.88	1.86
4 th	1.89	1.88
5 th	2.05	2.19
6 th	2.06	2.20

Table S5: P1 radical anion excitation energies

EXCITED STATE	EXCITATION ENERGY (eV)	
	B3LYP/6-31+G(d,p)	mPW1PW91/6-31+G(d,p)
1 st	0.40	0.40
2 nd	1.13	1.23
3 rd	1.57	1.61
4 th	1.65	1.66
5 th	1.67	1.75
6 th	1.81	1.83

5. Vertical Ionization Energies

In **Table S4**, the effect on VIE of using different QCs is reported. Extending the conjugation of the aromatic rings lowers the VIE.

Table S6: VIE estimates by considering as QC the thiophen-malononitrile group (S1), the triphenylamine group (TRPH) and the entire molecule.

Molecular moiety	VIE (eV)
S1	9.02
TRPH	7.17
P1 (entire molecule)	6.91

6. Electric dipole moments

In the following table, the ground state unperturbed and perturbed dipole moment components are reported for the neutral, radical cation (RC), and radical anion (RA) form of P1 dye:

Table S7: Unperturbed and perturbed (in the three different environments) dipole moment components for the ground state.

(D)	μ_x	μ_y	μ_z
UNPERTURBED			
Neutral P1	-0.836	7.475	-0.873
RC P1	-0.844	7.347	-0.863
RA P1	-0.527	15.094	-0.408
PERTURBED NEUTRAL ENSEMBLE			
Neutral P1	-1.2	6.6	-0.9
RC P1	-1.5	6.4	-0.9
RA P1	-1.6	14.6	-0.4
PERTURBED RC ENSEMBLE			
Neutral P1	-1.1	8.4	-0.8
RC P1	-1.5	7.6	-0.9
PERTURBED RA ENSEMBLE			
Neutral P1	-5.4	7.8	-0.8
RA P1	-11.6	14.9	-0.5

7. Perturbed electronic wavefunctions analysis

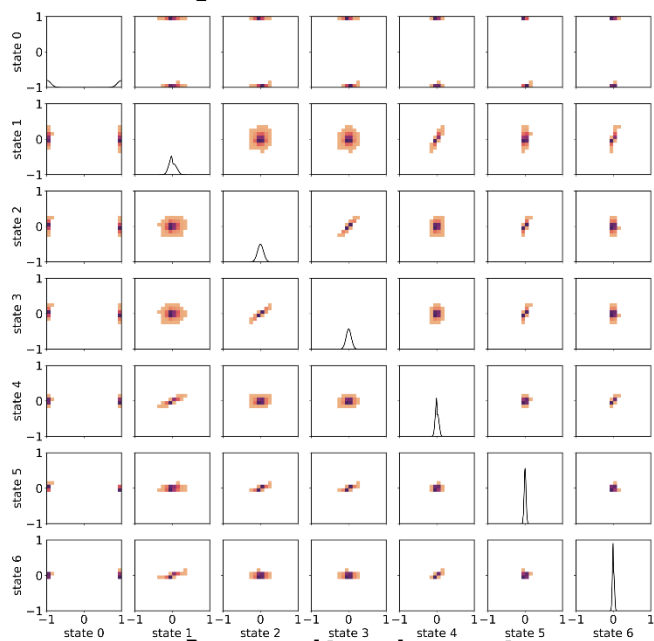
In this section the perturbed ground state electronic wavefunctions obtained by the MD-PMM calculations are described and analyzed. The P1 dye was considered in the following conditions: a) neutral QC in the neutral ensemble, b) radical anion QC in the radical anion ensemble, and c) radical cation QC in the radical cation ensemble. The perturbed wavefunctions (Φ_k), in the framework of the PMM theory, are expressed in terms of a linear combination of the unperturbed wavefunctions (Φ_l^0):

$$\Phi_k = \sum_l c_l^k \Phi_l^0$$

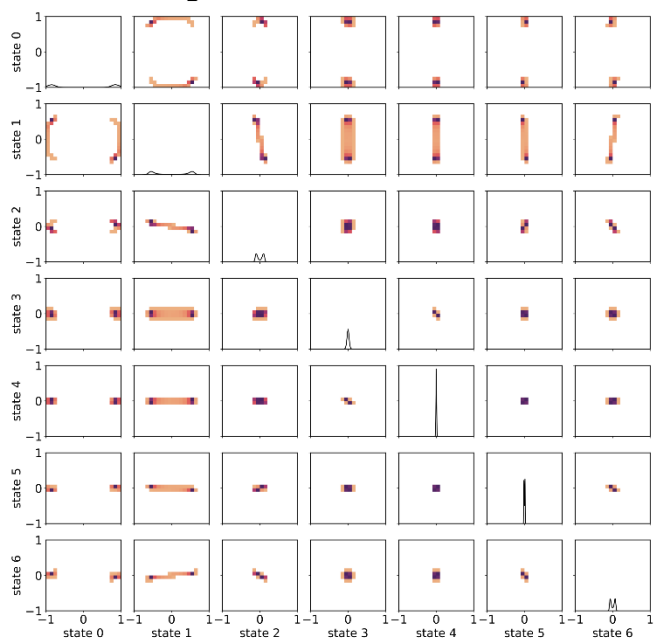
where the c_l^k coefficients (of the l -th unperturbed state for the k -th perturbed state) are obtained by the MD-PMM calculation for each frame.

In order to provide a dynamic picture of the characteristics of the perturbed wavefunctions, we plotted their projections (*i.e.* c_l^k) on the unperturbed basis set (*i.e.* the unperturbed electronic states) against each other for every frame of the simulations (see **Figure S2**). Similarly to **Figure 4** (main text), when P1 in the neutral form is considered, only a very limited amount of mixing between the unperturbed ground state and the excited states is observed (**Figure S2a**). On the other hand, a higher degree of mixing in the radical anion and radical cation is observed. In particular, while in the case of the radical anion the most representative electronic configuration is still mainly described by the unperturbed ground state (see **Figure S2c**), Φ_0^0 , in the case of the radical anion the most sampled electronic configuration is represented by a combination of mainly the unperturbed ground state and first excited state, corresponding to a probability (*i.e.* $|c_l^k|^2$) of 0.74 and 0.24 respectively (see **Figure S2b**).

a) Neutral



b) Radical anion



c) Radical cation

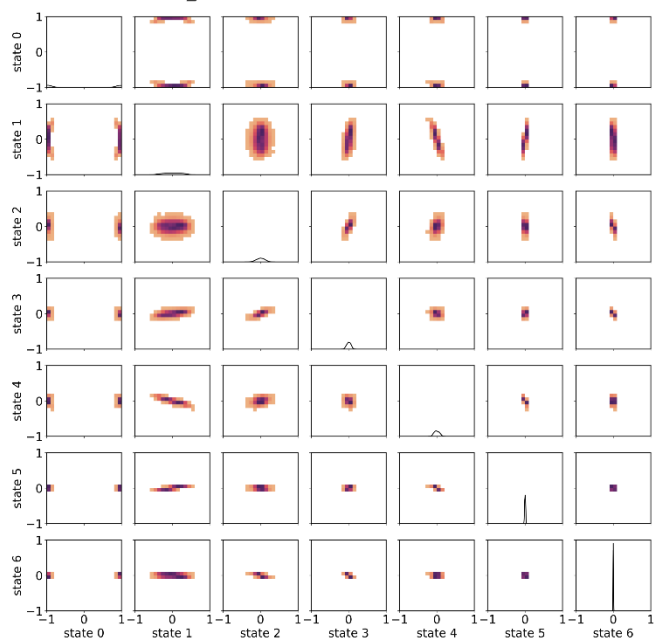


Figure S3: Projections of the perturbed electronic ground states of the neutral (a), radical anion (b) and radical cation (c) P1 dye on their corresponding unperturbed basis sets plotted against each other. The densities of sampled frames are shown through the colors of the bins (darker: higher density; lighter: lower density).