

## 論文の内容の要旨

化学的刺激による (3,5-ジクロロ-4-ピリジル)  
ビス (2,4,6-トリクロロフェニル) メチルラジカルの光機能制御

(Control of Photofunctions of (3,5-Dichloro-4-pyridyl)  
bis(2,4,6-trichlorophenyl)methyl Radical Using Chemical Stimuli)

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## Introduction

Luminescence of open-shell molecules (i.e., monoradicals) has attracted growing interest owing to the unique characteristics such as long emission wavelength and high efficiency in electroluminescence, based on their lowest-energy doublet excited ( $D_1$ ) and doublet ground ( $D_0$ ) states.<sup>[1]</sup> A rare class of luminescent radicals is triarylmethyl radicals. A pyridyl group containing-triarylmethyl radical PyBTM (PyBTM = (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)-methyl radical) exhibits excellent chemical stability in photoexcited condition.<sup>[2]</sup> The nitrogen atom in PyBTM acts as a metal-coordination site, and the coordination to gold(I) afforded increased photostability and absolute fluorescence quantum yield ( $\phi_{em}$ ) in  $[Au^I(PyBTM)PPh_3](BF_4)$ .<sup>[3]</sup> The coordination of PyBTM to metal ion is an efficient way to achieve novel doublet-based photofunctions, where one of the important steps for the future application is to develop stimuli-responsive photofunctions.

In this study, I focused on modulating the photofunctions of PyBTM using chemical stimuli, which has not been established so far, and developed two stimuli-responsive radical systems:  $Au^I(C_6F_5)(PyBTM)$  (**1**) and  $[(C_6F_5)_3B-PyBTM]$  (**2**). Complex **1** is the first example of luminescent organometallic paramagnetic complexes, and displayed solvent-sensitive emission properties. In **2**, the reaction between  $B(C_6F_5)_3$  as a Lewis acid and  $NEt_3$  as a Lewis base was shown to reversibly modulate the fluorescence characteristics of PyBTM.

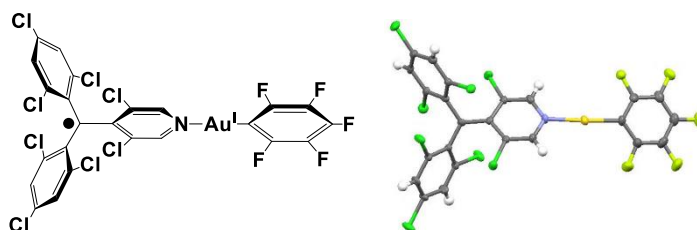
## Unique solvent-dependent optical properties of a novel luminescent gold(I) complex with a PyBTM radical

A neutral organometallic gold(I) complex **1** (Figure 1) containing PyBTM and a polar  $C_6F_5$  group was synthesised and its structure and novel optical properties were analysed. Single-crystal X-ray diffraction analysis revealed a two-coordinate linear structure around the gold(I) ion. In the PyBTM ligand, the central carbon atom formed  $sp^2$  hybridised geometry, confirming its radical character. ESR and SQUID measurements and DFT calculations indicated the existence of a spin of  $S = 1/2$  delocalised onto the PyBTM moiety.

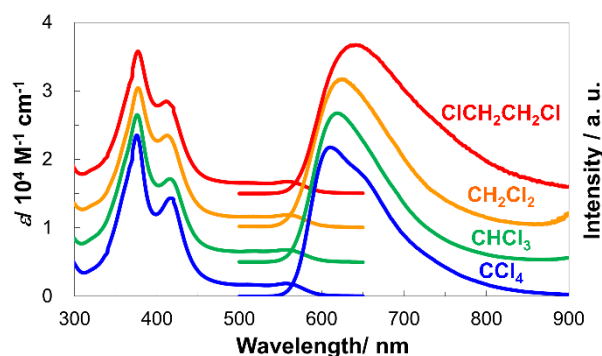
Complex **1** in  $CHCl_3$  displayed three characteristic transition bands at the absorption peak wavelengths ( $\lambda_{abs}$ ) = 557, 416, and 376 nm (Figure 2, Black dotted). Compared with the spectrum of PyBTM, the emergence of the second transition band and the bathochromic shift of the lowest-energy transition band at 550-600 nm region with increased  $\epsilon$  are detected; the spectral character is similar to those of  $[Au^I(PyBTM)PPh_3](BF_4)$  and the other N-modified PyBTMs. **1** exhibited luminescence with an emission peak wavelength ( $\lambda_{em}$ ) of 619 nm upon photoexcitation ( $\lambda_{exc} = 416$  nm), confirming that **1** is the first luminescent organometallic complex with a coordinated luminescent radical. The  $\Phi_{em}$  of 0.04 is higher than that of PyBTM in  $CHCl_3$ , showing improved luminescence upon coordination to the  $Au^I(C_6F_5)$  moiety.

Complex **1** displayed solvent-dependent luminescent characteristics in halogenated solvents  $CCl_4$ ,  $CHCl_3$ ,  $CH_2Cl_2$ , and  $ClCH_2CH_2Cl$  (Figure 2). The  $\lambda_{em}$  shifted bathochromically as the polarity (dielectric constant) of the solvents increased. The other optical properties were also affected by the polarity of solvents.

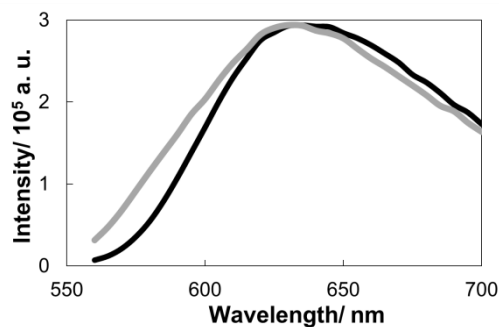
The  $\Phi_{em}$  and the fluorescence lifetime ( $\tau$ ) were 0.23 and 32 ns in  $CCl_4$ , 0.04 and 7.2 ns in  $CHCl_3$ , 0.01 and 6.8 ( $\tau_1$ ) and 1.2 ( $\tau_2$ ) ns in  $CH_2Cl_2$ , 0.01 and 7.2 ( $\tau_1$ ) and 1.2 ( $\tau_2$ ) ns in  $ClCH_2CH_2Cl$ . **1** in  $CCl_4$  showed the highest  $\phi_{em}$  among all the PyBTM derivatives in the solution state. The  $CH_2Cl_2$  and  $ClCH_2CH_2Cl$  solutions indicated the existence of two emissive components (i.e.,  $\tau_1$ - and  $\tau_2$ -components). The existence of two components in  $CH_2Cl_2$  was confirmed by the time-resolved fluorescence spectroscopy, in which the  $\tau_1$ -component showed  $\lambda_{em} = 625$  nm with a small shoulder at



**Figure 1.** The chemical (left) and the crystal (right) structures of **1**. Thermal ellipsoids are set at 50% probability (right).



**Figure 2.** The UV/vis absorption (left) and the fluorescence (right) spectra of **1**.  $CCl_4$ : red, the highest.  $CHCl_3$ : orange, middle upper.  $CH_2Cl_2$ : green, middle lower.  $ClCH_2CH_2Cl$ : blue, the lowest.

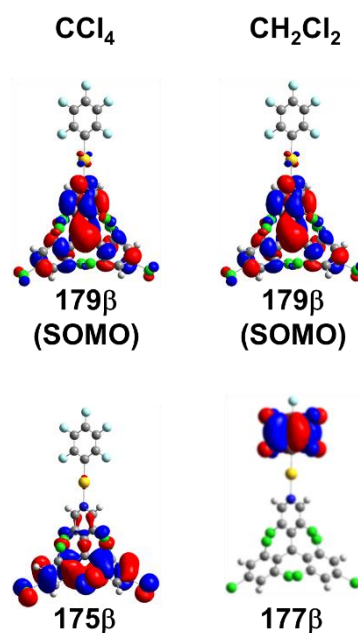


**Figure 3.** The time-resolved fluorescence spectra of **1** in  $CH_2Cl_2$ .  $\tau_1$ : grey.  $\tau_2$ : black.

580 nm while the  $\tau_2$ -component showed  $\lambda_{em}$  at around 635 nm (Figure 3). Namely, solvent-induced dual fluorescence was observed for the first time in radicals.

The exceptional  $\phi_{em}$  and  $\tau$  values observed in  $CCl_4$  suggest the nature of its emissive excited state different from those in other solvents. To confirm this suggestion, we examined solvent dependence of the electronic structure and transition energy calculated using DFT and time-dependent (TD-) DFT (UM06/SDD for Au, 6-31G(d) for C, H, N, Cl and F). TD-DFT calculations indicated that the lowest energy  $175\beta \rightarrow 179\beta$  transition induces a PyBTM-centred excited state in  $CHCl_3$ ,  $CH_2Cl_2$ , and  $ClCH_2CH_2Cl$  (Figure 4), observed typically in PyBTM derivatives and  $[Au^I(PyBTM)PPh_3](BF_4)$ . The similarity of  $\tau$  ( $\tau_1$  in  $CH_2Cl_2$  and in  $ClCH_2CH_2Cl$ ) in these solvents supports their similarity in the character of the excited states. In  $CCl_4$ , on the other hand, lowest-energy  $177\beta \rightarrow 179\beta$  electronic transition was predicted to form a ligand-to-ligand charge transfer (LLCT) excited state, where the  $C_6F_5$  and PyBTM moieties act as electron donor and acceptor, respectively (Figure 4). The emission from the LLCT excited state would cause the  $\phi_{em}$  and  $\tau$  values.

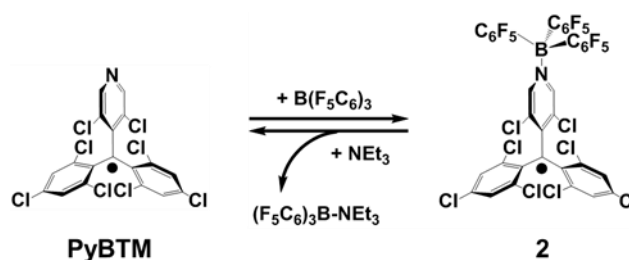
The polar character of  $C_6F_5$  group is expected to play an important role in forming the polarity-sensitive excited state in **1**. This study provides new molecular design principle for realising stimuli-responsive emissive radicals.



**Figure 4.** Molecular orbitals involved in the lowest-energy electronic transition in  $CCl_4$  and  $CH_2Cl_2$ . Solvent effects were treated using CPM model.

### Modulation of optical properties of PyBTM based on reversible Lewis acid-base reaction

The UV/vis absorption and emission spectral changes of PyBTM were investigated upon the Lewis acid-base compleximetric titrations with  $B(C_6F_5)_3$  and  $NEt_3$ , described as Scheme 1 and Figure 5. The absorption and emission maxima at 370 and 586 nm decreased and new transition bands at 442, 575 (absorption) and 666 nm (emission) appeared and enhanced progressively with gradual addition of  $B(C_6F_5)_3$ . The absorption maxima at 380 nm also emerged.



**Scheme 1.** The reaction of PyBTM upon addition of  $B(C_6F_5)_3$  and  $NEt_3$ .

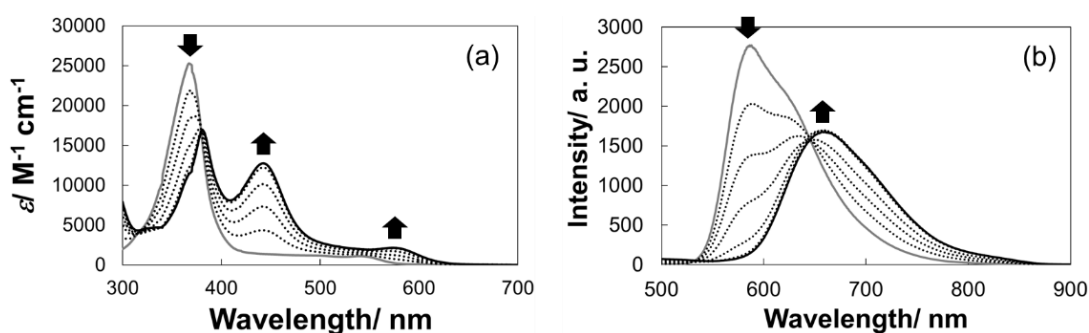
All the additional bands originated from the coordination of the nitrogen atom to the boron atom upon its complexation. The absorption spectral change was similar to that of the titration of  $H^+$  to the  $CH_2Cl_2$  solution of PyBTM, and, the final spectrum (black in Figure 4a) was also similar to that of  $[Me-PyBTM](BF_4)$ . The lowest-energy absorption band at 557 nm was attributed to the transition from the  $D_0$  state to the  $D_1$  state, which was bathochromically shifted in comparison with the original band of PyBTM. The shift indicated that the energy gap was reduced presumably owing to the decreased electron density on the pyridyl moiety. The estimated binding

constant  $K$  was  $2.8(5) \times 10^5 \text{ M}^{-1}$  with fitting the change of the absorbance at 442 nm upon the titration.

The emission band also changed upon addition of  $\text{B}(\text{C}_6\text{F}_5)_3$ , in which the emission band was red-shifted and extended beyond 850 nm, indicating NIR emission character of **2**. The bathochromically shifted emission band corresponded to that of the decreased lowest-energy absorption band.

When  $\text{NEt}_3$  was added to the solution of **2**, the absorption and emission spectra recovered as those of the initial spectra of PyBTM, suggesting that dissociation of  $\text{B}(\text{C}_6\text{F}_5)_3$  from PyBTM occurred and free PyBTM was regenerated. These results revealed that the optical properties including the fluorescent colour of PyBTM could be tuned reversibly using Lewis acid-base reaction.

The  $\phi_{\text{em}}$  ( $\lambda_{\text{exc}}$  at 380 nm) and the  $\tau$  ( $\lambda_{\text{exc}}$  at 464 nm) of **2** in  $\text{CH}_2\text{Cl}_2$ , which was prepared by adding 2.0 equivalents of  $\text{B}(\text{C}_6\text{F}_5)_3$  to the  $\text{CH}_2\text{Cl}_2$  solution of PyBTM, were 0.03 and 5.5 ns, respectively. It implies that the nature of its emission was fluorescence.



**Figure 5.** The UV/vis absorption (a) and fluorescence (b) spectra of PyBTM in  $\text{CH}_2\text{Cl}_2$  upon addition of  $\text{B}(\text{C}_6\text{F}_5)_3$ . The grey lines are the initial spectra of PyBTM. The black lines are the final spectra after total addition of  $\text{B}(\text{C}_6\text{F}_5)_3$ .

## Conclusion

The novel complex **1** was synthesised and its solvent-dependent optical properties were elucidated. Enhanced  $\phi_{\text{em}}$  and  $\tau$  were observed in  $\text{CCl}_4$ , which would be resulted from the emission from the LLCT excited state. In  $\text{CH}_2\text{Cl}_2$  and  $\text{ClCH}_2\text{CH}_2\text{Cl}$  solutions, dual fluorescence was observed for the first time in radicals. The optical properties of PyBTM was controlled reversibly using  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{NEt}_3$  based on the Lewis acid-base reaction. The  $\text{B}(\text{C}_6\text{F}_5)_3$  adduct **2** displayed red-shifted fluorescence. This study developed efficient methods to prepare stimuli-responsive luminescent radicals or to control their properties using chemical stimuli.

[1] (a) H. Namai; H. Ikeda; Y. Hoshi; N. Kato; Y. Morishita; K. Mizuno. *J. Am. Chem. Soc.* **2007**, *129*, 9032. (b) Q. Peng; A. Obolda; M. Zhang; F Li. *Angew. Chem. Int. Ed.* **2015**, *54*, 7091. [2] Y. Hattori; T. Kusamoto; H. Nishihara. *Angew. Chem. Int. Ed.* **2014**, *53*, 11845. [3] Y. Hattori; T. Kusamoto; H. Nishihara., *Angew. Chem. Int. Ed.* **2015**, *54*, 3731.