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Computational calculations of substitution pattern effects on the optical properties of benzobis(thiadiazole) derivatives as near-infrared-emitting organic compounds

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ABSTRACT

Organic materials with red to near-infrared (NIR) emission are of importance for organic light-emitting diodes (OLED). We designed novel organic compounds for OLED applications, incorporating benzobis(thiadiazole) (**BBT**) as the electron acceptor, thiophene as the electron donor, and using hexyl (C6) or triphenylamine (TPA) substituent groups. We studied the electronic and optical properties using theoretical methods to investigate effects of different substitution patterns. Optical properties were modeled using density functional theory (DFT) calculations. Absorption and emission wavelengths vary with the extent of twisting along the molecular axis; head-to-tail (HT) structures, with reduced steric hindrance, have redshifted spectra and are more energetically stable than the tail-to-tail (TT) configuration. Substituting C6 with TPA results in negligible increased in rotation angle. We also studied the effects of using TPA to end-cap the donor group; TPA end capping results in longer absorption and emission wavelengths. This work provides a useful theoretical screening method for new NIR organic materials.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted widespread attention since Tang and VanSlyke first described them in 1987 [1]. OLEDS require only a low driving voltage, have a wide view-angle, and are self-emitting [2–4]. Considerable effort has been invested in the search for highly efficient red-green-blue emitters, which are essential components for emission of the color spectrum, and are of great research interest, from both experimental and computational viewpoints [5–11]. A challenge for full-color OLED displays is to find materials that emit red, green, and blue (RGB) light with color purity. Among the various light-emitting materials available, there are few red-emitting materials at present; requirements for high temperature stability up to 150 °C and a small band gap present challenges to finding additional suitable materials [12]. In general, red emission covers the spectral region with wavelengths ranging from 620 to 760 nm, corresponding to an energy gap of approximately 1.6–2.0 eV. Materials that cover wavelengths greater than 750 nm are defined as near-infrared materials; thus, the next research challenge will be to develop low band-gap materials that can tune the redemission spectrum.

There have been a number of reports describing low-band-gap organic materials. In 1997, Yamashita et al. [13] synthesized a series of benzobis(thiadiazole) (**BBT**) as a class of low-band-gap material, which is of considerable interest because its derivatives exhibit near-infrared (NIR) absorption and fluorescence. Modification of the **BBT** core allows facile tuning of the emitted color. Further modification furnishes **BBT** derivatives containing a thiophene electron donor group; this change provides small band gaps and absorption maxima at 702 nm. Thomas et al. [14] researched ten **BBT** derivatives with various substitution groups. The group chose phenyl and thienyl **BBT** derivatives with no other substitution on the side rings for comparative studies. Thiophene substitution results in decreases in the HOMO-LUMO gap. The interesting result here is that the thiophene substituted **BBT** band gaps undergo NIR absorption. NIR absorption in the **BBT** derivatives arises because on substitution with thiophene, the **BBT** HOMO increases in energy, and the LUMO slightly decreases, thus closing the band gap. Thus, it is important to consider the influence of a thiophene substituting group on the HOMO-LUMO energy gap when designing materials.

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In 2006, Bundgaard and Krebs [15] reported a series of low-band-gap copolymers based on **BBT** derivatives containing up to four thiophene units. These derivatives had band gaps in the range of 1.7–2.1 eV. Interestingly, replacing the benzothiadiazole acceptor on **BBT** reduces the red-shifted band gap to approximately 0.7 eV. Therefore, the performance of **BBT** derivatives shows great promise for as the red-light-emitting device applications. The thiophene group is an important conjugated polymer often employed in band-gap engineering strategies. Although much effort is being spent on experimental research into OLED materials, experimental approaches may be limited by high costs and are time consuming. For these reasons, quantum chemistry calculations should first be used to predict the properties of new design materials, and so provide guidance for further experimental study.

In recent years, density functional theory (DFT) and Time-Dependent DFT (TD-DFT) have been employed to study OLEDs for two main reasons: (i) to gain insight into structural and electronic properties of materials and elucidate their structure-property relationships, (ii) to aid in the design of new molecules by screening for the most efficient candidates. DFT [16–18] is an effective calculation method that provides accurate groundstate electronic structures of molecules. TD-DFT [19–21] is an important approach to the calculation of excitation energies; the method has been used extensively to study the structure and absorption spectra of synthesized OLEDs. TD-DFT is an important tool with relatively low computational cost, and provides a good molecular orbital description of the ground-state electronic structure and the nature of the excitations therein. However, TD-DFT transition energies are affected by the nature of the functionals used for the calculations. The method provides consistent values for the maximum absorption wavelength (λ_{max}) and electronic transitions of dyes across different functionals; thus the functionals used are crucial to obtaining high quality calculated results.

Reports on the NIR properties of **BBT** derivatives [13–15] motivated us to investigate band-gap engineering of the **BBT** electron-acceptor group linked via a thiophene unit to form a conjugated polymer. In this study, we performed a computational chemistry study based on DFT/TD-DFT calculations of thiophene-conjugated-polymer **BBT** derivatives. The main objective of our study was to explore the effects on band gap, and the optical and chemical properties of substitution position in thiophene-conjugated-polymer **BBT** derivatives (chemical structures shown in Fig. 1). To the best of our knowledge, the effect of substituted positions of groups in these thiophene-conjugated-polymer **BBT** derivatives has not been previously reported. Thus, our computational study on introducing substituent groups into conjugated thiophene may provide useful for further investigation by experiment.

2. Calculation methods

All calculations on benzobis(thiadiazole) derivatives were performed using the Gaussian 09 program package [22]. The ground-state (S_0) geometries of all molecules were determined by full optimization with default convergence criteria. We applied DFT with the Becke-three–Lee–Yang–Parr (B3LYP) hybrid functional for S_0 geometry optimization [18,23] using a standard Pople type basis set 6-31G(d,p). The B3LYP functional has been demonstrated as a suitable method for predicting the S_0 geometry, and is widely used for calculations on various organic molecules used in OLED applications [24–28]. We determined configuration interactions of all singly excited determinants (CIS) [29] using the 631G (d,p) basis set to locate the excited-state geometry of photofunctional molecules and thus investigate excited-state (S_1) geometries. This approach provides suitable emission properties for most organic compounds.

The lowest excitation energy (E_{ex}) for a single electron transition from the ground state to the first excited state was evaluated using TD-DFT [19]. TDDFT calculations were performed on optimized S_0 geometries together with the consideration of solvation effects from dichloromethane by applying the Conductor-Polarizable Continuum Model (C-PCM) [30,31]. TDDFT currently uses varieties of functionals to interpret absorption spectra of different sized molecules [32–34]. In view of this, different DFT functionals were employed to calculate the absorption spectra, and for comparison with experimental results. Functionals closest experimental observations will be applied to shed light on the photophysical properties of benzobis(thiadiazole) derivatives. Additionally, the 10 lowest singlet-singlet electronic transitions were taken into account for TD-DFT calculations. We subsequently plotted the UV–vis absorption spectra derived from TD-DFT using the GaussSum program [35], in which each transition is based on the Gaussian distribution with full-width at half-maximum (fwhm) equal to 3000 cm^{-1}.

3. Results and discussion

3.1. BBT molecular orbital properties

Fig. 2 shows a schematic structure of **BBT** with atom numbering. The chemical structure for **BBT** comprises two five-membered rings with sulfur (S) and nitrogen (N) heteroatoms connected to a central benzene ring. Because of differences in electron affinity between S and N atoms and carbon, this molecular structure shows interesting properties as an electron acceptor. We performed DFT/B3LYP/6-31G(d,p) calculations to estimate the molecular orbital properties and aromaticity of benzobis(thiadiazole) (**BTT**). Atomic charges were determined following S_0 geometry optimization; the atomic charge distribution indicates that S atoms carry a positive charge (0.623) (Fig. 2), while the N atoms are negatively charged (−0.553). As expected, these two heteroatoms have greater atomic charges than those on the neighboring C atoms (0.218, −0.082), suggesting strong electron accepting properties. Moreover, the atomic charge distribution shows alternation between positive and negative alternation across the entire molecule. Thus, **BBT** exhibits resonance stabilization, which is a common characteristic of aromatic compounds.

Measurement of the electron density of the Frontier Molecular Orbitals (FMOs) is important because optical properties are strongly related to the electronic structures of molecules. A sketch map of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of **BBT** are presented in Fig. 2. The 4- and 8-positions on **BBT** have large atomic orbital coefficients in the HOMO, indicating that introduction of substituents on these positions would have a significant effect on molecular orbital properties. This will influence both the energy band-gab and the optical properties, which we discuss in detail in terms of the effect of substituted **BBT** derivatives.

3.2. Effect of thiophene substitution on BBT derivatives

Pristine **BBT** is sensitive to substitution at the 4- and 8-positions, and so we investigated the effects of incorporating up to three thiophene moieties in derivatives **BBTT1**, **BBTT2**, and **BBTT3** for comparison with **BBT**. Contour plots of the HOMOs and LUMOs of all molecules, together with their calculated energy levels are shown in Fig. 3. For the **BBT** molecule, the shapes of both HOMO and LUMO levels reveal that electrons are delocalized over the entire backbone of the molecule. The shapes of the HOMOs and