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Abstract of Thesis

Name (Tian Yi)

Title

Synthesis and Properties of Fluorenyl-based Hydrocarbon Radicals

(フルオレニルを基盤とする炭化水素ラジカルの合成と物性)

In recent years, interest is growing in the development of stable organic radicals as new functional molecular materials, because their open-shell electronic structures show unique technologically relevant properties. By virtue of having external stimuli (such as light, and electric and magnetic fields) responsive spin structures, stable organic radicals provide novel schemes for performing spin memory and logic operations, and open avenues for quantum information science and quantum computers. The synthesis of radicals with sufficient stabilities is the precondition for their further applications in material science. Because physical properties of hydrocarbon radicals depend predominantly on the topology of π -electrons array, the development of new hydrocarbon radicals is key to new basic molecular skeletons that promise novel and diverse applications of spin materials. Furthermore, studying structure-property relationship will provide valuable information for the molecular design.

The cyclopentadienyl (Cp) radical species is one of the simplest members of conjugated hydrocarbon radicals, but their further properties investigation and application have been hampered by the inherent high reactivity. By far, only a few of them have been isolated in crystalline form, and those radicals are stabilized by steric effect, hyperconjugative stabilization, or spin delocalization. And 9-anthryl group has stabilization effect for some radical centers, such as the newly reported fluorenyl monoradical. Inspired by those research, our strategy toward thermo-dynamic stabilization of fluorenyl-based radicals is by π -extension of the fluorenyl unit with two aromatic benzene rings, and based on the position of the extended benzene rings, we designed three types of target radicals, which can be called a-type, b-type, and c-type. The achievement of kinetic stabilization is by applying the steric hindrance of 9-anthryl group to the center position of fluorenyl. Such a design can possibly also improve the solubility due to orthogonal conformation of the anthryl with respect to dibenzofluorenyl moieties.

Three fluorenyl-based radical isomers (**1a**, **1b**, and **1c**) were prepared. The attachment of the 9-anthryl group at the most reactive site of fluorenyl moiety efficiently stabilizes the radicals in kinetic way, and benzannulation of the fluorenyl center increase stability of the radicals by thermodynamic method. Their electronic properties were systematically investigated by a bunch of experimental methods and assisted by DFT calculations. All three radicals showed significant stabilities; the half-lives of **1a**, **1b**, and **1c** in air-saturated toluene at ambient condition were 7, 3.5, and 43 days, respectively. **1b** could be isolated as an unassociated monoradical in crystalline form, whereas **1a** gave σ -dimers in crystal state. **1c** existed in solid state in both an unassociated monoradical and σ -dimer forms. The spin structures of those radicals were unambiguously determined by solution ESR and ENDOR measurements along with theoretical calculations. The ESR signals of **1a** were intensively decreased at low temperature, indicating that dimerization in solution proceeded. In contrast, **1b** and **1c** didn't show obvious signal decrease in VT ESR measurements. Three radicals showed amphoteric redox properties in CV measurements. **1c** needed 5–6 hours to finish dissociation of σ -dimer after dissolution whereas **1a** could dissociate immediately. UV and ^1H NMR spectra also revealed this phenomenon. Solid UV measurements disclosed mechanochromic properties of crystals of σ -dimers.

Different manner of benzannulation to fluorenyl radical leads to a variety of structures and properties in solution and solid states. Although these rich behaviors are ascribed to the difference of the conjugation style of spin delocalization (that is, cyclic for **1a** and **1c**, and linear for **1b**), anthracene as a substituent would also play an important role. Bulky and rigid skeleton of anthracene effectively protects a spin center with large spin density (~ 0.5) from σ -dimerization and oxygen attack, and at the same time, high ability of anthracene to pull an attached spin into its *meso*-position results in drastic conformation change from twisted to folded forms. Our results suggest that combination of spin-localized radicals and anthracene is a strategy for the molecular design that opens new avenues for spin-based materials.

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

空気中でも取り扱える安定な中性ラジカル種は、不対電子の特性を活かした新材料の構成成分として近年注目を集めている。申請者は、フルオレニルを基盤とする安定炭化水素ラジカルの開発を試み、実際に 9 位にアンスリル基を導入することで、空気中でも容易に取り扱える 3 種のラジカル種 (1, 2, 3) を合成・単離することに成功した。さらに、X 線構造解析、電子吸収スペクトル、電子スピン共鳴、電気化学測定、および量子化学計算を用いて、これらのラジカル種の性質を詳細に調べた。

3 種のラジカル種の室温での半減期は、空気を飽和させたトルエン溶液中でそれぞれ 7 日、3.5 日、および 43 日であり、これらのラジカルは、立体保護基を 1 つしか導入していないにもかかわらず、極めて安定であることがわかった。結晶中では、1 は σ ダイマーとして存在していたが、2 はモノラジカルの状態を保っており、さらに 3 は σ ダイマーとモノラジカルの双方の状態をとりうることもわかった。電気化学測定や電子吸収スペクトル測定では、1 と 3 は比較的良好な挙動を示すのに対し、2 にはそれらとは異なる振る舞いが見られた。これらの結果は、ベンゾ縮環位置の違いからうまく説明できることがわかった。

申請者はまた、ヘテロ原子導入の効果を調べるため、チオフェン環あるいはホウ素やカルボニル基を主骨格に組み込んだ中性ラジカル種の合成にも取り組んだ。

申請者は博士論文研究として、フルオレニル基盤の新規炭化水素ラジカルの合成とベンゾ縮環様式の違いによる電子構造の変化について調べてきた。電子構造の違いは、種々の電子物性、光学物性に違いを与え、大気中での寿命や結晶状態における会合様式にも違いを与えることが分かった。これらの結果は、安定中性ラジカル種の応用研究に対し、その設計指針を与えるものと期待される。

以上を踏まえ、本論文は博士（理学）の学位論文として十分価値あるものと認める。