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A bright blue emission material based on anthracene: Synthesis, characterization and luminescent properties

Lin Fang Shi [a,b], Bin Li [a,*], Li Ying Zhang [a,b]

[a] *Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China*
[b] *Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100039, China*

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Abstract

A blue light-emitting material, 2-(N-ethyl-anthraceneyl-9) imidazo [4,5-f] 1,10-phenanthroline (EAIP), has been synthesized and characterized by ^{1}H NMR, IR, elemental and single crystal X-ray diffraction analysis. The results of theoretical calculations indicate that the HOMO and LUMO distributions mainly locate at the anthracene fragment. It displays bright blue emission in both solid state and dichloromethane solution. The emission quantum yield calculated is 0.76.

Keywords: Crystal structure; X-ray diffraction; Luminescence

In recent years organic light-emitting materials have attracted much attention owing to their application in many fields, such as organic light-emitting diodes (OLEDs) [1], solar cells [2], and so on. The development of light-emitting materials has great influence on display technology. To achieve full color display, three primary color emission materials are required. Stability and efficiency of green and red light-emitting materials have reached commercial level, but those of blue light-emitting materials remain a challenge. Moreover, blue light-emitting materials can also be utilized to generate light of other colors by energy cascade to a suitable emissive dopant, which make the exploration of blue emission materials appear more important.

During the past decade a number of blue emission materials have been synthesized and some of them are anthracene-based [3–8]. In this paper, we have designed a new blue emission material containing anthracene unit, 2-(N-ethyl-anthraceneyl-9) imidazo [4,5-f] 1,10-phenanthroline (EAIP) which possesses wide energy band gap, high luminescence quantum yield, and good thermal stability.

1. Experimental

EAIP was synthesized according to the literature method [9,10] with some modification. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 9.256 (m, 2H), 9.148 (m, 1H), 8.718 (m, 2H), 8.151 (m, 2H), 7.777 (m, 2H), 7.571 (m, 4H), 7.468 (m,

* Corresponding author.
E-mail address: lib020@yahoo.cn (B. Li).

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2H), 4.329 (q, 2H), 1.320 (t, 3H). Anal. Calcd. for $C_{29}H_{20}N_4$: C, 82.05; H, 4.75; N, 13.20. Found: C, 82.03; H, 4.77; N, 13.19. IR (KBr pellet): ν 3052, 2985, 2931, 1627, 1598, 1562, 736, 688, 661, 688 cm^{-1}. Single crystals of EAIP suitable for X-ray diffraction studies were grown from slow evaporation of a CH_2Cl_2 solution. The crystals were measured on a Bruker Smart Apex CCD single crystal diffractometer using λ (Mo KR) radiation, 0.7107 Å at 293 K. An empirical absorption was based on the symmetry-equivalent reflections and applied to the data using the SADABS program. The structure was solved using the SHELXL-97 program.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer thermal analyzer at a heating rate of 10.0 °C/min. A 10 mL/min flow of dry nitrogen was used to purge the sample at all times.

Theoretical calculations: the starting geometry was from the single crystal structure. Density functional theory (DFT) calculations were carried out by B3LYP. The 6-31G* basis set was used to treat all of the atoms. The contours of the HOMO and LUMO orbits were plotted.

Absorption spectra were recorded on a Shimadzu Model 3100 spectrometer and the photoluminescence (PL) spectra were obtained by a Hitachi F-4500 fluorescence spectrophotometer equipped with a monochromator (resolution: 0.2 nm) and a 150 W Xe lamp as the excitation source. The room-temperature luminescence quantum yield was measured according to a reported method [11].

2. Results and discussion

The crystal structure of EAIP is presented in Fig. 1a, it is composed of two main components, one is the anthracene ring, the other is the imidazo [4,5-f] 1,10-phenathroline fragment. The dihedral angle of the two planes is 84.87°, which indicates that they are almost perpendicular. It is the reason for the absence of obvious π–π stacking in the crystal structure (Fig. 1b). We speculate that the absence of strong intermolecular π–π stacking makes EAIP a robust blue light-emitting material.

As shown in Fig. 2a, the decomposition temperature of EAIP is above 200 °C which indicates its good thermal ability. The absorption spectrum in dichloromethane solution (10^{-5} mol/L) is presented in Fig. 2b. The onset absorption is located at λ = 402.5 nm, and the optical band gap calculated according to it is 3.08 eV, which is slightly lower than the result of density function theory calculations, as presented in Table 1. The emission spectra in dichloromethane solution (10^{-5} mol/L) and that of in solid powder are presented in the inset of Fig. 2b. EAIP displays

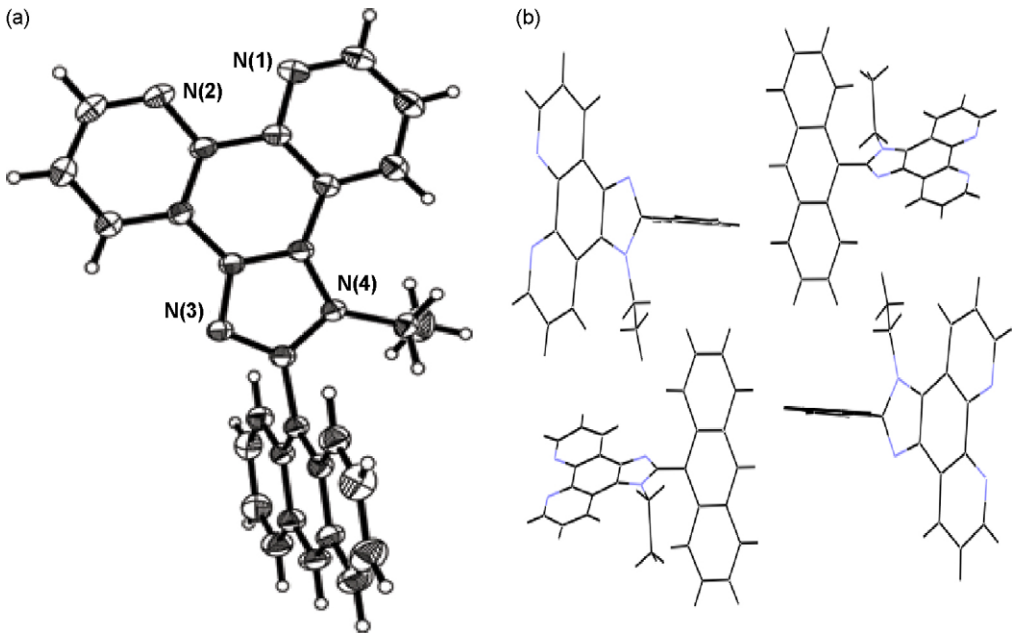


Fig. 1. (a) ORTEP drawing of a crystal of EAIP with displacement ellipsoids at the 30% probability level. (b) Crystal lattice packing diagram showing the absence of obvious π–π stacking.

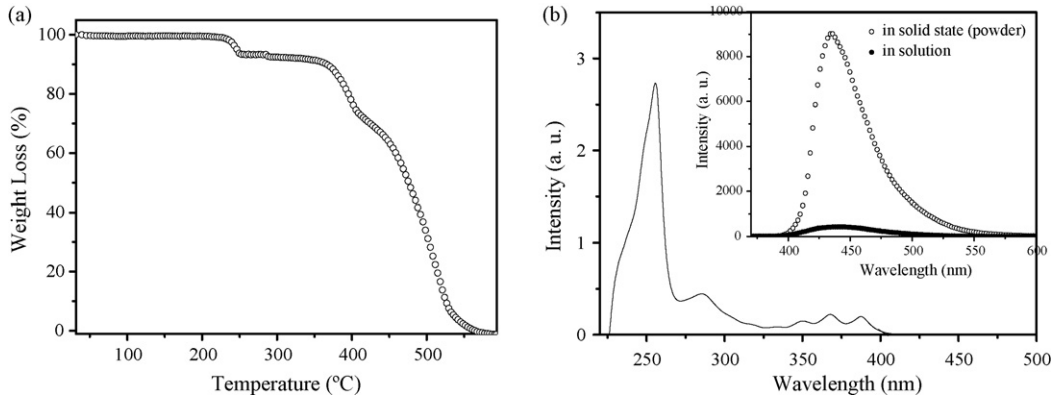
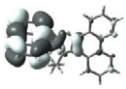
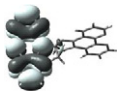


Fig. 2. (a) The TGA curve of EAIP. (b) UV–vis absorption spectrum of EAIP in dichloromethane solution (10^{-5} mol/L). Inset: emission spectra of EAIP in solid state (powder) and in 10^{-5} mol/L dichloromethane solution.

Table 1
HOMO and LUMO distributions of EAIP.

HOMO	LUMO	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)[a]	E_g (eV)[opt]
		−5.48	−1.83	3.65	3.08

[a] Band gap obtained from DFT calculations.
[opt] Band gap obtained from UV–vis absorption spectrum ($E_g = 1240/\lambda_{onset}$).

deep blue luminescence in both solid powder and in dichloromethane solution centering at about 434 and 440 nm, respectively. The strong emission of its powder indicates that the adverse intermolecular interaction in solid state can be overlooked as a result of the absence of strong intermolecular π–π stacking. The quantum yield measured in 10^{-5} mol/L dichloromethane solution (utilizing quinine sulfate ($\Phi = 0.546$) as the reference compound) is 0.76.

To further investigate the nature of the excited state, density functional theory calculations for EAIP were performed. As compiled in Table 1, both HOMO and LUMO distributions primarily reside on the anthracene ring indicating the emission coming from this unit. The calculated HOMO and LUMO levels together with calculated value of E_g are also listed in Table 1.

In conclusion, a bright blue emission material EAIP has been synthesized and characterized. The results of theoretical calculations display that the HOMO and LUMO distributions mainly locate at the anthracene unit suggesting the emission coming from anthracene fragment. The high radiative quantum yield together with its good stability implying EAIP can be utilized as a blue emission material.

Acknowledgments

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