



A study on the fluorescence property of the perylene derivatives with methoxy groups



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ABSTRACT

Perylene-based dyes with methoxy groups at various positions were synthesized to understand the effect of the methoxy groups on the fluorescence quenching. Additionally, perylene-based dyes with ethyl groups in place of the methoxy groups were also synthesized to serve as control. Absorption and fluorescence properties of the dyes were measured, and then, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) simulations were conducted. The methoxy groups of terminal-substituents had a lesser effect on fluorescence quenching than the methoxy groups of bay-substituents. Moreover, only the methoxy groups at the para-position of the bay-substituents strongly affected on fluorescence quenching. These results showed that the fluorescence of the dyes are influenced by the electron donating effect of the methoxy groups when the methoxy groups are involved in the main conjugation systems of the dyes.

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1. Introduction

Perylene-based dyes generally show superior thermal stability and optical properties owing to the planarity of their molecular structures [1–5]. Because of these advantages, perylene-based dyes are widely used as optical coloring materials for displays among many other useful applications [5–11]. Moreover, perylene dyes are easily functionalized through the introduction of substituents at their terminal- and bay-positions, which enables the modification of characteristics such as their spectral properties and solubilities [12–14]. Perylene diimide derivatives having two bulky substituents at their terminal-positions are commonly used, and these molecules are often modified for various purposes by the introduction of 1–4 substituents at their bay-positions.

Previously, we have reported many novel perylene-based dyes for use as the red colorants in LCD color filters [7,8,12–22]. Since the fluorescence of these dyes can negatively affect the optical performance of the color filters fabricated with them [21], we have also suggested solutions for this problem, in which the decrease of contrast ratios of color filters was inhibited by using perylene-based dyes with high solubility and low fluorescence [22]. Based

on our previous reports, the effect of methoxy groups on the fluorescence properties of perylene-based dyes and the relationships between the fluorescence of the dyes and the position of the introduced methoxy groups are studied in this paper, both experimentally and theoretically.

In this study, perylene-based dyes which contained methoxy groups in the terminal-, bay-, or both positions were synthesized. The methoxy groups were sequentially placed at the *ortho*-, *meta*-, or *para*-position of each substituent. Additionally, the dyes with ethyl substituents instead of methoxy groups were designed and synthesized, these dyes have similar geometrical molecular structures and conjugation systems with the dyes containing methoxy groups [22]. The absorption and fluorescence properties of the synthesized dyes were measured and compared. The geometrical structures of the dyes were analyzed by density functional theory (DFT) calculations, and excitations from the highest occupied molecular orbitals (HOMOs) to the lowest occupied molecular orbitals (LUMOs) of the dyes were simulated with time-dependent density functional theory (TD-DFT) [23,24]. Using these methods, the influence of the position of the methoxy groups on the electrochemical and the fluorescence properties of the dyes were studied.

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2. Experimental

2.1. Materials and instrumentation

Perylene-3,4,9,10-tetracarboxylic dianhydride, iodine, sulfuric acid, bromine, and acetic acid were purchased from Sigma-Aldrich, 2,6-diisopropylaniline, 2-methoxy-6-methylaniline, 4-methoxy-2-methylaniline, 4-methoxyphenol, 4-ethylphenol, 3-methoxyphenol, 3-ethylphenol, 2-methoxyphenol, and 2-ethylphenol were purchased from TCI. Potassium carbonate anhydrous, methylene chloride, and other chemical solvents were purchased from Samchun Pure Chemical. All chemicals were used without any additional purification.

Absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. Fluorescence spectra and quantum yield data were measured on a Perkin Elmer LS 55 and a PTI Quanta Master 40 fluorescence spectrometer, respectively. Elemental Analysis (EA) was completed on a CE Instruments EA1112 analyzer. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 500 spectrometer running at 500 MHz using chloroform- d as a solvent with TMS as an internal standard. Matrix Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE STR Biospectrometry Workstation using α -cyano-4-hydroxycinnamic acid (CHCA) as a matrix.

2.2. Syntheses of the dyes

All synthetic procedures were carried out by following our previous reports [20–22]. The dyes **PI-4EP**, **PI-4ME**, **P2M-4EP**, and **P2M-4ME** were already reported in our previous report [22]. The specified name of the dyes **P2M-4EP** and **P2M-4ME** were PM-4EP and PM-4ME in the report, respectively. The syntheses of these

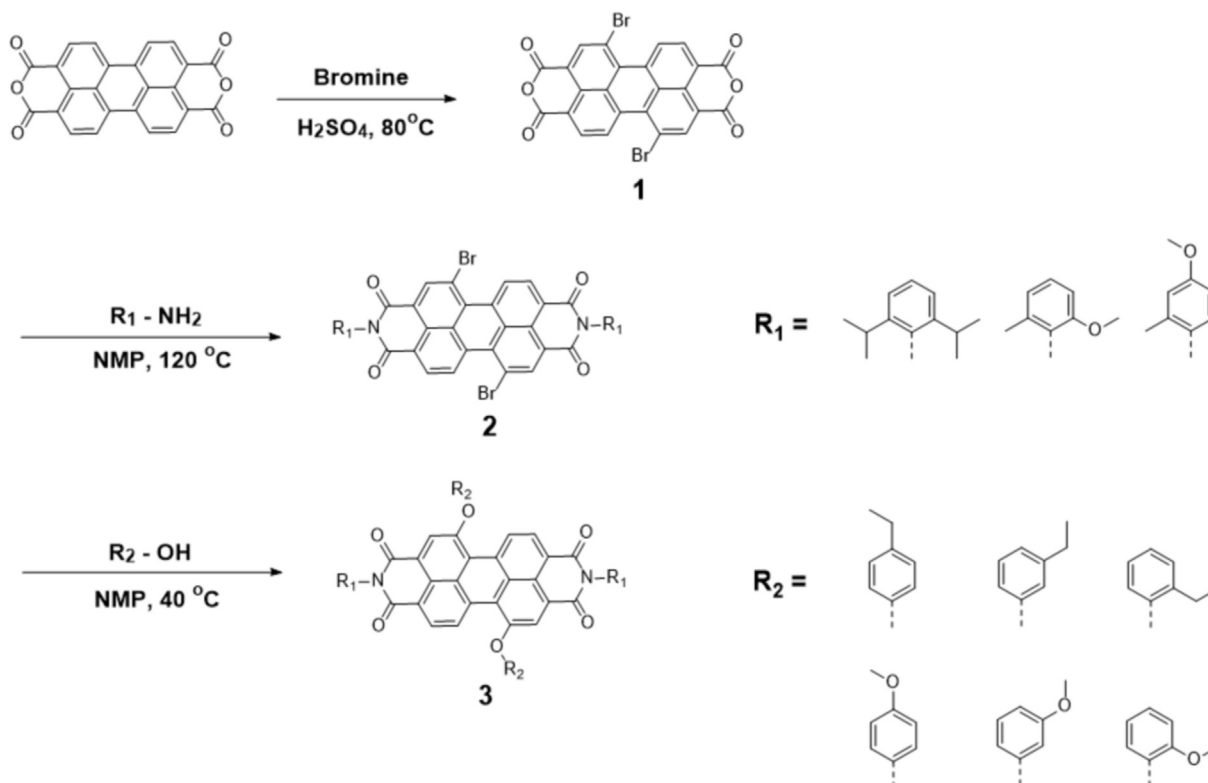
dyes are repeated in this paper.

2.2.1. 1,7-Dibromoperylene-3,4,9,10-tetracarboxydiimide: bromination

Perylene-3,4,9,10-tetracarboxylic dianhydride (32.00 g, 81.40 mmol), iodine (0.78 g, 3.04 mmol) and sulfuric acid (98%, 450 mL) were mixed and stirred for 2 h at room temperature. The temperature of the mixture was raised to 80 °C and bromine (8.33 mL, 162.80 mmol) was added dropwise over 1 h. The resulting mixture allowed to react for 16 h as sealed, upon which time, it was cooled to room temperature and the remaining bromine gas was displaced by nitrogen gas. The mixture was slowly poured into 3 L of ice water and the crude precipitate formed was collected by suction filtration followed by washing several times with distilled water. The crude product was dried at 80 °C under reduced pressure and used in the next step without further purification. The crude product containing both mono- and di-bromoperylene derivatives was separated by column chromatography in next step, after introducing bulky substituents in the terminal-position to increase their solubilities.

2.2.2. N,N' -bis(R_1)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide: terminal-position substitution

Crude 1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (8.00 g, 14.55 mmol), $R_1\text{-NH}_2$ (45.00 mmol), acetic acid (4.60 mL) and N -methyl-2-pyrrolidone (NMP, 100 mL) were mixed and heated to 120 °C under nitrogen atmosphere for 96 h. Water was added to the mixture and the resulting precipitate was collected by suction filtration. The crude product was washed with water and dried under reduced pressure. The crude product was purified by column chromatography in silica gel using CH_2Cl_2 as an eluent. Three bands were collected. The first band contained a small amount of tribrominated diimide, the second band contained the



Scheme 1. Synthetic routes of the designed dyes.

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