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Optical and electronic properties of organoboron compounds in solvent

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Abstract. Organoboron compounds 1-4 with an aryl ring directly bound to a $(FMes)_2B$ group through B-C bonds in vacuum, Hexane, Toluene, THF, CH_3CN were theoretically studied using DFT with B3LYP functional and 6-31G (d) basis set, and TD-DFT with CAM-B3LYP functional and 6-31G (d) basis set. The absorption and fluorescence spectra of compounds 1-4 are determined in the same and different solvents. It is found that the electronic transition is the most efficient when compounds 1-4 are in CH_3CN, the most polar solvent. The spectral contrast of compounds 3 and 4 is studied under different conditions. The charge difference density (CDD) is determined using the data from the intramolecular charge transfer of compounds 1-4 using 3D cube with large oscillator strength.

1. Introduction

Organoboron compounds have attracted considerable research interest in recent years due to their unique optoelectronic properties. It has been demonstrated that this kind of material can be used in a range of fields, such as nonlinear optics (NLO) [1-4], two-photon absorption (TPA) and emission materials [5-9], electron-transporting and emissive materials in organic light-emitting teleportation materials as well as chemosensors.

As early as 1955, Wittig and Herwig reported the photophysical properties of organoboron compounds [10], but it didn`t attract the attention of people because of their instability in air. In 1972 Williams demonstrated that the organoboron compounds become stable in air when two 1,3,5-trimethyl groups are added [11]. In order to improve the electron injecting and transporting properties in OLEDs, lower energy emission, and larger two-photon absorption cross sections and so on, many research groups looked for suitable organoboron compounds. However, most of these do not give sufficient steric protection to the boron centre to render it stable in air [12-16]. Marder et al. prepared three compounds using phenyl (1), 4-(1,1-Dimethylethyl) phenol (2) and 4-N,N-diphenylaminophenyl (3) groups attached to bis(fluoromesityl)boryl ((FMes)2B) by B – C bonds[17].

In this paper, we studied the influence of alternative acceptor groups bis(fluoromesityl) boryl($(FMes)_2B$, FMes= fluoromesityl = 2,4,6-tris(trifluoromethyl) phenyl), which is an analogue of $(Mes)_2B$ with the methyl groups replaced by CF_3 oxidation groups [18], under different conditions: in vacuum, in the nonpolar solvents Hexane and Toluene, and in the polar solvents THF and CH_3CN. By using 3D real-space analysis [19-24], we studied the properties of charge and energy transfer, transition of the dipole moment, electron-hole coherence and delocalization of compounds in different solvents at excited states. From the absorption spectra, emission spectra and analysis of the 3D real-space, we found that significant red shift or blue shift of both absorption maxima and fluorescence maxima of compounds 1-4 in more polar solvents, indicating a strong intramolecular charge transfer (ICT) feature and suggests that the bigger the polarity of the solvent, the greater the shift in red or blue.

2. Theoretical methods

The models in the calculations of compounds 1-4 can be seen in Figure 1. All of the calculations are done using Gaussian 09 software [25], the ground state geometries were optimised using the density functional theory (DFT), B3LYP functional, and 6-31G (d) basis sets, and the excited state electronic properties were calculated using time-dependent DFT (TD-DFT), CAM-B3LYP functional and 6-31G (d) basis sets [26-29].

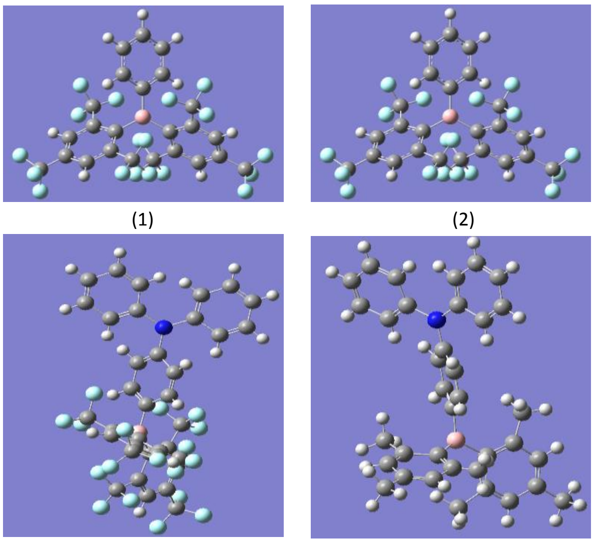
(1) (2) (3) (4)

Figure 1: Figures (1), (2), (3), (4) was the model of compound 1, 2, 3 and 4, respectively.

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The fluorescence of compounds 1-4 in the visible region were calculated using time-dependent DFT (TD-DFT), CAM-B3LYP functional and 6-31G (d) basis sets. Absorption and fluorescence spectra were obtained using Origin 8. The properties of the excited state was visualised using 3D real space analysis methods [30-33]. In the 3D cube representation, the charge difference density (CDD) shows results of the charge and energy transfer, calculated using [34]

$$\Delta\rho_{\mu\mu C}(\vec{\gamma})=\sum_{\substack{a\in unocc\\ i,j=occ}} C_{\mu aj}C_{\mu aj}\varphi_j(\vec{\gamma})-\sum_{\substack{a,b\in unocc\\ i=occ}} C_{\mu bi}C_{\mu ai}\varphi_b(\vec{\gamma})\varphi_a(\vec{\gamma})\quad ,$$

The first and second terms in the formula code for electron-hole by CDD [35].

3. Results and discussion

3.1 Electronic properties of compounds 1, 2, 3, 4 at ground state

We optimized the ground state geometry of compounds 1-4 using DFT at B3LYP/6-31G (d) level. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [36, 37] are seen under vacuum and in CH_3CN， Hexane， THF and Toluene, respectively (Figure 2). From Figure 2(a), we conclude that different solvents do not significantly affect the orbit of HOMO/LUMO for compound 1. The same analyses were carried out on the compounds 2, 3, 4, with similar conclusions. We can identify that the electron transfers from the lowest unoccupied molecular orbital (LUMO) is mainly an intramolecular charge transfer transition, where the red and green moieties represent the electron and hole [38].

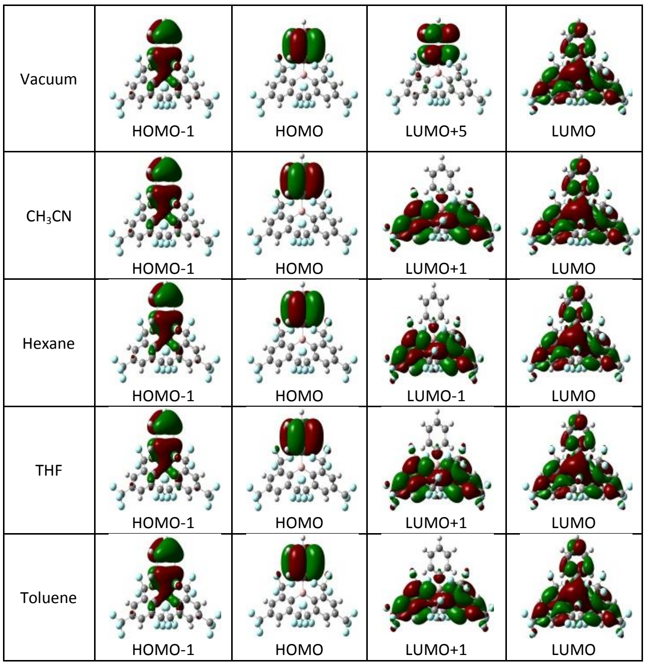

Figure 2(a): 3D Cube of compound 1 on the orbit of HOMO and LUMO

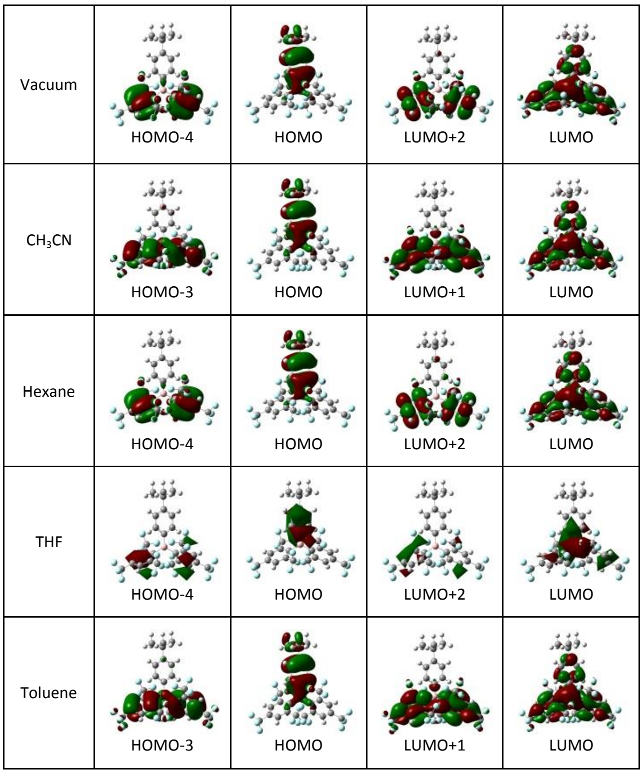

Figure 2(b): 3D Cube of compound 2 on the orbit of HOMO and LUMO

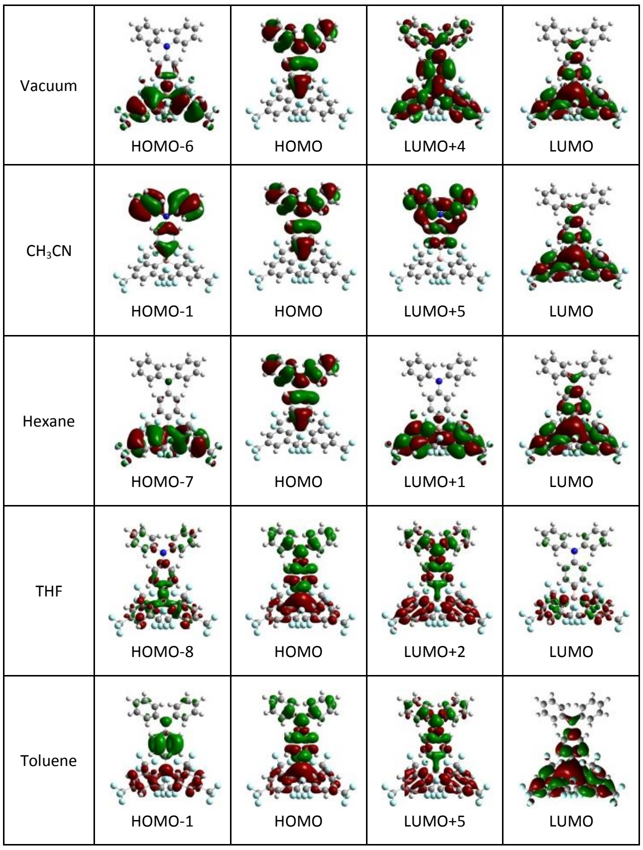

Figure 2(c): 3D Cube of compound 3 on the orbit of HOMO and LUMO