

A water reduction process performed by zinc metal under very mild conditions

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Supporting information

Experimental

Materials

All solvents, *o*-phenylenediamine, dansyl chloride, triethylamine, salicylaldehyde and tetraethylammonium perchlorate are commercially available and were used without further purification. Zinc metal (Ega Chemie) was used as ca. 2x2 cm² plate.

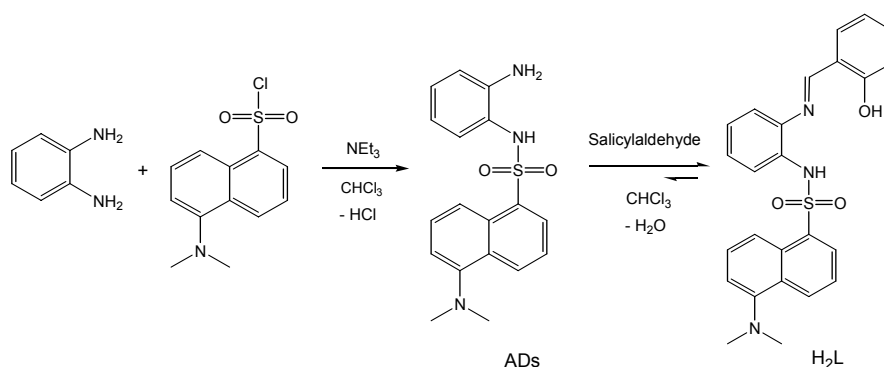
Physical Measurements

Elemental analysis of C, H, N and S were performed on a FISON S EA 1108 analyzer. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 spectrometer, using CDCl₃ and DMSO-d₆ 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⁻¹. Electronic impact (EI) mass spectrum was recorded on a HP 5988A quadrupole mass spectrometer. Electrospray ionisation (ESI) mass spectrum was recorded on an API4000 Applied Biosystems mass spectrometer with Triple Quadrupole analyser. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectra were registered in a Bruker Autoflex spectrometer using DCTB as matrix. 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 1×10⁻⁵ – 5×10⁻⁵ M.

Synthesis of N-(2-aminophenyl)-5-(dimethylamino)-1-naphtalenesulfonamide (ADs):

To a solution of *o*-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. 169-171°C; E. A. (Found: C, 63.4; H, 5.4 ; N, 12.2 ; S, 9.1; C₁₈H₁₉N₃O₂S required: C, 63.3; H, 5.6; N, 12.3; S, 9.4); EI-MS (*m/z*) 341.2 ([M]⁺, 51); ¹H NMR (DMSO-d₆, ppm): δ 8.53 (d, 1H, J= 8.5 Hz), 8.37 (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): ν(NH₂)+ν(NH) 3434, 3349, ν(SO₂)_{as} 1320, ν(SO₂)_s 1148.



Scheme S1: Synthesis of the ligand H₂L.

Synthesis of *E*-5-(dimethylamino)-*N*-(2-(2-salicylideneamino)phenyl)naphthalene-1-sulfonamide (H₂L): 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 (see Scheme S1). 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 °C; E. A. (Found: C, 66.9; H, 5.2 ; N, 9.3; S, 7.1; C₂₅H₂₃N₃O₃S required: C, 67.3; H, 5.2; N, 9.4; S, 7.2); ESI-MS (*m/z*) 446.1 ([H₂L+H]⁺); ¹H NMR (DMSO-d₆, ppm): δ 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, J₁= 7.3 Hz, J₂= 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); ¹³C NMR (DMSO-d₆, ppm): δ 164.79 (HC=N), 160.32 (C_{ar}), 151.01 (C_{ar}), 141.11 (C_{ar}), 133.87 (CH_{ar}), 133.72 (C_{ar}), 132.75 (CH_{ar}), 130.62 (CH_{ar}), 130.12 (CH_{ar}), 130.04 (C_{ar}), 129.22 (C_{ar}), 129.17 (C_{ar}), 128.65 (CH_{ar}), 127.37 (CH_{ar}), 125.83 (CH_{ar}), 122.61 (CH_{ar}), 121.96 (CH_{ar}), 119.14 (CH_{ar}), 118.90 (CH_{ar}), 118.61 (C_{ar}), 118.05 (CH_{ar}), 117.00 (CH_{ar}), 114.83 (CH_{ar}), 45.18 (CH₃); IR (KBr, cm⁻¹): ν(OH)+ν(NH) 3221, ν(C=N)+ν(C-N) 1616, 1567, ν(SO₂)_{as} 1338, ν(SO₂)_s 1164. UV/Vis (CH₃CN, λ_{max}): 260, 342 nm.

Electrochemical synthesis of $[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}_3(\text{L})_3(\mu_3\text{-O})]$ 1: A solution of the ligand H_2L (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. ***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; $\text{C}_{75}\text{H}_{75}\text{N}_9\text{O}_{16}\text{S}_3\text{Zn}_4$ required: C, 52.4; H, 4.4; N, 7.3; S, 5.6); MALDI-TOF MS (m/z) 1017.1 $[\text{Zn}_2\text{L}_2+\text{H}]^+$, 1037.1 $[\text{Zn}_2\text{L}_2(\text{O})+3\text{H}]^+$, 1546.1 $[\text{Zn}_3\text{L}_3(\text{O})+3\text{H}]^+$, 1628.0 $[[\text{Zn}(\text{H}_2\text{O})][\text{Zn}_3\text{L}_3(\text{O})]+2\text{H}]^+$, 1646.0 $[[\text{Zn}(\text{H}_2\text{O})_2][\text{Zn}_3\text{L}_3(\text{O})]+2\text{H}]^+$; ^1H NMR (DMSO- d_6 , ppm): δ 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^{-1}): $\nu(\text{OH})+\nu(\text{NH})$ 3433, $\nu(\text{C}=\text{N})+\nu(\text{C}-\text{N})$ 1612, 1576, $\nu(\text{SO}_2)_{\text{as}}$ 1317, $\nu(\text{SO}_2)_{\text{s}}$ 1153; Λ_{M} (Acetone, 10^{-3} M) = $106 \mu\text{S cm}^{-1}\text{mol}^{-1}$; UV/Vis (CH_3CN , λ_{max}): 246, 296, 320 sh, 350 sh, 414 nm.

Slow evaporation from mother liquors afforded single crystals of the compound $1 \cdot 3\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$, which was completely characterized.

$1 \cdot 3\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$: E. A. (Found: C, 52.5; H, 4.7; N, 9.0; S, 5.3; $\text{C}_{81}\text{H}_{86}\text{N}_{12}\text{O}_{17}\text{S}_3\text{Zn}_4$ required: C, 52.4; H, 4.7; N, 9.0; S, 5.2); MALDI-TOF MS (m/z) 1017.1 $[\text{Zn}_2\text{L}_2+\text{H}]^+$, 1037.1 $[\text{Zn}_2\text{L}_2(\text{O})+3\text{H}]^+$, 1546.1 $[\text{Zn}_3\text{L}_3(\text{O})+3\text{H}]^+$, 1628.0 $[[\text{Zn}(\text{H}_2\text{O})][\text{Zn}_3\text{L}_3(\text{O})]+2\text{H}]^+$, 1646.0 $[[\text{Zn}(\text{H}_2\text{O})_2][\text{Zn}_3\text{L}_3(\text{O})]+2\text{H}]^+$; ^1H NMR (DMSO- d_6 , ppm): δ 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^{-1}): $\nu(\text{OH})+\nu(\text{NH})$ 3447, $\nu(\text{C}=\text{N})+\nu(\text{C}-\text{N})$ 1611, 1576, $\nu(\text{SO}_2)_{\text{as}}$ 1316, $\nu(\text{SO}_2)_{\text{s}}$ 1153; UV/Vis (CH_3CN , λ_{max}): 246, 296, 320 sh, 350 sh, 414 nm.

Electrochemical synthesis of [Zn₂(L)₂] 2: The ligand H₂L (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; C₅₀H₄₂N₆O₆S₂Zn₂ required: C, 59.0; H, 4.2; N, 8.2; S, 6.3); MALDI-TOF MS (*m/z*) 1017.1 [Zn₂L₂+H]⁺; IR (KBr, cm⁻¹): ν(NH) 3449, ν(C=N)+ν(C-N) 1609, 1561, ν(SO₂)_{as} 1335, ν(SO₂)_s 1154.

The ¹H NMR spectrum of **2** showed a mixture of signals corresponding to complex **1** as major compound and signals of lower intensity assignable to complex **2** (Figure S5). This result indicates that **2** is not stable in solution and rapidly evolves to compound **1**.

Crystal Structure Determinations

Green prismatic crystals of **1**·3CH₃CN·H₂O were mounted on a glass fiber and used for data collection. Crystal data were collected at 293(2) K using a Smart-CCD-1000 BRUKER diffractometer. Graphite monochromated MoK(α) radiation (λ = 0.71073 Å) was used throughout. The data were processed with BRUKER SAINT¹ and corrected for absorption using SADABS.² The structure was solved by SIR-97³ and refined by full-matrix least-squares techniques against *F*² using SHELXL-97.⁴ Positional and anisotropic atomic displacement parameters were refined for all heteroatoms. The water protons were located in a difference map and their positions, with distance restraints, were refined isotropically [U_{iso}(H) = 1.2U_{eq}(O)]. Other H atoms were included as fixed contributions riding on attached atoms with isotropic thermal parameters (1.2-1.5 times those of their carrier atoms). Criteria of a satisfactory complete analysis were the ratios of "rms" shift to standard deviation less than 0.001 and no significant features in the final difference maps. Molecular graphics were done with ORTEP⁵ and DIAMOND.⁶ A summary of the crystal data, experimental details and refinement results are listed in Table S1. Significant bond distances and angles are summarized in Table S2 while hydrogen bond parameters are listed in Table S3.

CCDC 766560 contains 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.

Tables and Figures

Table S1: Main bond distances [Å] and angles [°] for the complex **1·3CH₃CN·H₂O**

[Zn(H₂O)₆][Zn₃(SAIDs)₃(μ₃-O)]·3CH₃CN·H₂O					
Zn1-Zn2	3.0790(10)	Zn1-O34	2.089(3)	Zn3-O1	2.024(3)
Zn2-Zn3	3.1560(11)	Zn2-O1	2.034(3)	Zn3-N10	2.031(3)
Zn1-Zn3	3.0898(10)	Zn2-N81	2.039(3)	Zn3-O34	2.052(3)
Zn1-O1	2.014(3)	Zn2-O66	2.104(3)	Zn3-O2	2.072(3)
Zn1-O66	2.010(3)	Zn2-N74	2.108(3)	Zn3-N17	2.084(3)
Zn1-N42	2.042(4)	Zn2-O2	2.111(3)	Zn4-O101	2.100(3)
Zn1-N49	2.057(3)	Zn1-O1-Zn2	99.05(11)	Zn3-O1-Zn2	102.10(11)
Zn1-O1-Zn3	99.84(12)	Zn1-O66-Zn2	96.88(12)	Zn3-O2-Zn2	97.97(11)
Zn3-O34-Zn1	96.50(12)	N49-Zn1-O34	162.83(13)	O1-Zn1-N42	146.51(12)
O1-Zn2-N74	158.42(12)	N81-Zn2-O66	155.91(12)	O1-Zn3-N10	162.40(12)
O2-Zn3-N17	153.71(13)	N42-Zn1-N49	80.44(14)	N42-Zn1-O34	86.47(13)
N81-Zn2-N74	79.18(13)	O66-Zn2-N74	82.74(13)	N10-Zn3-N17	79.97(13)
				N10-Zn3-O2	89.24(12)

Table S2: Hydrogen bond interactions in $1 \cdot 3\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$

D-H...A	D-H	H...A	D...A	∠DHA
O101-H11X...O19	0.77(3)	2.04(4)	2.808(4)	172(5)
O101-H11Y...O51	0.84(3)	2.09(4)	2.863(5)	153(5)
O102-H12X...O51	0.79(4)	2.15(4)	2.895(5)	157(5)
O102-H12Y...O83	0.91(4)	1.92(4)	2.760(4)	154(4)
O103-H13X...O84	0.74(3)	2.08(3)	2.809(4)	169(5)
O104-H14X...O20	0.90(3)	1.85(4)	2.725(6)	163(7)
O104-H14Y...N105	0.91(3)	2.01(3)	2.917(12)	170(7)

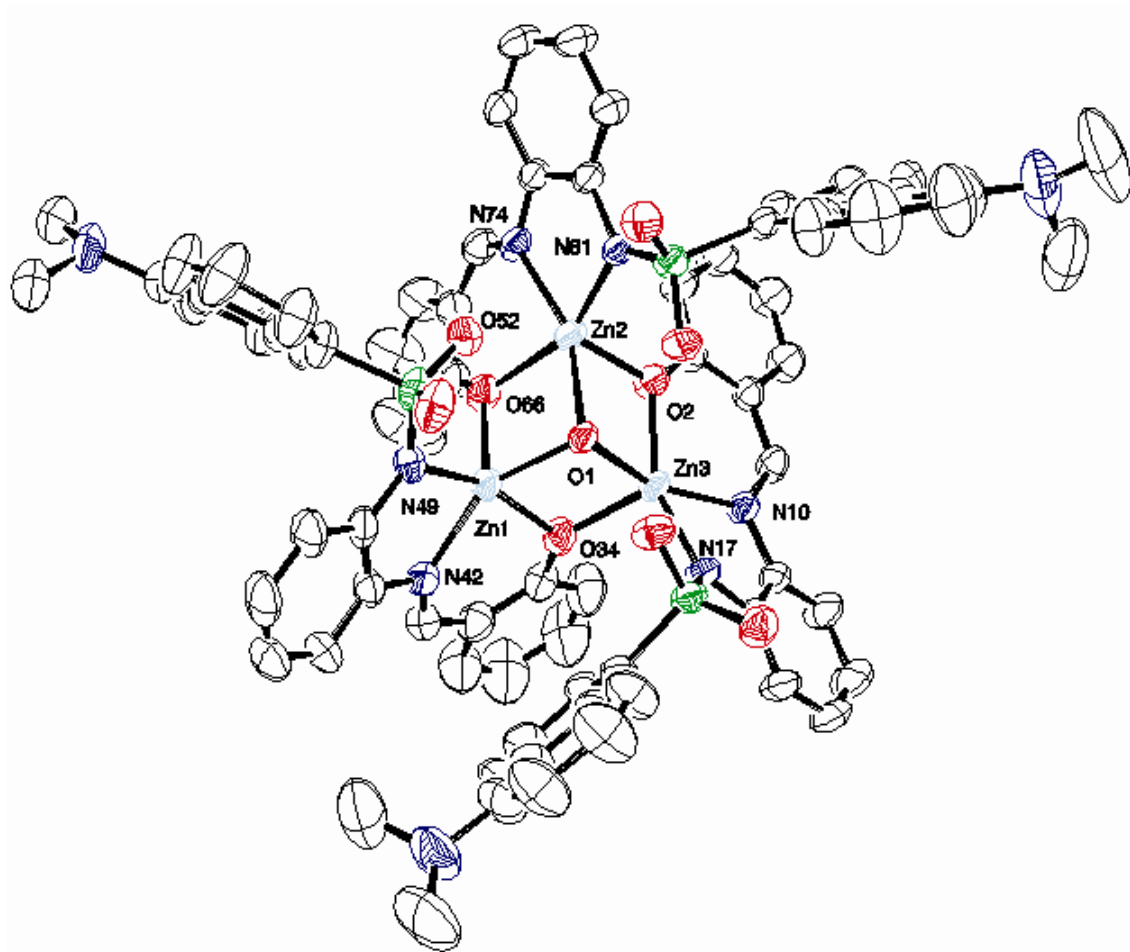


Figure S1. ORTEP diagram for 1·3CH₃CN·H₂O. The [Zn(H₂O)₆]²⁺ counterion, solvate acetonitrile and water molecules have not been depicted for clarity.

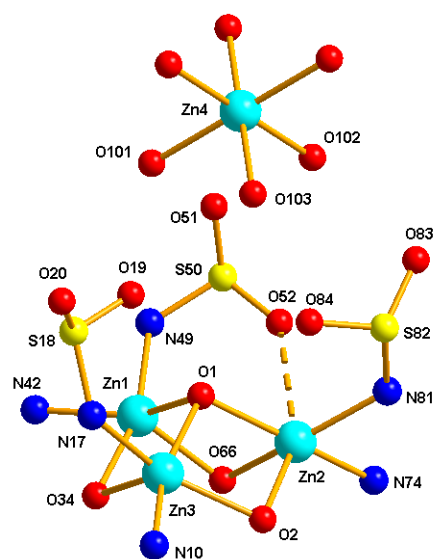


Figure S2. Orientation of the sulfonamide oxygen atoms towards the [Zn(H₂O)₆]²⁺ cation in 1·3CH₃CN·H₂O

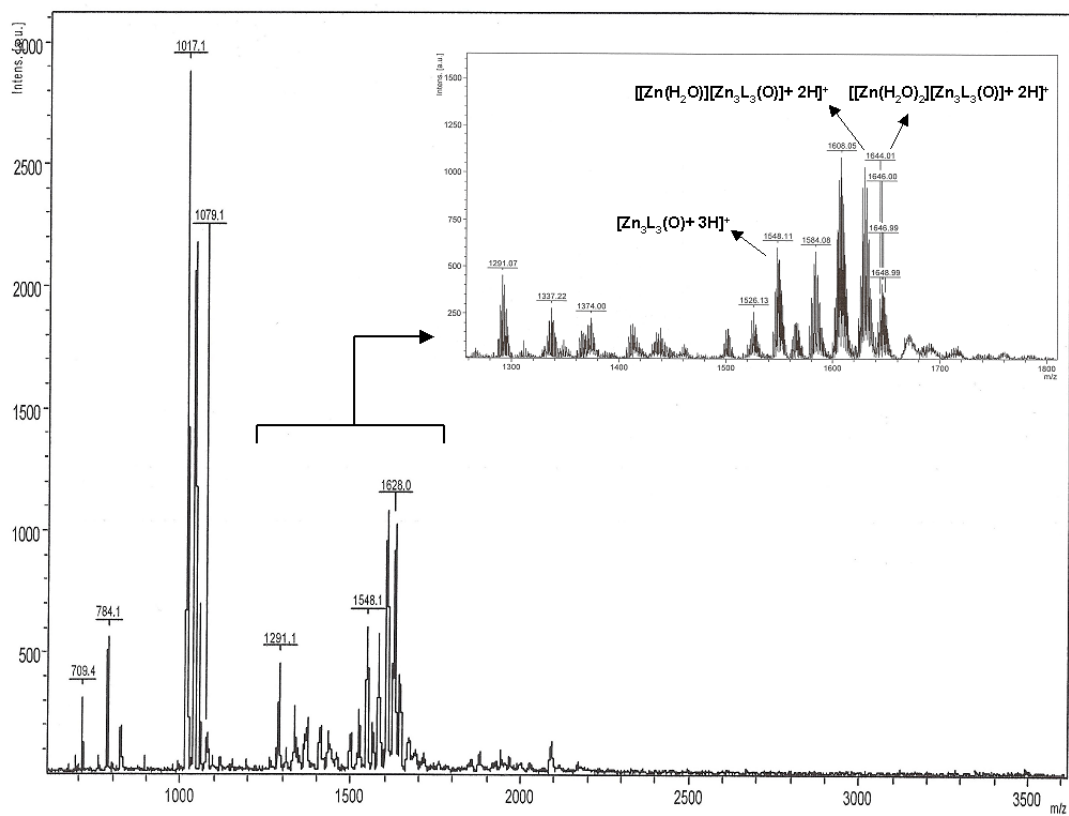


Figure S3. Maldi-TOF mass spectrum of **1**

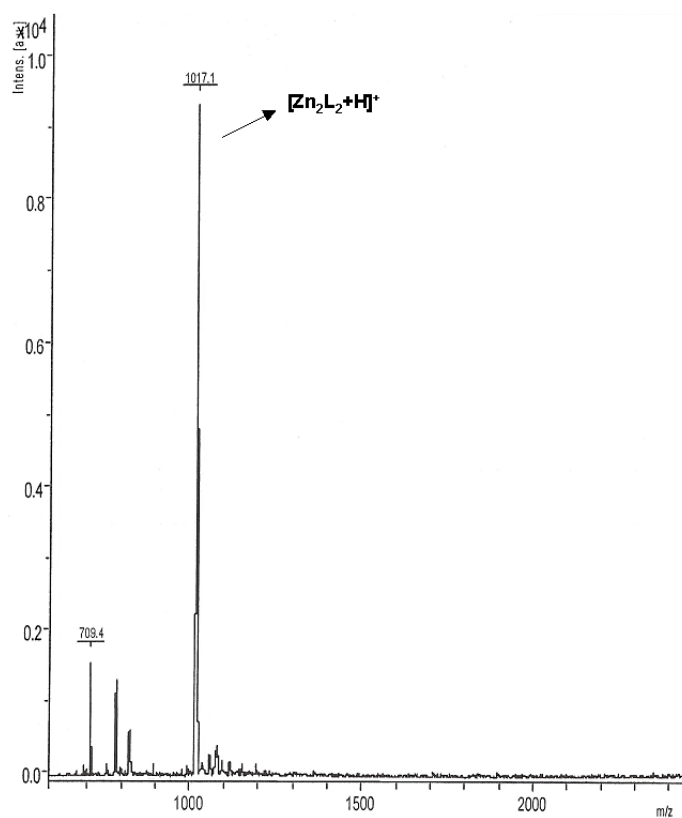


Figure S4. Maldi-TOF mass spectrum of **2**

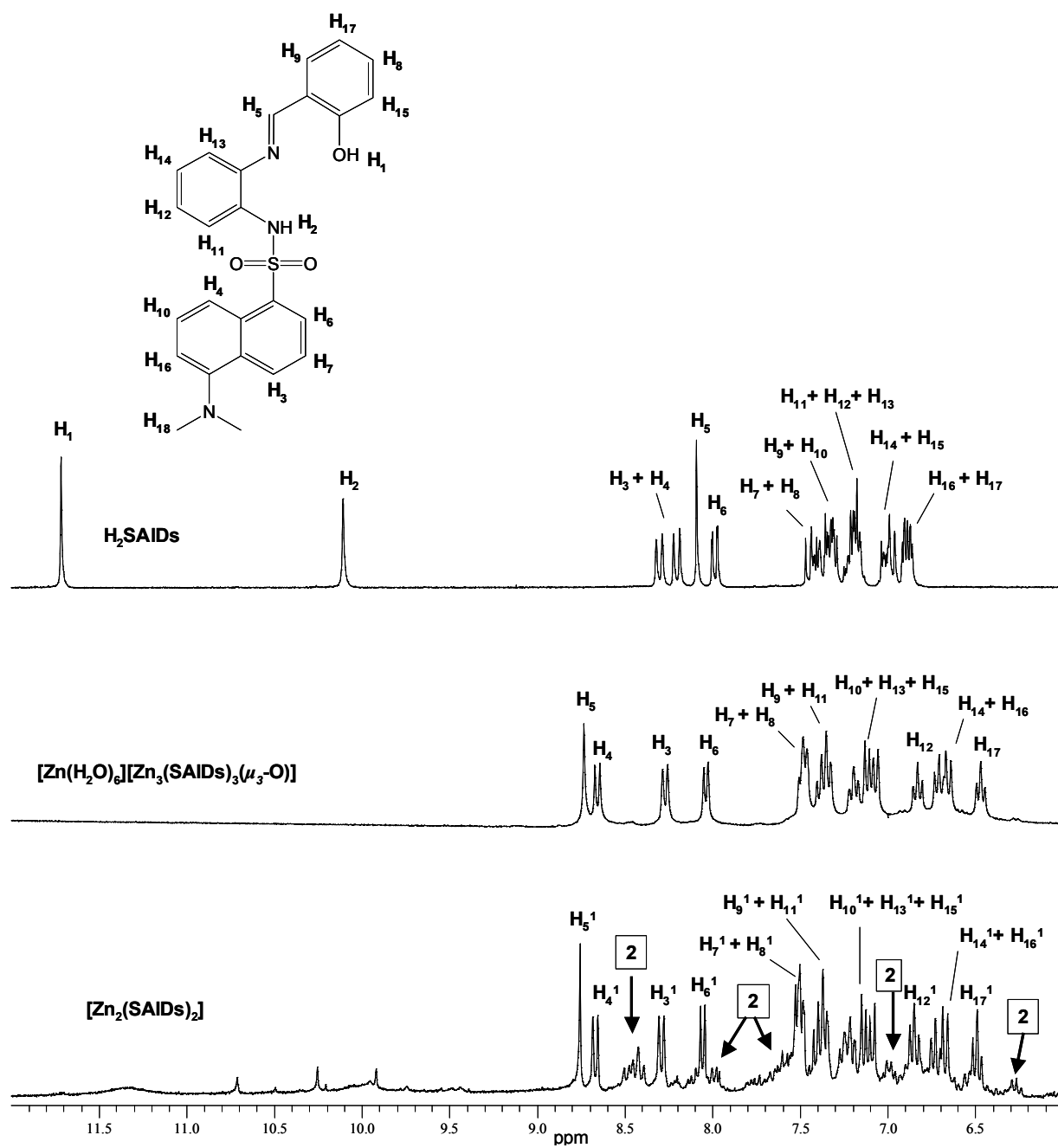


Figure S5. Overlapped 1H NMR spectra for the ligand H_2L and the complexes $[Zn(H_2O)_6][Zn_3(L)_3(\mu_3-O)]$ **1** and $[Zn_2(L)_2]$ **2**.

Supporting information references

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- ³ A. Altomare, C. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, M. C. Burla, G. Polidori, M. Camalli, R. Spagna, *SIR97*. University of Bari, Italy, 1997.
- ⁴ G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- ⁵ L. J. Farrugia, ORTEP-3 for Windows *J. Appl. Cryst.*, 1997, **30**, 565.
- ⁶ K. Brandenburg, DIAMOND, ver. 3.2; Crystal Impact GbR: Bonn, Germany, 2009.