

Doctoral thesis/dissertation Digest Form

Thesis/dissertation Title

Multi-Stimuli Responsive β -Diketonate Derivatives, from Molecules to Self-Assemblies

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Approved Digest

Multi-responsive fluorescent molecules can adjust their fluorescence properties in response to external stimuli such as changes in temperature, pressure, and chemical environment. This adaptability could efficiently direct the development of sensors, displays, and imaging technologies, providing various applications in the future. Mechanofluorochromism (MFC) is a fascinating property in multi-responsive systems, where materials undergo fluorescent changes under mechanical stress like compression, shear force, and friction. Difluoroboron β -diketonate (DFB) compounds draw attention for unique photophysical traits, featuring not only MFC but also polymorphism and intense fluorescence in both solid and solution. This research aims to explore innovative methodologies for designing and synthesizing multi-responsive DFB materials and their precursor compounds. Emphasis is placed on investigating these materials' photophysical characteristics and responsiveness to diverse stimuli. Additionally, the underlying mechanisms of MFC are studied. To achieve these objectives, a comprehensive approach is employed, integrating fluorescence spectroscopy, various microscopic techniques, anisotropic experiments, theoretical calculations, and other relevant methodologies.

In the first topic of this thesis, a novel multi-responsive and multicolor DFB is discussed. The synthesis of amino-methoxy-DFB (DFB-NH₂), involving the introduction of a primary amine into the phenyl ring through Curtius rearrangement, was undertaken. Thanks to the NH₂ group, the molecule exhibits intramolecular charge transfer (ICT) in solution and in the crystalline phase. A quinoid-like structure and a typical head-to-tail H-type dimer structure

are observed in the crystal state. The single crystal with dark-red weak emission demonstrates a blue-shifted emission after mechanical smearing, which constitutes an original MFC behavior. The drop-casted sample on a paper sheet also demonstrates significant MFC. Additionally, characteristic acid-/base-responsivity is observed in the solution phase, polymer-dispersed films, and powder samples.

In the second topic of this thesis, the multi-responsive system is delved into a C_3 -symmetrical molecule. A novel C_3 -symmetrical β -diketone compound, **BTA-D3**, and its monomeric counterpart, **D**, are successfully synthesized. Notably, Aggregation-induced emission (AIE) is observed in **BTA-D3** contrary to **D**. Additionally, **BTA-D3** displays polymorph-dependent fluorescence characteristics, forming 1D fibers with yellow emission in the THF/water system, while forming 2D sheets with blue emission. In addition, intramolecular energy transfer properties are demonstrated by **BTA-D3**, distinguishing it from **D**.

In the third topic of this thesis, energy migration in gel, assembly formations, mechanical effects, and boron complexation of **BTA-D3** were explored. I and my coworkers successfully obtained a gel demonstrating diverse emission characteristics, indicative of distinct aggregation modes that vary depending on the solvent systems employed, suggesting the gel adopts different structural conformations in response to its environment. Anisotropy analysis in gel offers insights into energy migration within and between molecules, highlighting crucial structures for efficient self-assembly. The unique structure contributes to diverse stimuli-responsive properties, such as chiral induction by chiral solvents and MFC. Notably, boronation of **BTA-D3** results in a highly luminescent molecule with a distinctive blue-shift in MFC.

These findings contribute to an enriched comprehension of C_3 -symmetrical molecules and offer insights into strategies for controlling molecular alignment to achieve diverse fluorescence coloration in molecular materials. The whole thesis seeks to provide practical guidelines and insights for developing new luminescent materials, contributing to advancements in the

field with potential applications.