C. R. Chimie 18 (2015) 954–959

Contents lists available at ScienceDirect

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Theoretical study of the optical and charge transport properties of star-shaped molecules with 1,3,5-triazine-core derivatives as organic light-emitting and organic solar cells materials

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ARTICLE INFO

Article history:
Received 6 March 2015
Accepted after revision 28 May 2015
Available online 21 August 2015

Keywords:
Star-shaped molecules
1,3,5-Triazine derivatives
Electronic and optical properties
Charge transport property
Organic electronics

ABSTRACT

A series of D–π–A star-shaped molecules has been investigated theoretically by using density functional theory (DFT) to reveal their optical, electronic, and charge transport properties for applications in organic light-emitting diodes (OLEDs) and organic solar cells (OSCs). The calculated results show that their optical, electronic, and charge transport properties are affected by the different end groups and π-bridges. Our results reveal that the molecules under investigation can serve as OSCs donor materials and/or luminescent materials for OLEDs. In addition, all molecules are expected to be promising candidates for hole- and electron-transport materials. On the basis of the obtained results, we propose a rational way for the design of multifunctional materials for OLEDs and OSCs applications.

1. Introduction

The development of organic electronics, including organic solar cells (OSCs) and organic light-emitting diodes (OLEDs), has received a significant amount of attention in recent years because of their light weight, of their potential low cost, because they can be used to make large-area flexible and transparent panels, and because the fabrication of the devices is easy [1–7]. Especially, small molecule-based organic electroactive molecules are of increasing importance for their optoelectronic applications in OSCs and OLEDs because they exhibit good light absorption, light-emitting, and charge-carrier transport properties. It is believed that small molecule-based organic electronics are promising for their commercial application in the future. Although enormous progresses have been made recently in the research and the development of new materials, the lower efficiency of small molecule-based organic electronics materials is still the main obstacle to their application. It is therefore necessary to develop novel high-efficiency multifunctional organic materials. They are capable of transporting charge in addition to serving as efficient light-absorption materials in OSCs as well as emitters with excellent performance in OLEDs, respectively [8–13]. Theoretical studies on multifunctional organic materials may provide useful insights into the understanding of the nature of the molecules [14–17]. Among the organic materials, star-shaped conjugated materials have become the most efficient strategy used in the design and synthesis of multifunctional OLEDs and OSCs materials [18–22]. The formation of an ordered, long-range, and coplanar *p*–*p* stacking can be prevented by the increased steric hindrance of star-shaped conjugated molecules. This may lead them to be good candidates as charge transport materials. At the same time, the absorption and emission spectra of these materials can be tuned effectively through adjusting the core and arm units, and π-conjugated bridge units or length when applied in organic electronics [23]. Recently, multifunctional star-shaped molecules with

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http://dx.doi.org/10.1016/j.crci.2015.05.021
1631-0748/

triazine core and various bithiophene branches have been reported for light-emitting materials in OLEDs, donor materials in OSCs, and active channels in organic field-effect transistors (OFETs) [24].

In this contribution, we designed a series of star-shaped D–π–A molecules with 1,3,5-triazine (TZ) as the core, aromatic derivatives as end groups, and thiophene or furan π-bridges for applications in organic electronics (Scheme 1). Furthermore, we explored the optical and electronic properties of the molecules with the aim to get a further insight into the relationship between topologic structure and optical as well as electronic properties. This provides a method for the rational design of good candidates for OLEDs and OSCs materials.

2. Computational methods

All calculations were carried out with the aid of the Gaussian 09 package [25]. The geometries of the compounds under investigation in ground states (S_0) were optimized using the B3LYP method. The corresponding geometries in the first excited singlet state (S_1) were optimized using TD-B3LYP. All geometry optimizations were performed using the 6-31G(*d,p*) basis set. The harmonic vibrational frequency calculations using the same methods as for the geometry optimizations were used to ascertain the presence of a local minimum. The absorption and fluorescent properties of the compounds under investigation were predicted using the TD-B3LYP/6-31+G(*d,p*) based on the optimized S_0 and S_1 geometries, respectively. To investigate the influence of solvents on the optical properties for the S_0 and S_1 states of the molecular systems in toluene as a solvent (dielectric constant: 2.374), we performed polarized continuum model (PCM) [26] calculations at the TD-DFT level.

The charge transfer rate can be described by the Marcus theory [27,28]:

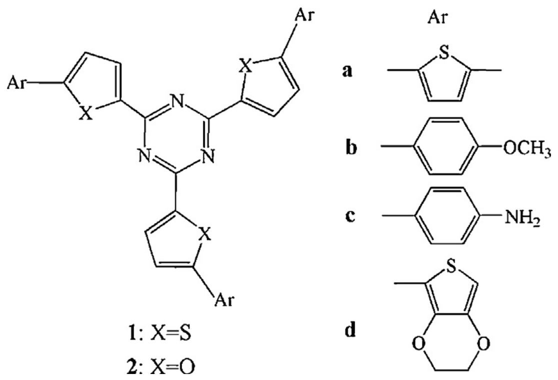
$$K = \left({}^{V^2}/_{\hbar}\right)\left({}^{\pi}/_{\lambda k_B T}\right)^{1/2} \exp\left({}^{-\lambda}/_{4k_B T}\right) \qquad (1)$$

where k_B is the Boltzmann constant, T is the temperature, λ corresponds to the reorganization energy, and V represents the intermolecular transfer integral. It can be seen from Eq. (1) that the λ and V values have a dominant impact on the charge transfer rate, especially the former. In order to predict V, crystal data are required. However, the investigated molecules may be noncrystal. Thus, in this paper, we focus on the reorganization energies λ to investigate their charge transport properties. The reorganization energy λ is further divided into two parts, external and internal reorganization energies [29]. We only study the internal reorganization energy because the external reorganization energy is quite complicated to evaluate at this stage. Furthermore, the computed values of the external reorganization energy in pure organic condensed phases are much smaller than their internal reorganization energy and can be neglected [30–32]. In addition, there is a clear correlation between internal reorganization energy and charge transfer rate in the literature [33,34]. Therefore, we study exclusively the internal reorganization energy in this work. Hence, the electron (λ_e) and hole (λ_h) reorganization energy can be calculated by Eqs. (2) and (3) [35]:

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

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

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 in the ground state. Furthermore, in order to compare with the results reported in literature [36,37], the λ_e and λ_h values of the molecules were predicted at the B3LYP/6-31G(*d,p*) level.



Scheme 1. Molecular structures of the investigated molecules.

3. Results and discussion

3.1. Frontier molecular orbitals

The qualitative frontier molecular orbitals (FMOs), including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the investigated molecules (**1a**–**d** and **2a**–**d**), are shown in Fig. 1. The total and partial densities of states (TDOS and PDOS) on each fragment of **1a**–**d** and **2a**–**d** around the HOMO–LUMO gaps were calculated based on the current level of theory. The FMOs energies E_{HOMO} and E_{LUMO}, HOMO–LUMO gaps E_g, and the contributions of individual fragments (in %) to the FMOs of **1a**–**d** and **2a**–**d** are given in Table 1. The distribution patterns and contributions of individual fragments (in %) of HOMOs – 1, HOMOs – 2, and LUMOs + 1 for the investigated molecules are given in Fig. SI and Table SI in the Supplementary data, respectively. The FMOs of **1a**–**d** and **2a**–**d** show π characteristics as visualized in Fig. 1. The HOMOs are mainly localized on the aromatic end groups (**AR**) and conjugate π-bridge fragments (**CB**) with only minor but nonzero contributions from the **TZ** fragments. On the contrary, the LUMOs mainly reside at the **TZ**, **CB**, and **AR** fragments of two arms. These results reveal that the different π-bridge units and end groups have obvious effects on the distribution of FMOs for the compounds under investigation. The distribution