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AUTHOR(S):
Tanaka, Kazuo; Kitamura, Narufumi; Inafuku, Kenichi; Chujo, Yoshiki

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Acceleration of Guanine Oxidation under Visible Light Irradiation by Photon Upconversion Based on Triplet–Triplet Annihilation

Kazuo Tanaka, Narufumi Kitamura, Kenichi Inafuku, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

ABSTRACT

We report the fluorescent polymer complex which can show fluorescence emission at 380 nm with the excitation of 520 nm in aqueous media. This photon upconversion based on triplet–triplet annihilation can efficiently take place via inter-molecular energy transfers between the Ru complex as a sensitizer and anthracene molecules as an emitter captured into the water-soluble network polymers. We performed the oxidation reaction of 2'-deoxyguanosine by riboflavin in the presence of the polymer complex with the visible light irradiation. It was clearly indicated that oxidative decomposition can be accelerated by UV light generation via upconversion based on triplet–triplet annihilation.

INTRODUCTION

Photoreactions are powerful methods to visualize and regulate biological events in the cells or vital body. Various kinds of molecular probes such as environmental-responsive fluorophores, photo-therapeutic anticancer drugs, and photo-manipulation systems of biomolecules have been developed, and some of them have been clinically used. In order to proceed photoreactions in high yields, short-wavelength light is favorable. However the photo-degradation of the drugs or the probe molecules and the damages to living organisms will take place under biological conditions. In addition, decay of light through vital organs should be considerable issue in the use of short-wavelength light for investigating deep positions inside body.

Upconversion (UC) to generate shorter-wavelength light emission than that of excitation is one of solves to overcome these problems. Indeed, the multi-photon step has been already applied for biotechnical analyzer, such as multi-photon microscopy. However, large power and coherent light should be required to raise multi-photon excitation. In contrast, UC via triplet–triplet annihilation (TTA) can proceed with weak power and non-coherent light such as sun light. Several groups have reported UC using nanoparticles for bioimaging. On the other hand, very few were the applications of TTA-supported UC process to the photoreaction with biomolecules.

RESULTS AND DISCUSSION

Herein, we present TTA-supported UC system which can show fluorescence emission at 380 nm with the excitation of 520 nm in the aqueous phase using the polymer complex. TTA-supported UC can efficiently occur in water via inter-molecular energy transfers between the Ru complex as a sensitizer and anthracene molecules as an emitter captured into the water-soluble network polymers. The oxidation reaction of 2'-deoxyguanosine (dG) by riboflavin was performed under visible light irradiation in the presence of the polymer complex, and it was confirmed that oxidative decomposition can be accelerated via UC. This is the first example, to our knowledge, for developing the water-soluble polymer material which can show anti-Stokes fluorescence and applying TTA-supported UC to the photochemical reaction with biomolecules in aqueous media.
Riboflavin can work as a photoreaction through DNA carcinogenesis but also one of solution processes. We have continuously challenged to apply photon UC system to the photochemical reactions in vivo.

**REFERENCES**


*Corresponding Author. Yoshiki Chujo, E-mail: chujo@chujo.synchem.kyoto-u.ac.jp*