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Synthesis and Characterization of Novel Porphyrinogen-Like Macrocycle Schiff Base Ligands

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ABSTRACT

In this paper, two novel porphyrinogen-like macrocycle ligands were synthesized and characterized with elemental analyses, ^{1}H NMR, FAB-Ms, and IR methods.

Key Words: Macrocycle schiff base; Porphyrinogen-like.

Novel pyrrole-containing macrocycle schiff bases have distinctive structures and properties. They are currently attracting interest because they may

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display unusual physical, chemical, or coordination properties, and play important roles in a number of areas in chemistry and biochemistry.[1–3] The porphyrin-like macrocycle and their rare earth metal complexes belong to a novel family of dye molecules, absorb strongly around 760–780 nm, and were suggested as potential photosensitizers for Photo Dynamic Therapy.[3] As we know, the formation of macrocyclic complexes depends significantly on the dimension of the internal cavity, on the rigidity of the macrocycle, on the nature of its donor atoms, and on the complexing properties of the anion involved in the coordination.[4] In this article we report the synthesis of two novel porphyrinogen-like macrocycle schiff base ligands with different internal cavities.

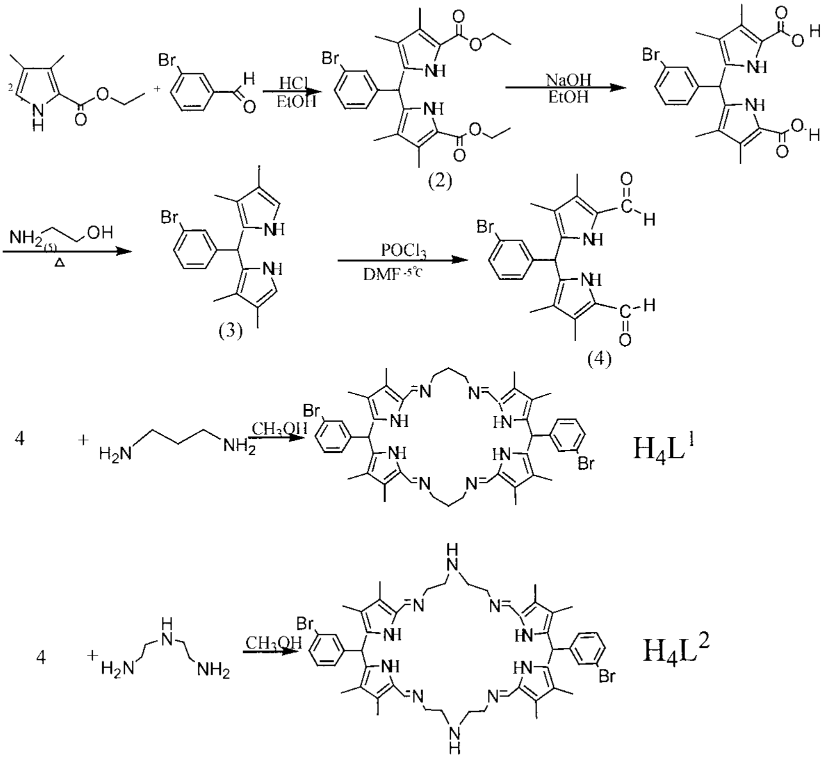
EXPERIMENTAL

Elemental analyses were determined with the Elementar Vario EL elemental analyzers. NMR spectra were obtained in $CDCl_3$ with Me_4Si as an internal standard. All melting points were uncorrected. All yields refer to isolated products.

3-Bromoformylbenzene (12 mmol) and 2-(ethoxycarbony1)-3,4-dimethylpyrrole[4] (24 mmol) were dissolved with heating in 40 mL absolute EtOH. The reaction mixture was then heated to reflux, and 1.2 mL of 6 mol/L HCL was added. The reaction was placed under N_2 and refluxed for 1 h. Upon cooling, the product crystallized. It was filtrated, washed with cold EtOH, and dried to yield 4.57 g (76%) of **2** ^{1}H NMR: δ 7.26 (4H, m, 4 × ArH, 2 × NH), δ 5.50 (1H, s, CH), δ 4.07 (4H, q, CH_2CH_3), δ 2.23 (6H, s, CH_3), δ 1.93 (6H, s, CH_3), δ 1.3 (12H, t, CH_2CH_3).

Ten mmol of **2** was suspended in 60 mL of absolute EtOH and brought to reflux. A total of 5 mL of 5 M NaOH solution was added, and the reaction mixture was refluxed for 20 h under N_2. The EtOH was removed under reduced pressure, and the residue was diluted with 100 mL of H_2O and filtrated. The filtrate was acidified with glacial HOAc, and the diacid was precipitated as a pink solid. The pink solid was dissolved in 60 mL of degassed ethanolamine. The mixture was placed under N_2 and refluxed for 2 h, after which the reaction mixture was poured into 80 mL of ice H_2O while still warm. A solid soon separated, which was filtrated and dried to yield 3.11 g (87%) of **3**. ^{1}H NMR: δ 7.20 (6H, m, 4 × ArH, 2 × NH), δ 6.32 (2H, s, α H), δ 5.38 (1H, s, CH), δ 2.01 (6H, s, CH_3), δ 1.87 (6H, s, CH_3).

Ten mmol of **3** was added to 30 mL of DMF. The mixture was cooled to -5°C, then 12 mL of $POCl_3$ was added, after which, the reaction mixture was stilled for 12 h under room temperature. The reaction mixture was placed under 50°C–60°C and refluxed for 2 h, after which the reaction mixture was poured into 100 mL of ice H_2O while still warm. The filtrate was basified with 5 M NaOH to pH = 9, a brown solid separated, which was filtrated and dried to yield 2.02 g (49%) of **4**. ^1H NMR: δ 9.30 (2H, s, CHO), δ 7.20 (6H, m, 4 × ArH, 2 × NH), δ 5.25 (1H, s, CH), δ 2.25 (6H, s, CH_3), δ 1.90 (6H, S, CH_3).



One mmol of **4** was dissolved with heating in 50 mL CH_3OH. The reaction mixture was then heated to reflux, 50 mL $NH_2{-}R{-}NH_2$(R_1 = $-CH_2CH_2CH_2-$, R_2 = $-CH_2CH_2NHCH_2CH_2-$) of CH_3OH solution (2.0×10^{-2} mol/L) was then added tardily. The reaction mixture was refluxed for 4 h. The CH_3OH was removed under reduced pressure. The residue was filtrated and recrystallized with CH_3OH, dried to yield 0.37 g (82%) of H_4L^1 and 0.41 g (81%) of H_4L^2. H_4L^1, $C_{48}H_{54}N_8Br_2$, [Found: C, 63.87 (63.86), H, 5.85 (6.03), N, 12.24 (12.41)] ^1H NMR: δ 8.01 (4H,s, HC=N) δ 7.11 (12H, m, 8 × ArH, 4 × NH), δ 5.50 (2H, s, CH), δ 3.50 (8H, t, CH_2), δ 2.09 (12H, s, CH_3), δ 2.01 (12H, s, CH_3), δ 1.22 (4H, tt, CH_2). FAB-MS m/z: 905 $[H_4L^1 + H]^+$. The melting point of H_4L^1 is 267–268°C.

H_4L^2, $C_{50}H_{60}N_{10}Br_2$, [Found: C, 62.87 (62.50), H, 6.18 (6.25), N, 14.06 (14.58)]. ^{1}H NMR: δ 8.05 (4H, s, HC=N) δ 7.16 (12H, m, 8 × ArH, 4 × NH), δ 5.53 (2H, s, CH), δ 4.82 (2H, t, NH), δ 3.53 (8H, t, CH_2), δ 2.30 (8H, t, CH_2), δ 2.06 (12H, s, CH_3), δ 1.98 (12H, s, CH_3). FAB-MS m/z: 963 $[H_4L^2 + H]^+$. TG-DTG shows that H_4L^2 begins to decompose at 254°C; the melting point of the ligand is not found.

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