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T-Shaped Donor−Acceptor Molecules for Low-Loss Red-Emission Optical Waveguide

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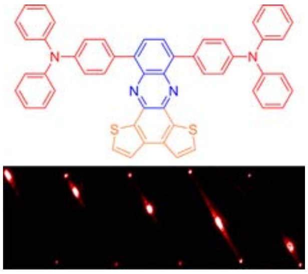
ABSTRACT



A series of T-shaped polycyclic molecules with high fluorescence were developed as optical waveguide materials. Their emissions covered almost the whole visible range from 450 to 800 nm. Compound 3-1 showed an optical loss coefficient about 0.29 dB/μm in red-emission waveguide. Our investigations demonstrated that these molecules held great potential for organic optical waveguide due to the high fluorescence quantum efficiency and large Stokes' shift.

Over the past decade, one-dimensional (1D) nano- and microstructures have attracted great attention due to their potential application in miniaturized optoelectronics, such as photodetectors,[1] chemical sensors,[2] field-effect transistors (FETs),[3] as well as optical waveguides.[4] Recently, 1D organic nano- and microstructures emerged as an effective flexible media to generate or propagate light.[5] Compared to their inorganic counterpart, organic materials have many advantages such as versatile modification from a molecular level, good flexibility, high luminescence efficiency, and low cost.[6] However, up to now, most of the reported organic materials for active waveguides emit light from 400 to 600 nm. The organic waveguide materials with red-emission above 600 nm are seldom reported.[7] Therefore, to develop new red-emissive organic waveguide materials with high performance is still a challenge for efficient full-color organic optical waveguides.

Organic materials for 1D active waveguides with high efficiency should be highly fluorescent and have large Stokes' shift. However, most 1D nano- and microstructures constructed by organic small molecules[8] or conjugated

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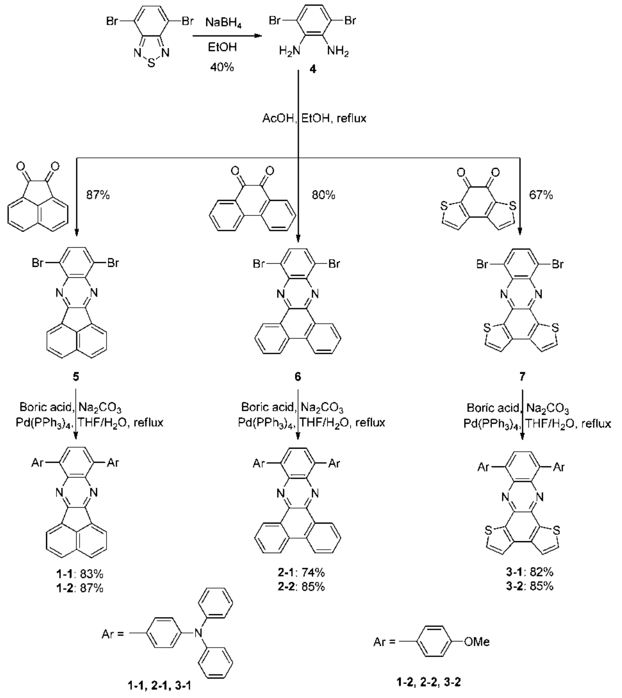
polymers[9] exhibit low fluorescence quantum efficiency, which is mainly caused by $\pi-\pi$ stacking of their planar backbones.[10] In order to achieve high fluorescence quantum efficiency in solid state, bulky groups are usually incorporated to decrease $\pi-\pi$ interactions.[11] Recently, Ma et al. found that triphenylamine (TPA) contained small donor−acceptor (D−A) molecules exhibited high fluorescence in solid state, which was attributed not only to the bulky TPA skeleton but also to the intercrossed excited state between the low-lying local exciton (LE) and charge transfer (CT) exciton resulting from the D−A structure.[12] On the other hand, the bandgap of D−A conjugated systems is usually small and can be tuned conveniently by changing donor and acceptor groups to achieve desired emission.[13]

Figure 1. Design strategy and structures of the T-shaped D−A molecules **1-1**, **2-1**, and **3-1**.

Herein, we developed a series of T-shaped polycyclic D−A molecules containing two electron-donor arms and an electron-acceptor core. As shown in Figure 1, the quinoxaline unit is chosen as the acceptor core, due to its strong electron-withdrawing properties.[14] To narrow the bandgap to achieve red emission, different aromatic cores are fused to the quinoxaline unit to enlarge the conjugated length.[15] In addition, bulky triphenylamine (TPA) donor arms are connected to the acceptor backbone due to their strong electron-donating property, which can further redshift their emission. Furthermore, these TPA-contained D−A molecules may efficiently use the excitation energy arising from the intercrossed excited state (LE and CT).[12]

Scheme 1. Synthetic Routes to T-Shaped D−A Molecules **1-1**, **1-2**, **1-3**, **1-2**, **2-2**, and **3-2**



Scheme 1 illustrates the synthetic approaches to the T-shaped D−A polycyclic molecules, **1-1**, **2-1**, **3-1**, **1-2**, **2-2**, and **3-2**. 4,7-Dibromo-2,1,3-benzothiadiazole was reduced by $NaBH_4$ in ethanol to afford **4** in 80% yield. Condensation reactions between **4** and different 1,2-diketone derivatives afforded compounds **5**, **6**, and **7**, respectively. A Suzuki coupling reaction between **5**, **6**, **7** and 4-(diphenylamino)phenylboronic acid catalyzed by $Pd(PPh_3)_4$ afforded T-shaped molecules **1-1**, **2-1**, and **3-1**. Following the same Suzuki coupling procedure, **1-2**, **2-2**, and **3-2** were also obtained using **5**, **6**, and **7** reacting them with *p*-methoxyphenylboric acid as references. The distributions of the donor arms in horizontal direction and the acceptor core in vertical direction facilitated the modification of the donor and the acceptor segments independently through different methods.

The absorption and emission spectra of all T-shaped D−A polycyclic molecules **1-1**, **2-1**, **3-1**, **1-2**, **2-2**, and **3-2** were measured in dilute CH_2Cl_2 solution (1×10^{-5} M) (Figures 2 and S1 and S2 in Supporting Information [SI]). Figure 2a shows the absorption spectra of **1-1**, **2-1**, and **3-1** in dilute CH_2Cl_2 solution. Note that these three compounds with the same donor arms exhibited similar absorption characteristics which was divided into three main parts. Taking **3-1** as an example, the first absorption band above 450 nm is attributed to the CT absorption. The second band, peaking at 425 nm, comes from $\pi-\pi^*$ transition of the acceptor core. This is concluded from the absorption spectra of **3-1** and **3-2**, which have the same acceptor core as shown in Figure 2b. The short wavelength band (280−300 nm) originates from the n$-\pi^*$ transition

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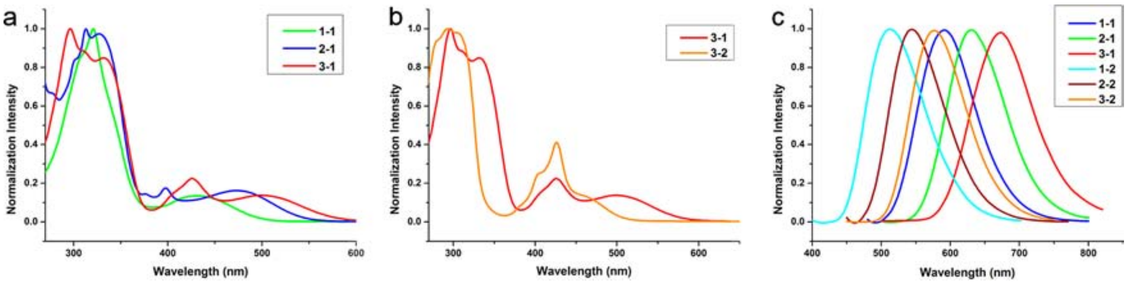

Figure 2. Absorption spectra of (a) **1-1**, **2-1**, and **3-1** and of (b) **3-1** and **3-2** in dilute CH_2Cl_2 solutions; (c) Emission spectra of all six T-shaped molecules in dilute CH_2Cl_2 solutions.

from the donor arm (TPA).[16] To further explore the photophysical properties of these molecules, we also performed the calculations using the method of B3LYP/6-31+g(d,p) to compute the electronic transitions of **3-1** and **3-2** (see Figures S7 and S8 in SI for a comparison between computed and observed spectra). The computed absorption spectra showed similar features with the experimental ones, which explained the origin of each absorption peak.

Photoluminescence (PL) behaviors of these molecules were explored by exciting the molecules at their absorption maxima, λ_{max} (Figure 2c). Compound **1-2** shows the shortest emission peaked at 513 nm, and **3-1** exhibits the longest emission around 669 nm, which are consistent with the trend in the absorption features. The emission peaks of **1-1** to **3-1** which contain stronger donor arms are more red-shifting compared to those of **1-2** to **3-2**. By fine-tuning the bandgap, a series of emission spectra from 450 to 800 nm were obtained. Significantly, all six T-shaped D−A molecules exhibit small overlaps between the absorption and emission spectra, thus decreasing their self-absorptions.

The electrochemical properties of these D−A molecules were investigated by cyclic voltammetry (CV) (Figures S5, S6 in SI) in CH_2Cl_2, and the data of **1-1**, **2-1**, **3-1** and **3-2** are summarized in Table 1. All compounds display reversible reduction bands and oxidation bands. Interestingly, for **1-1**, **1-2**, and **3-1** containing the same donor arms, the same HOMO levels (about −5.25 eV) but different LUMO levels are achieved. In addition, **3-1** and **3-2** exhibit the same LUMO levels (about −3.25 eV) but different HOMO levels, since they have the same acceptor core. The same trend is observed in all six compounds, implying that the oxidation potential is attributed to the oxidation of donor arms and the reversible reduction wave is decided by the reduction of the acceptor core. Figures S9 and S10 in SI illustrate the electron distributions in frontier molecular orbitals (FMOs) of compounds **1-1**, **2-1**, and **3-1** and **1-2**, **2-2**, and **3-2**. The HOMOs are mainly localized on donor arms, whereas the LUMOs are mostly distributed on acceptor cores. These results explain why the HOMO and LUMO levels depend on the donor arms and the acceptor cores, respectively. Such spatially separated FMOs in conjugate molecules are very interesting and have been reported in other D−A systems,[17] which lead to independent HOMOs and LUMOs of the T-shaped molecules.

Table 1. Electrochemical Properties of **1-1**, **2-1**, **3-1**, and **3-2**

compd	HOMO^a(eV)	LUMO^a(eV)	bandgap^a(eV)
1-1	−5.25 (−5.12)	−2.92 (−2.40)	2.33 (2.46)
2-1	−5.25 (−5.16)	−3.11 (−2.57)	2.14 (2.27)
3-1	−5.25 (−5.12)	−3.25 (−2.73)	2.00 (2.14)
3−2	−5.52 (−5.54)	−3.23 (−2.65)	2.29 (2.89)

[a] Calculated from CV, reference electrode: Ag/AgCl; computational results by the method of B3LYP/6-311+g(d,p) are in parentheses.

The red emissive molecule **3-1** grows into straight or bent microwires in mixed solvents of $CHCl_3$ and ethanol, as shown in a and b of Figure 3. The microwires are about 0.2−3 μm in width and 100−500 μm in length, with some of bent microwires. The microwires exhibit very bright red luminescence spots at both ends and relatively weaker emission from the body (Figure 3b). This is a typical feature of an optical waveguide,[5] suggesting that the microwires are able to absorb the excitation light and propagate the red emission toward the tips. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analyses were applied to determine the crystallinity of the microstructures. Both straight and bent microwires of **3-1** exhibit one set of single-crystal diffraction patterns, revealing that these microwires are well crystallized. Compared to the absorption spectrum of **3-1** in solution, the absorption of the microwires is not appreciably red-shifted (see Figure S3 in SI), indicating the relatively weak interactions among **3-1** molecules caused by the bulky TPA groups. The absolute fluorescence quantum efficiency of the microwires of **3-1** is 41%, which is very high in the solid state for red-emissive materials.[11] The large Stokes' shift is beneficial to efficient waveguiding, which decreases the

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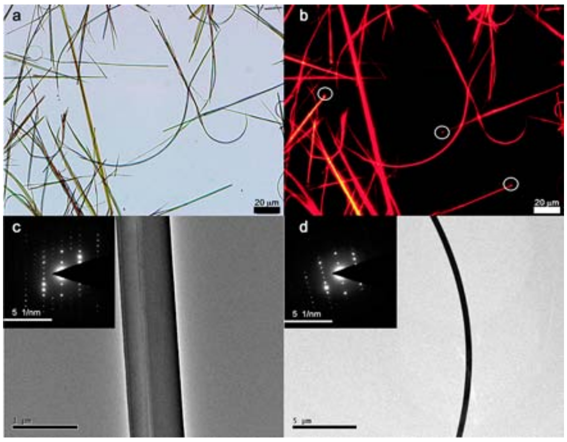

Figure 3. (a) Optical microscopy and (b) fluorescence microscopy images of microwires formed by **3-1**. Bright-red luminescence spots are marked with white circle at the ends of the microwires. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns of the (c) straight microwires and (d) bent microwires.

light loss caused by self-absorption. The emission spectra of **3-1** in solid state are shown in Figure S4 in SI. The Stokes' shift of the microwires is about 130 nm which is larger than those of the reported organic waveguide materials.[5]

A near-field scanning optical microscope (NSOM) was applied to investigate the distance-dependent fluorescence property of the microwires. The microwires were excited by a focused laser (325 nm) at different local positions along the length of the microwires with an NSOM collection-tip fixed over one of their ends. As shown in Figure 4a, b, both straight and bent microwires exhibit good waveguide properties. Such bent microwires may have potential applications in various optical or optoelectronic micro/nanodevices where shape-flexible material are needed. To investigate the waveguiding efficiency, the emission features at the excited site and the out-coupling light at the ends were measured separately. The fluorescence intensities at the excited site (I_{in}) and the emitting tip (I_{out}) were recorded to calculate the optical loss coefficient (α) by a single exponential fitting ($I_{\mathrm{in}}/I_{\mathrm{out}} = A\,\mathrm{e}^{-(-\alpha X)}$, where X is the distance between the excited site and the emitting tip) (Figures S11,12 in SI). The α of the microwires was thus calculated to be 0.29 dB/μm which is very low in those of reported red-emissive organic waveguide materials.[7]

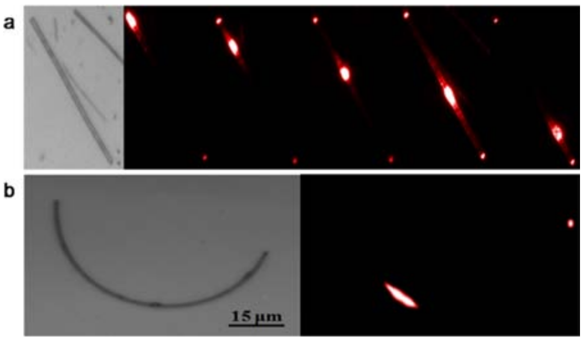

Figure 4. Waveguide properties of (a) straight microwires and (b) bent microwires.

In conclusion, we have developed a series of T-shaped D–A molecules through facile synthesis. These T-shaped molecules exhibit different emissions covered from 450 to 800 nm by changing the different donor arm and acceptor core. The red emissive molecule **3-1** can grow into straight or bent microwires in mixed solvent of $CHCl_3$ and ethanol with quite high fluorescence quantum efficiency up to 41%. The large Stokes' shift and high fluorescence quantum efficiency of **3–1** endow the microwires with a rarely low optical loss coefficient of 0.29 dB/μm as a red-emission waveguide materials. Our results demonstrate that intramolecular donor–acceptor molecules with high quantum efficiency can be rationally designed and used for red-emissive organic waveguide materials, thus presenting a new molecular family for full-color organic optical waveguides.

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Supporting Information Available. Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.