Deepening Insights of AIE plus TICT activated fluorescent sensor mechanism in Probe Molecule DPA-CI

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Abstract

The DPA-CI molecule is a novel fluorescent sensing probe synthesized with TICT and AIE properties. It can detect phosgene, generating DPA-CI-PS. We investigated their photophysical mechanisms in THF solvent using DFT and TD-DFT methods. Large torsion angles and noticeable charge separation confirmed that the TICT occurs in DPA-CI. Due to the formation of a robust cyclic structure, the TICT is inhibited in DPA-CI-PS. Besides, based on NBO analysis, we demonstrated that DPA-CI-PS exhibits significant AIE characters. This work clearly illuminates the detection mechanism, which offers theoretical insights valuable for developing efficient fluorescent sensing probes.

Keywords:
Twisted intramolecular charge transfer, aggregation-induced emission, density functional theory, natural bond orbital analysis, natural transition orbits
1. Introduction

Since Tang et al. proposed aggregation-induced emission (AIE) through solid-state dilution experiment in 2001, molecules with AIE phenomenon have become a new hot topic [1–7]. Due to its characteristics of a sharp increase in fluorescence intensity in the aggregated state, it can be well applied to organic light emitting diodes (OLEDs) and electroluminescent materials [8–12]. In contrast, molecules with twisted intramolecular charge transfer (TICT) characteristics can effectively promote the non-radiative transition, which may weaken the fluorescence intensity. The internal distortion within the molecules is limited to some extent when molecules are in aggregate state. This limitation hinders the energy loss generated by non-radiative TICT processes. In general, people prioritize effectively suppressing TICT process to enhance the AIE phenomenon[13–19]. Han et al observed the TICT and AIE properties of THF/water solution at different concentrations in NSTPE[20]. They confirmed that the emission behaved "on-off-on" TICT and AIE characteristics as the water concentration increased. Zhang et al. synthesized a fluorescent probe TPB-CN based on TICT and AIE characteristics to detect CLO [21]. They suggested that the reason why the fluorescence of TPB-CN reaction changed from yellow to blue at 440 nm was the inhibition of TICT by AIE effect. Li et al. explored the AIE properties of TDAPA molecules in THF/water solution by changing different pressures [22]. They demonstrated that the AIE effect could be effectively regulated by varying the pressure and successfully suppressed the TICT effect of the molecule.

Recently, Hu et al. synthesized an fluorescent probe molecule DPA-CI based on the properties of TICT and AIE for portable and visual identification of highly toxic phosgene [23]. They using fluorescence spectroscopy technology, confirmed that the detecting fluorescence characteristics before and after the change. At present, there is no in-depth analysis of its the specific internal mechanism. Therefore, it is important to explore the TICT and AIE mechanisms of DPA-CI and DPA-CI-PS molecules from a theoretical perspective.
In our work, the TICT and AIE process of DPA-CI and DPA-CI-PS molecules in THF solution were explored. We performed conformational optimization on DPA-CI and DPA-CI-PS molecules, and studied the excited-state dynamics properties of DPA-CI and DPA-CI-PS in THF solvent through density functional theory (DFT) calculations. We have obtained important information about the absorption of DPA-CI and DPA-CI-PS. And also elucidated the differences in frontier molecular orbitals, the fine spectrum, natural transition orbitals and the hole-electron analysis for different electronic states. From the charge transfer characteristics, we also calculated the charge transfer properties. The changes of optical properties caused by TICT plus AIE phenomenon are studied deeply.

2. Computational method

Our theoretical calculations are based on the Gaussian package. The ground ($S_0$) and excited ($S_1$) states geometry of DPA-CI and DPA-CI-PS molecules in THF solution are fully optimized at the B3PW91/6-31G(d) [24–30] level by using the density functional theory (DFT) [31–38] and the time-dependent density functional theory (TDDFT) [39–46]. The calculations were carried out in THF solvent using the polarized continuum model in integral equation form (IEFPCM) [47]. Five different functionals with 6–31G (d) basis set are selected to simulate the absorption spectra of DPA-CI in THF solvent (Table 1), and the results obtained by the B3PW91 (434.7 nm) functional are the closest to the experimental (425 nm) value. The hole-electron analysis and the frontier molecular orbitals are implemented using the Multiwfn program. Furthermore, the natural transition orbitals are obtained by the VMD soft-ware [48–51].

| Table 1 Calculated absorption peak (nm) of DPA-CI utilizing five different functionals. (Exp. is the experimental value) |
|---------------------------------|-------------|-------------|-------------|-------------|-------------|
| $\lambda_{abs}$                | B3LYP       | CAM-B3LYP   | M06-2X      | B3PW91      | PBE         | Exp.        |
|                                | 435.3       | 364.6       | 370.6       | 434.7       | 527.7       | 425         |

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3. Results and discussion

3.1 Optimized geometric structures

The optimized structures of DPA-CI and DPA-CI-PS molecules in the $S_0$ and $S_1$ states in THF solvent are depicted in Fig. 1. In DPA-CI, the twisting angles of the three benzene rings in the $S_0$ state are smaller than those in the $S_1$ state. However, in the case of the DPA-CI-PS molecule, similar twisting occurs in the three benzene rings. To further investigate the torsional differences between the two molecules, a detailed examination of their configurations was conducted. It was observed that, upon reaction with phosgene, a new cyclic structure was formed in the 3-(1H-benzimidazol-2-yl)-2H-chromen-2-imine moiety of the DPA-CI molecule, where one N-H bond was cleaved, forming a connection with a carbon atom. Due to the stability conferred by this cyclic structure, the DPA-CI-PS molecule lacks a rotatable dihedral angle compared to DPA-CI. This results in a more stable structure for DPA-CI-PS, thus, we can preliminarily infer that the TICT phenomenon is more significant in the DPA-CI molecule than in the DPA-CI-PS molecule.

![Optimized geometric structures of DPA-CI and DPA-CI-PS in THF solvent in the $S_0$ and $S_1$ states.](image)

**Fig. 1.** Optimized geometric structures of DPA-CI and DPA-CI-PS in THF solvent in the $S_0$ and $S_1$ states. ($C_2$-$N_1$-$C_3$-$C_4$ is $\delta_1$, $C_1$-$C_2$-$N_1$-$C_5$ is $\delta_2$, $C_2$-$N_1$-$C_5$-$C_6$ is $\delta_3$, $C_7$-$C_8$-$C_9$-$N_2$ is $\delta_4$)
Table 2 Calculated transition properties of DPA-CI and DPA-CI-PS in THF solvent at the TD-DFT/B3PW91/6-31G(d) theoretical level.

<table>
<thead>
<tr>
<th>Transition</th>
<th>λ_{abs}(nm)</th>
<th>f</th>
<th>Composition</th>
<th>CI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_0→S_1</td>
<td>434.7</td>
<td>1.1846</td>
<td>H→L</td>
<td>70.32%</td>
</tr>
<tr>
<td>S_0→S_2</td>
<td>337.9</td>
<td>0.0675</td>
<td>H-1→L</td>
<td>68.75%</td>
</tr>
<tr>
<td>S_0→S_3</td>
<td>321.3</td>
<td>0.0043</td>
<td>H-2→L</td>
<td>64.04%</td>
</tr>
<tr>
<td>S_0→S_4</td>
<td>316.2</td>
<td>0.0685</td>
<td>H→L+1</td>
<td>54.30%</td>
</tr>
<tr>
<td>S_0→S_5</td>
<td>307.4</td>
<td>0.0214</td>
<td>H-3→L</td>
<td>56.46%</td>
</tr>
<tr>
<td>S_0→S_6</td>
<td>300.6</td>
<td>0.1599</td>
<td>H→L+2</td>
<td>63.92%</td>
</tr>
<tr>
<td>DPA-CI-PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_0→S_1</td>
<td>688.1</td>
<td>0.0034</td>
<td>H→L</td>
<td>95.81%</td>
</tr>
<tr>
<td>S_0→S_2</td>
<td>505.0</td>
<td>0.0993</td>
<td>H→L</td>
<td>84.86%</td>
</tr>
<tr>
<td>S_0→S_3</td>
<td>462.0</td>
<td>0.0100</td>
<td>H→L+1</td>
<td>85.40%</td>
</tr>
<tr>
<td>S_0→S_4</td>
<td>446.3</td>
<td>0.5982</td>
<td>H→L+2</td>
<td>84.41%</td>
</tr>
<tr>
<td>S_0→S_5</td>
<td>425.5</td>
<td>0.0317</td>
<td>H→L+3</td>
<td>86.78%</td>
</tr>
<tr>
<td>S_0→S_6</td>
<td>403.6</td>
<td>0.1280</td>
<td>H→L+4</td>
<td>69.50%</td>
</tr>
</tbody>
</table>

3.2 Frontier molecular orbitals (FMOs)

After determining of molecular twisting structures is made, a comprehensive analysis of intra-molecular charge transfer phenomena is essential to comprehend the TICT characteristics between the two molecules. Consequently, we have summarized the transition properties in Table 2, encompassing absorption peaks, molecular orbital contributions, and oscillator strengths. It can be observed that the S_1 state transition of the DPA-CI molecule corresponds to the maximum oscillator strength, corresponding to the HOMO→LUMO transition. In contrast, the DPA-CI-PS molecule exhibits its maximum oscillator strength in the S_4 state transition (rather than the S_1 state), and corresponds to the HOMO→LUMO+2 transition.

To supplement findings, we have rendered fine absorption spectra for both molecules, as depicted in Fig. 2. It can be seen that the transition contributions in the DPA-CI molecule are almost entirely from the S_1 state, while in the DPA-CI-PS molecule, the S_2, S_4, and S_6 states significantly contribute to the molecular transitions,
with the $S_4$ state demonstrating the most pronounced influence. Remarkably, we have also discovered a redshift phenomenon in the maximum absorption peak of the DPA-CI molecule.

Therefore, we plotted the corresponding transition orbitals and calculated the energy gap difference ($E_{\text{gap}}$), as illustrated in Fig. 3. It revealed that the DPA-CI molecule has a smaller energy gap difference, elucidating the observed redshift. Furthermore, a narrower energy gap signifies heightened molecular reactivity, confirming that the DPA-CI molecule is a good probe molecule.

3.3 Electron fragment analysis

In the process of detecting phosgene, the excitation of the $S_0$ to $S_1$ state of two molecules is primarily involved. In order to observe the overall electron density distribution, we plotted the HOMO and LUMO orbitals of the two molecules and divided them into left and right parts, as shown in Fig. 4. Through calculations, we made a striking observation that the electron density distribution of fragment 1 in both molecules witnessed a decline from 70.621% and 40.446% in the HOMO orbitals to 36.946% and 18.066% in the LUMO orbitals, marking a substantial decrease of 33.675% and 22.380%, respectively. Therefore, we can conclude that although both molecules exhibit TICT, the DPA-CI molecule showcases a more intensified degree of TICT.
Fig. 2. Calculated absorption spectra with oscillator strength of DPA-CI and DPA-CI-PS in THF solvent.
Fig. 3. Frontier molecular orbitals and energy gaps of DPA-CI and DPA-CI-PS.

Fig. 4. Calculated electron density component of Fragment 1 and Fragment 2 in HOMO and LUMO based on Hirshfeld method.
3.4 Natural transition orbitals (NTOs) and hole-electron analysis

We have observed significant changes in the electron density distribution within the molecules before and after their reaction with phosgene, which play a crucial role in the dynamics of the excited state [52]. In light of this, visualizations of the electron density distribution in the excited states of DPA-CI and DPA-CI-PS were performed at the TD-DFT/B3PW91/6-31G(d) theoretical level, based on the NTOs theory proposed by Martin [53], as shown in Fig. 5. It is evident that the transitions from occupied to virtual states make substantial contributions for both molecules, amounting to 99.24% and 95.62%, respectively. For the DPA-CI molecule, the electrons in the occupied states are clearly concentrated in the diphenylamine (DPA) portion and extend to the 2-imine-3-benzo[d]imidazole portion in the virtual states. Compared with DPA-CI molecule, there is minimal change in the electron density within the diphenylamine portion of the DPA-CI-PS molecule. These findings strongly suggest that the charge transfer characteristics are more pronounced in the DPA-CI molecule.

**Fig. 5.** The occupied and virtual NTOs of DPA-CI and DPA-CI-PS in THF.

In order to provide a more visually compelling depiction of the charge transfer behavior during the excitation process, we utilized the Multiwfn program to perform hole-electron analysis for the two molecules. The resulting insights are illustrated in Fig. 6., where the electron and hole are represented by blue and orange iso surfaces. Describing the centroids of the \( C_{\text{hole}}(r) \) and \( C_{\text{ele}}(r) \) is made possible through the \( C_{\text{hole}}(r) \) and \( C_{\text{ele}}(r) \) functions. The expressions for these functions are as follows:
Among them, $A$ refers to the normalization coefficient, and $x, y, z$ stands for the three Cartesian components of the coordinate vector $r$.

Besides, we also mark the distances between $C_{\text{ele}}$ and $C_{\text{hole}}$ in Fig. 6. In general, the $C_{\text{ele}}$-$C_{\text{hole}}$ distance is closely related to the degree of charge transfer, that is, the longer the $C_{\text{ele}}$-$C_{\text{hole}}$ distance, the more intensive the degree of charge transfer. Specifically, the $C_{\text{ele}}$-$C_{\text{hole}}$ distances of DPA-CI and DPA-CI-PS in the $S_1$ state are 4.811Å and 2.557Å respectively, which confirms the intramolecular charge transfer behavior corresponding to the electron de-excitation process. It is worth noticing that the $C_{\text{ele}}$-$C_{\text{hole}}$ distance of DPA-CI is about twice that of DPA-CI-PS, which leads to stronger electron transfer.

$$C_{\text{ele}}(r) = A_{\text{ele}} \exp \left\{ -\frac{(x-X_{\text{ele}})^2}{2\sigma_{\text{ele},x}^2} - \frac{(y-Y_{\text{ele}})^2}{2\sigma_{\text{ele},y}^2} - \frac{(z-Z_{\text{ele}})^2}{2\sigma_{\text{ele},z}^2} \right\}$$  \hspace{1cm} (1)

$$C_{\text{hole}}(r) = A_{\text{hole}} \exp \left\{ -\frac{(x-X_{\text{hole}})^2}{2\sigma_{\text{hole},x}^2} - \frac{(y-Y_{\text{hole}})^2}{2\sigma_{\text{hole},y}^2} - \frac{(z-Z_{\text{hole}})^2}{2\sigma_{\text{hole},z}^2} \right\}$$  \hspace{1cm} (2)

Fig. 6. The $\text{Cele}(r)$ and $\text{Chole}(r)$ functions isosurfaces as well as the hole-electron distribution for DPA-CI and DPA-CI-PS.
Table 3. Indexes characterizing the distribution of holes and electrons and of DP-HPPI in DCM and ACN solvent

<table>
<thead>
<tr>
<th></th>
<th>D(Å)</th>
<th>Sr</th>
<th>H(Å)</th>
<th>t(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPA-CI</td>
<td>4.81</td>
<td>0.46</td>
<td>3.55</td>
<td>1.82</td>
</tr>
<tr>
<td>DPA-CI-PS</td>
<td>2.56</td>
<td>0.63</td>
<td>3.25</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

Among the Table, the index D symbolizes the distance between hole centroid and electron centroid, Sr describes the degree of hole and electron overlap, H reflects overall average distribution width for holes and electrons, and t represents degree of hole and electron separation. Based on the characterization data involving D and Sr, it is evident that the degree of electron transfer in the DPA-CI molecule is significantly stronger than in DPA-CI-PS. Furthermore, the t index for DPA-CI-PS is a negative value (-0.28 Å), indicating insufficient separation between the hole and electron. All of these observations collectively underscore the stronger TICT characteristics exhibited by the DPA-CI molecule.

3.5 Transition density matrix (TDM)

To delve deeper into the transition characteristics of the two molecules, we visualized the transition density matrix (TDM) from an atomic standpoint, as depicted in Fig. 7. The coordinates of the matrix correspond to the atomic indices, the intensity of the diagonal elements is represented by varying colors, with deeper shades of red indicating a stronger intensity of electron transitions associated with that particular atom. Conversely, the off-diagonal elements appear in red, indicating higher levels of electron-hole correlation between the corresponding pairs of atoms. By comparing the matrix with the molecular atom numbering diagram (Fig. 8.), we discovered that in the DPA-CI molecule, the 7th N atom exhibited the brightest color, indicating the most significant change in charge density for that N atom. Additionally, we observed a strong electron-hole correlation between the 7th N atom and the 21st, 22nd, and 23rd C atoms. Next, shifting our focus to the analysis of the DPA-CI-PS molecule, we observed the disappearance of electron transition characteristics in the 7th N atom, while the 21st C atom exhibited pronounced electron transition features. Additionally, the electron-hole
correlation observed between the 7th N atom and the 21st C atom in the DPA-CI molecule also vanished. In contrast, a strong electron-hole correlation was discovered between the 23rd and 21st C atoms. These findings validate the earlier conclusion that the DPA-CI molecule exhibits a more substantial charge transfer effect compared to the DPA-CI-PS molecule.

Fig. 7. Transition density matrix diagram for DPA-CI and DPA-CI-PS.

Fig. 8. Molecular configuration.
3.6 AIE properties

To validate the AIE properties of DPA-CI and DPA-CI-PS, we employed Natural Bond Orbital (NBO) analysis. We computed the charges on three carbon atoms (C₃, C₈, and C₉) bonded to the N atom (Fig. 9.). The charge values for the three carbon atoms in the DPA-CI molecule were 0.157 a.u., 0.169 a.u., and 0.155 a.u., respectively. In the DPA-CI-PS molecule, the corresponding charge values for the three carbon atoms were 0.132 a.u., 0.172 a.u., and 0.136 a.u.[54] Notably, the increasing asymmetry in the charge distribution of the three carbons neighboring N₁ indicates a more pronounced AIE property in DPA-CI-PS. Furthermore, the AIE properties can be quantified by the parameter D:

$$D = \sqrt{(E₁ - E₂)^² + (E₂ - E₃)^² + (E₃ - E₁)^²}$$

The D index of DPA-CI is 0.0186 a.u, and that of DPA-CI-PS is 0.0540 a.u. The D index of DPA-CI and DPA-CI-PS is much higher than 0.0135 a.u., which indicates that both molecules have AIE properties, but the AIE properties of DPA-CI-PS are stronger than that of DPA-CI.

![Fig. 9. Calculated charge values on the C₄, C₈, and C₉. (left) and D index (right).](image)

3.7 Mechanism Summary

Discovered from this study, it has been elucidated that a pronounced Twisted Intramolecular Charge Transfer (TICT) phenomenon exists within DPA-CI molecules. Furthermore, experimental evidence by Hu et al. demonstrates that an increase in solvent polarity enhances non-radiative transitions associated with TICT, leading to an intensification of fluorescence quenching. Analysis of the configurational changes
between the ground state and the S1 excited state of DPA-CI-PS molecules reveals a reduction in the twisting of the triphenylamine moiety. Whilst, a new cyclic structure in the benzimidazole portion. Experimentally, it is observed that an augmentation in water concentration suppresses molecular twisting. Consequently, at an 80% water concentration, the DPA-CI-PS molecule AIE and emits intense fluorescence. The disparate fluorescence behaviors between the two molecules underscore the superiority of DPA-CI molecules as probe molecules.

![Fluorescence Mechanism Diagrams of DPA-CI and DPA-CI-PS Molecules.](image)

**Fig. 10.** Fluorescence Mechanism Diagrams of DPA-CI and DPA-CI-PS Molecules.

4. Conclusion

We theoretically investigated the photo-physical properties and internal mechanisms of phosgene molecules in THF solvent before and after detection at the B3PW91/6-31G(d) level. Our analysis of geometric structures and frontier molecular orbitals indicates that both DPA-CI and DPA-CI-PS molecules exhibit pronounced TICT processes upon excitation to the S1 state. Through a detailed examination of electron-hole pairs and transition density matrices, we conclusively confirm the occurrence of the TICT process and ascertain its more significant manifestation in the DPA-CI molecule. Additionally, NBO analysis allowed us to quantify the D values for both molecules, with DPA-CI and DPA-CI-PS having D values of 0.0186 a.u. and
0.0540 a.u., respectively. The disparity in these D values highlights the more pronounced AIE characteristics in the DPA-CI-PS molecule. Importantly, our theoretical study provides valuable guidance for modulating the photo-physical behavior of fluorescence probes by effectively suppressing TICT while enhancing AIE.

Declaration of competing interest

The authors have no competing interests to declare.

CRediT authorship contribution statement

Yifu Zhang: Writing-Original draft preparation, Writing-Reviewing and Editing, Conceptualization, Data curation. Jiaan Gao: Writing-Original draft preparation, Writing-Reviewing and Editing, Conceptualization, Data curation. Hongyan Mu: Software. Hui Li: Writing-Reviewing and Editing, Conceptualization, Funding acquisition.

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References


