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Ab initio molecular orbital study of 1,3,5-triazine derivatives for phosphorescent organic light emitting devices

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Abstract

Novel triplet host materials 2,4,6-tris(diarylamino)-1,3,5-triazine derivatives (TRZ1–TRZ4) have been reported and from which TRZ2 as a host for $Ir(ppy)_3$ was particularly useful in producing high efficiency phosphorescent organic light emitting diodes (OLEDs). This Letter reports the molecular orbital and energy level of these derivatives determined by ab initio calculation. The calculated triplet bandgap energy of TRZ1 has been found to be larger than that of TRZ2 and the TRZ1 molecules and has the lowest dipole moment which infers the highest carrier mobility. Therefore, TRZ1 has the potential to be a superb triplet host material and electron transport material.

Phosphorescent organic light emitting devices (PHOLEDs) can achieve near 100% internal quantum efficiency [1]. Recently, Adachi and co-workers [2] synthesized four 2,4,6-tris(diarylamino)-1,3,5-triazine derivatives (TRZ1–TRZ4 as shown in Fig. 1) for use as host as well as electron transport material. They obtained high external quantum efficiency (~10%) by using TRZ2 with carbazole substituents. Since TRZ2 triplet gap was found to be higher than that of 4,4′-*N*,*N*′-dicarbazolyl-biphenyl (CBP), it was suggested that TRZ2 can effectively confine the triplet exciton of the green phosphorescent dopant *fac*-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$). However, it was also reported that the TRZ1 thin film had a polycrystalline morphology with which it was difficult to fabricate a robust OLED multilayer structure. Therefore, the triplet gap of TRZ1 has never been ascertained even though, from the structural point of consideration, it should have the largest triplet bandgap energy.

A number of theoretical electronic structural studies of OLED materials have been reported, but most dealt with tris(8-hydroxy-quinolinato)aluminum (Alq_3) which is the archetypical host electron transport materials for fluorescent OLEDs [3]. Recently, there are many studies about the triplet bandgap of Alq_3 [3] and we also calculated the triplet bandgap of Alq_3 by computer simulation (ab initio calculation) [4]. The simulation result is consistent with the experimental data [5]. In this Letter, we report on the simulation of the triplet bandgap of TRZ1 by ab initio calculation and discuss the electron distribution of HOMO and LUMO of TRZ1–TRZ4.

The structures of TRZ1–TRZ4 were optimized by using ab initio density functional theory (DFT) with the B3LYP (Becke three-parameter Lee–Yang–Parr) [6] exchange correlation function with 6-31G* basis sets, in GAUSSIAN 03 program [7]. Percentage compositions of molecular orbitals and density of states were calculated using the AOMIX program [8] whose analyses are based on the output coefficient matrix of wave functions and the discrete peaks are broadened using Gaussian functions with a broadening parameter of 0.5 eV. The triplet gap is determined by the energy

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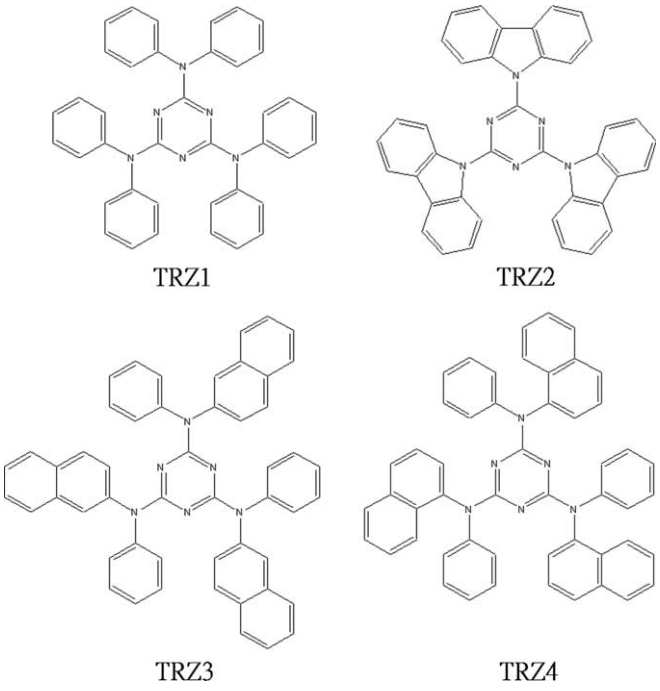

Fig. 1. Molecular structures of TRZ1–TRZ4.

difference between the unrestricted triplet state and the restricted singlet state in the optimized triplet state geometry.

The ground state and triplet state molecular geometries of TRZ1–TRZ4 are optimized by DFT with B3LYP basis sets. The calculated and experimental energy levels are shown in Table 1. The energy level difference of highest occupied molecular orbital (HOMO) is around 0.2 eV and lowest unoccupied molecular orbital (LUMO) energy difference is 0.5 eV by electrochemical experiments. From the simulation results, we also find that the energy level difference of LUMO is larger than that of HOMO. This phenomenon can be rationalized by the molecular orbital decomposition of the triazine moiety, from which we observed the carbon atoms are mainly occupied by the electron of LUMO state (Fig. 2). Therefore, the electron-donating substituents directly connected to the carbon atoms would alter the LUMO energy level. Connecting donor or acceptor to the HOMO site and LUMO site has been reported to be effective in adjusting the energy level and gap [9]. The ionization potential and oxidation potential of diphenylamine has been found to be smaller than that of carbazole [10], therefore we conclude that the diphenylamine is a stronger donor than carbazole and would cause

Table 1
Calculated energy levels as compared with experimental results

	TRZ1	TRZ2	TRZ3	TRZ4
HOMO (eV)	5.47(6.0)[a]	5.77(6.0)	5.36(5.8)	5.47(5.8)
LUMO (eV)	0.38(2.1)	1.41(2.6)	0.96(2.3)	1.06(2.2)
Singlet E_g (eV)	5.1(3.9)	4.4(3.4)	4.4(3.5)	4.4(3.6)
Triplet E_g (eV)	2.88(–[b])	2.63(2.81)	2.21(2.47)	2.11(2.42)
Dipole (D)	0.3	1.2	1.9	2.5

[a] The experimental value in brackets is cited from [2].
[b] The triplet gap of TRZ1 has not been measured by experiment.

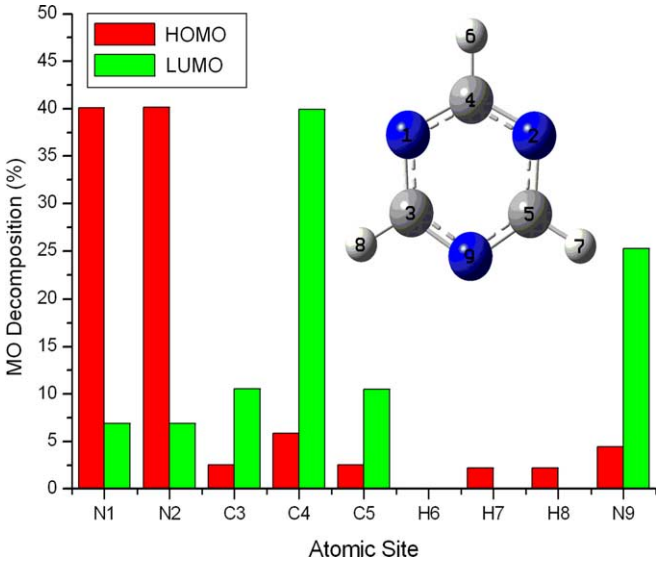

Fig. 2. The percentage compositions of triazine HOMO/LUMO molecular orbitals.

the TRZ1 to have the smaller LUMO energy level and result in a larger singlet energy gap. Hence, the singlet gap of TRZ1 is about 0.5 eV larger than that of TRZ2–TRZ4.

Fig. 3 depicts the calculated HOMO and LUMO electron distribution of TRZ1–TRZ4. We find TRZ1 has the most delocalized HOMO and LUMO molecular orbital. Molecular charge transporting property is related to the distribution of HOMO and LUMO. In general, a more delocalized HOMO would allow better intermolecular orbitals overlap which would lead to easier hole-transport by hopping. On the other hand, the more localized HOMO will not be favorable for hole-transport. Adachi in his Letter reported that TRZ2 also functions as an electron transport material (ETM) and hole blocking material. We note that the LUMO of TRZ2 shows a highly delocalized distribution and the HOMO electron density is located on only one side (see Fig. 3) of the molecule. Although TRZ3 and TRZ4 have not been reported in the literature as to their suitability for use as the ETM, our calculations suggest that TRZ3 and TRZ4 could not be an effective ETM due to their considerably localized LUMO electron density.

The charge carrier mobility through the organic thin film strongly depends on the molecular packing within the film. The carrier mobility μ exhibits a universal Poole–Frenkel [11] behavior

$$\mu = \mu_0 \exp(-\theta/kT) \exp(\gamma\sqrt{E}),$$

where k is Boltzmann's constant, the activation energy θ is temperature independent, and γ is the Poole–Frenkel factor. According to the disorder model (Bässler and co-workers) [12], $\Theta/kT = (2\sigma/3kT)^2$, and $\gamma = C(\beta^2\sigma^2 - \Sigma^2)$, where $\beta = 1/kT$, and C and Σ are constants, σ is the width of the energetic disorder [13]. The charge-dipole model from Young and Fitzgerald [14] describes the variance of σ depends on the molecular concentration and dipole moment, they studied several molecules and the dipole moment

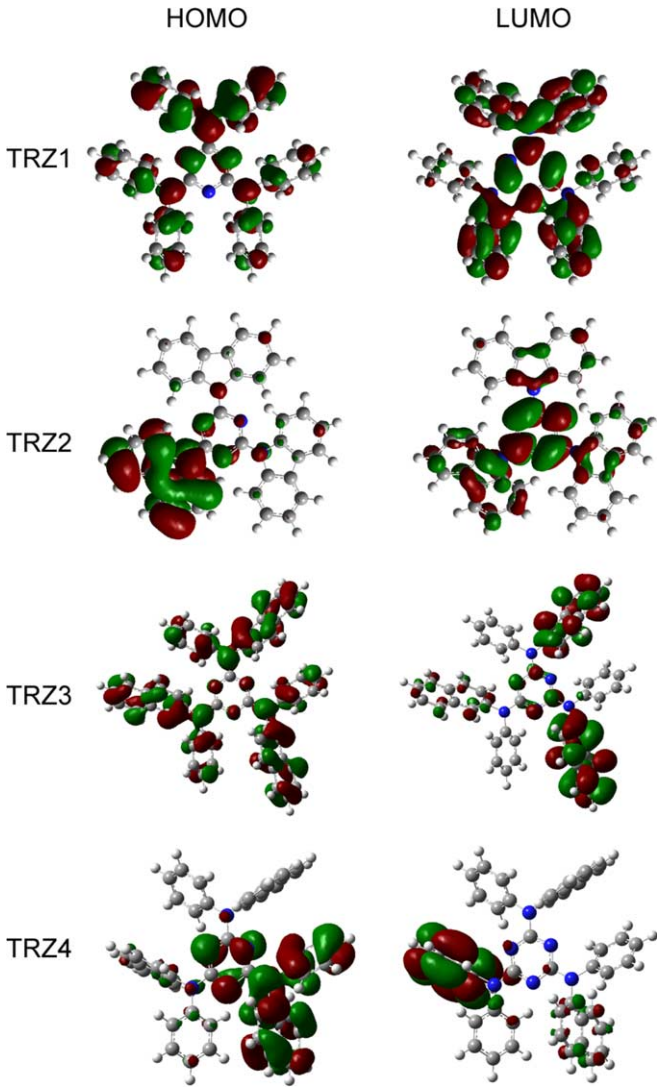

Fig. 3. The calculated HOMO/LUMO electron distribution of TRZ1–TRZ4.

range in 0–6.6 D. It was found the molecule with high dipole moment has lower carrier mobility and strongly depends on electric field. So and co-workers [15] has found that the hole mobilities of a series of naphthyl phenylamine (NPA) compounds can be correlated with the dipole moments, and the weak dipole moment will lead to low carrier mobility. The calculated dipole moments of TRZ1–TRZ4 are, respectively, 0.3, 1.2, 1.9 and 2.5 D (Table 1), therefore the TRZ1 can be predicted has the largest mobility in these compounds. On the other hand, the density of states (DOS) of TRZ1 and TRZ2 have been compared in Fig. 4 in which TRZ1 has been found to have more DOS on LUMO, that in turn means it can accommodate more electrons in LUMO.

Although TRZ2–TRZ4 has almost the same singlet gap, the calculated triplet gap of TRZ2 is observed to be larger than that of TRZ3 and TRZ4 by about 0.4 eV. The calculation is in good agreement with the experimental results, which suggest excellent triplet exciton confinement of

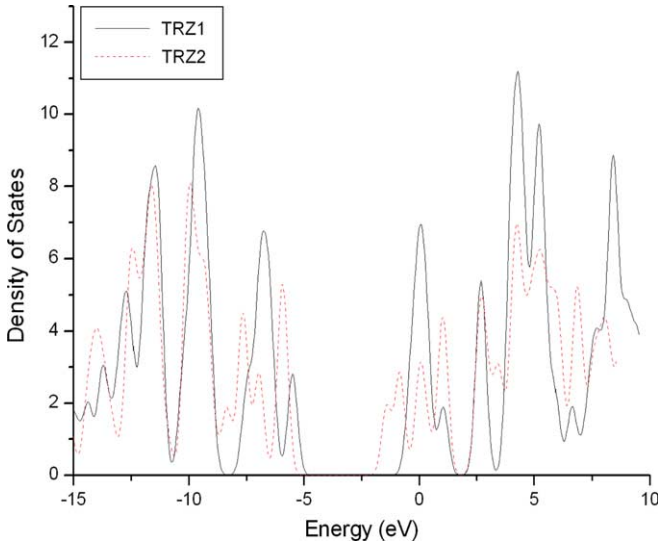

Fig. 4. Total density of states of TRZ1 and TRZ2.

$Ir(ppy)_3$ by TRZ2. However, the triplet gap of TRZ1 has not been measured experimentally because it was found to have a polycrystalline morphology. Here for the first time, our calculation has confirmed that the calculated triplet gap of TRZ1 is about 0.25 eV larger than that of TRZ2. The phosphorescent host materials are required to have large triplet gap to confine the triplet exciton of the phosphorescent dopant. Therefore, TRZ1 having not only high electron mobility but also large triplet energy gap is expected to be a good host material for a variety of phosphorescent dopants with smaller triplet bandgap energy. Unfortunately, TRZ1 as thin-film was shown to be morphologically unstable upon evaporation. But from this study, we find that the triplet gap of TRZ1 is the largest among the rest. Therefore, how to suppress recrystallization and maintain the conjugation system within TRZ1 are important criteria for the next generation of triplet host material design.

In summary, this Letter reports the calculated singlet gap and triplet gap of TRZ1–TRZ4 which are found in full agreement with experimental results. TRZ1 has the largest singlet gap due to the strong electron-donating substituents directly connected to the LUMO site of the triazine moiety. Although the triplet gap of TRZ1 has not been measured because of its polycrystalline thin-film morphology in experiment, we found TRZ1 has the largest triplet gap of the 2,4,6-tris(diarylamino)-1,3,5-triazine derivatives by ab initio calculation. The most delocalized electron distribution of TRZ1 also suggests that the charge would be more easily moved around the molecule which in turn would lead to improved intermolecular charge-transport by efficient and extensive orbital overlap. On the other hand, TRZ1 has been found with the smallest dipole moment, from which we infer that TRZ1 has the highest carrier mobility. Therefore, we conclude that TRZ1 should have the best capabilities in confining the green phosphorescent $Ir(ppy)_3$ triplet excitons and can be use as an electron transport material as well.

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