



#### Cluster Compounds

## Phosphorescence at Low Temperature by External Heavy-Atom Effect in Zinc(II) Clusters

Fumiya Kobayashi,<sup>[a]</sup> Ryo Ohtani,<sup>[a]</sup> Saki Teraoka,<sup>[a]</sup> Masaki Yoshida,<sup>[b]</sup> Masako Kato,<sup>[b]</sup> Yingjie Zhang,<sup>[c]</sup> Leonard F. Lindoy,<sup>[d]</sup> Shinya Hayami,<sup>\*[a, e]</sup> and Masaaki Nakamura<sup>\*[a]</sup>

**Abstract:** Luminescent Zn<sup>II</sup> clusters  $[Zn_4L_4(\mu_3-OMe)_2X_2]$  (X = SCN (1), Cl (2), Br (3)) and  $[Zn_7L_6(\mu_3-OMe)_2(\mu_3-OH)_4]Y_2$  (Y = I<sup>-</sup> (4), ClO<sub>4</sub><sup>-</sup> (5)), HL=methyl-3-methoxysalicylate, exhibiting blue fluorescence at room temperature ( $\lambda_{max}$ =416  $\approx$  429 nm,  $\Phi_{em}$ =0.09–0.36) have been synthesised and investigated in detail. In one case the external heavy-atom effect (EHE) arising the presence of iodide counter anions yielded phosphorescence with a long emission lifetime ( $\lambda_{max}$ =520 nm,  $\tau$ =95.3 ms) at 77 K. Single-crystal X-ray structural analysis and time-dependent density-functional theory (TD-DFT) calculations revealed that their emission origin was attributed to the fluorescence from the singlet ligand-centred (<sup>1</sup>LC) excited state, and the phosphorescence anions having strong CH–I interactions.

Luminescent transition-metal complexes have attracted much attention because of their characteristic photophysical properties that, for example, have led to the development of organic light-emitting devices (OLEDs),<sup>[1]</sup> chemical sensors,<sup>[2]</sup> molecular probes,<sup>[3]</sup> and photosensitizers.<sup>[4]</sup> Transition-metal complexes, particularly those of Ir<sup>III</sup>, Pt<sup>II</sup>, Ru<sup>II</sup>, and Au<sup>I</sup>, have been well studied due to their tendency to display strong emission as well as spin-orbit coupling (SOC), reflecting the presence of the heavymetal centres.<sup>[5]</sup> However, the high cost of those metals is a

[a]	F. Kobayashi, Dr. R. Ohtani, S. Teraoka, Prof. Dr. S. Hayami, Dr. M. Nakamura
	Department of Chemistry, Graduate School of Science and Technology Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto
	860-8555 (Japan)
	E-mail: hayami@kumamoto-u.ac.jp
	m_nakamura@kumamoto-u.ac.jp
[b]	Dr. M. Yoshida, Prof. Dr. M. Kato
	Department of Chemistry, Faculty of Science, Hokkaido University North-10 West-8, Kita-ku, Sapporo, Hokkaido 060-0810 (Japan)
[c]	Dr. Y. Zhang
	Australian Nuclear Science and Technology Organization
	Locked Bag 2001, Kirrawee DC, NSW, 2232 (Australia)
[d]	Prof. Dr. L. F. Lindoy
	School of Chemistry, The University of Sydney, NSW 2006 (Australia)
[e]	Prof. Dr. S. Hayami
	Institute of Pulsed Power Science (IPPS), Kumamoto University
	2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555 (Japan)
	Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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vices. Construction of luminescent Zn<sup>II</sup> complexes is, therefore, an attractive alternative approach for developing novel functional luminescent materials.<sup>[6]</sup> Zn<sup>II</sup> complexes have a further advantage in that their use can facilitate the otherwise relatively difficult to obtain blue emission because most such complexes show luminescence based solely on a ligand-centred (LC) transition.<sup>[7]</sup> However, it can be difficult to obtain long lifetime phosphorescence and to control emission wave lengths because of the weak SOC commonly exhibited by Zn<sup>II</sup> complexes, with exceptions being several Zn<sup>II</sup>-based luminescent metal-organic frameworks (MOFs).<sup>[8]</sup> In the present study we focused on a strategy involving application of an external heavy-atom effect (EHE) that introduces SOC into Zn<sup>II</sup> clusters. It is considered that the EHE is executed through orbital interactions between the heavy-atoms and the luminophore, resulting in increases of both the intersystem crossing (ISC) rates and the phosphorescence decay time of the excited-state luminophore.<sup>[9]</sup> Although the EHE has been routinely utilized to promote the phosphorescence of organic molecules,<sup>[10]</sup> very few reports of the application of the EHE to metal complex systems have appeared. In this study, we have designed and synthesised cationic Zn<sup>II</sup> clusters with heavy-atom counter anions. Clusters are a particularly suitable class of materials for achieving high quantum yields because their structural rigidity leads to thermo- and photostability relative to smaller monoor dinuclear complexes.<sup>[11]</sup>

significant issue for their continuing use in luminescent de-

Herein, we report the presence of anion-dependent blue emissions with high luminescence quantum yields and phosphorescence associated with the EHE in Zn<sup>II</sup> clusters of type  $[Zn_4L_4(\mu_3\text{-}OMe)_2X_2]$  (HL = methyl-3-methoxysalicylate; X = SCN, Cl, Br) and  $[Zn_7L_6(\mu_3\text{-}OMe)_2(\mu_3\text{-}OH)_4]Y_2$  (Y = I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>).

The three tetranuclear  $Zn^{II}$  clusters  $[Zn_4L_4(\mu_3-OMe)_2X_2]$  (X = SCN (1), Cl (2), Br (3)) and two wheel-type heptanuclear  $Zn^{II}$  clusters  $[Zn_7L_6(\mu_3-OMe)_2(\mu_3-OH)_4]Y_2$  (Y = I<sup>-</sup> (4), ClO<sub>4</sub><sup>-</sup> (5)) were synthesized using the methods, with minor modification, reported previously by us.<sup>[12]</sup> A 1:1:1 mixture of the required  $Zn^{II}$  salt, HL and triethylamine in methanol was stirred for 30 min at room temperature and the resultant solution was allowed to stand for a few days. 1, 2, 3, and 5 were obtained as colourless crystals while 4 was obtained as yellow crystals (Scheme 1). Elemental analyses for 1–5 were in accord with their formulations as  $[Zn_4L_4(\mu_3-OMe)_2(SCN)_2]$ ,  $[Zn_4L_4(\mu_3-OMe)_2(Cl)_2]$ ·0.5 CH<sub>3</sub>OH,  $[Zn_7L_6(\mu_3-OMe)_2(\mu_3-OH)_4]$ -(ClO<sub>4</sub>)<sub>2</sub>·4.5 CH<sub>3</sub>OH, respectively.

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Scheme 1. Synthesis scheme for 1-5.

Single-crystal X-ray structural analyses for **1–5** were carried out at 100 or 123 K (see Figure 1). Crystallographic data is displayed in Table S1, Supporting Information. Individual structures of the tetranuclear  $Zn^{\parallel}$  clusters **1–3** are shown in Figure S1, Supporting Information. Each consists of a "defective"



**Figure 1.** Crystal structures of the tetranuclear  $Zn^{\parallel}$  clusters  $[Zn_4L_4(\mu_3 - OMe)_2X_2]$  (X=SCN, Cl, Br) (1–3) and heptanuclear  $Zn^{\parallel}$  clusters  $[Zn_7L_6(\mu_3 - OMe)_2(\mu_3 - OH)_4]Y_2$  (Y=I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) (**4**, **5**). Hydrogen atoms, counter anions and solvent molecules are omitted for clarity.

double-cubane core  $[{Zn_4O_6}]$  in which four  ${Zn^{{{\scriptscriptstyle \parallel}}}}$  ions are bridged by  $\mu_3$ -methoxo groups and  $\mu_2$ -O atoms of the deprotonated methyl-3-methoxysalicylate ligands (Figure S1d, Supporting Information). In 1, two different octahedral Zn<sup>II</sup> coordination spheres are present (Figure S1e, Supporting Information). One is formed by six oxygen atoms: four arising from carbonyl and bridging phenoxo groups on the L<sup>-</sup> ligands and two from bridging methoxo groups. The other is formed by an anion and five oxygen atoms: four arising from methoxy and bridging phenoxo groups on the L<sup>-</sup> ligands and one from a bridging methoxo group. Compounds 2 and 3 have similar structures to 1 except that they contain two five-coordinated  ${\sf Zn}^{\scriptscriptstyle \|}$ ions which lack coordinating methoxy groups from the L<sup>-</sup> ligands (Figure S1b,c, Supporting Information). The crystal structures of the wheel-type heptanuclear  $Zn^{\parallel}$  clusters **4** and **5** are shown in Figure S2, Supporting Information. Each consist of a divalent cationic heptanuclear cluster,  $[Zn_7L_6(\mu_3-OMe)_2(\mu_3-Me)_2(\mu_3 OH_{4}]^{2+}$ , with their respective counter anions (I<sup>-</sup> or  $CIO_{4}^{-}$ ). The seven  $Zn^{\parallel}$  ions are bridged by two  $\mu_3$ -OMe, four  $\mu_3$ -OH, six phenoxo and six alkoxo groups to form a Zn<sub>7</sub> wheel core displaying a Zn@Zn<sub>6</sub> arrangement. The central Zn<sup>II</sup> ion is coordinated by two methoxo- and four hydroxo-groups with the Zn-O bond lengths spanning 2.096(9)-2.125(8) Å. The peripheral Zn<sup>II</sup> ions are coordinated by one methoxy, one carbonyl, and two deprotonated phenol groups from L<sup>-</sup> ligands, with Zn–O bond lengths of 1.991(9)-2.295(9) Å. The crystal void and solvent accessible area volume for **1–5** were calculated by Crystal Explorer<sup>[13]</sup> and PLATON<sup>[14]</sup> (Figure S8, Supporting Information). The results are listed in Table S2 and S3, Supporting Information. The calculations revealed that **1–5** have 9.7, 3.6, 5.0, 8.3, 10.4% crystal voids per one-cell unit, which contain solvent accessible area volume ratios of 2.0, 0, 0, 1.6, 3.8%, respectively.

UV/Vis absorption and emission spectra of the HL ligand in the solid state at room temperature are shown in Figure 2. The UV/Vis absorption spectrum shows an absorption band ( $\lambda_{abs}$ = 318 nm) attributed to the  ${}^{1}\pi\pi^{*}$  transition while the emission



**Figure 2.** UV absorption spectrum (red line,  $\lambda_{abs}$ =318 nm) and emission spectrum (blue line,  $\lambda_{ex}$ =318 nm,  $\lambda_{max}$ =402 nm) of HL in the solid state at room temperature.

spectrum displays a fluorescence band ( $\lambda_{max} = 402 \text{ nm}$ ) attributed to the  ${}^{1}\pi\pi^{*}$  transition. The solid-state excitation and emission spectra of 1-5 at room temperature and 77 K are shown in Figure 3 and Figure S9, Supporting Information. At room temperature, the solid (crystalline) samples of 1-3 each exhibited blue luminescence. The emission spectra for 1-3 show unstructured broad emission bands with maxima ( $\lambda_{max}$ ) at 416, 422, and 418 nm, respectively. Although slight changes in the maxima for 1-3 are observed, the emission spectra are quite similar. When compared with the emission maximum for HL, the maxima for 1-3 are significantly shifted. These differences are in accord with an increase in the HOMO energy in each case reflecting the different electronegativities between a proton and the Zn<sup>II</sup> ion.<sup>[7b]</sup> The above observations for 1-3 indicate that the emission maxima are essentially not affected by the coordinating anions. The solid-state excitation and emission spectra of 4 and 5 at room temperature and 77 K are

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Figure 3. Luminescence spectra of  $Zn^{\parallel}$  clusters 1–5 in the solid state at a) room temperature and b) 77 K.

shown in Figure S9, Supporting Information. At room temperature, crystalline samples of 4 and 5 also exhibited blue luminescence. Emission spectra for 4 and 5 showed unstructured broad emission bands with the maxima ( $\lambda_{max}$ ) occurring at 424 and 429 nm, respectively. Each showed related photoluminescent behaviour to 1-3, indicating a contribution of the intraligand  ${}^{1}\pi\pi^{*}$  transition to their luminescence. These results serve to demonstrate that differences in the coordinated environments of the Zn<sup>II</sup> ions and also the number of Zn<sup>II</sup> ions in the clusters do not greatly affect their emission maxima. Importantly, in the spectrum of 4, a shoulder around 520 nm was observed at 77 K, which is assignable to the phosphorescence, in addition to the emission band at 425 nm. CIE 1931 coordinates for emission spectra of 1-5 clearly show the emission colour change of 4 from deep blue to pale blue based on the expression of phosphorescence at low temperature (Figure S10, Table S4, Supporting Information), while the emission colours of 1-3 and 5 were almost unchanged even at 77 K.

Emission lifetimes ( $\tau$ ) and emission quantum yields ( $\Phi$ ) were measured for 1–5 (Table 1, Figure S11, Supporting Information). Each of 1–5 have emission lifetimes in the nanosecond range, 1 ( $\tau_{av}$ =4.84 ns), 2 ( $\tau_{av}$ =7.64 ns), 3 ( $\tau_{av}$ =4.45 ns) 4 ( $\tau_{av}$ = 2.26 ns), and 5 ( $\tau_{av}$ =5.40 ns), which are in accord with expected values arising from intraligand  ${}^{1}\pi\pi^{*}$  transitions in Zn<sup>II</sup> complexes.<sup>[7]</sup> Emission quantum yields ( $\Phi$ ) of 1–3 were found to decrease slightly in the order of 1 (0.36), 2 (0.29), 3 (0.23) at

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Table 1. Photophysical data for 1–5 in the solid state at 298 K.						
	$\lambda_{\max} \ [nm]^{[a]}$	$arPhi^{ ext{bl}}$	$\tau_{\rm av} \ [\rm ns]^{[c]}$	$k_{\rm r}  [{\rm s}^{-1}]^{\rm [d]}$	$k_{\rm nr}  [{\rm s}^{-1}]^{[{\rm e}]}$	
1	416	0.36	4.84	7.4×10 <sup>7</sup>	1.3×10 <sup>8</sup>	
2	422	0.29	7.64	$3.8 \times 10^{7}$	9.3×10 <sup>7</sup>	
3	418	0.23	4.45	$5.2 \times 10^{7}$	$1.7 \times 10^{8}$	
4	424	0.09	2.26	$4.0 \times 10^{7}$	$4.0 \times 10^{8}$	
5	429	0.29	5.40	5.4×10 <sup>7</sup>	1.3×10 <sup>8</sup>	

[a] Emission maximum,  $\lambda_{ex}$ =330 nm. [b] Emission quantum yields,  $\lambda_{ex}$ = 340 nm. [c] Averaged emission lifetimes,  $\lambda_{ex}$ =340 nm. [d] Radiative rate constants, estimated from  $\Phi/\tau_{av}$  [e] Nonradiative rate constants, estimated from  $k_r(1-\Phi)/\Phi$ .

298 K. Compound 5 exhibited a similar emission quantum yield to 1-3 of 0.29, whereas 4 showed a significantly smaller value at 0.09 than found for the others. This smaller value is likely due to ISC generated by the external heavy-atom effect (EHE) of the iodide counterions present in this case.<sup>[11]</sup> The shoulder present in the spectrum of 4 around 520 nm at 77 K was associated with a remarkably long emission lifetime of  $\tau =$ 95.3 ms, in agreement with this emission band resulting from phosphorescence involving the lowest-excited triplet state (T<sub>1</sub> state). An emission quantum yield ( $\Phi$ ) of **4** at 77 K was evaluated at 0.32. An emission spectrum of 4 at 77 K, measured after a delay time of 100 ms after the excitation, clearly exhibited a broad phosphorescence band with the maximum at  $\lambda_{phos}$  = 520 nm (Figure 4). Although this phosphorescence was not observed at room temperature due to the thermal deactivation, overall, the results illustrate the significant contribution of triplet excited states of 4 generated by the EHE (arising from the presence of the iodine ions).

To investigate the relationship between structures and emission origins for resultant clusters, DFT and TDDFT calculations for **2** were carried out because **2** is suitable molecular size for calculations rather than **4**, which consists of large heptanuclear clusters. The HOMO and LUMO are shown in Figure S12, Supporting Information (Table S5 and S6, Supporting Information).



**Figure 4.** Excitation (dotted lines) and emission (solid lines) spectra of **4** in the solid state at 77 K. Red and blue lines represent steady-state emission ( $\lambda_{ex}$ =330 nm,  $\lambda_{em}$ =450 nm) and phosphorescence spectra ( $\lambda_{ex}$ =330 nm,  $\lambda_{em}$ =550 nm, delay time = 100 ms), respectively.

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The singlet excited states were also calculated for **2** by using TDDFT. The lowest energy of the spin-allowed electronic vertical transitions  $[\Delta E(S_0-S_1)]$  was 3.69 eV (336 nm) (Figure 5, see Table S7, Supporting Information). These results support that the S<sub>1</sub> state of **2** is singlet ligand-centred (<sup>1</sup>LC) excited state



**Figure 5.** Natural transition orbitals for the key vertical excitation of **2**, in which *f* refers to the oscillator strength. The highest occupied transition orbital (HOTO) and the lowest unoccupied transition orbital (LUTO), show the occupied "hole" and the unoccupied "electron", respectively, for this excitation.

and that the intraligand transition occurs from the ligand  $\boldsymbol{\pi}$ HOMO delocalized in the benzene rings and methoxy groups to the ligand  $\pi^*$  LUMO delocalized in the benzene rings and carbonyl groups. A similar origin for the emission is anticipated for each of 1-5 due to their similar photoluminescence spectra and radiative rate constants. In the case of 4, strong CH-I interactions between the ligand and counter anion (I<sup>-</sup>) are observed (Figure S13 and S14, Supporting Information). For 5, although many hydrogen bonds are present between the ligand and the ClO<sub>4</sub><sup>-</sup> counter anions occur (Figure S15, Supporting Information), no phosphorescence was observed. The above contrasting behaviour is in keeping with 4 exhibiting orbital interactions between the ligand and the I<sup>-</sup> counter anion that give rise to the EHE promoting the ISC rates, yielding the phosphorescence caused by <sup>3</sup>LC.<sup>[15]</sup> Such generation of the EHE via orbital interaction clearly provides an efficient approach for introducing SOC into complexes associated with a ligand-centred (LC) transition than via direct coordination of heavy-atoms as occurs in 1-3.

In conclusion, we have synthesized the luminescent Zn<sup>II</sup> clusters of types [Zn<sub>4</sub>L<sub>4</sub>(µ<sub>3</sub>-OMe)<sub>2</sub>X<sub>2</sub>] (X=SCN, Cl, Br) and [Zn<sub>7</sub>L<sub>6</sub>(µ<sub>3</sub>-OMe)<sub>2</sub>(µ<sub>3</sub>-OH)<sub>4</sub>]Y<sub>2</sub> (Y=I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) and demonstrated that iodide counterions produced the external heavy-atom effect (EHE) for the expression of the phosphorescence ( $\lambda_{max}$ =520 nm) with the extremely long emission lifetime ( $\tau$ =95.3 ms). To the best of our knowledge, this is the first observation of long phosphorescence involving the EHE arising from counter anions in luminescent Zn<sup>II</sup> clusters.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** external heavy-atom effect · long emission lifetime · luminescence · phosphorescence · zinc

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# COMMUNICATION

#### Cluster Compounds

F. Kobayashi, R. Ohtani, S. Teraoka, M. Yoshida, M. Kato, Y. Zhang, L. F. Lindoy, S. Hayami,\* M. Nakamura\*

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Phosphorescence at Low Temperature by External Heavy-Atom Effect in Zinc(II) Clusters



 $\begin{array}{l} \mbox{Luminescent Zn}^{II} \mbox{ clusters } [Zn_4L_4(\mu_3-$$$$$$$ OMe)_2X_2] \ (X = SCN, \ CI, \ Br) \ and \ [Zn_7L_6(\mu_3-$$$$$$$$$ OMe)_2(\mu_3-OH)_4]Y_2 \ (Y = I^-, \ CIO_4^-), \end{array}$ 

HL = methyl-3-methoxysalicylate, exhibiting blue fluorescence at room temperature ( $\lambda_{max}$  = 416  $\approx$  429 nm,  $\Phi_{em}$  = 0.09– 0.36) have been synthesized and investigated in detail (see figure).

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