

## Development of Intramolecular Exciton-Coupled Bis-Squaraine Dyes for Application to Near-Infrared Organic Photodetectors

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### Abstract

We synthesized two bis-squaraine dyes consisting of benzo[1,2-*b*:5,4-*b'*]dipyrrole central components and indolenine-based semisquaraine or its dicyanovinylene analogue for application to electron donor materials for organic photodetectors with bulk heterojunction architecture. These dyes exhibited split electronic absorption bands attributed to intramolecular exciton coupling. The lower energy absorption band of the bis-squaraine dye with dicyanovinylene group was observed in the near-infrared region. In cyclic voltammograms of bis-squaraine dyes, broad redox waves were observed in oxidative scans, indicating that one-electron oxidized dyes have delocalized electronic states throughout two chromophores. The highest occupied molecular orbitals and the lowest unoccupied molecular orbitals of bis-squaraine dyes have suitable energy levels for electron donor materials toward the fullerene-based electron acceptor. A composite film comprised of a fullerene acceptor and a bis-squaraine dye showing near-infrared absorption exhibited a near infrared absorption with a maximum at ca. 780 nm, promising photo-induced electron transfer upon the irradiation of near infrared light. An organic photodetector with the composite film demonstrated a specific detectivity ( $D^*$ ) of  $4.6 \times 10^{11}$  Jones under 750 nm illumination and  $3.3 \times 10^{11}$  Jones under 800 nm illumination. This indicated that the bis-squaraine dye can work as the donor material in organic photodetectors responsive to near-infrared light.

**Key-words:** Exciton coupling, Squaraine, Donor, Near infrared, Photodetector

### 1. Introduction

Organic photodetectors (OPDs), that directly convert light into electrical signals enhanced by the organic photoactive layer, have attracted considerable interest due to their key advantages, including the elimination of toxic elements, compatibility with flexible substrates, and lightweight characteristics.<sup>1,2)</sup> Particularly, a bulk-heterojunction (BHJ) featuring an electron donor and an acceptor in a photoactive layer facilitates the dissociation of photogenerated excitons and the transport of holes and electrons to the respective electrodes.<sup>3,4)</sup> This enhances the efficiency of photocurrent generation in OPDs.<sup>5)</sup> These features enable their application in various fields as a viable alternative to inorganic compound-based photodetectors. Especially, OPDs designed for near-infrared (NIR) light (NIR-OPDs) are expected to find applications used for living tissues and organisms such as biometric authentication technology, since NIR light exhibits significant biological permeability due to the suppression of absorption, scattering, and autofluorescence in living tissues.<sup>6)</sup>

To date, various compounds with extended  $\pi$ -electron systems have been developed for integration into the photoactive layer of NIR-OPDs.<sup>7)</sup> These compounds exhibit strong absorption in the NIR region and demonstrate semiconducting properties due to a substantial overlap of  $\pi$  orbitals.

Squaraine dyes, derived from the condensation of squaric acid and electron-rich heterocycles, emerge as strong candidates for donor materials for NIR-OPD.<sup>8,9)</sup> They exhibit electron-donating properties owing to their relatively high oxidation potentials and display significant electronic absorption strength with adjustable electronic transition energy. This characteristic is primarily dependent on the structure of electron-rich heterocyclic components located at the 1,3-position of the central cyclobutenedione.<sup>10,11)</sup> Moreover, these dyes can be modified with diverse electron-poor substituents at the 2-position of cyclobutenedione, enabling them to exhibit intense NIR absorption properties.<sup>12,13)</sup> These versatile properties make them suitable for OPDs<sup>14–17)</sup> and enable a wide range of applications, including chemosensors,<sup>18)</sup> bioimaging,<sup>19,20)</sup> photoacoustic imaging,<sup>21)</sup> photothermal therapy,<sup>22)</sup> and organic photovoltaics.<sup>23)</sup>

The optimization of electronic absorption properties and oxidation potentials in squaraine dyes is typically achieved

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