

Development of Electroswitchable Organic π -Systems with Near-Infrared (NIR) Absorptions: Control of HOMO/LUMO Levels Based on Unique Structures

(¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, ²Faculty of Science, Hokkaido University) ○Takashi Harimoto,¹ Takanori Suzuki,² Yusuke Ishigaki²

Keywords: Redox System, NIR Absorption, Oligocation, Dyes and Pigments

Electrochromic systems capable of switching near-infrared (NIR) absorption are fascinating from the viewpoint of applications in the materials and life sciences, and thus the development of organic-based materials is needed to reduce the environmental impact and improve biocompatibility. Among such electrochromic systems, mono- and bisquinodimethane derivatives **1** and **2** with a folded form undergo one-stage multi-electron oxidation to produce twisted di- and tetracations with a planar acene skeleton. The HOMO of oligocations **1**²⁺ and **2**⁴⁺ is mainly located on the acene framework, and the corresponding LUMO is delocalized in peripheral diarylmethylium units. As a result, a NIR absorption band based on an intramolecular charge-transfer (CT) interaction from HOMO to LUMO was observed in these oligocationic dyes. Therefore, controlling the HOMO and LUMO levels of oligocations is an effective approach for the precise modulation of longer-wavelength absorption in the NIR region.

Herein, we propose two different strategies for modulating frontier orbital levels: (i) a “ π -extension strategy” that allows a red-shift of the NIR absorption band by elevating the HOMO levels of the acene core (Figure 1) and (ii) the “*ortho*-substitution strategy” that allows an enhancement of NIR-absorbing abilities by lowering the LUMO levels of the chromophores (Figure 2).³ Under these strategies, we designed and synthesized various quinodimethane derivatives and demonstrated quantitative redox interconversion with diarylmethylium-type dyes exhibiting NIR absorption bands due to the narrower HOMO-LUMO gaps. Their properties were characterized by electrochemical, spectroscopic and theoretical studies, and the NIR absorption properties can be drastically changed by controlling the HOMO of the donor unit and the LUMO level of the acceptor unit.

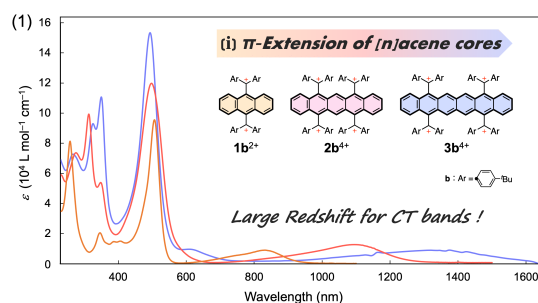


Figure 1. UV/Vis/NIR spectra of **1b**²⁺(SbCl₆)₂, **2b**⁴⁺(SbCl₆)₄, and **3b**⁴⁺(SbCl₆)₄ in CH₂Cl₂.

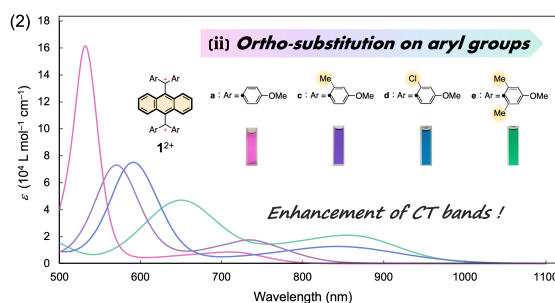


Figure 2. UV/Vis/NIR spectra of **1a**²⁺(SbCl₆)₂, **1c**²⁺(SbCl₆)₂, **1d**²⁺(SbCl₆)₂, and **1e**²⁺(SbCl₆)₂ in CH₂Cl₂.

- 1) Y. Ishigaki, K. Sugawara, T. Tadokoro, Y. Hayashi, T. Harimoto, T. Suzuki, *Chem. Commun.*, **2021**, 57, 7201.
- 2) Y. Ishigaki, T. Harimoto, K. Sugawara, T. Suzuki, *J. Am. Chem. Soc.* **2021**, 143, 3306.
- 3) T. Harimoto, T. Suzuki, Y. Ishigaki, *Chem. Eur. J.* **2023**, accepted.