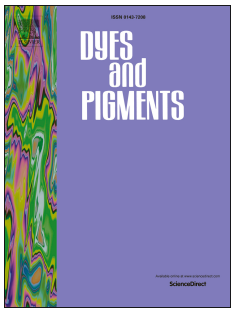
Accepted Manuscript



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PII: S0143-7208(18)31153-7

DOI: 10.1016/j.dyepig.2018.08.021

Reference: DYPI 6934

To appear in: *Dyes and Pigments*

Received Date: 22 May 2018

Revised Date: 31 July 2018

Accepted Date: 13 August 2018

Please cite this article as: Nguyen ML, Kim S, Kim H-J, Cho B-K, Morphology-dependent luminescent behavior of hexacatenar Luminogens based on naphthalenyl and 1,2,3-triazolyl groups, *Dyes and Pigments* (2018), doi: 10.1016/j.dyepig.2018.08.021.

Morphology-Dependent Luminescent Behavior of Hexacatenar Luminogens Based on Naphthalenyl and 1,2,3-Triazolyl groups

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Abstract:
The columnar assemblies and thermochromic properties of a hexacatenar molecule consisting of naphthalenyl and 1,2,3-triazolyl units were evaluated. The molecule formed 3D monoclinic crystalline (Cry_{mono}) and hexagonal columnar LC (Col_{hex}) phases as a function of temperature. Photoluminescence (PL) study revealed a noticeable change in the emission color at the Cry_{mono}-to-Col_{hex} transition. The aromatic cores in the Cry_{mono} phases were stacked in an edge-to-face geometry and thereby exhibited a monomeric emission in the ultra-violet (UV) region. In contrast, a bluish excimer emission was observed for the Col_{hex} phase with face-to-face stacking. Consequently, the fluorescent molecule exhibited different assembly features as a function of temperature, giving rise to distinct thermochromic phenomenon.

Keywords: thermochromism, crystalline phase, liquid crystalline phase, morphology, naphthalene, excimer emission.

1. Introduction

The self-organization of π-conjugated aromatic building blocks is an interesting research topic because the photophysical properties of such building blocks can be tuned by their morphological features, such as the stacking mode and order [1–8]. Understanding the correlation between the morphology and photophysical properties may facilitate practical applications of the molecules in temperature sensors, memory materials, etc., because their photoluminescence (PL) behavior is tunable in response to temperature [4,7], solvent [9–11], and mechanical pressure [7,12,13].

Polycatenar molecules composed of an aromatic rod and multiple peripheral chains have been known to organize into nanostructured domains due to the anisotropic aromatic stacking and space-filling of multiple chains [14,15]. In particular, hexacatenar molecules bearing six bulky alkyl chains commonly produce columnar liquid crystalline (LC) structures, where the six peripheral chains are sufficient to fill the matrix space, and the aromatic moieties occupy the core space [16–22]. Recent studies of hexacatenar systems have shifted to the use of heterocyclic rings such as oxadiazole [8,23–25], thiadiazole [17,26–28], and thiazole [29] as molecular components. In these previous studies, the primary motivation for adopting such heterocycles was to exploit their photoluminescent (PL) properties. It was found that most of these systems formed hexagonal columnar LC phases, and their bulk and solution states exhibited PL properties. Nevertheless, a drastic variation in the PL in response to stimuli such as temperature has rarely been reported to date. Therefore, the design of hexacatenar-type molecules with switchable PL function is still challenging.

In this context, we designed a hexacatenar molecule consisting of a luminescent naphthalenyl core and 1,2,3-triazolyl linkages (Scheme 1). To obtain switchable PL behavior, the naphthalenyl group was employed as the aromatic core because the PL