

# Self-assembly of bis(pyrrol-2-yl-methyleneamine)s bridged by flexible linear carbon chains

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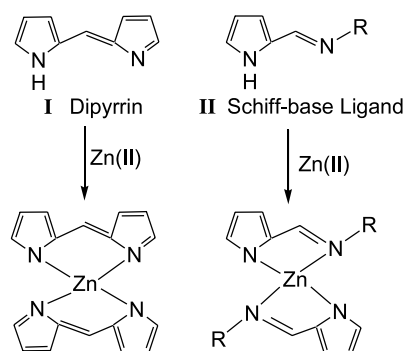
**Abstract**—Two linear bis(pyrrol-2-yl-methyleneamine)s linked by a carbon chain,  $-(CH_2)_n-$ ,  $n=2, 4$ , were synthesized in high yields by condensation of 2-formylpyrrole with the corresponding diamines. Self-assembly of the resulting bis(pyrrol-2-yl-methyleneamine) ligands with Zn(II) gave double-stranded helicates in excellent yields. Their structures were characterized by MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV–Vis spectroscopic studies, and were confirmed by an X-ray crystal analysis. In CH<sub>2</sub>Cl<sub>2</sub>, both complexes **4** and **5** displayed moderate fluorescence. © 2003 Elsevier Ltd. All rights reserved.

## 1. Introduction

Dipyrins **I**, formerly called dipyrromethylenes, are fully conjugated flat yellowish molecules containing 10π electrons. Their uses as a novel building block for supramolecular architectures were recently explored by Dolphin<sup>1</sup> and our group.<sup>2</sup> In dipyrin **I**, the hydrogen of N–H group could be removed and the resulting mono-anionic species function as resonance stabilized ligands. The complexes generated by dipyrins **I** and metal ions are neutral species, therefore, counterions are not required. Consequently, it is particularly convenient to purify the complexes by column chromatography since they are not charged, being generally the least polar component in the reaction mixtures.<sup>1,2</sup> However, the use of dipyrins for supramolecular architectures by self-assembly is still limited by their availability and solubility in organic solvents.

To take advantages of dipyrin ligands for self-assembly chemistry and to avoid the problems regarding their solubility and availability, we are interested in the pyrrole Schiff base ligand **II**, simplified analogues of **I**. Ligand **II** may possess similar coordinating properties to **I**, therefore may be an ideal building block for supramolecular architectures. Ligand **II**, a pyrrol-2-yl Schiff base or pyrrol-2-yl-methyleneamine, could be simply prepared by condensation of pyrrole-2-carbaldehyde with a primary amine. Indeed, the complexes formed between **II** and metal ions have been long known.<sup>3</sup> Linear spaced bis(pyrrol-2-yl-

methyleneamine) and their complexes with metal ions were recently reported,<sup>4</sup> which indicated that both the preparation of ligands and the complexes were highly efficient, and the metal complexes formed by pyrrol-2-yl-methyleneamines possessed good solubility in common solvents. The feasible synthesis, good solubility and excellent coordination ability with metal ions have attracted us to further explore their applications as a building block for supramolecular architectures. By changing the geometry of the space linker between two pyrrol-2-yl-methyleneamine units, we synthesized 1,2-, 1,3- and 1,4-bis(dipyrrol-2-yl-methyleneamine)benzene ligands, and have successfully used them to form supermolecules with interesting geometric shapes such as double-stranded helicates, trimeric triangles, and tetrameric squares.<sup>5</sup> In this paper we report the synthesis, characterization, optical properties and X-ray analysis of the Zn(II) complexes of bis(pyrrol-2-yl-methyleneamine) linked by linear carbon chains with different lengths (Scheme 1).



Scheme 1.

**Keywords:** crystal structure; pyrrole; self-assembly; pyrrol-2-yl-methyleneamine; Schiff base; double stranded helix; Zn(II)-complex.

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## 2. Results and discussion

### 2.1. Synthesis and characterization

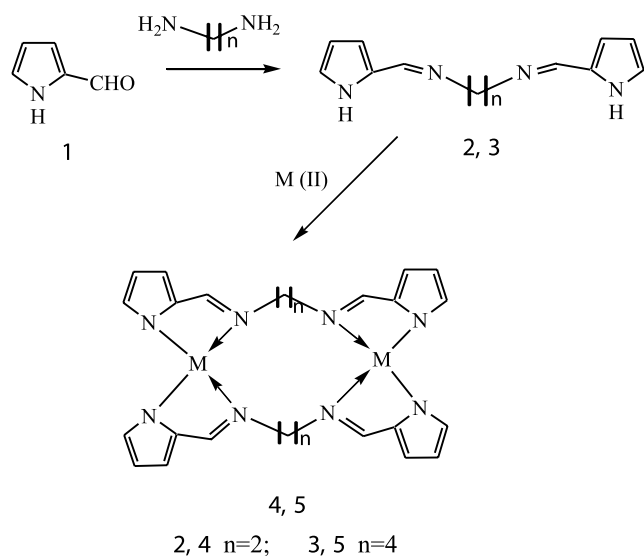
Bis(pyrrol-2-yl-methyleneamine) ligands **2** and **3** were synthesized in high yields by condensation of diamines with pyrrole-2-carbaldehyde **1** in ethanol (Scheme 2). They are symmetric and possess two Schiff-base units, and show good solubility in common solvents. Their structures were fully characterized by MS,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy.

The zinc (II) complexes **4** and **5** were prepared in yields of 60–65% by reaction of either ligands **2** or **3** with Zn(II) in methanol under basic conditions. Complexes **4** and **5** possess good solubility in common solvents such as dichloromethane, chloroform, THF, DMF, and DMSO, but they are less soluble in methanol, ethanol, hexane, benzene, toluene and water. Crystals of compounds **4** and **5** are stable at room temperature under darkness. Their solution in dichloromethane or chloroform slowly decomposed upon exposure to light and air. FAB, and MALDI-TOF mass spectroscopy were found to be especially informative in identifying the above reaction products. The peaks ( $m/z$ ) observed in the mass spectra of **4** and **5** were 553 and 609 respectively, which were assigned to the dimeric complexes with a ligand–metal ratio of 2:2.

### 2.2. NMR analysis of **4** and **5**

The  $^1\text{H}$  NMR spectra of the zinc complexes **4** and **5** in  $\text{CDCl}_3$  show a single set of proton resonances that could be fully assigned, which suggest that they exist as a single species in solution. As compared with the corresponding free ligands, complexes **4** and **5** exhibit upfield shifts for most protons except the protons at the pyrrole rings, in which they show downfield shifts of 0.15–0.32 ppm, indicating a likely deshielding on the pyrrole ring protons due to coordination of the pyrrole ring with the metal center.

$^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  revealed some chiral properties in the solution of complexes **4** and **5**. For example, the



Scheme 2.

protons of ethane-1,2-diyl spacer in free ligand **2** are equivalent and appear as a singlet at 3.78 ppm; however, in complex **4** they appear as two doublets (AA'BB' resonance pattern) at 3.40 and 3.56 ppm. The same behavior can be observed by comparing **3** and **5**. The butane-1,4-diyl chain in **3** reveals a multiplet at 1.73 ppm and a triplet at 3.55 ppm, and in **5** three multiplets at 1.35, 3.10, 3.58 ppm, respectively. All these results imply that the strong coordination of the pyrrol-2-yl-methyleneamine with zinc ion leads to the removal of the inherent enantiotropic nature of the protons, making them diastereotopic and chiral, which are very similar to the observations reported in literatures<sup>3d,4g</sup> and our recent work.<sup>5</sup> The  $^{13}\text{C}$  NMR spectra of complexes **4** and **5** in  $\text{CDCl}_3$  consisted of the anticipated peaks. Interestingly, the enantiomeric pairs of complex **4** are found in the crystal packing diagram as shown in Figure 1, which is consistent with our  $^1\text{H}$  NMR analysis. The  $^{13}\text{C}$  NMR spectra of complexes **4** and **5** in  $\text{CDCl}_3$  consisted of the expected peaks.

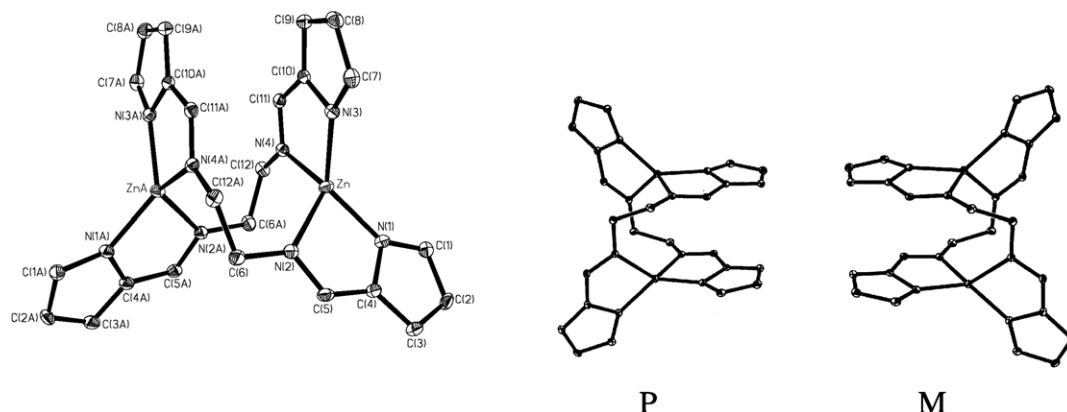
### 2.3. X-Ray analysis

Crystals suitable for an X-ray analysis were grown from  $\text{CH}_2\text{Cl}_2$ –MeOH. ORTEP views of compounds **4** and **5** are shown respectively in Figs. 1 and 2. The crystallographic data and structure analysis for complexes **4** and **5** are summarized in Table 1. Selected bond lengths and angles are shown in Table 2.

The complex structures are a double-stranded helical geometry with  $D_2$  symmetry, resulting from a major twist around the chain spacer of ethane-1,2-diyl (for **4**) or butane-1,4-diyl (for **5**). The coordination geometry around the metal center is almost tetrahedral. The two ligands wrapping around the metal–metal axis give rise to a double-stranded dinuclear helical compound. The dihedral angles between N–M–N planes around the same metal center are  $99.5^\circ$  for compound **4** and  $79.3^\circ$  for compound **5** respectively, indicating the deviation from the ideal tetrahedral geometry.

The complexes are dinuclear dimers which adopt an *anti*-opened conformation,<sup>4g</sup> with the Schiff bases acting as bis(bidentate) donors. Their structures are quite similar to other bis(pyrrol-2-yl-methyleneamine) metal complexes.<sup>4</sup> Each Schiff base, for example in complex **4**, uses the pyrrolic NH and imine nitrogen atoms corresponding to its arms [N(1), N(2), N(3), N(4)] to bind to the first zinc atom [Zn], and the nitrogen donor atoms of the remaining arm [N(1A), N(2A), N(3A), N(4A)] to bind to the second zinc atom [ZnA]. The distances between two zinc centers are 4.248 Å for **4** and 6.380 Å for **5**, which correspond to the lengths of the spacer between two Schiff base units. The Zn–N bond lengths for all complexes are in the range 1.96–2.05 Å. Analysis of the crystal structures reveals that the pyrrol-2-yl-methyleneamine units in all complexes are planar, as expected through conjugation. Both right- (*P*) and left-handed (*M*) helices<sup>6</sup> can simultaneously be observed in the crystals of **4**.

Interestingly, only a left-handed (*M*) helix is observed in the crystals of **5**, which shows the possibility of the same helical molecules packing together in a same crystal.



**Figure 1.** ORTEP view of complex **4** (hydrogen atoms and solvent molecules have been omitted for clarity), left: emphasizing the helical structure and right: the mirror image enantiomers coexist in the crystal.

**Table 1.** Crystal data and structure refinement

	4	5
Empirical formula	$C_{24}H_{24}N_8Zn_2$	$C_{28}H_{32}N_8Zn_2$
Formula mass	555.25	611.36
Temperature [K]	293 (2)	293(2)
Crystals system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)$
$a$ [Å]	13.8966 (6)	8.9733 (8)
$b$ [Å]	22.0405 (8)	16.1465 (16)
$c$ [Å]	8.0313 (7)	10.5094 (11)
$\beta$ [°]	112.671 (4)	109.958(3)
$V$ [Å <sup>3</sup> ]	2269.8(2)	1431.2 (2)
$Z$ , $\rho_{calc}$ [mg/cm <sup>3</sup> ]	4, 1.625	2, 1.419
$F(000)$	1136	632
Crystal size (mm)	0.30×0.15×0.04	0.47×0.47×0.24
Reflections collected/unique[ $R(int)$ ]	7662/2599 [0.0457]	6200/6200[0.0000]
Parameters	154	343
GOF	0.804	0.789
$R$	0.0272	0.0327
$wR$	0.0581	0.0548

## 2.4. Optical properties

Comparing the electronic absorption of free ligands **2** and **3** in  $CH_2Cl_2$  with that of Zn(II) complexes **4** and **5** in  $CH_2Cl_2$  (see Fig. 3), it is found that the absorption of the complexes have been red-shifted about 50 nm (for **4**) and 30 nm (for **5**), indicating a strong interaction between the pyrrol-2-yl-methyleneamine ligands and zinc centers. It is interesting to mention that both complexes **4** and **5** in  $CH_2Cl_2$  displayed

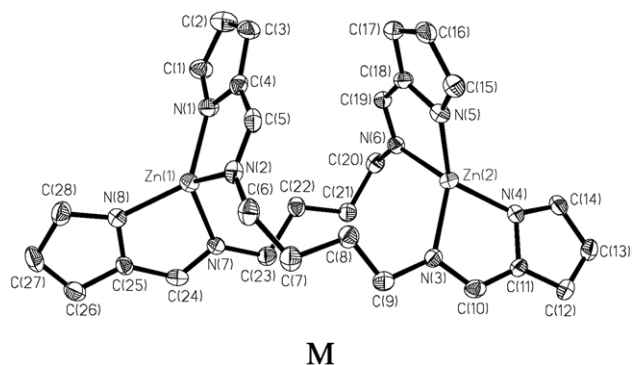
moderately fluorescence, while their corresponding free ligands **2** and **3** do not show such properties (see Table 3). The UV absorption of both **4** and **5** display a single peak, indicating that both complexes are not dissociated in the solution, and exist as single species, and is consistent with an NMR analysis.

## 3. Conclusions

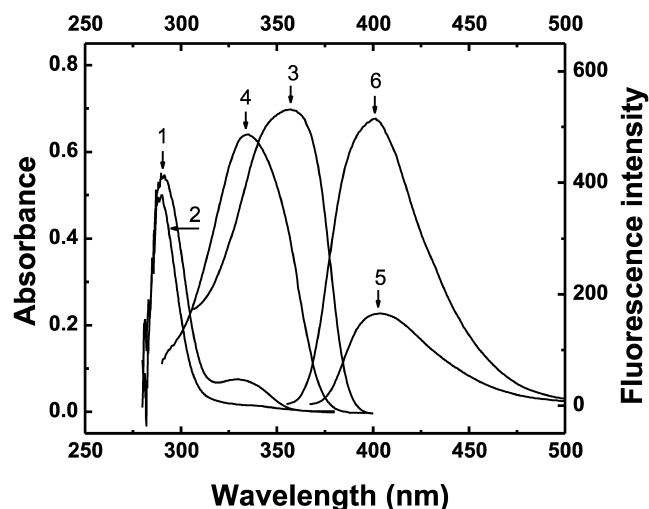
In summary, we have demonstrated that bis(pyrrol-2-yl-methyleneamine)s bridged by flexible linear carbon chains

**Table 2.** Selected bond lengths [Å] and angles [°] for compound **4** and **5**

	4	5	
Zn–N(1)	1.9836(18)	Zn(1)–N(1)	1.946(3)
Zn–N(2)	2.0626(17)	Zn(1)–N(2)	2.056(3)
Zn–N(3)	1.9795(17)	Zn(1)–N(7)	2.024(3)
Zn–N(4)	2.0450(17)	Zn(1)–N(8)	1.963(3)
N(3)–Zn–N(1)	130.95(7)	N(1)–Zn(1)–N(7)	126.07(11)
N(3)–Zn–N(4)	84.49(7)	N(1)–Zn(1)–N(2)	84.38(13)
N(1)–Zn–N(4)	123.74(7)	N(2)–Zn(1)–N(7)	112.11(11)
N(3)–Zn–N(2)	117.47(7)	N(1)–Zn(1)–N(8)	128.62(12)
N(1)–Zn–N(2)	84.70(7)	N(7)–Zn(1)–N(8)	85.22(11)
N(4)–Zn–N(2)	119.76(7)	N(2)–Zn(1)–N(8)	124.06(12)



**Figure 2.** ORTEP view of complex **5** (hydrogen atoms and solvent molecules have been omitted for clarity).



**Figure 3.** Absorption and emission spectra (in  $\text{CH}_2\text{Cl}_2$ ). Note: (1) UV for **2**,  $c=1.84\times 10^{-5}\text{ mol l}^{-1}$ ; (2) UV for **3**,  $c=1.74\times 10^{-5}\text{ mol l}^{-1}$ ; (3) UV for **4**,  $c=2.07\times 10^{-5}\text{ mol l}^{-1}$ ; (4) UV for **5**,  $c=2.98\times 10^{-5}\text{ mol l}^{-1}$ ; (5) fluorescence for **4**; (6) fluorescence for **5**.

**Table 3.** Absorption and fluorescence data

Compound	$\lambda_{\text{max}} (\epsilon)$ [nm] ( $\text{CH}_2\text{Cl}_2$ )	$\lambda_{\text{em max}}$ [nm] ( $\text{CH}_2\text{Cl}_2$ )	$\Phi^a$
<b>2</b>	289.6 ( $2.99\times 10^4$ )	397.0	/
<b>4</b>	358.4 ( $5.61\times 10^4$ )	404.0	$7\times 10^{-3}$
<b>3</b>	290.2 ( $2.88\times 10^4$ )	394.5	/
<b>5</b>	334.4 ( $5.92\times 10^4$ )	401.5	$1.1\times 10^{-2}$

<sup>a</sup> Anthracene (in ethanol) as the standard.<sup>7</sup>

can assemble to form dinuclear double-stranded helical complexes. The metal complexes possess an excellent solubility in most common solvents, which make spectroscopic characterization easy. Moreover, the supermolecules generated by pyrrol-2-yl-methyleneamines are uncharged without the need for counterions, thus making their isolation facile, via chromatography if necessary. Furthermore, as compared to dipyrin ligands, pyrrol-2-yl-methyleneamine ligands are much easier to prepare. Future work focused on synthesis and self-assembly of multiple pyrrol-2-yl-methyleneamine ligands is currently in progress.

## 4. Experimental

### 4.1. General procedure for the synthesis of **2** and **3**

Pyrrole-2-carbaldehyde<sup>8</sup> (**1**, 10 mmol) and linear diamino-alkane (5 mmol) were dissolved in ethanol (10 mL). The mixture was stirred while a few drops of glacial acetic acid were added. After a few seconds, white precipitate was observed. The suspension was allowed to stir at room temperature for 2 h. The white solid was collected by suction filtration, washed with cold ethanol and dried under vacuum to give the expected product. Analytical sample was crystallized from ethanol.

**4.1.1. 1,2-Bis(pyrrole-2-yl-methyleneamine)ethane (2).** Yield: 75%, mp 178–181°C, <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta=3.78$  (s, 4H;  $\text{CH}_2$ ), 6.23 (dd,  $J_1=3.5$  Hz,

$J_2=3.5$  Hz, 2H; pyrrole- $\text{H}_4$ ), 6.47 (dd,  $J_1=3.5$  Hz,  $J_2=1.3$  Hz, 2H; pyrrole- $\text{H}_3$ ), 6.89 (m, 2H; pyrrole- $\text{H}_5$ ), 8.04 (s, 2H; imine-H) ppm; <sup>13</sup>C NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta=61.4$ , 109.8, 114.5, 122.0, 130.1, 152.8 ppm; MS-FAB ( $m/z$ , %): 215 (M+1, 30).

**4.1.2. 1,4-Bis(pyrrol-2-yl-methyleneamine)butane (3).** Yield: 78%, mp 178–179°C, <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta=1.73$  (m, 4H;  $\text{CH}_2$ ), 3.55 (t,  $J=4$  Hz, 4H;  $\text{CH}_2$ ), 6.25 (dd,  $J_1=3.4$  Hz,  $J_2=3.4$  Hz, 2H; pyrrole- $\text{H}_4$ ), 6.52 (dd,  $J_1=3.4$  Hz,  $J_2=1.1$  Hz, 2H; pyrrole- $\text{H}_3$ ), 6.94 (m, 2H; pyrrole- $\text{H}_5$ ), 7.99 (s, 2H; imine-H) ppm; <sup>13</sup>C NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta=28.7$ , 59.8, 110.2, 115.3, 122.9, 129.7, 151.6 ppm; MS-FAB ( $m/z$ , %): 243 (M+1, 70).

### 4.2. General procedure for the synthesis of **4** and **5**

A solution of  $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$  (1 mmol) in methanol (20 mL) was added to a solution of ligand (**2** and **3**, 1 mmol) in methanol (10 mL). The colorless mixture was stirred for 10 min at room temperature. A solution of KOH (2 mmol in 30 mL methanol) was added. The mixture turned to pale-yellow in color and was stirred for a further 30 min. The solvent was removed under vacuum. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered to remove all insoluble materials. The filtrate was concentrated under vacuum to dryness, and was crystallized from  $\text{CH}_2\text{Cl}_2$ –MeOH to give the expected products as pale-yellow needles for **4** and white block crystals for **5**.

**4.2.1. 1,2-Bis(pyrrol-2-yl-methyleneamine)ethane Zn(II) complex (4).** Yield: 60%, mp >150°C (dec.), <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta=3.40$  (d,  $J=12$  Hz, 4H;  $\text{CH}_2$ ), 3.56 (d,  $J=12$  Hz, 4H;  $\text{CH}_2$ ), 6.39 (dd,  $J_1=3.4$  Hz,  $J_2=3.4$  Hz, 4H; pyrrole- $\text{H}_4$ ), 6.73 (d,  $J=3.0$  Hz, 4H; pyrrole- $\text{H}_3$ ), 7.03 (m, 4H; pyrrole- $\text{H}_5$ ), 7.44 (s, 4H; imine-H) ppm; <sup>13</sup>C NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta=53.5$ , 54.2, 113.2, 118.4, 135.3, 137.1, 161.0 ppm; FAB-MS ( $m/z$ ): 554 (M+2), HR-LSIMS calcd for  $\text{C}_{24}\text{H}_{25}\text{N}_8\text{Zn}_2$  (M+1)<sup>+</sup>: 553.0780, found: 553.0786.

**4.2.2. 1,4-Bis(pyrrol-2-yl-methyleneamine)butane Zn(II) complex (5).** Yield: 65%, mp >150°C (dec.), <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , 25°C TMS):  $\delta=1.35$  (m, 8H;  $\text{CH}_2$ ), 3.10 (m, 4H;  $\text{CH}_2$ ), 3.58 (m, 4H;  $\text{CH}_2$ ), 6.40 (dd,  $J_1=3.2$  Hz,  $J_2=3.2$  Hz, 4H; pyrrole- $\text{H}_4$ ), 6.84 (d,  $J=3.2$  Hz, 4H; pyrrole- $\text{H}_3$ ), 7.03 (m, 4H; pyrrole- $\text{H}_5$ ), 7.80 (s, 4H; imine-H) ppm; <sup>13</sup>C NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta=28.2$ , 56.0, 112.8, 117.5, 135.4, 136.2, 160.2 ppm. MALDI-TOF-MS ( $m/z$ ): 609 (M+1).

### 4.3. X-Ray crystallographic studies of complexes **4**–**5**

Crystals suitable for an X-ray analysis were grown by slow evaporation of a solution of the complex in MeOH or  $\text{CH}_2\text{Cl}_2$ –MeOH. Single crystal X-ray diffraction measurements were carried out on a Rigaku RAXIS RAPID IP diffractometer. The determination of unit cell parameters and data collection was performed with Mo  $\text{K}\alpha$  radiation 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 PSI scan method. Zn(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.

## 5. Supplementary materials

Crystal structure analyses were measured on a Rigaku RAXIS RAPID IP using graphic-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.71073$  Å) at 293(2) K. Experimental details are shown in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-208243/208244. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.): +1-44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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