Monatshefte für Chemie 135, 223–229 (2004)
DOI 10.1007/s00706-003-0099-9

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Molecular Rectangle Formed by Head-to-tail Self-Assembly of 1-(Dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methane

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Received July 18, 2003; accepted July 22, 2003
Published online November 10, 2003

Summary. 1-(Dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methane, the *N*-confused analog of biladiene-*ac*, is prepared by condensation of 2,3′-dipyrromethane with two molecules of 2-formylpyrrole in dichloromethane in the presence of hydrogen bromide. Self-assembly of the ligand with Zn(II) in dichloromethane and methanol offers a dinuclear dimeric complex with a ligand:metal ratio of 2:2. X-Ray crystal structure analysis reveals two ligands bound through a head-to-tail pattern to two zinc centers to form a severely distorted helical conformation, which has the shape of a rectangle.

Keywords. Self-assembly; Dipyrrin; 1-(Dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methane; Biladiene-*ac*; Dinuclear dimeric complex.

Introduction

Metal ion assisted self-assembly is one of the most powerful approaches to supramolecular architectures [1]. This strategy typically utilizes metal–ligand interactions to organize small molecules into large assemblies. Obviously, ligands are the key for such research. Dipyrrin ligands **1**, the important synthetic precursors for porphyrins, bile pigments, and linear and cyclic polypyrroles [2] have been recently explored for metal ion assisted self-assembly [3–8]. One of the advantages to use dipyrrins as the building block for self-assembly is their ability to form neutral complexes. Therefore, counter-ions are not required, which makes it particularly convenient to purify the complexes by column chromatography since the complexes are generally the least polar component in the reaction mixtures [3–8]. This may also avoid the disordering problem in the solid state caused by counter-ions.

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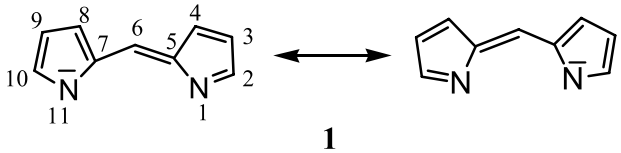

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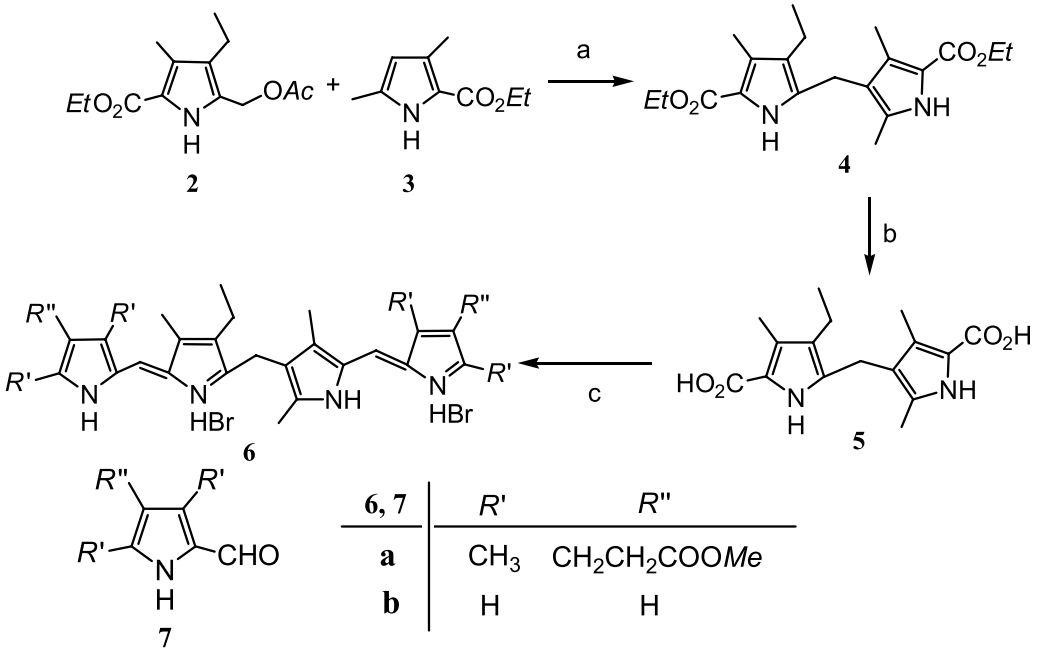
Ligands containing multiple dipyrrin units, such as biladiene-*ac* [3], hexapyrrins [3], 3,3′-bis(dipyrrin)methane [4, 5], bis(dipyrrin-3-yl)alkanes [6], and bis(dipyrrin-3-yl)sulfides [7] react with metal ions to offer helical complexes, while bi(dipyrrin-3-yl), a bis(dipyrrin-3-yl) ligand with no linker, gives a trinuclear trimeric triangle complex [4] of 3:3 of ligand:Zn(II). By examining the X-ray crystal structures of dimeric zinc complexes of bis(dipyrrin) ligands linked by an alkyl spacer between 3 and 3′ positions, *Dolphin* [6] recently has found that the angles between two dipyrrin planes and the extent of helicity in complexes differ as the length of the linker varies. All those results suggest that the self-assembly of bis(dipyrrin) ligands are controlled by the bridging spacers, whose length, flexibility, planarity, and rotary ability could remarkably affect the geometry of the supramolecular architectures. To the best of our knowledge, all bis(dipyrrin) ligands used for self-assembly reported in literature so far [2–7] are symmetric, and the bridging spacers are linked to two identical dipyrrin units at the 2- or 3-position. The corresponding asymmetric system thus remains to be investigated. In this paper, we report a novel molecular rectangle formed by head-to-tail self-assembly of 1-(dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methane (**6**), an asymmetric bis(dipyrrin)-methane ligand.

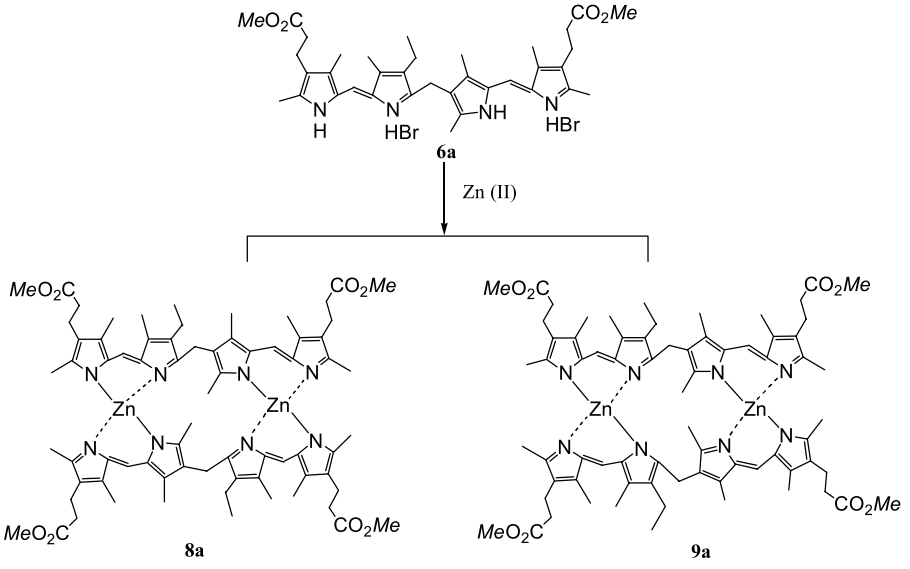
Results and Discussion

1-(Dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methanes **6** were synthesized by condensation of 2,3′-dipyrromethane **5** with 2-formylpyrroles **7** under acid-catalyzed conditions as shown in Scheme 1. The important precursor, the 2,3′-dipyrromethane **4**, is prepared in 86% yield by condensation of 5-acetoxypyrrole **2** [8] with the 3-unsubstituted pyrrole **3** [9] in acetic acid at reflux. Treating **4** with aqueous sodium hydroxide in ethanol at reflux offers the corresponding 2,3′-dipyrromethane diacid **5** in quantitative yield. Compound **5** is treated with trifluoroacetic acid, followed by condensation with two equivalents of 2-formyl-3,5-dimethyl-4-methoxycarbonylethylpyrrole (**7a**) [10] or 2-formyl-pyrrole (**7b**) [11] in methanol in the presence of HBr–HO*Ac* to give the expected 1-(dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methane **6**, a *N*-confused analog of biladienes-*ac*.

Ligands **6** were attempted to react with stiochiometric amounts of Zn(II), however, the reaction is very slow with very poor yield. Thus an excess of Zn(II) ion was used in the same reaction (Scheme 2), in which ligand **6a** or **6b** resulted in one major and more than two minor products as judged by TLC. The major products were isolated and purified by chromatography (dichloromethane:methanol = 95:5, v/v). The complexes were isolated as orange powders with a green metallic luster. Solutions of the complexes in dichloromethane or chloroform are stable for more than half a year in dark, but very slow photobleaching is observed if the solution is exposed to light, which is very similar to its bis(dipyrin-3-yl)methane analogues [5, 6].



Scheme 1. a) CH_3OH, *Ts*OH, 40°C, 4 hr (86%); b) 4.0 equiv. NaOH, reflux in 95% ethanol, 4 h, then 1 *M* H_2SO_4 (84%); c) *TFA*, N_2, then **7** and HBr–HO*Ac* were added (72% for **6a**)



Scheme 2

Analysis of the complex of **8a**, primarily by MALDI-TOF mass spectrometry (gave $m/z = 1320$), revealed that it is a dinuclear dimeric complex like its analogues such as biladiene-*ac* and bis(dipyrrin-3-yl)methane [4–7]. The ^{1}H NMR spectrum of the zinc complex **8a** in $CDCl_3$ shows a single set of proton resonances that can be fully

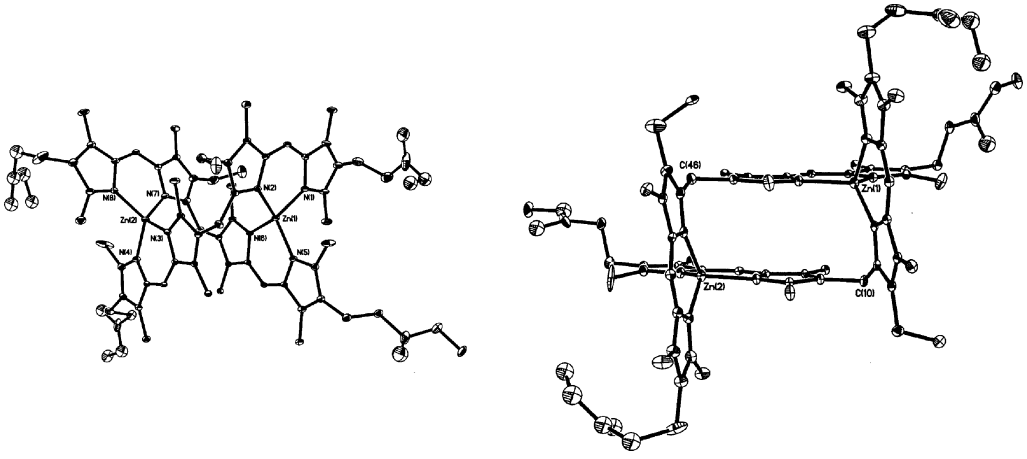


Fig. 1. X-Ray crystal structure of compound **8a**; left: emphasizing the helical conformation, and right: emphasizing the rectangle geometry (H atoms are omitted for clarity)

assigned, which suggest that **8a** exists as a single species in $CDCl_3$ solution. The disappearance of the NH protons present in the free ligands is also observed, which is in agreement with the bis(deprotonation) of the bis(dipyrrin)methane ligand. Compared to the corresponding free ligands, complex **8a** has upfield shifts for all protons indicating strong interactions between dipyrrin units and zinc centers. The ^{13}C NMR spectrum of **8a** in $CDCl_3$ shows the expected peaks.

In principle, the reaction of ligands **6** with zinc ions would generate two isomers through head-to-tail (compound **8**) and head-to-head patterns (compound **9**). It would be very hard to elucidate their structures by using current available NMR techniques. X-Ray crystal structure analysis finally provided unambiguous evidence of the identity of the isolated product from **6a** with Zn(II), namely that of **8a**, a head-to-tail dimeric complex with a severely distorted helical conformation resulting from a major twist around the CH_2-bridge (Fig. 1). As a result, the complex is shaped in a rectangular geometry with dimensions of 5.6×3.4 Å. Each Zn(II) center is coordinated by four N-donors (two from one ligand and two from another) forming a distorted tetrahedron geometry. The Zn–N distances are in the range of 1.956–2.010 Å. The distance between the two metal centers is 6.203 Å. The dihedral angles, which are defined by the intersection of two planes at the Zn(1) and Zn(2) centers, are 87.1° and 82.5°.

Ligand **6b** was reacted with Zn(II) following the same procedure as for **8a**. Although a major product **8b** was isolated in 45% yield (based on **5**), it failed to yield crystals suitable for X-ray analysis. Therefore, it is not clear if compound **8b** is the head-to-tail complex, although it most likely is as its analogue **8a**. The ^1H NMR spectrum of the zinc complex **8b** in $CDCl_3$ shows a single set of proton resonances that can be fully assigned, which suggest that **8b** exists as a single species in solution.

To conclude, the self-assembly of 1-(dipyrrin-2-yl)-1′-(dipyrrin-3-yl)methane directed by Zn(II), gives a dinuclear dimeric complex with severely distorted helical conformation. As a result, the complex is shaped in a rectangular geometry. To

a large content, this reflects the steric arrangement of two dipyrrin units in the ligand and the tetrahedral geometric requirement of Zn centers.

Experimental

IR spectra were recorded on a Tensor 27 spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument using *TMS* as internal standard. Mass spectra were determined on Brucker APEX II and KYKY-ZHP-5 spectrometers. The melting points were determined on a Yanaco MP-500 micro-melting point apparatus. Elemental analyses were performed on Carlo Erba-120 elemental analyzer and agreed favourably with the calculated values. All solvents were of reagent grade and were used as received. Compounds **2** and **3** were prepared according to Refs. [8, 9] and compounds **7** were prepared according to Refs. [10, 11]. X-Ray structure analysis was performed on a Bruker Smart 1000 CCD diffractometer instrument using MoKα radiation. The data were handled by means of the instrument software.

2′,4,4′-Trimethyl-3-ethyl-5,5′-diethoxycarbonyl-2,3′-dipyrrylmethane (**4**, $C_{20}H_{28}N_2O_4$)

Ethyl 5-acetyloxymethyl-4-ethyl-3-methyl-1*H*-pyrrole-2-carboxylate (**2**) (4 g, 15.8 mmol) and 2.7 g of ethyl 3,5-dimethyl-1*H*-pyrrole-2-carboxylate (**3**) (16.1 mmol) were dissolved in 40 cm^3 of methanol, 0.2 g of *p*-toluenesulfonic acid were added to the mixture, it was stirred at 40°C for 4 h under N_2, concentrated to 20 cm^3, and cooled to room temperature. Then the white solid was collected by filtration and recrystallized from ethanol to give 5.0 g of white solid (86%). EI-MS: $m/z = 360$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.08$ (t, $J = 7.4$ Hz, CH_3), 1.32 (t, $J = 7.4$ Hz, CH_3), 1.35 (t, $J = 7.4$ Hz, CH_3), 2.15 (s, CH_3), 2.18 (s, CH_3), 2.28 (s, CH_3), 2.45 (q, $J = 7.4$ Hz, CH_2), 3.67 (s, CH_2), 4.25 (q, $J = 7.4$ Hz, CH_2), 4.31 (q, $J = 7.4$ Hz, CH_2), 8.22 (s, NH), 9.19 (s, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 10.39$, 10.54, 11.25, 14.44, 15.13, 17.07, 20.86, 59.51, 59.77, 116.62, 116.68, 117.35, 122.95, 126.79, 127.12, 130.82, 131.89, 161.97 ppm.

2′,4,4′-Trimethyl-3-ethyl-2,3′-dipyrrylmethane-5,5′-dicarboxylic acid (**5**, $C_{16}H_{20}N_2O_4$)

2′,4,4′-Trimethyl-3-ethyl-5,5′-diethoxycarbonyl-2,3′-dipyrrylmethane (**4**) (4 g, 11.0 mmol) and 3 g of NaOH (75.0 mmol) were suspended in 40 cm^3 of 95% ethanol and 10 cm^3 of H_2O were added. The mixture was refluxed for 5 h. After ethanol was removed under reduced pressure, the solution was poured into 100 cm^3 of ice-water and it was acidified with H_2SO_4 (10%) to $pH = 6$. The white precipitate was collected and dried under vacuum to give 2.8 g of white solid (84%). EI-MS: $m/z = 216$ $(M–2CO_2)^+$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.10$ (t, $J = 7.4$ Hz, CH_3), 2.11 (s, CH_3), 2.15 (s, CH_3), 2.28 (s, CH_3), 2.41 (q, $J = 7.4$ Hz, CH_2), 3.66 (s, CH_2), 8.35 (s, NH), 9.58 (s, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 10.5$, 10.6, 11.3, 15.1, 15.6, 17.2, 21.0, 116.1, 117.0, 123.7, 129.4, 132.4, 133.4, 166.1 ppm.

1-(3-Ethyl-4,8,10-trimethyl-9-(methoxycarbonylethyl)dipyrrin-2-yl)-1′-(2,4,8,10-tetramethyl-9-(methoxycarbonylethyl)dipyrrin-3-yl)methane (**6a**, $C_{36}H_{46}N_4O_4$)

The preparation was achieved by following a procedure described in Ref. [5]. Yield 72%; mp > 250°C (decomp); FAB-MS: $m/z = 599$ $(M + 1)^+$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.4$ Hz, CH_3), 2.17 (q, $J = 7.4$ Hz, CH_2), 2.27 (s, CH_3), 2.32 (s, CH_3), 2.35 (s, CH_3), 2.49 (t, $J = 7.9$ Hz, CH_2), 2.51 (t, $J = 7.9$ Hz, CH_2), 2.63 (s, CH_3), 2.72 (s, CH_3), 2.74 (s, CH_3), 2.77 (t, $J = 7.9$ Hz, CH_2), 2.79 (t, $J = 7.9$ Hz, CH_2), 3.69 (s, CH_3), 3.70 (s, CH_3), 4.38 (s, CH_2), 7.09 (s, –CH=), 7.14 (s, –CH=), 13.12 (s, NH), 13.19 (s, NH), 13.22 (s, NH), 13.30 (s, NH) ppm; ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 10.0$, 10.3, 10.7, 12.9, 13.0, 13.2, 14.0, 17.3, 19.3, 22.8, 33.7, 51.8, 119.5, 119.7, 123.1, 125.7, 125.8, 126.6, 126.7, 127.3, 127.6, 130.6, 142.3, 142.6, 143.1, 143.3, 152.3, 153.7, 155.2, 155.6, 172.6 ppm.

Zn(II) Complex of 1-(3-Ethyl-4,8,10-trimethyl-9-(methoxycarbonylethyl)dipyrrin-2-yl)-1′-(2,4,8,10-tetramethyl-9-(methoxycarbonylethyl)dipyrrin-3-yl)methane (**8a**, $C_{72}H_{88}N_8O_8Zn_2$)

The preparation was achieved by following a procedure described in Ref. [5]. Yield 65%; mp > 280°C (decomp); MALDI-TOF-MS: $m/z = 1320$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (m, $2CH_3$), 1.27 (s, $2CH_3$), 1.50 (s, $2CH_3$), 1.66 (s, $2CH_3$), 2.04 (s, $2CH_3$), 2.16 (s, $2CH_3$), 2.21 (s, $2CH_3$), 2.27 (s, $2CH_3$), 2.31 (t, $J = 7.7$ Hz, $2CH_2$), 2.44 (t, $J = 7.7$ Hz, $2CH_2$), 2.46 (t, $J = 7.7$ Hz, $2CH_2$), 2.59 (t, $J = 7.7$ Hz, $2CH_2$), 2.75 (m, $2CH_2$), 3.39 (d, $J = 17$ Hz, $-CH_2-$), 3.55 (d, $J = 17$ Hz, $-CH_2-$), 3.58 (s, $2CH_3O$), 3.67 (s, $2CH_3O$), 6.60 (s, 2-CH=) ppm; ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 0.8$, 9.4, 9.5, 9.6, 13.5, 13.7, 14.3, 14.9, 15.7, 17.6, 19.3, 19.9, 20.0, 22.3, 23.7, 28.9, 29.3, 31.5, 34.3, 34.8, 50.9, 51.0, 119.7, 120.3, 123.6, 123.7, 125.7, 129.7, 134.5, 135.2, 135.5, 135.5, 136.1, 136.3, 136.9, 139.2, 152.5, 156.9, 157.0, 157.7, 173.1, 173.2 ppm.

X-Ray crystal data of **8a** (CCDC No. 209680) $C_{72}H_{88}N_8O_8Zn_2$: $M = 1324.24$, triclinic, space group P-1, $a = 14.974(5)$, $b = 15.700(5)$, $c = 18.449(6)$ Å, $\alpha = 66.838(6)$, $\beta = 67.552(6)$, $\gamma = 88.168(6)°$, $V = 3650(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.205$ g/cm^3, $F(000) = 1400$, $\mu = 0.713$ mm^{-1}, crystal size $0.32 \times 0.20 \times 0.18$ mm^3. A total of 18790 reflections were measured in the range $1.31° < \theta < 25.00°$ (*hkl* range: $-17/16$, $-18/14$, $-21/21$), 12746 unique [R(int) = 0.0495]. The structure was refined to final $R = 0.1249$, $Rw = 0.3298$ ($I > 2\sigma(I)$), and GOF = 1.148 on F^2 for 751 refined parameters.

Zn(II) Complex of 1-(3-Ethyl-4-methyldipyrrin-2-yl)-1′-(2,4-dimethyldipyrrin-3-yl)methane (**8b**, $C_{48}H_{48}N_8Zn_2$)

A solution of 0.25 mmol of **5** in 2 cm^3 of trifluoroacetic acid was stirred at room temperature for 10 min under N_2, then a solution of pyrrole-2-carbaldehyde (0.5 mmol) in 5 cm^3 of methanol was added, followed by 1 cm^3 of HBr–HOAc (45%). The mixture was stirred for 2 h, 0.1 g of zinc acetate and 1 g of sodium acetate in 20 cm^3 of methanol were added to the solution and it was stirred for 1 hour. The reaction mixture was poured into 40 cm^3 of H_2O and extracted with 3×30 cm^3 $CHCl_3$. The $CHCl_3$ extract was evaporated under vacuum and the residue was purified by silica gel chromatography using CH_2Cl_2 as eluent to give complex **8b**. Yield 45%; mp > 250°C (decomp); MALDI-TOF-MS: $m/z = 865$ $(M+H)^+$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.21$ (t, $J = 7.3$ Hz, $2CH_3$), 1.45 (s, $2CH_3$), 1.67 (s, $2CH_3$), 2.37 (s, $2CH_3$), 2.55 (q, $J = 7.3$ Hz, $2CH_2$), 3.65 (d, $J = 17$ Hz, CH_2), 3.68 (d, $J = 17$ Hz, CH_2), 6.55 (m, 4pyrrole-H), 6.96 (s, 2-CH=), 7.10 (m, 4pyrrole-H), 7.22 (s, 2-CH=), 7.49 (m, 4pyrrole-H) ppm; ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 8.6$, 10.0, 15.1, 16.5, 17.9, 24.4, 113.8, 115.3, 125.6, 126.1, 126.7, 126.9, 128.2, 133.0, 137.5, 137.7, 138.7, 139.2, 140.6, 142.9, 143.5, 145.9, 162.8, 163.3 ppm.

Acknowledgements

This work was supported by the Major State Basic Research Development Program (G2000078100), NSFC (20172055) and CAS (CMS CX-200205). We thank Ms. *S.-H. Zhou* (Institute of Biophysics) for the NMR spectra.

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