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Influence of the Pendant Arm, Halide, and Solvent on High-Efficient-Tuning [1 + 1] and [2 + 2] Schiff-Base Macrocyclic Complexes via a Zinc-Ion Template

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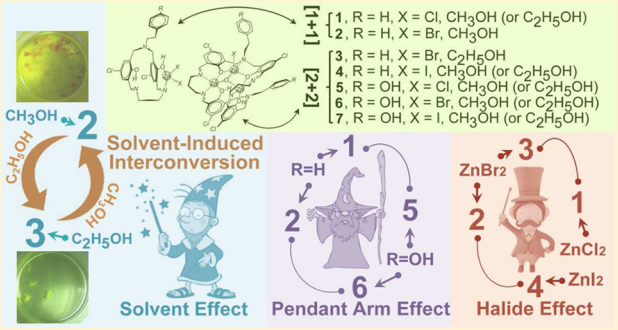
Supporting Information

ABSTRACT: A series of pendant-armed Schiff-base macrocyclic complexes **1**−**7** have been prepared by the condensation between extended dialdehydes with pendant arms (H_2hpdd/H_2pdd) and 1,3-propanediamine in the presence of ZnX_2 (X = Cl, Br, I), where 18-membered [1 + 1] mononuclear and 36-membered [2 + 2] half-fold trinuclear macrocyclic zinc(II) complexes are yielded. Three experimental variables, i.e., the pendant arm, halide, and solvent, are found to influence the organization of final macrocyclic complexes, in addition to the conventional metal-ion template effect promoting reversible formation and cleavage of Schiff-base imine bonds. It is noted that all of the reactions produce singular macrocyclic complexes in high yields if the experimental variables are fixed, and the selection of different pendant arms and halide counterions will generate different [1 + 1] mononuclear and [2 + 2] trinuclear macrocyclic zinc(II) complexes. More interestingly, [1 + 1] and [2 + 2] macrocyclic zinc(II) complexes **2** and **3** can be produced in methanol and ethanol, respectively, in the case of the reaction between $ZnBr_2$, H_2pdd, and 1,3-propanediamine. Further experiments reveal that red solid **2** and yellow-green solid **3** can be transformed to each other just by altering the type of solvent, and this tuning is complete and reversible.



INTRODUCTION

Schiff base, deriving from the reversible condensation between amino and carbonyl groups, was discovered by the German chemist Hugo Schiff in 1864.[1] During the past one and a half centuries, chemists have spent many efforts in the studies of Schiff-base compounds. As one of the very few covalent bonds with reversible character, many experimental parameters, such as the concentration, solvent, pH value, cation, anion, temperature, steric hindrance, hydrogen bond, and electronic factor, can influence the dynamic process of the reversible imine condensation reaction. However, it is only recently that the dynamic property of the imine bond has been a concern. From the viewpoints of dynamic covalent chemistry (DCC),[2] this equilibrium of imine formation leads to the most thermodynamically stable system. With regard to a multiple Schiff-base condensation, regulation of the relative experimental factors could make faster reaction rates and more ordered products. These characters are very important for the syntheses of sophisticated supramolecular assemblies based upon the dynamic covalent bonds. Actually, it is hard to realize the conceived architectures only by the template-directed synthetic method. At this moment, the noncovalent supramolecular bonding interactions could play very critical roles. Commonly, they could promote precursors to be preorganized into relative intermediates with definite geometries as a prelude of covalent bond formation and to generate thermodynamically preferential products in cooperation with the template ions. With the help of these experimental parameters, which could be used to finely tune the desired molecular architecture, chemists have achieved great success in Schiff-base-involved metal−organic container molecules,[3] imine macrocycles,[4,13−16] imine helicates,[5] catenanes,[6] rotaxanes,[7] suitanes,[8] hemicarcerands,[9] molecular knots,[6b,10] and so on.

After a review of these attractive assemblies, besides elegant structures and outstanding properties, the most impressive place is suggested to be the tunable formation of multiple Schiff-base condensation. However, it is still a great challenge for the selective construction of Schiff-base macrocyclic complexes with controllable sizes and nuclearities by alteration of the experimental factors. During painstaking exploration in the past half century, cations, especially the transition-metal and alkaline-earth-metal ions, have provided researchers a highly reliable approach to fulfilling this goal. The term "template effect" presented by Busch[11] explains that the final possible macrocycles should fit well with the metal-ion template's

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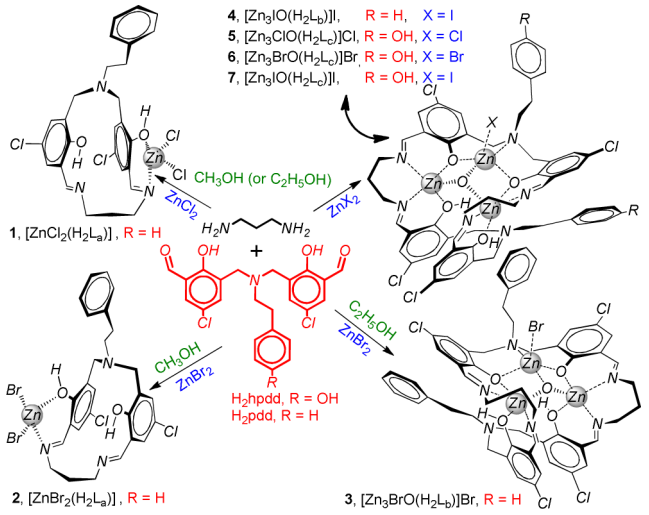
optimal coordination geometry and size. The representative pattern of this tunable method mainly relies on the type[4b−d,13d] and even the stoichiometric amounts of cations.[12] On the basis of a variety of dialdehydes, diamines, and metal templates, [1 + 1], [2 + 2], [3 + 3], [4 + 4], and even larger condensation products can be yielded.[4b−d,13] As for other nonmetal methods, such as pendant arms,[14] anions,[15] and solvents,[16] fine tuning from the precursors to the final products will be much more difficult to realize by means of weaker supramolecular interactions without the coordinative bond fixation of metal ions.

In our previous work, it is found that $Zn(NO_3)_2{\cdot}6H_2O$ is a suitable template for carrying out folded [2 + 2] Schiff-base dinuclear macrocyclic zinc(II) complexes by means of Schiff-base condensation between 1,2-bis(2-aminoethoxy)ethane and dialdehydes (H_2hpdd and H_2pdd with variable $-CH_2CH_2C_6H_4OH$ and $-CH_2CH_2C_6H_5$ pendant arms).[17] In order to reveal more of DCC and macrocyclic assemblies, we have taken great effort to explore whether other chemical factors could be used to regulate the macrocyclic zinc(II) products by varying several experimental variables. To this end, ZnX_2 (X = Cl, Br, I) salts have been used as templates to synthesize macrocyclic zinc(II) complexes having 1,3-propanediamine and H_2hpdd/H_2pdd components in ethanol or methanol (Scheme 1). As a result, two types of macrocyclic

Scheme 1. Schematic Illustration for the Formation of [1 + 1] Mononuclear and [2 + 2] Trinuclear Macrocyclic Zinc(II) Complexes Regulated by the Combination of Halide Anions, Pendant Arms, and Solvents



complexes are produced in high yields, i.e., 18-membered [1 + 1] mononuclear macrocyclic zinc(II) complexes and 36-membered [2 + 2] half-fold trinuclear macrocyclic zinc(II) complexes, because of the use of different pendant arms, halide anions, and solvents. It is found that the selection of different pendant arms and halide counterions will generate different [1 + 1] mononuclear and [2 + 2] trinuclear macrocyclic zinc(II) complexes. More interestingly, [1 + 1] and [2 + 2] macrocyclic zinc(II) complexes **2** and **3** with distinguishable color can be produced in methanol and ethanol, respectively, in the case of the reaction between $ZnBr_2$, H_2pdd, and 1,3-propanediamine, and they can be reversibly and completely transformed to each other just by changing the type of solvent.

RESULTS AND DISCUSSION

Pendant-Armed, Halide, and Solvent Effects on the Formation of [1 + 1] and [2 + 2] Schiff-Base Macrocyclic Complexes in the Presence of a Zinc-Ion Template. Although many experimental variables can influence the Schiff-base macrocyclic condensation containing paratactic formation of several imine bonds, not all of them work. In this paper, functional pendant arms of macrocycles were chosen as a primary focus because of the fact that the pH value could be subtly adjusted by the pendant arms of the dialdehyde components.[17] So, a pair of previously reported dialdehydes (H_2hpdd and H_2pdd) was selected to react with 1,3-propanediamine and $ZnCl_2$ in methanol. As a result, different products, namely, [1 + 1] mononuclear macrocyclic zinc(II) complex **1** and [2 + 2] trinuclear macrocyclic zinc(II) complex **5**, were obtained in high yield, respectively. The results suggested that the regulation of the sizes of Schiff-base macrocycles could be effectively realized by the pendant arms of the dialdehydes, which could be verified by the formation of similar [1 + 1] and [2 + 2] macrocyclic complexes **2** and **6** in the case of $ZnBr_2$ also. Nevertheless, only [2 + 2] trinuclear macrocyclic zinc(II) complexes **4** and **7** can be yielded when ZnI_2 was used in the above-mentioned cyclization reactions no matter what pendant arm was used.

Here, one can see the halide effect in the process of cyclization reactions in addition to the influence of pendant arms. Namely, only [2 + 2] macrocyclic complexes can be produced in the case of a $-CH_2CH_2C_6H_4OH$ pendant arm, while [1 + 1] or [2 + 2] macrocyclic complexes are generated for a $-CH_2CH_2C_6H_5$ pendant arm. The halide effect is suggested to originate from the combination of their different coordination capability, steric hindrance, and acidity, which can be regarded as the "secondary template effect", in addition to the primary zinc(II)-cation template.

In our experiments, F^-, Cl^-, Br^-, and I^- anions were utilized to synthesize the macrocyclic zinc(II) complexes, but the F^- ion was proved to be an unsuccessful secondary template even though the zinc(II) cation was an appropriate one. It is found that the pH value of the reaction mixture was about 8−9, which is higher than the conventional pH value of 5−6 in the cases of Cl^-, Br^-, and I^- anions. Distinguishable basicity of the F^- ion against the other three ions is responsible for alteration of the pH values, which will deter the effective Schiff-base condensation reaction.

Considering that [1 + 1] and [2 + 2] macrocyclic complexes can be yielded in the presence of ZnX_2 only for a $-CH_2CH_2C_6H_5$ pendant arm, further attempts have been performed on the solvent alteration in order to finely tune the formation of different macrocyclic complexes. Fortunately, [1 + 1] and [2 + 2] macrocyclic zinc(II) complexes **2** and **3** are produced in methanol and ethanol with 85 and 81% yield, respectively, merely in the case of the reaction between $ZnBr_2$, H_2pdd, and 1,3-propanediamine, and they are both very stable under general laboratory conditions. As demonstrated in Scheme 2, complexes **2** and **3** are easy to distinguish because they have different colors (red vs yellow green).

More interestingly, our experiments reveal that the red solid **2** and the yellow-green solid **3** can be transformed efficiently to each other just by altering the type of solvent. If the red solid **2** (picture a in Scheme 2) was dissolved in ethanol, the red solution could be transformed gradually and completely to yellow green after 48 h of reflux. The slow evaporation of the

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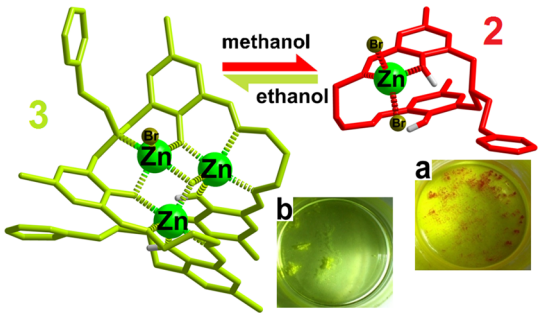
Scheme 2. Reversible Interconvertion between Red [1 + 1] Mononuclear and Yellow-Green [2 + 2] Trinuclear Macrocyclic Zinc(II) Complexes 2 and 3 in Methanol and Ethanol Solvents



resultant solution in air will only produce the yellow-green crystal **3** (picture b in Scheme 2), which can be verified by single-crystal XRD and spectral characterization. In contrast, the yellow-green complex **3** can be quickly and fully converted to the red complex **2** just by refluxing its methanol solution for 2 h. Further experiments reveal that the reversible transformation of [1 + 1] and [2 + 2] macrocyclic complexes cannot proceed at room temperature.

The ring contraction and expansion of the Schiff-base macrocycles are often induced by metal ions.[14e,18] When the introduced metal ion is too small or too big for the macrocyclic cavity, the dynamic imine covalent bond cleavage and formation allows for alteration of the Schiff-base macrocycle sizes to best accommodate the metal ion. However, these processes are often irreversible. Until now, examples of solvent-induced reversible rearrangement are rarely reported because a solvent does not make a significant difference in the relative stabilities of the equilibrated species.[16,19] These results indicate that **2** and **3** are in equilibrium in both methanol and ethanol. However, **2** preferentially crystallizes in methanol and eventually produces only **2** because of its relatively lower solubility. Similarly, **3** preferentially crystallizes in ethanol. Furthermore, it is assumed that **2** is a kinetic product, while **3** is the thermodynamic one in this equilibrium.[3g] The achievement of reversible interconversion of [1 + 1] and [2 + 2] macrocyclic zinc(II) complexes in this work could provide a new approach to the selective preparation of Schiff-base macrocyclic complexes and even the understanding of dynamic imine bond reassembly. Nevertheless, in comparison with $ZnBr_2$, our control experiments indicate that $ZnCl_2$ only produces [1 + 1] macrocyclic complex **1** and ZnI_2 only yields [2 + 2] macrocyclic product **4** in either methanol or ethanol. In addition, parallel reactions by using different stoichiometric zinc(II) salts will not change the type of final macrocyclic product.

Spectral Characterization and Crystal Structures of Macrocyclic Zinc(II) Complexes. Fourier transform infrared (FT-IR) spectra are used to monitor this type of macrocyclic Schiff-base condensation reaction. In comparison with the characteristic FT-IR absorption peaks at 1660 and 1664 cm^{-1} for aldehyde groups in H_2hpdd and H_2pdd, respectively, a new peak is observed for macrocyclic zinc(II) complexes **1** and **2** (1639 and 1638 cm^{-1}), indicating transformation from the aldehyde groups to the C═N Schiff-base units. Similar single peaks can be observed for complexes **3**−**7** in the range of 1626−1630 cm^{-1}. As shown in Figure SI8 in the SI, one can see that the FT-IR spectra of **1** and **2** as well as **3** and **4** are very similar to each other and those of **5**−**7** are almost identical. It is concluded that strikingly similar FT-IR spectra, especially in the fingerprint region, suggest construction of the same molecular structures for related macrocyclic complexes.

Furthermore, ^{1}H NMR spectral comparisons have been performed to reveal variations of the chemical shifts between extended dialdehydes and their relative macrocyclic zinc(II) complexes **1**−**7**. It is known that chemical shifts for the aldehyde protons of H_2hpdd and H_2pdd are the same as 10.01 ppm. In contrast, after formation of the Schiff-base macrocyclic complexes, the peaks of the aldehyde protons disappear in **1**−**7**, and two new peaks are observed instead at 8.27 and 7.90 ppm in **1** and **2** as well as 8.33 and 8.06 ppm in **3**−**7**, indicative of the presence of Schiff-base protons. Electrospray ionization mass spectrometry spectra for every complex have also been done, but nearly no valuable peaks could be observed.

All Schiff-base macrocyclic zinc(II) complexes except **7** are successfully determined by single-crystal XRD analysis, and the molecular structures of complexes **1**−**6** are shown in Figure 1. Both **1** and **2** are "dustpan"-type 18-membered [1 + 1] mononuclear macrocyclic zinc(II) complexes, and the Schiff-base macrocyclic skeleton is derived from the condensation between H_2pdd and 1,3-propanediamine. Differing from the "tripodal" structure of H_2pdd, the configuration of dialdehyde components in **1** and **2** looks like a "tuning fork" and the dihedral angles between two salicylaldehyde rings are 17.4(5) and 13.1(4)°, respectively. However, the dihedral angles between the benzene ring and two salicylaldehyde rings in **1** and **2** are entirely different with 86.7(4) and 88.0(4)° in **1** as well as 16.4(5) and 15.0(4)° in **2**. The basal coordination plane of each four-coordinate tetrahedral zinc(II) ion is composed of one phenolic oxygen, one nitrogen atom of the imine bond, and two halide ions. It is worth mentioning that half of the Schiff-base C═N units are not coordinated with the metal ions in both **1** and **2**. In addition, the tertiary nitrogen atom is not coordinated, and both of the phenolic protons are present in **1** and **2**.

Single-crystal XRD analysis of **3** and **4** reveals that 36-membered [2 + 2] half-fold trinuclear macrocyclic zinc(II) complexes are like swans spreading their wings. All of the metal centers in **3** and **4** are five-coordinate. The coordination geometry for two of the three zinc(II) centers in **3** is distorted trigonal-bipyramidal (τ = 0.582 and 0.932 for Zn1 and Zn2, respectively), while the third one is distorted pyramidal (τ = 0.300 for Zn3).[20] Similar results can be found in **4** (τ = 0.895, 0.395, and 0.540 for Zn1, Zn2, and Zn3, respectively). Moreover, the separations among the three zinc(II) centers are 3.154(1), 3.646(1), and 3.119(1) Å in **3**, while they are 3.712(2), 3.160(2), and 3.130(2) Å in **4**.

In each macrocyclic skeleton, two extended dialdehyde components have different configurations. One is "tuning fork" like **1** and **2**, and the other is "tripodal" like H_2pdd. With regard to the "tripodal" parts in **3** and **4**, the dihedral angels between two salicylaldehyde rings are 58.7(3) and 56.5(6)°, while those between the pendant-armed benzene ring and two salicylaldehyde rings are 61.6(4) and 87.8(3)° in **3** and 81.5(6) and 67.8(9)° in **4**. In contrast, the above-mentioned dihedral angles are much smaller as 15.0(3), 22.1(5), and 19.9(4)° in **3** and 15.2(6), 26.0(8), and 27.7(6)° in **4** with regard to the "tuning fork" parts. Compared with **1** and **2**, half of the phenolic protons are removed and all of the Schiff-base C═N units together with tertiary nitrogen atoms coordinate with the central zinc(II) ions in **3** and **4**.

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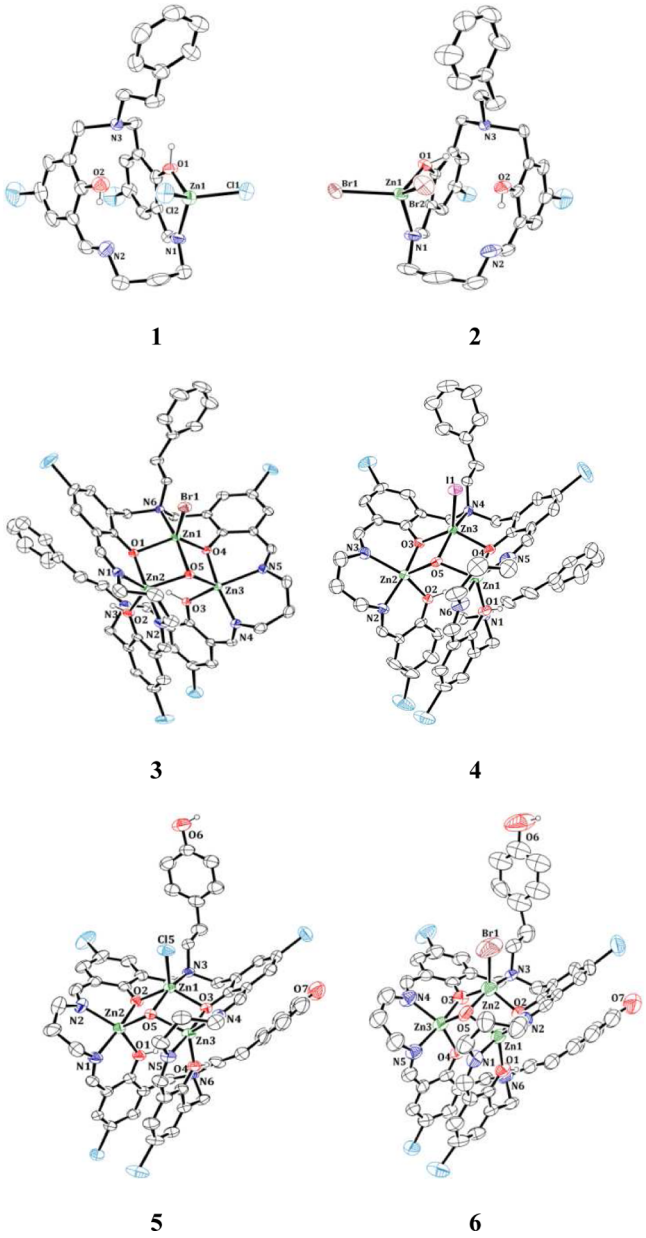

Figure 1. ORTEP drawings of **1**–**6** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and the phenolic protons are shown as small spheres of arbitrary radii.

The molecular structures of the two 36-membered [2 + 2] half-fold trinuclear macrocyclic zinc(II) complexes **5** and **6**, which are based upon the same H_2hpdd component, are analogous to those of **3** and **4**. As for the configuration of extended dialdehyde components in **5** and **6**, the dihedral angles between two salicylaldehyde rings for the "tripodal" parts are 49.3(5) and 51.2(9)°, while those for the "tuning fork" parts are 14.7(5) and 14.9(6)°. However, the coordination geometry for all three five-coordinate zinc(II) centers in **5** and **6** is distorted trigonal-bipyramidal (τ = 0.632, 0.507, and 0.768 for Zn1, Zn2, and Zn3 in **5** and τ = 0.790, 0.632, and 0.508 for Zn1, Zn2, and Zn3 in **6**). The separations among the three zinc(II) centers are 3.099(1), 3.593(2), and 3.171(2) Å in **5** and 3.215(3), 3.021(3), and 3.544(3) Å in **6**.

CONCLUSION

In summary, seven pendant-armed Schiff-base macrocyclic complexes, **1**–**7**, have been prepared by the condensation between extended dialdehyde (H_2hpdd/H_2pdd) and 1,3-propanediamine in the presence of ZnX_2 (X = Cl, Br, I), where 18-membered [1 + 1] mononuclear (**1** and **2**) and 36-membered [2 + 2] trinuclear (**3**–**7**) macrocyclic zinc(II) complexes are yielded. Three experimental variables, i.e., pendant arm, halide, and solvent, are found to influence the organization of the final macrocyclic complexes, in addition to the conventional metal-ion template effect promoting reversible cleavage and formation of Schiff-base imine bonds. It is noted that [1 + 1] and [2 + 2] macrocyclic zinc(II) complexes **2** and **3** can be obtained in methanol and ethanol, respectively, in the case of the reaction between $ZnBr_2$, H_2pdd, and 1,3-propanediamine. Further experiments reveal that the red solid **2** and the yellow-green solid **3** can be transformed efficiently to each other just by altering the type of solvent, and this tuning is complete and reversible.

In fact, the achievement of regulating the different size and number of nuclearity of the macrocyclic complexes is very challenging just by subtle variation of either the pendant arms of the macrocyclic ligands or the halide counterions. Herein we provide a remarkable example for high-efficient-tuning [1 + 1] and [2 + 2] Schiff-base macrocyclic complexes via a zinc-ion template, and we hope this successful tuning could throw some new insight on the design and construction of Schiff-base macrocyclic complexes from the viewpoint of DCC on the imine bond.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise specified, solvents of analytical grade were purchased directly from commercial sources and used without any further purification. Relative dialdehydes H_2hpdd and H_2pdd were synthesized following the literature procedure.[17]

^{1}H NMR spectroscopic measurements were performed on a Bruker AM 500 or AVANCE III HD 600 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at room temperature. Elemental analyses were measured with a PerkinElmer 1400C analyzer. IR spectra (4000–400 cm^{-1}) were collected on a Nicolet FT-IR 170X spectrophotometer at 25 °C using KBr plates. 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. Crystal data and structural refinements for macrocyclic zinc(II) complexes **1**–**6** are given in Table 1.

Synthesis of 1. $ZnCl_2$ (0.016 g, 0.12 mmol) was dissolved in ethanol (10 mL), and the resulting mixture was added to a solution of H_2pdd (0.046 g, 0.10 mmol) in hot ethanol (20 mL). The mixture was refluxed for 10 min, and then an ethanol (10 mL) solution of 1,3-propanediamine (0.008 g, 0.11 mmol) was added. The mixture was refluxed for an additional 2 h, cooled to room temperature, and filtered. The filtrate was concentrated to give complex **1** in a yield of 91% (0.029 g). ^{1}H NMR (600 MHz, CD_3OD): δ 8.27 (s, 1H), 7.90 (s, 1H), 7.43–7.25 (m, 5H), 4.77 (d, J = 13.5 Hz, 1H), 4.25 (d, J = 13.5 Hz, 1H), 4.15 (d, J = 13.7 Hz, 2H), 3.77–3.71 (m, 2H), 3.66 (s, 1H), 3.64 (d, J = 0.7 Hz, 1H), 3.61 (q, J = 7.1 Hz, 3H), 3.49 (q, J = 7.0 Hz, 2H), 3.42 (dd, J = 3.3 and 1.6 Hz, 2H). Anal. Calcd for $C_{27}H_{27}Cl_4N_3O_2Zn$: C, 51.25; H, 4.30; N, 6.64. Found: C, 51.11; H, 4.19; N, 6.50. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3049, 2924, 2858, 1640 (s, CH=N), 1549, 1452, 1219, 1041, 879, 777, 699. Red single crystals of complex **1** were grown from a mixture of ethanol/acetonitrile or methanol/acetonitrile (6:1, v/v) by slow evaporation in air at room temperature for 1 week.

Synthesis of 2. The synthetic process of **2** is the same as that of **1** except that $ZnBr_2$ (0.027 g, 0.12 mmol) was used. Yield: 89% (0.033 g). ^{1}H NMR (600 MHz, CD_3OD): δ 8.27 (s, 1H), 7.90 (s, 1H), 7.42–

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Table 1. Crystal Data and Structural Refinements for Macrocyclic Zinc(II) Complexes 1−6

	1	2·H_2O	3·C_2H_5OH	4·CH_3OH·$3H_2O$	5·$3H_2O$	6
empirical formula	$ZnC_{27}H_{27}Cl_4N_3O_2$	$Zn_2C_{54}H_{58}Br_4Cl_4N_6O_6$	$Zn_3C_{56}H_{58}Br_2Cl_4N_6O_6$	$Zn_6C_{109}H_{114}Cl_8I_4N_{12}O_{14}$	$Zn_6C_{108}H_{108}Cl_{12}N_{12}O_{17}$	$Zn_3C_{54}H_{52}Br_2Cl_4N_6O_7$
fw	632.71	1479.24	1408.81	2999.54	2663.68	1394.75
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$Pna2_1$	$C2/c$	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$
a (Å)	9.502(9)	21.456(2)	13.868(1)	15.084(1)	18.113(3)	18.138(3)
b (Å)	19.368(12)	15.867(2)	14.694(1)	14.105(1)	25.387(3)	25.593(5)
c (Å)	14.872(13)	20.628(3)	15.942(1)	58.538(4)	27.136(5)	26.533(5)
α (deg)	90	90	77.562(1)	90	90	90
β (deg)	90	120.608(3)	68.266(1)	93.285(1)	108.593(3)	107.924(3)
γ (deg)	90	90	87.571(1)	90	90	90
V (Å^3)	2737(4)	6044.0(14)	2944.3(4)	12434.2(16)	11826(3)	11719(4)
Z/D_{calcd} (g/cm^3)	4/1.536	4/1.626	2/1.589	4/1.602	4/1.496	8/1.581
F(000)	1296	2960	1424	5968	5440	5616
μ (mm^{-1})	1.319	3.666	2.804	2.365	1.535	2.819
h_{min}/h_{max}	−10/9	−25/25	−16/16	−17/17	−17/21	−21/21
k_{min}/k_{max}	−23/11	−18/18	−15/17	−11/16	−30/30	−30/23
l_{min}/l_{max}	−17/10	−24/24	−18/18	−69/69	−32/30	−31/28
data/param	3635/335	5212/343	10250/696	21880/1378	10428/688	10289/685
R1, wR2 [$I > 2\sigma(I)$][a]	0.0613, 0.1344	0.0510, 0.1468	0.0515, 0.1448	0.0860, 0.2045	0.0808, 0.2081	0.1247, 0.2869
R1, wR2 (all data)[a]	0.1180, 0.1572	0.0875, 0.1622	0.0759, 0.1776	0.1709, 0.2296	0.1690, 0.2354	0.2183, 0.3248
Flack parameter	0.03(3)					
S	0.92	1.05	1.03	1.04	1.04	0.95
max/min $\Delta\rho$ (e/Å^3)	0.51/−0.70	1.87/−0.84	2.13/−1.00	1.07/−2.26	0.96/−1.97	1.31/−1.24

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

7.33 (m, 5H), 7.14 (d, J = 2.6 Hz, 1H), 7.11 (d, J = 2.5 Hz, 2H), 7.09 (d, J = 2.5 Hz, 1H), 4.77 (d, J = 13.5 Hz, 1H), 4.25 (d, J = 13.4 Hz, 1H), 4.16 (d, J = 13.7 Hz, 2H), 3.77−3.71 (m, 2H), 3.66 (s, 1H), 3.64 (d, J = 0.8 Hz, 1H), 3.61 (dd, J = 14.1 and 7.1 Hz, 2H), 3.51−3.46 (m, 2H), 3.42 (dd, J = 3.3 and 1.7 Hz, 2H). Anal. Calcd for $C_{27}H_{29}Br_2Cl_2N_3O_3Zn$: C, 43.84; H, 3.95; N, 5.68. Found: C, 43.74; H, 3.90; N, 5.61. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3493, 3062, 2924, 2858, 1638 (s, CH═N), 1549, 1459, 1310, 1041, 777, 694. Red crystals of the solvent complex 2·H_2O were obtained by slow evaporation of a mixture of an ethanol/acetonitrile (8:1, v/v) solution for 1 week.

Synthesis of 3. The synthetic process of **3** is the same as that of **2** except that methanol was used and more $ZnBr_2$ (0.039 g, 0.17 mmol) was used. Yield: 87% (0.061 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.33 (s, 2H), 8.06 (s, 2H), 7.43 (s, 3H), 7.36 (s, 2H), 7.27 (s, 4H), 7.18 (s, 3H), 7.07 (s, 2H), 6.96 (d, J = 11.3 Hz, 4H), 4.75 (dd, J = 13.1 and 1.1 Hz, 2H), 4.21 (d, J = 12.3 Hz, 2H), 4.19−4.14 (m, 2H), 3.98 (d, J = 12.1 Hz, 2H), 3.80 (d, J = 23.8 Hz, 6H), 3.38 (d, J = 14.2 Hz, 2H), 2.83 (s, 2H), 2.53 (s, 2H), 2.33 (s, 2H), 2.22−2.10 (m, 4H). Anal. Calcd for $C_{56}H_{58}Br_2Cl_4N_6O_6Zn_3$: C, 47.74; H, 4.15; N, 5.96. Found: C, 47.61; H, 4.07; N, 5.85. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3439, 2924, 1628 (s, CH═N), 1555, 1448, 1297, 772. Light-yellow-green crystals of the solvent complex 3·C_2H_5OH were obtained by slow evaporation of a mixture of a methanol/acetonitrile (8:1, v/v) solution for 1 week.

Synthesis of 4. The synthetic process of **4** is the same as that of **3** except that ZnI_2 (0.055 g, 0.17 mmol) was used. Yield: 85% (0.064 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.33 (s, 2H), 8.06 (s, 2H), 7.44 (d, J = 2.2 Hz, 3H), 7.37 (s, 2H), 7.25 (d, J = 7.0 Hz, 4H), 7.17 (s, 3H), 7.06 (d, J = 6.6 Hz, 2H), 6.96 (d, J = 11.2 Hz, 4H), 4.75 (d, J = 12.9 Hz, 2H), 4.22 (d, J = 12.7 Hz, 2H), 4.17 (d, J = 12.7 Hz, 2H), 4.00 (d, J = 12.7 Hz, 2H), 3.90−3.75 (m, 6H), 3.62 (dd, J = 12.8 and 4.7 Hz, 2H), 3.40 (d, J = 12.6 Hz, 2H), 3.25 (dd, J = 8.5 and 5.0 Hz, 2H), 2.89−2.80 (m, 2H), 2.56−2.47 (m, 2H), 2.30 (dd, J = 14.6 and 5.5 Hz, 2H), 2.17 (d, J = 20.8 Hz, 2H). Anal. Calcd for $C_{109}H_{114}Cl_8I_4N_{12}O_{14}Zn_6$: C, 43.64; H, 3.83; N, 5.60. Found: C, 43.52; H, 3.75; N, 5.51. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3444, 3026, 2924, 1626 (s, CH═N), 1555, 1452, 1394, 1297, 1082, 879, 772, 699. Light-yellow-green crystals of the solvent complex 4·CH_3OH·$3H_2O$ were obtained by slow evaporation of a mixture of a methanol (or ethanol)/acetonitrile (8:1, v/v) solution for 1 week.

Synthesis of 5. $ZnCl_2$ (0.024 g, 0.17 mmol) was dissolved in ethanol (10 mL) and added to a solution of H_2hpdd (0.047 g, 0.10 mmol) in hot ethanol (20 mL). The mixture was refluxed for 10 min, and then an ethanol (10 mL) solution of 1,3-propanediamine (0.008 g, 0.11 mmol) was added. The mixture was refluxed for an additional 2 h, cooled to room temperature, and filtered. The filtrate was concentrated to give complex **5** in a yield of 81% (0.054 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.32 (s, 2H), 8.06 (s, 2H), 7.36 (s, 2H), 7.19 (s, 2H), 7.11 (d, J = 6.7 Hz, 2H), 6.96 (s, 4H), 6.87 (t, J = 7.5 Hz, 6H), 4.71 (d, J = 12.1 Hz, 2H), 4.21 (d, J = 12.3 Hz, 2H), 4.13 (s, 3H), 3.91 (d, J = 11.0 Hz, 2H), 3.77 (s, 6H), 3.35 (s, 4H), 3.16 (d, J = 8.3 Hz, 4H), 2.73 (s, 2H), 2.48 (s, 2H). Anal. Calcd for $C_{108}H_{108}Cl_{12}N_{12}O_{17}Zn_6$: C, 48.69; H, 4.09; N, 6.31. Found: C, 48.58; H, 4.01; N, 6.19. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3420, 2929, 1626 (s, CH═N), 1554, 1512, 1450, 1297, 770. Light-yellow-green single crystals of complex **5** were grown from a mixture of an ethanol (or methanol)/acetonitrile (7:3, v/v) solution by slow evaporation in air at room temperature for 1 week.

Synthesis of 6. The synthetic process of **6** is the same as that of **5** except that $ZnBr_2$ (0.038 g, 0.17 mmol) was used. Yield: 76% (0.053 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.32 (s, 2H), 8.06 (s, 2H), 7.36 (s, 2H), 7.30 (s, 1H), 7.22 (s, 1H), 7.16 (s, 2H), 7.11 (d, J = 7.5 Hz, 2H), 6.96 (s, 4H), 6.86 (d, J = 6.9 Hz, 4H), 4.71 (d, J = 13.1 Hz, 2H), 4.23−4.14 (m, 2H), 3.92 (d, J = 13.5 Hz, 2H), 3.78 (d, J = 7.2 Hz, 6H), 3.39 (s, 1H), 2.75 (s, 2H), 2.50 (s, 2H), 2.15 (s, 3H), 2.03 (s, 2H). Anal. Calcd for $C_{54}H_{52}Br_2Cl_4N_6O_7Zn_3$: C, 46.50; H, 3.76; N, 6.03. Found: C, 46.35; H, 3.68; N, 5.92. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3420, 2925, 1627 (s, CH═N), 1549, 1512, 1452, 1297, 772. Light-yellow-green crystals of the solvent complex **6** were

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obtained by slow evaporation of a mixture of an ethanol (or methanol)/acetonitrile (1:2, v/v) solution for 1 week.

Synthesis of 7. The synthetic process of 7 is the same as that of **5** except that ZnI_2 (0.054 g, 0.17 mmol) was used. Yield: 70% (0.054 g). ^{1}H NMR (500 MHz, CD_3OD): δ 8.32 (s, 2H), 8.07 (s, 2H), 7.36 (d, J = 2.6 Hz, 2H), 7.30 (s, 1H), 7.23 (s, 1H), 7.18 (s, 2H), 7.13 (s, 1H), 7.11 (s, 1H), 6.97 (s, 4H), 6.88 (s, 4H), 3.93 (s, 2H), 3.90 (s, 2H), 3.78 (s, 6H), 3.39 (s, 1H), 2.57 (s, 2H), 2.49 (d, J = 2.4 Hz, 2H), 2.19 (dd, J = 16.5 and 8.7 Hz, 5H). Anal. Calcd for $C_{54}H_{52}Br_2Cl_4N_6O_7Zn_3$: C, 46.50; H, 3.76; N, 6.03. Found: C, 46.38; H, 3.68; N, 5.94. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3427, 2924, 1630 (s, CH=N), 1551, 1514, 1450, 1296, 827, 770.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic details, characterization data, tables of selected bond distances and angles and hydrogen-bonding interactions, FT-IR, UV–vis, and ^{1}H NMR spectra, views of the packing structures of related complexes, and X-ray crystallographic data in CIF format (CCDC 1014709–1014714). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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