



Tuning the optical absorption of potential blue emitters



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ABSTRACT

The quest for more efficient blue emitters to be applied in organic light-emitting diodes is one of the challenging tasks of contemporary nanotechnologies. An approach to enhance substantially the intrinsic efficiency of luminescent organic molecules is the so-called thermally activated delayed fluorescence. A prerequisite for its occurrence is a vanishing energy separation between the first singlet and triplet excited states. A series of donor–acceptor molecules is investigated theoretically within this study in order to validate a molecular model for design of efficient organic blue emitters with closely spaced singlet and triplet excited states. The model is based on *meta*-linkage of the donor and acceptor residues to a spacer ensuring frontier molecular orbitals partitioning. The optimal geometries of the molecules are obtained with density functional theory (B3LYP/6-31G^{*}) and the singlet and triplet absorption spectra are simulated within the time-dependent density functional framework. The excited singlet–triplet energy gap is estimated and correlated to structural and energetic characteristics of the donors and acceptors. Several requirements for achieving high-energy triplet states at the molecular level in such donor–acceptor systems are outlined, the main being disjoint character of the molecular orbitals on the spacer and sufficient energy separation of the two topmost occupied orbitals. It is shown that by variation of the acceptor moiety the optical absorption transitions of the compounds can be fine-tuned in a systematic fashion. Molecules with degenerate singlet and triplet first excited states are proposed, combining bisdimethylaminotriphenylamine or phenoxazine as donors with diphenyloxadiazole or diphenyl-2,2'-bipyridine as acceptors. Bipolar molecules derived from this model could be used as prospective building blocks for efficient emissive materials in blue organic light-emitting diodes.

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1. Introduction

The development and production of new light-emitting devices has been a priority for science and industry during the past two decades. This is driven above all by the search for lower electric power consumption and additionally by longer life time, flexibility of shape and size, and faster reaction times. All these requirements are met by the or-

ganic light-emitting diodes (OLEDs) [1–4]. The OLED technology allows also the achievement of extremely high contrast and frequency, good luminance, and very wide viewing angles [5]. The OLED-based devices, however, still possess some disadvantages, one of the most important being the short lifetime and the unsatisfactory efficiency of the blue light-emitting diodes. The blue purely organic LEDs produced nowadays have varying external quantum efficiency from ca. 0.5% to ca. 7% [6–10]. However, upon application of phosphorescent metal-containing triplet emitters embedded in organic matrices, devices with efficiencies up to 25% have been realized [11,12]. Many new hybrid organic–inorganic systems are emerging constantly, e.g., based on different metal complexes and or-

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ganic matrices [13–16]. The purely organic materials, which are the subject of the current work, are all π -conjugated but vary enormously in the specificity of constituents and in molecular mass: from relatively small molecules to polymers. There are some technological benefits of the small-molecules diodes (SM-OLEDs) relative to the polymer ones. Namely, it is possible to form homogeneous layers and to fabricate complex multi-layer structures, which can furthermore improve the OLEDs efficiency. Therefore, we have focused on the investigation of small organic π -conjugated molecules.

A resourceful strategy for enhancing the performance of blue SM-OLEDs is the rational design of new π -electronic molecules employing quantum chemical modeling. Theoretical calculations on the geometry and photophysical properties of various entities have been reported [9,17–25]. The studies correlate primarily a specific molecular structure to the energy of the frontier molecular orbitals and to the wavelength of the absorption and fluorescence transitions. Just a few of the communications are more systematic. For example, the work of Li et al. tracks the influence of chain length on the optical properties of phenylene amine oligomers [19b]. However, no general molecular model for efficient blue luminescence of a class of small purely organic molecules has been proposed so far.

The emission efficiency can be increased by devising new organic compounds with higher internal quantum yield and employing them to obtain more productive emissive materials. According to quantum mechanics [26], the statistical limit for the internal quantum efficiency of purely singlet emission in OLEDs is 25% and it can be overcome only by making use of triplet excited states populations. Currently, there are two main directions for exceeding the limits of organic singlet emitters: (i) singlet fission or triplet–triplet fusion [27] and (ii) thermally activated delayed fluorescence (TADF). While the former processes most often count for efficiency on intermolecular excitation transfer, TADF can take place successfully even at the single molecule level. The TADF approach relies on improving the luminescence performance of organic substances by design of molecules with close-lying first excited singlet (S_1) and triplet (T_1) states. These are known to exhibit TADF through back population of S_1 from the triplet state and together with the fluorescence (primary emission) and phosphorescence (secondary emission) can result in almost complete overall quantum yield. For this purpose, dyes with significantly destabilized triplet excited state have to be proposed, which is a non-trivial task [28,29]. Verifying such a molecular model for a class of π -conjugated systems by theoretical calculations is the foremost aim of this study.

To-date, the most substantial efforts have been invested in designing and preparing molecules with high-lying triplet states, which could be used as host materials in phosphorescent OLEDs [12,17c,19a,13b,30–35]. Much fewer systems emitting via TADF have been suggested. Aromatic compounds like anthracene and fluorene are highly fluorescent but have stable triplet excited states [36]. On the contrary, some benzophenone derivatives are known to have comparatively narrow (0.1–0.2 eV) spacing between the singlet and the triplet excited state [37] but they prac-

tically do not fluoresce. More efficient blue TADF has been observed in some imidazole derivatives, for which also intramolecular proton transfer has been registered [38]. In this series one of the molecules was characterized by energy spacing between the singlet and the triplet excited state of 0.08 eV and showed increase of the internal quantum yield from 18% to 22% due to TADF. Recently, Adachi and coworkers have suggested several π -conjugated molecules as purely organic TADF-assisted blue emitters and have tested them in multilayer OLEDs. S_1 – T_1 energy differences ranging from 0.06 eV to 0.54 eV and prototype devices reaching external efficiency as high as 11% at low current densities have been reported [39]. Therefore, new blue luminescent molecules relying on TADF seem to be prospective OLED components and deserve to be sought.

A certain type of synthetically accessible donor–acceptor molecules are suggested as model blue emitters in this study and characterized theoretically. An understanding of the relationship between the molecular structure and the optical properties of the dyes is offered, facilitating the rational design of such materials.

2. Molecular models

Different donor–acceptor systems have been proposed as blue-emitting LED materials so far [40] but many of them are copolymers consisting of monomers with electron-donating or electron-withdrawing nature [41–43]. Some works report also the luminescent characteristics of small donor–acceptor molecules, which can be utilized as building blocks for SM-OLEDs [17c,19a,21,22a,38,44–48]. However, the classification of these materials based on general criteria is difficult. In order to be more systematic, we first summarize the requirements which our target molecules need to comply with.

The transition from the ground to the first excited state of donor–acceptor systems is usually HOMO–LUMO. Therefore, the representatives with potential for application are required to have large HOMO–LUMO gap (3–4 eV), thus enabling blue emission, and to be without overlap between the two frontier orbitals (destabilization of the triplet excited state) [38,49]. The strategy of connecting a donor and an acceptor moiety allows tuning of the HOMO–LUMO gap, since in the assembled molecule the HOMO usually originates from the donor and the LUMO – from the acceptor. The vanishing MO overlap provided by *meta*-linkage of the donor and the acceptor through a spacer should avoid the excessive electron density delocalization and guarantee small energy separation between the singlet and the triplet excited state [50]. The π -conjugation would ensure transport of charge carriers along the molecules.

Fig. 1 presents a scheme of the general molecular model, which can be utilized for achieving efficient blue fluorescence. The main feature is the presence of well-defined donor (D) and acceptor (A) moieties bridged by different spacers in a certain fashion to ensure the disjoint character of the donor and the acceptor molecular orbitals (MOs). In the simplest case this bridge can be a single bond but it can also be an organic residue with moderate elec-

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