



Theoretical investigations into optical and charge transfer properties of donor-acceptor 1,8-naphthalimide derivatives as possible organic light-emitting materials



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ARTICLE INFO

Article history:

Received 28 March 2015
Received in revised form
6 September 2015
Accepted 29 September 2015
Available online 3 October 2015

Keywords:

Naphthalimide derivatives
Fluorene derivatives
Optical and electronic properties
Charge transport property
Luminescent materials
Organic light-emitting diodes (OLEDs)

ABSTRACT

A series of D–A naphthalimide-substituted fluorene derivatives have been designed to explore their optical, electronic, and charge transport properties as charge transport and/or luminescent materials for organic light-emitting diodes (OLEDs). The frontier molecular orbitals (FMOs) analysis turned out that the vertical electronic transitions of absorption and emission are characterized as intramolecular charge transfer (ICT). The calculated results show that their optical and electronic properties are affected by the substituent groups in fluorene moieties. Our results suggest that all selected candidates are promising as luminescent materials for OLEDs. In addition, all derivatives can be used as promising hole and electron transport materials while derivatives with dibenzothiophene fragment can be used as hole transport material only for OLEDs.

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1. Introduction

Since Tang and Vanslyke reported the first thin film structure organic light-emitting diodes (OLEDs), the development of OLEDs materials has received considerable attention in connection with their potential applications in flat panel displays and solid-state light sources [1–5]. However, the lower efficiency of OLEDs is still the main obstacle for their commercialization application. To address this issue, the two most important parameters are the intense luminescence and high carrier mobility of OLEDs materials. Therefore, it has become one of the urgent research topics to develop high efficiency multifunctional organic materials that exhibit carrier mobility for use in OLEDs. Molecules with donor–acceptor (D–A) architecture represent a promising class of multifunctional materials for OLEDs [6,7]. The D–A organic compounds have become the most efficient strategy used in the design and synthesis of OLEDs materials with the tunable properties [8]. This type of molecular structure can improve the intense

luminescence and carrier mobility due to their planar geometry along with extended π -conjugated systems. At the same time, the electronic energy levels and band-gaps can be tuned effectively through adjusting the acceptor and donor units, and π -bridge units or length [9]. Among the various kinds of OLEDs materials, 1,8-naphthalimide derivatives are promising fluorescent materials and environmentally sensitive. They may be considered as the most important building blocks due to their strong fluorescence, a large Stokes shift, good chemical stability and film-forming properties, and high photoluminescence quantum yield [10–12]. 1,8-Naphthalimides derivatives contain a class of fluorophore whose electronic absorption and emission depend upon the properties of the surrounding medium. The fluorescent quantum yields can be increased and the emission spectrum can be conveniently tuned by introducing different electron-donating substituent groups, such as N-substituted groups, C-substituted groups, and O-substituted groups [13–15]. Moreover, 1,8-Naphthalimide derivatives generally exhibit high electron affinity owing to the existence of an electron-deficient center and can be used as electron-transporting or hole blocking material in OLEDs [16,17]. On the other hand, fluorene and its derivatives are also popular building block for the preparation of luminescent and charge-transporting materials because of their

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good charge transfer, high thermal stability, and excellent photoluminescence properties [18,19]. Because of these unique properties, it is expected to design and synthesis of novel fluorene derivatives with excellent optical and electrical properties [20,21]. Furthermore, chemical modifications can be easily made at the 2, 7, and 9-positions of the fluorene ring, which can improve the solubility and photophysical properties of fluorene derivatives. Theoretical study provides an essential role in developing materials. A number of studies demonstrate the interplay between theory and experiment, which is capable of providing useful insights to the understanding of the nature of molecules [22–25]. Recently, some 1,8-naphthalimide-substituted derivatives of fluorene has been reported [26]. It was found that these molecules have high fluorescence quantum yield and good charge transporting property.

In this paper, we report the investigation of both optical and charge transporting properties from theoretical point of view for a series of D–A naphthalimide-substituted fluorene derivatives **1–6** (Scheme 1) for OLEDs applications. Furthermore, we explored the optical and electronic properties of the molecules with the aim to get a further insight on the relationship between topologic structure and optical as well as electronic properties. This provides a demonstration for the rational design of novel luminescent and charge transporting materials for OLEDs.

2. Computational methods

All calculations were carried out with the aid of Gaussian 09 code [27]. Our previous work [28–30] suggested that the B3LYP appeared notably adapted to 1,8-Naphthalimide derivatives. The B3LYP method with the 6-31G(d,p) basis set was used in all the geometry optimization including neutral, cation, and anion molecules in ground states (S_0). The first excited singlet states (S_1) structures of **1–6** have been optimized using the TD-B3LYP/6-31G(d,p). The harmonic vibrational frequency calculations using the same methods as for the geometry optimizations were used to ascertain the presence of a local minimum. Absorption and fluorescent properties of **1–6** have been predicted using the TD-B3LYP/6-31G(d,p) method based on the S_0 and S_1 optimized geometries, respectively.

According to Marcus theory [31,32], the charge transfer rate can

be represented as follows equation:

$$K = \left(V^2 / \eta \right) \left(\pi / \lambda k_B T \right)^{1/2} \exp \left(-\lambda / 4 k_B T \right) \quad (1)$$

where T and k_B are the temperature and the Boltzmann constant respectively. λ is the reorganization energy and V is the electronic coupling matrix element (transfer integral). It can be seen from eq (1) that the λ and V are the two key parameters, which have a dominant impact on the charge transfer rate, especially the former. In order to predict V , crystal data in general are needed [33]. However, the investigated molecules may be noncrystal, and the electronic coupling matrix element value is very limited [34,35]. We cannot predict the V values for the investigated molecules because of the lack of available approaches. Therefore, in this paper, we focus on their reorganization energies λ to investigate their charge transport properties exclusively. For the reorganization energy λ , it can be generally divided into external reorganization energy (λ_{ext}) and internal reorganization energy (λ_{int}) two parts. λ_{ext} represents the effect of polarized medium on charge transfer; on the other hand, λ_{int} is a measure of structural change between ionic and neutral states [36]. The computed values of the external reorganization energy in pure organic condensed phases are not only small but also are much smaller than their internal counterparts [37,38]. Moreover, there is a clear correlation between λ_{int} and charge transfer rate in literature [39], and the λ_{ext} is quite complicated to evaluate at this stage. Therefore, we study the internal reorganization energy exclusively in this work. The electron (λ_e) and hole (λ_h) reorganization energy can be calculated by equations Eqs. (2) and (3) [34,40]:

$$\lambda_e = \left(E_0^- - E_-^- \right) + \left(E_0^0 - E_0^0 \right) \quad (2)$$

$$\lambda_h = \left(E_0^+ - E_+^+ \right) + \left(E_0^0 - E_0^0 \right) \quad (3)$$

Where $E_0^+(E_0^-)$ is the energy of the cationic (anionic) states at the geometry of the optimized neutral molecule. $E_+^+(E_-^-)$ is the energy of the cationic (anionic) states with the optimized cationic (anionic) structures. $E_+^0(E_-^0)$ is the energy of the neutral states at the cationic (anionic) structures. E_0^0 is the energy of the neutral molecule at the ground state. Furthermore, in order to compare with the interested results reported in literature [41,42], the λ_e and λ_h of the molecules were predicted at the B3LYP/6-31G(d,p) level.

To predict the stability of **1–6** from a viewpoint of conceptual density functional theory, the absolute hardness, η , of **1–6** were calculated using operational definitions [43,44] given by:

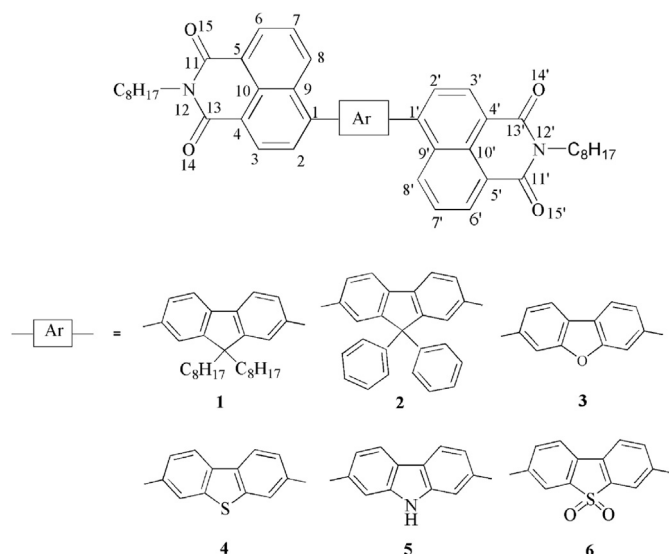
$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right) = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right) = \frac{IP - EA}{2} \quad (4)$$

where μ is the chemical potential and N is the total electron number. In this work, the values for IP (adiabatic ionization potential) and EA (adiabatic electron affinity) were determined according to the equation $IP = E_{\text{cr}} - E_{\text{p}}$ and $EA = E_{\text{p}} - E_{\text{ar}}$, where p, cr, and ar indicate the parent molecule and the corresponding cation and anion radical generated after electron transfer.

3. Results and discussion

3.1. Molecular structures in ground and first excited singlet state

A summary of the important bond lengths and dihedral angles in the S_0 and S_1 are given in Tables 1 and 2, respectively. The



Scheme 1. Molecular structures of the investigated molecules, along with atom numbering.

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