

論文内容の要旨

論文題目

Photostable Luminescent Radicals:

(3,5-Dihalo-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radicals

and Their Gold Complexes

(光安定な発光性ラジカル : (3,5-ジハロ-4-ピリジル)ビス
(2,4,6-トリクロロフェニル)メチルラジカル及びそれらの金錯体)

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Introduction

Luminescent molecules have been extensively researched for many applications, such as organic light-emitting diodes (OLED) and luminescent probes. While most known luminescent molecules are in the closed-shell ground state, luminescent open-shell radicals have attracted interest recently. They exhibit luminescence at long wavelengths without extended π -conjugated structures. The radicals display a spin-allowed fluorescence from the doublet lowest excited state to the doublet ground state. Unlike conventional closed-shell fluorescent molecules, the emission processes of radicals do not suffer from annihilation through the triplet state, which is produced by singlet-triplet intersystem crossing or charge recombination. These unique characteristics allow the luminescent radicals as possible candidates for applied luminescent materials; so far, the number of reports of the luminescent radical is limited. Perchlorotriphenylmethyl radical and tris(2,4,6-trichlorophenyl)methyl (TTM) radical are known as rare examples of luminescent radicals. However, they decompose rapidly under irradiation with light to yield non-fluorescent products. Hence, development of more (photo)stable luminescent radicals is an important step in expanding the scope of the luminescent radicals. In the Ph.D. course, I conducted three research topics on a novel photostable luminescent organic radical, its halogen-substituted derivatives, and their gold complexes.

An open-shell (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl (PyBTM) radical

I have prepared a novel luminescent stable radical (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl (PyBTM) radical, with a unique molecular design: a pyridine ring was incorporated into the TTM skeleton in order to lower the energies of the frontier orbitals owing to the electronegativity of the nitrogen atom. The absorption spectrum in dichloromethane displayed a weak visible absorption band and a strong near-UV absorption band. Time-dependent (TD) DFT calculations suggested that the weak visible absorption maximum at $\lambda = 541\text{nm}$ could be assigned to the transition mainly from 128β (π orbital of pyridine) to 129β (the lowest unoccupied spin orbital), to form the lowest excited state, whereas the strong near-UV band at $\lambda = 370\text{ nm}$ was assigned to the transition mainly from 129α (SOMO) to 130α and 131α (antibonding π^* orbitals). The fluorescence spectrum in dichloromethane displayed emission maximum at $\lambda = 585\text{ nm}$ with the absolute photoluminescence quantum yields (ϕ) of 2%. PyBTM was luminescent at 77 K with excellent quantum yield ($\phi = 81\%$) in EPA (diethyl ether:isopentane:ethanol 5:5:2 v/v). The PyBTM molecules dispersed in a poly(methyl methacrylate) film showed luminescence with $\phi = 0.26$ at room temperature. These high quantum yields resulted from the suppression of the molecular vibrations that promote nonradiative decay. The photostability of PyBTM was evaluated and compared with that of TTM. When acetone solutions of PyBTM and TTM were irradiated at $\lambda = 370\text{ nm}$, the decay of the fluorescence intensity of PyBTM was 115 times smaller than that of TTM. This study revealed the principles of the fluorescence of the radical, potential for highly efficient fluorescence, and acquiring of the photostability.

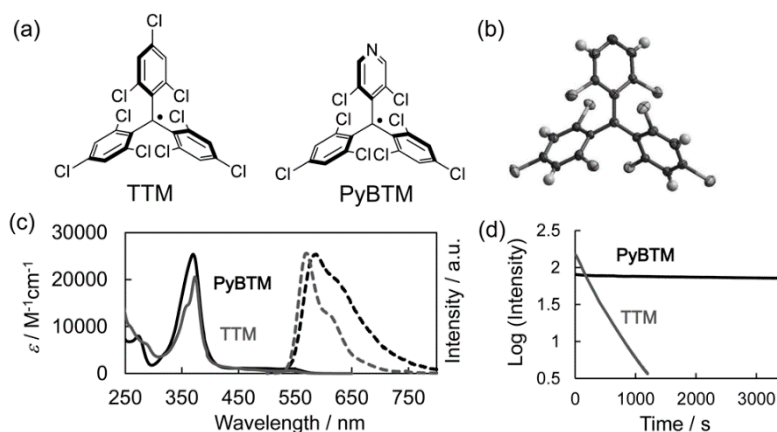


Figure 1 (a) Structures of TTM and PyBTM. (b) Crystal structure of PyBTM with thermal ellipsoids set at 50% probability. (c) Absorption and emission spectra of TTM (gray) and PyBTM (black). (d) Plots showing the emission decay of PyBTM and TTM in acetone under continuous excitation with light at $\lambda = 370\text{ nm}$.

(3,5-Dibromo-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (Br₂PyBTM) and (3,5-difluoro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (F₂PyBTM)

The six *ortho*-chlorine atoms in PyBTM sterically protect the radical center from reactions. Electron-withdrawing effect and electron resonance effect of the chlorine atoms are thought to provide further stability of the radical. I aimed to reveal how the choice of the halogen atoms on the pyridine ring affects the luminescent properties and stabilities of the radicals. I have prepared novel luminescent stable radicals (3,5-dibromo-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (Br₂PyBTM) and (3,5-difluoro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (F₂PyBTM). Spectroscopic studies showed the absorption and emission peak maxima shifted bathochromically in the order of F₂PyBTM < PyBTM < Br₂PyBTM. F₂PyBTM showed fluorescence quantum yield of 6% in chloroform, which is superior to those of PyBTM (3%) and Br₂PyBTM

(2%). Photostability in dichloromethane was also estimated. F₂PyBTM showed similar photostability to PyBTM, whereas Br₂PyBTM showed superior photostability. The improved photostability of Br₂PyBTM is probably because of the enhanced steric hindrance of the Br atoms, which more efficiently protect the radical center than the Cl or F atoms. This study elucidated that *ortho*-halogen atoms on the pyridine ring affect the fluorescence quantum yields and the photostability of the radicals.

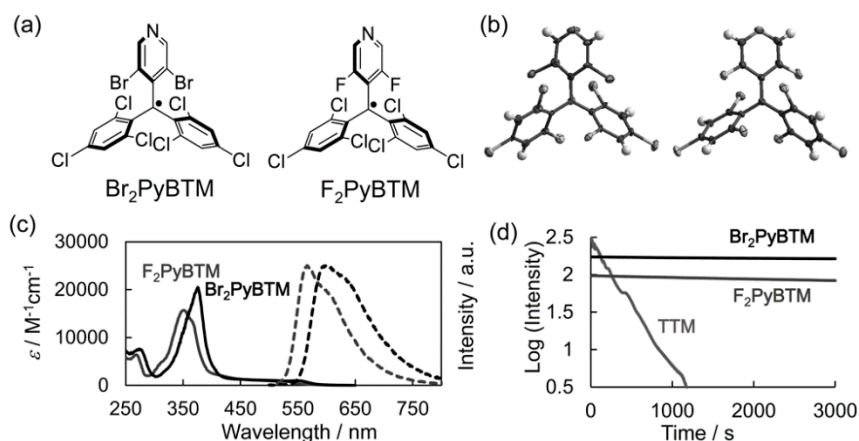


Figure 2 (a) Structures of Br₂PyBTM and F₂PyBTM. (b) Crystal structure of Br₂PyBTM (left) and F₂PyBTM (right) with thermal ellipsoids set at 50% probability. (c) Absorption and emission spectra of Br₂PyBTM (black) and F₂PyBTM (gray). (d) Plots showing the emission decay of Br₂PyBTM, F₂PyBTM and TTM in dichloromethane under continuous excitation with light at $\lambda = 370$ nm.

Enhancement of luminescent properties of PyBTM by coordination to gold

The nitrogen atom of PyBTM acts as a coordination site to proton, Lewis acids, or metal ions. Although the protonation of PyBTM quenched the fluorescence, here I report enhancement of the luminescent properties of PyBTM through its coordination to gold(I). Novel luminescent radical complex, [Au^I(PyBTM)PPh₃]⁺X⁻ (X = ClO₄⁻, BF₄⁻) was synthesized. As far as I know, it is the first example of a luminescent metal complex that contains a luminescent organic radical as a ligand. Single-crystal X-ray diffraction revealed a two-coordinate linear structure. The absorption spectrum in dichloromethane displayed three absorption maxima at $\lambda = 566, 434,$ and 380 nm, and the fluorescence band ($\lambda = 653$ nm) was bathochromically shifted compared with that of PyBTM. TDDFT calculations confirmed that frontier molecular orbitals related to absorption transitions were mainly on the PyBTM ligand. Their energies were lowered compared with PyBTM owing to coordination to Au^I

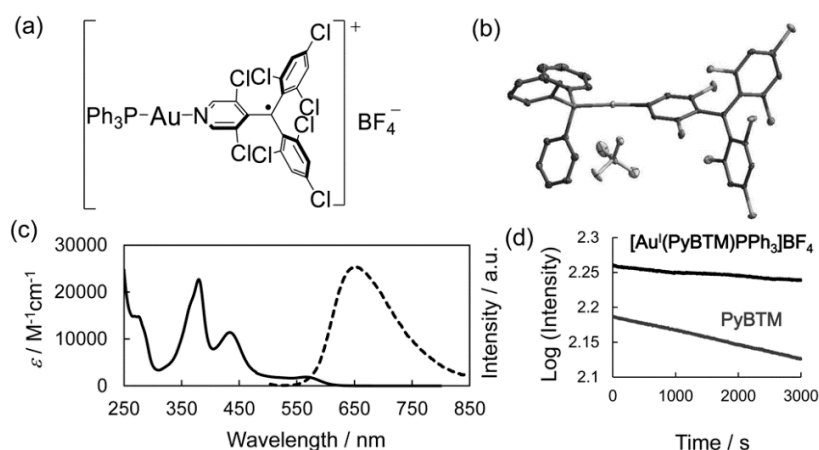


Figure 3 (a) Structure of [Au^I(PyBTM)PPh₃]⁺BF₄⁻. (b) Crystal structure of [Au^I(PyBTM)PPh₃]⁺BF₄⁻ with thermal ellipsoids set at 50% probability. (c) Absorption and emission spectra of [Au^I(PyBTM)PPh₃]⁺BF₄⁻. (d) Plots showing the emission decay of [Au^I(PyBTM)PPh₃]⁺BF₄⁻ and PyBTM in dichloromethane under continuous excitation with light at $\lambda = 370$ nm.

cation. Fluorescence quantum yield ($\phi = 8\%$) was four times that of PyBTM. The fluorescence lifetime measurements revealed that the doubling of the rate of fluorescence transition and halving of the rate of non-radiative decay caused the quadrupling of the quantum yield. Photostability under irradiation to UV light ($\lambda = 370$ nm) was investigated. The decay of the emission intensity of $[\text{Au}^{\text{I}}(\text{PyBTM})\text{PPh}_3]\text{BF}_4$ was three times slower than that of PyBTM. $[\text{Au}^{\text{I}}(\text{Br}_2\text{PyBTM})\text{PPh}_3]\text{BF}_4$ and $[\text{Au}^{\text{I}}(\text{F}_2\text{PyBTM})\text{PPh}_3]\text{BF}_4$ were prepared and studied similarly. Especially $[\text{Au}^{\text{I}}(\text{F}_2\text{PyBTM})\text{PPh}_3]\text{BF}_4$ showed the highest fluorescence quantum yield ($\phi = 20\%$) among these radicals. This study disclosed that the luminescent properties and the photostability can be modulated positively by external stimuli, such as gold(I).

Conclusion

Novel luminescent radicals were synthesized and their electronic structures and optical properties in solutions were investigated. They showed unprecedented high photostability for luminescent radicals, and photoluminescence quantum yield was improved by encapsulation in rigid solvent or polymer, chemical modification on pyridine ring, or coordination to gold cation. These studies showed the possibility of the luminescent radicals as useful, stable and efficient luminescent materials, which has not seriously considered previously. The methods established in this study give important insights to realize novel luminescent radicals with improved photostability and fluorescence quantum yields for their future application.

【Publications related to the thesis】

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