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Reference to a book :

2. Kinney JM, Tucker HN : Energy Metabolism. Tissue determinants and cellular corollaries. Raven Press, New York, 1992

Reference to a chapter in a book :

3. Takaue Y, Kawano Y, Kuroda Y : Mobilization of peripheral blood stem cells for autografts. In : Levit DJ, Mertelsmann R, eds. Hematopoietic Stem Cells. Biology and Therapeutic Application. Marcel Dekker Inc, New York, 1995, pp.611-639

Visible Light-Induced α-Oxyamination of Aldehydes with Flavin Organocatalysts

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Abstract

Flavin can be used as visible light photocatalysts for reductive quenching-based photoredox reactions. For example, α-oxyamination of aldehydes with TEMPO was successfully catalyzed by flavin molecules in the presence of catalytic amount of morpholine under blue LED irradiation. In addition, flavin molecules having secondary amino group can function both as the secondary amine catalyst and the flavin catalyst to efficiently promote the oxyamination reaction.

Introduction

Transition-metal complexes such as $Ru(bpy)_3^{2+}$ and $Ir(ppy)_3$ have become the most promising catalysts to carry out visible-light-driven photoredox reactions in organic synthesis, though they are expensive and potentially toxic.[1] On the other hand, a variety of organic dyes that exhibit unique redox properties under visible light irradiation have also been utilized as metal-free photoredox catalysts. Riboflavin is one of the most attractive candidates as photo-organocatalyst, since it is inexpensive and structurally versatile (Figure 1).

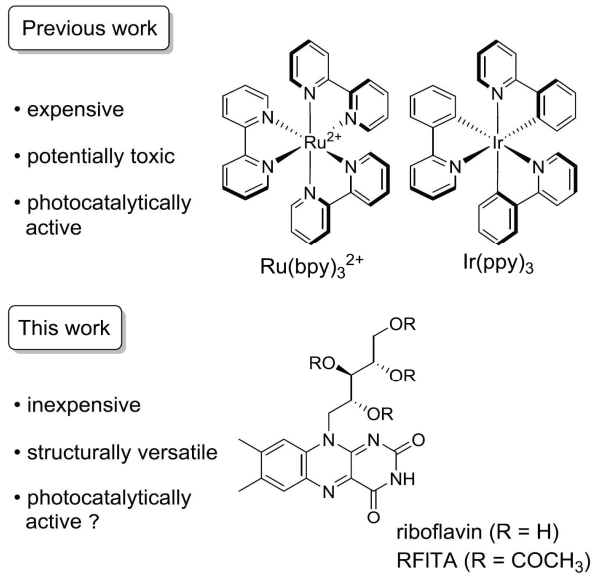


Figure 1. Typical photoredox catalysts and flavins.

In this work, we proved that a combination of riboflavin derivatives and secondary amines can concurrently catalyze α-oxyamination of aldehydes with TEMPO under visible light irradiation, which previously required the transition-metal catalysts.[2]

Experimental

A 5φ NMR tube was charged with TEMPO (100 μmol), photoredox catalyst (2 mol%), 1,3,5-trimethoxybenzene (17 μmol) as NMR internal standard, and CH_3CN (0.50 mL). 3-Phenylpropanal (**1a**, 50 μmol) and morpholine (5 mol%) were added to the mixture, which was then deaerated by N_2 bubbling and irradiated by LED visible light (465 nm, 1.1 W, I_F=350 mA, 1cm distance, Figure 2) at room temperature for a defined reaction time. The reaction yield was determined by ^1H NMR spectrospopy of the crude mixture.

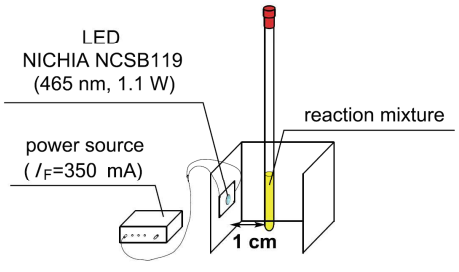


Figure 2. General setup for photoreaction.

Results and Discussion

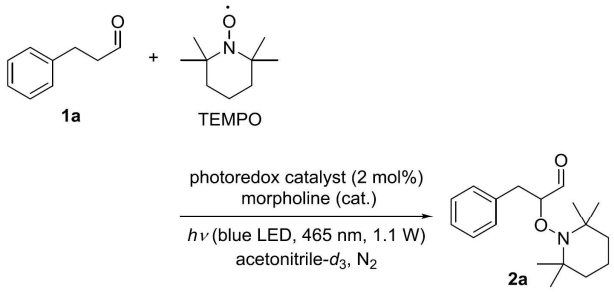
First of all, we explored the photocatalytic activity of riboflavin tetraacetate (**3a**) in the above

α-oxyamination reaction. To our delight, the aldehyde **1a** was fully consumed within 4 hours and the desired α-oxyaminated product (**2a**) was obtained in 80% yield (Table 1, entry 1). Typical transition metal-based photoredox catalyst, $Ru(bpy)_3(PF_6)_2$, was much less active under the same conditions (entry 2), probably due to its lower excited-state reduction potential ($^*E_{red}$ = 0.77 V vs SCE)[1] compared to that of **3a** ($^*E_{red}$ = 1.67 V vs SCE).[3] In fact, 3-methyllumiflavin (**3b**), which is known to be rather less oxidizing than **3a** in their ground state (**3a**: E_{red} = −725 mV, **3b**: E_{red} = −809 mV, vs Ag/AgCl),[4] showed lower photocatalytic activity under the same conditions as expected (entry 3). From a mechanistic viewpoint, the quantum yield of the α-oxyamination of **1a** catalyzed by **3a** (entry 1) was determined to be 0.59 by chemical actinometry with $K_3[Fe(C_2O_4)_3]$, indicating that the reaction takes place via non-radical chain pathway. It should be also noted that the lack of any one of flavin, morpholine, and LED light did not allow for the photoredox reaction. These results suggest one electron transfer mechanism similar to that of previous transition metal-based catalysis,[2] in which the formation of an enamine radical cation intermediate via one electron transfer from an enamine to an excited photocatalyst is involved as a key step.

Other aldehydes such as *n*-butanal, *n*-octanal and 3-methylbutanal were also used as substrates for the reaction catalyzed by **3a**, and in all cases the corresponding α-oxyaminated products were obtained in 71%, 78%, and 79%, respectively.

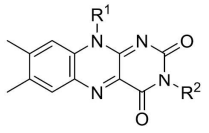
To further extend the versatility of flavin photoredox catalysts, we explored whether flavins bearing a secondary amino group can catalyze the α-oxyamination without adding external secondary amine cocatalyst. 7,8-Dimethyl-10-(2-*N*-benzylamino-ethyl)isoalloxazine (**3c**)[5] was selected as a test molecule. Remarkably, in the presence of 2 mol% of acetic acid salt of **3c** and trimethylamine, the photoinduced α-oxyamination reaction proceeded smoothly to give **2a** in 71% yield within 12 h (Table 1, entry 4), which is more efficient than the reaction using a combination of **3a** (2 mol%) and morpholine (2 mol%) (entry 5). This result shows that **3c** efficiently functioned both as the flavin photoredox catalyst and the secondary amine catalyst.

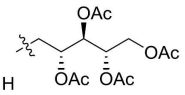
Table 1. Flavin-catalyzed α-oxyamination of 3-phenylpropanal



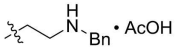
entry	photoredox catalyst	morpholine / mol%	time / h	NMR yield / %
1	**3a**	5	4	80
2	$Ru(bpy)_3(PF_6)_2$	5	4	14
3	**3b**	5	4	45
4[a]	**3c**	0	12	71
5	**3a**	2	12	58

[a] in the presence of 2 mol% of triethylamine as a base



3a : R^1 =  R^2 = H

3b : R^1, R^2 = Me

3c : R^1 =  • AcOH

R^2 = H

Conclusion

We found that flavins **3a**–**3c** can be used as efficient photoredox catalysts for α-oxyamination of aldehydes under visible light irradiation.

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Evaluation of the UVA-LED disinfection device in plant factory

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Abstract

Disinfection of nutrient solution is important to keep a sanitary condition in plant factory. We developed the disinfection device with UVA-LED which we apply to a plant factory. We carried in this device to the real plant factory and evaluated the effect of disinfection. As a result, it was possible to decrease the number of bacteria in nutrient solution, but it was time need longer than expectation. In addition, we found mixing nutrient solution in storage tank induced high disinfection ability. It was suspected that mixing nutrient solution in storage tank which made bacteria pass in the germicidal pipe by the uniform density should be useful for reducing the bacterial number.

Introduction

The plant factory tried to keep a constant quality by cultivate a lot of crops in artificial environment. Therefore, it is drawing attention as the steady supply method of the food, and building the plant factory is increase. In general, hydroponics which circulates the nutrient solution is carried out in the plant factory. When hydroponic nutrient solution is contaminated by the microbial pathogen, the pathogens will propagate and spread. Therefore, it is important to disinfect hydroponic nutrient solution, and we developed a circulating disinfection device with UVA-LED (1). Disinfection of light is excellent in not using a chemical substance (2-5). In addition, UVA irradiation has low damage to crops and nutrient solution (1,5). We confirm enough ability of disinfection of the device which we developed for 5L to 20L of nutrient solution used by model microorganism, *Escherichia coli* strain ATCC25922 (2). Furthermore, we evaluated basic performance of the disinfection in a small scale (200μL) and made a kinetics estimate equation as followed,

$$T(V) = 2.22 \times 10^{-6} \times V^2 - 2.28 \times 10^{-3} \times V + 0.975$$

T (V) ; Log survival ratio, V ; fluid volum

$$E(V) = -7.85 \times \frac{S^2}{T(V)^2} - 102 \times \frac{S}{T(V)} + 59.5$$

S ; sterilizing power of the target (Log survival ratio),
E (V) ; amount of irradiation energy

These equation can provide the required fluence, when log survival ratio of target and amount of the

nutrient solution were decided.

In this study, we developed the new disinfection device for 100L of nutrient solution in plant factory by the estimate equation, and estimate the ability of disinfection.

Materials and Methods

Inactivation of the bacteria in the 100L hydroponic unit in plant factory

We constructed the new disinfection device to the 100L hydroponic unit in plant factory and estimate the ability of disinfection. The irradiation intensity of UVA was 1.3kW m^{-2}. Then, we sampled 50ml nutrient solution from storage tank in 100L hydroponic unit in plant factory.

Effects of mixing nutrient solution on disinfection by UVA irradiation

Escherichia coli as model microorganism were suspended to 100 L of sterilized nutrient solution (OD_{600}=0.5). 100L was same amount of the nutrient solution in hydroponic unit in plant factory and the nutrient solution with *E. coli* keep in the storage tank which was same tank in hydroponic unit in plant factory. And then UVA was irradiated (1.3kW m^{-2}). We sampled 50ml nutrient solution from storage tank.

Evaluation of disinfection ability

Inactivation level was determined by a colony-forming assay. The sampled nutrient solution was inoculated on standard agar plates. After incubation at 37 ºC for 42h, the number of colonies was counted, and evaluated the effect of disinfection.

Log survival ratio was calculated using the following equation;

$$\text{Log survival ratio} = \log\left(\frac{N_t}{N_0}\right)$$

N_t ; the colony count of UVA irradiated sample

N_0; the colony count of the sample before UVA irradiation

Results

The bactericidal effect of -2.8log was observed by irradiation for 720 hours in the 100L hydroponic unit in plant factory, but it was a time-consuming results for disinfection as compared to the disinfection time which is estimated by the equation. (Fig1)

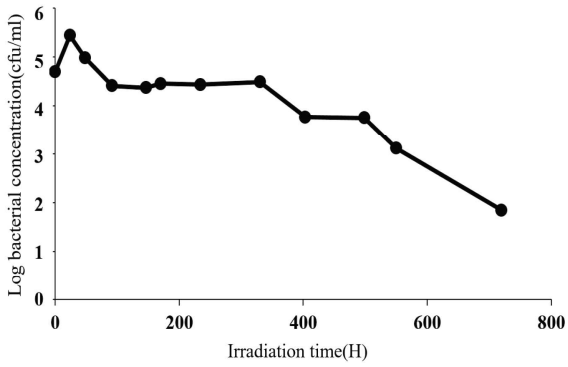

Fig1. Inactivation of the bacteria in the 100L hydroponic unit in plant factory. The bactericidal effect of -2.8log was observed by irradiation for 720 hours. Vertical axis indicated log bacterial concentration and horizontal axle indicated UVA irradiation time in the hydroponic nutrient solution.

The bacteria in the nutrient solution were classified seven geniuses. Then, we measured the changes of survival number of each of bacteria. *Burkholderia* sp. and *Staphylococcus* sp. were predominance bacteria in the nutrient solution and were decrease with irradiation time. (Fig 2A and Fig 2B). *Bacillus* sp. and *Stenotrophomonas* sp. were always existing bacteria and were not conspicuous changes. (Fig 2C and Fig 2D) *Leifsonia* sp., *Arthobacter* sp. and *Herbaspirillum* sp. were

increases accidentally and suppressed. (Fig 2E, Fig 2D, and Fig 2E) All groups of the bacteria in the nutrient solution were suppressed the growth by the UVA irradiation.

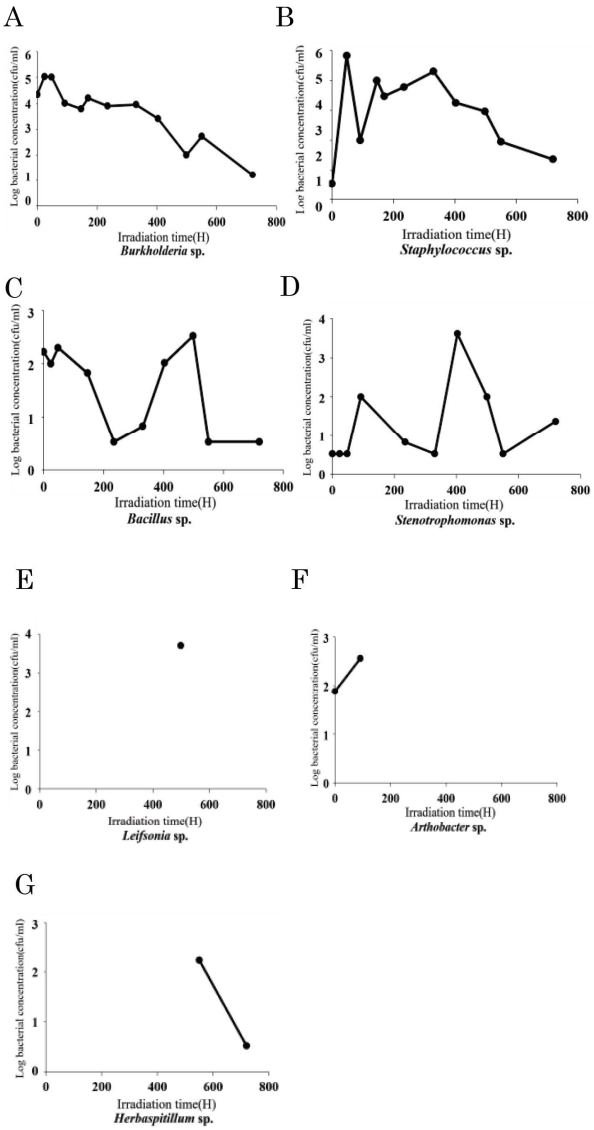

Fig2. Classification of bacteria in nutrient solution. Vertical axis indicated log bacterial concentration and horizontal axle indicated UVA irradiation time to the hydroponic nutrient solution. A and B; *Burkholderia* sp. and *Staphylococcus* sp. were predominance. C and D; *Bacillus* sp. and *Stenotrophomonas* sp. were always existing bacteria. E, F, and D ; *Leifsonia* sp., *Arthobacter* sp. and *Herbaspirillum* sp. occurs accidentally

Next, we examined why the time needed for disinfect the bacteria in nutrient solution in plant factory longer than the expectation by the estimated equation. Interestingly, mixing the nutrient solution in storage tank induced shorter disinfection time than non-mixing the nutrient solution. (Fig3)

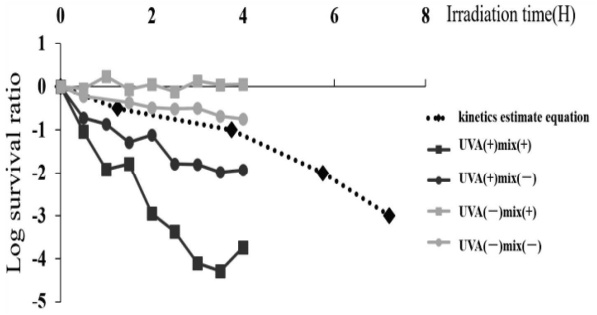

Fig3. Effects of mixing nutrient soultion on disinfection by UVA irradiation. We used *Escherichia coli* as model microorganism. UVA was irradiated to 100 L of nutrient solution with *E. coli* (OD_{600}=0.5). Vertical axis indicated log survival ratio of the bacteria and horizontal axle indicated UVA irradiation time in the hydroponic nutrient solution. It tended to be more sterilized by mixing the nutrient solution.

Discussion

We confirmed bacteria in nutrient solution in the plant factory decreased by UVA irradiation. But it was time need longer than expectation by the estimate equation. It was effective to mix the nutrient solution in the storage tank the bactericidal effect was strengthened and to reduce the germicidal time. It may be necessary to make a new equiation for mix nutrient solution enough with the present type, and to equalize the bacteria in nutrient solution.

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