

Synthesis and electronic properties of acetylene- and butadiyne-linked 3,3'-porphycene dimers

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ABSTRACT: The butadiyne- and acetylene-linked 3,3'-porphycene dimers **1** and **2** were synthesized from the common intermediate, 3-ethynyl-2,7,12,17-tetrahexylporphycene **4**. The butadiyne-linked dimer **1** was prepared from **4** by copper mediated Glaser-type homo-coupling. The acetylene-linked dimer **2** was synthesized by Sonogashira coupling of **4** and 2,7,12,17-tetrahexyl-3-iodoporphycene **5**. These porphycene dimers were characterized by ¹H and ¹³C NMR spectroscopies, mass spectroscopy, X-ray diffraction analysis, UV-vis absorption and fluorescence spectra, cyclic voltammetry and differential pulse voltammetry. Crystal structure of **1** showed a coplanar structure of two porphyrin units. The absorption spectra in CH₂Cl₂ indicated the small interaction between the porphycene units through the linkage at 3,3'-positions. The electrochemical measurement showed two one-electron oxidation potentials and four one-electron reduction potentials indicating the electric interaction between the porphycene units.

KEYWORDS: porphycene, dimer, crystal structure, optical property, electrochemical property

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INTRODUCTION

Porphycene is known as a first example of the porphyrin isomer reported by Vogel in 1986 [1]. Porphycene has a lower D_{2h} symmetric π -system compared with the D_{4h} symmetric π -system of porphyrin. Owing to this structural change, porphycene exhibits moderate intense Q-band absorption bands and fluorescence due to the non-degenerate LUMO and LUMO+1 orbitals compared with those of porphyrin [2]. These unique optical properties allowed us to investigate porphycenes as the possible materials for nonlinear optics [3], photodynamic therapy [4], protein mimicry systems [5] and so on.

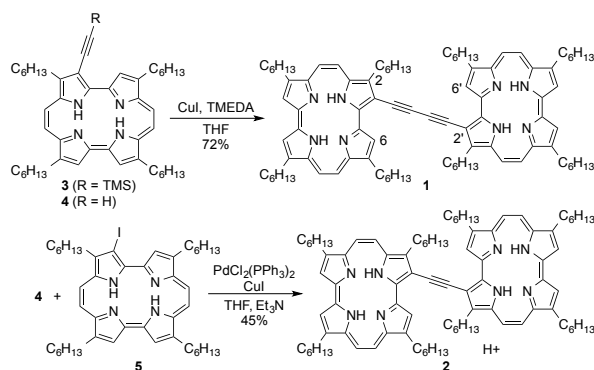
Covalently-linked oligoporphyrin systems have been well investigated to date [6] and have attracted attentions in the fields of non-linear materials [7], singlet oxygen sensitizer [8], and electron-conducting molecular wires [9]. The electronic interaction of each porphyrin in oligoporphyrins is well known to lead the unique optical and electrochemical properties by the exciton coupling. In particular, acetylene- and butadiyne-linked porphyrin dimers are highly conjugated [10]. In addition, these optical properties are dependent on the linkage mode such as β - β , *meso*- β and *meso-meso* linkage due to the difference of degree of the exciton couplings. However, porphyrin-related compounds based dimers and oligomers have been rarely reported. Recently, Matano et al. have reported the 5,15-diaazaporphyrin dimers connected directly and via acetylene- and butadiyne-bridges dimers which showed the different optical and electrochemical properties from porphyrin dimers because *meso*-nitrogen atoms are important for the formation of the coplanar *trans* geometry [11]. In addition, corrole dimers and oligomers [12] and subporphyrin dimers [13] have also been reported to investigate the electronic properties. These results suggested that the properties of porphyrin-related compounds based dimers and oligomers are affected by the nature of the parent compounds properties such as molecular shapes, orbital geometries and transition dipole moments to derive the unique optical and electrochemical properties.

Oligoporphycenes have little been studied due to the difficulty of the modification of porphycene. To the best of our knowledge, oligoporphycenes have been limited to the metal μ -oxodimers to date [14]. Recently, we have reported the selective iodination of porphycene to give 2,7,12,17-tetrahexyl-3-iodoporphycene and 2,7,12,17-tetrahexyl-3,13-diiodoporphycene [15]. Using the iodoporphycenes, the porphycene-diketopyrrolopyrrole conjugates linked by an ethynyl-linkage were also prepared. The intensities of Q-bands of these conjugates are much larger than that of 2,7,12,17-tetrahexylporphycene because of electronic interaction between porphycene and diketopyrrolopyrrole moieties. Herein we report a preparation of the first examples of the porphycene dimers **1** and **2** with butadiyne- and acetylene-bridges, respectively, to investigate the effects of the linkages on the opto- and electronic properties of porphycene dimers **1** and **2**. We also describe the crystal structure of the porphycene dimer **1** obtained by X-ray diffraction analysis.

RESULTS AND DISCUSSION

The synthetic scheme of porphycene dimers is shown in Scheme 1. The starting materials 3-ethynyl-2,7,12,17-tetrahexylporphycene **4** and 2,7,12,17-tetrahexyl-3-iodoporphycene **5** were prepared by referring to our previous report [15]. The butadiyne-linked dimer **1** was prepared from **4** by Glaser-Hay coupling condition using copper(I) iodide and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in 72% yield. Despite of using an excess amount of CuI, **1** was obtained as freebase without metal insertion to porphycene core. This is because the cavity of porphycene is small and strong hydrogen interaction exists between inner NH...N atoms. The acetylene-linked dimer **2** was synthesized from **3**

and **4** by Sonogashira coupling. After purification by silica gel column chromatography and gel permeation chromatography (GPC) with CHCl_3 as an eluent, dimer **2** was obtained in 45% yield. The obtained porphycene dimers **1** and **2** are the first examples of the covalently-linked porphycene dimers and have been characterized by ^1H and ^{13}C NMR spectroscopies, high-resolution matrix-assisted laser desorption/ionization time-of-flight (HR-MALDI-TOF) mass spectrometry and X-ray diffraction analysis. The HR-MALDI-TOF mass spectrum of **1** and **2** display parent positive ion peaks at $m/z = 1339.9870$ (calcd for $\text{C}_{92}\text{H}_{123}\text{N}_8$, $[\text{M}+\text{H}]^+$: 1339.9865) and $m/z = 1315.9865$ (calcd for $\text{C}_{90}\text{H}_{123}\text{N}_8$, $[\text{M}+\text{H}]^+$: 1339.9865), respectively.



Scheme 1. Synthetic Scheme of porphycene dimers **1** and **2**.

The structure of **1** is unambiguously determined by X-ray diffraction analysis (Fig. 1). The suitable single crystal was obtained from a slow diffusion of DMF into CHCl_3 solution. The porphycene dimer **1** displayed perfectly coplaner porphycene core-structures with torsional angle between the porphycenes of 0° due to a crystallographic inversion center at the center of the molecule. The bond distances in the central butadiyne unit are 1.410(5) ($\beta\text{-C-C}$), 1.209(5) ($\text{C}\equiv\text{C}$) and 1.371 (central C-C) Å. These distances are similar to the previously reported one of *meso-meso* butadiyne-linked porphyrin dimer [16].

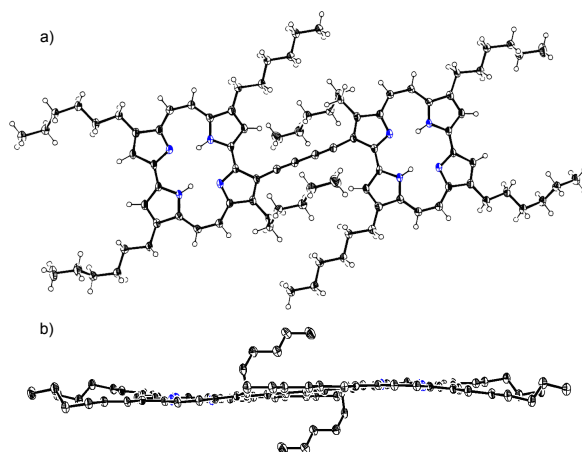


Fig. 1 Crystal structure of **1**. a) Top view and b) side view. The hydrogen atoms in the side view are omitted for clarity. Thermal ellipsoids represent 50% probability.

The ^1H NMR spectra of **1** and **2** in CDCl_3 are shown in Fig 2 in comparison with that of **4**. The pyrrolic β -position protons bound to the 6,6'-carbon atoms are observed at 10.30 ppm for **1** and 10.60 ppm for **2** as singlet peaks. The positions of these peaks were identified by NOE measurements (Figure S1). The protons of 6,6'-positions of **1** and **2** exhibit low-field shift compared with the protons of 6-position of **4** at 10.05 ppm due to the diatropic ring current effect

of the neighboring porphycene core. Similar phenomenon is known for porphyrin dimers. The NH protons are observed as two-sets of singlet peaks at 2.75 and 3.04 ppm for **1** and 3.09 and 3.28 ppm for **2**. In the case of **2**, the protons of terminal methyl groups of hexyl groups at 2,2'-positions are observed at 0.08 ppm as triplet peak which show large high-field shift compared with those of **1** (0.86 ppm) and **4** (0.92 ppm). According to the crystal structure of **1**, the hexyl groups at 2,2'-positions deviate from the molecular plane due to steric hindrance with neighboring hexyl groups. This structural character of **1** predict that hexyl groups at 2,2'-positions of **2** would locate above the porphycene core because the length of ethynyl linkage is shorter than that of hexyl groups. Therefore, these protons are strongly influenced by a diatropic ring-current of the adjacent porphycene to induce the large high-field shift.

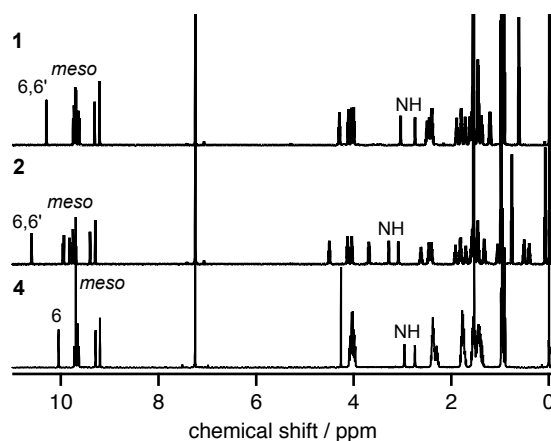


Fig. 2 ^1H NMR spectra of **1**, **2** and **4** in CDCl_3 .

To investigate the optical properties of these porphycene dimers, we have measured the absorption and fluorescence spectra in CH_2Cl_2 (Fig. 3). In general, porphycene has a Soret band with split shoulder peak and moderate intense Q-bands with three peak tops. The absorption peaks of the reference compound, 2,7,12,17-tetrahexyl-3-[(trimethylsilyl)ethynyl]porphycene **3**, are shown at 375 and 386 nm as Soret bands, and 573, 613 and 646 nm as Q-bands. In the case of porphycene dimers **1** and **2**, the shapes of the absorption bands are not largely different from that of **3**, while the molar absorption coefficients of **1** and **2** are almost twice as high as that of **3**. The Soret bands of **1** and **2** become slightly broadened and show slightly larger split width than **3**; the Soret bands are observed at 377 and 394 nm for **1** with 17 nm split-width and 373 nm and 392 nm for **2** with 19 nm split-width. The maximum absorption peaks of Q-bands of **1** and **2** are slightly red-shifted by 4 and 1 nm from **3**, respectively, indicating the limited expansion of the π -conjugation. Common porphycene molecules have the fluorescence bands in the NIR region with moderate fluorescence quantum yields ($\Phi_f = 0.20$ to 0.40). Fig. 3 shows the fluorescence spectra of **1**, **2** and **3**. The fluorescence of **3** is observed at 651 and 712 nm with $\Phi_f = 0.18$. In the dimer system, fluorescence of **1** and **2** were drastically quenched. The maximum peaks were observed at 660 nm and 714 nm for **1**, and 656 and 714 nm for **2** which fluorescence quantum yields were 0.7% and 0.6%, respectively. The fluorescence lifetimes have been measured by time correlated single photon counting method. Porphycenes **1**, **2** and **3** showed the single exponential decays with lifetimes of 0.19, 0.14, and 4.1 ns, respectively. We conclude from these results that porphycene dimers **1** and **2** have small electronic perturbation between each porphycene unit since triple-bonded linkage allows the free-rotation in the solution, and, therefore, the contribution of the non-radiative process is increased, thus the fluorescence quantum yields of **1** and **2** are decreased.

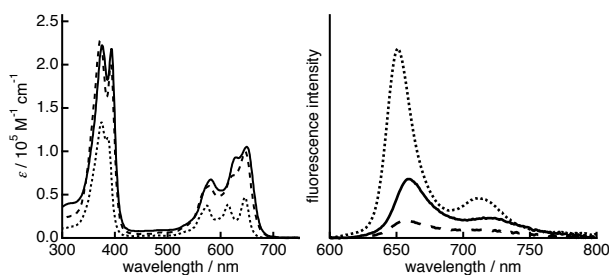


Fig. 3 UV-vis-NIR absorption (left) and fluorescence (right) spectra of **1** (solid line), **2** (dashed line) and **3** (dotted line) in CH_2Cl_2 .

Table 1. Optical and electrochemical properties of **1**, **2** and **3**.

	$\lambda_{\text{abs}} / \text{nm}^{[a]}$	$\lambda_{\text{em}} / \text{nm}^{[a,b]}$	$\Phi_{\text{fl}}^{[a,b]}$	$\tau_{\text{fl}} / \text{ns}^{[c]}$	$E_{\text{ox}} / \text{V}^{[d]}$	$E_{\text{red}} / \text{V}^{[d]}$
1	377, 394, 582, 629, 650	660, 720	0.007	0.19	0.48, 0.62	-1.33, -1.64, -1.78
2	373, 392, 578, 623, 647	656, 714	0.006	0.14	0.50, 0.63	-1.33, ^[e] -1.40, ^[e] -1.57, -1.65
3	375, 386, 573, 613, 646	651, 712	0.18	4.1	0.50	-1.33, -1.61

[a] in CH_2Cl_2 . [b] excited at Soret band. [c] excited at 380 nm. [d] Potential values were measured by DPV in *o*-dichlorobenzene:acetonitrile (5:1) with 0.1 M $n\text{Bu}_4\text{NPF}_6$. The ferrocene/ferrocenium cation redox couple was used as the internal standard. Scan rate = 100 mV s^{-1} . [porphycene] = 1.0 mM. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgNO_3 . [e] These potential values were determined by multi peak fitting with Voigt function.

To understand the electrochemical properties, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out in *o*-dichlorobenzene : acetonitrile (5 : 1) with 0.1 M $n\text{Bu}_4\text{NPF}_6$ as electrolyte at room temperature (Fig. 4). The reference compound **3** shows one quasi-reversible oxidation at 0.50 V (vs. ferrocene/ferrocenium cation) and two reversible reductions at -1.33 and -1.61 V. The porphycene dimer **2** showed two one-electron oxidation peaks at 0.48 and 0.62 V and a two-electron broad reduction peak around -1.35 V and two one-electron reduction at -1.57 and -1.65 V. The multi-peak fitting was carried out by Voigt function to attempt the separation of the first broad reduction peak of **1**. The broad reduction is able to be separated to two one-electron peaks at -1.33 and -1.40 V (Figure S2). Similarly, **1** also shows the split peaks at 0.48 V and 0.62 V for oxidation processes and -1.33, -1.64 and -1.78 V for reduction processes. However, multi peak fitting was failed to separate the first reduction broad peak since the bond distance of the butadiyne linker is longer than that of acetylene linker to decrease the electronic interactions of each porphycene units. These redox properties of the porphycene dimers indicate the electronic coupling of the two porphycene units though the triple bond bridges.

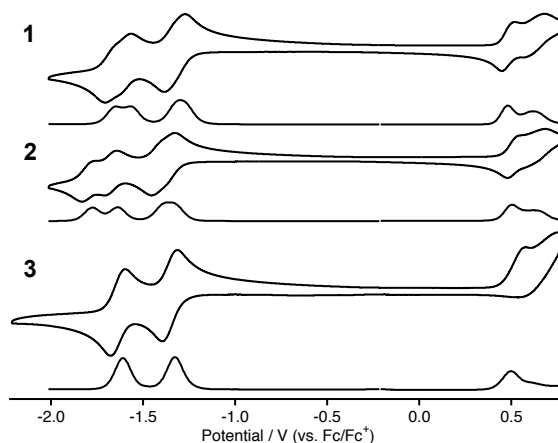


Fig. 4 Cyclic voltammograms and differential pulse voltammograms of **1**, **2** and **3** in *o*-dichlorobenzene:acetonitrile (5:1) with containing 0.1 M *n*Bu₄NPF₆. Scan rate is 100 mV s⁻¹.

CONCLUSION

We have successfully synthesized the first example of butadienyl- and acetylene-linked porphycene dimers **1** and **2**, and investigated the optical and electrochemical properties. The crystal structure of **1** displayed two porphycene units are coplanar to each other. The results of the absorption spectra and electrochemical measurement of the **1** and **2** indicated that porphycene units have small electronic interactions between the two porphycene units via triple bond. The fluorescence of the dimer exhibited the smaller fluorescence quantum yields and shorter fluorescence lifetimes compared to the reference monomer **3**, probably because of the increase of the molecular motion of the dimers in solution.

EXPERIMENTAL

¹H-NMR and ¹³C-NMR spectra were recorded on a JNM-ECX600 spectrometer using tetramethylsilane as an internal standard. Matrix assisted laser desorption/ionization (MALDI)-TOF-MS spectra were recorded on a JEOL, spiralTOF, JMS-S3000 spectrometer. UV-vis-NIR absorption spectra were recorded on a JASCO UV/VIS/NIR Spectrophotometer V-670. Fluorescence spectra and fluorescence quantum yields were obtained on a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. CV and DPV measurements were conducted in a solution of 0.1 M TBAPF₆ in dry *o*-dichlorobenzene/CH₃CN (5:1) with a scan rate of 100 mV s⁻¹ at room temperature in an argon-filled cell. A glassy carbon electrode and a Pt wire were used as a working and a counter electrode, respectively. An Ag/AgNO₃ electrode was used as a reference electrode, which was normalized with the half-wave potential of ferrocene/ferrocenium cation (Fc/Fc⁺) redox couple. TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. Gel permeation chromatography (GPC) was performed on JAI LC-9225NEXT with chloroform as eluent. All other solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification except as noted. For spectral measurements, spectral-grade dichloromethane.

Butadiyne-linked porphycene dimer (1). 3-Ethynyl-2,7,12,17-tetrahexyl-porphycene **3** (24 mg, 36 μmol), CuI (6 mg, 42 μmol), *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 0.1 mL) and THF (5 mL) were placed in flask. The mixture was stirred for 1 h under air at room temperature. After removal of the solvent under a reduced pressure, the residue was purified by column chromatography on silica gel by using a 1:9 mixture of CH₂Cl₂/hexane as eluent. Recrystallization from CHCl₃/hexane provided porphycene dimer **1** as a purple solid. Yield: 72% (17 mg, 13 μmol). UV-vis (CH₂Cl₂): λ_{max}, nm (log ε) 377 (5.34), 394 (5.34), 582 (4.82), 629 (4.97), 650 (5.01). ¹H NMR (400 MHz; CDCl₃; Me₄Si): δ_H, ppm 0.62 (6H, t, *J* = 7.6 Hz), 0.92 (6H, t, *J* = 7.6 Hz), 0.98 (12H, t+t, *J* = 7.6 Hz), 1.21 (4H, m), 1.38 (4H, m) 1.42-1.48 (12H, m), 1.53-1.65 (XH, m), 1.72 (4H, m), 1.77-1.83 (8H, m), 1.89 (4H, m), 2.37-2.53 (16H, m), 2.75 (2H, brs, -NH), 3.04 (2H, brs, -NH), 4.00 (4H, t, *J* = 7.6 Hz), 4.04 (4H, t, *J* = 8.3 Hz), 4.11 (4H, t, *J* = 8.3 Hz), 4.29 (4H, t, *J* = 7.6 Hz), 9.21 (2H, s), 9.31 (2H, s), 9.64 (2H, d, *J* = 11.0 Hz), 9.69 (2H, d, *J* = 11.0 Hz), 9.71 (2H, d, *J* = 11.0 Hz), 9.74 (2H, d, *J* = 11.0 Hz), 10.30 (2H, s). ¹³C NMR (150 MHz; CDCl₃; Me₄Si): δ_C, ppm (typical signals because the signals of alkyl chain was overlapped) 153.17, 148.67, 147.98, 145.69, 144.44, 143.06, 139.67, 139.30, 138.14, 136.50, 131.94, 130.86, 123.99, 122.79, 122.00, 118.71, 112.91, 111.97, 110.45, 109.04, 84.48, 81.74, 32.53,

32.55, 32.11, 32.09, 32.03, 31.92, 29.64, 29.80, 28.64, 28.41, 28.13, 22.92, 22.89, 22.73, 14.33, 14.04. HRMS (MALDI): m/z 1339.9870 (calcd. for $C_{92}H_{123}N_8$ $[M+H]^+$: 1339.9865). Elemental analysis C 81.18, H 9.40, N 8.37 (calcd. for $C_{92}H_{122}N_8 \cdot H_2O$ C 81.37, H 9.20, N 8.25).

Ethynyl-linked porphycene dimer (2). Triethylamine (0.5 g, 5 mmol), $Pd(PPh_3)_4$ (3.3 mg, 0.003 mmol) and CuI (1 mg, 0.006 mmol) were added to a solution of 3-ethynyl-2,7,12,17-tetrahexylporphycene **3** (15.9 mg, 0.024 mmol) and 2,7,12,17-tetrahexyl-3-iodo-porphycene **4** (18.3 mg, 0.024 mmol) in toluene (5 mL). The solvent was degassed with nitrogen by bubbling for 15 min. The resulted solution was stirred at 80 °C for 13 h. After removal of solvent, the crude product was purified by chromatography on silica gel a 1 : 1 mixture of CH_2Cl_2 /hexane as eluent and gel permeation chromatography (GPC) with $CHCl_3$. Recrystallization from $CHCl_3$ /hexane provided porphycene dimer **2** as a purple solid. Yield: 45% (14 mg, 11 μ mol). UV-vis ($CHCl_3$): λ_{max} , nm (log ϵ) 373 (5.36), 392 (5.30), 578 (4.78), 623 (4.86), 647 (5.00). 1H NMR (600 MHz; $CDCl_3$; Me_4Si): δ_H , ppm 0.08 (6H, t, J = 6.8 Hz), 0.40 (4H, m), 0.51 (4H, m), 0.76 (6H, t, J = 7.6 Hz), 0.97 (6H, t, J = 7.6 Hz), 0.99 (6H, t, J = 6.8 Hz), 1.05 (4H, m), 1.33 (4H, m), 1.46 (8H, m), 1.51-1.61 (12H, m), 1.70 (4H, m), 1.78-1.85 (8H, m), 1.92 (4H, m), 2.41 (4H, m), 2.46 (4H, m), 2.62 (4H, m), 3.09 (2H, brs, NH), 3.28 (2H, brs, NH), 3.69 (4H, t, J = 8.2 Hz), 4.04 (4H, t, J = 7.6 Hz), 4.13 (4H, t, J = 8.2 Hz), 4.50 (4H, t, J = 7.6 Hz), 9.30 (2H, s), 9.41 (2H, s), 9.70 (2H, d, J = 11.0 Hz), 9.76 (2H, d, J = 11.0 Hz), 9.82 (2H, d, J = 11.0 Hz), 9.95 (2H, d, J = 11.0 Hz), 10.60 (2H, s). ^{13}C NMR (150 MHz; $CDCl_3$; Me_4Si): δ_C , ppm (typical signals because the signals of some aromatic and alkyl chain was overlapped) 13.45, 14.16, 14.32, 22.08, 22.86, 22.88, 28.39, 28.44, 28.50, 28.63, 29.41, 29.80, 29.82, 30.10, 31.19, 31.57, 32.10, 32.12, 32.18, 32.24, 33.73, 96.02, 109.46, 110.20, 111.97, 112.76, 120.92, 122.07, 123.54, 123.87, 131.45, 132.62, 136.36, 137.78, 139.90, 140.14, 143.36, 144.42, 146.14, 147.65, 148.12, 150.27. HRMS (MALDI): m/z 1315.9865 (calcd. for $C_{90}H_{123}N_8$ $[M+H]^+$ 1315.9865). Elemental analysis C 81.22, H 9.67, N 8.29 (calcd. for $C_{90}H_{122}N_8 \cdot H_2O$ C 81.03, H 9.37, N 8.40).

Single crystal X-ray diffraction analysis

Single-crystal X-ray diffraction experiment of **1** was carried out with Rigaku Saturn 724 diffractometer using synchrotron radiation and a large cylindrical imaging plate camera at SPring-8 beam line BL40XU (Hyogo, Japan) [17], (Proposal No. 2014A1717). The structure was solved by the direct methods with SHELXS-97[18] and refined by the full-matrix least-squares techniques against F^2 (SHELXL-97)[18]. The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed by using Crystal Structure 4.0 or Yadokari-XG 2011.

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REFERENCES

1. (a) Vogel E, Köcher M, Schmickler H and Lex J. *Angew. Chem. Int. Ed. Engl.* 1986; **25**: 257-259. (b) Sánchez-García D and Sessler JL. *Chem. Soc. Rev.* 2008; **37**: 201-232 and reference cited therein.
2. Waluk J, Müller M, Swiderek P, Köcher M, Vogel E, Hohlneicher G and Michl J. *J. Am. Chem. Soc.* 1991; **113**: 5511-5527.
3. (a) Arnbjerg J, Jiménez-Banzo A, Paterson MJ, Nonell S, Borrell JI, Christiansen O and Ogilby PR. *J. Am. Chem. Soc.* 2007; **129**: 5188-5199. (b) Sarma T, Panda PK, Anusha PT and Rao SV. *Org. Lett.* 2011; **13**: 188-191. (c) Rao SV, Prashant TS, Swain D, Sarma T, Panda PK and Tewari SP. *Chem. Phys. Lett.* 2011; **514**: 98-103.
4. (a) Richert C, Wessels JM, Müller M, Kisters M, Benninghaus T and Goetz AE. *J. Med. Chem.* 1994; **37**: 2797-2807. (b) Gottfried V, Davidi R, Averbuj C and Kimel S. *J. Photochem. Photobiol. B* 1995; **30**: 115-121. (c) Arnbjerg J, Jiménez-Banzo A, Paterson MJ, Nonell S, Borrell JI, Christiansen O and Ogilby PR. *J. Am. Chem. Soc.* 2007; **129**: 5188-5199. d) Rubio N, Martínez-Junza V, Estruga J, Borrell JI, Mora M, Sagristá ML and Nonell S, *J. Porphyrins Phthalocyanines* 2009; **13**: 99-106.
5. (a) Matsuo T, Dejima H, Hirota S, Murata D, Sato H, Ikegami T, Hori H, Hisaeda Y and Hayashi T. *J. Am. Chem. Soc.* 2004; **126**: 16007-16017. (b) Hayashi T, Murata D, Makino M, Sugimoto H, Matsuo T, Sato H, Shiro Y and Hisaeda Y. *Inorg. Chem.* 2006; **45**: 10530-10536.
6. (a) Tanaka T and Osuka A. *Chem. Soc. Rev.* **2014**, advance article, DOI: 10.1039/C3CS60443H and reference cited therein. (b) Yang J, Yoon MC, Yoo H, Kim P and Kim D. *Chem. Soc. Rev.* 2012; **41**: 4808-4826 and reference cited therein. (c) Aratani N, Kim D and Osuka A. *Chem. Asia. J.* 2009; **4**: 1172-1182 and reference cited therein. (d) Shinokubo H and Osuka A. *Chem. Commun.* 2009; 1011-1021 and reference cited therein. (e) Burrell AK, Officer DL, Plieger PG and Reid DC. *Chem. Rev.* 2001; **101**: 2751-2796 and reference cited therein. (f) Anderson HL. *Chem. Commun.* 1999; 2323-2330.
7. (a) Kuimova MK, Collins HA, Balaz M, Dahlstedt E, Levitt JA, Sergent N, Suhling K, Drobizhev M, Makarov NS, Rebane A, Anderson HL and Phillips D. *Org. Biomol. Chem.* 2009; **7**: 889-896. (b) Anderson HL, Martin SJ and Bradley DDC. *Angew. Chem. Int. Ed. Engl.* 1994; **33**: 655-657.
8. Kuimova MK, Balaz M, Anderson HL and Ogilby PR. *J. Am. Chem. Soc.* 2009; **131**: 7948-7949.
9. (a) Kocherzhenko AA, Patwardhan S, Grozema FC, Anderson HL and Siebbeles LDA. *J. Am. Chem. Soc.* 2009; **131**: 5522-5529. (b) Grozema FC, Houarner-Rassin C, Prins P, Siebbeles LDA and Anderson HL. *J. Am. Chem. Soc.* 2007; **129**: 13370-13371.
10. (a) Victor SY, DiMagno SG and Therien MJ. *Science* 1994; **264**: 1105-1111. (b) Anderson HL. *Inorg. Chem.* 1994; **33**: 972-981.
11. Matano Y, Fujii D, Shibano T, Furukawa K, Higashino T, Nakano H and Imahori H. *Chem. Eur. J.* 2014; **20**: 3342-3349.
12. (a) Chen C, Zhu YZ, Fan QJ, Song HB and Zheng JY. *Chem. Lett.* 2013; **42**: 936-938. (b) Cho S, Lim JM, Hiroto S, Kim P, Shinokubo H, Osuka A and Kim D. *J. Am. Chem. Soc.* 2009; **131**: 6412- 6420. (c) Koszarna B and Gryko DT. *Chem. Commun.* 2007; 2994-2996. (d) Hiroto S, Furukawa K, Shinokubo H and Osuka A. *J. Am. Chem. Soc.* 2006; **128**: 12380-12381. (e) Hiroto S, Hisaki I, Shinokubo H and Osuka A. *Angew. Chem. Int. Ed.* 2005; **44**: 6763-6766. (f) Hirabayashi S, Omote M, Aratani N and Osuka A. *Bull. Chem. Soc. Jpn.* 2012; **85**: 558. (g) Barata JFB, Silva AMG, Neves MGPMS, Tomé AC, Silva AMS and Cavaleiro JAS, *Tetrahedron Lett.* 2006; **47**: 8171-8174. (h) Luobeznova I, Simkhovich L, Goldberg I and Gross Z. *Eur. J. Inorg. Chem.* 2004; 1724-1732. (i) Mahammed A, Giladi I, Goldberg I and Gross Z. *Chem. Eur. J.* 2001; **7**: 4259-4265.

13. (a) Kitano M, Sung J, Park KH, Yorimitsu H, Kim D and Osuka A. *Chem. Eur. J.* 2013; **19**: 16523-16527. (b) Kitano M, Hayashi Sy, Tanaka T, Yorimitsu H, Aratani N and Osuka A. *Angew. Chem. Int. Ed.* 2012; **51**: 5593-5597.
14. (a) Ito K, Matsuo T, Aritome I, Hisaeda Y and Hayashi T. *Bull Chem. Soc. Jpn.* 2008; **81**: 76-83. (b) Baba T, Shimakoshi H, Aritome I and Hisaeda Y. *Chem. Lett.* 2004; **33**: 906-907. (c) Hayashi T, Nakashima Y, Ito K, Ikegami T, Aritome I, Aoyagi K, Ando T and Hisaeda Y. *Inorg. Chem.* 2003; **42**: 7345-7347. (d) Bernard C, Le Mest Y and Gisselbrecht JP. *Inorg. Chem.* 1998; **31**: 181-190. (e) Guillard R, Pichon-Pesme V, Lachekar H, Lecomte C, Aukauloo AM, Boulas PL and Kadish KM. *J. Porphyrins Phthalocyanines* 1997; **1**: 109-119. (f) Kadish KM, Boulas P, D'Souza F, Aukauloo MA, Guillard R, Lausmann M and Vogel E. *Inorg. Chem.* 1994; **33**: 471-476. (g) Lausmann M, Zimmer I, Lex J, Lueken H, Wiegardt K and Vogel E. *Angew. Chem. Int. Ed.* 1994; **33**: 736-739.
15. Okabe T, Kuzuhara D, Suzuki M, Aratani N and Yamada H. *Org. Lett.* 2014; **16**: 3508-3511.
16. (a) Chen YJ, Chen SS, Lo SS, Huang TH, Wu CC, Lee GH, Peng SM and Yeh CY. *Chem. Commun.* 2006; 1015-1017. (b) Taylor PN, Huuskonen J, Rumbles G, Aplin RT, Williams E and Anderson HL. *Chem. Commun.* 1998; 909-910.
17. Yasuda N, Murayama H, Fukuyama Y, Kim J, Kimura S, Toriumi K, Tanaka Y, Moritomo Y, Kuroiwa Y, Kato K, Tanaka H and Takata M, *J. Synchrotron Rad.* 2009; **16**: 352-357. (b) Yasuda N, Fukuyama Y, Toriumi K, Kimura S and Takata M, AIP Conference Proceedings 2010; **1234**: 147-150.
18. Sheldrick, G. M. *Acta Cryst.* 2008, **A64**, 112.