Effect of hybridized local and charge transfer molecules rotation in excited state on exciton utilization

Gang Sun¹, Xin-Hui Wang¹, Jing Li², Bo-Ting Yang⁴, Ying Gao⁵ & Yun Geng³

The fluorescent molecules utilizing hybridized local and charge-transfer (HLCT) state as potential organic light-emitting diodes materials attract extensive attention due to their high exciton utilization. In this work, we have performed the density functional theory method on three HLCT-state molecules to investigate their excited-state potential energy surface (PES). The calculated results indicate the T₁ and T₂ energy gap is quite large, and the T₂ is very close to S₁ in the energy level. The large gap is beneficial for inhibiting the internal conversion between T₁ and T₂, and quite closed S₁ and T₂ energies are favor for activating the T₂ → S₁ reverse intersystem crossing path. However, considering the singlet excited-state PES by twisting the triphenylamine (TPA) or diphenylamine (PA) group, it can be found that the TPA or PA group almost has no influence on T₁ and T₂ energy levels. However, the plots of S₁ PES display two kinds of results that the S₁ emissive state is dominated by charge-transfer (CT) or HLCT state. The CT emission state formation would decrease the S₁ energy level, enlarge the S₁ and T₂ gap, and impair the triplet exciton utilization. Therefore, understanding the relationship between the S₁ PES and molecular structures is important for designing high-performance luminescent materials utilizing HLCT state.

Organic light-emitting diode (OLED) was widely studied since the first small molecules device was reported by Tang et al.¹. The luminescent materials, as the most important component of OLED, were always the focused study by materials scientists²–⁴. One most important requirement of the luminescent materials was a high photoluminescence quantum yield (PLQY). The pure organic materials utilizing hybridized local and charge-transfer (HLCT) state⁷–⁹ become potential high-efficiency OLED materials considering the low cost, less toxicity, and high exciton utilization.

Numerous highly luminous HLCT-state compounds containing triphenylamine (TPA, Fig. 1) group have been reported¹⁰–¹⁵. For example, in 2014, a series of twisting donor–acceptor (D–A) molecules with high exciton utilization efficiencies and full-color-range emissions were reported¹⁶. To enhance the proportion of radiative exciton, methods such as constructing orthogonal cyano substituted D–A structure imidazole derivative¹⁷, designing butterfly-shaped D–A chromophore¹⁸, modulating a fine proportion of charge-transfer (CT) state and locally excited (LE) state¹⁹ and choosing an appropriate substituted position, were suggested²⁰. Especially, a pure-blue emitting molecule consisting of phenanthroimidazole and phenylcarbazole-substituted anthracene (PAC, Fig. 1) was reported, and the external quantum efficiency (EQE) exceeds 10%²¹. Besides being the emitting materials, the 4-(2-(4-(diphenylamino)phenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (TPMCN, Fig. 1) was also used as host material with EQE up to 6.3% and exciton utilizing efficiency of 64%²². More recently, triphenylamine-acridine (TPA-9AC, Fig. 1) was reported to be a visualization and ultrasensitive fluorescence sensor for diethyl chlorophosphate vapor fast and accurate detection²³.

Taking the carbazole-dicyanobenzene molecule 4CzIPN (Fig. 1) and triphenylamine-thiadiazole molecule TPA-NZP (Fig. 1) as theoretical models, Pan et al. pointed out different reverse intersystem crossing (RISC) paths (T₁ → S₁ for 4CzIPN and T₂ → S₁ for TPA-NZP) by comparing the singlet exciton utilization formats using density functional theory calculation²⁴. The systematic calculations on accurate description of HLCT state also

¹College of Science, Beihua University, Jilin 132013, People’s Republic of China. ²Jilin Provincial Key Laboratory of Straw-Based Functional Materials, Institute for Interdisciplinary Biomass Functional Materials Studies, Jilin Engineering Normal University, Changchun 130052, People’s Republic of China. ³Faculty of Chemistry, Northeast Normal University, Changchun 130024, People’s Republic of China.

¹¹email: ybt199@126.com; gaoy029@163.com
demonstrate that the ωB97XD or optimally tuned range-separated functional can provide a better description of HLCT state\(^{25,26}\).

It is observed that molecules containing TPA group show a sharp emission wavelength dependence on solvent polarity\(^{27-30}\). For example, the work done by Xia et al. proposed the explanation that the emissions of cyano-substituted oligo a-phenylenevinylene-1,4-bis(\(R\)-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (CNDPASDB, Fig. 1) were from the LE state in a low-polarity solvent but were from the CT state in the high-polarity solvent\(^{31}\). An overall theoretical investigation of TPA-NZP also concluded the excited state changed from HLCT character to complete intramolecular CT with increasing solvent polarities, followed by increased non-radiative decay rate\(^{32}\).

Huang et al. also suggested an aggregation-induced emission mechanism that a conversion is from dark twisted intramolecular charge transfer (TICT) excited state to emissive quasi-TICT state because that the restriction of molecular rotation was lower in the amorphous film than in power and crystalline\(^{33}\). The fluorescent molecules atomistic molecular dynamics simulation of deposition process showed that the torsion angles between donor and acceptor groups have a broadened distribution around 90 degrees due to the thermal fluctuation and intermolecular interaction\(^{34}\). Based on reported compounds (Fig. 1), namely 1,2-bis(carbazol-9-yl)-4,5-dicyanobenzene (2CzPN) and (4CzIPN), the theoretical simulation of bulk amorphous phase also indicated that the torsion angles between donor and acceptor are in a broad distribution, and the RISC is a dynamical process with the varying molecular structures\(^{35,36}\).

Ma et al. have proposed the hot-exciton RISC path of the higher triplet state to the single state \((T_2 \rightarrow S_1/S_2)\) to explain the large proportion of radiative singlet exciton for HLCT-state molecules. However, we wonder whether the excited-state \((S_n, T_1, T_2)\) energy levels would lead to the variations between \(S_1\) and \(T_2\) gaps and affect the RISC process with molecular rotation. Thus, in this work, taking reported HLCT-state molecules (1, 2, and 3) as examples (Fig. 2a), we have calculated the excited-state potential energy surface (PES) by twisting TPA (Fig. 1) or diphenylamine (PA, Fig. 1) using the time-dependent density functional theory (TD-DFT) method. The calculated results indicate that twisting TPA or PA almost has no influence on \(T_1\) and \(T_2\) energy levels, but would affect the \(S_1\) energy level and the \(T_2 \rightarrow S_1\) RISC process. Therefore, understanding the relationship between the \(S_n\) PES and molecular structures is important for designing high-performance luminescent materials utilizing HLCT state.

**Computational details**

In this work, the ground-state \((S_0)\) geometries of 1, 2, and 3 (Fig. 2a) were optimized at density functional theory (DFT) calculations M06-2X/Def2SVP level. The lowest singlet excited state \((S_1)\) was obtained with time-dependent density functional theory (TD-DFT) M06-2X/Def2SVP level. Two low-lying triplet excited-state geometries \((T_1, T_2)\) were optimized using the same M06-2X/Def2SVP considering the Tamm-Dancoff approximation (TDA)\(^{37,38}\) for avoiding the issue of triplet instability. The corrected linear response (cLR) approach\(^ {39}\) was employed to obtain the total energies of \(S_n\), \(T_1\), and \(T_2\) excited-state structures. In all calculations, the dimethylsulfoxide (DMSO) solvent under the SMD model\(^ {40}\) was used to consider the solvent effect because that the high polar DMSO was prone to stabilize the charge-transfer state. To analyze the excited-state \((S_n, T_1, \text{and } T_2)\)
properties, the vertical singlet and triplet excited states with M06-2X/Def2SVP were calculated based on their S0 structures. Besides, the S1, T1, and T2 excited-state potential energy surface (PES) was performed by twisting TPA or PA group with a scan step of 10 degrees. All calculations were accomplished by Gaussian 16 program41. The natural transition orbitals, electron and hole analysis and structural comparison among S1, T1, and T2 excited states were obtained by Multiwfn program42.

Consent to participate. All authors agree to participate.

Consent for publication. All authors agree for publication.

Result and discussion

Excited-state properties of 1, 2 and 3. Most reported works explain the high exciton utilization of HLCT-state molecules by analyzing the vertical singlet and triplet excited-state energy levels. In this work, we have optimized the ground-state, singlet, and triplet excited-state structures (S0, S1, T1, and T2) and calculated their relatively adiabatic energies. For better describing the excited-state properties, we also illustrate the natural transition orbitals (NTOs) and the associated weights (v) for the singlet (S1), triplet (T1 and T2) states. However, the v values for some excited states are far away from 100% (in Fig. 2b), and the NOTs are not enough to describe the excited-state properties. Therefore, we further to depict the hole and electron distribution to supplement the NTOs. To analyze the excited states (S1, T1, and T2) properties, the hole and electron distribution were calculated with three methods (CAM-B3LYP, M06-2X, and ωB97XD) based on their S0 structures.

The overlap of hole and electron (Sr), separation degrees of hole and electron (t), distance between centroid of hole and electron (D), and overall mean span of hole and electron (H) (in Table S1-S3) were used to describe the quantitative representation of hole and electron distribution, and there are tiny differences in these parameters. However, three methods give similar excited-state characteristics for S1, T1, and T2 states. Figure S1 depicts the electron and hole distribution obtained with CAM-B3LYP, ωB97XD and M06-2X methods. According to the

Figure 2. (a) Molecular structures of 1, 2, and 3. (b) Natural transition orbitals of S1, T1, and T2 excited-state with M06-2X/Def2SVP based on ground-state structures. (c) Relative S1, T1, and T2 energy levels with M06-2X/Def2SVP and a structural comparison among S1, T1, and T2 structures. S1 (orange); T1 (green); T2 (cyan). (b) Drawn by GaussView 6.0 and Multiwfn programs; (c) is drawn by VMD 1.9.1. program.
hole and electron distribution, the $S_1$, $T_1$, and $T_2$ states of $1$, $2$, and $3$ display main locally excited (LE) and very slight charge-transfer (CT) natures.

We take the plot (Fig. 2b) with M06-2X as an example to discuss the NTOs. As seen in Fig. 2b, the $S_1$ states of $1$, $2$, and $3$ display main LE and very slight CT natures. For example, the NTOs of $1$ mainly locate on the anthracene group and the middle phenyl ring with little CT from the TPA to anthracene group. Both NTOs of $2$ and $3$ are delocalized over the whole molecules. Such high LE percentages in $S_1$ states were beneficial for high fluorescence radiative rate. Similarly, the $T_j$ states of $1$, $2$, and $3$ also possess main LE and little CT natures. For example, the NTOs of $1$ are mainly distributed on the anthracene group, and both $2$ and $3$ display the NTOs over 2-phenylquinazoline group and middle phenyl ring. As for $T_2$, $1$, $2$, and $3$ have dominant LE characteristics. $1$ has NTOs over the TPA group, and the NTOs of $2$ and $3$ locate over the whole molecules.

Taking $S_0$ as a reference, the relative $S_1$, $T_1$, and $T_2$ energy levels are depicted in Fig. 2c. For all molecules ($1$, $2$, and $3$), the $T_2$ is quite close to $S_1$ in energy levels, and such a small $T_2$ and $S_1$ gaps are apt to realize $T_2 \rightarrow S_1$ reverse intersystem crossing (RISC) path. Besides, compared to the $S_1$ and $T_2$ gaps, the $T_1$ and $T_2$ gaps of all molecules ($1$, $2$, and $3$) are relatively large and beneficial to suppress the $T_1$ and $T_2$ internal conversion, leading to more $T_2$ population. The combination of more $T_2$ population and negligible $T_2$ and $S_1$ gaps is advantage for $T_2 \rightarrow S_1$ RISC, which is consistent with the explanation of the large proportion of radiation singlet exciton for HLCT-state molecules. The $1$ and $2$ have similar structures, but the $T_1$ and $T_2$ gap of $1$ and $2$ are $1.14$ eV and $0.75$ eV, indicating a slight geometric variation has a huge influence on $T_1$ and $T_2$ energy gap. Consequently, a careful group combination for designing novel luminescent materials utilizing HLCT state is important.

To quantify the geometric change, we also summarize the typical bond lengths (BL1 and BL2) and dihedral angles (DA1 and DA2) (shown in Fig. 2a) and Table S4) in $S_0$, $S_1$, $T_1$, and $T_2$ structures. Upon electron excitation from $S_0$ to $S_1$, $T_1$, and $T_2$, the DA have more noticeable variation (−45.9° to −69.0° for $1$) than DA2 (−28.8° to −38.9° for $1$). Likewise, the BL2 variation between $S_0$ and excited state ($S_1$, $T_1$, and $T_2$) is smaller than BL1, and the differences are below 0.03 Å. The BL1 and BL2 variations show the opposite variations to DA1 and DA2. The larger rotations lead to shorten bond lengths between TPA (or PA) and various groups. Figure 2e depicts a geometric comparison among the $S_0$, $T_1$, and $T_2$, and the structure deviation are mostly originated from the DA1 and DA2.

**Singlet excited-state potential energy surface by twisting TPA or PA group.** The results with non-restricted optimized $S_0$, $S_1$, and $T_2$ structures are consistent with the hot-exciton RISC path proposed by Ma et al. However, upon the excited states ($S_1$, $T_1$, and $T_2$), the stable CT state formation by twisting TPA or PA would affect the $T_2$ and $S_1$ gap and RISC process. On one hand, if the CT state is the most stable emission state, the decrease of the $S_1$ state would affect the quantum efficiency by decreasing the fluorescence decay rate and aggravating the non-radiative relaxation. On the other hand, the enlarging $S_1$ and $T_2$ gap originated from the decreased $S_1$ energy level would weaken the $T_2$ exciton utilization. Like-TADF molecules based on donor and acceptor groups through a single bond, the molecular rotation was easily activated and would generate a large spectrum of conformations at room temperature. For $1$, $2$, and $3$ (Fig. 2a), the donor and acceptor groups are connected via a flexible single bond, therefore, the $S_0$, $S_1$, $T_1$, and $T_2$ CT states by twisting TPA or PA were calculated.

At first, we performed the triplet excited-state ($T_1$ and $T_2$) potential energy surface (PES) (in Figure S2) with twisting TPA or PA. It can be found that almost all $T_1$ and $T_2$ energies are increased with twisting TPA or PA, meaning that molecular rotations are difficult to realize upon $T_1$ and $T_2$ PES. Consequently, the $T_1$ and $T_2$ energy levels are almost constant. Further, the singlet excited-state potential energy surface ($S_1$ PES) with twisting TPA or PA with a scan step of 10 degrees has been performed.

The vertical $S_1$ states of three HLCT-state molecules based on $S_0$, structures (in Table S5) display large oscillator strength in a range from 0.3560 to 0.9085, indicating main LE transition and high fluorescence emission. Figure 3b depicts the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). All $S_1$ states are attributed to a mixture of more HOMO $\rightarrow$ LUMO and less HOMO $1$ $\rightarrow$ LUMO contributions (Fig. 3a). For example, $3$ possesses a total HOMO $\rightarrow$ LUMO (80%) transition with HOMO mainly diffused over TPA and LUMO localized on the 2-phenylquinazoline group (Fig. 3b). The HOMO $1$ of $3$ is distributed over the whole molecules, and the HOMO $1$ $\rightarrow$ LUMO transition presents the main LE characteristic. The $S_1$ states of $1$, $2$, and $3$ display a combination of CT and LE features.

In terms of twisting TPA (DA1) or PA (DA2) (Fig. 3c,d), the plots of $S_1$ PES show three variation tendencies. It can be concluded that the CT state of $3$ is very easy to realize by twisting TPA or PA. But the TPA or PA of $2$ is very different to twist on the $S_1$ PES. The CT state formation of $1$ is in a barrierless process by twisting TPA, but not for PA. To illustrate the excited-state properties, Table S6-S13 lists the oscillator strength, transition configuration, and frontier molecular orbitals of $1$, $2$, and $3$ with twisting TPA or PA.

On the $S_1$ PES of $1$ and $3$ with twisting TPA, the CT state is more stable than the HLCT state and would become the finally stable emission state, suppressing small energy barriers (0.05 eV for $1$ and 0.02 eV for $3$). At small DA1, the $S_1$ states of $1$ contain a main HOMO $\rightarrow$ LUMO transition, but a mixture of HOMO $\rightarrow$ LUMO and HOMO $1$ $\rightarrow$ LUMO transitions at 70°−80° is found. With increasing DA1, the HOMO shifts from the whole molecules to the TPA group, and LUMO moves from the anthracene and the middle phenyl ring to the whole anthracene (Table S8). Finally, the $S_1$ state (DA1 = 90 degrees) is a total CT character with a low f (nearly zero). The $S_1$ states of $3$ are assigned to HOMO $\rightarrow$ LUMO in a percentage range of 20%−90% with increased DA1. Considering orbital distribution (Table S10), the initial HOMO shows a high degree of localization of electron density on the whole molecule, and transfers to TPA with increasing DA1. Upon the TPA rotation process, LUMO is always distributed on the 2-phenylquinazoline and the middle phenyl ring. When DA1 = 90 degrees, a noticeably separated HOMO and LUMO for CT state is formed, and f is nearly approaching to zero. However, the $S_1$ energies of $2$ are increasing with twisting TPA (Fig. 3c). The energy is the highest point on the $S_1$ PES (DA1 = 90 degrees), indicating that TPA rotation of $2$ is restrained. Therefore, the relative $S_1$ and $T_1$ energy levels
are almost unchanged and have no influence on the $T_2 \rightarrow S_1$ RISC process. Different from other HLCT molecules, the $S_1$ states have large $f$ values in a range from 0.991 to 1.433 (Table S6). With twisting TPA group, the transition configurations (Table S9) change from HLCT to total LE, accompanied by high $f$.

As with twisting PA (Fig. 3d), the relative energies of $1$ and $2$ increase linearly with increasing $\Delta A_2$, indicating that the PA rotation of $1$ and $2$ on $S_1$ PES need to overcome the high energy barrier to realize. The $S_1$ states of $1$ contain a major HOMO $\rightarrow$ LUMO (Table S7). As with twisting PA, the HOMO is initially delocalized over the whole molecules and shifts to the anthracene and middle phenyl ring, and the LUMO show almost complete localization on the anthracene and middle phenyl ring. Finally, the $S_1$ state ($\Delta A_2 = 90$ degrees) of $1$ contains the main LE state and has non-zero $f$ (Table S6). The $S_1$ states of $2$ contain a major HOMO $\rightarrow$ LUMO and minor HOMO-1 $\rightarrow$ LUMO. Along twisting PA, the HOMO and HOMO-1 are always localized over the whole molecules, and LUMO is distributed on the phenanthrene and middle phenyl ring (Table S12). When the $\Delta A_2$ is 90 degrees, the $S_1$ state displays the main LE characteristic and large $f$ (Table S6). With increasing $\Delta A_2$, the $S_1$ energy of $3$ is decreasing, and a stable CT state would form in a barrierless process by twisting PA. The HOMO $\rightarrow$ LUMO (84–90%) transition gives dominant contributions to $S_1$ states along twisting PA. At small $\Delta A_2$, the HOMO is mostly distributed on the TPA and a small part on the 2-phenylquinoxaline but shift to the TPA group with increasing $\Delta A_2$, Table S13. When the $\Delta A_2$ is 90 degrees, the HOMO is centered on the PA group, while LUMO are distributed on 2-phenylquinoxaline and middle phenyl ring with $f$ nearly to zero for $S_1$ state.

In the excited state, the CT states ($\Delta A_1 = 90$ degrees) of $1$ and $3$ ($\Delta A_1/\Delta A_2 = 90$ degrees) are easy to populate via twisting TPA or PA, accomplished by decreased $f$ and $S_1$ emission efficiency. Moreover, the formation of stable CT states would enlarge the $S_1$ and $T_2$ gap, weaken the $T_2$ to $S_1$ RISC and decrease the triplet exciton utilization.

Figure 3. (a) $S_1$ transition configuration of $1$, $2$, and $3$, (b) HOMO-1, HOMO and LUMO distribution, (c) $S_1$ PES by twisting TPA, (d) $S_1$ PES by twisting PA.
Conclusion
In conclusion, taking molecules 1, 2, and 3 as examples, we have investigated the excited-state potential energy surface (PES) by twisting triphenylamine (TPA) or diphenylamine (PA) by density functional theory and time-dependent density functional theory calculations. The calculated relative total energy indicated that the T₂ and T₁ energy gap is large, and T₁ is closed to S₁ in energy levels under the case of non-restricted excited-state optimizations. Meanwhile, the S₁ states of 1, 2, and 3 have a mixture of locally excited (LE) and charge-transfer (CT) characteristics, high oscillator strength, and high fluorescence emission efficiency. Considering the excited state PES, the T₁ and T₂ energy levels are almost constant. However, for the S₁ PES, it can be found that twisting TPA or PA would stabilize the CT state, which would seriously damage the quantum efficiency. For example, the CT states of 3 are very easy to realize no matter by twisting TPA or PA. The stable CT state formation of 3 would enlarge the energy gap between S₁ and T₂ and decrease the T₂ exciton utilization. However, the TPA or PA group of 2 is very different to twist in the S₁ PES, and S₁ and T₂ energy gap is almost unchanged. For 1, the CT states are formed in a barrierless process by twisting TPA, but not for PA. Therefore, understanding the relationship between the S₁ PES and molecular structures is important for designing high-performance luminescent materials utilizing HLCT state.

Data availability
The authors declare that the data and manuscript are availability.

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Correspondence and requests for materials should be addressed to B.-T.Y. or Y.G.

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