Versatile coordination behaviour of an asymmetric half-salen ligand bearing a dansyl fluorophore

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Supporting information

Experimental

Materials
All solvents, \textit{o}-phenylenediamine, dansyl chloride, triethylamine, salicylaldehyde and tetraethylammonium perchlorate are commercially available and were used without further purification. Metals (Ega Chemie) was used as ca. 2x2 cm\textsuperscript{2} plate.

Physical Measurements
Elemental analysis of C, H, N and S were performed on a FISONS EA 1108 analyzer. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer, using CDCl\textsubscript{3} and DMSO-d\textsubscript{6} as solvents. Chemical shifts are expressed relative to tetramethylsilane. Infrared spectra were measured as KBr pellets on a BRUKER IFS-66V spectrophotometer in the range 4000-100 cm\textsuperscript{-1}. Electronic impact (EI) mass spectrum was recorded on a HP 5988A quadrupolar mass spectrometer. Electrospray ionisation (ESI) mass spectrum was recorded on an API4000 Applied Biosystems mass spectrometer with Triple Cuadrupole analyser. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectra were registered in a Bruker Autoflex spectrometer using DCTB as matrix. Room temperature magnetic
susceptibilities were measured using a Digital Measurement system MSB-MKI, calibrated using mercury tetrakis(isothiocyanato) cobalt(II). Conductivity of a 10\(^{-3}\) M solution in acetone was measured in a Crison micro CM 2200 conductivimeter. UV-Vis absorption spectra were registered in acetonitrile at room temperature using a Hewlett Packard 8452A spectrophotometer in a concentration range 8x10\(^{-5}\) – 8x10\(^{-6}\) M.

**Synthesis of N-(2-aminophenyl)-5-(dimethylamino)-1-naphtalenesulfonamide (ADs):**
To a solution of \(\alpha\)-phenylenediamine (1.2 g, 11.1 mmol) and dansyl chloride (3 g, 11.1 mmol) in 120 ml of chloroform was added triethylamine (1.56 ml, 11.1 mmol). The mixture was refluxed for 8 hours and monitored by TLC. After the reaction was complete, the organic layer was washed with water (2x100 mL), dried over anhydrous sodium sulphate and the resulting solution was concentrated to reduced volume. The solid formed was collected by filtration, washed with diethyl ether and dried in vacuo, yielding 3.3 g of a pale yellow product. Yield 90%; m.p. 169-171ºC; E. A. (Found: C, 63.4; H, 5.4; N, 12.2; S, 9.1; \(\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2\text{S}\) required: C, 63.3; H, 5.6; N, 12.3; S, 9.4); EI-MS (m/z) 341.2 ([M]+, 51); \(^1\text{H NMR (DMSO-d}_6\text{, ppm)}: \delta 8.58 (d, 1H, J= 8.5 Hz), 8.39 (d, 1H, J= 8.6 Hz), 8.06 (d, 1H, J= 7.2 Hz), 7.59 (t, 1H, J = 8.1 Hz), 7.41 (t, 1H, J= 7.9 Hz), 7.21 (d, 1H, J= 7.5 Hz), 6.95 (t, 1H, J= 7.6 Hz), 6.65 (d, 1H, J = 8.0 Hz), 6.46 (s, 1H), 6.35 (t, 1H, J= 7.5 Hz), 6.23 (d, 1H, J = 7.6 Hz), 4.95 (s, 2H), 2.91 (s, 6H); IR (KBr, cm\(^{-1}\)): v(NH\(_2\))+v(NH) 3434, 3349, v(SO\(_2\))s 1320, v(SO\(_2\))as 1148.

**Synthesis of E-5-(dimethylamino)-N-(2-(2-salicylideneamino)phenyl)naphtalene-1-sulfonamide (H\(_2\)L 1):** A solution of the amine ADs (1.15 g, 3.4 mmol) and salicylaldehyde (0.36 mL, 3.4 mmol) in 120 mL of chloroform was refluxed with a Dean-Stark trap for 7 hours. The reaction mixture was concentrated to ca. 20 mL, filtered and concentrated to dryness under reduced pressure. The oily product obtained was solidified under vacuum providing a yellow solid. Yield 80%; m.p. 136-138 ºC; E. A. (Found: C, 66.9; H, 5.2 ; N, 9.3; S, 7.1; \(\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_3\text{S}\) required: C, 67.3; H, 5.2; N, 9.4; S, 7.2); ESI-MS (m/z) 446.1 ([H\(_2\)L+H]+); \(^1\text{H NMR (DMSO-d}_6\text{, ppm)}: \delta 11.72 (s, 1H), 10.11 (s, 1H), 8.30 (d, 1H, J= 8.4 Hz), 8.21 (d, 1H, J= 8.6 Hz), 8.09 (s, 1H), 7.99 (dd, 1H, J\(_1\)= 7.3 Hz, J\(_2\)= 1.0 Hz), 7.49-7.38 (m, 2H), 7.36-7.29 (m, 2H), 7.26-7.12 (m, 3H), 7.07-6.93 (m, 2H), 6.92-6.84 (m, 2H), 2.73 (s, 6H); \(^{13}\text{C NMR (DMSO-d}_6\text{, ppm)}: \delta 164.79 (\text{HC=\text{N}}), 160.32 (\text{C}_{\text{ar}}), 151.01 (\text{C}_{\text{ar}}), 141.11 (\text{C}_{\text{ar}}), 133.87 (\text{CH}_{\text{ar}}), 133.72 (\text{C}_{\text{ar}}), 132.75 (\text{CH}_{\text{ar}}), 130.62 (\text{CH}_{\text{ar}}), 130.12 (\text{CH}_{\text{ar}}), 130.04 (\text{C}_{\text{ar}}), 129.22 (\text{C}_{\text{ar}}), 129.17 (\text{C}_{\text{ar}}), 118.84 (\text{C}_{\text{ar}}), 35.75 (\text{CH}_{\text{ar}}), 29.81 (\text{CH}_{\text{ar}}), 25.20 (\text{CH}_{\text{ar}}), 22.43 (\text{CH}_{\text{ar}}), 18.04 (\text{CH}_{\text{ar}}).
128.65 (CH\textsubscript{ar}), 127.37 (CH\textsubscript{ar}), 125.83 (CH\textsubscript{ar}), 122.61 (CH\textsubscript{ar}), 121.96 (CH\textsubscript{ar}), 119.14 (CH\textsubscript{ar}), 118.90 (CH\textsubscript{ar}), 118.61 (C\textsubscript{ar}), 118.05 (CH\textsubscript{ar}), 117.00 (CH\textsubscript{ar}), 114.83 (CH\textsubscript{ar}), 45.18 (CH\textsubscript{3}); IR (KBr, cm\textsuperscript{-1}): \(\nu\)(OH)+\(\nu\)(NH) 3221, \(\nu\)(C=N)+\(\nu\)(C-N) 1616, 1567, \(\nu\)(SO\textsubscript{2})\textsubscript{as} 1338, \(\nu\)(SO\textsubscript{2})\textsubscript{s} 1164. UV/Vis (CH\textsubscript{3}CN, \(\lambda\)\textsubscript{max}): 260, 342 nm.

**Electrochemical synthesis of [Zn(H\textsubscript{2}O)\textsubscript{6}][Zn\textsubscript{2}(L)\textsubscript{3}(\mu\textsubscript{3}-O)] \textsubscript{11}:** A solution of the ligand H\textsubscript{2}L (0.1 g, 0.22 mmol) containing tetraethylammonium perchlorate as supporting electrolyte, a platinum wire as cathode and a zinc plate as anode, was electrolysed in degassed acetonitrile (80 mL) for 1 h 12 min. The reaction was carried out at 10 mA (15 V) under argon atmosphere. The resulting yellow solution was concentrated under reduced pressure and diethyl ether was added until the precipitation was completed. The solid formed was filtered, washed with diethyl ether and dried in vacuo, providing 0.082 g of a yellow product (see Scheme S1). *Caution!* Perchlorate salts are potentially explosive and should be handled with care. Yield 64%; m.p.>300°C; E. A. (Found: C, 52.3; H, 4.6; N, 7.5; S, 5.4; \(C_75H_{72}N_6O_{16}S_2Zn_4\) required: C, 52.4; H, 4.4; N, 7.3; S, 5.6); MALDI-TOF MS (m/z) 1017.1 [Zn\textsubscript{2}L\textsubscript{2}+H]\textsuperscript{+}, 1037.1 [Zn\textsubscript{2}L\textsubscript{2}(O)+3H]\textsuperscript{+}, 1546.1 [Zn\textsubscript{3}L\textsubscript{3}(O)+3H]\textsuperscript{+}, 1628.0 [[Zn(H\textsubscript{2}O)]][Zn\textsubscript{3}L\textsubscript{3}(O)]+2H]\textsuperscript{+}, 1646.0 [[Zn(H\textsubscript{2}O)\textsubscript{2}][Zn\textsubscript{3}L\textsubscript{3}(O)]+2H]\textsuperscript{+}; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, ppm): \(\delta\) 8.75 (s, 1H), 8.67 (d, J = 8.6 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 7.2 Hz, 1H), 7.54-7.46 (m, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.85 (t, J = 7.7 Hz, 1H), 6.73 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 8.6 Hz, 1H), 6.49 (t, J = 7.3 Hz, 1H), 2.78 (s, 6H) ppm; IR (KBr, cm\textsuperscript{-1}): \(\nu\)(OH)+\(\nu\)(NH) 3433, \(\nu\)(C=N)+\(\nu\)(C-N) 1612, 1576, \(\nu\)(SO\textsubscript{2})\textsubscript{as} 1317, \(\nu\)(SO\textsubscript{2}) 1153; \(\Lambda\)\textsubscript{M} (Acetone, 10\textsuperscript{-3} M)= 106 \(\mu\)S cm\textsuperscript{-1} mol\textsuperscript{-1}; UV/Vis (CH\textsubscript{3}CN, \(\lambda\)\textsubscript{max}): 246, 296, 320 sh, 350 sh, 414 nm.

Slow evaporation from mother liquors afforded single crystals of \textbf{11-3CH\textsubscript{3}CN-H\textsubscript{2}O} (see Figure S1) and one crystal of [Zn\textsubscript{5}(L)\textsubscript{4}(\mu\textsubscript{3}-OH)\textsubscript{2}]-5CH\textsubscript{3}CN \textbf{12}, both being crystallographically characterized.

**Electrochemical synthesis of [Zn\textsubscript{2}(L)\textsubscript{3}]:** The ligand H\textsubscript{2}L (0.045 g, 0.10 mmol) was dissolved in degassed dry acetonitrile (40 mL) containing tetraethylammonium perchlorate as supporting electrolyte. The solution was electrolysed for 32 min at 10 mA (15 V) under argon employing a platinum wire as cathode and a zinc plate as anode. After the reaction was finished, the solvent was completely removed by bubbling argon.
through the yellow solution. The crude oil obtained was dissolved in 3 mL of hexane and filtered through a syringe filter. The resulting solution was concentrated as described above, providing 0.043 g of a yellow solid which was dried under vacuum.

*Caution!* Perchlorate salts are potentially explosive and should be handled with care.

Yield 85%; E. A. (Found: C, 58.9; H, 4.1; N, 8.2; S, 6.4; C_{50}H_{42}N_{6}O_{6}S_{2}Zn_{2} required: C, 59.0; H, 4.2; N, 8.2; S, 6.3); MALDI-TOF MS (m/z) 1017.1 [Zn_{2}L_{2}+H]^+ (see Figure S2); IR (KBr, cm\(^{-1}\)): \(\nu(\text{NH})\) 3449, \(\nu(\text{C} = \text{N})+\nu(\text{C}-\text{N})\) 1609, 1561, \(\nu(\text{SO}_{2})_{\text{as}}\) 1335, \(\nu(\text{SO}_{2})_{s}\) 1154.

The \(^1\text{H}\) NMR spectrum of \([\text{Zn}_{2}\text{L}_{2}]\) showed a mixture of signals corresponding to complex 11 as main compound and signals of lower intensity assignable to complex \([\text{Zn}_{2}\text{L}_{2}]\). This result indicates that the dimer is not stable in solution and rapidly evolves to compound 11.

**Crystal structure of \(\text{H}_{2}\text{L}\ 1\)**

In an attempt to gain a deeper understanding of the coordination behaviour of this ligand towards different metal ions, we determined its structure by X-ray diffraction. The unit cell of the ligand \(\text{H}_{2}\text{L}\ 1\) contains two independent conformers, both of which have an \(E\) conformation around the imine bond (Figure S3). The phenol and dansyl aromatic groups are almost parallel in both isomers [C1–C6/C14–C23 11.04(7)°; C26–C31/C39–C48 5.86(8)°], adopting a close arrangement that could be attributed to the establishment of weak ‘face to face’ \(\pi\)-stacking interactions (centroid-centroid distance of ca. 3.9 Å, Figure S4). Furthermore, the phenol group is oriented towards the imine nitrogen atoms N1/N4 because of the establishment of intramolecular hydrogen bonds. The dihedral angles between the phenol and phenylene rings C1–C6/C8–C13 [44.68(10)°] and C26–C31/C33–C38 [51.57(9)°] indicate that the sulfonamide NH group of each conformer is not coplanar with the corresponding phenol oxygen and imine nitrogen atoms.

Additionally, each conformer establishes two intermolecular hydrogen bonds, with a close different conformer (i.e. \(I\)--\(\cdot\)--\(II\), \(\text{II}\)--\(\cdot\)--\(I\)) engaging the sulfonamide NH group and the phenol oxygen atom (Table S3), as shown in Figure S5. In addition, three weak ‘edge to face’ \(\pi\)-stacking interactions are also observed between different ligand strands: one involving dansyl rings and two engaging phenol and phenylene aromatic systems. All of these interactions induce an almost perpendicular orientation between the two enantiomers, as revealed by the angle between the dansyl rings C14–C23/C39–C48 [76.40(5)°].
The imine, phenol, dansyl and sulphonamide bond distances are in the range expected for these groups and do not warrant further comment (Table S2).

**Table S1** Crystal data and structure refinement for the ligand H$_2$L 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{22}$H$</em>{23}$N$_3$O$_3$S</td>
</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.48 × 0.20 × 0.08</td>
</tr>
<tr>
<td>Formula weight</td>
<td>445.52</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a [Å]</td>
<td>11.5395(18)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>14.248(3)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>14.5284(17)</td>
</tr>
<tr>
<td>α [º]</td>
<td>75.654(13)</td>
</tr>
<tr>
<td>β [º]</td>
<td>78.072(8)</td>
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<tr>
<td>γ [º]</td>
<td>77.710(19)</td>
</tr>
<tr>
<td>Volume [Å$^3$]</td>
<td>2231.1(6)</td>
</tr>
<tr>
<td>Temperature [K]</td>
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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>μ [mm$^{-1}$]</td>
<td>1.553</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>9254</td>
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<tr>
<td>Independent reflections [Rint]</td>
<td>8886 [0.068]</td>
</tr>
<tr>
<td>$R_1$, $wR_2$ [$I&gt;2σ(I)$]</td>
<td>0.0510, 0.1338</td>
</tr>
<tr>
<td>$R_1$, $wR_2$ (all data)</td>
<td>0.1078, 0.1566</td>
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</table>

**Table S2** Main bond distances [Å] and angles [º] for the ligand H$_2$L 1

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<th>Bond Lengths and Angles</th>
<th>Value</th>
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<tr>
<td>O1–C1</td>
<td>1.362(3)</td>
</tr>
<tr>
<td>C7–N1</td>
<td>1.287(3)</td>
</tr>
<tr>
<td>C13–N2</td>
<td>1.427(3)</td>
</tr>
<tr>
<td>N2–S1</td>
<td>1.637(2)</td>
</tr>
<tr>
<td>S1–C14</td>
<td>1.775(3)</td>
</tr>
<tr>
<td>C19–N3</td>
<td>1.416(4)</td>
</tr>
<tr>
<td>O1–C1–C6</td>
<td>121.0(2)</td>
</tr>
<tr>
<td>C7–N1–C8</td>
<td>116.8(2)</td>
</tr>
<tr>
<td>C13–N2–S1</td>
<td>118.98(17)</td>
</tr>
<tr>
<td>N2–S1–C14</td>
<td>106.45(11)</td>
</tr>
<tr>
<td>C19–N3–C25</td>
<td>115.7(2)</td>
</tr>
<tr>
<td>C13–N2–S1–C14</td>
<td>60.1(2)</td>
</tr>
<tr>
<td>O4–C26</td>
<td>1.364(3)</td>
</tr>
<tr>
<td>C32–N4</td>
<td>1.278(3)</td>
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<tr>
<td>C38–N5</td>
<td>1.438(3)</td>
</tr>
<tr>
<td>N5–S2</td>
<td>1.630(2)</td>
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<tr>
<td>S2–C39</td>
<td>1.781(3)</td>
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<tr>
<td>C44–N6</td>
<td>1.418(4)</td>
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<tr>
<td>O4–C26–C31</td>
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<td>C32–N4–C33</td>
<td>118.7(2)</td>
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<tr>
<td>C38–N5–S2</td>
<td>119.35(17)</td>
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<tr>
<td>N5–S2–C39</td>
<td>105.95(11)</td>
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<tr>
<td>C44–N6–C50</td>
<td>115.7(3)</td>
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<tr>
<td>C38–N5–S2–C39</td>
<td>−68.4(2)</td>
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Table S3 Hydrogen bond parameters [Å] for 1, 6 and 12

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<tr>
<th>Parameter</th>
<th>D–H···A/Å</th>
<th>D–H/Å</th>
<th>H···A/Å</th>
<th>H–DHA/º</th>
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<td><strong>Ligand H2L 1</strong></td>
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<tr>
<td>O4–H4O···N4</td>
<td>0.873(18)</td>
<td>1.84(2)</td>
<td>2.629(3)</td>
<td>150(3)</td>
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<tr>
<td>O1–H1O···N1</td>
<td>0.890(18)</td>
<td>1.86(2)</td>
<td>2.652(3)</td>
<td>148(3)</td>
</tr>
<tr>
<td>N2–H2N···O4</td>
<td>0.851(17)</td>
<td>2.129(19)</td>
<td>2.951(3)</td>
<td>162(3)</td>
</tr>
<tr>
<td>N5–H5N···O1</td>
<td>0.828(17)</td>
<td>2.130(18)</td>
<td>2.931(3)</td>
<td>163(3)</td>
</tr>
<tr>
<td><strong>[Ni(L)∙3H2O]∙H2O∙(CH2CH3)2O 6</strong></td>
<td></td>
<td></td>
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<tr>
<td>O4–H4O···N4</td>
<td>0.822(18)</td>
<td>2.059(19)</td>
<td>2.875(3)</td>
<td>172(3)</td>
</tr>
<tr>
<td>O4–H4B···O3</td>
<td>0.79(3)</td>
<td>1.99(3)</td>
<td>2.681(3)</td>
<td>145(4)</td>
</tr>
<tr>
<td>O5–H5B···N3</td>
<td>0.92(4)</td>
<td>2.130(18)</td>
<td>2.931(3)</td>
<td>163(3)</td>
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<tr>
<td>O5–H5A···O8</td>
<td>0.821(14)</td>
<td>2.168(14)</td>
<td>2.977(4)</td>
<td>169(3)</td>
</tr>
<tr>
<td>O6–H6B···O1</td>
<td>0.795(18)</td>
<td>2.059(19)</td>
<td>2.875(3)</td>
<td>172(3)</td>
</tr>
<tr>
<td>O6–H6A···O7</td>
<td>0.817(18)</td>
<td>2.02(2)</td>
<td>2.843(3)</td>
<td>152(3)</td>
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<tr>
<td>O8–H8A···O2</td>
<td>0.813(19)</td>
<td>2.15(2)</td>
<td>2.952(3)</td>
<td>170(5)</td>
</tr>
<tr>
<td>O8–H8B···O3</td>
<td>0.814(19)</td>
<td>2.52(3)</td>
<td>3.233(3)</td>
<td>147(5)</td>
</tr>
<tr>
<td><strong>[Zn5(SAlDs)4(μ3-OH)]2·5CH3CN 12</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O13 H13O O2</td>
<td>0.77(4)</td>
<td>2.08(4)</td>
<td>2.659(4)</td>
<td>133(4)</td>
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<tr>
<td>O14 H14O O9</td>
<td>0.784(19)</td>
<td>2.03(3)</td>
<td>2.696(4)</td>
<td>143(4)</td>
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</table>

Symmetry transformations: (i) 1-x,-y, 1-z (ii) 2-x, 2-y, 1-z; (iii) 1+x, y, z ; (iv) x, 1+y, z ; (v) 2-x, 1-y, 2-z

Scheme S1. Proposed mechanism for the formation of 11.1
Figure S1. Crystal structure of the zinc(II) complex [Zn(H$_2$O)$_6$][Zn$_3$(L)$_3$(μ$_3$-O)]·3CH$_3$CN·H$_2$O 11.$^1$

Figure S2. Maldi-TOF mass spectrum of dimer Zn$_2$(L)$_2$ precursor of the complexes 11 and 12.$^1$
**Figure S3.** Conformers of the ligand H$_2$L 1.

**Figure S4.** $\pi$-stacking interactions in the ligand H$_2$L 1.
**Figure S5.** Intra and intermolecular hydrogen bond interactions between I···II conformers in the ligand H$_2$L 1.

**Figure S6.** Overlapped UV-Vis absorption spectra of the ligand H$_2$L 1 and its metal complexes recorded in acetonitrile solutions at room temperature (8x10$^{-5}$ – 8x10$^{-6}$ M).
Supporting information references