Title

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Syntheses and properties of amphiphilic zinc(II), nickel(II), and palladium(II) phthalocyanines with eight tri(oxyethylene) chains introduced at non-peripheral α positions

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Dedicated to Prof. Tomás Torres on the occasion of his 70th birthday

ABSTRACT: Amphiphilic zinc(II) (**1**), nickel(II) (**2**), and palladium(II) (**3**) complexes of 1,4,8,11,15,18,22,25-octakis(1,4,7,10-tetraoxaundecyl)phthalocyanine were synthesized and characterized by elemental analysis and MALDI-TOF mass and ^{1}H NMR spectroscopies. Electronic absorption spectra showed aggregation of the phthalocyanine molecules in H_2O for **2** and **3**, while the monomeric form for **1** in H_2O, and **1**, **2**, and **3** in CH_2Cl_2. The cyclic voltammograms of **1**, **2**, and **3** in CH_2Cl_2 showed that oxidation of the phthalocyanine ring occurs easily in these complexes. This may be due to the energetically increased HOMO, coming from the deformation of the phthalocyanine ring. Steric hindrance between the α-introduced 1,4,7,10-tetraoxaundecyl groups (tri(oxyethylene) chains) within the phthalocyanine molecule gives rise to the deformation of the phthalocyanine ring, which decreases the aggregating nature of the present complexes.

KEYWORDS: α-substituted phthalocyanines, tri(oxyethylene) chains, amphiphilic property, zinc(II) complex, nickel(II) complex, palladium(II) complex.

INTRODUCTION

Phthalocyanines and their metal complexes ([M(pc)]) have received continuous attention due to their unique properties derived from the extended π-system within the molecules, giving a strong absorption called the Q band in the near-infrared region (650–700 nm) [1–4]. This is the reason why they show remarkable blue or green colors and enable us to apply these compounds to many fields concerning pigments [1–5], photocatalysts for hydrogen generation [6], non-linear optics [7, 8], chemical sensors [7, 9], energy storage and conversion [7, 10], optically active compounds [11], dye-sensitized solar cells (DSSCs) [12, 13], perovskite-based solar cells (PSCs) [14, 15], and photodynamic therapy (PDT) [16–20], including magnetic materials such as single-molecule magnets [13, 21–23]. The chromogenic properties of the π-conjugated system may be expected to be modified by changing the central metal atom or adding functional groups to the phthalocyanine (pc) rings at their α and β-positions (Scheme 1), which are also called non-peripheral and peripheral positions, respectively, because the optoelectronic properties depend on the coupling between

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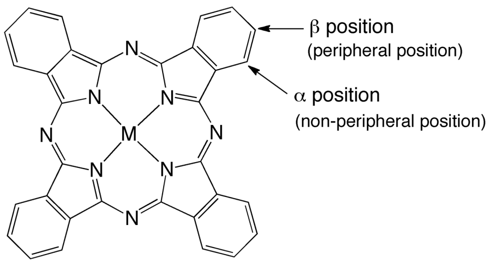


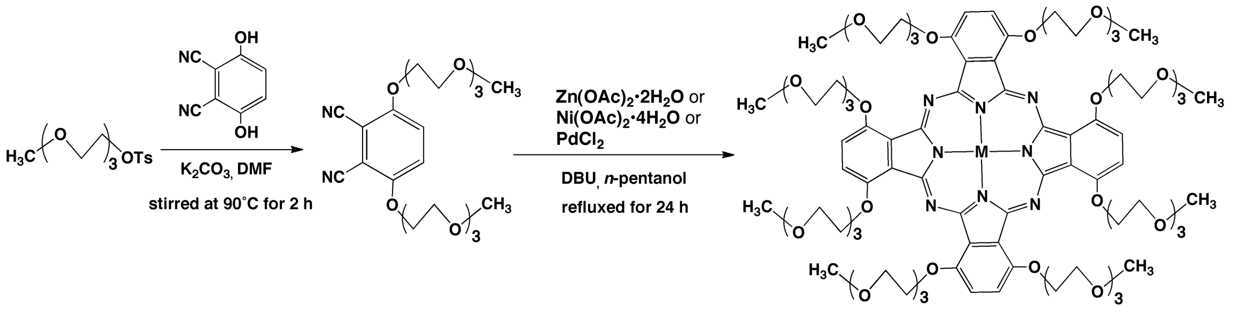
Scheme 1. Chemical structure of [M(pc)].

the delocalized electronic ligand system and the d-orbital electrons of the transition metal ion [13]. The addition of substituent groups to the α-position was reported to arise the red-shift of the Q-band absorption beyond 700 nm by the distortion of the phthalocyanine ring due to the steric hindrance between the α-substituent groups [24–30]. Among many phthalocyanine compounds, amphiphilic phthalocyanines substituted by tri(oxyethylene) chains are interesting, because such compounds are promising as materials for PDT [20]. Kobayashi *et al.* synthesized a β-substituted phthalocyanine with eight tri(oxyethylene) chains, 2,3,9,10,16,17,23,24-octakis(1,4,7,10-tetraoxaundecyl)-phthalocyanine and its zinc(II) complex [31]. They found that these compounds are amphiphilic, dissolving in dioxane as a monomer and in water as an aggregated species. Taking these results into the consideration, we decided to synthesize zinc(II), nickel(II), and palladium(II) complexes with an α-substituted phthalocyanine with eight tri(oxyethylene) chains, 1,4,8,11,15,18,22,25-octakis(1,4,7,10-tetraoxaundecyl) phthalocyanine ($H_2\alpha$-otoupc). Here, we report on these complexes' synthesis and spectroscopic and electrochemical properties.

RESULTS AND DISCUSSION

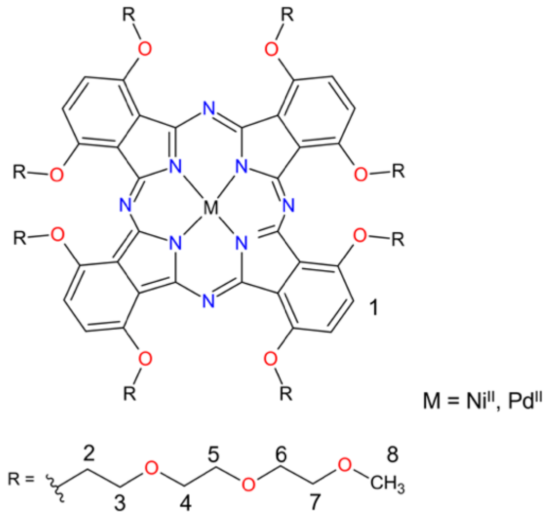
Syntheses of the phthalocyanine complexes [Zn(α-otoupc)] (**1**), [Ni(α-otoupc)] (**2**), and [Pd(α-otoupc)] (**3**) were successfully performed by the template reactions of metal ions with 3,6-bis(1,4,7,10-tetraoxaundecyl)phthalonitrile, which was obtained using the method reported by Ng *et al.* [32]. The synthesized complexes were identified by MALDI-TOF mass spectra and elemental analyses. The synthesis scheme is shown in Scheme 2. The synthesis of zinc(II) complex **1** was reported in the literature, along with its NMR and absorption spectra, measured in DMF-d_7 and DMSO, respectively [33]. In the report, details on the synthesis of **1** were not described. Hence, we synthesized complex **1** in the method described in the Experimental section and measured the NMR spectrum (in DMSO-d_6) as given in Fig. S1. The NMR spectra measured for **2** and **3** in $CDCl_3$ are given with their assignments in Fig. 1.

The absorption spectra (measured at the concentration of 1.0×10^{-4} M in DMSO and CH_2Cl_2) of **1** are given in Fig. 2. The spectrum measured in DMSO is the same as that given in the previous report [33]. There is no important difference between spectral features measured in DMSO and CH_2Cl_2; the Q band was observed at 740 nm in DMSO and 733 nm in CH_2Cl_2. A weak unknown band around 800 nm in CH_2Cl_2 was also observed in the previous report [33], although it was observed in the DMSO solution. The significant red-shift of the Q band beyond 700 nm should come from the introduction of eight tri(oxyethylene) chains at the α positions of the pc ring, when taking into account that a zinc(II) phthalocyanine with eight tri(oxyethylene) chains at the β positions ([Zn(β-otoupc)]) shows the Q band at λ_{max} = 670 nm in dioxane. The tri(oxyethylene) chains introduced at the α positions should lead to the distortion of the pc ring due to the steric hindrance between the chains. In fact, distorted pc rings are often found in crystal structures of α-substituted phthalocyanines [25–28, 30, 34–41]. It has been reported that the deformed phthalocyanines (with a distorted pc ring) decrease the HOMO-LUMO gap, which corresponds to the Q band energy [24, 25, 28]. The absorption spectra of **2** and **3** in CH_2Cl_2 at the concentration of 1.0×10^{-4} M are displayed in Fig. 3, respectively. The spectral features of both complexes are the typical ones of the non-aggregated species because the Q bands observed at λ_{max} = 733 nm (for **2**) and 723 nm (for **3**) are sharply strong. A heavier metal ion inserted into pc ring is known to make the Q band blue-shifted [4, 42–44].



[M(α-otoupc)] (M = Zn^{II} (**1**), Ni^{II} (**2**), Pd^{II} (**3**))

Scheme 2. The synthetic procedure of **1**–**3**.



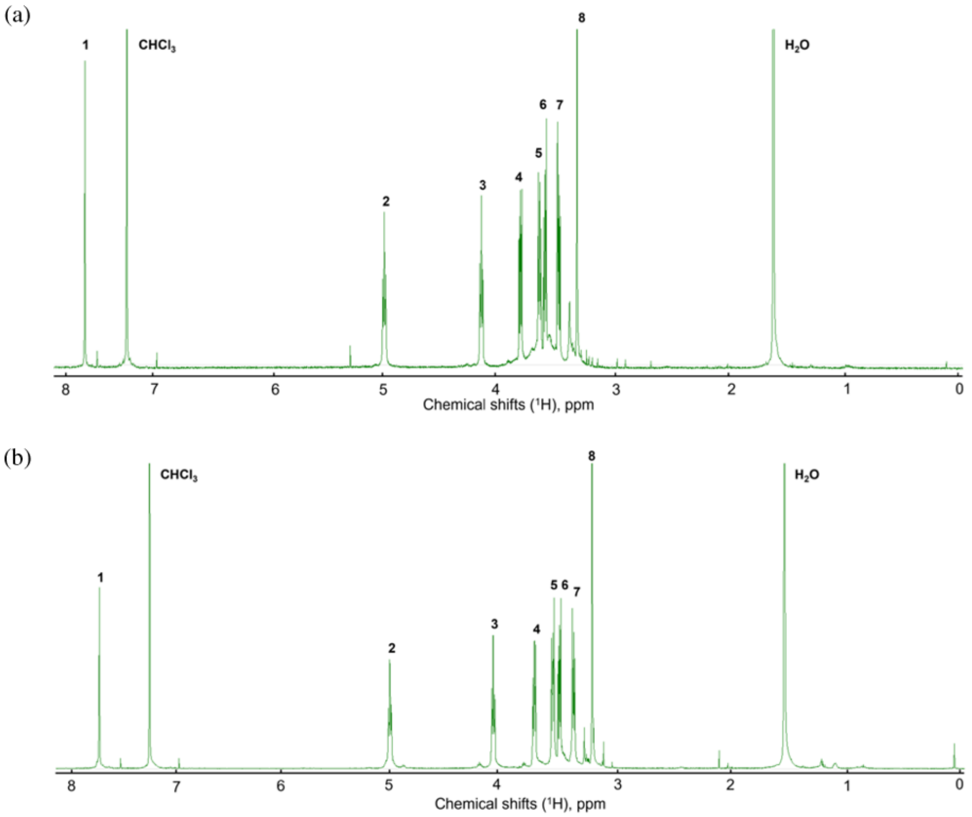


Fig. 1. ^{1}H NMR spectra of **2** (a) and **3** (b) in CDCl$_3$.

This may be the reason why the Q band of **3** is located at a shorter wavelength (723 nm) compared with that of **2** (733 nm). The fluorescence emission band was observed at 770 nm in CH_2Cl_2 for **1** (Fig. S2), with the peak position similar to that reported previously in DMSO for **1** (751 nm) [33], although no emission band was observed for **2** and **3**.

All the present complexes **1** – **3** are soluble in water. That is, they are amphiphilic compounds. The absorption spectra measured at the concentration of 1.0×10^{-4} M in water are shown in Fig. 4 for **1** and **3** and Fig. 5 for **2**, respectively. Complex **1** has a relatively sharp and strong Q band among the present complexes. The band position and intensity (λ_{max} = 750 nm, $\varepsilon_{max} = 1.28\times10^5$ M^{-1} cm^{-1}) are rather similar to that measured in CH_2Cl_2 (λ_{max} = 733 nm, $\varepsilon_{max} = 1.66\times10^5$ M^{-1} cm^{-1}). This result implies that the complex may exist mainly as monomeric species in water. This is one of the important points that originated from the introduction of eight tri(oxyethylene) chains at the α positions. The amphiphilic zinc(II)

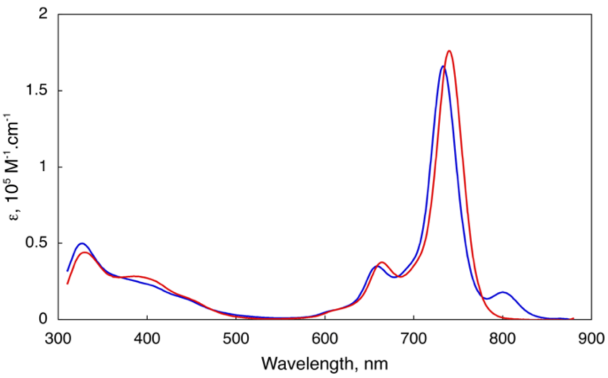


Fig. 2. Absorption spectra of **1** in DMSO (—) and CH_2Cl_2 (—) at the concentration of 1.0×10^{-4}M.

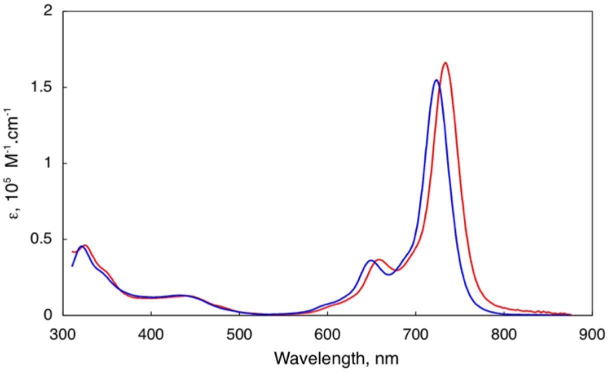


Fig. 3. Absorption spectra of **2** (—) and **3** (—) in CH_2Cl_2 at the concentration of 1.0×10^{-4} M.

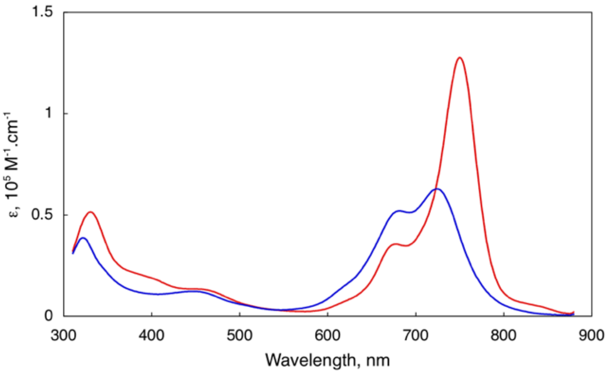


Fig. 4. Absorption spectra of **1** (—) and **3** (—) in H_2O at the concentration of 1.0×10^{-4} M.

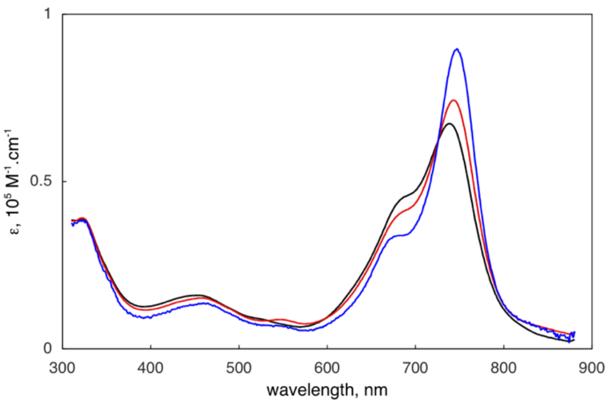


Fig. 5. Absorption spectra of **2** in H_2O at the concentrations of 1.0×10^{-4} (—), 1.0×10^{-5} (—), and 1.0×10^{-6} M (—).

phthalocyanine with the eight chains at β positions [Zn(β-otoupc)] shows a broad band around 630 nm (λ_{max} = 729 nm, ε_{max} ~ 3.5×10^4 M^{-1} cm^{-1}) whereas the complex shows a sharply strong Q band at λ_{max} = 670 nm (ε_{max} = 1.5×10^5 M^{-1} cm^{-1}) in dioxane [31]. It has been proposed that the distortion of the pc ring would depress the aggregation of pc molecules [32]. This could work for **1** in water, giving the relatively sharp Q band at nearly the same wavelength position as that observed in CH_2Cl_2. In water, **2** has a shoulder band around 680 nm and **3** has a band as a peak at 681 nm, at the shorter wavelength region relative to their Q band positions (739 nm for **2** and 724 nm for **3**). The shoulder band of **2** becomes less remarkable and the Q band becomes stronger when the concentration is decreased (Fig. 5). The blue shift of the Q band is known to be due to the face-to-face aggregation (H-aggregate) in the solution [4, 43]. The present results indicate that the aggregated species could be present in considerable amounts for **2** and **3** in water. Although it is difficult to explain the difference in the aggregating nature between **1** and the other complexes **2** and **3** in water, oxygen atoms of water molecules or tri(oxyethylene) chains could play an important role by occupying the axial site of the central zinc(II) ion for **1**. Nickel(II) and palladium(II) complexes with d^8 electron configuration prefer a tetragonal planar geometry without axial ligations when there are strong donations at the four equatorial coordination sites, like in the cases of phthalocyanine ligands.

It has been well established that HOMO and LUMO energies of phthalocyanines are correlated with their first oxidation and reduction potentials [25, 45–47]. Cyclic voltammograms (CVs) obtained in CH_2Cl_2 containing 0.1 M TBAP (tetra-*n*-butylammonium perchlorate) are displayed in Fig. 6. The potential values are quoted relative to Fc^+/Fc redox couple. On the oxidation side, there are two redox waves for all three complexes; $E_{1/2}$ (=(E_{pa} + E_{pc})/2) = -0.03 and 0.37 V for **1**, 0.07 and 0.49 V for **2**, and 0.12 and 0.56 V for **3**. The potential values are rather comparable to that reported for a deformed zinc(II) phthalocyanine with eight phenyl groups at α positions ([Zn(pcPh$_8$)]); $E_{1/2}$ = -0.2 and 0.27 V vs Fc^+/Fc in *o*-dichlorobenzene containing 0.1 M TBAP [25]. In this report, based on the MO calculation results, it has been explained that HOMO is energetically increased in the deformed pc complex, which is the main reason for the location of the Q band in a longer region (λ_{max} = 786 nm for [Zn(pcPh$_8$)] in pyridine). The first reduction potential ($E_{1/2}$ = -1.71 V vs. Fc^+/Fc in *o*-dichlorobenzene) of [Zn(pcPh$_8$)] is negatively

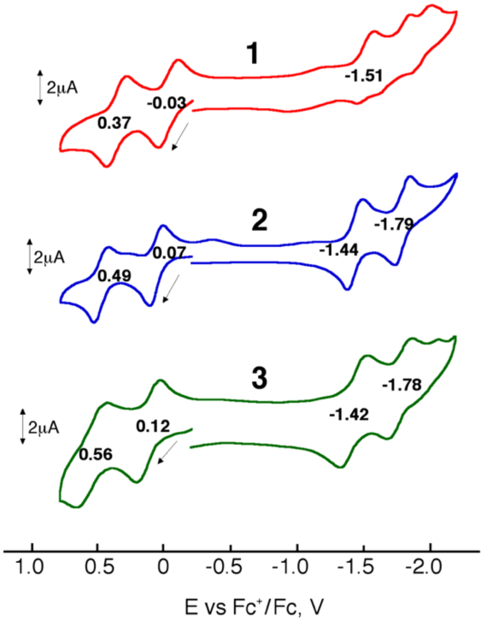


Fig. 6. Cyclic voltammograms of **1**, **2** and **3** in CH_2Cl_2 ([complex] = 5×10^{-4} M; [TBAP] = 0.1 M; scan rate = 50 mV.s^{-1}).

shifted by only 0.08 V compared with that of a planar complex [Zn(PcPh$_2$)] ($E_{1/2}$ = -1.63 V vs Fc$^+$/Fc). On the reduction side (Fig. 6), the potential values for the redox waves are estimated to be $E_{1/2}$ = -1.51 V for **1**, -1.44 and -1.79 V for **2**, and -1.42 and -1.78 V for **3**, respectively, although the second reduction potential is not given here for **1** because the redox behavior is complicated after the first reduction wave. The difference between the first oxidation and reduction potentials are 1.48 V for **1**, 1.51 V for **2**, and 1.59 V for **3**, which are close to that of [Zn(pcPh$_8$)] (1.51 V). The CV results support that the appearance at the longer wavelength region (~750 nm) of the Q band for **1**, **2**, and **3** in CH_2Cl_2 and water may be due to the deformed structures of the pc ring in the present complexes.

EXPERIMENTAL

Syntheses of complexes

3,6-Bis(1,4,7,10-tetraoxaundecyl)phthalonitrile was synthesized by the method reported by Ng *et al* [32].

1,4,8,11,15,18,22,25-Octakis(1,4,7,10-tetraoxaundecyl)phthalocyaninatozinc(II) [Zn(otoupc)] (1). 3,6-Bis(1,4,7,10-tetraoxaundecyl)phthalonitrile (453 mg, 1.0 mmol) and zinc(II) acetate dihydrate (109 mg, 0.5 mmol) were dissolved in a dried *n*-pentanol (5 mL) containing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.3 mL) and refluxed for 23 h under N_2. The solvent was removed by evaporation, followed by the addition of toluene (5mL × 3), filtration, and evaporation to dryness. Then, the residue dissolved in a small portion of chloroform was passed through an alumina column twice times using chloroform and chloroform/methanol (100:2 v/v). The collected fraction was evaporated to dryness and further dried under vacuum at 100°C for 6 h to give a green oil; Yield 210 mg (11.2%); Anal. Calcd for $C_{88}H_{128}N_8O_{32}Zn$: C, 56.36; H, 6.88; N, 5.98%. Found C, 56.09; H, 6.67; N, 5.96%. MALDI-TOF-MS: Found 1874.20 *m/z* (calcd for [M]$^+$ 1872.79). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (s, 8H, Ar$\underline{H}$), 5.06-5.04 (m, J = 4.9 Hz, 16H, ArO-C$\underline{H}_2$-), 4.09 (t, J = 4.9 Hz, 16H, -O-C$\underline{H}_2$-), 3.70-3.68 (m, 16H, -C$\underline{H}_2$-O-), 3.52-3.41 (m, 32H, -O-C$\underline{H}_2$-C$\underline{H}_2$-), 3.12 (s, 24H, -OC$\underline{H}_3$).

1,4,8,11,15,18,22,25-Octakis(1,4,7,10-tetraoxaundecyl)phthalocyaninatonickel(II) [Ni(otoupc)] (2). The complex was synthesized in a similar manner to [Zn(otoupc)] using nickel(II) acetate tetrahydrate in place of zinc(II) acetate dihydrate. The chromatographic purification was made by passing through the alumina column (eluent: chloroform) and subsequently passing through silica gel columns (eluent: chloroform/methanol (100:3 v/v)). The obtained material was green oil. The yield was 108 mg (5.8 %). Anal. Calcd for $C_{88}H_{128}N_8O_{32}Ni$: C, 56.56; H, 6.90; N, 6.00%. Found C, 56.23; H, 6.54; N, 6.04%. MALDI-TOF-MS: Found 1866.32 *m/z* (calcd for [M]$^+$ 1866.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 8H, ArH), 5.01-4.99 (t, J = 5.2 Hz, 16H, ArO-CH$_2$-), 4.16-4.14 (t, J = 5.2 Hz, 16H, -CH$_2$-O-), 3.82-3.79 (m, 16H,-OC$\underline{H}_2$-), 3.65-3.62 (m, 16H, -C$\underline{H}_2$-O-), 3.60-3.58 (m, 16H, -OC$\underline{H}_2$-), 3.48-3.46 (m, 16H, -C$\underline{H}_2$-O-), 3.31 (s, 24H, -OC$\underline{H}_3$). In the second chromatographic purification using a silica gel column, we found a violet fraction after the green fraction of **2**. The violet fraction was eluted with chloroform/methanol (100:7 v/v). The amount of the finally obtained material as a dark violet oil was too small to be characterized by the elemental analysis. MALDI TOF mass spectrum confirmed that the oily compound is a corresponding triazatetrabenzocorrole complex (Fig. S3; Found 1853.48 *m/z* (calcd for [M]$^+$ 1852.80)).

1,4,8,11,15,18,22,25-Octakis(1,4,7,10-tetraoxaundecyl)phthalocyaninatopalladium(II) [Pd(otoupc)] (3). The complex was obtained in a similar manner to [Zn(otoupc)] using palladium(II) chloride in place of zinc(II) acetate dihydrate. The chromatographic purification was made by passing through the alumina column (eluent: chloroform) and subsequently passing through silica gel columns (eluent: chloroform/methanol (100:3 v/v)). The obtained material was green oil. The yield was 45 mg (2.3%). Anal. Calcd for $C_{88}H_{128}N_8O_{32}Pd$: C, 55.15; H, 6.73; N, 5.85%. Found C, 55.20; H, 6.49; N, 5.67%. MALDI-TOF-MS: Found 1914.28 *m/z* (calcd for [M]$^+$ 1914.29). ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 7.71 (s, 8H, Ar$\underline{H}$), 5.13-5.10 (t, J = 5.2 Hz, 16H, ArO-C$\underline{H}_2$-), 4.19 (t, J = 5.2 Hz, 16H, -C$\underline{H}_2$-O-), 3.83-3.81 (m, 16H, -O-CH$_2$), 3.67-3.59 (m, 32H, -C$\underline{H}_2$-O-C$\underline{H}_2$-), 3.48-3.46 (m, 16H, -C$\underline{H}_2$-O-), 3.30 (s, 24H, -OC$\underline{H}_3$).

Measurements

Elemental carbon, hydrogen, and nitrogen analyses were carried out using a Yanako CHN CORDER MT-6. ^{1}H NMR spectra were recorded on a JEOL JNM-AL400 spectrometer. Chemical shifts were referenced to the solvent residual peaks of $CHCl_3$ (δ = 7.26) for nickel(II) and palladium(II) complexes (**2** and **3**), and DMSO-d_6 (δ = 2.50) for zinc(II) complex (**1**). Absorption spectra were measured in dichloromethane and water using a Shimadzu UV-2450 spectrometer. MALDI-TOF mass spectra were taken on Bruker Daltonics Autoflex-T1. Cyclic voltammograms were measured in dichloromethane containing tetra-*n*-butylammonium perchlorate, $[(n\text{-}C_4H_9)_4N](ClO_4)$, on a BAS 100BW Electrochemical Analyzer. A glassy carbon disk (1.5 mm radius), platinum wire, and saturated calomel electrodes were used as working, counter, and reference electrodes. All cyclic voltammograms were internally referenced to the Fc^+/Fc redox couple.

CONCLUSION

Amphiphilic zinc(II), nickel(II), and palladium(II) complexes of α-substituted phthalocyanine with eight 1,4,7,10-tetraoxaundecyl groups (tri(oxyethylene) chains) were synthesized by the template reaction of 3,6-bis(1,4,7,10-tetraoxaundecyl)phthalonitrile with each metal source. The distortion of the phthalocyanine ring due to the steric hindrance between the α-substituted groups was deduced from the red shift of the Q band beyond 700 nm. This is due to the increase of HOMO energy, coming from the distortion of the phthalocyanine ring. The increase in HOMO energy was confirmed by the cyclic voltammograms; oxidation of the phthalocyanine ring occurs easily in these complexes. Electronic absorption spectra showed aggregation of the phthalocyanine molecules in H_2O for the nickel(II) and palladium(II) complexes, while the monomeric form for the zinc(II) complex in H_2O, and the zinc(II), nickel(II), and palladium(II) complexes in CH_2Cl_2. The depression of aggregating nature of the present complexes is considered to be originated from the distortion of the phthalocyanine ring as well as the bulkiness of the introduced tri(oxyethylene) chains themselves.

Acknowledgments

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Supporting information

^{1}H NMR spectrum of **1** in DMSO-d_6 (Fig. S1), the fluorescence spectrum of **1** (Fig. S2), and MALDI-TOF mass spectrum of a nickel triazatetrabenzocorrole complex with eight tri(oxyethylene) chains are given in the supplementary material. This material is available free of charge *via* the Internet at https://www.worldscientific.com/doi/suppl/10.1142/S1088424622500948

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