

## Anion Effects on Crystal Structures of Cd<sup>II</sup> Complexes Containing 2,2'-Bipyridine: Photoluminescence and Catalytic Reactivity

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Anion effects on structures of Cd<sup>II</sup> complexes containing 2,2'-bipyridine (2,2'-bpy) ligands have been studied, and compared with Zn<sup>II</sup>-(2,2'-bpy) complexes. For each anion, different structures have been obtained in both Zn<sup>II</sup>-(2,2'-bpy) and Cd<sup>II</sup>-(2,2'-bpy). Polymeric structures of Cd<sup>II</sup>-2,2'-bpy complexes can be produced by hydrogen bonding interactions as shown in Zn<sup>II</sup>-2,2'-bpy complexes. In addition, the bigger size of a Cd<sup>II</sup> ion gives higher coordination numbers forming variety of structures, and it makes that chlorides can act as bridging ligands to form a one-dimensional structure. The compound **5** catalyzed efficiently the transesterification of a variety of esters with methanol, while the rest of the compounds have displayed very slow conversions. In addition, the emission bands of complexes **1**, **2**, **4**, and **6** are blue-shifted compared to the corresponding ligand 2,2'-bpy, whereas **3** and **5** showed the similar emission observed for the ligand.

**Key Words** : Cd<sup>II</sup> complexes, Photoluminescence, 2,2'-Bipyridine, Catalyst, Transesterification

### Introduction

Construction of coordination networks by self-assembly process has attracted considerable attention in the fields of supramolecular chemistry and crystal engineering,<sup>1-5</sup> because they have shown an intriguing variety of topologies and structural diversity and their potential applications as functional materials, such as gas storage,<sup>6,7</sup> photoluminescence,<sup>8,9</sup> catalysis,<sup>10-13</sup> magnetism,<sup>14</sup> and molecular sensing.<sup>15,16</sup> Therefore, many efforts have been devoted to the study of fundamental structural aspects to understand and control the several factors that affect the self-assembly of supramolecular architectures. There are several factors affecting the supramolecular assemblies, such as the coordination geometry of metal ions,<sup>17,18</sup> structure of organic ligands,<sup>19-22</sup> the hydrogen bonds,<sup>23-32</sup>  $\pi$ - $\pi$  stacking,<sup>4</sup> counter-anions,<sup>33-36</sup> pH value,<sup>38,39</sup> temperature,<sup>40,41</sup> ligand-to-metal ratio,<sup>42,43</sup> solvent system,<sup>44-48</sup> and template effect.<sup>49</sup> Among them, the anions play a very important role on the self-assembled construction.<sup>50</sup> For examples, we have recently shown that six new structures of Zn<sup>II</sup> complexes containing 2,2'-bipyridine (2,2'-bpy) ligands have been determined.<sup>37</sup> Halide anions were used as simple coordinating ligands to form a tetrahedral environment around a Zn<sup>II</sup> ion. Nitrate and benzoate anions were used as chelating ligands to form an octahedral environment. For non-coordinating ClO<sub>4</sub><sup>-</sup> and bridging SO<sub>4</sub><sup>2-</sup> anions, three 2,2'-bpy ligands chelate a Zn<sup>II</sup> to form an octahedral environment, and both ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions occupy empty positions between metal cations for charge balances. Polymeric structures of Zn<sup>II</sup>-2,2'-bpy complexes can be produced by hydrogen bonding. Moreover, [Zn(2,2'-bpy)(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] catalyzed efficiently the transesterification

reaction of esters with methanol under the neutral conditions, while the rest of compounds showed very slow conversions.

As a part of our continued interests (a) for a comparison of the structures and reactivities of Zn<sup>II</sup> and Cd<sup>II</sup> complexes with a chelating 2,2'-bipyridine ligand, (b) in the aim to fully understand the anion effect to the different metal ions (Zn vs. Cd), and (c) in order to find efficient catalysts capable of carrying out the transesterification reactions under mild reaction conditions, we have studied cadmium salts containing different counter-anions (Cl<sup>-</sup>,<sup>51,52</sup> Br<sup>-</sup>,<sup>53,54</sup> I<sup>-</sup>,<sup>55</sup> NO<sub>3</sub><sup>-</sup>,<sup>56,57</sup> C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub><sup>-</sup>,<sup>58</sup> ClO<sub>4</sub><sup>-</sup><sup>59,60</sup>).

We report here anion effects on six structures of Cd<sup>II</sup> complexes containing 2,2'-bipyridine ligands, and their fluorescence and catalytic activities for transesterification reactions have been also investigated.

### Experimental

**Materials.** Methanol, ethanol, acetone, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methylacetate, methylbenzoate, 2,2'-bipyridine, cadmium chloride, cadmium bromide, cadmium iodide, cadmium nitrate, ammonium benzoate, and cadmium perchlorate 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 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.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury 400 spectrometer. 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.

**Syntheses of  $[\text{Cd}(2,2'\text{-bpy})(\mu\text{-Cl})_2]_n$  (1),<sup>51,52</sup>  $[\text{Cd}(2,2'\text{-bpy})_2\text{X}_2]$  (X = Br for 2,<sup>53,54</sup> I for 3<sup>55</sup>),  $[\text{Cd}(2,2'\text{-bpy})_2(\text{NO}_3)_2][\text{Cd}(2,2'\text{-bpy})_2(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)$  (4),<sup>56,57</sup>  $[\text{Cd}(2,2'\text{-bpy})(\text{O}_2\text{CPh})_2(\text{H}_2\text{O})](\text{H}_2\text{O})$  (5),<sup>58</sup> and  $[\text{Cd}(2,2'\text{-bpy})_3](\text{ClO}_4)_2$  (6).<sup>59,60</sup>** Compounds 1-6 have been prepared by the literature procedures. All structures of 1-6 have been determined by X-ray crystallography.

**$[\text{Cd}(2,2'\text{-bpy})(\mu\text{-Cl})_2]_n$  (1):** 28.5 mg (0.125 mmol) of  $\text{CdCl}_2$  hemipentahydrate were dissolved in 4 mL  $\text{H}_2\text{O}$  and carefully layered by 4 mL ethanol solution of 2,2'-bpy ligand (39.4 mg, 0.25 mmol). Suitable crystals of compound 1 for X-ray analysis were obtained in 2 days. The yield was 42.5 mg (68.6%) for compound 1. IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3072 (w), 1593 (s), 1476 (m), 1440 (s), 1316 (w), 1170 (m), 1016 (s), 773 (s), 736 (s), 649 (w), 411 (w). Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{Cd}_2\text{Cl}_4\text{N}_4$  (678.97), 1: C, 35.38; H, 2.38; N, 8.25. Found: C, 35.53; H, 2.47; N, 7.98%.

**$[\text{Cd}(2,2'\text{-bpy})_2\text{Br}_2]$  (2):** 43.0 mg (0.125 mmol) of  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 4 mL  $\text{H}_2\text{O}$  and carefully layered by 4 mL methanol solution of 2,2'-bpy ligand (39.4 mg, 0.25 mmol). Suitable crystals of compound 2 for X-ray analysis were obtained in a day. The yield was 33.5 mg (45.8%) for compound 2.  $^1\text{H}$  NMR (DMSO, 400 MHz),  $\delta$  8.77 (d, 2H, pyridyl-H),  $\delta$  8.49 (d, 2H, pyridyl-H),  $\delta$  8.08 (t, 2H, pyridyl-H) and  $\delta$  7.60 (t, 2H, pyridyl-H). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3055 (w), 1592 (s), 1471 (s), 1436 (s), 1313 (m), 1172 (w), 1152 (w), 1057 (w), 1011 (s), 771 (s), 738 (m), 646 (w). Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{Br}_2\text{CdN}_4$  (584.59), 2: C, 41.09; H, 2.76; N, 9.59. Found: C, 40.85; H, 3.01; N, 9.62%.

**$[\text{Cd}(2,2'\text{-bpy})_2\text{I}_2]$  (3):** 73.9 mg (0.2 mmol) of  $\text{CdI}_2$  were dissolved in 4 mL  $\text{H}_2\text{O}$  and carefully layered by 4 mL a mixture solution (2 mL acetone, 1 mL ethanol, and 1 mL methanol) of 2,2'-bpy ligand (63.1 mg, 0.4 mmol). Suitable crystals of compound 3 for X-ray analysis were obtained in a few days. The yield was 52.16 mg (61.5%) for compound 3.  $^1\text{H}$  NMR (DMSO, 400 MHz)  $\delta$  8.76 (d, 2H, pyridyl-H),  $\delta$  8.51 (d, 2H, pyridyl-H),  $\delta$  8.11 (t, 2H, pyridyl-H) and  $\delta$  7.62 (t, 2H, pyridyl-H). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3055 (w), 1591 (s), 1470 (s), 1434 (s), 1311 (m), 1245 (w), 1174 (w), 1156 (w), 1060 (w), 1011 (s), 766 (s), 735 (m), 646 (w), 622 (w), 411 (w). Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{CdI}_2\text{N}_4$  (678.57), 3: C, 35.40; H, 2.38; N, 8.26. Found: C, 35.73; H, 2.51; N, 7.95%.

**$[\text{Cd}(2,2'\text{-bpy})_2(\text{NO}_3)_2][\text{Cd}(2,2'\text{-bpy})_2(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)$  (4):** 38.6 mg (0.125 mmol) of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 4 mL  $\text{H}_2\text{O}$  and carefully layered by 4 mL methanol solution of 2,2'-bpy ligand (39.4 mg, 0.25 mmol). Suitable crystals of compound 4 for X-ray analysis were

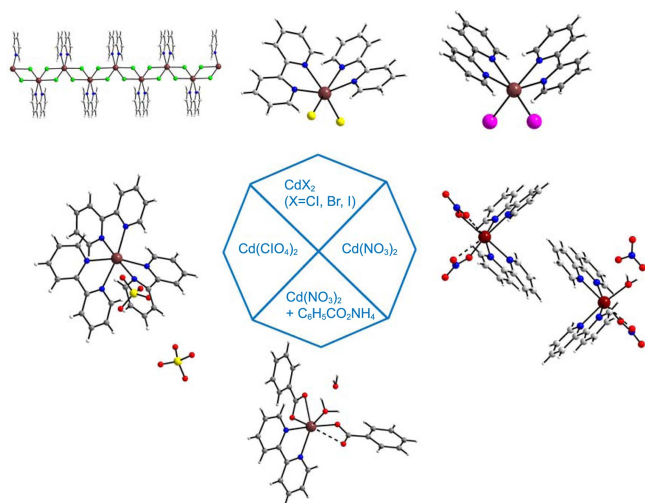
obtained in two months. The yield was 28.7 mg (41.9%) for compound 4.  $^1\text{H}$  NMR (DMSO, 400 MHz)  $\delta$  8.71 (d, 2H, pyridyl-H),  $\delta$  8.55 (d, 2H, pyridyl-H),  $\delta$  8.14 (t, 2H, pyridyl-H) and  $\delta$  7.65 (t, 2H, pyridyl-H). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3078 (w), 1603 (m), 1594 (m), 1568 (w), 1477 (m), 1439 (s), 1386 (s), 1290 (s), 1178 (w), 1157 (m), 1099 (w), 1062 (w), 1019 (s), 911 (w), 818 (m), 761 (s), 734 (s), 651 (s), 628 (s). Anal. Calcd. for  $\text{C}_{40}\text{H}_{34}\text{Cd}_2\text{N}_{12}\text{O}_{13}$  (1115.59), 4: C, 43.06; H, 3.08; N, 15.07. Found: C, 43.37; H, 2.86; N, 14.96%.

**$[\text{Cd}(2,2'\text{-bpy})(\text{O}_2\text{CPh})_2(\text{H}_2\text{O})](\text{H}_2\text{O})$  (5):** 38.6 mg (0.125 mmol) of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 34.8 mg (0.25 mmol) of ammonium benzoate were dissolved in 4 mL  $\text{H}_2\text{O}$  and carefully layered by 4 mL acetone solution of 2,2'-bpy ligand (39.4 mg, 0.25 mmol). Suitable crystals of compound 5 for X-ray analysis were obtained in a week. The yield was 39.9 mg (62.5%) for compound 5.  $^1\text{H}$  NMR (DMSO, 400 MHz)  $\delta$  8.82 (d, 2H, pyridyl-H),  $\delta$  8.52 (d, 2H, pyridyl-H),  $\delta$  8.10 (t, 2H, pyridyl-H),  $\delta$  7.95 (d, 2H, benzoate-H),  $\delta$  7.62 (t, 2H, pyridyl-H),  $\delta$  7.44 (m, 2H, benzoate-H) and  $\delta$  7.38 (m, 1H, benzoate-H). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3072 (w), 1597 (s), 1556 (s), 1476 (m), 1438 (m), 1390 (s), 1315 (w), 1171 (w), 1067 (m), 1017 (m), 831 (m), 771 (s), 735 (m), 717 (s), 677 (m), 649 (w). Anal. Calcd. for  $\text{C}_{24}\text{H}_{22}\text{CdN}_2\text{O}_6$  (546.84), 5: C, 52.71; H, 4.06; N, 5.12. Found: C, 72.84; H, 4.41; N, 5.48%.

**$[\text{Cd}(2,2'\text{-bpy})_3](\text{ClO}_4)_2$  (6):** 63.0 mg (0.2 mmol) of  $\text{Cd}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  were dissolved in 4 mL  $\text{H}_2\text{O}$  and carefully layered by 4 mL methanol solution of 2,2'-bpy ligand (63.1 mg, 0.4 mmol). Suitable crystals of compound 6 for X-ray analysis were obtained in a month. The yield was 61.54 mg (63.1%) for compound 6.  $^1\text{H}$  NMR (DMSO, 400 MHz)  $\delta$  8.67 (d, 2H, pyridyl-H),  $\delta$  8.48 (d, 2H, pyridyl-H),  $\delta$  8.06 (m, 2H, pyridyl-H) and  $\delta$  7.56 (m, 2H, pyridyl-H). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3567 (w), 3488 (w), 3064 (w), 1595 (s), 1489 (w), 1474 (m), 1438 (s), 1317 (w), 1249 (w), 1145 (s), 1089 (s), 1012 (m), 770 (s), 738 (m), 626 (s). Anal. Calcd. for  $\text{C}_{30}\text{H}_{24}\text{CdCl}_2\text{N}_6\text{O}_8$  (779.85), 6: C, 46.20; H, 3.10; N, 10.77. Found: C, 45.88; H, 3.27; N, 10.53%.

**Catalytic Activity of Compounds 1-6.** Catalytic reaction conditions: Ester (0.05 mmol) was dissolved in methanol (1 mL), and the compounds 1-6 (1.0 mg,  $1.47 \times 10^{-3}$  mmol for 1, 1.0 mg,  $1.71 \times 10^{-3}$  mmol for 2, 1.0 mg,  $1.47 \times 10^{-3}$  mmol for 3, 1.0 mg,  $0.90 \times 10^{-3}$  mmol for 4, 1.0 mg,  $1.83 \times 10^{-3}$  mmol for 5, and 1.0 mg,  $1.28 \times 10^{-3}$  mmol for 6) were added and shaken at 50 °C (450 rpm). Reaction conversion was monitored by GC/Mass analysis of 20  $\mu\text{L}$  aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average conversion yields are presented.

**Crystallography.** The diffraction data for all six compounds were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo  $\text{K}\alpha$  ( $\lambda = 0.71073$  Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SMART software package, and the structure was solved and refined using SHELXTL V6.12. The crystallographic data for compounds 1-6 are listed in Table S1, and the selected bond distances and angles are listed in Table S2.



**Scheme 1.** Structures of Cd<sup>II</sup> compounds containing 2,2'-bpy ligands.<sup>51-60</sup>

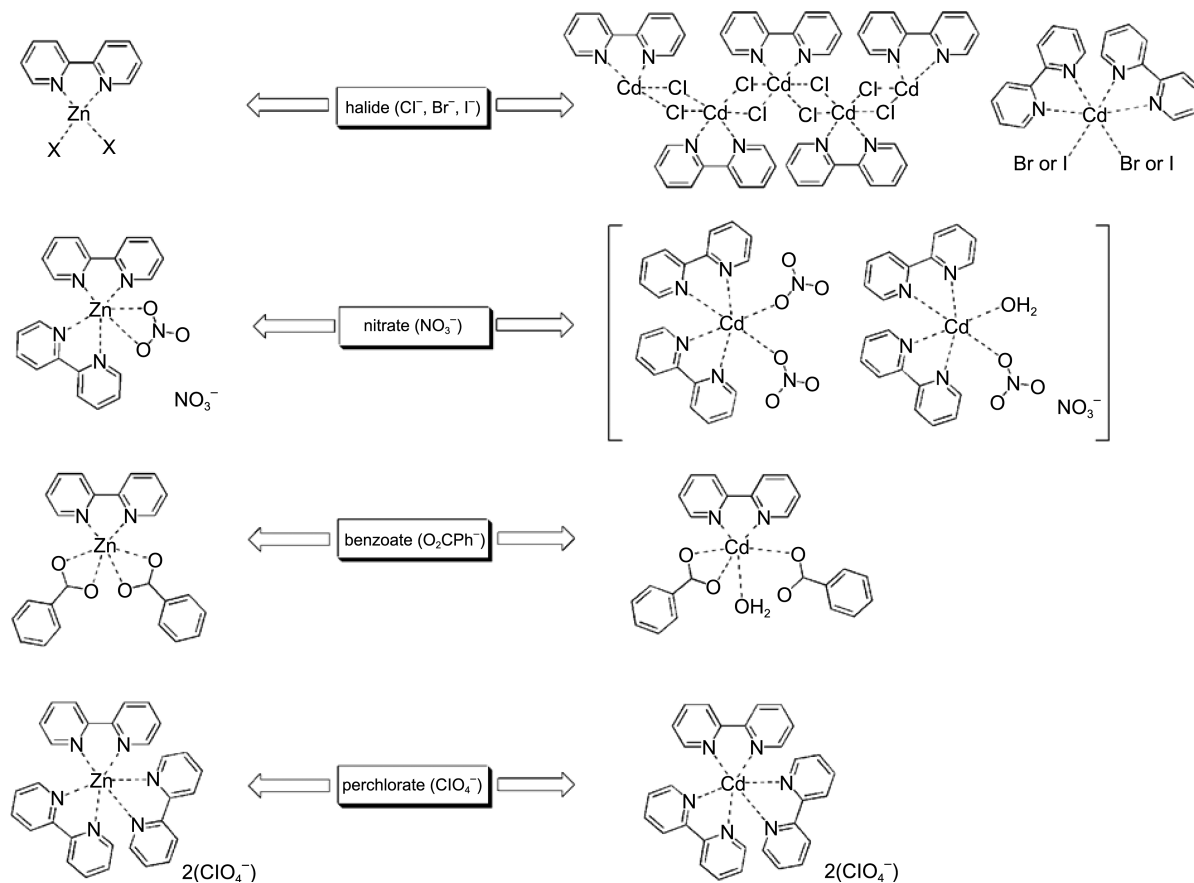
Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers: CCDC 849715 for **1**, 849714 for **2**, 849716 for **3**, 849712 for **4**, 849713 for **5**, and 849711 for **6**).

## Results and Discussion

In order to understand the anion effects on the construction of crystal structures with the rigid chelating 2,2'-bpy ligand,

we re-synthesized six compounds **1-6**. The structures of all six Cd<sup>II</sup> compounds containing 2,2'-bpy ligands are shown in the Scheme 1.

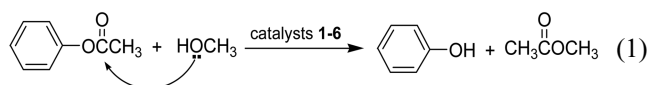
Anion effects of Zn<sup>II</sup> complexes containing chelating 2,2'-bpy ligands have been previously investigated,<sup>37</sup> and their structures have been compared with Zn<sup>II</sup> complexes containing other chelating Hdpa ligands.<sup>35</sup> To further investigate anion effects, the corresponding Cd<sup>II</sup> complexes containing a chelating ligand, 2,2'-bipyridine (2,2'-bpy), have been studied. Various cadmium salts (CdX<sub>2</sub> (X = Cl<sup>-</sup>,<sup>51,52</sup> Br<sup>-</sup>,<sup>53,54</sup> I<sup>-</sup><sup>55</sup>), Cd(NO<sub>3</sub>)<sub>2</sub>,<sup>56,57</sup> Cd(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>,<sup>58</sup> and Cd(ClO<sub>4</sub>)<sub>2</sub><sup>59,60</sup>) have been selected in this system. For each anion, different structures have been obtained in both Zn<sup>II</sup>-(2,2'-bpy) and Cd<sup>II</sup>-(2,2'-bpy) systems as shown in Scheme 2. Halide anions were used as simple coordinating ligands for the Zn<sup>II</sup> system. For the Cd<sup>II</sup> system, chloride anions bridge Cd<sup>II</sup> ions to form a one-dimensional structure while bromide and iodide anions act as simple coordinating ligands. The coordination geometry of a Cd<sup>II</sup> ion is octahedral while that of a Zn<sup>II</sup> ion is tetrahedral. Nitrate anions were used as monodentate ligands for the Cd<sup>II</sup> system while those were used as chelating ligands for the Zn<sup>II</sup> system. In addition, there are independent molecules containing two nitrates or both a nitrate and a water for this system. For benzoate anions, both Zn<sup>II</sup> and Cd<sup>II</sup> complexes have similar structures, but the Cd<sup>II</sup> complex contains a chelating benzoate, a monodentate benzoate, and a water ligands having octahedral geometry. For non-coordinating ClO<sub>4</sub><sup>-</sup> anions, three 2,2'-bpy



**Scheme 2.** Structures according to anions.

ligands chelate a  $Zn^{II}$  ion or a  $Cd^{II}$  ion. Polymeric structures of  $Cd^{II}$ -(2,2'-bpy) complexes can be produced by hydrogen bonding interactions as shown in  $Zn^{II}$ -(2,2'-bpy) complexes. These results confirm that inter-molecular hydrogen bonding interactions as well as anion effects play also very important roles in the construction of crystal structures in both  $Zn^{II}$ -(2,2'-bpy) and  $Cd^{II}$ -(2,2'-bpy) systems. In addition, the bigger size of a  $Cd^{II}$  ion gives higher coordination numbers forming variety of structures, and it makes that chlorides can act as bridging ligands to form a one-dimensional structure.

**Catalytic Transesterification Reactions by the Compounds 1-6.** We have previously reported that zinc and cadmium complexes containing a chelating 2,2-bipyridine and Hdpa ligands have shown efficient catalytic activities on transesterification reaction of a range of esters with methanol under the mild conditions.<sup>37,50,61,62</sup> These results led us to attempt the transesterification reaction using the compounds 1-6, in order to make a comparison of the reactivities of compounds 1-6 with  $Zn^{II}$  and  $Cd^{II}$  complexes having chelating 2,2-bipyridine and Hdpa ligands. Treatment of phenyl acetate and methanol in the presence of 1-6 at 50 °C produced methyl acetate quantitatively within 1 day for 5 and 8 days for 4, respectively, under the neutral conditions (eq. 1), while complexes 1, 2, 3, and 6 showed very slow conversions (50-100 days). Little transesterification occurred without the catalysts 1-6 in the same time period.<sup>37</sup>



Compound 5 with two labile benzoate ligands was most efficient and the reactivity of 5 is the best among the catalytic systems reported previously in Cd-containing coordination and polymeric compounds including the chelating 2,2-bipyridine and Hdpa ligands, to our best knowledge.<sup>18,50,63</sup>

Next, we have examined further the transesterification of other esters with 5 and the results are shown in Table 1. The substrates *p*-nitrophenyl acetate and benzoate with the electron-withdrawing substituent have undergone faster transesterification (0.21 and 3 days, entries 1 and 4). Moreover, *para*-substituted phenyl acetate groups (entries 1-3) have displayed better reactivity than *para*-substituted phenyl benzoate groups (entries 4-7). Furthermore, vinyl acetate was converted effectively to the product methyl acetate within 0.17 days by 5. The catalytic reactivity of 5 is comparable to those of Zn catalysts which are well known as the efficient catalysts for the transesterification reactions.<sup>37,61,62,64</sup>

**Photoluminescence Property.** The emission spectra of  $Cd^{II}$  complexes 1-6, together with that of the ligand 2,2'-bpy, were measured in the solid state at room temperature (Figure 1), based on their UV-vis spectra (Figure S1). Strong emission of compound 1 was observed at 369 nm ( $\lambda_{\text{ex}} = 285$  nm), but relatively very weak luminescences were observed under the same experimental conditions at 377-390 nm ( $\lambda_{\text{ex}} = 285$  nm) for 2, 415-430 nm ( $\lambda_{\text{ex}} = 285$  nm) for 3, 348 nm ( $\lambda_{\text{ex}} = 285$  nm) for 4, 415-430 nm ( $\lambda_{\text{ex}} = 285$  nm) for 5, 346 nm ( $\lambda_{\text{ex}} =$

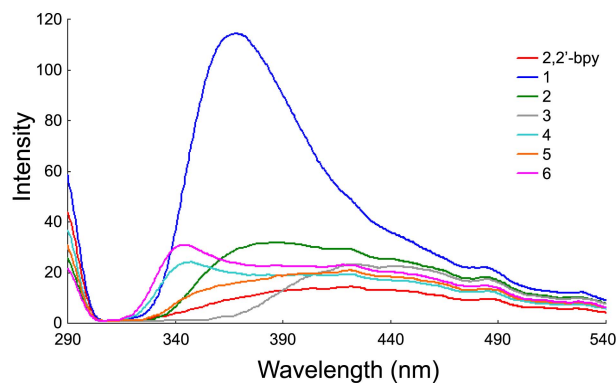
**Table 1.** Transesterification of esters by methanol in the presence of compound 5 at 50 °C<sup>a</sup>

Entry	Substrate	5
		(time/days) <sup>b</sup>
1	4-Nitrophenyl acetate	0.21
2	Phenyl acetate	1
3	4-Methylphenyl acetate	2
4	4-Nitrophenyl benzoate <sup>c</sup>	3
5	4-Chlorophenyl benzoate	3
6	Phenyl benzoate	4
7	4-Methylphenyl benzoate	4
8	Vinyl acetate	0.17

<sup>a</sup>All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters; 0.05 mmol, catalyst; 1.0 mg,  $1.83 \times 10^{-3}$  mmol for 5, solvent; methanol (1 mL). See the experimental section for the detailed reaction conditions.

<sup>b</sup>Time necessary for the complete conversion of substrate to product.

<sup>c</sup>The solvent was a mixture of  $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$  (1/1) because of low solubility of substrate in  $\text{CH}_3\text{OH}$ .



**Figure 1.** Emission spectra of complexes 1-6 and ligand (2,2'-bpy) at room temperature.

285 nm) for 6, and 415-430 nm ( $\lambda_{\text{ex}} = 285$  nm) for 2,2'-bpy, respectively. The emission bands of complexes 1, 2, 4, and 6 are blue-shifted compared to the corresponding ligand 2,2'-bpy, which indicates that the emission peaks of 1, 2, 4, and 6 may be due to the metal-to-ligand charge transfer (MLCT) and/or ligand-to-metal charge transfer (LMCT).<sup>37</sup> Such emissions of complexes 3 and 5 can be tentatively assigned to the intraligand transition of 2,2-bpy ligand, since the similar emission was observed for the ligand. Moreover, it is worthwhile to mention that the intense emission of 1 at room temperature may be a good candidate for a potential hybrid inorganic-organic photoactive material.<sup>65,66</sup>

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**Appendix A. Supplementary Data.** Table S1. The crystallographic data for compounds **1-6** and Table S2. The selected bond distances and angles. CCDC 849715 for **1**, 849714 for **2**, 849716 for **3**, 849712 for **4**, 849713 for **5**, and 849711 for **6** contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Figure S1. UV-Vis spectra of compounds **1-6**. Supplementary data associated with this article can be found, in the online version, at [doi:http://dx.doi.org/](http://dx.doi.org/)

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