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Synthesis and structural characterization of copper(II), cadmium(II) and zinc(II) complexes with 4,5-diazaspirobifluorene and bis-9-biphenyl-4,5-diazafluorenyl peroxide

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ABSTRACT

The synthesis and structural chemistry of four new divalent transition metal complexes of the fluorene ligands 4,5-diazaspirobifluorene (L1) and bis-9-biphenyl-4,5-diazafluorenyl peroxide (L2), $[Cu_3(L1)_4(NO_3)_6(H_2O)_2] \cdot 2CH_3CN$ (**1**), $[Cu(L1)(CH_3CO_2)_2(H_2O)] \cdot 2H_2O$ (**2**), $[Cd(L1)_2(NO_3)_2] \cdot DMF$ (**3**) (DMF = N,N-dimethylformamide) and $[Zn_2(L2)(\mu\text{-}Cl)_2Cl_2]_\infty$ (**4**) are described. Single-crystal X-ray diffraction analysis reveal that the four complexes exhibit various frameworks due to diverse coordination modes and different conformations of ligands L1 or L2, as well as nitrate, acetate or chloro counterions. L1 in complexes **1**, **2** and **3** present an asymmetric rigid bidentate ligand with two nitrogen atoms as the donor sites. Novel complex **4** was formed through complexation between conformationally bent shaped peroxide ligands and zinc(II) dichlorides that adopt a linear coordination geometry, which can also give rise to extended polymeric chains with a zigzag secondary structure.

1. Introduction

Organocopper, cadmium and zinc complexes have been widely explored due to their rich structural chemistry [1] and importance in organic synthesis [2], and in polymerization chemistry [3], e.g., as well-defined catalysts for the copolymerization of CO_2 and epoxides [4]. The applications of these complexes must be based on the fundamental understanding of their components and structure chemistry. Hence it is of interest to study the coordination modes and structural features of the complexes. Several rigid multidentate oxygen-donor ligands have been used to design and synthesize the metal–organic complexes [5,6]. At the same time, many rigid bidentate nitrogen-donor ligands, such as 2,2′-bipyridine and its derivatives have also been used to prepare the metal organic materials [7]. However, the nitrogen-donor ligands with larger volumes are not easy to coordinate with the metal ions because of the large steric hindrance, and larger crystals suitable for single-crystal XRD analysis are difficult to obtain due to the low coordination strength of the nitrogen-donor organic ligands caused by the less negative charge on the nitrogen compared with the oxygen [8]. The coordination chemistry of the rigid ligand 4,5-diazaspirobifluorene has rarely been reported, except for a complex with silver ion [9]. In order to study the structure feature of the transition metal complex with the rigid and bulky ligands and the coordination code of the nitrogen-donor ligands, herein, we report the synthesis, characterization, and crystal structure of copper(II), cadmium(II) and zinc(II) complexes bearing bipyridine-based N,N-chelate fluorene ligands, 4,5-diazaspirobifluorene (L1) and bis-9-biphenyl-4,5-diazafluorenyl peroxide (L2). Remarkably, we have obtained the first zinc complex with peroxide so far, which may have potential applications in catalysis chemistry in the future.

2. Experimental

2.1. General

All of the reagents were commercially available and used as purchased. 9-Biphenyl-4,5-diazafluorenol and 4,5-diazaspirobifluorene was prepared according to the literature [10]. Interestingly, along with the expected 4,5-diazaspirobifluorene, bis-9-biphenyl-4,5-diazafluorenyl peroxide was unexpectedly formed as a by-product by the oxidation of 9-biphenyl-4,5-diazafluorenol with H_2SO_4/HOAc.

The elemental analysis was carried out with a Perkin–Elmer 240C elemental analyzer. ^{1}H NMR spectra were performed on a Bruker model Advance DRX 500 spectrometer in DMSO-d_6 and were referenced to TMS. The FT-IR spectra were recorded from KBr pellets over the range 4000–400 cm^{-1} with a Vector 22 spectrometer. The emission/excitation spectra were recorded with a

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Hitachi 850 fluorescence spectrophotometer by using 1×10^{-4} M CH_3CN solution. Optical absorption spectra were collected on a Shimadzu 3100 spectrophotometer at room temperature. The absorbance was directly proportional to the concentration of complexes in the range from 1×10^{-4} M to 1×10^{-3} M.

*2.2. Preparation of $[Cu_3(L)_4(NO_3)_6(H_2O)_2] \cdot 2CH_3CN$ (**1**)*

Equimolar amounts of 4,5-diazaspirobifluorene (0.079 g, 0.25 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.061 g, 0.25 mmol) were stirred together in CH_3CN (30 ml) at room temperature for 2 h. The resulting glaucous solution was filtered and concentrated to 10 ml. Blue block crystals of complex **1** suitable for X-ray diffraction were obtained in 69% yield by slow diffusion of diethyl ether into the filtrate for several days. At room temperature, crystals of complex **1** are unstable and decompose slowly into blue powder over the course of several days. *Anal.* Calc. for $C_{96}H_{62}Cu_3N_{16}O_{20}$ (1950.24): C, 59.12; H, 3.21; N, 11.49. Found: C, 59.36; H, 3.44; N, 11.23%. ^1H NMR (DMSO-d_6): $\delta = 8.09$ (s, 4H, $H_{1,7}$), 7.44 (s, 4H, $H_{3,4}$), 7.17 (s, 4H, $H_{5,6}$), 6.68 (s, 2H, H_2), 2.07 (s, 3H, CH_3CN) (see Table 4 for the atom numbering arrangement). IR data (KBr, cm^{-1}): 3447 (s), 3053 (vw), 1578 (w), 1473 (m), 1447 (m), 1406 (s), 1384 (s), 1279 (s), 1169 (w), 1013 (w), 797 (w), 765 (m), 737 (m) cm^{-1}.

*2.3. Preparation of $[Cu(L)(CH_3CO_2)_2(H_2O)] \cdot 2H_2O$ (**2**)*

Similar procedures were performed to obtain blue crystals of complex **2**, except that $Cu(CH_3CO_2)_2 \cdot 4H_2O$ was used instead of $Cu(NO_3)_2 \cdot 4H_2O$, yield 55%. *Anal.* Calc. for $C_{27}H_{26}CuN_2O_7$ (554.04): C, 58.53; H, 4.73; N, 5.06. Found: C, 58.33; H, 4.77; N, 5.21%. ^1H NMR (DMSO-d_6): $\delta = 8.84$ (s, 2H, H_1), 8.07 = (d, 2H, H_7, $J = 7.31$), 7.46 (t, 2H, H_3, $J = 14.11$), 7.33 (s, 2H, H_4), 7.18 (s, 4H, $H_{5,6}$), 6.70 (d, 2H, H_2, $J = 7.00$), 2.45 (s, 6H, CH_3CO_2) (see Table 4 for the atom numbering arrangement). IR data (KBr, cm^{-1}): 3423 (s), 2927 (w), 1606 (s), 1404 (s), 1339 (w), 1163 (w), 807 (w), 762 (m), 737 (m), 676 (w) cm^{-1}.

*2.4. Preparation of $[Cd(L)_2(NO_3)_2] \cdot DMF$ (**3**)*

A mixture with a stoichiometric 2:1 solution of ligand L1 (0.079 g, 0.50 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.077 g, 0.25 mmol) in CH_3CN (30 ml) were stirred together for 2 h at room temperature. The clear solution thus obtained was evaporated under vacuum to form a white solid and recrystallized from CH_2Cl_2–DMF to give colorless crystals, yield 70%. *Anal.* Calc. for $C_{52}H_{42}CdN_8O_8$ (1019.34): C, 61.27; H, 4.15; N, 10.99. Found: C, 61.09; H, 3.99; N, 10.46%. ^1H NMR (DMSO-d_6): $\delta = 8.71$ (d, 2H, H_1, $J = 3.34$), 8.07 = (d, 2H, H_7, $J = 7.61$), 7.96 (s, 1H, DMF–H), 7.45 (d, 2H, H_3, $J = 7.49$), 7.26 (t, 2H, H_4, $J = 6.88$), 7.16 (d, 4H, $H_{5,6}$, $J = 7.08$), 6.70 (d, 2H, H_2, $J = 7.64$), 2.89, 2.73 (s, 6H, DMF–CH_3) (see Table 4 for the atom numbering arrangement). IR data (KBr, cm^{-1}): 3449 (w), 3074 (w), 2922 (w), 1661 (s), 1582 (m), 1432 (s), 1408 (s), 1383 (s), 1298 (s), 1166 (w), 1089 (w), 1028 (w), 954 (w), 803 (w), 762 (m), 738 (m), 652 (w) cm^{-1}.

*2.5. Preparation of $[Zn_2(L2)(\mu\text{-}Cl)_2Cl_2]_\infty$ (**4**)*

A solution containing anhydrous zinc dichloride (0.071 g, 0.50 mmol) and bis-9-biphenyl-4,5-diazafluorenyl peroxide (0.168 g, 0.25 mmol) in CH_3CN (30 ml) was stirred for 2 h at room temperature. The resulting light brown solution was filtered, and then it was left open for slow evaporation of the solvent at room temperature. After standing for two weeks, small needle-like crystals of complex **4** were obtained, yield 50%. Because the growing rate of crystal is too fast, the structure quality of complex **4** is not high. Calc. for $C_{23}H_{15}Cl_2N_2OZn$ (471.64): C 58.57, H 3.21, N 5.94. Found: C, 58.44, H, 3.60, N, 5.99%. ^1H NMR (DMSO-d_6): $\delta = 8.35$ (d, 2H, H_1, $J = 4.00$), 8.13 (d, 1H, H_7, $J = 8.00$), 7.57 (m, 1H, H_{10}, $J = 30.00$), 7.37 (t, 1H, H_6, $J = 14.50$), 7.19 (d, 2H, H_3, $J = 7.50$), 6.97 (t, 1H, H_4, $J = 12.00$), 6.85 (d, 1H, H_9, $J = 7.00$), 6.77 (t, 1H, H_8, $J = 14.50$), 6.54 (t, 2H, H_5, $J = 15.00$), 5.86 (d, 2H, H_2, $J = 7.00$) (see Table 4 for the atom numbering arrangement). IR (KBr pellet): $\nu = 3435$ (s), 1600 (m), 1586 (m), 1473 (w), 1438 (w), 1411 (s), 1161 (m), 1008 (m), 814 (w), 769 (m), 707 (m), 557 (w) cm^{-1}.

2.6. Crystal structure determination and refinement

Suitable single crystals were selected for indexing and intensity data were measured with a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298 K. The raw data frames were integrated into SHELX-format reflection files and corrected using the SAINT program. Absorption corrections based on multiscans were obtained from the SADABS program. The structures were solved with direct methods and refined with full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively. Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses, where they were refined with anisotropic thermal parameters on F^2. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of the water molecules were located using the different Fourier method and refined freely. Further details for structural analysis are summarized in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis of metal complexes

Complexes **1**–**4** have been prepared in moderate to good yields (50–70%) by mixing acetonitrile solutions of ligand L1 or L2 with a salt of a divalent metal, M^{II} = Cu, Cd, Zn (Scheme 1). Crystal of **1** or **2** can be obtained through slow diffusion of diethyl ether into the reaction mixture. Otherwise, crystals for cadmium and zinc complex have grown tardily from the solution along with the volatilization of the solvent acetonitrile, respectively. From the crystal structure of complex **1**, we could deduce that ligand L forms a

Table 1
Crystallographic data for complex **1–3**.

	Complex **1**	Complex **2**	Complex **3**
Formula	$C_{96}H_{66}Cu_3N_{16}O_2$	$C_{27}H_{26}CuN_2O_7$	$C_{52}H_{42}CdN_8O_8$
Formula weight	1954.27	554.04	1019.34
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Crystal size (mm)	0.21 × 0.19 × 0.16	0.23 × 0.15 × 0.11	0.30 × 0.24 × 0.22
a (Å)	12.2642(18)	10.0594(13)	12.0376(7)
b (Å)	12.9474(19)	23.117(3)	15.9870(10)
c (Å)	15.649(2)	11.4744(15)	13.0900(8)
α (°)	86.468(2)	90	90
β (°)	75.369(2)	108.732(2)	113.4070(10)
γ (°)	63.026(2)	90	90
V (Å3)	2138.7(5)	2527.0(6)	2311.8(2)
Z	1	4	2
D_{calc} (g cm^{-3})	1.517	1.456	1.464
F(000)	1001	1148	1044
μ (mm^{-1})	0.825	0.914	0.538
Goodness-of-fit on F^2 (S)	1.013	1.049	1.040
Data collected	11693	13716	12500
Unique data (R_{int})	8247 (0.0313)	4947 (0.0532)	4527 (0.0515)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0660, 0.1527	0.0624, 0.1228	0.0622, 0.1263
R_1, wR_2 [all data]	0.0898, 0.1597	0.0891, 0.1286	0.0856, 0.1311

Table 2
Crystallographic data for 9-biphenyl-4,5-diazafluorenol and complex **4**.

	9-Biphenyl-4,5-diazafluorenol	Complex **4**
Formula	$C_{46}H_{32}N_4O_2$	$C_{23}H_{15}ZnCl_2N_2O$
Formula weight	672.76	471.64
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Crystal size (mm)	0.25 × 0.15 × 0.11	0.20 × 0.13 × 0.11
a (Å)	8.0633(6)	8.8988(12)
b (Å)	15.4115(11)	18.567(3)
c (Å)	27.940(2)	12.2080(17)
α (°)	90	90
β (°)	90	94.785(2)
γ (°)	90	90
V (Å3)	3472.1(4)	2010.0(5)
Z	4	4
D_{calc} (g cm^{-3})	1.287	1.559
F(000)	1408	956
μ (mm^{-1})	0.080	1.505
Goodness-of-fit on F^2 (S)	1.000	0.756
Data collected	18394	10863
Unique data (R_{int})	3659 (0.0962)	3940 (0.1107)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0350, 0.0618	0.0504, 0.0604
R_1, wR_2 [all data]	0.0529, 0.0664	0.1502, 0.0721

4:3 complex with copper(II) nitrate (Fig. 1), although the reaction was processed in a 1:1 ratio.

Reactions of ligand L1 with one equivalent of copper(II) acetate yielded complex **2** whose chemical analysis suggested a 1:1 ratio of ligand to metal salt. This result parallels the reaction of substituted 2,2′-bipyridine with copper(II) acetate which forms a simple four-coordinate 1:1 complex [11]. In contrast, crystals from a mixture of ligand L1 and cadmium(II) nitrate with a 2:1 ratio in DMF/CH_2Cl_2 were shown by X-ray crystallography to be a DMF solvate.

The addition of ligand L2 in a 1:2 ratio to a acetonitrile solution of $ZnCl_2$ after two weeks, accompanied with slow evaporation of the solvent at room temperature, results in small needle-like crystals of complex **4**.

3.2. X-ray crystallography

Single crystals suitable for X-ray analysis could be obtained for all five compounds in this study. The solved crystal structures are shown in Figs. 1, 3, 5, 6 and 9, and the selected bond lengths and angles are collected in Table 3.

3.2.1. $[Cu_3(L1)_4(NO_3)_6(H_2O)_2] \cdot 2CH_3CN$ (**1**)

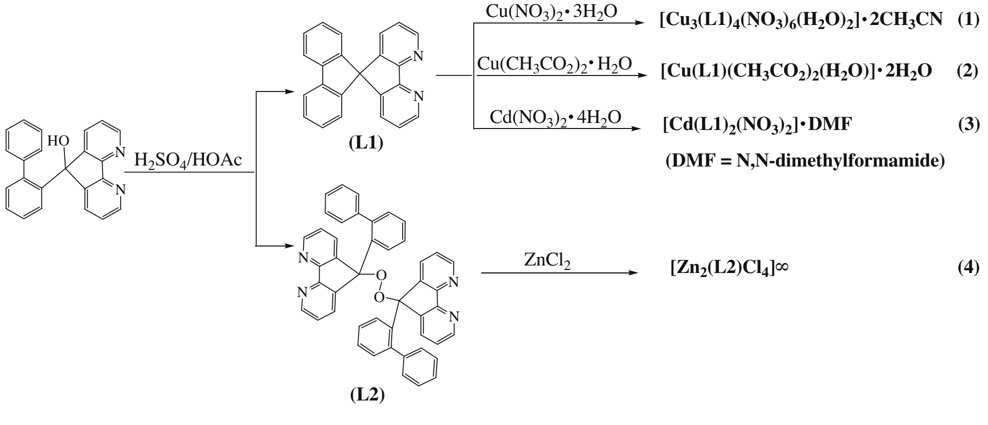
Single-crystal X-ray study reveals that the asymmetric unit of complex **1** consists of three crystallographically independent molecules. Thus, the structure of $[Cu_3(L1)_4(NO_3)_6(H_2O)_2] \cdot 2CH_3CN$ is best represented by the formula $[Cu(L1)_2(H_2O)_2] \cdot [Cu(L1)(NO_3)_3]_2 \cdot 2CH_3CN$, and for clarity, of two molecules with identical structures only one is shown in Fig. 1. From crystal structure of complex **1** we can see that the coordination geometry of Cu1 center is unusual in that the elongated Jahn–Teller axis of the molecule lies along the N–Cu–N vector [Cu1–N2 = 2.631(2) Å] and not in the O–Cu–O axis [Cu1–O1 = 2.002(3) Å], which is occupied by water molecules. To our knowledge, this is one of only two examples of $N_2O_2N'_2$ coordination to a Cu(II) center with two water molecules bound *trans* in the equatorial plane and the nitrogen atoms of the chelates directed along the *J*–*T* axis. [12] This $N_2X_2N'_2$ geometry has been observed in other Cu(II) complexes with the 4,5-diazafluorene template and other anions such as Cl^-, Br^- or NO_3^- [12,13], while complexes with transition metals other than Cu(II) (e.g., Re(I), [14] Co(II) [15]) typically exhibit a more symmetrical coordination.

On the other hand, the environment of Cu2 center is square pyramidal. The basal plane is built by a nitrogen atom from the ligand L1 and three oxygen atoms of three nitrate groups, whereas the apical position is occupied by the other nitrogen atom of the bidentate ligand L1. Main bond distances and angles for non-hydrogen atoms are listed in Table 3. Meanwhile, the structure analysis indicates that biphenyl and 2,2′-bipyridine units in two kinds of coordinated ligand L1 are both perpendicularly cross-linked by a carbon atom. The dihedral angles between the mean planes of the two units are 88.6° (L1 coordinated to Cu1) and 91.5° (L1 coordinated to Cu2), which are very similar to that in the crystal structure of the free ligand L1 we have reported previously [16].

Interestingly, as can be seen from Fig. 2, a one-dimensional supramolecular chain is formed by intermolecular hydrogen bonding involving the water molecules coordinated to the copper center which chelated by two bidentate ligands L1 and the nitrate oxygen atoms coordinated to the other copper center (Table 4). Undoubtedly, these hydrogen bonds contribute to the stability of the whole crystal structure.

3.2.2. $[Cu(L1)(CH_3CO_2)_2(H_2O)] \cdot 2H_2O$ (**2**)

Copper(II) acetate forms a variety of structures with unsubstituted 2,2′-bipyridine. The formation of multinuclear systems containing two or three copper ions [17–19], polymers [20] and a mononuclear cation [21] $[Cu(bipy)_2(acetate)]^+$ are facilitated by the possibility of acetate either acting as a bidentate ligand, or using one oxygen atom to bridge two metal centers. To determine the structure feature of the complex formed by 2,2′-bipyridine-based ligand L1 and copper(II) acetate, complex **2** was synthesized



Scheme 1. Synthetic routes of the ligands L1, L2 and complexes **1**–**4**.

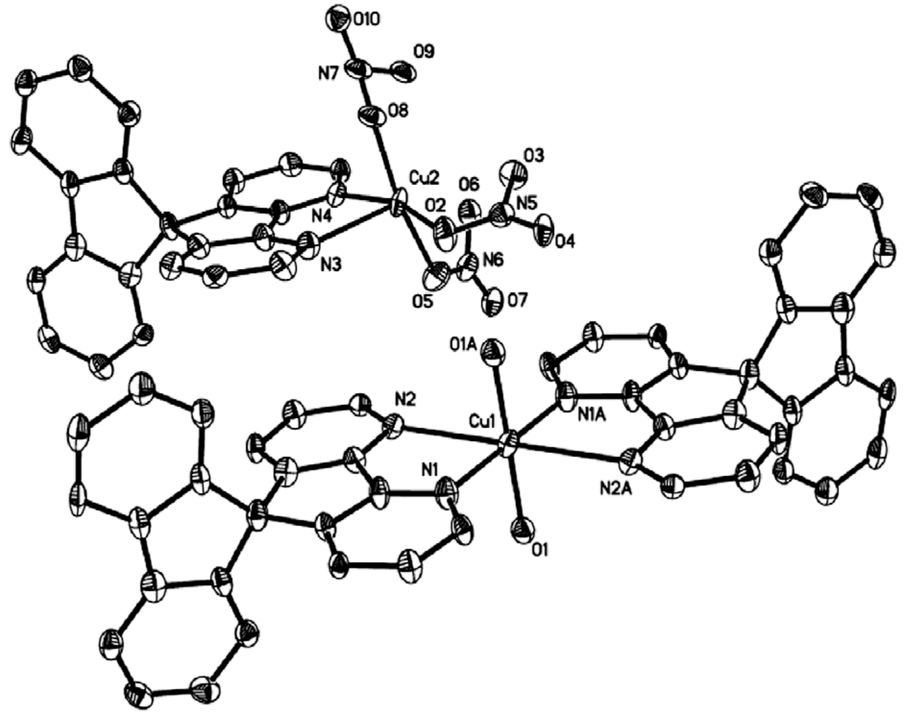


Fig. 1. X-ray single crystal structure of complex **1** (thermal ellipsoids at 30% probability).

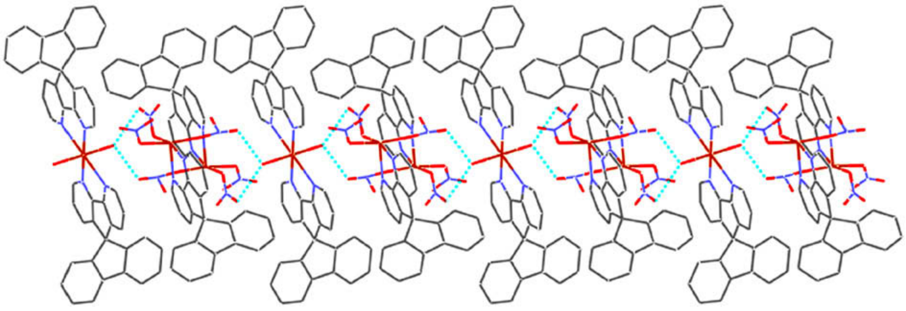


Fig. 2. 1D linear chain of complex **1** via the intermolecular hydrogen bonding, dashed lines indicate the intermolecular hydrogen bonds.

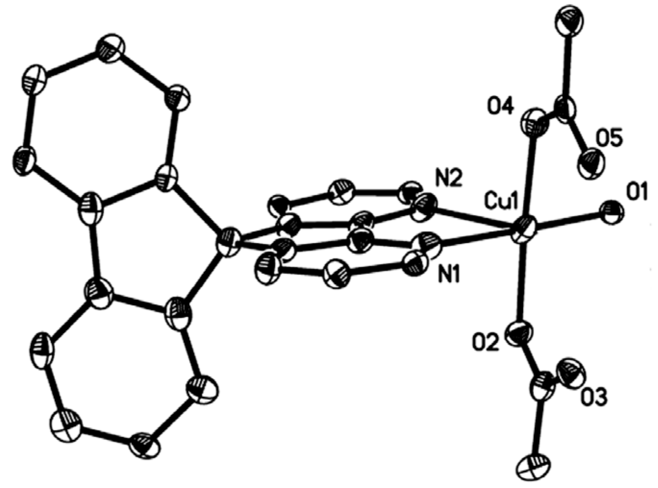


Fig. 3. X-ray single crystal structure of complex **2** (thermal ellipsoids at 30% probability).

in our case, which was characterized by X-ray crystallography. The molecular structure is shown in Fig. 3, which is different from the mononuclear copper(II) complexes mentioned above. The crystal structure of **2** consists of mononuclear units in which the copper(II) center surrounding is square pyramidal. A nitrogen atom (N2) from the bidentate ligand L1 is in the apical position. Two oxygen atoms (O2 and O4) from the monodentate acetate groups, one oxygen atoms (O1) from a water molecule and the other nitrogen atom of ligand L1 (N1) build the basal plane. The Cu–N bond distances are similar to those observed in the foregoing mononuclear five-coordinate molecular structure of complex **1**. However, the Cu–O (water oxygen atom) [1.961(3) Å] is slight shorter than the one [2.002(3) Å] observed in the foregoing another six-coordinate molecular structure of complex **1**. N1, O1, O2, and O4 atoms fall on a plane: the largest deviation from the mean plane is −0.0273 Å for O1. The copper(II) ion is 0.032(3) Å out of this plane. The value of the axial copper-nitrogen distance is 2.489(3) Å, which is much longer than the observed one [2.037(3) Å] in the quadrilateral plane.

In **2** there are no π–π aromatic interactions between the biphenyl or bipyridyl rings, Fig. 4, but there are several sets of intermo-

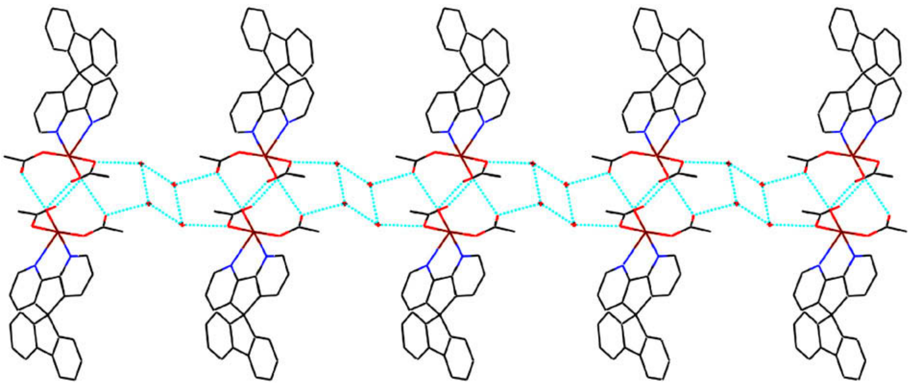


Fig. 4. Perspective view of the one-dimensional chain of complex **2**, dashed lines indicate the weak interaction and the intermolecular hydrogen bonds.

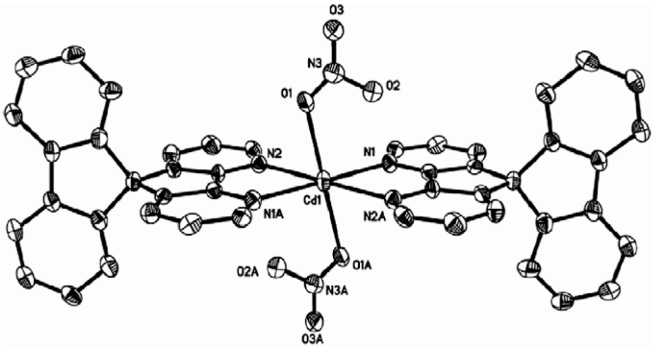


Fig. 5. Molecular structure of complex **3**. Thermal ellipsoids are at the 30% probability level.

lecular hydrogen bonding (see Table 4) between the waters of crystallization and the coordinated acetic groups which link the adjacent molecules into an infinite one-dimensional supramolecular chain (Fig. 4).

3.2.3. *[Cd(L1)$_2$(NO$_3$)$_2$] · DMF* (**3**)

The crystal structure of complex **3** unambiguously confirms the [Cd(L1)$_2$] stoichiometry as well as the bidentate nature of the ligand L1 (Fig. 5). The cadmium atom lies on a crystallographic inversion center. N_4O_2 coordination polyhedron around the Cd(II) center is Jahn–Teller distorted octahedron. Four N atoms from the two ligands L1 coordinate to the Cd(II) center in the equatorial plane, wherein, for each ligand moiety, one Cd–N distance is slightly longer than the other [2.447(4) and 2.329(3) Å]. Two nitrate counterions occupy the apical position, *d*(Cd–O) = 2.411(5) Å. The bite angle of the ligand L1 [77.14°] indicates that there is a certain strain in the six-membered chelate ring. According to the literatures, this is the first example of $N_2O_2N'_2$ coordination to a Cd(II) center with four nitrogens of the chelates bound in the equatorial plane and two *trans* nitrates directed along the *J*–*T* axis. [22,23] Similar $N_2O_2N'_2$ geometry has been observed in other Cd(II) complex with the 4,5-diazafluorene template and anions NO_3^-, while it typically exhibit a more symmetrical coordination by adopting *cis* structures for two nitrate anions and two bidentate ligands (e.g., 4′,5′-diaza-9′-(4,5-bis(ethylthio)-1,3-dithiole-2-ylidene)-fluorene) [23].

3.2.4. *[Zn$_2$(L2)(μ-Cl)$_2$Cl$_2$]$_\infty$* (**4**)

A section of the one-dimensional polymer [Zn$_2$(L2)(μ-Cl)$_2$Cl$_2$]$_\infty$ is illustrated in Fig. 6; selected intramolecular distances and angles are presented in Table 3. The asymmetric unit contains only one-half of the molecules, the remainder being generated by a center of symmetry located on the O–O bond. The structure features of the peroxide group in **4** are similar to those of ap-9-(*o*-isopropylphenyl)-9-fluorenyl peroxide. [24] They include a C–O–O–C dihedral angle of 180°, and C–O and O–O distances of 1.433(4) and 1.473(5) Å, respectively. One phenyl ring of the biphenyl group is nearly perpendicular to their respective fluorenyl rings [79.7°], and the other is parallel to the fluorenyl ring [21.3°]. Meanwhile, the symmetry requires the two fluorene-ring planes connected by the O–O bond to be anti-parallel, which is also the case for the corresponding four phenyl-ring planes. In the similar fluorene

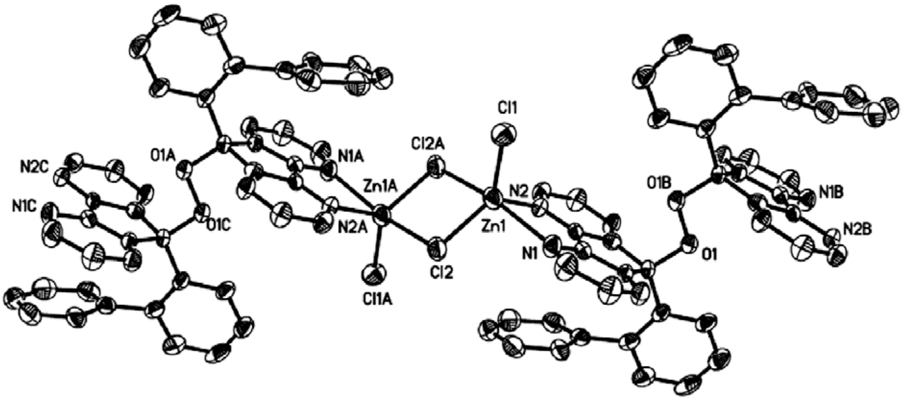


Fig. 6. View of a selected unit of the chain polymer **4** (thermal ellipsoids at 30% probability).

Table 3
Selected bond lengths (Å) and angles for complexes **1**–**4**.

Complex ***1***			
Cu1–O1	2.002(3)	Cu2–O5	1.916(3)
Cu1–N1	1.983(3)	Cu2–O8	2.008(3)
Cu1–N2	2.631(2)	Cu2–N4	2.037(3)
Cu2–O2	2.070(3)	Cu2–N3	2.348(4)
O2–Cu2–N4	161.5(1)	O2–Cu2–O5	82.57(2)
O2–Cu2–N3	80.92(1)	O8–Cu2–N3	86.20(1)
O1–Cu1–N1	88.86(2)	O8–Cu2–N4	91.54(1)
O8–Cu2–O5	171.0(2)		
Complex ***2***			
Cu1–O1	1.962(3)	Cu1–N1	2.037(3)
Cu1–O2	1.948(3)	Cu1–N2	2.489(3)
Cu1–O4	1.936(3)		
O1–Cu1–O2	88.41(1)	O2–Cu1–O4	177.12(1)
O1–Cu1–O4	89.11(1)	O2–Cu1–N1	91.74(1)
O1–Cu1–N1	178.3(1)		
Complex ***3***			
Cd1–N1	2.433(3)	Cd1–O1	2.411(5)
Cd1–N2	2.332(3)		
O1–Cd1–N1	103.4(2)	N1–Cd1–N2	102.7(1)
O1–Cd1–N2	84.10(1)	O1–Cd1–N1^{ii}	76.75(1)
Complex ***4***			
Zn1–N2	2.075(3)	Zn1–N1	2.447(4)
Zn1–Cl1	2.185(1)	Zn1–Cl2^{iii}	2.718(1)
Zn1–Cl2	2.233(1)	O1–O1^{iv}	1.473(5)
N2–Zn1–Cl1	113.9(1)	N2–Zn1–Cl2	124.75(1)
Cl2–Zn1–Cl1	121.2(5)	N2–Zn1–N1	78.78(1)
N1–Zn1–Cl1	96.26(10)	N1–Zn1–Cl2	91.41(1)
N2–Zn1–Cl2^{iii}	88.23(1)	Cl1–Zn1–Cl2^{iii}	99.99(5)
Cl2–Zn1–Cl2^{iii}	86.14(5)	N1–Zn1–Cl2^{iii}	162.3(1)
C11–O1–O1^{iv}	104.7(3)		

Symmetry codes: i, $-x, -y+2, -z+1$; ii, $-x+1, -y+1, -z+2$; iii, $-x+1, -y, -z+2$; iv, $-x, -y, -z+1$.

peroxide mentioned above [24], there only exists the perpendicular phenyl ring.

In complex **4**, zinc(II) centers are linked by bis-9-biphenyl-4,5-diazafluorenyl peroxide ligands to form an infinite zigzag chain. Terminal and bridged chloro groups complete the distorted trigonal–bipyramidal coordination around each metal ion. The coordination geometry of **4** is novel, in which one nitrogen atoms (N2, from the ligand L2) and two chloride ions (Cl1, Cl2) are in the basal plane, another nitrogen atom of the ligand (N1) and a chloride ion Cl2^{i} from the neighboring molecular unit occupy the axial position [symmetry code i: $1-x$, $2-y$, $-z$]. The distortion of the trigonal-bipyramid is indicated by the fact that the basal donor atoms not planar but deviate by as much as 0.0176 Å from their least-squares plane, and by the angle of N1–Zn1–Cl2^{i} [162.3(1)°]. As usual in the case of zinc(II) compounds, the axial Zn–Cl distance [2.718(1) Å] is much longer than the ones in the basal plane [2.233(1) and 2.185(1) Å].

An additional structural feature of interest is the involvement of four-membered Zn_2Cl_2 ring. The four-membered ring is coplanar completely with four atoms Zn1, Cl2, Zn1^{i} and Cl2^{i}. The Zn–Zn distance in the coordination dimmer is 3.630 Å, which is comparable with the Zn–Zn distance of 3.620 Å in the reported $[ZnCl_2(\mu\text{-bipy})]_\infty$ (bipy = 4,4′-bipyridine) polymer [1a].

Table 4
Hydrogen bonding geometries for complexes **1** and **2** (Å and °).

D–H···A	H···A	D···A	D–H···A
Complexe ***1***			
O(1)-H(1C)···O(4)^{i}	2.10(6)	3.010(5)	157(5)
O(1)-H(1C)···N(5)^{i}	2.62(6)	3.571(5)	171(4)
O(1)-H(1D)···O(10)^{ii}	1.83(6)	2.751(4)	160(5)
Complexe ***2***			
O(1)-H(1A)···O(3)^{iii}	1.69(5)	2.637(4)	173(4)
O(6)-H(6A)···O(7)^{iii}	2.08(6)	2.820(5)	157(5)
O(1)-H(1B)···O(5)^{iii}	1.90(6)	2.689(4)	157(5)
O(7)-H(7A)···O(6)^{iv}	2.15(6)	2.903(5)	175(6)
O(6)-H(6B)···O(2)	2.29(6)	2.959(4)	137(5)

Symmetry codes: i, $-x, -y+2, -z+1$; ii, $x-1, y, z$; iii, $-x+1, -y+1, -z+1$; iv, $x, y, z-1$.

Because of the flexibility of the ligand L2, the geometry arrangement between the biphenyl and 2,2′-bipyridine units in complex **4** differentiates markedly from that of the ligand L1. The most interesting characteristic is that one of the phenyl ring is approximately paralleled to the 2,2′-bipyridyl ring.

The role of π–π stacking interaction in the stability of structures in metal–organic coordination compounds has been a topic of much interest. [25,26] In the present complex, π–π interaction involving the 9-biphenyl-4,5-diazafluorenyl peroxide is also observed (Fig. 7). The centroid–centroid distance (*d*) between the phenyl and the bipyridyl rings is 3.495 Å and their interplanar angle (*θ*) is 20.9°. It should be noted that the intramolecular π–π interactions play an important role for the structural stability.

All efforts to obtain the crystal structure of the ligand L2 were not successful so far. However, we have determined the structure of the precursor of the ligands L1 and L2, 9-biphenyl-4,5-diazafluorenol. As it is shown from Fig. 8, in each independent fluorenol molecule there is an intramolecular π–π interaction which is extremely identical with the π-π interaction observed in complex **4.** So

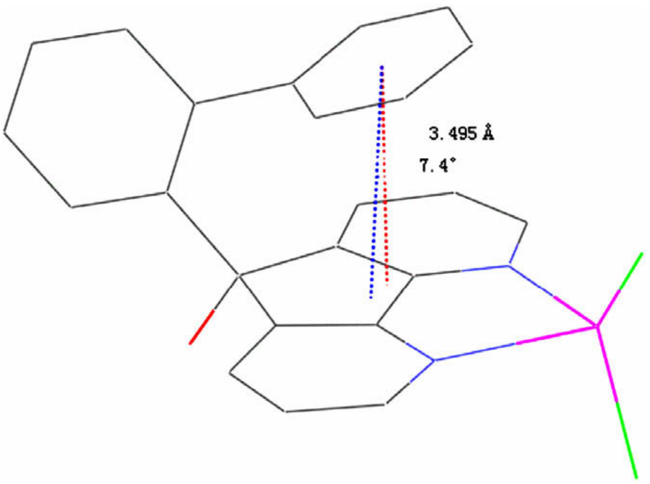


Fig. 8. Intramolecular π–π stacking interaction between the phenyl and fluorenyl rings in the complex **4**.

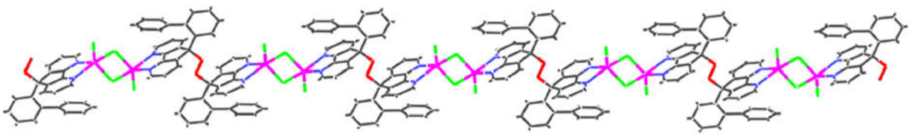


Fig. 7. Perspective view of the one-dimensional polymeric chain of complex **4**.

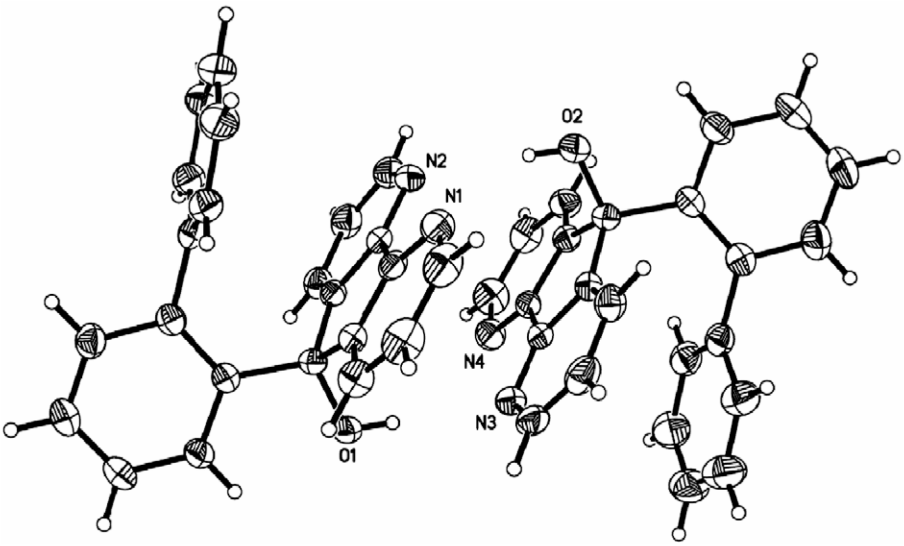
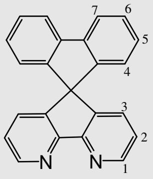
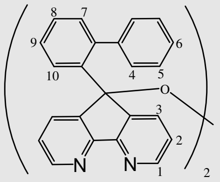


Fig. 9. X-ray single crystal structure of 9-biphenyl-4,5-diazafluorenol (30% probability thermal ellipsoids): showing the parallel stacking of the intermolecular fluorene domains or the intramolecular fluorene and phenyl rings.

Table 5
^{1}H NMR spectroscopic data for complexes containing L1 or L2.



L1



L2

	Hydrogen					
1	8.09 (1,7-H)		7.44 (3,4-H)	7.17 (5,6-H)		6.68 (2-H)
2	8.84 (1-H)	8.07 (7-H)	7.46 (3-H)	7.33 (4-H)	7.18 (5,6-H)	6.70 (2-H)
3	8.71 (1-H)	8.07 (7-H)	7.45 (3-H)	7.26 (4-H)	7.16 (5,6-H)	6.70 (2-H)
4	8.35 (1-H)		8.13 (7-H)	7.57 (10-H)	7.37 (6-H)	7.19 (3-H)
	6.97 (4-H)		6.85 (9-H)	6.77 (8-H)	6.54 (5-H)	5.86 (2-H)

it can be concluded that, when the biphenyl group is not fully fixed to the 9-position carbon atom appeared in the ligand L1, the conformation of one phenyl ring perpendicular to the fluorenyl ring and the other parallel is the most stable. Meanwhile, there also exists intermolecular π–π interaction for the fluorenyl rings between two adjacent 9-biphenyl-4,5-diazafluorenol in the unit cell, which contributes to the stability of the whole crystal structure.

3.3. ^{1}H NMR spectroscopy

All ^{1}H NMR spectra were measured in DMSO-d_6 for consistency. The ^{1}H NMR chemical shifts for complexes **1**–**4** are shown in Table 5.

From the ^{1}H NMR spectra of complexes **1**–**4** we can see that, different metal ions or coordination geometry have less affect on the chemical shift of the ligands in the complex except complex **1**. Both complex **2** and **3** exhibit six sets of aromatic hydrogen between 6.70 and 8.84 ppm. Only obvious difference for the protons at the 1 ortho-position of nitrogen-donor atoms can be found. But for complex **1**, due to the existence of two kinds of coordination geometry between ligand L1 and copper center, and the environment of some aromatic hydrogen have mixed a lot and shown only four

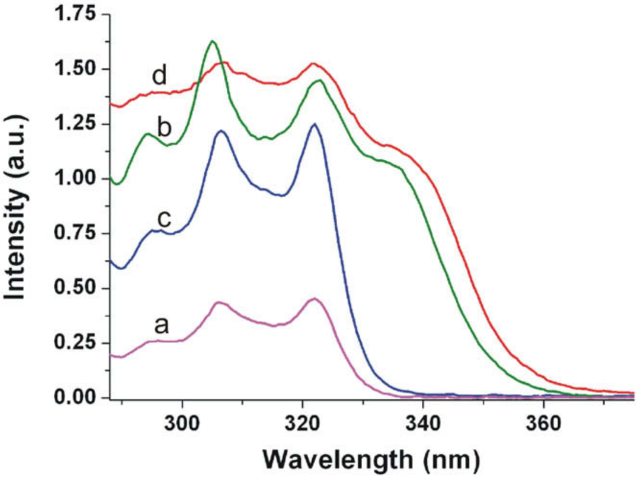


Fig. 10. Absorption spectra of L1 (a) and complex**1** (b), **2** (c), **3** (d) at 298 K in CH_3CN.

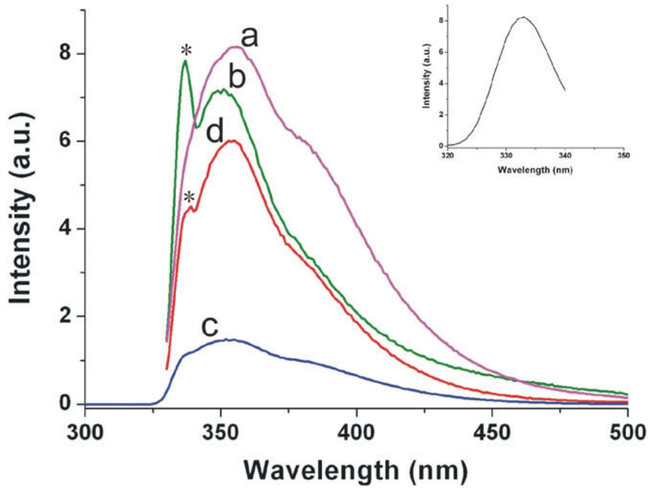


Fig. 11. Emission spectra of the free ligand L1 (a) and complex **1** (b), **2** (c), **3** (d) in CH_3CN solution at room temperature, excited at 333 nm (the peaks with a star are assigned to the scattering of the excitation; *inset:* excitation spectrum of the fluorescent species).

types of chemical shifts in the ^1H NMR spectra. Just like the proton environment of ligand L2 themselves, the ^1H NMR spectra of complex **4** shows ten sets of different types of aromatic hydrogen.

*3.4. UV–Vis and fluorescent spectra of complexes **1–3***

The UV–Vis spectral data of the ligand L1 and the three complexes in acetonitrile were measured. The dominant vibronic absorption peaks in complexes **1–3** at ~294, ~305, and ~322 nm can be ascribed to the ligand-centered (LC) π–π^* transitions. These spectral assignments were made on the basis of their spectral similarities with those of free ligand L1 (see Fig. 10) and a silver(I) complex with L1 [9]. Furthermore, for complex **1** and **3**, the Cu(II) and Cd(II) d–d transitions are observed as a single broad feature centered at 334 nm, consistent with a 6-coordinate mixed N, O coordination environment. [27]

In acetonitrile (CH_3CN), both the ligand L1 and corresponding metal complexes are emissive; fluorescent emission at UV wavelength (354 nm) of the free ligand L1 can be attributed to the ligand-centered π^*–π relaxation (Fig. 11). Ligand-based emission bands (~354 nm) are preserved in the corresponding Cu or Cd complexes, but the Ag complex reported previously is intrinsically nonluminescent throughout 350–800 nm in any organic solvent [9].

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Appendix A. Supplementary data

CCDC 671903, 668544, 668545, 668546, and 690767 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and 9-biphenyl-4,5-diazafluorenol. 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.2008.11.023.

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