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Light harvesting subphthalocyanine-pyrene dyad has been synthesized and characterized by linking pyrene (Py) with subphthalocyanine (SubPc) at its axial position with the B-O bond through the *para* position of the benzene group. Upon photoexcitation at the pyrene unit of the dyad, an efficient electron transfer from the singlet-excited state of Py to SubPc was observed. The electron transfer features were also observed by exciting the SubPc entity, but with slower rates (~ 10^8 s^{-1}). From the electrochemical measurements, the negative driving forces for charge separation via both singlet states of Py and SubPc in the polar solvents indicate that the electron transfer is thermodynamically feasible. Interestingly, the examined compounds showed relatively high efficiency for producing the singlet oxygen ($\Phi_{\Delta} = \sim 0.70$). The collected data suggested the usefulness of the examined subphthalocyanine-pyrene dyad as a model of light harvesting system, as well as a sensitizer for photodynamic therapy.

Introduction

Development of relatively simple donor-acceptor models designed to mimic the events of photosynthetic reaction center has been an important goal for light energy conversions and development of molecular electronic devices.¹⁻²⁵ In the past years, various conjugated macrocycles such as porphyrins, phthalocyanines and naphthalocyanines were widely employed as building blocks for the photoactive and electro-active assemblies.¹⁻²⁵ Among numerous

porphyrinoids, subphthalocyanines (SubPcs) have attracted special attention in the recent years as photoactive building blocks for the artificial photosynthetic systems,²⁶ organic solar cells,²⁷⁻²⁹ and organic light emitting diodes OLED^{30,31} applications for their conically shape with three *N*-fused units arranged around a central boron atom and aromatic π -electron, strong absorption in the visible region (500–700 nm), high energy of the singlet (2.16 eV) and triplet (1.40 eV) states, and relatively low reorganization energies.³²⁻⁴⁷ In the reported SubPc-based molecular systems, SubPcs were linked with other photoactive species via different routes involving peripheral and/or axial approaches.³²⁻⁴⁷

On the other hand, pyrene derivatives can utilize as electron donors and electron acceptors in the light harvesting systems.⁴⁸ Due to its planar and rigid structure, incorporation of pyrene unit into molecular materials would offer an effective way to control the π - π stacking interactions and enhance charge carrier mobility.⁴⁹ In addition, pyrene chromophores showed unique photophysical and photochemical properties, such as high fluorescence quantum yields, long excited-state lifetimes, and good thermal stabilities.⁵⁰⁻⁵³

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Electronic Supplementary Information (ESI) available: ¹H NMR and MALDI-TOFF spectra of SubPc-Py **3**, cyclic voltammograms of **3**, and nanosecond transient absorption spectra of SubPc reference and **3** in different solvents. See DOI: 10.1039/x0xx00000x

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ARTICLE

Taking these properties into consideration, we present here the photoinduced electron transfer of a dyad composed of subphthalocyanine (SubPc) covalently bonded with the pyrene entity (Py) at the axial position through B-O bond (Fig. 1). Such combination between the curved π -conjugation system of the SubPc and the planar π -conjugation of pyrene via axial approach has yet to be reported. Advantage of the axial approach is to preserve the electronic characteristics of the SubPc macrocycles.^{32-47,54-60} This behavior is quite different from the reported pyrene-fused subphthalocyanine molecule via peripheral approach, which causes an alteration of the spectroscopic properties of subphthalocyanine entity.⁶¹ The photochemical behavior of the subphthalocyanine-pyrene (SubPc-Py) dyad has been explored by using the steady-state absorption and fluorescence, cyclic voltammetry and timeresolved emission techniques. In addition, the ability of the examined subphthalocyanines to act as an efficient sensitizer for photodynamic therapy has been reported in this study.



Fig. 1 Molecular structure of the examined SubPc-pyrene (SubPc-Py) dyad.

Experimental

1,4-Dioxane and toluene were dried as described in Perrin and Armarego before use.⁶² Chlorosubphthalocyanine (1), 4iodophenol, pyreneboronic acid, Cs_2CO_3 and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich. The chromatographic methods such as thinlayer chromatography (TLC) (Silica gel 60 HF₂₅₄) and preparative thin-layer chromatography were performed for separation and purification of the target compounds.

FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Positive ion and linear mode MALDI-MS of complexes were obtained in 2,5dihydroxybenzoic acid (DHB) as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. ¹H-NMR spectra were recorded in CDCl₃ solutions on a Varian 500 MHz spectrometer. Optical absorption and fluorescence measurements were carried out on JASCO spectrophotometer (V-780) and JASCO spectrofluorometer (model FP-8300), respectively. Measurements of fluorescence quantum yields were carried out on a Hamamatsu C9920-0X(PMA-12) U6039-05 fluorescence spectrofluorometer. Fluorescence lifetimes and singlet oxygen measurements have been recorded by utilizing a high performance fluorescence lifetime spectrometer FluoTime 300 (PicoQuant, Germany). Lifetimes were evaluated with software FluoFit attached to equipment. Nanosecond time-resolved transient the absorption measurements were carried out using the laser system provided by UNISOKU Co., Ltd. Measurements of nanosecond transient absorption spectrum were performed according to the following procedure. A mixture solution in a quartz cell (1 cm \times 1 cm) was excited by a Nd:YAG laser (Continuum SLII-10, 4-6 ns fwhm). The photodynamic measurements were monitored by continuous exposure to a xenon lamp for the visible region and halogen lamp for the near-IR region as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. All measurements were carried out in deaerated solvents.

Electrochemical measurements in tetrahydrofuran were performed on a potentiostat / Galvan state / ZRA-05087 electrochemical analyzer. The measurements were taken by using carbon electrode as working electrode, silver-silver chloride (Ag/AgCl) as a reference electrode and platinum as a counter electrode. All measurements were carried out in tetrahydrofuran containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆, 0.1 M) as the supporting electrolyte at the scan rate = 40 mV s⁻¹.

Compound 2 was synthesized and characterised according to literature procedures (Scheme 1).⁶³ Compound 3 axially terminal iodophenol substituted boronsubphthalocyanine 2 (50 mg, 0.081 mmol) and pyreneboronic acid (40 mg, 0.16 mmol) were dissolved in 1,4-dioxane (5 mL) and then Pd(PPh₃)₄ (37.63 mg, 0.03 mmol) and Cs₂CO₃ (530.47 mg, 1.63 mmol) were added to this solution in argon atmosphere. This reaction mixture was stirred at reflux temperature until complete conversion of the starting material to the product. After cooling to room temperature, this mixture was extracted with CH₂Cl₂/water. The organic CH₂Cl₂ phase was dried by anhydrous Na₂SO₄ and then filtered off. The residue was purified by preparative thin-layer chromatography with silica gel using CH₂Cl₂ solution as an eluent. The target subphthalocyanine 3 was obtained as a pink solid. Yield 36 mg, (64%). FT-IR v_{max}/cm^{-1} : 3041 (Aromatic-CH), 1607, 1517, 1455, 1382, 1285, 1252, 1132, 1004, 915, 842, 734, 696. ¹H-NMR (CDCl₃), (δ :ppm): 8.91 (dd, J = 5.7, 3.0 Hz, ArH, 6H), 8.14-8.08 (m, pyrene-H, 3H), 8.02 (s, pyrene-H, 2H), 7.96 (s, pyrene-H, 1H), 7.94 (dd, J = 5.8, 2.8 Hz, ArH, 6H), 7.90 (s, pyrene-H, 2H), 7.74 (d, J = 7.9 Hz, pyrene-H, 1H), 7.02 (d, J = 8.3 Hz, phenyl-H, 2H), 5.57 (d, J = 8.3 Hz, phenyl-H, 2H) (Fig. S1). UV-Vis (DCM): λ_{max} 561. MALDI- Published on 19 July 2017. Downloaded by Cornell University Library on 19/07/2017 08:52:17.

TOF-MS m/z: Calcd. for C₄₆H₂₅BN₆O: 688.22, Found: 688.618 [M]⁺ (Fig. S2).



 $\label{eq:scheme 1} \begin{array}{l} \mbox{Scheme 1} & \mbox{Synthesis of pyrene-SubPc and its precursor, where (i)} \\ \mbox{toluene, (ii) pyreneboronic acid, 1,4-dioxane, Pd(PPh_3)_4, Cs_2CO_3.} \end{array}$

Results and discussion

The absorption spectra of the intense magenta solutions of SubPc-Py 3, as well as the control SubPc 2 and pyrene, in acetonitrile are shown in Fig. 2. The absorption spectrum of the SubPc 2 consists of a high-energy B-band (300 nm) and a lower energy Q-band (558 nm) arisen from π - π * transitions associated with 14 π -electron systems, analogous to those of porphyrins and phthalocyanines. The absorption spectrum of pyrene showed maxima at 335, 319 and 307 nm. In the case of SubPc-Py dyad 3, the absorption spectrum showed four absorption bands at 561, 508, 342, and 304 nm. Since these absorption bands are identical to the sum absorption of both SubPc and Py entities, one can suggest no ground state interaction between the SubPc and pyrene entities. Similar absorption bands were observed for SubPc-Py dyad in toluene (TN) and tetrahydrofuran (THF) and dimethylformamide (DMF), only there is a small red shift of the Q-band (~2 nm) in DMF (Supporting Information's, Fig. S3).



Fig. 2 Steady-state absorption spectra of SubPc-Py dyad, as well as SubPc and Py control compounds in acentonitrile.

Photophysical behavior was firstly investigated by steadystate fluorescence using 334-nm light excitation, which is selectively excited the pyrene moiety. As seen from Fig. 3 (left), the fluorescence spectrum of the control pyrene in acetontrile showed strong emission bands at 371 and 391 nm. In the case of SubPc-Py dyad in acetonitrile, the emission bands of the singlet pyrene were heavily quenched in all examined solvents (TN, THF, MeCN and DMF). Such fluorescence quenching of the singlet-excited state of pyrene can be explained by the electron transfer from the singlet state of pyrene to SubPc generating Py^{+} -SubPc⁻ and/or energy transfer from the singlet-excited state of Py to SubPc. The finding that the quenching process increases with increasing the solvent polarity may suggest that the electron transfer is dominant.

Upon exciting the SubPc with 500-nm light excitation, the fluorescence spectrum of SubPc **2** in toluene showed a maximum at 576 nm with fluorescence quantum yield (Φ_f) of 0.16. By the axial linkage of SubPc with Py, the emission intensity of the singlet SubPc in toluene exhibited no fluorescence quenching suggesting no electron transfer process from Py to the singlet-excited state of SubPc in toluene. When changing the solvent to more polar solvents, the emission intensity of the singlet SubPc was considerably decreased with increasing solvent polarities, THF ($\Phi_f = 0.12$), MeCN ($\Phi_f = 0.09$), and DMF ($\Phi_f = 0.08$). This observation suggests the occurrence of electron transfer from pyrene to the singlet-excited state of SubPc in the polar solvents, but not in the less-polar toluene.



Fig. 3 (Left) Fluorescence spectra of SubPc-Py **3** in the indicated solvents, as well as the pyrene control; $\lambda_{ex} = 334$ nm. (Right) Fluorescence spectra of SubPc-Py **3** in the indicated solvents, as well as the SubPc control; $\lambda_{ex} = 500$ nm.

The fluorescence lifetime measurements (Fig. 4) track the above considerations in a more quantitative way, giving kinetic data of the electron-transfer process in the polar solvents. In THF, the time-profile of the singlet-excited state of SubPc control exhibited a single exponential decay with a lifetime of 2.0 ns. In the case of SubPc-Py 3, the lifetimes of the singlet SubPc entity were found to be 1.80 ns (THF), 1.53 ns (MeCN), and 1.35 ns (DMF), which is considerably shorter than that of the SubPc control. In the less polar toluene, the lifetime of the singlet SubPc entity of 3 is nearly the same as that of SubPc control. These observations agree well with the steady-state fluorescence measurements. Based on the lifetimes of the singlet states of SubPc control and SubPc-Py 3, the rate constants of electron transfer (k_{et}) were determined to be 8.8×10^7 s⁻¹ (THF), 1.8×10^8 s⁻¹ (MeCN), and 3.3×10^8 s⁻¹ (DMF).

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The observed electron-transfer process of SubPc-Py 3 from both the steady state and time-resolved emission measurements was supported by the electrochemical measurements (Supporting Information, Fig. S4). The cyclic voltammogram of 3 in deaerated THF solution containing (n-C₄H₉)₄NClO₄ as a supporting electrolyte exhibited the first reduction potential (E_{ox}) of the SubPc entity at -1.0 V vs. Ag/AgCl, while the first oxidation potential (E_{ox}) of the Py entity was recorded at 1.0 V vs. Ag/AgCl. Based on the redox values, the driving force for the charge-recombination (ΔG_{CR}) process in THF was determined to be 2.0 eV.⁶⁴ From the electrochemical data and energy of the singlet-excited state of Py (3.12 eV), the driving forces of charge separation (- ΔG_{CS}) via the singlet Py were determined to be 0.69, 1.12, 1.32, and 1.42 eV in TN, THF, MeCN and DMF, respectively. The negative ΔG_{CS} of **3** via the singlet excited state of pyrene in both the polar and less polar solvents indicate the higher exothermicity for electron transfer, as shown in Fig. 3. Similarly, the driving forces of charge separation (- ΔG_{CS}) of **3** via the singlet SubPc were determined to be -0.45, 0.15, 0.35, and 0.45 eV in TN, THF, MeCN, and DMF, respectively. The estimated negative ΔG_{CS} via the singlet SubPc indicate that the electron transfer is thermodynamically feasible only in the polar solvents, but not in the less polar solvents.



Fig. 4 Decay time profiles of the singlet SubPc emission at 570 nm of the SubPc-Py 3 in the indicated solvents, as well as the SubPc 2 in THF; $\lambda_{ex} = 470$ nm.

The complementary nanosecond transient measurements of SubPc–Py **3** in the polar solvents with 570 nm laser excitation, which selectively excited the SubPc moiety, exhibited an absorption band in the visible region with a maximum at 450 nm (Figs. 5, S5 and S6) that assigned to the triplet-excited state of SubPc (3 SubPc*).⁶⁵ This assignment was confirmed by recording the transient absorption spectrum of SubPc control in acetonitrile (see supporting information, Fig. S7). From the first-order kinetic, the decay of 3 SubPc*-Py was determined to be 1.9×10^{4} s⁻¹, which is comparable to that of the SubPc control. Upon exciting the SubPc-Py **3** by using 355 nm light, which is selectively excited the Py moiety, the nanosecond transient absorption spectra of **3** showed similar features

(Supporting Informations, Figs. S8 and S9). This observation suggests that the singlet-excited state of pyrene donates its electron to the attached SubPc entity forming the charge-separated state (Py⁺-SubPc⁻), which in turn decayed to populate the low lying ³SubPc^{*} (Fig. 6).



Fig. 5 Nanosecond transient absorption spectra at the indicated time intervals of the SubPc-Py dyad 3 in deaerated acetonitrile solution. Inset shows the decay profiles of the triplet SubPc in argon-saturated and oxygen-saturated solutions.



(a) In polar solvents



Fig. 6 (Upper figure) Energy level diagram depicting the photoinduced intramolecular electron transfer events of SubPc-Py $\mathbf{3}$ via the singlet Py and SubPc entities in the polar solvents. (Lower figure) The singlet oxygen generation via the triplet SubPc of $\mathbf{3}$ in toluene.

As shown in Fig. 5, the decay of ³SubPc*-Py and SubPc control in the toluene, was accelerated on addition of oxygen $(k = 7.0 \times 10^5 \text{ s}^{-1})$ indicating that the triplet SubPc was significantly quenched because of the energy-transfer process yielding the singlet oxygen. By assuming that the concentration of O₂ = 0.2 mM, the rate constant of the

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energy-transfer process was determined to be 3.5×10^9 M⁻¹ s⁻¹. In order to determine the efficiency of the examined SubPc 2 and SubPc-Py 3 to produce singlet oxygen, which is the key to the application of photodynamic cancer therapy property,⁶ two methods are generally used. The first method is to measure singlet oxygen generation such as photooxidation of the chemical quenchers for singlet oxygen,⁶⁷ while second method is to measure directly photoluminescence of singlet oxygen at 1274 nm.⁶⁸ The ability of SubPc control and SubPc-Py dyad to generate the singlet oxygen was confirmed here by directly observing the characteristic emission band of the generated singlet oxygen in the NIR region. As shown in Fig. 6, a strong photoluminescence for the singlet oxygen at 1274 nm was observed in toluene. By comparison with fullerene C₆₀ as a standard (quantum yield of singlet oxygen in toluene = 0.95),⁶⁹ the quantum yield of singlet oxygen generation in toluene (Φ_{Δ}) was determined to be ~ 0.70 (for SubPc control) and ~ 0.68 (for SubPc-Py dyad). The finding that the ability of SubPc-Py 3 to produce the singlet oxygen is close to that of the SubPc 2 was rationalized by the absence of electron transfer from pyrene to the attached SubPc in the less polar toluene. Therefore, it is most likely that the ¹SubPc*-Py is mainly decayed via the intersystem crossing to populate the ³SubPc*-Py, which in turn, transfers the energy from the triplet SubPc to the oxygen generating the singlet oxygen (Fig. 7). The decay profile of the singlet oxygen generation was fitted with a single exponential decay, from which the lifetime of the singlet oxygen was determined to be 29.4 µs, which is similar to the reported value.⁷⁰



Fig. 7 Emission spectrum of singlet oxygen produced by SubPc-Py 3 in toluene; $\lambda_{ex} = 470$ nm.

CONCLUSIONS

We reported herein the synthesis, electrochemical, photophysical and photochemical properties of the subphthalocyanines dyad, as a model for the light harvesting system. The steady-state fluorescence measurements revealed a significant fluorescence quenching of the pyrene entity due to the electron-transfer process to the attached SubPc entity. Upon exciting the SubPc entity, similar electron-transfer features were observed. Based on the time-resolved emission measurements, the electron-transfer rate constant were determined to be 8.8×10^7 s⁻¹ (THF), 1.8×10^8 s⁻¹ (MeCN), and 3.3×10^8 s⁻¹ (DMF). The finding that the fluorescence quenching increase with increasing the solvent polarities support the electron transfer character. Interestingly, the examined SubPc showed higher ability to generate the singlet oxygen, which is the key to the application of photodynamic cancer therapy. These findings suggest the usefulness of the examined materials as light harvesting materials and sensitizers for the medical application such as photodynamic therapy.

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energy of the 0-0 transition of ${}^{1}SubPc^{*}$ (2.15 eV) and ${}^{1}Py^{*}$ (3.12 eV).

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Subphthalocyanine – pyrene dyad: Electron transfer and singlet oxygen generation



Good combination!! Electron transfer of the light harvesting dyad composed of curved π -conjugation of the subphthalocyanine and the planar π conjugation of pyrene *via* axial approach.

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