

Thesis Summary

Synthesis and Properties of New Cationic Nitrogen Radical Containing Compounds (新規カチオン性窒素ラジカル化合物の合成と性質)

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As one of the branches of radical chemistry, ion-radical chemistry features the properties and reactivities of both ion and radical. Their detection and isolation have been very challenging due to their highly reactive nature. With continuing efforts on synthesizing stable ion-radicals, two general strategies have been established, namely, to increase the electron delocalization over a π system, and to increase the steric protection by bulky substituent. In recent years, the stable ion-radical species have found potential applications in electronic, optical and magnetic fields. For instance, diradicals featuring partially bonded show enhanced two-photon absorption (TPA). However, there is no molecular design strategy through fine-tuning effect of the electron system to affect TPA. Therefore, we envisioned that weak hypervalent bond in a cation radical species may perturb the electron system and affect the optical properties of diradical species.

This thesis not only concentrates on design, synthesis and isolation of the stable nitrogen cation radical species, but also investigates their potential applications. It is composed of six chapters.

Chapter 1 (Introduction) is a general introduction of radical chemistry, ion-radical chemistry and cation radical chemistry in sequence.

Chapter 2 (Synthesis and Properties of Hypervalent Electron-rich Pentacoordinate Nitrogen Compounds) describes the isolation and structural characterization of the first air stable hypervalent electron-rich pentacoordinate nitrogen cationic radical (11-N-5) and neutral (12-N-5) species. The nitrogen centers adopt a trigonal bipyramidal geometry featuring a weak 3-center-4-electron hypervalent bond. The N-O bond distance in both neutral precursors and cationic radical species are shorter than the sum of N-O Van der Waals radii, indicating attractive interactions between N and O atoms. The atoms in molecules (AIM) studies showed the presence of bond critical points, confirming the formation of 12-N-5 and 11-N-5 hypervalent attractive interaction respectively. In addition, based on N-O distances in the solid-state structures, the apical hypervalent bonds in the cationic radical species are stronger than those in neutral compounds. This successful design strategy and isolation of air-stable pentacoordinate hypervalent nitrogen species allows us to further explore the effect of weak

electronic perturbation on the properties and/or reactivity of nitrogen containing compounds.

Chapter 3 (*Electronic Effect of Weak Hypervalent Bonding on Diradical Characters and Two-photon Absorption Properties*) concentrates on the electronic fine-tuning effect of the weak hypervalent bonding on two-photon absorption (TPA). We successfully synthesized, isolated, and structurally characterized the air-stable bromo-substituted triarylamine dication diradical dimers featuring the weak 3-center-4-electron hypervalent bond. Based on the relative bond length comparison between dication diradical species and neutral dimer compounds, dication species showed a contribution of both the quinoidal form with closed-shell structure and the nonquinoidal form with a singlet diradical structure. These dication diradicals with intermediate state showed an enhanced TPA as predicted. In addition, the increased magnitude in the order of isopropyl- (3000 ~ 3800 GM), methoxy- (4000 ~ 5300 GM) and hydrogen (6600 ~ 7800 GM) substituents indicates the sensitive electronic fine-tuning effect of the weak hypervalent bonding on decreasing the TPA properties.

Chapter 4 (*Synthesis and Magnetic Properties of Stable Nitrogen Centered Trication Triradical Trimers*) aims to synthesize and isolate a triarylamine analogue with high-spin quartet state. We designed three dendritic types of triarylamine analogues, and based on the cyclovoltammetry spectra, only trimer **25** showed three reversible peaks indicating the stability of the corresponding trication triradical species. With the treatment of different oxidants, UV-Vis spectra showed that employed AgPF_6 as oxidant, the corresponding trication triradical species can survive under ambient atmosphere for at least 30 mins, demonstrating a good stability. The theoretical studies showed a small energy difference between doublet state and quartet state, suggesting that the quartet state maybe observed in EPR spectrum at low temperature. Their high-spin quartet state will be investigated using low temperature EPR, precise and detail theoretical calculation will be carried out in the future.

Chapter 5 (*Synthesis and Properties of Bridged Triarylamine Helicenes with Electron Transfer Properties*) provides a new and mild synthetic route to synthesize the bridged triarylamine helicenes, which were isolated and structurally characterized. Furthermore, their respective radical cation species were synthesized via one-electron oxidation. The UV-Vis spectra of natural compounds showed a red-shift starting from trifluoromethyl- to methoxy-substituted compounds, indicating the electron-withdrawing group increases the HOMO-LUMO gap whereas the electron-donating group decreases the HOMO-LUMO gap. In addition, the cyclovoltammetry spectra of neutral bridged triarylamine helicenes showed small oxidation potentials, implicating their potentially applicable to charge transfer materials. The corresponding radical species still cannot be confirmed yet.

Chapter 6 (*Conclusion and Outlook*) is the total conclusion and outlook of this research.