Green emission band associated with defects in the crystal growth of a new chiral imine

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ABSTRACT

The morphological, structural and optical properties of a new chiral imine, namely (S)-(+)-[(1-phenyl)-N-(1-benzo [b]tiofen-2-yl)methylidene]ethylamine (**Bt**), are reported. Photoluminescence showed a band of intense green emission located at ~525 nm. The absorbance spectra displayed bands associated with $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions. The band gap was quantified by two electronic transitions at ~3.5 and ~4.7 eV, confirming those observed by absorbance. XRD studies showed a monoclinic phase. Additionally, by using Time Depending-Density Functional Theory (TD-DFT), the electronic and optical properties were examined.

1. Introduction

The design of organic optical materials have attracted much attention due to their applications in organic electroluminescent devices, organic light-emitting diodes, etc. [1], and likewise, an extensive number of organic molecules have displayed extremely high luminescence in the Vis-region [2]. Photoluminescence (PL) allows to investigate green emission band (GE) associated with crystalline defects. Usually, the GE band is generated by vacancies and crystalline interstices, stacking faults, grain boundaries, etc. On the other hand, the effect of introducing different functional groups in the *para*-position of the benzene ring in enantiopure imines can generate an increase in the GE intensity band, as the electron density of the phenyl ring is increased by $\delta \rightarrow \pi$ hyperconjugation effect, $\delta \rightarrow \delta^*$ and $n \rightarrow \pi^*$ transitions along with crystalline defects associated with molecular packing [3,4]. Such optical behavior can be associated with a $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition band with the long-wavelength edge at ~262 nm and a weak intraligand charge transfer band with the edge at ~305 nm [5]. Herein, the synthesis of (S)-(+)-[(1-phenyl)-N-(1-benzo [b]tiofen-2-yl)methylidene]ethylamine (**Bt**) in solvent-free conditions affording crystals in a multigram procedure is reported, along with its morphological, structural and optical properties. Worth-noting is the straightforward preparation of the enantiopure organic material, in a cost-effective, easier

and cleaner approach allowing a gram-scale and fast procedure to prepare suitable non-centrosymmetric crystals with a range of interesting properties for its potential application in the construction of optoelectronic devices. Its optical, morphological and structural properties displayed interesting features to build lasers, diodes, etc. as luminescence was found in the visible region and was related to crystalline defects.

2. Experimental

Benzo [b]thiophene-2-carboxaldehyde was allowed to react with the chiral amine in equimolar amounts under solvent-free conditions to yield enantiopure **Bt**, as reported earlier by us [2]. The molecular structure is showed in Fig. 1. Crystal data and structure refinement for **Bt** are displayed in Table 1. Single crystals suitable for X-ray studies were obtained by slow evaporation of a CH_2Cl_2 solution at room temperature and were handled in a non-controlled atmosphere. Diffraction data were collected at 298 K on an Agilent Xcalibur Atlas Gemini diffractometer with monochromatized MoKα (λ = 0.71073 Å) radiation. A cif file has been deposited with reference CCDC 1836718. X-ray Diffraction (XRD) patterns were obtained in a D8 Bruker Discover Series 2 diffractometer with Cu K$_\alpha$ radiation of wavelength λ ~1.5408 Å. Morphological images were registered by Scanning Electron Micro-
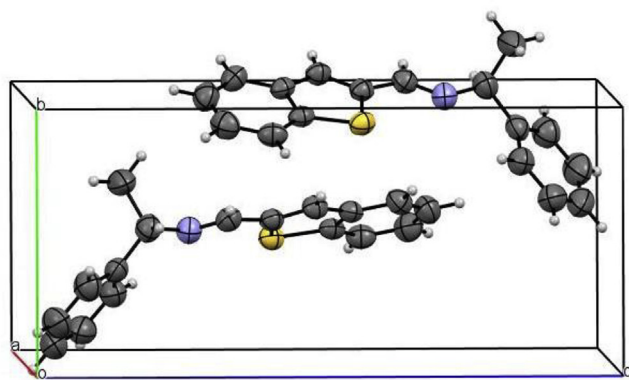
Fig. 1. Crystal packing and molecular structure of (*S*)-(+)-[(1-phenyl)-*N*-(1-benzo [*b*]tiofen-2-yl)methylidene]ethylamine (Bt).

Table 1
Crystal data and structure refinement for Bt.

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Empirical formula	$C_{17}H_{15}NS$
Formula weight	265.36
Temperature/K	293 (2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.7369 (3)
b/Å	7.6834 (3)
c/Å	16.6045 (9)
α/°	90
β/°	97.549 (5)
γ/°	90
Volume/Å³	726.59 (6)
Z	2
ρ_{calc}g/cm³	1.215
μ/mm⁻¹	0.209
F (000)	280.0
Crystal size/mm³	0.392 × 0.267 × 0.175
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.164 to 64.064
Index ranges	−8 ≤ h ≤ 8, −11 ≤ k ≤ 11, −24 ≤ l ≤ 24
Reflections collected	14126
Independent reflections	4926 [R_{int} = 0.0310, R_{sigma} = 0.0403]
Data/restraints/parameters	4926/1/173
Goodness-of-fit on F²	0.982
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0401, wR_2 = 0.0812
Final R indexes [all data]	R_1 = 0.0760, wR_2 = 0.0962
Largest diff. peak/hole/e Å⁻³	0.16/-0.17
Flack parameter	0.03 (3)
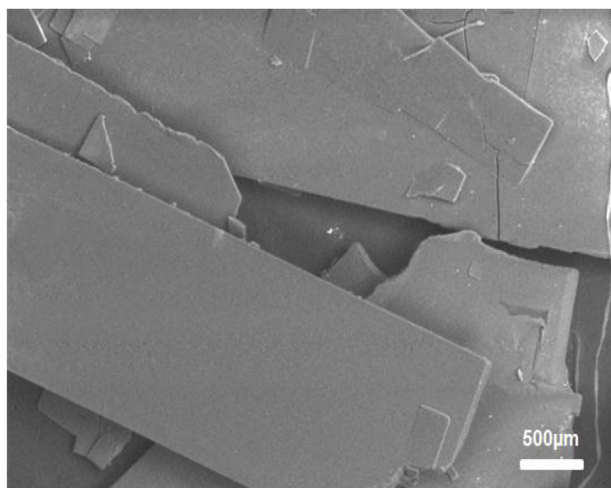
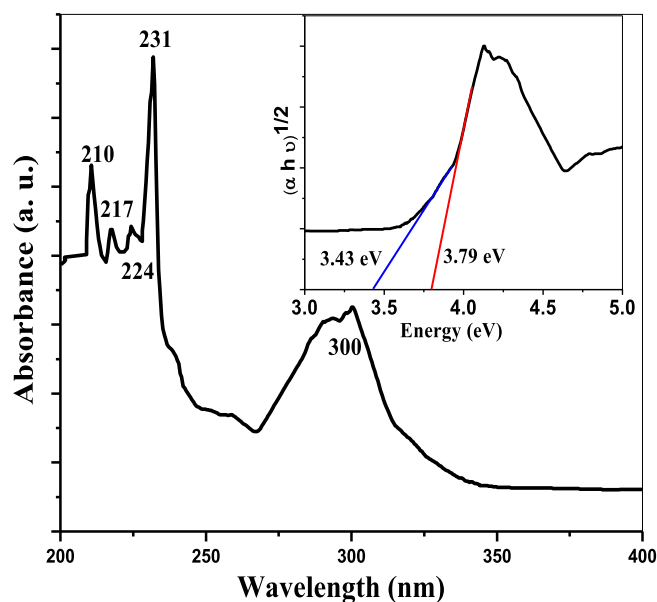**Fig. 2.** SEM image showing the morphology of Bt crystal.

Fig. 3. Absorbance *vs.* wavelength (nm) spectrum of Bt. Inset shows $(\alpha h\nu)^2$ *vs.* $(h\nu)$ plot.

scopy (SEM) by means of a Voyager II X-ray in an 1100/1110 SEM system from Noran Instruments. PL spectra was characterized by a main peak, under optical excitation provided by an Ar⁺ laser beam with a pump power of 10 mW, 450 nm as excitation using a Science-Tech model 9040 apparatus. The density functional theory (DFT) with the Truhlar functional (M06L) combined with 6-311 + G (d,p) basis set were employed to calculate the optimized full structure and vibrational frequencies of **Bt** from the X-ray structure, for assuring the global minimum in gas phase of the ground state. Electronic transition energies, energy gap ($E_g = E_{LUMO}-E_{HOMO}$) values and vertical excitation energy from the optimized geometry were carried out to reproduce UV-Vis absorption spectrum using the time depending-density functional theory (TD-DFT) by the TD-M06 L/6-311 + G (d,p) method. Calculations were performed using the Gaussian 16 package.

Bt. Mp 134–136 °C. ¹H NMR (500 MHz, CDCl₃/TMS): δ = 8.51 (s, 1H; H*C*=N), 7.82–7.75 (m, 2H; Ar-*H*), 7.50 (s, 1H; Ar-*H*), 7.43–7.41 (m, 2H; Ar-*H*), 7.38–7.32 (m, 4H; Ar-*H*), 7.26–7.23 (m, 1H; Ar-*H*), 4.59 (q, 1H; C*H*CH₃), 1.61 (d, 3H; CHC*H₃*). ¹³C NMR (500 MHz, CDCl₃/TMS): δ = 153.47 (H*C*=N), 144.79, 143.07, 140.63, 139.34, 128.61, 127.60, 126.97, 126.71, 125.95, 124.50, 124.48, 122.73 (Ar-*C*), 69.28 (*C*HCH₃), 24.85 (CH*C*H₃) ppm. FT-IR ν = 1625 cm⁻¹ (C=N). MS-I⁺: *m/z* calcd for $C_{17}H_{15}NS$: 265.0925; found: 265. $[\alpha]_D^{20}$ = + 142.1. Yield = 94%.

3. Discussion

A SEM image of **Bt** crystals with a lamellar morphology can be observed in Fig. 2, in the form of long, well-defined and compact sheets forming stacked plaques randomly, and such morphology is usually displayed in crystals of organic molecules with aromatic rings and/or conjugated bonds. A smooth surface, without holes, can be appreciated. The absorbance spectrum of **Bt** crystal in the ~200–400 nm (~6.2–3.1 eV) range of the UV region was measured under ambient conditions, the absorbance coefficient (α) was evaluated using T = (1-R)²e⁻αt equation, where T is transmittance and R reflectance. The absorption *vs.* wavelength (nm) spectrum is showed in Fig. 3. In the Vis-region (400–800 nm), typical absorption bands can be observed which are commonly associated with the π→π* (~343 nm) and n→π*