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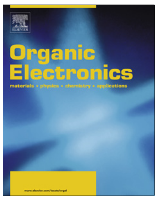

Charge transport and optical properties of cross-conjugated organic molecules: A theoretical study

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The structure, charge transport and optical properties of two-dimensional cruciform molecules 1,4-distyryl-2,5-bis(arylethynyl)benzenes, 1,4-distyryl-2,5-bis(arylethynyl)pyridines and 1,4-bis(ethylenediyl)dipyridine-2,5-bis(benzene) have been studied using density functional theory methods. The effective charge transfer integral and site energy corresponding to hole and electron transports in the above molecules were calculated directly from the matrix elements of Kohn–Sham Hamiltonian. The charge carrier mobility on the cruciform molecules was calculated using Monte Carlo simulation based on the Marcus rate theory and the results show that these cruciform molecules are the p-type organic semiconductors. The excited state calculations were performed using the time-dependent density functional theory method in gas phase, hexane and dichloromethane mediums. The trifluoromethyl substituted 1,4-distyryl-2,5-bis(arylethynyl)benzenes molecule possesses the maximum absorption and emission wavelength of 443 and 504 nm, respectively in dichloromethane medium.

1. Introduction

Organic π-conjugated molecules continue to be the subject of contemporary area of research due to its promising applications in sustainable and low-cost electronic devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaic cells (OPVs) [1–3]. The mobility of charge carriers is one of the key parameters that determine the device performance. Thus, organic molecules with various shapes have been synthesized and are extensively studied to find efficient materials with high charge carrier mobility [4–6]. As a consequence, there has been an increasing pursuit in the investigation of π-conjugated X-shaped organic molecules and their applications in opto-electronics [7–10]. It has been shown in earlier studies that the charge transport properties of organic molecules strongly depend on the orientation of the molecules, and a molecule with highly ordered structure will possess high charge carrier mobility [11]. It is expected that the X-shaped molecules in two dimensional form will possess higher ordering compared to linear structures and the distribution of excess charge in this type of molecules occurs in two dimensions thereby increasing the rate of charge transport between the molecules. An enormous amount of experimental and theoretical studies on charge transport in π-conjugated linear organic molecules and disc shaped liquid crystalline molecules [11–15] are available in the literature, but only few studies were reported on the charge transport properties of X-shaped molecules [10,16–21]. The charge transport analysis on different X-shaped molecules shows that these molecules exhibit high charge carrier mobility. Recently, Li et al. [17], have reported a high charge carrier mobility of around 0.80 $cm^2/V\,s$ for benzo dithiophene based cruciform molecules. Further, Choi et al. [19], have reported that

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anthracene based X-shaped molecules are p-type organic semiconductors and they exhibit a field-effect mobility of about 0.04 and 0.24 cm^2/V s. Therefore, a systematic theoretical study on the charge transport properties of recently synthesized X-shaped organic molecules is necessary to understand the structure property relationship and to design new molecules with improved properties.

It has been shown in earlier studies that the cruciform molecules possess high quantum yield and exhibit higher two-photon absorption cross section and photoluminescence efficiency [22]. Previous studies have reported the spectroscopic behavior of cruciform binding with metal ions in various solvent mediums due to their potential application as fluorescent sensors [23–25]. Bunz et al. [7,8,24–27], synthesized cruciform molecules of different types with the substitution of different electron withdrawing (EWG) and electron donating (EDG) groups and analyzed their spectral properties. In principle, the optical and electronic properties of π-conjugated organic molecules depend on the delocalization of electron density on the frontier molecular orbitals (FMO). Thus, the spectral and charge transport properties can be tuned by the modification in the spatial distribution of electron density on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). It has been shown in earlier studies that the substitution of certain EWG and EDG on the cruciform molecules leads to spatially separated electron density delocalization on the FMOs [7,28]. This separation of the FMOs in the cruciform molecules has significant consequences on the photophysical and charge transport property of the molecules. Hence, a systematic theoretical study on the optical properties of X-shaped molecules in terms of FMO's is necessary.

To the best of our knowledge, a detailed study on charge transport property of cruciform molecules synthesized by Bunz et al. [24,25], have not been reported so far and among the different cruciforms synthesized by Bunz et al., nine molecules have been chosen and their charge transport and optical properties have been analyzed using quantum chemical methods. The cruciform molecules studied in the present work, XF1–XF9 are shown in Fig. 1. (For more details about the molecules chosen see Supplementary Material) The charge transport and spectral properties of nine cruciform molecules have been studied by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. The TD-DFT is the common choice of method for studying the excited state geometry of organic molecules [29–33]. The results obtained from the theoretical calculations will be useful to understand the nature of electronic transition, intensity of the spectra and the effect of substitution on the absorption and emission spectra of the cruciform molecules. Further, it is necessary to analyze the suitability of the available DFT functionals to calculate the absorption and emission spectra by comparing the theoretical results with the available experimental results. In the present investigation, long-range separated functionals (LC-BLYP) developed by Hirao and co-workers [34,35], the Coulomb attenuating B3LYP (CAM-B3LYP) method proposed by Yanai et al. [36] and meta hybrid functionals M06-HF [37] and M06-2X [38] developed by Truhlar et al. are used to calculate the absorption and emission spectra of cruciform molecules.

2. Theoretical methodology

The ground state geometry of the cruciform molecules has been optimized at B3LYP/6-311G(d,p) level of theory. The B3LYP functional uses the Becke's three parameter exchange functional (B3) [39] together with the non-local correlation function provided by Lee–Yang–Parr (LYP) [40] and the local correlation functional of Vosko–Wilk–Nusair (VWN) [41]. It has been shown in a previous study that the ground state structure optimized at B3LYP, PBE0 and MP2 methods are nearly same [30]. Subsequently, vibrational frequency calculations were performed at B3LYP/6-311G(d,p) level of theory to confirm that the stationary points are true minima in the potential energy surface. To calculate the charge transfer integral and site energy, the single point energy calculations for the stacked dimers with different stacking angles were performed using the fragment orbital approach as implemented in Amsterdam Density Functional (ADF) theory program [42]. In ADF program, the single point energy calculations were performed with Becke's [43] exchange and Perdew's [44] correlation functionals and an atomic basis set of Slater-type orbitals (STOs) of triple-ζ quality including two sets of polarization functions on each atom (TZ2P) were used.

In the hopping regime, the rate of charge transfer between the adjacent molecules can be calculated using the Marcus equation [45,46],

$$K_{CT} = \frac{J_{eff}^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\exp\left(-\frac{\lambda}{4k_B T}\right) \qquad (1)$$

where λ is the reorganization energy, J_{eff} is the effective charge transfer integral, k_B is Boltzmann's constant and T is the temperature. The effective charge transfer integral is defined as

$$J_{eff} = J_{ij} - \frac{S(\varepsilon_i + \varepsilon_j)}{2} \qquad (2)$$

where J_{ij} represents the charge transfer integral (or electronic coupling) corresponding to HOMO (or LUMO) of nearby molecules i and j, which measures the strength of the overlap between the orbitals of nearby molecules. ε_i and ε_j are the energy of a charge when it is localized at ith and jth molecules, respectively and S is the spatial overlap integral. The charge transfer integral, the spatial overlap integral and site energy were calculated for different stacking angles between the cruciform molecules. As reported in previous studies [11,47], charge transfer integral and site energy are directly calculated as the matrix elements of the Kohn–Sham Hamiltonian, $H_{KS} = C^{-1}SCE$. Here, C and E are the coefficient and energy of the molecular orbital involved in charge transport.

The reorganization energy, λ is the change in energy of the molecule due to the structural relaxation upon the presence of excess positive (λ^+) or negative (λ^-) charge. The reorganization energies, λ^+ and λ^- are calculated

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