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Synthesis and self-assembly of novel tetra- and hexapyrroles containing dipyrrins linked by a sulfur bridge at the β-position

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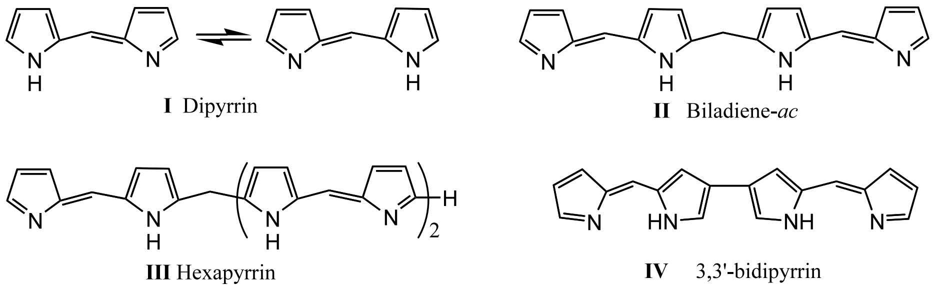
Abstract—Novel ligands containing two dipyrrin units linked by a sulfur bridge at the β-position have been synthesized and used to prepare double-stranded helical metal complexes. A structure was confirmed by X-ray analysis. © 2002 Elsevier Science Ltd. All rights reserved.

Dipyrrins **I** are basic, highly colored, fully conjugated flat molecules containing 10-π electrons, and have been extensively used for the synthesis of porphyrins,[1] macrocycles related to porphyrins, bile pigments, and linear polypyrroles.[2] Although their ability to coordinate transition metal ions has long been known, their use in supramolecular assembly as novel building blocks was only recently explored by our laboratory.[3] One advantage of using dipyrrins and divalent metal ions to assemble supramolecules is that the products are neutral, which makes separation and purification particularly convenient.[3] In contrast bipyridine ligands used by Lehn and his colleagues,[4–9] generate charged species, when coordinated to divalent metal ions, and may give rise to disorder in the solid state.[3]

We have previously used polydipyrrin ligands (Scheme 1), such as biladiene-ac (**II**), hexapyrrin (**III**), and 3,3′-bidipyrrin (**IV**), to generate helicates and triangular macrocycles. To expand our work, we became interested in the self-assembly of bis(dipyrrin-3-yl) sulfides,[3] in which two dipyrrin units are linked by a sulfur bridge at the β-position. In this paper we present their syntheses and self-assembly with Zn(II).

Tetrapyrrole **3a**[11] was synthesized in high yield by the condensation of bis(5-formylpyrrole-3-yl)sulfide **1a**[10] with **2a** in the presence of TFA and HBr. Compound **3b**,[12] on the other hand, was prepared by two methods: condensation of either **1a** with **2b** or **1b** with 3,4,5-trimethyl-2-formylpyrrole (Scheme 2). When a solution of $Zn(OAc)_2$ and MeOH was added to a solution of **3** in $CHCl_3$, complexes **4a**[13] and **4b**[14] were formed in 80–85% and their constitutions were confirmed by LSIMS. They are dimeric complexes with a ligand:metal stoichiometry of 2:2. The X-ray structure (Fig. 1) of **4a**[13] showed that it has a double stranded helical geometry resulting from a twist around the –S-


I Dipyrrin

II Biladiene-*ac*

III Hexapyrrin

IV 3,3'-bidipyrrin

Scheme 1.

Keywords: dipyrrins; helicates; hexapyrrin; bis(dipyrrin-3-yl) sulfides; self assembly; metal complexes.

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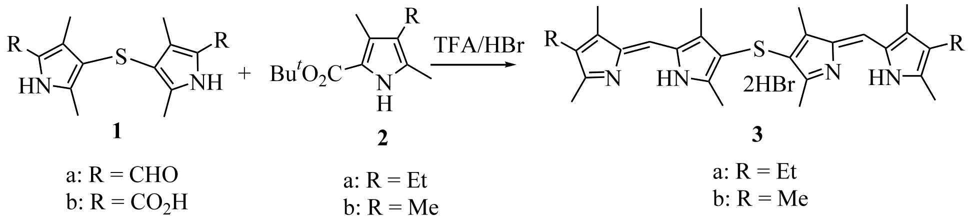


Scheme 2.

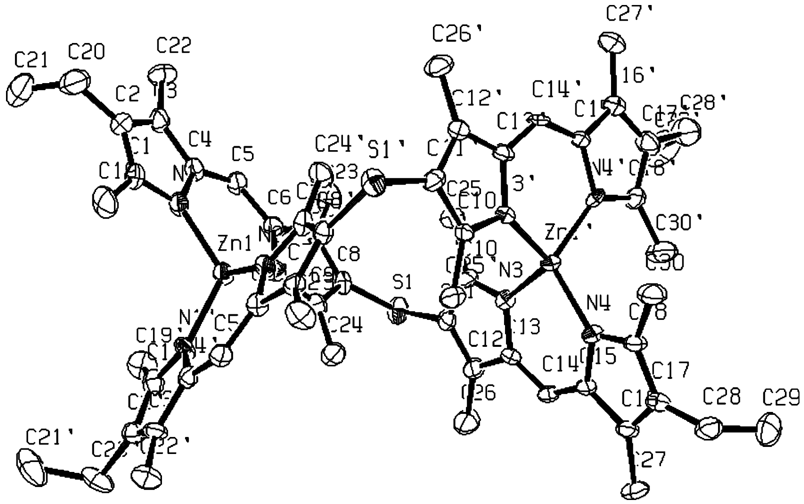
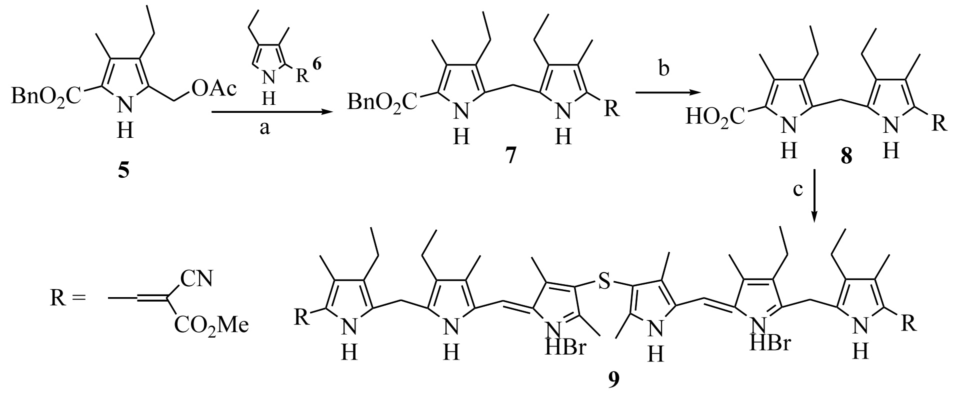


Figure 1. X-Ray structure of **4a** (hydrogen atoms are omitted for clarity). Selected bond angles (°): N(1)–Zn(1)–N(2) 96.4(2), N(1)–Zn(1)–N(1′) 121.6(2), N(2)–Zn(1)–N(2′) 113.1(2), C(8)–S(1)–C(11) 101.7(2), C(4)–C(5)–C(6), 131.1(5). Selected torsion angle (°): C(8)–C(9)–C(11)–C(10) 81.88. Selected bonded length (Å): Zn(1)–Zn(1′) 7.589, Zn(1)–N(1) 1.972(5), Zn(1)–N(2) 1.989, S(1)–S(1′) 8.813, S(1)–C(8) 1.756, S(1)–C(11) 1.758, N(1)–N(2) 2.969, N(1)–N(4) 10.131, N(2)–N(3) 5.551.



Scheme 3. *Reagents and conditions*: (a) IIOAc/TsOH, 64%; (b) H_2/Pd–C in THF, 95%; (c) **8** dissolved in TFA, then **1b** in CH_2Cl_2–MeOH and HBr, 85%. R = 2-methoxycarbonyl-2′-cycanovinyl.

bridge in **4a**. The distance between the two metal centers along the axis of the helix is 7.59 Å.

Similarly, hexapyrrin **9**[15] was prepared in 85% yield from the condensation of bis(5-formylpyrrole-3-yl)sulfide **1b**[10] and the monoacid dipyrromethane **8**[16] in the presence of trifluoroacetic acid and hydrogen bromide. Starting material **7**[17] was synthesized by the condensation of 5-acetoxymethylpyrrole **5** and the 2-unsubstituted pyrrole **6** under acidic conditions (Scheme 3). As expected, ligand **9** reacted with Zn(II) to form the $\mathbf{9}_2Zn_2$ complex **10**[18] in 75% yield.

In summary, we have synthesized several S-linked dipyrrin ligands, and used them to generate double helical dinuclear complexes by self-assembly. One of their structures was confirmed by X-ray. Future work will focused on the synthesis and self-assembly of multidipyrrins.

Acknowledgements

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11. Bis(2,4,7,9-tetramethyl-3-ethyldipyrrin-8-yl)sulfide dihydrobromide salt (**3a**) Yield 85%. Mp 285–288°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.03 (t, $J=7.32$ Hz, 6H, $2CH_3$), 2.20–2.60 (m, 28H, $8CH_3$, $2CH_2$), 7.02 (s, 2H, 2CH), 13.00 (s, 2H, 2NH), 13.20 (s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 10.06 (**CH_3**), 11.12 (**CH_3**), 13.11 (**CH_3**), 13.24 (**CH_3**), 14.22 (**CH_3**), 17.19 (**CH_2**), 117.78, 119.31, 124.92, 127.47, 132.29, 143.51, 144.56, 153.94, 158.48 ppm. MS (FAB): $m/e=487$ (M^++1). UV–vis ($CHCl_3$), λ: (ε) 465 (63,200), 510 (122,600) nm. Anal. calcd for $C_{30}H_{40}Br_2N_4S$, C, 55.56; H, 6.22; N, 8.64. Found: C, 55.35; H, 6.40; N, 8.49%.
12. Bis(2,3,4,7,9-pentamethyldipyrrin-8-yl)sulfide dihydrobromide salt (**3b**). Mp 245–247°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ : 1.60 (s, 6H, $2CH_3$), 2.01 (s, 6H, $2CH_2$), 2.25 (s, 9H, $3CH_3$), 2.60 (s, 9H, $3CH_3$), 7.00 (s, 2H, 2CH), 13.20 (s, 2H, 2NH), 13.25 (s, 2H, 2NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ : 10.26 (CH_3), 10.72 (CH_3), 12.81 (CH_3), 13.44 (CH_3), 15.22 (CH_3), 119.78, 120.31, 123.88, 128.57, 132.56, 144.01, 145.56, 152.84, 157.67 ppm. UV–vis ($CHCl_3$), λ: (ε) 464 (64,800), 512 (128,600) nm. MS (FAB): $m/e=459$ (M^++1). Anal. calcd for $C_{28}H_{36}Br_2N_4S$, C, 54.20; H, 5.85; N, 9.03. Found: C, 54.10; H, 5.53; N, 8.79%.
13. Bis(2,4,7,9-tetramethyl-3-ethyldipyrrin-8-yl)sulfide complex with zinc(II) (**4a**). Yield 90%. Mp >250 (dec.). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.85 (t, $J=7.6$ Hz, 6H, $2CH_3$), 1.45 (s, 6H, $2CH_3$), 1.55 (s, 6H, $2CH_3$), 1.80 (s, 6H, $2CH_3$), 1.85 (q, $J=7.6$ Hz, 4H, $2CH_3$), 2.00 (s, 6H, $2CH_3$), 6.50 (s, 2H, 2 -CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ : 9.86 (**CH_3**), 10.12 (**CH_3**), 12.11 (**CH_3**), 13.54 (**CH_3**), 15.22 (**CH_3**), 17.39 (**CH_2**), 121.78, 122.31, 123.92, 127.57, 133.29, 143.51, 144.26, 152.94, 157.58 ppm. UV–vis (CH_2Cl_2), λ: (ε)=374 (20,700), 480 (129,600), 515 (216,000) nm. MS (FAB): $m/e=1100$ (M^++2). $C_{60}H_{72}N_8S_2Zn_2$, required: C, 65.50; H, 6.60; N, 10.19. Found: C, 65.24; H, 6.69; N, 9.88%. Crystal data for **4a**: $C_{60}H_{72}N_8S_2Zn_2 \cdot 2CH_2Cl_2$, $M=1270.03$, monoclinic, space group $P2_1/C$ (#14), $a=14.4307(6)$, $b=12.4665(6)$, $c=36.281(2)$Å, $\beta=101.220(2)$°, $U=6402.3(5)$ Å^3, Z=4, $D_{calcd}=1.318$ g/cm^3. Rigaku AFC7/ADSC Quantum 1 CCD diffractometer, data were collected at a temperature of −100±2°, graphite-monochromated Mo-Kα radiation, $\lambda=0.71069$ Å, $2\theta_{max}=55.7$°, 37490 reflections measured, 11428 unique ($R_{int}=0.089$). The structure was solved by direct methods and using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The material was found to crystallize with two molecules of CH_2Cl_2 in the asymmetric unit. The final cycle of full-matrix least-squares refinement was based on 10976 observed reflections ($I>0.00\sigma(I)$) and 712 variable parameters and converged with unweighted and weighted agreement factors of $R_1=0.113$, $wR_2=0.148$. Calculations were performed using the *teXscan* structure analysis package (Molecular Structure Corporation, 1985–1997). CCDC 182/1158.
14. Bis(2,3,4,7,9-pentamethyldipyrrin-8-yl)sulfide complex with zinc(II) (**4b**). Mp >260 (dec.). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.75 (s, 6H, $2CH_3$), 1.85 (s, 6H, $2CH_3$), 1.95 (s, 6H, $2CH_3$), 2.06 (s, 6H, $2CH_3$), 2.20 (s, 6H, $2CH_3$), 6.55 (s, 2H, 2-CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 9.97 (**CH_3**), 11.16 (**CH_3**), 12.01 (**CH_3**), 13.94 (**CH_3**), 16.22 (**CH_3**), 120.78, 121.81, 124.95, 128.66, 134.29, 144.52, 145.56, 155.44, 156.08 ppm. UV–vis (CH_2Cl_2), λ: (ε)= 380 (25,700), 480 (130,600), 515 (210,000) nm. MS (FAB): $m/e=1044$ (M^++2). $C_{56}H_{64}N_8S_2Zn_2$, required: C, 64.42; H, 6.18; N, 10.73. Found: C, 64.04; H, 6.39; N, 10.53%.
15. Hexapyrrole dihydrobromide salt (**9**). Mp >280°C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.95 (t, $J=7.32$ Hz, 6H, $2CH_3$), 1.05 (t, $J=7.32$ Hz, 6H, $2CH_3$), 2.20 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 2.35 (q, $J=7.32$ Hz, 4H, $2CH_2$), 2.45 (q, $J=7.32$ Hz, 4H, $2CH_2$), 2.65 (s, 6H, $2CH_3$), 3.80 (s, 6H, $2OCH_3$), 4.40 (s, 4H, $2CH_2$), 7.10 (s, 2H, 2-CH=), 7.90 (s, 2H, 2-CH=), 9.70 (s, 2H, 2NH), 13.80 (s, 2H, 2NH), 14.05 (s, 2H, 2NH) ppm. UV–vis ($CHCl_3$), λ: (ε) 390 (92,300), 530 (80,600) nm. MS (LSIMS): $m/e=919$ (M^+). Anal. calcd for $C_{54}H_{62}Br_2N_8O_4S$, C, 60.00; H, 5.97; N, 10.37. Found C, 59.85; H, 5.49; N, 10.20%.
16. 5-Carboxy-5′-(2-methoxycarbonyl-2′-cycanovinyl)-4,4′-dimethyl-3,3′-dimethyl-dipyrromethane (**8**). Mp 250°C

(dec.). ^{1}H NMR (200 MHz, DMSO-d_6) δ: 1.35 (t, J= 7.60 Hz, 3H, CH_3), 1.38 (t, J=7.60 Hz, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.35 (q, J=7.50 Hz, 2H, CH_2), 2.39 (q, J=7.50 Hz, 2H, CH_2), 3.59 (s, 3H, OCH_3), 4.10 (s, 2H, CH_2), 7.88 (s, 1H, -CH=), 10.22 (s, 1H, NH), 12.55 (s, 1H, NH), 13.00 (s, 1H, COOH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ: 8.55 (CH_3), 9.24 (CH_3), 10.55 (CH_3), 13.46 (CH_3), 15.35 (CH_2), 16.23 (CH_2), 27.88 (CH_2), 56.54 (OCH_3), 109.22, 118.93, 120.45, 123.43, 125.33, 127.44, 128.87, 129.40, 131.21, 133.56, 137.34, 161.58 (COO), 162.35 (COO) ppm. UV–vis (DMSO), λ: (ε)=416 (59,000) nm. MS (FAB): m/e=384 (M^++1). $C_{21}H_{25}N_3O_4$, required: C, 65.78; H, 6.57; N, 10.96. Found: C, 65.58; H, 6.37; N, 10.59%.

17. 5-Benzoxycarbonyl-5′-(2-methoxycarbonyl-2′-cycanovinyl)-4,4′-dimethyl-3,3′-dimethyldipyrromethane (**7**). Mp 242–244°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.25 (t, J=7.50 Hz, 3H, CH_3), 1.30 (t, J=7.50 Hz, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.30 (q, J=7.50 Hz, 2H, CH_2), 2.35 (q, J=7.50 Hz, 2H, CH_2), 3.56 (s, 3H, OCH_3), 3.95 (s, 2H, CH_2), 5.25 (s, 2H, OCH_2), 7.25 (m, 5H, 5 Phenyl-H), 7.85 (s, 1H, -CH=), 8.25 (s, 1H, NH), 9.05 (s, 1H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 8.50 (CH_3), 9.00 (CH_3), 11.50 (CH_3), 14.45 (CH_3), 15.05 (CH_2), 16.25 (CH_2), 26.88 (CH_2), 55.44 (OCH_3), 65.66 (OCH_2), 109.55, 112.33, 119.44, 120.45, 123.33, 124.32, 125.56, 125.98, 127.34, 128.03, 128.34, 129.33, 131.11, 134.22, 137.89, 162.55 (COO), 164.33 (COO) ppm. UV–vis (CH_2Cl_2), λ: (ε)=420 (66,000) nm. MS (FAB): m/e= 474 (M^++1). $C_{28}H_{31}N_3O_4$, required: C, 71.02; H, 6.60; N, 8.87. Found: C, 70.78; H, 6.39; N, 8.52%.

18. Bis(5-(5-(2-methoxycarbonyl-2′-cycanovinyl)-4-methyl-3-ethylpyrrole-2-methylene)-4-ethyl-3-methylpyrrole-2-methylene)sulfide zinc(II) complex (**10**). Mp >280 (dec.). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.85 (t, J=7.6 Hz, 6H, $2CH_3$), 0.95 (t, J=7.60 Hz, 6H, $2CH_3$), 2.10 (s, 6H, $2CH_3$), 2.15 (s, 6H, $2CH_3$), 2.25 (q, J=7.6 Hz, 4H, $2CH_2$), 2.37 (q, J=7.6 Hz, 4H, $2CH_2$), 2.46 (s, 6H, $2CH_3$), 3.85 (s, 6H, $2OCH_3$), 4.30 (s, 4H, $2CH_2$), 6.20 (s, 2H, 2-CH=), 7.40 (s, 2H, 2-CH=) ppm. UV–vis ($CHCl_3$), λ: (ε) 400 (122,300), 530 (220,500) nm. MS (FAB): m/z= 1966 (M^++1), 1965 (M^+), 1964, 1963. HRMS: Found 1965.74175, required 1965.15584 for $C_{108}H_{120}N_{16}O_8S_2Zn_2$. Anal. calcd for $C_{108}H_{120}N_{16}O_8S_2Zn_2$: C, 66.01; H, 6.15; N, 11.40. Found: C, 66.40; H, 6.05; N, 11.20%.