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Zn(II) and Co(II) mediated self-assembly of bis(dipyrrin) ligands with a methylene spacer bridged at 3,3′-positions and their optical properties

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Abstract

Self-assembly of bis(2,4-dimethyldipyrrin-3-yl)methane (**1**) with Zn(II), and bis(2,4,8,10-tetramethyl-9-methoxycarbonylethyldipyrrin-3-yl)methane (**2**) with Co(II) give dinuclear dimeric helicates **3**, **4** respectively, the structures of which were characterized by X-ray diffraction analyses. Both compounds **3** and **4** are dinuclear dimeric complexes, in which each metal ion center is wrapped by two dipyrrin units from two distinct ligands and adopts tetra-coordination with distorted tetrahedron geometry. The similar spectral properties to metalloporphyrins and metallophthalocyanines are reported.

Keywords: Self-assembly; Optical property; Dipyrrin; Zn(II) complex; Co(II) complex

1. Introduction

The use of metal ions and ligands in supramolecular self-assembly has been extensively studied. Among many ligands designed by chemists, polybipyridine ligands developed by Lehn and his colleagues are particularly interesting with respect to their ability to generate helicates [1], grids [2], cages [3], ladders [4], and rings [5]. In contrast to bipyridine, dipyrrin **I** was recently found to be an ideal building block for supramolecular self-assembly [6,7]. Dipyrrin **I**, formerly called dipyrromethene, is yellow colored, fully conjugated, flat molecule containing 10π electrons, and is the important building block for porphyrins, bile pigments, and linear polypyrroles [8,9]. In dipyrrin **I**, the hydrogen at the N–H group can be removed and the resulting mono-anionic species is a resonance stabilized ligand. The complexes generated by dipyrrin **I** and metal ions are neutral species, therefore, counterions are not needed (Scheme 1). Consequently, the complexes are particularly convenient to be purified by column chromatography since they are not charged and are generally the least polar component in the reaction mixtures [6,7].

Self-assemblies of bis(dipyrrin)s such as biladiene-ac **II** [6], 3,3′-bidipyrrins **III** [7] and

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bis(dipyrrin-3-yl)methane **IV** have been reported. Interestingly, by varying the bridge spacers between two dipyrrin units, the self-assembly of the corresponding bis(dipyrrin) ligands with metal ion such as Zn(II) give supramolecules with different geometric shapes. For example, The Zn(II) complexes of ligands **II** and **IV** are dinuclear dimeric helicates [6], while that of ligand **III** is trinuclear trimeric triangle [7]. In this paper we report the synthesis of Zn(II) and Co(II) mediated self-assembly of bis(dipyrrin-3-yl)methane ligands **1** and **2**, and their absorption and fluorescence properties (Scheme 2).

2. Experimental

2.1. Materials and general methods

All reagents for syntheses and analyses were of analytical grade and used as received. Melting points were determined on a Yanaco MP-500

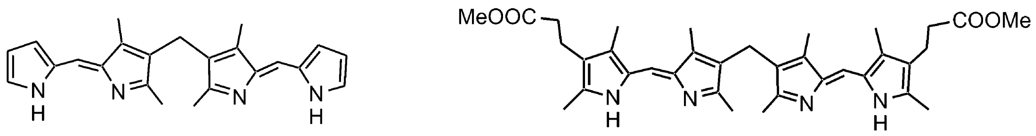
I Dipyrrin

II Biladiene-ac

III 3,3’-Bidipyrrin

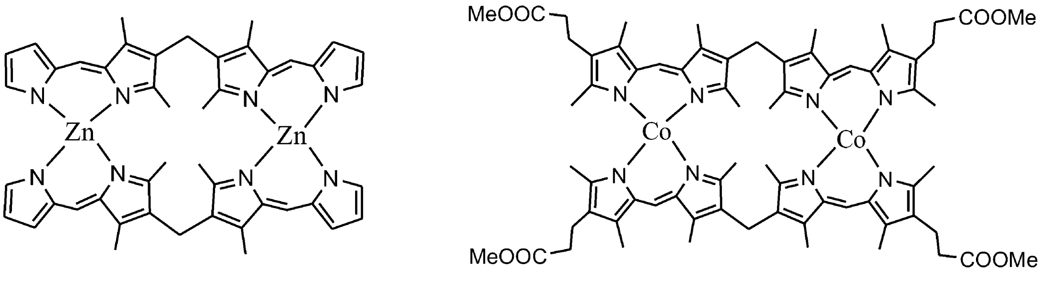
IV Bis(dipyrrin-3-yl)methane

Scheme 1.



1

2



3

4

Scheme 2.

micro-melting point apparatus. IR spectra were recorded on Bio-Rad FT-165 IR spectrometer. Elemental analyses were performed on Carlo Erba-120 elemental analyzer. Absorprion spectra were measured with a Hitachi UV-2001 ultra-vis spectrometer. Fluoresence emission spectra were obtained on a Hitachi F-4500 spectrofluorimeter.

2.2. Syntheses of the complexes

2.2.1. Zn(II) complex of bis(2,4-dimethyldipyrrin-3-yl)methane (**3**)

A solution of 2,2′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid [10] (0.25 mmol) in 2 ml 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 ml methanol was added, followed by 1 ml HBr–HOAc (45%). The mixture was stirred for 2 h, 0.1 g zinc acetate dihydrate and 1 g sodium acetate in methanol (20 ml) was added to the solution and stirred for 1 h. The reaction mixture was poured into 40 ml H_2O and extracted with $CHCl_3$ (30 ml×3). The $CHCl_3$ extract was evaporated under vacuum and the residue was purified over silica gel chromatography using CH_2Cl_2 as eluent to give complex **3**. Red crystals suitable for X-ray analysis were obtained by recrystalization in CH_2Cl_2. Yield: 65%. Anal. calcd for $C_{46}H_{44}N_8Zn_2\cdot(CH_2Cl_2)$: C, 61.06; H, 5.02; N, 12.12. Found: C, 60.85; H, 4.88; N, 11.91. IR (KBr pellet cm^{-1}): 3437, 2906, 1601, 1388, 1274, 1178, 1159, 1035, 852, 794.

2.2.2. Co(II) Complex of Bis(2,4,8,10-tetramethyl-9-methoxycarbonylethyldipyrrin-3-yl-)methane (**4**)

To a solution of 0.1mmol **2** [10] in chloroform (10 ml) was added a solution of 0.05 g cobalt(II) acetate dihydrate and 0.02 g sodium acetate in methanol (10 ml). The mixture was stirred for 1 h, then the solvent was concentrated to 10 ml. The precipitate was filtered and washed with methanol. Single crystal suitable for X-ray analysis was obtained by recrystallization from CH_2Cl_2–CH_3OH. Yield: 80%. Anal. Calcd for $C_{70}H_{84}N_8O_8\ Co_2\cdot(0.75CH_2Cl_2)$: C, 63.09; H, 6.40; N, 8.32. Found: C, 63.34; H, 6.60; N, 8.55. IR (KBr pellet cm^{-1}): 3439, 2909, 1738, 1595, 1439, 1390, 1365, 1225, 1166, 1101, 960, 851.

2.3. X-ray crystallographic studies of complexes **3** and **4**

Single crystal X-ray diffraction measurements were run on a Bruker Smart 1000CCD diffractometer. The determination of unit cell parameters and data collection were performed with *Mo Kα* radiation ($\lambda = 0.71073$ Å) and unit cell dimensions were obtained with least-squares refinements. The structure was solved by direct methods and semi-empirical absorption corrections were applied using the SADABS method. Zn(II) and Co(II) atoms in the complexes were located in successive difference Fourier syntheses. The final refinement was carried out by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen positions were calculated and refined riding on the concerned atoms with fixed thermal factors. Further details of the structure analyses of complexes **3** and **4** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Description of the crystal structures

The molecular structure of complex **3** with atomic labeling is shown in Fig. 1(a). Fig. 1(b) is the packing diagram of **3** viewed along the *b* axis. The X-ray analysis of compound **3** indicate that it possesses a double-stranded helical geometry, resulting from a twist around the $–CH_2–$ bridge. Each Zn(II) center was four-coordinated with four N-atoms from two distinct ligands to form distorted tetrahedron geometry. In compound **3**, ligand **1** perform as tetradentate ligands with two N atoms coordinated to one Zn(II) and the other two N atoms coordinated to another Zn(II). The mean bond length of Zn–N is in the range of 1.962(4)–2.005(4) Å, which is in the normal range for N–Zn bond length [11]. Both Zn(II) centers are equivalently bridged by two **1** ligands forming a 16-membered metallomacrocyle, which possesses C_2 symmetry, and is shaped as a diamond. Each edge of the diamond cavity was consisted of

Table 1
Crystallographic data and structure refinement for complexes **3** and **4**

	3	**4**
Formula	$C_{46}H_{44}N_8Zn_2\cdot(CH_2Cl_2)$	$C_{70}H_{84}N_8O_8Co_2\cdot(0.75CH_2Cl_2)$
Molecular weight	924.56	1347.00
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/c
Unit cell dimensions (Å, °)	$a = 28.278(8)$	$a = 11.812(4)$
	$b = 11.333(4)$	$b = 28.486(9)$
	$c = 17.900(5)$	$c = 21.625(7)$
	$\alpha = 90$	$\alpha = 90$
	$\beta = 122.799(4)$,	$\beta = 98.102(6)$
	$\gamma = 90$	$\gamma = 90$
Volume (Å^3)	4822(3)	7204(4)
Z	4	4
D_{calcd} (g cm^{-3})	1.274	1.242
Absorption coefficient (mm^{-1})	1.145	0.573
F(000)	1912	2838
Crystal size (mm^3)	0.35×0.30×0.20	0.32×0.24×0.20
Range of h, k, l	−35/33,−13/14,−22/15	−14/14,−33/27,−25/19
Theta range (°)	2.71/26.40	2.00/25.00
Reflections collected/unique	12,769/4827	35,861/12,327
parameters	322	903
R and R_w	0.0582 and 0.1232	0.0785 and 0.1505
Largest diff. peak and hole (e Å^{-3})	0.539 to −0.595	0.418 to −0.287
Goodness of fit	1.003	0.999

Table 2
Selected bond lengths (Å) and angles (°) for complex **3**

Zn1–N1	1.962(4)	Zn1–N2	2.005(4)
Zn1–N3	1.986(4)	Zn1–N4	1.971(5)
N1–Zn1–N3	122.55(17)	N1–Zn1–N4	119.00(18)
N4–Zn1–N3	95.89(18)	N1–Zn1–N2	95.85(16)
N3–Zn1–N2	106.25(16)	N4–Zn1–N2	118.27(17)

Table 3
Selected bond lengths (Å) and angles (°) for complex **4**

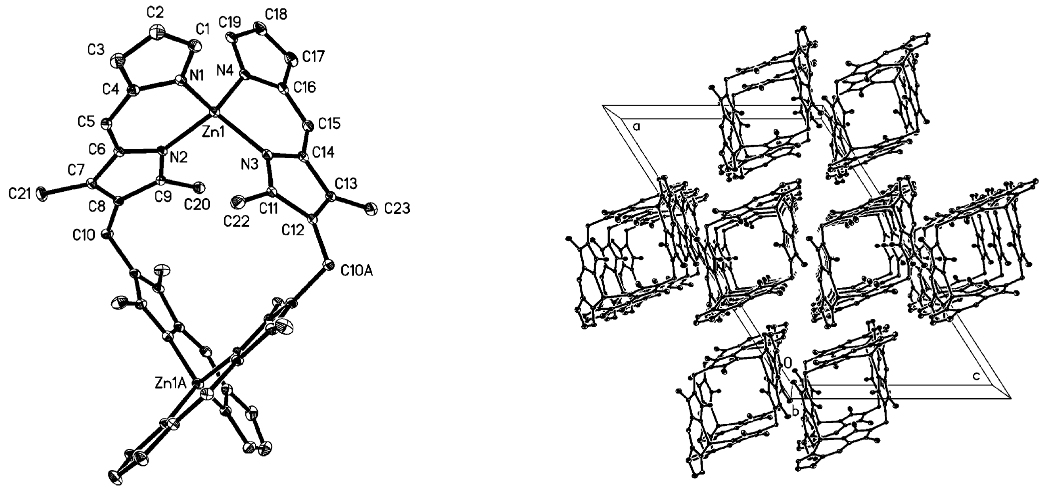
Co1–N1	1.984(4)	Co2–N3	1.964(5)
Co1–N2	1.981(4)	Co2–N4	1.967(5)
Co1–N5	1.975(5)	Co2–N7	1.985(4)
Co1–N6	1.981(4)	Co2–N8	1.968(5)
N5–Co1–N2	119.11(19)	N3–Co2–N4	96.07(19)
N5–Co1–N6	95.68(18)	N3–Co2–N8	118.15(19)
N2–Co1–N6	109.43(19)	N4–Co2–N8	117.4(2)
N5–Co1–N1	116.16(19)	N3–Co2–N7	109.67(19)
N2–Co1–N1	95.75(19)	N4–Co2–N7	121.71(19)
N6–Co1–N1	122.34(18)	N8–Co2–N7	95.34(18)

N–C–C–CH_2–C–C–N, and two Zn(II) atoms and two CH_2 groups occupy the four vertexes of the diamond. The Zn···Zn distance is 8.083 Å and that of C10···C10A is 7.744 Å. The dihedral angle defined by the intersection of two planes at the zinc center is 96.9°. CH_2Cl_2 is highly disordered in the crystal and didn't have connections with the main structure of the Zn (II) complex.

The molecular structure of complex **4** is similar to that of complex **3** and adopts double-stranded helical geometry as shown in Fig. 2. The Co(II) atom is also tetra-coordinated with four N-atoms from two distinct ligand 2 with distorted tetrahedron geometry. The distances of Co1–Co2 and C10···C45 are 7.981 Å and 7.819 Å respectively. The bond length of Co–N is found in the range of 1.964(5)–1.985(4) Å, which is close to the previous reports [6]. The dihedral angles defined by the intersection of two planes at the Co1 and Co2 centers, are 83.4° and 95.4° respectively.

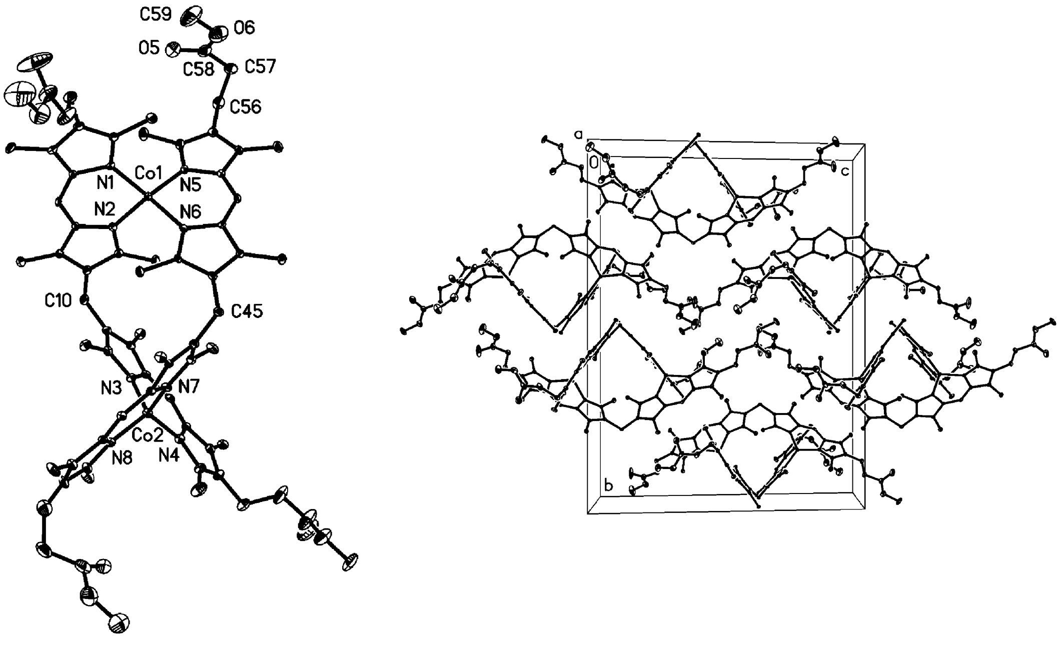
3.2. Optical properties

The UV–Vis analysis of shows that both complex **3** and **4** give strong absorption at 501.5 nn



(a) (b)

Fig. 1. (a) Structure and spatial labeling of **3**; (b) packing diagram of **3** viewed along the *b* axis. H atoms, CH_2Cl_2 molecules have been omitted for clarity.



(a) (b)

Fig. 2. (a) Structure and spatial labeling of **4**; (b) packing diagram of **4** viewed along the *a* axis.

and 525.5 nm (Fig. 3), which is similar to that of biladiene-a,c [8]. Co(II) complex **4** does not have emission in solution due to cobalt ions are electronically active in the ground and excited states of complex. In contrast to **4**, the Zn(II) complex **3** is moderately fluorescent in both solution and solid state at ambient temperature. The singlet excited-state lifetime of **3** in chloroform is found in the range of nano-second with quantum yield ϕ_{em} 0.13 (Rhodamine B in ethanol as standared [12]). Both **3** and **4** are stable in aprotic solution, and no disassociation is observed

The UV–Vis and emission data for **3** and **4** are summarized in Table 4. The structure of the metal complexes of bis(dipyrrin) ligands are partly similar to those of porphyrins and phthalocyanines. The absorption spectra of regular-type metalloporphyrins consist of several bands in visible region, the most intense band is called Soret band in the region 380–400 nm with ϵ value of 10^5 mol^{-1} dm^3 cm^{-1}. The strongest band for regular metallophthalocyanines is in the region 650–700 nm (Q band). Metal complexes of bis(dipyrrin)s have intense absorption in the region of 500–550 nm with ϵ value of 10^5 mol^{-1} dm^3 cm^{-1}. The absorption of three types of metal complexes covers the visible region from 400 to 700 nm. The moderate fluorescence and quantum yield of the Zn(II) complex of bis(dipyrrin) are comparable to those of porphyrins and phthalocynines (Table 4).

As we long known that the metalloporphyrins and metallophthalocynines have vast of application in industry and modern technology. The similarity in structures and optical properties makes a possibility of application for metallo-bis(dipyrrin) in the fields of new materials, such as electrochromic devices, molecular metal, liquid

Table 4
Absorption and fluorescence data in ethyl acetate

Compound	λ_{max} (ϵ) (nm)	$\lambda_{em\ max}$ (nm)	Φ	τ (ns)
3	454.4 (5.64×10^4)	516.2	0.13	$\tau_1=0.55$
	501.5 (1.55×10^5)			$\tau_2=2.96$
4	488.1 (5.60×10^4)	–	–	–
	525.5 (1.54×10^5)			
Zinc porphyrins[a]	380–400 (10^5)	675	0.003	60
Zinc phthalocyanines[a]	650–700 (10^5)	683	0.3	3.8

[a] The data for porphyrin and phthalocynine are from [13].

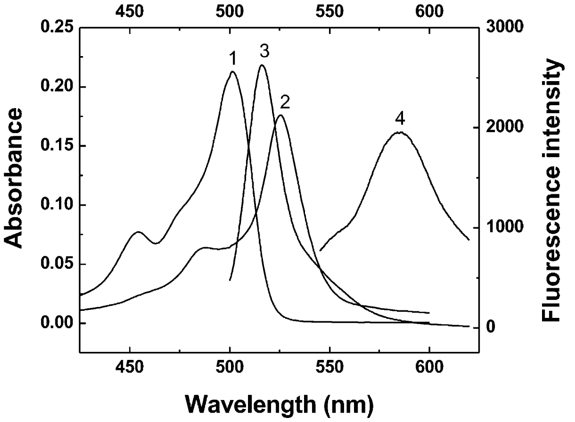


Fig. 3. Absorbance and fluorescence spectra for complex **3** and **4**: (1) UV for **3** in ethyl acetate. $c=1.37$ µM. (2) UV for **4** in ethyl acetate. $c=1.14$ µM. (3) Fluoresence for **3** in ethyl acetate. $\lambda_{em}=516.2$ nm. (4) Fluoresence for solide state Zn(II) complex **3**. $\lambda_{em}=583.8$ nm.

crystals, non-linear optic, and catalist etc, and industrial application, such as dyes and pigments.

4. Conclusion

Zn(II) or Co(II) assisted self-assembly of bis(dipyrrin-3-yl)methane ligands **1** and **2** give dimeric helicates **3** and **4** respectively, in which, the Zn(II) or Co(II) center are all four-coordinated by four N atoms of the ligands forming the distorted tetrahedron geometry. The 16-member rings in complex **3** and **4** are nearly the same size and the average N–Zn length (1.981 Å) in complex **3** is almost equal to that of Co–N (1.976 Å) in complex **4**, which can be attributed to the similarity of the **3** and **4** ligands and the similar coordination properties of Zn(II) and Co(II). The optical properties of both complexes may make possibility of application in the fields of new materials and industries.

5. Supplementary materials

Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Date Center as supplementary materials (No. CCDC-208378/208381). Copies of available material can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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