# Novel Benzothiazole based Highly Selective Ratiometric Fluorescent *turn on* Sensor for $Zn^{2+}$ and Colorimetric Chemosensor for $Zn^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ Ions

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## 1. Methods and Materials

### 1.1 UV-visible and fluorescence titration

UV-Visible and fluorescence titration of **compound-1** was carried out in 1:1 mixture of $CHCl_3$ and DMSO solutions. **Compound-1** (1 mL, $1 \times 10^{-5}$ M) were placed in a cuvette and was titrated with incremental amount of metal ion ($1\times10^{-3}$ M) solution in 1:1 mixture of $CHCl_3$ and DMSO solutions.

### 1.2 Details about the association constant[1,2]

**For compound Compound-1:**

Chloroform solution of compounds **compound-1** (1 mL, $1 \times 10^{-5}$ M) were placed in a cuvette and was titrated with incremental amount of metal ions ($1\times10^{-3}$ M) solution in 1:1 ratio of $H_2O$ and DMSO. The changes associated with the absorption band at 410 nm were monitored. The calculation for compound **compound-1** is shown below.

**compound-1**+ [Metal] $\longleftrightarrow$ **compound-1**•[Metal]$^2$

$I = k_s[\textbf{compound-1}] + k_p[\textbf{compound-1}\bullet[\text{Metal}]^2]$

$I_0 = k_s[\textbf{compound-1}]_0$

$[\textbf{compound-1}]_0 = [\textbf{compound-1}] + [\textbf{compound-1}\bullet[\text{Metal}]^2]$

$K = [\textbf{compound-1}\bullet[\text{Metal}]^2]/ [\textbf{compound-1}] [\text{Metal}]^2$ (K is association constant)

$I/I_0 = (k_s[\textbf{compound-1}] + k_p[[\text{Metal ion}]^2\bullet \textbf{compound-1}]) / k_s[\textbf{compound-1}]_0$

$= (k_s[\textbf{compound-1}] + k_p[[\text{Metal ion}]^2\bullet \textbf{compound-1}]) / k_s ([\textbf{compound-1}] + [\text{Metal ion}\bullet \textbf{compound-1}])$

$I/I_0 = (1 + (k_p/k_s) K[\text{Metal}]^2)/(1 + K[\text{Metal}]^2) (1 – I/I_0)/ [\text{Metal}]$

$k_p/k_s = \alpha$ (constant)

$I/I_0 = (1+ \alpha K[\text{Metal}]^2) / (1+K[\text{Metal}]^2)$

$1-I/I_0 = 1-(1+ \alpha K[Metal]^2) / (1+K[Metal]^2)$

$= (1+K[Metal]^2-1- \alpha K[Metal]) / (1+K[Metal]^2)$

$= (K[Metal]^2- \alpha K[Metal]^2) / (1+K[Metal]^2)$

$(1-I/I_0)*(1+K[Metal]^2) = K[Metal]^2- \alpha K[Metal]^2$

$(1-I/I_0) = K[Metal]^2 (I/I_0)- \alpha K[Metal]^2$

$(1-I/I_0)/ [Metal]^2 = K(I/I_0)- \alpha K$

Here, $I_0$ is initial absorbance of respective band, I is absorbance of respective band I upon addition of eqve of metal ions.

The association constant is obtained from the slope of $(1 – I/I_0)/ [Metal]^2$ Vs $I/I_0$ and are given in Table S1 (Figure 9).

A= εCl, here ε= molar extension constant, C= concentration of sample, l = path length

= εl [C]

=Ks [C] for substrate

=Kp [C] for product

**1.3 Calculation of Detection Limit**

The detection limit was calculated from the fluorescence quenching titration experiment. The intercept to X-axis (here log[metal]) was obtained by linear fitting of the $(I_{max}-I)/(I_{max}-I_{min})$ vs log[metal], where $I_{max}$, I and $I_{min}$ are the initial fluorescence intensity, intensity at particular concentration and intensity at saturation point respectively. The detection limits were calculated by the formula, ([metal] × MW of metal ions)/1000 (multiplied by $10^6$ to get the values in ppm), where MW [metal] is the molecular weight of metal.

**1.4 Fluorescence quenching titration study:**

The fluorescence quenching experiments were carried in 1:1 ratio of $CHCl_3$ and DMSO. The stock solution of **compound-1**is $1 \times 10^{-5}$ M placing 1 mL quartz cuvette and followed metal ions $1 \times 10^{-3}$ M were added gradually increasing amount. For each addition, at least three fluorescence spectrums were recorded repeatedly at 298 K to obtain a concordant value. **compound-1**were excited at 375 nm and the emission was monitored at 575 nm, whereas slit

width was kept 2 nm both source and detector through the experiment. Fluorescence quenching efficiency for each analyte was calculated by the following equation,

$\eta = (I_0\text{-}I)/I_0 \times 100\%$

where, $I_0$ is the initial intensity of the **Compound-1** and I is the intensity after the addition of a fixed volume of analytes.

Stern-Volmer constants ($K_{SV}$) were obtained for both cases, **compound-1**, from $I_0/I$ vs [metal ions] plots by fitting using Stern-Volmer equation,

$I_0/I = 1 + K_{SV}$[metal ions]

## 1.5 Fluorescence quantum yield

The fluorescence quantum yield of molecules can be determined as the ratio of number of the photons emitted to the number of photons that are absorbed. The quantum yield of an ideal molecule is 1.0, which is the maximum efficiency. The quantum efficiency can be calculated by using the acute luminescence of standard sample whose emission or absorption spectrum falls in the region of the unknown compounds. The quantum efficiency of an unknown sample can be determined from the comparison of absorbance and emission area of standard sample with unknown compound, using the standard equation 1.

$$\varphi_u = [(A_s F_u n_u^2)/A_u F_s n_s^2] \varphi_s \qquad (1)$$

Here the subscript u stands for unknown, s stands for known and φ is quantum efficiency, $A_s$ stands for absorbance of standard, $A_u$ is the absorbance of unknown, $F_s$ stands for integrated emission of standard, $F_u$ is integrated emission of unknown and n is the refractive index of solvents used. Generally, absorbance of a standard and unknown sample should be similar or small which is around 0.1. Maximum quantum yield (Φ) of compounds, can be achieved either by designing a material with a rapid rate of radiative decay, or by minimizing competing nonradiative processes.

## 2. Photophysical Properties

**Table S1**: Photophysical data of **compound-1-1**, **S compound-1+$Zn^{2+}$**, **compound-1+ $Ni^{2+}$**, **compound-1+$Cu^{2+}$** ions,

| | **compound-1** | **compound-1-$Zn^{2+}$** | **compound-1-$Ni^{2+}$** | **compound-1-$Cu^{2+}$** |
|---|---|---|---|---|
| Association constant, $K_a$ | | $4.9 \times 10^{11}$ | $1.6 \times 10^{11}$ | $6.0 \times 10^{10}$ |
| Quantum yield[a, b] | 0.55 | 0.69 | 0.07 | 0.05 |
| Quenching constant[c] | | $2.0 \times 10^{5}$ | $5.6 \times 10^{5}$ | $2.4 \times 10^{5}$ |
| Quenching efficiency[d] | | 69% | 98% | 96% |

b) Quantum yields are calculated using quinine sulphate (0.1 M in $H_2SO_4$, $\Phi_F = 57.7\%$) solution as reference and using the following formula $\Phi = \Phi_F \times I/I_R \times A_R/A \times \eta^2 / \eta R^2$ where $\Phi$ = quantum yield, I = intensity of emission, A = absorbance at $\lambda_{ex}$, $\eta$ = refractive index of solvent.

c) The quantum yields of compounds are determined in a 1:1 ratio of DMSO and $CHCl_3$ and the standard error is equal to the standard deviation of five independent measurements.

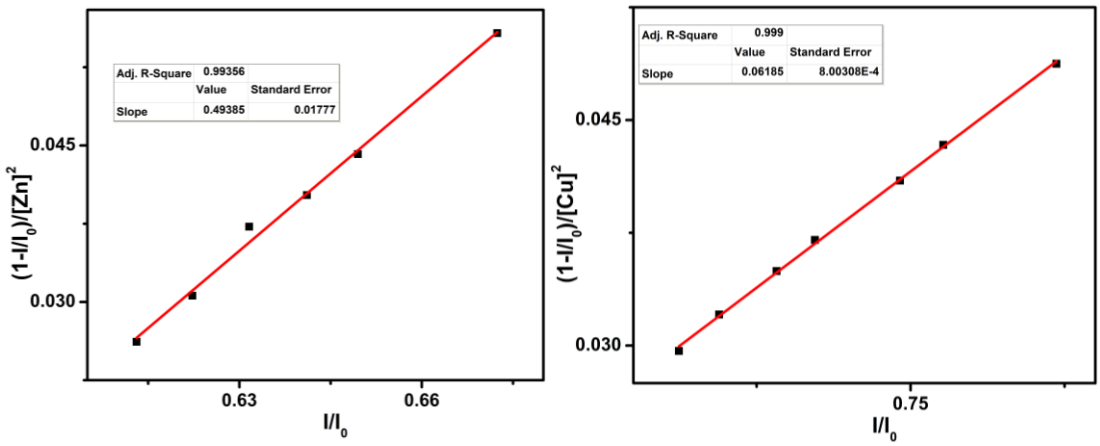


**Figure S1**: The $I/I_0$ vs $(1 - I/I_0)/[Metal]^2$ plot for absorption titration data of **compound-1** with $Zn^{2+}$ (left) and $Cu^{2+}$ (right) ions in 1:1 ratio of DMSO and $CHCl_3$

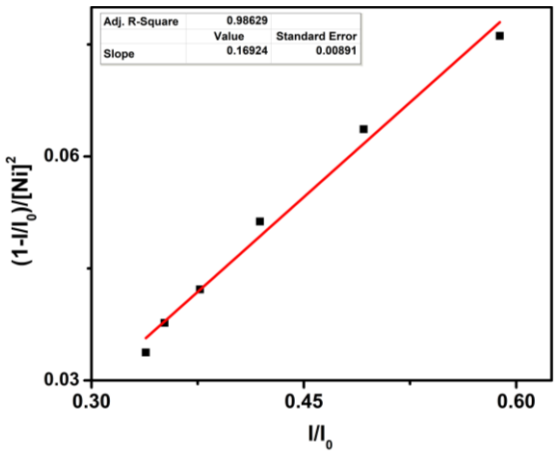


**Figure S2**: The $I/I_0$ vs $(1 - I/I_0)/[Metal]^2$ plot for absorption titration data of **compound-1** with $Ni^{2+}$ ions in 1:1 ratio of DMSO and $CHCl_3$

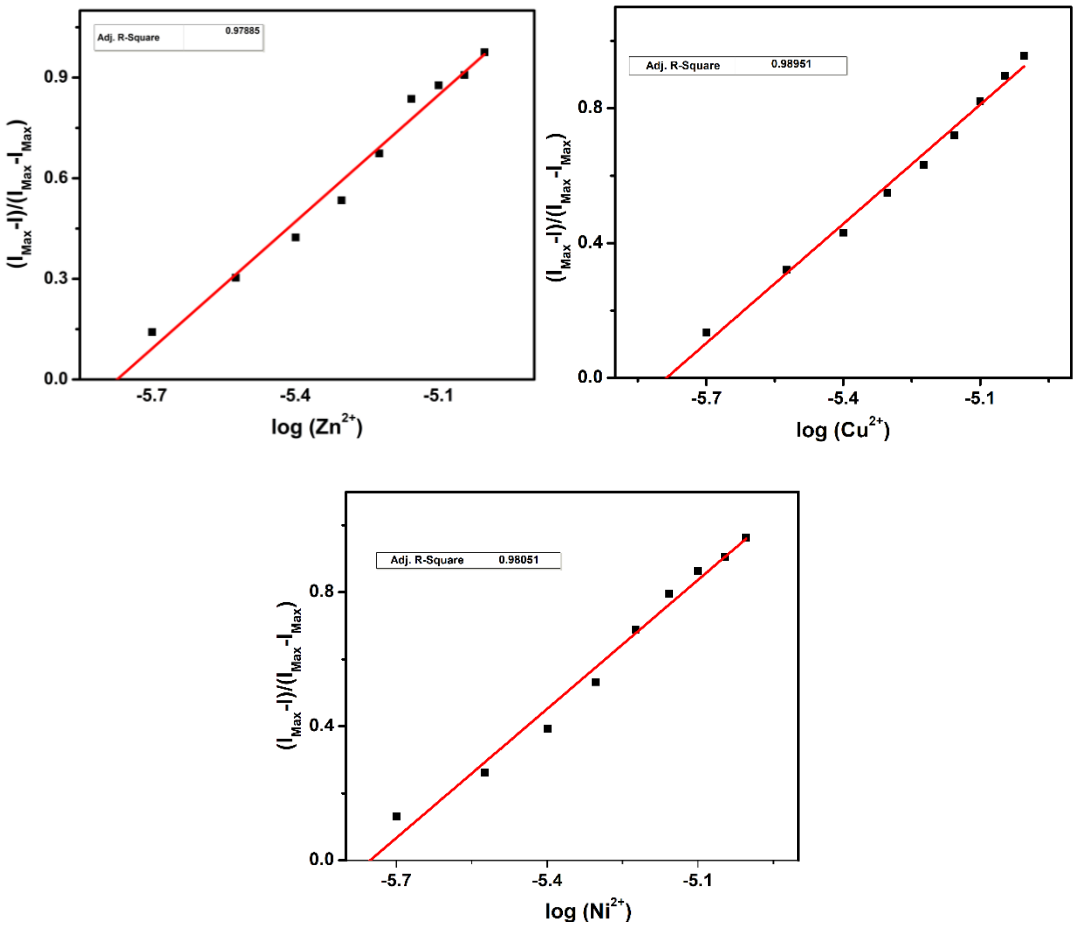


**Figure S3:** $(I_{max}-I)/(I_{max}-I_{min})$ vs log[metal ions] plots for **compound-1** with $Zn^{2+}$ (top left), $Cu^{2+}$ (top right) and $Ni^{2+}$ (bottom) ions in 1:1 ratio of DMSO and $CHCl_3$

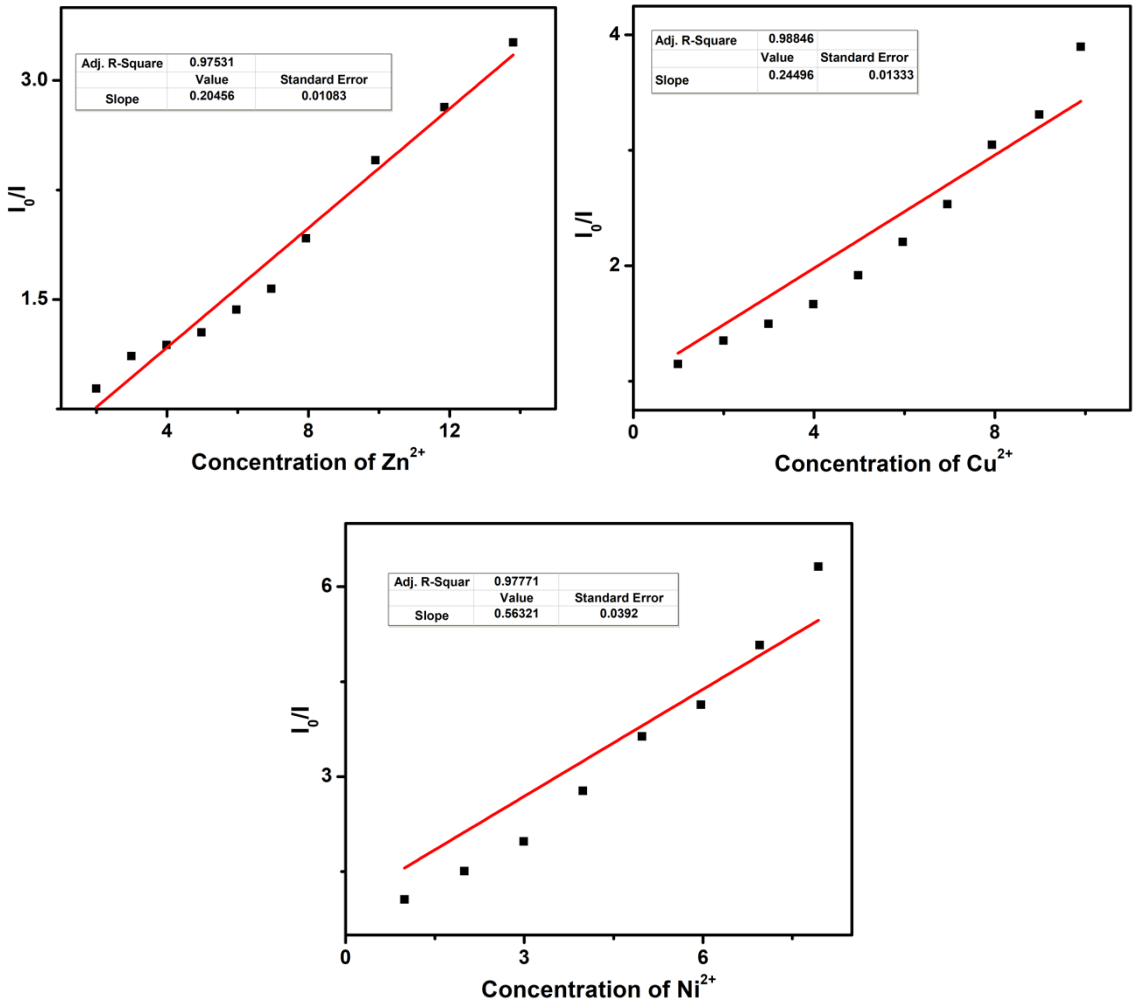


**Figure S4**: Stern-Volmer plots for **compound-1** with $Zn^{2+}$ (top left), $Cu^{2+}$ (top right) and $Ni^{2+}$ (bottom) ions in 1:1 ratio of DMSO and $CHCl_3$

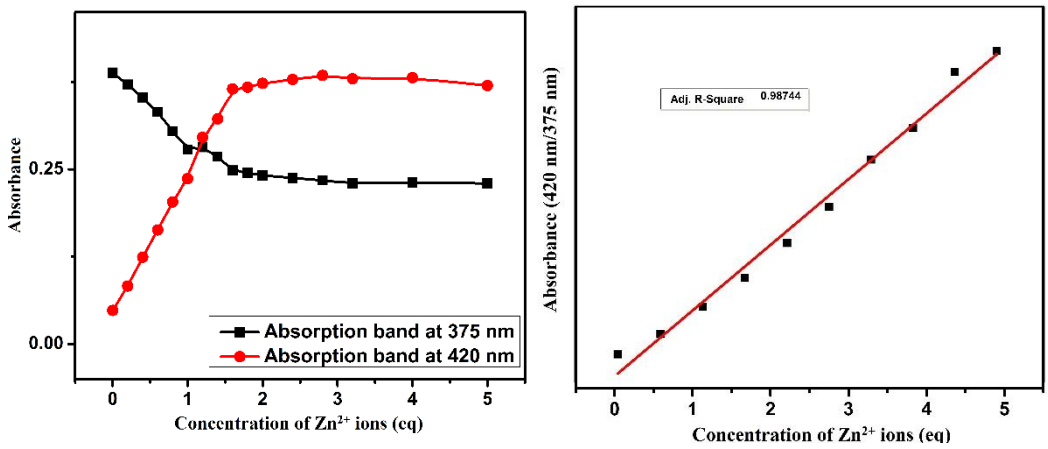


**Figure S5**: The compared absorption bands at 375 nm and 420 nm, which indicates the ratiometric response towards $Zn^{2+}$ ions (left) and linear fitting between the ratio of 420 nm/375 nm absorption bands and upon incremental of concentration of $Zn^{2+}$ ions

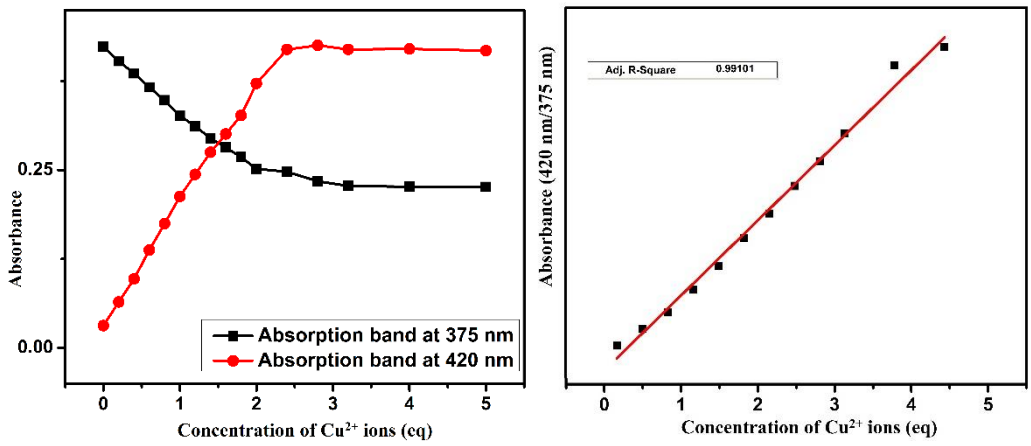


**Figure S6**: The compared absorption bands at 375 nm and 420 nm, which indicates the ratiometric response towards $Cu^{2+}$ ions (left) and linear fitting between the ratio of 420 nm/375 nm absorption bands and upon incremental of concentration of $Cu^{2+}$ ions

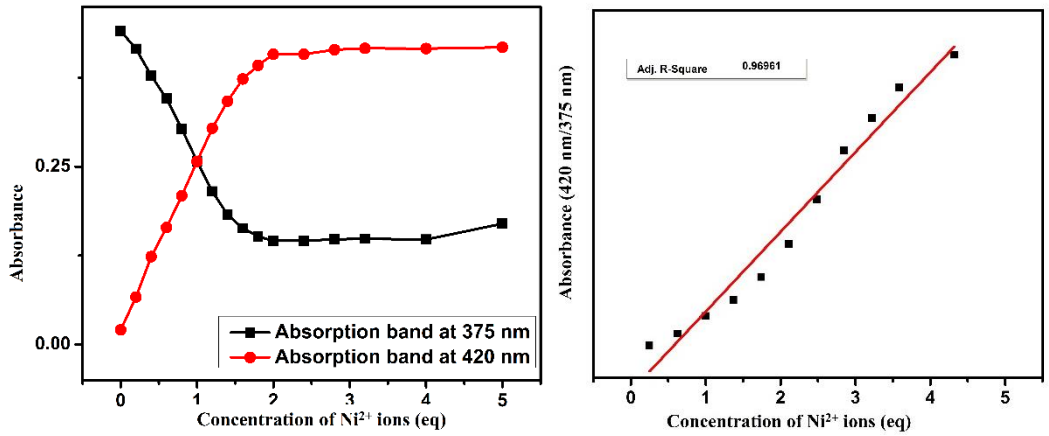


**Figure S7**: The compared absorption bands at 375 nm and 420 nm, which indicates the ratiometric response towards $Ni^{2+}$ ions (left) and linear fitting between the ratio of 420 nm/375 nm absorption bands and upon incremental of concentration of $Ni^{2+}$ ions

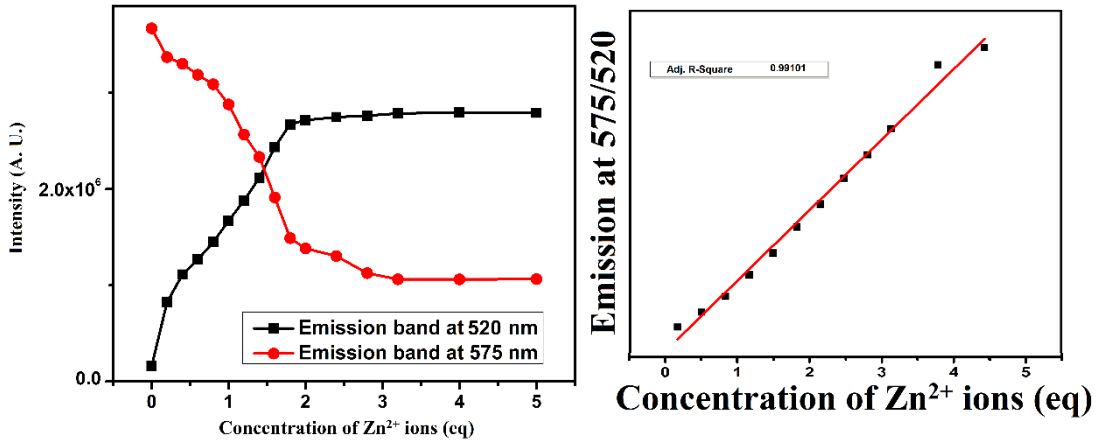

**Figure S8**: The compared emission bands at 375 nm and 420 nm, which indicates the ratiometric response towards $Zn^{2+}$ ions (left) and linear fitting between the ratio of 420 nm/375 nm emission bands and upon incremental of concentration of $Zn^{2+}$ ions

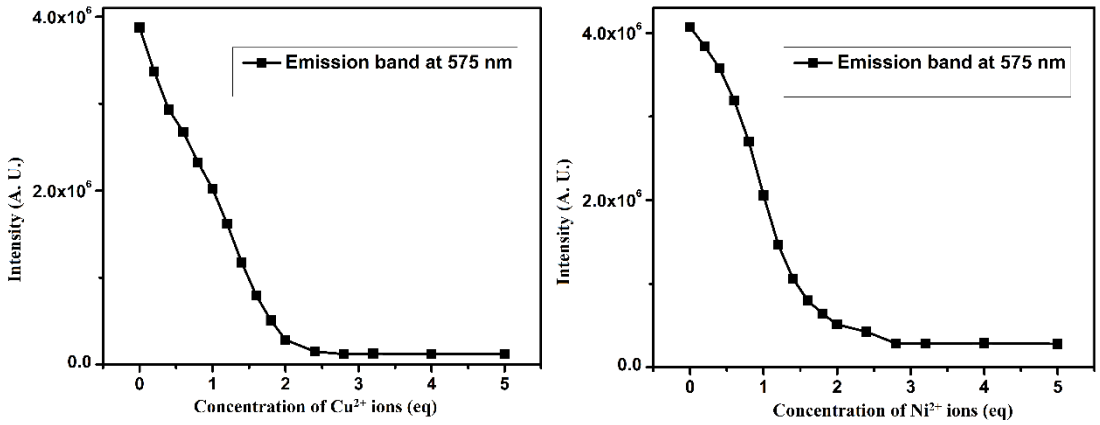


**Figure S9**: Change in emission spectra, upon addition of $Cu^{2+}$ (left) and $Ni^{2+}$ ions (right)

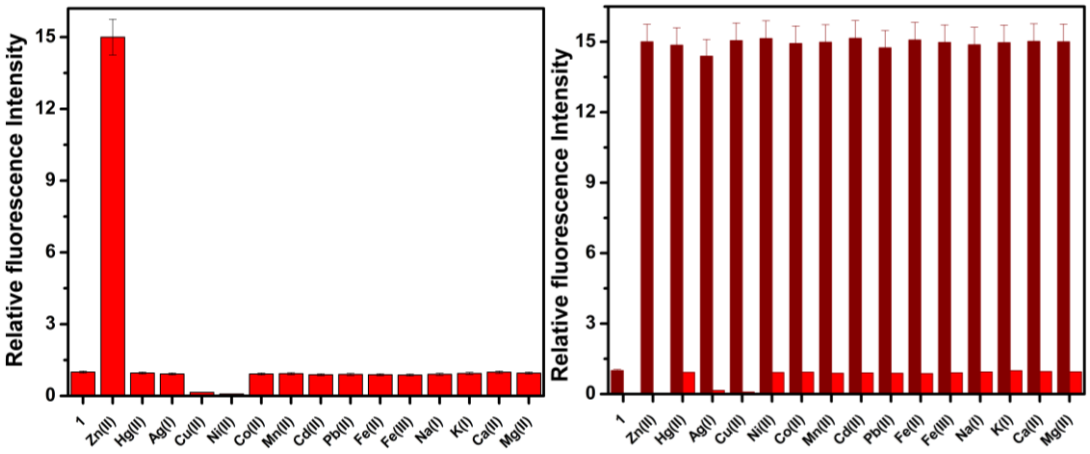


**Figure S10**: Examination of selectivity (left) and competitive (right) studies of **compound-1** (1μM) toward various metal ions (with error bar). The competitive binding ability of **compound-1** (1μM) were performed towards $Zn^{2+}$ in the presence of other interfering metal ions and the emission band was monitored at 520 nm.

## 3. $^{1}H$ and $^{13}C$ Nuclear Magnetic Resonance (NMR) and High-Resolution Mass Spectroscopic (HR MS) studies

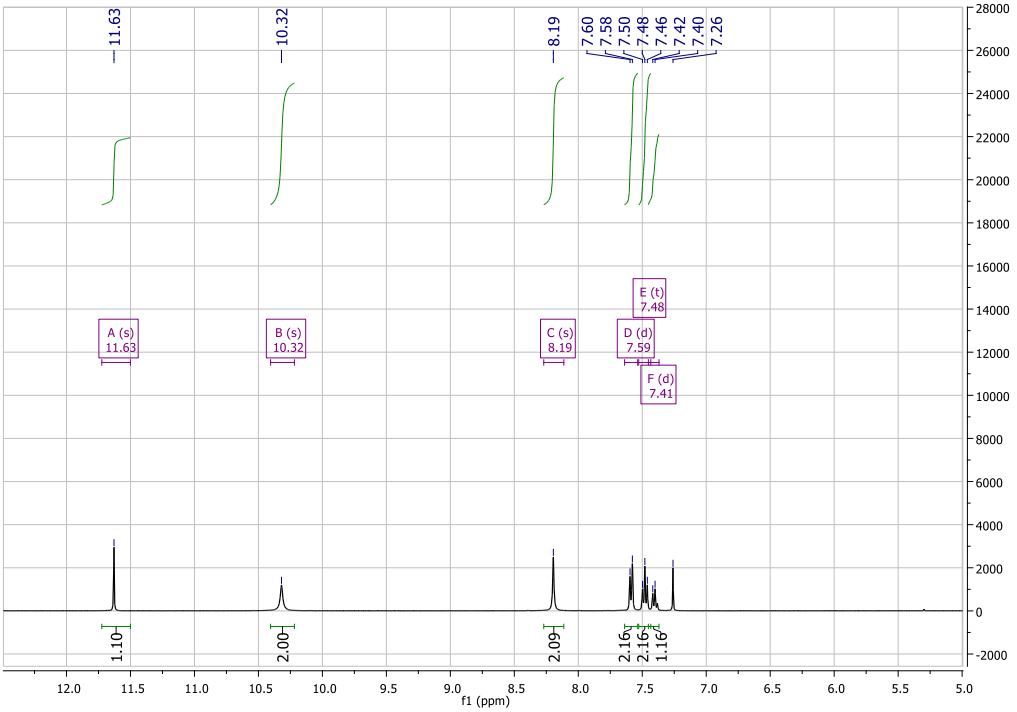


**Figure S11**: $^{1}H$ NMR of **A (**400 MHz, $CDCl_3$)

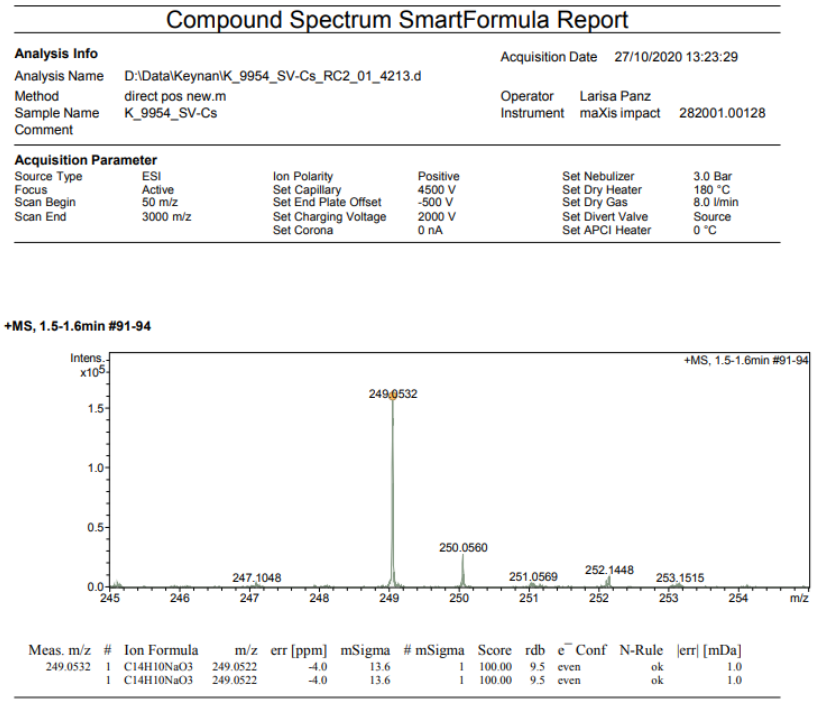


**Figure S12**: HRMS of **A**

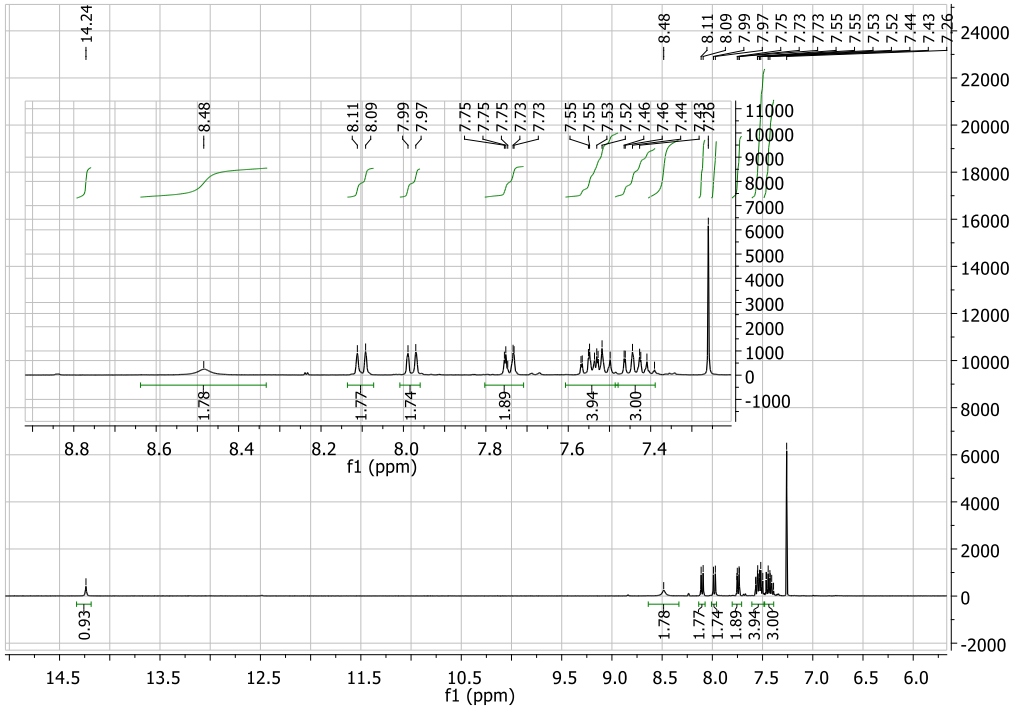


**Figure S13**: $^{1}$H NMR of **compound-1** (400 MHz, $CDCl_3$)

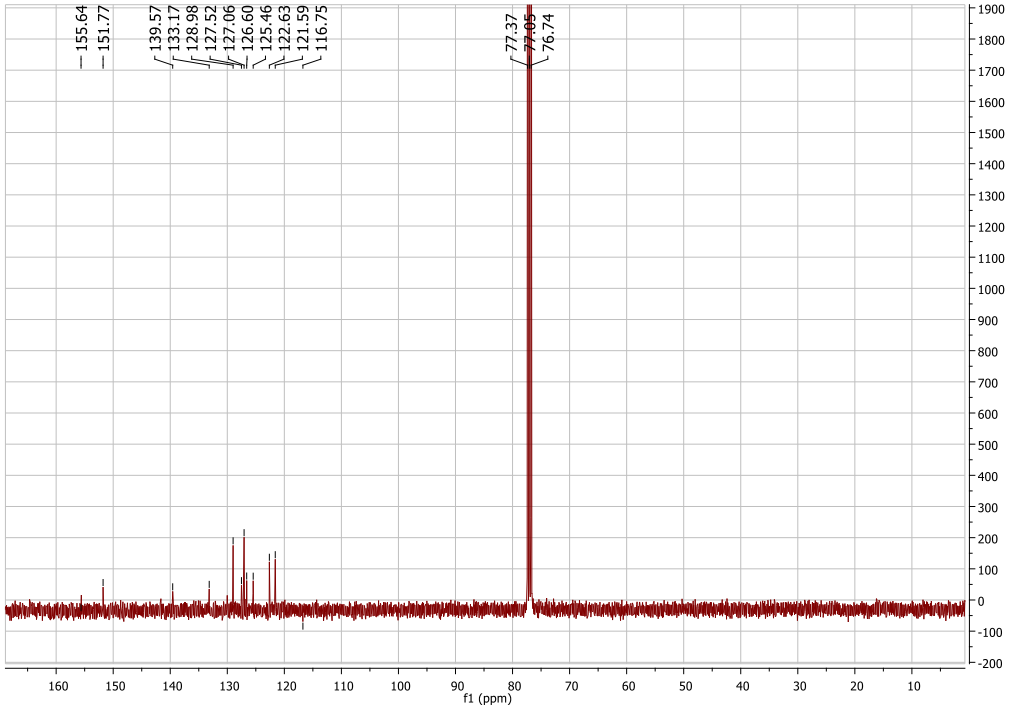


**Figure S14**: $^{13}$C NMR of **compound-1 (**101 MHz, $CDCl_3$)

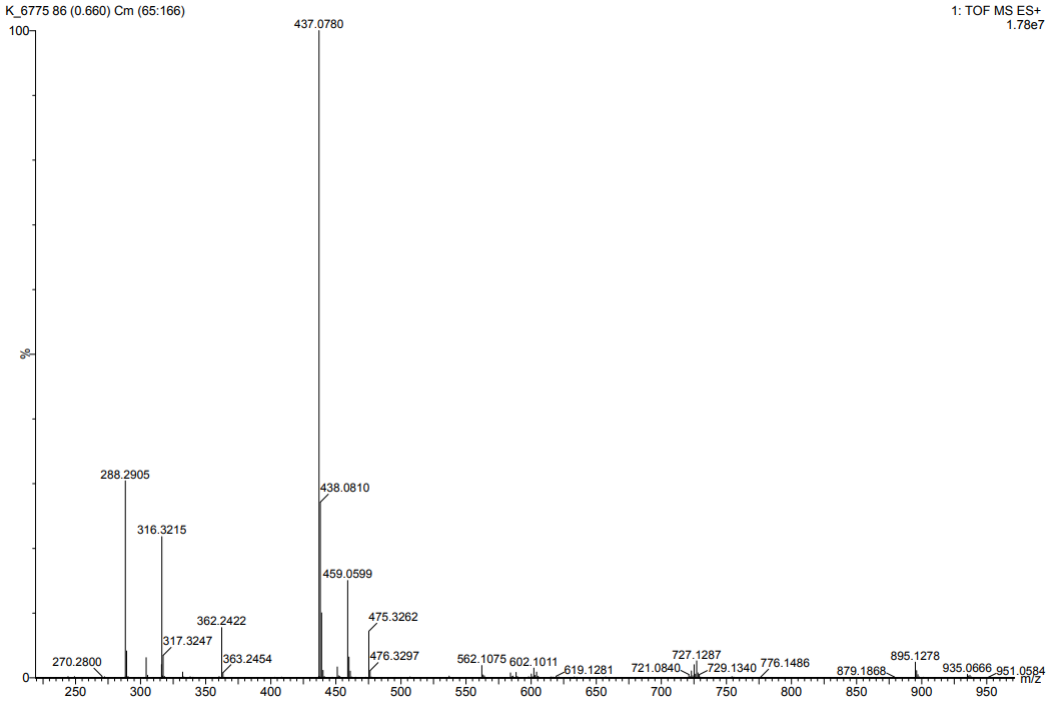


**Figure S15**: HRMS of **compound-1**

## 4. Density Functional Theory results

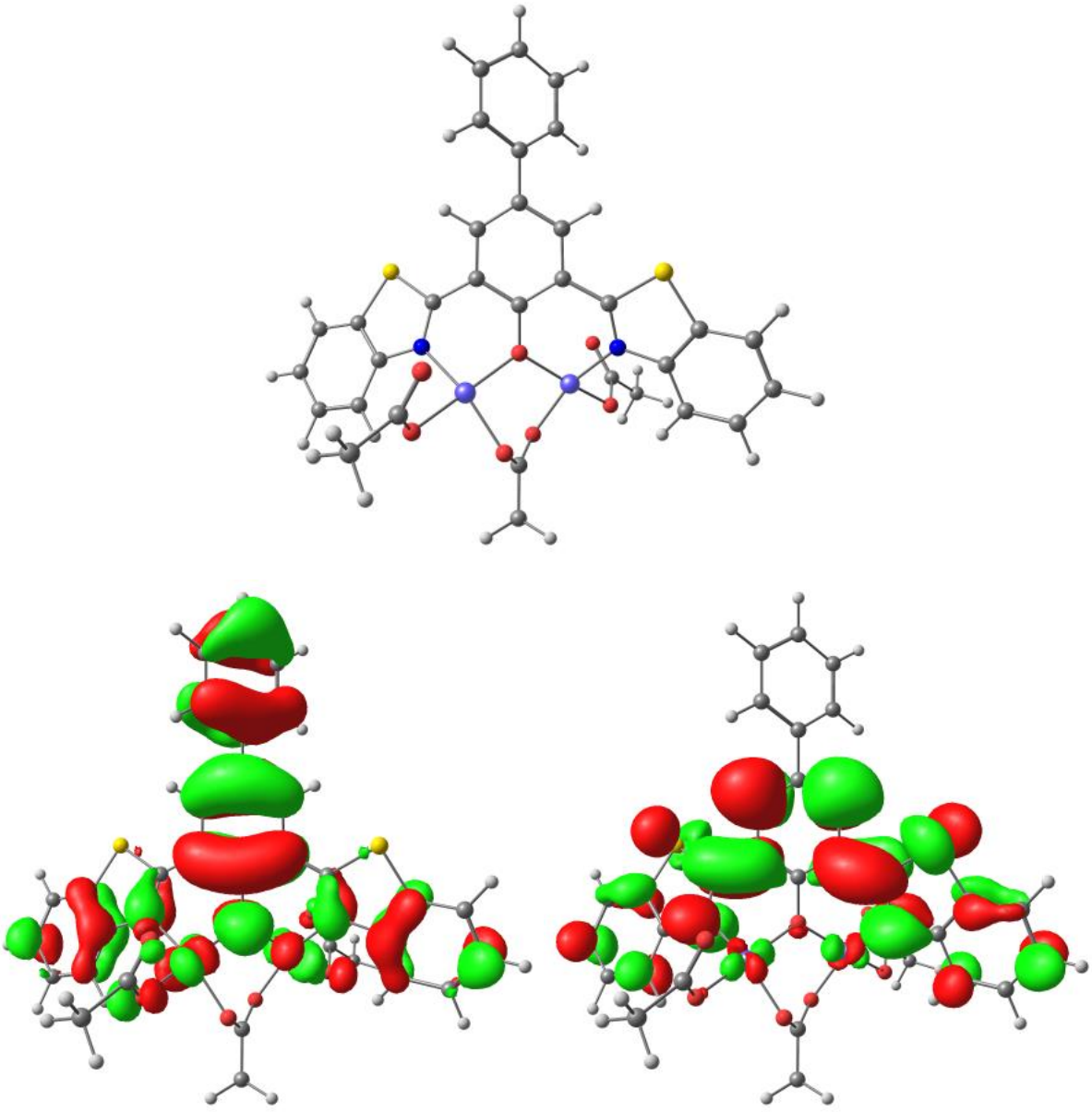

**Figure S16**: Density functional theory calculations of **compound-1+Ni$^{2+}$** ions, molecular structure (top) HOMO (left) and LUMO (right)

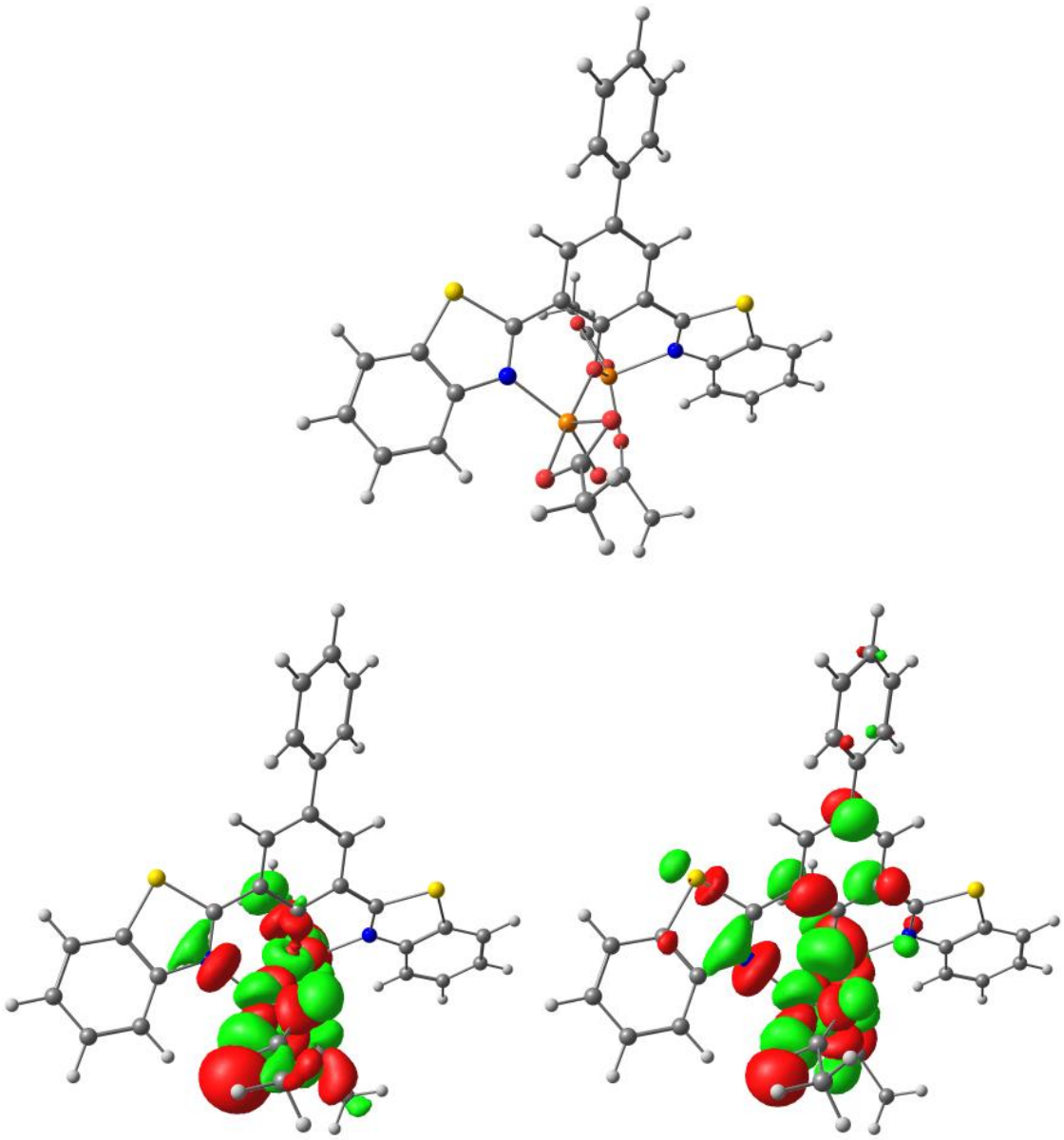

**Figure S17**: Density functional theory calculations of **compound-1+Ni$^{2+}$** ions, molecular structure (top) HOMO (left) and LUMO (right)

**Table-S2**: Band gap of **compound-1**, **compound-1+Zn$^{2+}$**, **compound-1+Cu$^{2+}$** and **compound-1+Ni$^{2+}$** ions obtained from DFT data

| Compound | HOMO (eV) | LUMO (eV) | LUMO-HOMO (eV) |
|---|---|---|---|
| **compound-1** | -6.2353 | -2.2158 | 4.0195 |
| **compound-1+Zn$^{2+}$** | -6.3549 | -2.4654 | 3.8894 eV |
| **compound-1+Cu$^{2+}$** | -5.7753 | -3.4104 | 2.3649 |
| **compound-1+Ni$^{2+}$** | -6.4761 | -2.6805 | 3.7955 |

**Table S3:** Selected electronic transition from TDDFT of **compound-1**

Excited State 1: Singlet-A 3.1842 eV 389.37 nm f=0.3326 <S**2>=0.000
113 -> 114 0.69364
Excited State 4: Singlet-A 4.0395 eV 306.93 nm f=0.2015 <S**2>=0.000
110 -> 114 0.55750
Excited State 9: Singlet-A 4.4048 eV 281.48 nm f=0.2330 <S**2>=0.000
111 -> 115 0.52239
Excited State 10: Singlet-A 4.4401 eV 279.24 nm f=0.3185 <S**2>=0.000
113 -> 116 0.60032

**Compound-1-$Zn^{2+}$**

Excited State 1: Singlet-A 3.0143 eV 411.32 nm f=0.3032 <S**2>=0.000
189 -> 190 0.69776
Excited State 3: Singlet-A 3.8039 eV 325.94 nm f=0.1024 <S**2>=0.000
188 -> 190 0.62059

Excited State 8: Singlet-A 4.0035 eV 309.69 nm f=0.3702 <S**2>=0.000
183 -> 190 0.51814
Excited State 9: Singlet-A 4.1981 eV 295.33 nm f=0.1164 <S**2>=0.000
188 -> 191 0.54358
Excited State 16: Singlet-A 4.4042 eV 281.51 nm f=0.5078 <S**2>=0.000
189 -> 192 0.61891

**Compound-1**+Ni

Excited State 9: Singlet-A 2.8988 eV 427.70 nm f=0.2085 <S**2>=0.000
187 -> 188 0.69139

Excited State 17: Singlet-A 3.5438 eV 349.86 nm f=0.0647 <S**2>=0.000
184 -> 188 0.49622

Excited State 18: Singlet-A 3.5580 eV 348.47 nm f=0.0253 <S**2>=0.000
187 -> 190 0.54301

Excited State 19: Singlet-A 3.6332 eV 341.25 nm f=0.0021 <S**2>=0.000
183 -> 188 0.62797

Excited State 20: Singlet-A 3.7099 eV 334.19 nm f=0.0445 <S**2>=0.000
182 -> 188 0.37806

**Compound-1**+Cu

Excited State 15: Singlet-A 2.2652 eV 547.35 nm f=0.0468 <S**2>=0.000
181 -> 189 0.29469

Excited State 16: Singlet-A 2.3998 eV 516.63 nm f=0.0252 <S**2>=0.000
169 -> 189 0.32584

Excited State 17: Singlet-A 2.4664 eV 502.70 nm f=0.0090 <S**2>=0.000
188 -> 190 0.68130

Excited State 18: Singlet-A 2.5276 eV 490.52 nm f=0.0022 <S**2>=0.000
167 -> 189 0.44917

Excited State 19: Singlet-A 2.7148 eV 456.70 nm f=0.0005 <S**2>=0.000
177 -> 189 0.70509

Excited State 20: Singlet-A 2.7289 eV 454.34 nm f=0.0038 <S**2>=0.000
165 -> 189 0.36985

**Table S4**: Computational results of optimized structure of **Compound-1**

| | | | | |
|---|---|---|---|---|
| 1 | 6 | 3.994961304 | -2.231732169 | -0.053181004 |
| 2 | 6 | 4.977383381 | -1.203880094 | 0.007291001 |
| 3 | 6 | 6.347216460 | -1.500002115 | 0.013706001 |
| 4 | 6 | 6.731137518 | -2.853008215 | -0.041811003 |
| 5 | 6 | 5.761300456 | -3.882807298 | -0.102161008 |
| 6 | 6 | 4.391482337 | -3.582221275 | -0.108468008 |
| 7 | 6 | 2.558159193 | -0.452437034 | 0.009948001 |

| | | | | |
|---|---|---|---|---|
| 8 | 1 | 7.096475564 | -0.715575056 | 0.060383005 |
| 9 | 1 | 7.787442618 | -3.108299238 | -0.037855003 |
| 10 | 1 | 6.084524460 | -4.919483378 | -0.143864011 |
| 11 | 1 | 3.637727280 | -4.362134330 | -0.153758012 |
| 12 | 6 | 1.276434099 | 0.237616018 | 0.024165002 |
| 13 | 6 | 1.189584090 | 1.646178128 | 0.068954005 |
| 14 | 6 | 0.076456006 | -0.550141040 | -0.006842001 |
| 15 | 6 | -0.046133004 | 2.312192178 | 0.070359005 |
| 16 | 1 | 2.105908160 | 2.228595170 | 0.125619010 |
| 17 | 6 | -1.184401090 | 0.112803009 | 0.015690001 |
| 18 | 6 | -1.217595093 | 1.517602117 | 0.040336003 |
| 19 | 1 | -2.187269168 | 2.007975152 | 0.031471002 |
| 20 | 6 | -0.127104009 | 3.799773292 | 0.113382008 |
| 21 | 6 | -1.176634091 | 4.451735342 | 0.805016060 |
| 22 | 6 | 0.844131064 | 4.601267349 | -0.534195040 |
| 23 | 6 | -1.253706095 | 5.854425439 | 0.846945065 |
| 24 | 1 | -1.920808145 | 3.862718296 | 1.335783100 |
| 25 | 6 | 0.771921061 | 6.004107457 | -0.488756037 |
| 26 | 1 | 1.642937124 | 4.128435317 | -1.100889083 |
| 27 | 6 | -0.278639021 | 6.639136508 | 0.201549015 |
| 28 | 1 | -2.065787158 | 6.332671494 | 1.389485108 |
| 29 | 1 | 1.525470114 | 6.598941527 | -0.999630074 |
| 30 | 1 | -0.336870026 | 7.724292616 | 0.234807018 |
| 31 | 6 | -2.443208189 | -0.650001052 | 0.000479000 |
| 32 | 6 | -4.029085310 | -2.201518170 | 0.456660035 |
| 33 | 6 | -4.812924368 | -1.436851108 | -0.457939035 |
| 34 | 6 | -4.579689348 | -3.344816253 | 1.069457081 |
| 35 | 6 | -6.132928462 | -1.800942137 | -0.765601060 |
| 36 | 6 | -5.897843427 | -3.710818284 | 0.762451058 |
| 37 | 1 | -3.971339303 | -3.916986301 | 1.762859134 |

| | | | | |
|---|---|---|---|---|
| 38 | 6 | -6.668366512 | -2.945702225 | -0.147346011 |
| 39 | 1 | -6.731320507 | -1.221054091 | -1.461941110 |
| 40 | 1 | -6.335344474 | -4.591251352 | 1.225936095 |
| 41 | 1 | -7.688561563 | -3.245676250 | -0.373446028 |
| 42 | 8 | 0.121055009 | -1.906499144 | -0.089856007 |
| 43 | 1 | 1.093648086 | -2.217222172 | -0.095291007 |
| 44 | 16 | -3.850586293 | -0.041459003 | -1.089600081 |
| 45 | 16 | 4.179126317 | 0.425809033 | 0.071678006 |
| 46 | 7 | -2.727311209 | -1.723434133 | 0.680292052 |
| 47 | 7 | 2.671115204 | -1.771321133 | -0.050950004 |

**Table S5**: Computational results of optimized structure of **Compound-1+$Zn^{2+}$** Complex

| | | | | |
|---|---|---|---|---|
| 1 | 6 | -4.121628240 | -0.778462067 | -0.432917262 |
| 2 | 6 | -4.827035271 | 0.188608826 | -1.195306099 |
| 3 | 6 | -6.133002388 | -0.043309983 | -1.648990922 |
| 4 | 6 | -6.732476601 | -1.272344252 | -1.320489857 |
| 5 | 6 | -6.040526547 | -2.236182402 | -0.546990943 |
| 6 | 6 | -4.736091398 | -2.000630262 | -0.092602844 |
| 7 | 6 | -2.476772309 | 0.827115153 | -0.473038951 |
| 8 | 1 | -6.669539434 | 0.696454940 | -2.235281213 |
| 9 | 1 | -7.743457564 | -1.480387113 | -1.660741303 |
| 10 | 1 | -6.531847514 | -3.171085139 | -0.292597976 |
| 11 | 1 | -4.216197506 | -2.716299099 | 0.534821983 |
| 12 | 6 | -1.208911246 | 1.516855363 | -0.221471262 |
| 13 | 6 | -1.176941003 | 2.926968266 | -0.224735757 |
| 14 | 6 | 0.002106125 | 0.777146004 | -0.000494781 |
| 15 | 6 | 0.006724784 | 3.656670354 | -0.005463226 |
| 16 | 1 | -2.099151953 | 3.471550394 | -0.409956261 |
| 17 | 6 | 1.215447114 | 1.513718929 | 0.217969167 |
| 18 | 6 | 1.188046846 | 2.923919147 | 0.216357822 |

| | | | | |
|---|---|---|---|---|
| 19 | 1 | 2.111992968 | 3.466169190 | 0.399753194 |
| 20 | 6 | 0.009132012 | 5.146895401 | -0.008017035 |
| 21 | 6 | 1.117041842 | 5.871221578 | -0.510179257 |
| 22 | 6 | -1.096429330 | 5.876503296 | 0.491668107 |
| 23 | 6 | 1.121221284 | 7.276631683 | -0.510615299 |
| 24 | 1 | 1.966403078 | 5.336841458 | -0.929551168 |
| 25 | 6 | -1.096059965 | 7.281913401 | 0.487314037 |
| 26 | 1 | -1.947499279 | 5.346284626 | 0.912857213 |
| 27 | 6 | 0.013730033 | 7.990038816 | -0.012860066 |
| 28 | 1 | 1.980023042 | 7.812351679 | -0.907914169 |
| 29 | 1 | -1.953113320 | 7.821762567 | 0.882795183 |
| 30 | 1 | 0.015491135 | 9.077212836 | -0.014701073 |
| 31 | 6 | 2.481000435 | 0.820704171 | 0.472181155 |
| 32 | 6 | 4.121028153 | -0.789931984 | 0.437542271 |
| 33 | 6 | 4.828995344 | 0.177348992 | 1.197287339 |
| 34 | 6 | 4.732227346 | -2.014801100 | 0.101059096 |
| 35 | 6 | 6.134036400 | -0.057013028 | 1.652369189 |
| 36 | 6 | 6.035726380 | -2.252805976 | 0.556825173 |
| 37 | 1 | 4.210796194 | -2.730573126 | -0.524933777 |
| 38 | 6 | 6.730082603 | -1.288768327 | 1.327898338 |
| 39 | 1 | 6.672400695 | 0.682942928 | 2.236738038 |
| 40 | 1 | 6.524472370 | -3.189853998 | 0.305378136 |
| 41 | 1 | 7.740240695 | -1.498792956 | 1.669369009 |
| 42 | 8 | 0.000031751 | -0.570510226 | 0.001839949 |
| 43 | 16 | 3.803510161 | 1.648980868 | 1.443967018 |
| 44 | 16 | -3.797231473 | 1.656371886 | -1.446965865 |
| 45 | 7 | 2.817384125 | -0.394984249 | 0.068207243 |
| 46 | 7 | -2.816793034 | -0.386215782 | -0.065178233 |
| 47 | 30 | 1.474247069 | -1.599366267 | -1.027498173 |
| 48 | 30 | -1.477866112 | -1.589738945 | 1.036070844 |

| | | | | |
|---|---|---|---|---|
| 49 | 8 | 1.038392874 | -3.450693402 | -0.452115283 |
| 50 | 6 | -0.009444226 | -4.056120330 | 0.004351954 |
| 51 | 8 | -1.052327169 | -3.443360063 | 0.462518908 |
| 52 | 6 | -0.028451215 | -5.571686617 | -0.024379196 |
| 53 | 1 | -0.483664831 | -5.901503217 | -0.967758295 |
| 54 | 1 | 0.990685957 | -5.963075635 | 0.019268931 |
| 55 | 1 | -0.633581804 | -5.957704486 | 0.799763039 |
| 56 | 8 | 3.010674052 | -2.152686170 | -2.597378154 |
| 57 | 6 | 2.213120328 | -1.594282990 | -3.452057092 |
| 58 | 8 | 1.095167243 | -1.063493867 | -3.000929253 |
| 59 | 6 | 2.519543060 | -1.554780967 | -4.929170185 |
| 60 | 1 | 1.861331231 | -2.260701301 | -5.451869246 |
| 61 | 1 | 2.312315133 | -0.555964201 | -5.327143227 |
| 62 | 1 | 3.560005017 | -1.831886221 | -5.112602599 |
| 63 | 8 | -3.014004165 | -2.132103291 | 2.610214407 |
| 64 | 6 | -2.217365917 | -1.565283019 | 3.460196367 |
| 65 | 8 | -1.099789077 | -1.037392200 | 3.004727158 |
| 66 | 6 | -2.524735347 | -1.511277305 | 4.936634230 |
| 67 | 1 | -3.558761450 | -1.808566967 | 5.124491624 |
| 68 | 1 | -1.849906294 | -2.193031172 | 5.469907311 |
| 69 | 1 | -2.340690146 | -0.501802910 | 5.319236260 |

**Table S6**: Computational results of optimized structure of **Compound-1+Cu$^{2+}$** Complex

| | | | | |
|---|---|---|---|---|
| 1 | 6 | -4.132728262 | -0.570840961 | -0.224804021 |
| 2 | 6 | -4.787656546 | 0.360659167 | -1.077563103 |
| 3 | 6 | -6.116187251 | 0.168637147 | -1.483590223 |
| 4 | 6 | -6.786390766 | -0.976837918 | -1.016621993 |
| 5 | 6 | -6.141315233 | -1.905690043 | -0.162193885 |
| 6 | 6 | -4.813494155 | -1.713420369 | 0.241961005 |
| 7 | 6 | -2.390023224 | 0.887438184 | -0.445769919 |

| | | | | |
|---|---|---|---|---|
| 8 | 1 | -6.618479650 | 0.875935988 | -2.136503400 |
| 9 | 1 | -7.816838573 | -1.149276145 | -1.316662847 |
| 10 | 1 | -6.685572446 | -2.779270133 | 0.185879859 |
| 11 | 1 | -4.301819443 | -2.409763123 | 0.898439250 |
| 12 | 6 | -1.064179152 | 1.487285996 | -0.264110248 |
| 13 | 6 | -0.916654060 | 2.884736217 | -0.348834172 |
| 14 | 6 | 0.081776935 | 0.677765987 | 0.024532128 |
| 15 | 6 | 0.322467915 | 3.529661464 | -0.157150826 |
| 16 | 1 | -1.791330077 | 3.486951039 | -0.578769095 |
| 17 | 6 | 1.343632895 | 1.323616236 | 0.225917939 |
| 18 | 6 | 1.441651338 | 2.722883122 | 0.132353051 |
| 19 | 1 | 2.407954395 | 3.194274216 | 0.290035171 |
| 20 | 6 | 0.444589853 | 5.009378639 | -0.258541187 |
| 21 | 6 | 1.620062389 | 5.607897158 | -0.773992107 |
| 22 | 6 | -0.612032118 | 5.855668529 | 0.157511196 |
| 23 | 6 | 1.736051163 | 7.004858419 | -0.869028108 |
| 24 | 1 | 2.432874939 | 4.981739182 | -1.133859095 |
| 25 | 6 | -0.497786984 | 7.252651486 | 0.061299893 |
| 26 | 1 | -1.513311992 | 5.424532478 | 0.586615206 |
| 27 | 6 | 0.677433135 | 7.834943314 | -0.451981930 |
| 28 | 1 | 2.643467376 | 7.443251606 | -1.277019004 |
| 29 | 1 | -1.317718026 | 7.884220829 | 0.394327011 |
| 30 | 1 | 0.766367192 | 8.915879922 | -0.526248782 |
| 31 | 6 | 2.530600219 | 0.519239829 | 0.509495030 |
| 32 | 6 | 3.964879059 | -1.273385144 | 0.514441779 |
| 33 | 6 | 4.753249442 | -0.396581835 | 1.306316903 |
| 34 | 6 | 4.435913487 | -2.563868005 | 0.199087065 |
| 35 | 6 | 6.002663385 | -0.784821190 | 1.810075122 |
| 36 | 6 | 5.681914238 | -2.955600989 | 0.705725067 |
| 37 | 1 | 3.853065494 | -3.204286249 | -0.453140299 |

| | | | | |
|---|---|---|---|---|
| 38 | 6 | 6.457419263 | -2.079993091 | 1.505329353 |
| 39 | 1 | 6.602679476 | -0.114145120 | 2.417583304 |
| 40 | 1 | 6.063036689 | -3.946192223 | 0.473939082 |
| 41 | 1 | 7.420719768 | -2.409719201 | 1.885456951 |
| 42 | 8 | -0.009794013 | -0.680709271 | 0.112041111 |
| 43 | 16 | 3.901637086 | 1.189530130 | 1.523670107 |
| 44 | 16 | -3.665105440 | 1.719044994 | -1.499795217 |
| 45 | 7 | 2.736883036 | -0.718098819 | 0.100815145 |
| 46 | 7 | -2.807162008 | -0.234030226 | 0.094321082 |
| 47 | 29 | 1.302060201 | -1.729340137 | -0.931982208 |
| 48 | 29 | -1.423308996 | -1.448315267 | 1.293230349 |
| 49 | 8 | 0.148081257 | -3.328513254 | -1.132901285 |
| 50 | 6 | -1.018359282 | -3.676351514 | -0.690447191 |
| 51 | 8 | -1.586271247 | -3.180266365 | 0.363092853 |
| 52 | 6 | -1.765732186 | -4.753571181 | -1.456475180 |
| 53 | 1 | -2.429470213 | -4.278180566 | -2.191103909 |
| 54 | 1 | -1.058886321 | -5.392899321 | -1.992013140 |
| 55 | 1 | -2.380418128 | -5.343439240 | -0.770245003 |
| 56 | 8 | 2.631244440 | -2.491924241 | -2.300444099 |
| 57 | 6 | 2.329756286 | -1.643599135 | -3.267578494 |
| 58 | 8 | 1.471894347 | -0.711632273 | -3.035826376 |
| 59 | 6 | 2.991326274 | -1.822729338 | -4.615343205 |
| 60 | 1 | 2.577753087 | -2.714086080 | -5.104196618 |
| 61 | 1 | 2.806178267 | -0.948511060 | -5.244747154 |
| 62 | 1 | 4.068039518 | -1.982205369 | -4.490821448 |
| 63 | 8 | -2.616712174 | -1.859892927 | 3.095786392 |
| 64 | 6 | -1.975054067 | -0.881297082 | 3.652863453 |
| 65 | 8 | -1.063837303 | -0.271553126 | 2.922303039 |
| 66 | 6 | -2.216947338 | -0.458810963 | 5.077659437 |
| 67 | 1 | -3.194207010 | -0.812189179 | 5.417063671 |

| | | | | |
|---|---|---|---|---|
| 68 | 1 | -1.441797920 | -0.896718895 | 5.720213441 |
| 69 | 1 | -2.150529243 | 0.630212003 | 5.165947370 |

**Table S7**: Computational results of optimized structure of **Compound-1+$Ni^{2+}$** Complex

| | | | | |
|---|---|---|---|---|
| 1 | 6 | 4.040978452 | -0.838231050 | 0.556081150 |
| 2 | 6 | 4.776523186 | 0.181815248 | 1.212105889 |
| 3 | 6 | 6.055396427 | -0.041165227 | 1.740807937 |
| 4 | 6 | 6.599615540 | -1.330258998 | 1.618251015 |
| 5 | 6 | 5.870985565 | -2.360938055 | 0.977703123 |
| 6 | 6 | 4.597113578 | -2.129711410 | 0.441907983 |
| 7 | 6 | 2.475344060 | 0.843811224 | 0.400443241 |
| 8 | 1 | 6.606280527 | 0.750886112 | 2.238899198 |
| 9 | 1 | 7.586951805 | -1.536093073 | 2.022809139 |
| 10 | 1 | 6.308015592 | -3.352268021 | 0.894436024 |
| 11 | 1 | 4.054095168 | -2.901783133 | -0.086827932 |
| 12 | 6 | 1.211952957 | 1.523794993 | 0.148148992 |
| 13 | 6 | 1.187293297 | 2.934084112 | 0.138441235 |
| 14 | 6 | -0.003043828 | 0.784744989 | -0.004224951 |
| 15 | 6 | -0.001798144 | 3.669307107 | -0.001827778 |
| 16 | 1 | 2.122554288 | 3.473252228 | 0.261549030 |
| 17 | 6 | -1.218107289 | 1.524830064 | -0.149898981 |
| 18 | 6 | -1.191810883 | 2.935277407 | -0.139713906 |
| 19 | 1 | -2.126763364 | 3.475580079 | -0.260017062 |
| 20 | 6 | -0.000721798 | 5.158683354 | -0.003156013 |
| 21 | 6 | -1.064687162 | 5.885215670 | 0.582785021 |
| 22 | 6 | 1.064521000 | 5.882094583 | -0.590656003 |
| 23 | 6 | -1.064969214 | 7.290589791 | 0.579823216 |
| 24 | 1 | -1.878845410 | 5.353480378 | 1.069981051 |
| 25 | 6 | 1.067275897 | 7.287469762 | -0.590724267 |
| 26 | 1 | 1.877697095 | 5.347809186 | -1.076698957 |

| | | | | |
|---|---|---|---|---|
| 27 | 6 | 0.001774860 | 7.999083513 | -0.006219949 |
| 28 | 1 | -1.887991181 | 7.829902372 | 1.042370170 |
| 29 | 1 | 1.891247208 | 7.824319552 | -1.054441232 |
| 30 | 1 | 0.002717854 | 9.086229487 | -0.007397898 |
| 31 | 6 | -2.484475013 | 0.846519024 | -0.391498029 |
| 32 | 6 | -4.056552138 | -0.831334812 | -0.529669913 |
| 33 | 6 | -4.797008167 | 0.191307101 | -1.176140887 |
| 34 | 6 | -4.615134180 | -2.121337180 | -0.410228258 |
| 35 | 6 | -6.082663344 | -0.027455832 | -1.689875156 |
| 36 | 6 | -5.895975431 | -2.348312944 | -0.931050856 |
| 37 | 1 | -4.067876532 | -2.895577472 | 0.110891209 |
| 38 | 6 | -6.629229357 | -1.315031923 | -1.561962961 |
| 39 | 1 | -6.636992387 | 0.766663002 | -2.180800299 |
| 40 | 1 | -6.334679246 | -3.338548042 | -0.843638183 |
| 41 | 1 | -7.621889675 | -1.517616849 | -1.954964911 |
| 42 | 8 | -0.002718913 | -0.580282013 | -0.009976049 |
| 43 | 16 | -3.833955316 | 1.718712141 | -1.256637213 |
| 44 | 16 | 3.816702550 | 1.711942906 | 1.281951994 |
| 45 | 7 | -2.771518216 | -0.410481205 | -0.094069194 |
| 46 | 7 | 2.762717998 | -0.413477935 | 0.105632775 |
| 47 | 28 | -1.479993934 | -1.574474298 | 0.731850019 |
| 48 | 28 | 1.482879008 | -1.566529231 | -0.750088113 |
| 49 | 8 | -0.408324807 | -3.150879035 | 1.028421058 |
| 50 | 6 | -0.014913802 | -3.757333096 | -0.056829932 |
| 51 | 8 | 0.409718131 | -3.125005443 | -1.114060987 |
| 52 | 6 | -0.029712773 | -5.268832656 | -0.078494978 |
| 53 | 1 | 0.848274834 | -5.639037651 | 0.467540800 |
| 54 | 1 | -0.922803100 | -5.644022501 | 0.429399291 |
| 55 | 1 | 0.020907264 | -5.630565523 | -1.107900835 |
| 56 | 8 | -2.787550170 | -2.404326356 | 1.778500174 |

| | | | | |
|---|---|---|---|---|
| 57 | 6 | -2.947414087 | -1.739670206 | 2.937161278 |
| 58 | 8 | -2.346696308 | -0.657325987 | 3.186749315 |
| 59 | 6 | -3.899071106 | -2.412543420 | 3.910730468 |
| 60 | 1 | -3.477984131 | -3.375077148 | 4.225862399 |
| 61 | 1 | -4.048157271 | -1.773411077 | 4.784386231 |
| 62 | 1 | -4.859671220 | -2.614583294 | 3.422733263 |
| 63 | 8 | 2.808130402 | -2.384237200 | -1.783512012 |
| 64 | 6 | 2.999523229 | -1.702494975 | -2.927316465 |
| 65 | 8 | 2.413761057 | -0.611433090 | -3.173972331 |
| 66 | 6 | 3.967422285 | -2.368752415 | -3.889564437 |
| 67 | 1 | 4.910195476 | -2.599015429 | -3.379970450 |
| 68 | 1 | 3.539109395 | -3.316178133 | -4.239074368 |
| 69 | 1 | 4.151366414 | -1.712441920 | -4.743637466 |