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Photodecarbonylation of Ruthenium Carbonyl Octaethylporphyrin via Stepwise Two-Photon Absorption of Visible Light

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The photoinduced decarbonylation of a ruthenium(II) carbonyl octaethylporphyrin (RuOEP(CO)(Py)) complex has been shown to occur upon nanosecond pulse laser irradiation as a visible light excitation source, which is reasonably interpreted by a stepwise two-photon absorption process.

Photochemistry has been useful not only for observing ultrafast chemical dynamics but also as an important methodology, where photoproducts which cannot be obtained by thermal activation are selectively synthesized.[1] Photodecarbonylation of carbonyl metallocomplexes is a well-known photochemical reaction, which usually occurs only through excitation with ultraviolet light.[2−6] However, in general, the ultraviolet light excites nearly all the molecules, which not only results in the occurrence of complex photochemical reactions[8] but also in unavailablity to biological systems.[9] Therefore, if the excitation source can be changed from ultraviolet light to visible light, we may achieve more effective and useful photochemical reactions without byproducts or photodamage.

We report here the first example of converting the excitation source from ultraviolet light to visible light in an efficient photodecarbonylation of carbonyl metallocomplexes. The examined system is photoinduced decarbonylation of a ruthenium(II) carbonyl octaethylporphyrin (RuOEP(CO)(Py)) complex, where it has been reported that the photochemical reaction yield is negligibly small using visible light excitation in contrast to ultraviolet light excitation.[7a,10,11] An important feature is the employment of a nanosecond pulse laser as the visible light excitation source. Using this system, we have succeeded in achieving efficient photodecarbonylation of RuOEP(CO)(Py) with visible light. The photochemical reaction is reasonably interpreted by a stepwise two-photon excitation.

RuOEP(CO)(Py) and RuOEP$(Py)_2$ were synthesized from octaethylporphine (Tokyo Kasei Kogyo Co., Ltd.) following the methods previously reported.[12,13] Extra pure grade pyridine (Wako Pure Chemicals) was used as the solvent. For photochemical reactions, concentrations of samples were 2−50 μM, and sample solutions were bubbled with nitrogen gas for 1 h beforehand. Electronic absorption spectra were measured with a Hitachi 330LC spectrometer. Photodecarbonyl reaction yields were determined by fitting of the difference electronic absorption spectra at around the Soret or Q-band region before and after photoexcitation with the difference spectrum of RuOEP(CO)(Py) and RuOEP$(Py)_2$. A Nd:YAG pulse laser (Spectra Physics INDI-30; 532 nm; 5−8 ns fwhm), a dye laser (Sirah CSTR-LG532-TRI-T) pumped with a Nd:YAG pulse laser (Spectra Physics INDI 40; 532 nm; 5−8 ns fwhm), the continuous wave (cw) of a 500 W ultrahigh-pressure mercury lamp (Ushio USH-500D), and a cw He−Ne green laser (Melles Griot, 543.5 nm) were used as excitation sources. In order to complete the cross

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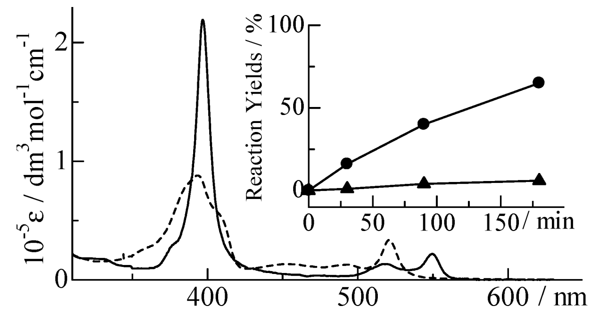
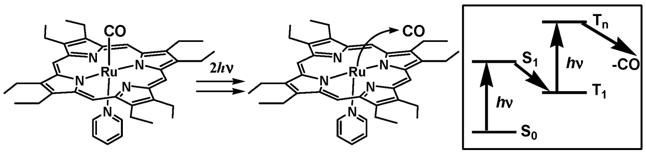


Figure 1. Electronic absorption spectra of RuOEP(CO)(Py) (—) and RuOEP(Py)$_2$ (- - -) in pyridine. Inset shows time-courses of photodecarbonylation reaction yields upon 543.5 nm excitation (▲, cw He−Ne laser; ●, pulse dye laser), respectively.

Chart 1



section, a pinhole (diameter ~ 2.5 mm) was inserted between the sample and light source.

Electronic absorption spectra of RuOEP(CO)(Py) and RuOEP(Py)$_2$ in pyridine are shown in Figure 1. The absorption peaks of RuOEP(CO)(Py) are located at 397.0 nm ($\epsilon = 2.19 \times 10^5$), 518.0 nm ($\epsilon = 1.33 \times 10^4$), and 550.0 nm ($\epsilon = 2.19 \times 10^4$), while those of RuOEP(Py)$_2$ occur at 393.0 nm ($\epsilon = 8.74 \times 10^4$) and 521.0 nm ($\epsilon = 3.35 \times 10^4$). Since the electronic absorption spectrum of RuOEP(Py)$_2$ is different from that of RuOEP(CO)(Py), the photodecarbonylation can be easily measured from the electronic absorption spectral change.

The inset of Figure 1 shows time courses of reaction yields upon excitation at 543.5 nm. Similarly to the previous studies,[7a,10] negligible reaction yields were observed on cw He−Ne laser irradiation (543.5 nm, 1 mW). On the other hand, the photodecarbonylation of RuOEP(CO)(Py) occurs efficiently upon pulse dye laser excitation (543.5 nm, 1 mW, fwhm = 5−8 ns, 5 Hz). Since isobestic points appear during the course of the irradiation (not shown), a simple photochemical reaction is expressed as shown in Chart 1. Hence, we have succeeded in achieving the efficient photodecarbonylation of RuOEP(CO)(Py) using a nanosecond pulse laser as the visible light excitation source.

It is important that the photon flux density of the pulse laser during lasing 5−8 ns is $\sim 10^7$ times that of the cw laser. Since a concentration dependence upon pulse Nd:YAG laser excitation (532 nm, 10 mW, 5 Hz) was not observed between 5 and 50 μM (not shown), intermolecular processes, such as triplet−triplet annihilation, are negligible. In addition, the temperature of the solution was not changed by the pulse laser irradiation. Therefore, multiphoton absorption processes are considered. The excitation wavelength dependence of the reaction yields was examined at around the Q-band region by using the pulse dye laser, since the action spectrum of photochemical reactions via the stepwise two-photon absorption is approximately the average of the ground-state absorption and excited-state absorption spectra, in contrast to simultaneous multiphoton absorption processes.[14−16] An action spectrum and a corresponding ground-state absorption spectrum are shown in Figure 2. The peak position (550 nm) and line shape of the action spectrum are similar to those of the ground-state absorption spectrum. In addition, the photon flux density of our pulse laser ($\sim 10^{25}$ photons/cm^2 s) is sufficient for stepwise absorption of two photons ($10^{23}-10^{28}$ photons/cm^2 s), while the simultaneous multiphoton absorption requires $>10^{28}$ photons/cm^2 s.[17] Thus, it is concluded that the photodissociation of a carbonyl ligand occurs via the stepwise two-photon absorption process.[18] The lowest excited triplet (T$_1$) state, ${}^3(\pi, \pi^*)$, immediately generated within ~30 ps after laser excitation, is considered to be an intermediate excited state (Chart 1), since the T$_1$ lifetime (=34 μs) is much longer than the pulse width of our pulse laser.[19] This is consistent with the similarity between the Q-band and action spectra, because the triplet−triplet absorption of the OEP complex in the ${}^3(\pi, \pi^*)$ state decreases with increasing wavelengths at 500−600 nm.[10,19a]

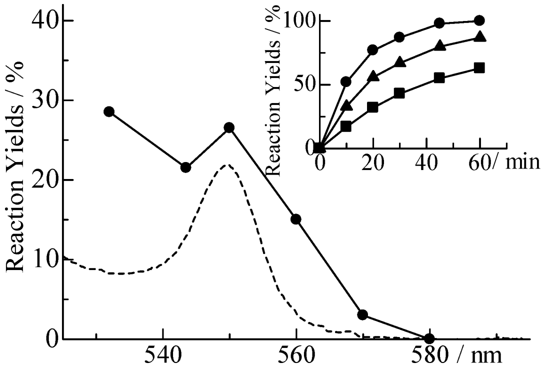


Figure 2. Excitation wavelength dependence of photodecarbonylation reaction yields (●) with the corresponding ground-state absorption spectrum of RuOEP(CO)(Py) (- - -). Inset shows time-courses of photodecarbonylation reaction yields using a cw mercury lamp (▲, [RuOEP(CO)(Py)] = 5 μM; ■, [RuOEP(CO)(Py)] = 50 μM) and pulse Nd:YAG laser (●, [RuOEP(CO)(Py)] = 5 or 50 μM), respectively.

To investigate the usefulness of this mechanism, reaction yields upon pulse Nd:YAG laser excitation are compared with a conventional ultraviolet excitation source, i.e., a cw

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(18) The laser power dependency of reaction yields was examined for 0.01−0.4 mJ/pulse. Here, filters were used for decreasing laser power, and relatively long reaction time (120 min) was employed for increasing reaction yields. The relationship between the reaction yield and laser power seems to deviate only a little from a straight line, but it is inadequate to prove the two-photon excitation process. This may originate from saturation of laser power examined.[16a] While it is difficult to examine the lower laser power because of the lower reaction yields, a stepwise two-photon excitation process was satisfactorily proven by the facts: (1) comparison between the cw laser and pulse laser, (2) photon density, (3) long triplet lifetime, and (4) excitation spectrum.

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mercury lamp (inset of Figure 2). While the power of the excitation light (10 mW) is similar between the pulse Nd:YAG laser and cw mercury lamp, the reaction yields are much larger for the pulse Nd:YAG laser. Indeed, in contrast to the pulse laser independence of the sample concentrations (5−50 μM), the reaction yields obtained by cw mercury lamp excitation dramatically decrease with increasing sample concentration. Previous studies suggest that the reaction yield increases with increasing excitation energy and that the photodecarbonylation of RuOEP(CO) occurs via a triplet charge transfer state between the Ru and OEP moieties (^{3}MLCT),[10,19b] which is higher than the S_1 and T_1 states. Therefore, our experimental results are reasonably interpreted by considering three advantages of the stepwise two-photon excitation, as follows. The first advantage is the solvent window. In the case of the cw mercury lamp, RuOEP(CO)(Py) is excited to the higher excited singlet (S_n) state, which is lower in energy than the pyridine solvent window (~32800 cm^{-1}, 305 nm). On the other hand, in the stepwise two-photon absorption upon 532 nm pulse laser excitation, RuOEP(CO)(Py) is initially excited from the S_0 state to the S_1 state, and then subsequently excited from the T_1 state (15300 cm^{-1}) to the higher triplet (T_n) state ($34100 = 15300 + 18800$ cm^{-1}),[12] which is higher in energy than the pyridine solvent window. The second advantage is the spin-multiplicity. While internal conversion (IC) to the S_1 state overcomes intersystem crossing (ISC) to the ^{3}MLCT state from the S_n state generated by the one photon absorption, the ^{3}MLCT state can be efficiently produced via IC from the T_n state generated by the stepwise two-photon absorption. The third advantage is the bleaching effect of the Q-band. While the absorbance at high concentrations is too large for the efficient excitation of the ground-state molecules, the bleaching of the Q-band upon pulse laser excitation allows synthesis at high concentrations.[20] Thus, the two-photon absorption process results in more efficient photodecabonylation than a one-photon absorption process, even using ultraviolet light.

In summary, we have demonstrated efficient photodecarbonylation of RuOEP(CO)(Py) via stepwise two-photon absorption using a visible-light pulse laser. This is a precious and important example of converting the excitation source of a photochemical reaction from ultraviolet light to visible light, utilizing a two-photon excitation. This conversion can be applied to photochemical reactions, where the excited-state lifetime is relatively long and both the ground state and excited state absorb visible light. Our methodology is promising, since this photochemical reaction can be utilized even at high concentrations, and since photochemical reactions using visible light will result in purer products without byproducts or photodamage.[21] Applications to other photochemical reactions, including various carbonyl metallocomplexes, are now in progress. In addition, from the viewpoint of photodynamic therapy of cancer, which is based on the combined use of selective uptake of porphyrinic photosensitizers into malignant tissues and local irradiation of these, resulting in photodamage with singlet oxygen ($^1\Delta_g$), the photosensitizers currently utilized have the drawback of causing phototoxicity in the skin. The conversion of porphyrinic compounds from photoinactive to photoactive upon pulse laser irradiation will be a novel approach for realizing functional photosensitizers, which exhibit high phototoxicity in tumor tissues upon pulse laser irradiation, in contrast to low phototoxicity in the skin with sunlight.[22]

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(20) In fact, the photodecarbonylation reaction was satisfactorily completed upon pulse Nd:YAG laser excitation (532 nm, 10 mJ, 10 Hz, 8 h), even at high concentration (5×10^{-4} M, 10 mg of RuOEP(CO)(Py)).

(21) HPLC analyses of our photoproducts indicated that byproducts were not observed upon either pulse Nd:YAG laser excitation (532 nm) or cw mercury lamp excitation.

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