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Photophysical properties and photostability of novel unsymmetric polycyclicphenazine-type D-π-A fluorescent dyes and the dye-doped films

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ABSTRACT

Structural isomers of unsymmetric polycyclicphenazine-type D-π-A fluorescent dyes have been newly synthesized and characterized in both solution and polymer films. The dyes exhibited two strong absorption bands at around 328–401 nm and 516–532 nm, and an intense fluorescence band at around 595–629 nm ($\Phi = 0.32–0.84$) in 1,4-dioxane. The dye-doped polymer films showed good ability of wavelength conversion; the films can efficiently convert ultraviolet and green-yellow lights into red light ($\Phi = 0.43–0.86$). Moreover, the photostability of the dyes-doped PS, PMMA, and PLA films has been investigated.

1. Introduction

Photosynthesis and photomorphogenesis in plant growth are significantly controlled by light quality. In general, many kinds of wavelength conversion films such as UV, visible and near-infrared light absorbing films have been used for various regulations of plant growth [1–5]. It is known that red and blue light efficiently promotes the plant growth in many kinds of plants [6–8]. However, there are few reports on fluorescent dye-doped films evaluated as wavelength conversion films [9,10]. For the polymer films, it is required to enhance red light without decrease of blue light of light source such as the sun light. To develop the fluorescent dyes which satisfy the above requisition, we have performed the semi-empirical molecular orbital calculations (AM1 and INDO/S) and estimated approximately the absorption wavelengths of the dye molecules. In this study, we have designed and synthesized novel unsymmetric polycyclic phenazine-type D-π-A fluorescent dyes **3a**, **3b**, and **6a**, **6b** which are structural isomers. The photophysical properties, photostability and the wavelength conversion ability of the dyes in both solution and polymer films have also been investigated.

2. Result and discussion

2.1. Semi-empirical MO calculations (AM1, INDO/S)

We have carried out semi-empirical molecular orbital (MO) calculations for the designed fluorophores **3** and **6** to elucidate the difference of photophysical properties. The structures of these compounds were optimized by MOPAC/AM1 [12] and then the electron transition spectra were calculated by the INDO/S [13–15]. The calculated first and second absorption wavelengths and the transition character of the bands are collected in Table 1. The change of electron density accompanying the first electronic excitation (HOMO → LUMO) is shown in Fig. 1, which reveals the migration of intramolecular charge transfer from the dibutylamino groups as a donor to the pyrazine ring with a butoxy carbonyl group as an acceptor. The calculated absorption wavelengths of **3a** (430 nm, $f = 0.63$) and **3b** (432 nm, $f = 0.47$), which have benzofuran skeleton, were longer than those of **6a** (420 nm, $f = 0.87$) and **6b** (422 nm, $f = 0.71$), which have benzopyran skeleton. Moreover, the oscillator strength of the fluorophores, which have benzopyrane skeleton, was larger than those of the fluorophores, which have benzofuran skeleton. The second absorption maxima were predicted to be appeared at around 330 nm for **3a** and **3b** and at around 355 nm for **6a** and **6b**. It is known that the absorption wavelengths of INDO/S calculations are blue-shifted by ca. 50–120 nm than the experimental values [16,17]. Therefore, we expected that the fluorophores **3** and **6** could convert green-yellow lights into red light.

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Table 1
Calculated absorption spectra for the fluorescent dyes **3** and **6**.

Dye	μ [D][a]	Absorption (calc.)		CI component[c]	$\Delta\mu$ [D][d]
		λ_{max} (nm)	f[b]		
3a	5.75	430	0.63	HOMO → LUMO (83%)	10.21
		329	0.76	HOMO-1 → LUMO (34%)	
				HOMO → LUMO + 1 (22%)	
				HOMO → LUMO + 5 (10%)	
				HOMO → LUMO + 2 (8%)	
				HOMO → LUMO + 4 (4%)	
3b	6.64	432	0.47	HOMO → LUMO (81%)	9.92
		331	1.01	HOMO-1 → LUMO (42%)	
				HOMO → LUMO + 1 (20%)	
				HOMO → LUMO + 5 (7%)	
				HOMO → LUMO + 2 (6%)	
				HOMO → LUMO + 4 (5%)	
6a	6.16	420	0.87	HOMO → LUMO (80%)	7.86
		357	0.17	HOMO → LUMO + 1 (38%)	
				HOMO-2 → LUMO (27%)	
				HOMO-1 → LUMO (11%)	
				HOMO → LUMO (5%)	
6b	6.77	422	0.71	HOMO → LUMO (80%)	7.81
		353	0.23	HOMO → LUMO + 1 (49%)	
				HOMO-2 → LUMO (17%)	
				HOMO-1 → LUMO (8%)	
				HOMO → LUMO + 2 (4%)	
				HOMO-3 → LUMO (3%)	

[a] The values of the dipole moment in the ground state.

[b] Oscillator strength.

[c] The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component.

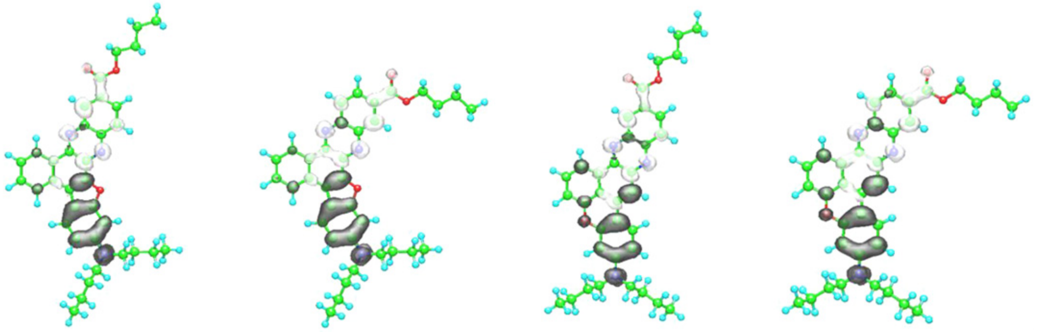
[d] The difference in dipole moment between the excited and the ground states.

2.2. *Synthesis of the unsymmetric polycyclic phenazine-type D-π-A fluorescent dyes*

The synthesis of the unsymmetric isomeric phenazine-type D-π-A fluorescent dyes **3a**, **3b**, **6a** and **6b** is shown in Schemes 1 and 2. We used polycyclic *o*-quinone derivatives **1** and **4** as starting materials [18]. The reaction of the polycyclic *o*-quinones **1** and **4** with 3,4-diaminobenzoic acid produced the intermediates **2a**, **2b**, **4a** and **4b**, which are structural isomers having polycyclicphenazine skeleton, respectively. The esterification of the intermediates produced the fluorescent dyes, **3a**, **3b**, **6a** and **6b** in 44%, 46%, 16% and 73%, respectively. These compounds were completely characterized by ^{1}H NMR, IR, and elemental analysis. A comparison of the observed and calculated UV–VIS spectra for the compounds **3a**, **3b**, **6a** and **6b** and the X-ray crystal analysis of **3a** were performed for identification of their structures, which will be described later on.

2.3. *Spectroscopic properties of the polycyclic phenazine-type D-π-A fluorescent dyes in solution*

The absorption and fluorescence spectra of **3a**, **3b**, **6a** and **6b** were measured in 1,4-dioxane, THF, and DMSO. The absorption and fluorescence spectra in 1,4-dioxane are shown in Figs. 2 and 3 as an example and all the spectroscopic data are summarized in Table 2. The shapes of the absorption spectra in solution were comparatively good agreement with the MO calculation data shown in Table 1. The substituent-isomers **3a** and **3b** which have a benzofuran skeleton exhibited two absorption maxima at around 517 nm and 350–390 nm and the fluorescence band appeared at around 625 nm in 1,4-dioxane. The wavelengths of the absorption and fluorescence maxima between the substituent-isomers were almost same, however, the fluorescence quantum yield of **3a** (Φ = 0.69) was higher than that of **3b** (Φ = 0.36). Similar relation was also



3a **3b** **6a** **6b**

Fig. 1. Calculated changes in electron density accompanying the first electronic excitation of **3a**, **3b**, **6a** and **6b**. The black and white lobes signify degreases and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change.