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# Zinc halide template effects on the construction of [1 + 1] flexible Schiff-base macrocyclic complexes having pendant-armed dialdehyde components†

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Two novel pendant-armed dialdehydes (**1a** and **1b**) were prepared by a one-step reaction between 5-chloro-3-(chloromethyl)-2-hydroxybenzaldehyde/5-methyl-3-(chloromethyl)-2-hydroxybenzaldehyde and cyclohexylamine involving two nucleophilic substitutions, and they were used to react with 1,3-propanediamine to prepare Schiff-base macrocyclic complexes in the presence of $ZnX_2$ salts (X = Cl, Br, and I). As a result, five dinuclear (**2a**, **2b**, **3b**, **4a**, and **4b**) and one mononuclear (**3a**) [1 + 1] flexible macrocyclic Zn(II) complexes have been structurally and spectrally characterized. The zinc centers in three pairs of macrocyclic complexes have the common four-coordinate tetrahedral geometry with one or two coordinated halide ions, where the template Zn(II) cations and the auxiliary halide anions with different sizes and coordination abilities are believed to play important roles in forming the resulting macrocyclic complexes. In addition, subtle alterations of electron-withdrawing and electron-donating substituted groups (Cl *versus* $CH_3$) in the macrocyclic backbone result in different $^1H$ NMR and UV-vis spectra.

## Introduction

There has been growing interest in Robson-type Schiff bases since they were first developed in the 1970s.[1] Studies on the approaches for forming this type of Schiff-base macrocyclic complexes have been performed by many groups and large numbers of such complexes have been synthesized and characterized during the last four decades and they were found to exhibit particular magnetic,[2] catalytic,[3] biological,[4] and nonlinear optical properties,[5] and so on. Commonly, there are two approaches to form this type of macrocyclic Schiff-base metal complexes, namely, metal-free and metal-ion templated methods of which the latter one has been proved to be more effective.[6] In our previous work, quite a number of Robson-type macrocyclic ligands and their metal complexes have been prepared through template synthetic approaches.[7]

The introduction of functional pendant arms into the macrocyclic ligands is a useful method to extend the applications of macrocyclic complexes.[8] Pendant arms are often introduced into the amine components to construct corresponding macrocyclic ligands.[9] In contrast, the expansion of dialdehyde components with functional pendant arms is much more challenging and has been less studied up to now.[10] Our motivation is to design and prepare novel flexible Schiff-base macrocyclic ligands bearing extended pendant-armed dialdehyde components, and to use them to build up macrocyclic complexes in the presence of certain templates. We report herein the syntheses and structural characterization of a series of flexible [1 + 1] Schiff-base macrocyclic Zn(II) complexes bearing two extended dialdehyde components derived from 5-chloro-3-(chloromethyl)-2-hydroxybenzaldehyde and 5-methyl-3-(chloromethyl)-2-hydroxybenzaldehyde, where $ZnX_2$ salts (X = Cl, Br, and I) were used to produce five dinuclear (**2a**, **2b**, **3b**, **4a**, and **4b**) and one mononuclear (**3a**) four-coordinate Zn(II) complexes countered by $Cl^-$, $Br^-$, and $I^-$ anions (Scheme 1). Both the template Zn(II) cation and the auxiliary halide anion with different sizes and coordination abilities are believed to play important roles in forming the resulting macrocyclic complexes.

## Experimental

### Materials and measurements

The reagents of analytical grade were purchased from commercial sources and used without any further purifi-

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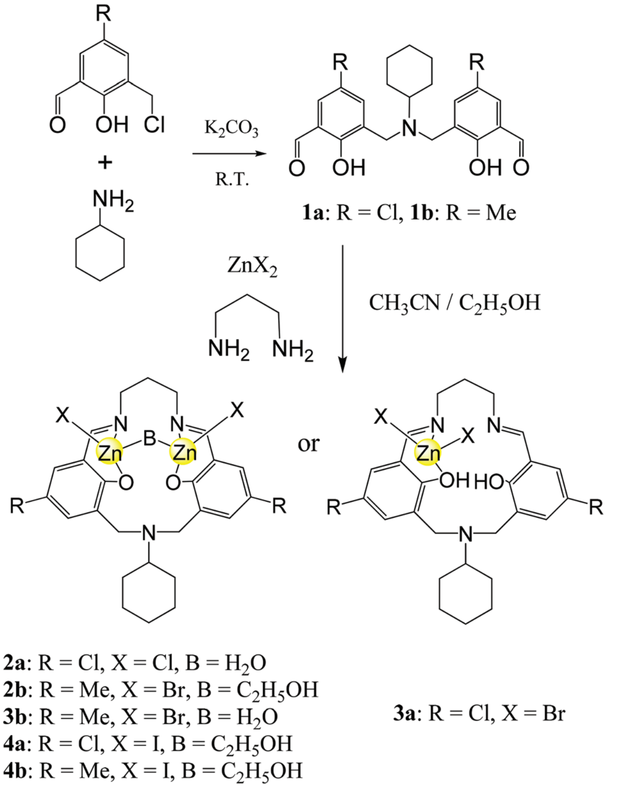
† Electronic supplementary information (ESI) available: FT-IR spectra of all eight compounds and powder X-ray diffraction patterns of six macrocyclic Zn(II) complexes. CCDC 988803–988809 for seven compounds. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00605d



**Scheme 1** Synthetic route for a pair of extended dialdehydes and six [1 + 1] flexible macrocyclic Zn(II) complexes.

cation. 5-Chloro-3-(chloromethyl)-2-hydroxybenzaldehyde and 5-methyl-3-(chloromethyl)-2-hydroxybenzaldehyde were prepared *via* our previously reported method.[11] Elemental analyses (EA) for carbon, hydrogen and nitrogen were performed using a Perkin-Elmer 1400C analyzer. Infrared (IR) spectra (4000–400 cm$^{-1}$) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks. UV-vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. Powder X-ray diffraction (PXRD) measurements were performed on a Philips X'pert MPD Pro X-ray diffractometer using Cu Kα radiation ($\lambda$ = 0.15418 nm), in which the X-ray tube was operated at 40 kV and 40 mA at room temperature. $^1$H NMR spectra were obtained using a Bruker 500 MHz NMR spectrometer.

### Synthesis of pendant-armed dialdehydes 1a and 1b

**Dialdehyde 1a.** An acetone solution (20 cm$^3$) of 5-chloro-3-(chloromethyl)-2-hydroxybenzaldehyde (1.154 g, 5.62 mmol) was added dropwise to a mixture of $K_2CO_3$ (7.067 g, 51.13 mmol) and 1-cyclohexanamine (0.248 g, 2.50 mmol) dissolved in acetone (40 cm$^3$), and the mixture was stirred for 1 h at room temperature. The solid was filtered off, washed with acetone, and the solvent of the filtrate was removed using a rotatory evaporator under reduced pressure. The yellow-green solid **1a** was purified by silica gel column chromatography using ethylacetate–petroleum ether (v/v = 1 : 8) as the eluent, and the final product **1a** was obtained in a yield of 0.553 g (51%). Mp: 149–150 °C. Main FT-IR absorptions (KBr pellets): 2968 (m), 2937 (w), 1674 (w), 1471 (m), 1386 (w), 837 (s), 557 (m). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 10.01 (s, 2H), 7.45(d, 2H), 7.30 (d, 2H), 3.82 (s, 4H), 2.67 (t, 1H), 2.01–1.84 (d, 4H), 1.69–1.65 (d, 1H), 1.46–1.42 (d, 2H), 1.27–1.22 (m, 3H). Anal. calc. for $C_{22}H_{23}Cl_2NO_4$: C, 60.56; H, 5.31; N, 3.21%. Found: C, 60.60; H, 5.59; N, 3.09%. UV-vis in methanol: $\lambda_{max}$ = 220, 256, and 343 nm.

**Dialdehyde 1b.** Dialdehyde **1b** was synthesized by using the same method as that of **1a** except that 5-methyl-3-(chloromethyl)-2-hydroxybenzaldehyde (1.030 g, 5.60 mmol) was used. Compound **1b** was obtained in a yield of 0.521 g (53%). Mp: 118–120 °C. Main FT-IR absorptions (KBr pellets): 2931 (m), 2875 (w), 1645 (w), 1470 (m), 1384 (w), 838 (s), 559 (m). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 10.06 (s, 2H), 7.28 (d, 2H), 7.16 (d, 2H), 3.81 (s, 4H), 2.69 (t, 1H), 2.26 (s, 6H), 2.02–1.87 (d, 4H), 1.68–1.66 (d, 1H), 1.48–1.46 (d, 2H), 1.27–1.22 (m, 3H). Anal. calc. for $C_{24}H_{29}NO_4$: C, 72.89; H, 7.39; N, 3.54%. Found: C, 72.66; H, 7.54; N, 3.62%. UV-vis in methanol: $\lambda_{max}$ = 218, 261, and 343 nm.

### Syntheses of [1 + 1] macrocyclic Zn(II) complexes 2–4

**Complex 2a.** $ZnCl_2$ (0.028 g, 0.20 mmol) dissolved in acetonitrile (10 cm$^3$) and 1,3-propanediamine (0.008 g, 0.11 mmol) dissolved in ethanol (10 cm$^3$) were added to a solution of **1a** (0.046 g, 0.10 mmol) in ethanol (20 cm$^3$) at reflux. After 2 h, the solution was cooled and filtered and the solvent evaporated gradually under room temperature to give product **2a** as yellow crystals in a yield of 0.024 g (70%). Main FT-IR absorptions (KBr pellets): 3442 (m), 2937 (w), 2857 (w), 1637 (s), 1433 (m), 1031 (w), 776 (w). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.05 (s, 2H), 7.02 (d, 4H), 4.54 (t, 2H), 4.10 (t, 2H), 3.95 (d, 2H), 3.61 (d, 2H), 2.74 (m, 1H), 2.23 (m, 2H), 2.07 (m, 2H), 1.88 (m, 2H), 1.77–1.64 (m, 2H), 1.39–1.24 (m, 6H). Anal. calc. for $C_{25}H_{29}Cl_4N_3O_3Zn_2$: C, 43.38; H, 4.22; N, 6.07%; found: C, 43.12; H, 4.45; N, 5.99%. UV-vis in methanol: $\lambda_{max}$ = 225 and 358 nm.

Complexes **3a** and **4a** were prepared by a similar method to that of **2a** by using $ZnBr_2$ (0.046 g, 0.21 mmol) and $ZnI_2$ (0.066 g, 0.21 mmol), respectively. **3a:** Yield, 0.025 g (68%). Main FT-IR absorptions (KBr pellets): 3526 (m), 2939 (w), 2859 (w), 1634 (s), 1551 (s), 1460 (s), 1220 (w), 1128 (w), 784 (w). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.37 (s, 1H), 8.07 (s, 1H), 7.07 (s, 2H), 7.02 (s, 2H), 4.62 (t, 2H), 4.16 (t, 2H), 3.97 (d, 2H), 3.65 (d, 2H), 2.74 (m, 1H), 2.24 (m, 2H), 1.88–1.24 (m, 10H). Anal. calc. for $C_{25}H_{35}Br_2Cl_2N_3O_4Zn$: C, 40.70; H, 4.78; N, 5.70%. Found: C, 40.55; H, 4.80; N, 5.68%. UV-vis in methanol: $\lambda_{max}$ = 224 and 360 nm. **4a:** Yield, 0.032 g, 72%. Main FT-IR absorptions (KBr pellets): 3452 (m), 2935 (w), 2370 (w), 1633 (m), 1548 (w), 1452 (w), 1083 (s), 789 (w), 466(m). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.38 (s, 1H), 8.17 (s, 1H), 7.11 (s, 2H), 7.07 (s, 2H), 4.65 (t, 2H), 4.28 (t, 2H), 3.94 (d, 2H), 3.66 (m, 2H), 2.74 (m, 1H), 2.25 (m, 2H), 1.91–1.07 (m, 16H). Anal.

calc. for $C_{27}H_{33}Cl_2I_2N_3O_3Zn_2$: C, 35.91; H, 3.68; N, 4.65%. Found: C, 35.62; H, 3.39; N, 4.56%. UV-vis in methanol: $\lambda_{max}$ = 221 and 357 nm.

**Complex 2b.** $ZnCl_2$ (0.028 g, 0.21 mmol) dissolved in ethanol (10 $cm^3$) was added to a solution of **1b** (0.039g, 0.10 mmol) in ethanol (20 $cm^3$). The mixture was refluxed for 10 min, and then 1,3-propanediamine (0.008 g, 0.11 mmol) dissolved in ethanol (10 $cm^3$) was added. After an additional 2 h of refluxing, the solution was cooled to room temperature and filtered. The solvent was removed to give the product **2b** as light orange crystals in a yield of 0.024 g (69%). Main FT-IR absorptions (KBr pellets): 3452 (m), 2936 (w), 2861 (w), 1631 (s), 1557 (m), 1467 (m), 1127 (w), 789 (w). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.00 (s, 2H), 6.80 (s, 2H), 6.77 (s, 2H) , 4.40 (t, 2H), 4.12 (t, 2H), 3.78 (d, 2H), 3.61 (d, 2H), 2.71 (m, 1H), 2.52 (s, 4H), 2.24 (m, 5H), 2.04 (s, 6H), 1.87–1.07 (m, 16H). Anal. calc. for $C_{30}H_{46}Cl_2N_3O_3Zn_2$: C, 51.59; H, 6.64; N, 6.02%. Found: C, 51.30; H, 6.91; N, 6.41%. UV-vis in methanol: $\lambda_{max}$ = 221, 239, 266, and 363 nm.

Complexes **3b** and **4b** were prepared in a way similar to that of **2a** by using $ZnBr_2$ (0.046 g, 0.21 mmol) and $ZnI_2$ (0.065 g, 0.21 mmol), respectively. **3b**: Yield, 0.028 g (71%). Main FT-IR absorptions (KBr pellets): 3501 (m), 2933 (w), 2858 (w), 1631 (s), 1556 (s), 1467 (s), 1220 (w), 1128 (w), 813 (w). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.04 (s, 1H), 8.02 (s, 1H), 6.84 (s, 1H), 6.80 (s, 1H), 6.71 (s, 1H), 6.61 (s, 1H), 4.52 (t, 2H), 4.12 (t, 2H), 3.76 (d, 2H), 3.61 (d, 2H), 2.75 (m, 1H), 2.25 (m, 4H), 2.07 (s, 6H), 1.88–1.24 (m, 10H). Anal. calc. for $C_{27}H_{35}Br_2N_3O_3Zn_2$: C, 43.81; H, 4.77; N, 5.68%; Found: C, 43.65; H, 4.98; N, 5.49%. UV-vis in methanol: $\lambda_{max}$ = 220, 241, 268, and 365 nm. **4b**: Yield, 0.034 g (78%). Main FT-IR absorptions (KBr pellets): 2968 (w), 2858 (w), 1631 (w), 1556 (w), 1471 (w), 1035 (w), 838 (s), 557 (m). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.12 (s, 1H), 8.08 (s, 1H), 6.91 (s, 1H), 6.86 (s, 1H), 6.74 (s, 1H), 6.63 (s, 1H), 4.57 (t, 2H), 4.16 (t, 2H), 3.77 (d, 2H), 3.61 (s, 2H), 2.76 (m, 1H), 2.25 (m, 2H), 2.07 (s, 6H), 1.88–1.07 (m, 16H). Anal. calc. for $C_{29}H_{39}I_2N_3O_3Zn_2$: C, 40.40; H, 4.56; N, 4.87%. Found: C, 40.25; H, 4.78; N, 4.62%. UV-vis in methanol: $\lambda_{max}$ = 219, 267, and 365 nm.

### X-ray crystallographic analysis

Single-crystal X-ray diffraction data were measured on a Bruker SMART CCD diffractometer using graphite monochromatic Mo Kα radiation ($\lambda$ = 0.71073). Data collection was performed by using the SMART program, and cell refinement and data reduction were made using the SAINT program.[12] The structures were solved by direct methods and refined on $F^2$ by using full-matrix least-squares methods with SHELXTL version 6.10.[13] All non-hydrogen atoms were refined on $F^2$ by the full-matrix least-squares procedure using anisotropic displacement parameters. Hydrogen atoms were inserted into the calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups and oxygen atoms) and allowed to ride on their respective parent atoms. All calculations were carried out using the SHELXTL PC program package. Details of the data collection and refinement for **1a** and complexes **2–4** are given in Table 1, and the selective bond lengths and angles of seven compounds are listed in Table 2.

## Results and discussion

### Syntheses and spectral characterizations

The two N-modified dialdehydes (**1a** and **1b**) can be prepared by a one-step reaction in medium yields between cyclohexylamine and 5-chloro-3-(chloromethyl)-2-hydroxybenzaldehyde and 5-methyl-3-(chloromethyl)-2-hydroxybenzaldehyde involving two nucleophilic substitutions (Scheme 1). The [1 + 1] Zn(II) Schiff-base complexes **2–4** have been produced by metal-ion templated condensation. In the synthesis of metal macrocyclic Schiff bases, the Zn(II) ion is found to show good template effects in comparison with other metal ions and the macrocyclic products can be isolated successfully. A pre-organized synthetic strategy is used in our reactions, where dialdehydes and metal ions are mixed together at first for 10 min, and then 1,3-propanediamine is added for another 2 h of refluxing.

Because of the strong coordination capability of the halide anion with the metal center, one or more coordination sites of the Zn(II) ion can be occupied by the halide anions, which will more or less influence the cationic template effects in the process of constructing macrocyclic complexes. Furthermore, large steric hindrance effects of coordinated halide anions favor to form lower coordination numbers for the metal coordination centers. As a result, six dinuclear or mononuclear four-coordinate macrocyclic Zn(II) complexes have been obtained in this work. Moreover, [1 + 1] Schiff-base macrocyclic Zn(II) complexes are found to be the main products, which may be attributed to the size-matching effect of the Zn(II) ion as well as the use of flexible dialdehyde and diamine compounds. Actually, the discrepancy of halide anions for forming different macrocyclic Zn(II) complexes is not obvious in this case, owing to the fact that similar [1 + 1] Schiff-base macrocyclic complexes are obtained. However, in the case of **3a**, only a mononuclear macrocyclic complex was obtained as the main product, which is different from all the other five dinuclear macrocyclic complexes. We have tried to do exact control experiments including the alterations of the molar ratios of the Zn(II) ion and the ligands and the reaction solvents, in order to produce corresponding [1 + 1] dinuclear Zn(II) complexes as the other five ones, but we were unsuccessful.

FT-IR spectra are very useful to monitor this type of macrocyclic Schiff-base condensation reactions. In our experiments, a medium FT-IR absorption peak at 1676 and 1681 $cm^{-1}$ in **1a** and **1b** (Fig. SI1 and SI2†) can be assigned to the existence of aldehyde groups. However, it disappears and a new absorption peak is observed for six macrocyclic Zn(II) complexes **2–4** in the range of 1632–1637 $cm^{-1}$ (Fig. SI3–SI8†), indicating the transformation from the aldehyde groups to the Schiff-base C═N

**Table 1** Crystal data and structural refinements for compounds **1a** and **2–4**

| Compound | **1a** | **2a** | **3a** | **4a** | **2b** | **3b**·CH$_3$CN | **4b** |
|---|---|---|---|---|---|---|---|
| Empirical formula | $C_{22}H_{23}Cl_2NO_4$ | $C_{25}H_{29}Cl_4N_3O_3Zn_2$ | $C_{25}H_{31}Br_2Cl_2N_3O_2Zn$ | $C_{27}H_{33}Cl_2I_2N_3O_3Zn_2$ | $C_{30}H_{46}Cl_2N_3O_3Zn_2$ | $C_{27}H_{35}Br_2N_3O_3Zn_2$ | $C_{29}H_{39}I_2N_3O_3Zn_2$ |
| Formula weight | 436.31 | 692.09 | 701.62 | 903.00 | 698.38 | 781.21 | 862.17 |
| Temperature/K | 291(2) | 291(2) | 291(2) | 291(2) | 291(2) | 291(2) | 291(2) |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Monoclinic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_12_12_1$ | $Cc$ | $Pnma$ | $P2_12_12_1$ | $Pnma$ |
| $a$/Å | 12.153(2) | 11.981(5) | 12.269(3) | 15.413(2) | 21.705(7) | 11.757(6) | 19.260(3) |
| $b$/Å | 8.604(1) | 13.858(6) | 13.851(3) | 13.516(2) | 12.007(4) | 13.684(7) | 12.236(2) |
| $c$/Å | 20.383(3) | 19.572(8) | 19.379(5) | 15.824(2) | 12.259(4) | 19.582(10) | 14.146(2) |
| $\alpha$/° | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| $\beta$/° | 105.492(2) | 100.091(7) | 90.00 | 93.866(3) | 90.00 | 90.00 | 90.00 |
| $\gamma$/° | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| $V$/Å$^3$ | 2053.9(5) | 3199(2) | 3293.5(14) | 3288.8(6) | 3194.8(18) | 3150(3) | 3333.5(9) |
| $Z/D_{\text{calcd}}$ (g cm$^{-3}$) | 4/1.411 | 4/1.437 | 4/1.415 | 4/2.824 | 4/1.452 | 4/1.647 | 4/1.718 |
| $F$(000) | 912 | 1408 | 1408 | 1760 | 1460 | 1576 | 1696 |
| $\mu$/mm$^{-1}$ | 0.345 | 1.862 | 3.358 | 3.530 | 1.703 | 4.095 | 3.323 |
| $h_{\min}/h_{\max}$ | −14/14 | −14/13 | −13/14 | −16/18 | −25/25 | −13/13 | −16/22 |
| $k_{\min}/k_{\max}$ | −10/8 | −16/16 | −15/16 | −16/14 | −11/14 | −12/16 | −14/14 |
| $l_{\min}/l_{\max}$ | −24/24 | −16/23 | −23/20 | −18/18 | −14/14 | −23/23 | −16/16 |
| Data/parameters | 3809/263 | 5586/334 | 6129/316 | 4929/353 | 2961/194 | 5547/335 | 3090/200 |
| Final $R$ indices | $R_1$ = 0.0705 | $R_1$ = 0.1036 | $R_1$ = 0.0389 | $R_1$ = 0.0585 | $R_1$ = 0.0999 | $R_1$ = 0.0924 | $R_1$ = 0.0483 |
| | w$R_2$ = 0.2104 | w$R_2$ = 0.2956 | w$R_2$ = 0.0879 | w$R_2$ = 0.1526 | w$R_2$ = 0.2735 | w$R_2$ = 0.2247 | w$R_2$ = 0.1449 |
| $S$ | 0.980 | 0.985 | 0.920 | 1.003 | 0.890 | 1.040 | 1.067 |
| Max./min. $\Delta\rho$/e Å$^{-3}$ | 0.388/−0.431 | 1.657/−1.104 | 0. 593/−0.268 | 2.253/−1.034 | 0.626/−1.032 | 4.279/−1.471 | 1.098/−1.066 |

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

**Table 2** Selected bond distances and bond angles of **1a** and **2–4**

| Bond distances | | Bond angles | |
|---|---|---|---|
| **1a** | | | |
| Cl1–C4 | 1.741(4) | C8–N1–C17 | 111.8(3) |
| Cl2–C12 | 1.746(4) | C8–N1–C9 | 111.4(3) |
| O1–C1 | 1.347(4) | C9–N1–C17 | 113.5(3) |
| O2–C7 | 1.205(5) | O1–C1–C6 | 119.4(3) |
| O3–C15 | 1.350(4) | O1–C1–C2 | 119.9(3) |
| O4–C16 | 1.195(5) | O2–C7–C6 | 124.8(4) |
| N1–C17 | 1.483(4) | N1–C8–C2 | 111.7(3) |
| N1–C8 | 1.483(4) | N1–C9–C10 | 112.1(3) |
| N1–C9 | 1.481(4) | N1–C17–C18 | 114.7(3) |
| | | N1–C17–C22 | 110.8(3) |
| **2a** | | | |
| Zn1–Cl3 | 2.217(5) | Cl3–Zn1–O1 | 112.2(2) |
| Zn1–O1 | 1.953(6) | Cl3–Zn1–O3 | 114.7(3) |
| Zn1–O3 | 2.037(10) | Cl3–Zn1–N3 | 110.6(3) |
| Zn1–N3 | 2.007(9) | O1–Zn1–O3 | 109.5(3) |
| Zn2–Cl4 | 2.202(5) | O1–Zn1–N3 | 95.3(3) |
| Zn2–O2 | 1.922(9) | O3–Zn1–N3 | 112.9(4) |
| Zn2–O3 | 2.241(10) | Cl4–Zn2–O2 | 115.6(3) |
| Zn2–N2 | 2.099(14) | Cl4–Zn2–O3 | 110.9(3) |
| | | Cl4–Zn2–N2 | 116.1(4) |
| | | O2–Zn2–O3 | 108.7(4) |
| | | O2–Zn2–N2 | 89.9(5) |
| | | O3–Zn2–N2 | 114.0(4) |
| **3a** | | | |
| Zn1–Br1 | 2.358(1) | Br1–Zn1–Br2 | 110.7(0) |
| Zn1–Br2 | 2.401(1) | Br1–Zn1–O2 | 111.5(1) |
| Zn1–O2 | 1.936(3) | Br1–Zn1–N2 | 119.1(1) |
| Zn1–N2 | 2.022(4) | Br2–Zn1–O2 | 113.1(1) |
| | | Br2–Zn1–N2 | 107.4(1) |
| | | O2–Zn1–N2 | 94.1(1) |
| **4a** | | | |
| Zn1–I1 | 2.549(2) | I1–Zn1–O1 | 117.5(2) |
| I2–Zn2 | 2.533(2) | I1–Zn1–O3 | 116.7(3) |
| Zn1–O1 | 1.951(7) | I1–Zn1–N1 | 109.3(2) |
| Zn1–O3 | 1.928(10) | O1–Zn1–O3 | 102.8(4) |
| Zn1–N1 | 2.024(8) | O1–Zn1–N1 | 93.6(3) |
| Zn2–O2 | 1.919(8) | O3–Zn1–N1 | 114.8(4) |
| Zn2–O3 | 1.897(12) | I2–Zn2–N2 | 112.1(3) |
| Zn2–N2 | 2.037(9) | O2–Zn2–O3 | 105.8(4) |
| | | O2–Zn2–N2 | 94.2(3) |
| | | O3–Zn2–N2 | 105.9(4) |
| **2b** | | | |
| Zn1–Cl1 | 2.214(4) | Cl1–Zn1–O1 | 117.8(2) |
| Zn1–O1 | 1.955(7) | Cl1–Zn1–O2 | 113.4(3) |
| Zn1–O2 | 1.963(7) | Cl1–Zn1–N1 | 112.3(3) |
| Zn1–N1 | 2.033(10) | O1–Zn1–O2 | 108.0(4) |
| | | O1–Zn1–N1 | 94.1(3) |
| | | O2–Zn1–N1 | 109.6(4) |
| **3b·CH$_3$CN** | | | |
| Zn1–Br1 | 2.374(3) | Br1–Zn1–O1 | 114.1(3) |
| Zn2–Br2 | 2.365(3) | Br1–Zn1–O3 | 114.9(3) |
| Zn1–O1 | 1.944(8) | Br1–Zn1–N1 | 109.7(3) |
| Zn1–O3 | 2.030(9) | O1–Zn1–O3 | 108.0(3) |
| Zn1–N1 | 2.028(12) | O1–Zn1–N1 | 95.9(4) |
| Zn2–O2 | 1.938(8) | O3–Zn1–N1 | 112.7(4) |
| Zn2–O3 | 2.106(9) | Br2–Zn2–O2 | 114.1(3) |
| Zn2–N2 | 2.047(11) | Br2–Zn2–O3 | 111.9(2) |
| | | Br2–Zn2–N2 | 114.1(3) |
| | | O2–Zn2–O3 | 110.6(4) |
| | | O2–Zn2–N2 | 93.7(4) |
| | | O3–Zn2–N2 | 111.2(4) |
| **4b** | | | |
| Zn1–I1 | 2.551(1) | I1–Zn1–O1 | 120.4(1) |
| Zn1–O1 | 1.928(4) | I1–Zn1–O2 | 113.0(2) |
| Zn1–O2 | 1.937(3) | I1–Zn1–N1 | 110.9(2) |
| Zn1–N1 | 2.016(6) | O1–Zn1–O2 | 106.3(2) |
| | | O1–Zn1–N1 | 94.6(2) |
| | | O2–Zn1–N1 | 109.9(2) |

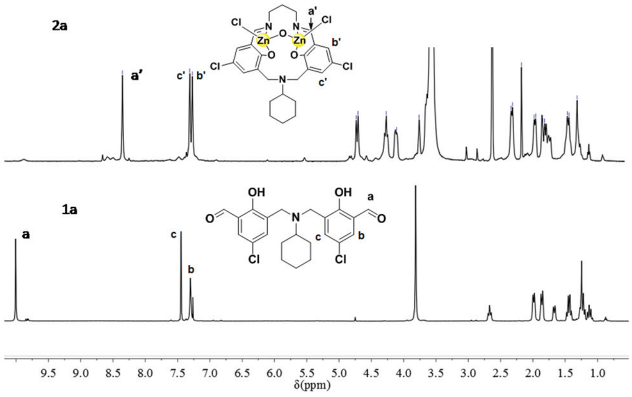


Fig. 1 $^1H$ NMR spectra of **2a** in DMSO-$d_6$ and **1a** in $CDCl_3$.

units after the condensation and the following metal-ion complexation.

With regard to the anti-magnetic Zn(II) complexes with a $d^{10}$ electronic structure, NMR spectroscopy has been proved to be a feasible technique to indicate the formation of Schiff-base macrocyclic Zn(II) complexes. $^1H$ NMR spectra have been recorded for both pendant-armed dialdehydes **1a** and **1b** in $CDCl_3$ and corresponding [1 + 1] macrocyclic Zn(II) complexes **2–4** in DMSO-$d_6$. In extended dialdehydes, the two *ortho* aromatic protons of the phenolic ring and the aldehyde protons are found at 7.30, 7.45, 10.01 ppm in **1a** and 7.16, 7.28, 10.06 ppm in **1b**, respectively, indicative of the discrepancy of the electron-withdrawing and electron-donating effects of Cl and $CH_3$ substituted groups. After the Schiff-base condensation, the aldehyde protons disappear and the *ortho* protons of the phenolic ring are shifted to around 7.02 ppm. In addition, new peaks are observed in the range of 8.00–8.07 ppm in **2–4**, corresponding to the formation of Schiff-base units (Fig. 1). In conclusion, by means of the variations of chemical shifts for certain protons in the $^1H$ NMR spectra, one can easily distinguish the starting dialdehydes and the formation of final Zn(II) macrocyclic products as well as the substituent effects (Cl and $CH_3$) in the macrocyclic backbone.

UV-vis spectra of **1–4** in $CH_3OH$ are shown in Fig. 2 for full comparison. In comparison with the absorption bands at 343 nm for both extended dialdehydes **1a** and **1b**, all six Schiff-base macrocyclic Zn(II) complexes **2–4** exhibit red shifts to different extents, namely 358 nm in **2a**, 360 nm in **3a**, 357 nm in **4a**, 363 nm in **2b**, and 365 nm in **3b** and **4b**, which can be attributed to the formation of the azomethine groups. Besides, the bathochromic shifts of several nanometers from **2a–4a** to **2b–4b** in their UV-vis spectra indicate the discrepancy of the electron-withdrawing and electron-donating effects of Cl and $CH_3$ substituted groups in the macrocyclic skeleton.

Furthermore, as illustrated in Fig. SI9–SI14,† the pure phase of the three pairs of Zn(II) macrocyclic complexes **2–4** was also confirmed by PXRD patterns which are in good agreement with their single-crystal diffraction simulative data that will be discussed below.

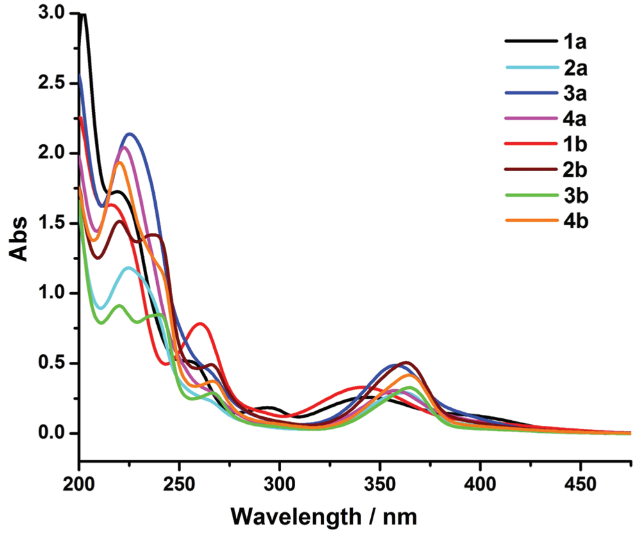


Fig. 2 UV-vis spectra in $CH_3OH$ at $1.0 \times 10^{-4}$ mol $L^{-1}$ for **1–4**.

### Description of single-crystal structures

The molecular structures of seven compounds **1a** and **2–4** with the atom-numbering scheme are illustrated in Fig. 3 and 4. In ligand **1a**, the two phenolic rings are staggered with the separation between two phenolic oxygen atoms of 4.985(4) Å. In contrast, the distance between two phenolic oxygen atoms is significantly shortened to 3.186(12) Å in **2a**, 3.108(7) Å in **3a**, 3.192(10) Å in **4a**, 3.093(8) Å in **2b**, 3.154(12) Å in **3b**, and 3.088(5) Å in **4b** in the three pairs of macrocyclic complexes because of the affixation of Zn–O coordinative bonds. Furthermore, strong intramolecular π–π stacking interactions between two offset phenolic rings are observed with the centroid-to-centroid separation of 3.489(4) Å in **1a**, and it is elongated to 3.503(6) Å in **2a**, 3.575(13) Å in **2b**, 3.508(3) Å in **3a**, 3.468(3) Å in **3b**, 3.467(8) Å in **4a**, and 3.597(6) Å in **4b**. Additionally, the dihedral angle between the two phenol rings in the extended dialdehyde **1a** is 18.7(3)°, while it changes to 15.4(3)° in **2a**, 18.4(3)° in **2b**, 14.8(1)° in **3a**, 12.7(3)° in **3b**, 13.6(4)° in **4a**, and 20.2(2)° in **4b**.

All five Zn(II) complexes (**2a**, **2b**, **3b**, **4a**, and **4b**) are 18-membered [1 + 1] macrocyclic dinuclear complexes where the coordination configuration for each four-coordinate Zn(II) center is distorted tetrahedra. It is found that each Zn(II) ion is coordinated by one halide atom, one oxygen atom from the bridging water/ethanol molecule, one imine nitrogen atom from the azomethine group, and one phenolic oxygen atom. In five dinuclear Zn(II) complexes, one oxygen atom from either a water or an ethanol molecule serves as the $\mu_2$ linker connecting two neighboring Zn(II) ions with the Zn⋯Zn separations of 3.382(6) Å in **2a**, 3.284(7) Å in **2b**, 3.326(3) Å in **3b**, 3.293(8) Å in **4a**, and 3.281(6) Å in **4b**. It was noted that the distance between the two *ortho* carbon atoms of each phenolic hydroxyl group has been elongated from 2.451(3) Å in **1a** to 2.545(6) Å in **2a**, 2.519(7) Å in **2b**, 2.513(3) Å in **3a**, 2.517(3) Å in **3b**, 2.517(8) Å in **4a**, and 2.525(6) Å in **4b**.

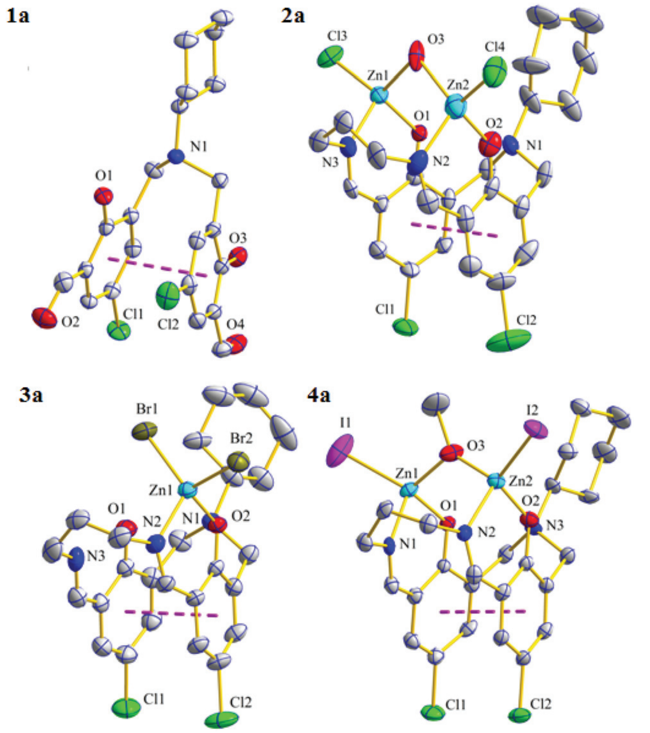


**Fig. 3** ORTEP diagrams (30% thermal probability ellipsoids, all H atoms and uncoordinated solvent molecules are omitted for clarity) of the molecular structures of **1a–4a**.

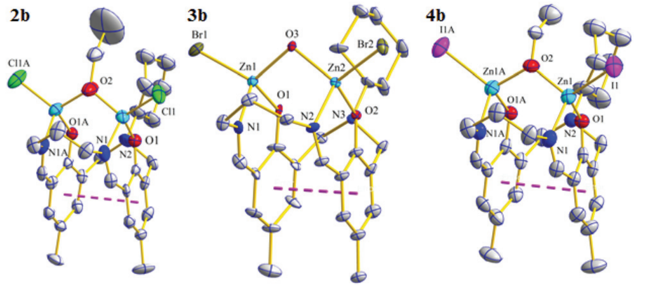


**Fig. 4** An ORTEP diagram (30% thermal probability ellipsoids, all H atoms and uncoordinated solution molecules are omitted for clarity) of the molecular structures of **2b**, **3b** and **4b**.

With regard to the 18-membered [1 + 1] mononuclear macrocyclic Zn(II) complexes **3a**, the central Zn(II) ion is four-coordinated by two bromide atoms, one phenolic oxygen atom, and one imine nitrogen atom from the azomethine group, also imposing a distorted tetrahedral environment. Additionally, the zinc–halogen bond distances in **2–4** are found to be elongated from 2.202(5) to 2.551(1) Å with the increase of the halogen atom size.

## Conclusion

In summary, two new extended dialdehydes (**1a** and **1b**) have been designed and synthesized, and they are used to react with 1,3-propanediamine to prepare Schiff-base macrocyclic complexes in the presence of $ZnX_2$ salts (X = Cl, Br, and I). As a result, five dinuclear (**2a**, **2b**, **3b**, **4a**, and **4b**) and one mononuclear (**3a**) [1 + 1] flexible Schiff-base macrocyclic Zn(II) complexes have been obtained and characterized by elemental analyses, FT-IR spectra, UV-vis and mass spectrometry, $^1$H NMR spectra, and single-crystal and powder X-ray diffraction analyses.

The zinc centers in three pairs of macrocyclic complexes exhibit a low coordination number of 4 with one or two co-ordinated halide ions adopting the common tetrahedral geometry, where the template Zn(II) cations and the auxiliary halide anions with different sizes and coordination abilities are believed to play important roles in forming the resulting Schiff-base macrocyclic complexes. In addition, subtle alterations of the electron-withdrawing and electron-donating substituted groups (Cl *versus* $CH_3$) in the macrocyclic backbone result in different $^1$H NMR and UV-vis spectra.

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