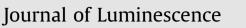
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The optical behavior of amorphous microribbons for hydroxy-naphthol based Schiff bases



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ABSTRACT

The optical behaviors of three hydroxy-naphthol based Schiff bases, L1, L2 and L3, in aggregated states in 1,4-dioxane (Diox) – H₂O mixture, were investigated. The intermolecular hydrogen bond between luminogen and water resulted in the twisting of benzothiazole group, which is favorable for the assembly of organic molecules into J-aggregates. And also a bathochromic shift in absorption and enhancement of the fluorescence emission (aggregation-induced enhanced emission, AIEE) can be observed. L1 and L2 in Diox-H₂O mixture with water volume fractions (f_w) 95% assembled into microribbons with 40–50 nm thickness, twisted together to make amorphous supramolecular organogels. Whereas L3 assembled into needle-like nanorods with the thickness up to ~200 nm, consistence with its lower emission intensity compared to L1, L2 aggregates. Moreover, a drastic blue-shift and an enhancement of emission efficiency of L1-L3 were also observed in solid states with the morphology change from the crystalline to the amorphous state by grinding. It was found that L1 aggregates showed fluorescence switch-off sensing towards Cu²⁺, with higher selectivity and sensitivity compared to L1 in Diox solution.

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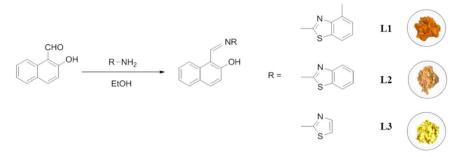
1. Introduction

The exploitation of efficient fluorescent materials has attracted substantial interest due to their potential application in photoelectronic devices and sensors. But the conventional organic luminophoric molecules undergo intermolecular π - π interactions and easily suffer from aggregation caused quenching (ACQ), which leads to poor solid state emission and limits their applications [1]. Fortunately, these years, Tang built a series of luminogens, such as tetraphenylethylene (TPE) derivatives, emit efficiently when aggregated in the solid state, known as aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) [2]. AIE/AIEE effect helps propeller-shaped luminogens to overcome the notorious ACQ effect and become highly fluorescent in the solid state, which is an essential requirement for mechanochromism. Various mechanisms, such as changes in intramolecular planarity or restrictions [3], the specific head-to-tail molecular arrangement, as well as intermolecular interactions of π - π stacking [4], and ACQ to AIE transformation, have been used to explain AIE phenomena [5]. Molecular structures and conformations of dye molecules, as well as their morphological packing

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Much effort has been devoted to the construction of AIE/AIEE systems, and various methods were developed to prepare organic nanoparticles, such as reprecipitation [7], template method [8], selforganization [9]. Different size and shaped organic particles, including one dimensional nanowire [3], two dimensional nanoplates [10] and three dimensional cubes [11] were obtained for improving optical or photovoltaic efficiency of organic materials. In a search of AIE/AIEE luminogens structures, silole TPE and some other conformational planarity or D- π -A systems are the archetypes [12]. Schiff base derivatives possess AIE/AIEE characters had been found in literature [13]. Triphenylamine or anthryl was found the core contributed group in Schiff Bases AIE/AIEE behavior. In the following, we first found three Schiff bases derivatives, consisting of the same hydroxy-naphthol group and different thiazole substituents (L1, L2 and L3, Scheme 1), exhibited AIEE effect with maximum fluorescence intensity in 1,4-dioxane (Diox) – H₂O mixture with 95% (for L1 and L2) or 99% (for L3) water content. The persistence of AIEE in these luminogens was attributed to the presence of intermolecular hydrogen bonding between luminogen and water, resulted in the destruction of the planarity of molecular and the



Scheme 1. Structure and synthesis of three luminogens.

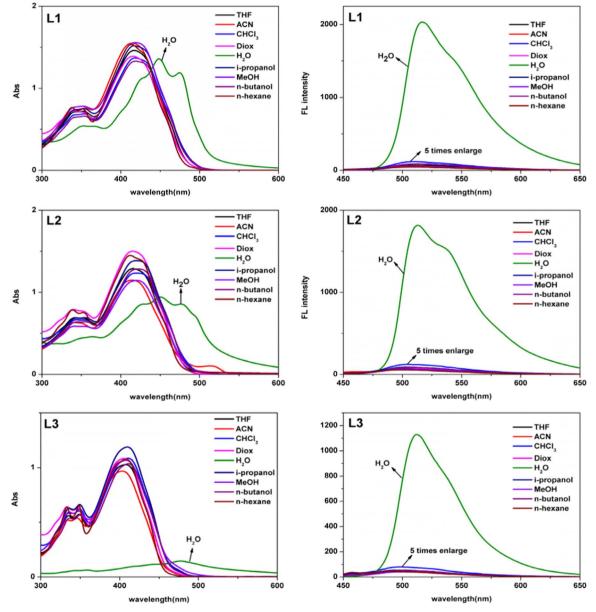


Fig. 1. Absorption and fluorescent spectra of L1, L2, L3 (50 μ M) in different solvents.

rotation of thiazole substituent. The molecular packing and morphologies of aggregated nanoparticles were evaluated, as a comparation of their crystal states, with the help of XRD and SEM measurements. Furthermore, it was found that L1 AIEE system could be constructed as a chemoprobe towards Cu^{2+} fluorescence recognition, and aggregated L1 had exhibited higher selectivity and sensitivity for Cu^{2+} compared to L1 in Diox solution.

2. Experimental sections

2.1. Material and apparatus

All starting materials used to synthesize luminogens were purchased from Aldrich Chemical and used as received. The chemical structures of these compounds were confirmed by ¹H-NMR, Download English Version:

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