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Photophysical and photochemical properties of difluoroboronated 1,3-diketones having the ferrocene moiety studied by steady-state and laser flash photolyses

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ABSTRACT

We synthesized 1,3-diketones having the ferrocene moiety (FcDKPhs) and the corresponding difluoroboronated complexes (Fc@Phs), and investigated the photophysical and photochemical properties in solution by steady-state and laser flash photolyses. FcDKPhs and Fc@Phs had absorption bands with large absorptivities in the UV-region and ones with small absorptivities in the Vis-region, but provided neither fluorescence nor phosphorescence. FcDKPhs decomposed upon exposure to UV–vis light while Fc@Phs were stable. No transient signals obtained upon laser flash photolysis of FcDKPhs and Fc@Phs demonstrated absence of intersystem crossing to the triplet states. Fc@Phs efficiently convert absorbed photon energy to heat.

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1. Introduction

It is reported that 1,3-dibenzoylmethane (DBM), a representative of 1,3-diketones, and their derivatives take enol forms as the molecular configuration at room temperature, and that they are non-fluorescent in solution due to the formation of non-chelated enols (NCE) in the excited singlet states [1–3]. The typical isomerism of DBM is shown in Scheme 1.

Some of photoirradiated DBMs decompose in solution according to the Norrish Type I mechanism [3]. Once aromatic 1,3-diketones are coordinated to difluoroboronated boron (BF₂), the BF₂ complexes of the 1,3-diketones (BF₂DK) are emissive in solution and the solid state [4–6]. Changing the arene systems as the chromophores in the BF₂DKs enables to tune the fluorescence colors and quantum yields [7]. It seems that the chromophores in BF₂DKs play important roles for controlling photophysical and photochemical properties.

Ferrocene (Fc) is a well-known metallocene that has cyclopentadienyl ligands and core metal of Fe(II), and has been used as a redox responsive unit owing to the stability, ease of functionalization and well-defined electrochemical properties [8]. Recently, preparation of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

(BODIPY) conjugated with the Fc moiety, and their chemical and electrochemical properties have been investigated [9–13]. The colors of ferrocenyl BODIPYs in solution are variable upon chemical and electrochemical oxidation [9,13]. Dy- and tri-ads of Fc and the BODIPY cores were studied as electron donor-acceptor systems for understanding the charge-separation mechanisms using ultrafast spectroscopic measurements [11]. However, photochemical and photophysical investigations for ferrocene-conjugated BF₂ complexes except BODIPYs are few because variety of the chelating ligands to BF₂ is limited [14,15]. To our knowledge, there are no reports on synthetic and photochemical researches of BF₂DK having the Fc moiety as the chromophore.

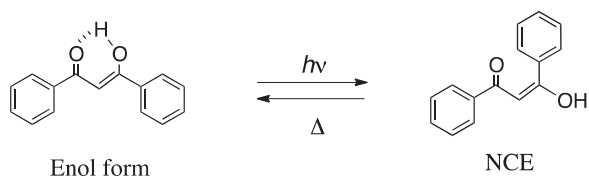
In the present communication, we report synthesis of the 1,3-diketones having the Fc moiety and the corresponding BF₂DK (FcDKPhs and Fc@Phs, respectively, see Chart 1), and the photochemical and photophysical properties studied by stationary and laser flash photolysis techniques. Fc@Phs were found to be nonluminescent and robust to UV–vis photoirradiation. FcDKPhs were also nonluminescent, but labile.

2. Experimental

The preparation procedures and the NMR data for FcDKPhs and Fc@Phs used in this study and experimental details are deposited in Supplementary data.

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Scheme 1. Isomerization processes of DBM.

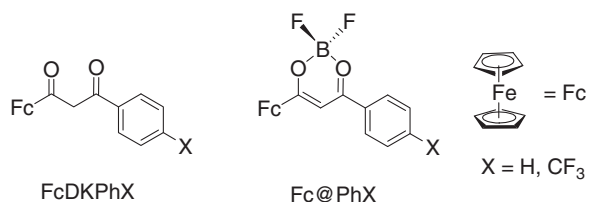


Chart 1. Molecular structures and abbreviations of 1,3-diketones (left) and BF_2DKs (right) used in this study. The keto form is representative for FcDKPhX.

3. Result and discussion

Fig. 1 shows absorption spectra of FcDKPhs and Fc@Phs in CHCl_3 .

The absorption spectra have large absorptivities ($10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) due to the $\pi\text{-}\pi^*$ transitions in the UV-region and ones with small absorptivities ($10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) due to metal-to-ligand-charge-transfer (MLCT) transitions originated from the Fc moiety in the Vis-region. The molar absorption coefficients (ϵ) determined for FcDKPhs and Fc@Phs are listed in Table 1.

Appearance of the intense absorption bands in the UVA region indicates that FcDKPhs take enol forms in the ground state. The absorption bands of Fc@Phs were found to undergo red shifts (ca. 20 nm for the $\pi\text{-}\pi^*$ band and ca. 70 nm for the MLCT band) compared with those of the corresponding FcDKPhs. The MLCT absorption bands of Fc@Phs were found to red-shift on introducing the electron withdrawing group ($-\text{CF}_3$) at the *para*-position of the benzene ring as the counter chromophore. The absorption spectra of Fc@Phs in cyclohexane (CH) and acetonitrile (ACN), deposited in Supplementary data as Fig. S1, are similar to those in CHCl_3 . From these observations, it is inferred that Fc@Phs have little charge-transfer character in the ground state. Fluorescence at 295 K and phosphorescence in a mixture of methylcyclohexane and isopentane (3:1, v/v, MP) at 77 K were absent from FcDKPhs and Fc@Phs, indicating that excited singlet states deactivate via nonradiative processes and chemical reactions.

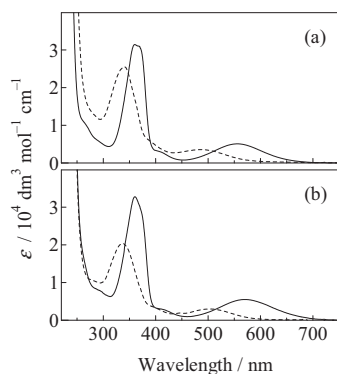


Fig. 1. Absorption spectra in CHCl_3 at 295 K for FcDKPh ((a), dash), Fc@Ph ((a), solid), FcDKPh CF_3 ((b), dash) and Fc@Ph CF_3 ((b), solid). Fluorescence at 295 K and phosphorescence in a mixture of methylcyclohexane and isopentane (3:1, v/v, MP) at 77 K were absent from FcDKPhs and Fc@Phs.

Table 1
Molar absorption coefficients (ϵ) of FcDKPhs and Fc@Phs in CHCl_3 .

Compound	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{abs}}/\text{nm}$)
FcDKPh	26100(340), 3400 (485)
FcDKPh CF_3	20300 (337), 2700 (504)
Fc@Ph	31700 (365), 4700 (555)
Fc@Ph CF_3	32500 (360), 5300 (570)

Fig. 2 shows absorption spectral changes upon steady-state photolysis ($\lambda > 290 \text{ nm}$) of FcDKPhs in aerated CH at 295 K.

With the lapse of irradiation time, the intensities of the absorption bands at 340 nm decreased. These observations indicate that FcDKPhs are labile to photoirradiation. The decomposition may proceed in the excited singlet state because the absorption spectra changed in aerated solution. The plausible photochemical reactions in the excited singlet states of FcDKPhs are the Norrish Type I and intramolecular electron transfer between the Fc moiety and the 1,3-diketone backbone. The quantum yields for the decomposition were too small to determine from the absorption changes, presumably, less than 10^{-4} . Conversely, we performed steady-state photolysis of Fc@Phs under the same conditions as for FcDKPhs. No changes in the absorption spectra of Fc@Phs were found, indicating that Fc@Phs are stable upon photoirradiation without apparent photochemical reactions. From these facts, it is inferred that coordinating FcDKPhs to the BF_2 unit results in an increase of photostability in Fc@Phs.

To understand relaxation processes of the excited states in FcDKPhs and Fc@Phs, we performed nanosecond laser flash photolysis. We observed no transient signals in the wavelength region 370–640 nm after 100 ns upon 355 nm laser pulsing in the CH solution of FcDKPhs and Fc@Phs. The observed transient spectra are deposited in Supplementary data as Fig. S2. Upon photoexcitation of 1,3-diketones, NCE formation is characteristic in the excited singlet states as shown in Scheme 1 [1–3], but no transient spectra due to the NCE of FcDKPhs were observed in the present study. Based on these experimental facts, no triplet states of FcDKPhs and Fc@Phs would be formed upon photolysis of these compounds. In other words, intersystem crossing from the lowest excited singlet states (S_1) to the triplet states is absent. We have confirmed that FcDKPhs and Fc@Phs showed no fluorescence in solution, that FcDKPhs underwent photodecomposition and that no appreciable photochemical reactions in the S_1 state were recognized upon steady-state photolysis of Fc@Phs in CH. Consequently, it is plausible that the excited singlet states of FcDKPhs deactivate competitively by decomposition and internal conversion to the ground state whereas those of Fc@Phs relax via

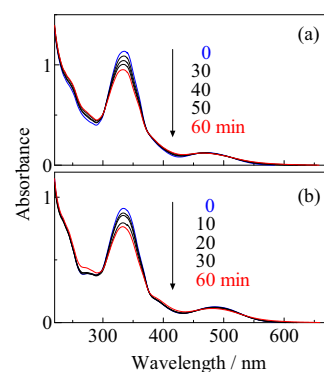


Fig. 2. Absorption spectral changes upon photolysis ($\lambda > 290 \text{ nm}$) of FcDKPh (a) and FcDKPh CF_3 (b) in aerated CH at 295 K.

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