

## Red to Near-Infrared Fluorescence in the Solid-State of Alkoxy-Substituted Bisazomethine Dyes Possessing a Dibutylamino Terminal Group

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### Abstract

Eleven novel bisazomethine dyes possessing a dibutylamino terminal group with diverse alkoxy substituents on the phenyl ring were prepared by a reaction of diaminomaleonitrile and aminobenzaldehydes. We observed that ten derivatives exhibited red-shifted fluorescence in a crystalline state with an improved quantum efficiency from that in a solution. They showed red to near-infrared fluorescence with a quantum efficiency in the range of 12 to 28%. X-ray crystal structure analysis was carried out for interpreting optical properties in a crystalline state. The solid-state fluorescence property of the derivatives with a long alkoxy side chain could be characterized by their structural feature, whereas no close correlation was found between the solid-state fluorescence property and structure feature in crystal structure in the derivatives with a short to middle alkoxy side chain.

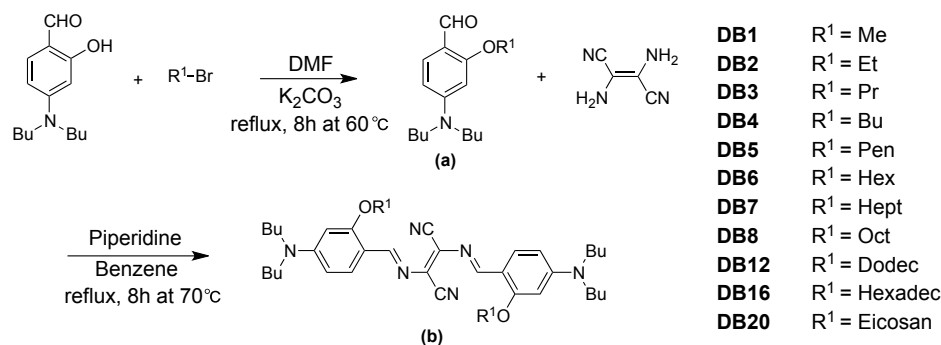
**Key-words:** Bisazomethine dye, Substituent effects, Crystal structure, Solid-state optical property, Near-infrared fluorescence

### 1. Introduction

Organic fluorescent materials have attracted extensive attention due to their applications for emitter such as solid-state dye laser<sup>1,2)</sup> and organic light-emitting diode (OLEDs) devices<sup>3,4)</sup>. Most of organic fluorophores become strongly emissive in dilute solution. However, they often exhibit no or weak emission in the solid state<sup>5-7)</sup>. In particular, near-infrared (NIR) fluorophores usually suffer from low quantum efficiencies in the solid state, because an extended  $\pi$ -conjugated system to reduce the energy gap of HOMO-LUMO promotes intermolecular contacts such as  $\pi$ - $\pi$  or dipole-dipole interactions<sup>8-11)</sup>.

The different molecular conformation and arrangement of organic molecules in the solid state are considered to play a critical role in the solid-state optical properties containing fluorescence quenching<sup>12-18)</sup>. Crystallization of the organic

dyes increases intermolecular interactions in the tightly packed crystalline state and the formation of delocalized exciton or excimer leading to weakened emission<sup>19,20)</sup>. The high fluorescence quantum yield of organic dye solids is possibly caused by the following factors. Firstly, the isolated molecules in the crystal prevent intermolecular interactions between neighboring molecules, whose increase could reduce the emission of organic dyes in the solid state<sup>9,16)</sup>. Secondly, molecules adopt a nonplanar conformation, which suppresses strong intermolecular interactions, such as  $\pi$ - $\pi$  stacking<sup>21-23)</sup>. Lastly, molecules form J-aggregates or a slipped  $\pi$ -stacked arrangement with a small slip angle, avoiding the trapping of the excitons of H-aggregates<sup>18,24-26)</sup>. However, such reported examples with high fluorescence intensity are very rare, especially for NIR fluorophores. To improve this point, various substituents are introduced into the fluorophores<sup>15,27-31)</sup>.



**Fig. 1** The synthetic route and chemical structures of novel bisazomethine dyes.