Enhanced blue thermally activated delayed fluorescence with rigid adamantane as non-conjugated linker for space-confined donor-acceptor charge transfer: a theoretical study

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Abstract—A lack of control over the relative orientation of donor and acceptor moieties in solid films is the main reason for poor electroluminescence efficiency found in most D–σ–A patterns. In this study, adamantane was introduced as the linker for the construction of a D–σ–A system since its rigid but non-conjugated nature. For a systematic study, the same donor (9,9-dimethyl-10-phenyl-9,10-dihydroacridine, DMTPA) and acceptor (2,4,6-triphenyl-1,3,5-triazine, TPZ) block were attached at different sites of the adamantine molecule, forming three kinds of configuration including face-to-face (FF), head-to-tail (HT), and chair (CH) style. DFT/TD-DFT simulation was carried out to investigate the electronic structures, optical characteristics, and charge transfer (ICT) properties of these three designed molecules. Attributed to a non-conjugated adamantane linker, the conjugation between donor and acceptor was disrupted for either of these molecules, resulting in high triplet energy of 2.79, 2.99, and 3.10 eV, respectively. Among them, the face-to-face style molecule presents the smallest ΔE_{ST} and greatest charge transfer excitation from donor to acceptor, suggesting an excellent potential for thermal activated delayed fluorescence (TADF). Face-to-face type molecule is a good option for a high-performance blue organic light-emitting diode (OLED) host material based on these results. Our investigation may open a door for designing new host molecule with other donor and acceptor groups to further enhance the efficiency and longevity of OLEDs.

1. Introduction
Organic light-emitting diode (OLED) materials and associated device fabrication methods have been subjected to extensive investigation with the purpose of determining their potential on display and lighting applications. One can attain 100% internal quantum efficiency (IQE) with thermally activated delayed fluorescence (TADF), which is possible because of the upconversion of triplet excitons to singlet ones via reverse intersystem crossing (RISC). In order for charge-transfer host molecules with spatially separated electron and hole wave functions to be successful, TADF requires a very tiny energy difference(ΔE_{ST}) between the singlet and triplet excited states of the lowest energy. The external quantum efficiencies (EQEs) of organic light-emitting diodes (OLEDs) based on excitable host molecule have recently reached as high as 16% due to the TADF mechanism and the development of suitable D/A pairings.

Recently, Molecular host materials for phosphorescent OLEDs can now be designed using the electron donor—acceptor (D–A) system because of its bipolar charge injection and transport capabilities (PhOLEDs). However, D–π–A host with an extended conjugated extension generally introduces intramolecular charge transfer (ICT) interactions, which reduces ET. A host material that can be used in...
blue and white PhOLEDs is severely constrained because of this fact. Because of this, there are just a handful of high-efficiency D–π–A type universal hosts for OLEDs that are available. The construction of bipolar universal hosts employing the D–π–A molecular system is greatly wanted because linking style efficiently reduces ICT between the donor and acceptor. As an example, the sp3 carbon site of Fluorene has been extensively studied for joining D or A components. Most fluorene compounds, on the other hand, fall short of achieving extraordinarily high ET. Fluorene’s neutrality allows it to be combined with electron-donating or electron-withdrawing groups via its conjugated sites, further reducing ET. As a result, the D–A molecule makes use of a stiff linker to regulate the distance between the donor and acceptor subunits and the orientation of those subunits in OLEDs.

In this study, three different host molecules by attaching at different sites of an adamantane molecule were designed, a host material, as π-conjugation interrupter between 9,9-dimethyl-10-phenyl-9,10-dihydroacridine (DMTPA) and 2,4,6-triphenyl-1,3,5-triazine (TPZ). By connect the donor and acceptor units via a rigid but non-conjugated linker, adamantane, they are confined into a closely packed coplanar configuration. Adamantane bridges inhibit the transfer of intramolecular charge from electron-donating DMTPA to electron-receiving TPZ and the conjugation between DMTPA and TPZ was disrupted, thus giving the molecule a higher triplet energy. The introduction of a rigid adamantane linker can also keep the low molecular weight host thermally stable. By comparing with head-to-tail (HT) and chair (CH) designs, a host molecule with donor and acceptor in a face-to-face (FF), with ΔEST less than 0.7 eV and high triplet energy of 2.79 eV, has the most strongly contributes in the CT state.

2. Computational details
The Gaussian 16 program package was used to do density functional theory (DFT) and time-dependent density functional theory. The B3LYP exchange-correlation function and the 6-31G* basis set with D3 correction were used to optimize the ground states. Optimizing excited state geometries was achieved by implementing TD-DFT calculations at cam-B3LYP level. Difference between lowest excited singlet state (S1) and lowest excited triplet state (T1) energies were used to compute EST values at their optimal geometries. TDDFT calculations were performed in the gas phase using the cam-B3LYP functionals and the 6-31G* basis sets and Multiwfn program. Analysis of hole electrons was carried out using the Multiwfn 3.5.1 software program after the findings of TD-DFT calculations.

3. Results and Discussions
3.1. Geometric and electronic structures
DMTPA (9,9-dimethyl-10-phenyl-9,10-dihydroacridine) and TPZ (2,4,6-triphenyl-1,3,5-triazine) were chosen as the donor and acceptor motifs respectively by using a rigid linker, adamantane. The first host molecule of molecules consisted of donor and acceptor with adjacent position in face-to-face (FF), as P. The second one was in a rectangular state with donor and acceptor of head-to-tail (HT), as R. The last one was that donor and acceptor are at chair (CH) style, as LP. All the triphenyltriazine acceptors were connected at the para position. Chemical structures of them are shown in Figure 1.
3.2. Frontier Molecular Orbitals (FMOs)

Ground-state and excited-state geometries were optimized in order to better understand the relationship between the compound's geometrical and electrical properties. It was necessary to compute the HOMO and LUMO electron populations in order to see where each population's electrons fall in relation to the molecular orbital energy map. As predicted, the HOMO was concentrated on the donor units, whereas the LUMO was dispersed over the electron-deficient acceptor moieties, according to the calculations (Figure 2). The LUMO and HOMO level of them were all suitable for electron injection from the cathode. However, in comparison with R and LP, which a little bit of the HOMO was on adamantane, the HOMO of P distributed in donor units with the most complete separation due to the nonconjugated adamantane linkage.

As Table 1 shown, R and LP had similar HOMO and LUMO levels, whereas the P possessed a lower HOMO and deeper LUMO level, -4.99 eV and -1.80 eV respectively. S1 and T1 energy levels were used to estimate the ΔE_ST for P, R, and LP, with P more likely to meet a requirement for efficient thermally triggered delayed fluorescence (TADF). These values were 0.64, 1.39, and 1.66 eV respectively. In addition, the dipole moments for the S1 states of P had the biggest number, with 18.85 Debye, in comparison with R (2.53 Debye) and LP (3.02 Debye).
Table 1. DFT and TD-DFT calculation results.

|        | HOMO  | LUMO  | S1    | T1    | ΔE_ST | Dipole Moment of S1 (Debye) |
|--------|-------|-------|-------|-------|-------|-----------------------------|
| P      | -4.99329 | -1.80357 | 3.4277 | 2.790964 | 0.636736 | 18.85297                   |
| R      | -5.1084  | -1.6969  | 4.3767 | 2.988655 | 1.38804   | 2.527885                   |
| LP     | -5.19194 | -1.69337 | 4.7617 | 3.097691 | 1.66401   | 3.020035                   |

3.3. Optical absorption and emission properties

The properties of electronic transition in the absorption and fluorescence emission process evaluated for all host molecule are summarized in Figure 3 at their optimized S1 geometry. The p–p* transition of the carbazole molecule is responsible for all absorption in the region of 310-350 nm and about 293 nm. [21-23]. As Figure 3(a), all of them had one peaks with almost same peak positions, between 270-300 nm, while the absorption intensities at the peaks were different, which P’s (about 35000.0 L mol⁻¹ cm⁻¹) was more than double the amount of anyone of R’s and LP’s. It was according with the dipole moments for the S1 states of P had the biggest number that had the strongest absorption. However, from Figure 3(b), the peak positions were different and the absorption intensities of P and LP were the same at the peaks. But, that of R was far from highest among them, above 12000.0 nm, which was because f value of R (Table 2) was the largest at optimized S1 geometry.

Figure 3. Simulated absorption(a) and fluorescence emission spectra(b) for P, R and LP at their optimized S1 geometry.

3.4. Charge transfer (CT) properties

Interfragment CT study on relaxed S1 states helped us better understand the various roles played by the fluorene spacer in the CT state development. There was negligible participation of the fluorene spacer in electron transitions involved with the development of the CT-state in P, as illustrated in Figure 4. However, for R and LP, there was no any or minimal electron transition. For Figure 5, hole-electron spatial distribution of P was completely separated, whereas that of R and LP got together. All of Figure 4-5 demonstrate that a pure CT intramolecular exciplex was made possible because to P's molecular design technique, but R and LP were not.
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Figure 4. During the excited state of S1, the electron contribution ratio ($\eta$) for the transitions from donor to acceptor, from donor to linker, and from linker to acceptor.

Table 2. D-DFT results and hole-electron analysis of S1 states. D_idx is the hole-electron centroid distance. Sr is the hole-electron overlap integral. T_idx is the CT character.

|                | eV  | f   | D_idx | Sr    | T_idx | Orbital Composition          |
|----------------|-----|-----|-------|-------|-------|------------------------------|
| P              | 3.4284 | 0.0641 | 4.645 | 0.26174 | 2.816 | H-L 93.4%                   |
| R              | 4.3767 | 0.3016 | 2.088 | 0.63102 | -0.057 | H1-L 44.0%, H2-L 24.7%, H4-L 16.2% |
| LP             | 4.7617 | 0.0578 | 9.455 | 0.38003 | 6.239 | H-L 84.2%, H4-L 6.4%        |

Figure 5. Hole-electron spatial distribution of S1 states of P, R and LP

4. Conclusion
To conclude, a new D–σ–A system by providing a rigid but non-conjugated adamantane to link a donor (9,9-dimethyl-10-phenyl-9,10-dihydroacridine, DMTPA) and an acceptor (2,4,6-triphenyl-1,3,5-triazine, TPZ) was designed. There is evidence that a face-to-face (FF) with high charge-transfer emission quantum yield, acceptable thermal qualities, and suitable photophysical parameters can be used for effective thermally activated delayed fluorescence (TADF). This outstanding device performance highlighted the tremendous potential of adamantane-based compounds as a host material for organic light-emitting diodes (OLEDs). Also, using these findings, new functionalized adamantane with other donor and acceptor groups can be designed to further enhance the efficiency and longevity of OLEDs.
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