Impact of substitution on the reorganization energy of bis-triarylamine derivatives

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ABSTRACT

The impact of substitution on the reorganization energy (λ) of N,N'-diphenyl-N,N'-bis (3-methyllphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) derivatives (TPDs) is evaluated from the results of quantum-mechanical calculations performed at density functional theory levels. In this article, models modified on the central biphenyl and on the side phenyl are designed. The relationship between reorganization energy and substitution is analyzed and qualitatively established. These results help us to design material for OLED with desirable hole carrier transport properties.

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1. Introduction

Charge-transport phenomena in semiconducting doped polymers in recent years has attracted considerable interest due to their widespread use in electroluminescent devices (OLEDs) [1–3], xerography [4,5], photovoltaic cells [6,7], and photorefractive systems [8]. Organic light emitting diodes (OLED) are generally multilayer composites, consisting of charge trans-porting donor or acceptor molecules dispersed in a polymer binder. The optoelectronic properties for OLED devices depend on suitable electron and hole mobilities. The mobilities are important in optimizing the performance of devices: high mobilities reduce the resistance of the device leading to high power efficiency. Additionally, the relative mobilities of electron and hole in the same material can also affect the power efficiency [9].

The hole trans-porting molecule TPD was known to be an electron donor in the charge transport layer (CTL) [10] in the past decade. Recently, it is expected to be significantly promising in laser applications [11]. Recent advances in methodologies have made the synthesis of a variety of new substituted TPD molecules possible, and several derivatives of TPD have been developed [12].

Although the guidelines for designing small molecules with desirable photo and thermal properties are well-known, analogous guide on the mobilities of charge carriers is unclear. The geometric and electronic properties of TPD are changed simultaneously by substitution, and the fundamental physical processes such as charge mobility are potentially influenced [13]. With the purpose of designing desirable hole transport properties TPD materials, it is necessary to catch thoroughly the relationship between geometric, electronic structure and hole transfer properties, i.e., the reorganization energy. The impact of substitution on the reorganization energy of TPD deserves considerable attentions. In this work, two types of substitutions on TPD are considered: (1) modifications on side phenyl of TPD (Fig. 1) (2) modifications on the central biphenyl (Fig. 2). The reorganization energy of them is calculated.

2. Methodology

Base on the Marcus theory [14–18], the hole intermolecular transfer can be described by Eq. (1)

$$M^+ + M^* \rightarrow M + M^{*+} \qquad (1)$$

In the Eq. (1), M^+ indicates the molecule in a cationic state. M^* is a neighboring molecule in a neutral state. The rate constant K_{ET} of Eq. (1) is given by Eq. (2).

$$K_{ET} = (4\pi^2/h)\Delta H_{ab}^2(4\pi\lambda T)^{-1/2}\exp(-\lambda/4K_BT) \qquad (2)$$

K_B is the Boltzmann constant. T is temperature. ΔH_{ab} is a constant [19,20]. h is the Plank constant. Then the hole transport property K_{ET} is only related to λ.

According to Fig. 3, reorganization energy can be carried out, by Eq. (3).

$$\lambda = E_2 + E_3 - E_1 - E_4 \qquad (3)$$

All the calculations are performed at density functional theory (DFT) levels, using the B3LYP functional. The Gaussian 98 [21] package is used in all calculations. B3LYP functional employs the gradient corrected exchange functional with three-parameters by Becke [22] and the correlation functional by Lee–Yang–Parr [23].

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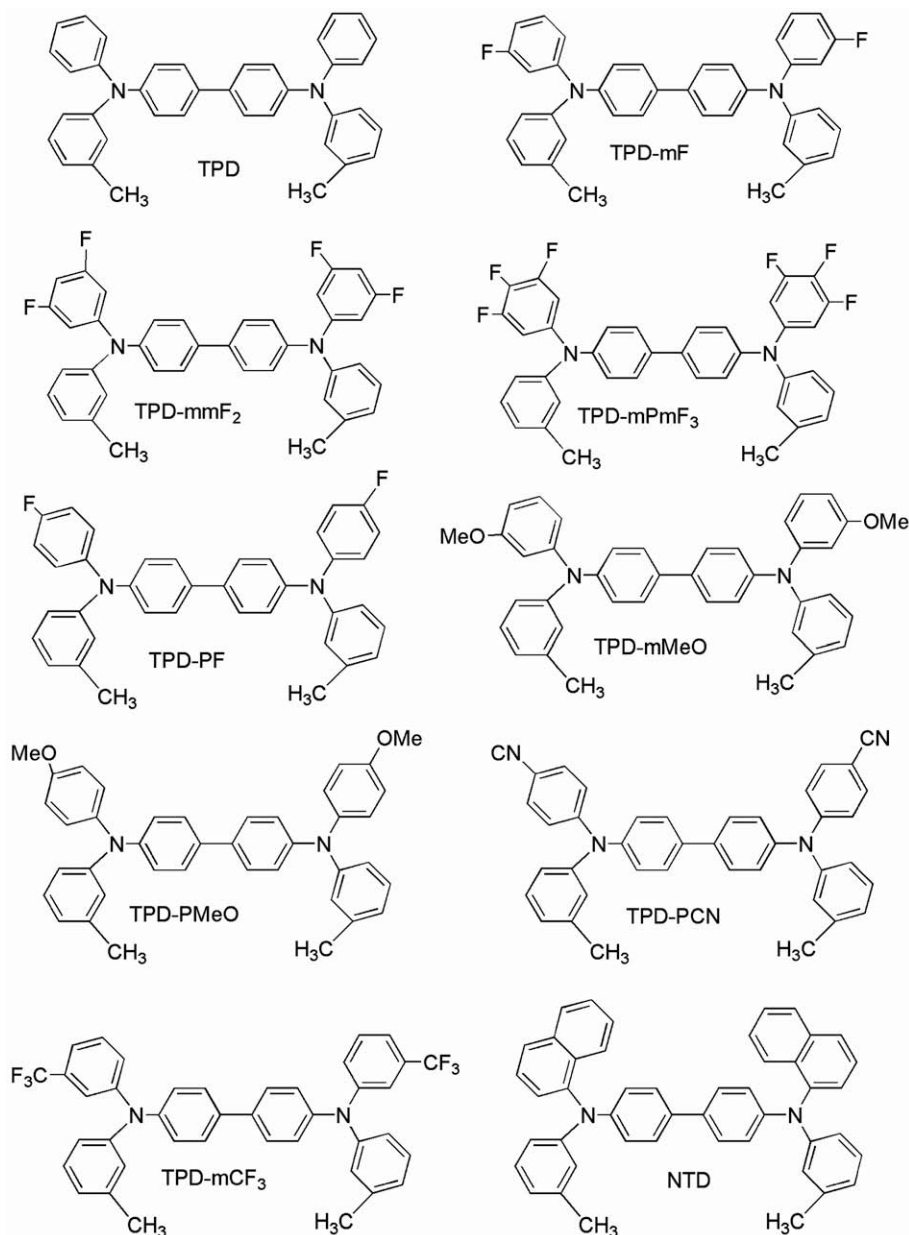*E-mail address:* Mishizhen909@163.com (S. Mi).

Fig. 1. Structures of TPD derivatives: modified on side phenyl.

6-31G** basis set is used [24–28]. Full geometry optimizations are carried out for all the TPD derivatives. The reorganization energy of them is also figured out. There is very little energy difference between cis- and trans-conformers [29]. Conformational difference is not considered in this calculation.

3. Results and discussion

3.1. Modified on the side phenyl

As we can see from Fig. 1, TPD molecule is modified by electron-withdrawing group (F, CN, CF$_3$), electron-donating group (MeO) on its side phenyl separately. The substituent's number and position on TPD are also varied. Energy and reorganization energy calculations are performed, shown in Table 1. Impact of substituents on side phenyl moiety on the reorganization energy of TPD is studied below.

First, reorganization energy of TPDs modified by group F is shown in column 2 of Table 1. The reorganization energy difference

between TPD and TPDs is shown in column 3. Substituting at meta-position (corresponding mF in Table 1), F will contribute about 0.0379 eV to λ, while at para-position (means pF), −0.0123 eV is contributed. Similarly, λ of mmFF2 increases to 0.3396 eV with another F substitute on meta-position of TPD. When the third F is added to para-position, λ of mPmF3 reduce to 0.2931 eV, even smaller than mF. The position variety of F group leads to the variety of λ. This result can still indicate that positive conjugated effect of meta-substitution will enhance the reorganization energy of TPD, while of para-substitution it will reduce λ.

Secondly, the data in right two columns are analyzed. Similar tendency is found in the reorganization energy change of TPD substituted by MeO (meta-substitution increase λ about 0.0284 eV, while para decrease 0.0400 eV). For F and MeO, one is electron-withdrawing group, another electron donating. The mainly reason why similar tendency appears can only be attributed to conjugated effect of substituents. The conjugated and inductive effects possibly contributing to reorganization energy