

Synthesis and photosensitizing properties of porphycene with imidazolium tag

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Dedicated to Professor Emanuel Vogel in memoriam

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ABSTRACT: Porphycene having an imidazolium cation tag was synthesized and characterized by elemental analysis, UV-vis, NMR and ESI-mass spectroscopies. This porphycene derivative easily dissolves in various ionic liquids and produces singlet oxygen under irradiation by visible light ($\lambda \ge 460$ nm). The photophysical parameters of the porphycene in ionic liquids were determined and the values were compared to those in acetonitrile. Photosensitizing reactions using this new porphycene for the oxidation of 1,5-dihydroxynaphthalene in ionic liquids were investigated and found to form 5-hydroxy-1,4-naphthoquinone. The recycled use of the porphycene was efficiently achieved in *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide ([TMPA][TFSA]) and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)amide ([P13][TFSA]).

KEYWORDS: porphycene, ionic liquid, singlet oxygen, imidazolium tag, recycled catalysis.

INTRODUCTION

Natural tetrapyrrole macrocycles, such as porphyrin, corrin, and chlorophyll, are attractive compounds in the bio- and organic chemistry fields because of their important role in biological processes and unique structure [1]. The main features of these macrocycles are visible light absorption, conjugated structure and they coordinate to a variety of metals. To expand these unique properties of the tetrapyrrole macrocycles, the preparation of new porphyrin analogs has been developed over the years [2–5]. Among the porphyrin analogs, porphycene, a structural isomer of porphyrin, was first synthesized by Vogel and co-workers in 1986 [6]. This porphyrin isomer exhibits geometries of the N₄ core, which deviates from the ideal square shape of the porphyrin core, and this unique structural property results

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in an interesting electronic structure of the porphycene [7–13]. For example, porphycene shows a more intense absorption than porphyrin in the red spectral region due to its lower molecular symmetry. Therefore, utilizations of porphycenes as a visible light photosensitizer and photocatalyst have been established by many groups [14–23]. Among the photochemical properties of the porphycene, singlet oxygen generation with visible light sensitization has been well studied in photodynamic therapy and photo-oxidation reactions. To develop this unique property of the porphycene, the combined use of the porphycene with an ionic liquid was achieved in this study. Immobilization of a catalyst on various supports is a desirable approach for the establishment of "Green Chemistry" since the catalyst is easily separated from the reaction medium and reused [24]. Ionic liquids have various advantages as a reaction medium because of the their low melting point, negligible vapor pressure, non-flammability and good solubility for many organic compounds [25-29]. Furthermore, ionic liquids allow for simple work-up procedures and straightforward isolation protocols for products from the catalytic reaction since

[◊]SPP full member in good standing

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ionic liquids are not miscible with a number of organic solvents. The reaction can be carried out in an ionic liquid and the product is isolated by extraction using an organic solvent. Therefore, dissolving and retaining the porphycene photosensitizer in an ionic liquid and the recycled use of the solution is a promising approach in this field. In this study, new porphycene photosensitizer having an imidazolium cation tag was synthesized in order to enhance the ionic liquid solubility, and its photophysical properties and photosensitizing reaction in ionic liquids were investigated.

EXPERIMENTAL

Reagents and apparatus

All solvents and chemicals used in the syntheses were of reagent grade, and were used without further purification. 2,7,12,17-tetra-*n*-propyl porphycene (H₂TPrPc) and 2,7,12,17-tetra-*n*-propyl porphycene-3sulfonyl chloride (1) were synthesized as described in the literature [6, 22]. The ionic liquids, N,N,N-trimethyl-Npropylammonium bis(trifluoromethanesulfonyl)amide ([TMPA][TFSA]), 1-butyl-3-methyl imidazolium bis-(trifluoromethanesulfonyl)amide ([bmim][TFSA]), and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)amide ([PP13][TFSA]) (Chart 1) were purchased from Kanto Chemical Co., Inc., and dried under reduced pressure for 1 day before use. Toluene and acetonitrile were of spectroscopic grade (Kishida Chemical, Japan). 1,5-dihydroxynaphthalene was purchased from Nacalaitesque (Japan) and used as received.

The ¹H, ¹³C and 2-D COSY NMR spectra were recorded by a Bruker Avance 500 spectrometer installed at the Center of Advanced Instrumental Analysis, Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer. The fluorescence (FL) spectra were measured by a Hitachi F-4500 spectrophotometer at room temperature. The IR spectra were measured by a JASCO FT-IR 460 plus KH spectrophotometer using KBr discs. The MALDI-TOF mass spectra were obtained using a Bruker autoflex II with dithranol as the matrix. The ESI-mass spectra were obtained using a Shimadzu



LCMS-IT-TOF in acetonitrile. The GC-mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25μ m).

Photophysical measurements

The Φ_f values of the porphycene were measured using an absolute photoluminescence quantum efficiency measurement system (Hamamatsu C9920-02) incorporating an integrating sphere. To measure the Φ_f , degassed solutions of the porphycene were prepared and the concentration was adjusted so that the absorbance of the solution at 337 nm would be less than 0.1. The excitation was performed at 337 nm.

The τ_s was determined by time-correlated single photon counting using a HORIBA FluoroCube. A light-emitting diode (LED) at 370 nm was used for the excitation. The fluorescence lifetimes (τ_s) were determined by curve fitting using a microcomputer. The concentration was adjusted so that the absorbance of the solution at 337 nm would be less than 0.1.

The transient absorbance spectra were obtained using a laser flash photolysis system (Unisoku TSP-1000M). To measure the transient absorbance spectra, degassed solutions of the porphycenes in [TMPA][TFSA] or [bmim]-[TFSA] or acetonitrile were prepared in a glove box and the concentration was adjusted so that the absorbance of the solution at 532 nm would be less than 0.1. A Xe arc lamp was employed as the source of the probe light to follow the spectral changes. For the laser flash photolysis, a sample was excited with 5 ns pulses (532 nm) from a Q-switched Nd:YAG laser (Surelite I, Continuum). The time course of the absorbance decay was analyzed by single-phase kinetics to determine the lifetimes of the triplet state $(\tau_{\rm T})$. The rate constant for the oxygen quenching $(k_{\rm q})$ was determined from a Stern-Volmer analysis of the triplet lifetime in degassed, air- and oxygen-saturated solutions. The measurements for both the air- and oxygen-saturated solutions were performed under similar conditions. The concentration of oxygen in the acetonitrile solution in air (0.0019 M⁻¹) and dioxygen (0.0091 M⁻¹) was obtained from published oxygen solubility data [30]. The concentration of oxygen in the [bmim][TFSA] solution in air (0.000423 M⁻¹) and dioxygen (0.0020 M⁻¹) were estimated from Henry's constant [31]. Due to the lack of a Henry's constant for [TMPA][TFSA] in the literature, the values were used of that for a similar structure of an ionic liquid, N-methyl-*N*,*N*,*N*-tributylammonium bis(trifluoromethanesulfonyl)amide, in air (0.00049 M⁻¹) and dioxygen (0.00237 M⁻¹) [31]. For the singlet oxygen phosphorescence measurements, an air-saturated toluene solution containing the sample in a quartz cell (optical path length 10 mm) was excited at 600 nm using a HORIBA JOBIN YUON FL3-21 at room temperature. Each Φ_{Λ} value (3) was determined from the slope of the plot with intensities at 1270 nm vs. **3** based on H₂TPrPc as the standard (Φ_{Δ} = 0.36) [32, 33].

Synthesis of imidazolium cation tag porphycene

Bromopropylamido porphycene (2). One mL of dry triethylamine (TEA) was added to a stirred mixture of a solution of 2,7,12,17-tetra-*n*-propyl porphycene-3-sulfonyl chloride (1) (27 mg, 0.046 mmol) and 3-bromopropylamine hydrobromide (200 mg, 0.91 mmol) in dry THF (20 mL) over 5 min at room temperature. The mixture was stirred for 2 h at room temperature. The solution was evaporated under reduced pressure and then chromatographed on silica gel (Silica Gel 60N, spherical, neutral; column size: $\phi = 5 \times 30$ cm) using dichloromethane as the eluent. Recrystallization from dichloromethane/n-hexane (1:1) gave the blue compound 2 (25 mg, 79%). UV-vis and FL (CH₂Cl₂): λ_{max} , nm 375, 387, 575, 620, 656; λ_{flu} , nm (excitation at 370 nm) 662, 722. MS (MALDI): m/z calcd. for $C_{35}H_{44}N_5Br_1O_2S_1$, 677.2. Found 678.3 [M + H]. Anal. calcd. for C₃₅H₄₄N₅Br₁O₂S₁: C, 61.94; H, 6.53; N, 10.32. Found C, 61.80; H, 6.62; N, 10.05. ¹H NMR (CDCl₃): δ, ppm 1.36–1.40 (m, 12H, -CH₃), 1.69 (t, 3H, -CH₂CH₂CH₂Br), 2.30–2.41 (m, 8H, β-CH₂-), 2.97 (q, 2H, -CH₂CH₂CH₂Br), 3.02 (t, 2H, -CH₂CH₂CH₂Br), 3.89-4.36 (tx4, 8H, a-CH2-), 5.43 (t, 1H, NH), 9.11 (s, 1H, pyrrole), 9.28 (s, 1H, pyrrole), 9.56 (d, 1H, methine), 9.61 (d, 1H, methine), 9.70 (d, 1H, methine), 9.83 (d, 1H, methine), 10.19 (s, 1H, pyrrole).

N-methyl 3-imidazolium-1-propylamido porphycene (3). To a solution of 2 (35 mg, 0.052 mmol) in 30 mL of ethanol was added 1-methylimidazole (144 mg, 1.81 mmol) under nitrogen, and solution was refluxed for 48 h. Ammonium hexafluorophosphate (85 mg, 0.52 mmol) was then added to the solution and stirred at room temperature. The solution was evaporated under reduced pressure and then chromatographed on silica gel (Silica Gel 60N, spherical, neutral; column size: $\phi = 5 \times 30$ cm) using dichloromethane/methanol (9:1) as the eluent. Recrystallization from acetonitrile/dichloromethane (1:1) gave the blue compound 3 (32 mg, 73%). UV-vis and FL ([bmim][TFSA]): λ_{max} , nm (ϵ) 373 (95400), 384 (86100), 571 (33600), 615 (23100), 651 (37500); λ_{flu} , nm (excitation at 371 nm) 655, 715. HR MS (ESI): m/z calcd. for C₃₉H₅₀N₇Br₁O₂S₁, 680.3747. Found 680.3744 $[M-PF_6]$. Anal. calcd. for $C_{39}H_{50}N_7F_6O_2P_1S_1$: C, 56.72; H, 6.10; N, 11.87. Found C, 56.58; H, 5.96; N, 11.82. ¹H NMR (CD₃CN): δ, ppm 1.29–1.40 (m, 12H, -CH₃), 1.65 (t, 3H, $-CH_2CH_2CH_2-Im$), 2.24–2.45 (m, 8H, β -CH₂-), 2.89 (t, 2H, $-CH_2CH_2CH_2-Im$), 3.05 (s, 3H, Im-CH₃), 3.72 (t, 2H, -CH₂CH₂CH₂-Im), 3.82–4.30 (tx4, 8H, a-CH₂-), 6.33 (t, 1H, NH), 6.55 (s, 1H, Im-H), 6.65 (s, 1H, Im-H), 7.35 (s, 1H, Im-H), 9.06 (s, 1H, pyrrole), 9.26 (s, 1H, pyrrole), 9.53 (d, 1H, methine), 9.57 (d, 1H, methine), 9.75 (d, 1H, methine), 9.86 (d, 1H, methine), 10.18 (s, 1H, pyrrole). ¹³C NMR (CD₃CN): δ, ppm 14.03, 14.11, 14.22, 14.71 (-CH₂CH₂CH₃), 25.04, 25.24, 25.84, 28.52 (-CH₂CH₂CH₃), 29.38, 29.48, 30.05, 30.37 (-<u>CH</u>₂CH₂CH₃), 29.41 (-NHCH₂CH₂CH₂-Im), 35.60 (Im-<u>C</u>H₃), 39.63 (-NH<u>C</u>H₂-), 46.78 (-CH₂CH₂CH₂-Im),

108.89, 112.15, 113.02, 115.36 (methine <u>C</u>H), 122.05, 123.36, 123.55, 124.81, 125.64, 130.33, 131.30, 131.52, 133.20, 135.78, 137.64, 139.95, 140.74, 143.42, 144.02, 145.03, 150.14, 152.02, 154.16 (pyr and Im).

General procedure of the photoreaction

A typical example of the photoreaction catalyzed by a sensitizer is shown below. A 5 mL [TMPA]-[TFSA] solution of porphycene (3) $(1.0 \times 10^{-6} \text{ M})$ and 1,5-dihydroxynaphthalene $(3.5 \times 10^{-3} \text{ M})$ was stirred in air under irradiation of a 500 W tungsten-lamp through a cut-off filter (TOSHIBA Y-46, ≥460 nm) for 3 h. The progress of the reaction was monitored by absorption at 427 nm, typical for the product, 5-hydroxy-1,4naphthoquinone (Juglone) [34]. After the photoreaction, the product was extracted by dipropyl ether and the resulting ionic liquid layer containing 3 was used for the recycling reaction. Juglone: ¹H NMR (CDCl₃, 293 K): δ, ppm 6.94 (s, 2H), 7.27 (dd, 1H), 7.60–7.65 (m, 2H), 11.90 (s, 1H, OH). GC-MS (EI): m/z 174 [M]⁺. A mixture of dipropyl ether: *n*-hexane (2:1 v/v) and toluene: diethyl ether:*n*-hexane (2:2:1, v/v/v) were used for extracting the solvent in case of the [PP13][TFSA] and [bmim][TFSA] reaction media, respectively.

Determination of rate constant for oxidation of 1,5-dihydroxynaphthalene by 3

Using the change in the absorption at 427 nm, the rate constant (k) for the 1,5-dihydroxynaphthalene oxidation was determined using the following equation at 25 \pm 1 °C, where k is the rate constant, A_{427} is the absorption at 427 nm, A_{∞} is the final absorption at 427 nm, t is the irradiation time and C is a constant. The temperature was directly determined using a thermometer on the surface of the reaction cuvette during the UV light irradiation.

 $\ln \left(A_{427} - A_{\infty} \right) = -kt + C$

RESULTS AND DISCUSSION

Synthesis and optical properties of imidazolium cation tag porphycene (3)

The parent porphycene, 2,7,12,17-tetra-npropylporphycene (H₂TPrPc), is slightly soluble in ionic liquids, such as the imidazolium or ammonium-type ionic liquids (e.g. $< 1 \times 10^{-4}$ M in [bmim][TFSA]). To enhance the solubility of porphyne in an ionic liquid, the imidazolium cation tag was covalently attached to the porphycene. The porphycene derivative having an imidazolium cation tag was synthesized from H₂TPrPc as shown in Scheme 1 and was identified by elemental analysis, UV-vis, fluorescence, NMR and high resolution (HR)-mass spectra. The imidazolium cation tag porphycene is soluble in a variety of ionic liquids and hard to extract in any kind of organic solvent. This is a





significant advantage for a catalyst used in a recycling reaction as already described. The UV-vis absorption and the fluorescence spectra of 3 in [TMPA][TFSA] are shown in Figs 1a and 1b, respectively. The absorption and fluorescence peaks of the solutions from the spectra are listed in Table 1. The Q-type absorption bands are red-shifted compared to those of H2TPrPc due to the sulfonamido substitution on the porphycene ring [19, 22] and its color changed to blue from purple of the parent H_2 TPrPc. The UV-vis spectra of **3** were almost similar in [TMPA][TFSA], [bmin][TFSA] and acetonitrile. The fluorescence maximum in 3 was shifted to 655 nm and the fluorescence intensity decreased compared to that of H₂TPrPc with the Φ_f value 0.20 (in H₂TPrPc, λ_{flu} = 641 nm, $\Phi_f = 0.36$ in toluene) [32, 33]. These spectral features were due to the sulfonamido substitution on the porphycene ring, while the imidazolium tag provided no significant change in the UV-vis and fluorescence spectra.

Photophysical properties of imidazolium cation tag porphycene (3)

The lifetimes of the singlet state (τ_s) and the triplet state (τ_T) were measured under degassed conditions in several solvents, and the τ_T values were also measured under air and oxygen to determine ($k_p + k_{nr}$) and k_q from the Stern–Volmer analysis where k_p is the phosphorescence rate constant, k_{nr} is the rate constant of the nonradiative decay, and k_q is the rate constant of oxygen quenching. The fluorescence rate constants (k_f) are readily calculated using the measured values, Φ_f and τ_s , as eqn. $k_f = \Phi_f / \tau_s$ [18]. These determined photophysical parameters for **3** are



Fig. 1. (a) UV-vis absorption spectrum of **3** in [TMPA][TFSA], (b) fluorescence spectrum of **3** in [TMPA][TFSA] at the excitation wavelength of 371 nm

 Table 1. UV-vis absorption and fluorescence maxima for 3 in several solvents

Solvent	λ_{abs} , nm	$\lambda_{\rm flu},nm^{\rm a}$	Viscosity, cP
[TMPA][TFSA]	373, 384, 571, 615, 651	655,716	72 ^b
[bmim][TFSA]	373, 384, 570, 615, 651	658, 720	52°
CH ₃ CN	371, 383, 570, 615, 651	657,718	0.345
$\mathrm{CH}_3\mathrm{CN}^\mathrm{d}$	367, 379, 559, 597, 629	635, 688	0.345

^aExcitation at 371 nm. ^bViscosity value (cP) was obtained from Kanto Chemical Co., Inc. ^cData from Ref. 36. ^dData for H_2 TPrPc.

Table 2. Photophysical parameters of 3 in several solvents^a

Solvent	$\Phi_{\rm f}^{\ b}$	τ_s , ns ^c	τ_t , us ^d	$k_f / 10^7 \text{s}^{-1}$	$k_p + k_{\rm nr} / 10^4 {\rm s}^{-1}$	k _q /10 ⁹ M ⁻¹ ,S ⁻¹
[TMPA][TFSA]	0.20	7.8	825	2.6	0.12	3.3
[bmim][TFSA]	0.20	8.0	660	2.5	0.16	4.2
CH ₃ CN	0.18	7.0	142	2.6	0.58	3.4

^aFluorescence quantum yield (Φ_f), lifetime of the singlet (τ_s), lifetime of the triplet (τ_T), the fluorescence rate constant (k_f), the phosphorescence rate constant (k_p), the rate constant for nonradiative decay (k_{nr}), the oxygen quenching rate constant (k_q). ^bExcitation at 337 nm. ^cExcitation at 370 nm. ^dExcitation at 532 nm.

summarized in Table 2. The fluorescence quantum yields and lifetimes of the singlet state slightly increased in an ionic liquid compared to those observed in acetonitrile. whereas the lifetimes of the triplet state under degassed conditions were quite different in the ionic liquids and acetonitrile of $\tau_t = 825 \,\mu s$, 660 μs and 142 μs in [TMPA]-[TFSA], [bmim][TFSA] and acetonitrile, respectively. The significant increase in the τ_t value in [TMPA][TFSA] and [bmim][TFSA] were explained by the increase in the medium viscosity (71 cP at 298 K for [TMPA][TFSA], 52 cP at 298 K for [bmim][TFSA]). Restriction of the intramolecular motion in a viscous medium should lead to a decrease in the nonradiative decay process with the relatively small $k_p + k_{nr}$ value to be $k_p + k_{nr} = 0.12 \times 10^4 \text{ s}^{-1}$, 0.16×10^4 s⁻¹ and 0.58×10^4 s⁻¹ in [TMPA][TFSA], [bmim][TFSA] and acetonitrile (0.345 cP at 298 K), respectively.

Photocatalysis of imidazolium cation tag porphycene with singlet oxygen generation (3)

The quantum yield of the singlet oxygen generation (Φ_{Δ}) for **3** was determined by the phosphorescence at 1270 nm in an air-saturated toluene solution. The values were determined by comparing the emission intensity of the standard H₂TPrPc (Φ_{Δ} =0.36) of 0.28 [32, 33]. Though similar emissions were observed in the ionic liquids, [bmim][TFSA] or [TMPA][TFSA] or [PP13][TFSA], we could not determine the exact quantum yields in these ionic liquids because of nostandard values (reference photosensitizers) in the ionic liquids. Alternatively, the

intensities of the 1270-nm emission by 3 were compared in acetonitrile and the ionic liquids, and the intensities were almost similar in these solvents except for [bmin][TFSA] as shown in Fig. 2. Thus, the singlet oxygen should be generated in the ionic liquids, and we tried to use the imidazolium cation tag porphycene as a photosensitizer in the ionic liquids. To investigate the photocatalytic activity of the porphycene, the photo-oxygenation of the 1,5-dihydroxynaphthalene was carried out under visible light irradiation ($\lambda \ge$ 460 nm). As expected, the photoreaction effectively proceeded and the oxygenated product, 5-hydroxy-1,4-naphthoquinone (Juglone), was quantitatively obtained in the ionic liquids as shown in Fig. 3, and the turnover number of the porphycene photosensitizer was 3500. From the UV-vis spectral changes of the solutions, the rate constant for the 1,5-dihydroxynaphthalene oxidation was determined to be $k = 2.33 \times 10^{-2} \text{ s}^{-1}$ and $1.47 \times 10^{-2} \text{ s}^{-1}$ in acetonitrile and [TMPA]-[TFSA], respectively. The efficiency in

the ionic liquid was lower than that in acetonitrile. The low efficiency in the ionic liquid is probably caused by the low oxygen solubility in the ionic liquid and its high viscosity: [TMPA][TFSA], 72 cP; acetonitrile, 0.345 cP at 298 K [35, 36]. The advantage of the ionic liquid in the photoreaction is the recycled use of the solution retaining the porphycene. After extraction of the product from the ionic liquid layer by an organic solvent, the imidazolium tag porphycene stably remained in the ionic liquid. The reaction proceeded with almost the same efficiency in the 3rd run, and the porphycene in the ionic liquid did not



Fig. 2. Phosphorescence spectra of singlet oxygen sensitized by $3 (4.7 \times 10^{-6} \text{ M})$ in air-saturated solutions at room temperature with excitation at 600 nm



Fig. 3. Oxidation of 1,5-dihydroxynaphthalene in various ionic liquids: $[3] = 1 \times 10^{-6}$ M, [substrate] = 3.5×10^{-3} M under air at room temperature with visible light irradiation (≥ 460 nm)

undergo any bleaching during the reaction. Interestingly, the reaction was dependent on the type of ionic liquid, and the quaternary ammonium-type ionic liquids, [TMPA][TFSA] and [PP13][TFSA] had good results as shown in Fig. 3. In contrast, the imidazolium cation-type ionic liquid, [bmim][TFSA], showed a low yield for the product of *ca*. 60%. The finding described here is a guideline for using an ionic liquid as a photoreaction medium.

CONCLUSION

Porphycene having an imidazolium cation tag was synthesized, and the photophysical parameters of the porphycene were determined in ionic liquids. The imidazolium cation tag porphycene generated singlet oxygen during visible light irradiation and shows a photosensitizing activity for the oxidation of an organic compound. The photooxidation reactions efficiently proceeded in an ammonium-type ionic liquid with the imidazolium cation tag porphycene and can be recycled without any loss of activity.

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