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著者(和文)	CHENXu
Author(English)	Xu Chen
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Thesis Outline

Synthesis and Antibacterial Application of Push-Pull Chromophores by [2 + 2] Cycloaddition-Retroelectrocyclization Reaction

CHEN Xu

In Chapter I, the history and mechanism of [2 + 2] cycloaddition-retroelectrocyclization (CA-RE) reaction were outlined, and the developments in the synthesis of molecular and polymeric push-pull chromophores were introduced. Additionally, the applications of CA-RE products were briefly reviewed, including their use in nonlinear optical materials, p-dopants for organic semiconductors, colorimetric sensors and so on.

In Chapter II, a series of 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives with various heterocyclic moieties, including pyridine, carbazole, indole, and benzothiadiazole, was newly synthesized through a [2 + 2] CA-RE reaction under ambient or mild heating conditions. Thermal analysis demonstrated the good stability of these TCBD derivatives. Their absorption spectra revealed strong intramolecular charge-transfer bands within the visible range. The electrochemical analysis indicated the oxidation waves ascribed to the heterocyclic donor moieties and reduction waves attributed to the acceptor moieties. The HOMO and LUMO energy levels, estimated from the onset potentials, confirmed that the energy levels and bandgaps can be modulated by altering the chemical structures. Furthermore, density functional theory (DFT) calculations for these compounds were performed, and the result was consistent with the experimental findings. Besides, the optimized structures from DFT calculations revealed the nonplanar structure of these derivatives, which was further verified by the single crystal structure of the pyridine-substituted TCBD derivative. It was found that the aminopyridine substituent is a promising unit for the synthesis of TCBD derivatives with relatively higher thermal stability and deeper LUMO energy levels.

In Chapter III, several pyridine-containing CA-RE adducts were synthesized in high yields under ambient or mild heating conditions. The thermal stability and optical and electrochemical properties of these derivatives were investigated using thermogravimetric analysis, ultraviolet-visible (UV-Vis) spectroscopy, and cyclic voltammograms, and the optimized structures and frontier molecular orbitals with their energy levels were determined by DFT calculations. These molecules featured relatively deep LUMO energy levels, which can be further reduced by coordination with tris(pentafluorophenyl)borane (BCF). The obtained complex was employed as a p-dopant for poly(3-hexylthiophene-2,5-diyl) (P3HT), and the doping performance was evaluated by UV-Vis-near infrared spectroscopy and photoemission yield spectroscopy in air.

In Chapter IV, *N,N*-dibutyl-4-((4-vinylphenyl)ethynyl)aniline was synthesized and copolymerized with *N,N*-dimethylacrylamide (DMA) to produce a polymer precursor containing electron-rich alkyne units. Subsequently, the water-soluble cyano-containing polymer additives were prepared via [2 + 2] CA-RE postfuctionalization with TCNE. The success of postfuctionalization was confirmed by observed color change, increased molecular weight, and characteristic variations in FT-IR and ^{1}H NMR spectra. Due to the multivalent complexation interaction between cyano groups and silver ions (Ag^+), the obtained polymeric additives were incorporated into polyvinyl alcohol (PVA)-based hydrogels to capture and fix silver ions for antibacterial application. The Ag^+-loading capability of the resulting hydrogels was determined by inductively coupled plasma mass spectrometry (ICP-MS) measurements, and the antibacterial performance of the Ag^+-loaded hydrogels was evaluated by halo tests against *E. coli*.

In Chapter V, the applications of [2 + 2] CA-RE reaction in chromophore synthesis and polymer postfunctionalization were summarized, and the prospects of CA-RE products in p-doping and Ag^+ capture were highlighted. First, the development of novel TCBD derivatives with lower LUMO energy levels can be achieved by replacing the substituent with electron-withdrawing units. Second, it is of great significance to prepare multi-functional, versatile hydrogels incorporating water-soluble TCBD-containing polymers. These achievements will lead to the development of advanced push-pull chromophore materials.