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# Toward highly fluorescence and ultralow-threshold amplified spontaneous emission in ordered solid state from twin-tapered bi-1,3,4-oxadiazole derivatives<sup>†</sup>

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We report several influential factors for achieving high fluorescent quantum yield and low ASE threshold from twin-tapered bi-1,3,4-oxadiazole derivatives by theoretical and experimental investigations. High fluorescence of BOXD-T3 in either apolar solvents or in the aggregating states were due to increased conjugation and a co-planar structure in the excited state, a four-level photophysical cycle between ground state and excited state, and co-planar formation of a rigid backbone with the tendency for slipped stacking. High fluorescence efficiency, high  $k_r$  value, high  $\sigma_e$  value, polarized and self-waveguided emissions in BOXD-T3 solution processed aligned film contributed to the ultralow ASE threshold. Extremely strong fluorescence of the microbelt-like organogel BOXD-T3 with fluorescence quantum yield of near unity was achieved. This work paves the way toward obtaining highly fluorescent and ultralow-threshold ASE in an ordered solid state from bi-1,3,4-oxadiazole derivatives.

## Introduction

Development of organic fluorescent materials is a hot topic of current interest because of its various applications in optoelectronic and photonic applications, such as organic light-emitting diodes (OLED),<sup>1</sup> organic light-emitting field-effect transistors (OLEFETs),<sup>2</sup> organic solid-state lasers<sup>3</sup> and organic fluorescent sensors.<sup>4</sup> However, most organic chromophores or laser dyes are highly emissive in their dilute solutions becoming weakly fluorescent in aggregating states due to severe fluorescence quenching as a result of certain intermolecular interactions, and which act as an obstacle to their applications in high-density optical systems.<sup>5</sup>

An effective method to achieve high fluorescence is to frustrate chromophore aggregation, such as the attachment of bulky alicyclics, encapsulation by amphiphilic surfactants, and blending with transparent polymers.<sup>6</sup> However, these processes often jeopardize the electronic conjugation in luminophores, by diluting the luminophore density or obstructing the charge transport in electroluminescent (EL) devices.

An important challenge is to explore the role of molecular structure and intermolecular interactions, which play a dominant role in determining the electronic and optical properties of molecular aggregates. It has been found that designing fluorescent molecules in certain packing manners, such as cross-dipole stacking,<sup>7</sup> aggregation-induced emission,<sup>8</sup> *J*-aggregate formation,<sup>9</sup> and enhanced intramolecular charge transfer (CT) transition,<sup>10</sup> could achieve an intense emission in ordered solid state. However, the examples of highly emissive organic ordered solids with a fluorescence quantum yield close to unity are still quite limited.

An attractive application based on organic fluorescent materials is to achieve electrically pumped organic lasers, which could open up the prospect of compact, low cost (even disposable) visible lasers suitable for applications from point-of-care diagnostics to sensing.<sup>3</sup> Optical pumped organic lasers have been realized in the visible region at various wavelengths for many decades, but huge obstacles still remain to be overcome with electrically pumped organic lasers. One of the main obstacles is how to prepare ideal organic laser materials for electrically pumped organic lasers, with not only high solid state

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fluorescence but also high stability, low amplified spontaneous emission (ASE) threshold and high carrier mobility, which is a challenge to achieve. The light emission of organic materials results from the exciton located on single molecule, and properties of photons (such as polarization) emitted from each single molecule are dependent on the molecular orientation and the orientation of molecular transition dipoles. Physical alignment of the small molecules or conjugated polymer chains results in alignment of their transition dipoles, which leads to new and interesting optical properties.<sup>11</sup> It is therefore of significant interest to prepare oriented organic films in which molecules with the same orientation and the emitted photons have the same characters, this may be beneficial to their correlation coupling for the amplification of light emission and thus achieve low threshold ASE. Furthermore, alignment of  $\pi$ -conjugated molecular films could increase the charge carrier mobility by orders of magnitude relative to their non-oriented films, thus offering simpler access to high current density devices.12

1,3,4-Oxadiazoles derivatives have enjoyed widespread use as electron-transporting/hole blocking (ECHB) materials, emitting layers in electroluminescent diodes and non-linear optical materials, due to the electron-deficient nature of the heterocycle, high photoluminescence quantum yield, good thermal and chemical stabilities.<sup>13</sup> Some 1,3,4-oxadiazoles derivatives have been demonstrated to be laser materials. Berggren et al. reported UV ASE of 392 nm from a thin film of 2-(4'-tert-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxiadiazole (PBD), which is known to be an excellent electron transporting material.<sup>14</sup> However, the pumping threshold for ASE was high ( $\sim 10 \text{ kW cm}^{-2}$ ) due to the large self-absorption (Scheme 1). Salbeck et al. reported a spiro 1,3,4-oxadiazole derivative (2',7'-bis-(biphenyl-4-yl)-2-(5-(4-tertbutylphenyl)-1,3,4-oxadiazole-2-yl)-9,9'-spirobifluorene) with high fluorescence quantum yields and a low ASE threshold, 1  $\mu J \text{ cm}^{-2} (2 \text{ kW cm}^{-2}).^{15}$ 

In our previous work, we reported a series of highly fluorescent liquid crystalline bi-1,3,4-oxadiazole derivatives which were useful model compounds for building functional architectures.<sup>16</sup> Strong ultraviolet ASE was observed in a twin-tapered bi-1,3,4oxadiazole derivative (BOXD-T3) cyclohexane solution.17 Aligned microbelts and BOXD-T3 film with strong fluorescence emissions and self-waveguided structure were prepared. Ultralow-threshold ASE (about 40 W cm<sup>-2</sup>) was realized in aligned ordered film of BOXD-T3, while no ASE phenomenon was observed in a vacuum evaporated film at excitation power below the laser damage threshold. An explanation of the reasons for different ASE properties between BOXD-T3 films is needed. In this work, we try to reveal the factors influencing high fluorescent quantum yield and low ASE threshold using twin-tapered bi-1,3,4-oxadiazole derivatives by theoretical and experimental investigations. This contribution reveals that: (1) the high fluorescence of BOXD-T3, either in apolar solvents or in aggregating





states, is due to increased conjugation and the co-planar structure which exists in the excited state, a four-level photophysical cycle between ground state and excited state, and the co-planar formation of a rigid backbone which has a tendency towards slipped stacking; (2) high fluorescence efficiency, high  $k_r$  value, high  $\sigma_e$  value, polarized and self-waveguided emissions of the BOXD-T3 solution processed aligned film contributed to the ultralow ASE threshold; (3) extremely strong fluorescence microbelt-like organogel of BOXD-T3 with a fluorescence quantum yield near to unity was achieved.

#### **Results and discussion**

#### Theoretical calculations

We calculated the geometry of BOXD-T1 with Becke3-Lee-Yang-Parr functional (B3LYP) methods for ground state and configuration-interaction singles (CIS) method for the excited state together with the 6-311+G\*\* basis set Fig. 1. The main calculated geometrical parameters of BOXD-T1 in ground state and excited state are listed in S-Table 1<sup>+</sup>. In the ground state, the four rings of BOXD-T1 molecule are co-planar, and the bond lengths of phenyl-oxadiazole and oxadiazole-oxadiazole are 1.45 Å and 1.44 Å, respectively, corresponding to the range for a C(sp2)-C(sp2) single bond (1.48 Å).<sup>18</sup> This indicates that the rigid backbone of BOXD-T1 is conjugated, which may be beneficial for aggregation through intermolecular  $\pi$ - $\pi$  interactions. In the excited state, the rigid backbone of the BOXD-T1 molecule is also co-planar, while the bond lengths of phenyloxadiazole and oxadiazole-oxadiazole are 1.42 Å and 1.39 Å, respectively, which are shorter than those of the ground state, indicating increased conjugation. We calculated the LUMO and HOMO levels of BOXD-T1 in ground state and excited state with B3LYP methods with 6-311+G\*\* basis set. The calculated LUMO and HOMO levels of BOXD-T1 in ground state are -2.09 eV and -5.72 eV, respectively. In excited state, the calculated LUMO level is decreased to -2.17 eV, and the calculated HOMO level is increased to -5.45 eV, indicating a four-level photophysical cycle beneficial for stimulated emission. The absorption spectrum of BOXD-T3 in cyclohexane



**Fig. 1** Calculated conformation of BOXD-T1 in excited state with geometry optimized with CI-singles method with 6-311+G\*\* basis set, a) top view and b) side view.

showed a lack of vibronic structure, while its emission spectrum exhibited a marked vibronic structure with a Stokes shift of 5078.7 cm<sup>-1</sup> (Fig. 6). This behavior is typical of a non-planar structure and co-planar structure in the excited state, indicating a four-level photophysical cycle between the ground state and excited state. Thus, it can be concluded that increased conjugation and the co-planar structure of BOXD-T3 in an excited state, and a four-level photophysical cycle between the ground state and excited state, may be the reason for the high fluorescence quantum yield (96%) and strong ASE phenomenon in the monomeric state in apolar solvents.

The BOXD-T1 dimer potential energy surface (PES) was computed as a function of the separate molecular plane (d), molecular shifts along the molecular long axis (y-displacement (y)) and the short axis (x-displacement (x)) are shown in Fig. 2a. The ground state PES was calculated with the M062x approach, which has a greatly improved performance for noncovalent interactions.<sup>19</sup> The ground state PES for d = 3.4 Å of BOXD-T1 dimer is shown in Fig. 2b. It can be seen that the face-to-face molecular packing geometry has the highest energy due to unfavoured electrostatic interactions. The global minimum is predicted at x = 0.6, y = 5.6 Å, with binding energy calculated to be  $E_{\text{bin}} = 68.56 \text{ kJ mol}^{-1}$  (Fig. 2c, d). It can be seen that BOXD-T1 dimer slipped stack form with its 1,3,4-bi-oxadiazole rings closed to neighbouring trialkoxyphenyl rings, in the global minimum, is consistent with findings in the single crystal structure of a linear bi-oxadiazole compound.16a

#### Experimental

In our previous work, aligned microbelts and BOXD-T3 film with strong fluorescence emissions, self-waveguide structure and ultralow-threshold ASE (about 40 W cm<sup>-2</sup>) were prepared, while no ASE phenomenon was observed in its vacuum evaporated film at the excitation power below its laser damage threshold.<sup>17</sup> The alignment of the solution prepared film of aligned microbelts of BOXD-T3 was demonstrated on polarized optical microscopy (POM), in which alternative changes in uniform darkness or brightness was observed by rotating the sample stage. The birefringence of BOXD-T3 vacuum evaporated film was weak and no obvious change was observed by rotating the sample stage, indicating random aggregating (Fig. S1<sup>†</sup>). Polarized emission could be observed by fluorescence microscopy for a BOXD-T3 solution prepared aligned film (Fig. 3). Careful study showed that the most intense emission was obtained when the polarizer was placed perpendicular to the growth direction of the BOXD-T3 solution prepared film, while emission intensity diminished to a minimum when the polarizer was rotated by 90° from this position. Under polarized UV excitation, the emission is more intense with polarization of the excitation light perpendicular to the growth direction of the BOXD-T3 solution prepared film, while the emission intensity diminished to a minimum upon rotating the sample by 90° from this position (Fig. S2). From computations, the transition dipole moment of BOXD-T1 polarized mainly along the long molecular axis (Table S2<sup>†</sup>). The polarized emission of the BOXD-T3 solution prepared aligned film indicated that the dipole moments of the molecules in this film are aligned in a certain direction (perpendicular to the growth direction of the solution prepared film) which is beneficial



**Fig. 2** (a) Intermolecular coordinates used for scanning the dimer potential energy surface; (b) computed potential energy surface of dimer BOXD-T1 ground state; calculated dimer with global minimum (c) side view and (d) top view.

for correlation coupling and amplification of light emission. Furthermore, a well aligned dipole moment of the molecules can efficiently absorb the pumping laser light within certain polarization directions, demonstrated by polarized UV excited fluorescent spectra (Fig. S2†). Random aggregated molecules with random dipole moments can not efficiently absorb the polarized pumping laser light, which would lead to high threshold ASE or no ASE phenomena. No anisotropic fluorescence was observed in the BOXD-T3 vacuum evaporated film. By comparing the PL microscopy images of two types of BOXD-T3 film, BOXD-T3 solution processed aligned film exhibited much brighter



**Fig. 3** (a), (b) Polarized photoluminescence microscopy images of solution processed aligned film of BOXD-T3 on glass (white arrows illustrate the directions of the emission polarizer and red arrows illustrate the growth direction of the solution prepared film); (c) polarized fluorescent emission spectra of BOXD-T3 solution processed aligned film (blue line: polarizer perpendicular to the growth direction; red line: polarizer parallel to the growth direction).

emissions at the edge of the film and relatively weaker emissions from the surface of the film, indicating waveguide behavior (Fig. 4a), while vacuum evaporated film exhibited nearly the same intense emissions both at the edge and the surface of the film, indicating an unefficient waveguide structure, leading to higher optical losses (Fig. 4b).

The rigid segment of BOXD-T3 is donor-acceptor-acceptordonor (D-A-A-D) type, which favors  $\pi$ -electron donor-acceptor interaction giving rise to slipped stacks as calculated by computer. The XRD pattern of BOXD-T3 vacuum evaporated



Fig. 4 Photoluminescence microscopy image of BOXD-T3 (a) solution processed aligned film and (b) vacuum evaporated film.

film showed sharp strong diffraction (18.5 Å) and up to fifth order diffractions, indicating a well-defined layer structure with sharp interfaces (Fig. 5c). The layer space of BOXD-T3 vacuum evaporated film was much shorter than the geometry optimized BOXD-T3 molecular length with fully extended alkyl tails (26 Å), this indicates that the BOXD-T3 molecules had large angle tilt in layers. A possible packing mode for BOXD-T3 in vacuum evaporated film is depicted in Scheme 2, which shows BOXD-T3 molecules tilted with the angle between the molecular plane and the aggregation direction of about 47°. The angle between the molecular plane and the aggregation direction decides between the present of an H- or J-aggregate: above a theoretical value of 54.7° an H-aggregate is usually found, whereas in J-aggregates the molecules slip more with respect to each other, giving a smaller angle.<sup>20</sup> The angle obtained by molecular modeling of BOXD-T3 in vacuum evaporated film is well below this theoretical value, indicating the formation of J-type aggregates. This is supported by spectral data, a bathochromic shift is observed in the absorption spectra of BOXD-T3 vacuum evaporated film ( $\lambda_{max} = 334$  nm) in contrast to its



Fig. 5 XRD profiles of BOXD-T3 (a) xerogel from DMSO, (b) solution processed microbelts and (c) vacuum evaporated film.



Scheme 2 Packing mode for BOXD-T3 in vacuum evaporated film.

cyclohexane solution ( $\lambda_{max} = 329$  nm) (Fig. 6). In general, the J-aggregation band is distinctly red-shifted and appears as an intense narrow absorption band due to motional narrowing,<sup>21</sup> but the band of BOXD-T3 vacuum evaporated film is relatively broad. This result suggests that BOXD-T3 molecules in vacuum evaporated film may be oriented in a less optimal way. Positional disorder of BOXD-T3 molecules in layers of its vacuum evaporated film, is supported by XRD patterns, no additional diffraction peak was observed in the wide angle region, which is considered as one of the possible reasons for this behavior.<sup>22</sup> In addition, J-aggregates in solid state generally exhibit small Stokes shift and enhancement in photoluminescence quantum yield. Based on computations of BOXD-T1 in the ground and excited statea, the relatively large Stokes shift of BOXD-T3 vacuum evaporated film (6630.1 cm<sup>-1</sup>) may be due to increased conjunction in the excited state. The maximum absorption peak of BOXD-T3 solution processed aligned film was nearly the same as its vacuum evaporated film, while the absorption band of BOXD-T3 solution processed aligned film was narrower Fig. 7. The narrower absorption band of BOXD-T3 aligned film may be



**Fig. 6** Absorption spectra of BOXD-T3 cyclohexane solution (solid black line), solution processed film (solid red line), and vacuum deposited film (solid blue line); fluorescence spectra of BOXD-T3 cyclohexane solution (dash black line), solution processed film (dash red line), and vacuum deposited film (dash blue line). (Excitation wavelength: 340 nm).



Fig. 7 Stimulated emission cross section spectra of BOXD-T3 in solution processed aligned film (red line) and vacuum evaporated film (blue line).

due to the more ordered structure, demonstrated by XRD patterns which show many diffraction peaks in both low- and wide-angle regions (Fig. 5b). Unfortunately, we could not obtain a crystal structure of BOXD-T3 in the aligned film. Based on computer calculations, we suppose that BOXD-T3 molecules also adopt slipped stacks in solution processed aligned film.

From the  $\Phi_{\rm F}$  and the  $\tau_{\rm F}$  values (Table 1) of the two types of BOXD-T3 film, we estimated the radiative decay rate ( $k_{\rm r} = \Phi_{\rm F}/\tau_{\rm F}$ ) and the stimulated emission cross section ( $\sigma_{\rm e}$ ). Here,  $k_{\rm r}$  is related to Einstein's B coefficient,  $B \propto (c^3/8\pi h v_o^3) k_{\rm r}$ , where *h* is Planck's constant,  $v_o$  is the frequency of light, and *c* is the velocity of light. Since the ASE threshold is inversely proportional to the *B* coefficient, we would expect a large  $k_{\rm r}$  to result in a low threshold ASE.<sup>23</sup> BOXD-T3 aligned film with ultralow ASE threshold had a higher  $k_{\rm r}$  of  $3.4 \times 10^8 {\rm s}^{-1}$  and  $\sigma_{\rm e}$  of  $8.6 \times 10^{-17} {\rm cm}^2$ , while its vacuum evaporated film had a lower  $k_{\rm r}$  of  $1.7 \times 10^8 {\rm s}^{-1}$  and  $\sigma_{\rm e}$  of  $4.9 \times 10^{-17} {\rm cm}^2$ , which may be the reason for the different ASE properties in the two solid states.

It can be concluded that the high fluorescence efficiency, high  $k_r$  value, high  $\sigma_e$  value, polarized and self-waveguided emissions in the BOXD-T3 solution processed aligned film contribute to the ultralow ASE threshold. It is believed that the obtained aligned microbelts and film of BOXD-T3 with polarized strong fluorescence emissions, self-waveguided structure and low-threshold ASE are expected as ideal gain media for solid-state lasers.

Organogels are the material in which 3-D networks are formed through self-assembly of low-molecular-weight compounds (gelators) through noncovalent interactions, and the net work can absorb a large amount of solvent. In the past few years,

 Table 1
 Photophysical properties of BOXD-T3 in different states at room temperature.<sup>a</sup>

	$\lambda_{abs} (nm)$	$\lambda_{\rm em} ({\rm nm})$	$\Phi_{\mathrm{F}}$	$\tau_{\mathrm{F}} \left( \mathrm{ns} \right)$	$k_{\rm r}  ({\rm s}^{-1})$	$\sigma_{\rm e}~({\rm cm}^2)$
SPF VEF	334, 364 334	418 429	0.82 0.68	2.4 3.9	$\begin{array}{c} 3.4\times10^{\scriptscriptstyle 8}\\ 1.7\times10^{\scriptscriptstyle 8} \end{array}$	$8.6  imes 10^{-17} \ 4.9  imes 10^{-17}$

<sup>a</sup> SPF: solution processed film, VEF: vacuum evaporated film.

preparing functional 3-D architectures based on  $\pi$ -conjugated gelators are of increasing interest for quite diverse applications.<sup>24</sup> We are excited to find BOXD-T3 can form a highly fluorescent gel in DMSO and the fluorescence quantum efficiency ( $\Phi_F$ ) of its xerogel is close to unity. BOXD-T3 completely dissolved in DMSO when heated to boiling point. Upon cooling to room temperature, an immobile gel formed within half an hour at concentrations above 1.2 wt%. The resulting organogel exhibited blue-shifted and large enhancement of fluorescence emissions at 415 nm in contrast to that occuring in isotropic solutions (Fig. 8a). The BOXD-T3 xerogel shows very strong fluorescence in the deep blue spectral region ( $\lambda_{max} = 417 \text{ nm}, \tau_F = 3.0 \text{ ns}$ ). The



**Fig. 8** (a) Fluorescent emission spectra of BOXD-T3 in isotropic state (green), gel (blue) and xerogel (red) from DMSO (2 wt%) (excitation wavelength:  $\lambda = 340$  nm). (b) SEM image of BOXD-T3 xerogel from 2 wt % gel in DMSO. (c) Photoluminescence microscopy image of BOXD-T3 xerogel from 2 wt% gel in DMSO.

FE-SEM image of BOXD-T3 xerogel from DMSO displayed three-dimensional networks of microbelts width of 1–4  $\mu$ m (Fig. 8b). The PL microscopy images of the BOXD-T3 xerogel exhibit blue emission with very bright luminescence spots at tips and relatively weaker emissions from the bodies of the microbelts, typical characteristics of an optical waveguide behavior (Fig. 8c). Refining the excitation UV light into a ~50  $\mu$ m spot, gave bright luminescence spots at the belt tips in the unirradiated area, also observed in (Fig. S4†). Almost all of the observed microbelts reveal this kind of waveguide behavior. The XRD profile of BOXD-T3 xerogel from DMSO consists of several sharp strong diffractions both in the low-angle range and high-angle range, indicating crystalline features (Fig. 5a), similar to the solution processed film.

## Conclusion

In conclusion, we reveal several influential factors to achieve high fluorescent quantum yield and low ASE threshold from twintapered bi-1,3,4-oxadiazole derivatives by theoretical and experimental investigations. High fluorescence of BOXD-T3 either in apolar solvents or in the aggregating states were due to the increased conjugation and co-planar structure in excited state, a four-level photophysical cycle between ground state and excited state, and the co-planar formation of the rigid backbone with a tendency for slipped stacking. High fluorescence efficiency, high  $k_r$  value, high  $\sigma_e$  value, polarized and self-waveguided emissions in the BOXD-T3 solution processed aligned film contributed to the ultralow ASE threshold. Extremely strong fluorescence microbelt-like organogel of BOXD-T3 with the fluorescence quantum yield near to unity was achieved. This work paves the way toward highly fluorescence and ultralowthreshold ASE in an ordered solid state from bi-1.3.4-oxadiazole derivatives. We expect further excellent performance from the highly fluorescent bi-1,3,4-oxadiazole derivatives in solid-state optoelectronic applications.

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