Preparation and Formation Mechanism of Organometallic Complex Co-Crystalline Micro- nanometer

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Abstract: Co-crystal is a product in which two or more molecules are co-crystallized by intermolecular forces. According to the force of crystallization, it is divided into 3 kinds: charge transfer conforming crystals, intermolecular π-π interaction, hydrogen bonding and halogen bonding co-crystal, and other types. Because of its shape and properties are diverse from single crystal, it has great designability, and has broad research prospects in the fields of luminescence, photo response, conductance, bipolar electrode transmission and so on. [1] The difficulty lies in the controllable preparation. Based on the demand for controllable preparation in the eutectic field, our group used $BeBq_2$ -TCNB as the main research object to prepare two kinds of $BeBq_2$ -TCNB microcrystals by solution volatilization method. First, this paper will introduce the basic properties of BeBq2, TCNB and its co-crystal and the theoretical basis for the possible formation of eutectic. Next, the preparation method independently explored by the group will be described in detail. In this way, the co-crystals of the one-dimensional regular hexagon structure of $BeBq_2$ -TCNB can be stably prepared. Next, the SEM, fluorescence microscope, fluorescence emission spectrum, optical waveguide and other test results will be used to illustrate the morphology and optical properties of the crystal. The growth mechanism was inferred by analyzing the results of single crystal analysis. Studies have indicated that the crystal has good optical waveguide performance, with optical loss coefficient as low as 0.022db/um, for which may provide potential applications in the field of optical logic gates and optoelectronic circuits.

1. Introduction

Co-crystal is a kind of special material which is crystallized by more than two components. Eutectic materials are rich in sources and relatively simple in preparation, so they have very important research significance and application value. Therefore, how to design, prepare and obtain high purity products is the focus of eutectic research. According to the types of intermolecular interaction, organic eutectic can be divided into charge transfer complex crystal, intermolecular π - π interaction crystal, hydrogen bond and halogen interaction formed eutectic, and other types. [2] therefore, the development of a simple, efficient and controllable method for the preparation of organic eutectic nanostructures will not only promote and promote the research in the field of nano photonics, but also have great significance in the study of exciton photon interaction, the construction of photoelectric functional devices, and biological sensing detection.

However, although the academic community has a deep understanding of eutectic, there are still some problems to be solved in the field of controllable preparation, such as the establishment of the database of molecular eutectic materials; [3] continue to explore the nucleation and growth mechanism of eutectic, and test the similarities and differences with the classical organic model of single crystal. Among them, the key difficulty in the field of micro and nano materials is controllable preparation, that is to overcome the influence of human error and environment, effectively use the designability of eutectic, and accurately prepare eutectic with stable properties and meet the application requirements.

In this work, we have successfully synthesized self-assembled regular hexagonal micro crystal of bebq2 tcnb by solution evaporation method. The crystal has good optical properties and the optical loss coefficient is as low as 0.022 dB / um, which may be used in optical logic gates and

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optoelectronic circuits. According to the similarity of the morphology of the bidb branched nanorods with the existing literatures, it is speculated that the prepared crystals may have the optical waveguide properties due to the reflection principle and unique morphology, which may have potential applications in the field of optoelectronic circuits in the future.

2. Chapter 1: the controllable preparation of BeBq2-TCNB

2.1 Introduction to materials

BeBq2 is a typical aromatic electron donor material. It has been reported that it can form stable and luminescent charge transfer complexes with aromatic donor compounds. According to the literature, BeBq2 single crystal has a regular lamellar structure and is yellow green. TCNB, as an electron acceptor, is a colorless hexagonal lamellar crystal. The purity of BeBq2 and TCNB, is 99% and 98% respectively. It is generally believed that the eutectic of the two is a regular orange red hexagonal micro nano structure.

2.2 Preparation Method

Bebq2-TCNB nanorods were prepared by solution evaporation method. In the general process, Bebq2 and TCNB powders were dissolved in 1ml tetrahydrofuran respectively, and then vibrated to form a solution of 0.012 mmol / ml. While using, mix the two solutions in 5ml plastic centrifuge tube to prepare a 6 mmol:6mmol mixed solution. After the two centrifuge tubes were keeping still at room temperature for 30 min, 400 μ l mixed solution was taken with syringe and dropped on the slide in the evaporating dish respectively. Then the evaporating dish was sealed with the sealing film and placed in a cool place for rest. One day later, the slide was taken out and orange red crystals were found on the slide. The regular yellow hexagonal eutectic was observed by optical microscope (400 *). Compared with the results of the original method of introducing bad solvent at room temperature, that is, after taking a certain amount of mixed solution and slowly dropping the bad solvent (water is used as the bad solvent in this paper), the comparison of the preparation effect of the original method after mixing is shown in Fig. 1 - (a). The crystal growth is observed under the microscope, and there are less crystal growth and more impurities (Fig. 1 - (a)). After mixing with the improved method, the crystal is more regular, forming a two-dimensional hexagonal structure, and the agglomeration phenomenon is significantly improved (Fig. 1 - (b)).

It is worth mentioning that this preparation method is stable and repeatable in summer to prepare the samples with uniform morphology. But in the winter, the finished product fell. Through the multi-layer investigation of the ratio, temperature, instrument, solvent, mixing method and other factors, the preparation method which can maintain the sample quality in winter to a certain extent is obtained. That is to say, the other conditions remain unchanged, and the heating temperature is reduced to 55 ℃. However, the morphology of the finished product is still not as regular as that obtained at room temperature in summer.

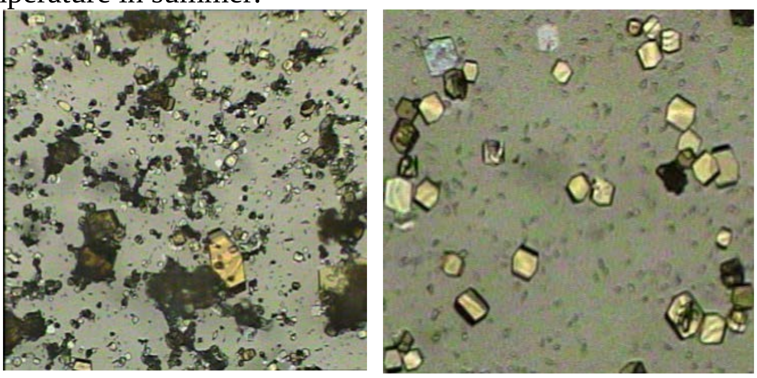


Fig 1. (a) bad solvent method; (b) direct evaporation method

3. Chapter 2 morphology characterization

3.1 characterization by optical microscope, SEM and TEM

As shown in Fig. 2 - (a) and (b), the regular two-dimensional hexagonal structure can be clearly seen under the optical microscope. Scanning electron microscopy (SEM) characterization (Fig. 2 - (c)) showed that the crystal structure was complete, and it was a very regular parallelhexagon. The crystal was clean and smooth with a side length of 4-6 nm.

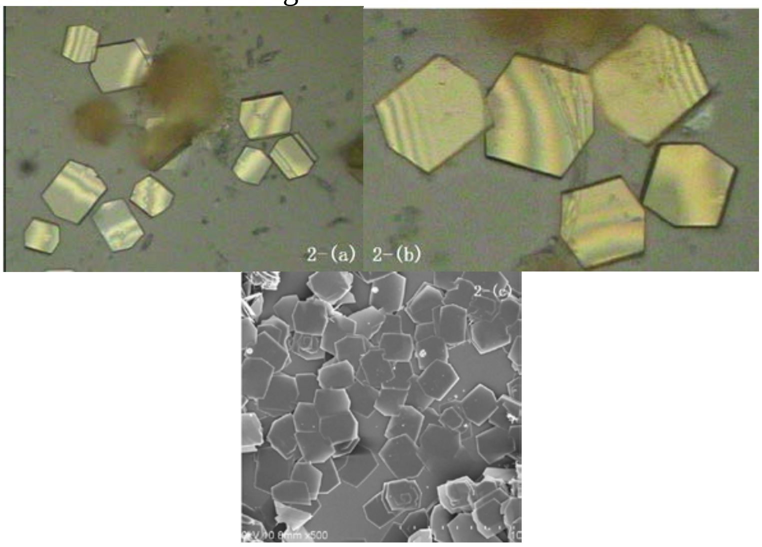


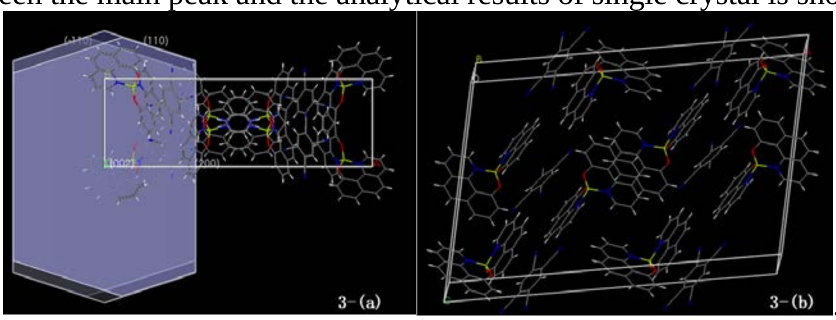
Fig 2. (a), (b) morphology of BeBq2 -TCNB under optical microscope; (c) Morphology under scanning electron microscope (SEM)

4. Chapter 3: The Formation Mechanism of eutectic BeBq2 -TCNB

4.1 Analysis of XRD and single crystal analysis results

In order to further determine the growth mechanism of the crystal, $BeBq_2$ -TCNB single crystal was prepared in a dark glass bottle by high concentration solvent evaporation method with a ratio of 50:50. The simulated growth morphology (3-a) and molecular arrangement (3-b) are shown in the figure. The crystal growth direction is along the crystal direction [110]. According to the side-by-side arrangement of the two kinds of molecules, combined with the literature, it can be inferred that this structure is a donor acceptor system formed by π charge transfer or π - π interaction between molecules.

The structure was further characterized by X-ray diffraction (XRD). The corresponding relationship between the main peak and the analytical results of single crystal is shown in Fig. 3 - (c).



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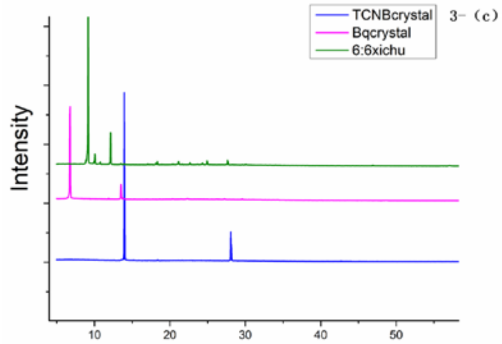


Fig 3. (a) simulated growth morphology of BeBq2-TCNB; (b) molecular arrangement of BeBq2-TCNB; (c) XRD spectra of of BeBq2, TCNB and of BeBq2-TCNB

5. Chapter 4: Optical Property Testing

5.1Qualitative analysis and fluorescence series test

Many eutectic crystals have the property of emitting fluorescence completely different from that of single crystal under the condition of specific wavelength laser excitation. [5] according to the previous experimental experience, we speculate that it may emit red light under the condition of ultraviolet excitation, and the second conjecture is confirmed by confocal fluorescence microscope. The red light emitted from BeBq2 crystal, which mainly emits blue light, indicates that it may have good luminescence properties. As shown in Fig. 4 - (a), after UV excitation, the edge intensity of the material is greater than that of the middle, indicating that there may be good optical waveguide properties. In order to quantitatively determine the excitation wavelength, a 400 nm laser was used to excite. The emission spectrum test results (Fig. 4 - (g) showed that the emission peak was 625-660 nm. In addition, the fitting results of fluorescence lifetime are shown in Fig. 4 - (b), τ1 = 4.46ns, τ2 = 4.47ns, X2 = 6.28.

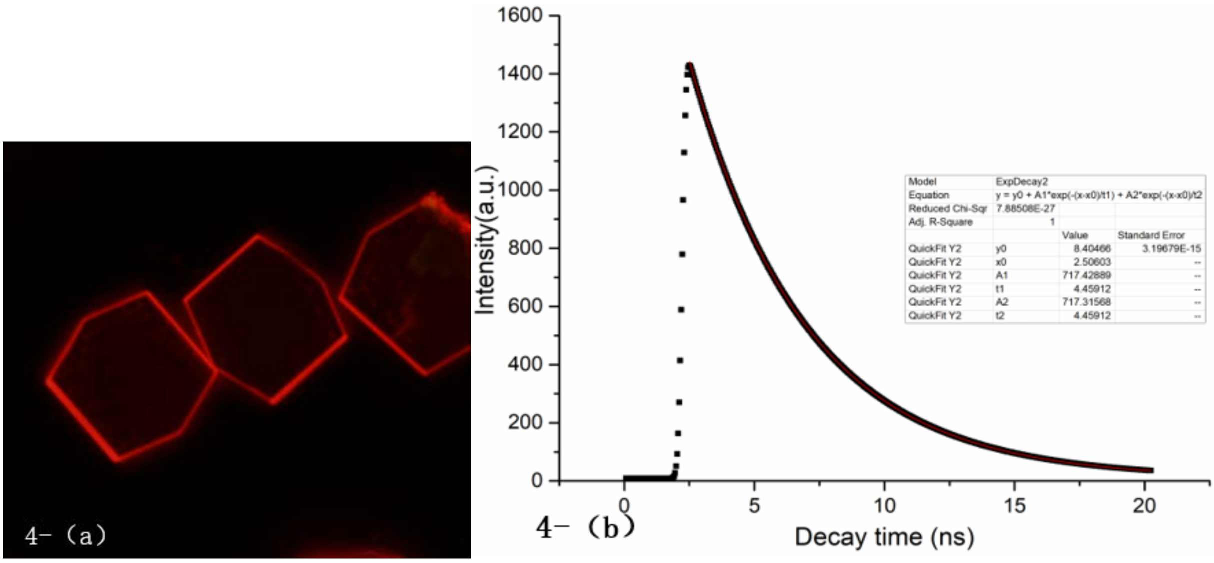
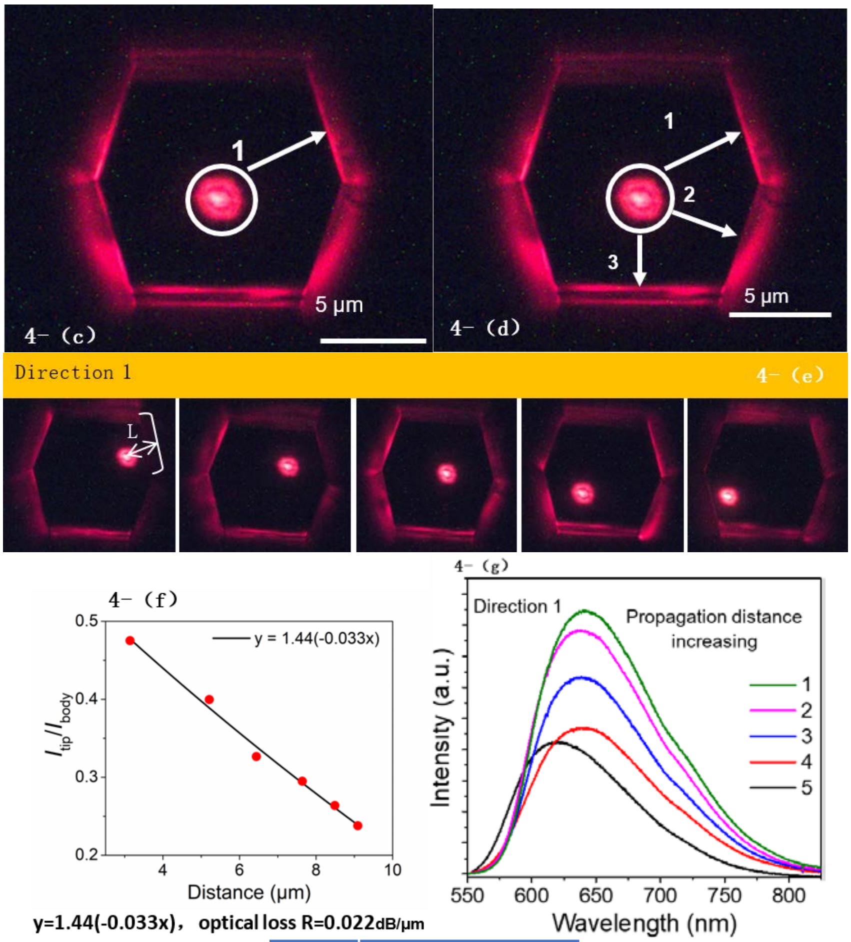


Fig 4. (a) Fluorescence micrograph of BeBq2-TCNB; (b) Fluorescence lifetime curve of BeBq2-TCNB.

5.2 Optical waveguide properties

In order to further explore the propagation behavior of light, a BeBq2-TCNB nanocrystal with the most regular shape is selected. As shown in Fig. 4 - (c), a light path direction 1 direction is selected, and a laser beam with wavelength of 400nm moves to focus continuously in this direction (Fig. 4-5e)). With the increase of the distance L between the laser point and the opposite side of the crystal, the ratio of the PL intensity to the peak value decreases exponentially. Fig. 4 - (g) shows the relative curves of PL intensity at the end and excitation point to D ratio at the peak. The curve conforms to the equation y = 1.44 (- 0.033x) (Fig. 4 - (f)). The optical loss coefficientαis calculated to be 0.022 dB / μm, which is a small value in the same kind of organic optical waveguide materials, indicating that this kind of micron single crystal rod has good optical waveguide performance.



Direction	Optical loss coefficient (dB/μm)
1	0.033
2	0.022
3	0.029

Fig 5. (c)(d)(e) Fluorescence microscope pictures; (f)(g) Optical waveguide results

6. Conclusion and Prospect

In this research, the most difficult part is to control the morphology and obtain the desired structure selectively. To solve this problem, we can stably prepare hexagonal BeBq2 -TCNB nanocrystals by changing the experimental conditions. After analyzing the single crystal, characterizing the morphology and testing the optical properties in detail, it is found that the two kinds of eutectic emit yellow green light under UV excitation, and have low optical waveguide loss. Based on the description of the optical logic gate formed by the asymmetric waveguide of BeBq2, the eutectic of BeBq2-TCNB may have similar application in the field of optoelectronic circuits.

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