

<Electronic Supplementary Information (ESI) available>

**Sandwich-shaped  $M_3L_2$  zinc(II) complex containing 1,3,5-tris(dimethyl(pyridin-3-yl)silyl)benzene: Selective photoluminescence recognition of diiodomethane**

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**Table S1.** Crystallographic data on  $[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$

| $[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ |   |
|--|---|
| Formula  | $\text{C}_{62}\text{H}_{83}\text{Cl}_3\text{N}_{10}\text{O}_{16}\text{Si}_6\text{Zn}_3$ |
| $M_w$ (g mol <sup>-1</sup> )   | 1695.38   |
| Crystal system   | Monoclinic  |
| Space group  | $P2_1/n$  |
| $a$ (Å)  | 20.8466(3)  |
| $b$ (Å)  | 16.4944(3)  |
| $c$ (Å)  | 23.9629(4)  |
| $\beta$ (°)  | 92.623(1)   |
| $V$ (Å <sup>3</sup> )  | 8231.1(2)   |
| $\sigma$ (g cm <sup>-3</sup> )   | 1.368   |
| $Z$  | 4   |
| $\mu$ (mm <sup>-1</sup> )  | 1.116   |
| $F(000)$   | 3512  |
| $R_{\text{int}}$   | 0.0895  |
| Completeness (%)   | 100.0   |
| GoF on $F^2$   | 1.012   |
| $R_1 [I > 2\sigma(I)]^{\text{a}}$  | 0.0509  |
| $wR_2$ (all data) <sup>b</sup>   | 0.1626  |

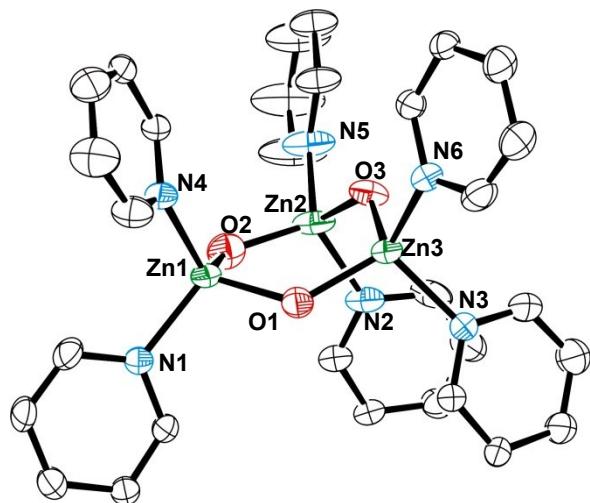
<sup>a</sup> $R_1 = \sum ||F_{\text{o}}| - |F_{\text{c}}|| / \sum |F_{\text{o}}|$ , <sup>b</sup> $wR_2 = (\sum [w(F_{\text{o}}^2 - F_{\text{c}}^2)^2] / \sum [w(F_{\text{o}}^2)^2])^{1/2}$

**Table S2.** Selected bond lengths (Å) and angles (°) of  $[Zn_3(\mu\text{-OH})_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ 

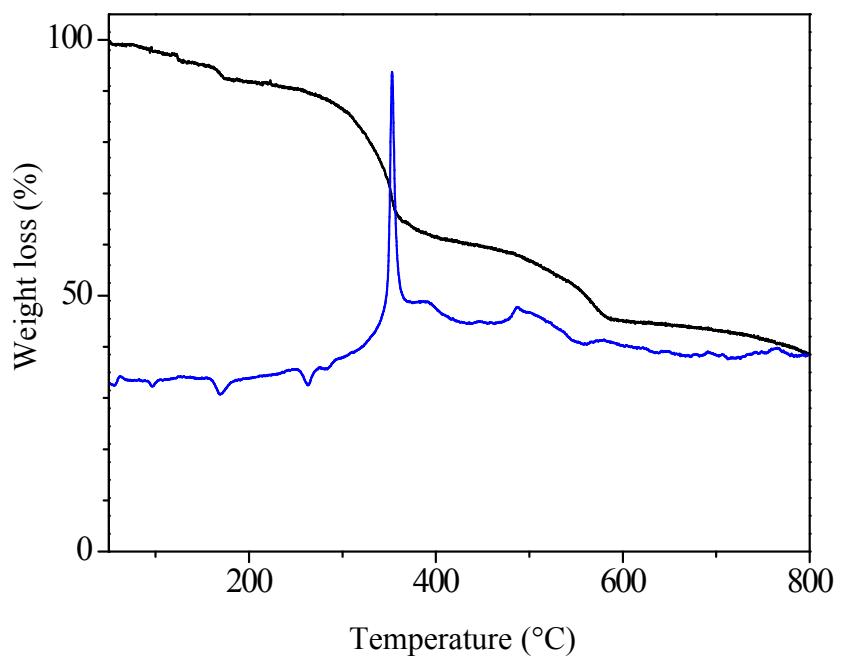
| $[Zn_3(\mu\text{-OH})_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ |          |
|---|----------|
| Zn(1)–O(2)  | 1.899(3) |
| Zn(1)–O(1)  | 1.923(2) |
| Zn(1)–N(1)  | 2.023(3) |
| Zn(1)–N(4)  | 2.032(3) |
| Zn(2)–O(2)  | 1.907(3) |
| Zn(2)–O(3)  | 1.923(3) |
| Zn(2)–N(5)  | 2.023(3) |
| Zn(2)–N(2)  | 2.029(3) |
| Zn(3)–O(1)  | 1.908(2) |
| Zn(3)–O(3)  | 1.930(3) |
| Zn(3)–N(6)  | 2.024(3) |
| Zn(3)–N(3)  | 2.029(3) |
|   |          |
| O(2)–Zn(1)–O(1)   | 106.1(1) |
| O(2)–Zn(1)–N(1)   | 116.2(1) |
| O(1)–Zn(1)–N(1)   | 106.3(1) |
| O(2)–Zn(1)–N(4)   | 116.6(1) |
| O(1)–Zn(1)–N(4)   | 107.3(1) |
| N(1)–Zn(1)–N(4)   | 103.6(1) |
| O(2)–Zn(2)–O(3)   | 105.3(1) |
| O(2)–Zn(2)–N(5)   | 114.5(1) |
| O(3)–Zn(2)–N(5)   | 107.4(1) |
| O(2)–Zn(2)–N(2)   | 112.9(1) |
| O(3)–Zn(2)–N(2)   | 106.9(1) |
| N(5)–Zn(2)–N(2)   | 109.4(1) |
| O(1)–Zn(3)–O(3)   | 102.9(1) |
| O(1)–Zn(3)–N(6)   | 123.3(1) |
| O(3)–Zn(3)–N(6)   | 103.1(1) |
| O(1)–Zn(3)–N(3)   | 106.6(1) |
| O(3)–Zn(3)–N(3)   | 112.1(1) |
| N(6)–Zn(3)–N(3)   | 108.6(1) |

**Table S3.** Fluorescence lifetime (ns) of  $[Zn_3(\mu\text{-OH})_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$  in presence of various  $CH_2I_2$  concentrations, 0,  $8.15 \times 10^{-5}$ , and  $1.62 \times 10^{-4}$  mol/L in a methanol solution state at room temperature

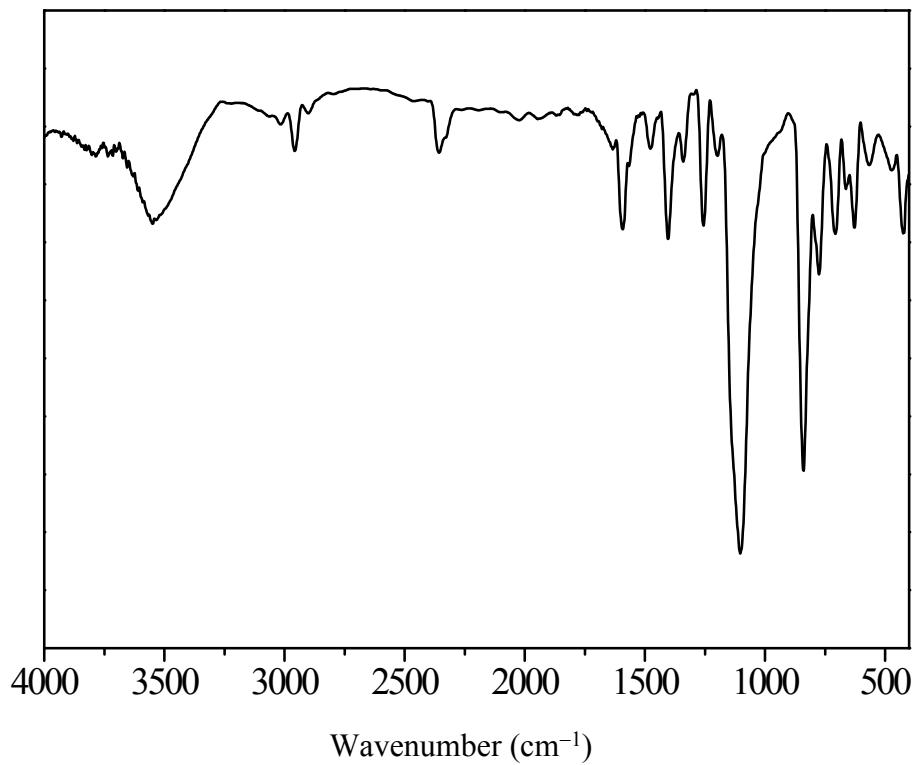
| $[Q] \times 10^5$ | $\lambda_{em}$ | $\tau_1$ | $\tau_2$ |
|-------------------|----------------|----------|----------|
| 0                 | 410 nm         | 1.077    | 7.987    |
| 8.1               | 410 nm         | 0.429    | 5.845    |
| 16.2              | 410 nm         | 0.268    | 4.362    |



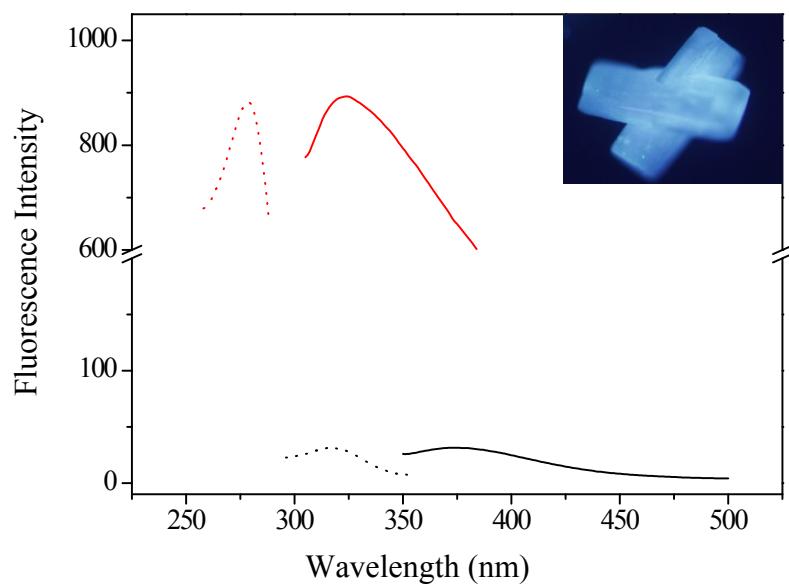
**Fig. S1.** ORTEP drawing showing local geometry of zinc(II) and 6-membered ring moiety of  $[Zn_3(\mu\text{-OH})_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ .



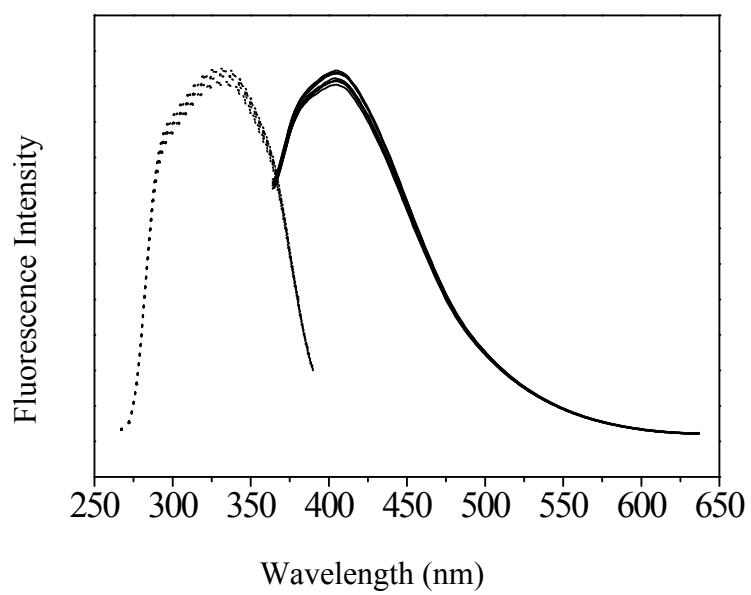
**Fig. S2.** TGA and DSC curves of  $[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ . Weight loss for solvate molecules: Calc. 11.8 %, Found 10.8 %.



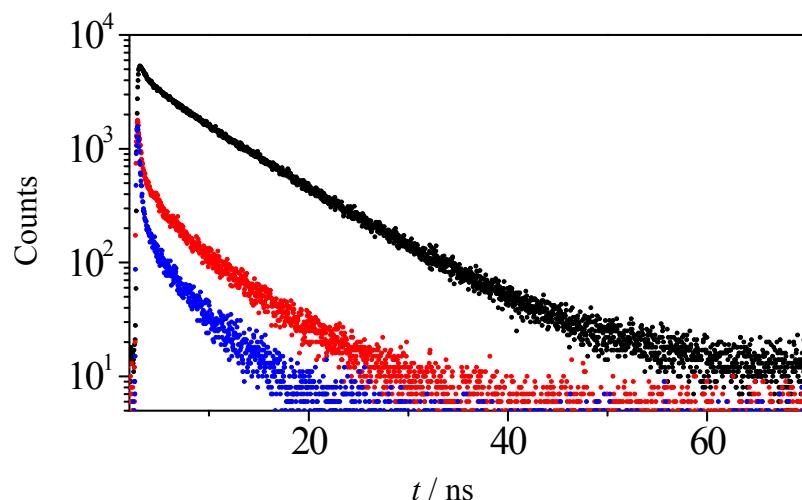
**Fig. S3.** FT-IR spectrum of  $[Zn_3(\mu\text{-OH})_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ .



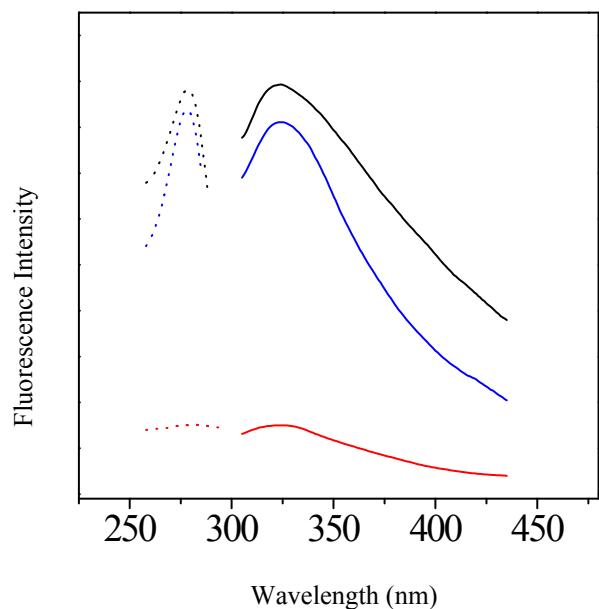
**Fig. S4.** Solid state fluorescence spectra of  $[Zn_3(\mu-OH)_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$  (red line),  $\lambda_{ex} = 275$  nm,  $\lambda_{em} = 324$  nm; L (black line),  $\lambda_{ex} = 317$  nm,  $\lambda_{em} = 373$  nm; Inset: fluorescent-microscopic image of  $[Zn_3(\mu-OH)_3L_2](ClO_4)_3 \cdot 4CH_3CN \cdot 2H_2O$ .



**Fig. S5.** Fluorescence excitation (dotted line) and emission (solid line) spectra of  $[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$  in methanol solution in presence of various dichloromethane concentration (0;  $5.22 \times 10^{-4}$ ;  $1.04 \times 10^{-3}$ ;  $1.57 \times 10^{-3}$ ;  $2.09 \times 10^{-3}$ ;  $2.61 \times 10^{-3}$ ;  $3.13 \times 10^{-3}$ ;  $3.65 \times 10^{-3}$ ;  $4.18 \times 10^{-3}$  mol/L).



**Fig. S6.** Fluorescence lifetime decays following excitation at  $\lambda = 375$  nm of  $[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$  (monitored at  $\lambda = 410$  nm) in presence of various  $\text{CH}_2\text{I}_2$  concentrations, 0 (black),  $8.15 \times 10^{-5}$  (red), and  $1.62 \times 10^{-4}$  (blue) mol/L.



**Fig. S7.** Photoluminescence spectra in a solid state of  $[\text{Zn}_3(\mu\text{-OH})_3\text{L}_2](\text{ClO}_4)_3 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$  (black), after addition of  $\text{CH}_2\text{I}_2$  (red), and after several washings with diethyl ether (blue).