# A Hexa-quinoline based $C_3$-Symmetric Chemosensor for Dual Sensing of Zinc (II) and PPi in Aqueous Medium *via* Chelation Induced "OFF-ON-OFF" Emission

*Sanghamitra Sinha,[†] Bijit Chowdhury,[†] Nayarassery N. Adarsh[#] and Pradyut Ghosh*[†]*

[†]Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Kolkata 700 032, India.

[#]Instituto Catalan de Nanociencia y Nanotecnologia (ICN2), Edifici ICN2, Campus UAB, Cerdanyola del Valles 08193, Spain

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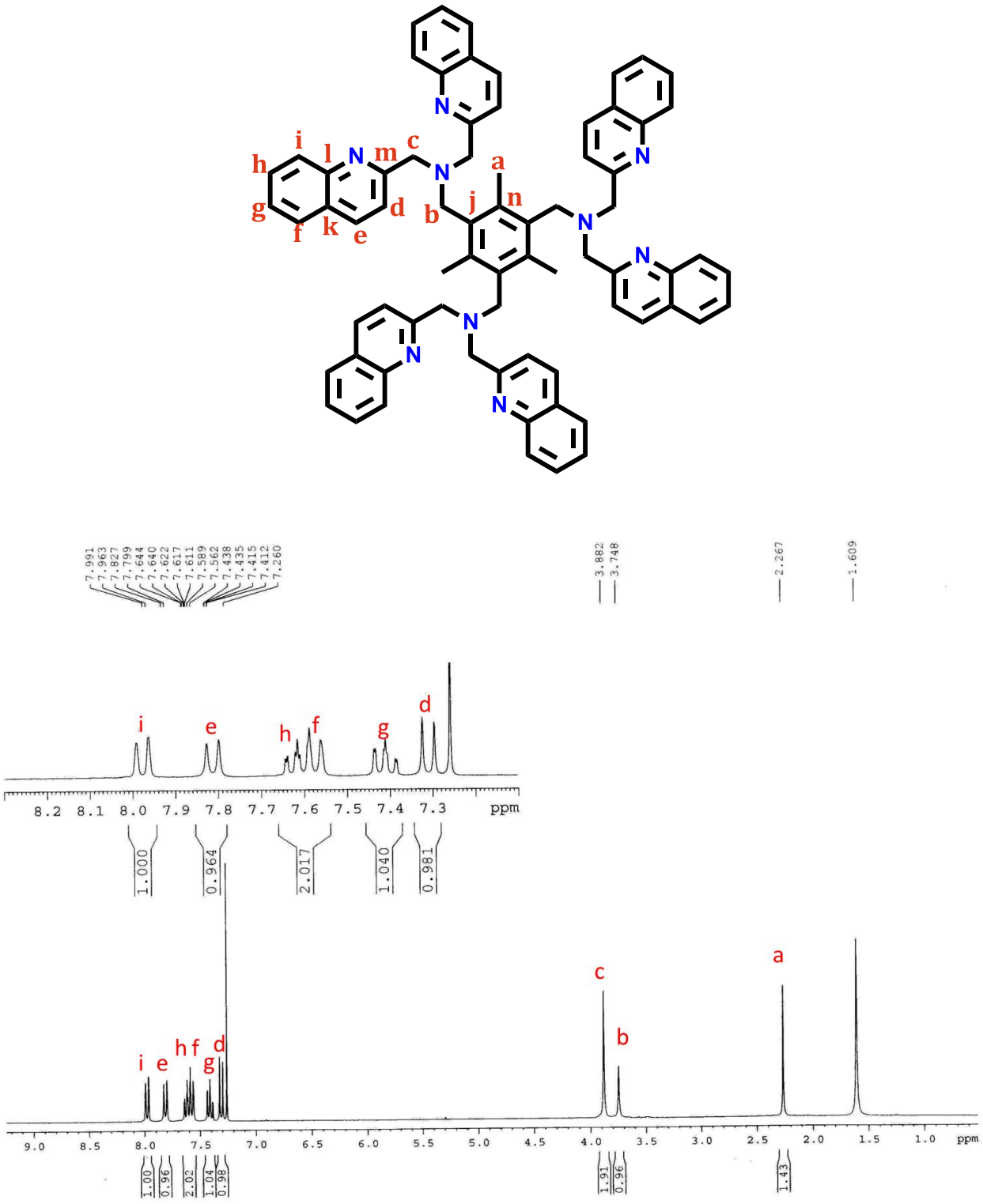



**Figure S1.** $^{1}$H-NMR (300 MHz) spectrum of **1** in $CDCl_3$.

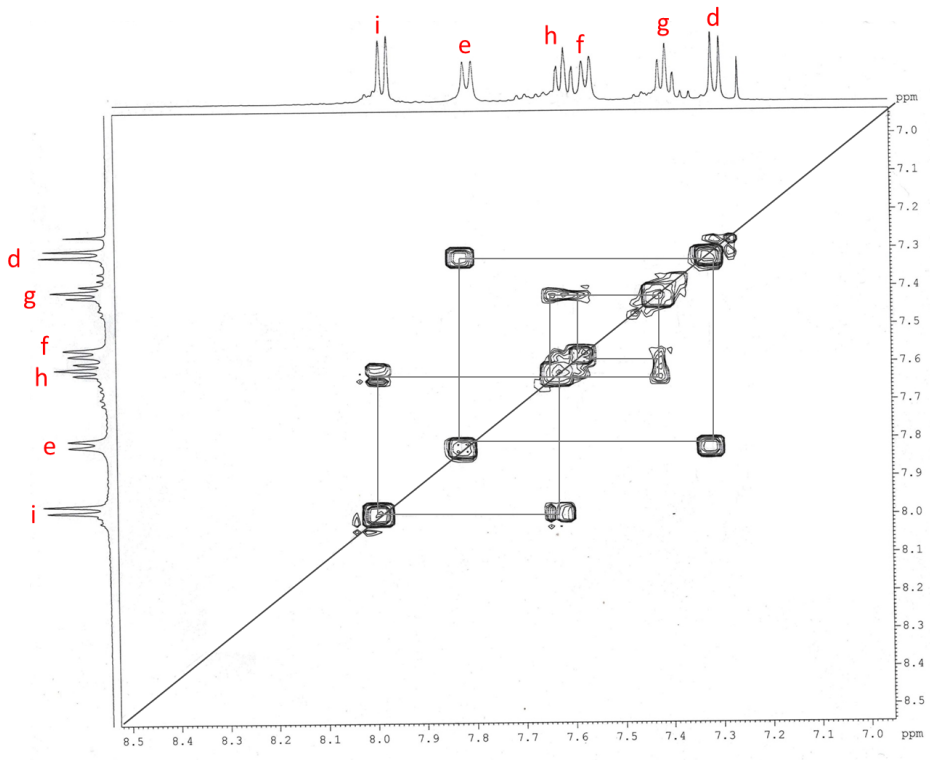



**Figure S2.** $^{1}$H-$^{1}$H COSY NMR (500 MHz) spectrum of **1** in $CDCl_3$.

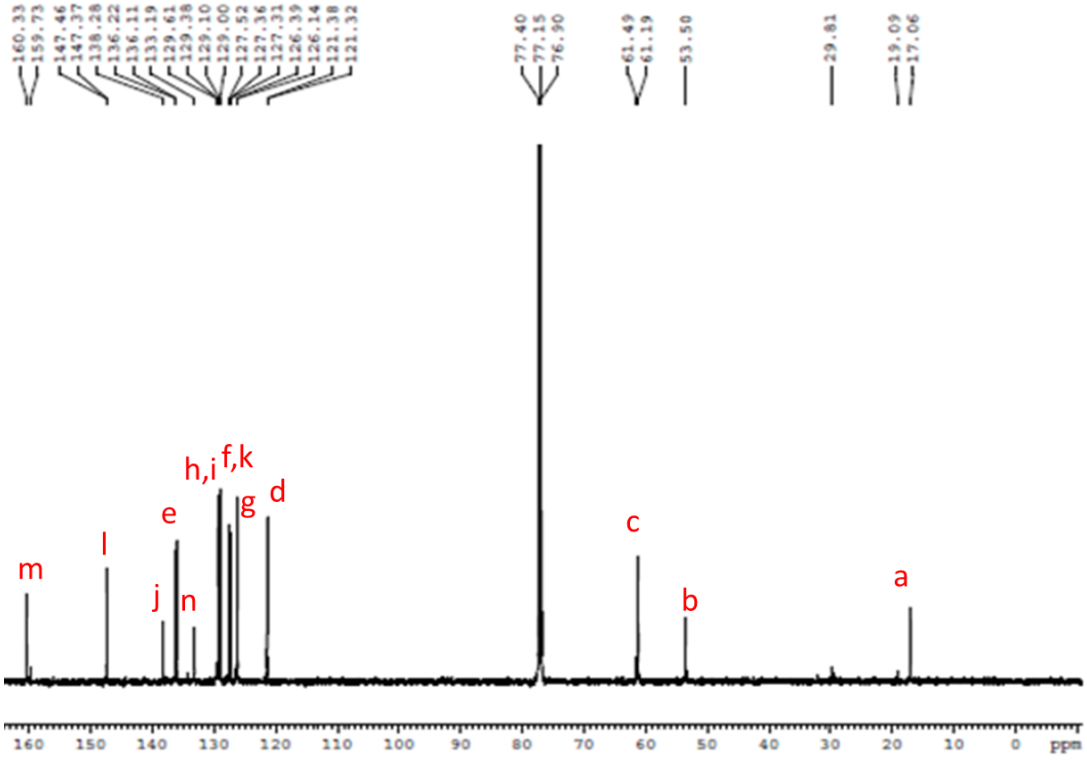



**Figure S3.** $^{13}$C-NMR (125 MHz) spectrum of **1** in $CDCl_3$.

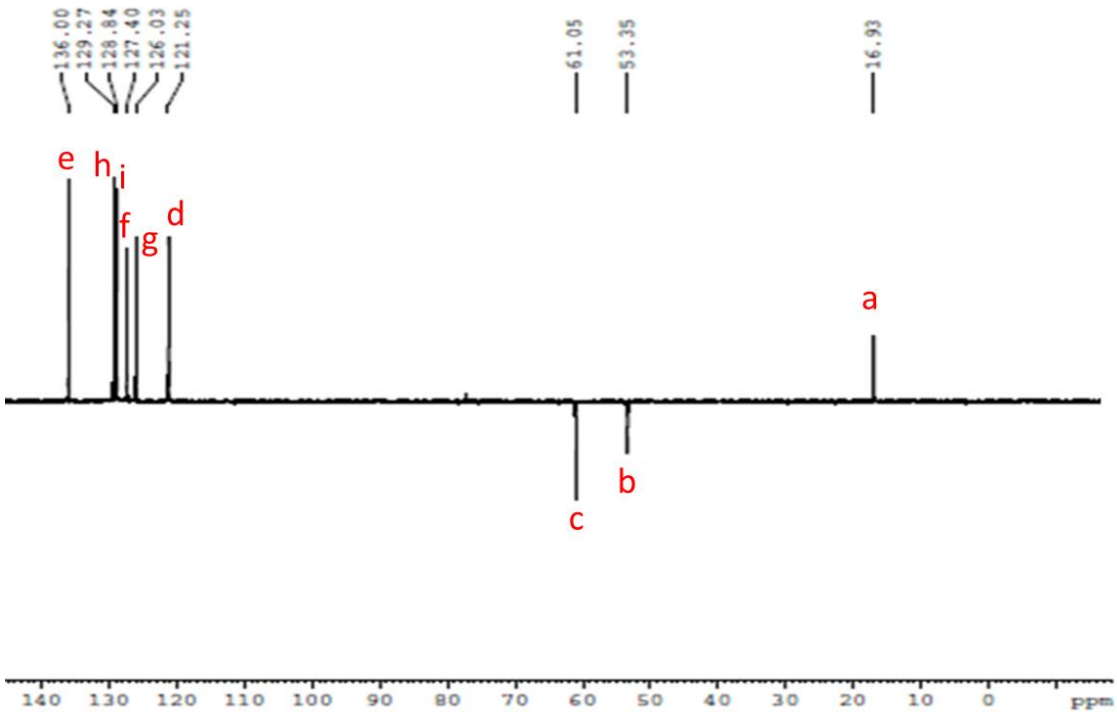



**Figure S4.** DEPT-135-NMR (125 MHz) spectrum of **1** in $CDCl_3$.

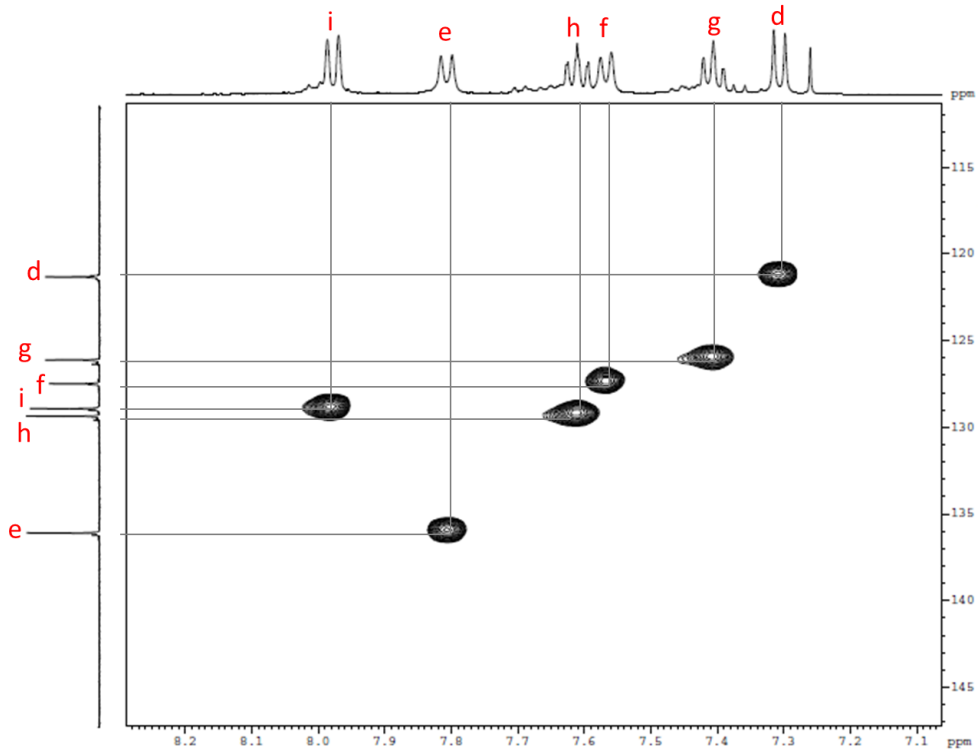



**Figure S5.** $^1$H-DEPT-135 HSQC NMR (500 MHz) spectrum of **1** in $CDCl_3$.

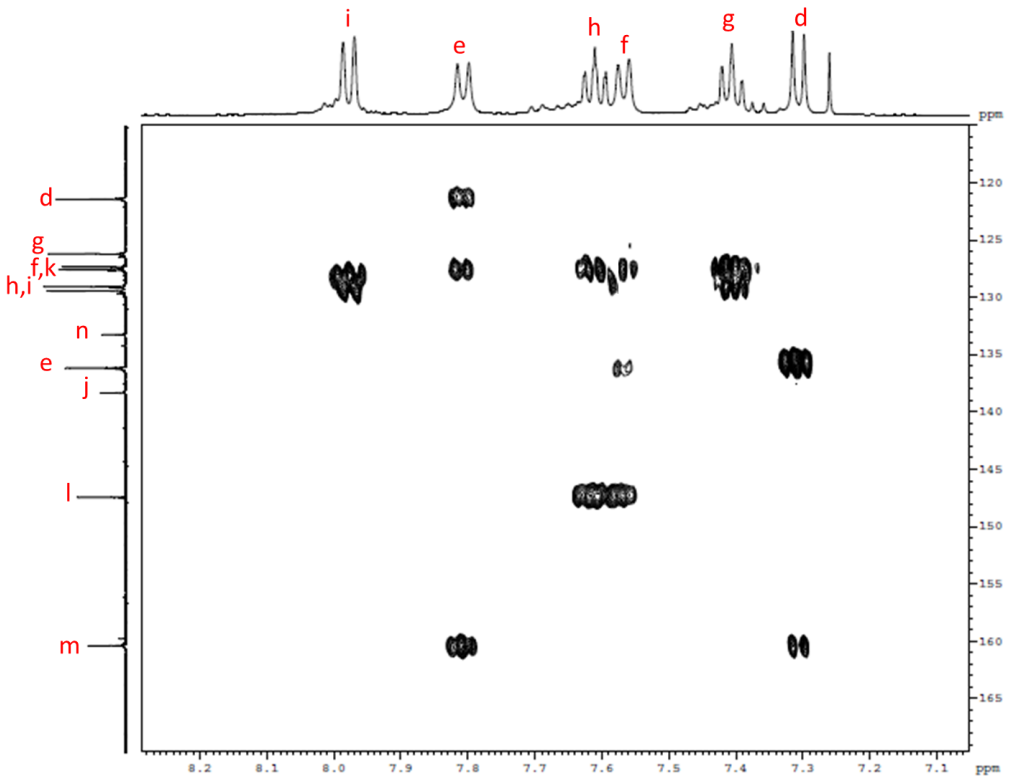



**Figure S6.** $^{1}H$-$^{13}C$ HMBC NMR (500 MHz) spectrum of **1** in $CDCl_3$.

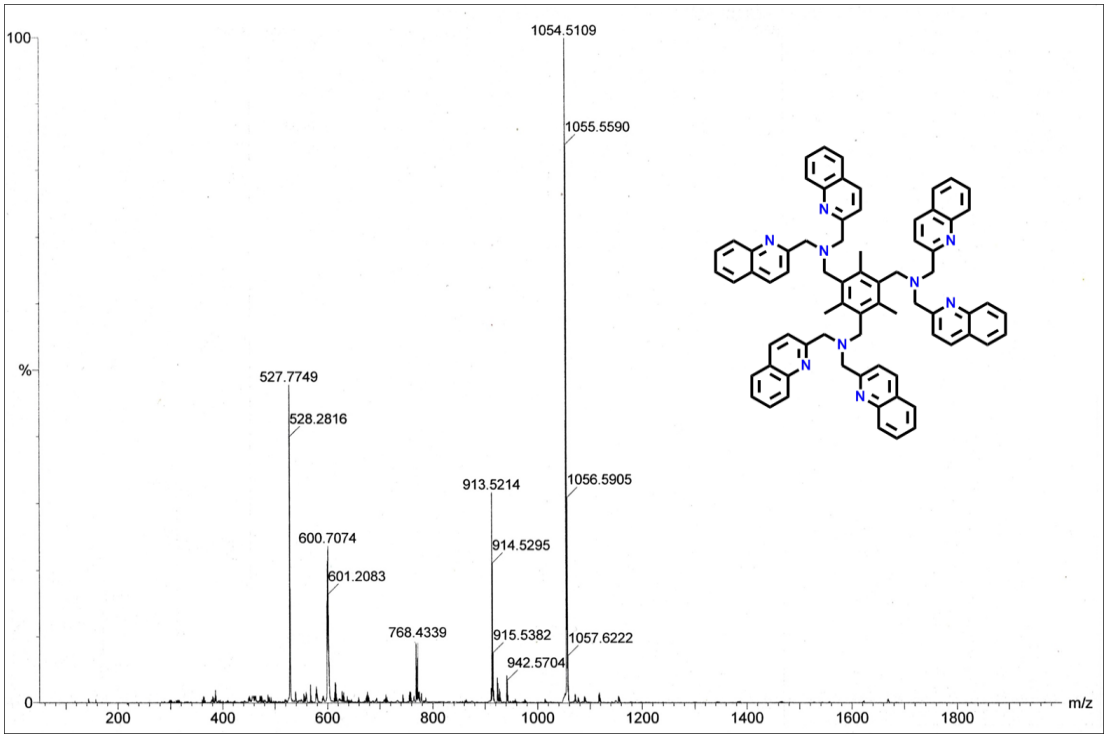



**Figure S7.** ESI-MS of **1**.

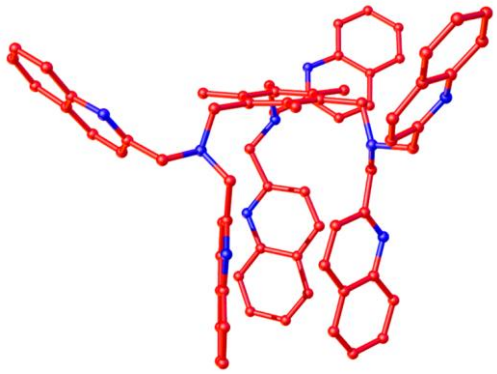


**Figure S8.** Ball and stick representation of single crystal X-ray structure of the ligand **1**. Colour code: N, blue; C, red; hydrogen and disordered atoms are omitted for clarity.

**Table S1.** List of crystallographic parameter details of ligand **1**.

| **Compound reference** | **1** |
|---|---|
| Chemical formula | $C_{72}H_{63}N_9$ |
| Formula Mass | 1054.31 |
| Crystal system | Monoclinic |
| *a*/Å | 25.704(3) |
| *b*/Å | 18.476(2) |
| *c*/Å | 13.0580(9) |
| *α*/° | 90 |
| *β*/° | 98.915(3) |
| *γ*/° | 90 |
| Unit cell volume/Å$^3$ | 6126.4(10) |
| Temperature/K | 100(2) |
| Space group | *P*21/*c* |
| No. of formula units per unit cell, *Z* | 4 |
| Radiation type | MoKα |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.068 |
| No. of reflections measured | 23077 |
| No. of independent reflections | 6010 |
| $R_{int}$ | 0.1165 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.1207 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.2679 |
| Final $R_1$ values (all data) | 0.1750 |
| Final $wR(F^2)$ values (all data) | 0.2966 |
| Goodness of fit on $F^2$ | 1.087 |
| CCDC number | 1583646 |

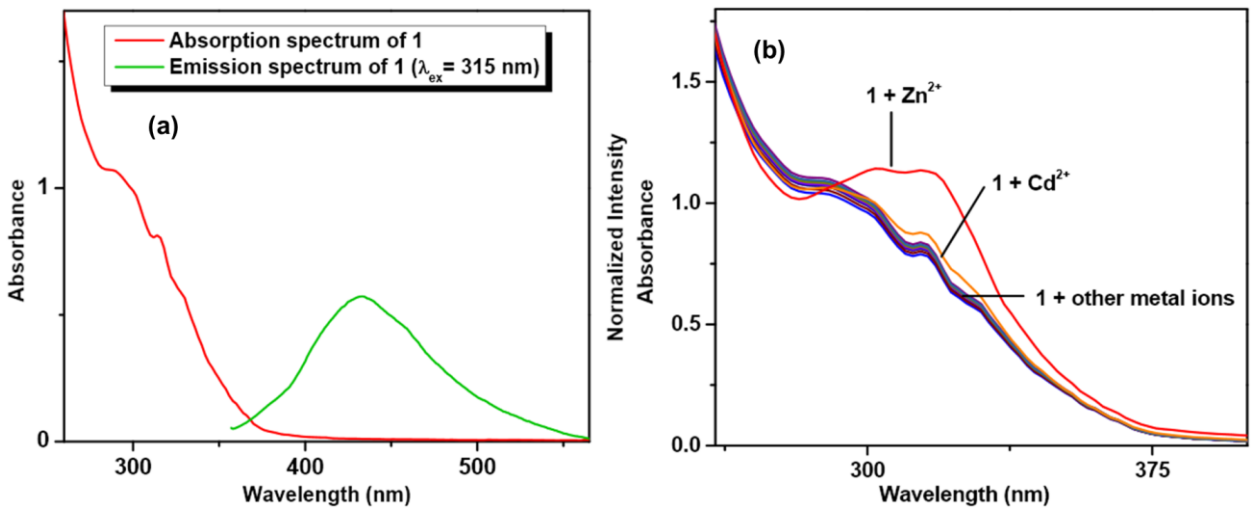



**Figure S9.** (a) Absorption and emission profiles of **1** and (b) Absorption spectral changes of **1** (6.5 x $10^{-5}$ M) in presence of various metal ions (10 equiv) in acetonitrile at room temperature.

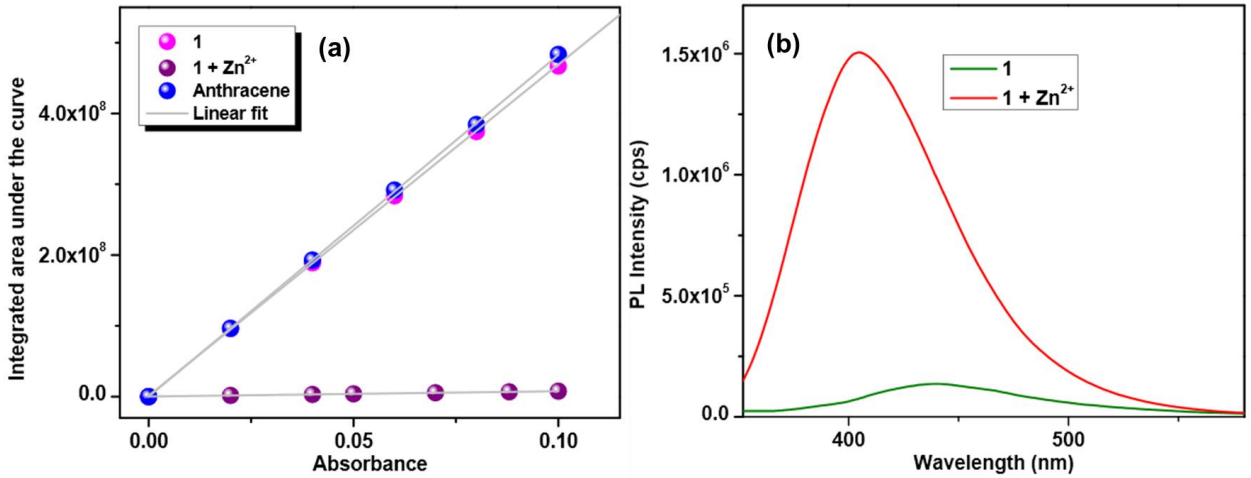



**Figure S10.** (a) Plot of integrated emission intensity versus absorbance for calculation of quantum yield ($\phi_f$) of **1** and its $Zn^{2+}$ adduct in acetonitrile using anthracene as the standard (b) Change in emission profile of **1** (8.5 x $10^{-6}$ M) upon addition of 10 equiv of $Zn^{2+}$ in DMSO.

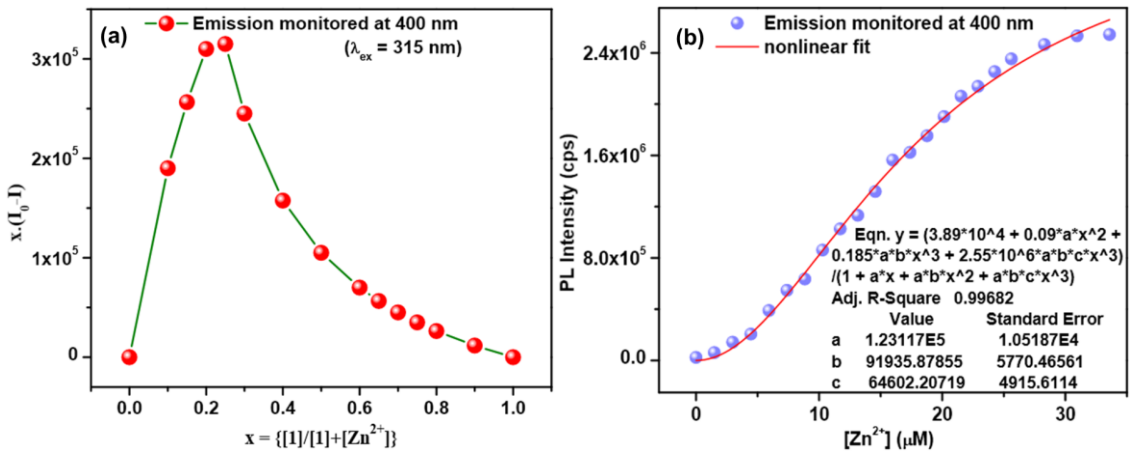


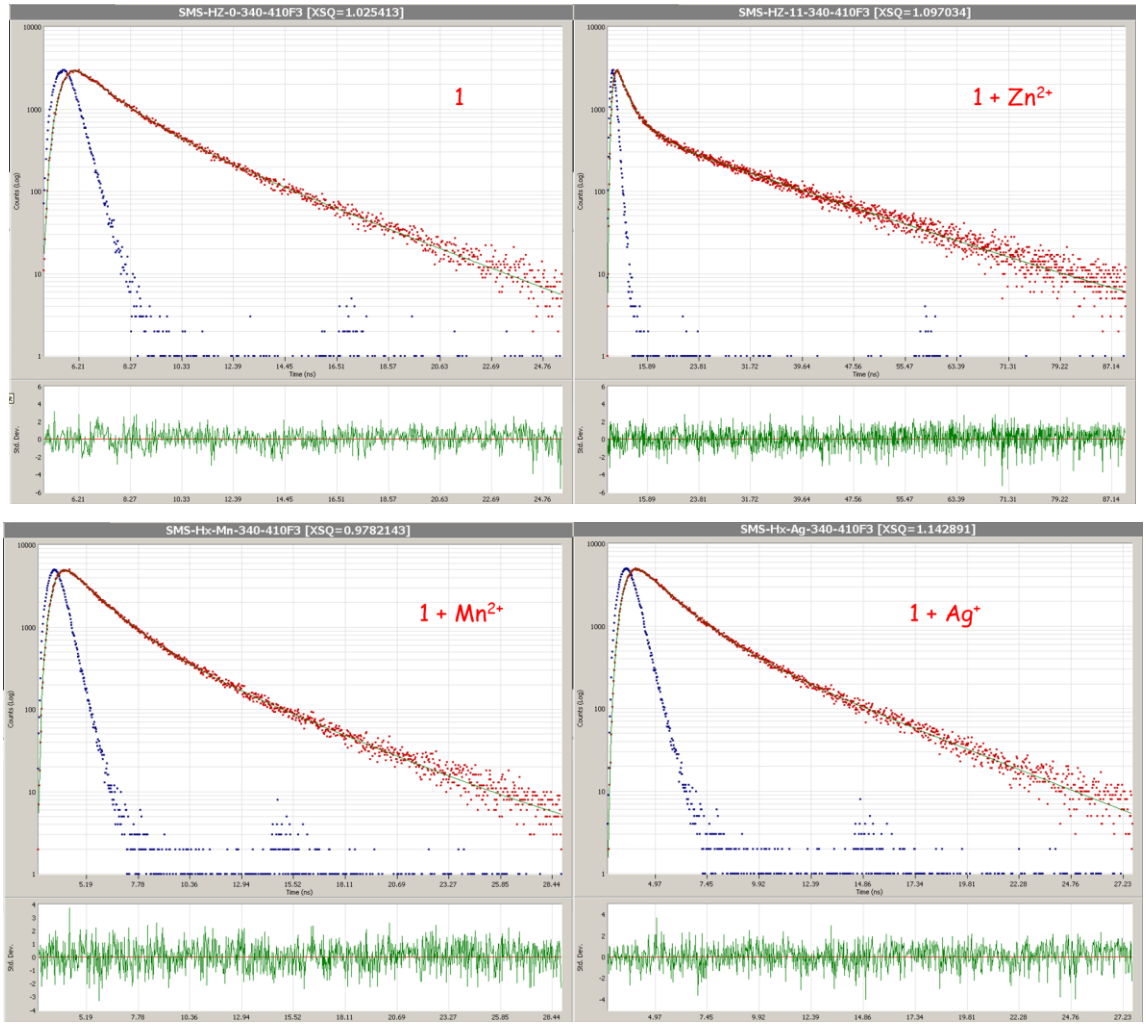

**Figure S11.** (a) PL Job's plot experiment of **1** (15 x $10^{-6}$ M) with $Zn^{2+}$ (15 x $10^{-6}$ M). (b) Non-linear 1:3 fitting of PL titration data to calculate association constant of **1** with $Zn^{2+}$ in acetonitrile at room temperature.

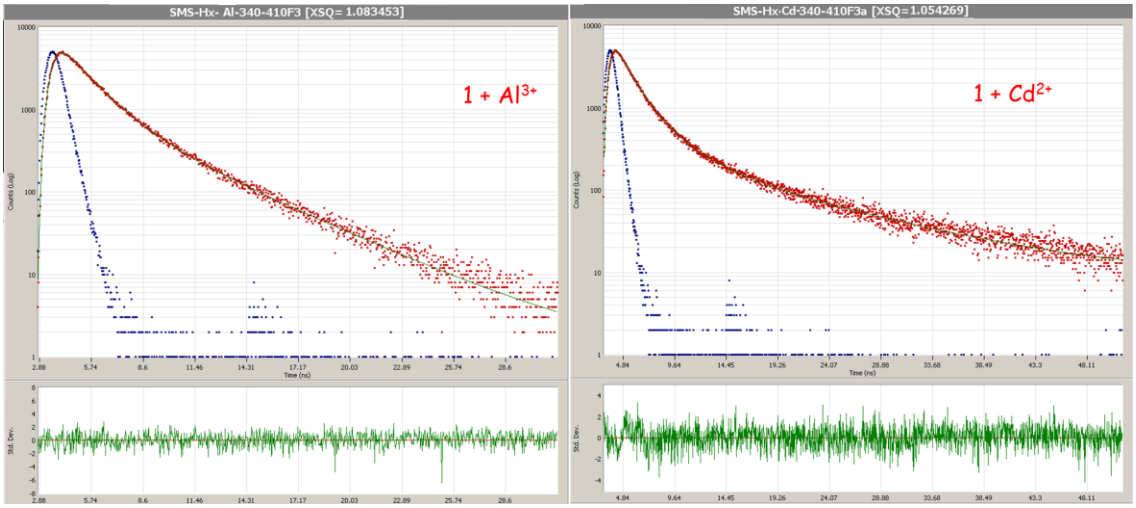
**Table S2.** Comparison of $Zn^{2+}$ sensing by sensor **1** with some of the previously reported sensors.

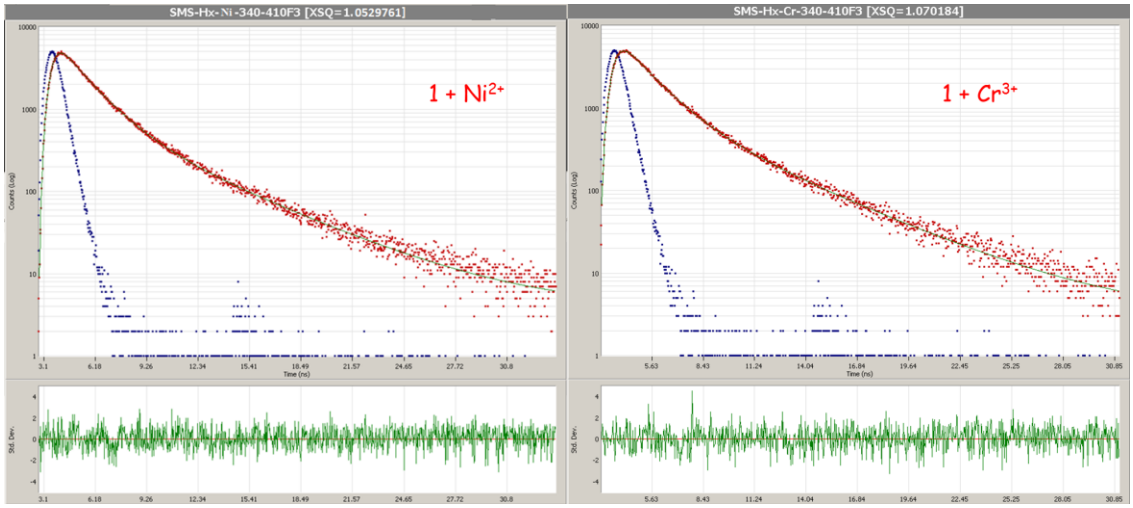
| **Ref.** | **$\lambda_{ex}$ (nm)** | **$\lambda_{em}$ (nm)** | **Log $K_a$** | **LOD** | **Nuclearity** | **Fluorophore** | **Solvent** |
|---|---|---|---|---|---|---|---|
| *Inorg. Chem.*, **2011**, *50*, 4229-4231. | 311 | 382 | 4.52 | 1.2 μM | Mononuclear | Quinoline | $CH_3CN$ |
| *Accounts of Chemical Research*, **2009**, *42*, 193-203. | 415 | 581 | 5.22 | 21 nM | Mononuclear | Quinoline | MeOH-HEPES buffer (3/7, v/v, pH 7.4) |
| *Pure Appl. Chem.*, **2011**, *83*, 2213-2228 | 319 | 480 | 11.92 | 3.8 μM | Mononuclear | Methoxy quinoline | ACN-$H_2O$ (9:1, v/v) |
| *ACS Sens.*, **2016**, *1*, 1408-1415 | 576<br>586 | 701<br>702 | | 0.2 μM<br>86 nM | Mononuclear | Rhodol-DPA | 10 mM HEPES buffer solution (pH 7.0) |
| *ACS Sens.*, **2016**, *1*, 739-747 | 410 | 532 | 4.84 | 0.1 μM | Mononuclear | Hydroxy-napthalene | DMF/ $H_2O$ (9:1, v/v) |
| *Chem. Rev.*, **2014**, *114*, 4564-4601 | 353;<br>360 | 405;<br>546 | 7.67;<br>7.40 | 1.3 μM<br>1.0 μM | Mononuclear | Napthalene | $CH_3CN$ /$H_2O$, 8:2 v/v |
| *J. Am. Chem. Soc.*, **2010**, *132*, 601-610 | 360 | 483 | ---- | 5.7 nM | Mononuclear | DPA-derivative | acetonitrile/water (50:50, v/v) |
| *J. Phys. Chem. A*, **2011**, *115*, 8234-8241 | 300 | 428 | 3.95 | 99.10 μM | Mononuclear | Quinoline | $CH_3CN/H_2O$ = 5/95, v/v |
| *Sensors and Actuators B*, **2016**, *234*, 616-624 | 344 | 515 | 6.83 | ---- | Mononuclear | Quinoline | tris-HCl (0.01 M) solution (MeOH/$H_2O$ ) 1:9, v/v, pH =7.22) |
| Present work | 315 | 400<br>430 | 5.09<br>4.10 | 35.60 nM<br>0.29 μM | Trinuclear | Quinoline | $CH_3CN$ aqueous buffer (10 mM HEPES, pH 7.4) / $CH_3CN$ (1:1 v/v) |

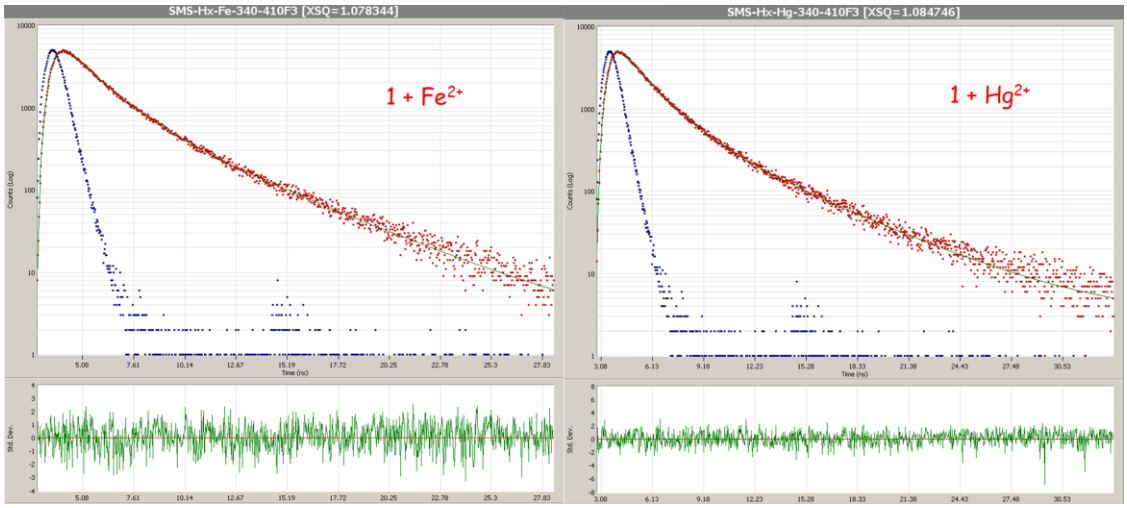
**Table S3.** List of lifetimes of **1** and **1** in presence of various metal ions in acetonitrile.

| | **B1** (x $10^{-2}$) | **T1** (ns) | **B2** (x $10^{-2}$) | **T2** (ns) | **τ** (ns) | **CHISQ** |
|---|---|---|---|---|---|---|
| **1** | 2.5675 | 0.2535 | 14.1647 | 1.6985 | 1.4768 | 1.0254 |
| **1** + $Ag^{+}$ | 2.3837 | 0.2753 | 17.9896 | 1.6692 | 1.5061 | 1.1429 |
| **1** + $Al^{3+}$ | 2.3535 | 0.2972 | 25.5737 | 1.6949 | 1.5771 | 1.0834 |
| **1** + $Cd^{2+}$ | 2.3459 | 0.3855 | 30.9823 | 2.2677 | 2.1352 | 1.0543 |
| **1** + $Co^{2+}$ | 2.2323 | 0.2798 | 10.8141 | 1.6196 | 1.3904 | 1.0621 |
| **1** + $Ni^{2+}$ | 2.3319 | 0.2448 | 5.8142 | 1.5255 | 1.1639 | 1.0530 |
| **1** + $Cr^{3+}$ | 2.1540 | 0.2580 | 12.5914 | 1.5577 | 1.3678 | 1.0702 |
| **1** + $Cu^{2+}$ | 2.4383 | 0.2829 | 10.2432 | 1.4086 | 1.1922 | 1.0909 |
| **1** + $Fe^{2+}$ | 2.3083 | 0.2793 | 26.9392 | 1.6783 | 1.5679 | 1.0783 |
| **1** + $Hg^{2+}$ | 2.2692 | 0.3002 | 28.1140 | 1.8577 | 1.7414 | 1.0847 |
| **1** + $Mn^{2+}$ | 2.3374 | 0.2836 | 19.0155 | 1.6390 | 1.4906 | 0.9782 |
| **1** + $Pb^{2+}$ | 2.2058 | 0.2895 | 20.2611 | 1.6719 | 1.5362 | 1.0818 |
| **1** + $Zn^{2+}$ | 2.2426 | 0.3010 | 3.9721 | 4.9011 | 3.2411 | 1.0970 |




SMS-Hx- Al-340-410F3 [XSQ= 1.083453]
1 + Al3+
SMS-Hx-Cd-340-410F3a [XSQ=1.054269]
1 + Cd2+


SMS-Hx- Ni -340-410F3 [XSQ=1.0529761]
1 + Ni2+
SMS-Hx-Cr-340-410F3 [XSQ=1.070184]
1 + Cr3+


SMS-Hx-Fe-340-410F3 [XSQ=1.078344]
1 + Fe2+
SMS-Hx-Hg-340-410F3 [XSQ=1.084746]
1 + Hg2+

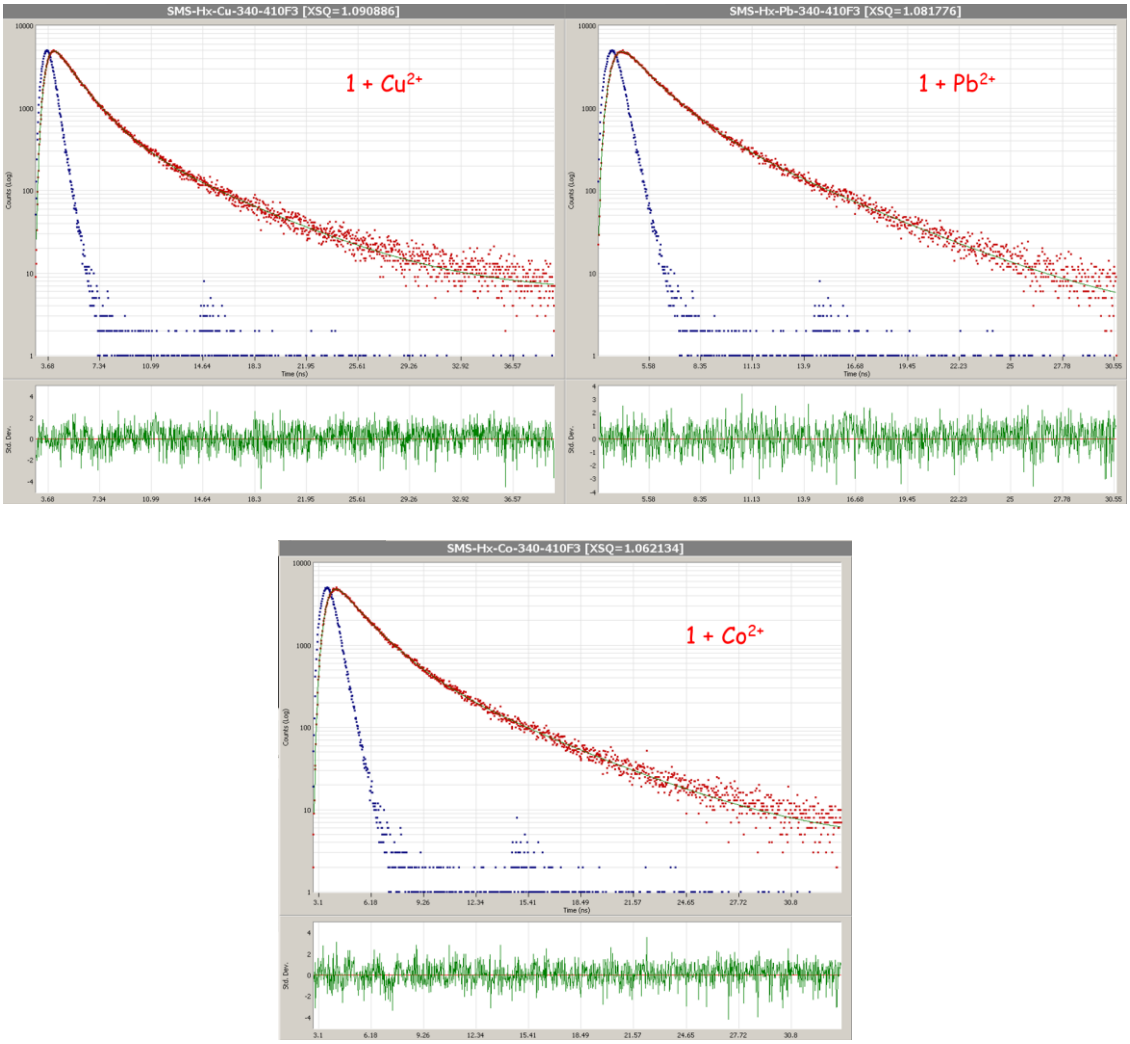



**Figure S12.** The residual plots for fitted decays of **1** in presence of various metal ions in acetonitrile at room temperature.

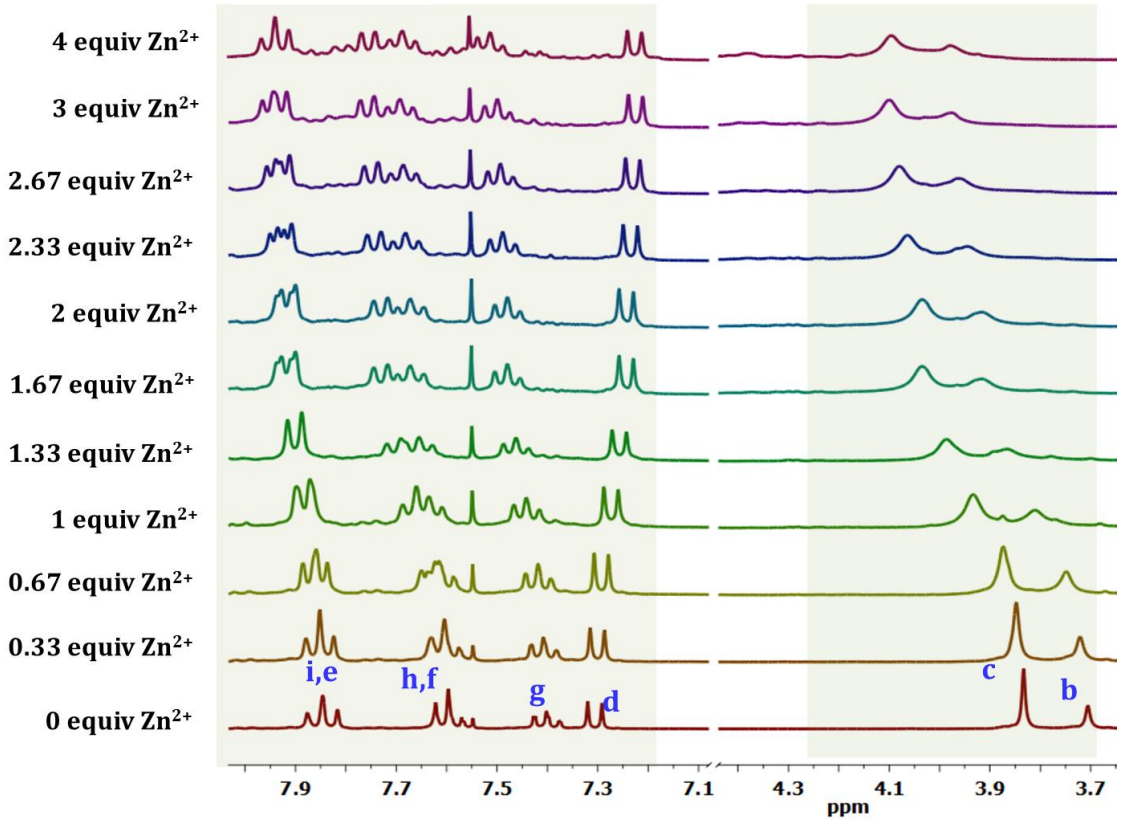



**Figure S13.** Changes in $^{1}$H NMR spectra of **1** (6.8 x $10^{-3}$ M) upon addition of increasing amount of $Zn^{2+}$ (0 - 4 equiv) in $CD_3CN$.

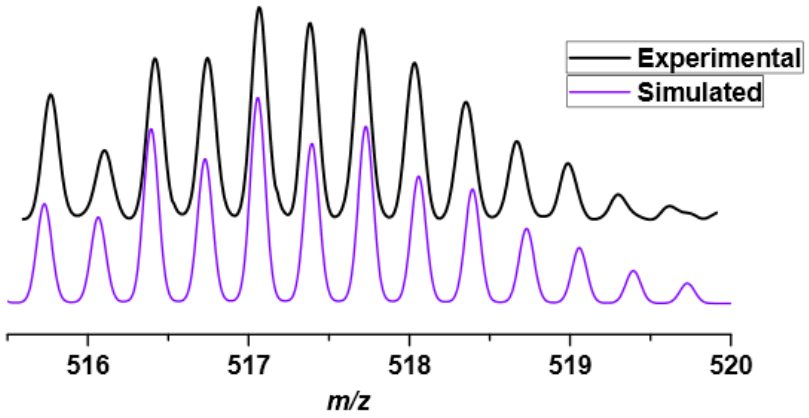



**Figure S14.** Isotopic distribution pattern of **1**$[ZnClO_4]_3^{3+}$ with its corresponding simulated pattern.

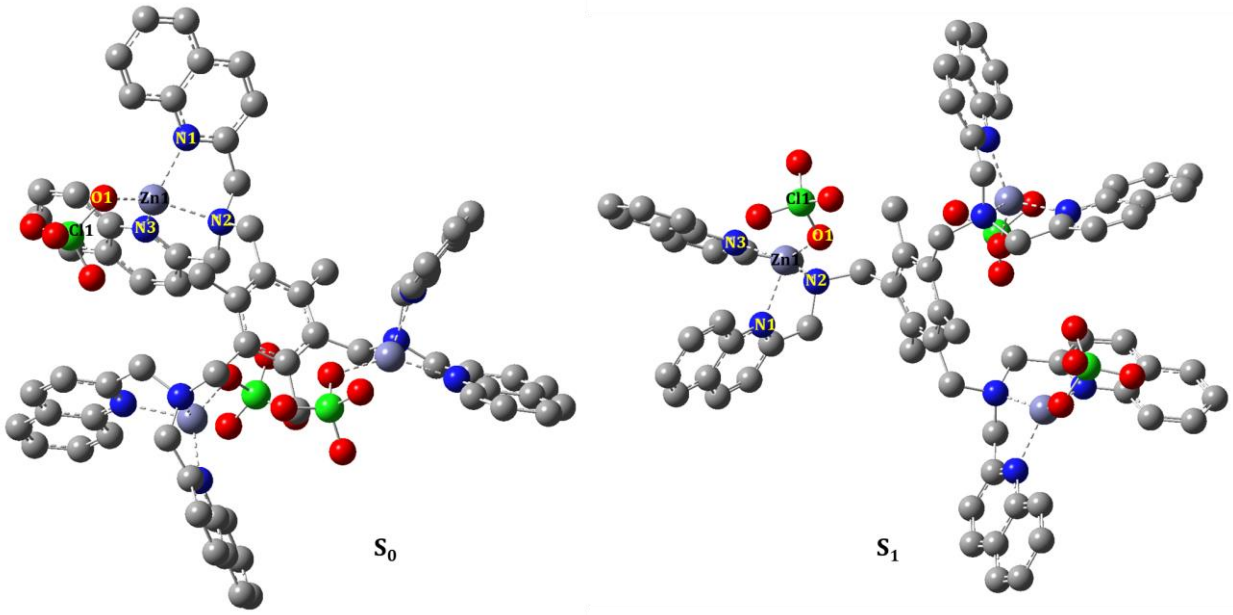



**Figure S15.** Theoretically (DFT B3LYP/6-31G(d); IEF-PCM for acetonitrile) optimized structures of the ground state ($S_0$) and first excited state ($S_1$) of **1**$[ZnClO_4]_3^{3+}$.

**Table S4.** The main geometric parameters for ground state ($S_0$) and first excited state ($S_1$) of **1**$[ZnClO_4]_3^{3+}$.

| Entry | Bond Angle (Degree) | | Entry | Bond Length (Å) | |
|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | | $S_0$ | $S_1$ |
| N1-Zn1-N2 | 82.35 | 80.74 | N1-Zn1 | 2. 174 | 2.154 |
| N1-Zn1-N3 | 90.67 | 117.04 | N2-Zn1 | 2.248 | 2.214 |
| N2-Zn1-N3 | 83.04 | 79.14 | N3-Zn1 | 2.169 | 2.176 |
| N1-Zn1-O1 | 119.57 | 106.89 | O1-Zn1 | 2.072 | 2.098 |
| N3-Zn1-O1 | 141.60 | 123.36 | O1-Cl1 | 1.559 | 1.560 |
| N2-Zn1-O1 | 122.08 | 144.32 | | | |

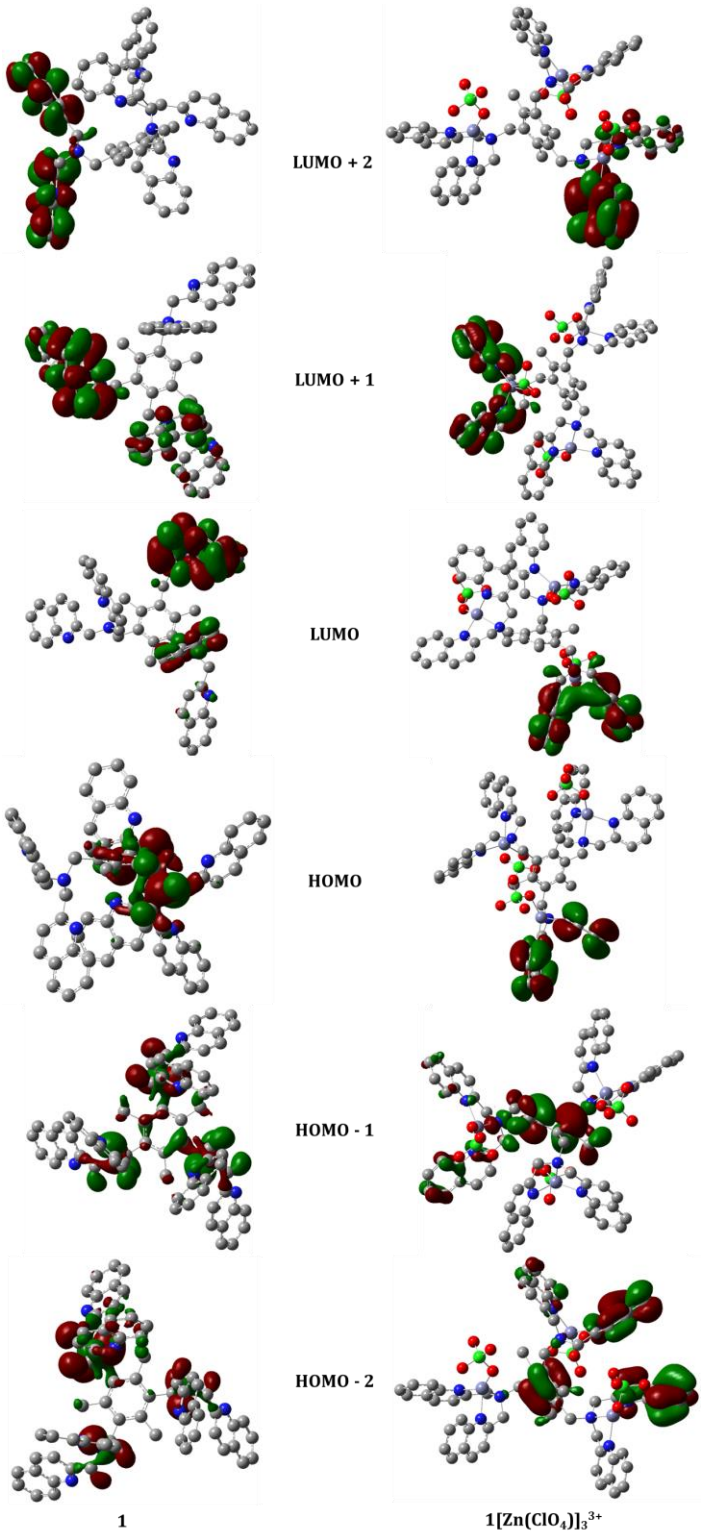



**Figure S16.** Selected MOs of **1** and **1**$[ZnClO_4]_3^{3+}$. as obtained from the DFT B3LYP/6-31G(d) level of computation using IEFPCM model to encounter the solvent effect of acetonitrile [isovalue = 0.02].

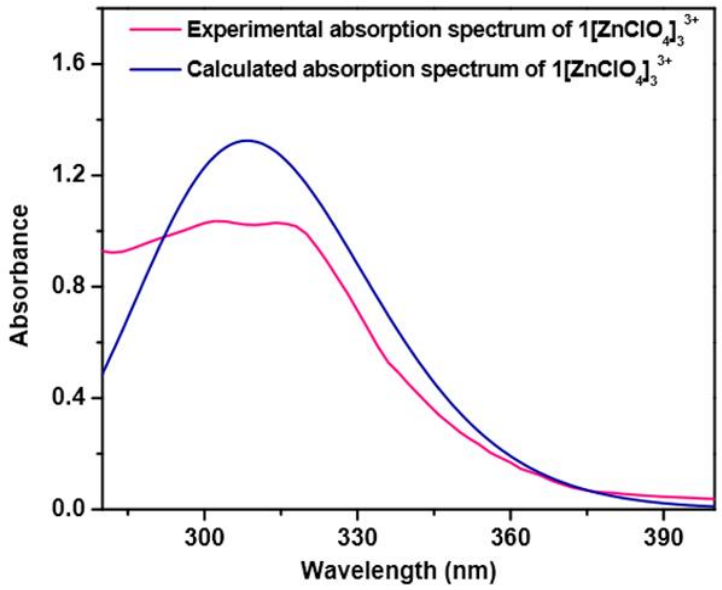



**Figure S17.** Theoretical (energy calculation by TD-DFT B3LYP/6-31G(d) level of computation (no of states = 20) using IEFPCM model for acetonitrile) and experimental UV-vis spectra of **1[**$ZnClO_4]_3^{3+}$.

**Table S5:** Main calculated optical transitions for **1** and **1[**$ZnClO_4]_3^{3+}$.

| **Entry** | **Computed vertical excitation** | | **Experimentally observed transition** | | **Corresponding MO** | **Oscillator strength (*f*)** |
|---|---|---|---|---|---|---|
| | Energy (eV) | $\lambda_{ex}$ (nm) | Energy (eV) | $\lambda_{ex}$ (nm) | | |
| **1** | 4.0386 | 307 | 4.0919 | 303 | HOMO-2 → LUMO+1 | 0.026 |
| | 3.9366 | 314.95 | 3.9360 | 315 | HOMO → LUMO+1 | 0.014 |
| **1**$[ZnClO_4]_3$ | 4.0766 | 304.14 | 4.0919 | 303 | HOMO-1→ LUMO+2 | 0.0527 |
| | 3.9969 | 310.20 | 3.9360 | 315 | HOMO-5 → LUMO | 0.0486 |
| | 3.9612 | 313.00 | 3.9360 | 315 | HOMO-1 → LUMO | 0.0121 |

**Table S6:** The (x,y,z) Cartesian coordinates of **1** calculated from Gaussian-09 at B3LYP/6-31G(d) computational level using IEF-PCM for acetonitrile.

| Ligand 1 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Centre No.** | **Atom** | **Coordinates (Å)** | | | **Centre No.** | **Atom** | **Coordinates (Å)** | | |
| | | **x** | **y** | **z** | | | **x** | **y** | **z** |
| 1 | C | 3.29676 | -6.15789 | -1.68758 | 73 | C | 3.3623 | 2.78263 | 5.2277 |
| 2 | C | 3.39964 | -5.00835 | -0.9454 | 74 | C | 2.7923 | 3.71545 | 6.13196 |
| 3 | C | 4.22004 | -3.94341 | -1.41955 | 75 | C | 1.64814 | 4.40231 | 5.79189 |
| 4 | N | 4.89516 | -4.00474 | -2.5541 | 76 | C | -4.45222 | -2.30224 | -0.81315 |
| 5 | C | 4.80299 | -5.14416 | -3.30862 | 77 | C | -2.51497 | -2.02743 | 0.60593 |
| 6 | C | 4.00559 | -6.26424 | -2.91405 | 78 | C | 4.35984 | -2.68353 | -0.58682 |
| 7 | C | 5.52588 | -5.21094 | -4.52841 | 79 | C | 3.12754 | -1.0887 | 0.75732 |
| 8 | C | 5.46033 | -6.33864 | -5.31896 | 80 | C | 0.27537 | 5.14032 | -0.6277 |
| 9 | C | 4.67132 | -7.44842 | -4.92654 | 81 | C | -0.62187 | 3.29967 | 0.671 |
| 10 | C | 3.95837 | -7.41213 | -3.74723 | 82 | H | 2.684 | -6.99034 | -1.35011 |
| 11 | C | 0.15317 | -1.35057 | -1.64025 | 83 | H | 2.87277 | -4.89144 | -0.00382 |
| 12 | C | -1.09864 | -0.7028 | -1.68166 | 84 | H | 6.12589 | -4.35177 | -4.81364 |
| 13 | C | -1.16833 | 0.70928 | -1.67769 | 85 | H | 6.01686 | -6.3811 | -6.2511 |
| 14 | C | 0.01823 | 1.46994 | -1.63714 | 86 | H | 4.63118 | -8.32944 | -5.56071 |
| 15 | C | 1.2751 | 0.82348 | -1.58975 | 87 | H | 3.35119 | -8.26023 | -3.4402 |
| 16 | C | 1.34158 | -0.58482 | -1.60987 | 88 | H | 2.65588 | -2.06482 | -2.43692 |
| 17 | C | 2.69197 | -1.28962 | -1.66402 | 89 | H | 3.47311 | -0.58796 | -1.99257 |
| 18 | C | 2.53659 | 1.66801 | -1.5498 | 90 | H | 2.9157 | 1.8738 | -2.56081 |
| 19 | C | -0.03842 | 2.99171 | -1.70679 | 91 | H | 2.34353 | 2.62247 | -1.06091 |
| 20 | C | -2.52737 | 1.3822 | -1.7551 | 92 | H | 3.34409 | 1.18179 | -0.99956 |
| 21 | C | -2.38073 | -1.51949 | -1.79604 | 93 | H | 0.70304 | 3.34226 | -2.43265 |
| 22 | C | 0.24376 | -2.86661 | -1.66327 | 94 | H | -1.0115 | 3.31993 | -2.10108 |
| 23 | N | 3.08953 | -1.96837 | -0.41144 | 95 | H | -2.79557 | 1.62188 | -2.79376 |
| 24 | N | 0.26721 | 3.68394 | -0.43343 | 96 | H | -3.30279 | 0.73615 | -1.34532 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 25 | N | -3.21692 | -1.5437 | -0.57437 | 97 | H | -2.55954 | 2.31819 | -1.19452 |
| 26 | C | -3.12303 | -1.93619 | 4.34052 | 98 | H | -3.0045 | -1.09163 | -2.58812 |
| 27 | C | -2.62737 | -2.27998 | 3.10959 | 99 | H | -2.15025 | -2.54272 | -2.12686 |
| 28 | C | -3.14114 | -1.64184 | 1.94094 | 100 | H | -0.54141 | -3.33329 | -1.06397 |
| 29 | N | -4.09273 | -0.72948 | 1.98685 | 101 | H | 0.14238 | -3.25994 | -2.68435 |
| 30 | C | -4.60815 | -0.37939 | 3.20771 | 102 | H | 1.19535 | -3.20743 | -1.25898 |
| 31 | C | -4.14923 | -0.95835 | 4.43196 | 103 | H | -2.74509 | -2.40356 | 5.2466 |
| 32 | C | -5.63529 | 0.59913 | 3.25746 | 104 | H | -1.8431 | -3.0255 | 3.01325 |
| 33 | C | -6.17887 | 0.98336 | 4.4653 | 105 | H | -5.97518 | 1.03364 | 2.32199 |
| 34 | C | -5.72232 | 0.40891 | 5.67697 | 106 | H | -6.96424 | 1.73369 | 4.49192 |
| 35 | C | -4.72619 | -0.54399 | 5.66013 | 107 | H | -6.16117 | 0.72301 | 6.61969 |
| 36 | C | -6.90735 | 0.336 | -1.99682 | 108 | H | -4.36996 | -0.99061 | 6.58526 |
| 37 | C | -5.98383 | -0.32185 | -1.22439 | 109 | H | -7.34319 | 1.27765 | -1.67131 |
| 38 | C | -5.44545 | -1.55902 | -1.68499 | 110 | H | -5.65213 | 0.06522 | -0.26631 |
| 39 | N | -5.7899 | -2.11319 | -2.83454 | 111 | H | -6.61926 | -3.00514 | -5.12706 |
| 40 | C | -6.70944 | -1.46863 | -3.61922 | 112 | H | -8.28319 | -1.90767 | -6.61835 |
| 41 | C | -7.30547 | -0.22456 | -3.24026 | 113 | H | -9.32034 | 0.25532 | -5.95575 |
| 42 | C | -7.08158 | -2.06089 | -4.85448 | 114 | H | -8.70273 | 1.32855 | -3.80955 |
| 43 | C | -8.00395 | -1.44681 | -5.67494 | 115 | H | 4.75182 | -0.75295 | 2.93661 |
| 44 | C | -8.59498 | -0.2153 | -5.29818 | 116 | H | 4.59329 | -1.91207 | 5.13645 |
| 45 | C | -8.25274 | 0.38365 | -4.10455 | 117 | H | 3.40935 | -3.63978 | 6.57093 |
| 46 | N | 2.13766 | -2.76324 | 2.22472 | 118 | H | 1.63592 | -5.35638 | 6.78735 |
| 47 | C | 3.07768 | -1.84361 | 2.07825 | 119 | H | 0.13032 | -5.85039 | 4.86839 |
| 48 | C | 3.99296 | -1.50885 | 3.11491 | 120 | H | 0.39464 | -4.62029 | 2.72093 |
| 49 | C | 3.90617 | -2.14981 | 4.32813 | 121 | H | 1.16174 | 7.5095 | -4.79619 |
| 50 | C | 2.91151 | -3.14083 | 4.52254 | 122 | H | 3.08117 | 8.42023 | -6.09373 |
| 51 | C | 2.04316 | -3.41885 | 3.4186 | 123 | H | 5.40289 | 8.16783 | -5.23493 |
| 52 | C | 2.74551 | -3.85732 | 5.73782 | 124 | H | 5.81818 | 7.00861 | -3.0849 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 53 | C | 1.7592 | -4.81164 | 5.85578 | 125 | H | 4.89187 | 5.79459 | -1.06049 |
| 54 | C | 0.90068 | -5.09174 | 4.76199 | 126 | H | 2.87963 | 4.92232 | 0.13879 |
| 55 | C | 1.03868 | -4.41333 | 3.5707 | 127 | H | -0.62542 | 5.57129 | 4.78411 |
| 56 | C | 2.18162 | 7.40839 | -4.43694 | 128 | H | -1.59022 | 5.07132 | 2.54082 |
| 57 | C | 3.24997 | 7.90988 | -5.14957 | 129 | H | 3.20526 | 1.83967 | 3.29717 |
| 58 | C | 4.57246 | 7.76654 | -4.66107 | 130 | H | 4.26366 | 2.24657 | 5.51153 |
| 59 | C | 4.80589 | 7.12205 | -3.46503 | 131 | H | 3.26332 | 3.88396 | 7.09613 |
| 60 | C | 3.72588 | 6.59484 | -2.71022 | 132 | H | 1.20455 | 5.11698 | 6.48071 |
| 61 | C | 2.39037 | 6.74024 | -3.20194 | 133 | H | -4.24996 | -3.28501 | -1.27356 |
| 62 | C | 3.89304 | 5.92027 | -1.47136 | 134 | H | -4.9206 | -2.48017 | 0.16001 |
| 63 | C | 2.79026 | 5.44185 | -0.80974 | 135 | H | -1.50168 | -1.6084 | 0.59268 |
| 64 | C | 1.49743 | 5.63498 | -1.37709 | 136 | H | -2.38471 | -3.12748 | 0.59858 |
| 65 | N | 1.30114 | 6.25747 | -2.5265 | 137 | H | 5.13657 | -2.04745 | -1.04601 |
| 66 | C | -0.15343 | 4.85188 | 4.11941 | 138 | H | 4.71807 | -2.96941 | 0.40915 |
| 67 | C | -0.68517 | 4.57733 | 2.88102 | 139 | H | 2.2479 | -0.4373 | 0.71255 |
| 68 | C | -0.03972 | 3.634 | 2.03516 | 140 | H | 4.01293 | -0.42719 | 0.75794 |
| 69 | N | 1.062 | 2.99057 | 2.39034 | 141 | H | -0.62597 | 5.49455 | -1.15732 |
| 70 | C | 1.60385 | 3.24789 | 3.61646 | 142 | H | 0.27406 | 5.60617 | 0.36496 |
| 71 | C | 1.02709 | 4.1861 | 4.53258 | 143 | H | -0.75667 | 2.2157 | 0.62308 |
| 72 | C | 2.78347 | 2.55288 | 3.99926 | 144 | H | -1.62181 | 3.76041 | 0.57846 |

**Table S7:** The (x,y,z) Cartesian coordinates of **1[**$ZnClO_4]_3^{3+}$ calculated from Gaussian-09 at B3LYP/6-31G(d) computational level using IEF-PCM for acetonitrile.

| **1[$ZnClO_4]_3^{3+}$** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Centre No.** | **Atom** | **Coordinates (Å)** | | | **Centre No.** | **Atom** | **Coordinates (Å)** | | |
| | | **x** | **y** | **z** | | | **x** | **y** | **z** |
| 1 | C | -1.61347 | -0.09038 | -1.19508 | 82 | C | -6.27813 | -3.12103 | 2.0573 |
| 2 | C | -0.67674 | -1.12648 | -1.41045 | 83 | Zn | -5.03841 | -0.44573 | 0.14551 |
| 3 | C | 0.20285 | -1.48907 | -0.36609 | 84 | C | -2.74087 | 0.14585 | -2.18204 |
| 4 | C | 0.2001 | -0.76222 | 0.8501 | 85 | H | -3.27492 | 2.01842 | -0.12584 |
| 5 | C | -0.52714 | 0.45188 | 0.92888 | 86 | H | -1.89324 | 2.67531 | -1.007 |
| 6 | C | -1.45032 | 0.78299 | -0.09614 | 87 | H | -1.95493 | 2.74198 | 0.74129 |
| 7 | C | -2.18846 | 2.11234 | -0.1135 | 88 | H | 0.75042 | -0.78146 | 2.96625 |
| 8 | C | 0.94285 | -1.33239 | 2.04733 | 89 | H | 0.61553 | -2.36095 | 2.23443 |
| 9 | C | -0.56337 | -1.75035 | -2.79302 | 90 | H | -1.49484 | -2.17215 | -3.17251 |
| 10 | C | -0.36954 | 1.39423 | 2.11475 | 91 | H | -0.24614 | -0.9824 | -3.5097 |
| 11 | N | 0.72614 | 2.4437 | 1.98442 | 92 | H | 0.17279 | -2.54962 | -2.83838 |
| 12 | C | 0.38436 | 3.63273 | 2.81617 | 93 | H | -1.29731 | 1.93555 | 2.28212 |
| 13 | C | 2.03359 | 1.88396 | 2.41786 | 94 | H | -0.18633 | 0.84771 | 3.04363 |
| 14 | C | 3.20757 | 2.7859 | 2.08618 | 95 | H | -0.22348 | 3.34022 | 3.67833 |
| 15 | C | 4.28794 | 2.89287 | 2.98915 | 96 | H | 1.31272 | 4.052 | 3.22094 |
| 16 | C | 5.37273 | 3.66449 | 2.64593 | 97 | H | 2.1859 | 0.93819 | 1.89305 |
| 17 | C | 5.40499 | 4.3232 | 1.39329 | 98 | H | 2.02643 | 1.66337 | 3.49218 |
| 18 | C | 4.27841 | 4.16967 | 0.52326 | 99 | H | 4.24657 | 2.36647 | 3.93546 |
| 19 | N | 3.19471 | 3.41341 | 0.91175 | 100 | H | 6.2121 | 3.77292 | 3.3268 |
| 20 | C | -0.29756 | 4.74876 | 2.04545 | 101 | H | -2.45647 | 7.3296 | 2.51904 |
| 21 | N | 0.07342 | 4.95481 | 0.78356 | 102 | H | -1.49817 | 5.3756 | 3.73195 |
| 22 | C | -0.41172 | 6.04 | 0.0889 | 103 | H | 0.74131 | 5.64013 | -1.71538 |
| 23 | C | -1.34376 | 6.93617 | 0.70214 | 104 | H | -0.13012 | 7.57644 | -2.93591 |
| 24 | C | -1.74076 | 6.67124 | 2.0351 | 105 | H | -1.77254 | 9.12132 | -1.88485 |
| 25 | C | -1.21766 | 5.59137 | 2.70705 | 106 | H | -2.54038 | 8.71832 | 0.44088 |
| 26 | C | 0.0187 | 6.29416 | -1.23695 | 107 | H | 7.35108 | 5.22985 | 1.65118 |
| 27 | C | -0.46944 | 7.38766 | -1.92197 | 108 | H | 7.34314 | 6.32999 | -0.57378 |
| 28 | C | -1.40214 | 8.26919 | -1.32378 | 109 | H | 5.40472 | 6.02284 | -2.10302 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 29 | C | -1.83054 | 8.04769 | -0.03449 | 110 | H | 3.48108 | 4.65836 | -1.44344 |
| 30 | C | 6.50596 | 5.11752 | 0.97817 | 111 | H | 0.56023 | -3.46096 | -1.12278 |
| 31 | C | 6.49955 | 5.72489 | -0.25683 | 112 | H | 1.26075 | -3.18358 | 0.4429 |
| 32 | C | 5.39349 | 5.5534 | -1.124 | 113 | H | 2.25087 | -0.4305 | -1.20765 |
| 33 | C | 4.30396 | 4.79441 | -0.74939 | 114 | H | 2.15463 | -1.16063 | -2.798 |
| 34 | Zn | 1.23688 | 3.35705 | -0.0079 | 115 | H | 1.90862 | -3.81422 | -2.78001 |
| 35 | C | 1.08814 | -2.71626 | -0.52415 | 116 | H | 3.60655 | -3.36051 | -2.72402 |
| 36 | N | 2.46567 | -2.51795 | -1.16708 | 117 | H | 2.11252 | -6.19951 | -2.82781 |
| 37 | C | 2.67723 | -1.21642 | -1.83662 | 118 | H | 2.82857 | -8.30144 | -1.693 |
| 38 | C | 2.75059 | -3.64108 | -2.10033 | 119 | H | 6.05087 | 1.16099 | -3.98561 |
| 39 | C | 3.10069 | -4.93018 | -1.38169 | 120 | H | 3.6601 | 0.55432 | -3.5973 |
| 40 | C | 2.71337 | -6.17383 | -1.92557 | 121 | H | 7.17628 | -2.71667 | -0.14769 |
| 41 | C | 3.11073 | -7.33039 | -1.29608 | 122 | H | 9.51928 | -2.19187 | -0.54335 |
| 42 | C | 3.88817 | -7.26203 | -0.11483 | 123 | H | 10.19033 | -0.4439 | -2.18257 |
| 43 | C | 4.23523 | -5.96754 | 0.3876 | 124 | H | 8.44834 | 0.78253 | -3.45985 |
| 44 | N | 3.82952 | -4.83068 | -0.27349 | 125 | H | 4.05486 | -9.3962 | 0.19243 |
| 45 | C | 4.14493 | -0.90122 | -2.07283 | 126 | H | 5.40493 | -9.18367 | 2.26399 |
| 46 | N | 5.07415 | -1.52644 | -1.3549 | 127 | H | 5.99655 | -6.93058 | 3.13679 |
| 47 | C | 6.41074 | -1.24759 | -1.56956 | 128 | H | 5.25686 | -4.89124 | 1.96746 |
| 48 | C | 6.79875 | -0.25619 | -2.52661 | 129 | H | -4.90965 | 0.98887 | -2.92866 |
| 49 | C | 5.77829 | 0.40616 | -3.25343 | 130 | H | -4.928 | -0.53754 | -3.80223 |
| 50 | C | 4.46224 | 0.07817 | -3.04348 | 131 | H | -2.87036 | -2.29478 | -1.58424 |
| 51 | C | 7.42521 | -1.94249 | -0.86366 | 132 | H | -3.82589 | -2.33528 | -3.07491 |
| 52 | C | 8.75492 | -1.64877 | -1.09081 | 133 | H | -4.89431 | -4.42205 | -2.86699 |
| 53 | C | 9.13805 | -0.65782 | -2.02406 | 134 | H | -6.28619 | -6.01026 | -1.54244 |
| 54 | C | 8.17434 | 0.02438 | -2.7318 | 135 | H | -9.60473 | -0.50216 | -3.77589 |
| 55 | C | 4.32391 | -8.41903 | 0.58303 | 136 | H | -7.19969 | -0.42601 | -4.4277 |
| 56 | C | 5.07226 | -8.29783 | 1.7321 | 137 | H | -10.0551 | -0.18428 | 2.12537 |
| 57 | C | 5.40921 | -7.01454 | 2.22737 | 138 | H | -11.878 | -0.35142 | 0.43978 |
| 58 | C | 5.00189 | -5.86957 | 1.57465 | 139 | H | -11.3175 | -0.45959 | -1.97772 |
| 59 | Zn | 4.18799 | -2.76072 | 0.20278 | 140 | H | -7.42617 | -6.56014 | 0.60747 |
| 60 | N | -4.04087 | -0.5933 | -1.86306 | 141 | H | -8.03091 | -5.91428 | 2.92716 |
| 61 | C | -5.07131 | -0.08816 | -2.81189 | 142 | H | -7.2759 | -3.72803 | 3.84265 |
| 62 | C | -3.84728 | -2.06099 | -2.01358 | 143 | H | -5.95071 | -2.1814 | 2.4878 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 63 | C | -4.82361 | -2.95632 | -1.27578 | 144 | H | -3.00346 | 1.20049 | -2.21177 |
| 64 | C | -5.20615 | -4.18601 | -1.8557 | 145 | H | -2.4485 | -0.13057 | -3.19996 |
| 65 | C | -5.96966 | -5.06104 | -1.11946 | 146 | Cl | 0.9549 | 2.60573 | -3.10495 |
| 66 | C | -6.34563 | -4.73059 | 0.20472 | 147 | O | 1.75554 | 3.84008 | -3.32098 |
| 67 | C | -5.92875 | -3.46362 | 0.7262 | 148 | O | 1.36746 | 1.5179 | -4.02357 |
| 68 | N | -5.18371 | -2.60165 | -0.04685 | 149 | O | 1.24955 | 2.09244 | -1.66976 |
| 69 | C | -6.51488 | -0.26399 | -2.38128 | 150 | O | -0.49814 | 2.88065 | -3.21101 |
| 70 | N | -6.81368 | -0.20818 | -1.08704 | 151 | O | 4.79104 | -2.69298 | 2.21152 |
| 71 | C | -8.13354 | -0.25317 | -0.68651 | 152 | Cl | -4.88865 | 1.15094 | 2.87476 |
| 72 | C | -9.1832 | -0.35085 | -1.65601 | 153 | O | -4.08181 | 0.37193 | 1.79224 |
| 73 | C | -8.82527 | -0.41678 | -3.02403 | 154 | O | -3.95077 | 1.38467 | 3.9921 |
| 74 | C | -7.50147 | -0.37733 | -3.38724 | 155 | O | -6.03274 | 0.29441 | 3.28495 |
| 75 | C | -8.47955 | -0.19647 | 0.68782 | 156 | H | 2.0281 | -1.35891 | 1.91544 |
| 76 | C | -9.8053 | -0.23149 | 1.06967 | 157 | O | -5.35801 | 2.42078 | 2.27434 |
| 77 | C | -10.8433 | -0.32621 | 0.11261 | 158 | H | -7.71202 | -0.12078 | 1.4499 |
| 78 | C | -10.5357 | -0.38589 | -1.22737 | 159 | Cl | 5.27968 | -1.37476 | 2.88691 |
| 79 | C | -7.11329 | -5.60461 | 1.01865 | 160 | O | 6.73082 | -1.2434 | 2.63208 |
| 80 | C | -7.44639 | -5.24431 | 2.30444 | 161 | O | 4.52242 | -0.24736 | 2.27869 |
| 81 | C | -7.01932 | -3.99779 | 2.82258 | 162 | O | 4.98426 | -1.51265 | 4.3276 |

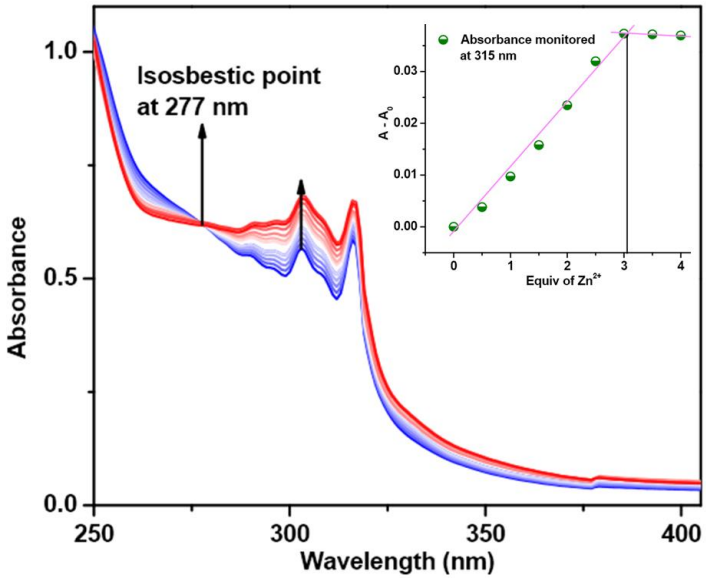



**Figure S18.** Absorption titration profile of **1** with $Zn^{2+}$ (Inset: Corresponding equivalent plot) in aqueous buffer (10 mM HEPES, pH 7.4) / acetonitrile (1:1 v/v).

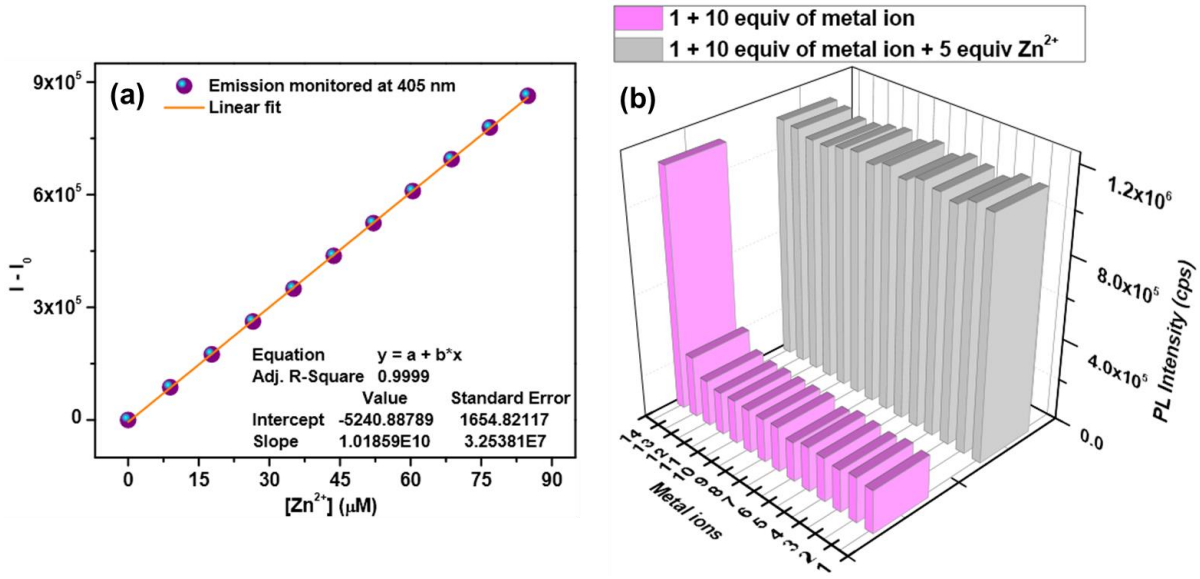



**Figure S19.** (a) The calibration curve for $Zn^{2+}$ over the concentration range between 0 and 90 μM derived from the PL titration data and (b) selectivity graph of **1** with $Zn^{2+}$ in presence of other metal ions in aqueous buffer (10 mM HEPES, pH 7.4) / acetonitrile (1:1 v/v) at room temperature. Magenta bars represent the fluorescence intensities of **1** in presence of all metal ions (10 equiv) and the light grey bars correspond to the same in presence of all metal ions and $Zn^{2+}$. Codes used: (1) Only **1** (2) $Mn^{2+}$ (3) $Mg^{2+}$ (4) $Cu^{2+}$ (5) $Cr^{3+}$ (6) $Co^{2+}$ (7) $Ni^{2+}$ (8) $Ag^{+}$ (9) $Fe^{2+}$ (10) $Pb^{2+}$ (11) $Al^{3+}$ (12) $Hg^{2+}$ (13) $Cd^{2+}$ (14) $Zn^{2+}$.

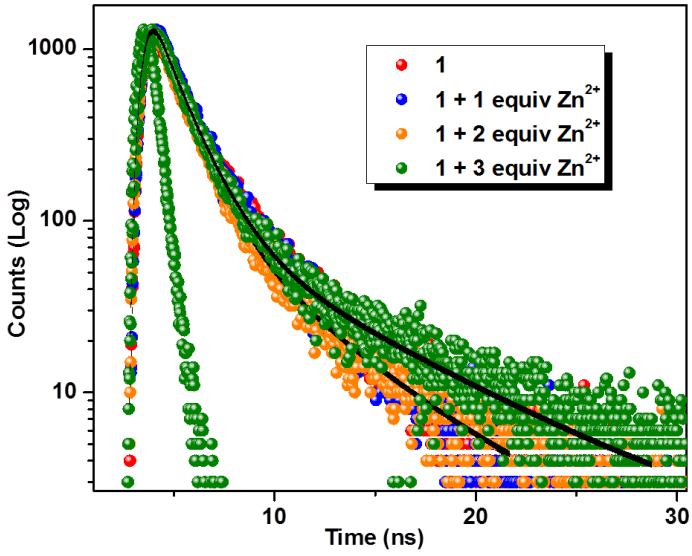



**Figure S20.** Time-resolved luminescence decays of **1** (10 μM; $\lambda_{ex}$ = 340 nm and $\lambda_{em}$ = 410 nm) in the presence of various metal ions as their perchlorate salts and in aqueous buffer (10 mM HEPES, pH 7.4) / acetonitrile (1:1 v/v) at room temperature.

**Synthesis of trinuclear $Zn^{2+}$ complex.** Crystallization of the zinc complex was done by slow evaporation of a solution of the ligand with 3.2 equivalent of $Zn^{2+}$ (1:1 (mole/mole) mixture of $Zn(NO_3)_2.6H_2O$ and $Zn(ClO_4)_2.6H_2O$) in MeOH/$H_2O$/DMF (3:1:1).

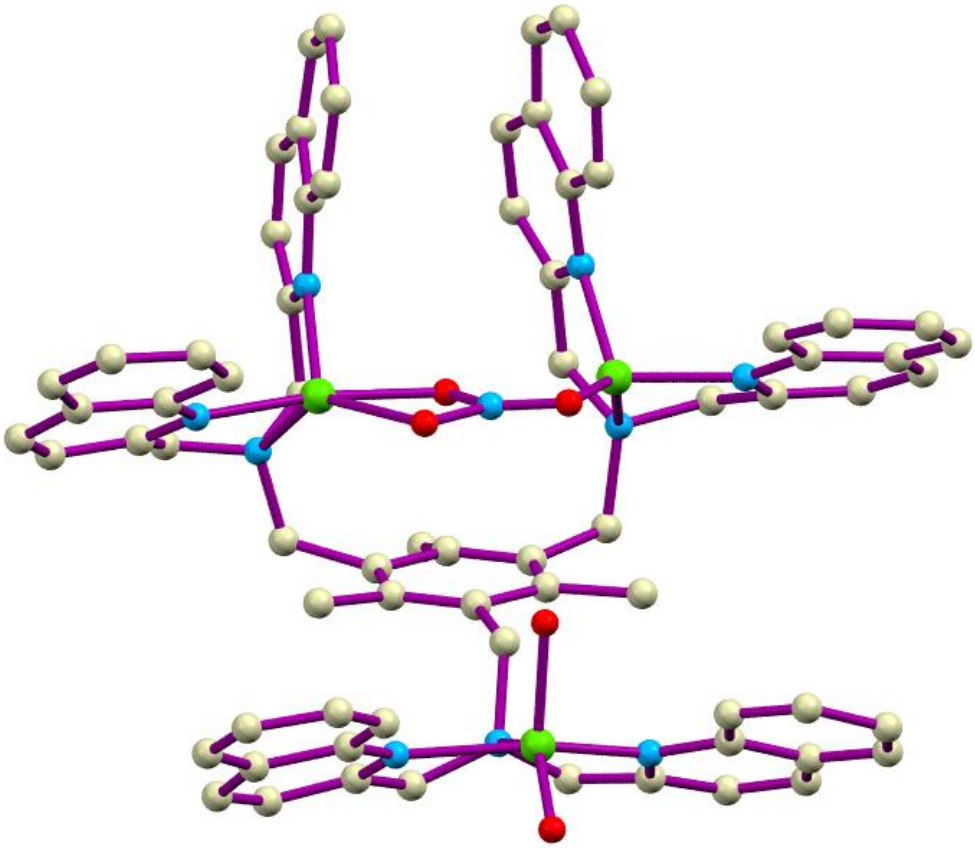


**Figure S21.** Ball and Stick representation of single crystal X-ray structure of the zinc complex. Color code: N, blue; C, grey; O, red; Zn; green. Hydrogen and non-interacting counter anions are omitted for clarity.

**Table S8.** List of crystallographic parameter details of trinuclear $Zn^{2+}$ complex.

| **Compound reference** | **trinuclear $Zn^{2+}$ complex** |
|---|---|
| Chemical formula | $C_{72}H_{63}Cl_3N_{12}O_{26}Zn_3$ |
| Formula Mass | 1814.80 |
| Crystal system | Monoclinic |
| *a*/Å | 12.002(2) |
| *b*/Å | 21.828(4) |
| *c*/Å | 17.522(3) |
| *α*/° | 90 |
| *β*/° | 103.674(7) |
| *γ*/° | 90 |
| Unit cell volume/Å$^3$ | 4460.3(13) |
| Temperature/K | 106(2) |
| Space group | *P*21 |
| No. of formula units per unit cell, *Z* | 2 |
| Radiation type | MoKα |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.967 |
| No. of reflections measured | 32257 |
| No. of independent reflections | 9306 |
| $R_{int}$ | 0.2683 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.1024 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.2381 |
| Final $R_1$ values (all data) | 0.1673 |
| Final $wR(F^2)$ values (all data) | 0.2763 |
| Goodness of fit on $F^2$ | 1.209 |
| CCDC number | 1583647 |

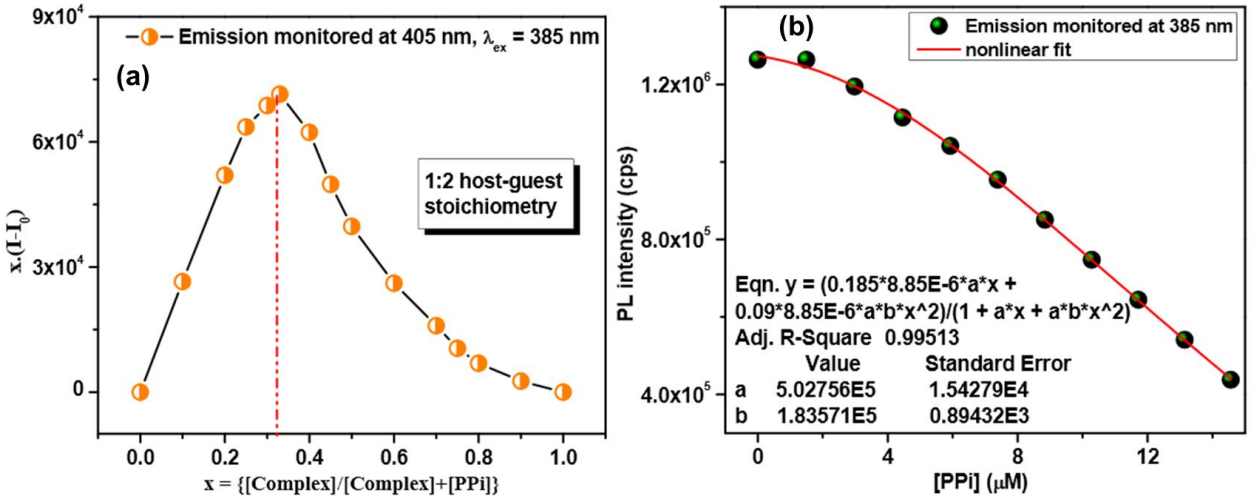



**Figure S22.** (a) PL Job's plot experiment of the tri nuclear $Zn^{2+}$ complex (8.5 x $10^{-6}$ M) with PPi (8.5 x $10^{-6}$ M) and (b) Non-linear 1:2 fitting of PL titration data to calculate association constant of the trinuclear $Zn^{2+}$ complex with PPi in acetonitrile at room temperature.

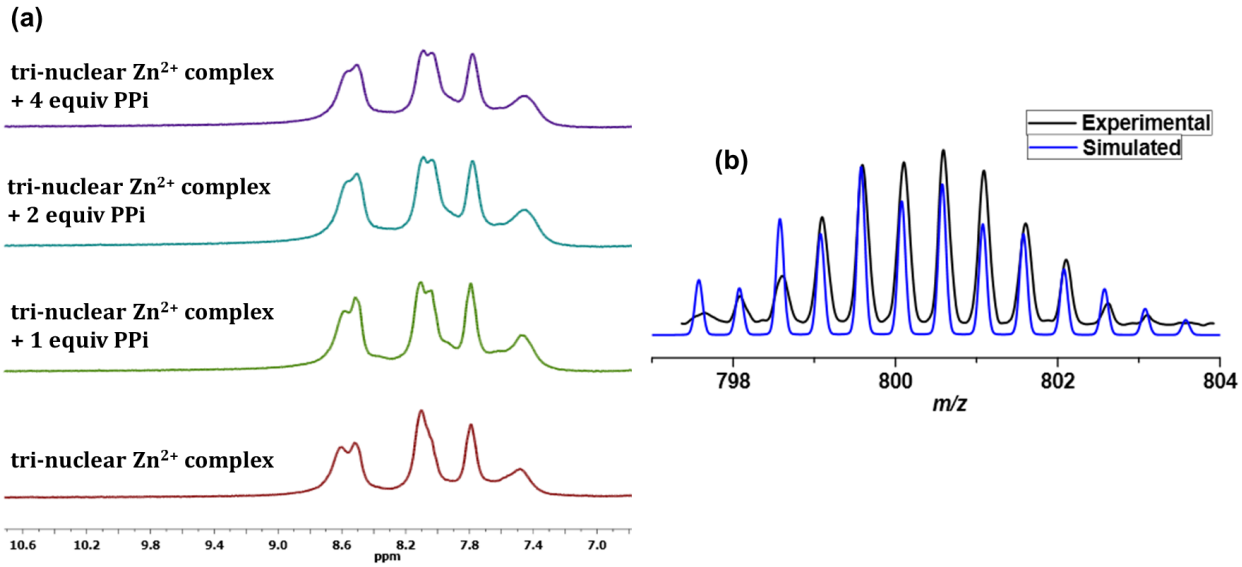
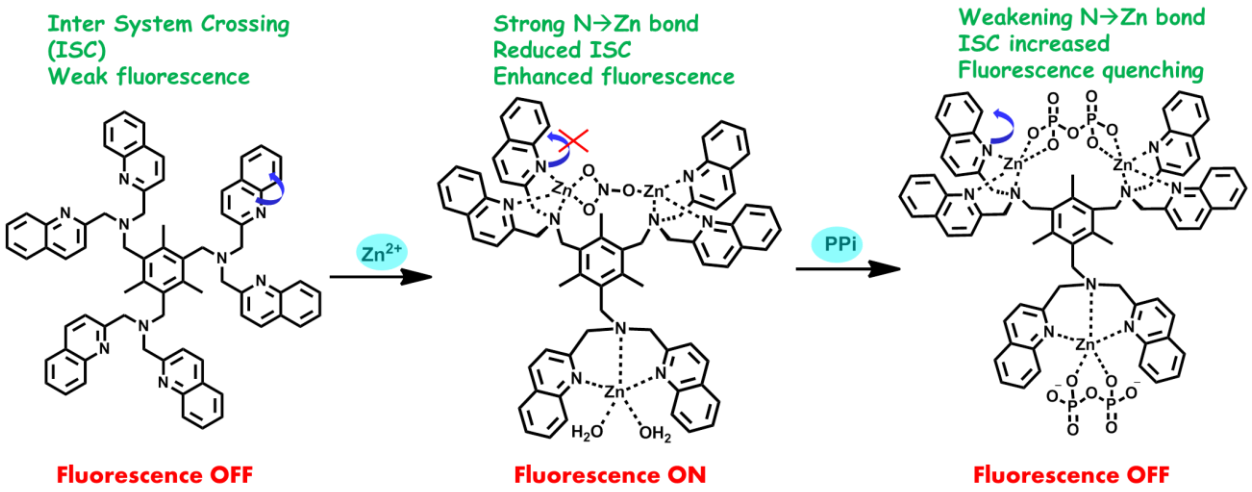



**Figure S23.** (a) Changes in $^{1}H$ NMR spectra of the trinuclear Zn-complex (6.8 x $10^{-3}$ M) upon addition of increasing amount of PPi (0 - 4 equiv) in 70 % $D_2O$-$CD_3CN$ media and (b) isotopic distribution pattern of the phosphate adduct ($[\mathbf{1}(Zn^{2+})_3(P_2O_7^{4-})_2(4H^{+})]^{2+}$; chemical formula: $[C_{72}H_{67}N_9O_{14}P_4Zn_3]^{2+}$ ) with its corresponding simulated pattern.




**Scheme S1.** Probable binding mode of PPi by the tri nuclear $Zn^{2+}$ complex.

**Table S9.** Comparison of PPi sensing by trinuclear $Zn^{2+}$ complex of **1** with some of the previously reported sensors.

| Ref. | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | Log $K_a$ | LOD | Host-guest stoichiometry | Mode | Solvent |
|---|---|---|---|---|---|---|---|
| *Org. Lett.*, **2008**, *10*, 473-476 | 315 | 376 | 5.67 | -- | 2:1 | Turn Off | tris-HCl (0.01 M) solution (MeOH/$H_2O$) 1:9, v/v, pH 7.22 |
| *Org. Lett.*, **2011**, *13*, 1362-1365 | 430 | 512 | 4.10 | 2.18 µM | 2:1 | Turn On | HEPES buffer |
| *Tetrahedron Letters*, **2016**, *57*, 5022-5025 | 352 | 453 | 5.61 | -- | 1:1 | Turn Off | $CH_3CN$-HEPES buffer (0.02 M, pH 7.2) (v/v = 5:5) |
| *New J. Chem.*, **2017**, *41*, 4806-4813 | 350 | 450 | -- | 74 nM | 1:1 | On-On | 6:4 ($H_2O$:EtOH, v/v) |
| *Inorg. Chem.*, **2016**, *55*, 2212-2219 | 302 | 380 | 6.22 | 300 nM | 1:1 | Turn On | MOPS Buffer |
| *Anal. Chem.* **2013**, *85*, 8369-8375 | 350 | 480 | 4.24 | 2 ppb | 1:1 | Turn Off | MeOH/aqueous HEPES buffer (1 mM, pH 7.4; 3:2 v/v) |
| *J. Am. Chem. Soc.* **1999,** *121*, 9463-9464. | 312 | 476 | 8.08[a] | -- | 2:1 | Turn On | MeOH |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Inorg. Chem.*, **2009**, *48*, 2993-2999 | 352 | 453 | 4.52 | -- | 1:1 | Turn On | 10 mM HEPES buffer solution ($H_2O$, pH 7.4) |
| *Inorg. Chem.* **2016**, *55*, 259-271. | 465 | 600 | 14.96 | 0.02 μM | 1:3 | Turn On | $CH_3CN$ |
| *J. Am. Chem. Soc.*, **2014**, *136*, 5543-5546 | 440 | 591 | -- | 0.8 nM | 3:1 | Turn On | 10 mM HEPES buffer (pH 7.4) |
| Present work | 315 | 385 | 5.70[a], 5.26[b] | 45.37 nM | 1:2 | Turn Off | 70% aqueous buffer (10 mM HEPES, pH 7.4) / acetonitrile |

[a]: $K_{a1}$; [b]: $K_{a2}$