

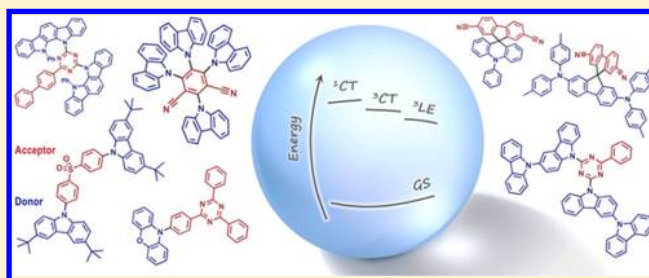
# Computational Prediction for Singlet- and Triplet-Transition Energies of Charge-Transfer Compounds

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## S Supporting Information

**ABSTRACT:** Our work reveals a high dependence on charge-transfer (CT) amounts for the optimal Hartree–Fock percentage in the exchange–correlation functional of time-dependent density functional theory (TD-DFT) and the error of a vertical transition energy calculated by a given functional. Using these relations, the zero–zero transition energies of the first singlet and first triplet excited states of various CT compounds are accurately reproduced. <sup>3</sup>CT and locally excited triplet (<sup>3</sup>LE) states are well distinguished and calculated independently.



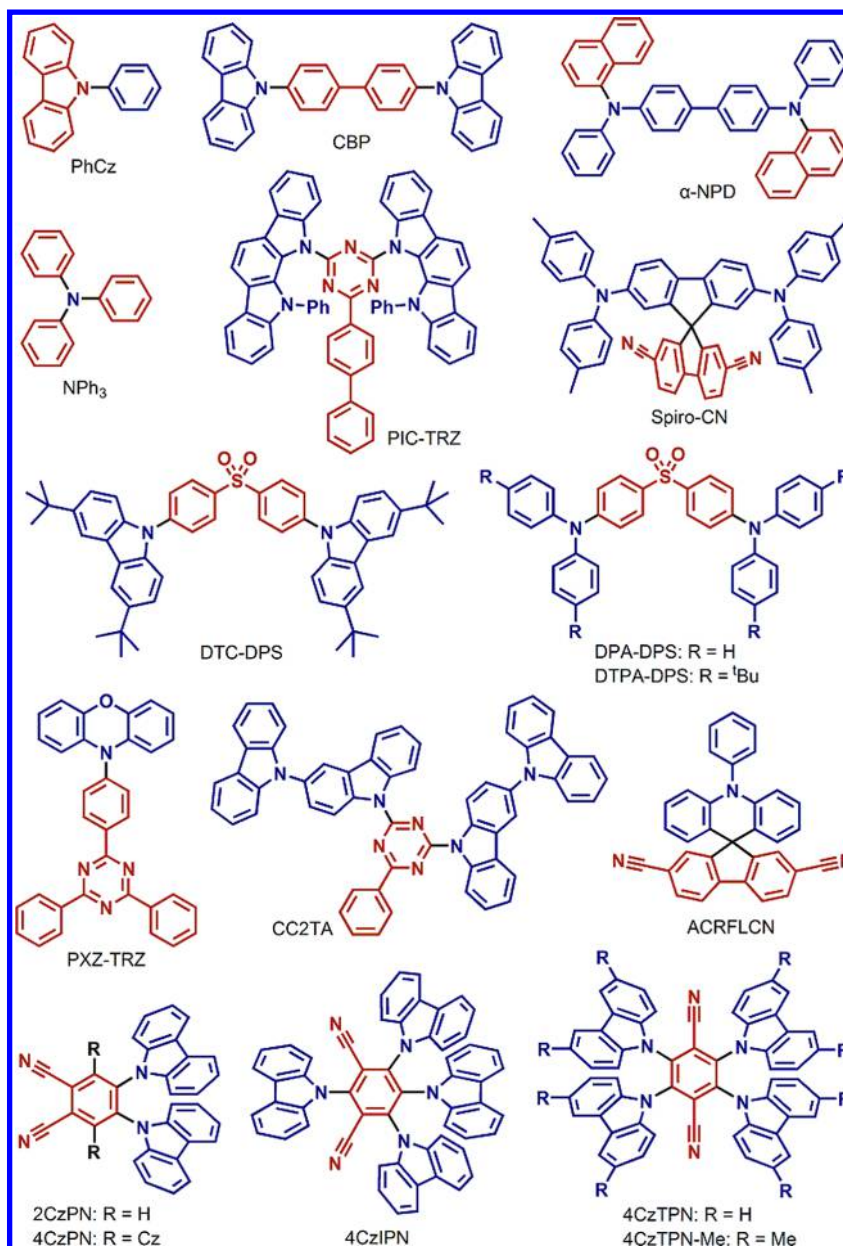
Conjugated molecules containing electron-rich and/or electron-poor units have great potential for applications in organic photonics and electronics owing to the charge-transfer (CT) character in their excited states. The zero–zero transition energies ( $E_{0-0}$ ) of the first singlet ( $S_1$ ) and the first triplet ( $T_1$ ) excited states are important parameters for these materials that determine not only their optical and electronic band gaps, but also the energy-transfer process in multi-molecular systems.<sup>1,2</sup> In particular, when the difference ( $\Delta E_{ST}$ ) between  $E_{0-0}(S_1)$  and  $E_{0-0}(T_1)$  of a conjugated system is small enough, the efficient energy conversion between  $S_1$  and  $T_1$  is possible.<sup>3</sup> On the basis of this concept, a number of efficient thermally activated delayed fluorescence (TADF) compounds have recently been developed by our group and used to harvest triplet excitons in organic light emitting diodes (OLEDs).<sup>4–10</sup> The maximum efficiencies of the devices containing these compounds are finally comparable to those of the best phosphorescent OLEDs.<sup>6,10</sup> If theoretical calculations can predict accurate transition energies of CT molecules, the time and cost in development of new materials with specific performance can be greatly reduced.

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT)<sup>11,12</sup> are certainly the most widely used methods for theoretical interpretation of the ground- and excited-state properties of medium to large molecular systems. By mixing a flexible fraction of Hartree–Fock (HF) exchange into exchange–correlation (XC) functionals,<sup>13–25</sup> the DFT and TD-DFT performed at the optimized ground- and excited-state geometries can reproduce the vertical absorption and emission energies ( $E_{VA}$  and  $E_{VE}$ ), respectively, for which average values approximate the  $E_{0-0}$  according to the Franck–Condon principle (Figure S1).<sup>26,27</sup> In fact, until now, accurate predictions of  $E_{0-0}(S_1)$  and  $E_{0-0}(T_1)$

were still difficult for two reasons: (1) there is no rationale for how much exact exchange should be included for a particular system, and (2) the XC functional applied to the  $S_1$  transition of a CT compound might not be applicable to its  $T_1$  transition.<sup>28–31</sup> In this Letter, we establish a new correction method for TD-DFT results based on the amount of separated charges in the excited state and make individual and exact predictions of  $E_{0-0}(S_1)$  and  $E_{0-0}(T_1)$  of various CT compounds.

This work involves the investigation of phenylcarbazole (PhCz), triphenylamine (NPh<sub>3</sub>), and various CT compounds based on carbazole or a diphenylamine donor, including common organic semiconductors, 4,4'-bis(carbazol-9-yl)-biphenyl (CBP) and *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,10-biphenyl-4,4'-diamine ( $\alpha$ -NPD), and all TADF materials that we report on. Their structural forms are illustrated in Figure 1. To understand the influence of HF exchange percentage (HF%) in XC functionals on calculated  $E_{VA}(S_1)$ , TD-DFT calculations using the BLYP (0%HF),<sup>13,14</sup> MPWLYP1M (5%HF),<sup>15</sup> TPSSH (10%HF),<sup>16</sup> B3LYP\* (15%HF),<sup>17</sup> B3LYP (20%HF),<sup>18,19</sup> PBE0 (25%HF),<sup>20,21</sup> MPW1B95 (31%HF),<sup>22</sup> BMK (42%HF),<sup>23</sup> M06-2X (56%HF),<sup>24</sup> and M06-HF (100%HF)<sup>25</sup> functionals were performed to obtain  $E_{VA}(S_1)$  of all these molecules at their  $S_0$  geometry optimized using B3LYP. As Figures 2 and S3 show, the variation of  $E_{VA}(S_1)$  strongly depends on the HF% for all molecules, almost regardless of the difference in the expression of these XC functionals. The continuous and monotonic dependence of  $E_{VA}(S_1)$  on HF% allows for an optimal HF% (OHF) in the TD-DFT calculation. We know that TD-DFT with nonhybrid functionals usually describes non-CT excited states well but

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**Figure 1.** Molecular structures of compounds investigated. The blue and red denote the positive and negative charges, respectively, after the cancellation of hole and electron in the excited state (see Figure S2).

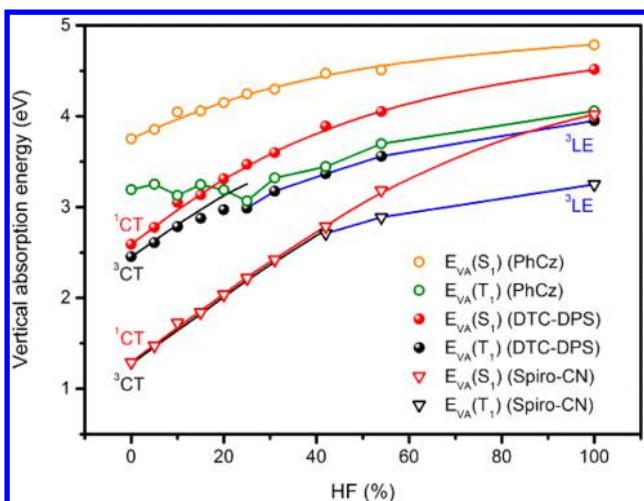
drastically underestimates transition energies for CT states, owing to a neglect of long-range Coulombic attraction between the separated electron and hole.<sup>32–34</sup> TD-HF completely removes such a self-interaction error; however, it suffers from the so-called electron correlation problem and tends to overestimate transition energies.<sup>34,35</sup> Consequently, the OHF in hybrid functionals might be related to the degree of excited-state charge separation, i.e., the amount of charge transferred from donor to acceptor. In previous studies, two indexes defining the orbitals overlap and spatial extent of a CT transition were proposed to warn of possible TD-DFT failures.<sup>36–38</sup> Herein, to establish the relationship between OHF and the CT amount ( $q$ ), a simplified approach is adopted to evaluate the new index  $q$ :

$$q_+ = e \sum_i |a_i - b_i|, a_i - b_i > 0$$

$$q_- = e \sum_i |a_i - b_i|, a_i - b_i < 0$$

where  $\sum_i a_i = 1$ ,  $\sum_i b_i = 1$ , and  $q = q_+ = q_-$ . The index  $i$  denotes the number of fragments (atoms, phenyl groups, or carbazole groups);  $a_i$  and  $b_i$  are the contribution percentages of different molecular fragments in the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO), respectively. The orbital composition analysis was done using Multiwfn.<sup>39</sup> According to the definition,  $q$  is 0.097 for PhCz, 0.764 for DTC-DPS, and 0.940 (the largest) for Spiro-CN based on their  $S_0$  geometry. As shown in Figure 2, the larger the  $q$ , the more pronounced the variation in  $E_{VA}(S_1)$  with HF%, which is expected because the transition energy errors produced by pure functionals increase with increasing degree of CT in the excitations.<sup>36</sup>

To assess the optimal HF%, we identify the experimental  $E_{VA}(S_1)$  of all studied molecules from their absorption and

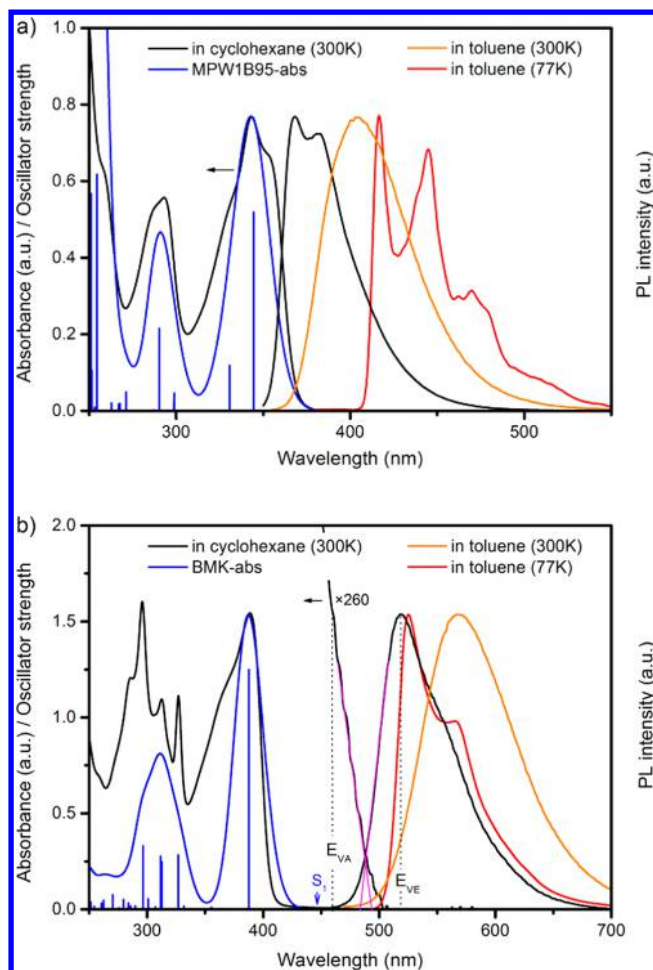


**Figure 2.** Dependence of  $E_{VA}(S_1)$  and  $E_{VA}(T_1)$  of PhCz, DTC-DPS, and Spiro-CN on the HF% in TD-DFT functionals.

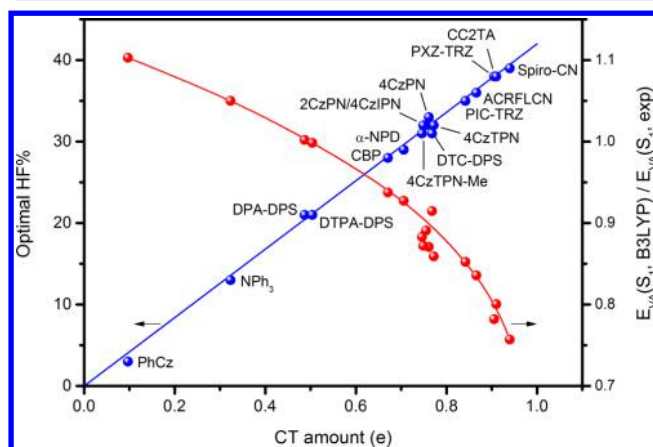
emission spectra in the nonpolar solvent cyclohexane. If the  $S_1$  transition exhibits well-defined vibronic structure, the energy of the absorption peak is  $E_{VA}(S_1)$ , such as for DTC-DPS shown in Figure 3a. If the  $S_1$  transition, which corresponds to a weak absorption or overlaps with other higher transitions, is not easily recognizable, the experimental  $E_{VA}(S_1)$  is determined from  $E_{VE}(S_1)$  and the onset of absorption and emission edges utilizing the mirror image rule (see the experimental section in the SI), such as the case of Spiro-CN shown in Figures 3b and S10a. To verify the rationality of the determination of the experimental  $E_{VA}(S_1)$ , we simulated the absorption spectra of all the molecules we studied using functionals with HF% close to the optimal HF%.<sup>40</sup> As expected, the low energy sides of the absorption spectra are satisfactorily reproduced (Figures 3 and S6–S21).

After the determination of experimental  $E_{VA}(S_1)$ , we can take the optimal HF% from the  $E_{VA}(S_1)$ -HF% curve and further assess the effect of HF% on the error of TD-DFT results. Finally, we found two significant relations: (1) the optimal HF% is proportional to the CT amount with a relation of  $\text{OHF} = 42q$ ; (2) the relative error of a vertical transition energy obtained with a given functional is highly dependent on the CT amount (Figures 4 and S22). Both relations should be independent of molecule structures because they are obtained from various compounds with different types of donors, acceptors, and molecular conformations. In fact, the prime determinant of the amount of HF exchange in a XC functional or the error of TD-DFT is the electrostatic attraction between the separated charges in the CT state, which is neglected within the pure TD-DFT functional as mentioned above. As a consequence, the above relations should also be theoretically independent of the spin direction of excited electrons.

In the following, we show how to predict the  $E_{0-0}(S_1)$  and  $E_{0-0}(T_1)$  of CT compounds by employing the above two relations. After the calculation of  $q$  based on the B3LYP-optimized  $S_0$  geometry, we can calculate the optimal HF% by the first relation to obtain  $E_{VA}(S_1)$  from the  $E_{VA}(S_1)$ -HF% curve. Considering that the above relations are independent of molecular structures, they are applied equally to the calculation of  $E_{VE}(S_1)$ . Because the optimized  $S_1$  geometries are generally sensitive to the HF% in TD-DFT,<sup>41,42</sup> the geometry optimization of the  $S_1$  state was carried out on the basis of the functional with a HF% close to the optimal HF% employed



**Figure 3.** Absorption and emission spectra of DTC-DPS (a) and Spiro-CN (b) in cyclohexane at 300 K and their 300 K emission spectra and 77 K phosphorescence spectra (delayed by 10 ms) in toluene. The theoretical absorption spectra are generated using the SWizard program with a half-bandwidth of 0.24 eV.<sup>40</sup> The local excitation energies calculated at the MPW1B95 and BMK levels are corrected by dividing by empirical factors 1.09 and 1.11, respectively.



**Figure 4.** Dependence of the optimal HF% for the calculation of  $E_{VA}(S_1)$  and the correction factor of  $E_{VA}(S_1)$  calculated using the B3LYP functional (i.e.,  $E_{VA}(S_1, \text{B3LYP})/E_{VA}(S_1, \text{exp})$ ) on the CT amount calculated at the B3LYP/6-31G\* level based on  $S_0$  geometry.

for the  $E_{VA}(S_1)$  calculations. Note that the effect of the solvation on the CT emission is stronger than on its absorption



Table 1. Comparison of Calculated  $E_{VE}(S_1)$ ,  $E_{0-0}(S_1)$ ,  $E_{0-0}(T_1)$ , and  $\Delta E_{ST}$  with Experimental Data

compound	calculated data				calculated data (in toluene)				experimental data (in toluene)			
	at gas-phase $S_0$ geometry <sup>a</sup>		at solvated $S_1$ geometry <sup>b</sup>		$E_{0-0}(^3CT)^d$ (eV)	$E_{0-0}(^3LE)^d$ (eV)	$\Delta E_{ST}^d$ (eV)	$E_{VE}(S_1)$ (eV)	$E_{0-0}(S_1)^e$ (eV)	$E_{0-0}(T_1)^f$ (eV)	$\Delta E_{ST}^f$ (eV)	
	$q$ (e)	OHF (%)	$E_{VA}(S_1)$ (eV)	$q$ (e)	OHF (%)	$E_{VE}(S_1)$ (eV)						
PhCz	0.097	4	3.68	0.186	8	3.36	3.59	3.03 (T <sub>1</sub> )	3.58	3.03 ( <sup>3</sup> LE)	0.55	
NPh <sub>3</sub>	0.323	14	3.77	0.324	14	3.45	3.53 (3.61)	3.02 (T <sub>1</sub> )	3.60	3.03 ( <sup>3</sup> LE)	0.57	
CBP	0.671	28	3.78	0.536	23	3.17	3.54 (3.48)	2.88 (T <sub>1</sub> )	3.54	2.83 ( <sup>3</sup> LE)	0.71	
$\alpha$ -NPD	0.706	30	3.34	0.851	36	2.90	3.10 (3.12)	2.45 (T <sub>1</sub> )	3.10	2.37 ( <sup>3</sup> LE)	0.73	
PhC-TRZ	0.842	35	3.34	0.858	36	2.58	3.10 (2.96)	2.74 (T <sub>1</sub> )	2.91	2.73 ( <sup>3</sup> LE)	0.18	
Spiro-CN	0.940	39	2.69	0.936	39	2.08	2.45 (2.39)	2.38 (T <sub>1</sub> )	2.44	2.38 ( <sup>3</sup> LE)	0.06	
DPA-DPS	0.487	20	3.54	0.735	31	3.07	3.30 (3.31)	2.76 (T <sub>1</sub> )	3.28	2.76 ( <sup>3</sup> LE)	0.52	
DTPA-DPS	0.504	21	3.48	0.847	36	2.90	3.24 (3.19)	2.73 (T <sub>1</sub> )	3.19	2.73 ( <sup>3</sup> LE)	0.46	
DTC-DPS	0.768	32	3.62	0.893	37	3.10	3.38 (3.36)	2.95 (T <sub>1</sub> )	3.34	2.98 ( <sup>3</sup> LE)	0.36	
CC2TA	0.910	38	3.62	0.929	39	2.72	3.38 (3.17)	2.95 (T <sub>1</sub> )	3.15	2.95 ( <sup>3</sup> LE)	0.20	
ACRFLCN	0.866	36	3.07	0.856	36	2.56	2.83 (2.82)	2.57 (T <sub>1</sub> )	2.83	2.59 ( <sup>3</sup> LE)	0.24	
PXZ-TRZ	0.905	38	2.76	0.911	38	2.21	2.52 (2.49)	2.44 (T <sub>1</sub> )	2.53	2.47 ( <sup>3</sup> CT)	0.06	
2CzPN	0.755	32	3.18	0.862	36	2.35	2.94 (2.77)	2.68	2.94	2.63 ( <sup>3</sup> LE)	0.31	
4CzPN	0.761	32	2.83	0.819	34	2.20	2.59 (2.52)	2.48	2.60	2.45 ( <sup>3</sup> LE)	0.15	
4CzIPN	0.750	32	2.83	0.767	32	2.31	2.59 (2.57)	2.49 (T <sub>1</sub> )	2.63	2.53 ( <sup>3</sup> LE)	0.10	
4CzTPN	0.772	32	2.60	0.779	33	2.08	2.36 (2.34)	2.23 (T <sub>1</sub> )	2.43	2.34 ( <sup>3</sup> CT)	0.09	
4CzTPN-Me	0.746	31	2.53	0.774	33	1.99	2.29 (2.26)	2.19 (T <sub>1</sub> )	2.33	2.24 ( <sup>3</sup> CT)	0.09	

<sup>a</sup>Optimized via DFT at the B3LYP/6-31G\* level. <sup>b</sup>Optimized via TD-DFT in toluene at the levels listed in Table S5. <sup>c</sup>The data outside parentheses are calculated by  $E_{VA}(S_1) - \Delta E_V - \Delta E_{Stokes}$  where  $\Delta E_V$  is 0 for PhCz and 0.15 eV for other compounds. The data in parentheses are calculated by  $(E_{VA}(S_1) + E_{VE}(S_1))/2$ . <sup>d</sup>Calculated through the TD-DFT results based on  $S_0$  geometry. <sup>e</sup> $E_{0-0}(S_1)$  of PhCz is determined from the highest energy peak of the emission spectrum at 300 K.  $E_{0-0}(S_1)$  of other compounds are determined from the crossing point of the normalized ( $S_1$  band) absorption and emission spectra or the emission onset at 300 K (see the Experimental Section and Figures S5–S21 in SI). <sup>f</sup>If  $T_1$  is a LE state,  $E_{0-0}(T_1)$  is determined from the highest energy peak of its phosphorescence spectrum in toluene at 77 K. If  $T_1$  is a CT state,  $E_{0-0}(T_1)$  is calculated by  $E_{0-0}(S_1) - \Delta E_{ST}$ , where  $\Delta E_{ST}$  is an experimental value (see the experimental section in the SI).

because the CT state is always more polar than its ground state. For the purpose of device application, we would prefer to obtain the zero-zero energy levels in aromatic media, and thus  $E_{VE}$  is calculated at the solvated  $S_1$  geometry with toluene. The CT amount and the calculated vertical transition energies of our studied molecules at their relaxed  $S_1$  states in toluene are listed in Table 1. We find that the calculated  $E_{VE}(S_1)$  are in reasonable accord with the peak energy of the emission bands in toluene, and the  $E_{0-0}(S_1)$  calculated by averaging  $E_{VA}(S_1)$  and  $E_{VE}(S_1)$  reproduce the experimental results with an error of  $\pm 0.06$  eV.

The TD-DFT excited state optimization for large molecules is time-consuming and is suspected to generally overestimate the CT-induced excited-state twisting,<sup>41</sup> so we considered calculating  $E_{0-0}(S_1)$  and  $E_{0-0}(T_1)$  only through a ground-state electronic structure. In principle, we can derive  $E_{0-0}(S_1)$  from the calculated  $E_{VA}(S_1)$  using

$$E_{0-0}(S_1) = E_{VA}(S_1, \text{OHF}) - \Delta E_V - \Delta E_{\text{Stokes}}$$

Here,  $\Delta E_{\text{Stokes}}$  is the Stokes-shift energy loss (0.09 eV),<sup>43</sup> derived from the PhCz energy difference between its 0-0' absorption peak in cyclohexane and its 0'-0 emission peak in toluene, which includes the contribution of solvation ( $\sim 0.06$  eV).  $\Delta E_V$  is the vibrational energy level difference between the 0-0' transition and the vertical transition. If the vertical transition agrees with the 0-0' transition,  $\Delta E_V$  is 0. If it corresponds to the 0-1' transition,  $\Delta E_V$  is about 0.15 eV for conjugated molecules. As illustrated by the absorption and emission spectra of the studied molecules in toluene, the vertical  $S_1$  transition corresponds to the 0-1' transition for most CT compounds, except for PIC-TRZ and CC2TA, for which small steric effects between the donor and acceptor allow a significant structural distortion and energy loss in the excited state. As listed in Table 1, if  $\Delta E_V$  is set to 0.15 eV, the calculated  $E_{0-0}(S_1)$  of these CT compounds shows good agreement with experiment (error  $\pm 0.03$  eV), excluding PIC-TRZ and CC2TA.

The prediction of the  $T_1$  state of a CT compound is more complicated because it could be either a CT state or a locally excited (LE) state of the donor or acceptor, with different errors in  $E_{VA}$  and different relations between  $E_{VA}$  and  $E_{0-0}$ . The analysis of the nature of the  $T_1$  state is also difficult owing to different results produced using different functionals. However, we find that the  $E_{VA}(T_1)$  points corresponding to the  $^3\text{CT}$  or  $^3\text{LE}$  transitions can be distinguished by looking at the change in  $E_{VA}(S_1) - E_{VA}(T_1)$  difference with HF%. Taking DTC-DPS as an example (Figure 2), the calculated  $S_1-T_1$  energy differences using functionals with HF% over 25% are distinctly greater than those with HF% smaller than 20%. From our previous study, the  $T_1$  of DTC-DPS is known to be a  $^3\pi\pi^*$  state localized at the PhCz moieties.<sup>6</sup> As seen in Figure 2, if the HF% is higher than 25%, the calculated  $E_{VA}(T_1)$  of DTC-DPS is close to that of PhCz. However, if the HF% decreases from 25% to 0%, the  $E_{VA}(T_1)$  of DTC-DPS tends to be lower than that of PhCz and close to its  $E_{VA}(S_1)$ . From the comparison, we could infer that the  $^3\text{CT}$  state contributes mainly the obtained  $T_1$  state of DTC-DPS at the functionals with less than 20% HF exchange. Because the CT excitations are exquisitely sensitive to the asymptotic behavior of the XC potential than local excitations,<sup>35</sup> the  $^3\text{CT}$  states of DTC-DPS, calculated using functionals with small HF%, are underestimated and lying below the  $^3\text{LE}$  states to be  $T_1$  states.

To accurately predict  $E_{0-0}(T_1)$  for CT compounds, we suggest calculating  $E_{0-0}(^3\text{CT})$  and  $E_{0-0}(^3\text{LE})$  independently and make a comparison. Because  $^3\text{CT}$  and  $^1\text{CT}$  have the same orbital transitions and the same CT amount, the relative error of their energies calculated by a given functional should be the same according to the second relation. For example, if  $E_{VA}(T_1, \text{BLYP})$  is the energy of a  $^3\text{CT}$  transition, we can obtain an accurate  $E_{0-0}(^3\text{CT})$  with

$$E_{0-0}(^3\text{CT}) = E_{0-0}(S_1) - [E_{VA}(S_1, \text{OHF}) - C \cdot E_{VA}(T_1, \text{BLYP})]$$

where  $C = E_{VA}(S_1, \text{OHF})/E_{VA}(S_1, \text{BLYP})$ . It is known that the splitting energy between  $^1\text{CT}$  and  $^3\text{CT}$  highly depends on the overlap of the involved orbitals,<sup>44</sup> as well as the CT amount. Herein, we assume that the twisting distortion in the CT state, a large-amplitude nuclear rearrangement, is not significant, and therefore the CT amount and the energy difference between  $^1\text{CT}$  and  $^3\text{CT}$  are close at their nonrelaxed and relaxed  $S_1$  states. This is expected as these CT compounds are doped into organic semiconductor films and might also happen in the less polar solvent toluene, because the photophysical properties (e.g., emission maximum and fluorescence rate) of these compounds in toluene are close to those in the doped films.<sup>4-10</sup>

Similarly, according to the second relation, we can anticipate that the relative error of  $E_{VA}(^3\text{LE})$  calculated using a given functional should be close for different CT compounds because the CT amount is smaller for a locally excited state. For PhCz, the calculated  $E_{VA}(T_1)$  using BMK, M06-2X, and M06-HF is 1.10, 1.18, and 1.30 times higher than the experimental value, respectively, and hence provides the correction factor  $C$  in the following:

$$E_{0-0}(^3\text{LE}) = [E_{VA}(T_1)/C] - \Delta E_{\text{Stokes}}$$

Eliminating the data points which do not belong to  $^3\text{LE}$  transitions in 42–100%HF, we calculated the  $E_{0-0}(^3\text{LE})$  of all studied molecules in toluene using this equation with the same correction factors as for PhCz and found that the average  $E_{0-0}(^3\text{LE})$  reproduced experimental values with an error as small as  $\pm 0.03$  eV (Tables 1 and S6). Employing this method, we further examined  $E_{0-0}(T_1)$  of some small planar  $\pi$ -conjugated molecules with  $E_{0-0}(T_1)$  varying from 1.5 to 3.0 eV and obtained satisfactory results (Table S7).

After obtaining the  $E_{0-0}(^3\text{CT})$  and  $E_{0-0}(^3\text{LE})$  of all CT compounds in toluene independently, we assessed which was  $T_1$  and found the result is in good agreement with experimental ones (Table 1). For example, Figure 3 and previous studies indicated that the  $T_1$  of DTC-DPS and Spiro-CN is a  $^3\text{LE}$  state with an  $E_{0-0}$  of 2.98 and 2.38 eV,<sup>6,45</sup> respectively, and our calculated values are 2.95 and 2.38 eV, respectively. Except for the triazine compounds CC2TA and PIC-TRZ, the calculated  $\Delta E_{\text{ST}}$  is also consistent with the experimental results.

Note that another approach to treat CT compounds with TD-DFT is to use range separated hybrid functionals, including the widely used CAM-B3LYP,<sup>46</sup> LC- $\omega$ PBE,<sup>47-49</sup>  $\omega$ B97XD,<sup>50</sup> and LC-BLYP.<sup>51</sup> For comparison purposes, they have also been used in this work but found to dramatically overestimate the  $E_{VA}(S_1)$  of our studied molecules (Table S4), which may be due to the fact that the present intramolecular CT transitions are shorter ranged.

In short, our study showed that a strong relation exists between the amount of charge transferred in the excitation

process and the optimal HF% in XC functional, and that the relative error of a vertical transition energy calculated using a given functional is significantly dependent on the CT amount. Making full use of these relations, predicting the  $E_{\text{VA}}(S_1)$ ,  $E_{\text{VE}}(S_1)$ ,  $E_{0-0}(S_1)$ , and  $E_{0-0}(T_1)$  of CT compounds is possible in TD-DFT. More applications of our excited-states method to TADF molecular design will be reported elsewhere.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental details and photophysical and raw computed data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

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### Notes

The authors declare no competing financial interests.

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## ■ REFERENCES

- (1) Brütting, W.; Adachi, C. *Physics of Organic Semiconductors*, 2nd Completely New Revised ed.; Wiley-VCH: New York, 2012.
- (2) Köhler, A.; Bässler, H. *Mater. Sci. Eng., R* **2009**, *66*, 71–109.
- (3) Valeur, B. *Molecular Fluorescence Principles and Applications*; Wiley-VCH: New York, 2002; p 41.
- (4) Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. *Appl. Phys. Lett.* **2011**, *98*, 083302.
- (5) Nakagawa, T.; Ku, S.-Y.; Wong, K.-T.; Adachi, C. *Chem. Commun.* **2012**, *48*, 9580–9582.
- (6) Zhang, Q.; Li, J.; Shizu, K.; Huang, S.; Hirata, S.; Miyazaki, H.; Adachi, C. *J. Am. Chem. Soc.* **2012**, *134*, 14706–14709.
- (7) Lee, S. Y.; Yasuda, T.; Nomura, H.; Adachi, C. *Appl. Phys. Lett.* **2012**, *101*, 093306.
- (8) Mehes, G.; Nomura, H.; Zhang, Q.; Nakagawa, T.; Adachi, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 11311–11315.
- (9) Tanaka, H.; Shizu, K.; Miyazaki, H.; Adachi, C. *Chem. Commun.* **2012**, *48*, 11392–11394.
- (10) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234–238. 4CzTPN-Ph is not included in this work due to its poor solubility in cyclohexane and excessive size for excited state geometry optimization.
- (11) Runge, E. E.; Gross, K. U. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
- (12) Marques, M. A. L.; Gross, E. K. U. *Annu. Rev. Phys. Chem.* **2004**, *55*, 427–455.
- (13) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (15) Schultz, N.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127–11143.
- (16) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129–12137.
- (17) Reiher, M.; Salomon, O.; Hess, B. A. *Theor. Chem. Acc.* **2001**, *107*, 48–55.
- (18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (19) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (20) Adamo, C.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *111*, 2889–2899.
- (21) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (22) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908–6918.
- (23) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405–3416.
- (24) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (25) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126–13130.
- (26) Serrano-Andrés, L.; Serrano-Pérez, J. J. Calculation of Excited States: Molecular Photophysics and Photochemistry on Display. In *Handbook of Computational Chemistry*; Leszczynski, J., Ed.; Springer: New York, 2012; p 488.
- (27) Jacquemin, D.; Planchat, A.; Adamo, C.; Mennucci, B. J. *Chem. Theory Comput.* **2012**, *8*, 2359–2372.
- (28) Jacquemin, D.; Perpète, E. A.; Ciofini, I.; Adamo, C. *J. Chem. Theory Comput.* **2010**, *6*, 1532–1537.
- (29) Sears, J. S.; Koerzdoerfer, T.; Zhang, C.-R.; Brédas, J.-L. *J. Chem. Phys.* **2011**, *135*, 151103.
- (30) Pabst, M.; Sundholm, D.; Köhn, A. *J. Phys. Chem. C* **2012**, *116*, 15203–15217.
- (31) Milián-Medina, B.; Gierschner, J. *Org. Electron.* **2012**, *13*, 985–991.
- (32) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 2943–2946.
- (33) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007–4016.
- (34) Dreuw, A.; Head-Gordon, M. *Chem. Rev.* **2005**, *105*, 4009–4037.
- (35) Magyar, R. J.; Tretiak, S. *J. Chem. Theory Comput.* **2007**, *3*, 976–987.
- (36) Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J. *J. Chem. Phys.* **2008**, *128*, 044118.
- (37) Bahers, T. L.; Adamo, C.; Ciofini, I. A. *J. Chem. Theory Comput.* **2011**, *7*, 2498–2506.
- (38) Ciofini, I.; Bahers, T. L.; Adamo, C.; Odobel, F.; Jacquemin, D. *J. Phys. Chem. C* **2012**, *116*, 11946–11955.
- (39) Lu, T.; Chen, F. W. *J. Comput. Chem.* **2012**, *33*, 580–592.
- (40) The UV-Vis spectra were calculated using the SWizard program. Gorelsky, S. I.; Lever, A. B. P. *J. Organomet. Chem.* **2001**, *635*, 187–196.
- (41) Harbach, P. H. P.; Dreuw, A. The Art of Choosing the Right Quantum Chemical Excited-State Method for Large Molecular Systems. In *Modeling of Molecular Properties*; Comba, P., Ed.; Wiley-VCH: New York, 2011; pp 37–38.
- (42) Guido, C. A.; Knecht, S.; Kongsted, J.; Mennucci, B. J. *Chem. Theory Comput.* **2013**, *9*, 2209–2220.
- (43) Stokes-shift is the gap between the 0–0 transitions of absorption and fluorescence: Petr, K.; Jakob, W. *Photochemistry of Organic Compounds: From Concepts to Practice*; Wiley-VCH: New York, 2009; p 43.
- (44) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH: Weinheim, Germany, 1995; p 14.
- (45) Ku, S.-Y.; Hung, W.-Y.; Chen, C.-W.; Yang, S.-W.; Mondal, E.; Chi, Y.; Wong, K.-T. *Chem. Asian J.* **2012**, *7*, 133–142.
- (46) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (47) Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 234109.
- (48) Vydrov, O. A.; Heyd, J.; Krukau, A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 074106.
- (49) Vydrov, O. A.; Scuseria, G. E.; Perdew, J. P. *J. Chem. Phys.* **2007**, *126*, 154109.
- (50) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
- (51) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540–3544.