

論文内容の要旨

Creation of Functional π -Conjugated Systems: Tetraceneimide Disulfide Metal Complexes and Fluorenylideneacridane

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1. Introduction

Creation of a practical material applicable to high performance electronic devices is one of the ultimate targets in organic chemistry. The organic compounds possess some characteristics that are light weight and flexible. The characteristics are of advantage against inorganic materials that are usually heavy and inflexible. On the other hand, electronic device performances composed of organic materials are lower than those of inorganic materials because of organic materials' carrier mobility. As a widely studied organic material, I can pick up polycyclic aromatic hydrocarbons (PAHs). In addition, distorted structures of PAHs have been also investigated to control the aggregated structure and improve the solubility. PAHs involve some fused aromatic rings, which often require multistep synthetic routes. Planar and rigid structures are derived from π - π interactions in PAHs, but those features also evoke low solubility and difficulty to introduce distortion for the molecules. To overcome the issues, I decided to explore different molecular structures rather than PAHs.

In my PhD research, I have spotted on development of long-wavelength light absorption materials toward application to organic photovoltaics. For long-wavelength light absorption, I designed extended π -conjugated systems, which also have an advantage in efficient charge transporting. Herein, I proposed two methods to expand π -conjugated systems. One is to construct metal complex. In this method, I confirmed that introduction of metal can extend π -system by using d-orbitals. As a ligand for this

study, I used tetracenenimide disulfide (TIDS) that I previously developed for organic semiconductors. Coordination of TIDS with metal atom extended the π -system by $d\pi$ - $p\pi$ interaction, which gave different system from $p\pi$ - $p\pi$ interaction in PAHs. Since just one-step reaction of metal insertion is needed to extend the π -system, the π -system can be more easily widened than fused polycyclic aromatic compounds.

2. Results and Discussion

2.1. Platinum Tetraceneimide Disulfide Complex

Platinum complex materials have been enthusiastically examined as light emitting material, thin film organic photovoltaic material, non-linear optical material, and so on. The applicability would be derived from electron-donating properties of platinum, high stability of the complexes in the air, and heavy atom effect to smoothly undergo intersystem crossing. On the other hand, I considered that coordination of aromatic components to metal by using disulfide group is an efficient way to get metal complex materials. Nonetheless, almost all of literatures on metal dithiolate complexes are about synthesis and characterization. Among them, few platinum complexes have been reported, but none of them discussed photophysical property.

The TIDS platinum complex was easily obtained as a mononuclear complex (Pt-TIDS) by reacting TIDS with $\text{Pt}(\text{PPh}_3)_3$ through oxidative insertion in 70% yield (Scheme 1). In contrast to platinum naphthalene dithiolate complexes, Pt-TIDS did not react with $\text{Pt}(0)$ and $\text{Pd}(0)$ to give multinuclear structures. The difference of reactivity could be explained by X-ray structural analysis (Figure 1). The distances of Pt–S in Pt-TIDS are slightly shorter than those in naphthalene dithiolate complexes, deriving twisted structure between tetracene moiety and platinum coordination plane in Pt-TIDS, but naphthalene dithiolate complexes have envelope-like conformation. The twisted structure sterically protects disulfide group from coordination of additional metals.

Scheme 1. Synthesis of Pt-TIDS.

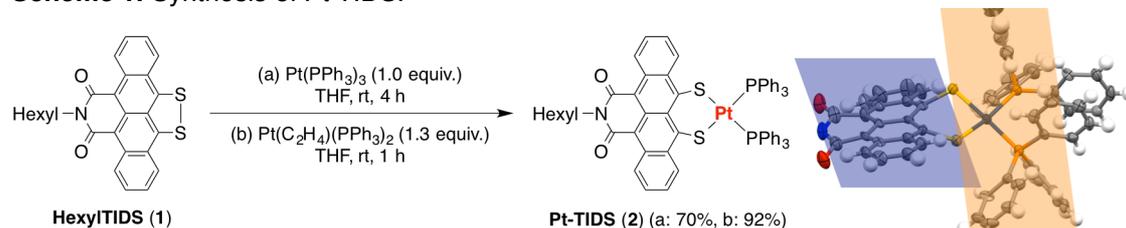


Figure 1. Crystal structure of Pt-TIDS.

Light absorption measurements were carried out to confirm if the π -system was extended by insertion of platinum into TIDS. The light absorption spectra clearly displayed the longer wavelength absorption and higher molar absorption coefficient in Pt-TIDS than TIDS (Figure 2). This result suggested the π -conjugated system was successfully expanded by insertion of platinum. This was further investigated by DFT

calculations with the analog model compound **3** (Figure 3). The structural optimization calculation output fully delocalized orbitals in HOMO and LUMO. The result also exhibits conjugation between d-orbital of platinum and π -orbital of TIDS.

The effect of platinum was further explored by transient absorption measurements. The measurements carried out with excitation at 387 and 670 nm gave the energy diagram of Pt-TIDS, which included a triplet state with lifetime of 0.18–0.28 μ s (Figure 4). The fast relaxation transition would be derived from the large π -conjugated system (energy gap law).

In summary, I have synthesized platinum mononuclear complex with TIDS ligand. Red shift of light absorption spectrum implied π -expansion by introduction of platinum atom. DFT calculation clearly showed $d\pi$ - $p\pi$ conjugation contributes to extend the π -system. Triplet state confirmed by transient absorption measurements provided the applicability of this molecular design toward materials utilizing triplet state with this molecular design.

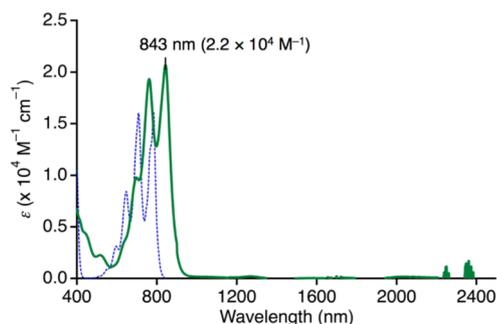


Figure 2. Light absorption spectra of free TIDS (---), Pt-TIDS (—).

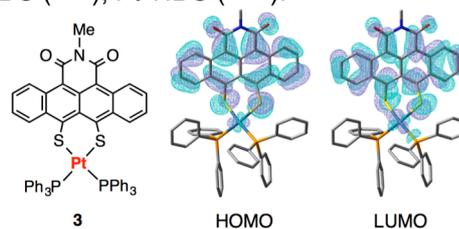


Figure 3. Structure of model compound and optimized structures with HOMO and LUMO.

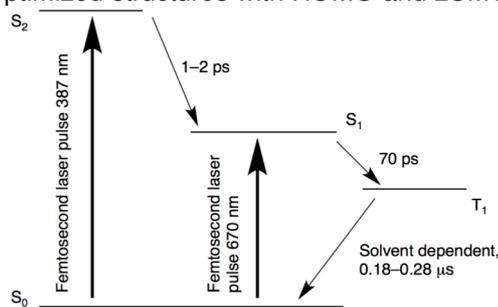


Figure 4. The energy diagram of Pt-TIDS obtained by transient absorption studies.

2.2. Extended π -System in Tri-palladium Tetraceneimide Disulfide Complex

Organic compounds showing long-wavelength light absorption in infrared region have been developed for porphyrinoids, rylene derivatives and so on. Such compounds, however, have complicated and multistep synthetic routes. In contrast, bisdithiolene complexes and multidecker phthalocyanine holding aromatic components longitudinally are known to show long wavelength light absorption to near-infrared region although those can be synthesized in a few steps. Metal complexes demand less number of synthesis steps, but generally two or more aromatic ligands are necessitated.

The reaction with TIDS and $\text{Pd}(\text{PPh}_3)_4$ resulted in trinuclear palladium TIDS complex (*tri*-Pd-TIDS) (Scheme 2). By modifying the condition of solvent and synthetic methods, mono-palladium TIDS complex (*mono*-Pd-TIDS) was obtained as an unstable component. In the crystal structure of *tri*-Pd-TIDS, the palladium coordination planes constructed envelope-like formation unlike Pt-TIDS. The manner is the same in the crystal structure of *mono*-Pd-TIDS. Because of the structural difference,

tri-palladium structure was easily formed.

The π -conjugation structure was evaluated by light absorption measurements and DFT studies. The light absorption spectrum of *tri*-Pd-TIDS denoted an intense peak at infrared region (Figure 5). According to DFT studies, the infrared absorption was attributed to HOMO–LUMO transition. The orbital structures depicted by optimization calculations illustrated π -systems in TIDS ligands interact via d-orbital of the central palladium atom (Figure 6). The π -conjugation comes from parallel ligation of TIDS ligands.

In summary, I developed the tri-palladium complex with two TIDS ligands. Light absorption measurement obviously demonstrated intense infrared absorption peak. The DFT calculations deeply revealed the origin of the infrared absorption as HOMO–LUMO transition. In the optimized structures, HOMO and LUMO delocalize to both of the TIDS ligands through d-orbital of the central palladium atom presumably because of parallel ligation of TIDS ligands.

Scheme 2. Synthesis of palladium TIDS complexes.

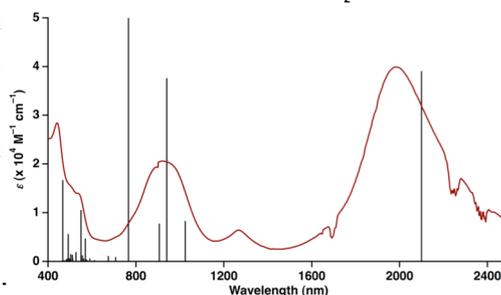
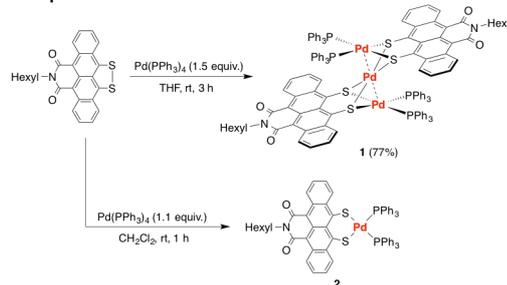


Figure 5. Light absorption spectrum of *tri*-Pd-TIDS with simulated absorption bands by TD-DFT.

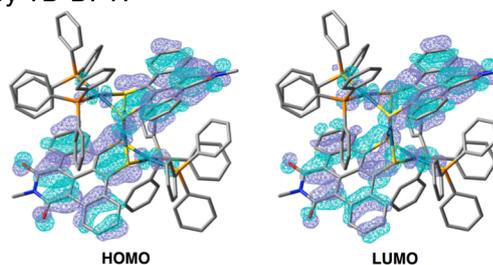


Figure 6. HOMO and LUMO structures of *tri*-Pd-TIDS provided by DFT calculations.

3. Conclusion

In my PhD works, I have developed two kinds of methods to extend the π -conjugated systems. One is metal complex involving $d\pi$ - $p\pi$ conjugation to show long-wavelength light absorption. In the first topic, I demonstrated the extended π -system can be easily constructed by coordinating aromatic disulfide ligand with metal. In addition, parallel ligation of the aromatic ligands generates expanded π -conjugation via d-orbital of metal to form a huge π -conjugated system. These achievements would contribute to development of metal complex material science.