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Synthesis of L-prolinol substituted novel optically active phthalocyanines

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ABSTRACT

The novel optically active **Pc-4** (neutral) and **Pc-5** (ionic), zinc(II) phthalocyanines having four *N*-benzyl protected L-prolinol unit were synthesized. L-prolinol has binucleophilic character and can be anchored to phthalonitrile derivative from both nitrogen and oxygen atoms. In order to overcome this problem and to enhance the solubility of phthalonitrile (*S*)-(-)-**3** and the target phthalocyanines, the nitrogen atom of L-prolinol was first protected with benzyl chloride. All the compounds were characterized by ^{1}H and ^{13}C NMR, MALDI–TOF MS, IR, UV–vis, and Circular Dichroism (CD) spectroscopy. **Pc-4** is highly soluble in most common organic solvents, whereas ionic **Pc-5** is soluble in water. The CD results showed that the chiral information was transferred from the peripheral chiral L-prolinol side chains to the phthalocyanine chromophore at the molecular level.

1. Introduction

Phthalocyanines (Pcs) have unique properties due to their conjugated core units which have found widespread application as dyes and catalysts [1]. Moreover, in the years, they have attracted increasing interest for their application in the construction of molecular devices. For example they have found utility in many popular areas of research such as photodynamic therapy (PDT) [2–4], organic photovoltaic (OPV) devices [5–9], and organic field-effect transistors (OFETs) [10].

Although a wide range of studies on the synthesis, properties and applications of many phthalocyanines has received more research interest than porphyrins, chiral phthalocyanines have received less attention than chiral porphyrins. However, optically active Pcs are more available than porphyrins in some respects. For instance, Pcs are prone to co-facial aggregation and may form helical superstructures. In addition, to analyze their circular dichroism (CD), Pcs are superior to porphyrins, since the Q-band is much more intense. The studies on the chiral Pcs have emerged over the last few decades. In particular, after 1990, Kobayashi and co-workers [11–16] made very valuable contributions in this emerging field [17–21].

In this study, we report the synthesis and the photophysical evaluation of a novel family of optically active phthalocyanines with L-prolinol peripheral units (Fig. 1). The reason for choosing this class of Pcs is that the bulky and ionic peripheral substitutions on Pcs core enhance solubility in organic and aqueous media and control the aggregation behavior [1,22]. In our synthetic strategy, the *N*-benzyl protected L-prolinol unit was first anchored to the core scaffold of phthalocyanines and subsequent cyclotetramerization afforded the optically active target ZnPcs. Since the nitrogen atom of L-prolinol unit has the capacity to form quaternary ammonium salt, the neutral L-prolinol substituted Pc was easily transformed into the ionic Pc, which is soluble in water. To the best of our knowledge, L-prolinol type chiral peripheral units have never been utilized before for the construction of optically active phthalocyanines. The combined structure of L-prolinol and Pc may be a valuable candidate as an organocatalyst in the application of asymmetric transformation reactions.

2. Experimental

2.1. General

All experiments were carried out in pre-dried glassware (1 h, 150 °C) under an inert atmosphere of argon. The following reaction solvents were distilled from the indicated drying agents: DMAE (CaH_2), DMF (CaH_2). Melting points were obtained on a Thomas

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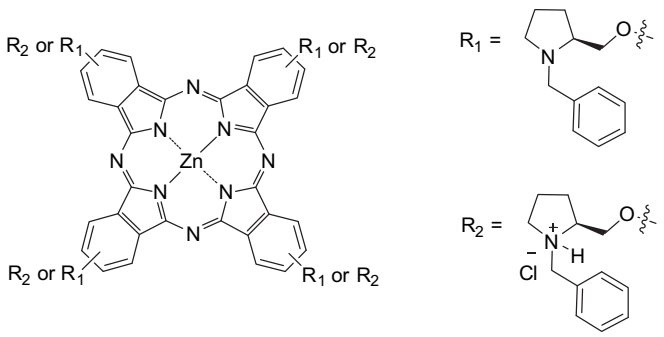


Fig. 1. Target optically active phthalocyanine structures.

Hoover capillary melting point apparatus and are uncorrected. All other chemicals were purchased from commercial suppliers and used without further purification.

Flash column chromatography was performed by using thick-walled glass columns with a flash grade (Merck Silica Gel 60). Reactions were monitored by thin layer chromatography using precoated silica gel plates (Merck Silica Gel PF-254), visualized by UV-light and polymolybden phosphoric acid in ethanol as appropriate. All extracts were dried over anhydrous magnesium sulphate and solutions were concentrated under vacuum by using rotary evaporator.

2.2. Spectroscopy

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 spectrometer. ^{1}H (400 MHz) and ^{13}C NMR were recorded in $CDCl_3$ and D_2O. The chemical shifts were expressed in ppm relative to $CDCl_3$ (δ 7.26 and 77.0 for ^{1}H and ^{13}C NMR, respectively) and D_2O as the internal standards. Infrared spectra were recorded on a Thermo Nicolet IS10 ATR–FT-IR spectrophotometer. The mass spectra were recorded on Thermo Scientific DSQ II Single Quadrupole GC/MS. HRMS and MALDI–TOF spectra were detected on a Waters Synapt mass spectrometer at central laboratory of Middle East Technical University. Optical rotations were measured employing a Rudolph research analytical, autopol III automatic polarimeter. Circular Dichroism (CD) measurements were recorded on JASCO J-815 at UNAM of Bilkent University. UV–visible spectroscopy was measured on a VARIAN CARY 100 Bio Spectrophotometer.

2.3. Synthesis

2.3.1. (S)-(-)-(1-Benzylpyrrolidin-2-yl)methanol, (S)-(-)-2

To a stirred mixture of (*S*)-pyrrolidin-2-yl-methanol (**1**) (2.02 g, 20 mmol), benzyl chloride (3.80 g, 30 mmol), and anhydrous potassium carbonate (2.76 g, 20 mmol) in 15 cm^3 of toluene was refluxed under argon for 16 h. Dilute hydrochloric acid was then added until the aqueous layer was strongly acidic. The aqueous layer was separated, shaken with ether, basified with ammonium hydroxide, and extracted several times with DCM. The organic layer was dried over $MgSO_4$, and the solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/methanol (10/1) to afford (*S*)-(-)-(1-benzylpyrrolidin-2-yl)methanol (*S*)-(-)-**2** as a viscous oil (3.52 g, 92%) [23]. $[\alpha]_D^{25} = -33.3$ (*c* 1, EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–7.17 (m, 5H), 3.84 (d, J_{AB} = 13.0 Hz, 1H), 3.46 (dd, J_{AB} = 4.2 Hz, J_{AB} = 10.8 Hz, 1H), 3.32 (dd, J_{AB} = 2.8 Hz, J_{AB} = 10.8 Hz, 1H), 3.20 (d, J_{AB} = 13.0 Hz, 1H), 2.78–2.83 (m, 1H), 2.51–2.57 (m, 1H), 2.11 (q, *J* = 8.8 Hz, 1H), 1.72–1.82 (m, 1H), 1.59–1.70 (m, 1H), 1.50–1.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 127.2, 126.8, 125.5, 62.8, 60.2, 57.0, 52.9, 26.2, 21.9.

2.3.2. (S)-(-)-4-((1-Benzylpyrrolidin-2-yl)methoxy)phthalonitrile, (S)-(-)-3

(*S*)-(-)-(1-Benzylpyrrolidin-2-yl)methanol (*S*)-(-)-**2**, (3.52 g, 18.4 mmol) was added to a mixture of 4-nitrophthalonitrile (3.18 g, 18.4 mmol), anhydrous potassium carbonate (20.33 g, 147.3 mmol) and 30 cm^3 DMF at room temperature. The reaction mixture was stirred at room temperature for 24 h under argon atmosphere, and then distilled to remove DMF under reduced pressure. Dilute hydrochloric acid (0.1 M) was then added. The aqueous layer was shaken with ether and basified with ammonium hydroxide, and extracted several times with DCM. The organic layer was dried over $MgSO_4$, and the solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/methanol (10/1) to afford (*S*)-(-)-4-((1-benzylpyrrolidin-2-yl)methoxy)phthalonitrile (*S*)-(-)-**3** as a yellow oil (1.45 g, 28%). $[\alpha]_D^{25} = -277.5$ (*c* 3.9, $CHCl_3$). FT-IR (ATR System, cm^{-1}): 3083, 3027, 2969, 2974, 2797, 2229, 1737, 1596, 1561, 1491, 1453, 1319, 1251, 1095, 1017. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.8 Hz, 1H), 7.11–7.24 (m, 5H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.97 (dd, *J* = 2.6 Hz, *J* = 8.8 Hz, 1H), 3.88 (d, J_{AB} = 13.1 Hz, 1H), 3.82 (dd, J_{AB} = 5.1 Hz, J_{AB} = 9.4 Hz, 1H), 3.75 (dd, J_{AB} = 6.3 Hz, J_{AB} = 9.4 Hz, 1H), 3.53 (d, J_{AB} = 13.1 Hz, 1H), 2.90–2.97 (m, 2H), 2.28 (q, *J* = 9.9 Hz, 1H), 1.90–1.97 (m, 1H), 1.61–1.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 139.5, 135.2, 128.8 (overlapped 2C signals), 128.4 (overlapped 2C signals), 127.1, 119.8, 119.4, 117.2, 115.9, 115.4, 107.0, 72.4, 61.9, 60.0, 55.0, 28.6, 23.3. Exact mass: 317.15. GS–MS measured *m*/*z*: 317.2. HRMS: *m*/*z* $[M + H]^+$ calcd. for $C_{20}H_{19}N_3O$: 318.1606; found $[M + H]^+$: 318.1601.

2.3.3. Synthesis of (S)-4-(1-benzylpyrrolidin-2-yl)methoxy substituted Zn phthalocyanine, Pc-4

(*S*)-(-)-**3**, (1.23 g, 3.86 mmol) was dissolved in 12 cm^3 of dry DMAE and DMF mixture (1:2) and then, stirred for 1 h. $Zn(OAc)_2$ (0.21 g, 0.97 mmol) was added and stirred for another 1 h under argon atmosphere and then refluxed at 160 °C for 24 h. Reaction mixture was poured into water–methanol mixture (1:1). Precipitate was filtered off and the residue was purified by column chromatography on silica gel eluting with ethyl acetate/methanol (10/1) to afford **Pc-4** as a dark-green solid (0.71 g, 55%). FT-IR (ATR System, cm^{-1}): 2953, 2917, 2849, 1710, 1667, 1605, 1487, 1452, 1377, 1336, 1280, 1260, 1228, 1116, 1089, 1047, 936, 861, 845, 817, 745. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93–7.60 (m, 32H), 3.92–4.07 (d, J_{AB} = 13.1 Hz, 4H), 3.87 (dd, J_{AB} = 5.4 Hz, J_{AB} = 9.3 Hz, 4H), 3.77 (dd, J_{AB} = 6.5 Hz, J_{AB} = 9.3 Hz, 4H), 3.26–350 (d, J_{AB} = 13.1 Hz, 4H), 2.81–2.97 (m, 8H), 2.20–2.28 (m, 4H), 1.90–2.00 (m, 4H), 1.60–1.75 (m, 12H). UV–vis λ_{max} (nm) (log ε) in $CHCl_3$: 345 (4.44), 623 (4.04), 683 (4.42). MALDI–TOF MS: *m*/*z* $[M]^+$ calcd. for $C_{80}H_{76}N_{12}O_4Zn$: 1334.9474; found $[M]^+$:1334.4724.

2.3.4. Synthesis of (S)-4-((1-benzylpyrrolidinium-2-yl)methoxy) substituted Zn phthalocyanine complex, Pc-5

To a solution of **Pc-4**, (0.50 g, 0.37 mmol) in DCM (50 cm^3), dilute hydrochloric acid (15 cm^3, 0.1 M) was added and the stirring continued at room temperature until pH became 1. The complete dark-green colour transferring of organic phase to water phase was observed. The water phase was separated and evaporated *in vacuo* to afford quantitatively **Pc-5**. FT-IR (ATR System, cm^{-1}): 3210, 1710, 1635, 1404, 1327, 1080, 948, 741. ^{1}H NMR (400 MHz, D_2O): δ 7.01–7.56 (m, 32H), 4.28–4.44 (m, 4H), 4.04–4.14 (m, 6H), 3.86–3.96 (m, 3H), 3.73–3.77 (m, 3H), 3.32–3.54 (m, 8H), 2.31–2.35 (m, 4H), 2.07–2.20 (m, 4H), 1.75–2.01 (m, 12H). ^{13}C NMR (100 MHz, D_2O): δ 169.3, 169.0, 160.7, 133.0, 129.0 (overlapped 2C signals), 128.4, 128.3, 127.7 (overlapped 2C signals), 123.8, 123.2, 118.5, 107.7, 63.8, 61.0, 57.3, 53.8, 24.5, 20.3. UV–vis λ_{max} (nm) in

H_2O: 345, 623, 683. HRMS: *m/z* $[M + 4H]^+$ calcd. for $C_{80}H_{84}Cl_4N_{12}O_4Zn$: 1484.8230; found $[M + 4H]^+$:1484.4760.

3. Results and discussion

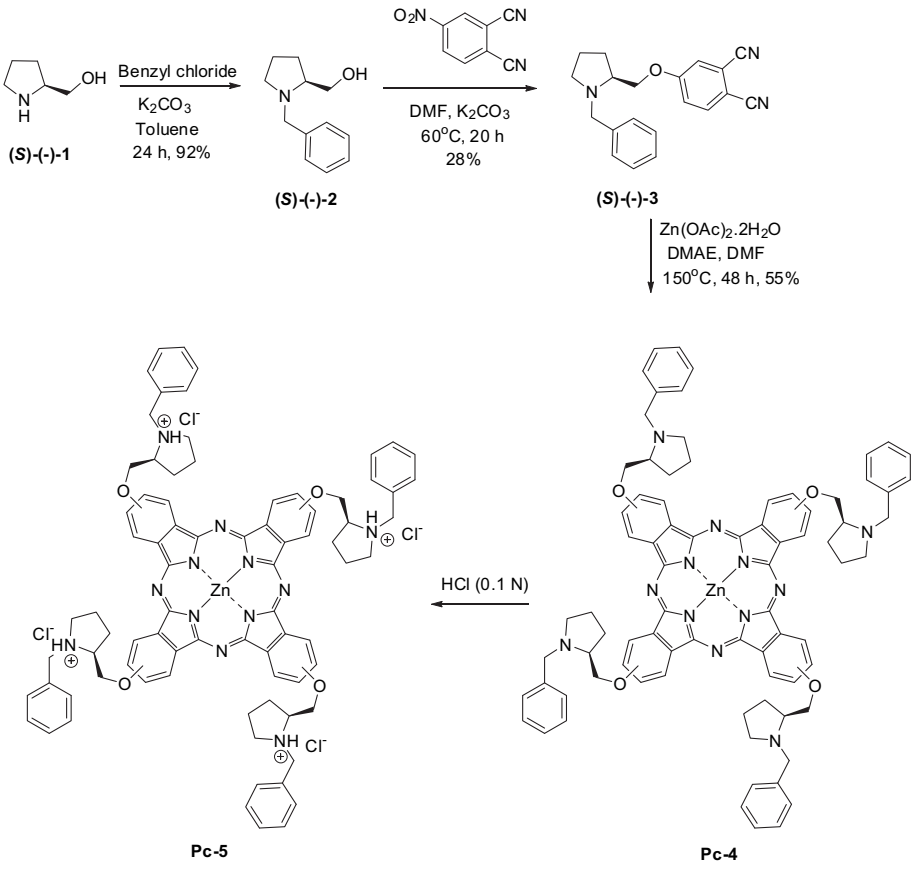
3.1. Synthesis

From the documented literature on phthalocyanines, it is well known that bulky peripheral substitutions can be used for enhancing the solubility in organic and aqueous media and can influence the aggregation behavior [1,22]. Moreover, as mentioned above, chiral phthalocyanines remain extremely rare so far. Motivated by the potential value of chirally anchored phthalocyanine derivatives, we formulated a general strategy of synthesis based on the use of commercially available L-prolinol as the chiral peripheral unit. Since L-prolinol has binucleophilic character, it can be anchored to 4-nitrophthalonitrile from both nitrogen and oxygen atoms. In order to overcome this problem and to enhance the solubility of phthalonitrile (*S*)-(-)-**3** and the target phthalocyanines, the nitrogen atom of L-prolinol was successfully functionalized to the desired *N*-benzyl protected derivative (*S*)-(-)-**2** with benzyl chloride and anhydrous K_2CO_3 by refluxing in toluene in high chemical yield [23]. The synthesis of novel chiral phthalonitrile (*S*)-(-)-**3** was performed by the ***S*$_N$*Ar*** type substitution reaction between (*S*)-(-)-**2** and 4-nitrophthalonitrile (Scheme 1). The chiral phthalonitrile (*S*)-(-)-**3** was isolated by column chromatography in 28% yield. The structure of (*S*)-(-)-**3** was assigned on the basis of ^1H and ^{13}C NMR spectra. The isomeric mixture of chiral phthalocyanine **Pc-4** was synthesized under standard conditions by using Zn $(OAc)_2.2H_2O$, DMEA (*N*,*N*-dimethylethanamine) afforded a 55% yield after purification by column chromatography. Alternative conditions (DBU and pentanol) were attempted but proved low yielding. The solubility test of **Pc-4** showed that it was highly soluble in most organic solvents, such as CH_2Cl_2, $CHCl_3$, toluene and THF, however, it was insoluble in water. We turned our attention to the synthesis of water soluble phthalocyanines that are potent photosensitizers in the application of photodynamic therapy [2,24–26]. It is envisaged the aforementioned L-prolinol peripheral units could be available candidates for that purpose. For the synthesis of water soluble phthalocyanine derivative, the **Pc-4** was reacted with dilute HCl solution (0.1 M) to afford water soluble **Pc-5** in almost quantitative yield. The structures of novel Pc compounds **Pc-4** and **Pc-5** were characterized by IR, UV, ^1H and ^{13}C NMR, MALDI–TOF, LC–HRMS and CD techniques.

3.2. Structure elucidation

The FT-IR spectrum of the monomer (*S*)-(-)-**3** exhibits a characteristic absorption band at 2229 cm^{-1} assignable to C≡N vibration. The disappearance of this signal in the FT-IR spectrum of **Pc-4** is a proof of cyclomerization. Absorption bands at 745, 817–861, 936, 1047–1280 and 1452–1487 cm^{-1} are observed for **Pc-4**, these can attribute to phthalocyanine skeletal vibrations [27]. FT-IR spectrum of **Pc-5** shows very similar absorption peaks at around 741–1404 cm^{-1} which are broader than **Pc-4** peaks. In addition to these, we observed a very intense and broad band at 3210 cm^{-1} for **Pc-5**, this is due to newly formed N–H bond on the peripheral chiral unit.

The structures of **Pc-4** and **Pc-5** were mainly assigned on the basis of ^1H NMR spectra. The most conspicuous features in the ^1H



Scheme 1. Synthesis of (*S*)-4-((1-benzylpyrrolidinium-2-yl)methoxy) substituted Zn phthalocyanine complexes **Pc-4** and **Pc-5**.

NMR spectrum of **Pc-4** are the diastereotopic methylene proton resonances of chiral L-prolinol peripheral units. To determine the exact structure of **Pc-4**, first we made full assignments for the diastereotopic benzylic and CH_2–O protons of phthalonitrile (*S*)-(-)-**3** with the help of the COSY spectrum. The diastereotopic benzylic methylene protons resonate as two doublets at δ 3.88 and 3.53 ppm with a coupling constant of $J = 13.1$ Hz, whereas the other diastereotopic methylene protons next to the stereogenic center reveal signal sets at δ 3.82 as doublet of doublets with coupling constants of $J = 9.4$ and 5.1 Hz (A-component of AB system) and at δ 3.75 ppm as doublet of doublets with coupling constant values of $J = 9.4$ and 6.3 Hz (B-component of AB system) due to the coupling with stereogenic center methine proton as given in Fig. 2 (part a). Our expectation was to observe similar sets of signals in ^{1}H NMR spectrum of **Pc-4**. Fortunately, expanding the 4.10–3.30 ppm part of ^{1}H NMR spectrum of **Pc-4**, it was observed that similar sets of protons with almost the same coupling constant and with slightly different chemical shift values were obtained as expected. Diastereotopic methylene protons of **Pc-4** resonate at δ 3.92–4.07 and δ 3.30–3.50 ppm regions as two separate sets of doublets with coupling constants of $J = \sim 13$ Hz as well as (*S*)-(-)-**3** diastereotopic methylene signals (Fig. 2, part b). The other diastereotopic methylene protons next to stereogenic centers reveal signal sets at δ 3.86 ppm as doublet of doublets with coupling constants of $J = 9.1$ and 5.3 Hz (A-component of AB system) and δ 3.76 ppm as a doublet of doublets with coupling constant values of $J = 9.1$ and 6.6 Hz (B-component of AB system) as well as the phthalonitrile derivative (*S*)-(-)-**3** (Fig. 2, part c). ^{1}H NMR spectrum of **Pc-5** in D_2O shows similar signal sets to that of **Pc-4** as given in experimental part except that the signals shift to down field region and broaden because of the ionic form of **Pc-5**. In addition, we compared the ^{13}C NMR spectra of phthalonitrile (*S*)-(-)-**3** with **Pc-5**. ^{13}C NMR spectrum of (*S*)-(-)-**3** reveals two characteristic signals at 115.4 and 115.9 ppm for C≡N carbons and another characteristic signal at 162.2 ppm for prolinol unit attached to aromatic carbon. In the ^{13}C NMR spectrum of **Pc-5**, disappearance of C≡N carbon signals, a slight shifting of prolinol attached carbon signal from 162.2 ppm to 160.7 and the presence of newly formed inner core pyrrol unit carbon signals at 169.0 and 169.3 ppm confirm strongly the structure of **Pc-5**.

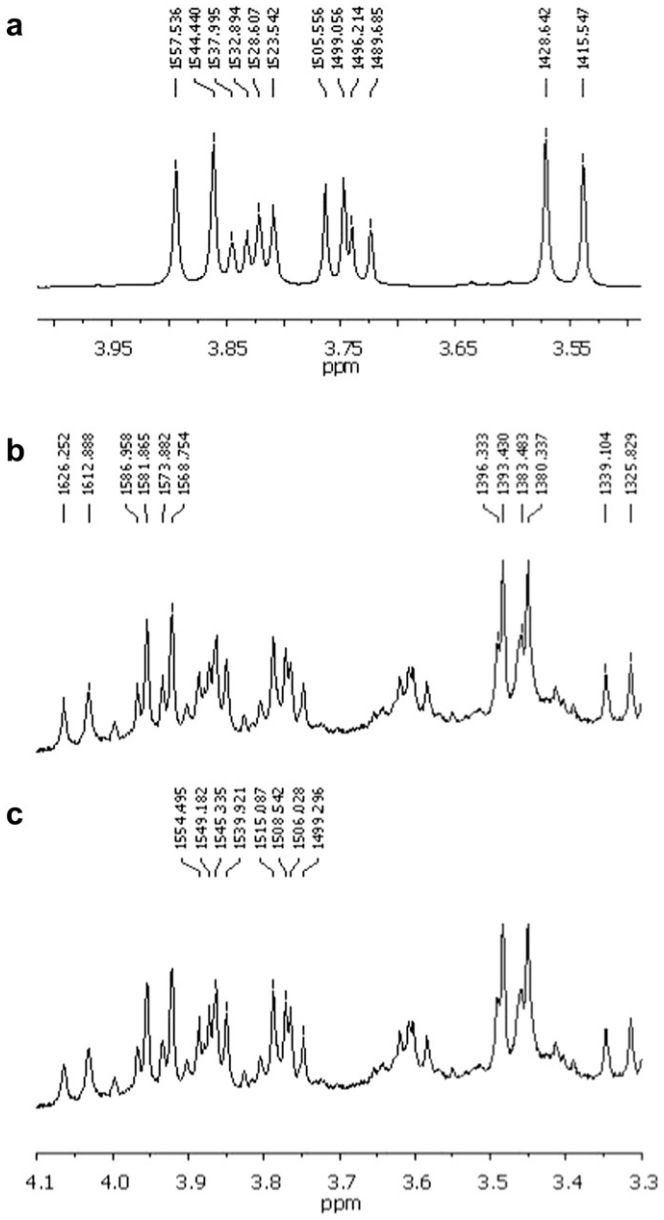


Fig. 2. ^{1}H NMR spectra (a) expanded ^{1}H NMR spectrum of (*S*)-(-)-**3** (3.50–4.00 ppm region) for diastereotopic benzylic and methylene protons next to the stereogenic center; (b) expanded ^{1}H NMR spectrum of **Pc-4** (3.30–4.10 ppm region) for diastereotopic benzylic protons; (c) expanded ^{1}H NMR spectrum of **Pc-4** (3.30–4.10 ppm region) for diastereotopic methylene protons next to the stereogenic center.

The mass spectra of Pcs also confirm the proposed structures. The linear mode positive ion MALDI–TOF mass spectrum of **Pc-4** is shown as an example in Fig. 3. The molecular ion peak was easily identified at 1334.4724 Da. When the molecular mass region of complex was expanded, we observed the protonated molecular ion of **Pc-4** at 1335, 1336, 1337 and 1338 Da as [M + H], [M + 2H], [M + 3H] and [M + 4H], respectively.

3.3. UV–vis and CD absorption spectra

The electronic absorption spectra of **Pc-4** and **Pc-5** were recorded in $CHCl_3$ and H_2O over a wide concentration range (10^{-5}–10^{-4} M), respectively. Fig. 4 compares the electronic absorption spectra in the range 300–750 nm of the two compounds. All the absorption spectra show a typical phthalocyanine Soret band around 335 nm for both **Pc-4** and **Pc-5**. An intense long wavelength π–π^* transition, the Q-band, which is characteristic of the UV–vis absorption spectra of phthalocyanines [1], and a peak at 683 nm with a shoulder at the higher-energy side (620–640 nm) in the UV–vis absorption spectrum of **Pc-4** in $CHCl_3$, was assigned to this transition. The

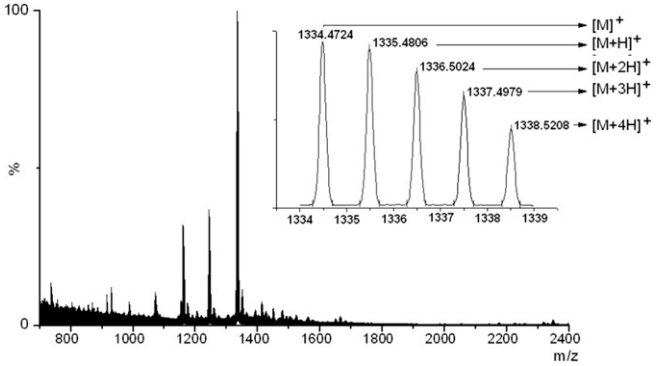


Fig. 3. The positive ion and linear mode MALDI–TOF MS spectrum of **Pc-4**, obtained in α -cyano-4-hydroxycinnamic acid (CHCA) MALDI matrix. Inset spectrum shows the expanded molecular mass region.

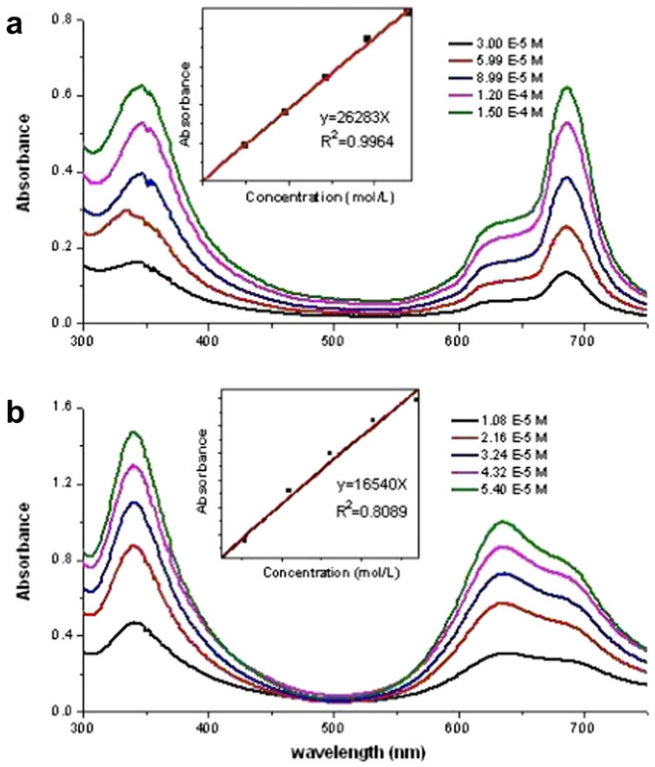


Fig. 4. Absorption spectra of **Pc-4** in $CHCl_3$ and **Pc-5** in H_2O at different concentrations.

sharpness of the peak indicates nonaggregated solution of **Pc-4** [1]. The inset of Fig. 4a also displays nonaggregation behavior of **Pc-4** solutions. The Q-band in the absorption spectrum of **Pc-5** (Fig. 4b), which is the HCl salt of **Pc-4**, was broadened, and the maximum (630 nm) was blue shifted in H_2O. This spectral change can be attributed to the formation of aggregated phthalocyanine species possessing a co-facial arrangement [28–32].

Since **Pc-4** and **Pc-5** have chiral peripheral units, they should have circular dichroism (CD) activity. The CD spectra of **Pc-4** and **Pc-5** were recorded in $CHCl_3$ and H_2O, respectively. Fig. 5 shows the CD spectra in the range 300–750 nm. The shape of the CD spectra of **Pc-4** and **Pc-5** is similar to the electronic absorption spectra. The CD spectra of **Pc-4** and **Pc-5** show the characteristic Q and Soret bands at about 683, 630 nm and 335 nm, respectively. In the CD spectra, the L-prolinol-anchored phthalocyanines show negative CD corresponding to these bands. These CD signals imply the effective chiral information transfer from the peripheral chiral L-prolinol side chains to the phthalocyanine chromophore at the molecular level [33–35].

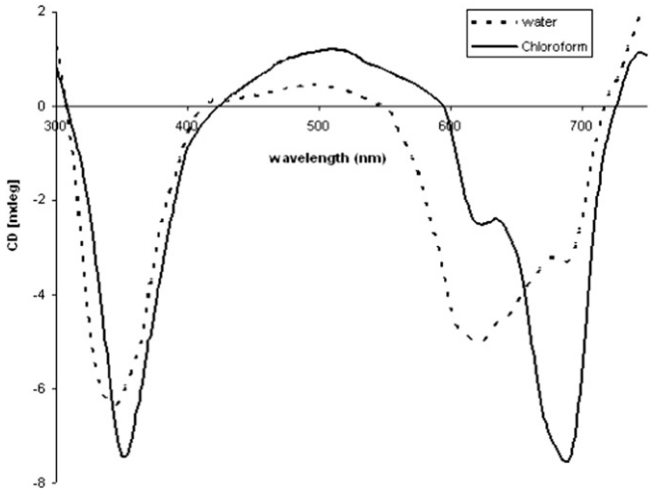


Fig. 5. CD spectra of **Pc-4** in $CHCl_3$ and **Pc-5** in H_2O.

4. Conclusion

In summary, we have reported the synthesis of a novel chiral L-prolinol-anchored phthalocyanine **Pc-4** with high solubility in many common solvents. In our synthetic strategy, *N*-benzyl protected L-prolinol was anchored to 4-nitrophthalonitrile via ***S*$_N$*Ar*** type substitution reaction to yield optically active phthalonitrile derivative (*S*)-(-)-**3** and subsequent cyclotetramerization afforded optically active target phthalocyanine **Pc-4**. Depending upon the salt formation ability of nitrogen on the chiral peripheral unit, it was transformed into its HCl salt **Pc-5** in almost quantitative yield. Thus, we have obtained optically active phthalocyanines which are soluble in most common organic solvents and water. The structures of all synthesized compounds were fully characterized by using FT-IR, ^{1}H NMR, ^{13}C NMR, MALDI–TOF MS, LC–HRMS, UV–vis and CD spectroscopic techniques. In particular, the electronic absorption spectroscopy indicates that **Pc-4** shows nonaggregated solution whereas, **Pc-5** displays aggregated solution. The perfect CD signals of both can prove the effective chiral information transfer from peripheral chiral L-prolinol units to the phthalocyanine chromophores at the molecular level. These findings may offer new possibilities towards to use these chiral macrocyclic molecules as catalyst in various asymmetric transformation reactions [36]. Our ongoing studies will be published in due course.

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References

[1] Leznoff CC, Lever ABP. Phthalocyanines, properties and applications, vols. 1–4. New York: VCH; 1989, 1992, 1993, 1996.
[2] Bonnett R. Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy. Chemical Society Reviews 1995;24:19–33.
[3] Pandey RK, Zheng G. Porphyrin handbook, vol. 6; 2000. 157–230.
[4] Moreira LM, dos Santos FV, Lyon JP, Maftoum-Costa M, Pacheco-Soares C, da Silva NS. Photodynamic therapy: porphyrins and phthalocyanines as photosensitizers. Australian Journal of Chemistry 2008;61:741–54.
[5] Yoo S, Domercq B, Donley CL, Carter C, Xia W, Minch BA, et al. SPIE: Organic photovoltaics IV, vol. 5215; 2004. 71–78.
[6] Shaheen SE, Ginley DS, Jabbour GE. Organic-based photovoltaics: toward low-cost power generation. Materials Research Society Bulletin 2005;30:10–9.
[7] Thompson BC, Frechet JMJ. Polymer–Fullerene composite solar cells. Angewandte Chemie International Edition 2008;47:58–77.
[8] Brumbach M, Placencia D, Armstrong NR. Titanyl phthalocyanine/C_{60} heterojunctions: band-edge offsets and photovoltaic device performance. The Journal of Physical Chemistry C 2008;112:3142–51.
[9] Xue J, Rand BP, Uchida S, Forrest SR. A hybrid planar-mixed molecular heterojunction photovoltaic cell. Advanced Materials 2005;17:66–71.
[10] Bouvet M. Phthalocyanine-based field-effect transistors as gas sensors. Analytical and Bioanalytical Chemistry 2006;384:366–73.
[11] Kobayashi N, Kobayashi Y, Osa T. Optically active phthalocyanines and their circular dichroism. Journal of the American Chemical Society 1993;115:10994–5.
[12] Kobayashi N. Optically active 'adjacent' type non-centrosymmetrically substituted phthalocyanines. Chemical Communications; 1998:487–8.
[13] Kobayashi N, Higashi R, Titeca BC, Lamote F, Ceulemans A. Substituent-induced circular dichroism in phthalocyanines. Journal of the American Chemical Society 1999;121:12018–28.

[14] Kobayashi N. Optically active phthalocyanines. Coordination Chemistry Reviews 2001;219–221:99–123.
[15] Kimura M, Kurado T, Ohta K, Hanabusa K, Shirai H, Kobayashi N. Self-organization of hydrogen-bonded optically active phthalocyanine dimers. Langmuir 2003;19:4825–30.
[16] Kobayashi N, Narita F, Ishii K, Muranaka A. Optically active oxo(phthalocyaninato) vanadium(IV) with geometric asymmetry: synthesis and correlation between the circular dichroism sign and conformation. Chemistry-A European Journal 2009;15:10173–81.
[17] Liu HW, Chen CF, Ai M, Gong AJ, Jiang J, Xi F. Synthesis of optically active 1,1 binaphthyl-phthalocyanines linked via a crown ether unit. Tetrahedron: Asymmetry 2000;11:4915–22.
[18] Liu H, Liu Y, Chen C, Xi F. Synthesis and properties of optically active 6,6′-didodecyl-1,1′-binaphthyl-phthalocyanine linked through crown ether units. Tetrahedron Letters 2001;42:7083–6.
[19] Adachi K, Chayama K, Watarai H. Control of optically active structure of thioether-phthalocyanine aggregates by chiral Pd(II)-BINAP complexes in toluene and at the toluene/water interface. Chirality 2006;18:599–608.
[20] Nemykin VN, Koposov AY, Subbotin RI, Sharma S. Preparation and characterization of first optically active rigid phthalocyanine dimers. Tetrahedron Letters 2007;48:5425–8.
[21] Wu L, Wang Q, Lu J, Bian Y, Jiang J, Zhang X. Helical nanostructures self-assembled from optically active phthalocyanine derivatives bearing four optically active binaphthyl moieties: effect of metal-ligand coordination on the morphology, dimension, and helical pitch of self-assembled nanostructures. Langmuir 2010;26:7489–97.
[22] McKeown NB. Phthalocyanine materials synthesis, structure and function. Cambridge University Press; 1998.
[23] Zhu L, Cheng L, Zhang Y, Xie R, You J. Highly efficient copper-catalyzed *N*-arylation of nitrogen-containing heterocycles with aryl and heteroaryl halides. The Journal of Organic Chemistry 2007;72:2737–43.
[24] Moser JG. Photodynamic tumor therapy: 2nd and 3rd generation photosensitizers. Amsterdam: Harwood Academic; 1998.
[25] Ben-Hur E, Chan WS. Phthalocyanines in photobiology and their medical applications. Cht.117. In: Kadish KM, Smith KM, Guilard R, editors. Porphyrin handbook, phthalocyanine properties and materials, vol. 19. Boston: Academic Press; 2003.
[26] Tedesco AC, Rotta JCG, Lunardi CN. Synthesis, photophysical and photochemical aspects of phthalocyanines for photodynamic therapy. Current Organic Chemistry 2003;7:187–96.
[27] Gladkov LL, Shkirman SF, Sushko NI, Konstantinova VK, Sokolov NA, Solovyov KN. IR spectra of Zn phthalocyanine and Zn phthalocyanine-d_{16} and their interpretation on the basis of normal coordinate analysis. Spectroscopy Letters 2001;34(6):709–19.
[28] Kobayashi N, Lam H, Nevin A, Janda P, Leznoff CC, Koyama T, et al. Synthesis, spectroscopy, electrochemistry, spectroelectrochemistry, Langmuir–Blodgett film formation, and molecular orbital calculations of planar binuclear phthalocyanines. Journal of the American Chemical Society 1994;116:879–90.
[29] Kobayashi N, Ojima F, Osa T, Vigh S, Leznoff CC. Tetrakis-[3-(dimethylamino) propyl]- and tetrakis-[3-(diethylmethylammonio)propyl] phthalocyanines: the first amphiphilic phthalocyanines. Bulletin of the Chemical Society of Japan 1989;62:3469–74.
[30] Kobayashi N, Nishimura Y. A copper phthalocyanine with four crown ether voids. Journal of the Chemical Society, Chemical Communications; 1986: 1462–3.
[31] Sielcken OE, van Tilborg MM, Roks MFM, Hendriks R, Drenth W, Nolte RJM. Journal of the American Chemical Society 1987;109:4261–5.
[32] Kimura M, Muto T, Takimoto H, Wada K, Ohta K, Hanabusa K, et al. Fibrous assemblies made of amphiphilic metallocyanines. Langmuir 2000;16: 2078–82.
[33] Berova N, Nakanishi K. In principles and applications of exciton chirality method. In: Berova N, Nakanishi K, Woody RW, editors. Circular dichroism, principles and applications. New York: Wiley-VCH; 2000.
[34] Huang X, Nakanishi K, Berova N. Porphyrins and metalloporphyrins: versatile circular dichroic reporter groups for structural studies. Chirality 2000;12: 237–55.
[35] Harada N, Nakanishi K. Circular dichromic spectroscopy, exciton coupling in organic stereochemistry. California: University Science Books; 1983.
[36] Berkessel A, Gröger H. Asymmetric organocatalysis. Weinheim: Wiley-VCH; 2005.