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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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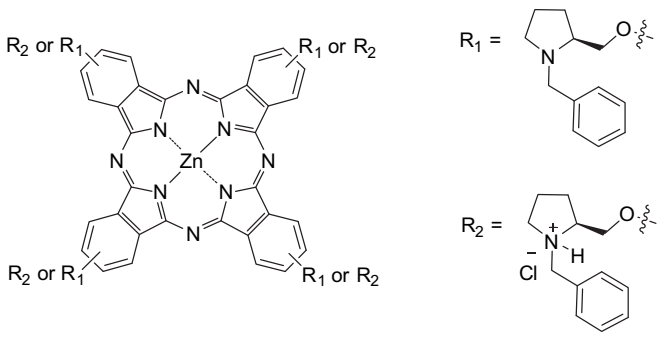

Fig. 1. Target optically active phthalocyanine structures.

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