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Construction of Cd(II) compounds with a chelating ligand 2,2'-dipyridiylamine (Hdpa): Anion effect, catalytic activities and luminescence

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ABSTRACT

Six new structures of Cd(II) complexes containing Hdpa ligands have been determined. With chloride and bromide, Cd(II) ions produce halide-bridged dinuclear units **1** and **2** while Cdl₂ produces mononuclear unit **3** without halide-bridging. Cd(II) ions produce mono-Hdpa complex **4** with chelating benzoate, di-Hdpa complex **5** with coordinating NO₃⁻ anion, and tri-Hdpa complexes **6** and **7** with non-coordinating ClO_4^- and BF_4^- anions. One-, two-, or three-dimensional structures of Cd(II)-Hdpa complexes can be produced by hydrogen bonding interactions and π - π interactions. The compounds **4**, **5**, and **6** catalyzed efficiently the transesterification of a variety of esters with methanol, while **1**, **2**, **3** and **7** have displayed a very slow conversion. The transesterification reactivity shown by the catalyst **6** is very efficient and the best among the compounds **1**–**7**. In addition, all compounds **1**–**7** and ligand (Hdpa) have shown the similar luminescent properties at $\lambda_{max} = 352$ nm which suggest that their emissions seem to be attributed to the π - π^* intraligand fluorescence.

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1. Introduction

Construction of coordination networks [1–6] by self-assembly process has been affected by the hydrogen bonds [7–16], $\pi - \pi$ stacking [17], and anion effect [18-23] as well as ligand design [24] and coordination numbers [25,26]. Among them, anion effect has been realized as a very important role on the self-assembled construction when anions can be coordinated to the metal centers. In recent years, we and others have shown that 2,2'dipyridylamine(Hdpa) as a chelating ligand mostly formed mononuclear Zn(II) complexes (zinc salts used; (Zn(NO₃)₂, Zn(CN)₂, Zn(O₂CCH₃)₂, Zn(O₂CC₆H₅)₂, Zn(ClO₄)₂, Zn(BF₄)₂, ZnCl₂, ZnBr₂, ZnI₂, and Zn(CF₃SO₃)₂)) [27-31], and then these Zn(II) complexes can be used as building blocks for one- or two-dimensional structures through weak hydrogen bonding and π - π interactions. With sulfate anion, the chelating ligand 2,2'-dipyridylamine(Hdpa), unexpectedly, forms a one-dimensional chain compound [30]. These results demonstrated that both anion effect and intermolecular hydrogen bonds are very important roles for formation of crystal structures in Zn(II)-Hdpa system. Some of Zn(II) complexes containing Hdpa have shown, surprisingly, unusual heterogeneous catalytic activities on transesterification reaction of esters [30,31].

As a part of our continued interests in the syntheses, structures, and reactivities of coordination complexes with chelating Hdpa ligands, and with the aim to fully understand the anion effect on construction of metal complexes in order to find efficient catalysts to mediate various catalytic reactions that could be carried out under mild reaction conditions, we employed cadmium salts with different counter-anions (halides, benzoate, nitrate [32], perchlorate, and tetrafluoroborate) to develop new Cd(II) complexes. Here we report the structures of several Cd(II) complexes with Hdpa, and compare them with Zn(II) complexes, and examine their catalytic activities and luminescence.

2. Experimental

2.1. Materials

2,2'-Dipyridylamine (Hdpa), methanol, ethanol, acetone, isopropyl ether, methylene chloride, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methyl acetate, methyl benzoate, ammonium benzoate, and cadmium salts were purchased from Aldrich and were used as received. 4-Fluorophenyl acetate and 4nitrophenyl benzoate were obtained from Lancaster.



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2.2. 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. 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.

2.3. Syntheses of $[{Cd(Hdpa)Cl(H_2O)}_2(\mu-Cl)_2]$ (1), $[{Cd(Hdpa)Br}_2(\mu-Br)_2]$ (2), and $[{Cd(Hdpa)I_2}]$ (3)

28.5 mg (0.125 mmol) of CdCl₂ hemipentahydrate were dissolved in 4 mL H₂O and carefully layered by 4 mL acetone solution of 2,2'-dipyridylamine ligand (42.8 mg, 0.25 mmol). Suitable crystals of compound **1** for X-ray analysis were obtained in 3 weeks. The yield was 47.7 mg (64.0%) for compound **1**. ¹H NMR (DMSO, 300 MHz): δ 9.70 (s, 1H, N–H) and δ 8.23, 7.66 and 6.87 (m, 8H, pyridyl-H). IR (KBr): $v(\text{cm}^{-1}) = 3485(\text{brm})$, 3308(brm), 3209(s), 3149(m), 1644(s), 1581(s), 1531(s), 1487(s), 1425(s), 1383(m), 1278(s), 1229(s), 1158(s), 1060(s), 1005(s), 909(s), 868(s), 832(m), 769(s), 696(m), 640(brm), 523(s). *Anal.* Calc. for C₂₀H₂₂Cd₂Cl₄N₆O₂ (745.04), **1**: C, 32.24; H, 2.98; N, 11.28. Found: C, 32.47; H, 2.78; N, 11.20%.

Tubic 1	Table	1
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43.0 mg (0.125 mmol) of CdBr₂·4H₂O and 2,2'-dipyridylamine ligand (42.8 mg, 0.25 mmol) were stirred in 10 mL methanol for 15 h at room temperature and carefully layered by 3 mL isopropyl ether. Suitable crystals of compound **2** for X-ray analysis were obtained in 2 months. The yield was 35.0 mg (30.2%) for compound **2**. ¹H NMR (DMSO, 300 MHz): δ 9.67 (s, 1H, N–H) and δ 8.21, 7.68 and 6.86 (m, 8H, pyridyl-H). IR (KBr): $\nu(\text{cm}^{-1}) = 3282(\text{m})$, 3196(w), 1623(s), 1581(s), 1523(s), 1461(s), 1415(s), 1349(s), 1270(m), 1232(s), 1157(s), 1056 (m), 1005(s), 903(s), 874(w), 842(w), 768(s), 743(w), 718(w), 634(brm), 598(w), 529(s), 411(s). Anal. Calc. for C₂₀H₁₈Br₄Cd₂N₆ (886.84), **2**: C, 27.08; H, 2.05; N, 9.48. Found: C, 26.89; H, 2.13; N. 9.41%.

45.8 mg (0.125 mmol) of CdI₂ were dissolved in 4 mL methanol and carefully layered by 4 mL methylene chloride solution of 2,2'dipyridylamine ligand (42.8 mg, 0.25 mmol). Suitable crystals of compound **3** for X-ray analysis were obtained in a month. The yield was 23.1 mg (34.0%) for compound **3**. ¹H NMR (DMSO, 300 MHz): δ 9.69 (s, 1H, N–H) and δ 8.22, 7.66 and 6.87 (m, 8H, pyridyl-H). IR (KBr): $v(\text{cm}^{-1}) = 3349(\text{brs})$, 1630(s), 1583(s), 1523(s), 1480(s), 1377(s), 1270(m), 1226(s), 1159(s), 1059 (m), 1011(s), 908(m), 829(m), 770(s), 645(m), 607(w), 565(\text{brm}), 514(s), 409(s). Anal. Calc. for C₁₀H₇CdI₂N₃ (535.39), **3**: C, 22.43; H, 1.32; N, 7.85. Found: C, 22.61; H, 1.33; N, 7.62%.

2.4. Synthesis of $[Cd(Hdpa)(O_2CC_6H_5)_2]$ (4)

38.6 mg (0.125 mmol) of Cd(NO₃)₂·4H₂O and 34.8 mg (0.25 mmol) of ammonium benzoate were dissolved in 4 mL

5 6 1	1						
	1	2	3	4	5 ^a	6	7
Empirical formula	C ₂₀ H ₂₂ Cd ₂ Cl ₄ N ₆ O ₂	C ₂₀ H ₁₈ Br ₄ Cd ₂ N ₆	C ₁₀ H ₇ CdI ₂ N ₃	$C_{24}H_{19}CdN_3O_4$	C ₂₀ H ₁₈ CdN ₈ O ₆	C ₃₀ H ₂₇ CdCl ₂ N ₉ O ₈	C30H27B2CdF8N9
Formula weight	745.04	886.82	535.39	525.82	578.82	824.91	799.63
T (K)	293(2)	293(2)	170(2)	170(2)	170(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	ΡĪ	ΡĪ	P2 ₁ /c	$P2_1/n$	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	7.0014(19)	8.5690(10)	13.342(3)	7.5480(15)	8.6546(12)	19.3572(12)	19.208(4)
b (Å)	9.959(3)	8.6892(11)	8.1330(16)	16.603(3)	16.497(2)	11.0908(7)	10.969(2)
c (Å)	10.386(3)	9.4616(12)	12.958(3)	17.683(3)	7.7313(11)	15.8297(9)	15.868(3)
α (°)	109.838(4)	105.007(2)	90.00	90.00	90.00	90.00	90.00
β (°)	98.966(4)	110.066(2)	103.08(3)	101.057(3)	94.572(2)	102.8440(10)	102.65(3)
γ (°)	107.849(4)	95.899(2)	90.00	90.00	90.00	90.00	90.00
V (Å ³)	620.5(3)	624.74(13)	1369.6(5)	2174.9(7)	1100.3(3)	3313.4(3)	3262.1(11)
Ζ	1	1	4	4	2	4	4
Density (calc.) (Mg/m ³)	1.994	2.357	2.596	1.606	1.747	1.654	1.628
Absorption coefficient (mm ⁻¹)	2.175	8.188	6.080	1.040	1.049	0.885	0.753
Crystal size (mm ³)	$0.10 \times 0.05 \times 0.05$	$0.10 \times 0.08 \times 0.08$	$0.35 \times 0.10 \times 0.10$	$0.20 \times 0.15 \times 0.15$	$0.15 \times 0.05 \times 0.03$	$0.10 \times 0.08 \times 0.06$	$0.25 \times 0.10 \times 0.10$
Reflections	3479	3513	7108	12 020	6023	18 080	17 926
Independent reflections	2379 [0.0549]	2405 [0.1116]	2628 [0.0367]	4277 [0.0678]	2160 [0.0636]	6506 [0.0400]	6413 [0.0212]
Data/restraints/	2379/0/166	2405/1/149	2628/0/165	4277/0/294	2160/1/164	6506/3/458	6413/0/457
parameters	2373707100	2 103/1/1 13	2020/0/103	1277 0 23 1	2100/1/101	0500151 150	0113/0/137
Goodness-of-fit (GOF) on F^2	0.977	0.854	1.092	0.858	0.866	0.913	1.048
Final R indices	$R_1 = 0.0355$,	$R_1 = 0.0542$,	$R_1 = 0.0430$,	$R_1 = 0.0299,$	$R_1 = 0.0322$,	$R_1 = 0.0399$,	$R_1 = 0.0416$,
$[I > 2\sigma(I)]$	$wR_2 = 0.0845$	$wR_2 = 0.1155$	$wR_2 = 0.1199$	$wR_2 = 0.0582$	$wR_2 = 0.0703$	$wR_2 = 0.1012$	$wR_2 = 0.1180$
R indices (all data)	$R_1 = 0.0389$,	$R_1 = 0.0702$,	$R_1 = 0.0484$,	$R_1 = 0.0400$,	$R_1 = 0.0468$,	$R_1 = 0.0603$,	$R_1 = 0.0485$,
	$wR_2 = 0.0852$	$wR_2 = 0.1186$	$wR_2 = 0.1240$	$wR_2 = 0.0593$	$wR_2 = 0.0719$	$wR_2 = 0.1054$	$wR_2 = 0.1242$
Largest difference in peak and hole (e Å ⁻³)	1.207 and -1.064	2.027 and -1.570	1.189 and -1.138	0.607 and -0.740	0.956 and -0.758	1.171 and -0.637	0.837 and –0.892

^a The crystal structure of **5** was re-determined, and all the parameters were similar to the results reported by Amma et al. [32].

H₂O and carefully layered by a mixture solution (2 mL acetone, 1 mL ethanol, and 1 mL methanol) of 2,2'-dipyridylamine ligand (42.8 mg, 0.25 mmol). Suitable crystals of compound **4** for X-ray analysis were obtained in 3 weeks. The yield was 22.8 mg (34.7%) for compound **4**. ¹H NMR (DMSO, 300 MHz): δ 9.68 (s, 1H, N–H), δ 7.96 and 7.42 (m, 10H, benzoate-H), and δ 8.21, 7.70 and 6.86 (m, 8H, pyridyl-H). IR (KBr): $v(\text{cm}^{-1}) = 3321(\text{w})$, 3213(w), 3069(w), 1647(s), 1596(s), 1538(s), 1484(s), 1397(s), 1233(m), 1163(m), 854(m), 772(s), 731(s), 685(m), 520(w), 432(w). Anal. Calc. for C₂₄H₁₉CdN₃O₄ (525.82), **4**: C, 54.82; H, 3.65; N, 8.00. Found: C, 54.65; H, 3.83; N, 8.22%.

2.5. Synthesis of [Cd(Hdpa)₂(NO₃)₂] (5)

Complex 5 has been synthesized and its structure was reported previously [32], but we re-synthesized, re-collected data and redetermined the structure.

38.6 mg (0.125 mmol) of Cd(NO₃)₂·4H₂O were dissolved in 4 mL methanol and carefully layered by acetone solution of 2,2'-dipyridylamine ligand (42.8 mg, 0.25 mmol). Suitable crystals of compound **5** for X-ray analysis were obtained in a week. The yield was 43.9 mg (60.6%) for compound **5**. ¹H NMR (DMSO, 300 MHz): δ 9.67 (s, 1H, N–H) and δ 8.20, 7.65 and 6.86 (m, 8H, pyridyl-H). IR (KBr): $v(\text{cm}^{-1})$ = 3305(s), 3202(m), 1629(s), 1580(s), 1527(s),



Scheme 1. Structures according to anions.

1479(s), 1328(brs), 1270(m), 1236(s), 1161(s), 1051(m), 882(m), 819(w), 773(s), 639(m), 527(m), 418(m). Anal. Calc. for $C_{20}H_{18}CdN_8O_6$ (578.82), **5**: C, 41.50; H, 3.14; N, 19.36. Found: C, 41.32; H, 3.10; N, 19.51%.

2.6. Syntheses of $[Cd(Hdpa)_3(ClO_4)_2]$ (**6**) and $[Cd(Hdpa)_3(BF_4)_2]$ (**7**)

38.9 mg (0.125 mmol) of Cd(ClO₄)₂·H₂O were dissolved in 4 mL H₂O and carefully layered by 4 mL acetone solution of 2,2'-dipyridylamine ligand (42.8 mg, 0.25 mmol). Suitable crystals of compound **6** for X-ray analysis were obtained in 2 months. The yield was 18.5 mg (27.0%) for compound **6**. ¹H NMR (DMSO, 300 MHz): δ 9.67 (s, 1H, N–H) and δ 8.21, 7.67 and 6.86 (m, 8H, pyridyl-H). IR (KBr): ν (cm⁻¹) = 3340(brs), 3148(w), 1631(s), 1582(s), 1530(s), 1472(s), 1434(w), 1419(w), 1355(s), 1273(w), 1233(s), 1161(m), 1094(brs), 1000(m), 903(w), 770(s), 621(s), 527(m), 415(w). Anal. Calc. for C₃₀H₂₇CdCl₂N₉O₈ (824.91), **6**: C, 43.68; H, 3.31; N, 15.29. Found: C, 43.82; H, 3.52; N, 15.21%.

35.8 mg (0.125 mmol) of Cd(BF₄)₂ 45% solution in water and 2,2'-dipyridylamine ligand (42.8 mg, 0.25 mmol) were stirred in 10 mL methanol for 15 h at room temperature and carefully layered by 16 mL isopropyl ether. Suitable crystals of compound **7** for X-ray analysis were obtained in a week. The yield was 13.8 mg (17.0%) for compound **7**. ¹H NMR (DMSO, 300 MHz): δ 9.73 (s, 1H, N–H) and δ 8.21, 7.67 and 6.88 (m, 8H, pyridyl-H). IR (KBr): ν (cm⁻¹) = 3294(m), 1631(s), 1582(s), 1530(m), 1476(s), 1435(m), 1419(w), 1352(m), 1232(m), 1160(m), 1083(s),

1032(w), 766(s), 526(w). *Anal.* Calc. for C₃₀H₂₇B₂CdF₈N₉ (799.63), **7**: C, 45.06; H, 3.41; N, 15.77. Found: C, 44.93; H, 3.32; N, 16.01%.

2.7. Catalytic activity of compounds 1-7

Catalytic transesterification reaction conditions: Esters (0.05 mmol) were dissolved in methanol (1 mL), and the catalyst (1.0 mg, 1.34×10^{-3} mmol for **1**, 1.0 mg, 1.13×10^{-3} mmol for **2**, 1.0 mg, 1.87×10^{-3} mmol for **3**, 1.0 mg, 1.90×10^{-3} mmol for **4**, 1.0 mg, 1.73×10^{-3} mmol for **5**, 1.0 mg, 1.21×10^{-3} mmol for **6**, and 1.0 mg, 1.25×10^{-3} mmol for **7**) was added and shaken at room temperature (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.

2.8. X-ray crystallography

The diffraction data for compounds **1–7** were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo K α (λ = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12 [33]. Hydrogen atoms were located in the calculated positions. The crystallographic data for compounds **1–7** are listed in Table 1.



Fig. 1. (a) Structure of [{Cd(Hdpa)(OH₂)(Cl)}₂(µ-Cl)₂] (1) with 50% ellipsoid. All hydrogen atoms are omitted for clarity. (b) Two-Dimensional structure derived by inter- and intra-hydrogen bonds.

3. Results and discussion

Hdpa has been used as a chelating ligand to mostly form mononuclear Zn(II) complexes [27–31], and then these Zn(II) complexes

Table 2

Selected bond distances for compounds 1–7.

1			
Cd(1)–N(3)	2.316(4)	Cd(1)-N(1)	2.333(4)
Cd(1)-O(1)	2.400(4)	Cd(1)-Cl(1)	2.6186(13)
Cd(1)-Cl(2)	2.6209(12)	Cd(1)-Cl(2)#1	2.6261(13)
Cl(2)-Cd(1)#1	2.6262(13)		
N(3)-Cd(1)-N(1)	80.90(12)	N(3)-Cd(1)-O(1)	87.63(13)
N(1)-Cd(1)-O(1)	93.11(14)	N(3)-Cd(1)-Cl(1)	101.41(9)
N(1)-Cd(1)-Cl(1)	94.21(9)	O(1)-Cd(1)-Cl(1)	169.16(10)
N(3)-Cd(1)-Cl(2)	169.77(9)	N(1)-Cd(1)-Cl(2)	96.32(9)
O(1)-Cd(1)-Cl(2)	82.68(10)	Cl(1)-Cd(1)-Cl(2)	88.58(4)
N(3) - Cd(1) - Cl(2) = 1	94.72(9)	N(1) - Cd(1) - Cl(2) = 1	173.75(8)
O(1) - Cd(1) - Cl(2) = 1	82.20(12)	CI(1) - Cd(1) - CI(2) = 1	91.02(4)
Cl(2) - Cd(1) - Cl(2) = 1	87.22(3)	Cd(1) - Cl(2) - Cd(1) # 1	92.78(3)
Symmetry transformations used to generate equiva	lient atoms: $\#1 - x + 1$, $-y + 1$, $-z + 1$		
2			
Cd(1)-N(3)	2.284(7)	Cd(1)–N(1)	2.307(7)
Cd(1)-Br(2)	2.5349(11)	Cd(1)-Br(1)#1	2.7635(11)
Cd(1)-Br(1)	2.7729(11)	Br(1)-Cd(1)#1	2.7634(11)
N(3)-Cd(1)-N(1)	82.3(2)	N(3)-Cd(1)-Br(2)	112.58(17)
N(1)-Cd(1)-Br(2)	103.16(16)	N(3)-Cd(1)-Br(1)#1	90.92(17)
N(1)-Cd(1)-Br(1)#1	152.29(16)	Br(2)-Cd(1)-Br(1)#1	104.25(4)
N(3)-Cd(1)-Br(1)	138.69(17)	N(1)-Cd(1)-Br(1)	85.79(17)
Br(2)-Cd(1)-Br(1)	108.62(4)	Br(1)#1-Cd(1)-Br(1)	81.72(3)
Symmetry transformations used to generate equiva	lent atoms: $\#1 - x + 1$, $-y + 1$, $-z + 1$		
3			
N(1)-Cd(1)	2.260(6)	N(3) - Cd(1)	2,259(6)
Cd(1) - I(2)	2,6900(8)	Cd(1) - I(1)	2,6956(8)
N(3) - Cd(1) - N(1)	84 2(3)	N(3) - Cd(1) - I(2)	110 95(15)
N(1)-Cd(1)-I(2)	115.49(14)	N(3)-Cd(1)-I(1)	113.61(15)
N(1)-Cd(1)-I(1)	113.23(14)	I(2) - Cd(1) - I(1)	115.48(3)
· · · · · · · · · · · · · · · · · · ·			
4 C-{(1), O(11)	2 2449(10)		2 274(2)
Cd(1) = O(11)	2.2446(19)	Cu(1) = N(3)	2.274(2)
Cd(1) = N(1)	2.200(2)	Cl(1) = O(21)	2.5210(19)
Cd(1) = O(22)	2.5000(19)	Cd(1) = O(12)	2.4421(10)
C(1) - C(11) O(11) - C(11) - N(2)	2.071(3)	C((1) - C(21)) O(11) Cd(1) N(1)	2.090(3)
N(2) Cd(1) N(1)	103.27(7)	O(11) - Cd(1) - N(1) O(11) - Cd(1) - O(21)	1/2 20(7)
N(2) - Cd(1) - N(1)	100 20(7)	N(1) = Cd(1) = O(21)	143.39(7)
O(11) Cd(1) O(21)	100.30(7)	N(1) - Cd(1) - O(21) N(2) - Cd(1) - O(22)	99.00(7)
N(1) - Cd(1) - O(22)	154 91(7)	O(21) - O(1) - O(22)	55 83(7)
O(11) Cd(1) O(12)	55 02(6)	N(2) Cd(1) - O(22)	157 45(7)
N(1) Cd(1) O(12)	06 29(7)	O(21) Cd(1) O(12)	102.09(6)
N(1) - Cd(1) - O(12) O(22) - Cd(1) - O(12)	90.28(7)	O(21) - CO(12)	102.08(0)
O(22) - Cu(1) - O(12)	54.09(7)		
6			
Cd(1)–N(31)	2.302(3)	Cd(1) - N(11)	2.319(3)
Cd(1)-N(21)	2.341(3)	Cd(1)–N(33)	2.360(3)
Cd(1) - N(23)	2.365(3)	Cd(1)-N(13)	2.373(3)
N(31)-Cd(1)-N(11)	92.98(12)	N(31)-Cd(1)-N(21)	173.23(11)
N(11)-Cd(1)-N(21)	93.14(12)	N(31)-Cd(1)-N(33)	77.81(11)
N(11)-Cd(1)-N(33)	93.55(12)	N(21)-Cd(1)-N(33)	98.90(11)
N(31)-Cd(1)-N(23)	95.38(12)	N(11) - Cd(1) - N(23)	162.79(12)
N(21) - Cd(1) - N(23)	79.49(12)	N(33)-Cd(1)-N(23)	102.90(12)
N(31) - Cd(1) - N(13)	95.31(11)	N(11)-Cd(1)-N(13)	76.38(12)
N(21)-Cd(1)-N(13)	88.96(11)	N(33)-Cd(1)-N(13)	167.62(12)
N(23)-Cd(1)-N(13)	87.87(12)		
7			
Cd(1)-N(33)	2.307(3)	Cd(1)-N(21)	2.316(3)
Cd(1)-N(11)	2.342(3)	Cd(1)-N(13)	2.359(3)
Cd(1)-N(31)	2.365(3)	Cd(1)-N(23)	2.374(3)
N(33)-Cd(1)-N(21)	92.33(10)	N(33)-Cd(1)-N(11)	173.82(9)
N(21)-Cd(1)-N(11)	92.80(10)	N(33)-Cd(1)-N(13)	96.06(10)
N(21)-Cd(1)-N(13)	162.30(10)	N(11)-Cd(1)-N(13)	79.95(10)
N(33)-Cd(1)-N(31)	77.54(10)	N(21)-Cd(1)-N(31)	94.32(11)
N(11)-Cd(1)-N(31)	98.63(10)	N(13)-Cd(1)-N(31)	102.69(11)
N(33)-Cd(1)-N(23)	94.75(10)	N(21)-Cd(1)-N(23)	76.54(11)
N(11)-Cd(1)-N(23)	89.79(10)	N(13)-Cd(1)-N(23)	87.23(10)
N(31)-Cd(1)-N(23)	167.92(10)		

zoate, nitrate, perchlorate, and tetrafluoroborate) have been adopted in this system. For each anion, different structures have been obtained in both Zn(II) and Cd(II) systems as shown in Scheme 1. Halide anions can be used as bridging ligands in Cd(II) system while they were used for Zn(II) ions as simple coordinating ligands. For halide ligands, smaller Zn(II) ion prefers tetrahedral geometry, but depending on the size of the halide ions, the coordination on Cd(II) ion changes from octahedral in 1 to trigonal bipyramidal in 2 and tetrahedral in 3. Compounds 1 and 2 form dimeric compounds by halide bridges, and hydrogen bond interactions provide two- and three-dimensional structures. In addition, the bridging capability decreases from chloride down to iodide as described below. Benzoate anions were used as chelating ligands in both Zn(II) and Cd(II) systems with very similar structures. Nitrate anions were used as chelating ligands for Zn(II) ions, in contrast they can be used simple O-donor coordinating ligands for Cd(II) ions. Its structure was reported previously [32]. For non-coordinating ClO_4^- and BF_4^- anions, Cd(II) produces the same cation complexes containing three chelating Hdpa ligands with octahedral environments, but previous Zn(II) complexes showed different structures in those anions. Both anions for Cd(II) ions occupy empty positions between metal cations for charge balances. One-, two-, and three-dimensional structures of Cd(II)–Hdpa complexes can be produced by hydrogen bonding interactions and π - π interactions as shown in Zn(II)-Hdpa complexes. These results confirm

Table 3

Hydrogen bonds for compounds 1-7.

that both inter-molecular hydrogen bonds and π - π interactions as well as anion effects play also very important roles in the construction of crystal structures in Cd(II) system. In addition, the bigger size of a Cd(II) ion compared to that of a Zn(II) ion gives variety of structures, and it makes that halides can act as bridging ligands to form a dinuclear Cd(II) complex.

3.1. Crystal structures of compounds containing cadmium halides and Hdpa ligands, $[{Cd(Hdpa)Cl(H_2O)}_2(\mu-Cl)_2]$ (**1**), $[{Cd(Hdpa)Br}_2(\mu-Br)_2]$ (**2**), and $[{Cd(Hdpa)I_2}]$ (**3**)

Reactions of CdX₂ (X = Cl⁻, Br⁻, I⁻) yield the structures of $[{Cd(Hdpa)Cl(H_2O)}_2(\mu-Cl)_2]$ (1), $[{Cd(Hdpa)Br}_2(\mu-Br)_2]$ (2), and $[{Cd(Hdpa)I_2}]$ (3). Chloride and bromide act as both a simple coordinating ligand and a bridging ligand to form halide-bridged dinuclear compounds 1 and 2 (Scheme 1). Bridging ability of halides decreases from chlorides down to iodides. Iodide acts as a simple coordinating ligand to form a mononuclear compound 3, but the molecules are packed alternatively. Depending on the size of the halide ions the coordination changes from octahedral in 1 to square pyramidal in 2 and tetrahedral in 3.

In compound **1**, an asymmetric unit consists of a Cd atom, a Hdpa ligand, a chloride, a water and a bridging chloride, and whole dinuclear molecule has been generated through the inversion center in the middle of the molecule (Fig. 1a). The geometry

D–H···A	d(D-H)	d(H····A)	$d(D \cdot \cdot \cdot A)$	∠(DHA)
Compound 1				
C(7) - H(7) - Cl(1) = 2	0.93	2.84	3.635(5)	144.6
$O(1)-H(1B)\cdots Cl(1)#1$	0.83(6)	2.57(7)	3.361(4)	162(5)
$O(1)-H(1A)\cdots Cl(1)#3$	0.68(6)	2.52(6)	3.191(5)	174(7)
Symmetry transformations used to generate	e equivalent atoms: #1 $-x$ + 1,	-y + 1, $-z + 1$; #2 $-x + 2$, $-y + 2$	2, - <i>z</i> + 2; #3 <i>x</i> - 1, <i>y</i> , <i>z</i>	
Compound 2				
C(10)−H(10)···Br(2)#2	0.93	3.07	3.761(9)	132.6
$N(2)-H(2N)\cdots Br(1)#3$	0.830(2)	2.82(5)	3.584(8)	154(10)
$C(2)-H(2)\cdots Br(1)#4$	0.93	2.98	3.863(10)	158.5
$C(10)-H(10)\cdots Br(1)#1$	0.93	2.94	3.504(9)	120.3
Symmetry transformations used to generat	e equivalent atoms: #1 $-x + 1$,	-y + 1, $-z + 1$; #2 $-x + 1$, $-y$, $-$	z + 1; #3 $-x$, $-y + 1$, $-z + 1$; #4	-x, -y + 1, -z
Compound 4				
C(16)−H(16)···O(12)#1	0.95	2.46	3.370(4)	160.8
C(23)–H(23)···O(11)#2	0.95	2.33	3.259(4)	164.1
N(2)-H(2N)···O(21)#3	0.75(2)	2.22(3)	2.954(3)	165(3)
Symmetry transformations used to generat	e equivalent atoms: #1 x + 1, y	, z; #2 $x - 1$, y, z; #3 $-x + 1$, $-y$	+2, - <i>z</i>	
Compound 5				
N(2) - H(2N) - O(2) = 0	0.859(2)	2.250(14)	3.058(4)	157(3)
Symmetry transformations used to generat	e equivalent atoms: #1 $-x$. $-y$.	-z: #2 x. $-v + 1/2$. $z + 1/2$		
Compound 6	1			
N(22) H(22N) O(12)#1	0.820(2)	2 129(16)	2.014(6)	159(1)
N(12) = H(12N) = O(12) + 1 N(12) = U(12N) = O(22) + 2	0.830(2)	2.128(10)	2.514(0)	171(4)
N(22) = H(12N) = O(24) # 2	0.830(2)	2.550(8)	2 015(5)	169(4)
$N(22) = \Pi(22N) \cdots O(24) \# 3$	0.050(2)	2.130(3) $1/2$ $7 \pm 1/2 \cdot #2$ \times $1/2$	3.013(3)	108(4)
symmetry transformations used to generat	e equivalent atoms. $#1 - x + 1$,	y = 1/2, -2 + 1/2, #2 - x, y = 1/2	2, -2 + 1/2, # 3 x, y - 1, 2	
Compound 7				
$C(17) - H(17) \cdots F(14)$	0.93	2.32	3.119(8)	143.1
$C(14)-H(14)\cdots F(12)$	0.93	2.73	3.614(9)	159.6
$C(13)-H(13)\cdots F(12)#1$	0.93	2.48	3.243(9)	138.8
$C(29)-H(29)\cdots F(23)#2$	0.93	2.48	3.268(10)	142.8
$C(28)-H(28)\cdots F(12)#3$	0.93	2.58	3.260(9)	130.4
C(27)−H(27)···F(13)#4	0.93	2.54	3.418(7)	157.2
$N(22)-H(22A)\cdots F(11)#4$	0.86	2.35	3.024(5)	135.3
$C(24)-H(24)\cdots F(11)#4$	0.93	2.52	3.306(5)	142.0
C(32)−H(32)···F(23)#5	0.93	2.56	3.460(9)	162.3
C(33)−H(33)···F(22)#5	0.93	2.62	3.292(10)	130.0
N(32)−H(32A)···F(22)#6	0.86	2.02	2.868(10)	166.7
C(37)−H(37)···F(22)#6	0.93	2.75	3.368(10)	124.5
C(37)−H(37)···F(21)#6	0.93	2.46	3.379(5)	171.3
Symmetry transformations used to generate 2, $z - 1/2$; #6 $-x$, $-y + 1$, $-z + 1$	e equivalent atoms: #1 -x + 1, -	- <i>y</i> + 1, - <i>z</i> + 1; #2 <i>x</i> , <i>y</i> , <i>z</i> - 1; #3 <i>y</i>	x, -y + 3/2, z - 1/2; #4 - x + 1, y	-1/2, -z + 1/2; #5 x, -y + 1/

around the Cd(II) ion is distorted octahedral constructed by two N atoms of the chelating Hdpa ligand, a simple coordinating chloride, a bridging chloride, and an O atom of water. Hdpa ligand is a little bent with the angle between two pyridyl rings of 8.21°. The Cd–N_{pyridyl} bond distances are 2.316(4) and 2.333(4) Å which are typical and the Cd–O_{water} bond distance is 2.400(4) Å (Table 2). The Cd–Cl and Cd–Cl_{bridge} distances are 2.6186(13) and 2.6261(13) Å, respectively. Intra- and inter-molecular hydrogen bonds between a water hydrogen atom and a chloro atom (O–H…Cl) produce rectangular rings to form an 1-D chain, and inter-molecular hydrogen bonds between 1-D chains (C–H…Cl) form a 2-D sheet (Fig. 1b and Table 3). In the dinuclear unit in **1**, the Cd–Cl–Cd angle is 92.78(3)°, and the Cd…Cd distance is 3.799(15) Å.

Compound **2** also shows bromide-bridged dinuclear Cd(II) units, but differently a Cd(II) unit contains one Hdpa, a bromide, and no water ligand (Fig. 2a). The geometry around Cd(II) ion is distorted square pyramidal constructed by two N atoms of Hdpa, a bridging bromide, and a simple coordinating bromide occupying an apical position. Hdpa ligand is a little bent with the angle between two pyridyl rings of 13.76°. The Cd–N_{pyridyl} bond distances are 2.284(7) and 2.307(7) Å which are typical (Table 2). The Cd–Br distance is 2.5349(11) Å which is much shorter than the Cd–Br_{bridge} distances (2.7635(11) and 2.7729(11) Å). This implies that the bridging character of the bromide is weaker than that of the chloride. Intra- and inter-molecular hydrogen bonding interactions between bridging bromides and hydrogen atoms (C/N–H) produce 2-D sheets, and inter-molecular hydrogen bonds between simple bromides and carbon hydrogen atoms form a 3-D network (Fig. 2b and Table 3). In the dinuclear unit in **2**, the Cd–Br–Cd angle is 98.28(3)°, and the Cd···Cd distance is 4.187(7) Å which is much longer than that in the chloride-bridged compound **1**.

In compound **3**, it is recognized that the bridging character of the iodide is much weaker than those of the chloride and the bromide. The Cd(II) atom and the amine nitrogen atom (N2) are disordered in two sites with occupancies of 77% and 23%.



Fig. 2. (a) Structure of [{Cd(Hdpa)Br}₂(µ-Br)₂] (2) with 50% ellipsoid. (b) Three-Dimensional structure derived by non-classical hydrogen bonds between Br atoms and pyridyl hydrogen atoms and amine hydrogen atoms.



Fig. 3. (a) Structure of [{Cd(Hdpa)l₂] (**3**) with 50% ellipsoid. (b) Packing diagram along the *a* axis.



Fig. 4. (a) Structure of $[Cd(Hdpa)(O_2CC_6H_5)_2]$ (4) with 50% ellipsoid. (b) One-dimensional structure derived by hydrogen bond interactions and π - π interactions between pyridyl rings.

Considering only 77% Cd(II) ion, the structure of **3** is a di-iodide mononuclear complex as shown in Fig. 3a. The diagram down to the *a* axis shows that di-iodide complexes are packed alternatively (Fig. 3b). The geometry around Cd(II) ion can be described distorted tetrahedral constructed by two N atoms of Hdpa and two simple coordinating iodides. Hdpa ligand is a little bent with the angle between two pyridyl rings of 5.12° . The Cd–N_{pyridyl} bond distances are 2.260(6) and 2.259(6) Å which are typical (Table 2). The Cd–I distances are 2.6956(8) and 2.6900(8) Å.

3.2. Crystal structure of compound [Cd(Hdpa)(O₂CC₆H₅)₂] (**4**)

With chelating benzoate anions, Cd(II) produces a mononuclear $[Cd(Hdpa)(O_2CC_6H_5)_2]$ unit **4** whose structure is very similar to the corresponding Zn(II) complex with the similar cell dimension (Fig. 4a) [31]. The Cd–O_{benzoate} distances range from 2.2448(19) to 2.4421(18) Å, and the Cd–N_{pyridyl} distances are 2.280(2) and 2.274(2) Å (Table 2). There are inter-molecular hydrogen bond

interactions (Table 3) and $\pi - \pi$ interactions between pyridyl rings (C6…N1ⁱ 3.751(5), C7…C1ⁱ 3.686(5), C8…C2ⁱ 3.758(3), C9…C3ⁱ 3.848(3), C10…C4ⁱ 3.866(3) Å, symmetry operation i = (1 - x, 2 - y, -z)) (Fig. 4b). Two pyridyl rings are somewhat tilted with the angle of 9.57°.

3.3. Crystal structure of compound $[Cd(Hdpa)_2(NO_3)_2]$ (5)

Its structure was reported previously [32], but we re-collected data and re-determined the structure to fully understand the role of hydrogen bonds to form a 2-D sheet.

An inversion center on a Cd(II) ion produces a whole molecule $[Cd(Hdpa)_2(NO_3)_2]$. Two Hdpa ligands and two nitrate ligands coordinate to a Cd(II) ion to form a distorted octahedral environment [34,35]. There are hydrogen bonds between an amine hydrogen atom and a nitrate oxygen atom (N-H···O-N_{nitrate}) to form a 2-D sheet (Fig. 5 and Table 3). In the 2-D structure, the Cd···Cd distances are 7.731(1) and 9.109(1) Å.



Fig. 5. Two-Dimensional structure of 5 derived by hydrogen bonds between amine hydrogen atoms and nitrate oxygen atoms.

3.4. Crystal structures of compounds $[Cd(Hdpa)_3(ClO_4)_2]$ (6) and $[Cd(Hdpa)_3(BF_4)_2]$ (7)

With non-coordinating ligands ClO_4^- and BF_4^- , Cd(II) produces mononuclear complexes containing (tri-Hdpa)-chelated Cd(II) and two anions for charge balance (Fig. 6a for **6** and Fig. 7a for **7**). The $Cd-N_{pyridyl}$ distances range from 2.302(3) to 2.373(3) Å for **6** and from 2.307(3) to 2.374(3) Å for **7** (Table 2). Two pyridyl rings in three chelating Hdpa ligands of both **6** and **7** are all bent with 11.90°, 29.56°, and 31.95° for 6 and 10.46°, 29.64°, and 32.02° for 7. There are hydrogen bonds in **6** between amine nitrogen atoms and perchlorate oxygen atoms (N–H···O_{perchlorate}) to form a three-dimensional structure (Fig. 6b and Table 3). There are also non-classical N–H···F and C–H···F hydrogen bonds in **7** to form a three-dimensional structure (Fig. 7b and Table 3).





Fig. 6. (a) Structure of $[Cd(Hdpa)_3(ClO_4)_2]$ (6) with 50% ellipsoid. (b) Threedimensional structure derived by hydrogen bonds between amine hydrogen atoms and perchlorate oxygen atoms.



Fig. 7. (a) Structure of $[Cd(Hdpa)_3(BF_4)_2]$ (7) with 50% ellipsoid. (b) Threedimensional structure derived by hydrogen bonds between amine and pyridyl hydrogen atoms and tetrafluoroborate fluorine atoms.



Scheme 2. Structures of seven compounds containing chelating Hdpa ligands as transesterification catalysts.

Table 4					
Transesterification	of esters by	methanol ii	n the presence	of compounds 4	I-6 at 50 °C. ^a

Entry	Substrate	4 (time/days) ^b	5 (time/days) ^b	6 (time/days) ^b
1	4-Nitrophenyl acetate	0.5	0.38	0.25
2	Phenyl acetate	4	1	0.92
3	4-Methylphenyl acetate	35	44	13
4	4-Nitrophenyl benzoate ^c	2	4	4
5	4-Chlorophenyl benzoate	4	2	1
6	Phenyl benzoate	4	2	2
7	4-Methylphenyl benzoate	6	2	1
8	Vinyl acetate	0.21	0.25	0.17

^a All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. *Reaction conditions*: esters; 0.05 mmol, catalyst; 1.0 mg, 1.90×10^{-3} mmol for **4**, 1.0 mg, 1.73×10^{-3} mmol for **5**, 1.0 mg, 1.21×10^{-3} mmol for **6**, solvent; methanol (1 mL). See Section 2 for the detailed reaction conditions.

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

^c The solvent was a mixture of CH₃OH/CH₂Cl₂ (1/1) because of low solubility of substrate in CH₃OH.



Scheme 3.

3.5. Homogeneous catalytic activities of compounds 1-7

As part of our efforts to develop transesterification catalysts based on metal ions that are not redox-active, we have previously reported that $Zn(Hdpa)X_2$ (X = NO₃⁻, SO₄²⁻, $^{-}O_2C_6H_5$, Cl⁻, Br⁻, and I⁻) could carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions [30,31]. In addition, we have recently shown for the first time that $[Cd_2(O_2CPh)_4(4,4'-bpy)_2]_n$ Cd-containing polymers and $[Cd(O_2CPh)_2(bpa)_{1.5}]_n$ (4,4'-bpy = 4,4-bipyridine, bpa = 1,2-bis(pyridyl)ethane and $^{-}O_2CPh$ = benzoate) catalyzed efficiently the transesterification reactions of a series of esters in spite of being well known as an inert metal [34,35]. This experience led us to test the transesterification with the compounds 1-7 (see Scheme 2 for structures of seven compounds as transesterification catalysts). Thus, the compounds 1–7 were treated with phenyl acetate and methanol at 50 °C under the neutral conditions (Eq. (1)).



This reaction produced quantitatively the corresponding product methyl acetate within 0.9–20 days, while a control reaction carried out in absence of the complexes showed trace amounts of the conversion of the ester to the product in the same time period. Complexes **4**, **5**, and **6** have shown efficient catalytic reactivities (0.92–4 days; see Table 4), while **1**, **2**, 3 and **7** has displayed a very slow conversion (12–20 days; data not shown). Importantly, the transe-sterification reactivity shown by the catalyst **6** are very efficient and the best among the catalytic efficiencies reported previously with Cd-containing compounds, to our best knowledge [36]. In addition, the catalytic reactivity of **6** is comparable to those of Zn catalysts which are well known as the efficient catalysts for the transesterification reactions [30,31,34–36].

Once having established that 4-6 represents an excellent catalyst for the tansesterification reaction of phenyl acetate with methanol, we have investigated the transesterification of various *p*-substituted phenyl acetates and benzoates with them. The substrates with the electron-withdrawing substituents have undergone faster transesterification (entries 1, 4 and 6), while those with the electron-donating ones have shown slow reaction (entries 3 and 7).

In a certain case, transesterification of esters with alcohol cannot achieve high conversions because of the reversibility of the reaction. To solve this problem, therefore, we have used an enol ester as an acylating agent, since the resultant enolate is converted to an aldehyde or ketone that is unable to participate in the reverse reaction [37–41]. In this work, vinyl acetate was used as the acylating agent and, expectedly, converted efficiently to the product methyl acetate within 0.17–0.25 day by **4**, **5**, and **6** (entry 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, we are able to propose the possible transesterification reaction mechanism based on the structure of the complexes **4**, **5**, and **6**. With **4** and **5** having the labile ligands NO_3^- and benzoate, respectively, the plausible mechanism shown in Scheme 3, based on our previous proposed mechanism [30]. The substrate phenyl acetate substitutes an anion (NO_3^-) to give the adduct (Hdpa)₂Cd(NO_3)(Sub). Then, the nucleophile methanol would attack the carbon atom of carbonyl moiety of the adduct to produce the product methyl acetate.

With **6** having no labile ligand, we can presume that there is no direct interaction between the substrate ester and cadmium ion of the complex as Lewis acid, since it is saturated with three Hdpa ligands. Therefore, we propose that the hydrogen atom of amine N–H moiety in the complex can do the acid-catalyzed transesterification, as we have previously proposed with the Zn complexes of bis(2-pyridylmethyl)amine ligands [42]. Thus, this acidic hydrogen

 Table 5

 Emission data for complexes 1–7 and ligand (Hdpa) at room temperature.

Compound	Excitation (λ /nm)	Emission (λ_{max} /nm)
Ligand (Hdpa)	314	352
1	315	354
2	315	353
3	315	354
4	315	354
5	315	352
6	314	350
7	314	351



Scheme 4.



Fig. 8. Emission spectra of complexes 1–7 and ligand (Hdpa) at room temperature.

interacts with the oxygen atom of carbonyl of ester, resulting in that the carbonyl is more electrophilic. Then, the resultant activated carbonyl could be easily attacked by methanol to produce the product methyl ester as shown in Scheme 4. Further explorations into the uses of this catalyst family in organic transformations as well as mechanistic investigations are ongoing.

3.6. Luminescent study

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display [43]. The luminescent properties of compounds 1-7 have been investigated. The photoluminescent spectra of compounds 1-7 and Hdpa ligand have been measured at room temperature, and the wavelengths of the emission maximums and excitations are listed in Table 5 for compounds 1-7 and Hdpa ligand. The emissions for the complexes (Fig. 8) were found to be similar to that of the free ligand ((λ_{max} = 352 nm). Upon complexation, the emissions of the complexes are not shifted compared to the free ligand. Therefore, the emissions of 1-7 seem to be attributed to the π - π ^{*} intraligand fluorescence [27,44,45]. In addition, the enhancement of luminescence in 1, 2 and 5–7 may be attributed to the ligation of ligand to the metal center, which effectively increases the rigidity and reduces the loss of energy by radiationless decay. These observations indicate that they may be excellent candidates for potential photoactive materials [46].

4. Conclusion

We have shown six new structures of Cd(II) complexes containing Hdpa ligands to study anion effects. With chloride and bromide, Cd(II) ions produce halide-bridged dinuclear units 1 and 2while CdI₂ produces mononuclear unit 3 without halide-bridging. Cd(II) ions produce mono-Hdpa complex **4** with chelating benzoate, di-Hdpa complex **5** with coordinating NO₃⁻ anion, and tri-Hdpa complexes **6** and **7** with non-coordinating ClO₄⁻ and BF₄⁻ anions. One-, two-, or three-dimensional structures of Cd(II)-Hdpa complexes can be produced by hydrogen bonding and π - π interactions. These results indicate that both inter-molecular hydrogen bonds and π - π interactions as well as anion effects play very important roles in the construction of crystal structures in Cd(II)-Hdpa system.

We have also shown that the homogeneous catalysts **4**, **5**, and **6** catalyzed efficiently the transesterification of a variety of esters with methanol, while **1**, **2**, 3 and **7** have displayed very slow conversion. Importantly, the transesterification reaction catalyzed by the catalyst **6** is the best among the catalytic systems reported previously in Cd-containing coordination compounds, to our best knowledge. This result offers the opportunity to use many Cd-containing complexes reported to date as a potential catalyst for the transesterification reactions. In addition, the luminescent properties of compounds **1–7** have been investigated at room temperature, and the emissions for the complexes were found to be similar to that of the free ligand ($\lambda_{max} = 352$ nm), suggesting that the emissions of **1–7** seem to be attributed to the π – π * intraligand fluorescence.

Supplementary data

CCDC 737385, 737386, 737387, 737388, 737389 and 737390 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **6** and **7**. 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.

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