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Anions-Induced Assembly: Structures and Luminescent Properties[1]

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Abstract—Self-assembly of a multidentate ligand containing pyridyl groups, namely, 6-phenyl-4-(4'-[2-(2-naphthalene)ethenyl]phenyl)-2,2'-bipyridine (L) with corresponding zinc(II) salts, affords a series of coordination complexes, $ZnLI_2$ (**I**), $[ZnLCl_2]_2 \cdot 2CH_2Cl_2$ (**II**), $ZnLBr_2$ (**III**). Complexes **I** and **II** were characterized by single crystal X-ray diffraction (CIF files CCDC nos. 943273 (I), 944798 (II)). In complex **I**, the π–π stacking and C–H···π interactions based on the pyridyl group constructed the 1D and 2D structures. While in complex **II**, various weak interactions including hydrogen bonds (C–H···Cl and C–H···π) played significant roles in the final supramolecular structures. The luminescent properties of ligand and the complexes were investigated. The results reveal that different anions have shown a great influence on both the molecular structures and luminescent properties of the complexes.

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INTRODUCTION

In recent years, the design and synthesis of organic-inorganic hybrid complexes based on strong coordinate bonds and multiple weak non-covalent forces have become hot spots along with the rapid development in coordination chemistry and crystal engineering owing to their fascinating structural features and interesting properties as new functional materials with tremendous potential applications in the areas of luminescence, catalysis, separation, adsorption, biological chemistry, and so on [1–3]. Many supramolecular coordination complexes with specific topologies and excellent properties have been synthesized by assembly of metal salts and organic ligands [4, 5]. So far, considerable progress has been achieved in dominating the assembly and orientation of individual building blocks into structures with specific topologies andfunctions including ion/molecular recognition, selective guestinclusion, ion exchange, etc. [6, 7]. However, it is still very difficult to design and synthesize supramolecular architectures with predicted structures due to multiple weak intermolecular interactions to control the molecular packing [8]. Moreover, although a lot of interesting metal-organic frameworks have been constructed from mixed ligands, the effects of the counter-anions on the assembly process of anionic and neutral mixed ligands with metal ions have also seldom been investigated. Hence, it is a challenge to predict and control the exactly discrete coordination architectures or infinite polymeric networks through the self-assembly process of metal ions and mixed ligands in crystal engineering since the structures are highly influenced by the coordination preferences of metal ions, the nature of organic ligands, and some very subtle factors, such as counter-anions [9].

The chemistry of anions as components in supramolecular assemblies is an area of increasing interest. Anions are of critical importance due to the vital roles they play in biological and industrial processes. Anions also have proven ability to afford structural control of supramolecules through interactions with other components [10–12]. The organic ligands can control the topology of coordination complexes. The design and synthesis of new organic ligands is a key approach for construction of metal-organic complexes with desired structures and properties. In designing coordination complexes, pyridyl derivatives have been widely used as ligands due to their ability to coordinate with several metal centers in various modes [13].

We have an on-going interest in nitrogen based on heterocyclic ligands and the fascinating structural diversity possible in their combination with zinc salts [14]. Taking the above into consideration and in order to construct new coordination complexes with specific structures and properties, a multidentate ligand containing pyridyl groups, namely, 6-phenyl-4-(4'-[2-(2-naphthalene)ethenyl]phenyl)-2,2' (**L**) has been designed and synthesized according to the following Scheme:

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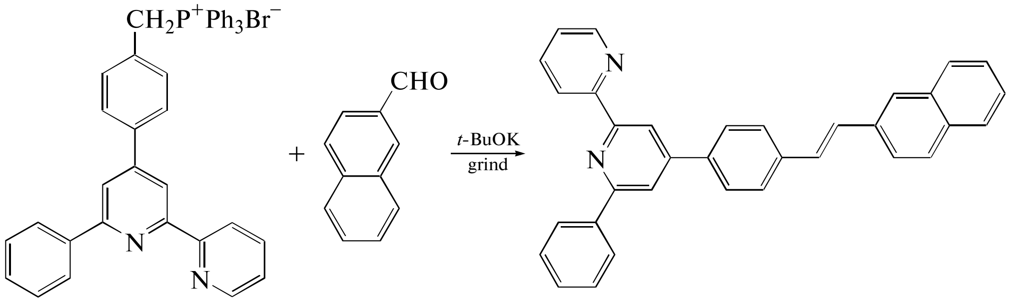
[1] The article is published in the original.



(M) (L)

Herein, we present structures and luminescent properties of the following complexes: ZnLI$_2$ (**I**), [ZnLCl$_2$]$_2$ · 2CH$_2$Cl$_2$ (**II**), ZnLBr$_2$ (**III**).

EXPERIMENTAL

General methods. All commercially available chemicals are of reagent grade and used without further purification. Elemental analyses were carried out on a PerkinElmer 240 analyzer. IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr disks) from 4000 to 400 cm^{-1}. The solid state luminescence spectra were measured on a F-4500FL spectrophotometer. For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA HuoroMax-4P). The decays were analyzed by least-squares. The quality of the exponential fits was evaluated by the goodness offit (χ^2).

Synthesis of L. To construct new coordination complexes with specific structures and properties, a multidentate ligand (L) containing pyridyl group has been designed and synthesized.

Intermediate (M) (0.97 g, 1.5 mmol) and *t*-BuOK (0.84 g, 7.50 mmol) was placed into a dry mortar and milled into powder, then 2-naphthaldehyde (0.23 g, 1.47 mmol) was added and milled vigorously [15, 16]. After completion of the reaction (monitored by thin layer chromatography (TLC), the mixture was dispersed in 100 mL dichloromethane. The filtrate was washed with water for three times and organic phase was dried with anhydrous magnesium sulfate. The filtrate was concentrated and 30 mL is *o*-propanol was added. Gray solid was gained after the suction filter, then the crude product was recrystallized by ethylacetate, 0.52 g creamy white solid was obtained, the yield was 75.3%.

^{1}H NMR (400 MHz; CD$_2$CCl$_2$; TMS; δ, ppm): 7.33–7.41 (m., 3H), 7.45–7.51 (m., 3H), 7.56 (t., 2H, *J* = 7), 7.76 (d., 2H, *J* = 7.6), 7.81–7.93 (m., 8H), 8.08 (s., 1H), 8.25 (d., 2H, *J* = 7.6), 8.70–8.75 (m., 3H). ^{13}C NMR (100 MHz; CDCl$_3$; TMS; δ, ppm: 117.66, 118.51, 122.25, 123.48, 124.14, 126.06, 126.41, 126.98, 127.13, 127.21, 127.61, 127.73, 128.08, 128.18, 128.40, 128.80, 129.25, 129.85, 133.17, 134.62, 137.28, 138.34, 139.28, 147.77, 149.80, 155.42, 157.44.

FT-IR (ν, cm^{-1}): 3448 w, 3055 m, 2026 w, 1686 w, 1600 v.s, 1584 s, 1567 s, 1543 s, 1513 s, 1498 s, 1451 m, 1473 s, 1391 v.s, 1261 m, 1124 m, 1075 m, 963.4 v.s, 856 v.s, 826 s, 792 s, 772 s, 753 s, 734 m, 695 s, 681 m, 618 m, 537 s, 516 w. LDI-TOF MS: *m*/*z* = 460.96 ([M + 1]$^+$, C$_{34}$H$_{24}$N$_2$ requires 460.19).

Synthesis of complex I. A methanol solution (15 mL) of ZnI$_2$ (0.016 g, 0.05 mmol) was added to a dichloromethane solution (15 mL) of L (0.0230 g, 0.05 mmol). The clear mixture solution was left to evaporate slowly at room temperature for a few days, and pale yellow, block shape crystals of I suitable for single crystal X-ray diffraction were obtained. The yield was 28.4 mg (73%).

For C$_{34}$H$_{24}$N$_2$I$_2$Zn

anal. calcd., %:	C, 52.37;	H, 3.10;	N, 3.59.
Found, %:	C, 52.35;	H, 3.12;	N, 3.60.

FT-IR (ν, cm^{-1}): 3448 w, 3052 w, 2346 w, 2026 w, 1599 v.s, 1540 s, 1485 v.s, 1459 w, 1445 w, 1429 w, 1399 s, 1365 m, 1241 m, 1123 m, 1063 m, 1024 m , 967 s, 893 w, 853 s, 821 s , 770 s, 750 s, 738 s, 670 v.s, 681 m, 651 m, 613 w, 536 m, 503 w, 478 m.

Synthesis of complex II. The reaction was carried out using ZnCl$_2$ in the same method for I, and the pale yellow, needle-like crystals of II suitable for single crystal X-ray diffraction were obtained. The yield was 26.9 mg (79%).

For C$_{70}$H$_{52}$N$_4$Cl$_8$Zn$_2$

anal. calcd., %:	C, 61.66;	H, 3.84;	N, 4.11.
Found, %:	C, 61.75;	H, 3.80;	N, 4.13.

FT-IR (ν, cm^{-1}): 3444 w, 3054 m, 2352 w, 2026 w, 1599 v.s, 1584 s, 1538 s, 1513 s, 1486 m, 1470 m, 1445 m, 1416 w, 1391 v.s, 1259 m, 1124 s, 1072 s, 1024 m , 963 v.s, 856 v.s, 826 v.s, 791 s, 752 s, 697 s, 681 m , 640 m, 615 m, 537 s, 516 w, 485 w.

Synthesis of complex III. By the same method with using of ZnBr$_2$, we obtained the complex III.

Table 1. Crystalloraphic data and structure refinement for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	779.72	681.75
Crystal system	Tetragonal	Triclinic
Space group	$P4_32_12$	$P\bar{1}$
a, Å	13.901(4)	13.6254(17)
b, Å	13.901(3)	13.7778(17)
c, Å	31.497(2)	18.119(2)
α, deg	90	87.596(2)
β, deg	90	88.320(2)
γ, deg	90	67.961(2)
V, Å^3	6086(2)	3149.7(7)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.702	1.438
μ, mm^{-1}	2.861	1.147
θ, Range, deg	1.60–25.55	1.12–25.00
F(000)	3024	1392
Reflections collected/unique	45052/5658	22546/10982
R_{int}	0.0560	0.0314
GOOF on F^2	1.023	0.958
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0838$ $wR_2 = 0.2450$	$R_1 = 0.0838$ $wR_2 = 0.2450$
R indices (all data)	$R_1 = 0.1374$ $wR_2 = 0.3058$	$R_1 = 0.1374$ $wR_2 = 0.3058$
$\Delta\rho_{max}\Delta\rho_{min}$, e Å^{-3}	1.248/–1.126	1.737/–0.862

The yield was 27.8 mg (81%).

For $C_{34}H_{24}N_2Br_2Zn$

anal. calcd., %:	C, 59.55;	H, 3.53;	N, 4.08.
Found, %:	C, 59.56;	H, 3.64;	N, 4.23.

FT-IR (ν, cm^{-1}): 3443 w, 3055 m, 2926 w, 2026 w, 1795 w, 1600 v.s, 1538 m, 1485 m, 1445 w, 1391 m, 1242 w, 1123 m, 1070 m, 1025 w, 963 m, 870 w, 855 w, 825 m, 790 m, 772 w, 699 m, 681 w, 640 w, 615 w, 538 m, 517 w, 477 w.

From the elemental analysis result, we can infer the unit of this compound contains only one $ZnLBr_2$ molecule.

X-ray crystallography. X-ray diffraction data of single crystals were collected on a Siemens Smart 1000 CCD diffractometer. Determination of unit cell parameters and data collections were performed with MoK_α radiation (λ = 0.71073 Å). Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods using SHELXS-97 [17]. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed using full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms on F^2. Hydrogens were added theoretically, riding on the concerned atoms. The crystal data collection parameters are summarized in Table 1. Selected bonds lengths and angles are listed in Table 2.

Supplementary material for complexes I and II has been deposited with the Cambridge Crystallographic Data Centre (nos. 943273 (I), 944798 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structures of complexes I and II were determined by X-ray crystallography. In complex I, Zn^{2+} ion locates in a four coordination environment as illustrated (Fig. 1a), coordinated with two iodine atoms and two N of pyridyl groups derived from one ligand. The coordination geometry of the Zn(II) center is distorted tetrahedron. The bond angles around the Zn^{2+} ion are in the rang of 80.9(4)°–127.6(3)°. A 1D linear chain is well-organized *via* π–π stacking interactions of two benzene ring from adjacent molecules with a centroid-centroid distance of 3.828 Å (Fig. 1b). These 1D chains were further linked by C–H···π bonds to

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–I(1)	2.552(2)	Zn(1)–N(1)	2.042(11)
Zn(1)–I(2)	2.520(2)	Zn(1)–N(2)	2.093(12)
		II	
Zn(1)–Cl(2)	2.2022(17)	Zn(2)–N(2)	2.070(4)
Zn(1)–Cl(1)	2.2253(16)	Zn(2)–N(1)	2.073(4)
Zn(1)–N(5)	2.056(5)	Zn(2)–Cl(4)	2.1806(16)
Zn(1)–N(6)	2.082(4)	Zn(2)–Cl(3)	2.2304(18)
Angle	ω, deg	Angle	ω, deg
		I	
N(1)Zn(1)N(2)	80.9(4)	I(2)Zn(1)I(1)	119.75(9)
N(1)Zn(1)I(1)	111.1(3)	N(1)Zn(1)I(2)	104.9(3)
N(2)Zn(1)I(1)	105.0(3)	N(2)Zn(1)I(2)	127.6(3)
		II	
N(5)Zn(1)N(6)	80.41(17)	N(2)Zn(2)N(1)	79.69(16)
N(5)Zn(1)Cl(2)	112.22(14)	N(2)Zn(2)Cl(4)	111.78(12)
N(6)Zn(1)Cl(2)	110.41(12)	N(1)Zn(2)Cl(4)	115.73(13)
N(5)Zn(1)Cl(1)	103.34(14)	N(2)Zn(2)Cl(3)	118.19(12)
N(6)Zn(1)Cl(1)	120.25(13)	N(1)Zn(2)Cl(3)	103.70(13)
Cl(2)Zn(1)Cl(1)	121.61(7)	Cl(4)Zn(2)Cl(3)	120.31(7)

generate a 2D structure (Fig. 1c). The H(12)···centroid distance is 3.193 Å.

Similar to I, each Zn^{2+} ion atom in II coordinated with two chlorine atoms and two N atoms of pyridyl groups from one ligand. The local coordination environment around Zn^{2+} ion can be also regarded as a slightly distorted tetrahedron. It is obvious that there is apparent difference between the two complexes. In the molecular structure of complex II, there are two crystallographically and conformationally independent $ZnLCl_2$ molecules with two CH_2Cl_2 solvent molecules in the asymmetric unit (Fig. 2a). The solvent molecules play a vital role in building the supramolecular structures by hydrogen bonding. The neighboring asymmetric units are linked each other *via* CH_2Cl_2 molecule in head to tail configuration by C(26)–H(26)···Cl(10) hydrogen bonding interactions (H···Cl 2.82 Å) and C(100)–H(10*B*)···Cl(2) (H···Cl 2.83 Å) to giving rise to a 1D structure (Fig. 2b). Also contributed by another C(32)–H(32)···π interaction with the distance of 3.833 Å, a 2D structure is produced along the *x* axis (Fig. 2c). Multiple C(18)–H(18)···Cl(2) interactions with the distance of 2.846 Å based on the 2D structure contributed to the formation of the 3D supramolecular structure (Fig. 3).

Coordination complexes with d^{10} metal atoms show fluorescence properties and are promising candidates for photoactive materials with potential applications. For potential applications as luminescent materials, the luminescent properties of ligand and complexes have been investigated in the solid state at room temperature.

The emission spectra of I–III and L are depicted in Fig. 4. The free ligand shows an intense fluorescent emission maximum at 429 nm with a shoulder peak at 452 nm upon excitation at 372 nm, which is attributed to the ligand-centered π–π* electronic transitions. In contrast to the free ligand, complexes I, II, and III exhibit broader fluorescent emission band at 470, 471, and 454 nm (corresponding excitation under 389, 393, and 383 nm for I–III), respectively, which may be assigned to the intraligand π–π* transition because of the resemblance of the emission spectra [18]. Compared with the emission spectra of the ligand, varying degree of red shifts of 41, 42, and 25 nm for I–III have been observed, respectively, which may be attributed to the coordination ofligand to the metal centers [19].

To further understand the fluorescent properties, the fluorescence quantum yield and lifetime of complexes I–III and ligand L were investigated. The fluorescence decay profiles of L and complexes were measured at their optimal wavelengths in solid state at room temperature, and the detailed data of the fluo-

Table 3. Fluorescence lifetimes (t), fractional contribution (*A*), fluorescence quantum yields (F), maximum excitation wavelength (λ_{det}), fitted value (χ^2) of ligand and complexes **I–III**

Compound	Φ	τ_1, ns^a (A_1^b)	τ_2, ns^a (A_2^b)	τ_3, ns^a (A_3^b)	$\langle\tau\rangle$, ns^c (χ^2)	λ_{det}, nm^d
L	0.099	0.81 (0.88)	3.0 (0.12)		1.07 (1.99)	372
I	0.014					389
II	0.103	1.71 (0.16)	0.24 (0.82)	5.79 (0.02)	0.56 (1.19)	393
III	0.030					383

[a] Fluorescence lifetime; [b] fractional contribution; [c] weighted mean lifetime; [d] detection wavelength.

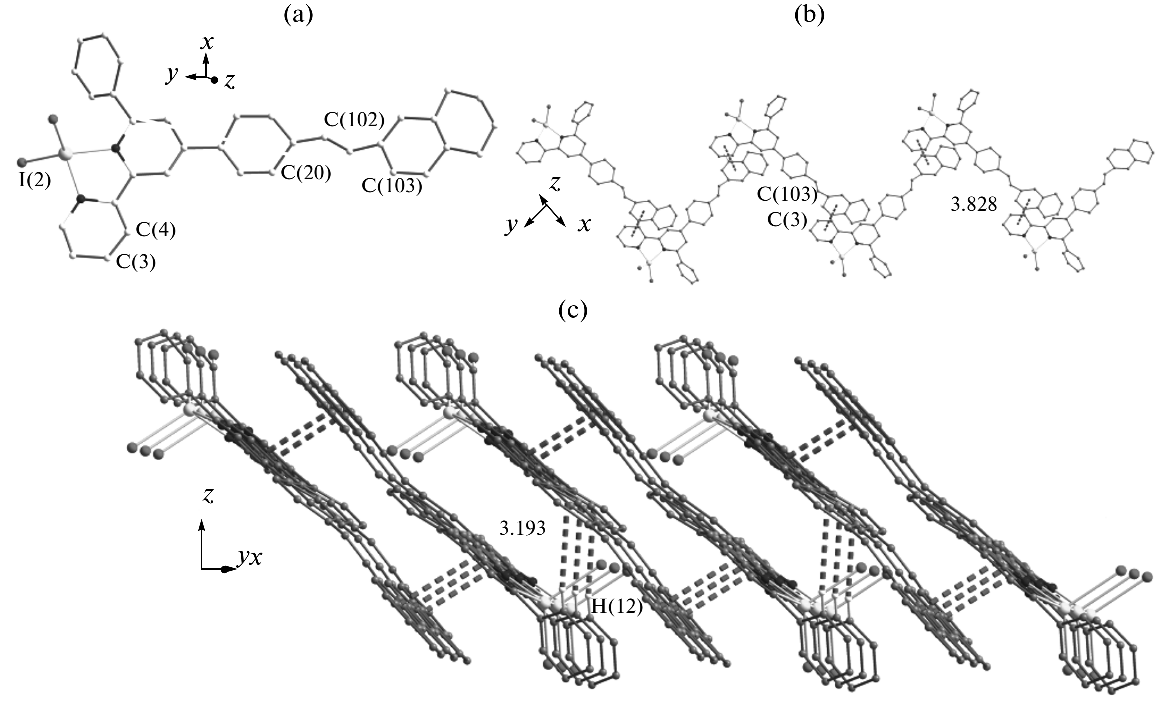


Fig. 1. Coordination environment of Zn atom with the atom numbering scheme (a); 1D framework of I showing the π–π stacking interactions (b); the 2D framework of complex I showing the C–H···π and π–π stacking interaction (c). Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

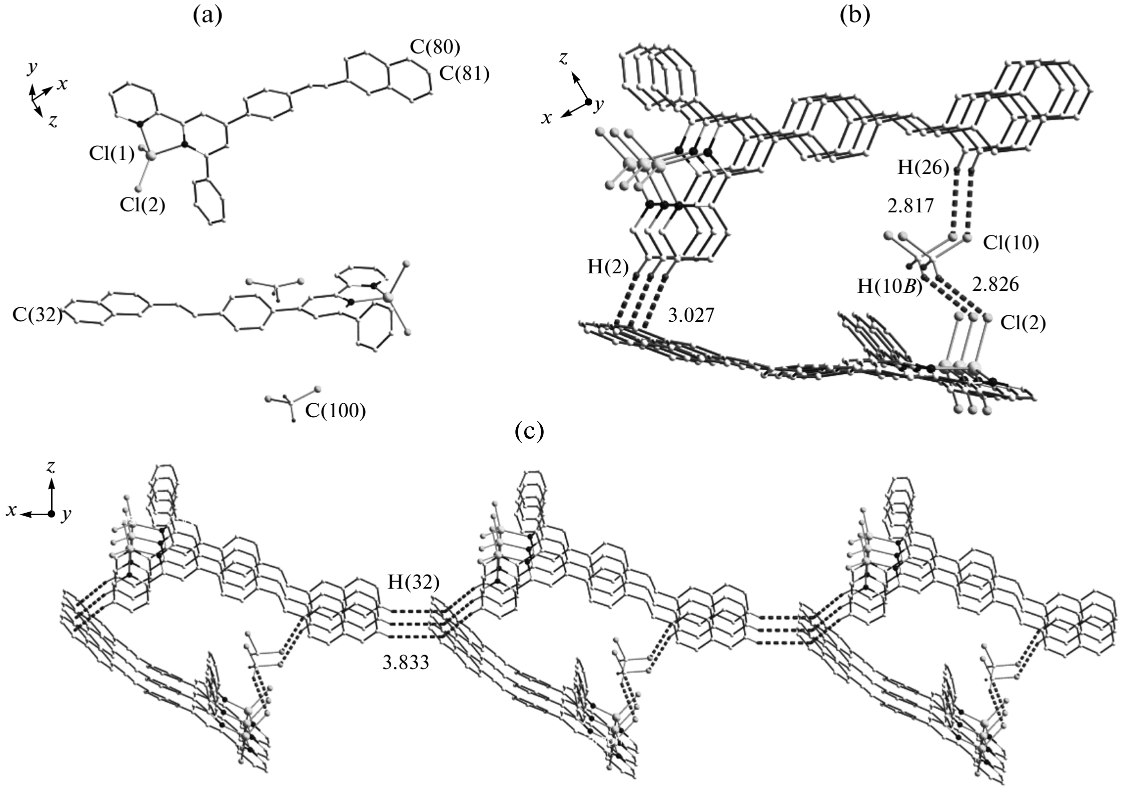


Fig. 2. The structural unit of complex II (a); the one-dimensional structure of complex II formed by C–H···π and CH···Cl interactions (b); the two-dimensional structure of complex II formed by multiple C–H···π interactions (c). Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

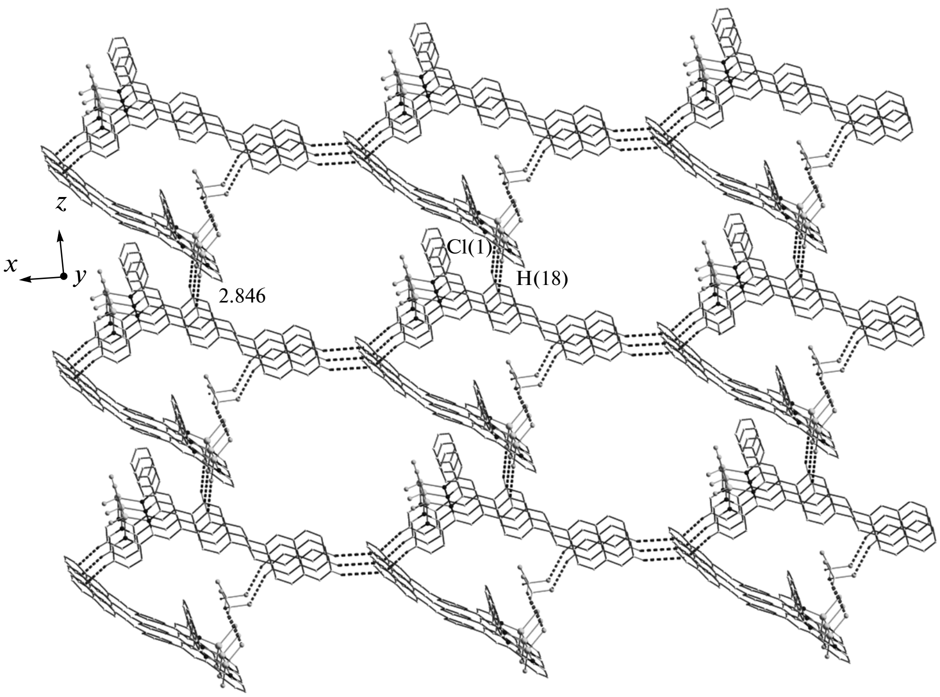


Fig. 3. The three dimensional structure of complex II formed by multiple C–H···Cl hydrogen bonding interactions. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

rescence decay curves (Fig. 5, Table 3). The fluorescence lifetime of complexes II (0.56 ns) is shorter than that of L (1.07 ns). The different anions and coordination environments of metal centres would have an effect on the emission wavelength, intensity, and fluorescence lifetimes of the complexes. Meanwhile, we also explored the lifetimes of complexes I and III. However, according to the original theoretical data, we can draw a conclusion that the two complexes have no lifetimes, the possible explanation is the heavy-atom effect of Br and I ions in complexes I and III [20].

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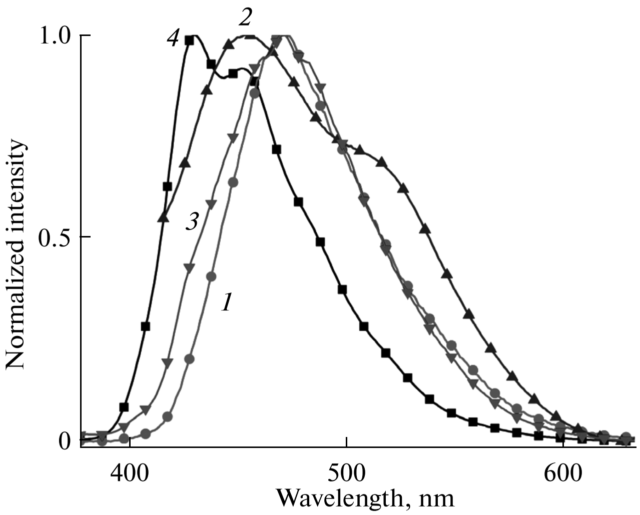

Fig. 4. Solid-state emission spectra of complexes I–III (*1*–*3*) and L (*4*) at room temperature.

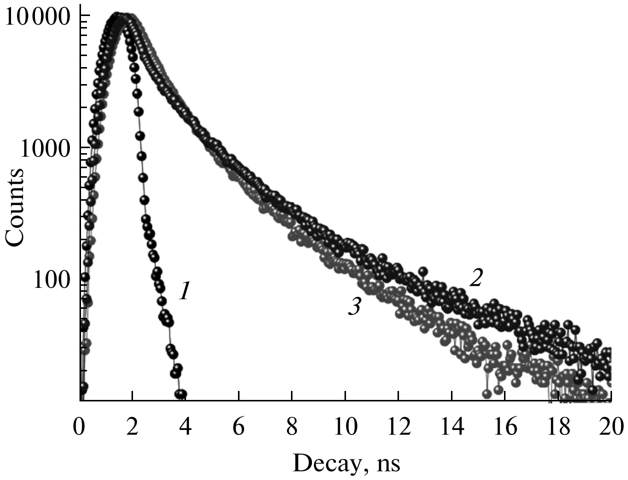

Fig. 5. Time-resolved fluorescence curves: SiO_2 (*1*), complexes II (*2*) and L (*3*) in the solid state at room temperature.

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