Ground State Orbital Analysis Predicts S_1 Charge Transfer in Donor–Acceptor Materials

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Abstract: Donor-acceptor (D-A) materials, such as D-A co-crystals and D-A copolymers, can exhibit a wide range of unique photophysical properties with applications in next-generation optoelectronics. The properties of D-A dimer models, computed with electronic structure calculations, are often employed to predict properties of D-A materials. One of the most important D-A dimer quantities is the degree of charge transfer (DCT) in the S_1 state, which correlates with properties such as fluorescence lifetimes and intersystem crossing rates. Predictive metrics of the S_1 DCT generally require an excited state quantum chemistry calculation. Presented here is a novel metric for predicting the degree of charge transfer (DCT) in the S_1 electronic state of D-A materials, computed solely with ground state orbital analysis. This metric computes the average of two quantities: (1) the degree of similarity between the highest occupied molecular orbital (HOMO) in the donor molecule and the D-A complex and (2) the degree of similarity between the lowest occupied molecular orbital (LUMO) in the acceptor molecule and the D-A complex. A linear relationship between this similarity metric and the DCT in the S_1 state (HOMO → LUMO transition) is demonstrated for a data set of 31 D-A dimers. The integration of this novel *orbital structure*-function relationship into high-throughput screening methods is discussed alongside best practices for choosing molecular geometries and quantifying the DCT.

In the search for next-generation optoelectronic devices, there has been a growing interest in donor-acceptor (D-A) materials, including D-A co-crystals and D-A copolymers, for their application in organic solar cells and organic light-emitting diodes.[1–3] D-A complexes, by definition, exhibit charge transfer (CT) in their ground and select excited states.[4] In the search for structure-function relationships to integrate into high-throughput screening and machine learning protocols,[5–9] several studies have assessed ways to predict the degree of CT (DCT), or ionicity parameter, in the S_0 state of D-A materials from molecular quantities such as orbital energies, vibrational frequencies, and geometric parameters.[10–14] Early evidence shows a relationship between DCT in S_0 to the magnitude of effective CT integrals,[11] commonly used in models of charge transport.[13–18] The DCT in the first electronically excited state of D-A dimers, S_1, has emerged as a key quantity for predicting radiative and non-radiative lifetimes in D-A materials, including intersystem crossing rates and fluorescence lifetimes.[2,19–23] These lifetimes are particularly difficult to compute directly using D-A dimer models, as energy levels and transition dipoles ofter differ substantially between the molecular cluster and material.[24,25]

A variety of DCT metrics for excited-state calculations have been put forward, as reviewed recently.[26,27] A widely-used example is the "Λ metric" introduced by Peach *et al.*[28] as a diagnostic for time-dependent density functional theory calculations. The definition of Λ is based on spatial overlaps of occupied and virtual orbitals, evaluated by numerical quadrature and weighted by excitation amplitudes, but importantly this and other standard DCT metrics require an excited-state calculation. Here, we consider whether ground-state orbital overlaps are sufficient to indicate CT character in the $S_0 \to S_1$ transition.

We construct a similarity metric, η, as follows. First, define a molecular orbital

$$|\phi_i\rangle = \sum_\mu C_{\mu i}\,|\chi_\mu\rangle, \tag{1}$$

where ϕ_i is the sum of atomic basis functions χ_μ, with MO coefficients $C_{\mu i}$. We compute the overlap O_{ij} between MOs ϕ_i and $\tilde{\phi}_j$, where $\tilde{\phi}_j$ uses the same atomic basis functions as ϕ_i at a displaced geometry. This overlap is

$$O_{ij} = \langle \phi_i | \tilde{\phi}_j \rangle = \sum_{\mu\nu} C_{\mu i} S_{\mu\nu} \tilde{C}_{\nu j} \tag{2}$$

where $S_{\mu\nu} = \langle \chi_\mu \mid \tilde{\chi}_\nu \rangle$ is the overlap matrix involving displaced basis functions. We compute O_{ij} twice: once between the HOMO of the isolated donor molecule (HOMO^i) and the HOMO of the donor molecule within the complex (HOMO^c), using ghost functions to ensure that both calculations have the same basis functions; and second, between the LUMO of the isolated acceptor molecule (LUMO^i) and the LUMO of the acceptor molecule within the complex (LUMO^c). We define η as the average of these two quantities:

$$\eta = \frac{1}{2}\left(O_{\mathrm{HOMO}^i,\mathrm{HOMO}^c} + O_{\mathrm{LUMO}^i,\mathrm{LUMO}^c}\right). \tag{3}$$

The two geometries are maximally oriented using the Kabsch algorithm,[29] in order to maximize the overlap. Each computation of η requires three ground state calculations to obtain the orbitals of the isolated donor molecule, the orbitals of the isolated acceptor molecule, and the orbitals of the D-A complex. The calculation of O_{ij} is performed in a locally-modified version of Q-Chem.[30]

To assess the correlation between η and the S_1 DCT of D-A dimers, we screened 31 D-A complexes with donor and acceptor molecules shown in Figure 1 and whose S_1 states are dominated by a HOMO → LUMO transition. The donor and acceptor molecules chosen are augmented from a data set recently chosen in a screening of S_0 DCT.[14] The donor molecules exhibit a diversity of molecular structures, while the acceptor molecules are 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its fluorinated derivatives, F_xTCNQ. Geometries are optimized with Gaussian G16 at the CAM-B3LYP/6-31+G(d,p) level of theory with Grimme dispersion.[28,31–33] We calculated the DCT using natural bond orbital (NBO) population analysis implemented in Gaussian G16 and transition density matrix (TDM) analysis in Theodore.[34,35]

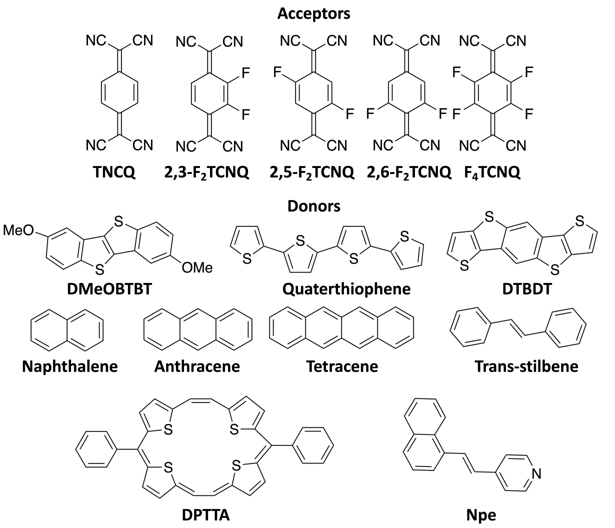

Figure 1. Chemical structures of the donor and acceptor molecules.

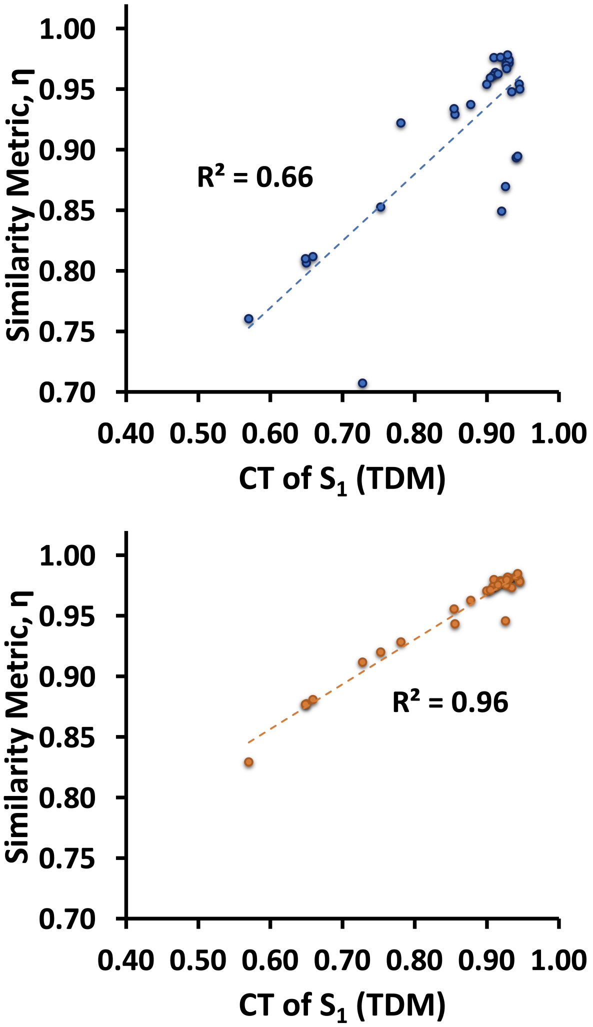

Figure 2. η vs. S_1 DCT. Left: Values computed at optimized monomer geometries and optimized dimer geometries. Right: Values computed at the optimized dimer geometries only.

We investigate the impact of geometries used to compute η by plotting η vs. S_1 DCT in two ways. First, we optimize both the isolated monomers and their dimer complex and compute η vs. S_1 DCT (Figure 2, left). Second, we optimize the dimer complex and take the geometries of the isolated monomers to be the same as in their dimer complex (Figure 2, right). In each case, the S_1 DCT is computed using TDM analysis. Notably, we observe significant variations in the η values when the monomers were optimized, as evidenced by the outliers shown in the left plot of Figure 2. Additionally, the R^2 value from linear regression is 0.66 when comparing optimized monomers vs. optimized dimers, while the R^2 value is 0.96 when monomer geometries are unrelaxed from those found in the dimer complex. In both cases, our analysis reveals a positive linear correlation between the S_1 DCT and η, indicating that S_1 DCT is large when the HOMO (LUMO) orbital of the donor (acceptor) retains its character from the isolated molecule. That the unrelaxed monomer geometries provide superior performance presents certain practical advantages, including avoiding the computational cost associated with optimizing the monomer geometries. Moreover, computing η at a single geometry eliminates the necessity of evaluating the atomic overlap integrals at displaced geometries. This simplifies the calculation of η, as $S_{\mu\nu}$ becomes the atomic basis self-overlap matrix, which is commonly printed in the output of electronic structure programs.[31]

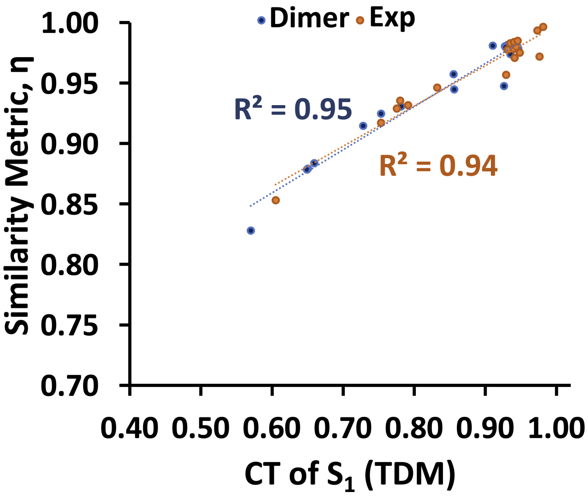

Figure 3. Plot of η vs. S_1 DCT at the experimental crystal structures (orange) and optimized D-A dimer geometries (blue).

To assess the sensitivity of η to the dimer geometry, bridging the gap between D-A dimers and D-A co-crystals, we perform an analysis of the S_1 DCT vs. η for geometries from experimental crystallographic data (where available) and compare to the results found in Figure 2. S_1 DCT is again computed using TDM analysis. Figure 3 shows the results obtained using the geometries from experiment in comparison to the dimer geometries, and indicates that the positive linear correlation still holds when the D-A geometries are taken from experimental crystal structures. In fact, when linear regressions are performed separately, the trend lines are almost indistinguishable. In Table 1, we report the value of η computed at each geometry (dimer complex vs. experiment) and the percent deviation between the two. The values of η obtained from these two geometries have very small percent deviations, from 0.1% to 6% with an average of 1.3%. This shows that η can bridge between different types of molecular structures (isolated dimer and experimental crystal), indicating reliability of the metric for different data sources. This is challenging for predictive metrics that rely on orbital energies.

Table 1. η values using the experimental crystal (exp) and dimer geometries and the percentage deviation (%D) of η_{dimer} from η_{exp}.

System	η_{exp}	η_{dimer}	%D
4T:F$_2$TCNQ	0.932	0.945	1.4
4T:F$_4$TCNQ	0.917	0.931	1.5
4T:TCNQ	0.946	0.957	1.2
Anthracene:F$_4$TCNQ	0.983	0.981	0.2
DMeO-BTBT:F$_2$TCNQ	0.975	0.980	0.5
DMeO-BTBT:F$_4$TCNQ	0.971	0.974	0.3
DMeO-BTBT:TCNQ*	0.957	0.948	1.0
DPTTA:25F$_2$TCNQ*	0.929	0.915	1.5
DPTTA:26F$_2$TCNQ	0.935	0.879	6.1
DPTTA:F$_4$TCNQ	0.853	0.828	3.0
DTBDT:F$_2$TCNQ	0.978	0.980	0.1
DTBDT:F$_4$TCNQ	0.972	0.975	0.3
DTBDT:TCNQ	0.980	0.981	0.1
Naphthalene:TCNQ	0.997	0.975	2.1
Npe:TCNQ	0.993	0.985	0.9
STB:F$_4$TCNQ	0.978	0.964	1.4
STB:TCNQ	0.984	0.974	1.0
Tetracene:F$_4$TCNQ	0.985	0.973	1.2
Average %D			**1.3**

* Acceptor and donor molecules are perpendicular and do not interact via π–π stacking.

We next assess two methodologies for calculating the correlation of S$_1$ DCT with η. Using unrelaxed molecular geometries taken from the dimer complexes, Figure 4 plots η vs. S$_1$ DCT using either TDM analysis (as in Figure 2), or alternatively using NBO analysis. The linear regression analysis of the TDM-analyzed data ($R^2 = 0.96$) is significantly improved compared to that of the NBO-analyzed data ($R^2 = 0.57$). The poor fit in the latter case is due to the method's inability to treat delocalized electron transfer.[34] Conversely, TDM provides a spatial mapping of the electron–hole pair associated with an electronic transition between two states and can successfully treat such delocalized electron transfer.[35,36] While both methods are commonly used to calculate the charges in molecules, we recommend TDM analysis over NBO.

In the left panel of Figure 5, the HOMO for DMeO-BTBT, the LUMO for TCNQ, and the HOMO and LUMO of their dimer complex are visualized; this D-A dimer has the greatest S$_1$ DCT in the data set. The visual similarity between the monomer orbitals and those in the complex is apparent, and the localization onto donor and acceptor moieties in the complex is striking. In the right panel of Figure 5, the HOMO of DPTTA HOMO, the LUMO of F$_4$TCNQ, and HOMO and LUMO of their dimer complex are visualized; this D-A dimer has the smallest S$_1$ DCT in the data set. While there is significant visual similarity between the monomer MOs and those in the complex, there is also substantial delocalization of the HOMO onto the acceptor molecule and similar delocalization of the LUMO onto the donor. To maximize S$_1$ DCT, the electron density must be localized on the electron donor in the HOMO and transferred completely to the acceptor LUMO. The value of η quantifies the degree to which the isolated HOMO (LUMO) of the donor (acceptor) correlates with that in the complex, which predicts S$_1$ DCT.

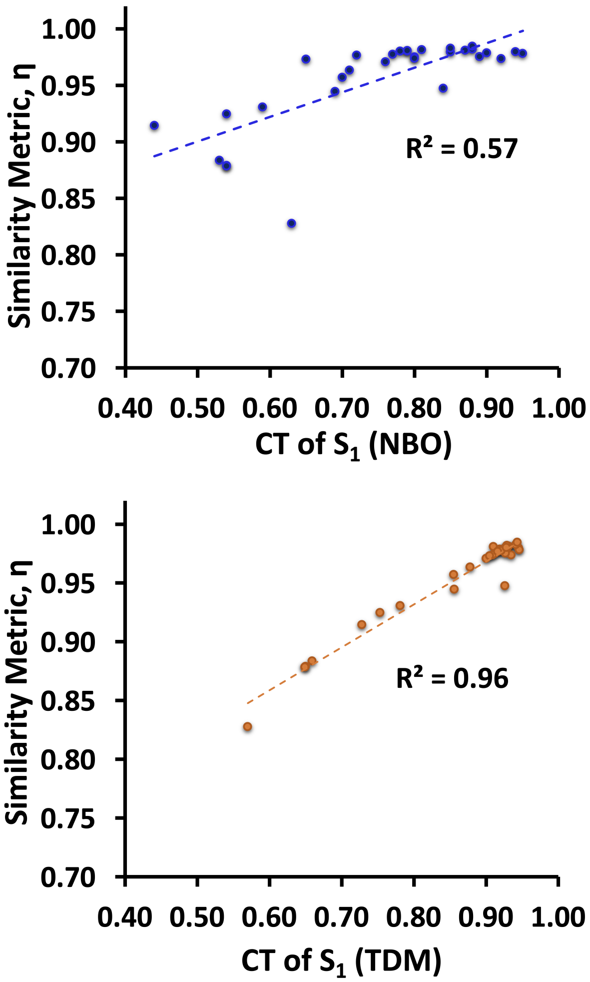

Figure 4. Plot of η vs. S$_1$ DCT using NBO (left) and TDM (right) at the D-A dimer geometries.

We have shown that the S$_1$ (HOMO→ LUMO) DCT can be predicted by a novel metric, η, that computes the average similarity between a donor (acceptor) molecule's HOMO (LUMO) and that of the corresponding orbital in the D-A complex. We find that η exhibits a positive linear correlation with S$_1$ DCT for a set of 31 D-A pairs. In choosing molecular geometries to compute η, we find that in comparing orbitals between isolated donor and acceptor molecules and their corresponding D-A complexes, one should use the same molecular geometries in the isolated molecules as in the D-A complex. Alternatively, experimental crystal structure data for the D-A complex can be used instead of optimized D-A dimer geometries. This allows flexibility in input data for inclusion in high-throughput screening and machine learning protocols. Lastly, we compare two methods for determining DCT, NBO and TDM analysis, and find that TDM is more reliable due to its ability to treat electron delocalization. Future work will aim to generalize the η metric to characterize the DCT of other electronic states, with the goal of uncovering further *orbital structure-function relationships.*

Conflicts of Interest J.M.H. serves on the board of directors of Q-Chem Inc.

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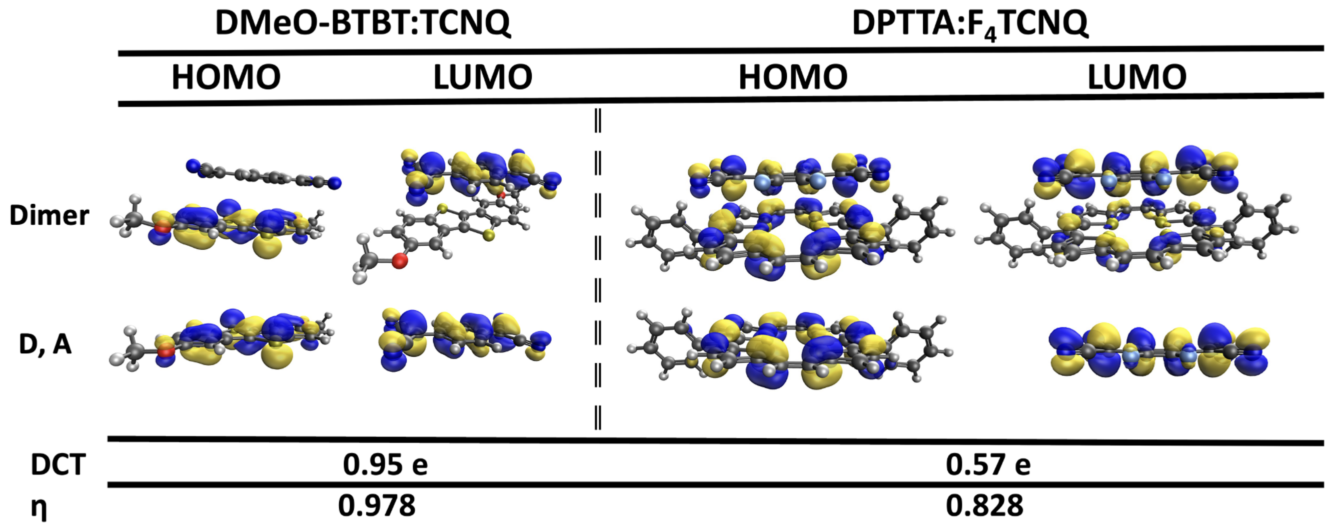

Figure 5. HOMO and LUMO for the D-A complex (top) and for the isolated molecules (bottom, donor at left and acceptor at right) using an isosurface value of 0.03 a.u.. Associated S_1 DCT and η values are also shown.

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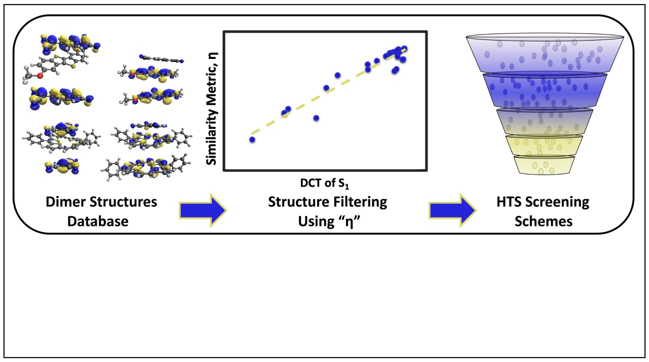
TOC Graphic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