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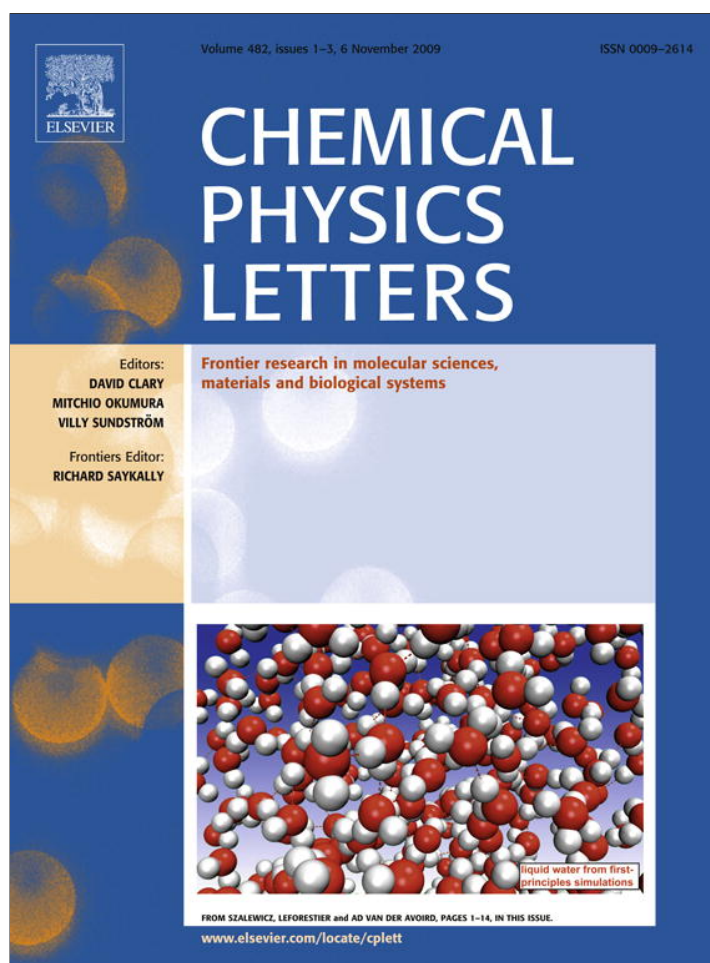


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Photophysics of a new photosensitizer with high quantum yield of singlet oxygen generation and its application to stereo-selective synthesis of (+)-deoxoartemisinin

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ABSTRACT

A new photo-catalyst of [5,10,15-triphenyl-20-(4-methoxycarbonylphenyl)-porphyrin] platinum was synthesized and its photophysical study revealed that it had a high quantum yield of singlet oxygen generation. As an application study, a stereo-specific synthesis of (+)-deoxoartemisinin was performed. The induced high triplet quantum yield (0.96 ± 0.03) of [5,10,15-triphenyl-20-(4-methoxycarbonylphenyl)-porphyrin] resulted the high singlet oxygen quantum yield of 0.90 ± 0.04 . The photo-catalytic effect was compared with that of methylene blue (MB) which was generally used as a photo-catalyst for these types of stereo-specific syntheses of organic compounds. The yield of synthesized (+)-deoxoartemisinin was correlated with singlet oxygen quantum yield.

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1. Introduction

Porphyrin derivatives have been the subject of extensive studies because of their broad applications such as photodynamic therapy (PDT), photovoltaic device, light harvesting coating, and photo-catalyst, etc. [1–4]. Among the applications, the photo-catalytic efficiency shows a great dependence on the singlet oxygen generation of photosensitized porphyrin [5]. Recently, the application area of singlet oxygen has been expanded into water disinfectants, DNA-programmed control, drug delivery system, and stereo-specific synthesis of drugs in life science [6–10]. Therefore, syntheses of new porphyrins with high efficiency of singlet oxygen generation are still in a great demand. As an effort to meet such demand, the evaluation of the photophysical property is essential for newly synthesized porphyrin in order to maximize their singlet oxygen generation efficiencies.

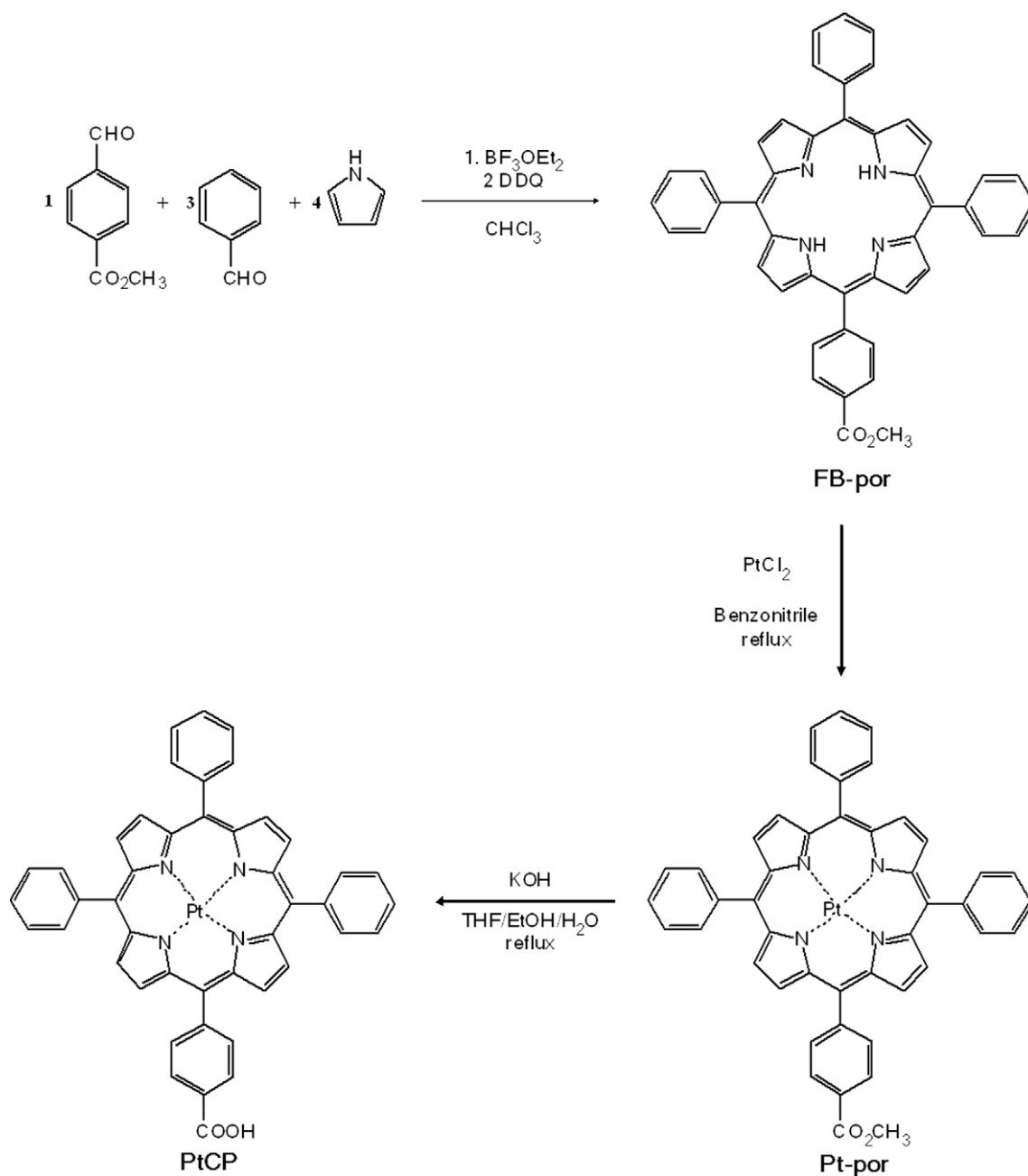
Moreover, for a specific application, chemical modification of synthesized porphyrins are often needed without altering the photophysical properties in a less favourable way. Since the detailed photophysical properties such as triplet state quantum yield, O_2 quenching fraction of the triplet state, energy transfer efficiency

between triplet oxygen and triplet state of the photosensitizer, and deactivation rate of singlet oxygen provide comprehensive understanding about the mechanism from photoexcitation of photosensitizer to singlet oxygen generation depending on their molecular structures, such photophysical factors must be newly investigated even with the modified ones.

Till now, a few synthesized porphyrins with high singlet oxygen quantum yields have been reported. From Refs. [11,12], it is known that [5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl)-porphyrin] zinc (ZnP), [5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl)-porphyrin] palladium (PdP), and [2-ethoxy-5,10,15,20-tetrakis(pentafluoro-phenyl)-3,7-diaza-21,22-dicarboxyphthalocyanine] silver ($Ag^{III}HN_2CP$) show the singlet oxygen quantum yields of 0.77, 0.88, and 0.92, respectively. In this work, we report a synthesis of new core-modified porphyrin of [5,10,15-triphenyl-20-(4-methoxycarbonylphenyl)-porphyrin] platinum (PtCP) and its photophysical properties with the singlet oxygen quantum yield of 0.90 ± 0.04 . Various spectroscopic methods were applied to understand the photophysical factors which determined the high efficiency of singlet oxygen generation of this new core-modified porphyrin. In order to check the application possibility as a photo-catalyst for stereo-specific syntheses of drugs, PtCP was applied to the synthesis of (+)-deoxoartemisinin which was an anti-malaria agent [13]. Its photo-catalytic efficiency was 50% more than that of the general photosensitizer of MB.

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Scheme 1. Synthesis of PtCP.

2. Experimental details

2.1. Materials

The overall synthetic route of the PtCP is shown in Scheme 1.

2.1.1. 5,10,15-Triphenyl-20-(4-methoxycarbonylphenyl)-porphyrin (FB-por)

The chemicals of methyl-4-formylbenzoate (Fluka, 1.5 g, 9.14 mmol), benzaldehyde (Aldrich, 2.79 mL, 27.41 mmol), and pyrrole (Aldrich, 2.54 mL, 36.55 mmol) were condensed in chloroform (914 mL) with $\text{BF}_3\cdot\text{OEt}_2$ (Aldrich, 1.39 mL, 10.96 mmol) at room temperature for 1 h. Then, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Aldrich, 6.22 g, 27.41 mmol) was added. After the mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure. The residue was dis-

solved in CHCl_3 and passed through a short silica gel column to remove the non-porphyrinic components from the crude reaction mixture. This mixture was further purified with a second column (silica, CHCl_3) to afford the compound of FB-por (680 mg, 11%). ^1H NMR (300 MHz; CDCl_3): δ (ppm) 8.95–8.97 (d, 6H, β -pyrrole), 8.88–8.89 (d, 2H, β -pyrrole), 8.52–8.55 (d, 2H, Ar-H), 8.39–8.42 (d, 2H, Ar-H), 8.31–8.33 (m, 6H, Ar-H), 7.83–7.84 (m, 9H, Ar-H), 4.11 (s, 3H, $-\text{OCH}_3$), 2.68 (s, 2H, NH).

2.1.2. [5,10,15-Triphenyl-20-(4-methoxycarbonylphenyl)-porphyrin] platinum (Pt-por)

FB-por (650 mg, 0.97 mmol) and PtCl_2 (Aldrich, 642 mg, 2.42 mmol) were suspended in anhydrous benzonitrile. The mixture was purged with N_2 and slowly heated to 160 °C. It was then brought to reflux under N_2 until there was no free base left as revealed by TLC (30 h). The mixture was cooled to room temperature

and the solvent was removed by vacuum distillation. The crude product left behind was then dried completely and purified with a column (silica, CH_2Cl_2) to afford the compound of Pt-por (690 mg, 82%). ^1H NMR (300 MHz; CDCl_3): δ (ppm) 8.76 (s, 6H, β -pyrrole), 8.69 (d, 2H, β -pyrrole), 8.50 (d, 2H, Ar-H), 8.30 (d, 2H, Ar-H), 8.27 (d, 6H, Ar-H), 7.75 (m, 9H, Ar-H), 4.11 (s, 3H, $-\text{OCH}_3$).

2.1.3. [5,10,15-Triphenyl-20-(4-carboxyphenyl)-porphyrin] platinum (PtCP)

Pt-por (680 mg, 0.79 mmol) and KOH (441 mg, 7.85 mmol) were dissolved in a mixed solution of THF–EtOH– H_2O (1:1:0.1, 50 mL), and the solution was refluxed for 12 h. The mixture was cooled to room temperature and acidified with conc. HCl (pH \approx 2). And then, it was extracted with CH_2Cl_2 . The organic phase was washed with sodium bicarbonate solution and water, and dried with sodium sulfate. Removal of the solvent yielded PtCP (630 mg, 94%). ^1H NMR (300 MHz; DMSO): δ (ppm) 8.76 (s, 6H, β -pyrrole), 8.69 (d, 2H, β -pyrrole), 8.50 (d, 2H, Ar-H), 8.30 (d, 2H, Ar-H), 8.27 (d, 6H, Ar-H), 7.75 (m, 9H, Ar-H).

2.2. Methods

Degassed toluene was prepared by thaw–freeze–pump cycles of 10 times. Steady-state absorption and phosphorescence spectra were obtained by using a UV–VIS spectrophotometer (Hitachi, U-2800) and a spectrofluorimeter (Hitachi, F-4500), respectively.

For time-resolved triplet–triplet absorption measurements, transient pump and probe experiment was employed. The probe light from a xenon lamp was shaped by iris and then perpendicularly focused into the sample which was excited by the pump beam from Nd-YAG (BMI series, 7 ns FWHM pulse) pumped optical parametric oscillator (OPO) laser (B.M. Industries OP901-355, 5 ns FWHM pulse). The transmitted beam was collected by focusing optics and then detected with a monochromator (Jobin Yvon, H20) and PMT (Hamamatsu, R-928). The signal was processed by 500 MHz digital oscilloscope (Hewlett Packard, 54520A) and transferred to a computer for data analysis. Triplet quantum yield was determined from various excitation powers by the power-dependent comparative method [14]. The Nd-YAG pumped OPO laser was also utilized as an excitation source for the detection of time-resolved singlet oxygen phosphorescence. Phosphorescence signal was collected at the perpendicular angle to the excitation beam and detected with a monochromator (Optometrics LLC, mini-chrom04) and NIR-PMT (Hamamatsu, H9170-45). The signal was acquired by 500 MHz digital oscilloscope and transferred to a computer for data analysis [15]. Singlet oxygen quantum yield was comparatively determined from the singlet oxygen phosphorescence signal with the reference porphyrin of H_2TPP ($\Phi_A^R = 0.68$ in toluene, $\Phi_A^R = 0.62$ in methylenechloride) [15,16].

Synthesized (+)-deoxoartemisinin was purified by column chromatography (Merk Kieselgel 60, 230–400 mesh), then it was confirmed with Infrared spectra (Nicolet Impact 400 FT-IR spectrometer), nuclear magnetic resonance spectra (Bruker AC250 spectrometer) and LC-MS (Waters ZQ 4000).

2.3. Sterospecific synthesis by singlet oxygen

2.3.1. Synthesis of (+)-deoxoartemisinin with PtCP

A solution of dihydro artemisinic alcohol (50 mg, 0.211 mmol) in dry CH_2Cl_2 (20 mL), containing the catalytic amount of PtCP (2.6×10^{-4} mmol, O.D. = 0.23 at 510 nm), was irradiated with Nd-YAG laser (510 nm, 3.2 mW) at room temperature under aerated condition (Scheme 2A). After irradiation for 90 min, the solvent was evaporated at room temperature, and the residue was taken up in ethyl acetate and filtered to remove PtCP. After removal of the ethyl acetate, the reaction mixture was dissolved in

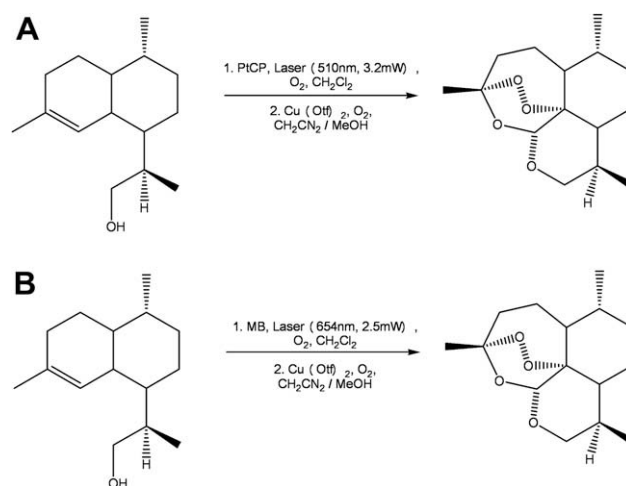
$\text{CH}_3\text{CN}/\text{MeOH}$ (1/1) (50 mL) and followed by in situ treatment of catalyst $\text{Cu}(\text{OTf})_2$ at room temperature. The mixture was stirred at room temperature under oxygen for 24 h. The reaction mixture was extracted with ethyl acetate using water, NaHCO_3 , brine, and dried with MgSO_4 . The extract was concentrated in vacuo to give crude product and was purified by a silica gel column chromatography (hexane/ethyl acetate = 5/1 as eluent) to obtain (+)-deoxoartemisinin (9.2 mg) in 15% yield as white solid [13,17,18]; ^1H NMR (250 MHz, CDCl_3): δ 5.20 (s, 1H), 3.76 (dd, 1H, $J = 4.1, 11.7$ Hz), 3.50 (t, 1H, $J = 11.7$ Hz), 2.69 (m, 1H), 2.42 (ddd, 1H, $J = 4.0, 3.9, 4.0$ Hz), 1.43 (s, 3H), 0.97 (d, 3H, $J = 6.1$ Hz), 0.79 (d, 3H, $J = 7.2$ Hz); ^{13}C NMR (63 MHz, CDCl_3): δ 104.9, 92.2, 80.9, 66.3, 52.2, 44.9, 37.3, 36.2, 34.0, 28.0, 26.2, 24.7, 20.8, 20.4, 13.2; IR (KBr) ν_{max} 2925, 2872, 1454, 1376, 1061, 878 cm^{-1} ; LCMS (ESI): m/z 291 ($[\text{M}+\text{Na}]^+$).

2.3.2. Synthesis of (+)-deoxoartemisinin with methylene blue

For the comparison study, the exactly same procedure for the photooxidative cyclization of dihydro artemisinic alcohol was performed with methylene blue (MB). A solution of dihydro artemisinic alcohol (50 mg, 0.211 mmol) in dry CH_2Cl_2 (20 mL), containing catalytic amount of MB (1.6×10^{-4} mmol, O.D. = 0.23 at 654 nm), was irradiated with Nd-YAG laser (654 nm, 2.5 mW) at room temperature under oxygen (Scheme 2B). The average power of the excitation laser beam was adjusted to be 2.5 mW in order to maintain the same photon numbers with the previous case of PtCP (510 nm, 3.2 mW). After irradiation for 90 min, the synthetic procedure was the same as the above case of PtCP. (+)-Deoxoartemisinin of 6.1 mg was obtained in 10% yield as white solid [13,17,18]; ^1H NMR (250 MHz, CDCl_3): δ 5.20 (s, 1H), 3.84 (dd, 1H, $J = 4.2, 11.6$ Hz), 3.49 (t, 1H, $J = 11.7$ Hz), 2.69 (m, 1H), 2.38 (ddd, 1H, $J = 4.0, 3.9, 4.0$ Hz), 1.43 (s, 3H), 0.97 (d, 3H, $J = 5.9$ Hz), 0.79 (d, 3H, $J = 7.2$ Hz); ^{13}C NMR (63 MHz, CDCl_3): δ 104.2, 92.2, 80.8, 66.2, 52.1, 44.8, 37.3, 36.2, 34.0, 28.0, 26.1, 24.7, 20.7, 20.4, 13.2; IR (KBr) ν_{max} 2921, 2847, 1454, 1372, 1057, 874 cm^{-1} ; LCMS (ESI): m/z 291 ($[\text{M}+\text{Na}]^+$).

2.3.3. Reactivity of singlet oxygen to (+)-deoxoartemisinin

The reactivity of singlet oxygen to dihydro artemisinic alcohol which was the precursor of (+)-deoxoartemisinin was investigated by measuring the singlet oxygen lifetimes in the presence of various concentrations of the precursor. Dihydro artemisinic alcohol was added to the PtCP solution (1.2×10^{-2} mM, methylene chloride) and the range of applied concentrations was 5.2–21 mM.



Scheme 2. Synthesis of (+)-deoxoartemisinin by singlet oxygen.

3. Results and discussion

3.1. Photophysics of PtCP

Steady-state absorption and phosphorescence spectra are presented in Fig. 1. For PtCP, there are two absorption regions of B band (Soret band) in the near-UV ($\lambda_{\max} = 400$ nm) range and Q-bands in the visible ($\lambda_{\max} = 510$ and 538 nm) range. Two peaks of the Q-bands are assigned to Q(1, 0) and Q(0, 0) [19]. Such Q-band nature of the peaks suggests that the molecular symmetry of PtCP is D_{4h} while H_2TPP has D_{2h} symmetry that presents the Q-bands of four peaks [19]. The fluorescence spectrum was not observed for PtCP. The phosphorescence spectrum only observed in Fig. 1, at 510 nm excitation, presents the peaks at 660 and 725 nm.

Time-resolved triplet–triplet absorption signal was measured at the probe detection of 450 nm under degassed condition with the excitation of 510 nm. The signal was fitted by a monoexponential decay, as shown in Fig. 2, which presents the triplet state lifetime of 38 μ s. Triplet quantum yield was determined with the power-dependent comparative method which has the following relationship between the excitation energy (E) and the difference in zero time transient triplet absorbance ($\Delta O.D.$) [20]:

$$\Delta O.D. = a \cdot (1 - \exp(-b \cdot E)). \quad (1)$$

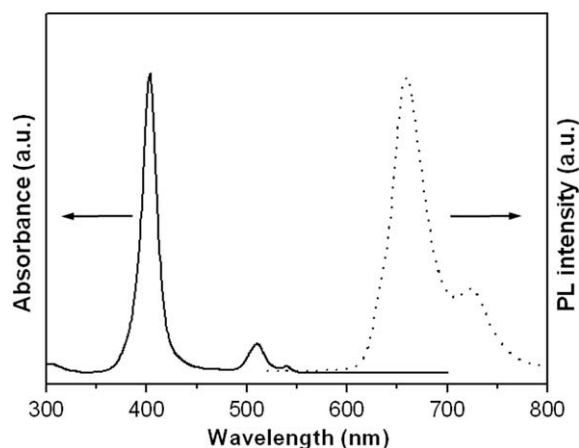


Fig. 1. Absorption (solid line) and phosphorescence (dot line) spectra of PtCP in toluene.

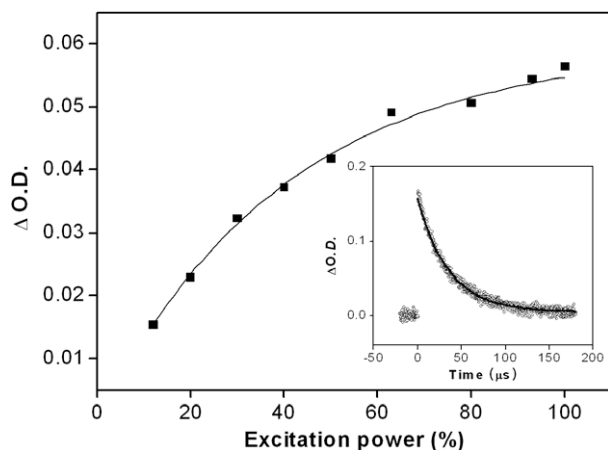


Fig. 2. Excitation power-dependence of zero time optical density for triplet–triplet transition under degassed condition. Inset represents the transient triplet state decay signals of PtCP in degassed conditions.

In Eq. (1), where a is a proportionality constant and b is equal to $k\Phi_T\epsilon_g$ (Φ_T is a triplet quantum yield, ϵ_g is an absorption coefficient of the transition, and k is an instrumental constant). With the reported value ($\Phi_T^R = 0.72$) of the reference H_2TPP and the estimated values of b and ϵ_g for both the reference and the sample, triplet quantum yield of PtCP was calculated as the following equation [20]:

$$\Phi_T^S = \Phi_T^R \frac{b^S \cdot \epsilon_g^R}{b^R \cdot \epsilon_g^S}. \quad (2)$$

In Eq. (2), S and R stand for sample and reference, respectively. The triplet quantum yield (Φ_T^S) of PtCP was estimated to be 0.96 ± 0.03 under degassed condition. The triplet quantum yield of PtCP is much higher than those of H_2TPP and the other porphyrins [20–22]. The molecular structure of PtCP presents the heavy atom effect of Pt and more distortion effect of D_{4h} than the D_{2h} molecules, which induces the enhanced intersystem crossing rates [23,24]. Therefore the high triplet quantum yield can generally be expected from the enhanced intersystem crossing rate [25].

As shown in Fig. 3, decays of singlet oxygen phosphorescence were measured at various detection wavelengths between 1195 and 1345 nm under air-saturated condition. Fitting of phosphorescence decays resulted 29 μ s in toluene, which correlated with the reported values of 27–29 μ s [15]

$$\Phi_A^S = \Phi_A^R \frac{I_S \times (1 - 10^{-A_R})}{I_R \times (1 - 10^{-A_S})}. \quad (3)$$

The singlet oxygen quantum yield (Φ_A^S) of PtCP was estimated to be 0.90 ± 0.04 under air-saturated condition by using the reference value $\Phi_A^R = 0.68$ [15,26] of H_2TPP and Eq. (3) where I was the phosphorescence signal intensity at zero time and A was the absorbance at the excitation wavelength [15,20]. The high singlet oxygen quantum yield of PtCP was analogous with our expectation from the high triplet quantum yield of 0.96 ± 0.03 . Photophysical factors of the relationships between triple state and singlet oxygen can be obtained by the following expressions [15,22,27–32]:

$$\Phi_A^S = \Phi_T \cdot P_{O_2}^T \cdot S_A^T, \quad (4)$$

$$P_{O_2}^T = \frac{k_q^T [O_2]^a}{k_T^0 + k_q^T [O_2]^a}, \quad (5)$$

$$K_T^a = k_T^0 + k_q^T [O_2]^a, \quad (6)$$

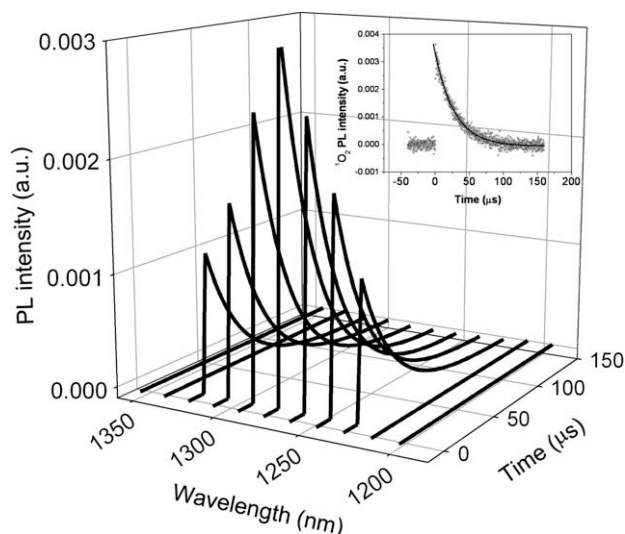


Fig. 3. Fitted decay signals of time and wavelength resolved singlet oxygen phosphorescence of PtCP in toluene. Typical phosphorescence decay of singlet oxygen from PtCP detected at 1270 nm with a single exponential fitted line (solid line) (inset).

where Φ_T is the triplet quantum yield of the sample in degassed condition, $P_{O_2}^T$ is the fraction of the triplet states quenched by oxygen, and S_A^T is the efficiency of singlet oxygen generation induced by the energy transfer during the oxygen quenching of the triplet state. k_q^T is the oxygen quenching rate constant of triplet state, and a and d are air-saturated and degassed conditions, respectively [22]. The oxygen concentration of air-saturated solution ($[O_2]^a$) of toluene at the room temperature was reported to be 2.1×10^{-3} M [22]. k_T^a was obtained with the measured lifetime of the triplet state in air-saturated condition. Since the intrinsic decay rate constant of the triplet state (k_T^0) was known to be 1.0×10^3 s $^{-1}$ in toluene from Ref. [33], the oxygen quenching rate constant of triplet state (k_q^T) could be estimated to be 1.6×10^9 s $^{-1}$ from Eq. (6). Therefore, with the estimated values of k_q^T , k_T^0 and, $[O_2]^a$ Eq. (5) resulted in the $P_{O_2}^T$ value of ~ 1 . Such high value of $P_{O_2}^T$ is also reasonably expected from the fact that the triplet decay rate of PtCP is much smaller than the oxygen quenching rate in air-saturated condition. From Eq. (4), S_A^T was estimated to be 0.95 ± 0.05 with the parameters obtained above. The high value of 0.95 ± 0.05 implies that the triplet state quenching of ground state oxygen results highly efficient generation of singlet oxygen through triplet–triplet energy transfer process. Therefore it is concluded that the high value of Φ_A^S (PtCP) is resulted from the high triplet quantum yield of PtCP and the efficient energy transfer process from the triplet state of PtCP to the ground state of triplet oxygen.

3.2. Stereo-specific synthesis of (+)-deoxoartemisinin

Amounts of the synthesized (+)-deoxoartemisinin by PtCP and MB were 9.2 mg and 6.1 mg under the same experimental conditions, respectively. It simply suggests that the yield of (+)-deoxoartemisinin with PtCP was 51% higher than that with MB. As one of the factors, the difference of singlet oxygen quantum yields of PtCP and MB is considered to be the determining one for the different (+)-deoxoartemisinin yields of 51%.

For the exact comparison, the solvent condition has to be the same as the methylene chloride which is used for the synthesis of (+)-deoxoartemisinin. Therefore the measurement of singlet oxygen quantum yield was repeated with PtCP in methylene chloride as shown in Fig. 4 (inset). The singlet oxygen quantum yield (Φ_A^S) of PtCP was determined to be 0.84 ± 0.01 under air-saturated condition in methylene chloride by using the same reference value of H_2TPP ($\Phi_A^R = 0.62$) [16] and Eq. (3).

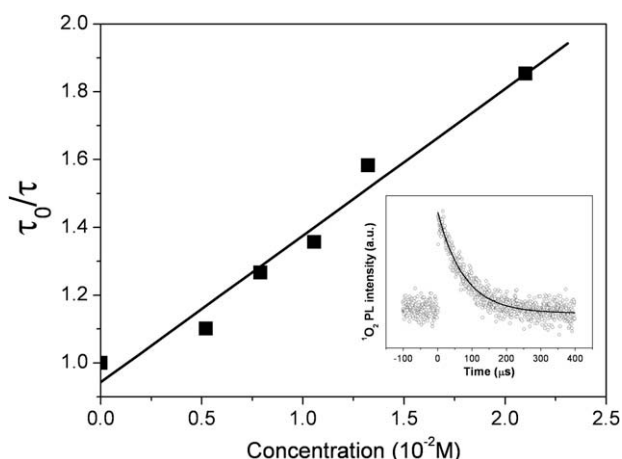


Fig. 4. Stern–Volmer plot for the phosphorescence quenching of 1O_2 at 1270 nm by dihydro arteminin alcohol in methylene chloride. The photosensitizer of PtCP was excited at 510 nm. Inset shows a typical 1O_2 decay signal in methylene chloride without the precursor.

The 51% enhancement of the (+)-deoxoartemisinin yield with PtCP well matches to 47% higher singlet oxygen quantum yield of PtCP ($\Phi_A^S = 0.84 \pm 0.01$) than the reported value of MB ($\Phi_A^S = 0.57$) [34]. Therefore it can be considered that such high quantum yield of singlet oxygen generated with PtCP is one major contributing factor to the enhanced synthesis yield of the stereo-specific of (+)-deoxoartemisinin.

The decay of singlet oxygen phosphorescence was measured in the presence of dihydro arteminin alcohol to obtain the bimolecular rate of the addition reaction. As shown in Fig. 4, the singlet oxygen lifetimes decreased from 76 to 41 μ s with increasing the concentration of dihydro arteminin alcohol [35]. From the results, Stern–Volmer plot was applied to estimate the quenching rate constant of singlet oxygen to dihydro arteminin alcohol. Stern–Volmer equation is expressed by $\tau_0/\tau = 1 + (k_q\tau_0 [Q])$; the symbols mean that τ_0 : singlet oxygen lifetime in the absence of dihydro arteminin alcohol, τ : singlet oxygen lifetime in the presence of dihydro arteminin alcohol, $[Q]$: dihydro arteminin alcohol concentration, k_q : quenching rate constant [36]. The equation results k_q of $0.45 \pm 0.12 \times 10^6$ M $^{-1}$ s $^{-1}$.

4. Conclusions

In this study, a new core-modified porphyrin of PtCP was synthesized and its photophysical parameters were investigated to understand the high singlet oxygen quantum yield (0.90 ± 0.04) in toluene solution. Singlet oxygen generation of the high quantum yield for this new photosensitizer can be expected from the experimental values of high triplet state quantum yield (0.96 ± 0.03) and highly efficient generation of singlet oxygen through triplet–triplet energy transfer process (0.95 ± 0.05). Such excited state properties of PtCP are considered to be determined by the molecular structure that presents the heavy atom effect of Pt and more distortion effect of D_{4h} than the D_{2h} molecules.

As a photo-catalytic application, stereo-specific synthesis was performed with PtCP and the dihydro arteminin alcohol. Under the same experimental condition, the syntheses of (+)-deoxoartemisinin were performed with PtCP and MP. The 15% yield and the 10% yield of (+)-deoxoartemisinin were obtained with PtCP and MB, respectively, where MB is a general photo-catalyst for this type of reaction. Such synthetic yield difference of 50% is considered to be due to the 47% higher singlet oxygen quantum yield of PtCP than that of MB under same environment. Therefore it suggests that the consideration of singlet oxygen quantum yield with a specific photo-catalyst can be often needed for high reaction yield of a photo-catalytic organic reaction such as the stereo-specific synthesis of (+)-deoxoartemisinin which is an anti-malaria agent [13].

Acknowledgments

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