

# Efficient amplified spontaneous emission based on $\pi$ -conjugated fluorophore-cored molecules studied by density functional theory

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## ABSTRACT

The  $\pi$ -conjugated molecules, anthracene, pyrene and perylene with stepwise enhanced conjugation, have become a key ingredient in the design of new organic semiconductors for light emission and energy harvesting applications. Here, new biphenyl disubstituted anthracene, pyrene and perylene derivatives are synthesized and investigated as blue-emitting materials. The designed molecules exhibited typical amplified spontaneous emission (ASE) behavior in solid thin films for the compounds dispersed in the inert polystyrene host at a rather large (5 wt%) chromophore concentration. Theoretical analysis assists in understanding the emission properties and optical gain performance. The calculations reveal enhanced transition density and increased transition dipole moment accompanying by stepwise enhanced molecular conjugation of fluorophore-cores. In addition, enhanced fluorescence quantum yield, significant shortened fluorescence lifetimes and increased radiative decay rate for designed compounds promote the occurrence of ASE behavior compared with anthracene, pyrene and perylene. As well, the vibration analysis show that the intramolecular vibrational modes of researched molecules possessed small Huang-Rhys factors, which thus bring in effective competition between radiative and non-radiative decay process in favor of optical gain. The experimental and theoretical provide evidence that the reported molecules are promising candidates for organic laser applications.

## 1. Introduction

Rational design and synthesis of novel molecular structures demonstrating superior properties rapidly improve the performance of organic optoelectronic devices. So far, the best light-emitting-device performance in terms of efficiency and lifetime has been achieved through the utilization of low-molecular-weight compounds [1]. Among them, organic semiconductor lasers have been the subject of intensive studies during the last two decades, leading to great progress in terms of lasing threshold and operational device stability [2–4]. Thus, a search for new small-molecule compounds with superior optical and amplified spontaneous emission (ASE) properties is in demand.

Organic materials targeted for laser applications must have high fluorescence quantum yields, high radiative decay rate and negligible absorption in the spectral region of stimulated emission ensuring low ASE threshold [2]. Furthermore, owing to extended  $\pi$ -electron conjugation and rigid molecular structure, anthracene, pyrene and perylene result in noteworthy emission properties, thus, making the

molecules attractive as organic optical gain materials. As we know, anthracene, pyrene and perylene moieties are the most important materials in the OLED field due to the high fluorescence quantum yields [5–7].

In addition, in reported work, R. Scholz and co-authors have proposed that the high-frequency Raman-active modes contribute to the vibronic progression observed in PL, whereas the elongation of low-frequency modes results in a substantial broadening of the vibronic subbands defined by the high-frequency modes [8]. Our previous works [9,10] found that strongly elongated high-frequency modes in the carbon rings contribute to distinct first vibronic sideband in the PL spectra, and form an effective vibrational state contained in “four-level” system for light amplification. For  $\pi$ -conjugated units, anthracene, pyrene and perylene possess remarkable high-frequency modes but weak low-frequency modes evidenced by Raman spectra [5,11,12]. Thus, in the view of vibration analysis, the dominant high-frequency modes originating from anthracene, pyrene and perylene groups and weak low-frequency modes are benefit for the formation of effective

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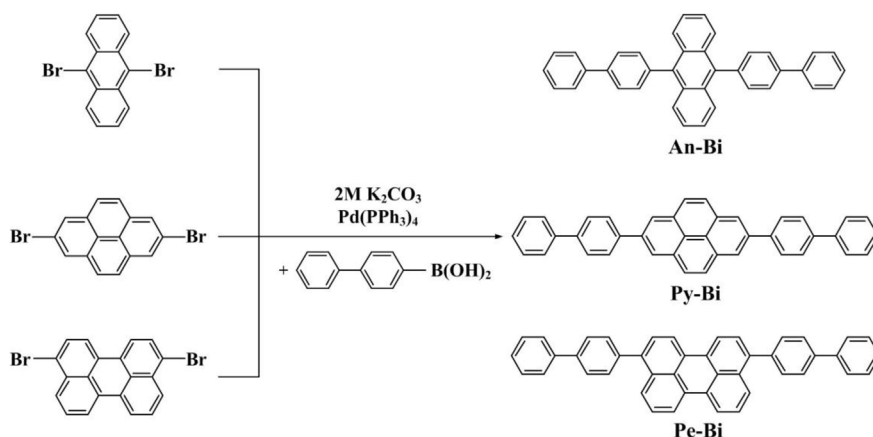
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Scheme 1. Synthesis of An-Bi, Py-Bi and Pe-Bi compounds.

and distinct “four-level” system for lasing.

However, to rigid low-molecular-weight molecules for the development of electronic applications, solubility of the chromophores and concentration quenching became an important issue [13–16]. In most cases, the multifragment compounds possess twisted conformations, which ensure suppressed luminescence quenching and glass-forming properties, need to be addressed [17,18]. In fact, in some cases, introduction of substituents to  $\pi$ -conjugated skeletons may bring out strong elongation of low-frequency modes due to small rotation barrier [19]. Therefore, rational design for rigid fluorophores is demanded to obtain twisted conformations but unnoted low-frequency vibrational modes for good ASE performances.

Within this context, considering illustrated factors above, we choose  $\pi$ -conjugated units anthracene, pyrene and perylene accompanying by enhanced plane conjugation as fluorophore-cores, and biphenyl as substituent to achieve ASE performance. The photoluminescence derives from anthracene, pyrene and perylene, and owing to the twisted conformation between biphenyl units and rigid fluorophore-cores could prevent luminescence quenching to some extent [20]. We synthesized three blue-emitting materials 9,10-Bis-[(1,1'-biphenyl)-4-yl]-anthracene (**An-Bi**), 2,7-Bis-[(1,1'-biphenyl)-4-yl]-pyrene (**Py-Bi**) and 3,10-Bis-[(1,1'-biphenyl)-4-yl]-perylene (**Pe-Bi**) with optical gain behavior. Compared to anthracene, pyrene and perylene with no ASE performance, the designed molecules exhibited typical ASE performance with ASE threshold of 29.7  $\mu\text{J}/\text{cm}^2$ , 7.32  $\mu\text{J}/\text{cm}^2$  and 23.7  $\mu\text{J}/\text{cm}^2$  in solid thin films for the compounds doped in the inert polystyrene host at a rather large (5 wt%) chromophore concentration. The theoretical calculations assist in analyzing the emission properties and intramolecular vibrational modes to provide evidence supporting for emission properties and ASE performance. Our work reports three organic emitters with typical ASE performance and offers valuable guidance for the design of new organic optical gain materials.

## 2. Theoretical methodology

The ground and excited-state equilibrium molecular geometries of **An-Bi**, **Py-Bi** and **Pe-Bi** were calculated with DFT using the hybrid functional B3LYP and the basis set 6–31 g respectively in the Gaussian 09 program package. The optimized molecular geometries were confirmed to be stable by frequency analysis at the same level of theory. Using the same functional and basis set, the oscillator strengths and vertical excitation energy were obtained with TDDFT in the adiabatic approximation. The vibrational frequency ( $\hbar\omega_i$ ) and Huang-Rhys factors ( $S$ ) for each normal mode are calculated using the DUSHIN program developed by Weber, Cai, and Reimers [21]. The electronic density distribution was analyzed with the aid of Multiwfn software.

## 3. Experimental section

The thin film doped with polystyrene (PS) in a certain amount (5 wt %) of **An-Bi**, **Py-Bi** and **Pe-Bi** were spin-coated onto quartz substrates. Due to limited solubility, for anthracene, pyrene and perylene, the thin film doped with PS in a certain amount (3 wt%) were spin-coated onto glass substrates. The absorption and PL spectra were obtained by UV-Vis spectrophotometer (HITACHI U-3010, Japan) and Fluorescence Spectrometer (fluoromax-4 spectrofluorometer) respectively.

ASE measurements (5 wt% doped films) were carried out for thin film samples 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 PL quantum yield (PLQY) of the doped films was measured using an integrating sphere with an absolute PL quantum yield measurement system (Hamamatsu C11347). PL transient decays were measured for 150 nm thickness doped films of three compounds excitation at 360 nm. The pump stripe was perpendicular to the surface of the samples and the emitted light was collected with Fiber Optic Spectrometer (Ocean Optics SpectraSuite, USB2000). All the measurements were carried under air.

The Raman Spectra for the three samples with similar thickness (around 320 nm) were performed on a LabRam HR800 spectrometer (from Horiba Jobin Yvon) and measured using a 600 groove/mm grating, using 514 nm emission line of a Ar + laser.

## 4. Results and discussion

### 4.1. Synthesis

Scheme 1 describes the synthesis route of **An-Bi**, **Py-Bi** and **Pe-Bi**. The synthesis details are given in the Supplementary Information. Scheme 1 also shows the chemical structures of the three  $\pi$ -conjugated fluorophore-cored molecules, comprising a plane-rigid core and same side substituents: anthracene, pyrene and perylene serve as fluorophore-cores and two side biphenyl units substitute the two sides of fluorophores.

### 4.2. Photoluminescence and absorption spectra

The normalized absorption and PL spectra of the investigated **An-Bi**, **Py-Bi** and **Pe-Bi** compounds in dilute PS matrixes are shown in Fig. 1. The details of the emission properties of the compounds are summarized in Table 1. The PL spectra of **An-Bi**, **Py-Bi** and **Pe-Bi** compounds feature a dominant band peaked at 426 nm, 417 nm and 468 nm respectively, and main peaks of the absorption spectra are located at 392 nm, 366 nm and 437 nm. Taking into account the insets in Fig. 1 of

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