

Synthesis and Near-Infrared Photoluminescence Properties of Novel D- π -A-Type Pyridinium Betaine Dyes Based on Thiophene-Derived π -Skeleton

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Near-infrared (NIR) light, which shows high transmittance to the living body and is invisible to the naked eye, has attracted much attention from the viewpoint of application in biomedical science and security technology. However, there are few examples of NIR luminescent dyes with high quantum yields (Φ_{PL}) due to facilitation of nonradiative decay according to the energy gap law. To develop novel NIR fluorescent dyes, we here focus on donor- π -acceptor (D- π -A)-type pyridinium-cyclic enolate betaines (Fig. 1). We recently reported that **PB-Th** (π -spacer: 2,5-thienylene) exhibited deep red fluorescence at 669 nm with Φ_{PL} of 0.75 in dichloromethane.¹ The *N,N*-diphenylamino donor group leads to achievement of red-shifted fluorescence through the intramolecular

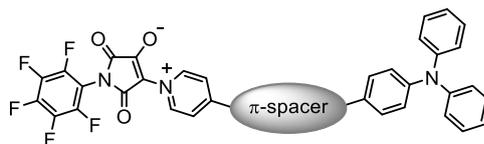


Fig. 1. General structure of D- π -A-type pyridinium-cyclic enolate betaine dyes.

charge transfer character and plays an essential role in reduction of the non-radiative decay rate. Also, as demonstrated in our previous work,² the electron-deficient five-membered cyclic enolate based on maleimide promises the improvement of Φ_{PL} due to suppression of twisted intramolecular charge transfer at the pyridinium-enolate moiety upon photoexcitation. In this research, we develop D- π -A-type pyridinium-cyclic enolate betaine dyes bearing extended π -skeletons, aimed at highly efficient red-shifted photoluminescence (PL) to the NIR region. Thiophene-derived extended π -spacers were effective to achieve NIR fluorescence. For example, one of the present betaine dyes exhibited intense NIR emission at 719 nm with Φ_{PL} of 0.66 in dichloromethane. Theoretical calculations indicate that it adopts a quinoidal electronic structure at the excited state, and thus the structural relaxation upon photoexcitation should be suppressed to achieve high Φ_{PL} . In the presentation, we report the synthesis of the NIR-fluorescent pyridinium betaine dyes and discuss their PL properties in detail.

1) M. Saikusa, S. Yagi, *et. al.*, 2021 Japan Society of Colour Material Annual Conference, 2A01 (online). 2) Y. Hayashi, S. Yagi, *et. al.*, *New J. Chem.*, **2021**, 45, 9770–9779.