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Takashi Harimoto

Design, Synthesis, and Properties of Redox-Active Bisquinodimethanes

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Takashi Harimoto

Design, Synthesis, and Properties of Redox-Active Bisquinodimethanes

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Supervisor's Foreword

Electrochromic systems capable of switching absorption in the NIR region (750–2500 nm) are attractive from the viewpoints of applications for materials and life science. To reduce the environmental impact and improve biocompatibility, development of organic-based systems is needed. Redox-active π-conjugated systems such as *para*-Quinodimethane (*p*-QD) and 9,10-anthraquinodimethane (AQD) have been recognized as useful scaffolds in constructing reversible redox pairs for electrochromism. However, switching of NIR absorption is still a challenging issue even using the AQD derivatives, in which triarylmethylium chromophores are generated upon two-electron oxidation. Thus, a new molecular design concept is necessary to construct *p*-QD/AQD systems which enable ON/OFF switching of NIR absorption.

The Ph.D. thesis of Dr. Takashi Harimoto focuses on the novel molecular design of *p*-QDs and AQDs endowed with unique redox properties. The voltammetric and crystallographic techniques are the strong tools for Takashi to accomplish the Ph.D. work along with the density functional theory (DFT) calculation. Takashi conducted syntheses of systematically designed series of compounds with different aryl substituents and molecular skeletons, thus realizing the NIR electrochromicity up to the 1400 nm region, which were accompanied by isolation and thorough characterization of the polycationic species. Noteworthy, the work on bisquinodimethane (BQD) disclosed unprecedented domino-type electron-transfer behavior, thus demonstrating that the molecules with multiple redox-active units can serve as promising materials for simultaneous multiple-electron transfer to generate multivalent ionic species. These groundbreaking results in the thesis are deserving of a place in the Springer Theses series.

Sapporo, Japan
October 2024

Takanori Suzuki

Parts of this thesis have been published in the following journal articles

Hysteretic Three-State Redox Interconversion among Zigzag Bisquinodimethanes with Non-fused Benzene Rings and Twisted Tetra-/Dications with [5]/[3]Acenes Exhibiting Near-Infrared Absorptions.
Y. Ishigaki, **T. Harimoto**, K. Sugawara, T. Suzuki, *J. Am. Chem. Soc.* **2021**, *143*, 3306–3311.
Geometrical and Electronic Structure of Cation Radical Species of Tetraarylanthraquinodimethane: An Intermediate for Unique Electrochromic Behavior.
Y. Ishigaki, R. Fukagawa, K. Sugawara, **T. Harimoto**, T. Suzuki, *Chem. Asian J.* **2022**, *17*, e202200914.
Enhancement of NIR-Absorbing Ability of Bis(diarylmethylium)-Type Dicationic Dyes Based on an *Ortho*-Substitution Strategy.
T. Harimoto, T. Suzuki, Y. Ishigaki, *Chem. Eur. J.* **2023**, *29*, e202203899.
Double Dynamic Structural Change Enabling Tricolor Chromism by the Realization of Apparent Two-Electron Transfer to Skip the Open-Shell State.
T. Harimoto, Y. Sugai, K. Sugawara, T. Suzuki, Y. Ishigaki, *Chem. Eur. J.* **2023**, *29*, e202301476.
Domino-Redox Reaction Induced by An Electrochemically Triggered Conformational Change.
T. Harimoto, T. Tadokoro, S. Sugiyama, T. Suzuki, Y. Ishigaki, *Angew. Chem. Int. Ed.* **2024**, *63*, e202316753.

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Chapter 1
General Introduction

1.1 Redox-Active π-Conjugated Systems

Over the past couple of decades, various stimuli-responsive organic molecules have been developed as a result of remarkable advances in synthetic and material sciences (Fig. 1.1) [1, 2], and these molecules are attracting attention for their potential application in optoelectronic devices or medical materials [3–8]. Such stimuli-responsive molecules change their properties in response to changes in physical stimuli such as heat, light, and electric potential, or to a change in the chemical environment such as in pH or concentration. Therefore, these molecules function as nano-actuators that can change their form in response to external input. Electrical stimulation is particularly suitable for controlling the physical properties of a specific molecule because electrons can be used for precise manipulation and target selectivity at the nano-level [9, 10]. In this regard, various redox-active species that respond to electric potential have been developed. Since the precise control of the redox properties is essential for achieving the high performance of electronic devices, switching behavior as well as the characteristics such as crystal structure, charge distribution, and spin density of redox-active species have been studied for a long time.

In 1965, Gomes et al. achieved the structural determination of the ClO_4^- salt of triphenylmethylium by a single-crystal X-ray structure analysis [11]. This was the first direct observation of the structure of a π-conjugated carbocation. Since then, the physical properties of cations based on aromatic hydrocarbons such as naphthalene, fluoranthene and perylene have been actively investigated by experimental and theoretical approaches [12–14], and their crystal structures have been successfully determined [15–20]. Since it is difficult to stabilize such charged species without heteroatoms, the development of pure hydrocarbon-based redox systems is challenging from the viewpoint of the stability of cationic (anionic) species. Therefore, the successful isolation of charged species composed of pure hydrocarbons and elucidation of their intrinsic redox properties have led to significant advances in the field of redox chemistry (Fig. 1.2) [21–25].

T. Harimoto, *Design, Synthesis, and Properties of Redox-Active Bisquinodimethanes*, Springer Theses, https://doi.org/10.1007/978-981-96-1591-9_1

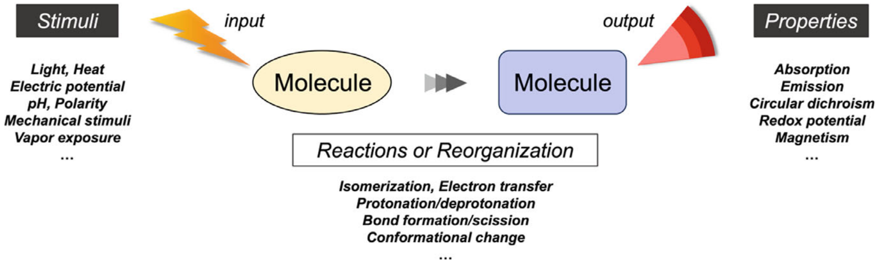


Fig. 1.1 Schematic illustration of stimuli-responsive molecules

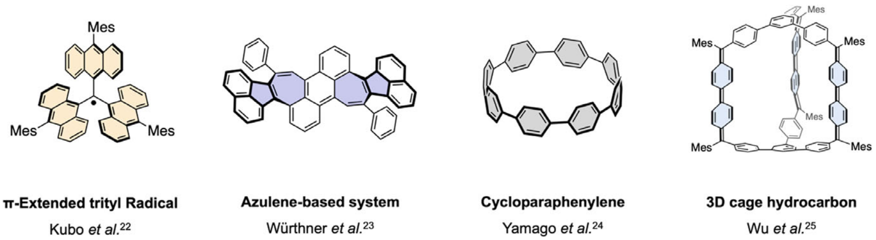
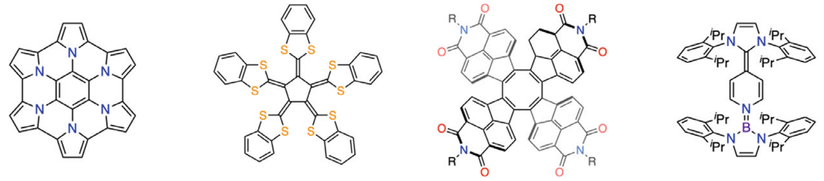


Fig. 1.2 Examples of previously reported well-designed redox-active π-conjugated hydrocarbons

On the other hand, the incorporation of heteroatoms, for example, nitrogen and oxygen atoms, into the molecule is an effective method for stabilizing charged species and modulating the electronic properties of organic molecules. In addition, delocalization of a charge over an extended π-conjugation is effective for the synthesis and isolation of charged species as stable entities with carbon-centered ions. Indeed, aromatic hydrocarbons are known to exhibit unique electrochemical and spectroscopic properties based on their π-conjugated systems, and several systems capable of redox interconversion between neutral and cationic (anionic) states have been reported by effectively stabilizing the charged-state(s) by embedding heteroatoms or introducing heteroatom-substituents into the π-skeleton (Fig. 1.3) [26–36]. These redox-active molecules have potential applications in electronic equipment such as semiconductors, batteries, and memory devices, due to the high reversibility of electron transfer among two or more redox states [37–43].

1.2 Near-Infrared (NIR) Electrochromic Systems

Electrochromic systems can induce a drastic change in color based on interconversion among differently charged species upon electron transfer (Fig. 1.1) [44–47]. Representative examples include robust inorganic compounds, such as tungsten oxide (WO_3), which have been used in auto-dimming mirrors, smart windows, and displays [48–52]. On the other hand, due to the advantages of organic molecules



Hexapyrrolohexaazacoronene Müllen *et al.*[27]

1,3-Dithiol-2-ylidenes Misaki *et al.*[28]

Tridecacyclene tetraimide Stępień *et al.*[30]

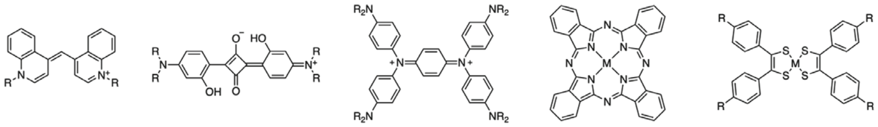
BN-Doped Thiele's analogue Aldridge *et al.*[35]

Fig. 1.3 Examples of previously reported well-designed redox-active π-conjugated systems with heteroatoms

in terms of affordability, flexibility, modularity, and biocompatibility, organic and related materials with redox activity have also been actively studied in the past decades [53–58].

Especially, NIR absorbing properties in the range of 750–2500 nm can be utilized to increase the efficiency of photovoltaic power generation by harvesting NIR light in sunlight [59–61]. In addition, since NIR light shows a superior penetration of biological tissues, they are also expected to be applied to chemotherapy and imaging of deep tissues in vivo [62–70]. Since organic dyes such as cyanines, squaliums and diimmonium, and organometallic complexes such as phthalocyanines and dithiolenes exhibit NIR-absorbing properties due to a narrow energy gap, they have attracted much attention from the viewpoint of various optical applications in electronics and life sciences to date (Fig. 1.4) [71–73].

In this context, some organic polymeric materials including covalent organic frameworks (COFs) and/or metal–organic frameworks (MOFs) have been reported as NIR switchable electrochromic systems (Fig. 1.5) [74–79]. In these systems, multiple electrophores are needed to be integrated and controlled by the corresponding operating potential to output multiple colors. On the other hand, a well-designed single molecule, which can adopt multiple redox states with different colors, would be very useful, since it could work under a simple setup without the fabrication of multiple layers (Fig. 1.6) [80–84]. Despite this attractiveness, since stabilization and/or isolation of all redox states (neutral and anionic and/or cationic states) is needed for the modulation of NIR absorption based on reversible redox interconversion, it remains challenging to establish a smart guideline of molecular design for organic dyes that



Cyanine

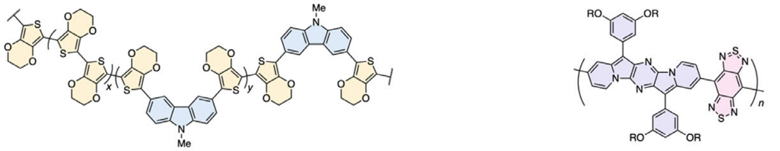
Squalium

Diimmonium

Phthalocyanine

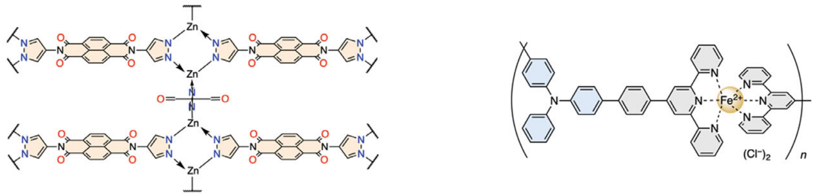
Dithiolene complex

Fig. 1.4 Examples of well-studied NIR dyes



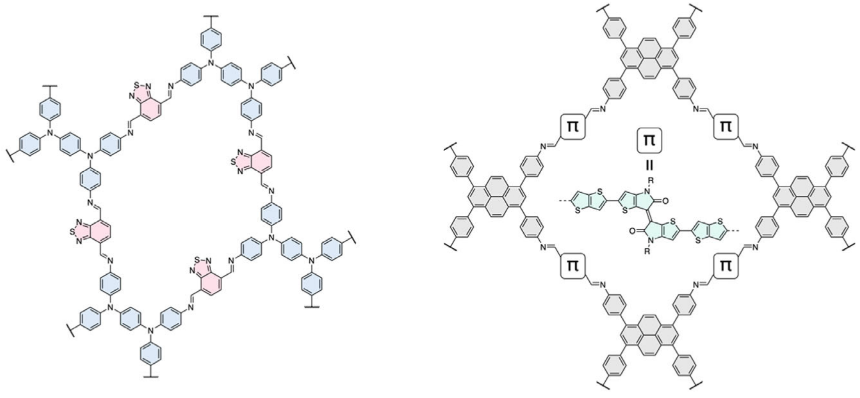
3,4-Ethylenedioxy-thiophene-based polymer
Reynolds *et al.*[74]

Heterocyclic π-conjugated polymer
Lu and Liu *et al.*[75]



Naphthalene-diimide-based MOF
Dincă *et al.*[76]

Metallo-supramolecular polymer
Higuchi *et al.*[77]



Donor-acceptor type COF
Zuo and Zhang *et al.*[78]

Pyrene-based COF
Auras and Bein *et al.*[79]

Fig. 1.5 Examples of previously reported organic polymeric NIR electrochromic materials

enable ON/OFF switching of NIR absorption, especially when some of the states are open-shell species.

1.3 *p*-Quinodimethanes

Para-quinodimethane (*p*-QD) [85, 86], a representative skeleton in cross-conjugated systems, is known to have a contribution of resonance structure with a planar aromatic sextet ring. Therefore, the *p*-QD skeleton is expected to be useful for the design of advanced π-conjugated systems that can switch photophysical and electrochemical