

COMPARISONS OF CYANOSTILBENE DERIVATIVES BETWEEN 2-DIMENSIONAL AGGREGATION USING LB TECHNIQUE AND 3-DIMENSIONAL AGGREGATION

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1. Abstract

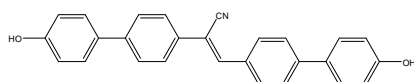
After the first observation of fluorescence property of organic Π -conjugated compounds, various research works were conducted to achieve high performance in photophysical and electronic application of such compounds. Most conjugated molecules with a rigid structure show high fluorescence in dilute solution but become weakly luminescent in the solid state. It was recognized that this was a general phenomenon for many aromatic compounds. This concentration quenching effect was found to be caused by the formation of sandwich-shaped excimers and exciplexes aided by the collisional interactions between the aromatic molecules in the excited and ground states [1]. Recently, novel properties originated from the nano-scale assembly of organic cyano-group containing fluorophores which are clearly discriminated from their macro-scale assembly have attracted a lot of attention. Consequently increasing attention has been paid to enhancing the solid state efficiency of luminescent materials.

We have synthesized cyanostilbene derivatives with various chemical functional groups. And we evaluated a spectroscopic characterization of optical property to consider the chemical functional group effects on the aggregation of those stilbene derivatives. We studied properties of these cyanostilbene aggregates that can do self-assembling at the air-water interface to form two- and three dimensional nanostructures having different optical properties

2. Introduction

Most conjugated molecules with a planar and rigid structure show high fluorescence in their dilute solutions but become weakly luminescent in the solid state. This is ascribed to the aggregate formation such as excimers [2]. However, the chromophoric molecules must have high luminescence property in the solid state, because various devices are only fabricated by film or crystalline formation. Many groups are making researches in enhancing the solid state efficiency of luminescent materials. Recently, unusual strong fluorescence in solid state was reported in a few organic compounds. That can be a clue to solve the concentration quenching dilemma in nanostructured molecular aggregation state. Among them, certain cyanostilbene derivatives have aggregation-induced enhanced emission (AIEE) properties [3, 4]. Aggregation is in some sense inherent in film formation and is formed due to the ordered arrangements of molecules. Since Langmuir-Blodgett techniques are appropriate for the control of the molecular arrangement, they are widely used to study such aggregations. The Langmuir-Blodgett (LB) method has provided a technique for the fabrication of organic ultra thin films at the molecular scale. The method enables the control of the molecular orientation in the films. LB films are built up from a condensed monolayer formed on air-water interface by multiple depositions onto solid supports, and this technique provides uniform films with controlled thickness and well-defined molecular orientation [5].

We have synthesized cyanostilbene derivatives with chemical functional groups. (CN-HBE, shown in Scheme 1) And we studied properties of these cyanostilbene aggregates that can do self-assembling at the air-water interface to form two- and three dimensional nanostructures having different optical properties.



Scheme 1. Structure of CN-HBE

3.1 UV absorption spectra of molecules

As reported in the literature, CN-TFMBE shows the remarkable fluorescence increase in the gel state. This is attributed to the cooperative effect of the strong Π - Π stacking interactions of rigid rodlike aromatic segments and supplementary intermolecular interactions induced by four CF_3 units [6]. We have designed and synthesized CN-HBE that has attached $-\text{OH}$ groups with a cyanostilbene structure like CN-TFMBE which show the aggregation induced enhanced emission phenomenon (AIEE). We expected that this molecule shows AIEE property and possibility of monolayer using LB technique.

Fig.1 shows UV absorption spectra for solution state and LB film of CN-HBE. For CN-HBE solution, the maximum peak in THF appeared at 355nm. As water is added into the CN-HBE solution to 60% volume fractions, the maximum peaks are red-shifted (361nm). This bathochromic effect indicates that effective conjugation length of CN-HBE is extended by aggregation. However From 80% volume fractions of water addition, the maximum peak shows blue-shift from 361nm to 351nm. This hypsochromic effect is thought that the molecules in nanoparticles may be more twisted by intermolecular hydrogen bonding.

For CN-HBE LB films, UV absorption of film appeared at only monolayer film and the maximum peak located around 355nm. These results suggest

that the stable monolayer can make using LB method and multilayer film form H-type aggregation.

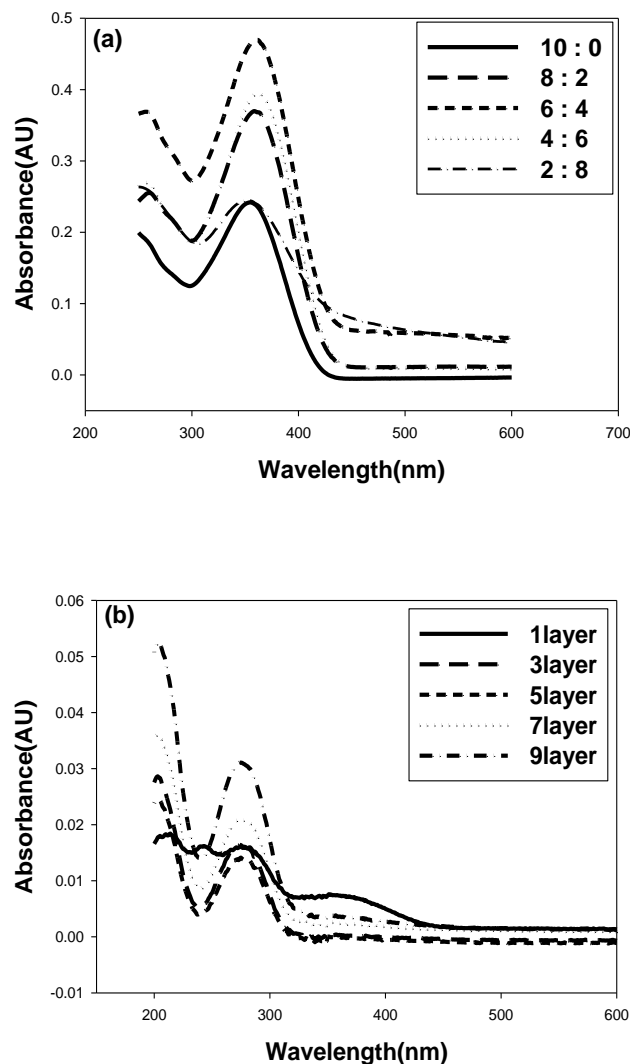


Fig. 1. UV absorption spectra for (a) solution state and (b) LB film of CN-HBE.

3.2 Emission property of molecules

Fig. 2 shows PL spectra changes for solution state and LB film of CN-HBE. As water is added into CN-HBE solution, the maximum peaks are red-shifted and the PL intensities are very little change. It is supposed that molecular packing helps with extended conjugation length and the origin of nanoparticles packing is not Π - Π stacking but packing structure with hydrogen bonding such as interaction between water and OH-groups of CN-HBE, intra- and intermolecular interaction of CN-HBE molecules. In particular, the hydrogen bonding prevents compact packing of molecules. As a result, CN-HBE aggregates have intramolecular vibrational and rotational motions. These intramolecular vibrational and rotational motions, which behave strongly in these twisted conjugated molecules, lead to the fast nonradiative relaxation and reduced fluorescence quantum yield in solutions [7]. Therefore, PL intensity of aggregates is similar to isolated molecules.

For CN-HBE LB films, PL intensity of film appeared at only monolayer and multilayer films show fluorescence quenching. These results are in concordance with UV absorption spectra of LB film.

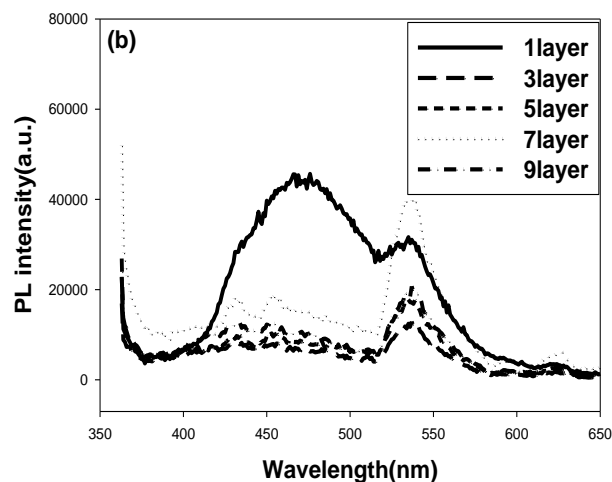
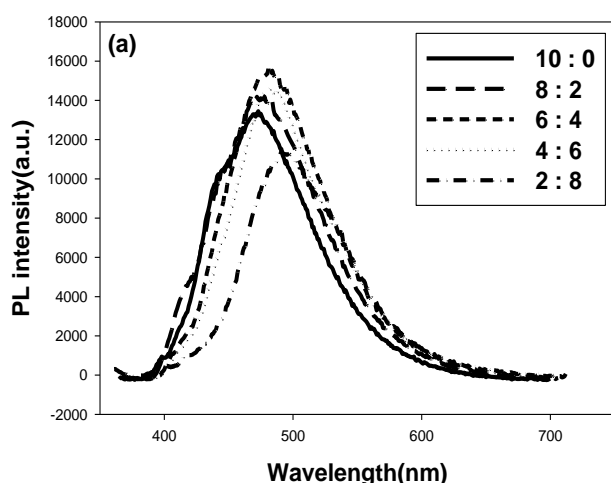


Fig. 2. PL spectra changes for (a) solution state and (b) LB film of CN-HBE.

4. Summary

We synthesized cyanostilbene derivatives in order to make LB film with AIEE property. And we studied properties of these cyanostilbene aggregates that can do self-assembling at the air-water interface to form two- and three dimensional nanostructures having different optical properties.

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