Supplementary Information for: Exploring the Mechanisms Behind Non Aromatic Fluorescence with Density Functional Tight Binding Method

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Supporting Information Available

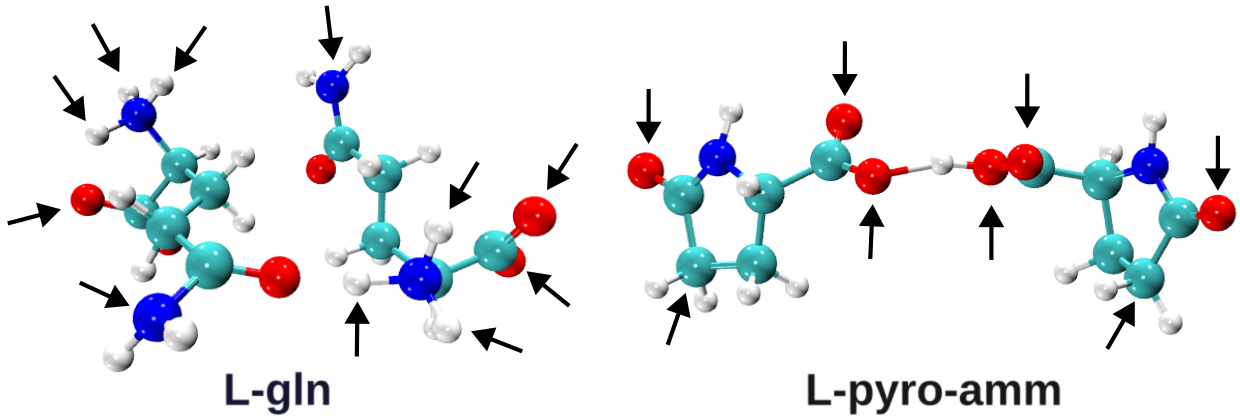

Figure S1: Molecular structures of the dimer models systems for L-gln and L-pyro-amm employed in the vacuum simulations. The black arrows indicate the positions of the atoms where the soft constraint were applied.

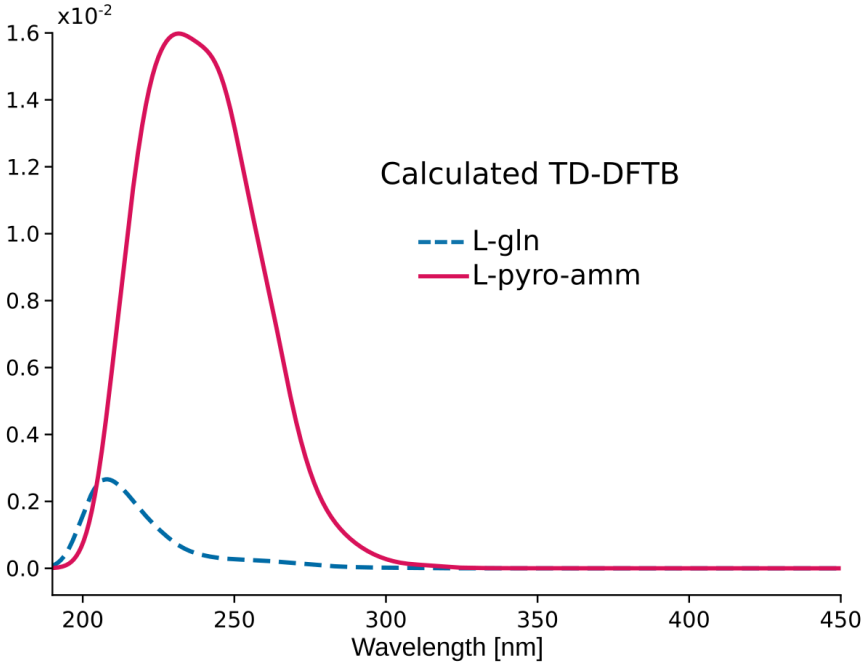

Figure S2: Full range of the calculated absorption spectra for L-Glutamine (L-gln, blue dashed line) and L-Pyroglutamine-Ammonium (L-pyro-amm, red solid line). The final spectra were obtained performing a calculation of 100 excitations using TD-DFTB and then making the average between the different conformations. A total of 1000 different conformations extracted from *ab-initio* ground state molecular dynamics in PBC were analyzed for each system.

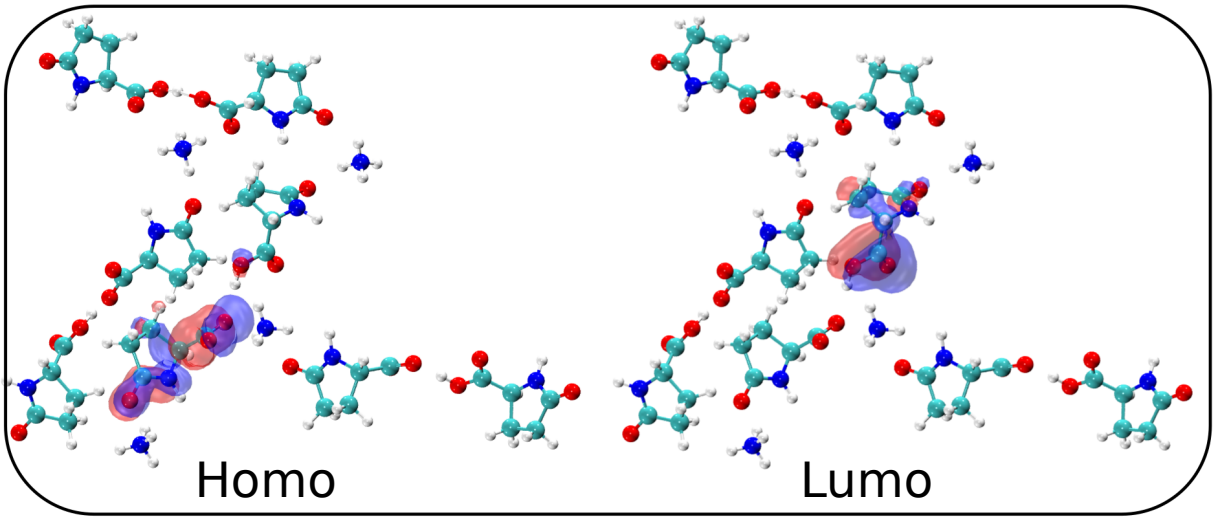

Figure S3: Molecular Orbitals involved in the transition $S_0 \rightarrow S_1$ in L-pyro-amm system.

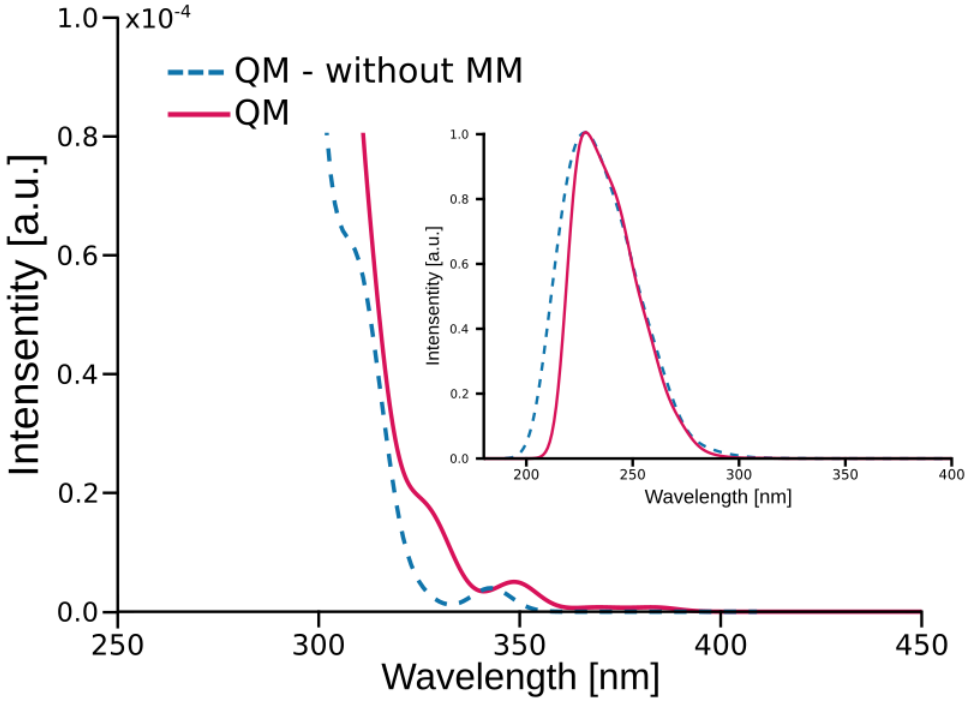

Figure S4: Absorption spectra calculated for the unit cell of the L-pyro-amm system. The absorption spectra obtained from *ab-initio* ground state dynamics in PBC are labeled as QM (the same spectra are depicted in Figure S2 and in Figure 2 in the main text). The spectra derived from a QM/MM ground state simulation with the MM molecules removed are denoted as QM - without MM. The inset displays the full-range spectra. All spectra were computed using TD-DFTB, as described in the main text.

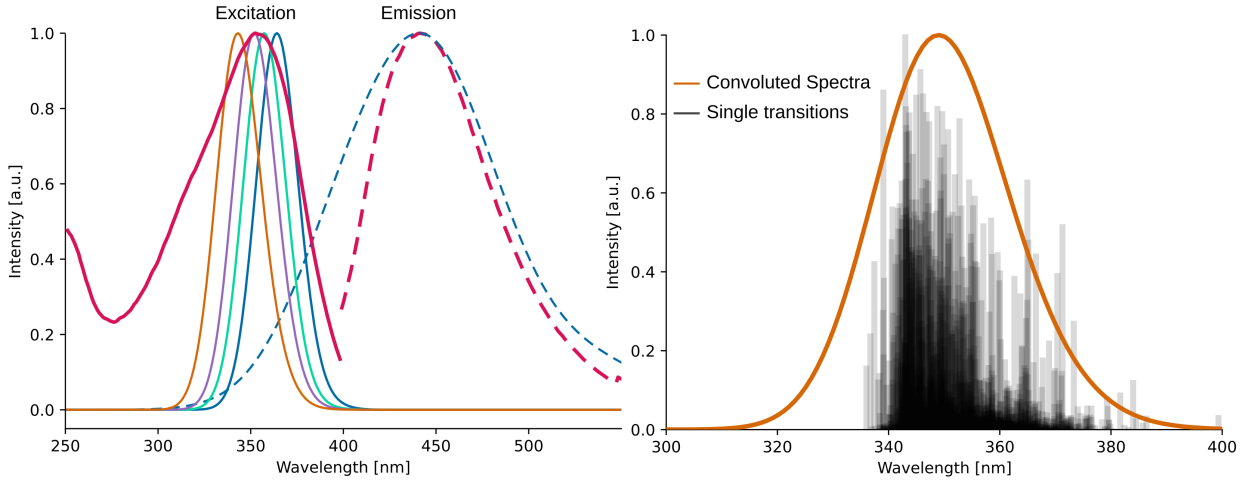

Figure S5: Excitation and Emission spectra of L-pyro-amm system. Left panel: The experimental data (red lines) were extracted from the reference.[1] The calculated spectra corresponds to emission (blue dashed line), excitation with 1 state (blue solid line), with 5 (green line), with 10 (purple line), with 20 states (brown line). Right panel: Excitation spectra calculated with 20 states (brown line, same that shown in left panel) and all the single transitions (grey bars). All the calculated spectra represent the average obtained using different conformations from a QM/MM ground state simulation where the QM is the unit cell. Each individual transition was broadened using a gaussian function of FWHM of 5 nm.

Table S1: Stokes shift for the unit cell QM/MM including an increasing number of states in the excitation spectra for L-pyro-amm system.

# States	Max. excitation [nm][a]	FWHM [nm][b]	Stokes shift [nm]
1	364	27	77
5	357	27	84
10	352	27	89
20	343	29	98
Exp.[c]	352	99	87

a The maximum of the theoretical excitation spectra were calculated using the same shift value to match the experimental and calculated fluorescence spectra.
b FWHM stands for Full Width at Half Maximum of the excitation spectra.
c The experimental data is extracted from reference.[1]

References

(1) Stephens, A. D.; Qaisrani, M. N.; Ruggiero, M. T.; Díaz Mirón, G.; Morzan, U. N.; González Lebrero, M. C.; Jones, S. T.; Poli, E.; Bond, A. D.; Woodhams, P. J., et al.

Short hydrogen bonds enhance nonaromatic protein-related fluorescence. *Proceedings of the National Academy of Sciences* **2021**, *118*, e2020389118.