

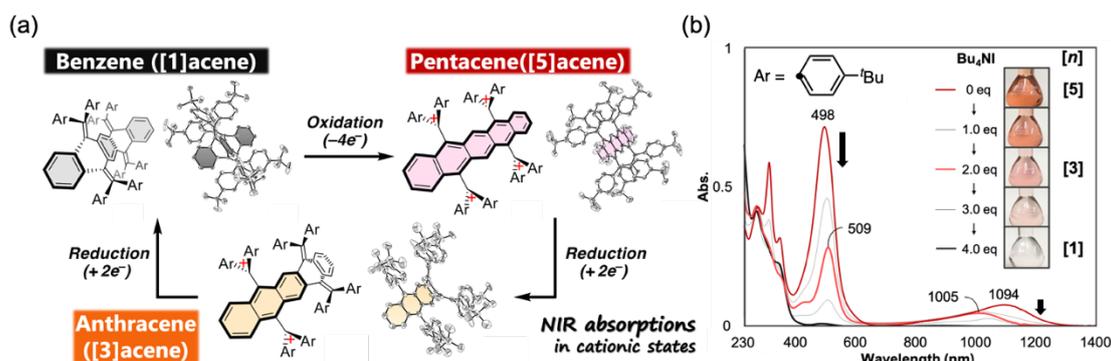
Electrochemical synthesis and dynamic control of $[n]$ acene structures

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$[n]$ Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings (n indicates the number of annulated benzene rings). $[n]$ Acenes are highly attractive molecules because their HOMO/LUMO levels and small band gap can be easily modulated by a change in n . Thus, their physical properties can be fine-tuned, and $[n]$ acenes are widely used as functional organic materials such as semiconductors. In addition, $[n]$ acenes have been reported to show dynamic interconversion through photo and thermal dimerization/dissociation and reversible endoperoxidation reactions. While these switching behaviors are fascinating from the viewpoint of control of HOMO/LUMO levels arising from the change in acene units, it is still challenging to attain reversible and selective switching of $[n]$ acene units that can be observed in a unimolecular fashion rather than as an intermolecular reaction of two molecules.

Herein, we designed and synthesized zigzag-structured bisquinodimethanes (BQDs) with non-fused benzene rings, which undergo one-stage four-electron oxidation to produce tetracationic $[5]$ acenes with a doubly twisted conformation. When tetracationic $[5]$ acenes were reduced, two-stage two-electron reduction occurred via dicationic $[3]$ acenes to the original BQDs (Figure a). Such hysteretic three-state redox interconversion among them demonstrates perfect control of n ($1 \rightarrow 5 \rightarrow 3 \rightarrow 1$) in the $[n]$ acene structure by redox conversion. Moreover, since these cations exhibit significantly red-shifted NIR absorptions (~ 1400 nm) based on an intramolecular charge-transfer interaction, changes in structure as well as UV-vis-NIR absorptions can be controlled by electrochemical input (Figure b). All structures were determined by X-ray analyses, and their properties were characterized by spectroscopic and theoretical studies.¹ Recent progress will be also presented.



1) Y. Ishigaki, **T. Harimoto**, K. Sugawara, T. Suzuki, *J. Am. Chem. Soc.* **2021**, *143*, 3306.