# Coordinated halide and pseudo halide-dependent structures and photoluminescence of defective double cubane Zn(II) clusters

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# Coordinated halide and pseudo halide-dependent structures and photoluminescence of defective double cubane Zn(II) clusters

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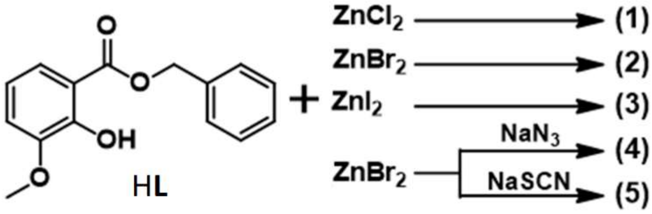
**Abstract:** Tetranuclear Zn(II) complexes, $[Zn_4(\mathbf{L})_4(\mu_3\text{-}OCH_3)_2(X)_2]$ (**L** = 2-((benzyloxy)carbonyl)-6-methoxyphenolate; X = $Cl^-$ (**1**), $Br^-$ (**2**), $I^-$ (**3**), $N_3^-$ (**4**), or $NCS^-$ (**5**)), have provided "defective" double-cubane core $[Zn_4O_6]$, which were bridged by two $\mu_3$-methoxo and four $\mu_2$-phenolato oxygens in each discrete complex. In halide complexes **1**, **2** and **3**, two Zn(II) ions are in slightly distorted octahedral coordinations and the other two in geometries close to the severely distorted trigonal bipyramid, respectively, while all four Zn(II) in pseudo halide complexes **4** and **5** show slightly distorted octahedral geometries. Each complex exhibited blue fluorescence ($\lambda_{max}$ = 415 - 428 nm) with high photoluminescence quantum yields (PLQYs, $\Phi_{em}$) in the range of 0.22-0.53 at room temperature in the solid state, of which **5** showed the highest $\Phi_{em}$ among the alkoxo-bridged multinuclear Zn(II) clusters ever reported.

## Introduction

The luminous transition metal complexes have long been attracting much interest because of their characteristic photophysical properties for the development of optical devices,[1] chemical sensors,[2] molecular probes[3] and photosensitizers.[4] Among them, Ir(III), Ru(II) and Pt(II) complexes have been well studied due to their strong emission properties as well as spin-orbit coupling (SOC) which reflect the presence of heavy metal centres.[5] Given the high prices of rare metals for application as luminescent devices, the construction of Zn(II) complexes with such properties may be attractive alternative candidates, many of which represent luminescence based solely on a ligand-centered (LC) transition, so they have further advantages that can be used to obtain a blue emission.[6] In addition, since the emission quantum yields (QYs) of the reported mononuclear Zn(II) complexes tend to be lowered due to thermal deactivation resulting from their structural flexibility that promote nonradiative transitions,[7] multinuclear ones with rigid cores are one approach to obtaining high efficiency luminescent materials. Numerous polynuclear complexes have been reported to improve thermal- and photo-stability by their structural rigidity,[8] but there are few examples of multinuclear Zn(II) ones with high luminescent properties.[9] We have previously successfully synthesized methoxo-bridged tetranuclear $[Zn_4(mmsa)_4(\mu_3\text{-}OCH_3)_2X_2]$ (mmsa = methyl-3-methoxy-salicylate; X = $SCN^-$, $Cl^-$, $Br^-$) and heptanuclear $[Zn_7(mmsa)_6(\mu_3\text{-}OCH_3)_2(\mu_3\text{-}OH)_4]Y_2$ (Y = $I^-$, $ClO_4^-$) complexes, which exhibited blue luminescence with quantum yields in the range of 0.09-0.36.[10] To further explore compounds with higher photoluminescent properties, we report "defective" double-cubane-type tetranuclear Zn(II) clusters with benzyl 2-hydroxy-3-methoxybenzoate (H**L**) as an organic ligand.

## Results and Discussion

Tetranuclear Zn(II) clusters, $[Zn_4(\mathbf{L})_4(\mu_3\text{-}OCH_3)_2X_2]$, coordinated with various monodentate anions ($Cl^-$ (**1**), $Br^-$ (**2**), $I^-$ (**3**), $N_3^-$ (**4**), and $NCS^-$ (**5**)) were prepared by slightly modifying our previous method[11] and reacting with appropriate Zn(II) salts and benzyl 2-hydroxy-3-methoxybenzoate under basic condition (Scheme 1).




**Scheme 1.** Synthetic route of complexes **1**-**5**.

Crystals of **1** to **5** suitable for structure determinations were obtained by slow evaporation of methanol solutions over several days. Single-crystal X-ray diffraction measurements were successfully carried out, and basic crystallographic parameters are summarized in Table S1 and selected bond distances and angles for the five complexes are given in Table S2. All crystal structures are shown in Figure S2 and consist of a "defective" double-cubane core $[Zn_4O_6]$ in which four Zn(II) ions are bridged by $\mu_3$-methoxo and $\mu_2$-phenolato oxygens. (Figure 1). The geometry of central metal ions in each complex varies depending on the anions used for the synthesis. Of the four Zn(II) ions in complexes **1**, **2**, and **3**, two are slightly distorted octahedral geometries and occupied by two $\mu_2$-phenolato, two $\mu_3$-methoxo, and two ester carbonyl oxygens, respectively, with axial bond angles of ∠O-Zn-O, 160.51 to 171.07°. The other two Zn(II) ions coordinated halide ions ($Cl^-$, $Br^-$, and $I^-$) show geometries close to the severely distorted trigonal bipyramid and are occupied by two $\mu_2$-phenolato, one $\mu_3$-methoxo, and one ethereal oxygens, respectively. Their axial bond angles ∠O-Zn-O are in the range of 148.04–149.64° with $\tau$ values of 0.54 (**1**), 0.54 (**2**), and 0.62 (**3**), respectively (Table S3).[12] The geometric parameter, $\tau$, is defined as $\tau = (\beta - \alpha)/60$, which can be applied to an index of the degree of trigonality in five coordinate geometries.[12] In complexes **4** and **5**, all four Zn(II) ions exhibit slightly distorted octahedral structures with axial bond angles of 146.15 to 150.15° (∠O-Zn-O) and 143.0 to 147.5° (∠X-Zn-O) (Table S2), of which two with pseudo halides ($N_3^-$ (**4**) and $NCS^-$ (**5**)) are coordinated by additional ethereal oxygen to complete their octahedral geometries.

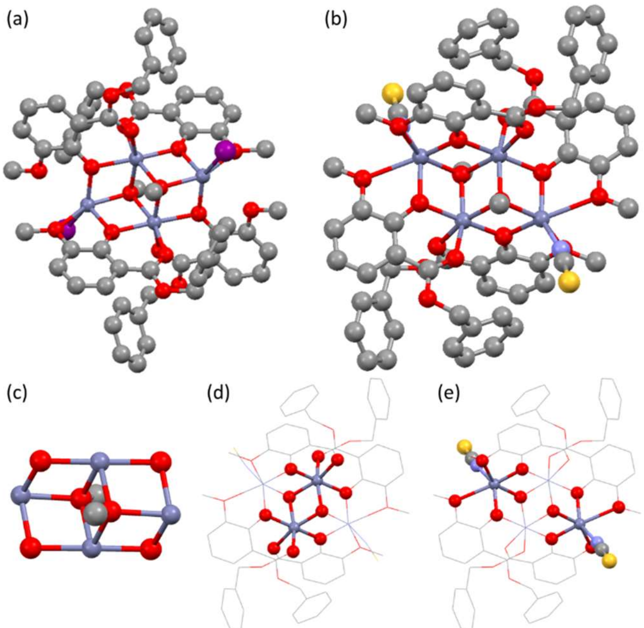



**Figure 1.** Crystal structures of complexes **3** (a) and **5** (b). Defective double-cubane core [$Zn_4O_6$] (c). Two kinds of Zn(II) octahedral coordination spheres exists in **5** (d) (e).

The diffuse reflectance and photoluminescence spectra of H**L** in the solid-state were measured at room temperature (298 K) (Figure 2a). The diffuse reflectance spectrum shows an absorption band ($\lambda_{abs}$ = 323 nm) attributed to the $^1\pi$-$\pi^*$ transition. Its emission spectrum displays a fluorescence band ($\lambda_{max}$ = 363 nm).[10] All complexes (**1** to **5**) exhibit photoluminescence properties in the solid state (Figure. 2b and S7), displaying blue luminescence at room temperature (298 K). The emission spectra of each complex show unstructured broad emission bands with maxima ($\lambda_{max}$) at 415–428 nm, which are quite similar with slight differences. Their photoluminescent behaviors indicate the contributions of intraligand $^1\pi$-$\pi^*$ transition to their luminescence.[10] The emission maxima of the complexes shift to significantly lower energy than H**L**, which are consistent with the increase in HOMO energy in cases that reflect different electronegativities between protons and the Zn(II) ions.[13] The above observations indicate that the emission maxima of **1** to **5** are not necessarily affected by coordinated halides or pseudo halide ions. Their excitation and emission spectra at low temperature (77 K) were also measured (Figure S8), with the latter displaying broadened peaks in comparison to those at room temperature, especially for complex **3**. The shoulder of the spectrum around 500 nm is derived from phosphorescence involving the lowest-excited triplet state. The use of heavy atoms such as iodide and lanthanide ions increases both inter-system crossing (ISC) rate and phosphorescence decay time of the excited-state luminophore due to the orbital interaction between the heavy atoms and the luminophore.[10, 14] The phosphorescence spectra of complexes **1** to **5** measured at 77 K after a 20 ms delay after excitation show broad bands with maximum values around 520 nm (Figure S9). Although the measurement of phosphorescence lifetime was not successful in this study, phosphorescence peaks were observed and in particular, complex **3** with coordinated iodide was more prominent than others.

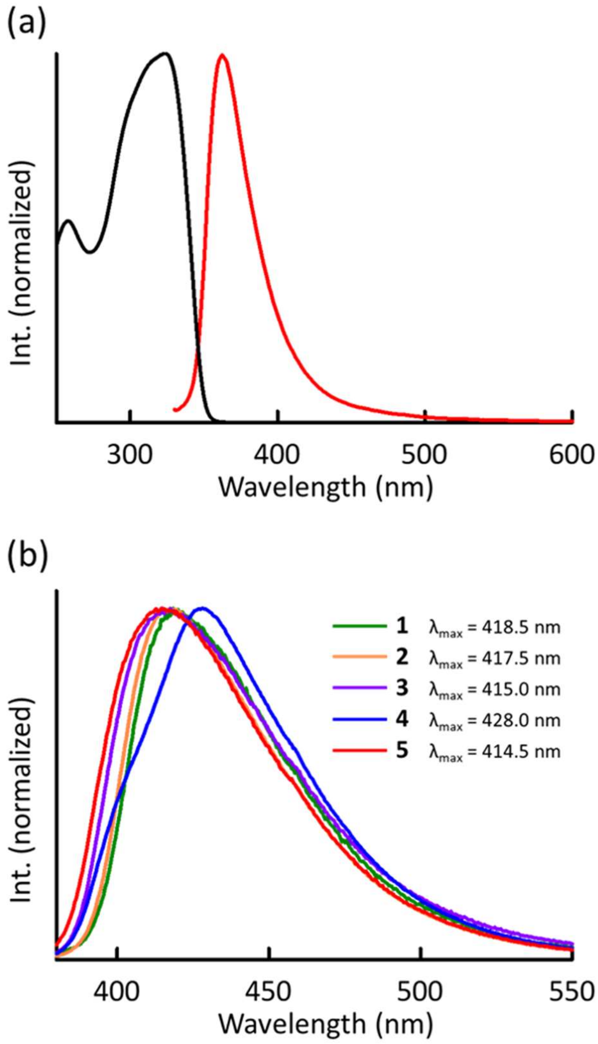



**Figure 2.** (a) UV absorption spectrum (black line, $\lambda_{abs}$ = 323.2 nm) and emission spectrum (red line, $\lambda_{ex}$ = 323.2 nm, $\lambda_{max}$ = 362.5 nm) of H**L** in the solid state at room temperature (298 K). (b) Luminescence spectra of Zn(II) clusters **1** – **5** in the solid state at room temperature (298 K).

Emission quantum yields (QYs, $\Phi_{em}$) and their lifetimes ($\tau$) were measured to further investigate the fluorescence properties of the complexes (Table 1 and S4; Figure S10 and S11). Each complex shows an average emission lifetime ($\tau_{av}$) of 3.10 to 7.07 nanoseconds (ns) at 298 K, which are consistent with the expected values from intraligand $^1\pi$-$\pi^*$ transitions in Zn(II) complexes.[10] Their QYs range from 0.22 to 0.53. At low temperature (77 K), meanwhile, $\tau_{av}$ range from 4.77 to 8.45 ns, with QYs ranging 0.70~0.88 ns, which are higher than those at

298 K because, in general, the fluorescence life time and QYs of most fluorescent materials are decreased by thermal quenching via multiphoton relaxation pathways as the temperature increases from cryogenic to ambient temperatures. The high QYs of multinuclear Zn(II) clusters seem to be mainly due to the strong coordination of 2-((benzyloxy)carbonyl)-6-methoxyphenolate ligands, **L**⁻, to the central metal ions to produce a rigid tetranuclear core.

**Table 1.** Photophysical data for **1** – **5** in the solid state at R.T.(298 K) and 77K.

| | $\lambda_{max}$ [nm] [a] | $\Phi$[b] | $\tau_{av}$ [ns] [c] |
|---|---|---|---|
| **1** (298 K) | 418.5 | 0.22 | 3.76 |
| **2** (298 K) | 417.5 | 0.44 | 5.50 |
| **3** (298 K) | 415 | 0.30 | 3.10 |
| **4** (298 K) | 428 | 0.52 | 7.07 |
| **5** (298 K) | 414.5 | 0.53 | 6.61 |
| **1** (77 K) | 413 | 0.70 | 8.07 |
| **2** (77 K) | 412 | 0.81 | 7.32 |
| **3** (77 K) | 424 | 0.70 | 4.77 |
| **4** (77 K) | 415 | 0.82 | 7.83 |
| **5** (77 K) | 417 | 0.88 | 8.45 |

[a] Emission maximum. [b] Emission quantum yields, $\lambda_{ex}$ = 300 nm. [c] Emission lifitimes, $\lambda_{ex}$ = 340 nm.

To the best of our knowledge, QY of complex **5** at room temperature ($\Phi_{em}$= 0.53) is the second-highest among the reported multinuclear Zn(II) complexes,[9a] and it is higher than that of $[Zn_4(mmsa)_4(\mu_3\text{-}OCH_3)_2(NCS)_2]$ ($\Phi_{em}$ = 0.36) which we have previously reported.[10] Unlike our previous tetranuclear Zn(II) cluster where methyl-esterified ligands were coordinated, benzyl substituents in the ligand of complex **5** seem to play an important role in improving QY, so their Hirshfeld surfaces and energy framework analyses[15] were applied to evaluate them. Hirshfeld surface appears to be particularly suitable for visualizing variations in the intermolecular interactions of compounds. Hirshfeld surface of complex **5** shows π-π interactions between the benzene rings of ligands but no other apparent interaction is confirmed (Figure 3a), which means that the integrated structure is mainly stabilized by π-π stacking. Energy framework analysis supporting these results provides the quantitative visualization of intermolecular interactions. This is a mapping of the interaction between molecules in crystals based on the strength of interaction energies (*IE*) of molecular pairs, and is represented as a cylindrical tube, whose thickness exhibits the intensity of the interaction between two molecules (Figure S12). *IE* of complex **5** based on π-π stacking is -92.5 kJ mol$^{-1}$ (Figure 3c, S12). The S---H interactions between NCS⁻ and benzyl group like CH-π interactions are also observed and its *IE* is ≤ −53 kJ mol$^{-1}$. Intermolecular interactions through NCS⁻ in previously reported $[Zn_4(mmsa)_4(\mu_3\text{-}OCH_3)_2(NCS)_2]$[10] are observed in several spots, as shown on the Hirschfeld surface (Figure 3b), of which interactions mainly contribute to stabilizing the packing arrangement (Figure 3d and S13). The most stabilized energy (*IE* = −130.5 kJ mol$^{-1}$) is the interaction consisting of a phenyl group and NCS⁻, which is arranged along the *c*-axis and represented in purple (Figure S13). The second stabilized energy is −83.0 kJ mol$^{-1}$, which is also involved by NCS⁻ and represented along *ab* plane, and the others seem to be very weak (-18.2, -16.0 and -1.7 kJ mol$^{-1}$). The comparison of complexes $[Zn_4(mmsa)_4(\mu_3\text{-}OCH_3)_2(NCS)_2]$ and **5** shows that the presence of benzyl groups serves to prevent strong interaction with adjacent multinuclear units. The introduction of a benzyl substituent to the ligand skeleton led to the dispersion of luminescence in the parent molecules and attenuation of the exciton interactions between the adjacent molecules. That is, increasing the intermolecular distance can effectively improve the solid-state luminous efficiency due to the loss of charge transfer between molecules.[16]

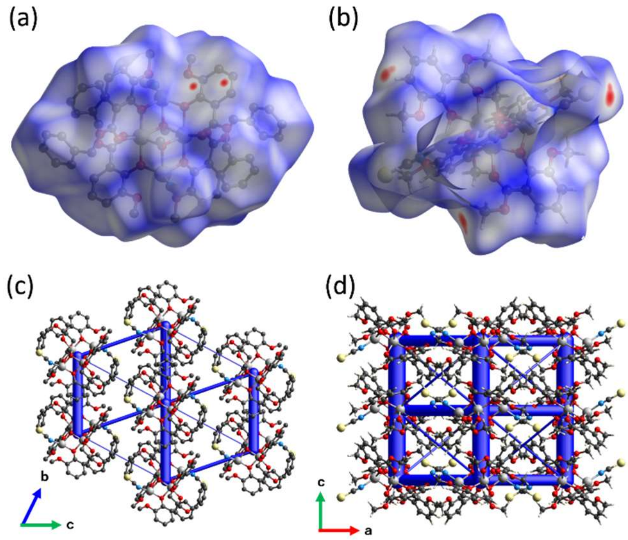



**Figure 3.** Hirshfeld surfaces for complex **5** (a) and $[Zn_4(mmsa)_4(\mu^3\text{-}OCH_3)_2(NCS)_2]$ (b). Energy framework in total interaction strengths for **5** (c) and $[Zn_4(mmsa)_4(\mu^3\text{-}OCH_3)_2(NCS)_2]$ (d).

## Conclusion

Tetranuclear Zn(II) clusters (**1**-**5**) with different anions (Cl⁻, Br⁻, I⁻, $N_3^-$ and NCS⁻) were synthesized using benzyl 2-hydroxy-3-methoxybenzoate, which exhibited blue fluorescence ($\lambda_{max}$ = 415 - 428 nm) with quantum yields ranging 0.22 to 0.53 in the solid-state at room temperature, of which **5** showed the highest emission quantum yield among the alkoxo-bridged multinuclear Zn(II) complexes reported so far. Detailed analysis of the crystal structures revealed that the introduction of benzyl substituents in the ligand eliminates the emission quenching due to the change in the assembly structure, which results in highly efficient luminescent metal complexes. The present study demonstrates that modulating monodentate anionic co-ligand as well as changing substituent of 3-methoxysalicylate ester are useful strategies to develop highly efficient molecular emitters by suppressing nonradiative transition in multinuclear Zn(II) complexes.

## Experimental Section

### Materials and Instrument

All reagents and solvents were purchased from Tokyo Kasei Co. and Wako Pure Chemical Industries and used without further purification. All reactions were carried out under ambient atmosphere. Elemental analyses (C, H, N) were carried out on a J-SCIENCE LAB JM10 analyzer at the Instrumental Analysis Centre of Kumamoto University.

**Ligand Synthesis**

Benzyl 2-hydroxy-3-methoxybenzoate (H**L**) was prepared by a slightly modified method to that reported previously.[8]

*N,N'*-Dicyclohexylcarbodiimide (DCC; 4.12 g, 20 mmol) was added to a solution of 2-hydroxy-3-methoxybenzoic acid (3.36 g, 20 mmol) in THF (100 mL) containing benzyl alcohol (2.16 g, 20 mmol). The mixture was stirred overnight at room temperature and the white precipitate was removed by filtration. The filtrate was concentrated to an oily liquid under reduced pressure and ethanol (50 mL) added. The solution was then allowed to stand for a few days to give colorless crystals, which were collected by filtration and dried in vacuo. Yield, 27%. Anal. Calc. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46; Found: C, 69.34; H, 5.53%. $^1$H NMR (500 MHz) in $CDCl_3$: $\delta$ 3.90 (d, 3H), 5.37 (s, 2H), 6.79 (t, 1H), 7.03 (d, 1H), 7.25-7.45 (m, 6H).

**[$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$(Cl)$_2$]·$H_2O$ (1)**

H**L** (129 mg, 0.50 mmol) was dissolved in methanol (30 mL) and $ZnCl_2$ (68.1 mg, 0.50 mmol) added with stirring. Triethylamine (50.6 mg, 0.50 mmol) in methanol (20 mL) was added before stirring for 30 minutes. Slow evaporation of the mixture at ambient temperature yielded colorless crystals suitable for a structure determination, which were collected by filtration and washed with methanol before drying. Yield, 58%. Anal. Calc. for $C_{62}H_{60}Cl_2Zn_4O_{19}$ = [$Zn_4$(**L**)$_4$($\mu_3$-$OCH_3$)$_2$(Cl)$_2$]·$H_2O$: C, 51.76; H, 4.49. Found: C, 51.66; H, 4.20%.

**[$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$(Br)$_2$]·2$H_2O$ (2)**

The preparation procedure was the same as that of **1**, except $ZnBr_2$ was used as a starting material. After workup, colorless crystals suitable for a structure determination were collected. Yield, 52 %. Anal. Calc. for $C_{62}H_{62}Br_2Zn_4O_{20}$ = [$Zn_4$(**L**)$_4$($\mu_3$-$OCH_3$)$_2$(Br)$_2$]·2$H_2O$: C, 48.29; H, 4.11. Found: C, 48.09; H, 4.04%.

**[$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$(I)$_2$]·$H_2O$ (3)**

The preparation procedure was the same as that of **1**, except $ZnI_2$ was used as a starting material. After workup, colorless crystals suitable for a structure determination were collected. Yield, 56%. Anal. Calc. for $C_{62}H_{60}I_2Zn_4O_{19}$ = [$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$(I)$_2$] ·$H_2O$: C, 45.77; H, 3.98. Found: C, 45.84; H, 3.72%.

**[$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$($N_3$)$_2$]·2$CH_3OH$ (4)**

Triethylamine (50.6 mg, 0.50 mmol) in methanol (20 mL) and $NaN_3$ (32.5 mg, 0.50 mmol) were sequentially added to a mixture of H**L** (129 mg, 0.50 mmol) and $ZnCl_2$ (68.1 mg, 0.50 mmol) in methanol (30 mL) with stirring. After further stirring for 30 minutes, the mixture was slowly evaporated at ambient temperature to yield colorless crystals suitable for a structure determination, which were collected by filtration and washed with methanol before drying. Yield, 59%. Anal. Calc. for $C_{64}H_{66}N_6Zn_4O_{20}$ = [$Zn_4$(**L**)$_4$($\mu_3$-$OCH_3$)$_2$($N_3$)$_2$]·2$CH_3OH$: C, 51.00; H, 4.45. N, 5.32. Found: C, 51.22; H, 4.43; N, 5.60 %.

**[$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$(NCS)$_2$]·2$CH_3OH$ (5)**

The preparation procedure was the same as that of **4,** except NaSCN was used instead of $NaN_3$. After workup, colorless crystals suitable for a structure determination were collected. Yield, 57%. Anal. Calc. for $C_{66}H_{66}N_2Zn_4O_{20}S_2$ = [$Zn_4$(L)$_4$($\mu_3$-$OCH_3$)$_2$(NCS)$_2$] ·2$CH_3OH$: C, 51.79; H, 4.39; N, 1.71. Found: C, 51.71; H, 4.34; N, 1.83 %.

**Physical measurements**

Single-crystal X-ray diffraction data were collected either on a Bruker D8 QUEST (**1** and **2**), or a Rigaku XtaLAB mini II diffractometer (**3**, **4** and **5**), at 100 or 173 K, respectively. The structures were solved by intrinsic phasing (SHELXT[17]) and refined by full-matrix least-squares using the SHELXL[18] program. Hydrogen atoms were introduced at calculated positions and were treated as riding atoms. For complexes **1** and **4**, PLATON/SQUEEZE[19] was used to take into account the contribution of disordered solvent molecules to structure factors, but it did not improve results for the void-containing structure of **2**. CCDC 2050848 (for **1**), 2050849 (for **2**), 2050850 (for **3**), 2050851 (for **4**), and 2050852 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Luminescence and excitation spectra at 77 K were recorded on a LS55 Fluorescence Spectrometer (PerkinElmer). Luminescence and excitation spectra at room temperature were recorded on a Fluorolog 3–22 (Horiba Jobin Yvon) spectrometer. Absolute luminescence quantum yields and luminescence lifetimes were determined using an absolute luminescence quantum yield C9920-02 spectrometer (Hamamatsu Photonics K. K.) and a Quantaurus-Tau C11367-12 spectrometer (Hamamatsu Photonics K. K.), respectively, with pulsed excitation light sources.

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**Keywords:** cubane • emission quantum yield • energy framework analysis • luminescence • multinuclear complex • zinc

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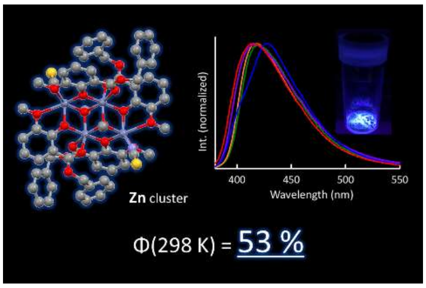
## Entry for the Table of Contents




Tetranuclear Zn(II) clusters of defective double cubane structures with monodentate anions and benzyl-functionalized *o*-vanillic acid ligands exhibited blue fluorescence ($\lambda_{max}$ = 415 - 428 nm) with high photoluminescence quantum yields (PLQY$_S$, $\Phi_{em}$) in the range of 0.22-0.53.