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## ARTICLE

# Semidirected vs. holodirected coordination and single component white light luminescence in Pb(II) complexes

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Ling Chen<sup>a</sup>, Cheng Yan<sup>a</sup>, Mei Pan<sup>a,b\*</sup>, Yuan-Zhong Fan<sup>a</sup>, Lu-Yin Zhang<sup>a</sup>, Shao-Yun Yin<sup>a</sup>, Ya-Jun Hou<sup>a</sup>, Kai Wu<sup>a</sup>, Ji-Jun Jiang<sup>a\*</sup>, and Cheng-Yong Su<sup>a\*</sup>

HMq (2-methyl-8-hydroxyquinoline) or tripodal ligands triBZ-NTB (4,4',4''-(2,2',2''-nitrilotris(methylene)tris(1*H*-benzo[*d*]imidazole-2,1-diyl)tris(methylene))tribenzonitrile) and H<sub>3</sub>triCB-NTB (4,4',4''-(2,2',2''-nitrilotris(methylene)tris(1*H*-benzo[*d*]imidazole-2,1-diyl)tris(methylene))tribenzoic acid) were applied to assemble mono-, tetra- or hetero-nuclear Pb(II) complexes, in which the Pb(II) coordination centers are either semidirected or holodirected coordinated with the ligands and counter anions (small solvent molecules), leading to varied coordination geometries. Moreover, the combination of LMCT (ligand to metal charge transfer) and MC (metal-centered) emissions in semidirected Pb(II) complexes results in single-component white light luminescence.

## Introduction

Due to the booming development of supramolecular coordination chemistry, the past few decades have witnessed a fast progress in the design and construction of photoluminescent coordination complexes, with potential applications in chemical sensors,<sup>1,2</sup> emitting devices,<sup>3,4</sup> biological imaging purposes,<sup>5</sup> and so on. Among which, as a choice for the urging demand of white light emitting (WLE) materials, different types of single component WLE coordination complexes have emerged rapidly in recent reports.<sup>6-8</sup> Comparatively, the assembly and photoluminescence properties of *p*-block metal complexes have been rarely studied. Despite the environmental concern, Pb(II), as a heavy *p*-block metal ion, has unique lone pair electron effects (with *ns*<sup>2</sup>*np*<sup>0</sup> configuration), large radius and flexible coordination contributes, which provides special opportunities for the construction of novel photoluminescent coordination structures.<sup>9-11</sup> For example, using H<sub>2</sub>pydc (pyridine-2,5-dicarboxylic acid) ligand, zur Loye\* et al assembled two single component white-light-emitting bismuth (Bi) and lead (Pb) MOFs, whose luminescence was originated from the intraligand  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and LMCT transitions.<sup>12</sup> In another example, two white light emitting Pb(II)-MOFs with 3D net structures were obtained, based on the composition of LC (ligand-centered) emission, LMCT (ligand to metal charge transfer) emission, and tailing emission which can be assigned to MC (metal-centered) transitions involving the *s* and *p* orbitals of Pb(II) clusters.<sup>13</sup> The characteristic white light luminescence in

these complexes makes them attractive candidates for WLE device materials.

We report herein four Pb(II)-containing coordination complexes from N,O-ended 2-methyl-8-hydroxyquinoline (HMq) or two tripodal ligands (triBZ-NTB and H<sub>3</sub>triCB-NTB). Due to the variation of pH value in the assembling process, Mq<sup>-</sup> coordinates with Pb(II) into 4-coordinated mononuclear (complex **1**) or 5-coordinated tetranuclear (complex **2**) complexes, in which the coordination geometries of Pb(II) ions are both semidirected. While two triBZ-NTB ligands encapsulate Pb(II) into a mononuclear complex (complex **3**), in which the Pb(II) centers are holodirected surrounded by eight N atoms from the ligands. In comparison, the bifunctional {HtriCB-NTB}<sup>2-</sup> ligands co-assemble Pb(II) and Zn(II) ions into a heteronuclear infinite coordination polymer (complex **4**), in which the coordination geometry of Pb(II) center is also holodirected, comprising six O atoms from triCB-NTB ligands and DMF, and an additional Cl anion. For the semidirected coordination in complexes **1** and **2**, significant lone pair electron effect brings wider LMCT emission as well as additional MC emission in longer wavelength region, affording single-component white light photoluminescence.

## Experimental

### Materials and methods

All raw materials and solvents were obtained from commercial sources and used without further purification. <sup>1</sup>H NMR spectra were

measured on a Varian/Mercury-Plus 300 instrument. The C, H, and N elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ). Photoluminescence spectra were taken at room temperature on an EDINBURGH FLS920 or 980 fluorescence spectrophotometer.

### Crystallography

Single-crystal reflection data were collected on an Agilent Gemini S Ultra or SuperNova diffractometer at 293 K with the Enhance X-ray Source of Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) or Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) using the  $\omega$ - $\phi$  scan technique. Structural solution and refinement against  $F^2$  were carried out using the OLEX2 programs. All the non-hydrogen atoms were refined with anisotropic parameters, while H atoms were placed in calculated positions and refined using a riding model, except for the H atoms of water molecules. Squeeze method has been used to remove all solvent molecules in complex **4**. Crystallographic data and structural refinement information are listed in Table 1. The selected bond lengths and bond angles for compounds are listed in Table S1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1055420-1055423.

### Synthesis of ligand

The ligands triBZ-NTB (4,4',4''-(2,2',2''-nitrioltris(methylene)tris(1*H*-benzo[*d*]imidazole-2,1-diyl)tris(methylene))tribenzonitrile) and H<sub>3</sub>triCB-NTB (4,4',4''-(2,2',2''-nitrioltris(methylene)tris(1*H*-benzo[*d*]imidazole-2,1-diyl)tris(methylene))tribenzoic acid) were synthesized according to our earlier report.<sup>14</sup>

### Synthesis of complexes

**[Pb(Mq)<sub>2</sub>]<sub>2</sub>·3(H<sub>2</sub>O) (1)**: A solution of Pb(NO<sub>3</sub>)<sub>2</sub> (0.1 mmol, 33 mg) in water (2 mL) was added to the bottom of a tube. And then, in turn, 4 mL mixed solution (water-ethanol, v/v=1:1) and 2 mL solution of HMq ligand (0.1 mmol, 16 mg) in ethanol (pH=7-8) were carefully added into the tube. After layering at room temperature for two weeks, yellow crystals of **1** suitable for single crystal diffraction were obtained from the middle layer in 70% yield according to HMq. Anal. Calc. (%) for [Pb(C<sub>10</sub>H<sub>8</sub>NO)<sub>2</sub>]<sub>2</sub>·(H<sub>2</sub>O): C, 44.27; H, 3.35; N, 5.17. Found: C, 44.35; H, 3.57; N, 5.06.

**[Pb<sub>4</sub>(Mq)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (2)**: A solution of Pb(NO<sub>3</sub>)<sub>2</sub> (0.1 mmol, 33 mg) in water (2 mL) was added to the bottom of a tube. And then, in turn, 4 mL mixed solution (water-ethanol, v/v=1:1) and 2 mL solution of HMq ligand (0.1 mmol, 16 mg) in ethanol (pH was adjusted to 5-6 by perchloric acid) were carefully added into the tube. After layering at room temperature for two weeks, brown crystals of **2** suitable for single crystal diffraction were obtained from the middle layer in 60% yield according to HMq. Anal. Calc. (%) for [Pb<sub>4</sub>(C<sub>10</sub>H<sub>8</sub>NO)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>·(C<sub>2</sub>H<sub>5</sub>OH) (2·C<sub>2</sub>H<sub>5</sub>OH): C, 36.78; H, 2.73; N, 4.25. Found: C, 38.08; H, 2.73; N, 4.29.

**[Pb(triBZ-NTB)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> (3)**: A mixture of triBZ-NTB (0.1mmol) in 2 ml DMF and Pb(NO<sub>3</sub>)<sub>2</sub> (0.05 mmol) in 2 ml water was sealed in a 15 ml Teflon-lined stainless steel container. The container was heated to 120 °C and held at that temperature for 100 h, and then cooled to room temperature. Colorless crystals of **3** were collected in 70% yield. Anal. Calc. (%) for [Pb(C<sub>48</sub>H<sub>36</sub>N<sub>10</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>4</sub> (3·2H<sub>2</sub>O): C, 60.28; H, 4.19; N, 16.12. Found: C, 60.40; H, 4.22; N, 16.13.

**{[PbZn(HtriCB-NTB)(DMF)Cl<sub>2</sub>]<sub>n</sub>·solvents (4·solvents)}**: A mixture of H<sub>3</sub>triCB-NTB (0.1mmol) in 2 ml DMF, Pb(NO<sub>3</sub>)<sub>2</sub> (0.1 mmol) and ZnCl<sub>2</sub> (0.1 mmol) in 2 ml water was sealed in a 15 ml Teflon-lined stainless steel container. The container was heated to 120 °C and held at that temperature for 20 h, and then cooled to room temperature. Colorless crystals of **4** were collected in 45% yield. Anal. Calc. (%) for [PbZn(C<sub>48</sub>H<sub>37</sub>N<sub>7</sub>O<sub>6</sub>)(C<sub>3</sub>H<sub>7</sub>NO)Cl<sub>2</sub>·(C<sub>3</sub>H<sub>7</sub>NO)(H<sub>2</sub>O)<sub>4</sub> (4·DMF·4H<sub>2</sub>O): C, 47.37; H, 4.31; N, 9.21. Found: C, 46.74; H, 4.21; N, 9.33.

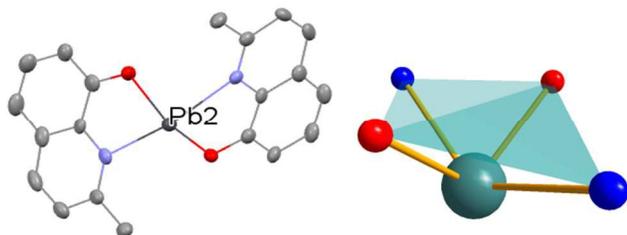
## Results and discussion

Table 1. The crystal data and structure refinement summary for complexes **1-4**.

Complex	1	2	3	4
Formula	C <sub>20</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub> 5Pb	C <sub>60</sub> H <sub>48</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>14</sub> Pb <sub>4</sub>	C <sub>96</sub> H <sub>76</sub> N <sub>22</sub> O <sub>8</sub> Pb	C <sub>51</sub> H <sub>43</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>7</sub> PbZn
F. w.	550.56	1976.70	1872.98	1223.39
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P-1
<i>a</i> (Å)	22.6209(13)	10.0789(2)	15.6793(4)	13.0328(5)
<i>b</i> (Å)	12.2218(7)	21.1453(3)	21.2137(5)	14.6898(5)
<i>c</i> (Å)	16.4211(9)	13.7167(2)	26.0127(5)	16.6176(8)
$\alpha$ (°)	90	90	90	94.303(3)
$\beta$ (°)	128.697(1)	102.148(2)	99.137(1)	108.155(4)
$\gamma$ (°)	90	90	90	108.110(3)
Volume (Å <sup>3</sup> )	3543.2(3)	2857.86(8)	8542.5(3)	2820.8(2)
Z	8	2	4	2
Dcalc (g cm <sup>-3</sup> )	2.064	2.297	1.456	1.440
$\mu$ (mm <sup>-1</sup> )	9.549	11.914	2.048	7.565
GOF	1.039	0.989	1.022	1.086
<i>R</i> <sub>1</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.0307	0.0379	0.0438	0.0855
<i>wR</i> <sub>2</sub> (all data)	0.0619	0.0688	0.1157	0.2925

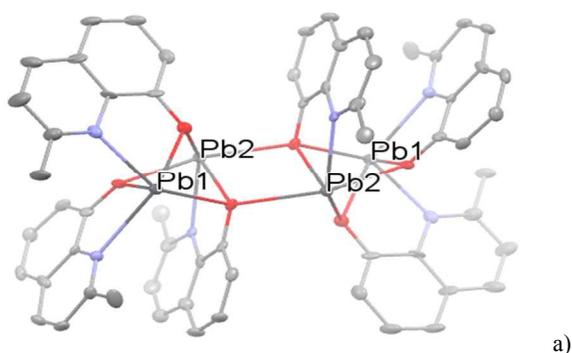
The coordination of Pb<sup>2+</sup> with HMq in pH range 7-8 resulted in

mononuclear complex **1**,  $[\text{Pb}(\text{Mq})_2]_2 \cdot 3(\text{H}_2\text{O})$ , whose structure is similar to that reported before,<sup>15</sup> which crystallizes in monoclinic space group  $C2/c$  and the asymmetric unit consists of one  $\text{Pb}^{2+}$  and two  $\text{Mq}^-$  ligands, as well as one and a half uncoordinated  $\text{H}_2\text{O}$  molecules. The  $\text{Pb}^{2+}$  ion is coordinated with two N and two O atoms from two  $\text{Mq}^-$  ligands, forming semidirected 4-coordination geometry (Fig. 1). We can see that the underneath direction of  $\text{Pb}^{2+}$  center is noncoordinated and vacant, leaving free  $6s^2$  lone pair position, which will induce special photoluminescence behavior in this complex.

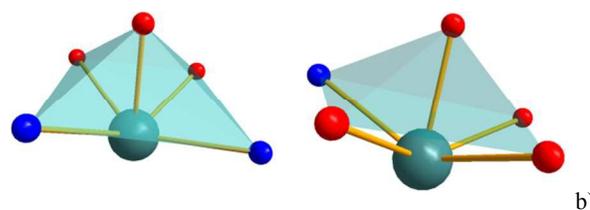


**Fig. 1** Crystal structure (left) and coordination geometry of central  $\text{Pb}^{2+}$  ion (right) in complex **1**. The coordination geometry of  $\text{Pb}^{2+}$  is semidirected. The hydrogen atoms and uncoordinated solvent molecules are omitted for clarity.

In comparison, the coordination of  $\text{Pb}^{2+}$  with HMq in pH range 5-6 resulted in tetranuclear complex **2**,  $[\text{Pb}_4(\text{Mq})_6] \cdot (\text{ClO}_4)_2$ , which crystallizes in monoclinic space group  $P2_1/n$  and the asymmetric unit consists of two different  $\text{Pb}^{2+}$  ions and three  $\text{Mq}^-$  ligands, as well as one uncoordinated  $\text{ClO}_4^-$  anion. Both  $\text{Pb1}$  and  $\text{Pb2}$  ions are 5-coordinated, among which  $\text{Pb1}$  is coordinated with two N and three O atoms from three different  $\text{Mq}^-$  ligands, while  $\text{Pb2}$  is coordinated with one N and four O atoms from four different  $\text{Mq}^-$  ligands (Fig. 2a). An inversion center links two of the above  $\{\text{Pb}_2\text{Mq}_3\}^+$  units into a tetranuclear structure. We can see that both of the two different kinds of  $\text{Pb}^{2+}$  centers are semidirected-coordinated (Fig. 2b), with free  $6s^2$  lone pair positions, similar to that in complex **1**, although the coordination geometries are different. The pH-dependent coordination structure of complexes **1** and **2** should be mainly related with the variation in linking abilities of hydroxyl O atoms on HMq ligands under different pH values.



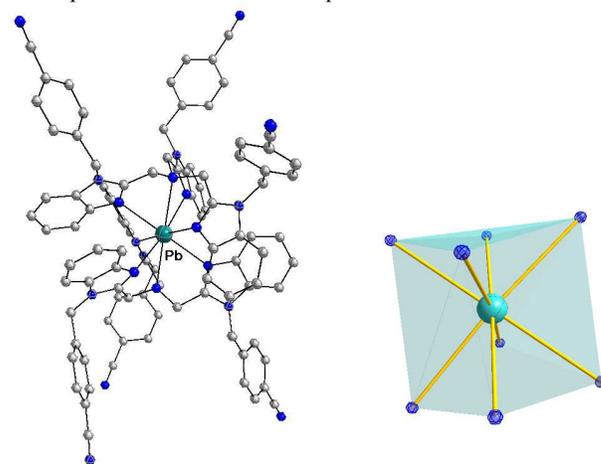
a)



b)

**Fig. 2** Crystal structure (a) and coordination geometries of two different kinds of  $\text{Pb}^{2+}$  ions (b) in complex **2**. The coordination geometries of the two different kinds of  $\text{Pb}^{2+}$  ions are both semidirected. The hydrogen atoms and uncoordinated anions are omitted for clarity.

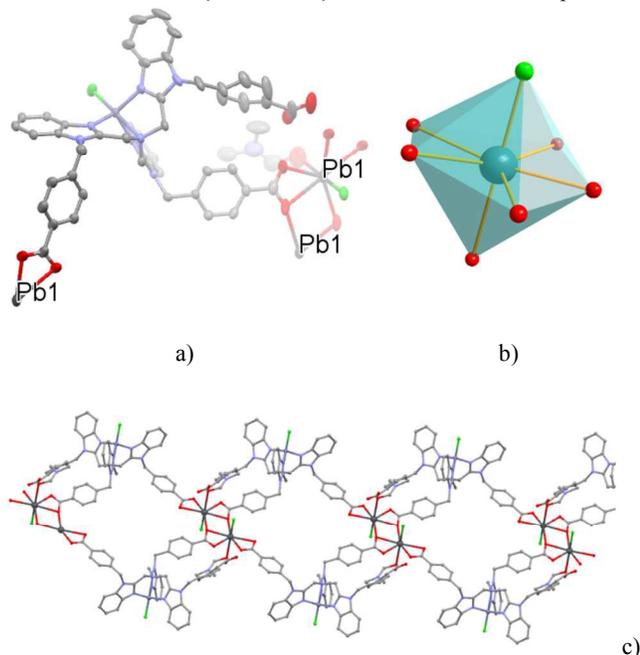
Reaction of tripodal ligand triBZ-NTB having only N ending coordination atoms with  $\text{Pb}(\text{NO}_3)_2$  resulted in mononuclear complex **3**, which crystallizes in monoclinic space group  $P2_1/c$  and the asymmetric unit consists of one  $\text{Pb}^{2+}$  and two triBZ-NTB ligands, as well as two uncoordinated  $\text{NO}_3^-$  anions and two water molecules. The  $\text{Pb}^{2+}$  ion is encapsulated by two triBZ-NTB ligands, forming 8-coordinated polyhedron by six benzimidazole N and two apical N atoms (Fig. 3). We can see that the coordination geometry of  $\text{Pb}^{2+}$  center is holodirected and the Pb-N distances are within 2.652-2.875 Å. The  $-\text{CN}$  groups in triBZ-NTB ligands are not coordinated in complex **3** and present a freely-stretching configuration, which makes complex **3** to be a discrete complex.



**Fig. 3** Crystal structure (left) and coordination geometry of central  $\text{Pb}^{2+}$  ion (right) in complex **3**. The coordination geometry of  $\text{Pb}^{2+}$  is holodirected distorted cube. The hydrogen atoms and uncoordinated anions/solvent molecules are omitted for clarity.

The co-assembly of another tripodal ligand  $\text{H}_3\text{triCB-NTB}$  having both N and O ending coordination atoms with  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  affords a heteronuclear coordination polymer (complex **4**), which crystallizes in triclinic  $P-1$  space group. According to the empirical soft-hard acid theory,<sup>16</sup>  $\text{Zn}^{2+}$  centers have potential affinity to the N coordination sites from the central NTB core, while  $\text{Pb}^{2+}$  ions prefer the carboxyl O atoms. Therefore, the coordination geometry of  $\text{Zn}^{2+}$  in complex **4** is 5-coordinated, surrounded by four N atoms from one  $\{\text{HtriCB-NTB}\}^{2-}$  ligand and one additional chloride anion. And the  $\text{Pb}^{2+}$  center is 7-coordinated by five carboxyl O atoms from three different  $\{\text{HtriCB-NTB}\}^{2-}$  ligands, one O atom from DMF, and

another chloride anion, forming holodirected pentagonal bipyramid geometry (Figs. 4a and b). The linking of two  $\text{Pb}^{2+}$  centers by carboxyl groups from four  $\{\text{HtriCB-NTB}\}^{2-}$  ligands results in a  $\{\text{Pb}_2\text{O}_{10}\text{Cl}_2\}$  cluster in complex **4**, which further extends the complex into a 1D loop-and-chain structure along  $a$  direction (Fig. 4c). It is noted that one carboxyl group on  $\text{H}_3\text{triCB-NTB}$  ligand in complex **4** is not deprotonated and not involved in coordination, therefore, it exists as  $\{\text{triCB-NTB}\}^{2-}$  anion state in the complex.



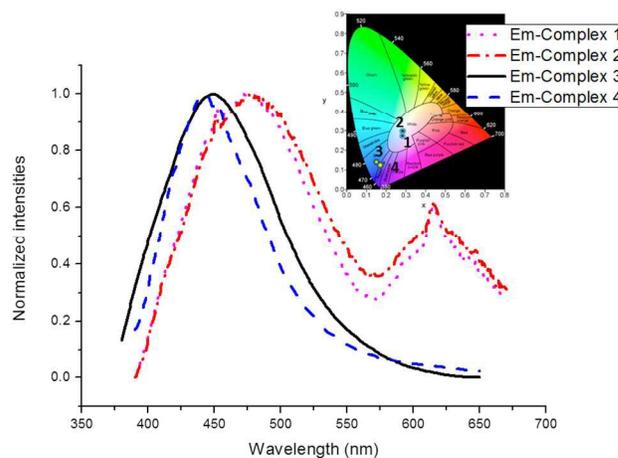
**Fig. 4** Crystal structure showing coordination of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions (a), coordination geometry of  $\text{Pb}^{2+}$  ion (b), and loop-and-chain linking structure (c) in complex **4**. The coordination geometry of  $\text{Pb}^{2+}$  is holodirected pentagonal bipyramid. The hydrogen atoms and uncoordinated solvent molecules are omitted for clarity.

Table 2. Photophysical properties of complexes **1-4**.

Complex	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
$\lambda_{\text{max}}(\text{EM})/\text{nm}$	480/615	475/616	450	443
$\tau/\text{ns}$	0.04/0.03	0.08/0.19	0.80	0.90
Assignment	LMCT/MC	LMCT/MC	LC	LC

The photoluminescence properties of complexes **1-4** were investigated in the solid state (Fig. 5 and Table 2). As we can see, complexes **3** and **4** show broad emission peaks centered at 443-450 nm, related with the intraligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the triBZ-NTB and  $\text{H}_3\text{triBZ-NTB}$  ligands (Fig. S3). This is in accordance with the fact that complexes **3** and **4** have no obvious  $\text{Pb}^{2+}$  lone pair electron effect dictated by nearly holodirected coordination geometry described above. Therefore, no obvious  $\text{Pb}^{2+}$ -perturbation is involved in the ligand photoluminescence. In comparison, the photoluminescence peaks of complexes **1** and **2** are obviously red-shifted to 475-480 nm, featuring LMCT (ligand-to-metal charge transfer) character from the ligand  $\text{Mq}^-$  to  $\text{Pb}^{2+}$ .

Furthermore, another obvious emission spreading well into the red region beyond 600 nm is observed in complexes **1** and **2**, suggestive of metal-centered (MC) transitions involving the  $s$  and  $p$  orbitals of  $\text{Pb}^{2+}$ , which is obviously related with the semidirected coordination geometry in these two complexes. As a result, different from the blue emission tone in complexes **3** and **4**, white light photoluminescence was observed in complexes **1** and **2**, both due to the LMCT red shift of the main luminescence peaks and the appearance of MC emissions.

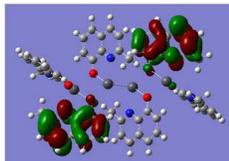
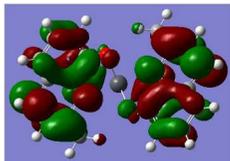


**Fig. 5** Photoluminescence spectra of complexes **1-4** in the solid state at room temperature ( $\lambda_{\text{exc}} = 345 \text{ nm}$ ). And the inset denotes the calculated CIE coordinates, located at (0.29, 0.29), (0.29, 0.30), (0.16, 0.15), and (0.17, 0.11), respectively.

Table 3. Schematic representation of the optimized geometrical structure and HOMO-1, HOMO, LUMO, and LUMO+1 orbitals of complexes **1-2**.

Complex	<b>1</b>	<b>2</b>
HOMO-1		
HOMO		
LUMO		

LUMO+1



To further elucidate the photoluminescence origins in the white light emitting Pb(II) complexes **1-2**, DFT calculations were performed using the B3LYP hybrid functional implemented in the Gaussian-09 suite of programs.<sup>17</sup> The basis sets used were 6-31G(d) for C, H, N, O and LanL2DZ for Pb. As we can see, the HOMO and HOMO-1 orbitals of the two complexes comprise contributions mainly from the  $\pi$  orbitals of Mq<sup>-</sup> ligands and  $d$  orbitals of Pb<sup>2+</sup> ions. We can also detect clearly the existence of 6s<sup>2</sup> lone pair electrons on Pb<sup>2+</sup> positions. While the LUMO and LUMO+1 orbitals are mainly contributed by the  $\pi^*$  orbitals of the ligands, as well as the vacant  $p$  orbitals of Pb<sup>2+</sup> (Table 3). This manifests the strong LMCT and MC transition tendency in these two complexes and supports the observation of white light photoluminescence combination.

## Conclusions

We have successfully synthesized four Pb(II)-containing mononuclear, tetranuclear or heteronuclear coordination compounds using N, O-ended HMq or substituted NTB ligands. Either holodirected or semidirected coordination geometries are presented in the compounds, resulting in different photoluminescence behaviour. Among which, compounds **1** and **2** with semidirected coordination geometry show obvious lone pair electron effect related with the s<sup>2</sup> state of Pb<sup>2+</sup> ions, affording single component white light photoluminescence, and making them attractive luminescent materials for solid-state WLE device applications.

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## Notes and references

<sup>a</sup> MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, Lehn Institute of Functional Materials, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

panm@mail.sysu.edu.cn;

jiangjij@mail.sysu.edu.cn;

cesscy@mail.sysu.edu.cn

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

Electronic Supplementary Information (ESI) available: [PXRD, TG, more emission and crystallographic information]. See DOI: 10.1039/b000000x/

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