



# Theoretical insight into the deep-blue amplified spontaneous emission of new organic semiconductor molecules

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## ABSTRACT

As for the lasing of organic semiconductor materials, novel semi-conducting materials  $N,N'$ -bis(3-methylphenyl)- $N,N'$ -diphenyl-[1,1':4',1''-terphenyl]-4,4''-diamine (BMT-TPD) and  $N,N'$ -bis(3-methylphenyl)- $N,N'$ -diphenyl-[1,1':4',1'':4'',1'''-quaterphenyl]-4,4'''-diamine (BMQ-TPD) were synthesized. In contrast to the  $N,N'$ -diphenyl- $N,N'$ -bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), the well known organic gain medium for the lasing, the two new materials have lower amplified spontaneous emission (ASE) thresholds and enhanced lasing performance. The molecular geometries in the electronic ground state and the first optically excited state as well as the vibrational modes of the three compounds have been studied by means of the dependent density functional theory (DFT). Theoretical analysis shows that, accompanying with the increased number of central phenyl rings, the uniform high-frequency modes (around at 1200, 1300 and 1650  $\text{cm}^{-1}$ ) of the three compounds are enhanced, which is driven by the C–H bending and C–C stretching in the central phenyl rings. Correspondingly, the enhanced vibration strength of the high-frequency modes and reinforced vibronic peak intensity bring out the distinct “four-level” energy level scheme which benefits population inversion for lasing and leads to the decreased ASE threshold. These results indicate that the synthesized materials are good candidates to act as active laser materials and our work provides an insight into the lasing of small organic molecules.

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## 1. Introduction

Molecular semiconducting materials, i.e. small molecules and oligomers, are one of the laser material classes investigated in recent years. Many of these systems have shown amplified spontaneous emission (ASE) thresholds much lower than those of traditional dyes, mostly due to the possibility of increasing the amount of materials in the films without significant PL quenching.  $N,N'$ -diphenyl- $N,N'$ -bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) receives significant attention serve as solid state laser material over the years due to the broad

photoluminescence and the tunable wide laser wavelength range [1–4] on account of its optical properties, absorption and emission behavior [5,6]. TPD shows stimulated emission in neat films that were fabricated by spin-coating, vacuum thermal evaporation and ink-jet printing as well as the blends that is diluted in polystyrene (PS) [7–10].

A lot of experiments have been carried out to study the ASE characteristics in TPD. It was considered that the factors of stokes shift, the radiative decay rate, the fluorescence lifetime and the fluorescence quantum yield are correlated with the stimulated emission phenomenon [10–12]. There are some density functional theoretical studies about the geometric structure and energetic of TPD [13,14], but as for the lasing mechanism of small molecules, up to now, few theoretical explanations were proposed in the molecu-

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lar structure and energy level point of view. Hence, the mechanism of organic semiconductor material for stimulated emission is ambiguity. In our previous work [15], we proposed that a handful of low-frequency modes and the strongly elongated high-frequency modes in the carbon rings contribute to distinct first vibronic sideband in the PL spectra. These formed an effective “four-level” system, which would be the key for lasing.

In this paper, based on TPD, following the idea in our previous work, we developed two compounds: N,N'-bis(3-methylphenyl)-N,N'-diphenyl- [1,1':4',1''-terphenyl]-4,4''-diamine (BMT-TPD) and N,N'-bis(3-methylphenyl)-N,N'-diphenyl- [1,1':4',1''':4''',1''''-quaterphenyl]-4,4'''-diamine (BMQ-TPD). On the one hand, in theory, by contrast with TPD, the increased number of central phenyl rings in BMT-TPD and BMQ-TPD lead to enhanced uniform strongly elongated high-frequency vibrational modes (around at 1200, 1300 and 1650  $\text{cm}^{-1}$ ). The high-frequency modes arise from the elongation of C—H in plane bending, C—C inter-ring stretching and C—C intra-ring stretching modes within the central phenyl rings. The intensive high-frequency vibrational modes, resulting in more remarkable vibronic peak in PL spectra, which is conducive to achieve more distinct “four-level” energy level scheme for the population inversion. Therefore, a significant low threshold is achieved. On the other hand, as we expected, the experimental results of resonant Raman peaks of BMT-TPD and BMQ-TPD were enhanced, which corresponds to reinforced elongation of high-frequency modes. Furthermore, the lower ASE thresholds for BMT-TPD and BMQ-TPD with deep-blue emission were achieved with the increased number of central phenyl rings, reduced by 2 times and 3.6 times compared with TPD respectively.

## 2. Experimental and theoretical methodology

### 2.1. Spectra measurement and ASE characteristics

Thin films, consisting of polystyrene (PS: inert polymer), doped with a certain amount (33 wt%, Sample:PS = 1:2) of TPD, BMT-TPD and BMQ-TPD (see Fig. 1), were spin-coated (around 500 nm) onto glass substrates at a speed of 3000 rpm and then the spin-coated films were annealed at 110 °C for 10 min in an oven.

Absorption and PL spectra were obtained by UV–Vis spectrophotometer (HITACHI U-3010, Japan) and Fluorescence Spectrometer (fluoromax-4 spectrofluorometer) respectively. As shown in Fig. 2, the normalized absorption spectra of TPD, BMT-TPD and BMQ-TPD possess two visible peaks and the lower energy peaks are the dominant. The PL

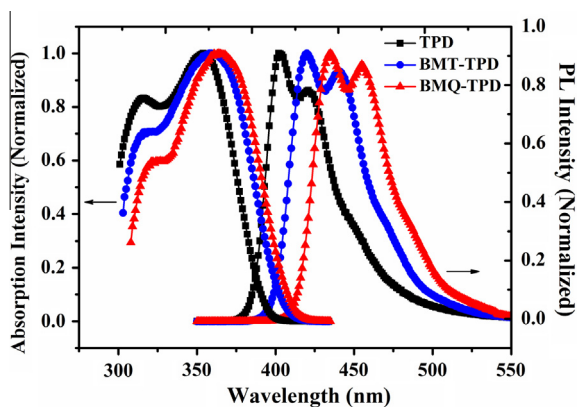


Fig. 2. Absorption and PL spectra of the three samples.

spectra of all three compounds show resolved vibrational progression, consisting of three emission peaks: a main band (0–0 transition) with a maximum at around 402 nm, 420 nm and 438 nm, the first visible vibronic peak (0–1 transition) at around 421 nm, 440 nm and 458 nm separately, and the second blurry vibronic peak (0–2 transition). Enhanced vibronic sideband, which was calculated as the product of the most strongly elongated in-plane modes, signify the intensive elongation of high-frequency modes with the increased number of central phenyl rings. The distinct first vibronic peak is beneficial to form distinct vibrational energy level included within electronic energy level.

To investigate ASE characteristics, the thin films were photopumped at normal incidence with a pulsed Nd:YAG laser (5.55 ns, 10 Hz) (Surelite I, Continuum Corp, USA), using the third harmonic (355 nm). The output beam of the Nd:YAG laser were shaped into a narrow stripe of approximately 1 mm width and 7 mm length by a cylindrical lens and an adjustable slit. The pump stripe was placed right up to the edge of the film where the emitted light was collected with a fiber spectrometer. The emission spectra were detected by a fiber-coupled CCD spectrometer (JY SPEX CCD3000).

Fig. 3 shows the emission spectra and the full-width half-maximum (FWHM) as a function of photon-pump energy for TPD, BMT-TPD and BMQ-TPD, which reflects their ASE characteristics. This spectral collapse is normally accompanied by a large enhancement of the output intensity and accounts for the presence of gain due to the stimulated emission. The specific parameters are listed in Table 1. These compounds show similar ASE characteristics, a significant increase of emission intensity and a rapid

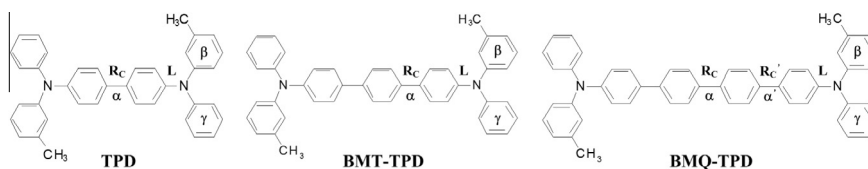


Fig. 1. Chemical structure of TPD, BMT-TPD and BMQ-TPD.

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