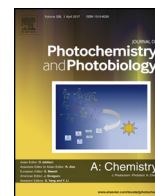




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A:  
Chemistryjournal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

Invited feature article

Visible-light-mediated C(sp<sup>3</sup>)-H activation by photo-induced hydrogen-atom transfer

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## ARTICLE INFO

## Article history:

Received 17 July 2017

Received in revised form 18 September 2017

Accepted 30 September 2017

Available online xxx

## Keywords:

Triplet-excited flavin

Hydrogen-atom-transfer

C–H activation

Visible light

## ABSTRACT

Visible-light-mediated C(sp<sup>3</sup>)-H activation has recently emerged as a powerful tool for functionalization of C–H bonds. In this work, we reported that the triplet state of Lumiflavin is a good candidate to directly abstract hydrogen atom from C(sp<sup>3</sup>)-H substrates. Following photoexcitation by visible light (440 nm), the organic molecule Lumiflavin (LF) can form the excited-state <sup>3</sup>\*LF, which is competent to oxidize a range of C–H substrates. Product analysis and kinetic data showed that these reactions occurred via rate determining hydrogen-atom-transfer (HAT), with a linear correlation for log(*k*) vs BDE (C–H) and KIE = 3.2 for 9, 10-dihydroanthracene (DHA).

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## 1. Introduction

Photoredox catalysis is a leading strategy extensively applied in energy conversion process such as water splitting and dye-sensitized solar cell [1]. Recently, this has also been applied to organic synthesis including C(sp<sup>3</sup>)-H functionalization [2]. A key step in photoredox catalytic C(sp<sup>3</sup>)-H functionalization is that the photosensitizer could engage in single-electron transfer (SET) events after excitation [3]. However, the SET initiation way also limits the application of photoredox catalysis in C(sp<sup>3</sup>)-H activation since the weak electron donor ability of most of C(sp<sup>3</sup>)-H substrates except activated C(sp<sup>3</sup>)-H such as α-H of amine [4]. To this extent, photoinduced hydrogen atom transfer is a promising protocol for visible-light-mediated C(sp<sup>3</sup>)-H functionalization because the energetics and kinetics of this HAT reaction between the light absorbing catalyst and a given C(sp<sup>3</sup>)-H substrate predominately rely on the bond dissociation energy (BDE) rather than the redox potential. In addition, the selectivity of catalytic HAT C(sp<sup>3</sup>)-H functionalization could be controlled by a combination of steric and electronic factors. Actually, photo-catalytic HAT C(sp<sup>3</sup>)-H functionalization is an old strategy in photochemistry. The simple (aromatic) ketones, such as benzophenone [5], were classical photocatalyst for C(sp<sup>3</sup>)-H functionalization via HAT pathway. Unfortunately, only UV light absorption has limited the

number of applications of organic photochemical C–H bonds activation. A photocatalyst with visible light absorption and with the ability of hydrogen atom abstraction from C(sp<sup>3</sup>)-H bond should be very interesting for C(sp<sup>3</sup>)-H functionalization.

As for the physical and chemical properties of flavin derivatives (Fig. 1), with maximum absorption around 365 nm and 445 nm and resulting in their characteristic yellow color, have been of considerable experimental interest due to the central role that flavins play as biological redox reagents and relevant photosensitive fluorochrome [6]. The core chemistry behind the unique physicochemical processes involving flavins stems from a coupled electron-proton transfer involving the isoalloxazine ring [7,8]. The versatility of flavin's chemical behavior is largely due to its unique ability to undergo both sequential (two 1e<sup>-</sup>/1H<sup>+</sup>) and simultaneous (one 2e<sup>-</sup>/2H<sup>+</sup>) reductions [9,10]. Irradiation with blue light results in spin-allowed transition to highly fluorescent short-lived singlet-excited state [11–14]. Intersystem crossing with high quantum yield generates the triplet-excited state very efficiently, and the resulting triplet-excited state (<sup>3</sup>\*Rib) is relative long-lived and as a bi-radical which is a powerful oxidant with E<sup>o</sup> ~ +1.7 V vs NHE compared to the ground state riboflavin (E<sup>o</sup> = -0.3 V vs NHE) leading to direct oxidation of most types of biomolecules such as tyrosine and tryptophan. [15–18] Here we reported that the triplet state of Lumiflavin (<sup>3</sup>\*LF, Fig. 1) is a good hydrogen atom acceptor to abstract hydrogen atom from C(sp<sup>3</sup>)-H substrates.

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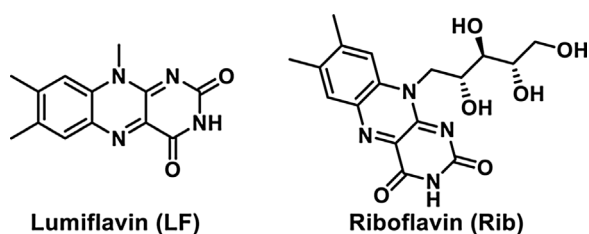


Fig. 1. The structure of Lumiflavin (LF) and Riboflavin (Rib).

## 2. Material and methods

### 2.1. Chemicals and reagents

All reagents of commercial quality were from freshly opened containers or were purified according to the standard methods before use. Reagent grade (HPLC) acetonitrile was distilled over  $P_2O_5$  under argon before use. Lumiflavin (LF) was purchased from Aldrich and was used without further purification. As for C–H substrates, 9, 10-dihydroanthracene (DHA), Xanthane, Triphenylmethane, Cumene, Fluorene, Indene and Cyclohexa-1, 4-diene

were obtained from commercial suppliers and used without further purification.

$d_4$ -DHA was synthesized according to reference [19]. The samples for laser flash photolysis were all performed via freeze-pump-thaw cycles (at least three times).

### 2.2. Laser flash photolysis

Transient absorption spectra were obtained using Continuum Surelite Laser, delivering ca 5 ns pulses at 355 nm. A pulsed Xenon lamp of XP920 setup provided analyzing light that was passed through  $1 \times 1$  cm optical glass sample cuvette in a right-angle configuration and through a monochromator before hitting photomultiplier detector. The PMT signal was converted and digitized using a digital real-time oscilloscope (TDS3012C). Transient absorption traces were recorded by LP920 spectrometer by Edinburgh Instruments (EI) and the data was analyzed by L900 software.

### 2.3. UV-vis spectrum and GC-MS

UV-vis spectrum was recorded on Agilent Cary 100UV-Vis spectrometer using  $1 \times 1$  cm optical glass sample cuvette.

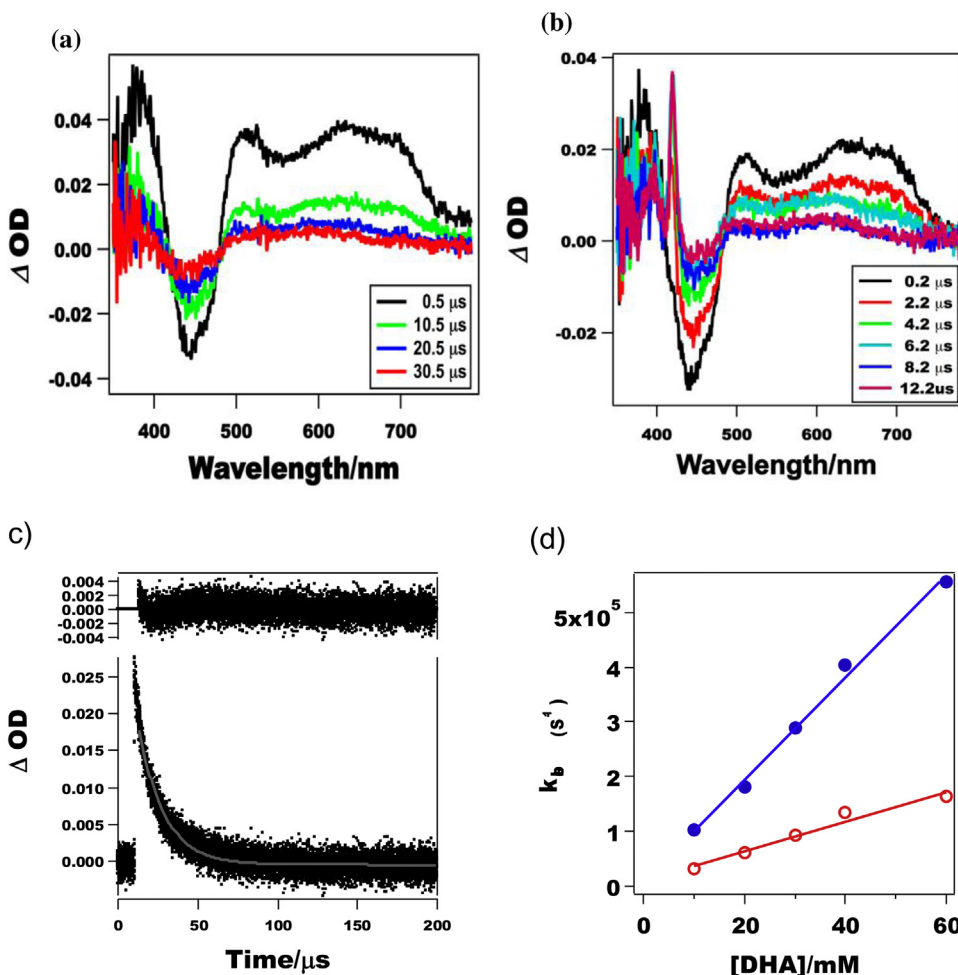


Fig. 2. (a) Transient absorption spectroscopy of LF after the laser flash (440 nm) at 0.5, 10.5, 20.5 and 30.5  $\mu$ s. The absorbance at 390, 510, 640 and 700 nm, as well as the bleach at 445 nm, is due to the formation of  $^3LF$ . The lifetime of this triplet state can be obtained by monitoring its absorbance decay or the bleach recovery. (b) Transient absorption spectroscopy of LF in the presence of 10 mM DHA after the laser flash (440 nm) at 0.2, 2.2, 4.2, 6.2, 8.2 and 12.2  $\mu$ s. The decay of  $^3LF$  can be obtained by monitoring the decay at 700 nm where have no other absorption. The final absorption at 418, 391 and 355 nm was due to the formation of anthracene; and the weak absorption around 500 and 604 nm was due to the neutral radical of Lumiflavin, LFH $^{\bullet}$ . (c) Kinetic traces for triplet-excited state,  $^3LF$  decay monitored in real-time at 700 nm following laser pulses at 440 nm; (d) Plots of  $k_{obs}$  versus [DHA] (blue dot) or [ $d_4$ -DHA] (red circle) for the reaction with  $^3LF$ . Observed pseudo first-order rate constant as function of [DHA] or [ $d_4$ -DHA]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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