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Tuning structural topology of zinc(II)-benzoate coordination complexes with 1,2-bis(4-pyridyl)ethene by controlling metal-to-ligand ratios and solvent systems: Their photoluminescence and catalytic activities

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ABSTRACT

Zinc-benzoates can be rationally tuned to form four different types of structures with a bridging bpe (1,2-bis(4-pyridyl)ethene) ligand by controlling zinc(benzoate)-to-ligand ratios and solvent systems, and they reveal three coordination polymers having different 1-D characteristics and a dinuclear Z-type molecule. Reactivity study of the compounds **1**–**4** for the transesterification of a variety of esters showed that the coordination polymers **1**–**3** have better activity than the discrete dinuclear molecule **4**. Strong emissions of compounds **1**–**3** were observed at 393 nm for **1**, 378 nm for **2**, and 393 nm for **3**, respectively, but weak luminescence was observed at 380 nm for **4** under the same experimental conditions. The thermal stabilities of these complexes were also examined.

1. Introduction

Metal–organic coordination polymers have recently attracted much attention not only due to their structural and topological novelty [1–9], but also due to their potential applications as functional materials such as gas storage [10–16], ion-exchange [17,18], catalysis [19–28], magnetism [29–31], and molecular sensing [32]. The design and construction of these coordination polymers are highly affected by several factors: the coordination geometry of metal ions [33,34], the structure of organic ligands [35–37], the solvent system [38,39], pH value [40–42], temperature [43,44], the counteranion [45,46], and the ligand-to-metal ratio [47,48]. A subtle change of those factors can control coordination network assembly, and provide new complexes with different structural topologies and different functional properties. The ligand-to-metal stoichiometry and solvent system among those factors are notable in copper- and silver-containing coordination polymers [49–54]. Their influence on the formation of coordination polymers with zinc ions is also studied [55–58], but systematic studies of their role are very scarce.

Recently, we have studied about coordination polymers formed from zinc-benzoate with the 1,2-bis(4-pyridyl)ethane (bpa) bridging ligand [59]. From this previous work, zinc-benzoates can be rationally tuned to form four different structures with a bridging bpa ligand by controlling zinc(benzoate)-to-ligand molar ratios and by using different solvent systems, and they reveal three coordination polymers having similar one-dimensional characteristics but having different mono-, di-, trinuclear nodes, and a dinuclear ring type molecule. This previous work revealed that the metal-to-ligand ratio and solvent play very important roles in the formation of different coordination structures.

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)ethene (bpe) in order to further 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 four types of structures of zinc-benzoate coordination polymers containing bpe ligands controlled by zinc(benzoate)-to-bpe ratios and different solvent systems: $[Zn_2(\mu\text{-}O_2CC_6H_5)_4(\mu\text{-}N_2C_{12}H_{10})]$ (**1**), $[Zn_2(O_2CC_6H_5)_2(\mu\text{-}N_2C_{12}H_{10})]$ (**2**), $[Zn_2(\mu\text{-}O_2CC_6H_5)_2(O_2CC_6H_5)_2(\mu\text{-}N_2C_{12}H_{10})_2]$ (**3**), and $[Zn_2(O_2CC_6H_5)_4(N_2C_{12}H_{10})_2(\mu\text{-}N_2C_{12}H_{10})]\cdot 4H_2O$ (**4**·4H₂O). Their physical properties and catalytic reactivity are also discussed.

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2. Experimental

2.1. Materials

1,2-Bis(4-pyridyl)ethene, methanol, ethanol, acetone, acetonitrile, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methyl acetate, methyl benzoate, ammonium benzoate, and $Zn(NO_3)_2{\cdot}6H_2O$ were purchased from Aldrich and were used as received. 4-Fluorophenyl acetate and 4-nitrophenyl benzoate were obtained from Lancaster.

2.2. Instrumentation

Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using a vario MACRO (Elemental Analysensysteme, Germany) in the Laboratory Center of Seoul National University of Science and Technology, 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). The emission/excitation spectra were recorded on a Perkin–Elmer LS45 fluorescence spectrometer. Thermogravimertic analyses (TGA) were carried out on a Shimadzu TA50 integration thermal analyzer.

2.3. Synthesis of 1-D containing paddle-units $[Zn_2(\mu\text{-}O_2CC_6H_5)_4(\mu\text{-bpe})]$ **1**

2.3.1. **1**·$2CH_3CN$

37.9 mg (0.125 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 35.5 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL acetonitrile solution of 1,2-bis(4-pyridyl)ethene (11.7 mg, 0.0625 mmol). Suitable crystals of compound **1**·$2CH_3CN$ for X-ray analysis were obtained in 4 days. The yield was 59.7 mg (54.4%) for compound **1**·$2CH_3CN$. IR (KBr): ν(cm^{-1}) = 3433(brw), 3066(w), 1636(s), 1612(s), 1573(s), 1407(s), 1209(w), 1175(w), 1070(m), 1029(m), 839(m), 718(s), 680(m), 570(w), 552(m), 464(w). *Anal. Calc. for $C_{44}H_{36}N_4O_8Zn_2$ (879.51), **1**·$2CH_3CN$: C, 60.08; H, 4.13; N, 6.37. Found: C, 60.00; H, 4.02; N, 5.95%.*

2.3.2. **1**·$2(CH_3)_2CO$

37.9 mg (0.125 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 35.5 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 (11.7 mg, 0.0625 mmol). Suitable crystals of compound **1**·$2(CH_3)_2CO$ for X-ray analysis were obtained in 4 days. The yield was 37.2 mg (32.6%) for compound **1**·$2(CH_3)_2CO$. IR (KBr): ν(cm^{-1}) = 3442(brw), 3067(w), 1712(w), 1637(s), 1613(s), 1573(m), 1504(w), 1401(s), 1222(w), 1206(w), 1068(w), 1029(w), 839(w), 719(s), 677(w), 572(w), 551(w). *Anal.* Calc. for $C_{46}H_{42}N_2O_{10}Zn_2$ (913.56), **1**·$2(CH_3)_2CO$: C, 60.47; H, 4.64; N, 3.07. Found: C, 60.18; H, 4.61; N, 3.38%.

2.4. Synthesis of 1-D zigzag chain, $[Zn_2(O_2CC_6H_5)_2(\mu\text{-}N_2C_{12}H_{10})]$ **2**

2.4.1. **2**·$0.5H_2O$

151.8 mg (0.5 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 142.0 mg (0.1 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL solution of mixture of acetone, methanol and ethanol (2/2/2) of 1,2-bis(4-pyridyl)ethene (93.9 mg, 0.5 mmol). Suitable crystals of compound **2**·$0.5H_2O$ for X-ray analysis were obtained in a month. The yield was 50.3 mg (10.1%) for compound **2**·$0.5H_2O$. IR (KBr): ν(cm^{-1}) = 3420(brw), 3051(w), 1613(s), 1568(m), 1505(w), 1430(w), 1367(s), 1252(w), 1222(w), 1208(w), 1171(w), 1089(w), 1026(m), 842(m), 722(s), 683(w), 569(w), 553(w), 443(w). *Anal.* Calc. for $C_{52}H_{42}N_4O_9Zn_2$ (997.68), **2**·$0.5H_2O$: C, 62.60; H, 4.25; N, 5.62. Found: C, 62.81; H, 3.92; N, 5.57%.

2.4.2. **2**·$(CH_3)_2CO{\cdot}0.5H_2O$

37.9 mg (0.125 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 35.5 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL solution of mixture of acetone, methanol and ethanol (2/2/2) of 1,2-bis(4-pyridyl)ethane (47.0 mg, 0.25 mmol). Suitable crystals of compound **2**·$(CH_3)_2CO{\cdot}0.5H_2O$ for X-ray analysis were obtained in 10 days. The yield was 43.9 mg (33.3%) for compound **2**·$(CH_3)_2CO{\cdot}0.5H_2O$. IR (KBr): ν(cm^{-1}) = 3433(brw), 3049(w), 1710(w), 1614(s), 1572(m), 1507(w), 1434(w), 1346(m), 1251(w), 1224(w), 1210(w), 1069(w), 1026(m), 985(w), 838(m), 718(m), 687(w), 569(w), 551(m), 442(w). *Anal.* Calc. for $C_{55}H_{47}N_4O_{9.5}Zn_2$ (1046.71), **2**·$(CH_3)_2CO{\cdot}0.5H_2O$: C, 63.11; H, 4.54; N, 5.35. Found: C, 62.85; H, 4.37; N, 5.23%.

2.4.3. **2**·CH_3CH_2OH

37.9 mg (0.125 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 35.5 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL ethanol solution of 1,2-bis(4-pyridyl) ethene (47.0 mg, 0.25 mmol). Suitable crystals of compound **2**·CH_3CH_2OH for X-ray analysis were obtained in 10 days. The yield was 44.3 mg (66.1%) for compound **2**·CH_3CH_2OH. IR (KBr): ν(cm^{-1}) = 3421(brw), 3063(w), 1614(s), 1566(m), 1379(brm), 1252(w), 1224(w), 1209(w), 1173(w), 1069(w), 1026(w), 840(w), 719(m), 685(w), 553(m), 444(w). *Anal.* Calc. for $C_{28}H_{26}N_2O_5Zn$ (535.88), **2**·CH_3CH_2OH: C, 62.75; H, 4.90; N, 5.23. Found: C, 62,58; H, 4.93; N, 5.47%.

2.5. Synthesis of 1-D ladder type, $[Zn_2(\mu\text{-}O_2CC_6H_5)_2(O_2CC_6H_5)_2(\mu\text{-}N_2C_{12}H_{10})_2]$ **3**

2.5.1. **3**·$2(CH_3)_2CO$

37.9 mg (0.125 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 35.5 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)ethene (47.0 mg, 0.25 mmol). Suitable crystals of compound **3**·$2(CH_3)_2CO$ for X-ray analysis were obtained in half a month. The yield was 16.3 mg (11.9%) for compound **3**·$2(CH_3)_2CO$. IR (KBr): ν(cm^{-1}) = 3443(brw), 3057(w), 1607(s), 1567(s), 1504(w), 1368(brs), 1251(w), 1221(w), 1174(w), 1070(w), 1026(m), 978(w), 834(m), 720(m), 702(m), 683(w), 552(m), 435(w). *Anal.* Calc. for $C_{58}H_{52}N_4O_{10}Zn_2$ (1095.78), **3**·$2(CH_3)_2CO$: C, 63.57; H, 4.79; N, 5.11. Found: C, 63.71; H, 5.02; N, 4.82%.

2.5.2. **3**·$2CH_3OH$

37.9 mg (0.125 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 35.5 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)ethene (47.0 mg, 0.25 mmol). Suitable crystals of compound **3**·$2CH_3OH$ for X-ray analysis were obtained in a month. The yield was 15.8 mg (12.1%) for compound **3**·$2CH_3OH$. IR (KBr): ν(cm^{-1}) = 3421(brw), 3063(w), 1614(s), 1566(m), 1379(brm), 1252(w), 1224(w), 1209(w), 1173(w), 1069(w), 1026(w), 840(w), 719(m), 685(w), 553(m), 444(w). *Anal.* Calc. for $C_{54}H_{48}N_4O_{10}Zn_2$ (1043.70), **3**·$2CH_3OH$: C, 62.14; H, 4.65; N, 5.37. Found: C, 61.78; H, 4.51; N, 5.38%.

Bulk samples of **1**·$2CH_3CN$, **2**·$0.5H_2O$, and **3**·$2(CH_3)_2CO$ were checked by powder XRD (Figs. S1–S3).