



# UNIVERSITÀ DI PARMA

## ARCHIVIO DELLA RICERCA

University of Parma Research Repository

Thermally activated delayed fluorescence: A critical assessment of environmental effects on the singlet-triplet energy gap

This is the peer reviewed version of the following article:

*Original*

Thermally activated delayed fluorescence: A critical assessment of environmental effects on the singlet-triplet energy gap / Dhali, Rama; Phan Huu, Dang Khoa Andrea; Terenziani, Francesca; Sissa, Cristina; Painelli, Anna. - In: THE JOURNAL OF CHEMICAL PHYSICS. - ISSN 0021-9606. - 154:13(2021), p. 134112. [10.1063/5.0042058]

*Availability:*

This version is available at: 11381/2891619 since: 2021-05-07T16:42:18Z

*Publisher:*

American Institute of Physics Inc.

*Published*

DOI:10.1063/5.0042058

*Terms of use:*

openAccess

Anyone can freely access the full text of works made available as "Open Access". Works made available

*Publisher copyright*

(Article begins on next page)

# Thermally activated delayed fluorescence: a critical assessment of environmental effects on the singlet-triplet energy gap

Rama Dhali,<sup>1</sup> D. K. Andrea Phan Huu,<sup>1</sup> Francesca Terenzi,<sup>1</sup> Cristina Sissa,<sup>1</sup> and Anna Painelli<sup>1, a)</sup>  
*Department of Chemistry, Life Science and Environmental Sustainability, University of Parma,  
Italy*

(Dated: 2 March 2021)

The effective design of dyes optimized for thermally activated delayed fluorescence (TADF) requires the precise control of two tiny energies: the singlet-triplet gap, that has to be maintained within thermal energy, and the strength of spin-orbit coupling. A subtle interplay among low-energy excited states having dominant charge-transfer and local character then governs TADF efficiency, making models for environmental effects both crucial and challenging. The main message of this paper is a warning to the chemists, physicists and material scientists community working in the field: the adiabatic approximation implicitly imposed to the treatment of fast environmental degrees of freedom in quantum-classical and continuum solvation models leads to uncontrolled results. Several approximation schemes were proposed to mitigate the issue, but we underline that the adiabatic approximation to fast solvation is inadequate and cannot be improved, rather it must be abandoned in favour of an antiadiabatic approach.

## I. INTRODUCTION

Thermally-activated delayed fluorescence (TADF) occurs in fluorescent systems where triplet states sit very close in energy to the emissive singlet state. Triplet states, that are populated upon intersystem crossing (ISC) following photoexcitation or directly via charge recombination in electrically operated devices, can undergo a thermally-activated reverse intersystem crossing (RISC) process and be converted into emissive singlet states. TADF emitters thus typically show a fast emission regime (prompt fluorescence) and a slow emission regime (delayed fluorescence). First observed in 1961,<sup>1</sup> TADF gained wide popularity in 2011 when Adachi proposed its exploitation to harvest triplets in organic light-emitting devices (OLED).<sup>2</sup> Indeed, using TADF-based materials it is possible to increase the theoretical internal quantum efficiency of OLED from 25% to 100%, maintaining a high color purity of emission.<sup>3-6</sup> Almost immediately, it was recognized that organic charge transfer (CT) dyes are good candidates as TADF emitters, as long as the conjugation between electron-donor (D) and electron-acceptor (A) moieties is low, as to guarantee for a small energy gap between singlet and triplet CT states. This condition is easily met in systems where D and A moieties are arranged almost orthogonally.<sup>7</sup> The inherent synthetic flexibility of organic compounds made it possible to synthesize a large collection of dyes, that differ not just in the nature of the D and A units, but also in the ways these units are connected: other than dipolar emitters, quadrupolar and octupolar emitters have been synthesized and studied, as well as more exotic systems with through-air CT interaction or conjugated DA structures.<sup>7-15</sup>

Quantum chemical calculations can help the work of synthetic chemists and material scientists: the systematic *in-silico* study of a large amount of novel chemical structures can indeed reduce the expensive and time-consuming work in the experimental laboratory, allowing the experimentalists

to focus on just the most promising structures. To this effect, cheap, fast and reliable computational approaches are needed. Time-dependent density functional theory (TD-DFT) arguably represents one of the most effective computational tools in this respect, thanks to the favorable trade-off between accuracy and computational cost. However, modeling CT transitions is non-trivial in TD-DFT, relevant results being strongly dependent on the adopted functional. Progress in this direction is offered by the development of tuned range-separated hybrid functionals, where the proper amount of exact exchange for each system is selected, without the need for a comparison with experimental data.<sup>16-18</sup>

Once the proper functional is selected, reliable TD-DFT results can be obtained for isolated (*gas phase*) dyes, but material scientists need to address the properties of the dyes in condensed phases (either in solution or in a matrix). In the following, we adopt the generic term *solvent* to address either the liquid solvent surrounding the dye in solution, or the solid matrix surrounding the dye, as e.g. in a device. Models where both the dye and the surrounding solvent are treated quantum-mechanically are clearly impractical and approximation strategies must be devised to separate the solute and solvent problem. In this perspective, effective solvation models are introduced where a quantum mechanical Hamiltonian is defined for the solute, implicitly accounting for the effects of the surrounding medium.

When constructing an effective solvation model, a hierarchy of approximations must be considered. The first step is the separation of the solute and solvent problems, relying on the different timescales of relevant degrees of freedom (DoF). Specifically, being interested to model the solute optical spectrum in the visible-near UV regions, we can safely assume that polar solvation, related to the orientational motions of polar solvent molecules around the solute, represents a slow motion and can be treated adiabatically. On the opposite, electronic solvation accounts for the rearrangement of the electronic clouds of solvent molecules in response to the charge distribution in the solute: the corresponding DoF have typical frequencies far in the ultraviolet, and are therefore much faster than the solute DoF. The adiabatic approxi-

<sup>a)</sup>Electronic mail: anna.painelli@unipr.it

mation must then be abandoned in favor of the antiadiabatic (AA) approximation.<sup>19</sup> Of course, cases may occur where the timescales of solute and solvent motions are comparable. In these special cases effective solvation models cannot be reliably defined.

Once the framework for the solute-solvent separation is set, models for the solute and solvent and for their interaction must be defined. As for the solute, a vast variety of quantum-mechanical models is possible, ranging from parametric models accounting for just few electronic degrees of freedom, semiempirical models, first-principle DFT and TD-DFT models, high-quality ab-initio etc. The choice of the model Hamiltonian and of the relevant basis of course heavily affects the quality of the results and their reliability. The solvent in turn can be described as a continuum dielectric medium, linearly responding to electrostatic perturbations (elastic medium).<sup>20,21</sup> Alternatively, one can rely on atomistic pictures for the solvent, in MM or MD approaches.<sup>22-24</sup> Quite interestingly, in these mixed approaches a number of solvent molecules can be included into the portion of system treated quantum-mechanically, and, when this number is large enough, the limit of a full quantum mechanical treatment of the solute and solvent is reached.<sup>25</sup>

The solute-solvent interaction can be simplified to a dipolar interaction in an approach that can be extended to multipolar terms. In more refined approaches, the solute is contained in a cavity carved in the solvent, whose shape and dimensions are defined according to several approximation schemes with variable degrees of details. In continuum solvation models, the solute generates charges at the cavity surface, that in turn affect the potential felt by the solute. In atomistic models, the solute affects the orientation of surrounding molecules and (in polarizable models) also their charge distribution. In turn, the charges on the surrounding molecules affect the potential felt by the solute.

Fixing all the details in the approximation ladder leads to a proliferation of effective solvation models, that cannot be reviewed here. However the first approximation, related to the separation of solute and solvent degrees of freedom, leads to two qualitatively different approaches to effective solvation. In the adiabatic approximation the molecular Hamiltonian is diagonalized for a fixed value of the potential generated by the surrounding medium (that, depending on the model, means fixed charges on the surrounding molecules or on the surface cavity, or a fixed reaction field, etc). The calculation can be repeated for different values of the potential, typically fixing it at the equilibrium value relevant for each state (hence leading to state-specific approaches). In any case, in the adiabatic approximation, each Hamiltonian is defined and diagonalized for a fixed potential. The adiabatic approach to solvation closely resembles the adiabatic approach adopted to separate electronic and vibrational DoF in molecular systems (most often in the so-called Born-Oppenheimer scheme).<sup>26</sup> It is well known that the adiabatic approximation can be reliably applied to separate electronic and vibrational DoF when the nuclear dynamics is much slower than the electronic dynamics. Analogously, the adiabatic approximation applied to separate solvation degrees of freedom works well when sol-

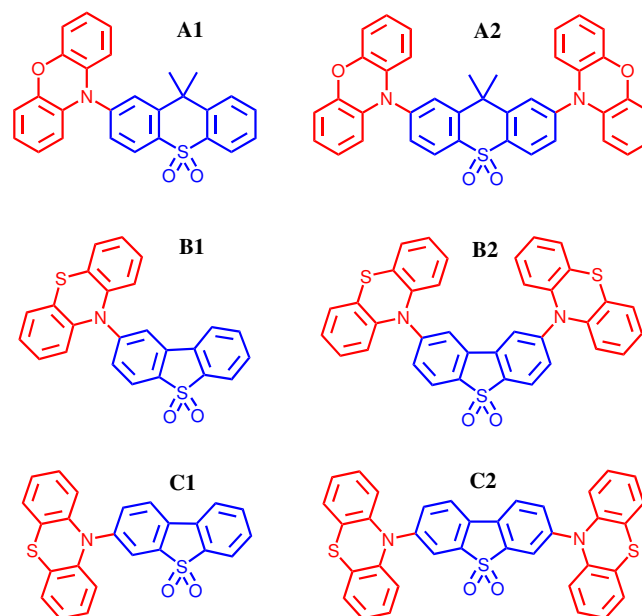


FIG. 1. Molecules considered in this work. **A1**: PO-TXO2. **A2**: DPO-TXO2. **B1**: 2-PTZ-DBTO2. **B2**: DPTZ-DBTO2. **C1**: PTZ-DBTO2. **C2**: 3,7-DPTZ-DBTO2. In all molecules red and blue color refer to the donor and acceptor groups, respectively.

vation charges (and the resulting potential) move slowly with respect to the solute DoF of interest. However, when dealing with electronic solvation we are considering fast DoF: the adiabatic approximation must be abandoned since it relies on a molecular Hamiltonian where the charges in the surrounding solvent are considered frozen, while they actually move faster than the solute DoF. Rather an AA approximation can be invoked, assuming an instantaneous rearrangement of the solvent charges and of the resulting potentials to the charge fluctuations in the solute. A single AA Hamiltonian is thus obtained, whose diagonalization leads in a single shot to all molecular eigenstates.

In this paper, with reference to TADF dyes, we show how current implementations of continuum solvation models do not properly address environmental effects on the singlet-triplet gap, with results that wildly depend on the adopted approximation scheme and lead, in some cases, to an inversion of the order of the lowest singlet and triplet states. In Section II we briefly introduce the three available implementations of continuum solvation model (PCM) in Gaussian package. In Section III we report results obtained with the three approaches on 6 different TADF dyes. In section IV we demonstrate that the observed inversion of the singlet and triplet states is indeed a spurious result obtained imposing the adiabatic approximation to fast solvation. Finally, the last Section puts main results in perspective.

## II. COMPUTATIONAL APPROACH

In this work we consider three dipolar emitters (**A1**, **B1** and **C1**) and their quadrupolar counterparts (**A2**, **B2** and **C2** respectively), as shown in Fig. 1. For each emitter, single point TD-DFT calculations on the optimized ground state geometry are performed to obtain excitation energies (in the Tamm-Dancoff approximation),<sup>27</sup> both in gas phase and accounting for non-equilibrium solvation in PCM. All DFT and TD-DFT calculations are performed using Gaussian 16 B.01.<sup>28</sup> The optimized ground state structures of **A2**, **B2** and **C2** are obtained at the B3LYP/6-31G(d) level. Ground state geometries for **A1**, **B1** and **C1** are obtained substituting one of the donor units with an hydrogen atom. TD-DFT calculations are performed at the M06-2X/6-31G(d) level (the choice of the functional is addressed in the SI) imposing the Tamm-Dancoff approximation.

As discussed in Ref.<sup>19</sup>, the ground state properties of the solute are not properly addressed when the adiabatic approximation is adopted to fast solvation. Since in current PCM implementations the ground state geometry is optimized in this approximation, leading to unreliable results, all data below are obtained for the optimized geometry in gas phase. Moreover, in order to exclude any contribution from polar solvation, we consider custom non-polar solvents, setting the static dielectric constant equal to the squared refractive index (results for a few natural solvents are available in SI). Calculations are repeated for different values of the refractive index,  $\eta$ . Results are displayed as a function of  $f(\eta^2) = (\eta^2 - 1)/(2\eta^2 + 1)$ , the region corresponding to most organic solvents and polymeric hosts covering the  $0.175 < f(\eta^2) < 0.225$  interval.

Three different implementations of PCM are currently available in the Gaussian package,<sup>28</sup> named linear response (LR), corrected linear response (CLR) and external iteration (EI). In all cases, the calculation starts with a reference (initial) state with equilibrated fast and slow solvent DoF, and a final state, defined in different ways in the three approaches.<sup>29,30</sup> LR represents the default approach in TD-HF and TD-DFT calculations. In LR,<sup>31</sup> excitation energies are determined directly as singularities of the frequency-dependent linear-response functions of the solvated molecule in the ground state, avoiding explicit calculations of the excited state wavefunctions, leading to a fast and computationally convenient approach. Specifically, defining the frozen-solvent transition energy as the transition energy calculated maintaining the fast and slow solvent DoF equilibrated to the reference state (the ground state for absorption, the excited state for emission), LR corrections are applied that only depend on the transition dipole moment between the reference and the final state. While computationally convenient, LR does not account for the variation of the charge distribution in the solute upon excitation, and therefore its use for CT transitions is not recommended.<sup>31</sup>

State-specific approaches were then proposed, accounting for the variation of the solute charge distribution upon excitation. Specifically, in EI, the fast DoF of the solvent are equilibrated to the excited state charge density, in a self-consistent procedure.<sup>32,33</sup> The non-equilibrium transition energy is then

computed as the difference between the energy of the final state and of the initial state, both states being obtained with the fast solvent DoF equilibrated for the relevant state (for polar solvents slow solvent DoF are maintained fixed to the equilibrium value for the ground state, when referring to absorption processes, and to the excited state when referring to emission). It is important to underline that in EI two different potentials for the ground and the excited states are considered in an effort to account for the fast relaxation of the solvent DoF. However the approach is still strictly adiabatic, as each Hamiltonian is defined and diagonalized for a specific constant potential. Moreover, since transitions are computed between eigenstates obtained from the diagonalization of different Hamiltonians, the calculation of fundamental spectroscopic properties such as the transition dipole moments is precluded.<sup>32,33</sup>

CLR bridges the gap between LR and EI and represents a perturbative approximation to EI.<sup>30,34</sup> As in LR, the zero-order transition energy is calculated as the frozen-solvent transition energy. Corrections are then applied that depend on the variation of the charge distribution upon excitation. According to Ref. 35 the correction is computed by considering the orbital response to the excitation of interest, in turn obtained as the solution of the Kohn–Sham Z-vector equations (relaxed density). CLR relies on a first order perturbative approach, so that corrections only apply to the energies, while wavefunctions are not affected. Transition dipole moments are therefore accessible and indeed coincide with those obtained in LR. However, CLR represents just a linear perturbative approximation to the complete EI calculation, and, apart from computational convenience, it is unclear why a linear perturbative treatment should be used rather than a nominally exact calculation.

## III. COMPUTATIONAL RESULTS

### A. PO-TXO2 (**A1**) and DPO-TXO2 (**A2**)

**A1** and **A2** are TADF emitters with dipolar (D-A) and quadrupolar (D-A-D) structure, respectively, where A is 9,9-dimethylthioxanthene-S,S-dioxide (TXO2) and D is the phenoxazine (PO) group. The optimized ground state structure has the D and A moieties almost orthogonal. Both **A1** and **A2** have a negligible permanent dipole moment. Fig. 2 shows the  $f(\eta^2)$ -dependence of the transition energies for the first few excitations of both molecules, calculated in the different implementations of PCM, discussed above. The nature of each state is defined with reference to the natural transition orbital (NTO), displayed in Fig. S3 and S5.

In gas phase, the lowest triplet excitation of **A1** at 3.389 eV is fully localized on the donor and has a negligible dipole moment; we call it  $^3\text{LE}_D$ . The second triplet at 3.487 eV and the lowest singlet at 3.504 eV are instead almost pure CT states, labeled  $^3\text{CT}$  and  $^1\text{CT}$ , respectively, and have a large permanent dipole moment oriented along the CT axis (see Table S2). Increasing  $f(\eta^2)$ , LR excitation energies marginally increase due to the solvent stabilization of the ground state, without any significant effect on the energies of the excited states.

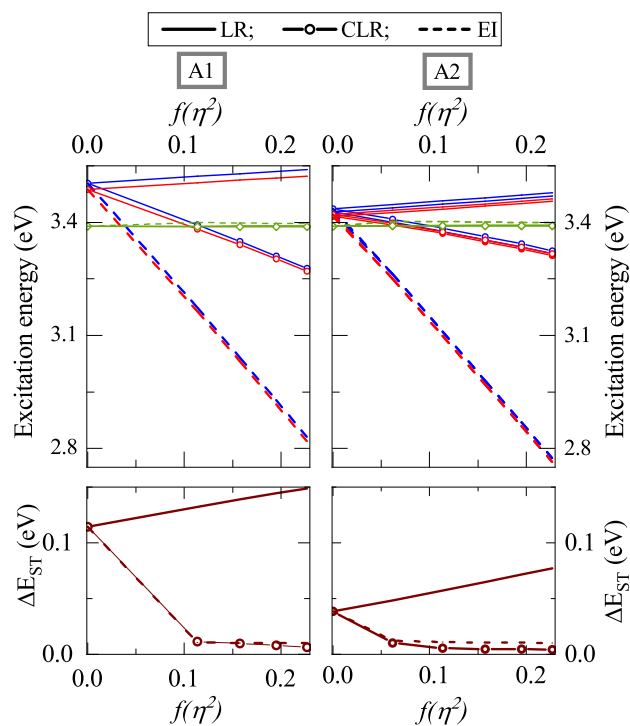


FIG. 2. Results for **A1** (left) and **A2** (right) molecules. Top panels: excitation energies vs  $f(\eta^2)$  for states  $^1\text{CT}$  (blue),  $^3\text{CT}$  (red),  $^3\text{LE}_D$  (green). Bottom panels: the calculated energy gap between the lowest singlet and triplet states. In all panels solid lines refer to LR, symbols refer to CLR, dashed lines refer to EI.

CLR and EI give qualitatively different results from LR: indeed already in non-polar solvents both approaches point to a different nature of the lowest excited triplet that becomes a CT state rather than an LE state. This has enormous spectroscopic consequences,<sup>8,9,36</sup> and it is important to realize that LR, the default approach to solvation, gives the wrong order of excited states for TADF dyes. In fact, not accounting for the large charge reorganization upon CT excitation, LR does not capture the large stabilization of CT states when going from gas-phase to condensed phases, leading to unreliable results already in non-polar media. On the other hand, CLR and EI lead to wildly different results, with energy differences  $\approx 0.5\text{eV}$  for typical  $f(\eta^2)$  values for organic media. CLR and EI results for the energy gap between the lowest singlet and triplet states,  $\Delta E_{ST}$ , are similar, even if largely different from the LR result.

In **A2**, the number of relevant excited states doubles with respect to **A1**, as symmetric and antisymmetric CT and  $\text{LE}_D$  states enter into play. In gas phase, the lowest triplets ( $\approx 3.39\text{eV}$ ) are two degenerate states localized on the donors,  $^3\text{LE}_D$ , while CT states are at higher energies: a pair of almost degenerate triplets,  $^3\text{CT}$ , at  $\approx 3.42\text{eV}$  and a pair of singlets,  $^1\text{CT}$ , at  $3.428\text{eV}$  and  $3.436\text{eV}$ . Despite the different structure and higher number of excited states, the dependence of LR, CLR and EI transition energies on  $f(\eta^2)$  (Fig. 2, right panel)

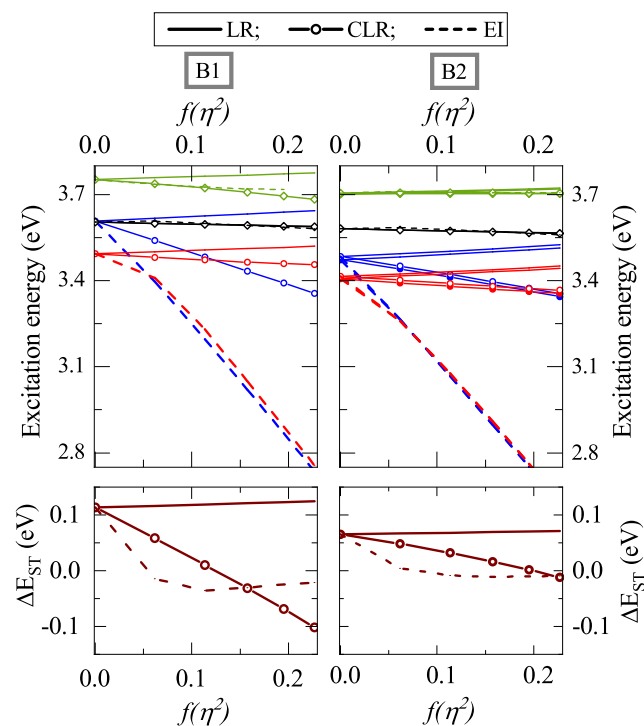


FIG. 3. Results for **B1** (left) and **B2** (right) molecules. Top panels: Calculated excitation energies vs  $f(\eta^2)$  for states  $^1\text{CT}$  (blue),  $^3\text{CT}$  (red),  $^3\text{LE}_A$  (black),  $^3\text{LE}_D$  (green). Bottom panels: the calculated energy gap between the lowest singlet and triplet states. In all panels solid lines refer to LR, symbols refer to CLR, dashed lines refer to EI.

can be explained in a similar way as for **A1**, with the caveat that EI and CLR corrections are due to the variation of the molecular quadrupolar moment of **A2** upon excitation. Once again,  $\Delta E_{ST}$  results from CLR and EI calculations are similar but largely different from LR results.

### B. 2-PTZ-DBTO2, 2,8-DPTZ-DBTO2 (**B1** and **B2**) and 3-PTZ-DBTO2, 3,7-DPTZ-DBTO2 (**C1** and **C2**)

**B1** and **B2** have been extensively studied both from a theoretical and experimental perspective.<sup>8,9</sup> The D and A units (phenothiazine, PTZ, and dibenzo[b,d]thiophene 5,5-dioxide, DBTO, respectively) are connected as shown in Fig. 1. In the optimized ground state, D and A moieties lie on nearly orthogonal planes. Results for **B1** and **B2** are displayed in Fig. 3. Several states must be considered for these systems. In fact the gas phase NTO and MO analysis (Fig. S6 and S7) reveals that **B1** lowest triplet ( $3.493\text{eV}$ ) has a predominant CT character, so that we dub it as  $^3\text{CT}$ , but with a non-negligible contribution from a local state. The next triplet,  $^3\text{LE}_A$ , at  $3.604\text{eV}$ , is almost entirely localized on the A unit. The lowest singlet state at  $3.607\text{eV}$ ,  $^1\text{CT}$ , is a pure CT state, with a large permanent dipole moment aligned approximately along the DA

axis. The third triplet at 3.753 eV is a localized excited state on the D unit,  ${}^3\text{LE}_D$  state, with a non-negligible CT character. As before, the LR corrections to the excitation energies are minor for all states, in view of the very small transition dipole moments of relevant excitations. On the opposite, CT states are largely stabilized in CLR and EI but, as before, the two approaches yield very different results.

**B2** is the quadrupolar counterpart of **B1** and more states enter into play. However, the nature and relative energies of the states in gas phase is similar in **B1** and **B2**. The lowest triplets ( $\approx 3.41$  eV) are mostly  ${}^3\text{CT}$ , but have a non-negligible LE component, as shown from the NTO analysis (Fig. S8). Interestingly, the low energy triplet in **B2** has a larger CT character than in **B1**. The next triplet at 3.580 eV is localized on A. The pair of degenerate  ${}^3\text{LE}_D$  states at  $\approx 3.70$  eV has a non-negligible CT component. The lowest singlets,  ${}^1\text{CT}$ , at 3.473 eV and 3.484 eV are essentially pure CT states.

As already discussed, LR corrections are negligible due to the very small transition dipole moments in TADF dyes. In CLR, corrections to the  ${}^3\text{LE}_A$  and  ${}^3\text{LE}_D$  states are also negligible. On the other hand,  ${}^3\text{CT}$  and  ${}^1\text{CT}$  states are stabilized as the transitions occur with a significant change in the charge distribution. However another serious problem emerges: both CLR and EI show an inversion in the order of the lowest singlet and triplet states. In other terms, according to these calculations, the lowest excited state of both **B1** and **B2** dissolved in an organic non-polar medium would correspond to a singlet and not to a triplet state. As discussed below, this result originates again from the mishandling of fast solvation. In **B1**, the lowest triplet has dominant CT character but with a sizable contribution from the triplet excitation localized on A, while the lowest singlet state is an almost pure CT state. The variation of the charge distribution upon excitation is therefore larger for the lowest singlet than for the lowest triplet excitation, leading to a larger stabilization of the singlet state with respect to the triplet state, with an effect that is most apparent in CLR. Indeed in CLR the nature of the states is frozen, while in EI the nature of the states changes in the iterative process. Specifically, in our case, during the EI iterations the weight of the LE component in the lowest triplet state decreases, reducing  $\Delta E_{ST}$ , that stays small but negative. In any case, the three implementations of the solvation model lead to very different values for  $\Delta E_{ST}$ . Due to the larger CT component in  ${}^3\text{CT}$  states in **B2** with respect to the same state in **B1**, the singlet-triplet inversion occurs at larger  $f(\eta^2)$  values.

**C1** and **C2** are very similar to **B1** and **B2**, respectively, as they share the same D and A units, even if connected in a different way. Result in Fig. 4 are self explanatory now. NTOs (see Fig. S9 and S11) show a smaller mixing of local and CT triplet states than observed in **B1/B2**. Accordingly, for both **C1** and **C2**,  ${}^3\text{CT}$  states have a larger weight of CT character than for **B1** and **B2**, resulting in larger charge separation. However, negative  $\Delta E_{ST}$  are observed again with most prominent effects in CLR.

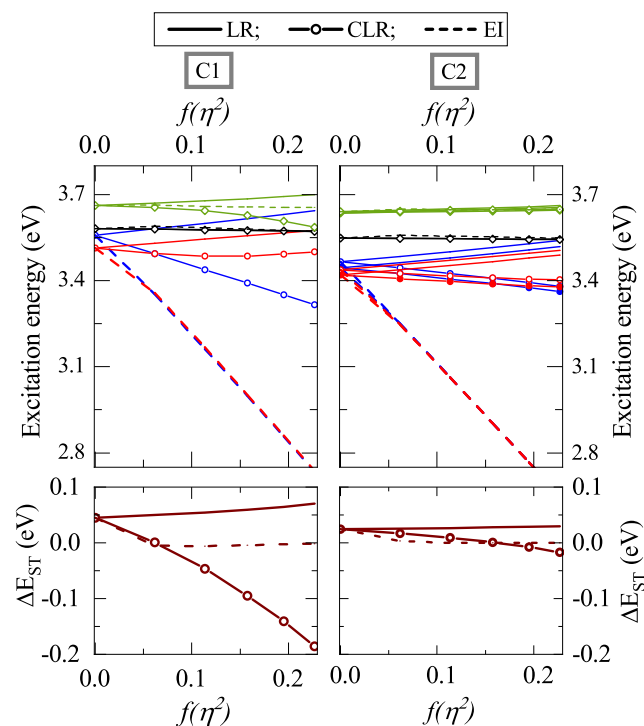


FIG. 4. Results for **C1** (left) and **C2** (right) molecules. Top panels: Calculated excitation energies vs  $f(\eta^2)$  for states  ${}^1\text{CT}$  (blue),  ${}^3\text{CT}$  (red),  ${}^3\text{LE}_A$  (black),  ${}^3\text{LE}_D$  (green). Bottom panels: the calculated energy gap between the lowest singlet and triplet states. In all panels solid lines refer to LR, symbols refer to CLR, dashed lines refer to EI.

#### IV. AN ANTIADIABATIC APPROACH

The scattering of the results obtained in the three current PCM implementations available in Gaussian package, the impossibility to calculate the transition dipole moment in the formally exact EI approach, addressed by limiting the analysis to first order perturbation theory in CLR, clearly point to some fundamental problem in solvation models, that can be traced back to the adiabatic approximation, as discussed in Ref.<sup>19</sup>. To demonstrate that also the singlet-triplet inversion calculated in CLR and EI for some dyes in non-polar solvents is a spurious effect resulting from the adiabatic approximation to fast solvation, we focus on **B1** dye and compare adiabatic and AA results.

At present, AA implementations of PCM are not available, therefore, following ref.<sup>19</sup>, we adopt a simplified model for the solvated molecule that relies on the dipolar approximation to describe the solute-solvent interaction and on the choice of a small electronic basis. With these approximations, we build a model that can be solved both in the adiabatic and in the AA approximation to fast solvation, allowing for a stringent comparison of the two approaches.

In the dipolar approximation, the solute dissolved in a non-polar solvent feels the electric field generated  $\vec{F}$  generated by

the polarization of the surrounding solvent molecules. At the equilibrium, the field is proportional to the molecular dipole moment through a constant  $r$  that, assuming a spherical shape for the cavity occupied by the solute, reads:<sup>37,38</sup>

$$r = \frac{2}{4\pi\epsilon_0 a^3} f(\eta^2) = \frac{2}{4\pi\epsilon_0 a^3} \frac{\eta^2 - 1}{2\eta^2 + 1} \quad (1)$$

where  $a$  is the cavity radius and  $\epsilon_0$  is the vacuum permittivity. A quadratic potential energy is associated to the field, with the force constant fixed to the inverse of the corresponding  $r$ , to guarantee for the proportionality between the reaction field and the solute dipole moment at equilibrium.<sup>39</sup> The effective Hamiltonian for the solvated molecule then reads:

$$H = H_{gas} + \left[ \frac{\vec{F}^2}{2r} + \hat{T} - \hat{\mu} \cdot \vec{F} \right] \quad (2)$$

where  $H_{gas}$  is the gas phase molecular Hamiltonian,  $\hat{\mu}$  the molecular dipole moment operator and  $\hat{T}$  the kinetic energy associated to the electronic polarization.

In the adiabatic approximation the kinetic energy is neglected, so that  $\vec{F}$  becomes a classical variable and the problem is solved for fixed  $\vec{F}$ . In other terms, in the adiabatic approximation the potential generated by the medium on the solute is frozen. In the AA approximation, instead, the medium responds instantaneously to the charge fluctuations in the solute, and it is not possible to define a molecular Hamiltonian at frozen field, since each state feels its own reaction field. A single effective Hamiltonian is obtained in the AA approximation that reads:<sup>19</sup>

$$\hat{H}_{AA} = \hat{H}_{gas} - \frac{1}{2} r_{el} \hat{\mu}^2 \quad (3)$$

The diagonalization of the AA Hamiltonian gives in a single shot all molecular eigenstates, properly renormalized to account for the effects of fast solvation.

To address the AA problem, we define a few state molecular model, writing the Hamiltonian in Eq. 3 on the basis of the eigenstates of the gas-phase Hamiltonian. Specifically, we neglect spin-orbit coupling and consider two independent subspaces formed by the first  $n$  singlets and the first  $m$  triplets, as obtained from the TD-DFT calculation for the gas-phase molecule. On this basis  $H_{gas}$  is clearly diagonal. The dipole moment matrices were obtained using the MULTIWFN software.<sup>40</sup> Results of course depend on the number of states included in the basis sets and, since the diagonalization is performed independently in the singlet and triplet subspaces, it is important to consistently choose the number of states in the two subspaces. Setting the same small number of states in both subspaces (see Fig. S12 for details) indeed gives rise to the crossing of singlet and triplet states. The reason for this result is easily recognized in a basis that spans a much wider energy interval for the singlet vs the triplet subspace. Increasing the number of triplet states, so that the same energy window is roughly spanned in both subspaces, leads to more reliable results. Data in Fig. S12 show that spanning a range of  $\sim 6$  eV with 17 singlets and 26 triplets leads towards convergence.

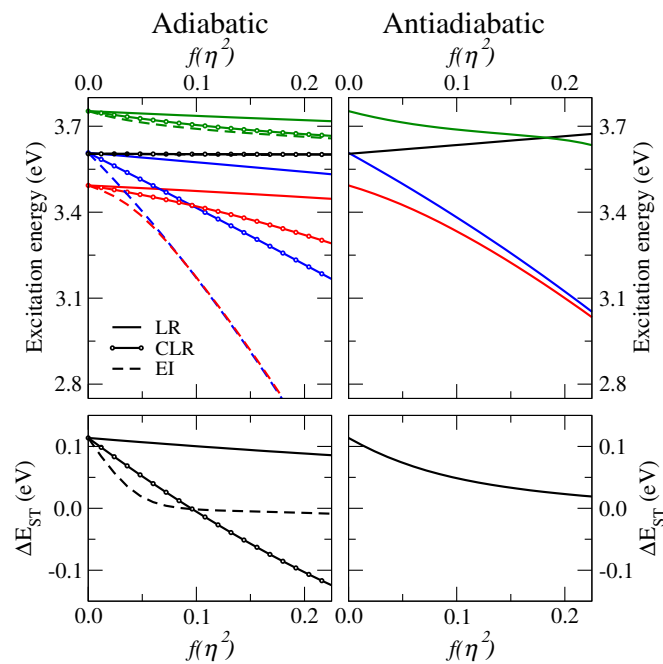


FIG. 5. Comparison between adiabatic and AA results (left and right panels, respectively) for **B1** in the few state model accounting for 17 singlet and 26 triplet states. Top panels: Calculated excitation energies vs  $f(\eta^2)$  for states  $^1\text{CT}$  (blue),  $^3\text{CT}$  (red),  $^3\text{LE}_A$  (black),  $^3\text{LE}_D$  (green). Bottom panels: the calculated energy gap between the lowest singlet and triplet states. In left panels (adiabatic results) solid lines refer to LR, symbols refer to CLR, dashed lines refer to EI.

Right panels of Fig. 5 collect AA results for **B1**, obtained setting the cavity radius to the Onsager's radius,  $a = 5.44 \text{ \AA}$ . These results clearly point to an excitation spectrum where the transition energies for the state with CT character (either singlet or triplet) are lowered due to the medium polarizability while LE states are less affected. As expected, LR results are completely off for CT states. On the other hand, EI largely overestimates the stabilization of CT states and CLR underestimates it (cf Fig. 3). At variance with EI and CLR, AA results point to a normal order of excited states, with the lowest excited state having a triplet nature.

Comparing AA results in the right panels of Fig. 5 with PCM results in Fig. 3 may however be misleading due to the approximations introduced to build the few-state model adopted to run AA calculations. For a stringent comparison of AA and adiabatic approximations, left panels of Fig. 5 show results obtained in the adiabatic approximation (and specifically in its LR, CLR and EI variants, see SI for relevant equations) for precisely the same model adopted for the AA approach (same basis set and dipole moment matrices).

The first observation is that adiabatic results in Fig. 5 compare favourably with PCM results in Fig. 3, suggesting that the adopted approximations capture most of the relevant physics. More important is however the comparison between adiabatic and AA results in Fig. 5, relevant to the same model. Solvation effects on LE states are marginal, but, as for CT states, neither EI nor CLR properly capture the stabi-

lization of either the singlet or triplet states with differences in the estimated transition energies of several tenths of eV at  $f(\eta^2) \sim 2$ , as relevant to common organic media. Moreover, the singlet-triplet gap decreases considerably as a result of the medium polarizability, but at variance with CLR and EI results, it stays positive. Quite irrespective of the quality of the proposed molecular model, results in Fig. 5 unambiguously demonstrate that the adiabatic approach, when applied to describe the spectroscopic effect of the medium polarizability, leads to unreliable results.

## V. DISCUSSION AND CONCLUSIONS

TADF dyes are particularly delicate to model since the subtle interplay between localized and CT states makes environmental or matrix effects crucial in the definition of the tiny energies, the singlet-triplet gap and the spin-orbit coupling, that define the system performance.<sup>8,9,23,36,41–45</sup> Explicit-solvent quantum-classical approaches<sup>23,24,46–53</sup> are applied in several papers to investigate matrix effects in TADF-dyes. Even more popular are continuum solvation models, with LR,<sup>42–44,54–62</sup> CLR<sup>63</sup> and EI implementations.<sup>46,47,62,64–67</sup> As extensively discussed here, none of these approaches properly accounts for the electronic polarizability of the medium, leading to results that need a careful consideration.

Two main approaches are possible to separate the relevant DoF of the solute from the solvent DoF: an adiabatic and an antiadiabatic approach. Both approaches rely on the distinctively different dynamics of solute and solvent DoF. In the adiabatic approximation, one separates the relevant system (in our case the low-lying electronic excitations of the solute, typically in the visible and near-UV spectral region) from slow solvent DoF, so that the relevant Hamiltonian may be defined while maintaining the slow environmental DoF fixed. Accordingly, one diagonalizes several Hamiltonians as relevant to the different configurations of the slow DoF. This is indeed what is done in EI, where different molecular Hamiltonians are defined with the solvent DoF specifically equilibrated to each state, in an approach that is perfectly adequate to deal with polar solvation. As the name suggests, the antiadiabatic approximation applies to the opposite case, i.e. when the DoF to be renormalized away are much faster than the relevant ones. In this approximation one assumes that the solvent DoF readjust instantaneously to the motion of the relevant DoF. Therefore, a single Hamiltonian is defined for the relevant system in the antiadiabatic approximation.<sup>19</sup> This is very well apparent if one works with a basis of diabatic states, as in ref. 68: the antiadiabatic Hamiltonian describes a system where the fast DoF of the solvent are equilibrated to each diabatic basis state.

Here a fairly simple implementation of the AA approximation is introduced to demonstrate that the anomalous results obtained when the adiabatic approximation is applied to fast DoF are quite naturally solved when the proper approximation scheme is adopted. To implement an AA calculation, a model is introduced, relying on a limited electronic basis and describing the solute-solvent interaction in the dipolar approx-

imation. Moreover, the molecular geometry is always maintained fixed at the gas-phase equilibrium. Therefore, AA results in the left panel of Fig. 5 must be taken with care and we do not pretend that they offer an accurate description of the system. Yet, the comparison with adiabatic results obtained for precisely the same model is solid and unambiguously demonstrates that the adiabatic approximation, implicitly adopted in all effective solvation models, leads to unreliable results.

Several variants of continuum solvation models are discussed in the literature,<sup>20,21,29–33</sup> that face the problem of fast solvation from slightly different perspectives, however, with the notable exception of early attempts,<sup>69,70</sup> all approaches rely on the diagonalization of molecular Hamiltonian obtained for a fixed potential from environmental charges. Whatever choice is made for the definition of the excited states of interest for absorption and emission processes, these methods are bound to fail, since the actual molecular states for a molecule in a polarizable environment should all be obtained diagonalizing a single Hamiltonian where the environmental polarizability affects in different ways the energy of the states of the systems and their coupling. Indeed, the adiabatic approximation leads to an incorrect description of the molecular ground state itself.<sup>19</sup> Just as an example, in polar dyes with a largely neutral ground state, the adiabatic approximation underestimates the increase of the ground state dipole moment as due to the polarizability of the environment, simply because the equilibrium reaction field for a largely neutral ground state is small and cannot account for the large stabilization of polar charge fluctuations.<sup>19</sup> Similarly quantum-classical approaches with explicit solvent models do not properly account for the solvent polarizability, even when a *polarizable environment* is considered. In fact in polarizable models, one allows the charges on the solvent molecules to reorganize in response to the solute perturbation, but the molecular Hamiltonian is always defined accounting for a frozen potential generated by the surrounding charges.

While the adiabatic approximation can never be applied to electronic solvation, whose dynamics is faster than the relevant solute DoF, the AA approximation works well when the solvent degrees of freedom are much faster than the solute ones. The AA approximation therefore should be considered with care when the solvent excitation spectrum comes very close in energy to the solute spectrum, as it is the case for some matrices used in TADF applications. For common solvents and polymeric matrices used in spectroscopy, the UV-cutoff is typically larger (and often much larger) than 4 eV. Moreover, it must be recognized that the UV cutoff signals the frequency where the solvent absorption starts, the relevant absorption bands being located at much larger energy (just as an example, the water cutoff is at 6.5 eV, but the absorption spectrum peaks at  $\sim 15$  eV<sup>71</sup>, with a large UV tail that moves the central frequency to  $\sim 24$  eV<sup>19</sup>). In systems where the AA approximation to fast solvation breaks down, due to similar timescales of the solute and solvent motions, the adiabatic approximation does not represent a viable alternative. Rather, solute and solvent degrees of freedom cannot be disentangled and one must resort to a full quantum mechanical approach



to the solute and the solvent. Along these lines, the beautiful work reported in ref.<sup>25</sup> for water solvated dyes, offers another independent demonstration of the failure of the adiabatic approximation to fast solvation. In that work, a QM-MM approach is adopted, where the potential generated in the QM region by the charges on water molecules in the MM region is described (as usual) in the adiabatic approximation. In order to get reliable results, the solvation sphere described by QM must include a large number of water molecules (of the order of at least 200, depending on the solute and on the state of interest).

Of special concern here is the inversion of the lowest singlet and triplet states calculated in the adiabatic CLR and EI implementations of PCM for some TADF-dyes. Indeed the breaking of the Hund rule was reported in some very special molecular systems, typically with highly symmetric structures and a very characteristic spatial separation of HOMO and LUMO orbitals that are delocalized on the whole molecular structure.<sup>72-76</sup> The molecules discussed here do not show these characteristics. Moreover, the singlet triplet inversion in these very special structures was only observed in high quality ab initio calculation, involving at least double excitations.<sup>72,73</sup> Quite interestingly, the inclusion of a standard TADF dye in a polarizable environment was also suggested as a possible origin for singlet-triplet inversion.<sup>23,72</sup> However these results were obtained and discussed treating the medium polarizability in the adiabatic approximation and deserve a careful reconsideration, either adopting the more adequate AA approximation or possibly addressing both the solute and its surrounding medium in a fully quantum mechanical approach.

In the early 90's antiadiabatic approaches were proposed for fast solvation, but never gained traction.<sup>69,70</sup> Most probably, this is related to the choice of a wrong name for the approximation that was called Born-Oppenheimer rather than antiadiabatic. Indeed the Born-Oppenheimer approximation is a specific flavor of the most general adiabatic approximation that allows to separate slow DoF from relevant electronic DoF, through the definition of an electronic Hamiltonian that parametrically depends on slow coordinates.<sup>26</sup> It is true that also slow DoF are finally treated in the adiabatic approximation, but this is only possible after the adiabatic electronic Hamiltonian (defined for frozen slow coordinates) is diagonalized. Using the name Born-Oppenheimer to address an antiadiabatic approximation, where instead a single electronic Hamiltonian is defined, was therefore unfortunate and may be the reason why the strategy was not recognized until very recently as the only viable approach to renormalize out the of the problem the DoF related to fast solvation.

The term antiadiabatic, borrowed from the physics community working on polarons and superconductivity,<sup>77</sup> was used in the context of fast solvation by one of the authors of this paper in 1999,<sup>39</sup> with reference to semiempirical model Hamiltonians, and was proposed again in the context of quantum chemical approaches.<sup>19</sup> Other authors have also recently recognized the value of the antiadiabatic approach to treat fast solvation.<sup>78</sup> Unfortunately, they stick on the Born-Oppenheimer notation, that obscures the qualitatively different nature of the antiadiabatic approach with respect to the adiabatic approximation.

As extensively discussed in Ref. 19 the antiadiabatic approximation can be applied to solute DoF slower than the electronic DoF of the solvent, typically located deep in the UV (energies much larger than 6 eV): applying it to all electronic excitations in the solute is bound to fail, as also demonstrated in Ref. 78. However, a clever choice of the basis states can be made as to renormalize only relevant DoF, and, as the results in Fig. S12 show for a specific example, converged antiadiabatic results can be obtained working in an energy window well within the critical threshold for common solvents.

Effective solvation models are of paramount importance in material science, since molecular properties are largely affected by the local molecular environment. Treating the active molecule and its environment on the same foot is a formidable task. Quantum-classical and continuum solvation models are therefore widely adopted in the community of computational chemists, physicists and material scientists. The main message of this work is a warning to these communities: the adiabatic approximation implicitly assumed in all these approaches to deal with fast solvation, i.e. to account for the medium polarizability, yields uncontrolled results, exemplified here by the prediction of a singlet excited state lying at lower energy than the lowest triplet state. The adiabatic approximation of course works very well to deal with slow solvation DoF, including e.g. polar solvation. However it cannot be applied to fast solvation: there is no way to improve on it. A different scheme, based on the antiadiabatic approximation, must rather be adopted.

## VI. AVAILABILITY OF DATA

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## SUPPLEMENTARY MATERIAL

See supplementary material for additional information and results on TD-DFT calculations (NTO/MO analysis,  $\omega$ -tuning functional) and for details about the convergence of AA calculations.

## ACKNOWLEDGMENTS

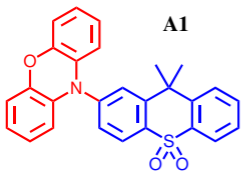
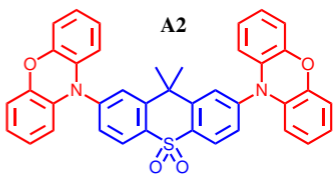
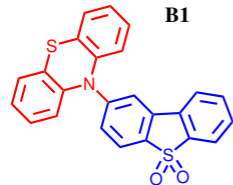
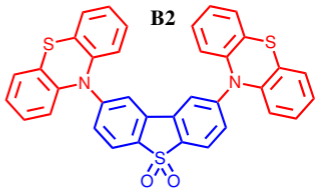
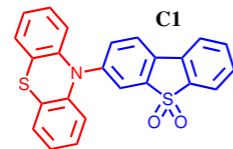
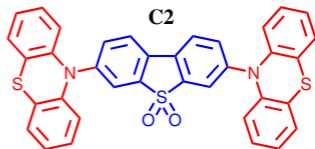
This project received funding from the European Union Horizon 2020 research and innovation programme under Grant Agreement No. 812872 (TADFlife), and benefited from the equipment and support of the COMP-HUB Initiative, funded by the "Departments of Excellence" program of the Italian Ministry for Education, University and Research (MIUR, 2018-2022). We acknowledge the support from the HPC (High Performance Computing) facility of the University of Parma, Italy.

<sup>1</sup>C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.* **57**, 1894 (1961).

- <sup>2</sup>A. Endo, K. Sato, K. Yoshimura, T. Kai, A. Kawada, H. Miyazaki, and C. Adachi, *Applied Physics Letters* **98**, 083302 (2011), <https://doi.org/10.1063/1.3558906>.
- <sup>3</sup>H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda, and C. Adachi, *Nature Communications* **5**, 4061 (2014).
- <sup>4</sup>E. Zysman-Colman, *Nature Photonics* **14**, 593 (2020).
- <sup>5</sup>L.-S. Cui, A. J. Gillett, S.-F. Zhang, H. Ye, Y. Liu, X.-K. Chen, Z.-S. Lin, E. W. Evans, W. K. Myers, T. K. Ronson, H. Nakanotani, S. Reineke, J.-L. Brédas, C. Adachi, and R. H. Friend, *Nature Photonics* **14**, 636 (2020).
- <sup>6</sup>Y. Wada, H. Nakagawa, S. Matsumoto, Y. Wakisaka, and H. Kaji, *Nature Photonics* **14**, 643 (2020).
- <sup>7</sup>Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi, and M. P. Aldred, *Chemical Society Reviews* **46**, 915 (2017).
- <sup>8</sup>M. K. Etherington, J. Gibson, H. F. Higginbotham, T. J. Penfold, and A. P. Monkman, *Nat. Commun.* **7** (2016), 10.1038/ncomms13680.
- <sup>9</sup>M. K. Etherington, F. Franchello, J. Gibson, T. Northey, J. Santos, J. S. Ward, H. F. Higginbotham, P. Data, A. Kurowska, P. L. D. Santos, D. R. Graves, A. S. Batsanov, F. B. Dias, M. R. Bryce, T. J. Penfold, and A. P. Monkman, *Nat. Commun.* **8** (2017), 10.1038/ncomms14987.
- <sup>10</sup>X. Wang, S. Wang, J. Lv, S. Shao, L. Wang, X. Jing, and F. Wang, *Chem. Sci.* **10**, 2915 (2019).
- <sup>11</sup>H. Tsujimoto, D.-G. Ha, G. Markopoulos, H. S. Chae, M. A. Baldo, and T. M. Swager, *J. Am. Chem. Soc.* **139**, 4894 (2017).
- <sup>12</sup>A. Pershin, D. Hall, V. Lemaire, J.-C. Sancho-García, L. Muccioli, E. Zysman-Colman, D. Beljonne, and Y. Olivier, *Nat. Commun.* **10** (2019), 10.1038/s41467-019-08495-5.
- <sup>13</sup>F. B. Dias, T. J. Penfold, and A. P. Monkman, *Method. Appl. Fluoresc.* **5**, 012001 (2017).
- <sup>14</sup>M. Y. Wong and E. Zysman-Colman, *Advanced Materials* **29**, 1605444 (2017), <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.201605444>.
- <sup>15</sup>S. Madayanad Suresh, D. Hall, D. Beljonne, Y. Olivier, and E. Zysman-Colman, *Advanced Functional Materials* **30**, 1908677 (2020), <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adfm.201908677>.
- <sup>16</sup>T. Stein, L. Kronik, and R. Baer, *Journal of the American Chemical Society* **131**, 2818 (2009).
- <sup>17</sup>H. Sun and J. Autschbach, *ChemPhysChem* **14**, 2450 (2013).
- <sup>18</sup>H. Sun, C. Zhong, and J.-L. Brédas, *Journal of Chemical Theory and Computation* **11**, 3851 (2015), pMID: 26574466, <https://doi.org/10.1021/acs.jctc.5b00431>.
- <sup>19</sup>D. K. A. Phan Huu, R. Dhali, C. Pieroni, F. Di Maiolo, C. Sissa, F. Terenziani, and A. Painelli, *Phys. Rev. Lett.* **124**, 107401 (2020).
- <sup>20</sup>J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.* **105**, 2999 (2005).
- <sup>21</sup>A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *The Journal of Physical Chemistry B* **119**, 958 (2014).
- <sup>22</sup>T. Vreven and K. Morokuma (Elsevier, 2006) pp. 35 – 51.
- <sup>23</sup>Y. Olivier, B. Yurash, L. Muccioli, G. D'Avino, O. Mikhnenko, J. C. Sancho-García, C. Adachi, T.-Q. Nguyen, and D. Beljonne, *Physical Review Materials* **1** (2017), 10.1103/physrevmaterials.1.075602.
- <sup>24</sup>J. Li, G. D'Avino, I. Duchemin, D. Beljonne, and X. Blase, *Phys. Rev. B* **97**, 035108 (2018).
- <sup>25</sup>J. M. Milanese, M. R. Provorse, E. Alameda, and C. M. Isborn, *Journal of Chemical Theory and Computation* **13**, 2159 (2017).
- <sup>26</sup>M. Stanke, in *Handbook of Computational Chemistry* (Springer Netherlands, 2015) pp. 1–51.
- <sup>27</sup>S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.* **314**, 291 (1999).
- <sup>28</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, "Gaussian 16 Revision B.01," (2016).
- <sup>29</sup>B. Lunkenheimer and Köhn, *J. Chem. Theory Comput.* **9**, 977 (2013).
- <sup>30</sup>C. A. Guido and S. Caprasecca, *International Journal of Quantum Chemistry* **119**, e25711 (2019), <https://onlinelibrary.wiley.com/doi/pdf/10.1002/qua.25711>.
- <sup>31</sup>R. Cammi, S. Corni, B. Mennucci, and J. Tomasi, *The Journal of Chemical Physics* **122**, 104513 (2005), <https://doi.org/10.1063/1.1867373>.
- <sup>32</sup>R. Improta, V. Barone, G. Scalmani, and M. J. Frisch, *The Journal of Chemical Physics* **125**, 054103 (2006), <https://doi.org/10.1063/1.2222364>.
- <sup>33</sup>R. Improta, V. Barone, G. Scalmani, and M. J. Frisch, *J. Chem. Phys.* **125**, 054103 (2006).
- <sup>34</sup>A. V. Marenich, C. J. Cramer, D. G. Truhlar, C. A. Guido, B. Mennucci, G. Scalmani, and M. J. Frisch, *Chem. Sci.* **2**, 2143 (2011).
- <sup>35</sup>M. Caricato, B. Mennucci, J. Tomasi, F. Ingrosso, R. Cammi, S. Corni, and G. Scalmani, *The Journal of Chemical Physics* **124**, 124520 (2006), <https://doi.org/10.1063/1.2183309>.
- <sup>36</sup>T. J. Penfold, E. Gindensperger, C. Daniel, and C. M. Marian, *Chem. Rev.* **118**, 6975 (2018).
- <sup>37</sup>E. G. McRae, *J. Phys. Chem.* **61**, 1128 (1957).
- <sup>38</sup>S. Di Bella, T. J. Marks, and M. A. Ratner, *J. Am. Chem. Soc.* **116**, 4440 (1994).
- <sup>39</sup>A. Painelli, *Chem. Phys.* **245**, 185 (1999).
- <sup>40</sup>T. Lu and F. Chen, *J. Comput. Chem.* **33**, 580 (2012).
- <sup>41</sup>Z. Tu, G. Han, T. Hu, R. Duan, and Y. Yi, *Chem. Mater.* **31**, 6665 (2019).
- <sup>42</sup>Y. Gao, Y. Geng, Y. Wu, M. Zhang, and Z.-M. Su, *Dyes and Pigments* **145**, 277 (2017).
- <sup>43</sup>P. K. Samanta, D. Kim, V. Coropceanu, and J.-L. Brédas, *J. Am. Chem. Soc.* **139**, 4042 (2017).
- <sup>44</sup>T.-T. Huang and E. Y. Li, *Organic Electronics* **39**, 311 (2016).
- <sup>45</sup>R. Dhali, D. K. A. P. Huu, F. Bertocchi, C. Sissa, F. Terenziani, and A. Painelli, *Phys. Chem. Chem. Phys.* (2021), 10.1039/d0cp05982j.
- <sup>46</sup>T. Northey, J. Stacey, and T. J. Penfold, *J. Mater. Chem. C* **5**, 11001 (2017).
- <sup>47</sup>L. Lv, K. Yuan, Y. Zhu, G. Zuo, and Y. Wang, *The Journal of Physical Chemistry A* **123**, 2080 (2019).
- <sup>48</sup>T. Hu, G. Han, Z. Tu, R. Duan, and Y. Yi, *J. Phys. Chem. C* **122**, 27191 (2018).
- <sup>49</sup>H. Sun, X. Yin, Z.-P. Liu, S.-L. Wei, J.-Z. Fan, L.-L. Lin, and Y.-P. Sun, *Int. J. Quantum Chem.* (2020), 10.1002/qua.26490.
- <sup>50</sup>J. Fan, Y. Zhang, Y. Ma, Y. Song, L. Lin, Y. Xu, and C.-K. Wang, *J. Mater. Chem. C* **8**, 8601 (2020).
- <sup>51</sup>K. Zhang, L. Cai, J. Fan, Y. Zhang, L. Lin, and C.-K. Wang, *Spectrochim. Acta A* **209**, 248 (2019).
- <sup>52</sup>Y.-J. Gao, W.-K. Chen, Z.-R. Wang, W.-H. Fang, and G. Cui, *Phys. Chem. Chem. Phys.* **20**, 24955 (2018).
- <sup>53</sup>Q. Wang, Y.-J. Gao, T.-T. Zhang, J. Han, and G. Cui, *RSC Adv.* **9**, 20786 (2019).
- <sup>54</sup>C. Tu and W. Liang, *ACS Omega* **2**, 3098 (2017).
- <sup>55</sup>G. Valchanov, A. Ivanova, A. Tadjer, D. Chercka, and M. Baumgarten, *J. Phys. Chem. A* **120**, 6944 (2016).
- <sup>56</sup>G. Grybauskaitė-Kaminskiene, K. Ivaniuk, G. Bagdziunas, P. Turyk, P. Stakhira, G. Baryshnikov, D. Volyniuk, V. Cherpak, B. Minaev, Z. Hotra, H. Ågren, and J. V. Grazulevicius, *J. Mater. Chem. C* **6**, 1543 (2018).
- <sup>57</sup>T. Cardeynals, S. Paredis, A. Danos, D. Vanderzande, A. P. Monkman, B. Champagne, and W. Maes, *Dyes and Pigments*, 109022 (2020).
- <sup>58</sup>C. Wang, C. Deng, D. Wang, and Q. Zhang, *J. Phys. Chem. C* **122**, 7816 (2018).
- <sup>59</sup>L. Wang, T. Li, P. Feng, and Y. Song, *Phys. Chem. Chem. Phys.* **19**, 21639 (2017).
- <sup>60</sup>C. He, Z. Li, Y. Lei, W. Zou, and B. Suo, *J. Phys. Chem. Lett.* **10**, 574 (2019).
- <sup>61</sup>H. Sun, Z. Hu, C. Zhong, X. Chen, Z. Sun, and J.-L. Brédas, *J. Phys. Chem. Lett.* **8**, 2393 (2017).
- <sup>62</sup>M. Moral, J. Tolosa, J. Canales-Vázquez, J. C. Sancho-García, A. Garzón-Ruiz, and J. C. García-Martínez, *J. Phys. Chem. C* **123**, 11179 (2019).
- <sup>63</sup>I. Lyskov, M. Etinski, C. M. Marian, and S. P. Russo, *Journal of Materials Chemistry C* **6**, 6860 (2018).
- <sup>64</sup>T. J. Penfold, F. B. Dias, and A. P. Monkman, *Chem. Commun.* **54**, 3926 (2018).
- <sup>65</sup>R. Ishimatsu, S. Matsunami, K. Shizu, C. Adachi, K. Nakano, and T. Imato, *J. Phys. Chem. A* **117**, 5607 (2013).

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.  
PLEASE CITE THIS ARTICLE AS DOI:10.1063/1.50042058

- <sup>66</sup>H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, *Nature* **492**, 234 (2012).
- <sup>67</sup>M. Hong, M. K. Ravva, P. Winget, and J.-L. Brédas, *Chem. Mater.* **28**, 5791 (2016).
- <sup>68</sup>D. K. A. P. Huu, C. Sissa, F. Terenziani, and A. Painelli, *Physical Chemistry Chemical Physics* **22**, 25483 (2020).
- <sup>69</sup>H. J. Kim and J. T. Hynes, *The Journal of Chemical Physics* **96**, 5088 (1992).
- <sup>70</sup>M. V. Basilevsky, G. E. Chudinov, and M. D. Newton, *Chemical Physics* **179**, 263 (1994).
- <sup>71</sup>H. Hayashi, N. Watanabe, Y. Udagawa, and C.-C. Kao, *Proceedings of the National Academy of Sciences* **97**, 6264 (2000).
- <sup>72</sup>P. de Silva, *The Journal of Physical Chemistry Letters* **10**, 5674 (2019).
- <sup>73</sup>J. Ehrmaier, E. J. Rabe, S. R. Pristash, K. L. Corp, C. W. Schlenker, A. L. Sobolewski, and W. Domcke, *The Journal of Physical Chemistry A* **123**, 8099 (2019).
- <sup>74</sup>R. Pollice, P. Friederich, C. Lavigne, G. dos Passos Gomes, and A. Aspuru-Guzik, (2020), 10.26434/chemrxiv.13087319.v1.
- <sup>75</sup>J. Sanz-Rodrigo, G. Ricci, Y. Olivier, and J. C. Sancho-García, *The Journal of Physical Chemistry A* **125**, 513 (2021).
- <sup>76</sup>G. Ricci, E. San-Fabián, Y. Olivier, and J. C. Sancho-García, *ChemPhysChem* (2021), 10.1002/cphc.202000926.
- <sup>77</sup>D. Feinberg, S. Ciuchi, and F. De Pasquale, *Int. J. Modern Phys. B* **4**, 1317 (1990).
- <sup>78</sup>C. A. Guido, M. Rosa, R. Cammi, and S. Corni, *The Journal of Chemical Physics* **152**, 174114 (2020).

**A1****A2****B1****B2****C1****C2**

— LR; —○— CLR; - - - EI

A1

A2

$f(\eta^2)$

$f(\eta^2)$

0.0 0.1 0.2 0.0 0.1 0.2

