# Supporting Information for "Modeling TADF in Organic Emitters Requires a Careful Consideration of the Environment and Going Beyond the Franck-Condon Approximation"

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## General

This document gives an overview about the supplementary data, contains further information on the methodology and computational protocol used, and provides a more detailed characterization of the excited states of ACRXTN.

In addition to this document, the input and output files of almost all calculations (the output files of the optimizations along the twisting coordinate are left out due to their large size) detailing all parameters and molecular geometries are supplied. Also the electron and hole plots of the lowest excited states of all molecules at the relaxed geometries of the relevant states are available. These can be viewed with any browser by opening the .html in the respective folder. All these files are contained in a self-exploratory folder structure in the archive *ESI.zip* 

In addition to the raw data, three spreadsheets collecting the data from the output files are provided. The first one, (*energies\_and\_methods.ods*) contains the adiabatic energies of all systems in the different environments and with different methods, as well as the data on basis set and functional studies described below. The second one, (*rates.ods*) contains the formalism to calculate the rISC and TADF rates from the vertical and adiabatic singlet-triplet gaps and transition properties. It furthermore allows to investigate the influence of a systematic bias of the gaps as discussed in the main article. The third one, (*twist.ods*) collects all energies, oscillator strengths and spin-orbit couplings calculated along the twisting coordinate, as well as the functions for Boltzmann and arithmetic averaging and the full data for all three molecules. These documents can be viewed with the open-source software LibreOffice (https://www.libreoffice.org/).

### Choice of the Functional for DFT/TDA

Regarding the choice of the exchange-correlation functional, the major consideration was that it should provide accurate energies and structures for the TADF emitters at the Kohn-Sham DFT level, *i.e.*, for the  $\Delta$ DFT calculations, preferably in a small basis set. Hence, Grimme's recently introduced PBEh-3c composite functional is well suited.

Clearly, systematic differences between TDA calculations with PBEh-3c vs.  $\omega$ PBE and CAM-B3LYP are to be expected. However, testing these other functionals for ACRXTN (see spreadsheet energies\_and\_methods.ods), it was established that none of the three above-mentioned functionals was able to correctly reproduce the ordering of the lowest (singlet and triplet) CT,  $n\pi^*$  and  $\pi\pi^*$  states compared to the ADC(2) level of theory. While CAM-B3LYP was found to provide the best general agreement concerning energies and dipole moments of the singlet states, PBEh-3c is the only functional that agrees with ADC(2) on the character of  $S_1$  and  $T_1$ . Since furthermore the energies obtained at the TDA level are not central to this work, but rather those obtained with the  $\Delta$ DFT and ADC methods, we have used the PBEh-3c functional throughout this work.

#### **Basis Sets**

TDA and DFT calculations are carried out with the PBEh-3c composite method which is tied to the def2-mSVP basis. For the ADC(2) calculations, we have studied the influence of the basis set for F1 using the def2-SV (266 bf), def2-SV(P) (396 bf), and def2-SVP (444 bf) basis sets. While we find large differences between def2-SV and def2-SVP (on average 0.14 eV for the singlet excitation energies), these differences are much smaller between def2-SV(P) and def2-SVP (on average < 0.02 eV). More importantly, the influence of the basis set is larger for the singlet states in apolar environments and gas phase, which leads to systematic errors of 0.05 eV comparing def2-SV and def2-SVP. For def2-SV(P) these errors are reduced to 0.006 eV in gas phase, and < 0.002 eV in the all environments. See spreadsheet energies\_and\_methods.ods for the full data.

Based on this data, we decided to use the def2-SV(P) throughout, which is just possible for the larger emitters (476 bf for AXRXTN, 444 bf for PTZ-DBTO2). To manage the computational effort in the solvent-field optimization, we reduce the basisset quality to def2-SV, and do a final calculation in the converged solvent field with the def2-SV(P) basis. This has been tested for PTZ-DBTO2, whose sulfur atom lets us expect the largest influence of the basis set using the most apolar environment cyclohexane, for which we observed the largest basis-set effects before. Here, the resulting differences in the excitation energies are below 0.02 eV, and the difference between the total energies of  $S_1$  and  $T_1$  is only 0.1 meV.

### Electron-Hole Plots and more details about ACRXTN

ACRXTN has a weakly polar  $S_0$  with a dipole moment of 2.4 D and a twisting angle between acridin and xanthone close to 90°. According to ADC, the lowest excited states at the  $S_0$  geometry are a pure  $S_{\rm CT}$  at 3.45 eV with a dipole moment of 19.5 D as well as a mixed  $T_{\rm CT}$  state at 3.44 eV, which has a smaller dipole of 14.2 D due to an admixture of  $n\pi^*$  character.  $S_2$  and  $T_2$  correspond to  $n\pi^*$  excited states and are situated 0.3 eV and 0.06 eV about  $S_1$  and  $T_1$ , whereas  $T_{n\pi^*}$  exhibits admixture of  $T_{\rm CT}$  character. The triplet excited states corresponding to a local  $\pi\pi^*$  excitation of the donor (LED,  $T_{\rm LED}$ ) and acceptor (LEA,  $T_{\rm LEA}$ ) are found as  $T_3$  and  $T_4$ , 0.36 eV and 0.37 eV above  $T_1$  with dipole moments very similar to  $S_0$ . Note that TDA provides a slightly different ordering



Figure 1: Plots of the electron and hole densities for the lowest excited states of ACRXTN at the relaxed structures in gas phase (a-d), apolar (e) and polar environments (f). While the excitation hole of the  $T_{\rm CT}$  is delocalized in gas phase (b), as evident from the larger hole size  $\sigma_h$ , the effect is diminished in apolar cyclohexane and completely vanishes in polar DCM. Gas-phase calculations are conducted at the ADC(2)/def2-SV(P) (ADC) and TDA/PBEh-3c/def2-mSVP (TDA) levels of theory, and condensed phase calculations employ ADC/SS-PCM for  $\Delta$ DFT/PBEh-3c/PCM structures. Visualization using two isodensity surfaces with isovalues of 0.0080 and 0.00027 with VMD.

of the states with the  $T_{\text{LEA}}$  and  $T_{\text{LED}}$  at lower energies as  $T_2$  and  $T_3$ , and  $T_{n\pi^*}$  at higher energies and thus as  $T_4$ . Also the LRC functionals CAM-B3LYP and LRC-wPBE fail to reproduce the ordering of ADC(2). With these, already  $T_1$  differs and becomes a locally excited state, while  $T_{\text{CT}}$  is shifted to  $T_3$  (see spreadsheet "energies\_and\_methods.ods").

Nuclear relaxation for  $S_1$  at the ADC level yields a structure with a twist of 90°, an adiabatic energy of 3.17 eV, and a dipole moment of about 18.5 D. The kink observed for the ADC optimized structure of F1 is present also in ACRXTN, but less pronounced. Since the same arguments apply here as well, only the linear structures obtained with other approaches will be considered in the following. The TDA optimization affords a very similar but completely linear structure, while the  $\Delta$ DFT approach provides a reduced twist of 76°. Despite the different twisting angle, adiabatic energies of the approaches are very consistent.

Nuclear relaxation for  $T_1$  at the ADC level in gas phase yields a structure with a reduced twist of 60° similar to F1. The state attains an intermediate dipole moment 12.8 D and an adiabatic energy of 3.08 eV, that is 0.09 eV below  $S_1$ . The TDA and  $\Delta$ DFT optimizations afford a very similar PES along the twisting coordinate exhibiting twisting angles of 61° and 59°, and virtually identical adiabatic energies and dipole moments. The reason for the reduced twist is the same hole-delolicalization already encountered in F1 (*cf.* fig. 1b). Also here, this apparent mixing between the states is despite an energy difference of 0.8 eV in gas phase (even more in solution), corroborating the hypothesis that the delocalization of hole density is a feature of the  $T_{\rm CT}$  state.

Nuclear relaxation for the  $S_{n\pi^*}$  and  $T_{n\pi^*}$  states in gas phase renders them  $S_1$  and  $T_1$ , and with adiabatic energies of 3.18 eV and 2.97 eV also the global the minima of excitedstate PES. Their relaxed structures are very similar to each other, and differ from the  $S_0$  structure by an elongated carbonyl bond. Both states are of pure character and have a dipole of similar size as the ground state. The next higher excited states at the  $n\pi^*$ optimized structures are the pure CT states and are situated 0.20 eV ( $S_{\rm CT}$ ) and 0.45 eV ( $T_{\rm CT}$ ) above the NPI state. As is typical for  $S_{n\pi^*}$  states, f for the transition to the ground state is vanishingly small with  $2 \cdot 10^{-5}$ .

Regarding the methodology, ADC//TDA and  $\Delta$ DFT are in excellent agreement in gas-phase for the  $S_{\rm CT}$  (3.19 eV vs 3.20 eV),  $T_{\rm CT}$  (3.05 eV vs 3.09 eV), and  $T_{n\pi^*}$  (2.99 eV vs 2.97 eV) states, whereas  $\Delta$ DFT is slightly too low for the  $S_{n\pi^*}$  state (3.06 eV vs 3.18 eV). The deviation for latter is most certainly due to the wrong spin state of the  $\Delta$ DFT wave function in combination with the significant electron-hole overlap and singlet-triplet splitting for this  $n\pi^*$  state. These results nicely illustrate the capabilities and limitations of the  $\Delta$ DFT approach.

SOCs of the  $n\pi^*$  excited states are difficult to calculate at their respective minima due a strong mixing with the  $T_{\text{LEA}}$  state at the TDA level of theory. Estimating the SOCs at the similar  $S_{\text{CT}}$  relaxed structure, where the mixing is less severe, the direct SOC between the  $T_{n\pi^*}$  and  $S_{n\pi^*}$  states is found to be small with about 0.1 cm<sup>-1</sup>, while the SOC between the  $T_{n\pi^*}$  and  $S_{\text{CT}}$  amounts to 0.4 cm<sup>-1</sup>.