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Prediction of Excited State Energies and Singlet-Triplet Gaps of Charge-Transfer States Using a Restricted Open-Shell Kohn-Sham Approach

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Abstract

Organic molecules with charge-transfer (CT) excited states are widely used in industry, and are especially attractive as candidates for fabrication of energy efficient OLEDs, as they can harvest energy from nonradiative triplets by means of thermally activated delayed fluorescence (TADF). It is therefore useful to have computational protocols for accurate estimation of their electronic spectra, in order to screen candidate molecules for OLED applications. However, it is difficult to predict the photophysical properties of TADF molecules with LR-TDDFT, as semi-local LR-TDDFT is incapable of accurately modeling CT states. Herein we study absorption energies, emission energies, zero-zero transition energies and singlet-triplet gaps of TADF molecules using a restricted open-shell Kohn-Sham (ROKS) approach instead, and discover that ROKS calculations with semi-local hybrid functionals give good agreement with experiment– unlike TDDFT, which significantly underestimates energy gaps. We also propose a

cheap computational protocol for studying excited states with large CT character, that is found to give good agreement with experimental results without having to perform any excited state geometry optimizations.

1 Introduction

Extensively π conjugated organic molecules with distinct charge donor and acceptor subunits are known to exhibit interesting optoelectronic[1,2] properties on account of the high charge-transfer (CT) behavior of their first few excited electronic states, and thus can be used in fields like non-linear optics,[3] organic photovoltaics[4] or organic field-effect transistors.[5] The spatial separation of the transferred electron (effectively in the ground state LUMO localized on the acceptor) and the resulting hole (effectively in the ground state HOMO localized on the donor) also minimizes the exchange interaction between the two singly occupied orbitals in excited CT states, resulting in a reduced energy gap between singlet and triplet states.[6–11] This permits such molecules to exhibit Thermally Activated Delayed Fluorescence (TADF)[12,13] where the "dark" first excited triplet (T_1) state indirectly fluoresces back into the singlet ground (S_0) state via thermally activated reverse intersystem crossing to the "bright" first excited singlet (S_1) state (as depicted in Fig. 1). Molecules exhibiting TADF are considered to be useful for OLED applications, as they can significantly increase energy efficiency by harvesting some of the energy that is normally wasted in generating non-radiative triplet excitons.[14–18]

TADF is however only possible at appreciable rates if the energy gap (ΔE_{ST}) between the S_1 and T_1 states is smaller than or comparable to $k_B T$. OLED applications also frequently require emitted radiation of a particular color, thereby constraining suitable values of emission energy (E_{emit}) to a narrow interval. It is therefore useful to have computational protocols for prediction of photophysical properties like $E_{\text{emit}}, \Delta E_{ST}$, quantum yields etc., of molecules with CT excited states,[19,20] as it allows screening of molecules for use in TADF based OLEDs. Unfortunately, many of the molecules of interest are too large (>100 atoms) to be studied
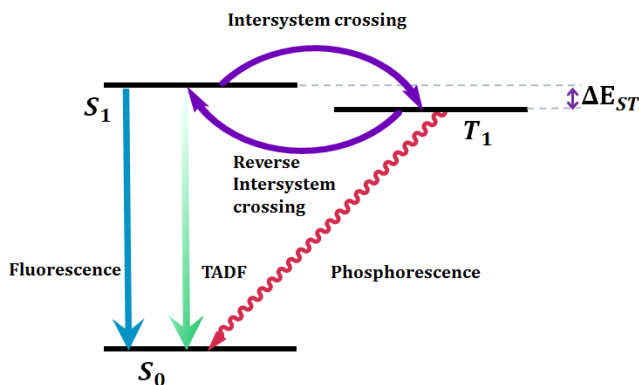
Figure 1: Simplified Jablonski diagram for TADF molecules. Phosphorescence is spin forbidden and hence much slower than fluorescence, but reverse intersystem crossing is permitted as ΔE_{ST} is small. This allows $T_1 \rightarrow S_1$ transition, permitting indirect fluorescence of T_1.

with high-level *ab-initio* wavefunction based methods like CASPT2[21,22] or coupled-cluster,[23] which are known to give quite accurate results for small organic molecules.[24,25] As a result, Density Functional Theory (DFT)[26–28] based approaches are the only viable post Hartree-Fock[23] computational tools for studying such molecules.

Consequently, a large amount of effort has gone into developing DFT based protocols for estimation of photophysical properties of potential OLED molecules. One of the earliest protocols was devised by Adachi and coworkers,[9,16] who attempted to obtain estimates for ΔE_{ST} from the difference between S_1 and T_1 energies obtained at S_0 optimized geometries with Linear Response Time-Dependent Density Functional Theory (LR-TDDFT),[29,30] employing semi-local hybrid functionals like B3LYP[31] or PBE0.[32] This approach however, was only effective for molecules with relatively low CT character,[16,33] as semi-local LR-TDDFT systematically underestimates the energy of CT states in general.[34–37] A later method proposed by Adachi and coworkers[38] tried to determine the ideal TDDFT functional for each structure by empirically calculating an "optimal" percentage of exact-exchange from ground-state calculations that estimated the extent of CT. Any semi-local hybrid functional employing close to the calculated exact-exchange percentage was postulated to be effective for TDDFT studies.

An alternative approach would be to use range-separated hybrid functionals[39,40] that

were developed for the purpose of performing TDDFT on CT states. This was also tested by Adachi and coworkers,[38] who however reported that range-separated functionals like CAM-B3LYP[41] or LC-ωPBE[42] tended to overestimate absorption energies (E_{abs}) for common TADF molecules, indicating that the range separation parameters for such molecules were not optimal for the length-scale of charge transfer in such systems. This was not particularly surprising, as such parameters are often strongly system dependent,[43,44] although it is possible to "tune" them for individual systems.[45] Recently, Penfold[10] and Brédas et al.[11] independently used tuned range separated functionals to investigate TADF molecules, and discovered that such an approach gave ΔE_{ST} values that are fairly consistent with experimental data.

There also exist time-independent excited state DFT techniques like ΔSCF,[46] which offer alternate routes for studying CT excited states. Such methods generally do not rely on linear response theory and can therefore be expected to not share the deficiencies of semi-local LR-TDDFT with regards to CT states. In particular, it is possible to use a Restricted Open Shell Kohn-Sham (ROKS)[47–50] approach to obtain energies of the S_1 state, which offers a new way to estimate emission wavelengths. Additionally, the Hohenberg-Kohn theorem[26] indicates that ground-state spin density functional theory (SDFT) should be able to estimate the energy of the first excited triplet (T_1) state, as it is the ground-state within the subspace of all triplet electronic states. This indicates that a combination of ROKS and SDFT could also be employed to calculate ΔE_{ST}, thereby implying that such a combination could be useful as a fast and reliable computational screen for potential TADF molecules.

In this article, we address these questions by devising two computational protocols that use a combination of ROKS and SDFT to estimate photophysical properties like E_{abs}, E_{emit}, E_{0-0} (gap between the minimum S_1 energy and the minimum S_0 energy) and ΔE_{ST}. Consequently, these protocols were compared with two TDDFT derived protocols against a test-set of 27 TADF compounds (Fig. 2) with available experimental data.[33,38,51,52] This revealed that while it was possible to use cancellation of errors to obtain some useful results from TDDFT,
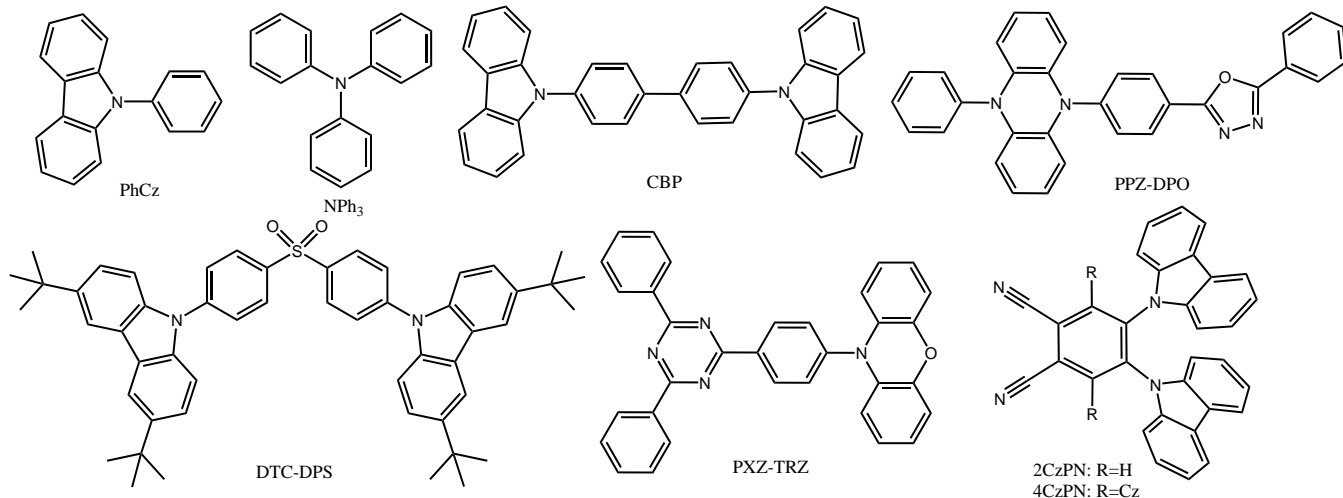
Figure 2: Representative members of the test-set. Experimental data obtained from Adachi et al.[33,38,51,52] Structures of all the molecules in the test-set can be found in the SI.

such approaches in general do not lead to accurate estimations of all desired parameters. On the other hand, semi-local hybrid functional based ROKS/SDFT based approaches led to very accurate predictions of $E_{\text{emit}}, \Delta E_{\text{ST}}$ etc., without having to resort to cancellation of errors or parameter optimization. Overall, it appears that ROKS with semi-local hybrid functionals provides a reliable and fast alternative to estimating properties of CT states, and can thus be used as a screen for potential TADF molecules.

2   Computational Details

All the calculations were done with the Q-Chem 4.2 Package,[53] employing the PBE,[54] B3LYP,[31] PBE0[32] and LC-ωPBE[42,55] (with the Q-Chem default Coulomb attenuation parameter $\omega = 0.3$ bohr^{-1} and zero short-range HF exchange[55]) functionals. Most calculations employed the 6-31G* basis[56] set, although some B3LYP calculations were repeated with the larger cc-pVTZ[57] basis to investigate the basis set dependence of the paratmeters measured. The Tamm-Dancoff approximation (TDA)[58–60] was not invoked in TDDFT calculations. Solvent effects were not taken into consideration in this study, nor was the effect of zero-point energy of molecular vibrations taken into account.
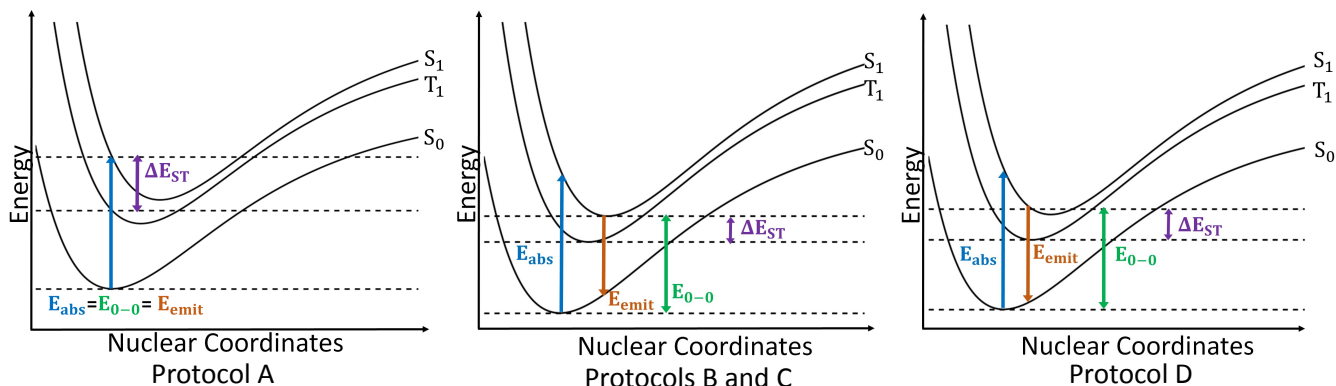
Figure 3: Photophysical parameters measured by the Protocols. The arrows only indicate energy gaps, and not nuclear coordinates of transitions.

The protocols themselves were as follows:

1. **Protocol A**: S_0 geometry is optimized using ground-state DFT, and TDDFT is then employed to find the energies of the S_1 and T_1 states at this geometry. The resulting vertical absorption energy E_{abs} is then assumed to be a reasonable estimate for both E_{emit} and E_{0-0} (Fig. 3, left panel). ΔE_{ST} is assumed to be the difference between S_1 and T_1 energies at the equilibrium S_0 geometry. This is the computationally cheapest of all the protocols, as it involves only one ground-state geometry optimization. However, it compromises the physics as real TADF molecules have non-zero experimental Stokes shifts, and is not at all likely to be effective when the exact functional is employed.

2. **Protocol B**: S_0 geometry is optimized using ground-state DFT, while both S_1 and T_1 geometries are optimized by TDDFT. TDDFT is then employed to find E_{abs} and E_{emit} as the vertical transition energy between the S_0 and S_1 surfaces, starting from the equilibrium S_0 and S_1 geometries respectively. E_{0-0} is obtained from the difference in the equilibrium S_1 and S_0 energies (found by TDDFT and ground-state DFT respectively) and ΔE_{ST} is given by the difference between equilibrium S_1 and T_1 energies (found by TDDFT). Unlike Protocol A, this Protocol does not compromise the physics, as the calculated parameters correspond exactly with experimentally measured ones.

3. **Protocol C**: S_0 geometry is optimized by ground state DFT while the T_1 geometry is optimized with Restricted Open-Shell DFT (RO-DFT). The equilibrium S_1 geometry

6

is obtained via ROKS. The energy differences are then found in the same manner as Protocol B, except that ROKS and RO-DFT are used instead of TDDFT to calculate S_1 and T_1 energies respectively. RO-DFT is preferred over unrestricted open-shell DFT for accessing T_1 energies in order to avoid systematic errors in ΔE_{ST}, as discussed in the results section. Like Protocol B, the parameters calculated with this Protocol also correspond exactly to experimentally measured ones.

4. **Protocol D**: S_0 geometry is optimized by ground state DFT while the T_1 geometry is optimized with RO-DFT. It was assumed that the equilibrium S_1 geometry is fairly well approximated by the T_1 geometry (which is definitely the case for molecules with large CT character where ΔE_{ST} is small), and the energy differences were then found in the same manner as Protocol C. Overall, only two geometry optimizations (both of which were formally in the ground-state) were employed, making this significantly cheaper than Protocol C.

The accuracy of the different protocols were compared by applying them to a set of relevant TADF chromophores, some of which are shown in Fig. 2. The experimental results were collected from work by from Adachi et al.[33,38,51,52] A complete listing of the molecules in the set and the associated experimental absorption and emission energies and singlet-triplet gaps is provided in the supporting information.

3 Results and discussion

3.1 Qualitative Agreement

Parameters calculated with all the protocols have positive coefficients of correlation against experimental data, irrespective of the functional employed. The r values are given in Table S1 in the Supporting Information, but they are all larger than 0.5, indicating that all the protocols reproduce the correct qualitative trends in energy gaps with all four functionals.

3.2 Quantitative Agreement

The errors associated with Protocols A & B are given in Table 1, while the errors for Protocol C & D can be found in Table 2. Because of the wide spectrum of values for the experimental ΔE_{ST} associated with the test-set, we report the errors in $\log(\Delta E_{\mathrm{ST}})$ instead of errors in ΔE_{ST}.

3.2.1 TDDFT Results: Protocols A & B

Table 1: Errors associated with Energy estimates from TDDFT derived protocols (RMSE= Root Mean Squared Error, ME= Mean Error). Errors in $E_{\mathrm{abs}}, E_{\mathrm{emit}}$ and $E_{\text{0-0}}$ have unit eV. Both protocols calculate absorption energy in the same manner, and thus have same errors associated with that parameter.

Parameter Measured	PBE RMSE (ME)	B3LYP RMSE (ME)	PBE0 RMSE (ME)	LC-ωPBE RMSE (ME)
E_{abs} (Protocols A and B)	1.38 (-1.31)	0.57 (-0.45)	0.43 (-0.28)	0.74 (0.72)
E_{em} (Protocol A)	0.81 (-0.75)	0.25 (0.11)	0.35 (0.28)	1.29 (1.28)
E_{em} (Protocol B)	1.48 (-1.45)	0.65 (-0.62)	0.49 (-0.44)	0.66 (0.63)
$E_{\text{0-0}}$(Protocol A)	1.00 (-0.95)	0.26 (-0.10)	0.23 (0.07)	1.04 (1.03)
$E_{\text{0-0}}$(Protocol B)	1.30 (-1.25)	0.52 (-0.46)	0.37 (-0.28)	0.82 (0.81)
$\log(\Delta E_{\mathrm{ST}})$ (Protocol A)	0.92 (-0.74)	0.68 (-0.37)	0.45 (-0.09)	0.76 (0.71)
$\log(\Delta E_{\mathrm{ST}})$ (Protocol B)	1.45 (-1.34)	1.04 (-0.85)	0.85 (-0.60)	0.74 (0.69)

Protocol A fares quite badly in estimating E_{abs}, with all the functionals. This is unsurprising for semi-local PBE, B3LYP and PBE0 calculations in light of the large CT nature of the S_1 state[34–37]–which leads to systematic underestimation of S_1 energy. Even the long-range corrected LC-ωPBE is not successful in estimating E_{abs}, although it systematically overestimates energy unlike the other three. This behavior indicates the length-scale of charge-transfer for the test-set molecules is smaller than $\dfrac{1}{\omega}$ and is consistent with what was reported earlier by Adachi et al.[38] However, the spurious TDDFT red-shift of energies in the B3LYP and PBE0 calculations were comparable to the Stokes shift for many of the molecules, resulting in a cancellation of errors that permitted $E_{\mathrm{abs}}^{\mathrm{TDDFT}}$ to be a fairly accurate estimate of $E_{\text{0-0}}^{\mathrm{Expt}}$. With B3LYP, it was also possible to get reasonable estimates of $E_{\mathrm{emit}}^{\mathrm{Expt}}$ by using $E_{\mathrm{abs}}^{\mathrm{TDDFT}}$, although PBE0 significantly overestimated this parameter (possibly on

account of using a greater percentage of exact-exchange than B3LYP). The energy-shifts for PBE were too large for a similar cancellation of errors to occur there and LC-ωPBE overestimated energies, making such a cancellation impossible.

This cancellation of errors however is not applicable to the ΔE_{ST} estimates, and Protocol A does not perform particularly well on that front. PBE and B3LYP both have large systematic errors as TDDFT artificially increases the extent of CT in the S_1 and T_1 states in a bid to lower their energies. This spuriously increased CT character leads to a smaller than expected energy gap, causing underestimation of ΔE_{ST}. PBE0 however has a smaller systematic error in ΔE_{ST}, possibly on account of the larger proportion of exact-exchange being employed in the functional (a trend that can also been seen in the decreased errors on going from PBE to B3LYP). LC-ωPBE on the other hand, significantly overestimates ΔE_{ST}, which is consistent with the CT length-scale being smaller than $\dfrac{1}{\omega}$. Consequently, single-functional Protocol A calculations cannot generally be used to get accurate ideas about ΔE_{ST} and E_{emit} simultaneously. The former is predicted best with PBE0 and the latter by B3LYP. However, Protocol A does not require excited-state geometry optimizations and is thus attractive as a preliminary screen for OLED materials, even if two calculations with different functionals are required.

Protocol B has no cancellation of errors to fall back upon, and thus consistently underestimates E_{emit} and E_{0-0} with PBE, B3LYP and PBE0. The ΔE_{ST} estimates are also considerably underestimated (by nearly an order of magnitude), and are in fact much worse than Protocol A estimates. This is a consequence of TDDFT further enhancing the CT character of S_1/T_1 states by distorting the equilibrium geometry in an attempt to spuriously lower the energy. LC-ωPBE again overestimates parameters significantly, for the same reason as earlier. Despite Protocol B being the most computationally expensive of the protocols tested (as it requires three geometry optimizations, two of which were in the excited state), it proves to be the least effective in predicting energies. This behavior is consistent with earlier studies,[38] and only serves to reinforce the notion that TDDFT with traditional functionals

is unsuitable for predicting energies of CT states.

3.2.2 ROKS Results: Protocols C & D

Table 2: Errors associated with Energy estimates from ROKS derived protocols (ME= Mean Error, RMSE= Root Mean Squared Error). Errors in $E_{\text{abs}}, E_{\text{emit}}$ and $E_{\text{0-0}}$ have unit eV. Both protocols calculate absorption energy in the same manner, and thus have same errors associated with that parameter.

Parameter Measured	PBE RMSE (ME)	B3LYP RMSE (ME)	PBE0 RMSE (ME)	LC-ωPBE RMSE (ME)
E_{abs} (Protocols C and D)	0.69 (-0.64)	0.18 (-0.06)	0.28 (0.11)	0.82 (0.75)
E_{em} (Protocol C)	0.53 (-0.49)	0.19 (0.00)	0.20 (0.10)	0.79 (0.45)
E_{em} (Protocol D)	0.52 (-0.48)	0.22 (0.02)	0.23 (0.11)	0.85 (0.79)
$E_{\text{0-0}}$ (Protocol C)	0.56 (-0.54)	0.14 (0.02)	0.17 (0.11)	0.70 (0.66)
$E_{\text{0-0}}$ (Protocol D)	0.55 (-0.52)	0.23 (0.10)	0.27 (0.19)	1.09 (1.03)
$\log{(\Delta E_{\text{ST}})}$ (Protocol C)	0.73 (-0.55)	0.35 (-0.17)	0.27 (-0.07)	0.58 (-0.06)
$\log{(\Delta E_{\text{ST}})}$ (Protocol D)	0.49 (-0.34)	0.35 (-0.03)	0.32 (0.04)	0.64 (0.25)

Protocols C and D attempt to circumvent the red-shifting of energies by using ROKS and Restricted Open-Shell DFT (RO-DFT) instead of TDDFT to access the S_1 and T_1 surfaces, respectively. While it is possible to use Unrestricted Open-Shell DFT (UO-DFT) to access T_1 energies instead, we chose to use RO-DFT as S_1 energies are always accessed by a restricted method (ROKS), and thus using UO-DFT triplet energies could lead to a systematic error in ΔE_{ST} from the extra stabilization recovered by the unrestricted calculation on the triplet. Nonetheless, we compared UO-DFT and RO-DFT calculation results for the case of the B3LYP functional and found that the numbers are not significantly different (the UO-DFT numbers are given in SI), further suggesting that performing RO-DFT was sufficient.

Though Protocol C is not a particularly cheap protocol (it requires three geometry optimizations, although only one of them is in the excited state), it gives quite accurate estimates of $E_{\text{abs}}, E_{\text{emit}}$ and E_{0-0} with B3LYP and PBE0. The near zero mean errors of B3LYP calculations are of particular interest, as they indicate there is no systematic bias unlike Protocol B with B3LYP. Interestingly, PBE0 mean errors are consistently greater than B3LYP errors by approx 0.1 eV, possibly on account of PBE0 blue-shifting the energies more due to greater

exact-exchange. PBE still underestimates energies, but the deviation is still much less than Protocol B (by approximately 0.5 eV) or even Protocol A. LC-ωPBE still overestimates energies, and the deviations here are comparable to the TDDFT deviations, suggesting that these are more a consequence of the functional than the method.

The trends in ΔE_{ST}'s obtained from Protocol C are somewhat more interesting. B3LYP and PBE0 have the smallest RMS errors, which coupled with their relatively small mean errors indicate that these two are best suited for calculating ΔE_{ST} (PBE0 being somewhat better than B3LYP). Like in TDDFT calculations, PBE significantly underestimates ΔE_{ST}, although the errors are smaller. On the other hand, LC-ωPBE has an extremely small mean error along with a fairly large RMS error, indicating that a lot of noise is associated with calculations based on this functional, but not much of a bias–which stands in direct contrast to the large Protocol A and B mean errors. This indicates that the ROKS/RO-DFT combination does not add a systematic bias to ΔE_{ST} for LC-ωPBE calculations, unlike TDDFT–although ΔE_{ST} calculations are still fairly inaccurate because this functional causes a large blue-shift of the S_1 and T_1 energies, which leads to a lot of noise. Overall, Protocol C is found to give very accurate energies with B3LYP and PBE0 and should be the method of choice if sufficient computational resources for S_1 geometry optimization are available. It is also possible to reduce the S_1 optimization cost by using T_1 optimized geometries as the starting guess, as those are expected to be closer to equilibrium S_1 geometry than S_0 geometries or ground-state forcefield fits for TADF molecules.

Protocol D aimed to attain accuracy comparable to Protocol C at a lesser computational cost by approximating the equilibrium S_1 geometry with the equilibrium T_1 geometry. This approach is reasonable for systems exhibiting TADF, as ΔE_{ST} is very small in these cases, indicating that the S_1 and T_1 surfaces are near parallel. Overall, Protocol D E_{emit} estimates are quite close to Protocol C estimates, and thus correspond well to experimental values for B3LYP and PBE0 functionals. PBE calculations also give E_{0-0} similar to Protocol C, although the other three functionals overestimate this parameter relative to Protocol C

(although the shift is only of the order of 0.1 eV on average for PBE0 and B3LYP).

This deficiency is somewhat compensated by the lack of apparent systematic bias in ΔE_{ST} calculated with PBE0 and B3LYP. PBE underestimates ΔE_{ST} as in all previous calculations, while LC-ωPBE overestimates ΔE_{ST} on average–unlike in Protocol C. Overall, all the functionals overestimate ΔE_{ST} with Protocol D, relative to Protocol C as Protocol D slightly overestimates S_1 energy as it is evaluated close to, but not at the minima. However, this slight blue shift of ΔE_{ST} improves the mean accuracy of both PBE0 and B3LYP–and allows Protocol D with these two functionals to be either better than or as effective as Protocol C in estimating E_{emit} and ΔE_{ST}, the two parameters of greatest interest for OLED screening. Protocol D with B3LYP/PBE0 is therefore the method we recommend be used first, with Protocol C only being used for the cases where D predicts large ΔE_{ST} (> 0.5 eV), indicating smaller than expected CT character that causes our assumption about similarities in equilibrium S_1 and T_1 geometries to break down.

Overall, it can be seen that ROKS derived protocols employing B3LYP or PBE0 yield numbers that are much closer to experiment than the equivalent LR-TDDFT based protocols. We believe this is on account of ROKS computing the optimal orbitals for the excited state self-consistently without any interference from the S_0 state (though S_0 orbitals serve as an initial guess). LR-TDDFT on the other hand accesses excited states via linear response from the S_0 density, leading to the possibility of ground-state contamination when employed with approximate functionals despite LR-TDDFT being guaranteed to be exact with the exact functional.[29] Such contamination would be especially problematic for CT states as these states are very far off from the S_0 state in terms of density, leading to a spurious lowering of energy that SCF methods like ROKS avoid by explicitly calculating the excited state density independent of the S_0 state. Similar reasons explain the lesser accuracy of T_1 energies obtained by LR-TDDFT compared to formally exact SCF methods[26] like RO-DFT and UO-DFT. The ROKS part of this analysis is functional dependent: LR-TDDFT is guaranteed to give the exact answer with the exact functional while no equivalent assurance

exists for ROKS. However, ROKS appears to give a more accurate picture of CT states than LR-TDDFT with commonly used semi-local hybrid density functionals like B3LYP and PBE0 at least, and both seem to be incorrect to a roughly equal extent with PBE or LC-ωPBE functionals.

3.2.3 Basis Set Effects

Several B3LYP single-point calculations were repeated with the larger cc-pVTZ[57] basis (using the 6-31G*[56] optimized geometries). It was found that neither the calculated parameters nor the associated errors were significantly altered, indicating that calculations with the smaller 6-31G* basis were sufficient.

4 Conclusions

In this paper we evaluated four computational protocols for calculating energies associated with CT states, in order to determine a method that gives accurate estimates of parameters like ΔE_{ST} and E_{emit} with minimal computational expense. We tested these protocols with four functionals (PBE, B3LYP, PBE0, LC-ωPBE) against a test-set of 27 compounds and determined TDDFT with all four functionals gave poor results, although fortuitous cancellation of errors can oftentimes give acceptable estimates for E_{emit} (with B3LYP) or ΔE_{ST} (with PBE0). We further discovered that protocols based on ROKS/RO-DFT with B3LYP and PBE0 were well suited for this problem, as they led to quite accurate predictions for TADF molecules, without having to do any form of tuning or fitting. Protocol D in particular seems to be very well suited for studying molecules with large CT character, as it requires only two ground-state geometry optimizations and yet gives accuracy comparable to methods that rely on computationally expensive excited state optimizations. We believe that other SCF excited state methods like ΔSCF[46] and CDFT[61] will also give similar accuracy to ROKS, and overall such methods are better suited for studying CT states than

TDDFT.

Our results however neglected the impact of the surroundings on the photophysics of these TADF molecules, mainly because the effects of the surrounding molecules are difficult to account for. This study only performed calculations on molecules that were experimentally studied in non-polar solvents like cyclohexane ($\epsilon_r = 2.02^{62}$) or toluene ($\epsilon_r = 2.38^{62}$), in part because the small dielectric constants should have a proportionately small effect on the photophysics. In future it would be interesting to examine how these protocols could be extended to deal accurately with the effects of the surroundings – for example, to tell the difference between the stokes shift in solution versus in a film. We are also currently unable to predict quantum yields from first principles, which is another important parameter to be considered for practical applications. Our future work therefore shall focus on properly accounting for solvent effects on photophysical properties and *ab-initio* quantum yield prediction, in order to enable more efficient design of organic semiconductors involving CT states.

Supporting Information Available

Equilibrium geometries, raw calculated energies and correlation coefficients (against experimental data).   This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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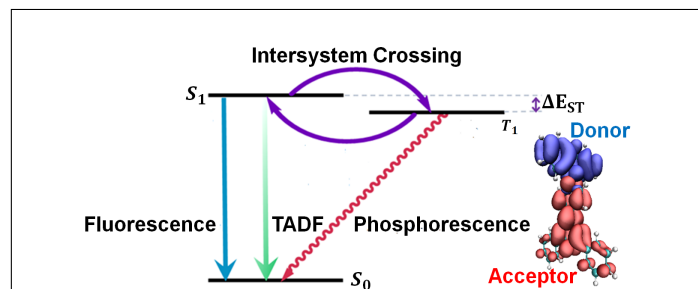(62) Haynes, W. M., Ed. *CRC Handbook of Chemistry and Physics*; CRC press: Boca Raton, Florida, 2013.

Graphical TOC Entry

Figure 4: For Table of Contents Only