Tetrahedron 64 (2008) 8264-8270

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Tetrahedron



journal homepage: www.elsevier.com/locate/tet

Translation of helical chirality from polymer into monomer: supramolecular polymerization of a chirality-memory molecule with an asymmetric Pd(II) complex

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ARTICLE INFO

Article history: Received 1 April 2008 Received in revised form 17 May 2008 Accepted 30 May 2008 Available online 5 June 2008

Keywords: Porphyrin Helical polymer Supramolecular polymerization Depolymerization Chiral memory

ABSTRACT

A chirality-memorizing saddle-shaped porphyrin (1_{2H}) with 3,5-dipyridylphenyl side arms at the opposite *meso* positions underwent supramolecular polymerization in CH₂Cl₂ with a chiral Pd(II) complex of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (Pd^{II}(BINAP)), forming a ladder-shaped polymer (**3**_{2H}) with a prevailing one-handed helical chirality. When this polymer was poured into AcOH containing 1,3-bis(diphenylphosphino)propane (DPPP) as a decomplexing agent, **3**_{2H} was depolymerized in a stereo-chemically retentive way to give optically active **1**_{2H}, hydrogen-bonded with AcOH. Although a cyclodimeric reference of **3**_{2H}, formed from **2**_{2H} having two 3-pyridylphenyl *meso* substituents in conjunction with Pd^{II}(BINAP), behaved similar to **3**_{2H}, the translation efficiency of helical chirality was lower than that in the case with **3**_{2H}.

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1. Introduction

Helical polymers are an attractive chiral motif in a variety of aspects. Since the discovery of synthetic helical polymers,¹ their chemistry has been studied extensively.² One of the attractive subjects in relation to supramolecular chemistry is the chiroptical sensing of asymmetric small molecules by helical polymers, where the guest chirality is translated into a prevailing one-handed helical chirality of the hosting polymers.³

In the present study, we explored an interesting possibility that such a one-handed or enantiomerically biased helical chirality might be translated from polymers into the constituting monomers. In order to realize this concept, we paid attention to a certain family of saddle-shaped porphyrins (SP) with a symmetry group D_2 .⁴ Because of the steric repulsion among the neighboring *meso* and pyrrole- β substituents on the periphery, SP adopts a nonplanar, saddle-shaped conformation.⁵ Due to this nonplanar structure along with the presence of two different substituents (Scheme 1, green and blue) at the neighboring *meso* positions, SP is chiral. However, the enantiomers of SP are not separable from one another because of a rapid saddle-to-saddle macrocyclic inversion. In 1997, we reported that such a thermodynamic equilibrium can be shifted to either of the two enantiomeric forms of SP by a 1:2 hydrogenbonding interaction with chiral acids such as mandelic acid (MA) (Chart 1).^{4a} Furthermore, the induced enantiomeric bias can be fixed by pouring this hydrogen-bonded complex into achiral acids such as acetic acid (AcOH) (Scheme 1). In this system, the hydrogen-bonded MA molecules are kicked out from SP by AcOH, but the inversion of the porphyrin macrocycle, leading to racemization of SP, can be suppressed by regenerated hydrogen bonds with AcOH. Because of this unique feature, we named SP as a chirality-memory molecule. After this work, some other molecular and supramolecular systems such as poly(phenyl acetylene) derivatives⁶ and assembled calixarenes⁷ have been found to possess an analogous chiroptical feature that may be referred to as 'chirality memory'.⁴

In our previous study,⁸ we demonstrated that compound $\mathbf{1'_{2H}}$ having 3,5-dipyridylphenyl side arms at the opposite *meso* positions (Chart 1) undergoes supramolecular polymerization by coordination with a Pt(II) complex of 1,3-bis(diphenylphosphino)-propane (DPPP), forming a ladder-shaped polymer.^{9,10} Of interest, we found that interaction of $\mathbf{1'_{2H}}$ in the ladder polymer with MA forms a prevailing one-handed helical chirality along the main chain. This is due to conformational interlocking of the *meso*-aryl groups with the porphyrin macrocycle. Namely, if the two *meso*-

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^{0040-4020/\$ -} see front matter \circledast 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2008.05.126



Scheme 1. Schematic representations of (1) chirality transfer from mandelic acid (MA) to a D_2 -symmetric saddle-shaped porphyrin (SP) through hydrogen-bonding interactions (SP·MA₂) and (2) memorization of the resulting configurations in acetic acid (AcOH) in the form of SP·(AcOH)₂.

aryl groups are twisted in a clockwise or counterclockwise direction relative to one another, the nonplanar porphyrin macrocycle is inverted from one enantiomeric form to the other through a planar transition structure. This interlocked conformation gave us a new idea that use of a chiral metal complex as the linker for the ladder polymer $(\mathbf{3}_{2H})$ might give rise to a helical twist of the main chain, and this helical twisting might bias the chirality of the porphyrin macrocycle to either of the two enantiomeric forms. If this mechanism indeed operates, one should obtain 1'2H, hydrogenbonded with AcOH, in an optically active form by stereochemically retentive depolymerization of 32H in AcOH containing DPPP as a decomplexing agent. As reported in the present paper, we succeeded in translating the helical chirality of supramolecular polymer 3_{2H} into the monomer porphyrin (Scheme 2). Here we used 1_{2H} , an advanced version of $1'_{2H}$ in terms of its enhanced solubility, in combination with a chiral Pd(II) complex of BINAP (Pd^{II}(BINAP)) for supramolecular polymerization. For comparison, we utilized compound 2_{2H}, which was intended to form a cyclic dimer by coordination with Pd^{II}(BINAP).

2. Results and discussion

Saddle-shaped porphyrin 1_{2H} was newly synthesized by a procedure analogous to that reported previously,⁸ and unambiguously characterized by means of ¹H NMR, absorption, and IR spectroscopies, along with MALDI-TOF mass spectrometry (see Section 4). The self-assembling behavior of 1_{2H} via coordination with chiral metal complex Pd^{II}(BINAP) was investigated by electronic absorption, circular dichroism (CD), and ¹H/³¹P/¹⁹F NMR spectroscopy, together with dynamic light-scattering analysis. When 1_{H2} was titrated with Pd^{II}(BINAP) in CH₂Cl₂, the Soret and Q bands at 473 and 686 nm, respectively (Fig. 1, purple curve), were intensified at the expense of the original absorbances of 1_{H2} at 446 and 540 nm (Fig. 1, black curve). These absorption spectral changes reached a plateau when 2 equiv of Pd^{II}(BINAP) with respect to 1_{H2} were added to the solution (Fig. 1, inset). Dynamic light-scattering (DLS) analysis of a 1:2 mixture of 1_{2H} and Pd^{II}(BINAP) indicated the





Scheme 2. Schematic representations of (1) induction of a helical chirality by supramolecular polymerization of chirality-memorizing $\mathbf{1}_{2H}$ with chiral Pd^{II}(BINAP) and (2) its translation into the chirality of monomer $\mathbf{1}_{2H}$ (hydrogen-bonded with AcOH) by stereochemically retentive depolymerization in AcOH containing 1,3-bis(diphenylphosphino)-propane (DPPP) as a decomplexing agent.



Figure 1. Electronic absorption spectra of $\mathbf{1}_{2H}$ (5.0×10^{-6} M) in CH₂Cl₂ at 20 °C upon titration with Pd^{II}(BINAP) (15.0×10^{-6} M). Inset shows plots of the absorbances of $\mathbf{1}_{2H}$ at 473 nm at different ratios of [Pd^{II}(BINAP)]/[$\mathbf{1}_{2H}$].

presence of light-scattering particles with dimensions ranging from 100 to 500 nm (average diameter=350 nm, Fig. 2). Because of this association, ¹H NMR signals of **1**_{2H} in CD₂Cl₂ were very broad. Similar broadening was observed for the 31 P NMR signal at 25 ppm and 19 F NMR signal at -79 ppm, due to BINAP and CF₃SO₃, respectively, suggesting that both the triflate anion and the Pd^{II}-(BINAP) cation are included in the assembly.¹¹ For structural elucidation of polymeric assembly 3_{2H} , we synthesized 2_{2H} , a reference saddle-shaped porphyrin bearing only one pyridyl group in each meso-aryl group (Chart 1), with an expectation that 2_{2H} could form a metal-bridged cyclic dimer⁸ in a manner analogous to that expected for the supramolecular polymerization of 1_{2H} (Scheme 2). To avoid analytical complexity due to protonation of 2_{2H} , its nickel complex 2_{Ni} was allowed to coordinate with Pd^{II}(BINAP) in CH₂Cl₂. Similar to the case with Pt^{II}(DPPP) reported previously,⁸ cold-spray ionization mass spectrometry (CSI-MS)¹² of their equimolar mixture displayed intense peaks at m/z=1937, 1241, and 893, assignable to the 2:2 complex losing two, three, and four $CF_3SO_3^-$ counter anions, respectively, at the ionization step.¹¹ No peaks assignable to higher oligomers were detected. In CD₂Cl₂ at 20 °C, the 1:1 mixture showed a sharp singlet ³¹P NMR signal at δ 25.03 ppm¹¹ (cf. 36.43 ppm for Pd^{II}(BINAP)) due to pyridine-coordinated Pd^{II}-(BINAP), along with a sharp singlet ¹⁹F NMR signal at δ –78.8 ppm¹¹ due to non-coordinated CF₃SO₃⁻¹³ Because of this coordinative interaction, the pyridyl groups of 2_{Ni} in the cyclodimeric assembly showed downfield-shifted ¹H NMR signals from those of monomeric $\mathbf{2}_{Ni}$.¹¹ In contrast, other peripheral groups of assembled $\mathbf{2}_{Ni}$



Figure 2. Histogram profile in dynamic light scattering (DLS) in CH₂Cl₂ at 20 °C of a 1:2 mixture of $1_{2H}~(1.5\times10^{-3}~M)$ and Pd^{II}(BINAP) (3.0 $\times10^{-3}~M)$.

displayed upfield-shifted signals most likely due to their mutual magnetic shielding. The selective cyclodimerization of 2_{Ni} with Pd^{II}(BINAP),⁸ thus observed, may support our hypothesis that 1_{2H} possibly forms polymer 3_{2H} with bridging Pd^{II}(BINAP) units (Scheme 2).

A 1:2 mixture of $\mathbf{1}_{2H}$ and (*R*)-Pd^{II}(BINAP) in CH₂Cl₂ (polymer $\mathbf{3}_{2H}$) displayed a distinct circular dichroism (CD) spectral feature at the absorption bands due to the binaphthyl ligands (300–400 nm) and saddle-shaped porphyrin moieties (400–550 nm) (Fig. 3, pink solid curve). When the (*S*)-isomer of Pd^{II}(BINAP) was allowed to coordinate with $\mathbf{1}_{2H}$, the observed CD spectral feature was a mirror image (Fig. 3, blue solid curve) of the above. Figure 4 shows plots of the CD intensities of $\mathbf{1}_{2H}$ at 485 nm upon complexation with Pd^{II}(BINAP) of different enantiomeric excess (ee) values. A linear correlation indicates that the chiroptical feature of the resulting polymer is given by the added chiral Pd^{II}(BINAP).¹⁴ As a control



Figure 3. CD spectra in CH₂Cl₂ at 20 °C of mixtures $\mathbf{1}_{2H}/(R)$ -Pd^{II}(BINAP) (pink solid curve) and $\mathbf{1}_{2H}/(S)$ -Pd^{II}(BINAP) (blue solid curve), together with $\mathbf{2}_{2H}/(R)$ -Pd^{II}(BINAP) (pink broken curve) and $\mathbf{2}_{2H}/(S)$ -Pd^{II}(BINAP) (blue broken curve). [$\mathbf{1}_{2H}$ =[$\mathbf{2}_{2H}$]= 5.0×10^{-6} M. [Pd^{II}(BINAP)]= 11.7×10^{-6} M for $\mathbf{1}_{2H}$ and 5×10^{-6} M for $\mathbf{2}_{2H}$.



Figure 4. Plots of CD intensities at 485 nm of self-assembled $\mathbf{1_{2H}}/Pd^{II}(BINAP)$ in CH₂Cl₂ observed at different enantiomeric excess (ee) values of Pd^{II}(BINAP). [$\mathbf{1_{2H}}$]=5×10⁻⁶ M. [Pd^{II}(BINAP)]=11.7×10⁻⁶ M.

experiment, we added (*R*)- or (*S*)-Pd^{II}(BINAP) to a reference saddleshaped porphyrin without any pyridyl side arms. However, no CD signal emerged at the Soret absorption band of the porphyrin, indicating that the observed CD for 1_{2H} upon mixing with (*R*)- or (S)-Pd^{II}(BINAP) is the consequence of the complexation of its dipyridylphenyl side arms, rather than its nitrogen core, with Pd^{II}-(BINAP). We assume that supramolecular polymer 3_{2H} , formed from **1**_{2H} and Pd^{II}(BINAP), may adopt a helical structure, where the dipyridylphenyl side arms in each porphyrin unit are twisted relative to one another in either clockwise or counterclockwise direction, and the helical sense is determined by the absolute configuration of bridging chiral Pd^{II}(BINAP). This structural feature could result in a twisted array of the porphyrin units, thereby exerting an efficient exciton coupling between the neighboring porphyrin units. While the cyclic dimer of 2_{2H} , bridged by (R)- or (S)-Pd^{II}(BINAP) ([Pd^{II}]/[**2**_{2H}]=1.25), displayed a CD spectral feature (Fig. 3, pink and blue broken curves, respectively) similar to its polymeric version, the CD intensity at the Soret absorption band (475–520 nm) was obviously smaller (Fig. 3). Thus, the cyclic dimer, as expected, may possess a greater geometrical freedom than its polymeric version.

As described in the introductory part, the possibility of translating the helical chirality of 32H into 12H (Scheme 2) was investigated by taking advantage of the chirality-memorizing ability of **1**_{2H} (vide ante) hydrogen-bonded with acids (Scheme 1).⁴ Thus, supramolecular polymer $\mathbf{3}_{\mathbf{2H}}$ was poured into DPPP-containing AcOH ([DPPP]/[Pd(II)]=5), with an expectation that it may dissociate into the protonated form of the monomer with retention of its configuration (Scheme 2).⁸ As shown in Figure 5 (solid curves), the intensity of the CD spectrum decreased entirely, most likely due to the disappearance of the exciton coupling, operating among the assembled porphyrin units, upon dissociation into 1_{2H} (AcOH)₂. However, the spectral change subsided immediately, where the resultant CD spectrum remained unchanged for the next 5 h at 20 °C. The CD spectral profile is virtually identical to that observed for the hydrogen-bonded 1_{2H}, formed by pouring the binary mixture of **1**_{2H} and (*R*)-MA into DPPP-containing AcOH (Fig. 6, pink solid curve). In fact, the formation of hydrogen-bonded 1_{2H} from polymeric 3_{2H} was confirmed by ¹H NMR spectroscopy measured in AcOH-*d*₄.¹¹ Although the final CD intensity after the dissociation of polymer $\mathbf{3}_{2H}$ was just 37% as large as those observed for AcOH-treated MA complex of 12H (Fig. 6), one can conclude that the helical chirality of $\mathbf{3}_{2H}$ gives rise to an enantiomeric bias of its monomer component⁸ (Fig. 5, solid curves). As a control



Figure 5. CD spectra in DPPP-containing AcOH (DPPP/Pd=5) at 20 °C of mixtures $\mathbf{1}_{2H}/(R)$ -Pd^{II}(BINAP) (pink solid curve) and $\mathbf{1}_{2H}/(S)$ -Pd^{II}(BINAP) (blue solid curve), together with $\mathbf{2}_{2H}/(R)$ -Pd^{II}(BINAP) (pink broken curve) and $\mathbf{2}_{2H}/(S)$ -Pd^{II}(BINAP) (blue broken curve). [$\mathbf{1}_{2H}$]=[$\mathbf{2}_{2H}$]=5×10⁻⁶ M. [Pd^{II}(BINAP)]=11.7×10⁻⁶ M for $\mathbf{1}_{2H}$ and 5×10⁻⁶ M for $\mathbf{2}_{2H}$.



Figure 6. CD spectra in DPPP-containing AcOH (DPPP/Pd=5) at 20 °C of mixtures $\mathbf{1}_{2H}/(R)$ -MA (pink solid curve), $\mathbf{1}_{2H}/(S)$ -MA (blue solid curve), $\mathbf{1}_{2H}/(R)$ -Pd^{II}(BINAP) (pink broken curve), and $\mathbf{1}_{2H}/(S)$ -Pd^{II}(BINAP) (blue broken curve) after immersion for 60 min. $[\mathbf{1}_{2H}]$ =5×10⁻⁶ M, [MA]=11.0×10⁻⁶ M, and [Pd^{II}(BINAP)]=11.7×10⁻⁶ M.

experiment, we simply immersed polymer 32H in DPPP-containing CH₂Cl₂ in the absence of AcOH. While **3**_{2H} dissociated into **1**_{2H} by the action of DPPP, the CD spectrum lost the activity at the Soret absorption band of 12H (450-525 nm) and simply displayed CD bands characteristic of Pd^{II}(BINAP)(DPPP) in CH₂Cl₂.¹¹ Thus, the assay we employed here indeed takes advantage of the chiralitymemorizing ability of the hydrogen-bonded form of 12H. Meanwhile, the cyclic dimer composed of 2_{2H} and Pd^{II}(BINAP), upon being poured into DPPP-containing AcOH, showed a CD spectral change (Fig. 5, broken curves) similar to its polymeric version. However, the CD intensity finally attained was only a half of that observed for the case starting from the polymeric version. From these results, we consider that coordinating Pd^{II}(BINAP) in the main chain of 3_{2H} with a much smaller geometrical freedom than in the cyclodimeric reference can give rise to a more twisted geometry of the porphyrin array, resulting in a larger enantiomeric bias of the chiral saddle.

3. Conclusions

A chirality-memorizing saddle-shaped porphyrin (1_{2H}) with 3,5-dipyridylphenyl side arms at the opposite *meso* positions undergoes supramolecular polymerization with a chiral Pd(II) complex of BINAP, forming a ladder-shaped polymer (3_{2H}) having a prevailing one-handed helical chirality. By stereochemically retentive depolymerization of 3_{2H} in DPPP-containing AcOH, optically active 1_{2H} , hydrogen-bonded with AcOH, was obtained. The results presented here indicate the successful translation of a helical chirality from polymer 3_{2H} into monomer 1_{2H} . The principle of this idea may not be limited to the system reported here but might be extendable to general asymmetric syntheses.

4. Experimental section

4.1. General

All reagents and solvents were used as-received from commercial sources without further purification. The enantiomers of mandelic acid (MA) (>99%), 1,3-bis(diphenylphosphino)propane (DPPP), [(*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]palladium(II) chloride, and CF₃SO₃Ag were purchased from Aldrich. The enantiomers of [Pd^{II}(BINAP)][(OTf)₂],^{10c} 5-(2,6-dimethoxyphenyl)-2,3,7,8-tetramethylpyrromethane,^{4a} and 2,3,7,8, 12,13,17,18-octamethyl-5,15-bis(2,6-dimethoxyphenyl)-10,20-bis[3(4-pyridyl)phenyl]porphine⁸ were synthesized according to the literature methods.

For column chromatography, Wakogel C-300HG (particle size 40–60 μ m, silica), C-400HG (particle size 20–40 μ m, silica), aluminum oxide 90 standardized (Merck), or Bio-BeadsTM S-X1 (BIO RAD) was used.

Circular dichroism (CD) and electronic absorption spectra were recorded on a IASCO type I-820 spectropolarimeter equipped with a JASCO type PTC-423L temperature/stirring controller and a JASCO type V-570 UV/vis/NIR spectrometer equipped with a JASCO type ETC-505T temperature/stirring controller, respectively. ¹H, 19 F, and 31 P NMR spectra were recorded on a JEOL model EX-270 or GSX-500 spectrometer, where chemical shifts (δ in parts per million) were determined with respect to tetramethylsilane (TMS), hexafluorobenzene (C_6F_6), and phosphoric acid (H_3PO_4), respectively, as internal standards. Matrix-assisted laser desorption/ ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed with 9-nitroanthracene as a matrix on an Applied Biosystems BioSpectrometry Workstation[™] model Voyager-DE[™] STR spectrometer. Fast atom bombardment (FAB) mass spectrometry was performed with 3-nitrobenzylalcohol as a matrix on a JEOL type JMS-BU30 LC MATE spectrometer. Cold-spray ionization (CSI) mass spectrometry was performed on a JEOL model JMS-700T spectrometer with a CSI source. Dynamic light-scattering (DLS) measurement was performed on an Otsuka model ELS-Z2 instrument.

4.2. Procedures for the synthesis of saddle-shaped porphyrin $\mathbf{1}_{2H}$ and its nickel complex $\mathbf{1}_{Ni}$

4.2.1. 3,5-Dibromo-4-dodecyloxybenzaldehyde (4)

A THF/DMF (4:1) solution (100 mL) of a mixture of 3,5-dibromo-4-hydroxybenzaldehyde (3.00 g, 10.7 mmol), 1-bromododecane (2.70 g, 10.8 mmol), and K₂CO₃ (4.50 g, 32.5 mmol) was refluxed for 24 h under Ar. The reaction mixture was filtered off from an insoluble fraction and the filtrate was evaporated to dryness. The residue was poured into water and extracted with CHCl₃. The combined organic extract was dried over Na₂SO₄ and chromatographed on silica gel with $CHCl_3/hexane (3/7 v/v)$ as an eluent, where the first fraction was collected and evaporated to give **4** as white solid in 73% yield (3.5 g, 7.81 mmol), mp 47 °C. ¹H NMR (270 MHz, CDCl₃, 20 °C): δ 9.80 (1H, s, aldehyde), 7.97 (2H, s, ArH), 4.04 (2H, t, J=6.5 Hz, alkyl), 1.91-1.81 (2H, m, alkyl), 1.57-1.24 (18H, m, alkyl), 0.85 (3H, t, *J*=6.6 Hz, methyl); IR (KBr): 2918, 2851, 1686, 1579, 1544, 1471, 1450, 1365, 1263, 1207, 1185, 1065, 1027, 1016, 984, 945, 925, 884, 741, 716, 661, 579, 543 cm⁻¹; FABMS *m*/*z* calcd for M⁺ (C₁₉H₂₈Br₂O₂) 448, found 449 (M+H⁺).

4.2.2. 3,5-Bis(4-pyridyl)-4-dodecyloxybenzaldehyde (5)

A 1.4-dioxane solution (80 mL) of a mixture of 4 (2.00 g. 4.46 mmol), 4-pyridineboronic acid (2.00 g, 16.27 mmol), and $K_3PO_4 \cdot nH_2O$ (5.5 g) was bubbled with Ar for 30 min. Tetrakis-(triphenylphosphine)palladium(0) (2.50 g, 2.16 mmol) was added to this solution and the mixture was refluxed for 3 days in an Ar atmosphere. To this reaction mixture were successively added CHCl₃, water, and ethylene diamine (20, 20, and 0.5 mL, respectively). The reaction mixture was filtered off from an insoluble fraction and the filtrate evaporated to dryness. The residue was poured into water and extracted with CHCl₃. The combined organic extract was dried over Na₂SO₄ and chromatographed on silica gel with CHCl₃/MeOH (98/2 v/v) as an eluent, where the first fraction was collected and evaporated to give 5 as white solid in 76% yield (1.5 g, 3.37 mmol). ¹H NMR (270 MHz, CDCl₃, 20 °C): δ 10.04 (1H, s, aldehyde), 8.71 (4H, d, J=5.9 Hz, pyridyl), 7.93 (2H, s, ArH), 7.57 (4H, d, J=5.9 Hz, pyridyl), 3.27 (2H, t, J=6.2 Hz, alkyl), 1.27–0.89 (20H, m, alkyl), 0.85 (3H, t, J=6.7 Hz, methyl); IR (KBr): 2924, 2853, 1699, 1599, 1547, 1438, 1405, 1380, 1339, 1230, 1185, 1120, 1070, 994, 932, 837, 775, 754, 722, 697, 614, 540, 504 cm⁻¹; FABMS *m*/*z* calcd for M⁺ ($C_{29}H_{36}N_2O_2$) 445, found 446 (M+H⁺).

4.2.3. Nickel complex of 2,3,7,8,12,13,17,18-octamethyl-5,15-bis-(2,6-dimethoxyphenyl)-10,20-bis[3,5-bis(4-pyridyl)-4dodecvloxyphenyl]porphine (**1**_{Ni})

To a propionic acid solution (300 mL) of 3,5-bis(4-pyridyl)-4dodecyloxybenzaldehyde (1.75 g, 3.93 mmol) was added at 0 °C a CHCl₃ solution (20 mL) of 5-(2,6-dimethoxyphenyl)-2,3,7,8tetramethylpyrromethane^{4a} (1.32 g, 3.36 mmol). The mixture was stirred for 12 h at room temperature and evaporated to dryness. The residue was dissolved in AcOH (200 mL) containing Ni(OAc)₂·4H₂O (3.34 g, 13.4 mmol) and the mixture was stirred under reflux for 12 h. The reaction mixture was evaporated to dryness under reduced pressure and the residue was dissolved into CHCl₃, treated with NaHCO₃ for neutralization, and extracted with CHCl₃/water. The combined organic extract was washed with brine, dried over anhydrous Na₂SO₄, and evaporated to dryness. The residue was chromatographed on silica gel with CHCl₃/MeOH (100:3) as an eluent, where the reddish purple fraction was collected. Evaporation of this fraction and recrystallization of the residue from CH2Cl2/hexane gave 1Ni (161 mg, 8% yield) as purple solid. UV/vis (CH₂Cl₂), λ_{max} (ε / M^{-1} cm⁻¹)=432 (45,000), 551 (3200), and 589 (3100) nm; ¹H NMR (270 MHz, CDCl₃, 20 °C): δ 8.69 (8H, d, *J*=5.6 Hz, PyH), 7.97 (4H, s, o-H of C₆H₃Py₂), 7.71 (8H, d, *J*=5.9 Hz, PyH), 7.57 (2H, t, *I*=8.2 Hz, *p*-H of C₆H₃(OMe)₂), 6.83 (4H, d, *I*=8.4 Hz, *m*-H of C₆H₃(OMe)₂), 3.63 (12H, s, OCH₃), 3.42 (4H, t, *I*=6.2 Hz, OCH₂), 2.01 (12H, s, CH₃ at pyrrole- β), 1.96 (12H, s, CH₃ at pyrrole- β), 1.65–1.07 (40H, m, CH₂), and 0.87 (6H, t, *J*=6.7 Hz, CH₃); IR (KBr): 2922, 2852, 1593, 1547, 1471, 1402, 1380, 1355, 1340, 1314, 1249, 1175, 1109, 1070, 1034, 992, 970, 899, 855, 825, 775, 730, 671, 648, 605, 545 cm⁻¹; MALDI-TOF MS m/z calcd for M⁺ (C₁₀₀H₁₁₂N₈NiO₆) 1580, found 1580.

4.2.4. 2,3,7,8,12,13,17,18-Octamethyl-5,15-bis(2,6-dimethoxyphenyl)-10,20-bis[3,5-bis(4-pyridyl)-4-dodecyloxyphenyl]porphine (**1**_{2H})

To a CHCl₃ solution (30 mL) of **1**_{Ni} (97 mg, 80 µmol) was added 35% aq HCl (10 mL) and the mixture was stirred for 12 h at room temperature. The reaction mixture was neutralized with aq NaHCO₃ and extracted with CH₂Cl₂. The combined organic extract was washed with brine, dried over anhydrous Na₂SO₄, and evaporated to dryness. A benzene solution of the residue was freezedried to give **1**_{2H} (89 mg 96% yield) as brown solid. UV/vis (CH₂Cl₂), λ_{max} (ϵ/M^{-1} cm⁻¹)=456 (47,000), 542 (3600), 582 (3600), 632 (3800), and 688 (3200) nm; ¹H NMR (270 MHz, CDCl₃, 20 °C): δ 8.72 (8H, d, *I*=5.0 Hz, PyH), 8.22 (4H, s, o-H of C₆H₃Py₂), 7.77 (8H, d, J=5.0 Hz, PyH), 7.65 (2H, t, J=8.1 Hz, p-H of C₆H₃(OMe)₂), 6.92 (4H, d, J=8.1 Hz, m-H of C₆H₃(OMe)₂), 3.66 (12H, s, OCH₃), 3.46 (4H, t, *J*=6.2 Hz, OCH₂), 2.05 (12H, s, CH₃ at pyrrole-β), 1.98 (12H, s, CH₃ at pyrrole-β), 1.35–1.08 (40H, m, CH₂), and 0.87 (6H, t, *J*=6.7 Hz, CH₃); IR (KBr): 3367, 2923, 2852, 1595, 1546, 1470, 1445, 1404, 1382, 1318, 1250, 1229, 1159, 1131, 1109, 1070, 1033, 957, 866, 822, 775, 732, 644, 605, 545 cm⁻¹; MALDI-TOF MS m/z calcd for M⁺ (C₁₀₀H₁₁₄N₈O₆) 1524, found 1524.

Acknowledgements

The present work was sponsored by a Grants-in-Aid for Scientific Research (No. 17350044) and Encouragement of Young Scientists (No. 18750113) from the Ministry of Education, Science, Sports, and Culture, Japan. M.A.A. thanks the JSPS Postdoctoral Fellowship for Foreign Researchers.

Supplementary data

Synthetic schemes of saddle-shaped porphyrin 1, ¹H, ³¹P, ¹⁹F NMR. CSI mass, and CD spectra of complexes $\mathbf{1}_{2H}$ and $\mathbf{2}_{Ni}$ with/ without Pd^{II}(BINAP) are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/ i.tet.2008.05.126.

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