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Controlling self-assembly of zinc(II)-benzoate coordination complexes with 1,4-bis(4-pyridyl)ethane by varying solvent and ligand-to-metal ratio: Their catalytic activities

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ABSTRACT

Four new coordination polymers formed by zinc-benzoate with the 1,2-bis(4-pyridyl)ethane (bpe) bridging ligand have been prepared and characterized. Zinc-benzoates can be rationally tuned to form four different structures with a bridging bpe ligand by controlling ligand-to-zinc-benzoate molar ratios and by using different solvent systems, and reveal three coordination polymers having similar one-dimensional characteristics but having different mono-, di-, trinuclear nodes (**1**–**3**), and a dinuclear ring type molecule (**4**). This work reveals that the ligand-to-metal ratio and solvent play very important roles in the formation of different coordination structures. We have also shown that the compounds **1**–**4** catalyzed efficiently the transesterification of a variety of esters. The complex **3** showed the most efficient reactivity and is the best among the catalytic efficiencies reported previously with zinc-containing coordination and polymeric compounds. The substrates with the electron-withdrawing substituents have undergone faster transesterification than those with the electron-donating ones. In addition, the scope of the application of **1**–**4** as transesterification catalysts has been expanded to now include ethanol and propanol, suggesting that this catalytic system can be potentially useful for preparing various esters by transesterification. Moreover, the transesterification reaction mechanism was discussed by ^{1}H NMR study.

1. Introduction

The design and construction of metal-organic coordination polymers has recently attracted much attention not only due to their structural and topological novelty [1–8], but also for their potential applications as functional materials such as gas storage [9–15], ion-exchange [16,17], catalysis [18–27], magnetism [28–30], and molecular sensing [31]. The rational design of these coordination polymers is highly affected by several factors such as the coordination geometry of metal ions [32,33], the structure of organic ligands [34–36], the solvent system [37,38], pH value [39–41], temperature [42,43], the counteranion [44,45], and the ligand-to-metal ratio [46,47]. Therefore, an investigation for understanding the relationships between the structures of complexes and those factors is at the center of controlling coordination network assembly.

Though numerous coordination polymers and macrocycles have been generated from transition metal nodes with a variety of organic spacers over the past few years, there is still little understanding of how ligand-to-metal stoichiometry and solvent system among several factors can be used to control the type of polymeric structures. While these two factors are relatively notable in copper- and silver-containing coordination polymers [48–53], their influence on the formation of coordination polymers, especially, with zinc ion is much less well understood and systematic studies of their role are very scarce [54–56].

Quite recently, we have reacted zinc-benzoate with pyrazine and its derivatives, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, and quinoxaline, and characterized five new Zn(II)-benzoate coordination architectures, from dinuclear, trinuclear and pentanuclear complexes to one-dimensional and two-dimensional coordination polymers [57]. These results have shown that the substituents of pyrazine are very important roles for construction of various zinc-benzoate complexes. Interestingly, the compounds catalyzed efficiently the transesterification of a variety of esters.

As an extension of our previous work, in this study, we have investigated the complex formation of zinc-benzoate with another bridging ligand 1,2-bis(4-pyridyl)ethane (bpe) in order to further

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prepare functional supramolecular complexes with intriguing structures and potential applications especially in catalysis and to systematically investigate the influence of the concentration and solvent effects less studied on the assembly processes of the structure of zinc-carboxylate containing coordination polymers. Here, we report the syntheses, characterization and crystal structures of four zinc coordination complexes $[Zn_2(O_2CPh)_4(H_2O)_2][Zn(O_2CPh)_2\text{-}(bpe)]_n$ (**1**), $[Zn_3(O_2CPh)_6(bpe)]_n$ (**2**), $[(Zn_3(O_2CPh)_6)(\mu\text{-}bpe)(Zn_2(O_2CPh)_4)]_n$ (**3**), and $[Zn_2(O_2CPh)_4(bpe)_2]$ (**4**) from the reaction of zinc-benzoate and bpe which were obtained by tuning solvent mixtures and ligand-to-zinc-benzoate ratios. These complexes contain mononuclear nodes **1**, trinuclear nodes **2**, and trinuclear alternating with dinuclear nodes **3** and a discrete dinuclear complex **4**, respectively. These results illustrate how both stoichiometry and solvent play a vital role in affecting the product formation, their structures and topology. We have also reported that the compounds **1**–**4** catalyzed efficiently the transesterification of a variety of esters with different alcohols, and discussed about the reaction mechanism of the transesterification reaction based on ^{1}H NMR study.

2. Experimental

Materials: Acetone, methanol, ethanol, methylene chloride, propanol, 2-propanol, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methylacetate, methylbenzoate, 1,2-bis(4-pyridyl)ethane (bpe), ammonium benzoate, and zinc nitrate hexahydrate were purchased from Aldrich and were used as received. 4-Fluorophenyl acetate and 4-nitrophenyl benzoate were obtained from Lancaster.

Instrumentation: Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using an EA1108 (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Product analysis for the transesterification reaction was performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with Hewlett–Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using 30-m capillary column (Hewlett–Packard, HP-1, HP-5, and Ultra 2). ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer. Chemical shifts (δ) are reported in ppm, relative to TMS (0.00).

Synthesis of $[Zn_2(O_2CPh)_4(H_2O)_2][Zn(O_2CPh)_2(bpe)]_n$ *(**1**):* 38.0 mg (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 ml water and carefully layered by 4 ml acetone solution of 1,2-bis(4-pyridyl)ethane (11.6 mg, 0.0625 mmol). The yield was 34.5 mg (21.2%) for compound **1**. Suitable crystals of compound **1** for X-ray analysis were obtained in a week. The structure **1** was also obtained with the same ratio of bpe to zinc-benzoate in methylene chloride (4 ml) /methanol (4 ml) system. *Anal.* Calc. for $C_{66}H_{56}N_4O_{13}Zn_3$ (1309.26), **1**: C, 60.54; H, 4.32; N, 4.28. Found: C, 60.45; H, 4.30; N, 4.55%. IR (KBr): ν (cm^{-1}) = 3422(br), 3064(w), 2362(m), 1619(s), 1572(m), 1364(s), 1229(w), 1070(w), 1030(w), 940(w), 720(s), 684(w), 550(m).

Synthesis of $[Zn_3(O_2CPh)_6(bpe)]_n$ *(**2**):* 38.0 mg (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 ml methanol and carefully layered by 4 ml methylene chloride solution of 1,2-bis(4-pyridyl)ethane (23.3 mg, 0.125 mmol). The yield was 53.7 mg (38.9%) for compound **2**. Suitable crystals of compound **2** for X-ray analysis were obtained in 5 days. The structure **2** was also obtained with the ratio of bpe to zinc-benzoate (0.5:1) in ethanol/water system. *Anal.* Calc. for $C_{54}H_{42}N_2O_{12}Zn_3$ (1107.01), **2**: C, 58.58; H, 3.83; N, 2.53. Found: C, 58.64; H, 3.93; N, 2.65%. IR (KBr): ν (cm^{-1}) = 3078(w), 2958(w), 2362(w), 1613(s), 1572(m), 1445(m), 1367(s), 1227(m), 1066(m), 1032(m), 939(w), 842(w), 812(m), 715(s), 683(m), 558(w), 524(m), 431(w).

Synthesis of $[(Zn_3(O_2CPh)_6)(\mu\text{-}bpe)(Zn_2(O_2CPh)_4)]_n$ *(**3**):* 38.0 mg (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 ml water and carefully layered by 4 ml acetone solution of 1,2-bis(4-pyridyl)ethane (26.6 mg, 0.25 mmol). The yield was 58.3 mg (24.5%) for compound **3**. Suitable crystals of compound **3** for X-ray analysis were obtained in a week. *Anal.* Calc. for $C_{94}H_{74}N_4O_{20}Zn_5$ (1906.42), **3**: C, 59.22; H, 3.92; N, 2.94. Found: C, 59.51; H, 3.81; N, 2.72%. IR (KBr): ν (cm^{-1}) = 3077(brm), 1619(s), 1573(s), 1438(m), 1364(s), 1229(m), 1173(m), 1069(m), 1032(m), 940(w), 841(m), 811(m), 719(s), 684(m), 558(w), 524(m), 439(w).

Synthesis of $[Zn_2(O_2CPh)_4(bpe)_2]$ *(**4**):* 38.0 mg (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 ml water and carefully layered by 4 ml methanol solution of 1,2-bis(4-pyridyl)ethane (23.3 mg, 0.125 mmol). The yield was 78.0 mg (63.4%) for compound **4**. Suitable crystals of compound **4** for X-ray analysis were obtained in five days. The structure **4** was also obtained with the ratios of bpe to zinc-benzoate (2:1 and 4:1) in methanol/water and (3:1 and 4:1) in ethanol/water system, respectively. *Anal.* Calc. for $C_{52}H_{44}N_4O_8Zn_2$ (983.65), **4**: C, 63.49; H, 4.52; N, 5.70. Found: C, 63.70; H, 4.49; N, 5.47%. IR(KBr): ν (cm^{-1}) = 3078(m), 2958(w), 1612(s), 1572(s), 1429(m), 1367(s), 1227(m), 1171(w), 1066(m), 1032(m), 939(w), 842(m), 812(m), 715(s), 683(m), 558(m), 524(m), 431(m).

*Catalytic activity of compounds **1**–**4**:* Catalytic homogeneous reaction conditions: Ester (0.05 mmol) was dissolved in an appropriate solvent (1 ml), methanol or propanol, and the catalyst (1.3 mg, 1.10×10^{-3} mmol for **1**, 1.9 mg, 1.01×10^{-3} mmol for **2**, 1.0 mg, 1.00×10^{-3} mmol for **3**, and 0.986 mg, 1.00×10^{-3} mmol for **4**, respectively) were added and shaken in an incubator at 50 °C (450 rpm). Reaction conversion was monitored by GC/Mass analysis of 20 μl aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average conversion yields are presented.

*NMR experiments for the structural determination of the complex **4** before and after the transesterification reaction:* ^{1}H NMR spectra of ammonium benzoate and bpe were obtained in CD_3OD at room temperature. For ammonium benzoate, ^{1}H NMR (CD_3OD, 400 MHz): δ 7.91–7.94 (m, 2H, aromatic-*ortho*-H), δ *7.30–7.44* (m, 3H, aromatic-*meta*-H and aromatic-*para*-H). For bpe, ^{1}H NMR (CD_3OD, 400 MHz): δ 8.38–8.40 (d, 2H, aromatic-*meta*-H), δ *7.27–7.29* (d, 2H, aromatic-*ortho*-H), δ 3.032 (s, 4H, CH_2). ^{1}H NMR spectrum of the complex **4** was obtained in CD_3OD; ^{1}H NMR (CD_3OD, 400 MHz): δ 8.02–8.05 (m, 2H, aromatic-*ortho*-H for benzoate), δ *7.45–7.50* (q, 1H, aromatic-*para*-H for benzoate), δ *7.37–7.42* (q, 2H, aromatic-*meta*-H for benzoate), δ *8.40–8.43* (d, 2H, aromatic-*meta*-H for bpe), δ *7.29–7.32* (d, 2H, aromatic-*ortho*-H for bpe), δ 3.045 (s, 4H, CH_2 for bpe). ^{1}H NMR spectrum of the complex **4** was again obtained after the reaction mixture of **4** and phenyl acetate in CD_3OD was incubated for 1 day at 50 °C. The transesterification reaction of phenyl acetate was found to be complete by GC and ^{1}H NMR. ^{1}H NMR (CD_3OD, 400 MHz): 8.02–8.05 (m, 2H, aromatic-*ortho*-H for benzoate), δ *7.45–7.50* (q, 1H, aromatic-*para*-H for benzoate), δ *7.37–7.41* (q, 2H, aromatic-*meta*-H for benzoate), δ *8.41–8.43* (d, 2H, aromatic-*meta*-H for bpe), δ *7.29–7.31* (d, 2H, aromatic-*ortho*-H for bpe), δ 3.045 (s, 4H, CH_2 for bpe).

X-ray crystallography: The X-ray diffraction data for all four compounds were collected on a Bruker SMART AXS diffractometer equipped with a monochromater n the Mo Kα (λ = 0.71073 Å) incident beam. Each crystal was mounted on a glass iber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12 [58]. All hydrogen atoms were placed in the calculated positions. The crystallographic data for compounds **1**–**4** are listed in Table 1.

Table 1
Crystallographic data for compounds **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{66}H_{56}N_4O_{13}Zn_3$	$C_{54}H_{42}N_2O_{12}Zn_3$	$C_{94}H_{74}N_4O_{20}Zn_5$	$C_{52}H_{44}N_4O_8Zn_2$
Formula weight	1309.26	1107.01	1906.42	983.65
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	11.9043(14)	10.2901(8)	10.1724(6)	19.617(5)
b (Å)	14.5166(17)	11.0667(8)	10.8612(7)	12.185(3)
c (Å)	19.116(2)	13.1179(10)	22.0757(14)	21.739(6)
α (°)	77.967(2)	76.1630(10)	81.6880(10)	90.000
β (°)	73.248(2)	67.4350(10)	83.8290(10)	115.665(4)
γ (°)	79.207(2)	64.9150(10)	66.2990(10)	90.000
Volume (Å^3)	3065.0(6)	1244.13(16)	2206.6(2)	4684(2)
Z	2	1	1	4
$D_{calc.}$ (Mg/m^3)	1.419	1.478	1.435	1.395
Absorption coefficient (mm^{-1})	1.232	1.500	1.412	1.083
Crystal size (mm^3)	0.30 × 0.25 × 0.20	0.15 × 0.05 × 0.05	0.10 × 0.05 × 0.05	0.15 × 0.10 × 0.08
Reflections collected	19307	6994	12504	12342
Independent reflections [R_{int}]	13650 (0.0482)	4776 (0.0179)	8479 (0.0204)	4597 (0.0469)
Data/restraints/parameters	13650/0/781	4776/0/322	8479/0/556	4597/0/298
Goodness-of-fit on F^2	0.935	1.044	0.972	1.012
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0423$, $wR_2 = 0.1112$	$R_1 = 0.0312$, $wR_2 = 0.0823$	$R_1 = 0.0371$, $wR_2 = 0.0865$	$R_1 = 0.0566$, $wR_2 = 0.1451$
R indices (all data)	$R_1 = 0.0661$, $wR_2 = 0.1157$	$R_1 = 0.0400$, $wR_2 = 0.0852$	$R_1 = 0.0556$, $wR_2 = 0.0920$	$R_1 = 0.0809$, $wR_2 = 0.1629$
Largest difference between peak and hole (e Å^{-3})	1.930 and −0.546	0.307 and −0.430	0.367 and −0.375	1.603 and −0.744

3. Results and discussion

To investigate the effect of solvent and ligand-to-metal ratio on the structures of zinc-containing coordination polymers, we have reacted Zn(II)-benzoate with 1,2-bis(4-pyridyl)ethane (bpe) by changing the solvent systems and ligand-to-zinc-benzoate ratios. The coordination complexes **1**–**4** were prepared cleanly as single phase crystalline products, respectively. The infrared spectra of **1**–**4** were fully consistent with their formulations. Asymmetric and symmetric C═O stretching modes of the ligated benzoate moieties were evidenced by very strong, slightly broadened bands at ~1600 cm^{-1} and ~1400 cm^{-1} [59–61]. The absence of any bands in the area of ~1710 cm^{-1} indicates full deprotonation of all carboxylate groups in **1**–**4** [59–61].

The reaction of zinc-benzoate with the bpe ligand revealed four different structures as a function of ligand concentration in the different solvent systems. The relationship between the molar ratio of bpe-to-zinc-benzoate and the solvent system is shown in Table 2. Compound **1** was obtained with the molar ratio of bpe-to-zinc-benzoate of 0.5:1 both in the acetone/H_2O system and in the methylene chloride/methanol system. Compound **2** was obtained with the molar ratios of bpe-to-zinc-benzoate of 0.5:1 in the ethanol/H_2O system and of 1:1 in the methylene chloride/methanol system, respectively, and compound **3** was obtained with the molar ratio of 2:1 in the acetone/H_2O system. When we use the methanol/H_2O system, only compound **4** was obtained with any molar ratios of bpe-to-zinc-benzoate (1:1, 2:1, and 4:1). **4** was also obtained with the molar ratios of both 3:1 and 4:1 in the ethanol/H_2O system, and **4** could not be obtained from the acetone/H_2O system. These results indicate that the formation of compounds **1–4** depends primarily on both the bpe ligand-to-zinc-benzoate ratios and the solvent systems.

*The structure of compound (**1**):* An X-ray structural analysis revealed that compound **1** consists of mononuclear $Zn(O_2CC_6H_5)_2$ units bridged by bpe (bpe = 1,2-bis(4-pyridyl)ethane) ligand to form a one-dimensional zigzag chain (Fig. 1a). Zn(II) ion is coordinated by two monodentate benzoate ligands, two bridging bpe ligands with a tetrahedral geometry. The Zn–$O_{benzoate}$ bond distances are 1.932(2) and 1.964(1) Å that are similar to those found in $[Zn(O_2CCH_3)_2(\mu\text{-bpe})] \cdot 2H_2O$ (1.922(3) and 1.949(3) Å) [62] and $[Zn(O_2CCH_3)_2(py)_2]$ (1.941(4) and 1.945(2) Å, py = pyridine)[63] and the Zn–N_{bpe} bond distances range from 2.036(2) to 2.075(2) Å which are typical in Zn complexes (ranging from 2.010(3) to 2.044(3) Å) [62,63]. The packing diagram of the one-

Table 2
Relationship between bpe-to-zinc-benzoate molar ratios and solvent systems.

bpe: zinc-benzoate	Acetone/H_2O[a]	Ethanol/H_2O[b]	Methanol/H_2O[c]	Methylene chloride/methanol[d]
0.5:1	**1**[e]	**2**[f]	–[i]	**1**
1:1	–	–	**4**[h]	**2**
2:1	**3**[g]	–	**4**	–
3:1	–	**4**	–	–
4:1	–	**4**	**4**	–

[a] Zinc-benzoate ($Zn(NO_3)_2 \cdot 6H_2O + C_6H_5COONH_4$) was dissolved in water and layered by an acetone solution of bpe.
[b] Zinc-benzoate ($Zn(NO_3)_2 \cdot 6H_2O + C_6H_5COONH_4$) was dissolved in water and layered by an ethanol solution of bpe.
[c] Zinc-benzoate ($Zn(NO_3)_2 \cdot 6H_2O + C_6H_5COONH_4$) was dissolved in water and layered by a methanol solution of bpe.
[d] Zinc-benzoate ($Zn(NO_3)_2 \cdot 6H_2O + C_6H_5COONH_4$) was dissolved in methanol and layered by a methylene chloride solution of bpe.
[e] A one-dimensional zigzag chain containing $Zn(O_2CPh)_2$ units bridged by bpe ligands with dinuclear paddle-wheel $Zn_2(O_2CPh)_4(H_2O)_2$, $[Zn_2(O_2CPh)_4(H_2O)_2]$-$[Zn(O_2CPh)_2(bpe)]_n$.
[f] A one-dimensional chain containing trinuclear $Zn_3(O_2CPh)_6$ units bridged by bpe ligands, $[Zn_3(O_2CPh)_6(bpe)]_n$.
[g] A one-dimensional chain containing trinuclear $Zn_3(O_2CPh)_6$ units and dinuclear $Zn_2(O_2CPh)_4$ units bridged by bpe ligands alternatively, $[(Zn_3(O_2CPh)_6)(\mu\text{-bpe})(Zn_2(O_2CPh)_4)]_n$.
[h] A dinuclear ring molecule containing two $Zn(O_2CPh)_2$ bridged by two bpe ligands, $[Zn_2(O_2CPh)_4(bpe)_2]$.
[i] We could not obtain any crystals suitable for X-ray analysis under these conditions.

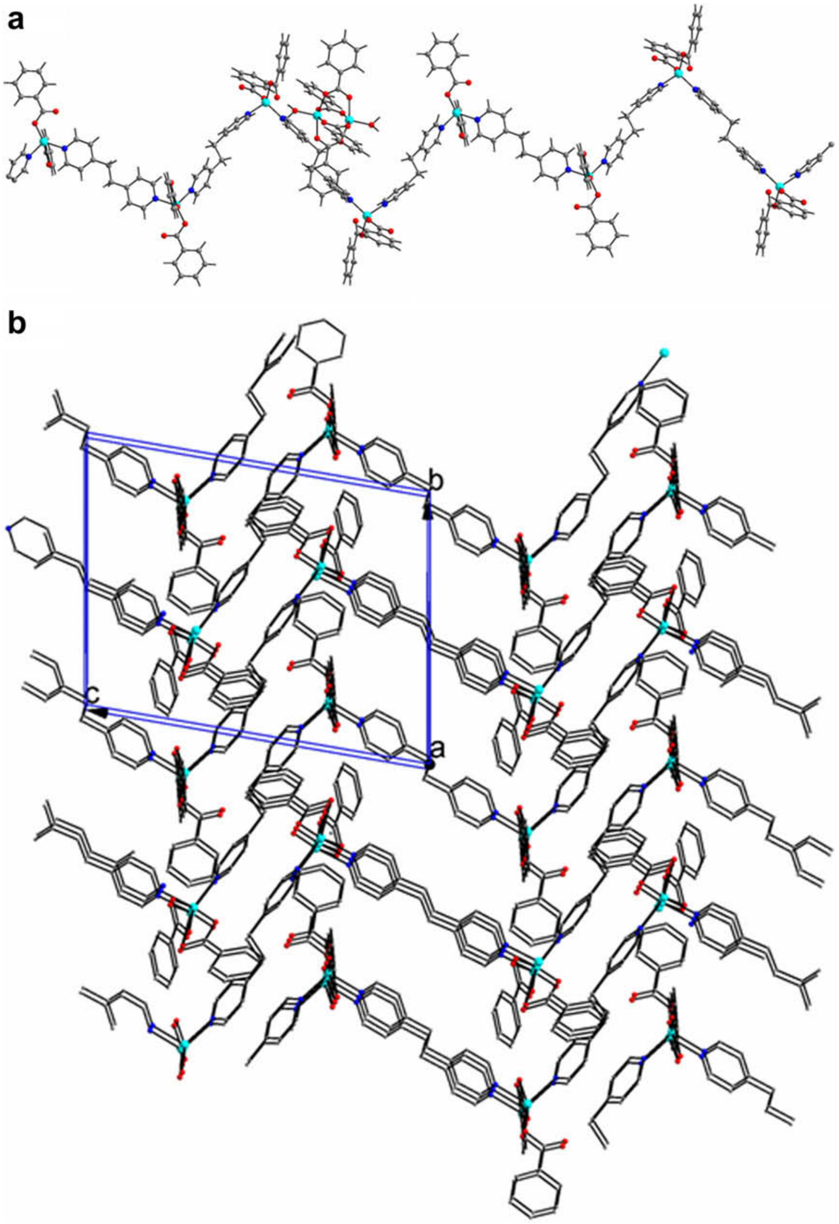


Fig. 1. (a) Structure of one-dimensional zigzag chain coexisting with dinuclear paddle-wheel Zn complex, **1**. (b) The packing diagram of the one-dimensional zigzag chains along an axis. All hydrogen atoms were omitted for clarity.

dimensional zigzag chains is shown in Fig 1b. There coexist dinuclear paddle-wheel type $Zn_2(O_2CC_6H_5)_4$ molecules with water axial ligands (Fig. 1a). Each Zn atom in this unit has distorted square-pyramidal environment, with four oxygen atoms from benzoates, which form the equatorial plane, and one water oxygen atom. The $Zn–O_{benzoate}$ bond distances range from 2.042(2) to 2.062(2) Å longer than those of the 1-D zigzag chain, but similar to those of the paddle-wheel type complexes [64–67], and the $Zn–O_{water}$ bond distance is 1.986(1) Å (Table 3). The Zn···Zn distance is 2.983(2) Å similar to those found in $Zn_2(MeCH{=}CHCO_2)_4$ $(quinoline)_2$] (2.976 Å) [64], $[Zn_2(O_2CPh)_4(py)_2]$ (2.927(4) Å) [65], $[Zn(bdc)\cdot(DMF)(H_2O)]$ (2.940(3) Å) [66], and $[Zn_2(bdc)_2(dabco)]$ (2.909(1) Å, bdc = 1,4-benzenedicaboxylate and dabco = 1,4-diazabicyclo[2.2.2]octane) [67]. There is a hydrogen bond interaction between oxygen atom of a benzoate ligand in a zigzag chain and the axial water hydrogen atom of a dinuclear unit ($O22_{benzoate}$···H15A–$O15_{water}$ 1.657(2) Å). Importantly, this is the first example of coexistence of 1-D and Zn dinuclear paddle-wheel type, to our best knowledge.

*The structure of compound (**2**):* An X-ray structural analysis revealed that compound **2** consists of trinuclear $Zn_3(O_2CC_6H_5)_6$ units bridged by bpe ligand to form a one-dimensional chain (Fig. 2a). A trinuclear Zn(II)-benzoate unit is constructed by six bridging benzoate ligands and similar to the previously described trinuclear zinc-carboxylate with axial N- or O-donor ligands [57,65,68–70]. There is an inversion center on the central Zn atom. Out of three Zn centers the central Zn is all O-donor hexa-coordinated from six benzoate groups to form a distorted octahedral geometry. The other two Zn centers are symmetric to each other, and each has a bridging bpe ligand and four oxygen atoms from benzoate ligands. Thus each Zn1 center has NO4 coordination environment with distorted trigonal bipyramid geometry. The coordination modes of benzoate ligands show two kinds of bridging modes [71–73]: one mode is a typical bridging mode, and the other is

Table 3
Selected bond distances for compounds **1**, **2**, **3**, and **4**.

	1	2	3	4
Zn–O (Å)	1.932(2)–2.062(2)	1.9628(16)–2.2640(19)	1.9607(19)–2.373(2)	1.950(3), 1.951(3)
Zn–N (Å)	2.036(2)–2.075(2)	2.0384(18)	2.035(2)	2.039(3), 2.064(3)
Zn–Zn (Å)	2.9827(7) (paddle-wheel type unit)	3.370(2)	2.9541(5) (paddle-wheel type unit), 3.347(2) (trinuclear unit)	8.502(14)

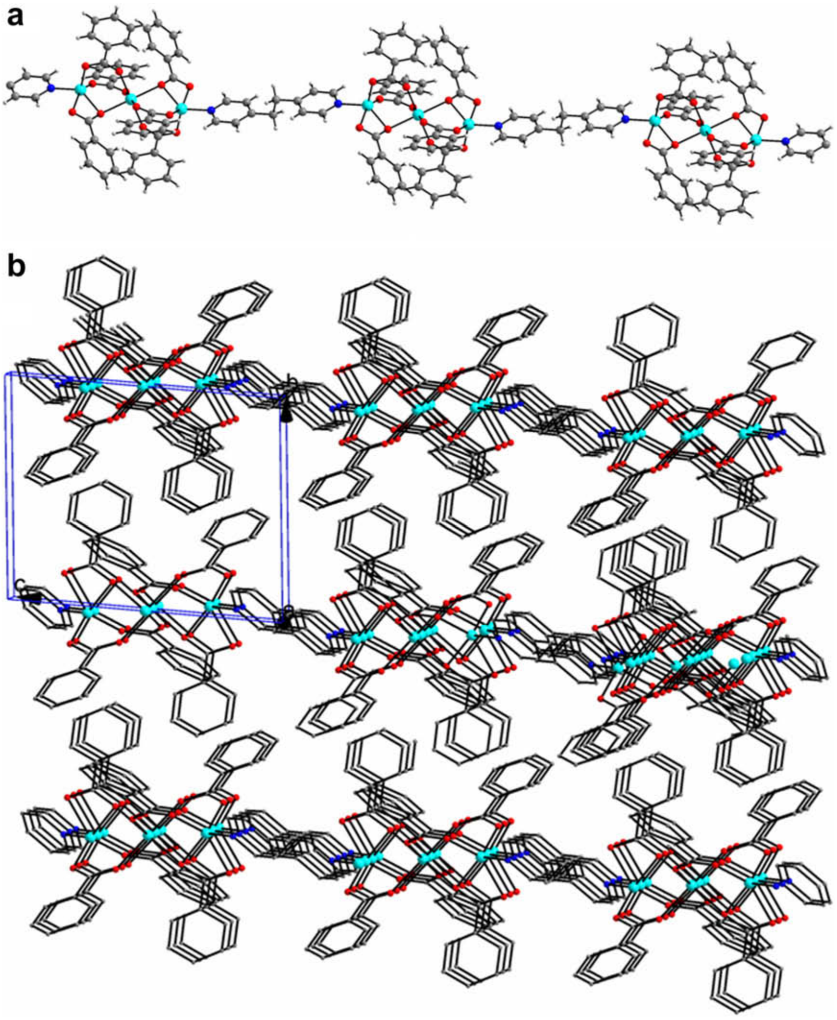


Fig. 2. (a) Structure of one-dimensional chain **2** containing trinuclear Zn units bridged by bpe ligands. (b) The packing diagram of the one-dimensional zigzag chains along an axis. All hydrogen atoms were omitted for clarity.

the unusual coordination mode, a monatomic coordination mode, that chelates to one Zn2 atom and, at the same time, bridges the other Zn1 atom as shown in Fig. 2a. This unusual coordination mode of carboxylate group provides a big distortion around Zn1. The packing diagram is shown in Fig. 2b. In the typical bridging carboxylate coordination mode, $Zn1–O_{bridging}$ distances are 1.963(1) and 1.968(1) Å, and $Zn2–O_{bridging}$ distances are 2.014(1) and 2.098(1) Å. In the unusual coordination mode, $Zn2–O_{bridging}$ distance is 2.207(2) Å which is a little longer than typical one, and $Zn1–O_{chelating}$ distances are 2.103(1) and 2.264(1) Å. Zn–N bond distance is 2.038(1) Å which is typical in Zn complexes (Table 3) [68–70]. The Zn···Zn distance is 3.370(2) Å that is much longer than that of dinuclear one in the compound **1**, and that can be comparable to those found in $[Zn_3(MeCH{=}CHCO_2)_6(quinoline)_2]$ (3.26 Å) [68], $[Zn_3(O_2CPh)_6(2,3\text{-diMepz})_2]$ (3.362(4) Å, 2,3-diMepz = 2,3-dimethylpyrazine) [57], $\{[Zn_3(1,4\text{-BDC})_3(DEF)_2]\cdot DEF\}_\infty$ (3.228(4) and 3.528(4) Å, 1,4-BDC = 1,4-benzene dicarboxylate and DEF = diethylformamide) [70].

*The structure of compound (**3**):* An X-ray structural analysis revealed that compound **3** consists of dinuclear paddle-wheel type $Zn_2(O_2CC_6H_5)_4$ units and trinuclear $Zn_3(O_2CC_6H_5)_6$ units bridged by bpe ligands alternatively to form a one-dimensional chain (Fig. 3a). Trinuclear $Zn_3(O_2CC_6H_5)_6$ units are similar to that of compound **2**, and dinuclear paddle-wheel type $Zn_2(O_2CC_6H_5)_4$ units are similar to that of the dinuclear one in compound **1**. While the trinuclear zinc-carboxylate units and the dinuclear paddle-wheel zinc-carboxylate units of structures from zinc-carboxylates have been often reported in literature [63,64–70], this arrangement in which bipyridyl ligands bridge dinuclear units and trinuclear units alternatively is unprecedented, to our best knowledge. On the other hand, it is worthwhile to mention that in $Cu_2(maa)_4$/bpp systems (Hmaa = 2-methylacrylic acid, bpp = 1,3-bis(4-pyridyl)pro-

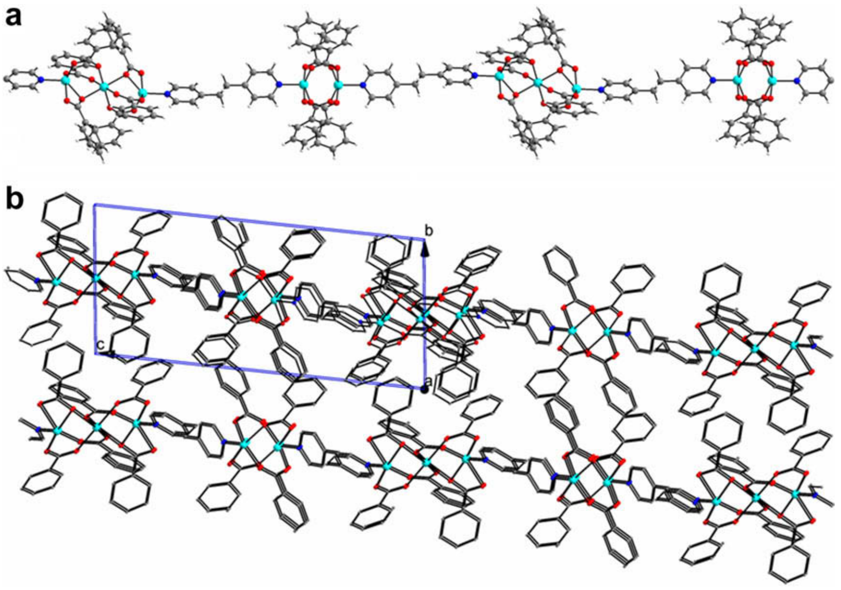


Fig. 3. (a) Structure of one-dimensional chain **3** containing dinuclear and trinuclear units bridged by bpe ligands alternatively. (b) The packing diagram of the one-dimensional zigzag chains along an axis. All hydrogen atoms were omitted for clarity.

pane), dinuclear and mononuclear alternating paddle-wheel 1-D instead of trinuclear and dinuclear alternating 1-D has been observed [48]. However, we could not obtain the dinuclear and mononuclear alternating polymer systems in our Zn systems. The packing diagram is shown in Fig. 3b. In the dinuclear unit, the Zn–$O_{bridging}$ bond distances range from 2.0240(19) to 2.054(2) Å similar to those of the dinuclear unit in the compound **1**, and the Zn–N bond distance is 2.035(2) Å which is typical in Zn complexes [64–67]. In the trinucelar unit, the Zn–$O_{bridging}$ bond distances of the typical bridging mode range from 1.9607(19) to 2.0903(19) Å, the Zn2–$O_{chelating}$ bond distances of the unusual coordination mode are 2.0491(17) and 2.373(2) Å, and the Zn1–$O_{bridging}$ bond distance of the unusual mode is 2.2428(17) Å which is a little longer than that of compound **2**. The Zn–N bond distance of the unusual mode is 2.035(2) Å which is typical in Zn complexes (Table 3) [68–70]. The Zn···Zn distances of dinuclear and trinuclear units are 2.9541(5) and 3.347(2) Å, respectively, which are shortened from dinuclear unit of **1** and trinuclear unit of **2**.

*The structure of compound (**4**):* An X-ray structural analysis revealed that compound **4** consists of two $Zn(O_2CC_6H_5)_2$ bridged by two bpe ligands to form a dinuclear molecule (Fig. 4). The Zn(II) ion has a distorted tetrahedral environment with two monodentate benzoate ligands and two bridging bpe ligands. The bpe ligand adopts a gauche conformation to form a ring type molecule. The Zn–O bond distances are 1.950(1) and 1.951(1) Å which are a little shorter than those of compounds **1**, **2**, and **3**, and the Zn–N bond distances are 2.039(2) and 2.064(6) Å which are typical in Zn complexes (Table 3). The Zn···Zn distance is 8.502(14) Å.

Structural diversity of zinc polymeric compounds by tuning ligand-to-metal ratio and solvent system: Zinc-benzoates can be rationally tuned to form four different structures with a bridging bpe ligand by controlling ligand-to-zinc-benzoate molar ratios and by using different solvent systems, and reveal three coordination polymers having similar one-dimensional characteristics but having different mono-, di-, trinuclear nodes, and a dinuclear ring type molecule. In case of the low concentration of the bpe ligand such as the bpe-to-zinc-benzoate molar ratio of 0.5:1 in both acetone/H_2O and CH_2Cl_2/MeOH solvent systems, compound **1** was obtained and revealed unprecedented one-dimensional zigzag chains coexisting with the paddle-wheel type dinuclear Zn_2 units which would not participate to form an one-dimensional chain. If the concentration of bpe ligand increases such as 1:1 molar ratio in acetone/MeOH solvent system, compound **2** was obtained and revealed trinuclear units connected by bpe ligands to form one-dimensional chains without the paddle-wheel type Zn_2 units. In ethanol/H_2O solvent system, **2** was also obtained in 0.5:1 bpe-to-zinc-benzoate molar ratio. If the concentration of bpe ligands increases more such as 2:1 molar ratio in acetone/H_2O system, compound **3** was obtained and revealed trinuclear and dinuclear units connected by bpe ligands alternatively, that is the first example in zinc-carboxylate systems. If the concentration of bpe ligands increases much more such as 4:1 molar ratio in EtOH/H_2O system, compound **4** was obtained and revealed the dinuclear ring type molecule which is a totally different structure from the previous structures. In MeOH/H_2O solvent system, importantly, only **4** was obtained without respect to the molar ratio of bpe-to-zinc-benzoate.

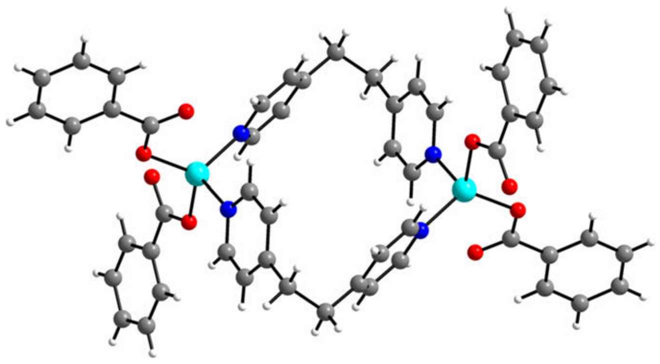


Fig. 4. Structure of dinuclear molecule **4**.

This result indicates that the solvent and the ligand-to-metal ratio are simultaneously playing a controlling role over the structure. Further, solvent seems to have more effect than the ligand-to-metal ratio, because in a certain case only one class of complexes was obtained (e.g., only **4** in MeOH/H_2O system), although the ratios of bpe-to-zinc-benzoate increase from 1 to 2 to 4. Interestingly, the solvents used in this work were not involved in the structures of

Table 4
Transesterification of esters by methanol and propanol in the presence of compounds **1**, **2**, **3**, and **4** at 50 °C.[a]

Entry	Substrate	**1**		**2**		**3**		**4**	
		MeOH[c] (time/days)[b]	PrOH[d] (time/days)[b]	MeOH[c] (time/days)[b]	PrOH[d] (time/days)[b]	MeOH[c] (time/days)[b]	PrOH[d] (time/days)[b]	MeOH[c] (time/days)[b]	PrOH[d] (time/days)[b]
1	4-Nitrophenyl acetate	0.7	2.5	0.9	1.5	0.3	0.5	0.6	1
2	4-Fluorophenyl acetate	2.5	11	4.5	9	2	11	3	15
3	Phenyl acetate	1.5	5	1.5	7	0.5	2	1	4
4	4-Methylphenyl acetate	5.5	18	4.5	18	4	14	3	17
5	4-Nitrophenyl benzoate [e]	2.5	6	3.5	10	0.3	9	0.7	18
6	4-Chlorophenyl benzoate	2	17	2.5	17	0.5	5	2	10
7	Phenyl benzoate	5	24	5	33	2	7	2	17
8	4-Methylphenyl benzoate	5	24	5	12	2	17	4	35
9	Vinyl acetate	1.5	2.5	0.9	3.5	0.3	0.5	0.7	1

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters; 0.05 mmol, catalyst; 1.10×10^{-3} mmol for **1**, 1.01×10^{-3} mmol for **2**, 1.00×10^{-3} mmol for **3**, 1.00×10^{-3} mmol for **4**, solvent; methanol or propanol (1 ml). See Section 2 for the detailed reaction conditions.

[b] Time necessary for the complete conversion of substrate to product.

[c] Transesterification of esters was carried out in methanol (MeOH).

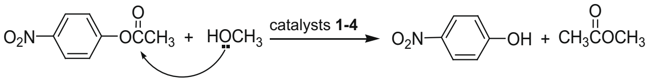
[d] Transesterification of esters was carried out in propanol (PrOH).

[e] The solvent was a mixture of MeOH/CH_2Cl_2 or PrOH/CH_2Cl_2 (1/1) because of low solubility of substrate in MeOH or PrOH.

1–**4** which means that the coordinating solvents such as H_2O, methanol, and ethanol, act as the "templating" role rather than the "coordination" one [38]. Therefore, the solvent used in this preparation should be considered as an innocent one instead of a potential participant in any coordination polymer formation.

In addition, the structural diversity of compounds **1**–**4** shows that the dinuclear paddle-wheel Zn(II) units can be rationally controlled and can serve as mono-, di-, and trinuclear nodes towards a dipyridyl ligand, respectively, and that four classes of mixed-ligand complexes can be obtained simply by manipulating the ligand-to-zinc-benzoate molar ratio and the solvent. This result led us to suggest that the ligand concentration as well as the solvent system can tune topology in the system of zinc-benzoate with a variety of bipyridyl bridging ligands.

Catalytic transesterification reactions by the compounds ***1***–***4***: Transesterifications are important transformations in organic synthesis in industrial as well as in academic laboratories [74–76]. As part of our efforts to design transesterification catalysts based on metal ions that are not redox active, therefore, we have recently synthesized several discrete complexes and coordination polymers and reported that some of them could carry out efficiently the catalytic transesterification of a range of esters with methanol under the mild conditions [77–79]. While these catalyst systems constitute a promising class of catalysts that appears to be an efficient, mild, and easily recyclable method for the alcoholysis of esters, there is still more demand to develop new types of catalysts that show better efficiency. With our previous experience, therefore, compounds **1**–**4** have been also employed as a catalyst for transesterification reaction in methanol under a homogeneous condition. The ester, *p*-nitrophenyl acetate, was initially used as a substrate (Eq. (1)):

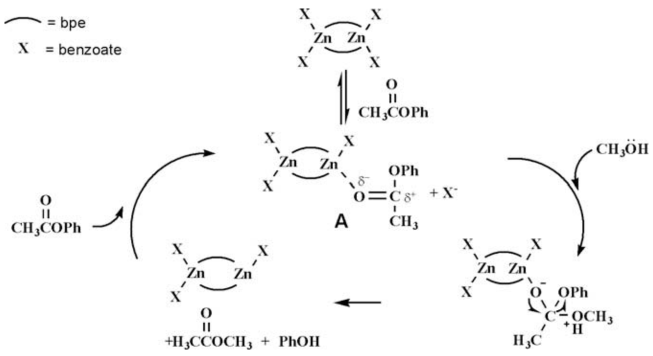


(1)

We observed that compounds **1**–**4** catalyzed the reaction of *p*-nitrophenyl acetate with methanol, with quantitative conversion to methyl acetate in 0.3–0.9 day (see the entry 1 of Table 4) at 50 °C under the neutral conditions. Among them, the complex **3** shows the most efficient reactivity. Importantly, this result is the second best among the catalytic efficiencies reported previously with zinc-containing coordination and polymeric compounds, to our best knowledge [77–84]. Since we have established that **1**–**4** represent excellent catalysts for the tansesterification reaction of *p*-nitrophenyl acetate with methanol, we have investigated the transesterification of various *p*-substituted phenyl acetates and benzoates. As shown in Table 4, the substrates with the electron-withdrawing substituents have undergone faster transesterification (entries 1 and 5) than those with the electron-donating ones (entries 4 and 8). In addition, vinyl acetate as a precursor widely used for ester synthesis [85–87] was converted efficiently to the product methyl acetate by **1**–**4** within 0.3–1.5 day (entry 9). This result suggests that this catalytic system can be useful for preparing various esters by transesterification. Moreover, it is worthwhile that 4-nitrophenyl acetate and 4-nitrophenyl benzoate with nitro substituents at the *para*-position, which are known to be problematic substrates for the transesterification reaction due to undesirable side reactions such as isomerization or polymerization [88], were also converted quantitatively to the corresponding products.

Furthermore, this promising result led us to test the transesterification with more challenging nucloephiles such as ethanol, 2-propanol, and propanol, in the presence of the catalysts **1**–**4**. Phenyl acetate reacted very slowly with either ethanol (70 days) or 2-propanol (90 days), respectively, whereas with propanol the transesterification reaction was complete within 2–7 days in the presence of **1**–**4**, respectively (entry 3). The complex **3** again shows the most efficient reactivity. This result is the best among the catalytic efficiencies reported previously with zinc-containing coordination and polymeric compounds, to our best knowledge [77–84]. Various esters were also examined with propanol as a nucleophile in the presence of **1**–**4**. The substrates with the electron-withdrawing substituents have undergone faster conversion to the corresponding products (entries 1 and 5), while those with the electron-donating ones have shown slow transesterification reaction (entries 4 and 8).

Though we do not know, at this moment, about the exact reactive species and the reaction mechanism for the transesterification reaction by the catalysts, it has been proposed that the mechanism of metal ion catalyzed transesterification probably involves electrophilic activation of the carbon center of the carbonyl moiety by binding of the metal to the carbonyl oxygen [89–93]. Therefore, Lewis acidity of the metal center may be important in catalytic transesterification. Based on this idea and our previous proposal on the transesterification reactions [79,94,95], a possible transesterification mechanism in these catalyst systems can be proposed with the catalyst **4** as shown in Scheme 1. The complex **4** could



Scheme 1. Plausable transesterification mechanism.

possibly be a catalytic species because only **4** has been obtained in methanol/H_2O without respect to the ligand-to-metal ratios and because the transesterification reactions were carried out in methanol. At the first step, the substrate phenyl acetate substitutes a labile ligand benzoate to give the adduct **A** (Scheme 1). Then, the nucleophile methanol would attack the carbon atom of carbonyl moiety of the adduct to produce the product methyl acetate. After the catalytic reaction, the structure of **4** was proved to be kept, based on ^1H NMR experiments. ^1H NMR data of benzoate and bpe of **4** appear at different positions from those of free benzoate and free bpe (see Section 2). ^1H NMR data of benzoate and bpe of the complex **4** taken after the transesterification reaction were exactly identical to those of benzoate and bpe of the starting complex **4** and we were not able to observe any free benzoate and bpe separated from **4** (see Section 2). This result indicates that there is no structural change of **4** after the transesterification reaction. This investigation was consistent with the proposed transesterification mechanism. Further detailed mechanistic studies are currently under investigation.

4. Conclusion

We have shown here how the structures of the coordination compounds of the bpe ligand with zinc-benzoate are able to be varied not only by the traditional method such as solvent control but also by changes in the ratio of ligand-to-zinc-benzoate. This work reveals that both the ligand-to-metal ratio and the solvent play very important roles in the formation of different coordination structures, and this offers the possibility to control the formation of such structures by varying those factors. Furthermore, these results led us to suggest that many of zinc-containing coordination polymers previously reported on specific solvents and ligand-to-metal ratios may be converted to yet unknown new structures according to the change of the reaction conditions such as solvent and ligand-to-metal ratio.

We have also shown that the compounds **1**–**4** catalyzed efficiently the transesterification of a variety of esters. Importantly, the overall transesterification reactivity shown by the catalyst **3** is the best among the catalytic efficiencies reported previously with zinc-containing coordination and polymeric compounds, to our best knowledge. In addition, the scope of the application of **1**–**4** as transesterification catalysts has been expanded to now include ethanol and propanol. Further explorations into the uses of this catalyst family in organic transformations as well as mechanistic investigations are ongoing.

Taken all together, this observation is very significant since it encourages us to construct new polymeric compounds that might be efficiently used as homogeneous or heterogeneous catalysts friendly to the environment simply by altering the ratio of ligand-to-metal and solvent system in the reaction mixtures.

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Appendix A. Supplementary data

CCDC 687836, 687837, 687838, and 687839 contain the supplementary crystallographic data for **1**, **2**, **3**, and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.11.048.

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