

# Supporting Information:

## Photoinduced Charge-Transfer in Chromophore-Labeled Gold Nanoclusters: Quantum Evidence of the Critical Role of Ligands and Vibronic Couplings

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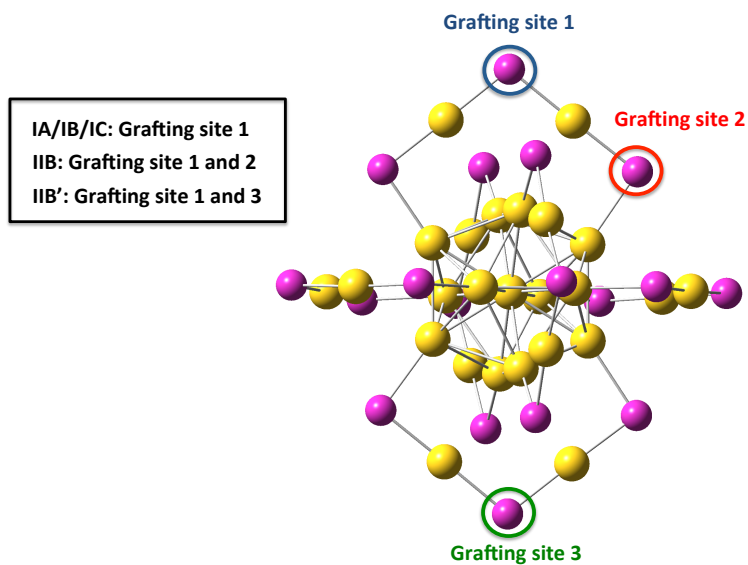
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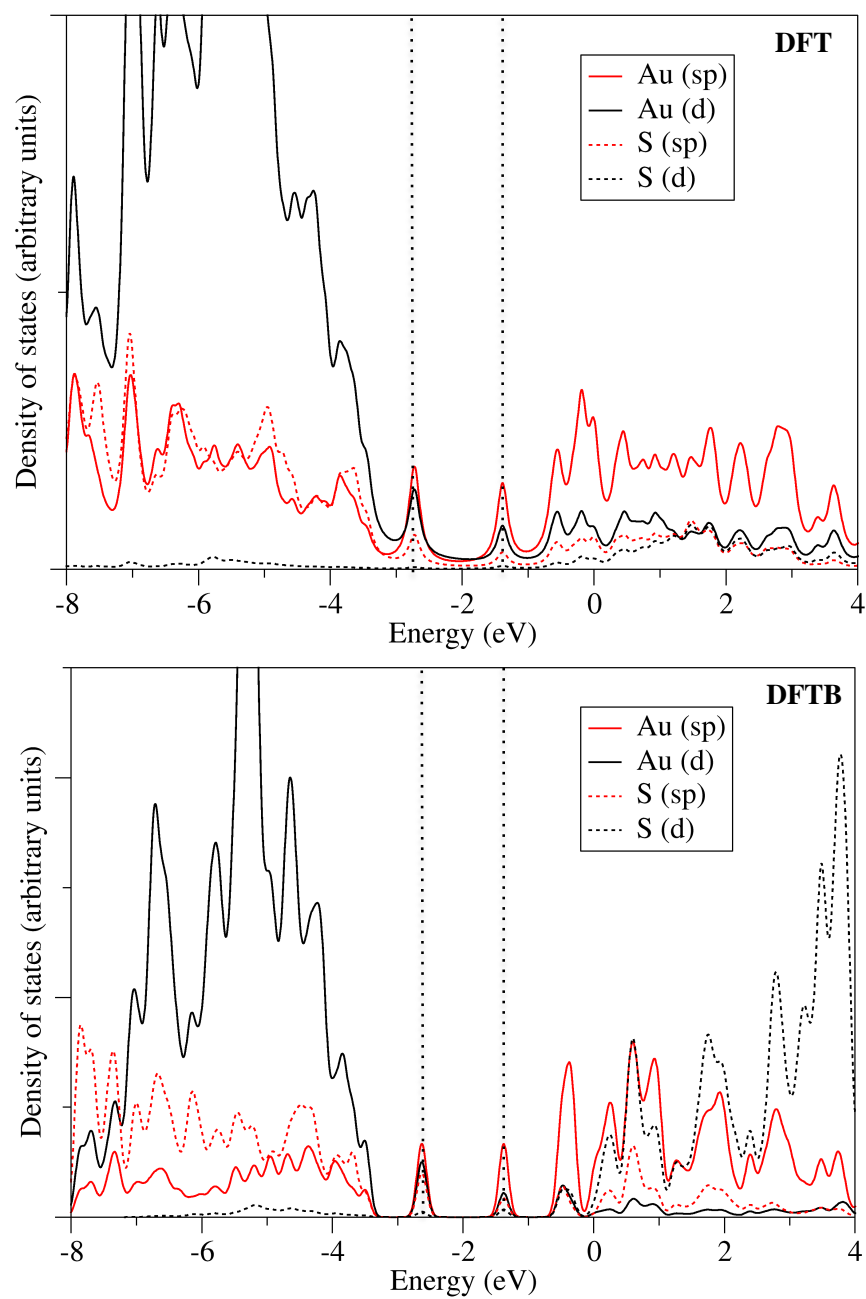
# 1 Substitution positions



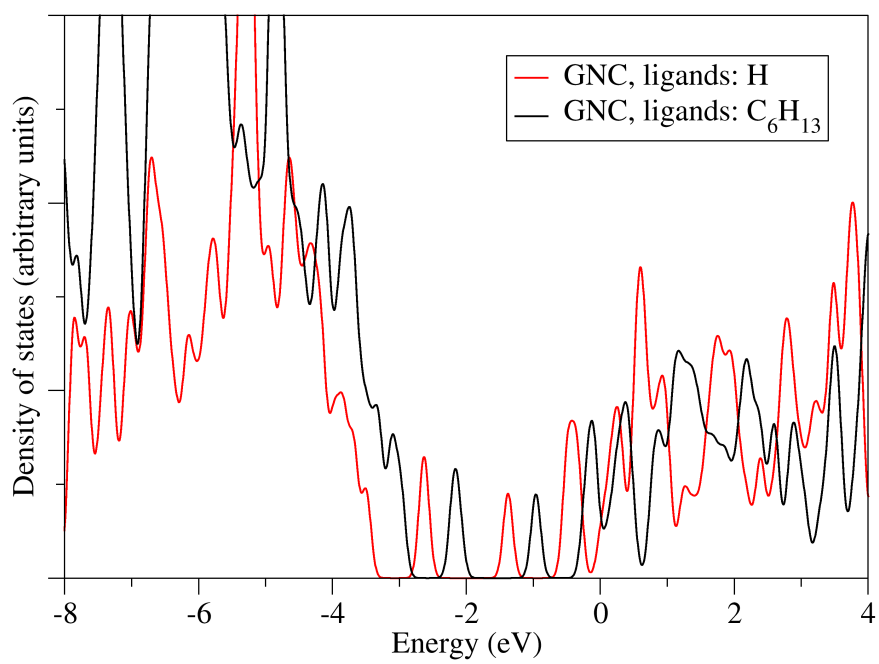
S 1: Schematic representation of positions of the pyrene derivative for the GNC substitution in the different systems.

## 2 Electronic structure - Density of states

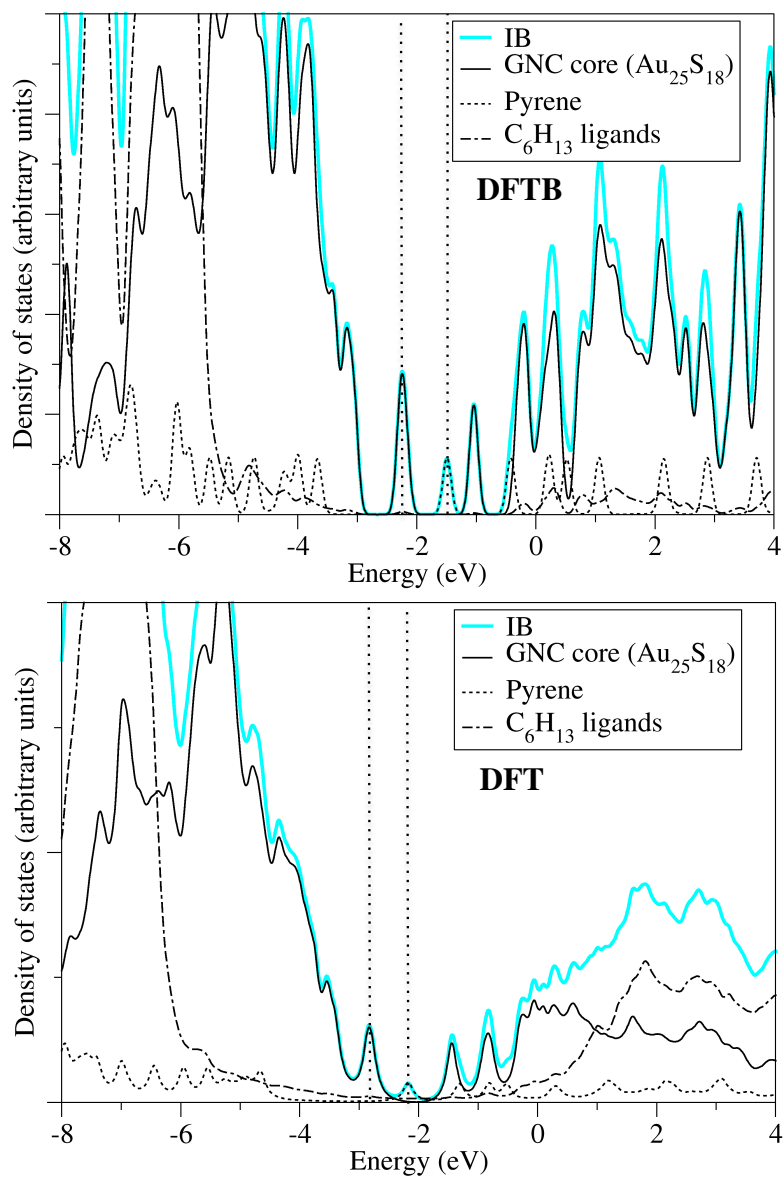
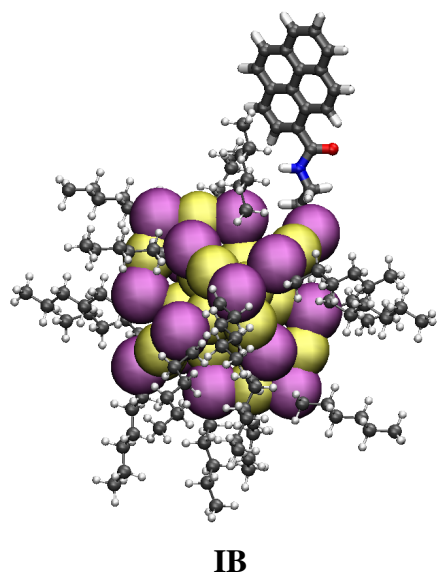
All DFTB density of states plot are obtained with a gaussian broadening function using a 0.10 eV width. The DFT density of state is made using Lorentzian functions of the same width.



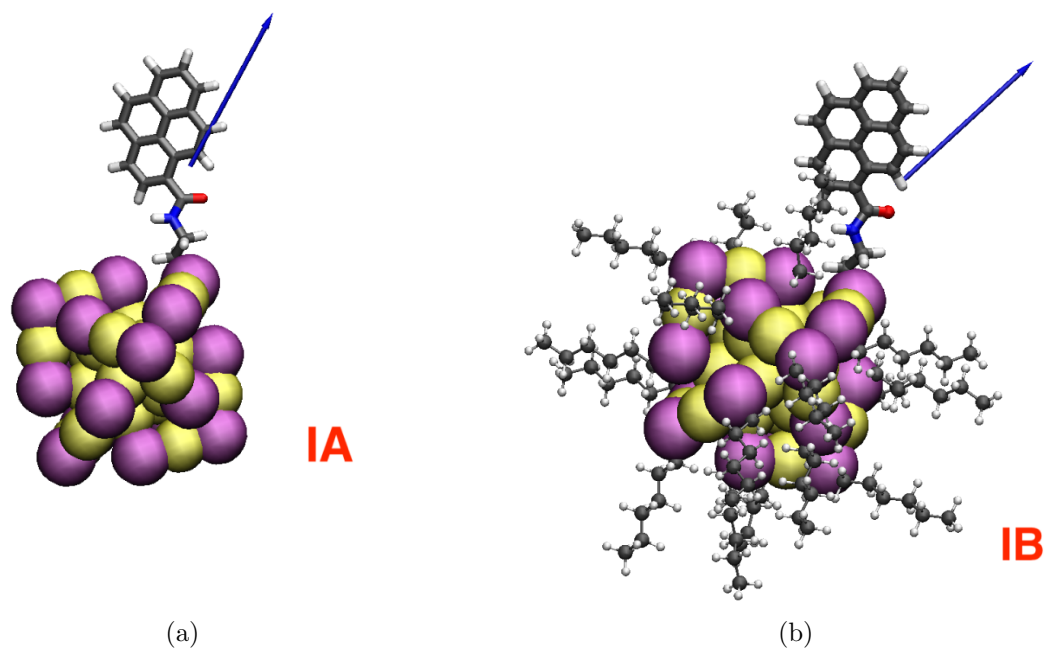
S 2: Projected density of states of the  $\text{Au}_{25}(\text{SH})_{18}^-$  GNC, obtained with DFT (PBE/6-31G(d,p)) and DFTB. Dotted black vertical lines represent the last occupied and first unoccupied levels.



S 3: Total DFTB Density of states of the GNC, in the case of simplified H ligands and full C<sub>6</sub>H<sub>13</sub> ligands.



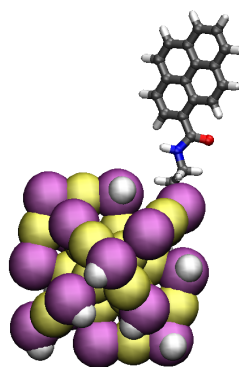
S 4: DFTB and DFT density of states of IB projected on the different part of the system. Dotted black vertical lines represent the last occupied and first unoccupied levels. DFT density of states is obtained at the DFTB ground state geometry, as a full DFT geometry optimization of IB is unreachable.



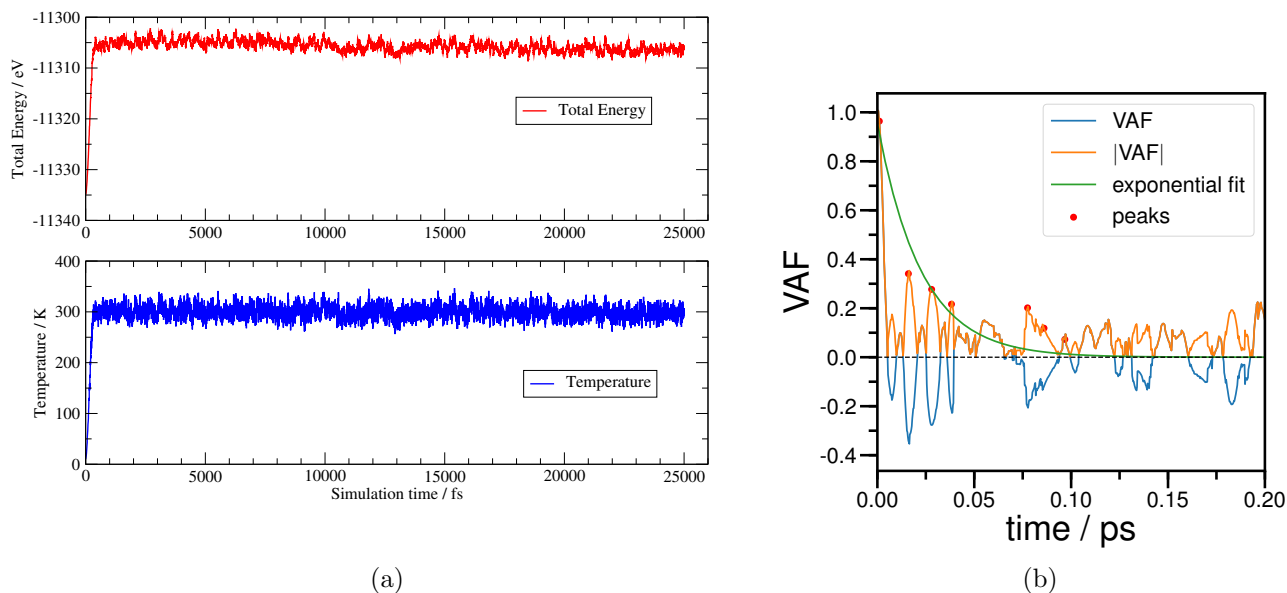
S 5: Transition dipole moment for system IA (a) and IB (b) at the pyrene lowest energy band (400 nm). To obtain the direction of the transition dipole vector, we calculate the second rank polarizability tensor at the energy of interest. After diagonalization of the tensor, the corresponding eigenvector with the largest eigenvalue represents the maximal polarizability direction and can be associated with the transition dipole moment.

### 3 Study of the effect of the Temperature in the charge-transfer processes: A configuration sampling

All the calculations were performed using the DFTB+ code.[1] For the Bohr-Oppenheimer MD simulations, 25 ps were simulated. The equation of motion is integrated using the Velocity Verlet algorithm, with a time step of 0.25 fs. Temperature was set by a linear increasing during the first 1000 steps and controlled at  $T = 300$  K, using Andersen thermostat. Were selected 25 configurations. The initial configuration was taken at 12.5 ps, and every 0.5 ps between each one, in order to ensure decorrelation. The interval time is bigger than the decorrelation time calculated of 90 fs and 80 fs for Au25 cluster-thiolated-pyrene system and Au25 cluster-thiolated with  $C_6H_{13}$  chains-pyrene system, respectively. ( See below VAF Figures). Ehrenfest dynamics for each selected configuration and initial velocities sampled from the MD were performed. For the Ehrenfest dynamics, an electromagnetic wave, a  $\sin^2$  shaped pulse is employed describing the electron dynamics during the light absorption with an electric field of  $0.1 \text{ V/\AA}$  and an energy laser of 400 nm (expressed in eV units equal to 3.0996). The total duration of the pulse is 100 fs in all cases. This method employed had been used with success in previous studies.[2–4] The geometrical structures for the systems under study are described using a color legend as follow: Gold, Sulfur, Carbon, Oxygen, Nitrogen, Hydrogen atoms are represented by yellow, purple, gray, red, blue and white, respectively.

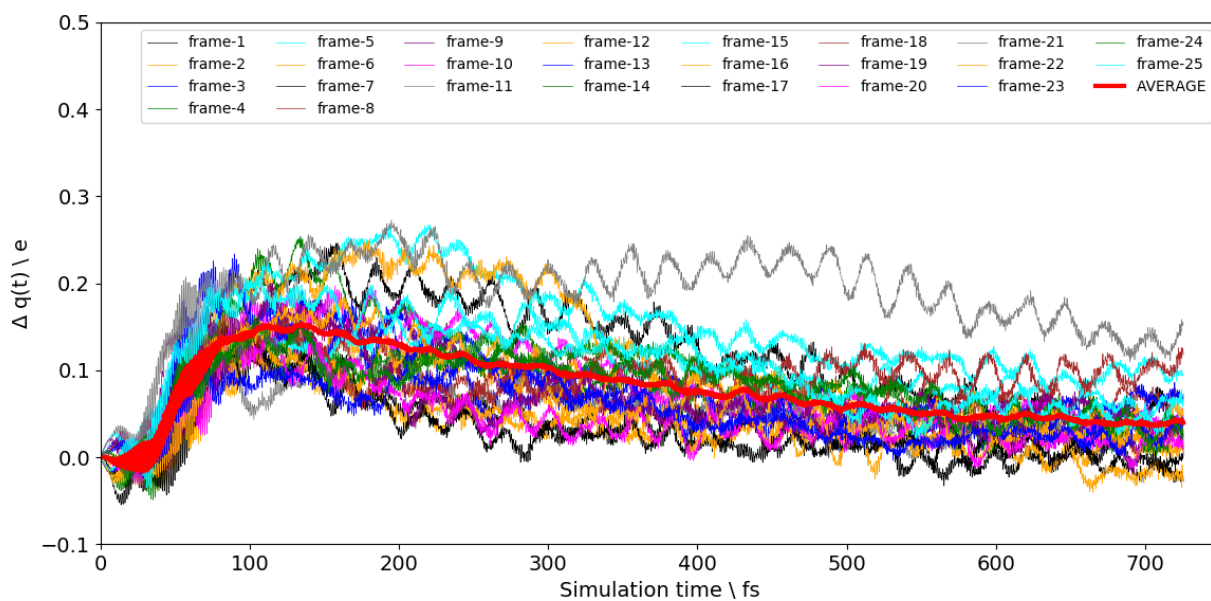


S 6: IA system under study.

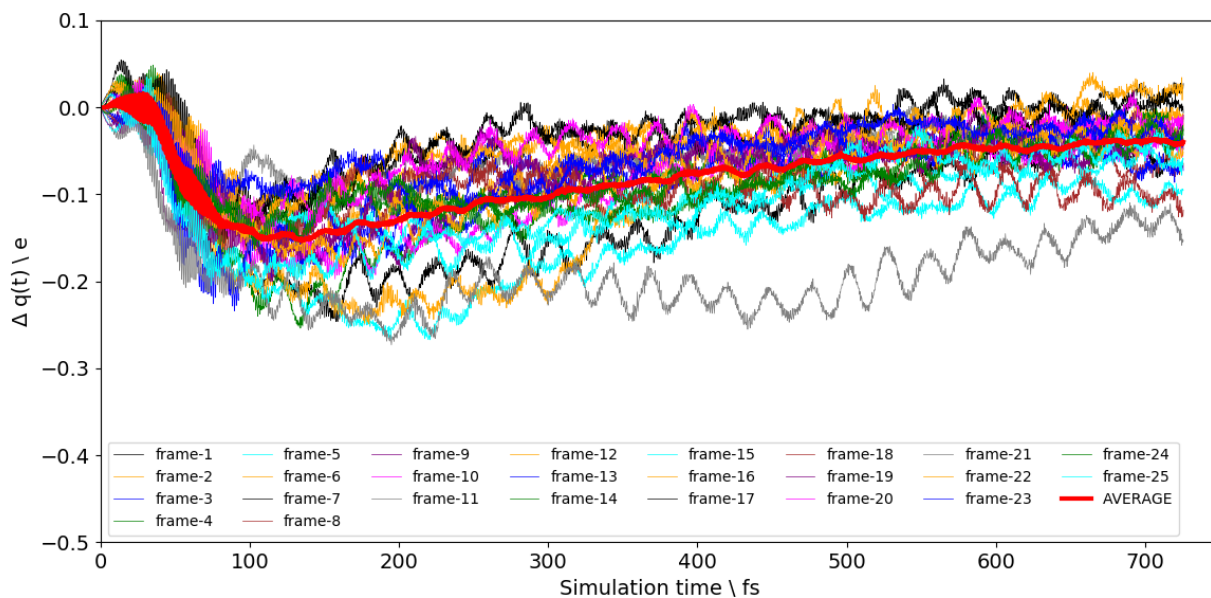


S 7: (a) Classical MD analysis: (up) Total Energy (bottom) Temperature during the simulation time for the IA system. (b) Velocities autocorrelation function corresponding to the second half of the NVT dynamic.

Figures S5 (a) and S9 (a) are represented the Classical MD Analysis demonstrating the stability of the systems under study here and validating the simulations. Figures S5 (b) and S9 (b) correspond with the VAF calculation for each case studied, respectively. And Figures S6, S7, S10, S11 the changes in the Mulliken charges with respect to their ground-state values as a function of time, are shown. Note, that in the first case under study (Figure S4) donor is referred as the Au25 cluster-thiolated and acceptor is referred as the Pyrene residue. For the second case under study (Figure S8) donor is referred Au25 cluster-thiolated with  $C_6H_{13}$  chains cluster and acceptor is referred as the Pyrene residue.

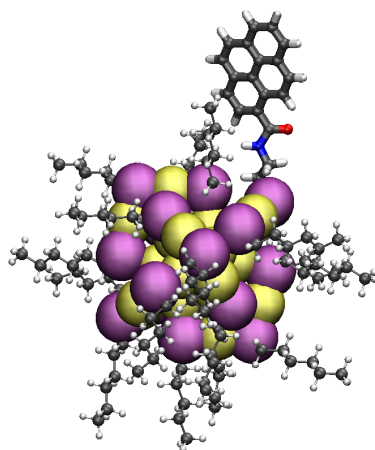


S 8: Changes in the Mulliken charges with respect to their ground-state values as a function of time for the donor in the IA system. The average curve calculated from all the configuration sampled is represented in red.

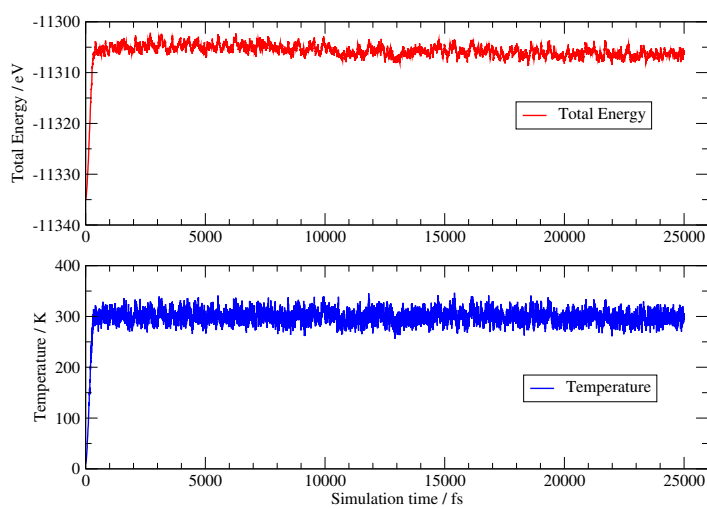


S 9: Changes in the Mulliken charges with respect to their ground-state values as a function of time for the acceptor in the IA system. The average curve calculated from all the configuration sampled is represented in red.

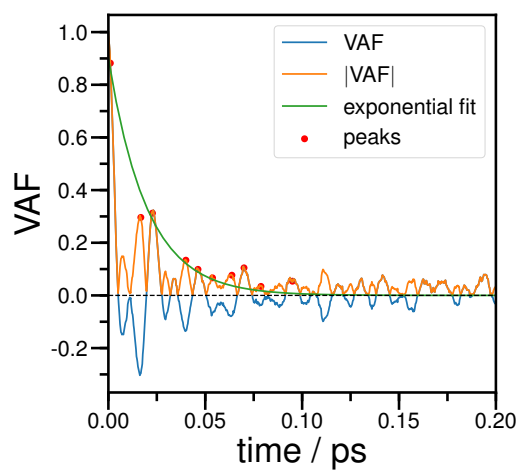




S 10: IB system under study.

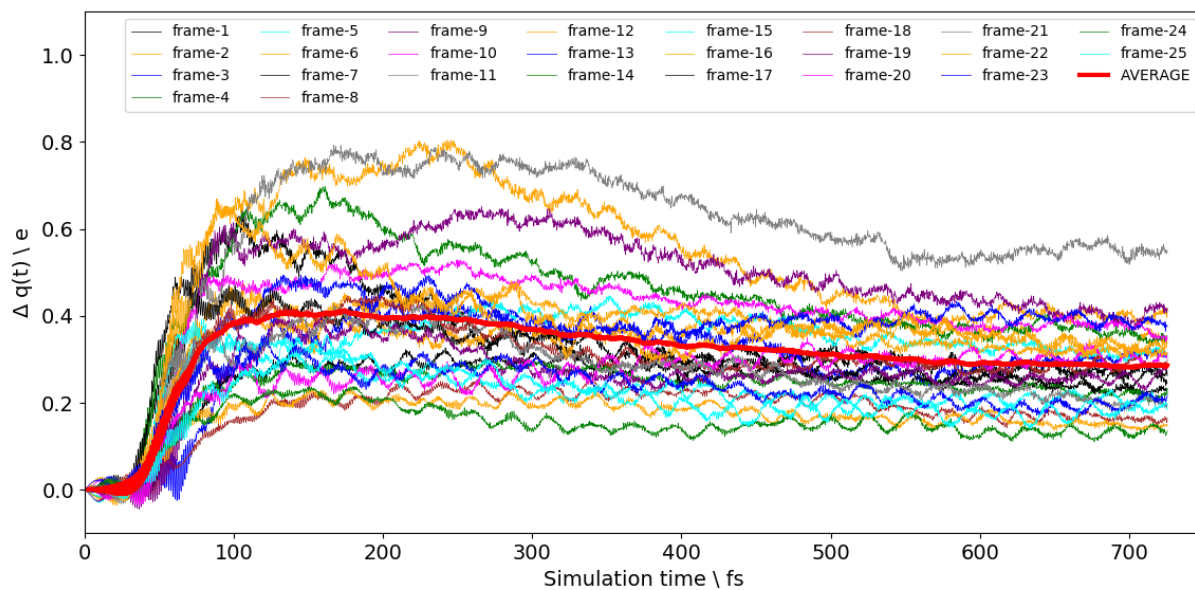


(a)

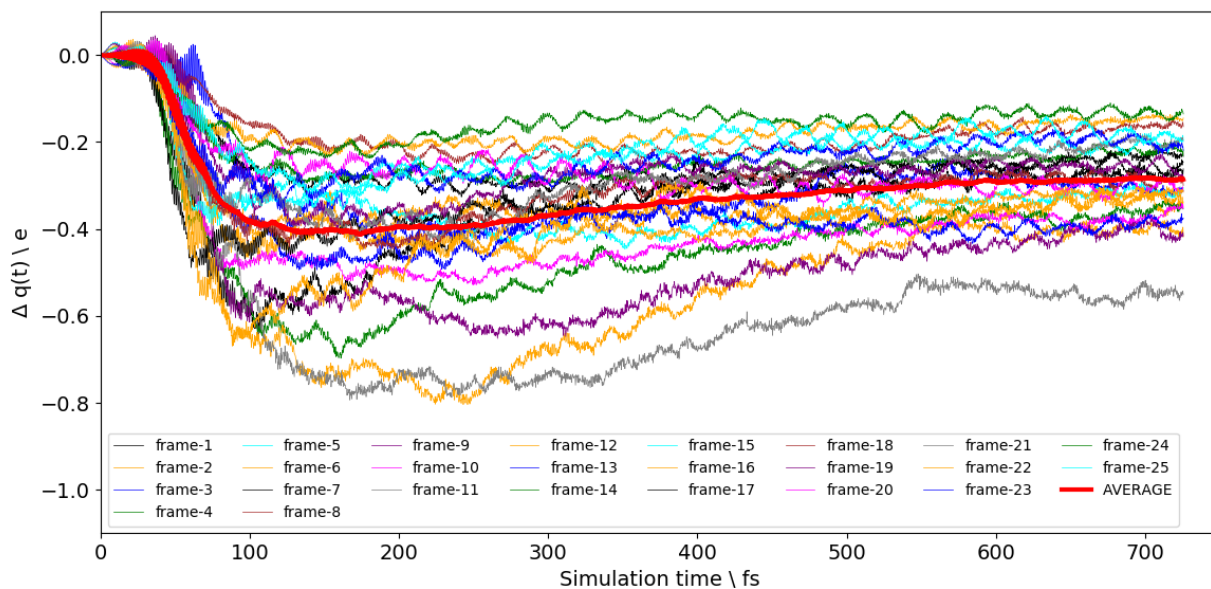


(b)

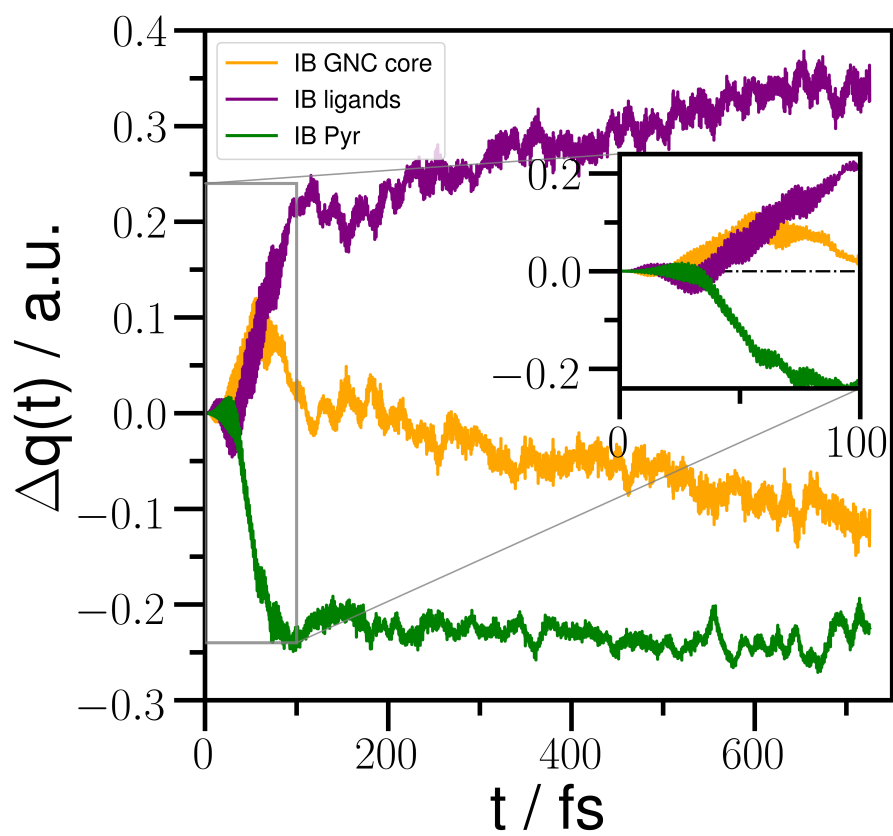
S 11: (a) Classical MD analysis: (up) Total Energy (bottom) Temperature during the simulation time for the IB system. (b) Velocities autocorrelation function corresponding to the second half of the NVT dynamic.



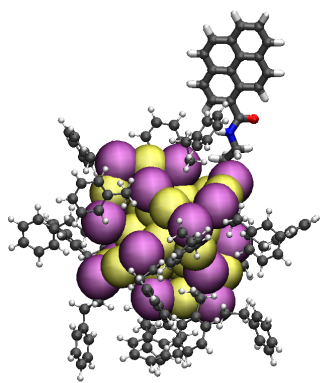
S 12: Changes in the Mulliken charges with respect to their ground-state values as a function of time for the donor in the IB system. The average curve calculated from all the configuration sampled is represented in red.



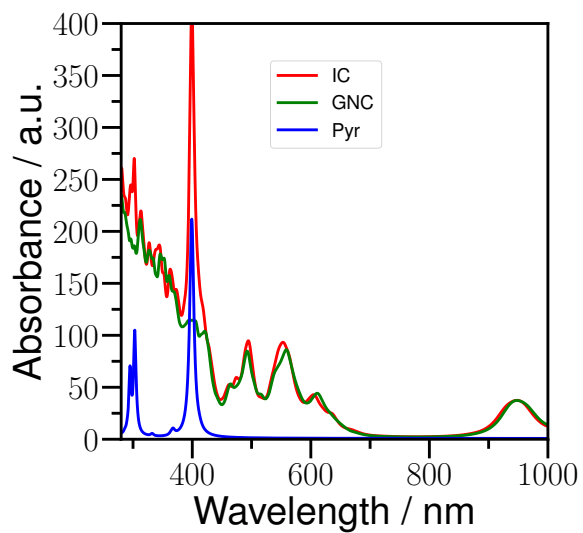
S 13: Changes in the Mulliken charges with respect to their ground-state values as a function of time for the acceptor in the IB system. The average curve calculated from all the configuration sampled is represented in red.



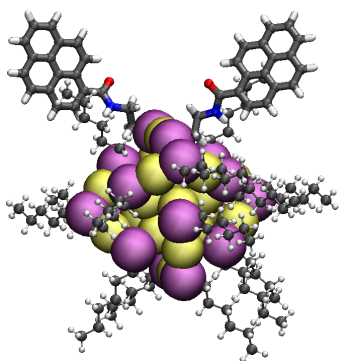
S 14:  $\Delta q$  as a function of time for IB system showing the different contributions of the cluster and the alkyl chains (Ehrenfest dynamic at 0 K).



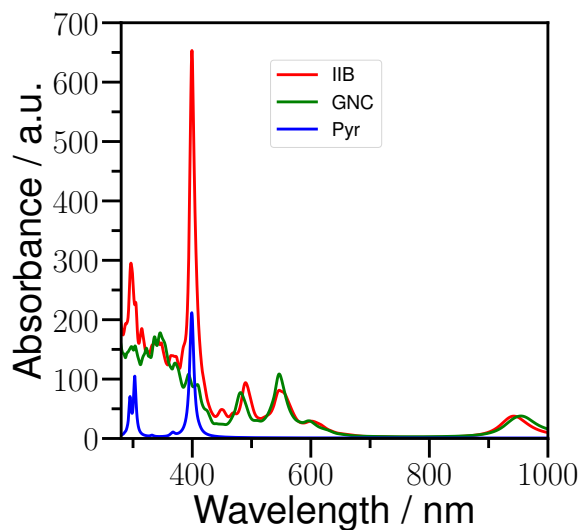
(a)



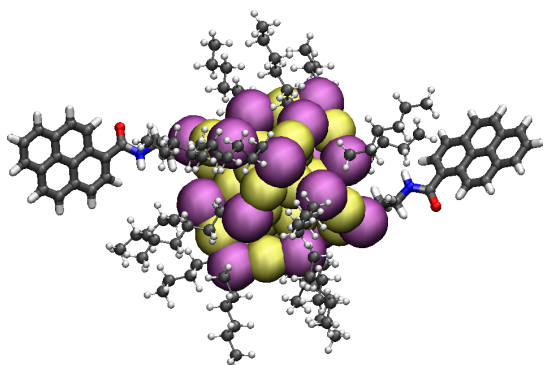
(b)



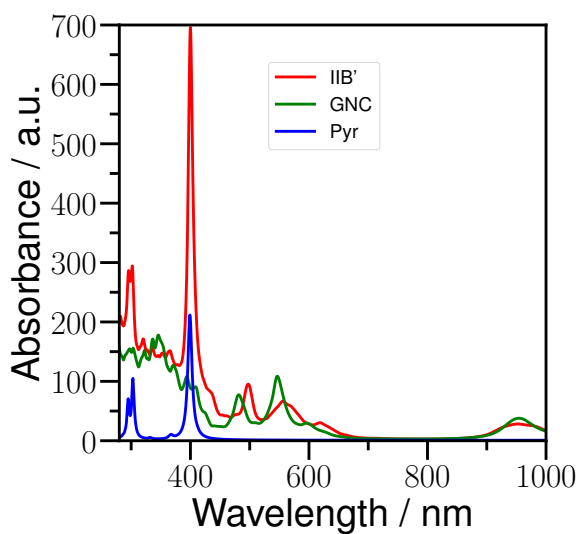
(c)



(d)

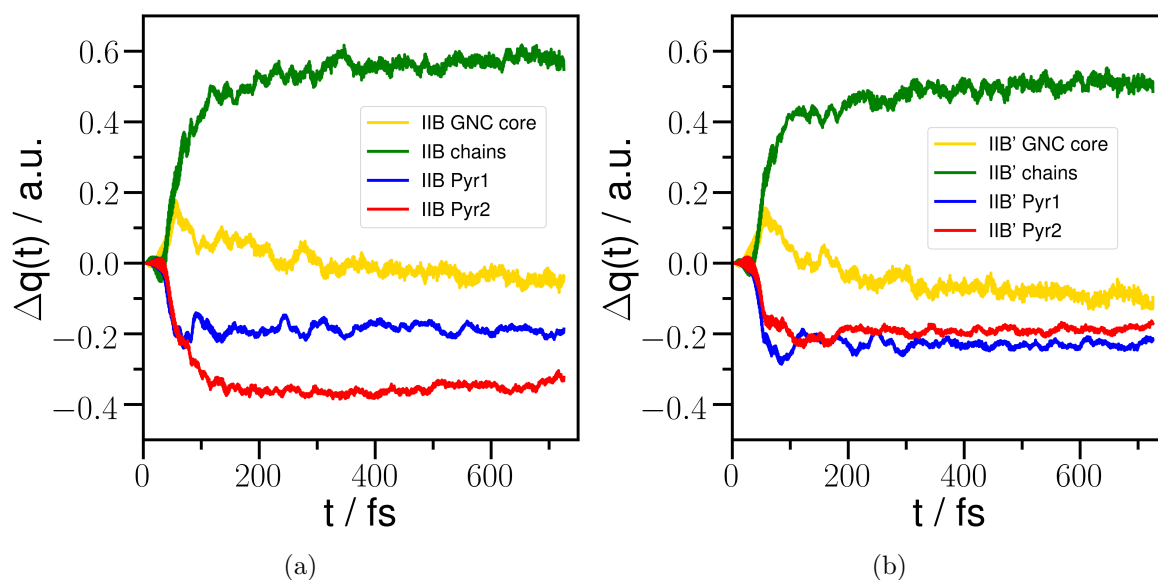


(e)



(f)

S 15: (a) IC system. (b) Absorption spectra for IC system. (c) IIB system (d) Absorption spectra for IIB system.(e) IIB' system (f) Absorption spectra for IIB' system



S 16: (a) Contribution analysis for the  $\Delta q$  as a function of time for the IIB system. (b) Contribution analysis for the  $\Delta q$  as a function of time for the IIB' system.

## References

- [1] B. Aradi, B. Hourahine, and T. Frauenheim, *J Phys Chem A* (2007) 111:5678
- [2] F. P. Bonafé, B. Aradi, M. Guan, O. A. Douglas-Gallardo, C. Lian, S. Meng, T. Frauenheim and C. G. Sánchez, *Nanoscale* (2017) 9, 12391-12397
- [3] F. P. Bonafé, F. J. Hernández, B. Aradi, T. Frauenheim, and C. G. Sánchez, *J. Phys. Chem. Lett.* (2018) 9, 4355-4359
- [4] F. P. Bonafé, B. Aradi, B. Hourahine, C. R. Medrano, F. J. Hernández, T. Frauenheim, and C. G. Sánchez, *J. Chem. Theory Comput.* (2020), 16, 7, 4454–4469