

# **Influence of intermolecular interactions on the reorganization energy of charge transfer between surface attached dye molecules**

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## Abstract

The parameters controlling the kinetics of intermolecular charge transfer are traditionally estimated from electronic structure calculations on the charge donor and charge acceptor in isolation. Here, we show that this procedure results in inaccuracies for hole transfer between a pair of organic dye molecules by comparing charge-constrained DFT calculations on a dye cation / neutral dye pair to the conventional DFT calculations on the isolated molecules. We quantify the error made in the reorganization energy of hole exchange between dye molecules ( $\lambda_i$ ). We choose three indolene based organic dyes with application to Dye Sensitized Solar Cells (DSSCs), namely D149, D102 and D131 for which experimental values of  $\lambda$  are available. We find that, although highly system dependent, the intermolecular interaction between the charge donor and acceptor can lead to a 0.25 eV change in  $\lambda_i$ , illustrating the limitations of the widely used original method in predicting rate of charge transfer.

Electronic structure and properties of materials are routinely calculated with quantum chemistry methods.<sup>1-5</sup> Although diverse in their approach and implementation, the concept behind any quantum chemical scheme is to describe the motion of electrons in the field of fixed nuclei within the Born-Oppenheimer approximation.<sup>6,7</sup> The choice of one technique over another is often made according to the balance between computational cost, accessibility and accuracy in predicting the properties one is interested in. This makes ground-state Density Functional Theory (DFT) one of the most widely used type of quantum chemistry calculation methods.<sup>6,8</sup> It allows a wide range of properties to be estimated, from molecular orbital energy levels to band structure in crystals. Recent developments, such as linear scaling for example, extend the range of systems which can be studied with DFT.<sup>9,10</sup> Thus, it becomes a powerful tool for evaluating electronic properties of large molecular assemblies. In the field of electronic devices, DFT is used to resolve experimental trends and guide the design of highly conductive materials.<sup>11,12</sup> For example, transport properties can be rationalised from the estimation of the rate of charge transfer between donor and acceptor moieties. In the context of non adiabatic charge transfer in the high temperature limit, we can compute a rate with Marcus's formula from DFT calculation of the electronic coupling, reorganization energy and free energy difference associated with the transfer of an electron from donor

to acceptor.<sup>13-15</sup> These predictions are then framed within the natural limitations of DFT, such as overestimation of true ground state energy, failure of basis set to describe the system, failure of the functional to approximate the relevant interactions, to name a few.<sup>6,8</sup> However, in the case of charge transfer, there is another shortcoming which is often overlooked. The quantities we aim to calculate depend on the pair "charge donor - charge acceptor" where an excess charge is localised on one of these entities. For example, the reorganization energy of hole exchange between identical molecules,  $\lambda$ , is the energy difference between the donor and acceptor at equilibrium and right after the charge transfer. Conventional DFT cannot simulate such a system where an excess charge is localised on one molecular entity. Hence, calculations are traditionally performed on the charge donor alone and then on the charge acceptor with or without the charge being transferred. The total energy of the system is taken as the sum of the energies of the individual components. This is true in the limit of large separation between the donor and acceptor, where the distribution of electron density of one entity does not influence the electron density of the other.<sup>15</sup> Intuitively, we expect this limit to depend on the size of the entities involved in the charge transfer as well as the magnitude and localisation of the excess charge. More sophisticated (hence expensive) methods, such as charge-constrained DFT,<sup>16</sup> have been proposed for cases where this limit can never be reached, as in intramolecular charge transfer.<sup>15</sup> However, for intermolecular charge transfer in solar cells for example, which often involves larger molecular assemblies, conventional ground state DFT is still the method of choice. Note that charge-constrained DFT is a ground state method and as such suffers from all the limitations stated above but the inability to deal with localised excess charges.

This letter aims to test the validity of the use of conventional ground-state DFT to calculate reorganization energies of intermolecular charge transfer. The intermolecular interactions accounted for in DFT energy calculations are electronic interactions, due to the adaptation of the electron density of the charge donor to the electron density of the charge acceptor and vice versa. We compare charge-constrained and conventional DFT calculations of the energy cost associated with the hole transfer between neighboring dye molecules, with direct application to lateral hole diffusion within dye monolayers anchored to metal oxide surfaces as in Dye Sensitized Solar Cells (DSSC).<sup>17-22</sup>

In this case, the charge donor is a cationic dye molecule while the charge acceptor is a neutral dye molecule and the dyes are separated according to their anchoring point to the subjacent substrate. We seek to quantify the error made when performing DFT calculation of the reorganization energy of intermolecular charge transfer on isolated molecules. We choose dye molecules of a typical size over 50 atoms for conjugated molecular materials, which makes difficult the use of more elaborate quantum chemical calculations. We calculate the inner-sphere reorganization energy,  $\lambda_i$  (i.e. without solvent effect) in two ways: using charge-constrained DFT (CDFT) as implemented in NWChem to directly calculate the total energy of the pair "neutral dye - cationic dye" for a range of intermolecular distances and using conventional DFT (NWChem) on the isolated molecules. We compare our results and evaluate the error on the reorganization energy for intermolecular separations relevant to devices. We select the widely used functional B3LYP of our study in order to relate the findings to common practice in the literature. We perform this study for three indole dyes, D102, D131 and D149, commonly used in solid state DSSCs and for which we have experimental values of the reorganization energy ( $\lambda_{\text{exp}}$ ).<sup>23</sup>

*Total energy variation of a pair of dye molecules*

We consider a charge transfer reaction of the form  $\text{dye}^+ + \text{dye} \rightarrow \text{dye} + \text{dye}^+$  between dyes whose chemical structure is given in Figure Figure 1a-c. In this work, a pair of dyes is built by translating one molecule along a vector normal to the anchoring group (see geometries in Supporting Information). We call  $d$  the intermolecular distance between dyes as illustrated in Figure Figure 1. Figure Figure 1d shows the Mulliken population analysis for D131 which illustrates the variation in partial charges between the hole donor (cationic dye) and acceptor (neutral dye). Similar variations in partial charges are obtained for D102 and D149.

The CDFT energy components (B3LYP/6-311G) of the pair of dyes (neutral and cation) are given in Figure Figure 2 as a function of the inverse intermolecular distance. In DSSC, the spacing between dye molecules is set by the spacing of the anchoring sites on the subjacent  $\text{TiO}_2$  surface. For the organic dyes studied here, it ranges from 8 to 12 Å in full coverage conditions.<sup>13,24</sup> In DFT (as in CDFT), the total energy is the sum of the Coulomb energy accounting for electrostatic

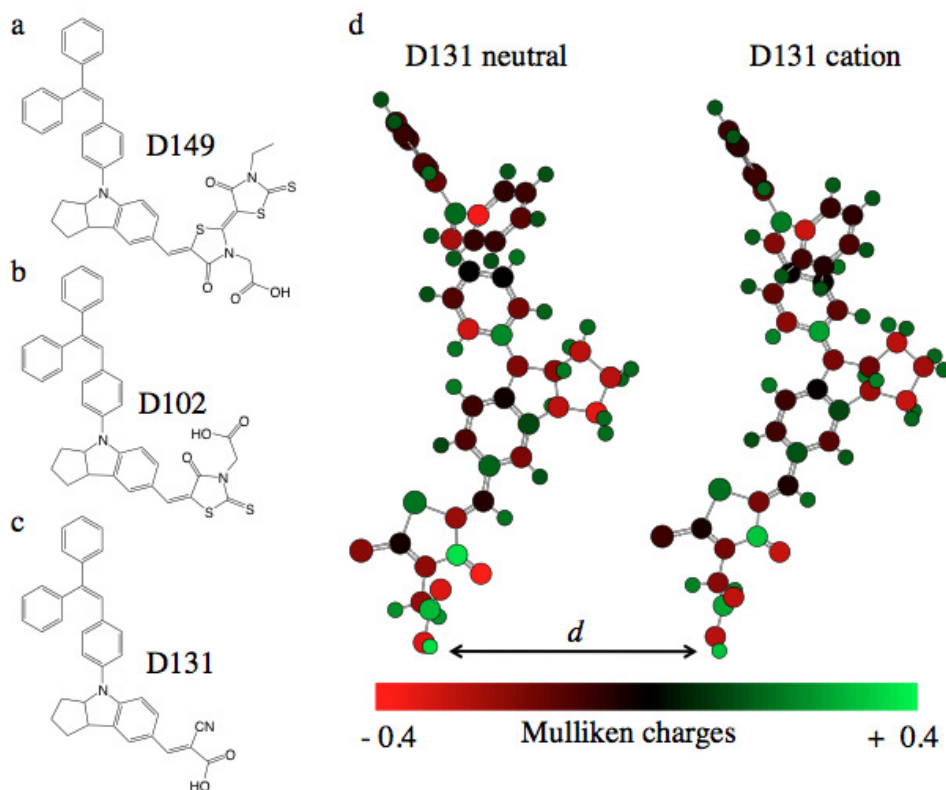


Figure 1: Chemical structure of the organic dyes considered: (a) D149, (b) D102 and (c) D131. (d) Mulliken population analysis of D131 in neutral (left) and cationic (right) state.

interactions between electrons, the nuclear repulsion energy, the one electron orbital energy, sum of the Kohn-Sham orbital energies of the non-interacting Kohn-Sham system and the exchange correlation energy accounting for multi electron effects.<sup>6,8</sup> To make sure the data presented in Figure Figure 2 do not result from spurious electron correlation effect, we reproduced the trends using the Hartree Fock method (see Figure Figure 5 in Supporting Information).

We observe that the coulomb and one electron energies vary linearly with the inverse of the intermolecular spacing  $d^{-1}$  (from 8 to 15 Å and 11 to 18 Å for D131, D102 and D149 respectively). Furthermore, the coulomb and nuclear repulsion energies have identical gradients. This suggests that, at these distances, the intermolecular interactions do not influence the electrostatics of the system (otherwise we would expect different dependences of Coulomb energy and nuclear repulsion on separation since the latter does not dependent on the electron density). However, the exchange correlation energy, and consequently the total energy, depend on the intermolecular separation. As

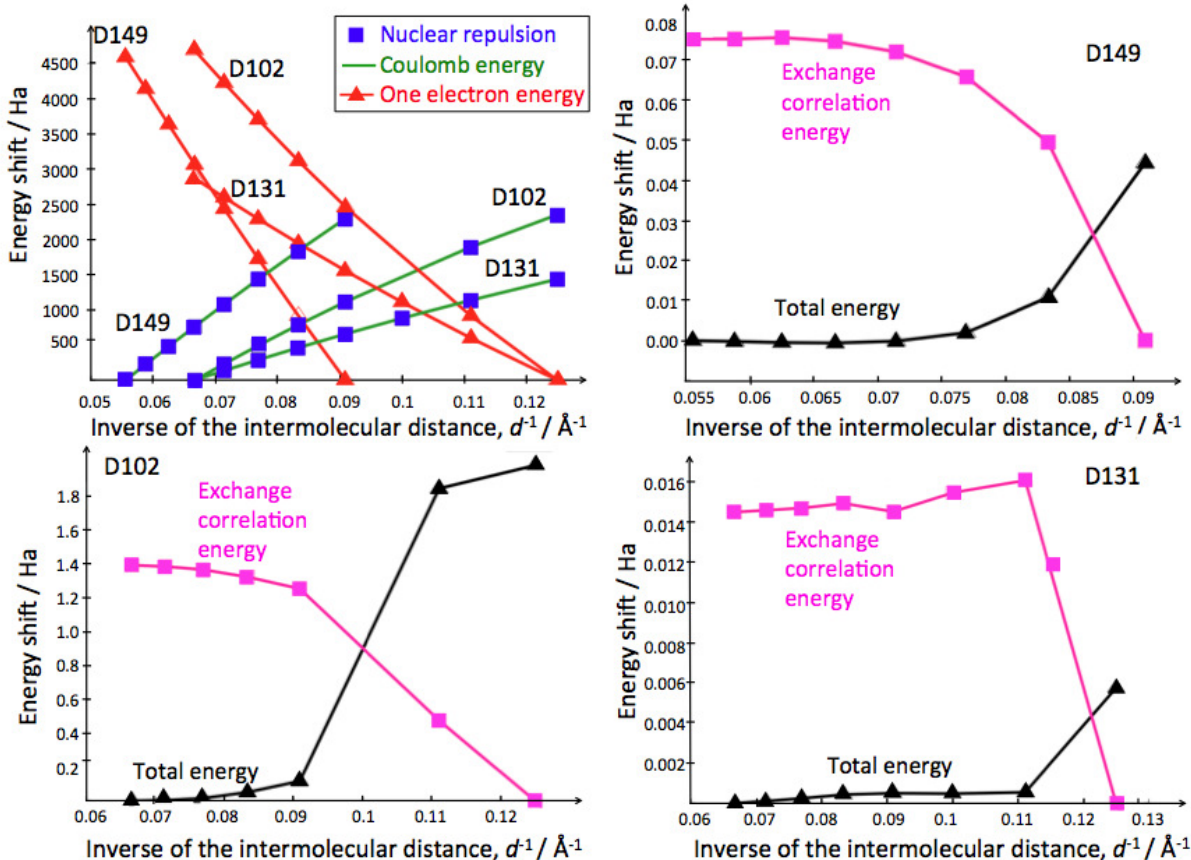


Figure 2: Charge constrained DFT energy components of the pair dye cation (hole donor) and dye neutral (hole acceptor) as a function of the inverse of the intermolecular distance  $d$ . In all cases, the energies are shifted by the minimal value obtained for this range. (a) One electron, coulomb and nuclear repulsion energies of D149, D102 and D131. (b) Exchange correlation and total energy of D149. (c) Exchange correlation and total energy of D102. (d) Exchange correlation and total energy of D131.

$d$  decreases towards  $10 \text{ \AA}$ , the total energy increases for all three dyes. Therefore, performing DFT calculations on isolated molecules results in an error in the total energy. To see how this error is translated when calculating the parameters controlling the kinetics of charge transfer, we calculate the reorganization energy of hole exchange between dye molecules.

#### *Calculation of the reorganization energy of hole exchange between dye molecules*

We want to quantify the error in reorganization energy due to the intermolecular interaction between dye molecules. Hence, we calculate with CDFT the inner-sphere reorganization energy,

$\lambda_i$  (e.g. no solvent contribution), according to:

$$\lambda_i(d) = E_{\text{noneq}}(\text{dye} + \text{dye}^+) - E_{\text{eq}}(\text{dye} + \text{dye}^+), \quad (1)$$

where the equilibrium energy component, "eq", refers to the dyes being in their equilibrium geometry (i.e. the neutral and cation equilibrium structures have null and +1 excess charge respectively) while the non-equilibrium energy component, "noneq", refers to the system immediately following charge transfer where the charge state has changed but not the geometry (i.e. the neutral and cation equilibrium dye structures have +1 and null excess charge respectively). The set of calculations is repeated for several intermolecular distances. In the limit of large  $d$ , we have:

$$\lim_{d \rightarrow \infty} \lambda_i = E_{\text{noneq}}(\text{dye}) + E_{\text{noneq}}(\text{dye}^+) - E_{\text{eq}}(\text{dye}) - E_{\text{eq}}(\text{dye}^+), \quad (2)$$

where the energy calculations are performed with conventional DFT on the isolated molecules. **The comparison of the values of  $\lambda_i$  calculated by Equation Eq. (1) for intermolecular spacings found in DSSC and the values obtained by Equation Eq. (2) for the three dyes D149, D102 and D131 is shown in Figure Figure 3.** We observe that in all cases,  $\lambda_i$  calculated with CDFT (Equation Eq. (1)) tends towards the value obtained from DFT calculations on the isolated molecules (infinite distance limit showed with dashed lines). However, for the range of intermolecular distances studied here, only  $\lambda_i$  for D131 seems to converge towards the limit. Computationally, it is difficult to calculate the reorganization energy at larger separation. Nevertheless, using a smaller basis set (3-21G\*) and the smallest dye (D131), we were able to verify the convergence of the CDFT calculations:  $\lambda_{i,d=20} = 0.36\text{eV}$  while  $\lambda_{i,d=\infty} = 0.37\text{eV}$ .

The inner-sphere reorganization energy of hole exchange between D149 and D102 increases as the intermolecular separation decreases. At distances relevant for DSSC,  $\lambda_i$  is about 0.2 eV higher than  $\lambda_i$  calculated from DFT on isolated molecules. This is a significant difference which would lead to a one order of magnitude change in the rate of charge transfer. The effect of the intermolecular interactions between the molecules reconciles slightly theoretical and experimental data,<sup>23</sup> for

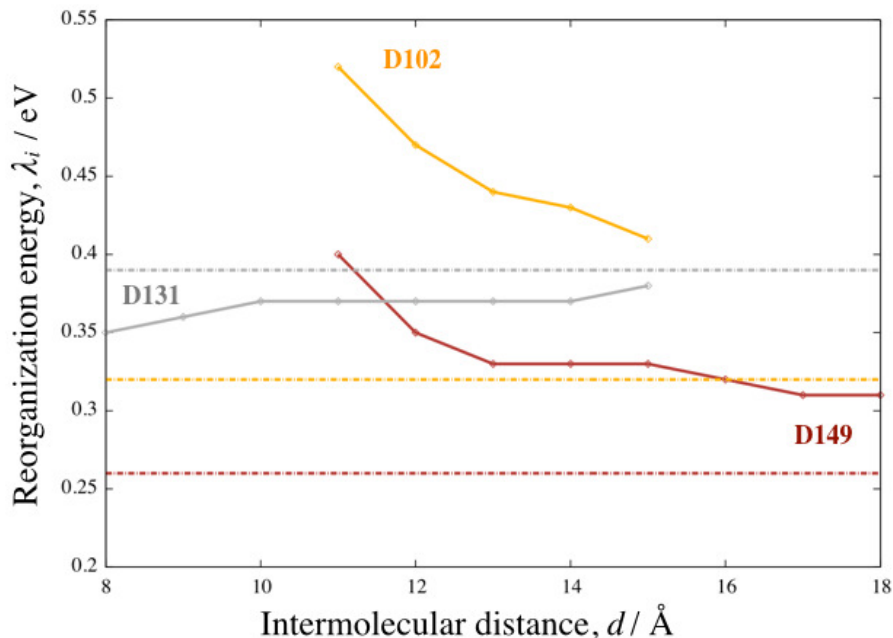


Figure 3: Reorganization energies in eV for hole exchange between pairs of the dyes D149, D102 and D131 as a function of the intermolecular distance  $d$ . The solid and dashed lines are the values computed from Equations Eq. (1) and Eq. (2) respectively.

D149 and D102 (i.e. the experimental values are too large compared with those calculated with DFT) although it does not help to resolve the disagreement of theory and experiment for D131.

It has to be noted that we look for relative agreement when comparing with experimental data as neither the solvent nor the metal oxide surface are included in these calculations. We expect, since we study similar dyes here, that the outer-sphere reorganization energy, incorporating both solvent and surface effects, will be of similar magnitude. More detailed consideration can be found in our earlier work.<sup>25,26</sup> Furthermore, we calculated  $\lambda_i$  for a specific configuration of the dye molecules.

In a real system, we expect the properties of the dye monolayer to be affected by energetic and configurational disorders. Energetic disorder would affect the experimental data which are a measure of the combined contributions of the reorganization energy and energetic disorder, as discussed in details in Ref.<sup>23</sup> This is consistent with the higher experimental reorganization energies. Indeed, energetic disorder in the experimental system would lead to experimental estimates of reorganization energy that overestimate the true values. Configurational disorder would give a variety of pair



configurations, each with a specific  $\lambda_i$  contributing to the total reorganization energy. To further address the influence of configurational disorder on the the reorganization energy of hole exchange we would need to first resolve the structural arrangement of the dye monolayer at the surface of the metal oxide. This is an unsolved problem and is outside the scope of this letter.

Finally, we note that the magnitude of the effect of intermolecular interaction on the total energy of a pair charge donor - charge acceptor will depend on the magnitude of the excess charge on both entities. To illustrate this point we provide in supporting information CDFT calculations on the system  $C_2F_4^-$  (electron donor) /  $C_2H_4^+$  (electron acceptor), where both the charge donor and acceptor carry an excess charge. In this system the intermolecular interaction affects every component of the total energy but the nuclear repulsion energy. Furthermore, in contrast to the pair of dyes, the total energy is seen to decrease with decreasing separation between the molecules. This has important implications for the design of materials for solar cells because the error made by using conventional DFT is not a systematic shift of the total energy. For example the error made by computing the rate of recombination reactions (as in the example in supporting information) differs in sign from the error made in computing charge transport.

In summary, we used charge constrained DFT to quantify the influence of the intermolecular interaction between dye molecules on the calculation of the energy barrier to hole exchange. **Accurate prediction of the kinetics of hole hopping would be beneficial for the design of solid state DSSC<sup>27</sup> but also of DSSC where the dye monolayer is the light absorber as well as the hole transporting medium.<sup>28</sup>** Both theoretical and experimental studies are relevant to complete the picture of interfacial charge exchange. In this paper, we observe that the intermolecular interaction between dyes cannot be neglected for the average intermolecular distance in DSSC. This illustrates some of the limitations in the traditional method of calculation of charge transfer parameters with DFT calculations on isolated molecules. We found that the reorganization energy can be underestimated by up to 0.25 eV when neglecting the intermolecular interactions. In other electronic devices, the charge donor and acceptor are often two charged entities. In this case, we expect the strength of the intermolecular interaction to be higher than between a neutral and cationic dye molecules.

Hence, it is likely that performing DFT calculations on the isolated components systematically underestimate the energy barrier to charge transfer. This is important to take into consideration when designing

## Acknowledgement

V. Vaissier was supported through a studentship in the Centre for Doctoral Training on Theory and Simulation of Materials at Imperial College funded by EPSRC under grant number EP/G036888/1. P. Barnes thanks the EPSRC for his Career Acceleration Fellowship EP/J002305/1. J. Nelson thanks the Royal Society for a Wolfson Merit Award and the support from EPSRC grant number EP/K010298/1 and the Supergen program (EP/G031088/1).

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## Supporting Information Available

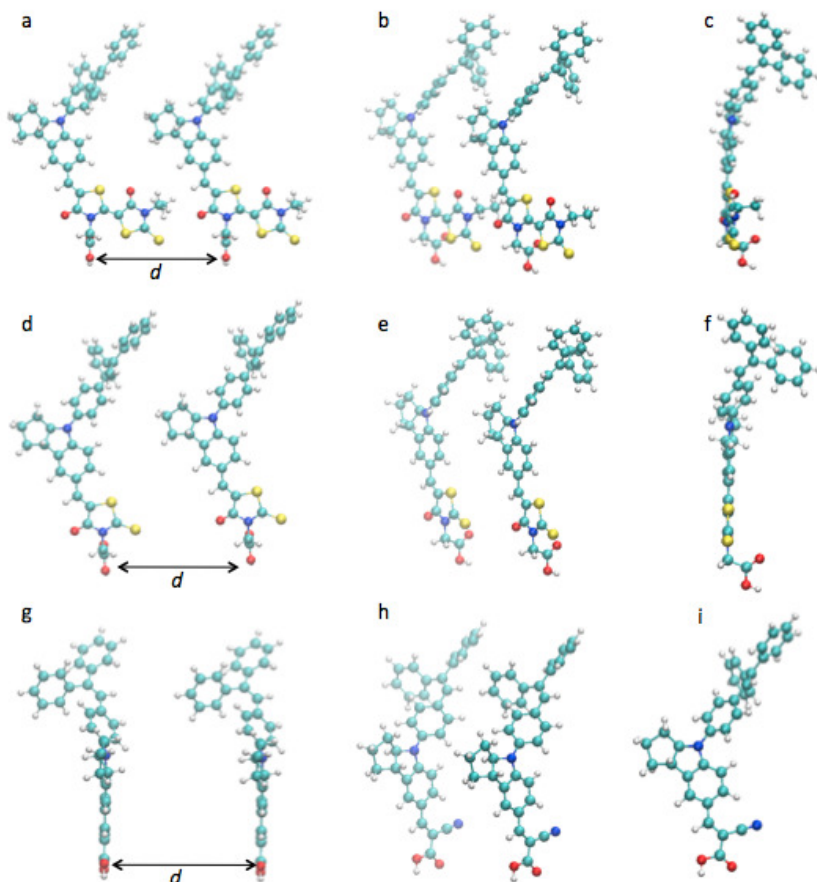
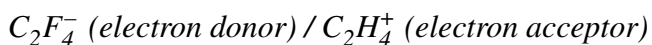


Figure 4: Geometries of the pair of dyes studied here. D149 front (a), 45° tilt (b) and side (c) view. D102 front (a), 45° tilt (b) and side (c) view. D131 front (a), 45° tilt (b) and side (c) view.



Here, we consider the system,  $C_2F_4^- / C_2H_4^+$ , lying in the same plane with the C-C axes collinear and with centres separated by a distance  $d$  as shown in Figure Figure 6. The Mulliken population analysis shows a drastic difference in charge localisation between the two molecules. We show in Figure Figure 6 the variations of the total energy as well as the different contributions to the total energy of the pair, calculated with CDFT (B3LYP/6-311G++), for  $d$  ranging from 4 to 12 Å. We also report the total energy from DFT (B3LYP/6-311G++) calculations on the isolated molecules (dashed line).

As expected, at large distances (over 10 Å in this case), the total energy of the pair is equivalent

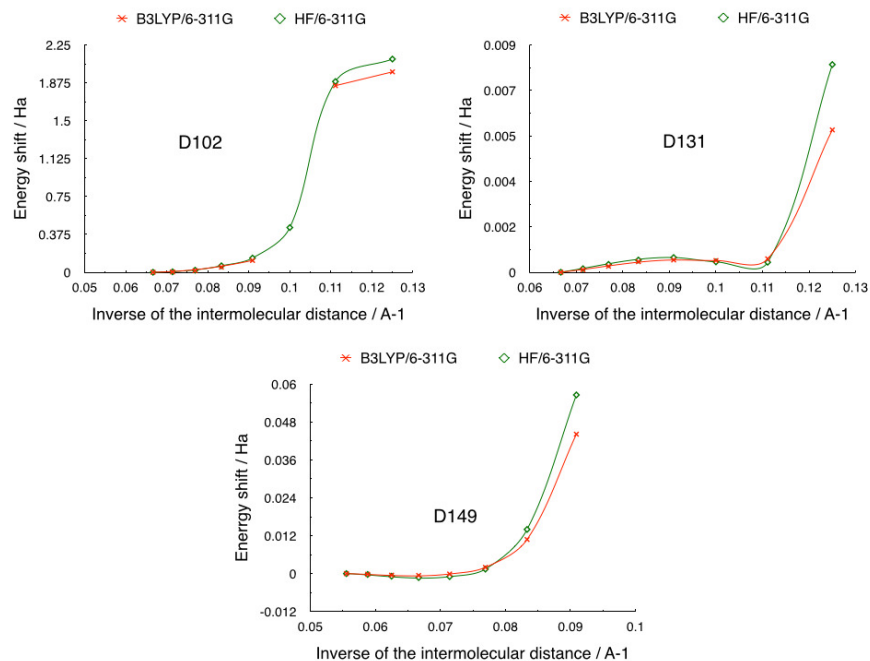


Figure 5: Comparison of the CDFT total energy shift and the Hartree Fock equivalent for the three organic dyes studied in this work. In all cases the two level of theory predict the same trend.

to the sum of the energies of each individual molecules. However, we observe a sharp change at  $d = 10 \text{ \AA}$  in all energy components of the pair but the nuclear repulsion. This is consistent with an increased electronic interaction between  $\text{C}_2\text{F}_4^-$  and  $\text{C}_2\text{H}_4^+$  when separated by less than  $10 \text{ \AA}$  which results in a decrease in total energy. The limiting distance above which the two entities effectively do not interact with each other is quite large relative to the size of the molecules. This result would suggest that, for configurations of charge donor and acceptor found in electronic devices (separated by about  $1 \text{ nm}$ ), electronic interaction cannot generally be neglected. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

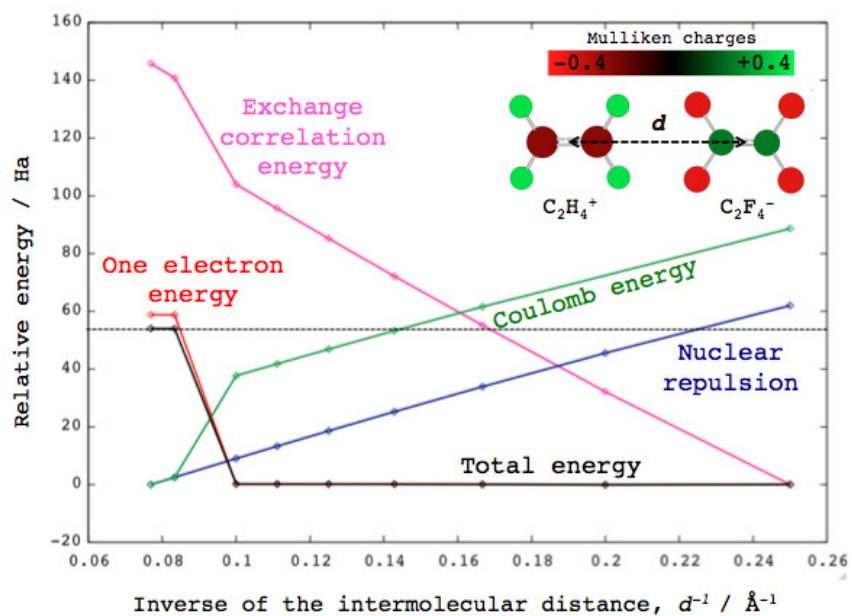


Figure 6: Charge constrained DFT energy components of the pair  $\text{C}_2\text{F}_4^-$  (electron donor) and  $\text{C}_2\text{H}_4^+$  (electron acceptor) as a function of the inverse of the intermolecular distance  $d$ . The total energy (solid black line) is the sum of the one electron energy (red), the coulomb energy (green), the nuclear repulsion energy (blue) and the exchange correlation energy (pink). The sum of the energies of  $\text{C}_2\text{F}_4^-$  alone and  $\text{C}_2\text{H}_4^+$  alone is represented by the dashed black line, for comparison.



# Graphical TOC Entry

