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Exploration the inherent mechanism of polymorphism and mechanochromism based on isomerism and AIE theory

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ABSTRACT

Polymorphism plays an important role in the fields of drugs, pigments and multicolor conversion materials, however, obtaining polymorphism mainly depend on accident and fortune until now. To explore the intrinsic mechanism of polymorphism and mechanochromism, TPEB2T and TPEB3T were designed and synthesized based on isomerism effect and aggregation-induced emission (AIE) theory. Photo-physical properties of the two complexes indicate they exhibit solvent-dependent fluorescence spectra, similar AIE property and markedly different mechanochromism and polymorphism. By diffusion n-hexane into dichloromethane solution of luminogens, the crystals of TPEB2T (2O) and TPEB3T (3Y and 3O) were obtained. The emission maxima of crystals 20, 30 and 3Y display 23, 40 and 66 nm red-shift respectively after grinding, accompanied by significantly enhanced fluorescence quantum efficiency for 3Y from 0.09 to 0.39 and over 50% decline for 2O and 3O. Compared with 20 and 30, the high contrast mechanochromism and weak emission intensity for crystal 3Y were attributed to different intermolecular head to head overlap rather than heavy atom effect of sulfur based on single crystal analysis and theoretical calculation. By extracting molecular pairs from crystals and constructing hypothetical molecular pairs based on molecular isomerization between sulphur and boron atoms, the minimum energy and dipole moment calculation results reveal that the formation polymorphism mainly depend on dipole moment of molecular pairs and culture solvent.

1. Introduction

One single substance exists in two or more than two different crystal types, which is called as polymorphism [1-4]. Generally, polymorphs have different physical and chemical properties, such as melting point, hardness, stability, colors and dissolution rate. For example, copper phthalocyanine, used as organic pigment, can exhibit different color due to existing eight crystal types including α , β , γ and so on [5–9]. In medicine aspect, optimization of crystal type can improve the bioavailability of drugs, reduce toxicity, and improve the therapeutic effect [10]. In addition, polymorphs are favorable for integrating multiple functions such as mechanochromism, aggregation-induced emission (AIE) and thermally activated delayed fluorescence into one single luminogen [11-14]. Recently, multicolor conversion materials induced by mechanical forces have attracted widespread attention and generated potential applications in terms of mechano-sensors, security

papers, and optical storage [15-19]. However, the design strategies for the multicolor conversion materials are lack due to limited quantity and unclear internal mechanism. Based on phase transition of crystal-crystal or crystal-amorphous-crystal, polymorphism provides a high-efficient and low-cost method to realize multicolor conversion. Further, luminogens with polymorphism have been obtained by careful screening solvents, anionic/cationic surfactant and temperature [20-23]. However, most reports focus on describing the conformation, arrangement and packing of crystals, while the inner relevance between polymorphism and solvents, surfactant or temperature are lack of in-depth discussion. Meanwhile, it is difficult for mechanochromic materials to predict red/blue shift of emission wavelength and enhancement/attenuation of fluorescence intensity after external forces stimulation [24].

Isomers have exhibited different physical and chemical properties, leading to interesting and magical phenomena. Isomers can be divided

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Scheme 1. Synthetic routes of TPEB2T and TPEB3T.

into structural isomers and stereoisomers, for examples, ethanol and methyl ether, stereoisomers R- and S- thalidomide. The former have the same molecular formula but different connection orders of atom or group, while discrepancy of the latter lies in the relative space positions of group. Furthermore, Isomers produce a huge impact on intermolecular interactions and stacking patterns, triggering high-contrast optical properties such as AIE, mechanochromism and room temperature phosphorescence [25-38]. To explore mechanism of polymorphism and mechanochromism, TPEB2T and TPEB3T were designed and synthesized by adopting AIE unit and isomerism (Scheme 1). The subtle structural discrepancy leads to high contrast mechanochromism and polymorphism. By diffusion n-hexane into dichloromethane solutions of luminogens, polymorphs 3Y (Yellow color) and 3O (Orange color) are discovered in sample TPEB3T, while only one orange color single crystal 20 was obtained for TPEB2T. Further, TPEB2T and TPEB3T exhibit almost identical solvatochromism and AIE activity but different mechanochromism. Combining photophysical properties of TPEB2T and TPEB3T with X-ray crystallographic analysis, the minimum energy and dipole moment calculations of molecular pairs extracted from crystals, in this paper, the relationships of structurephotophysical properties and inherent mechanism of polymorphism were analysed and discussed in depth.

2. Results and discussion

As shown in Fig. 1, donor-receptor donor (D-A-D)type **TPEB2T** and **TPEB3T** show similar solvatochromism, as well two main absorption

bands located at 200–400 nm and 400–500 nm (Table S1) belong to π - π^* transitions and intramolecular charge transfer (ICT) respectively. Compared with absorption maxima, the emission maxima show significant redshift with increasing the polarity of solvents, meaning easily polarized the excited state in comparison with the ground state. Meanwhile, the bathochromic emission of TPEB2T relative to TPEB3T indicates better conjugation effect. The reason is that the electron cloud density of 2-position is larger than that of 3-position for thiophene, which is conducive to ICT and reduction of energy gap. Next, the fluorescence emission spectra of two dyes were tested in different ratios of THF/H₂O solution to demonstrate their AIE properties (Fig. 2). Both luminogens emit very weakly in pure THF, but the fluorescence intensity of the solution increases significantly when the water fraction (f_w) reaches 80%. Subsequently, the fluorescence intensity of TPEB2T and TPEB3T reaches the strongest at 90% fw, illustrating typical AIE scene. In the aggregated state, the rotations and vibrations of C-C bonds are suppressed, which reduces non-radiation losses, thereby fluorescence enhancement is observed. Furthermore, the AIE absorption tests indicate maximum absorption wavelengths of two dyes display zigzag fluctuation with the increase of f_w from 0 to 70%, which is due to combined action of increased solvent polarity and twisted intramolecular charge transfer (TICT) (Fig. 2). Increase in solvent polarity promotes red-shifted absorption wavelength, while TICT causes the effective conjugation length becomes small. When f_w reaches 80%, absorption wavelength of TPEB2T gets to the maximum and then goes down at $f_w = 90\%$, but absorption maxima of **TPEB3T** exhibits linear redshift until 90%, which is attributed to formation of different aggregated state. On the one hand aggregation is beneficial to red shift of absorption wavelength due to intermolecular J-type stacking, but on the other it reduces the polarity of the environment around aggregated nanoparticles, leading to blue shift of absorption wavelength.

TPE moiety with propeller like molecular configuration endow two luminogens with AIE characteristic, and the propeller-like configuration easily lead to loose molecular packing and the resulting mechanochromism [39,40]. Fig. 3 and Table S2 in detail provide photographs of two luminogens under UV light and natural light and their emission



Fig. 1. Normalized UV–vis absorption spectra of (A) **TPEB2T** and (C) **TPEB3T** (Inset: Photographs under 365 nm UV illumination) and fluorescence spectra of (B) **TPEB2T** and (D) **TPEB3T** in various solvents (the concentration is 1×10^{-5} mol L⁻¹).



Fig. 2. Fluorescence spectra of (A) TPEB2T and (C) TPEB3T in THF/water mixtures with different fractions of water. Luminogen concentration: $1 \times 10^{-5} \text{ mol L}^{-1}$. The dependence of the intensity on the water fraction for (B) TPEB2T and (D) TPEB3T. The concentration is 1×10^{-5} mol L⁻¹. Inset: Photographs in THF/water mixtures with different fractions of water under 365 nm UV illumination. UV-vis absorption spectra of (E) TPEB2T, (G) TPEB3T in the THF/water mixtures with different fractions of water. Solution concentration: 10 µM. Chart of relationship between the maximum absorption wavelength and water fraction for (F) TPEB2T, (H) TPEB3T. Solution concentration: 10 µM.

spectra before/after grinding, fuming and heating. After light grinding, **3Y** and **3O** relative to **2O** show obvious the color change, even so, shifts of emission maxima are not exceed 7 nm, which indicates that the two luminogens are not suitable for the detection of weak pressure. By contrast, the three crystals show high-contrast mechanochromism before/after forceful grinding, especially for **3Y** with color change from yellow to orange and 66 nm red shift probably due to planarization of molecular configuration after destroying intermolecular weak

interactions. Further, ground **3Y** cannot return to the initial crystalline state by fuming and heating and displays irreversible mechanochromism, while reversibility of **2O** and **3O** is much better than **3Y**. More importantly, **3Y** displays weak fluorescence emission compared with **2O** and **3O**, however, the enhanced sharply emission with quantum efficiency change from 8.77% to 39.373% after grinding, while quantum efficiency of ground **2O** and **3O** reduced to less than half their crystalline state. In comparation with **2O**, the blue-shifted



Fig. 3. Photographic images of crystals 2O, 3Y and 3O under natural light and UV light (365 nm).

fluorescence emission and low quantum efficiency of 3Y obviously do not conform to the law of energy. To explain the contradiction, heavy atom effect is investigated due to sulfur atom can promote intersystem crossing (ISC) process from singlet to triplet, named as phosphorescence emission, which is sensitive toward oxygen and molecule vibration, and leads to low fluorescence quantum-yield [41,42]. In general, the aggregates have increased crossing channels compared with the monomer. Thus, DFT calculation of molecule pair derived from crystals 20 and 3Y was carried out (Table S3, Table S4). The result indicate there are the same two main channels for 20 (H-1 \rightarrow L, H \rightarrow L+1) and 3Y $(H-1 \rightarrow L, H \rightarrow L+1)$. Moreover, all the channels are not involve in triplet state. Therefore, there is not the tiny energy difference between S₁ and T_1 for **20** and **3Y** favoring the spin-orbit coupling between S_1 and T_1 states. The inferior fluorescence emission of **3Y** has nothing to do with the heavy atom effect. Further, crystal analysis indicate that the crystal density of **3Y** is 1.317 g cm⁻³, which is bigger than 1.201 g cm⁻³ of **2O**, while denser packing usually lead to the improvement of quantum efficiency by inhibiting rotation of molecular bonds, obviously, crystal density is not responsible for quantum efficiency degradation of 3Y. Generally, the optical properties of luminogens depend on spatial configuration, intermolecular weak interactions, arrangement and stacking. The single crystal X-ray diffraction analysis indicate 20 (CCDC 1912227), 3Y (CCDC 1912228) and 3O (CCDC 1912229) adopt twisted molecular conformation, especially for TPE unit forming rigid steric hindrance. While the B plane and its 1,3-bisubstituted benzene and thiophene units present V-shaped configuration and maintain almost planar configuration with the dihedral angle of 6.73° and 9.49° for 20, 3.72° and 5.56° for 3Y, 7.46° and 20.40° for 3O(Fig. 4). Obviously, plane A, B and C of 3Y maintain the minimum dihedral angle and the best planar configuration compared with that of 20 and 30. Moreover, the asymmetric molecular conformation easily produces antiparallel head to head stacking (TPE unit was defined as tail, and the other units were defined as head) to avoid steric hindrance of TPE unit. To



Fig. 4. Single crystal structure and conformation with hydrogen bond and weak interaction sites (A) 20, (B) 3Y, (C) 30 and intermolecular stacking modes ignoring hydrogen atoms (D) 20, (E) 3Y, (F) 30.

maintain the rigid molecular configuration, various hydrogen bonds and intermolecular weak interactions are involved, such as C-H...F, C…F, C-H…C, C-H…B, C…B and C-H…O, etc (Fig. S1). Even so, there are still obvious differences among of them. All the sulfur atoms are not involved in the formation of intermolecular hydrogen bonds and weak interactions in **30**. Different from **30**, two dimer linked by a pair of C-H…F and S…F (3.160 Å) can be observed in 2O, but only a part of sulfur atoms participated in S…F, while 3Y contained C-H…S (2.964 Å) interactions for all the sulfurs(Fig. S1 and Fig. 4). Meanwhile, conformational isomerism exists between sulfur and boron atoms in the crystals due to rotatable C-C single bond. Sulfur atom is located on the same side of the boron atom in 20 and 3Y, while 30 at different side. More importantly, although 20, 3Y and 30 are all to adopt antiparallel head to head stacking, the dimer with different overlap moiety can be observed in crystals. The intermolecular overlap of dimer located between B planes in 20 with 3.694 Å centroid-centroid (Cg-Cg) distances, and **30** with 3.539 Å plane-plane (C_p - C_p) and 3.687 Å C_g - C_g distances. For 3Y, the overlap occurs between thiophene and B plane, with 3.885 Å Cg-Cg distances (Fig. S2). The overlap between electron-donating unit and electron-withdrawing unit for 3Y could result in the dimer formation and the decreasing ICT effect and hypochromic shift of emission maxima, meanwhile, the best planar configuration combined with the short C_p - C_p distance, parallel arrangement mode favor π - π stacking and fluorescence quenching. By grinding, mechanical force would break the dense packing and π - π stacking of **3Y** to some extent and result in turn-on emission. Further, 20 and 30 with significantly reduced quantum efficiency adopt similar B plane overlap by grinding, but 3Y adopts the overlap between electron donor and electron acceptor, which produces enhanced quantum efficiency and high-contrast mechanochromism after grinding. Thereby, the stacking modes of crystal may be a good way to forecast the fluorescence change before/ after grinding. To provide further theoretical support for optical physical properties of the luminogens, we obtained the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) electron distribution of molecular pair extracted from single crystal based on theoretical calculation at B3LYP/6-31G* basis set level using Gaussian 09. As shown in Fig. 5, The HOMO orbital of 20, 3Y and 30 distribute on TPE moiety and B plane, but LUMO orbital is mainly



Fig. 5. B3LYP/6-31G(d,p) calculated molecular orbital amplitude plots of HOMO and LUMO levels for stacking molecule pairs extracted from crystals **20**, **3Y** and **30**.

located on B plane, and benzene and thiophene moiety directly linked with B plane, indicating similar ICT effect. Compared with **20**, HOMO and LUMO of **3Y** and **30** display the opposite movement, resulting in increased bandgap, which is consistent with the blue shifted emission of **3Y** and **30**. In addition, electron distribution did not spread on sulfur of two crystals based on HOMO electron cloud distribution, meaning absence of ISC process (Fig. 5).

To further explore mechanochromism behavior, we tested powder X-ray diffraction (PXRD) and differential scanning calorimetry (DSC) for 20, 3Y and 30 in different solid states. From Fig. 6 we can see that the sharp peaks of the crystal disappeared after grinding, and a diffuse and broad diffraction appeared, indicating a phase transition from crystalline to amorphous. After the ground sample is fumed, the disappearing peak appears again, indicating the transformation of molecular random patterns to ordered aggregates, but irreversible mechanochromism behavior and multi-state emission properties are obvious for 3Y due to appearance of some new diffraction peaks. In addition, a small amount of diffraction peaks mean that heating compared with fumigation is weaker stimulus mode for the recovery of crystalline state. The DSC curves (Fig. S3) reveal that the three crystals did not exhibit any thermal transition before the melt transition, while their corresponding ground samples show a distinct cold crystallization transition before melting, which show grinding produces a new metastable state.

Based on the above crystal analysis, the main difference among the crystals lies in spatial isomerization caused by boron and sulphur



Fig. 6. Normalized fluorescence emission spectra of (A) 20, (B) 3Y, (C) 3O in different solid states, PXRD patterns of (D) 2O, (E) 3Y, (F) 3O in various solid states (solid: original state of compounds, sg: slightly ground.).

atoms, intermolecular hydrogen bonds or weak interactions participated by sulphur atoms, overlap of stacking molecular pairs. Furthermore, the different factors affect stability of crystals, while the minimum energy of stacking molecular pairs have been used to evaluate the stability of crystals, moreover, polymorphism was usually obtained by adjusting the polarity of solvents according to the reported literature [43,44], thereby it is inferred that polymorphism are related to the minimum energy and dipole moment of aggregates in crystals. To provide theoretical supports for polymorphism, the minimum energy and dipole moment of stacking molecular pair extracted from single crystals were completed with the B3LYP/6-31G* basis set using Gaussian 09. Theoretically, there are four possibilities for each stacking molecular pair based on spatial isomerization between boron atom of B plane and sulfur and thiophene ring, therefore hypothetical molecular pair 2Y, 3Y_{a-c} and 3O_{a-c} were constructed by referring to crystals 3Y (Fig. S4). As a result, $3Y_{b}$ is not stable due to appearance of virtual frequency. Besides 3Y_b, 2O, 2Y, 3Y_a, 3Y_c 3O_{a-c} and 3O have almost the same the minimum energy in their respective crystals, obviously, the minimum energy is not the main reason of the absence of the other crystals except **3Y**, **3O** and **2O**. However, it is a wonder that the crystals possess wide span dipole moments. In addition, molecular pairs of 3Y, 20 and 30 relative to the hypotheticals exhibit much smaller dipole moments. By inference, the dipole moments of stacking molecular pair determine whether polymorphism exists or not. In consideration of dipole moments of dichloromethane (1.60D) and n-hexane (0D), the dipole moments of culture solvents does not exceed 1.60D. Obviously, the dipole moments of 20, 30 and 3Y are in the range from 0 to 1.6D, while the dipole moments of the hypotheticals are far beyond 1.6D. Therefore, it is difficult to obtain the hypotheticals according to dipole moments of conventional solvents.

3. Conclusions

In summary, two novel difluoroboron β-diketonate complexes named as TPEB2T and TPEB3T were designed and synthesized based on propeller-shaped TPE unit and isomerism effect of thiophene, and displayed significant AIE effects, solvatochromism and mechanofluorochromic properties. The crystals of TPEB2T (20) and TPEB3T(3Y and 30) were obtained by solvent diffusion method, based on X-ray diffraction single crystal analysis, 3Y compared with 2O and 3O displays hypochromic fluorescence emission due to different head to head overlap, further, the discrepancy lead to the most significant wavelength shift (66 nm) and enhanced fluorescence quantum efficiency from 8.77 to 39.37 for 3Y before/after grinding, while quantum efficiency of 20 and 30 reduced to less than 50% of the original crystal. As far as we known, the high contrast and off-on mechanofluorochromic materials are rare. The intrinsic mechanism of mechanochromism are attributed to the phase transition from crystalline to amorphous transitions according to the results of XRD and DSC. Theoretical calculation indicated that electron clouds in HOMO distributed in the whole molecule pairs, while electron clouds of LUMO mainly concentrated on the boron heterocyclic moiety, indicative of ICT effect. By contrast, 3Y possesses wide bandgap confirming blue-shifted emission compared with that of 20 and 30. Theoretical calculations combined with crystal analysis also confirm that inferior fluorescence intensity for 3Y was correlated with intermolecular stacking, but was not correlated with the heavy atom effect of sulfur. Last but not least, whether polymorphism exists or not may depend on the dipole moments of culture solvents and stacked molecular pairs according to theoretical calculations.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107663.

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