Synthesis and electronic properties of trimeric octaethylporphyrin (OEP) derivative connected with diacetylene linkage. A comparative study with vinylene-group connected OEP trimer

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Abstract

A new trimeric octaethylporphyrin (OEP) derivative was synthesized, in which each porphyrin ring is connected with diacetylene linkage. Its electronic absorption spectrum was examined, proving that the diacetylene linkage induces splitting of Soret band of OEP into two main bands with clear maxima at 429 and 481 nm and more bathochromic shift of Q band to appear in such a longer wavelength region at $\lambda_{\text{max}} = 670$ nm in chloroform, in contrast with that of the corresponding vinylene-group connected OEP trimer. It was shown that the spectrum of the present diacetylene-group connected OEP derivative drastically changed in pyridine, suggesting a coordination of pyridine molecule as the fifth ligand onto Ni(II) metal of the central ring. Furthermore, Vilsmeier formylation, a typical electrophilic substitution on the aromatic compounds, was examined for further oligomerization of OEP, proving that it takes place at the central ring exclusively.

Keywords: Porphyrin; Trimer; Diacetylene; Vinylene; Electronic property; Vilsmeier formylation

1. Introduction

In order to develop the new organic functional materials supporting the present opto-electronic society life, the extended $\pi$-electronic conjugation systems of porphyrin nuclei connected with various linkages have been vastly demonstrated, by virtue of their high susceptibilities to the optical and electronic stimulations [1]. Especially at the molecular design for functional materials, it is very important to construct the electronic structure of the molecule both purposively and precisely. For example, the intensification of particular bands participating in a material functionality in the electronic absorption spectra would lead to an enhancement of their responses and sensing capabilities to the outside stimulations. In addition to such an auxiliary modification of the main electronic structure, the extension of $\pi$-electronic conjugation system would make an electronic activation of the molecule much easier, leading to the wider versatility of photo-sensing functionalities such as non-linear optical (NLO) phenomena and to the further processibility for the material devices as well.

In connection with such intensive applicative investigations of porphyrin derivatives, the trinucleic porphyrin derivative 1 has been synthesized, in which each porphyrin ring is connected with a rigid and straight linkage of diacetylene (Chart 1). The electronic properties of 1 will be described, from the viewpoint of the $\pi$-electronic conjugation aspect as a functional unit of opto-electronic devices, as compared with those of the related compounds including the vinylene-group connected octaethylporphyrin (OEP) trimer 2 [2].

2. Results and discussion

2.1. Synthesis

The synthesis of 1 was carried out by an oxidative coupling between the corresponding terminal acetylenes (Scheme 1) [3], in which non-substituted porphyrin ring was employed as a central one in place of OEP ring due to a synthetic reason. Thus, coupling of bis(acetylene) 8 [4] with an excessive amount of the OEP acetylene 9 [5] yielded the desired
compound 1 as deep green crystalline powder (CHCl₃–MeOH).

2.2. Electronic absorption spectra

The diacetylene- and vinylene-group connected OEP dimers 4 [5] and 5 [6] demonstrate a typical difference between their absorption spectra, in reflecting the respective linkage effects on the spectrum of OEP 3 (Fig. 1). In the case of 4, the diacetylene linkage plays an important role in a drastic change of the electronic structure, with respect to that of 3, wholly exhibiting a bathochromicity of the spectrum and particularly splitting Soret band into three bands with clear maxima ($\lambda = 423, 455$ and $482$ nm) [5]. In contrast with the diacetylene linkage, the spectrum of 5 shows that the vinylene linkage does not affect Soret band of 3 so much, but rather changes Q band to elongate its absorption terminal over 800 nm [6].

In the case of trinucleic OEP derivatives 1 and 2, the characteristic features of the respective linkages were also observed in their individual spectra (Fig. 2). The vinylene-group connected OEP trimer 2 exhibits a further extension from the spectrum of the OEP dimer 5, with broadening each absorption band and elongating the terminal of Q band over 900 nm up to the near infrared region [7]. It was also shown that the vinylene linkage enhances the acidity and electron-releasing ability of OEP efficiently [8]. The spectrum of 2, however, clearly shows that the vinylene linkage possesses no ability enough to perturb the electronic structure of Soret band owing to $\pi-\pi^*$ transitions seriously even in such an extended $\pi$-electronic conjugation system. On the other hand, the trinucleic OEP derivative 1 showed a large splitting of Soret band, though by a little bit smaller as compared with the splitting width of the OEP dimer 4, to afford the clear maxima at 429 and 481 nm. Q band of 1 also showed further bathochromicity to afford an intensified and broad band at such a longer wavelength maximum of 670 nm, suggesting that the higher $\pi$-electronic conjugation system was constructed in 1. Also in the further oligomeric OEP derivatives, the diacetylene linkage would be expected to serve as a spacer linkage for an electronic communication between the constituent OEP chromophores with higher efficiency. In other words, it could be concluded that the diacetylene linkage with sp-C::sp-C character holds a high planarity throughout the molecule to take part in an extension of $\pi$-electronic conjugation smoothly probably due to its straight and rigid linkage, while the vinylene linkage with sp²-C::sp²-C character deviates enormously from the $\pi$-electronic conjugation plane with OEP ring to exist in a stairway form probably due to its steric repulsion with peripheral ethyl substituents in OEP ring.

2.3. Solvent effect on the electronic spectra

Among all the oligomeric porphyrin derivatives in this study, the diacetylene-group connected trinucleic OEP derivative 1 was found to show an intensive bathochromic shift ($\Delta\lambda = 70$ nm) of Q band in pyridine from that in CHCl₃ (Fig. 3). Not the vinylene-group connected OEP trimer 2 nor the constituent derivative 8 of 1 exhibited particular differences between their spectra in CHCl₃ and pyridine. Therefore, the present solvent-dependent spectral behavior is entirely independent in 1. At the present stage, it is proposed as a plausible feature that the sterically strain-free central porphyrin ring is readily coordinated with pyridine molecule as the fifth ligand, probably due to its lower electron density caused by the two diacetylene linkages and to the inherently low LUMO in such an extended $\pi$-electronic conjugation system. Under such a specific situation, the back-donative interaction from Ni(II) metal to the 18 $\pi$-electronic ring system of OEP would be weakened by
coordination of pyridine, recovering its much lower LUMO and thus reducing a NBMO–LUMO gap in consequence (Chart 2). In all the other OEP derivatives, which do not show such a solvent-dependent spectral change, it is likely that the peripheral ethyl substituents prevent the porphyrin ring from the coordination attack by pyridine ligand efficiently.

2.4. Linkage effect on Vilsmeier formylation

For extension of the meso-substituted conjugation systems of porphyrin nuclei, as a synthetic methodology, the formyl substituent is generally and naturally introduced into a starting material, because it is readily convertible into the desired forms such as alcohol and terminal acetylene. In fact, in the respective synthetic sequences for these OEP oligomeric derivatives 2, 4 and 5, formylation of the respective OEP constituents connected with vinylethylene or diacetylene linkage was essentially the key step [5–7]. Thus, the formylation effect on monoformylation of the trinucleic OEP derivatives 1 and 2 was examined from an isomerism viewpoint of the product distributions, because there are two different reaction sites at the outer ring (site-selectivity) and two different porphyrin rings in both 1 and 2 (position-selectivity) (Scheme 2).

Since the formylation of OEP is a fairly mild reaction, a large excessive amount of the Vilsmeier reagent to OEP is generally used and thus the polyformylation products are likely accompanied [9]. Therefore, the reactions in this study were carried out under the limited conditions where only monoformylation of OEP efficiently occurs at 50–55 °C in 1,2-dichloroethane, and were terminated before the starting OEP materials were completely consumed (see Section 3.1) [10]. In case of the vinylethylene-group connected OEP trimer 2, to be surprised, the complete position-selectivity was observed. Thus, the formylation did not occur at the outer OEP rings, but afforded the product 10 formylated at the central ring in 66% yield [11]. As is also deducible from the less steric repulsion of the central ring with the Vilsmeier reagent, the position-selectivity was similarly observed in 1, affording the monoformylation product 11 solely [12]. The position-selectivity in Vilsmeier formylation of 1 and 2 has been unclear as yet [13]. These results clearly indicate that both diacetylene and vinylethylene linkages are effective for incorporation of the electrophilic substituents predominantly in

Fig. 1. Electronic absorption spectra of 3: OEP(Ni); 4: diacetylene-group connected OEP(Ni) dimer; and 5: vinylethylene-group connected OEP(Ni) dimer (CHCl3).

Fig. 2. Electronic absorption spectra of trinucleic OEP(Ni) derivatives 1 (—) and 2 (—–) (CHCl3).

Fig. 3. Electronic absorption spectra of 1 in CHCl3 (—) and pyridine (—––).
the central ring of the trinucleic porphyrin derivatives, based on which the new two-dimensional extended molecular systems could be developed. However, it is noted that under the same conditions, a fair amount of the starting material \( \text{1} \) was recovered and the yield of \( \text{11} \) was only 35% yield, apparently indicating that the diacetylene linkage reduces its reactivity in electrophilic substitution of the porphyrin ring, as compared with the vinylene linkage (Chart 3).

3. Conclusion

The diacetylene-group connected trinucleic OEP derivative \( \text{1} \) was successfully synthesized by an oxidative coupling of the corresponding terminal acetylenes. Electronic absorption spectrum and Vilsmeier monoformylation of \( \text{1} \) were examined and were compared with those of the vinylene-group connected OEP trimer \( \text{2} \), proving that the diacetylene linkage affects not only the electronic spectral properties but also the electrophilic substitution of OEP nucleus more intensively than the vinylene linkage. Based on the results from the present study, the construction of the further extended \( \pi \)-electronic conjugation systems of new type is now in progress [13].

3.1. Experimental

The melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a Jasco FT-IR 7300 spectrophotometer as KBr disk; only significant absorptions are reported. EI and FAB mass spectra were recorded with JEOL JMS-700 and/or AX-505 spectrometers. In case of the hard ionization by the above techniques, ESI-FT-ICR mass spectra were performed with a Bruker BioAPEX 70e spectrometer equipped with a 7 T superconducting magnet, using a sample in a solution of CHCl\(_3\):MeOH (3:2). \(^1\)H NMR spectra were measured in CDCl\(_3\) solutions, unless otherwise stated, at 25 °C on JEOL Delta ECP-NMR 600 (600 MHz) spectrometer and were recorded in \( \delta \) values (per ppm) with TMS as an internal standard. The coupling constants (\( J \)) are given in Hertz. Electronic absorption spectra were measured in CHCl\(_3\) solution on a Shimadzu UV-2200A spectrophotometer. SiO\(_2\) (Fujisilycia BW 820MH or BW 127ZM) and aluminum oxide (Al\(_2\)O\(_3\), CAMAG 504-C-1) were used for column chromatography. THF was distilled over calcium hydride and then over sodium diphenylketyl under argon (Ar) before use. The reactions were followed by TLC aluminum sheets precoated with Merck SiO\(_2\)-F\(_{254}\) or with Merck Al\(_2\)O\(_3\)-GF\(_{254}\). Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate (MgSO\(_4\)) prior to removal of the solvents.

3.1.1. 5,15-Bis(trimethylsilyl)ethynyl)porphyrin and its terminal acetylene \( \text{8} \) [4]

A solution of dipyrromethane \( \text{6} \) (736 mg, 5.04 mmol) and trimethylsilylpropynal \( \text{7} \) (762 mg, 6.05 mmol) in MeOH
(90 cm$^3$) was stirred at $-30^\circ$C in the presence of $p$-toluene sulfonic acid monohydrate ($p$-TsOH·H$_2$O, 319 mg, 1.68 mmol) for 3 h and then gradually warmed up to room temperature. To the reaction mixture, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 2.23 g, 9.82 mmol) was added and then stirred for 30 min. After adding triethylamine (NEt$_3$, 1.8 cm$^3$), the mixture was concentrated under reduced pressure. The solid was triturated with CHCl$_3$ thoroughly and filtered. The residue obtained after removal of the solvent was chromatographed on SiO$_2$ with hexane–CHCl$_3$ (3:2) to afford the corresponding nickel derivative (80 cm$^3$) was added NaH (390 mg, 9.92 mmol, 60% in oil) at an ambient temperature and kept there for 1 h. To the reaction mixture, sat. aq. sodium bicarbonate, brine and then dried. The residue obtained after removal of the solvent was chromatographed on SiO$_2$ with hexane–CHCl$_3$ (7:3) to afford the bromovinyl OEP derivative (640 mg, 70%).$^1$H NMR (CDCl$_3$); $\delta$ = 9.49 (2H, s, meso-H), 9.47 (1H, s, meso-H), 9.41 (1H, d, $J$ = 14.0 Hz, vinyl-H), 5.47 (1H, d, $J$ = 14.0 Hz, vinyl-H), 3.90–3.70 (16H, m, CH$_2$), 1.79–1.60 (24H, m, CH$_3$).

To a solution of DSMSO (1 cm$^3$) in 1,2-dimethoxyethane (100 cm$^3$) was added NaH (390 mg, 9.92 mmol, 60% in oil) at room temperature. To the resulted solution, the bromovinyl OEP derivative (900 mg, 1.29 mmol) obtained above was added and stirred under reflux for 4 h. Poured onto crashed ice, the mixture was extracted with CHCl$_3$. The extracts were washed with brine and then dried. The residue obtained after removal of the solvent was chromatographed on SiO$_2$ with hexane–CHCl$_3$ (4:1) to afford the ethynyl OEP derivative 9 (690 mg, 86%).$^1$H NMR (CDCl$_3$); $\delta$ = 9.43 (2H, s, meso-H), 9.42 (1H, s, meso-H), 4.50 (1H, s, CCH), 4.17 (4H, q, $J$ = 7.2 Hz, CH$_2$), 3.84–3.75 (12H, m, CH$_2$), 1.78–1.69 (24H, m, CH$_3$).

3.1.3. Diacetylene-group connected trinuclear OEP derivative 1

A solution of $M$ = Ni, $Y$ = H, 90 mg, 0.217 mmol) and 9 (670 mg, 1.08 mmol) in pyridine (300 cm$^3$) was added to a solution of anhydrous copper(II) acetate [Cu(OAc)$_2$, 1.18 g, 6.50 mmol] in pyridine (50 cm$^3$) at 40 $^\circ$C over 4 h. Stirred for additional 10 h, the reaction mixture was poured into water and extracted with CHCl$_3$. The organic extracts were washed with 3 N HCl, sat. aq. sodium bicarbonate, brine and then dried. The residue obtained after removal of the solvent was recrystallized from CHCl$_3$–MeOH to afford 1 (79 mg). The residue from mother liquor was chromatographed on SiO$_2$ with CHCl$_3$ to give an additional 10 mg of 1 (total 89 mg, 25%), together with the diacetylene-group connected OEP dimer 4 [5] (102 mg). Selected structural properties of 1: mp; gradually decomposed at around 270 $^\circ$C. MS-FAB; $m/z$ at around 1640 for an isotope fragmentation group of C$_{100}$H$_{76}$N$_{12}$Ni$_3$ (MW = 1641.965). IR (KBr); $\nu$ = 2962, 2928, 2868 (C–H), 2180, 2129 cm$^{-1}$ (C–C–).$^1$H NMR (CDCl$_3$;pyridine-d$_5$ 1: 1 v/v); $\delta$ = 9.771 (2H, s, meso-H in the central ring), 9.541 (4H, d, $J$ = 5.2 Hz, pyrrole-H in the central ring), 9.358 (2H, s, meso-H, in the outer ring), 9.329 (4H, d, meso-H, in the outer ring), 9.247 (4H, d, $J$ = 5.2 Hz, pyrrole-H, in the central ring), 4.626–3.93 (32H, m, CH$_2$), 1.995–0.884 (48H, m, CH$_3$). Other physical properties of 1 will be reported elsewhere in detail.

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[10] The reactions were carried out for 6–7 h, at 50–55 °C in 1:2-dichloroethane (20 cm3) using 1.7–2.0×10–2 mmol of the starting materials and 15–20 eq. amount of the Vilsmeier reagent, under the limited conditions of which the monoformalization product from 3 was obtained in 70–75% yield. Also see Experimental part as general procedure for Vilsmeier formalization of 3.
[11] Selected structural properties of 10: FAB-MS: m/z 1850.382 for C113H132N12ONi3 (MW = 1850.376). 1H NMR (CDCl3); δ = 11.503 (1H, s, CHO), 9.465 (1H, s, meso-H in the outer ring), 9.423 (2H, s, meso-H in the outer ring), 9.418 (1H, s, meso-H in the outer ring), 9.370 (2H, s, meso-H in the outer ring), 8.866 (1H, s, meso-H in the central ring formylated), 7.860 (1H, d, J = 16.2, vinylene-H), 7.691 (1H, d, J = 15.6, vinylene-H), 7.232 (1H, d, J = 16.2, vinylene-H), 7.145 (1H, d, J = 15.6, vinylene-H), 3.842–2.835 (48H, m, CH3), 1.829–0.856 (72H, m, CH2).
[12] Selected structural properties of 11: FAB-MS: m/z 1669.965 for C109H88Ni13ONi3 (MW = 1669.968). 1H NMR (1:1 v/v CDCl3/pyridine-d5); δ = 11.758 (1H, s, CHO), 9.551 (2H, d, J = 5.4, pyrrole-H in the central ring), 9.502 (2H, d, J = 5.8, pyrrole-H in the central ring), 9.350 (4H, s, meso-H in the outer ring), 9.322 (2H, s, meso-H in the outer ring), 9.277 (2H, d, J = 5.4, pyrrole-H in the central ring), 9.269 (1H, d, J = 15.6, vinylene-H), 9.219 (2H, d, J = 5.8, pyrrole-H in the central ring), 9.065 (1H, s, meso-H in the central ring formylated), 4.266–3.183 (32H, m, CH2), 1.922–0.898 (48H, m, CH3).
[13] Studies on the quantitative analysis of the spectral change of I in pyridine and on the theoretical interpretation of the position-selectivity in Vilsmeier monoformalization are now underway. The results will be reported in detail properly, together with an application of the present result to the construction of the Studies on the quantitative analysis of the spectral change of I in pyridine and on the theoretical interpretation of the position-π-electronic conjugation systems of the new type such as two-dimensional diacetylene- and vinylene-groups connected OEP oligomers.