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A new ambipolar blue emitter for NTSC standard blue organic light-emitting device

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ABSTRACT

A novel blue emitter, **In2Bt**, featured with a rigid and coplanar distyryl-*p*-phenylene backbone flattened by two different bridging atoms (i.e. carbon and sulfur) exhibits high thermal and morphological stability ($T_g \sim 192$ °C) and ambipolar charge carrier mobilities in the range of $10^{-4} \sim 10^{-5}$ $cm^2 V^{-1} s^{-1}$. OLED device: ITO/PEDOT:PSS (300 Å)/α-NPD (200 Å)/TCTA (100 Å)/**In2Bt** (200 Å)/TPBI (500 Å)/LiF (5 Å)/Al (1500 Å) utilized **In2Bt** as an emitter gave a maximum brightness as high as 8000 cd m^{-2} (12 V) and saturated-blue emission with CIE chromaticity coordinates of (0.16, 0.08), which is very close to the National Television Standards Committee (NTSC) standard blue gives an enlarged palette of colors for color displays.

1. Introduction

In recent years, the development of deep blue emitters for OLED, which can match the National Television System Committee (NTSC) standard blue CIE (*x*,*y*) coordinates of (0.14, 0.08) has drawn considerable attentions [1–5]. Such a device not only can effectively reduce the power consumption of a full-color OLED but also can be utilized to generate emission of other colors through energy transfer. However, the molecular design for a deep blue emitter is quite challenging in terms of molecular structures. Molecules that can emit deep blue light normally have a restricted π-conjugated length, which consequently limits the spaces for tailoring the desired chromophore with sufficient thermal and thin film morphological stability. Thus, only few materials can meet these requirements so far [1–5]. Recently, the ladder-type oligomers and polymers [6–14], due to their rigid and coplanar structures which can enhance the π-conjugation, charge mobility, and luminescence intensity have emerged as potential materials for optoelectronic applications. In this regard, the physical properties and possible applications of ladder-type oligo- or poly(*p*-phenylene)s with various heteroatom bridges have been extensively studied [15–18]. More importantly, the physical properties of ladder-type materials can be

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tailored by modulating the degree of conformational flexibility between consecutive backbone units or, more effectively, manipulating the electronic properties by flattening the π-conjugated molecular framework with heteroatoms. In this paper, we report a new blue light-emitting material based on a coplanar molecular structure, in which benzothiophene was fused to neighboring phenylene ring through intramolecular annulation via sp^3-hybridized carbon atoms bearing two p-tolyl groups as peripheral substituents [19]. The non-doped OLED device shows an external quantum efficiency of 1.3% and saturated-blue emission with CIE chromaticity coordinates (0.16, 0.08), which is almost the National Television Standards Committee (NTSC) standard blue.

2. Results and discussion

Fig. 1 depicts the molecular structure of blue emitter: 7,14-dihydro-7,7,14,14-tetrakis(4-methylphenyl)-s-indaceno[1,2-b:5,6-b′]bis[1]benzothiophene (**In2Bt**) featured with a rigid and coplanar distyryl-*p*-phenylene backbone flattened by two different bridging atoms (i.e. carbon and sulfur). The synthesis and X-ray structural analysis of **In2Bt** have been reported by our group previously [19]. The peripheral *p*-tolyl substituents occupy the top and bottom faces of the main conjugated backbone prevent undesirable aggregation and improve thermal and morphological stability efficiently. We characterized the morphological and thermal properties of **In2Bt** using differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA), respectively. **In2Bt** exhibits a distinct glass transition temperature ($T_g \sim 192$ °C), which allows to form homogeneous and stable amorphous films upon thermal evaporation, a critical issue for OLED application. We ascribed the amorphous behavior and high values of T_g to the rigidity of the conjugated backbone and the presence of the *p*-tolyl substituents, which can effectively suppress intermolecular interactions and crystallization. The aryl substituents impart the oligomers with a high tolerance to heat, as indicated by their high decomposition temperatures ($T_d \sim 408$ °C, corresponding to a 5% weight loss).

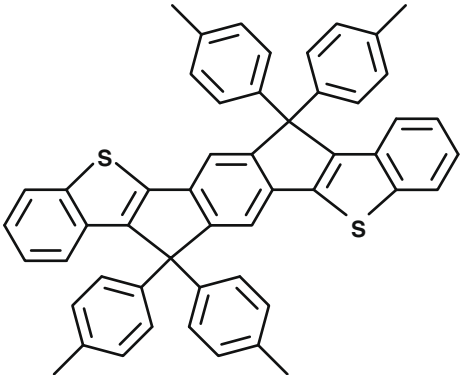

Fig. 1. Chemical structure of **In2Bt**.

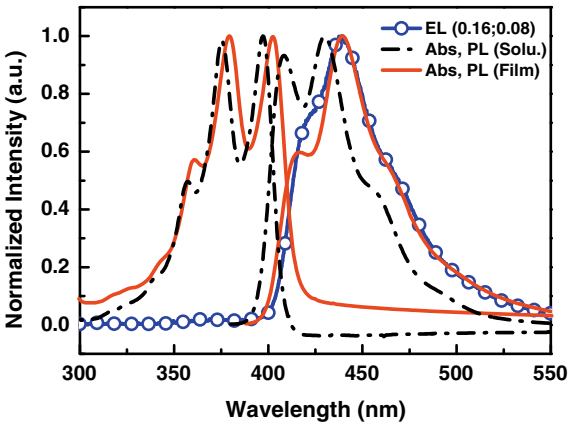

Fig. 2. The optical absorption, photoluminescence (PL) spectra of **In2Bt** in solution and thin film, and the electroluminescence (EL) spectra of device using **In2Bt** as an emitter.

Fig. 2 summarizes the electronic absorption (Abs) and photoluminescence (PL) spectra of **In2Bt** in chloroform solution and as solid films. Due to the coplanar conformation of the main chromophore, the absorption spectra of **In2Bt** in dilute solution and in thin film are almost superimposable with slightly red-shifted maxima in solid state (Abs λ_{max} in solution, 375, 397 nm, and in film, 385, 402 nm). The thin film emission spectra of **In2Bt** exhibit slightly red-shifted maxima (PL λ_{max} in solution 408, 430 nm, and in film 416, 439 nm). In addition, the small Stokes shifts ($\Delta\lambda \sim 11$ nm in solution) and the mirror images of the absorption and emission spectra are consistent with the molecular rigidity observed in the solid state structures [19,20]. We estimated the π–π^* band gap ($\Delta E_g \sim 3$ V) from the lowest energy absorption edges (ca. 413 nm) in the UV–Vis absorption spectra. The thin film photoluminescence quantum yield (PLQY) of **In2Bt** measured by a calibrated integral sphere (HAMAMATSU C9920) is ca. 14%. In order to gain more insight into the low PLQY of **In2Bt** in thin film, we have employed time-correlated single photon counting measurement with a time resolution of ~30 ps. Upon excitation at 390 nm and monitoring the emission at e.g. 450 nm, the observed lifetime (τ_{obs}) for **In2Bt** in thin film was determined to be 268 ps. From the PLQY and observed lifetime, the radiative (k_r) and non-radiative (k_{nr}) decay rate constants, deduced by Eq. (1), were 5.2×10^8 s^{-1} and 3.2×10^9 s^{-1}, respectively,

$$\mathrm{PLQY}(\Phi) = \frac{\tau_{obs}}{\tau_r} = \frac{k_r}{k_{obs}} = \frac{k_r}{k_r + k_{nr}}. \quad (1)$$

Normally, a skeleton possessing a rigid distyryl-*p*-phenylene backbone is expected to provide a reasonably high PLQY. The large k_{nr} (c.f. k_r) value and hence low PLQY for **In2Bt** in thin film is of fundamental interest and, to our viewpoint, can be tentatively attributed to two factors associated with the sulfur atom and/or the molecular framework. On one hand, sulfur atoms embedded inside the chromophore backbone may facilitate the non-radiative processes due to the heavy atom effect, a common phenomenon occasionally reported in sulfur-containing oligoaryls [21]. On the other hand, the soft sulfur atom pos-