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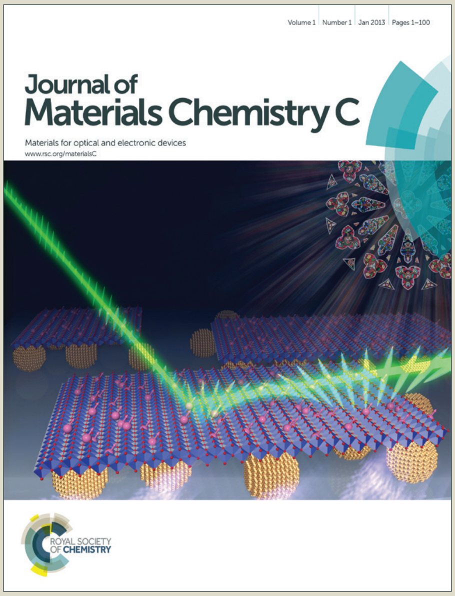

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Computational study on tri-s-triazine-based molecules as ambipolar host materials for phosphorescent blue emitters: effectively geometric and electronic tuning

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ABSTRACT

A series of host molecules for blue electrophosphorescence have been designed using density functional theory by incorporating carbazole and tri-s-triazine. It is found that carbazole ring should be coplanar with tri-s-triazine ring for obtaining high triplet energy (E_T). Results obtained from the electronic structure calculations show that the triplet energy, HOMO and LUMO energy levels and reorganization energy (λ) of the designed hosts can be modulated efficiently through different substitution patterns. This study provides theoretical insights into the nature of host molecules, and shows that the designed molecules with NH_2 group in tri-s-triazine ring and alkyl group in carbazole ring can meet the requirements of the host materials for blue emitting phOLEDs owing to their high E_T value, appropriate energy level alignment, balanced charge transfer, high triplet exciton-formation fraction (χ_T) and small difference between S_1 and T_1 excitation energy (ΔE_{ST}).

1 Introduction

As a "mystery molecule", tri-s-triazine and its derivatives attract more and more attention for their interesting properties and potential applications.[1] Compared with most organic or other C/N-moieties, the thermal stability of the tri-s-triazine framework is very high, i.e. decomposition starts above 500 ºC. It has been proved that tri-s-triazines have many useful properties such as electron deficiency, photoluminescence, electroluminescence, and nonlinear optical activity, etc.[2-5] Several theoretical and in some cases experimental studies suggest a lot of useful applications of tri-s-triazine-based materials in many fields such as polymer, adsorption and sensors.[6-12] Furthermore,

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several patents and work show the potential application as photo stabilizer and sensitiser,[2, 5, 13] as functional (semiconducting) components for organic electronics or luminescent devices.[14, 15] Recently, these molecules are proved to be efficient photocatalysts for the splitting of water and hydrogen evolution as well as metal-free catalysts for several different organic reactions such as selective C-H oxidation, transesterifications, or CO_2 activation.[16-18]

In 2013, Huang and co-worker synthesized a series of ternary asymmetric s-triazines with tunable singlet and triplet excited states and constructed a series of interesting s-triazine-based ambipolar phosphorescent OLED (PhOLED) host materials which maintained high triplet energy levels (above 2.7 eV) and independently modified LUMOs (from -1.81 to -2.17 eV).[19] In the same year, Chen et al. synthesized three propylene-, meta-, and para-linked triazine and found E_T values of these compounds were suitable for hosting red-emitting $Ir(piq)_3$.[20] Compared with s-triazines, tri-s-triazines have more conjugated system, more electron-deficiency, and more thermal stability besides the similarities of symmetry and aromaticity. These properties provide a possibility for the construction of PhOLED host materials based on tri-s-triazine molecules.

Phosphorescent OLED have received considerable attention because of the efficient harvesting of both singlet and triplet excitons simultaneously through efficient intersystem crossing, thus enhancing the internal quantum efficiency.[21-24] Generally, in compounds consisting of lighter elements, such as conventional organic materials, the decay of a triplet state is forbidden by the conservation of spin symmetry. It becomes weakly allowed by introducing heavier elements due to spin-orbit coupling. In such cases, the decay of the triplet state may still be very slow, but phosphorescence is generated.

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The solution to the utilization of phosphorescent materials in OLEDs could be found by doping the phosphor into a host material. Emission occurs by exciton formation in the host and energy transfer to the luminescent guest (phosphor) through triplet–triplet transfer. This is a short-range process where excitons diffuse from donor (host) to acceptor (guest) sites via intermolecular electron exchanging at a rate proportional to the orbital overlap of the donor and acceptor molecules. High efficiencies could be obtained by transition from the host singlet and triplet states to the guest triplet states via energy transfer and intersystem crossing.

The development of host materials for the fabrication of efficient device is a challenging task. To obtain high efficient PhOLEDs, the hosts would possess the following properties: (i) A high triplet energy level, which prevents the reverse energy transfer from the guest to the host;[25, 26] (ii) Suitable highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) energy levels matching those of hole transport layer (HTL) and electron transport layer (ETL) are required to reduce the driving voltage for charge injection; (iii) High and balanced hole and electron mobility; (iv)High thermal stability and film formation ability.

By using host-guest system, efficient and stable red and green emitting PhOLEDs are well developed with high quantum efficiency around 20%.[27-29] Owing to the lack of efficient host molecules with a high triplet energy (E_T ~ 3.0 eV) and efficient charge injection for blue emitters, the realization of high performance blue PhOLEDs is still a challenge.

Recently, ambipolar host molecules are receiving increasing attention since these molecules can transport both holes and electrons and simplify the device structure, in

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addition to reducing the driving voltage of the device.[30, 31] With suitable molecular design, the incorporation of hole transport (HT) and electron transport (ET) moieties integrates the advantages of both HT- and ET-type materials into the multifunctional host materials. The ambipolar host materials are the molecules composed of an electron-donating moiety capable of mediating hole injection and transportation and an electron-withdrawing moiety capable of mediating electron injection and transportation. In most cases, carbazole and diarylamines are used as the HT blocks whereas electron deficient systems including N-heterocyclic arenes, such as triazine, pyridine, quinoline, 1,2,3-triazole, 1,10-phenanthroline, 1,3,4-oxadiazole, benzimidazole, diarylphosphine oxide, and phenylsulfonyl group, are utilized to perform the ET function.[32]

In this paper, we theoretically predict the performance of tri-s-triazine combined with carbazole as ambipolar host materials for blue PhOLEDs. The geometric and electronic effects on the performance of these host molecules and the natures of these effects are explored in detail. The study provides a very promising outlook for the future of the branch of tri-s-triazine chemistry and blue PhOLEDs.

2 Computational details

All the structures in their ground state (S_0) and exited state (T_1) were optimized at B3LYP/6-31G* level of theory and frequency analysis was used to confirm that each structure was a minimum (with no imaginary frequency) on the potential surface.[33, 34] The adiabatic triplet energy (E_T) was obtained by means of the ΔSCF method on the basis of the optimized structures of the S_0 and T_1 states. Based on the ground state equilibrium geometries, ΔE_{ST} was estimated by calculating the difference between the lowest vertical singlet (S_0 - S_1) and triplet (S_0 - T_1) excitation energies. Subramanian et al. tested five

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DFT based functionals with the 6-31G* basis set to evaluate electronic properties, such as E_T and ΔE_{ST} values.[35] They found that the results obtained with different functionals remain akin to those of the B3LYP/6-31G * level. Wu et al. tested nine DFT based functionals with the 6-31G * basis set for estimating the ΔE_{ST} value.[36] Among the nine functionals they concluded that the B3LYP functional with a 6-31G * basis set is reliable for calculating ΔE_{ST}. All the calculations were carried out by the Gaussian 09 programs.[37]

The hole and electron transport processes at the molecular level in the electroluminescent layer can be described as the electron/hole transfer reactions between the neighboring molecules as

$$M^{+/-} + M^0 \rightarrow M^0 + M^{+/-} \qquad (1)$$

where $M^{+/-}$ indicates the molecule in a cationic or anionic state and M^0 is a neighboring molecule in the neutral state. In the case of hole transport, the interaction can be considered between a molecule in the neutral state and a cation, and in case of electron transport, the interaction can be considered between a molecule in the neutral state and with a anion. This process can be accounted by the Marcus electron transfer theory, and the hole/electron-transfer rate ($K_{h/e}$) is given by following equation[38]:

$$K_{h/e}=(\pi/\lambda_{h/e}kT)^{1/2} * V^2_{h/e}/ \hbar * \exp(-\lambda_{h/e}/4kT) \qquad (2)$$

where ħ and k refer to the Planck and Boltzmann constants respectively, T is the temperature, V is the electronic coupling matrix between donor and accepter molecules and $\lambda_{h/e}$ is the reorganization energy for hole/electron transport. In particular, the V and $\lambda_{h/e}$ terms play an important role for determining $K_{h/e}$. However, it is most likely that V would vary over a limited range for analogous molecules, and the experimental results have shown that V values for a series of organic molecules show a narrow range due to

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direct contact in the amorphous solid.[39, 40] Therefore, the charge (hole and electron) mobility of the designed hosts will be dominated by the respective reorganization energies. The hole/electron reorganization energy ($\lambda_{h/e}$) is calculated by the following equations:

$$\lambda_h=\lambda_1+\lambda_2 \qquad \lambda_1=E^+(M_0)-E^+(M^+) \qquad \lambda_2=E^0(M^+)-E^0(M_0)$$

$$\lambda_e=\lambda_3+\lambda_4 \qquad \lambda_3=E^-(M_0)-E^-(M^-) \qquad \lambda_4=E^0(M^-)-E^0(M_0)$$

where the $E^0(M_0)$, $E^+(M^+)$ and $E^-(M^-)$ represent the total energy of the neutral, cationic and anionic species at their respective optimized geometries. $E^+(M_0)$ and $E^0(M^+)$ denote the total energy of the cations and neutral species at the optimized geometries of M_0 and M^+ respectively. In the same way, $E^-(M_0)$ and $E^0(M^-)$ denote the total energies of the anions and neutral species at the optimized geometry of M_0 and M^- respectively.

3 Results and Discussion

In order to understand the charge injection and charge transfer process, iridium(III) bis[4,6-difluorophenyl)-pyridinato-*N*,C′] picolinate (FIrpic) is chosen to represent the guest in the host-guest system. N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)benzidine (NPB) is used as hole-transporting layer, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is used as the electron-transporting layer. In addition, 4,4′,4′′-tri(N-carbazolyl)triphenylamine (TCTA) is used to confine excitons in the emissive layer (EML) and to reduce the energy barrier between the HOMO levels of NPB and EML.

3.1 Model of newly designed tri-s-triazine-based host molecules

In this work, different host molecules as seen in Scheme 1 were designed. Owing to the high electron affinity, tri-s-triazine core is used as electron transporting moiety in the ambipolar host materials. Carbazole (CBZ) is combined with tri-s-triazine ring to act as

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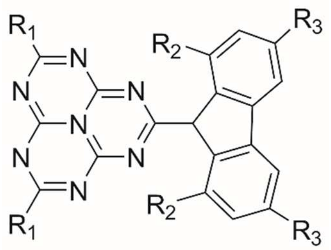
hole transporting moiety, and 1,8-substituted carbazole is used for considering steric effects. A series of halogen, electron-donating, electron-withdrawing and alkyl groups are introduced to tri-s-triazine and carbazole rings to explore the electronic effect on the performance of the designed host materials. Based on the substitution, the model systems are classified as (1) planar systems (series A–G) and (2) nonplanar systems (series H). The optimized structures of all studied molecules in S_0 and T_1 states are depicted in Supporting Information.

Scheme 1 The design of the tri-s-triazine derivatives. (R=F, Cl, Br, CN, NO_2, COOH, NH_2, OH, OPh, SPh, methyl, ethyl, propyl, i-propyl, butyl, i-butyl and t-butyl.)



3.2 Triplet energy E_T

Triplet energy E_T is one of the most important parameters which determine the potential performance of host molecules for use in phosphorescent blue emitters. As mentioned in previous reports, the triplet energy should be higher than that of phosphorescent guest to prevent back-transfer of energy from the guest to the host. For deep blue emitters, the triplet energy of the host should be higher than 2.70 eV.[41] Table 1 lists the triplet energies E_T for all the newly designed host molecules, and the E_T of FIrpic is also listed under the same level (B3LYP/6-31G*).

Table 1 The triplet energies E_T for all the newly designed host molecules and FIrpic (in series C and G.

Host	Planar			
	R_1	R_2	R_3	E_T
A	H	H	H	2.80
B1	F	H	H	2.82
B2	Cl	H	H	2.80
B3	Br	H	H	2.80
B4	CN	H	H	2.29
B5	NO_2	H	H	2.26
B6	COOH	H	H	2.35
C1	NH_2	H	H	3.02
C2	OH	H	H	2.93
C3	OPh	H	H	2.94
C4	SPh	H	H	3.01
D1	methyl	H	H	2.92
D2	ethyl	H	H	2.92
D3	propyl	H	H	2.92
D4	i-propyl	H	H	2.92
D5	butyl	H	H	2.92
D6	i-butyl	H	H	2.93
D7	t-butyl	H	H	2.91
E1	H	H	F	2.79
E2	H	H	Cl	2.80
E3	H	H	Br	2.79
E4	H	H	CN	2.81
E5	H	H	NO_2	2.80
E6	H	H	COOH	2.80
F1	H	H	NH_2	2.24
F2	H	H	OH	2.59
F3	H	H	OPh	2.57
F4	H	H	SPh	2.52
G1	H	H	methyl	2.75
G2	H	H	ethyl	2.74
G3	H	H	propyl	2.73
G4	H	H	i-propyl	2.75
G5	H	H	butyl	2.73
G6	H	H	i-butyl	2.74
G7	H	H	t-butyl	2.73
Host	nonplanar			
H1	H	CH_3	H	2.27
H2	H	$N(CH_3)_2$	H	2.08
	Guest			
	FIrpic			2.60

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3.2.1 Geometric effect on E_T

Initially, we designed three host molecules A, H1 and H2. The carbazole plane is coplanar with the tri-s-triazine ring in A, while nonplanar in H1 and H2 because of steric repulsion (Supporting Information). It can be seen from Table 1 that E_T value of A is 0.53 eV higher than that of H1 and 0.72 eV higher than that of H2. It seems that the planar geometry of the molecule has a most critical influence on obtaining a high E_T value. To take insight into this geometric effect, we calculated the E_T values for three conformations of A by constraining only the dihedral angle between tri-s-triazine and carbazole planes to 30, 60 and 90 degree (see Figure SI1 in Supporting Information). The energy diagram for these conformations is shown in Figure 1. It is clear that with the variation of dihedral angle from 0 to 90 degree, the ground-state energy for the molecule is increased by 0.71 eV, while the lowest triplet excited-state energy is only increased by 0.2 eV, which indicates that the decrease of E_T value is mainly caused by the increase of ground-state energy. The result suggests that the geometry change of the molecule has a large influence on the stability of the ground state but a small influence on that of triplet state. Actually, tri-s-triazine ring is a high electron-deficient fragment in the ground state, and electron-rich CBZ segment could stabilize it efficiently through conjugation effect in the planar molecular geometry. The natural bond orbital analysis shows that the stabilization is mainly contributed by the p-π conjugation between the nitrogen atom (N_{CBZ}) of CBZ and the tri-s-triazine ring, and the second order stabilization energy $E^{(2)}$ (see Table SI1 in Supporting Information) between N_{CBZ} lone pair and tri-s-triazine π^* orbital is calculated to be 67.52 kcal/mol for the planar molecule A. The data in Table SI1 reveals that the p-π conjugation is strongly dependent on the planar geometry. But in the excited state T_1, the p-π conjugation is limited because the excited electron has been transferred from CBZ moiety to the tri-s-triazine ring, which is reflected by the small $E^{(2)}$ value between N_{CBZ} lone pair and tri-s-triazine π* orbital in T1 state.

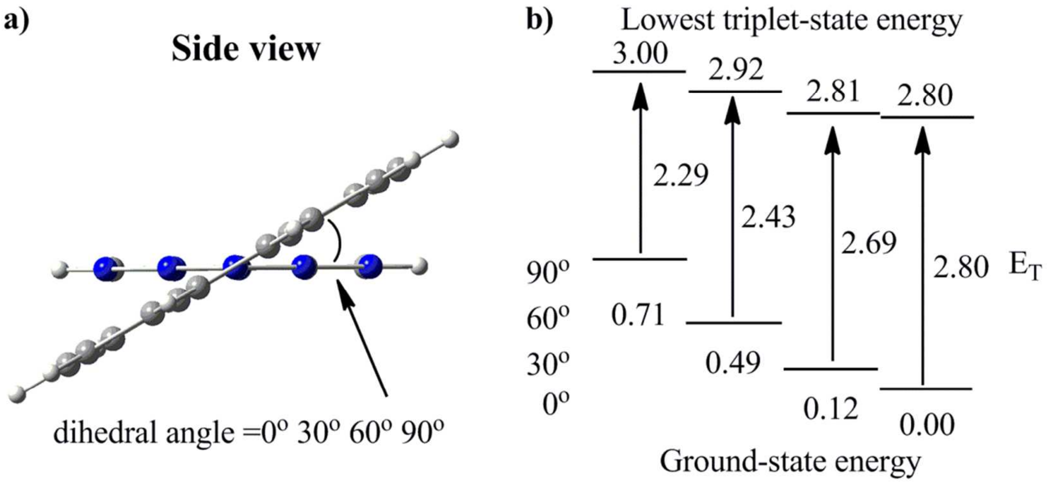

Figure 1 The energy diagram for conformations of A.

Thus, in order to get a high E_T value of designed host molecule, it is necessary to make carbazole ring coplanar with tri-s-triazine ring. This result is verified by the low E_T values of non-coplanar molecules H1 and H2 listed in Table 1.

3.2.2 Electronic effect on T1

In order to inspect the electronic effect on E_T, electron-withdrawing group (F, Cl, Br, CN, NO_2, COOH), electron-donating group (NH_2, OH, OPh, SPh,alkyl group) were introduced to the tri-s-triazine ring (series B, C and D) and CBZ ring (series E, F and G). Considering the geometric effect discussed above, only planar molecules were taken into account in this section.

Inspection of the E_T values listed in Table 1 shows that the triplet energies of

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halogen-substituted hosts (B1-B3 and E1-E3) are almost identical to that of reference host molecule A with the most deviation of 0.02 eV. For the electron-withdrawing substituted hosts, the E_T values are also almost identical to that of A with the most deviation of 0.01 eV for E4-E6, while decrease to 2.26-2.35 eV for B4-B6. For the electron-donating and alkyl substituted hosts, the E_T values increase to 2.91-3.02 eV when the substitution occurs in the tri-s-triazine ring (series C and D), while decrease to 2.24-2.75 eV when the substitution occurs in the CBZ ring (series F and G).

It should be noted that the hosts with electron-donating substituents on carbazole unit exhibit significantly lower triplet energies, when compared to the systems with other substituents. For example, the triplet energies of E1, F1 and G1 were 2.79, 2.24, and 2.75 eV respectively. To understand this behavior, the triplet spin density patterns of E1, F1, and G1 were calculated (Figure 2). It can be seen that the triplet spin densities of systems are all localized on the full tri-s-triazine unit and partial carbazole units. Therefore, the E_T value is contributed by both units. Since the tri-s-triazine unit for three hosts is identical, the variation in the triplet energy for them is most attributed to the change of carbazole moiety. We calculated the triplet energies for corresponding substituted carbazoles. The E_T values for 3,6-difluorocarbazole, 3,6-dicyanocarbazole, 3,6-dimethylcarbazole and 3,6-diaminocarbazole were calculated to be 3.11, 3.24, 3.15 and 2.56 eV, respectively. It is clear that the triplet energy of the molecule decreases significantly when electron-donating group NH_2 is introduced to the carbazole molecule. The reason for this is that carbazole is an electron-rich system. When an electron-donating group is introduced, the energy gap of carbazole will decrease abundantly owing to the significant increase of HOMO energy, leading to a decrease of E_T value. The energies of

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HOMO/LUMO and HOMO-LUMO gap for substituted carbazole molecules are presented in Table SI2 (Supporting Information).

Similarly, the hosts with electron-withdrawing groups on tri-s-triazine ring also show remarkably lower triplet energies. For an instance, the E_T values of B5, C1 and D1 were 2.26, 3.02, and 2.92 eV respectively. As shown in Figure 2, the triplet spin densities of B5, C1 and D1 are localized on the full molecule of B5 and D1 while full carbazole unit and partial tri-s-triazine unit of C1, indicating that the E_T value is contributed by both units. For the identical carbazole unit of three hosts, the variation in the E_T values for them is owing to the change of tri-s-triazine moiety. The E_T values of corresponding substituted tri-s-triazines were calculated to be 2.35 eV for dinitrotri-s-triazine, 3.05 eV for diaminotri-s-triazine and 2.71 eV for dimethyltri-s-triazine. It is clear that the E_T value of the molecule decreases significantly when electron-withdrawing group NO_2 is introduced to the tri-s-triazine molecule. This is because that tri-s-triazine is an electron-deficient system. When an electron-withdrawing group is introduced, the energy gap of tri-s-triazine decreases abundantly owing to the significant decrease of LUMO energy, leading to a decrease of E_T value.

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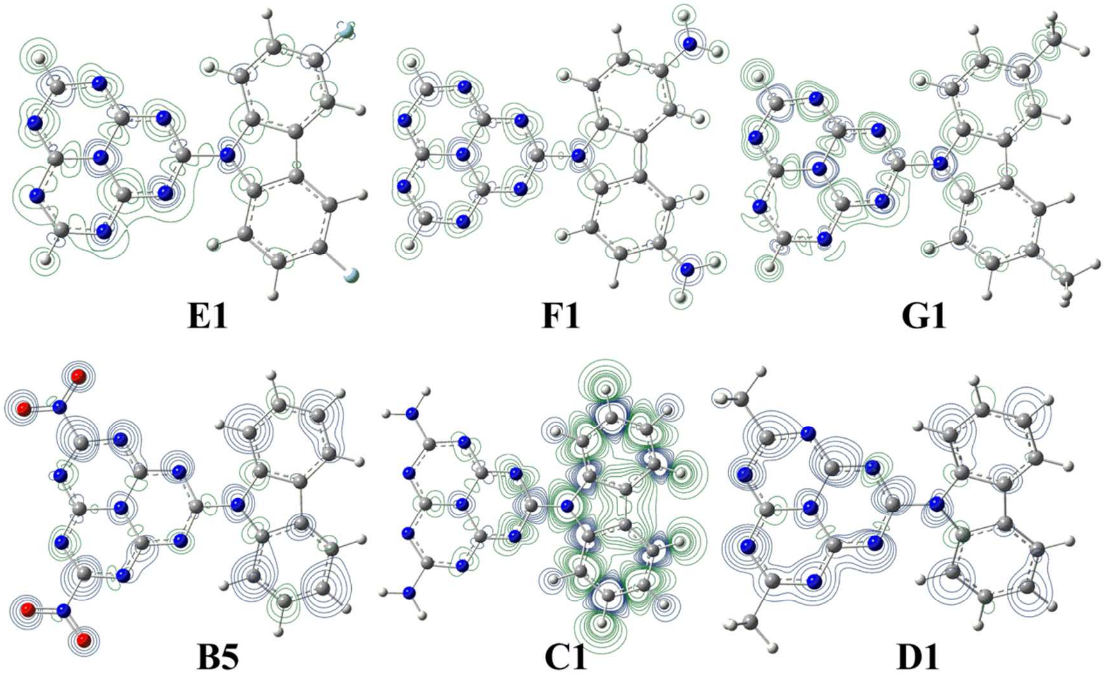

Figure 2 Triplet spin density distribution of E1, F1, G1, B5, C1, and D1 at the B3LYP/6-31G* level of theory.

In order to quantify the trends in substituent effects, we explored linear relationships between the E_T values and the Hammett σ parametrs of.[42] Plotting E_T values against σ parameters (shown in Figure 3) gives a calculated ρ-value of -0.62 for R1 substituent and 0.17 for R3 substituent. The results imply that electron effect of tri-s-triazine substitution is larger than that of carbazole substitution, which is consistent with the results discussed above. The introduction of electron-donating groups to tri-s-triazine ring could enhance the E_T values of the studied host molecules; the introduction of electron-withdrawing groups to carbazole ring almost has no influence on E_T values of the host molecules.

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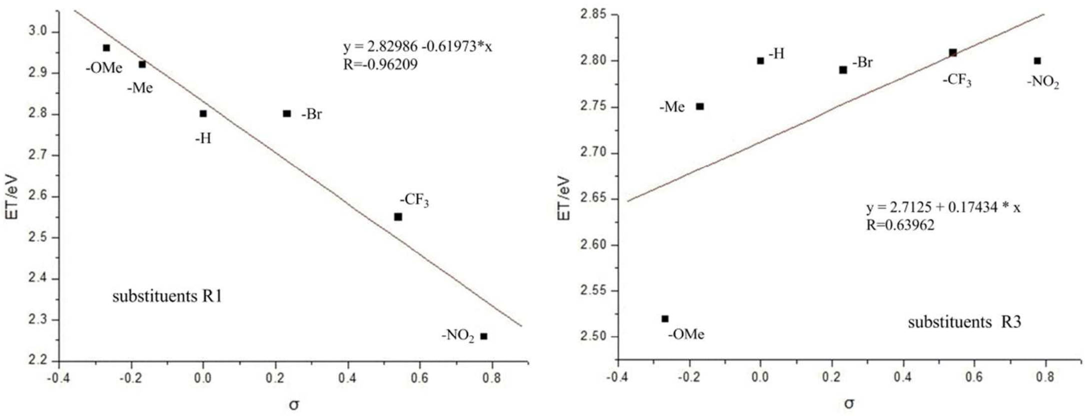

Figure 3 Hammett analysis of the host molecules for quantifying the trends in substituent effects.

3.3 Frontier molecular orbitals

3.3.1 Electron density distributions

Complete separation in the spatial distributions between HOMO and LUMO is necessary for efficient hole and electron transfer and also can prevent back energy transfer. The electron density distribution of the designed hosts is displayed in Figure 4.

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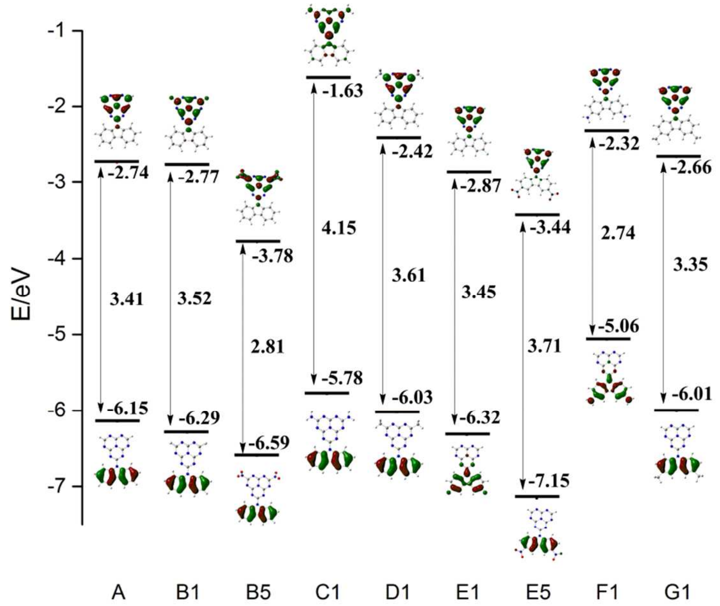

Figure 4 Contour plots and energies of FMO for the designed hosts in the ground state.

It can be seen that all the frontier molecular orbitals show π character and all molecules show significant spatial separation between the HOMO and LUMO. The HOMO is localized on the electron-rich carbazole moiety for all the designed hosts. The LUMO is predominantly concentrated on the electron-deficient tri-s-triazine moiety. This feature implies that the one-electron transition between the HOMO to LUMO is a typical charge transfer, which is preferable for facile hole and electron transfer and the prevention of reverse energy transfer. Figure 4 also clearly point out that the substitution has no influence on the spatial distribution of HOMO and LUMO. All the designed molecules can act as potential ambipolar hosts.

3.3.2 HOMO and LUMO levels

Besides a high triplet energy, a good host material is required to have high HOMO and low LUMO levels for reducing charge injection barriers from neighboring layers and electrodes, thus lowering the device driving voltage.

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The calculated HOMO/LUMO energies and HOMO-LUMO energy gaps of the designed host molecules are listed in Table 2. The table indicates that the energies of the frontier molecular orbitals of the hosts are affected by the substituent group largely. When halogen or electron withdrawing groups are introduced into A, the HOMO and LUMO levels move downward, indicating the improvement of electron transport abilities; while when electron donating or alkyl groups are introduced, the HOMO and LUMO levels go upward, making the host to accept a hole more easily.

Table 2 The calculated HOMO/LUMO energies and HOMO-LUMO energy gaps of the designed host molecules and other layers in the device.

Host	HOMO	LUMO	Eg	Host	HOMO	LUMO	Eg
A	-6.15	-2.74	3.41	E1	-6.32	-2.87	3.45
B1	-6.29	-2.77	3.52	E2	-6.44	-2.99	3.46
B2	-6.31	-3.01	3.29	E3	-6.38	-2.98	3.40
B3	-6.29	-2.99	3.29	E4	-6.97	-3.33	3.64
B4	-6.52	-3.86	2.66	E5	-7.15	-3.44	3.71
B5	-6.59	-3.78	2.81	E6	-6.55	-3.05	3.50
B6	-6.27	-3.34	2.94	F1	-5.06	-2.32	2.74
C1	-5.78	-1.63	4.15	F2	-5.78	-2.63	3.15
C2	-6.07	-2.24	3.83	F3	-5.75	-2.61	3.14
C3	-5.98	-2.14	3.84	F4	-5.58	-2.65	2.92
C4	-5.97	-2.32	3.65	G1	-6.01	-2.66	3.35
D1	-6.03	-2.42	3.61	G2	-6.03	-2.66	3.37
D2	-6.01	-2.41	3.61	G3	-6.02	-2.66	3.36
D3	-6.00	-2.39	3.61	G4	-6.00	-2.66	3.34
D4	-6.01	-2.39	3.62	G5	-6.01	-2.65	3.36
D5	-5.99	-2.37	3.62	G6	-6.01	-2.67	3.34
D6	-6.01	-2.40	3.61	G7	-6.01	-2.64	3.37
D7	-6.00	-2.40	3.60				
Other layers							
NPB	-4.74	-1.15	3.59	BCP	-5.78	-1.28	4.50
TCTA	-5.06	-0.91	4.15	FIr	-5.47	-1.72	3.75

It is worthy to note that there occurs a small shift of HOMO energy but a large change of LUMO value when the substitution occurs at tri-s-triazine ring; on the contrary,

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when the substitution occurs at carbazole ring, the variation is much more pronounced for the HOMO energy than for the LUMO value. This is in consistent with the spatial distribution of HOMO and LUMO. Since the HOMO is localized on the carbazole moiety, the HOMO energy is sensitive to the carbazole substitution; on the other hand, the LUMO is concentrated on the tri-s-triazine moiety, its energy is sensitive to the tri-s-triazine ring substitution.

According to these results, the HOMO and LUMO energies of these compounds could be effectively tunable to match the charge injection from the neighboring layer via different substitution patterns.

3.4 Reorganization energy

As mentioned in the introduction, the optimizing OLED needs to meet the requirement of an adequate charge transfer rate and comparable balance of charge transfer. Berlin concluded that the reorganization energy (λ) could be an important factor that governs the mobility of charge carriers.[43] The smaller the λ value is, the larger the rate of charge transport will be.

The calculated reorganization energies for hole (λ_h) and electron (λe) transport of the designed host molecules are collected in Table 3. As shown in the table, for the reference molecule A, the λ_h value of 0.40 eV is almost as twice as λe value of 0.24 eV, indicating that the electron transport is much faster than the hole transport. The λ_h and λe values of the compounds in series B1-B3, D, E1-E3 and G are approximately equal to those of A, with the largest variation of 0.08 eV, suggesting that the halogen and alkyl group substitution has limited impacts on the reorganization energy. As compared with A, the λ_h values of the compounds in series C show a slight variation, but λe values of them

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increase significantly to 0.38–0.41 eV, indicating that the introduction of electron-donating groups to the tri-s-triazine ring could increase the λe value efficiently. In addition, the differences between λ_h and λe of compounds in series C are less than 0.07 eV. It will improve a balance between hole and electron transfer, which may be beneficial to increase the produce of the exciton. Thus, the effective luminescence is enhanced. Interestingly, compared with A, B5, F1 and F4 have a slightly decreased λ_h value but a much increased λe value of 0.74, 0.42 and 0.54 eV respectively, implying that the introduction of NH_2 and SPh groups to carbazole ring and NO_2 group to tri-s-triazine ring could enhance the hole-transfer ability but suppress the electron-transfer ability of the host molecule.

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Table 3 The calculated reorganization energies for hole (λ_h) and electron (λe) transport of the designed host molecules.

Host	λ1	λ2	λh	λ3	λ4	λe
A	0.19	0.21	0.40	0.11	0.12	0.24
B1	0.22	0.22	0.43	0.14	0.15	0.29
B2	0.22	0.23	0.45	0.12	0.14	0.26
B3	0.23	0.23	0.46	0.12	0.13	0.25
B4	0.22	0.22	0.44	0.16	0.18	0.34
B5	0.22	0.22	0.44	0.43	0.31	0.74
B6	0.21	0.22	0.43	0.28	0.25	0.53
C1	0.16	0.20	0.36	0.18	0.20	0.38
C2	0.22	0.22	0.44	0.17	0.20	0.37
C3	0.18	0.17	0.35	0.18	0.20	0.39
C4	0.21	0.19	0.40	0.19	0.23	0.41
D1	0.20	0.21	0.41	0.10	0.10	0.20
D2	0.17	0.22	0.39	0.10	0.10	0.20
D3	0.17	0.21	0.38	0.10	0.10	0.20
D4	0.17	0.21	0.38	0.10	0.10	0.20
D5	0.16	0.21	0.38	0.10	0.10	0.20
D6	0.19	0.21	0.40	0.11	0.12	0.22
D7	0.20	0.21	0.41	0.11	0.13	0.24
E1	0.19	0.20	0.40	0.11	0.12	0.24
E2	0.17	0.18	0.35	0.10	0.11	0.21
E3	0.16	0.16	0.32	0.10	0.11	0.21
E4	0.13	0.14	0.27	0.08	0.08	0.16
E5	0.13	0.19	0.32	0.08	0.08	0.16
E6	0.20	0.23	0.43	0.10	0.10	0.20
F1	0.17	0.17	0.34	0.35	0.07	0.42
F2	0.20	0.21	0.41	0.13	0.14	0.27
F3	0.24	0.15	0.40	0.13	0.15	0.28
F4	0.14	0.13	0.27	0.41	0.13	0.54
G1	0.19	0.20	0.40	0.11	0.13	0.24
G2	0.20	0.21	0.41	0.12	0.13	0.24
G3	0.26	0.17	0.43	0.12	0.13	0.24
G4	0.19	0.20	0.39	0.12	0.13	0.24
G5	0.26	0.19	0.44	0.12	0.13	0.25
G6	0.19	0.20	0.39	0.12	0.13	0.24
G7	0.17	0.17	0.34	0.12	0.13	0.25

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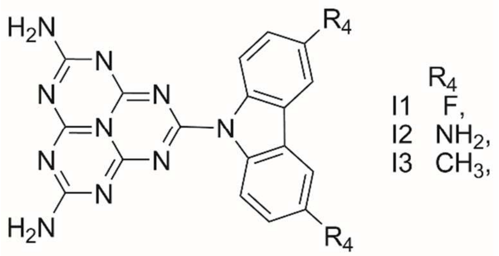
3.5 Potential host molecules used in OLED

Appropriate energy level alignment between host and neighboring layers is very important for the design of OLEDs. A typical device configuration of blue-OLEDs is ITO/MoO_3/NPB/TCTA/Host:FIrpic/BCP/LiF/Al.[44] MoO_3 and LiF are used as anode and cathode respectively; N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)benzidine (NPB) is used as the hole-transporting layer; 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is used as electron-transporting layer; 4,4′,4′′-tri(N-carbazolyl)triphenylamine (TCTA) is used to confine excitons in the emissive layer (EML) and to reduce the energy barrier between the HOMO levels of NPB and EML; FIrpic doped in host is used as the emitting layer. For an ideal host molecule, the HOMO level should be lower than that of TCTA and higher than that of BCP, while the LUMO level should be lower than that of BCP and TCTA, to lead to good charge transport and exciton blocking. Moreover, electron and hole trapping will be most favorable when the LUMO level of host is higher and the HOMO level is lower than that of guest. Specifically, for the host molecules designed in this study, the HOMO level should be lower than -5.47 eV and higher than -5.78 eV, while the LUMO should be lower than -1.28 eV and higher than -1.72 eV.

Scheme 2 Sketch map of the structures of I1-I3.



From Table 2, only the LUMO level of C1 fits the device. In order to obtain better interlayer matching of the HOMO and LUMO properties, three new host molecules I1–I3

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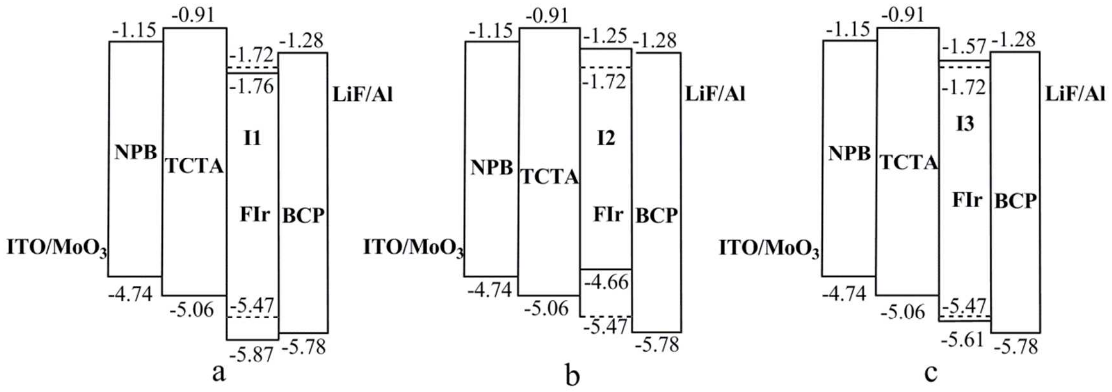
were designed (Scheme 2) according to the substitution effects discussed above. The calculated HOMO/LUMO energies, reorganization energies and triplet energies of newly designed host molecules are listed in Table 4. Moreover, the configurations and energy level diagrams of devices are shown in Figure 5. It can be seen from the table and the figure that I3 has a good interlayer matching of the HOMO and LUMO levels, a balanced transfer of hole and electron and a high triplet energy. This result suggests that the performance of the hosts would be significantly enhanced by introducing NH_2 group to tri-s-triazine ring and alkyl groups to carbazole ring of the reference molecule A. Thus, a series of host molecules I4−I9 were designed and investigated. The calculated HOMO/LUMO energies, reorganization energies and triplet energies of them are also listed in Table 4. As expected, the E_T values of I4−I9 are higher than that of FIrpic (2.60 eV). The HOMO levels of I4−I9 are in a narrow range of -5.58 to -5.63 eV, which is moderately lower than those of TCTA (-5.06 eV) and FIrpic (-5.47 eV) , but higher than that of BCP (-5.78 eV). Simultaneously, the LUMO levels of them are also in a narrow range (-1.55 to -1.58 eV), which is lower than those of TCTA (-0.91 eV) and BCP (-1.28 eV), but higher than that of FIrpic (-1.72 eV). Considering these energy levels above, I4−I9 may fit the OLED device well. In terms of charge transport rate, I6 and I9 exhibit a balanced charge and hole transfer owing to their comparable λ_h and λe.



a: ITO/MoO3/NPB/TCTA/I1:FIrpic/BCP/LiF/Al;

b: ITO/MoO3/NPB/TCTA/I2:FIrpic/BCP/LiF/Al;

c: ITO/MoO3/NPB/TCTA/I3:FIrpic/BCP/LiF/Al.

Figure 5 The configurations and energy level diagrams of devices.

Table 4 The calculated HOMO/LUMO energies, reorganization energies and triplet energies of newly designed host molecules (series I)

Host	E_T	HOMO	LUMO	Eg	λ1	λ2	λh	λ3	λ4	λe
I1	3.23	-5.87	-1.76	4.10	0.19	0.20	0.38	0.18	0.20	0.38
I2	2.64	-4.66	-1.25	3.41	0.18	0.19	0.37	0.18	0.20	0.38
I3	2.95	-5.61	-1.57	4.04	0.16	0.17	0.33	0.18	0.20	0.37
I4	2.97	-5.61	-1.57	4.04	0.16	0.17	0.34	0.25	0.27	0.52
I5	2.97	-5.60	-1.57	4.04	0.16	0.17	0.33	0.25	0.27	0.52
I6	2.96	-5.62	-1.57	4.05	0.16	0.17	0.33	0.18	0.20	0.38
I7	2.97	-5.59	-1.56	4.03	0.16	0.17	0.34	0.25	0.27	0.52
I8	2.96	-5.63	-1.58	4.05	0.16	0.19	0.35	0.25	0.28	0.53
I9	3.21	-5.58	-1.55	4.03	0.16	0.17	0.33	0.18	0.20	0.38

It must be noted that our prediction is based on the single molecular calculations. For the solid-state devices, some other factors should be considered, such as coupling between molecules, excitonic effects, crystal packing effects on conformations, and the low conductivity of molecular crystals.

3.5.1 Triplet exciton formation fraction

Previous studies reveal that the triplet exciton-formation fraction (χ_T) is an indicator to identify the potential host molecules which is related to triplet exciton formation in the host molecule. Higher the χ_T values are associated with better performance. In this study, the triplet exciton-formation fraction (χ_T) of I3-I9 was calculated according to the

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following equation[45]:

$$\chi_T = \frac{3\sigma_T}{\sigma_S + \sigma_T}$$

where σ_S and σ_T represent the formation cross-sections of singlet and triplet excitons respectively. The ratio σ_S/σ_T of the formation cross-section of the singlet and triplet is

$$\frac{\sigma_S}{\sigma_T} = \frac{E_{bT}}{E_{bS}} = \frac{E_g - E_{T1}}{E_g - E_{S1}}$$

where E_{bS} and E_{bT} are the binding energies of the singlet and triplet excitons, respectively, E_g is the HOMO-LUMO energy gap, and E_{S1} and E_{T1} are excitation energies from the ground state to the lowest excited singlet state and the lowest excited triplet state, orderly.

The exciton binding energy (E_{bT} and E_{bS}), the ratio (σ_S/σ_T) of the singlet-to-triplet exciton-formation cross-section, and triplet exciton-formation fractions (χ_T) for I3-I9 are collected in Table 5. The calculated values of σ_S/σ_T are in the range 1.98-2.12 with the corresponding triplet exciton-formation fractions (χ_T) of 58-60%, which is comparable to the reported values for previous studied host molecules in literature,[46,47] suggesting their potential as the efficient host molecules.

Table 5 The exciton binding energy (E_{bT} and E_{bS}), the ratio (σ_S/σ_T) of the singlet-to-triplet exciton-formation cross-section, and triplet exciton-formation fractions (χ_T) for hosts I3-I9.

Host	E_{bT}	E_{bS}	σ_S/σ_T	χT（%）
I3	1.06	0.53	2.00	59.99
I4	1.03	0.50	2.04	59.51
I5	1.02	0.50	2.04	59.49
I6	1.05	0.53	1.98	60.21
I7	1.02	0.50	2.04	59.56
I8	1.05	0.53	2.00	60.02
I9	0.98	0.46	2.12	58.57

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3.5.2 Singlet *versus* triplet energy

The difference between the S_1 and T_1 excitation energy (ΔE_{ST}) is an additional indicator of the potential performance of host molecules, which is related to the driving voltage and triplet exciton formation in the host molecules. A smaller ΔE_{ST} is proposed to correlate to a better performance. We calculated the ΔE_{ST} of I3-I9 at the optimized ground state geometry by TD-DFT method.

The calculated ΔE_{ST} of I3-I9 is presented in Table 6. It can be seen from the table that the ΔE_{ST} values vary from 0.52 to 0.53 eV, which is comparable to the reported values for previous studied host molecules in literature,[35,45] suggesting efficient triplet exciton formation in the host and can exhibit a reduced driving voltage.

Table 6 The difference between the S_1 and T_1 excitation energy (ΔE_{ST}) of hosts I3-I9.

Host	S0→S1	S0→T1	ΔE_{ST}
I3	3.51	2.98	0.53
I4	3.54	3.01	0.53
I5	3.53	3.01	0.52
I6	3.52	3.00	0.52
I7	3.53	3.01	0.52
I8	3.52	2.99	0.53
I9	3.57	3.05	0.52

3.6 Effect of different functionals on E_T and ΔE_{ST}

It is well known that application of the B3LYP functional leads to a severe underestimation of excitation energies in the charge-transfer states. In order to analyze how the variation in the choice of functional can alter the results, we carried calculations with functionals like BLYP (0%HF), B3LYP* (15%HF), B3LYP (20%HF), PBE1KCIS (22%HF), M06 (27%HF), BMK (42%HF), M06-2X (56%HF), M06-HF (100%HF) and CAM-B3LYP (19% HF at short range and 65% at long range) in conjugation with the 6-31G* basis set to evaluate E_T and ΔE_{ST} of compound A. The calculated results shown

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in Figuer X indicate that the more HF-like exchange employed, the larger triplet energy has. E_T value evaluated by B3LYP is in the middle. The Figure 6 also indicates that the functional influences ΔE_{ST} little.

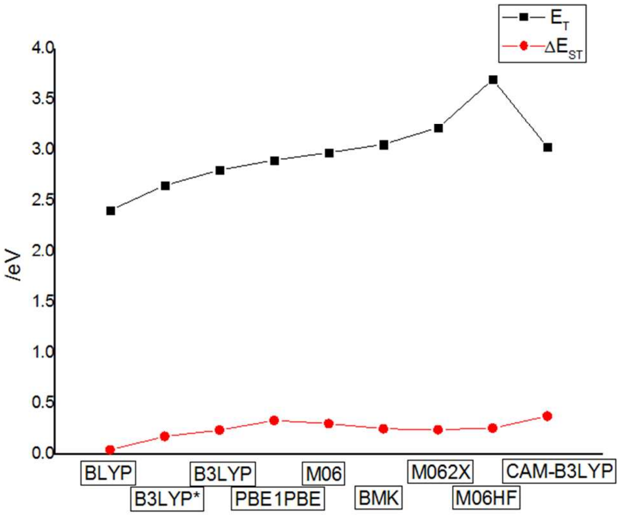

Figure 6 Evolution of E_T and ΔE_{ST} of the designed hosts using different DFT functionals.

4 Conclusion

A comprehensive DFT study of the structure and electronic properties of a series of carbazole combined with tri-s-triazine host molecules has been performed. Forty four host molecules were designed by substituting carbazole and tri-s-triazine rings. Our theoretical calculations revealed that various properties like triplet energy (E_T), HOMO and LUMO energy levels, and the charge transporting property of the designed host molecules can effectively be tuned by introducing halogen, electron-withdrawing, electron-donating and alkyl groups. Among the newly designed host molecules, the systems containing NH_2 in tri-s-triazine and alkyl groups in carbazole were found to be good host materials for blue emitting phOLED. We hope the findings described in this theoretical work are useful for the development of the branch of tri-s-triazine chemistry and blue PhOLEDs.

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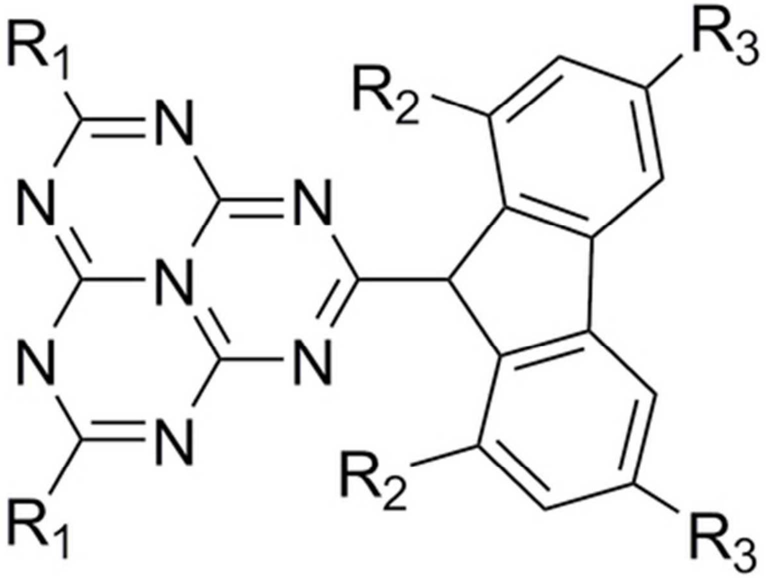

The design of the tri-s-triazine derivatives for host materials
33x25mm (300 x 300 DPI)

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