Decreasing the Singlet–Triplet Gap for Thermally Activated Delayed Fluorescence Molecules by Structural Modification on the Donor Fragment: First-principles Study

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ABSTRACT

The small energy gap between singlet excitons (S) and triplet excitons (T) of organic molecules is a dominant condition for high efficient thermally activated delayed fluorescence (TADF). In this study, influence of modification in donor groups of a series of molecules on their geometries, S-T energy gaps, and photophysical properties, is investigated based on first-principles calculations. Investigation shows that, as the electron donating ability is increased, both S-T energy gap and overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are decreased. This work provides strategy for designing high efficient and multi-color TADF devices.

Introduction

Organic light emitting diodes (OLEDs) have attracted much attention recently, since the new-typed high-efficient thermally activated delayed fluorescence (TADF) molecules are reported.¹⁻⁴ The internal quantum efficiency (IQE) of TADF molecules could approach 100%, which breaks the traditional opinion that the IQE of organic molecules can't exceed 25%.⁵ The electroluminescent mechanism of TADF molecules is that the utilization efficiency of excitons can be enhanced by up-conversion of the triplet excitons (T) to the singlet excitons (S). It has been found that the up-conversion process is strongly dependent on the spin-orbit coupling (SOC) and the energy gap between S and T ($\lambda \propto \frac{V_{SOC}}{\Delta E_{ST}}$). As the SOC is quite small for pure organic molecules, one efficient way to enhance the up-conversion is to decrease the S-T energy gap. Up to now, several groups have devoted to this work.⁶⁻⁸ It is found that the S-T energy gap depends largely on the exchange interaction between electrons in molecular orbitals involved in an electronic excitation.⁹ The general way to decrease the S-T energy gap is to connect electron-donating (D) groups and electron-accepting (A) groups to form D-A molecules which can form charge transfers states.^{10,11} Besides, the small S-T energy gap can be further decreased by connecting donor and acceptor moieties with a steric hindrance structure,

such as twist, bulky, or spirojunction *et. al*, because such steric hindrance can effectively separate the spatial overlaps between HOMO and LUMO.

For TADF-OLEDs, many investigations have been carried out and remarkable results have been achieved experimentally such as high efficient blue, green, and white OLEDs as well as high efficient exciplex systems.¹² Some useful molecular groups such as the N-containing aromatics: carbazole, diphenylamine and phenoxazine, are explored.^{13,14} In order to obtain a better understanding of the structure-property relationships in TADF emitters and look for TADF molecules with high IQE, we investigate properties of a series of molecules composed of the DPS group as acceptor and the diphenylamine, carbazole, DMAC, and PXZ groups as well as their derivatives as donors on the basis of first-principles calculation. The influence of the donor groups on the S-T energy gap as well as their photophysical properties are presented, and strategies to decrease the S-T energy gap by performing modification on the donor groups are demonstrated.

Theoretical methods

In this study, nine molecules (with short name **No1** to **No9** as shown in Fig. 1) are systematically studied. The geometry and the electronic structures are investigated using the density functional theory (DFT) at the B3LYP/6-31G* level. The time dependent

density functional theory (TD-DFT) method is employed to investigate the excitation property. Correct calculation of the S-T energy gap theoretically is one challenging work, and several methods have been reported.¹⁵⁻¹⁷ In this paper, the optimal HF method that has been proven reliable is adopted.¹⁵ In this method, different functionals with different percentage of HF exchange (HF%) are employed for different molecules. The percentage of HF exchange adopted is determined by the charge transfer amount (q) for the first singlet state (S1) of various molecules with the relationship HF%=42q. Since it is quite time-consuming to obtain the S1 and T1 state with the TD-DFT method, we predict the S-T energy gap according to the reliable formula as follows.

$$E_{0-0}(S1) = E_{VA}(S1, OHF) - \Delta E_v - \Delta E_{stokes} \quad (1)$$

$$E_{0-0}(^3CT) = E_{0-0}(S1) - [E_{VA}(S1, OHF) - C * E_{VA}(T1, BLYP)] \quad (2)$$

$$E_{0-0}(^3LE) = [E_{VA}(T1, OHF) / \omega - \Delta E_{stokes}] \quad (3)$$

Here $E_{0-0}(S1)$ is the minimum energy for the S1 state. $E_{VA}(S1, OHF)$ is the vertical excitation energy of S1 calculated with an optimal HF functional. ΔE_{stokes} (Stokes-shift energy loss) is assumed as 0.09 eV which includes the contribution of solvation (~0.06 eV). ΔE_v is the vibrational energy level difference between the 0-0' transition and the vertical transition. For most CT compounds, the vertical S1 transition corresponds to the

0-1' transition,¹⁵ so ΔE_v is set to 0.15eV in our calculation. $E_{0-0}(^3CT)$ and $E_{0-0}(^3LE)$ are the minimum energy of the T1 when the state is a CT state or a LE state. $E_{VA}(T1,BLYP)$ is the vertical excitation energy for the T1 state calculated with the BLYP functional where $C = E_{VA}(S1,OHF)/E_{VA}(S1,BLYP)$. The parameter ω in Equation (3) is the correction factor which is dependent on the functionals used (see **Table 1**). In this table, the fourteen functionals with different HF% are tested on the N-phenylcarbazole (PhCz) molecule with the method mentioned in Ref. 15. As we can see, the correction factor ω is around 1.0 when the HF% is smaller than 42%. When the HF% is 100%, the factor becomes 1.30. It can be deduced that the correction is quite necessary when the charge transfer amount is relatively large. Besides, the charge transfer amount (q) for the S1 state is calculated with the Multiwfn (a multifunctional wavefunction analyzer) program.¹⁸

It is to note that all the calculations are performed in the toluene with the Polarizable Continuum Model (PCM) through Gaussian09 package,¹⁹ which is thought suitable to predict the property of the molecules in the OLED.²⁰

Results and discussions

In this study, nine molecules named as **No1** to **No9** are shown in **Fig. 1**. From this figure, we can see that the donor groups for **No1**, **No3**, **No6** and **No8** are diphenylamine, carbazole, DMAC and PXZ respectively. Other molecules are their derivatives with a

little modification on the four kinds of donor groups mentioned above. For **No2**, the *tert*-butyl group is added at the *para*-position of two benzene rings in comparison with **No1**. For **No4** and **No5**, the *tert*-butyl and methoxy groups are added on the carbazole group respectively. The methoxy groups are also added on the DMAC group and the PXZ groups to form **No7** and **No9**. In fact, the donor of **No9** is one kind of resorufin derivatives which are perfect fluorescence materials with high PL efficiencies.^{21,22} In the following sections, we will systematically study the influence of the donor groups on the molecular geometry, the S-T energy gaps and their photophysical properties.

Influence on the geometry

As the relative position between D and A can significantly influence the charge transfer property and excitation property of the molecules, the bond length and dihedral angles between A and D groups are specifically noted (see **Table 2**). It is interesting that the bond lengths for **No1**, **No2**, **No3**, **No4** and **No5** are almost the same, while the dihedral angles for **No3** and **No4** are a little larger than that of **No1** and **No2**. The bond lengths of **No6**, **No7** and **No8** are about 0.02 Å larger than that of the former five molecules. The dihedral angles for **No6** and **No7** are around 90 degree. The bond lengths for **No9** is 1.42 Å, which is 0.1 Å smaller than **No6**, **No7** and **No8**, but 0.1 Å larger than the former five molecules. The dihedral angles for **No8** and **No9** are about 80 and 70

degree respectively, which is still much larger than the dihedral angles of the former five molecules. It is indicated that the modification of the D groups can change the relative position of D and A groups. Based on the analysis of the geometric structure, we can deduce that there will be relatively weaker orbital overlap between D and A groups for the latter four molecules in comparison with the former five molecules, due to relative farther distance and also larger dihedral angles between D and A groups. It can be confirmed in the latter section.

Influence on the S-T energy gap

The S-T energy gap is one of the most important parameters that determine the up-conversion process. To calculate the adiabatic S-T energy gap is quite time-consuming, thus a simple and reliable way is adopted here. Of course, the functional that relies on the charge transfer amount should be determined first. The charge transfer amount for nine molecules is calculated as shown in **Table 3**. It is found the charge transfer amounts for **No1** and **No2** are almost equal (0.276 and 0.262), thus the same functional O3LYP is adopted for them. **No4** and **No9** have the same charge transfer amount (0.514), and the MPW3LYP functional will be used for these two systems. In addition, **No5** and **No7** adopt the same functional PBE1PBE due to the same charge transfer amount obtained for them. For **No6**, the charge transfer amount is as large as 0.851, and the PBE38 functional

is employed. For **No3** and **No8**, the charge transfer amount is 0.481 and 0.523 respectively, so the functional of B3LYP and PBE1KCIS are selected. Based on the functionals chosen, the vertical excitation energy for S1 and T1 is calculated with both the BLYP functional and the OHF functional. Based on these values, $E_{0-0}(S1)$, $E_{0-0}(^3CT)$ and $E_{0-0}(^3LE)$ are obtained. By comparing the values of $E_{0-0}(^3CT)$ and $E_{0-0}(^3LE)$, the energy of the T1 state can be determined and the S-T energy gap can also be calculated. As we can see, the T1 states for **No1** to **No4** are LE states. From **No5** to **No9**, the T1 states are all CT states. It can be seen that the S-T energy gap from **No1** to **No7** becomes smaller and smaller. The energy gaps for **No8** and **No9** are also quite small, though they are a little larger than **No6** and **No7**. In comparison with the experimental results, good agreement is obtained, which further proves the reliability of the method we used to calculate the S-T energy gap. Specifically, the S-T energy gaps from **No1** to **No5** are all larger than 0.1 eV (a criterion for TADF molecules¹). Although TADF can be observed in these emitters, their up-conversion efficiency should be relatively poor. It is lucky to find that the energy gap of **No6**, **No7**, **No8** and **No9** are all smaller than 0.1 eV, which shows potential application as TADF emitters. In comparison of the S-T energy gap for **No1** with that for **No3**, **No6** and **No8**, we can see the import of the donor groups with better planarity will efficiently decrease S-T gap, and this change also brings a

nearly perpendicular angle between DPS and DMAC which is advantageous to further narrow the S-T gap.

As we have seen, a little modification on the D groups can significantly change the S-T gap of the molecules. From **Table 3**, we can see that the S-T energy gap varies from 0.01 eV to 0.43 eV. The direct reason is that the overlap between two excitation orbitals becomes weak especially when the DMAC and PXZ groups are used. Based on the analysis of the excitation component of the S1 state, the HOMO→LUMO transition performs dominate contribution in all these systems (see **Table 4**). The electron distribution of the HOMOs and LUMOs are analyzed (as shown in **Fig. 2**). One can see that the electrons mainly distributed on the D groups in the HOMOs and mainly on the A groups in the LUMOs for all the systems. Besides, there are also some electron distribution on the A groups in the HOMOs for **No1** to **No5**. In other words, there is relative significant overlap between HOMO and LUMO for **No1** to **No5**. Of course, the HOMO-LUMO overlap from **No1** to **No5** becomes weaker and weaker. Nevertheless, they should be much stronger than the HOMO-LUMO overlap of the latter four molecules. To quantitatively analyze the overlap between HOMO and LUMO, the integral of electron-hole overlap is introduced. S is defined as the minimum of the electron density $\rho^{ele}(r)$ and hole density $\rho^{hole}(r)$ everywhere, where $\rho^{ele}(r)$ and

$\rho^{hole}(r)$ are taken as Ψ_{LUMO}^2 and Ψ_{HOMO}^2 approximately. As shown in **Table 4**, the value of S varies significantly, when D is changed. Besides, it proves our deduction that the HOMO-LUMO overlap of latter four molecules becomes much smaller than the former five molecules. To get a better understanding of the relationship between the S-T energy gap and the overlap, one can see the black line in **Fig. 3**. A linear relationship can be found between the S-T energy gap and the value of S . With the value of S decreasing, the S-T energy gap becomes smaller. It further confirms that the S-T energy gap can be efficiently decreased by weakening the HOMO-LUMO overlap. Of course, modification of D is one efficient way to change the HOMO-LUMO overlap.

As we know, different D groups have different electron-donating ability. The electron-donating ability may be one of the main factors that determine the molecular orbital property and the S-T energy gap. The atomic charge of the S0 and S1 states for the nine molecules are calculated with the Natural population analysis (NPA) method (see **Table 5**). It can be found that the charge of the donor groups for the S0 states and S1 states are negative and positive respectively for all the nine molecules. While an opposite results are found for the acceptor group. In addition, the charge difference between S1 and S0 are also shown, and the values vary from 0.335 to 0.852 for the donor groups. It indicates that the D groups donating electrons in the transition process. The larger the charge difference is, the stronger the electron-donating ability of the D group will be.

Specifically, the charge difference of diphenylamine, carbazole, DMAC and PXZ in **No1**, **No3**, **No6** and **No8** are 0.335, 0.627, 0.822 and 0.797. The electron-donating ability for the four D groups are diphenylamine < carbazole < PXZ < DMAC. The introduction of the *tert*-butyl group and the methoxy group in the four D groups can influence their electron-donating ability, but the results are different. Comparing **No1** and **No2**, the introduction of the *tert*-butyl group increases the donating ability of the diphenylamine, while it weakens the donating ability of the carbazole (see **No3** and **No4**). Nevertheless, the introduction of the methoxy group makes the electron-donating ability of the carbazole and DMAC a little stronger, but weaker of the PXZ. This may be induced by different interaction between the *tert*-butyl group and the methoxy group and the four donor groups. Correspondingly, the introduction of the *tert*-butyl group to the diphenylamine group can decrease its S-T energy gap, while it makes the gap of the carbazole wider. For the carbazole, the methoxy group is more efficient to decrease the S-T energy gap than the *tert*-butyl group. To make out the influence of the donor groups on the S-T energy gap, the relationship between the S-T energy gap and the charge difference of the donor groups is shown in **Fig. 3**. It is indicated that the S-T energy gap varies as the function of the charge difference. With the increase of the charge difference, the S-T energy gap becomes smaller. It is indicated that one can decrease the S-T energy gap by introducing D groups with relatively strong electron-donating ability. As

mentioned above, the S-T energy gap can be also decreased by weakening the HOMO-LUMO overlap. Consequently, the electron-donating ability of the D groups may be also the main factors to influence the HOMO-LUMO overlap (see the insert of **Fig. 3**). The stronger the electron-donating ability is, the weaker the HOMO-LUMO overlap is. From **Fig. 3**, we can conclude that both the S-T energy gap and the HOMO-LUMO overlap will decrease with the increase of the electron-donating ability of donor groups.

Influence on the charge-transfer length and other photophysical parameters

In order to investigate the charge transfer (CT) nature of the S1 state for all molecules, the index Δr and S which represent the charge-transfer length during electron excitation and the integral of overlap between hole and electron respectively are analyzed. From **Table 4**, we can see that the charge transfer distance for **No3-No9** are all larger than 2.0 (the threshold value was proposed in the original papers^{23,24}) and their S values are all very small. It confirms that the S1 states for **No3-No9** are relatively pure CT states. The Δr values for **No1** and **No2** are smaller than 2.0, while the values of S are bigger than that of **No3-No9**. It indicates that the S1 states of **No1** and **No2** are not a simple CT states but mixed with local excited (LE) states, and it has been clearly displayed by the electron distribution of HOMO and LUMO in **Fig 2**. Meanwhile, compared with **No3-No9**, the values of oscillator strength (f) and transition dipole

moment (μ) of **No1** and **No2** are bigger. It can be deduced that the prompt fluorescence efficiency (Φ_{prompt}) of **No1** and **No2** may be higher than other molecules, but the delayed fluorescence efficiency (Φ_{delayed}) may be lower due to a relatively larger S-T energy gap for them. In addition, the energy gaps between HOMO and LUMO for all molecules are also calculated as shown in **Fig. 2**. It is indicated that the energy gap becomes small from **No1** to **No9** exclude **No 8**. The energy gap for **No1** is 4.01 eV (310 nm), while it is as small as 2.85 eV (435 nm) for **No9**.

Besides, the spin-orbit coupling between the S1 and T1 state is one important parameter that determines the reverse intersystem crossing. In this paper, the spin-orbit coupling constants between S1 and T1 are calculated with quadratic response function methods using the Dalton program.²⁵ It is found that the Spin-orbit coupling values for all the molecules investigated are quite small. Comparing the spin-orbit coupling constant of **No1** (0.184cm⁻¹) with **No2** (0.277cm⁻¹) and **No6** (0.110cm⁻¹) with **No7** (0.444cm⁻¹), we find that the *tert*-butyl group and methoxy group can decrease the dihedral angles between D and A groups, but increase the coupling constant. The relationship between the dihedral angles and the spin-orbit coupling is consistent with the research of Bredas' group.²⁶ Besides, comparing the data of **No3** (0.278cm⁻¹), **No4** (0.282cm⁻¹) and **No5** (0.518cm⁻¹), similar relationship between the spin-orbit coupling and the dihedral angles can be found, while opposite relationship is found for **No8** (0.048cm⁻¹) and **No9**

(0.019cm⁻¹). We conclude that the relationship between the dihedral angles and the spin-orbit coupling constant is system-dependent.

Conclusions

In conclusion, the influence of the modification in the donor groups of molecules on their S-T energy gaps and photophysical properties is systematically investigated. It is found that the dihedral angles between the D and A groups will change to nearly 90 degree when the DMAC is adapted as the donor unit. Correspondingly, the HOMOs and LUMOs become more localized. As a result, the molecule with DMAC has the narrowest S-T energy gap. Furthermore, the ability of the donor part to decrease S-T gap is shown as an order of diphenylamine < carbazole < PXZ < DMAC. The donor groups are further modified, and the substitution with the methoxy group is shown to be more efficient than that with the *tert*-butyl group for decreasing the S-T energy gap. The results indicate that planarity of the donor group is advantageous to decrease the S-T energy gap. More importantly, analysis of electron donating ability of the donor groups shows that the S-T gap and HOMO-LUMO overlap decrease as the electron donating ability increases. Our results provide some instructive information for the design of high efficient TADF emitters.

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Figure 1. Structure diagram of the molecules investigated.

Figure 2. Electron distribution of HOMOs and LUMOs for the molecules studied. The values of their energy levels and energy gaps are also presented.

Figure 3. Change of the S-T energy gap with the integral of e-h overlap (S) (black line) and charge difference (Δ) (red line). The relationship between Δ and S is also shown in the insert.

Table 1. Correction factor (ω) calculated with various functionals based on the PhCz molecule. The percentage of the HF component (HF%) in different functionals is also presented.

functional	HF%	ω
Tpssh	10	1.00
O3lyp	11.61	1.05
Tpss1kcis	13	1.03
Mpw1kcis	15	1.04
B3lyp	20	1.02
Mpw3lyp	21.8	1.02
Pbe1kcis	22	1.03
Pbe0	25	0.98
Mpw1b95	31	1.06
Pbe33	33.33	0.94
Pbe38	37.5	0.91
BMK	42	1.10
M062x	54	1.18
M06-HF	100	1.30

Table 2. Bonds lengths (B) and dihedral angles (D) between donor groups and the acceptor (C-N link) of the molecules in the ground state (S0).

system	bond length/Å		dihedral angle/°	
	B1	B2	D1	D2
No1	1.41	1.41	30.48	30.48
No2	1.41	1.40	29.67	29.91
No3	1.41	1.41	50.90	51.55
No4	1.41	1.41	48.58	49.40
No5	1.41	1.41	48.65	49.01
No6	1.43	1.43	92.49	92.49
No7	1.43	1.43	88.65	91.91
No8	1.43	1.43	76.06	78.63
No9	1.42	1.42	69.55	73.25

Table 3. CT amount from S0 to S1 for all molecules. The calculated percentage of HF component (HF%) and the chosen functionals are shown in the third and fourth column respectively. The vertical excitation energy of S1 and T1 states calculated by BLYP and OHF respectively are also listed. E_{0-0} (S1), E_{0-0} (³CT) and E_{0-0} (³LE) are shown in the following columns. Finally, we listed the calculated S-T energy gap and the experimental values for comparison. (Unit of energy: eV)

system	q(e)	HF%	functional	E_{VA} (S1,BLYP)	E_{VA} (T1,BLYP)	E_{VA} (S1,OHF)	E_{VA} (T1,OHF)	E_{0-0} (S1)	E_{0-0} (³ CT)	E_{0-0} (³ LE)	ΔE_{S-T} (cal.)	ΔE_{S-T} (exp.)
No1	0.276	11.6	O3LYP	2.84	2.57	3.25	2.81	3.01	2.70	2.58(T1)	0.43	0.54
No2	0.262	11.0	O3LYP	2.77	2.51	3.18	2.75	2.94	2.64	2.53(T1)	0.41	0.45
No3	0.481	20.2	B3LYP	2.66	2.54	3.38	3.04	3.14	2.99	2.89(T1)	0.25	----
No4	0.514	21.6	MPW3LYP	2.55	2.44	3.33	2.99	3.09	2.94	2.84(T1)	0.25	0.32
No5	0.573	24.1	PBE1PBE	2.25	2.14	3.19	2.83	2.95	2.79(T1)	2.80	0.16	0.24
No6	0.851	35.7	PBE38	1.98	1.97	3.39	2.98	3.15	3.14(T1)	3.18	0.01	0.09
No7	0.572	24.0	PBE1PBE	1.58	1.58	2.58	2.56	2.34	2.33(T1)	2.53	0.01	----
No8	0.523	22.0	PBE1KCIS	1.68	1.66	2.53	2.49	2.29	2.26(T1)	2.33	0.03	0.08
No9	0.514	21.6	MPW3LYP	1.52	1.46	2.36	2.27	2.12	2.03(T1)	2.14	0.09	----

Table 4. Oscillator strength and transition dipole moment for all the molecules are listed. The index of Δr (Å) and S are also presented. Spin-orbit coupling between S1 and T1 as well as the transition component for $S0 \rightarrow S1$ of **No1-No9** are assigned.

system	f	μ (au)	Δr (Å)	S	$\langle S1 H_{so} T1 \rangle$ (cm ⁻¹)	transition component
No1	0.7058	2.9755	1.2202	0.3622	0.184	HOMO→LUMO (99.3%)
No2	0.7297	3.0625	1.3624	0.3502	0.277	HOMO→LUMO (99.3%)
No3	0.4082	2.2200	2.3019	0.1678	0.278	HOMO→LUMO (96.1%)
No4	0.4928	2.4580	2.4095	0.1705	0.282	HOMO→LUMO (95.6%)
No5	0.4621	2.4334	4.3269	0.1518	0.518	HOMO→LUMO (92.7%)
No6	0.0026	0.1772	2.4555	0.0440	0.110	HOMO→LUMO (85.0%)
No7	0.0002	0.0611	2.5557	0.0422	0.444	HOMO→LUMO (92.0%)
No8	0.0337	0.7370	4.4659	0.0524	0.048	HOMO→LUMO (93.4%)
No9	0.1129	1.3986	2.5078	0.0786	0.019	HOMO→LUMO (94.1%)

Table 5. Atomic charges of all molecules investigated when they are in the ground state (S0) and first singlet excited state (S1) using NPA method. Δ is the charge difference between the S1 and S0 states.

		atomic charge	
		acceptor	donor
No1	S0	0.172	-0.172
	S1	-0.163	0.163
	Δ	-0.335	0.335
No2	S0	0.159	-0.159
	S1	-0.193	0.193
	Δ	-0.352	0.352
No3	S0	0.348	-0.348
	S1	-0.279	0.279
	Δ	-0.627	0.627
No4	S0	0.326	-0.326
	S1	-0.293	0.293
	Δ	-0.619	0.619
No5	S0	0.309	-0.309
	S1	-0.320	0.320
	Δ	-0.629	0.629
No6	S0	0.394	-0.394
	S1	-0.428	0.428
	Δ	-0.822	0.822
No7	S0	0.385	-0.385
	S1	-0.440	0.440
	Δ	-0.825	0.825
No8	S0	0.399	-0.399
	S1	-0.398	0.398
	Δ	-0.797	0.797
No9	S0	0.359	-0.359
	S1	-0.377	0.377
	Δ	-0.736	0.736