



Dual fluorescence polymorphs: Wide-range emission from blue to red regulated by TICT and their dynamic electron state behavior under external pressure



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ABSTRACT

Organic fluorescence molecules have attracted great interest in the last decades, due to their adjustable fluorescence properties and broad applications in organic electroluminescence display, fluorescence labelling, biological imaging, and so on. Conformation is one of the most important factors that determines organic molecular fluorescence properties. Herein, a compound, DBTO-PTZ, with five polymorphs was demonstrated. Distinctive polymorph-dependent optical characteristics were observed in these polymorphs, which gives an ideal model for the investigation of relationship between conformation and fluorescence property. Three of them display distinct dual fluorescence which is not observed in solution or the other two crystals. It is found that the twist angle between DBTO and PTZ units is a critical factor to determine the polymorphs of DBTO-PTZ and corresponding fluorescence behaviors. This result provides a direct proof to support the TICT model. Moreover, the external pressure was applied to adjust the fluorescence behavior from a dual emission to a single LE emission, which further proves the mechanism of TICT. This work will contribute to the understanding between conformation and optical characteristics. It also sheds light on a new strategy to fine-tune the fluorescence property.

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1. Introduction

Fluorescence occurs when an orbital electron of a molecule or an atom relaxes to its ground state by emitting a photon of light after being excited to a higher quantum state by some type of energy [1]. Organic fluorescence molecules, whose fluorescence properties can be tuned by various design strategies, have drawn great attentions due to their wide practical applications, including organic electroluminescence display, chemical sensors, fluorescent labelling, and biological imaging [2]. The molecular conformation is one of the main factors that would affect the fluorescence i.e. photoluminescence efficiency, emitting color etc. [3] In order to

investigate the basic relationship between molecular conformation and fluorescence behaviors, fluorescent organic crystals with definite molecular conformation and precise packing mode are favorable visualized models. Especially those organic crystals with conformational polymorphism, that is, different crystalline modifications of the same chemical substance, provide a convenient and efficient method to study and regulate the emission properties in various conformations and aggregated states [4].

Dual fluorescence effect, firstly discovered by Lippert et al. in a typical example of (N,N-dimethylamino)benzonitrile molecule (DMABN), is a particular phenomenon with respect to the appearance of two clearly distinct emission bands upon light excitation [5]. With the development of organic light emitting materials, many new materials with dual fluorescence have been reported [6]. The study of dual fluorescence mechanism is particularly important and highly challenging, which needs to consider not only the molecule itself but also the complicated environment. So far, different views on dual fluorescence mechanism are proposed

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based on experimental and theoretical investigations, one of the widely acceptable explanations is the appearance of intramolecular transfer states (CT) with twisted intramolecular charge transfer states (TICT) [7]. According to the TICT model, the emitting species are assumed to have a twisted geometry, the CT would be enhanced furthest when the torsion angle between the donor and acceptor group close to 90° , which triggers a red-shifted emission. Many attempts to elucidate the nature of the excited states using quantum chemical calculations have been made, however, direct measurement of the conformational structure of the emitting species still remains experimentally difficult and an urgent challenge.

In this work, we used phenothiazine as the electron donor and dibenzothiophene as the electron acceptor to construct a D-A-D type organic molecule 2,8-di (10H-phenoxazin-10-yl) dibenzo [b,d] thiophene 5,5-dioxide (DBTO-PTZ), which was reported as a thermally activated delayed fluorescence (TADF) molecule [8]. The donor and acceptor with relatively big steric hindrance were connected with a freely rotatable single bond to fabricate mutually perpendicular D-A alignment for efficient charge separation. The sulfur atom and sulfide sulfone moiety in the system are in favor of the occurrence of multiple intermolecular interactions and provide the possibility for polymorphism. Five polymorphisms of DBTO-PTZ were obtained and their single crystals were investigated in detail (Fig. 2 and Fig. 3). These five polymorphisms showed distinctive polymorph-dependent fluorescent properties. For example, three of them showed dual fluorescence, and the rest gave a single long wavelength pure CT emission. And their spectra which are induced mainly by conformations covered the whole visible region (from 427 nm to 643 nm). The outstanding diversity enables DBTO-PTZ single crystal an excellent model for the study of dual fluorescence effect and mechanism. Furthermore, hydrostatic pressure was used as an effective tool to regulate their conformation and fluorescent property, and to further prove the mechanism [9]. The remarkable properties inspire the exploration on the fluorescence mechanism and shed light on the connection between conformation and fluorescence.

2. Result and discussions

2.1. Polymorphs and dual fluorescence

DBTO-PTZ was prepared by Ullmann reaction between phenothiazine and 2,8-dibromodibenzo [b,d]thiophene 5,5-dioxide with high yield of 75%. The molecular structure of DBTO-PTZ was fully characterized by NMR spectra, high-resolution MS spectrum, and corroborated well with its expected structure. We firstly tried to grow crystals under different conditions and five polymorphs, labeled as A, B, C, D and E, with quite different molecular conformations, packing styles, and emission colors were obtained. These results allowed us to have a better understanding on the internal relationship among them and separately deal with the relationship between molecular conformation/arrangement and fluorescent properties derived from a single organic compound. The crystal A with pale yellow fluorescence and E with red fluorescence were obtained from a mixture of ethanol/dichloromethane (CH_2Cl_2) solution, respectively. Green slice-like crystal B was achieved by vacuum thermal sublimation of DBTO-PTZ. Form C was a faint yellow block which was prepared by layering n-hexane onto CH_2Cl_2 solution. Finally, slow evaporation of tetrahydrofuran (THF) gave crystal D exhibiting a yellow color. In general, the DBTO adopts a planar conformation and PTZ presents a butterfly-like structure. However, significant conformation difference was observed among these polymorphs and resulted in various fluorescence behaviors.

Fig. 1 shows the emission spectra of these five polymorphs. Crystal A, B, C clearly displayed dual fluorescence with the maximum emission at 430 nm and a longer wavelength emission ranged from 537 nm to 570 nm. While crystal D and E only exhibited one emission band, peaking at 580 nm and 643 nm, respectively. In addition, the fluorescence lifetime and quantum yield of polymorphs exhibited greatly difference (Table 1). The emission spectra of DBTO-PTZ in different polar solvents, in spin-coated film as well as the emission spectrum of PTZ moiety were also collected to assign the origin of emission peaks. PTZ showed stable blue emission peaking at 438 nm in organic solvents of different polarities. And the spin-coated film only gave a single emission which illustrate the dual fluorescence is generated by special conformation in crystal. As shown in Fig. 1, with the increase of solvent polarity, the fluorescence emission peaks of DBTO-PTZ showed continuous red-shift, accompanied by the gradually decreased fluorescent intensities. This solvatochromic effect was a typical feature of CT state transition [10]. Accordingly, dual fluorescence in crystal A, B, and C could be assigned to the LE state from PTZ groups and the CT state from PTZ to DBTO. The LE state was completely disappeared in emission spectra of crystals D and E, indicating the fluorescence was mainly from the CT state.

The single-crystal study revealed that crystal A belongs to the triclinic space group $P-1$ with $Z = 1$. The two PTZ units arranged symmetrically along the DBTO fragment. For easy identification, θ_L and θ_R are marked as the left angle and right angle between PTZ group major axis and plane of DBTO, which are 2.7° and 2.6° , respectively (Fig. 2). The dihedral angle between the PTZ and DBTO is 114.6° . In one unit of A, a dimer similar was formed through the anti-parallel alignment between the adjacent molecules. Each of the oxygen atoms in the DBTO interacts with a hydrogen atom of the neighboring DBTO and PTZ to form $\text{CH}\cdots\text{O}$ hydrogen bonds with distances of 0.26 nm, which are the major driving forces for the spatial arrangements of crystal A. Furthermore, there exists a weak π - π interaction between adjacent benzene rings of PTZ unit with a distance of 0.37 nm which further helps stabilize the molecular arrangement. The detailed intermolecular interactions are listed in Fig. S5 and Table S1 in the Supporting Information.

Crystal B belongs to the monoclinic space group $P2_1/c$ with $Z = 4$,

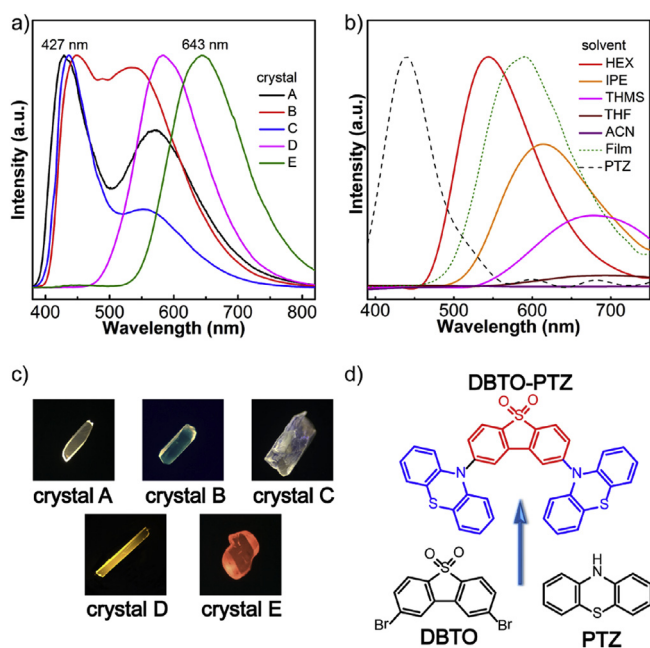


Fig. 1. a) Normalized emission spectra of polymorphs A, B, C, D, and E. b) The emission spectra of DBTO-PTZ in different polar solvents, the spectra of PTZ and film of DBTO-PTZ at room temperature. c) Photos of the polymorphs under 365 nm UV irradiation at room temperature. d) A diagram of synthetic route.

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