論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	陳 旭 CHEN Xu	審査員主査： Chief Examiner	道信 剛志

要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

The [2 + 2] cycloaddition-retroelectrocyclization (CA-RE) reaction, which typically occurs between electron-rich alkynes and electron-deficient alkenes, has been attracted extensive attention due to its advantages as a click reaction, including high-yielding, mild conditions, atom-economic and no side reaction. Therefore, it has been employed as an effective tool for constructing push-pull chromophores and for polymer postfunctionalization. Given its significant role in tuning energy levels and intramolecular charger transfer (ICT), the obtained CA-RE products exhibit great potential as functional materials in applications such as organic nonlinear optics, p-dopants for semiconducting polymers, colorimetric sensors and organic photovoltaics.

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 in 60-80% yields under ambient or mild heating conditions. Thermal analysis demonstrated the good thermal stability of these TCBD derivatives, and pyridine-substituted derivatives exhibited the highest stability, with the 5% decomposition temperature up to 327 ℃. The absorption spectra of these derivatives showed their strong intramolecular charge-transfer (ICT) bands within the visible range, with the new donor incorporating benzothiadiazole exhibiting the narrowest bandgap. The electrochemical analysis revealed 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 tuned by altering the chemical structures. Furthermore, density functional theory (DFT) calculations were performed, and the calculated energy levels aligned well with the experimental results. The calculation also revealed a clear separated localization of HOMOs and LUMOs, explaining the strong ICT behavior observed in the TCBD derivatives. Additionally, the optimized structures from DFT calculations suggested the nonplanar structure of these derivatives, which was verified by the single-crystal structure of the pyridine-substituted derivative.

In chapter Ⅲ, several pyridine-substituted CA-RE products were synthesized in high yields under ambient or mild heating conditions, based on the observation that pyridine-containing TCBD derivatives exhibited relatively high thermal stability and low LUMO energy levels. The pyridine-based monoalkynes, including symmetric alkynes and asymmetric alkynes with hydroxyl end groups, smoothly underwent the [2 + 2] CA-RE transformation in the yield over 86%. The thermal analysis

revealed that TCBD derivatives exhibited better thermal stability compared to TCNQ adducts. Besides, the optical and electrochemical properties of these derivatives were investigated using UV-Vis spectroscopy and cyclic voltammetry (CV) measurements, while their optimized structures and frontier molecular orbitals were determined through DFT calculations. These molecules featured deep LUMO energy levels, with the TCNQ adduct demonstrating a relatively low LUMO energy level of -4.26 eV. Furthermore, the LUMO energy level can be further reduced by coordinating with tris(pentafluorophenyl)borane (BCF) through cyano groups. The doping performance for P3HT was evaluated by UV-Vis-NIR spectroscopy and photoemission yield spectroscopy in air. Before coordinating with BCF, the doping efficiency was limited due to their relatively shallow LUMO levels. After coordinating with BCF, the hydroxyl-containing TCBD derivative induced a more significant shift in HOMO energy levels than BCF alone, highlighting its potential as p-dopants. In contrast, the TCNQ adduct exhibited poor doping performance even after the coordination with BCF, possibly induced by the highly nonplanar structure.

In chapter Ⅳ, *N,N*-dibutyl-4-((4-vinylphenyl)ethynyl)aniline was synthesized via Sonogashira coupling in 74% yield and subsequently copolymerized with *N,N*-dimethylacrylamide (DMA) to produce a polymeric precursor containing electron-rich alkyne units. The water-soluble cyano-containing polymer additives were then prepared through [2 + 2] CA-RE postfuctionalization with TCNE in almost quantitively yield. The successful postfuctionalization was confirmed through observed color changes, increased molecular weights, 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 synthesized polymeric additives were incorporated into polyvinyl alcohol (PVA)-based hydrogels to capture and fix Ag^{+}. The prepared hydrogel films exhibited excellent Ag^{+} loading capacity after immersing in a 0.1 mM aqueous solution of CF_3SO_3Ag for 16 hours, achieving an average loading amount of 35×10^{-3} mmol g^{-1} determined by inductively coupled plasma mass spectrometry (ICT-MS) measurement. Since Ag^{+} is a well-known antibacterial agent, the antibacterial performance of the Ag^{+}-loaded hydrogels was evaluated by the halo test against *E. coli*, and the significant antibacterial performance was revealed with an antibacterial halo diameter of 17.0 ± 0.3 mm. Besides, it was speculated that the rapid release of Ag^{+} from the hydrogel films was achieved, endowing the hydrogels with long-term durable antibacterial performance.

These studies expand the range of donor structures capable of activating the alkyne unit for CA-RE transformations, underscoring the exceptional potential of the [2 + 2] CA-RE reaction in synthesizing novel push-pull chromophores with extended UV-Vis absorptions and narrow bandgaps. The introduction of rich cyano groups effectively lowers the LUMO energy levels, making them highly suitable for the design of p-dopants. Furthermore, the LUMO levels of these p-dopants can be finely tuned by replacing the end groups. The successful preparation of water-soluble TCBD-containing polymers opens new possibilities for the development of multifunctional and versatile hydrogels incorporating TCBD derivatives.

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