



Theoretical studies on electroluminescent mechanism of a series of thermally activated delayed fluorescence emitters possessing asymmetric-triazine-cored triads

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ABSTRACT

A series of thermally activated delayed fluorescence (TADF) emitters using asymmetric-triazine-cored triad as the electron-accepting unit have been investigated theoretically. Based on two experimentally reported TADF molecules (**TPXZ-*as*-TAZ** and **oDPXZ-*as*-TAZ**), two new molecules (**mDPXZ-*as*-TAZ** and **pDPXZ-*as*-TAZ**) have been designed to explore the isomeric effect on their TADF properties. The present results reveal that the absorption and emission spectra calculated by the time-dependent density functional theory (TD-DFT) method at the M06-2X level are match well the available experimental findings, and **mDPXZ-*as*-TAZ** and **pDPXZ-*as*-TAZ** are found to exhibit the same yellow emission as their analogue **oDPXZ-*as*-TAZ**. In addition, the rates of reverse intersystem crossing of **mDPXZ-*as*-TAZ** and **pDPXZ-*as*-TAZ** estimated by the semiclassical Marcus theory are 2.51×10^6 and $4.57 \times 10^6 \text{ s}^{-1}$, respectively, one order of magnitude larger than that of **oDPXZ-*as*-TAZ** ($1.27 \times 10^5 \text{ s}^{-1}$), which suggests that our newly designed two molecules **mDPXZ-*as*-TAZ** and **pDPXZ-*as*-TAZ** can be also considered as potential yellow-light TADF emitters.

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1. Introduction

In recent years, the thermally activated delayed fluorescence (TADF) emitters have attracted a great deal of interest in that these TADF emitters are capable of harvesting both singlet and triplet excitons in organic light-emitting diodes (OLEDs) devices to achieve the internal quantum efficiency (IQE) of 100%, which is desirable to realize high-performance OLEDs for flexible flat-panel displays and solid-state lighting [1–46].

It is known that TADF molecules usually comprise electron donor (D) and acceptor (A) units, and their excited states are observed to exhibit a charge transfer (CT) characteristic from D to A framework. Owing to the strongly electron-deficient character, a symmetric 1,3,5-triazine (*s*-TAZ) group has been extensively adopted as the A moiety of a D-A or D- π -A system that shows significant TADF property [47–54]. A representative example is the report of 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9H,9'H-3,3'-bicarbazole exhibiting a sky-blue emission in OLEDs device with a maximum external quantum efficiency (EQE) of 21.7% [49]. As an isomer of *s*-TAZ, an asymmetric 1,2,4-triazine (*as*-TAZ) unit has recently received attention from researchers. One main motivation is to make it clear whether or not *as*-TAZ can be used as an efficient A unit in the TADF emitters. Based on the speculation, Yang

and co-worker designed two asymmetric-triazine-cored triads, that is, 10,10',10''-((1,2,4-triazine-3,5,6-triyl)tris(benzene-4,1-diyl))tris(10H-phenoxazine) (**TPXZ-*as*-TAZ**) and 10,10''-(3-phenyl-1,2,4-triazine-5,6-diyl)bis(4,1-phenylene))bis(10H-phenoxazine) (**oDPXZ-*as*-TAZ**) (see Fig. 1), in which the *as*-TAZ core is used as the A unit, phenyl groups as the π -bridges, and phenoxazine (PXZ) groups as the D moieties [55]. It was found that both compounds exhibits remarkable TADF character with short delayed fluorescence lifetimes (1.10 μs for **TPXZ-*as*-TAZ** and 0.98 μs for **oDPXZ-*as*-TAZ**) in doped CBP films. More importantly, OLEDs devices incorporating the two compounds as the emitters deliver yellow emission with EQEs of 11.5% and 8.4%, respectively.

To our best knowledge, theoretical investigations on **TPXZ-*as*-TAZ** and **oDPXZ-*as*-TAZ** only focus on the structural optimizations for ground state and spectral simulations by employing the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations, respectively [55]. It has been widely accepted that the intersystem crossing (ISC) from the lowest singlet excited S_1 state to the lowest triplet excited T_1 state and reverse ISC (RISC) from T_1 to S_1 are two very important processes for the TADF molecules. Therefore, a comprehensively theoretical studies on ISC and RISC are highly required. In the present calculations, herein, we performed a systematic computational investigation on four D- π -A-type molecules shown in Fig. 1. Two of them are experimentally synthesized molecules (**TPXZ-*as*-TAZ** and **oDPXZ-*as*-TAZ**), and the other two molecules (**mDPXZ-*as*-TAZ** and **pDPXZ-*as*-TAZ**) are newly designed from a

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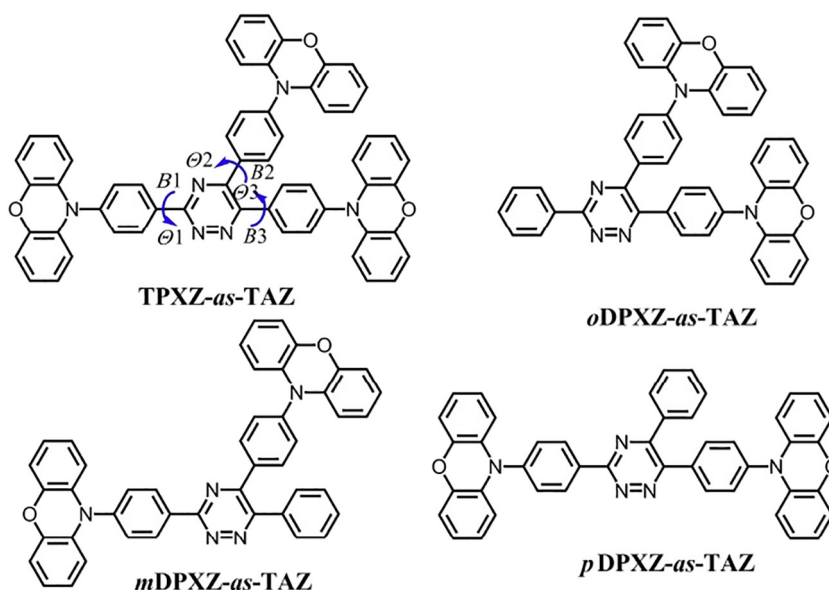


Fig. 1. Chemical structures of four donor- π -acceptor-type molecules investigated in this work. θ_1 , θ_2 and θ_3 denote dihedral angles, and B_1 , B_2 and B_3 represents bond length between the acceptor and phenyl bridges.

theoretical point of view, which are isomers of **oDPXZ-as-TAZ**. A main objective is to elucidate the isomeric effect on their TADF properties. It is expected that the present computational results can serve as a theoretical guide for developing the new efficient TADF-based OLED emitters.

2. Computational Details

Geometry optimizations of molecules as shown **Fig. 1** were performed to determine minimum energy structures in the gas phase for the ground S_0 state by DFT, and for the S_1 and T_1 excited states by TD-DFT using the hybrid meta-generalized gradient approximation (meta-GGA) exchange correlation functional M06-2X [56]. This functional provides a reasonable description of the ground-state and excited-state geometries [33]. Here, Pople's 6-31G(d) basis set was used in both cases. In addition, their absorption and emission spectra were also estimated by employing the TD-M06-2X/6-31G(d) calculations. Considering that the absorption spectra of **TPXZ-as-TAZ** and **oDPXZ-as-TAZ** were measured in dichloromethane solution, the polarizable continuum model (PCM) using CH_2Cl_2 ($\epsilon = 8.93$) as solvent was adopted [57,58].

Based upon the optimized structures, the adiabatic excitation energy method was applied to evaluate the singlet-triplet energy differences between the S_1 and T_1 states. **Fig. 2** plots the potential energy surfaces (PESs) of the S_0 , S_1 and T_1 electronic states. $E_{00}(S_1)$ and $E_{00}(T_1)$ represent the adiabatic excitation energies between the energy minima of S_0 and S_1/T_1 along PESs.

$$E_{00}(S_1) = E_{S_1}(S_1\text{-geometry}) - E_{S_0}(S_0\text{-geometry}) \quad (1)$$

$$E_{00}(T_1) = E_{T_1}(T_1\text{-geometry}) - E_{S_0}(S_0\text{-geometry}) \quad (2)$$

Therefore, the adiabatic excitation energy difference (ΔE_{ST}) can be defined as:

$$\Delta E_{ST} = E_{00}(S_1) - E_{00}(T_1) \quad (3)$$

The (R)ISC rates can be calculated by using semiclassical Marcus theory expression [59–61]:

$$k = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{k_B T \lambda}} \exp \left[-\frac{(\Delta E_{ST} + \lambda)^2}{4k_B T \lambda} \right] \quad (4)$$

where k_B is Boltzmann constant and T is temperature, which is set to 300 K. V denotes the spin-orbital coupling (SOC) matrix element between the S_1 and T_1 states, which could be treated as a perturbation on the basis of the scalar relativistic (SR) orbitals after the SCF and TD-DFT calculations [62], together with an Slater-type all-electron DZP basis set [63]. Additionally, λ is the reorganization energy induced by the electron or the energy transfer. For the S_1 and T_1 states, λ could be formulated as (see **Fig. 1**):

$$\lambda_S = E_{S_1}(T_1\text{-geometry}) - E_{S_1}(S_1\text{-geometry}) \quad (5)$$

$$\lambda_T = E_{T_1}(S_1\text{-geometry}) - E_{T_1}(T_1\text{-geometry}) \quad (6)$$

where $E_{S_1}(T_1/S_1\text{-geometry})$ is the S_1 energy at the T_1/S_1 minimum geometry, and $E_{T_1}(T_1/S_1\text{-geometry})$ is the T_1 energy at the T_1/S_1 minimum geometry. It should be mentioned that in calculation of the k_{ISC} rate, the λ_T value is used and $\Delta E_{ST} = E_{00}(T_1) - E_{00}(S_1)$.

All the DFT and TD-DFT computations were carried out with the Gaussian 09 package [64]. The SOC calculations were performed using the ADF2016 package [65].

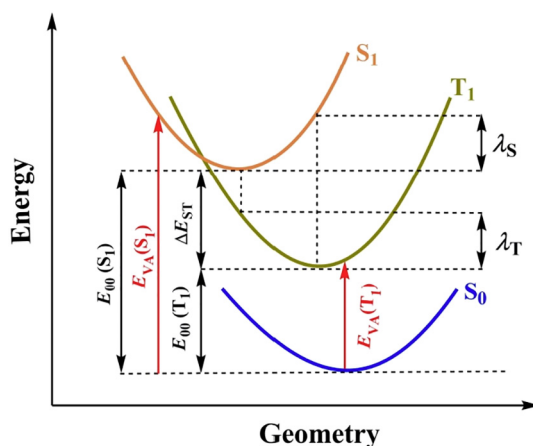


Fig. 2. Potential energy surfaces of the ground S_0 state, the lowest singlet excited S_1 state, and the lowest triplet excited T_1 state.

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