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Four new families of polynuclear Zn-Ln coordination clusters. Synthetic, topological, magnetic and luminescent aspects.

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Running Title : Zinc - Lanthanide polynuclear Coordination Clusters

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ABSTRACT:

The employment of three structurally related Schiff bases $H_2\mathbf{L1}$**,** $H_2\mathbf{L2}$, and $H_3\mathbf{L3}$ with zinc and lanthanide salts under various reaction conditions, gave four families of compounds formulated as $[Zn^{II}_2Ln^{III}_2(\mathbf{L1})_4(EtOH)_6][ClO_4]_2$ (**1-3**), $[Zn^{II}_5Ln(OH)(\mathbf{L1})_6(H_2O)]$ (**4-6**), $[(Zn^{II}_4Ln^{III}_2(OH)_2(\mathbf{L2})_4(OAc)_2(NO_3)_2(DMF)_3])$ (**7-9**), $[Zn^{II}_2Ln^{III}_2(\mathbf{L3})_2(NO_3)_2(CO_3)_2(CH_3OH)_2]$ (**10-12**) with robust and novel topologies. Synthetic aspects are discussed. A comprehensive topological analysis of all reported Zn^{II}/Ln^{III} CCs with a core nuclearity of four and above is presented and identifies that families **(4-6)** and **(7-9)** are the first examples of the 2,3,4M6-1 motif in Zn^{II}/Ln^{III} chemistry. Magnetic studies are presented for the Dy^{III} analogues (**1**, **7** and **10**) are presented, **7** demonstrates field-induced slow relaxation of the magnetization. Fluorescence studies are also discussed.

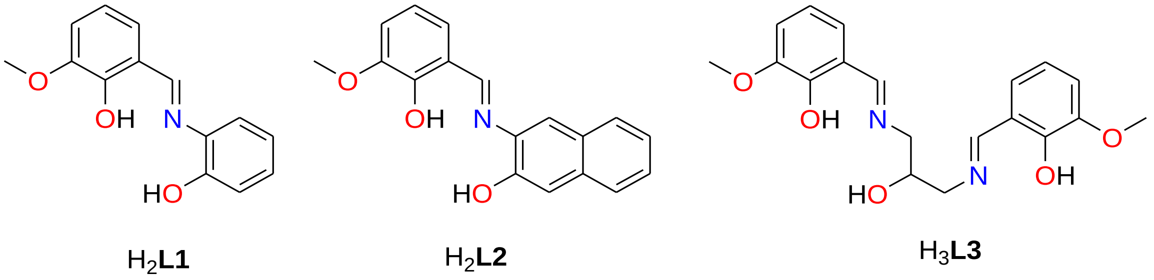
KEYWORS : Coordination Clusters, Zinc, Lanthanide, Topology, Magnetism,

Introduction

In recent years, 3d-4f polynuclear Coordination Clusters (CCs) have attracted increasing interest as a result of their extraordinary and fascinating structural characteristics[1–5] as well as their many potential applications in fields such as molecular magnetism,[6–8] optical materials[9–13] and catalysis.[14–18] In particular, the first heteronuclear Zn^{II} – Eu^{III}/Sm^{III} CCs were reported in 1995 by Brennan et al[19,20] ; more recent Zn^{II}/Ln^{III} examples followed.[13,21,22], in 2009 Murugesu et al[10] reported a multifunctional pentanuclear $Zn^{II}{}_2Dy^{III}{}_3$ CC exhibiting Single Molecule Magnet (SMM) and fluorescent properties. Since then the synthesis of Zn^{II}/Ln^{III} CCs has gained remarkable attention, this since to a) magnetic behaviour that can be explained due to the diamagnetic character of the Zn^{II} ion, which has also been shown to enhance the energy barrier in Zn^{II}/Dy^{III} SMMs[23] and b) Eu^{III} and Tb^{III} are attractive luminescent centres, due to their long lived $^5D_0$ and $^5D_4$ excited states and the accompanying large Stokes' Shifts. In addition, the combination with Zn^{II} ions may produce species with enhanced luminescent properties via f –d energy transfer,[24] a plethora of such mixed metal species have been reported and the magnetic and luminescent properties of such compounds have been very well investigated.[9,25–46]

Several organic ligands have been employed to build Zn^{II}/Ln^{III} CCs and Schiff Base ligands represent an ideal host to accommodate both elements and allow them to interact.[27,35,47,48] The synthesis of the Schiff base ligand (*E*)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol H_2**L1** (Scheme 1, left), was initially reported in 1971 and used to sequester UO_2.[49] Since then, a number of 3d/4f compounds bearing this ligand have been reported.[15,50–55] Recently, we employed H_2**L1** in Zn^{II}/Ln^{III} chemistry, to assemble a family of bimetallic tetranuclear CCs formulated as $[Zn_2Ln_2(\mathbf{L1})_4(NO_3)_2(DMF)_2].2DMF$ (Ln is Sm, Eu, Tb, Gd, Dy and Yb) which promote Fiedel Crafts[17,56] and multicomponent catalysis.[57] An interesting feature of these molecules is the retention of their topology into solution, presenting further importance to the rigidity of the ligands and allows some synthetic control over topology.

H_2**L1** is particularly versatile and straightforward to synthesise, and readily modified to enhance the luminescent properties eg. by the introduction of chromophoric moieties such as napthol, are often employed to transfer absorbed energy efficiently to the lanthanide ions[58] . We therefore used a systematic synthetic study using H_2**L1** and its structurally related organic ligands H_2**L2** and H_3**L3** (Scheme 1, centre and right) in the synthesis of Zn^{II}/Ln^{III} CCs. This study is limited to the formation and characterization of the Dy^{III}, Tb^{III} and Eu^{III} derivatives which are expected to show interesting magnetic (Dy^{III}) and fluorescent (Tb^{III}/Eu^{III}) properties. Herein, we describe twelve new CCs formulated as $[Zn^{II}_2Ln^{III}_2($**L1**$)_4(EtOH)_6]\ 2(ClO_4)$ (**1-3**) where Ln is Dy^{III} (**1**), Tb^{III} (**2**) or Eu^{III}(**3**). $[Zn^{II}_5Ln(OH)($**L1**$)_6(H_2O)]$ (**4-6**) where Ln is Dy^{III} (**4**), Tb^{III} (**5**) or Eu^{III}(**6**). $[Zn^{II}_4Ln^{III}_2(OH)_2($**L2**$)_4(OAc)_2(NO_3)_2(DMF)_3].DMF$ (**7-9**) where Ln is Dy^{III} (**7**), Tb^{III} (**8**) or Eu^{III} (**9**). $[Zn^{II}_2Ln^{III}_2($**L3**$)_2(CO_3)_2(NO_3)_2(CH_3OH)_2]$ (**10-12**) where Ln is Dy^{III} (**10**), Tb^{III} (**11**) and Eu^{III} (**12**). Magnetic studies of the dysprosium analogues are presented, as well as luminescent analyses in solution.



Scheme 1. Schiff Base ligands used in this study

EXPERIMENTAL SECTION

Materials. Chemicals (reagent grade) were purchased from Sigma Aldrich and Alfa Aesar. The synthesis and characterization of the HL ligand are described in the ESI. All experiments were performed under aerobic conditions using materials and solvents as received. *Safety note*: Perchlorate salts are potentially explosive; such compounds should be used in small quantities and handled with caution and utmost care at all times.

Instrumentation. IR spectra were recorded over the range of 4000-650 cm^{-1} on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a UATR polarization accessory. ESI-MS data were obtained on a VG Autospec Fissions instrument (EI at 70 eV). TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, UK) under nitrogen and at a scan rate of 10 °C/min (University of Sussex). All steady-state UV-Vis absorbance measurements (University of Kent) were made by use of a Shimadzu UV-1800 UV-Vis Spectrophotometer in examples were dissolved in DMF as indicated. with quartz cuvettes, while all stead-state solutions fluorescence emission measurements were carried out using a Cary Eclipse Fluorescence Spectrometer in either acetonitrile, or DMF as indicated with quartz cuvettes.

Magnetic studies. Variable-temperature magnetic studies were made by use of a MPMS-5 Quantum Design magnetometer operating at 0.03 T in the 300-2.0 K range. Magnetization measurements were made under a magnetic field range of 0 - 5 T. Diamagnetic corrections were applied to the observed paramagnetic susceptibility using Pascal's constants.

Ligand synthesis. The syntheses of $H_2\mathbf{L1}$[59] and $H_2\mathbf{L2}$ and $H_3\mathbf{L3}$ were by the reported procedures.

Experimental

Preparation of Complexes

$[\mathrm{Zn^{II}_2Ln^{III}_2}(\mathbf{L1})_4(\mathrm{EtOH})_4]\ [\mathrm{ClO_4}]_2$ (**1-3**) where Ln is $\mathrm{Dy^{III}}$ (**1**), $\mathrm{Tb^{III}}$ (**2**) or $\mathrm{Eu^{III}}$(**3**). To a solution of $H_2\mathbf{L1}$ (48.2 mg, 0.2 mmol) in EtOH (20 mL), $\mathrm{Zn(ClO_4)_2\ 6H_2O}$ (74 mg, 0.2 mmol) and $\mathrm{Ln(OTf)_3}$ (61 mg, 0.1 mmol) were added and the resultant solution was stirred for 5 minutes, $\mathrm{Et_3N}$ (62 µL, 0.45 mmol) was added and the mixture was stirred for a further 1h. The resulting cloudy yellow solution was filtered and allowed to stand at room temperature. After 4 days, small yellow crystals were obtained with yields in the range of 52% based on Zn. For 1, CHN $[\mathrm{Zn^{II}_2Dy^{III}_2}(\mathbf{L1})_4(\mathrm{EtOH})_6][\mathrm{ClO_4}]_2$ observed: C-43.19%, H-4.06%, N-2.79%; expected: C-43.08%, H-4.26%, N-2.96%. for **2** CHN $[\mathrm{Zn^{II}_2Tb^{III}_2}(\mathbf{L1})_4(\mathrm{EtOH})_6][\mathrm{ClO_4}]_2$ observed: C-43.21%, H-4.44%, N-3.04%; expected: C-43.30%, H-4.28%, N-2.97%., for **3** CHN $[\mathrm{Zn^{II}_2Eu^{III}_2}(\mathbf{L1})_4(\mathrm{EtOH})_6][\mathrm{ClO_4}]_2$ observed: C-43.53%, H-4.26%, N-2.92%; expected: C-43.59%, H-4.31%, N-2.99%.,

$[Zn^{II}_5Ln(\mathbf{L1})_6(OH)(H_2O)]$ (**4-6**) where Ln is Dy^{III} (**4**), Tb^{III} (**5**) and Eu^{III}(**6**). To a solution of $H_2\mathbf{L1}$ (48.2 mg, 0.2 mmol) in MeCN (20 mL), $LnCl_3.xH_2O$ (37 mg, 0.1 mmol) and $ZnCl_2$ (27.2 mg, 0.2 mmol) were added and the mixture was stirred for 5 minutes, Et_3N (62 µL, 0.45 mmol) was added and the mixture stirred for a further 1h. The resulting cloudy yellow solution was filtered and allow to stand at room temperature. After 3 days, small yellow crystals were collected with yields in the range of 67% based on Zn. CHN (**4**) $[Zn^{II}_5Dy(\mathbf{L1})_6(OH)(H_2O)]$ observed: C- 51.32%, H-3.41%, N-4.19%; expected C-51.29%, H-3.53%, N-4.27% , for **5** $[Zn^{II}_5Tb(\mathbf{L1})_6(OH)(H_2O)]$ observed: C-51.41%, H-3.50%, N-4.35%; expected C-51.29%, H-3.53%, N-4.27% , for **6** $[Zn^{II}_5Eu(\mathbf{L1})_6(OH)(H_2O)]$ observed: C- 51.45%, H-3.60%, N-4.14%; expected C-51.58%, H-3.55%, N-4.29% ,.

$[Zn^{II}_4Ln^{III}_2(OH)_2 (\mathbf{L2})_4(OAc)_2(NO_3)_2(DMF)_3].DMF$ (**7-9**) where Ln is Dy^{III} (**7**), Tb^{III} (**8**) or Eu^{III} (**9**). To a solution of $H_2\mathbf{L2}$ (52 mg, 0.2 mmol) in DMF (10 mL), $Ln(NO_3)_3.5H_2O$ (44 mg, 0.1 mmol), $Zn(CH_3CO_2)_2.2H_2O$ (45 mg, 0.2 mmol) and Et_3N (62 µL, 0.45 mmol) were added and the solution was stirred for 1h. The clear yellow solution was filtered and underwent vapour diffusion with Et_2O. After 7 days, yellow needle-like crystals were obtained with yields of 44%. CHN $[Zn^{II}_4Dy^{III}_2(OH)_2(\mathbf{L2})_4(OAc)_2(NO_3)_2(DMF)_3].DMF$ observed: C-45.41%, H-3.86%, N-6.19%; expected C-45.59%, H- 3.83%, N-6.05%. for **5** $[Zn^{II}_4Tb^{III}_2(OH)_2(\mathbf{L2})_4(OAc)_2(NO_3)_2(DMF)_3].DMF$ observed: C-45.67%, H-3.79%, N-6.11%; expected C-45.79%, H- 3.85%, N-6..07%, for **6** $[Zn^{II}_4Eu^{III}_2(OH)_2(\mathbf{L2})_4(OAc)_2(NO_3)_2(DMF)_3].DMF$ observed: C-45.99%, H-3.90%, N-6.15%; expected C-46.03%, H- 3.86%, N-6.10%.

$[Zn^{II}_2Ln^{III}_2(\mathbf{L3})_2(CO_3)_2(NO_3)_2(CH_3OH)_2]$ (**10-12**) where Ln is Dy^{III} (**10**), Tb^{III} (**11**) and Eu^{III}(**12**). To a solution of $H_3\mathbf{L3}$ (71.6 mg, 0.1 mmol) in MeOH (20 mL), Et_3N (61.5 µL, 0.45 mmol) was added and the solution was stirred for 10 min. $Ln(NO_3)_3.5H_2O$ (44 mg, 0.1 mmol) and $Zn(NO_3)_2.6H_2O$ (58 mg, 0.2 mmol) were added and the resultant solution was stirred for a further 40min. The clear yellow solution was filtered and left to stand at room temperature. After 5 days, small yellow crystals were obtained with a yield of 80 % based on Zn. CHN (**10**) $[Zn^{II}_2Dy^{III}_2(\mathbf{L3})_2(CO_3)_2(NO_3)_2(CH_3OH)_2]$

observed C-34.89%, H-3.16%; N-5.88%; expected C-34.95%,H-3.21%,N-5.83%. for **11** [$Zn^{II}_2Tb^{III}_2$(**L3**)$_2$(CO_3)$_2$(NO_3)$_2$(CH_3OH)$_2$] observed C-35.21%, H-3.34%; N-5.81%; expected C-35.19%, H-3.23%, N-5.86%. for 12 [$Zn^{II}_2Eu^{III}_2$(**L3**)$_2$(CO_3)$_2$(NO_3)$_2$(CH_3OH)$_2$] observed C-34.55%, H-3.24%; N-5.89%; expected C-35.49%,H-3.26%,N-5.91%.

X-ray Crystallography. Data and unit cells(Tables S1-S4) for **1-6**, **10**, **11** and **12** (ω- scans) were obtained at the University of Sussex by use of an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo Kα radiation (λ = 0.71073 Å). CRYSALIS CCD and RED software was used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multi-scan method. Data for **7**, **8**, **9**, **13** and **14** were collected at the National Crystallography Service, University of Southampton[61] on a Rigaku CrystalClear, processed with CrysAlisPro and solved by intrinsic phasing methods with SHELXT[62]. All crystal structures were then refined on Fo2 by full-matrix least-squares refinements using SHELXL.[62] All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Structures **7**, **8** and **9** are isostructural with a large solvent channel parallel to the b-axis present in each structure. From the difference map a large peak of electron density is present in each of these structures which has proved impossible to assign in a chemically sensible manner. For each of these structures we performed the elemental and TGA analysis three times for each sample and obtained the expected results at all times. The absence of Cl was confirmed by ICP analysis. Additionally, data were collected at 30K for **9** in an attempt to better characterize the structure within the solvent channel but this was unsuccessful. The electron contribution from this large peak along with that of the diffuse solvent has been taken into account using the SMTBX solvent masking as implemented in Olex2. Geometric/crystallographic calculations were performed using PLATON,[63] Olex2,[64] and WINGX[65] packages; graphics were prepared with Crystal Maker.[66] Crystallographic details are given in Tables S1-S4. CCDC 1505845-1505854

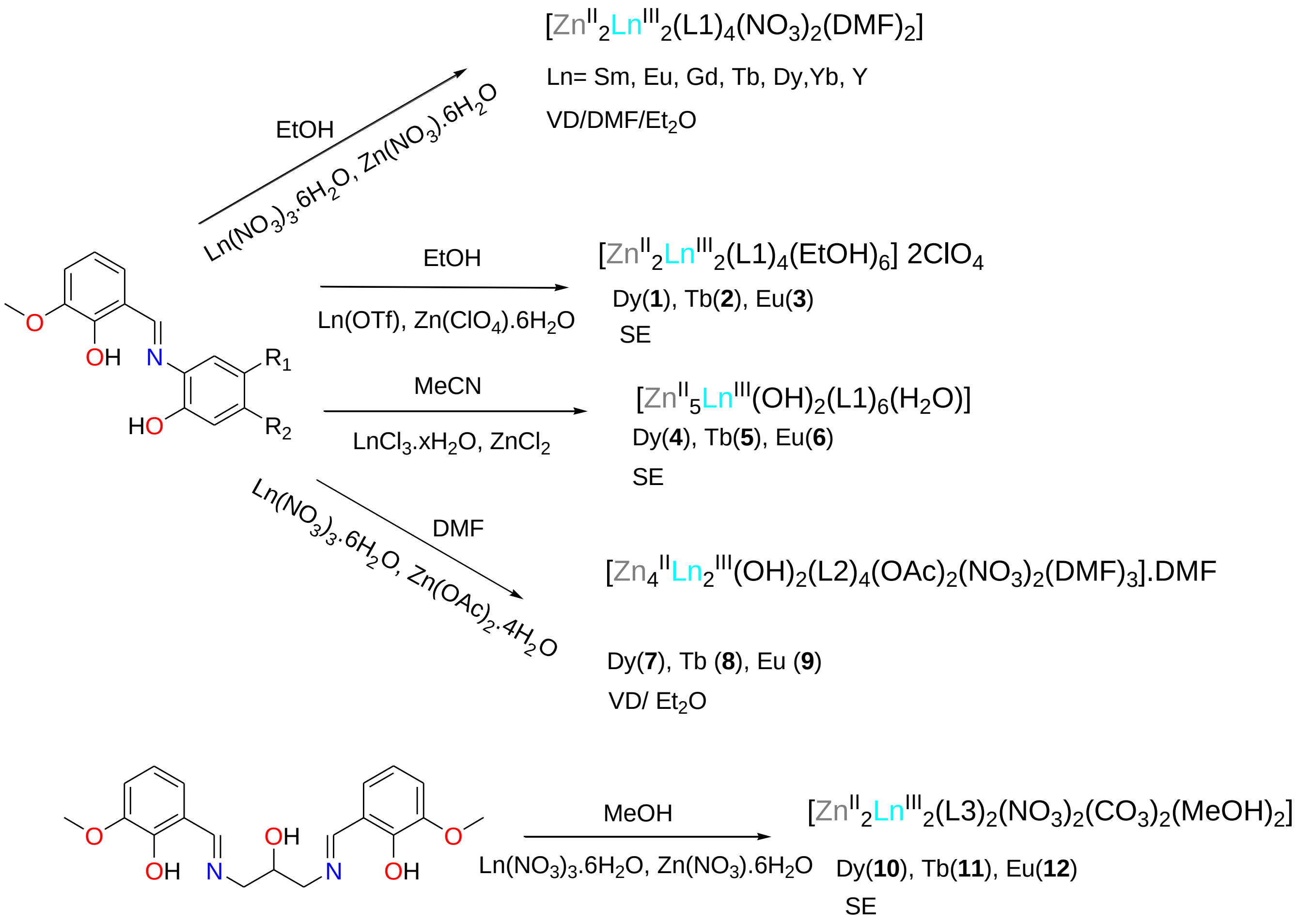
RESULTS AND DISCUSSION

Synthetic issues. It is well-known that the stoichiometric ratio, metal salt, temperature, atmosphere, solvent, time of reaction, can all affect the nature of the final product. The semi-rigid H_2**L1** ligand has two pockets-I(ONO) and –II(ONO) (Scheme 1, left) which are suitable for binding both 3d and 4f metal ions. The reaction between, $Dy(OTf)_3$, $Zn(ClO_4)_2$ and H_2**L1** in the presence of base (Et_3N) in EtOH in the molar ratio 1:2:2:4.5, afforded yellow needle like crystals of **1** in a tolerable yield (57%) after 1 week. The reactions with similar ratios but different counter anions and solvent yielded the recently reported isoskeletal[59] CCs formulated as $[Zn_2Ln_2(\mathbf{L1})_4(NO_3)_2(DMF)_2]$.[17] Aiming to synthesize the isoskeletal tetranuclear zinc analogue of $[Ni_2Ln_2(\mathbf{L1})_4Cl_2(CH_3CN)_2]$,[15] we performed the reaction with similar ratios in MeCN with $DyCl_3$ and $ZnCl_2$ that yielded after 2 weeks jagged crystals of **4** possessing a topology unseen in the literature for these metals. A modified form of this ligand (E)-3-((2-hydroxy-3-methoxybenzylidene)amino)naphthalen-2-ol (H_2**L2**, Scheme 1 middle) that offers similar pockets to H_2**L1** has been employed to act as a sensitizer to enhance luminescence of the resulting complexes. The same molar reactant ratios in DMF, with $Dy(NO_3)_3$ and $Zn(OAc)_2$., After 1 week of vapour diffusion with Et_2O, large yellow plate like crystals of **7** were afforded in a good yield (70%). With the retention of the o-vanillin unit and replacement of the aminophenol by 1,3-diamino-2-propanol the ligand H_3**L3** (Scheme 1, right), offering similar pockets to that in H_2**L1** and H_2**L2** and one extra pocket was obtained. The use of H_3**L3** for the first time in Zn^{II}/Ln^{III} chemistry, gave the tetranuclear compounds **10** – **12**. A summary of these synthetic procedures is shown in **Table 1** and **Scheme 2**.

Table 1. Synthetic Strategies of preparing Zn^{II}/Ln^{III} CCs.

Ratio[a]	Ligand	Ln source	Zn source	Crystallisation method/ time(days)	Solvent	Compound
A:B:C:D = 1:2:2:4.5	H_2**L1**	$Ln(OTf)_3$	$Zn(ClO_4)_2.6H_2O$	SE / 7	EtOH	Zn_2Ln_2 **(1,2,3)**
A:B:C:D = 1:2:2:4.5	H_2**L1**	$Ln(NO_3)_3.5H_2O$	$Zn(NO_3)_2.6H_2O$	VD Et_2O / 9	DMF	Zn_2Ln_2[17]
A:B:C:D = 1:2:2:4.5	H_2**L1**	$LnCl_3.XH_2O$	$ZnCl_2$	SE / 3	MeCN	Zn_5Ln (**4,5,6**)
A:B:C:D = 1:2:2:4.5	H_2**L2**	$Ln(NO_3)_3.5H_2O$	$Zn(CH_3CO_2)_2.2H_2O$	VD Et_2O / 7	DMF	Zn_4Dy_2 (**7,8,9**)
A:B:C:D = 1:2:2:4.5	H_3**L3**	$Ln(NO_3)_3.xH_2O$	$Zn(NO_3)_2.6H_2O$	SE / 5	MeOH	Zn_2Ln_2 (**10,11,12**)

(a) A= Dy^{III} salt, B = Zn^{II} salt, C= H_xLY, D = Et_3N



Scheme 2. Synthetic scheme for the preparation of (**1-12**)

Crystal Structure Description. Compounds **1 – 3** crystallize in the monoclinic *P*21/*n* space group and are isoskeletal, thus only **1** will be described. The asymmetric unit of **1** contains one Zn^{II} ion; one Dy^{III} ion; two doubly deprotonated organic ligands (**L1**); three coordinated ethanol molecules; one to the Zn^{II} and the other two to the Dy^{III} ion; one perchlorate and one ethanol molecule. The main core of **1** can be described as defect dicubane [67] and is isoskeletal to the previous reported Ni_2Ln_2,[15,50] and Co_2Ln_2[15,51] cores. The organic ligands exhibit two different coordination modes (modes I and II, Scheme 2). In the first mode (mode I, Scheme 2), the two phenoxide oxygen atoms and the imine nitrogen atom are chelated to the Zn^{II} centre, and the two phenoxide atoms are further bonded to two Dy^{III} ions (Dy(1) and its symmetry related) and the methoxide oxygen atoms is and bound to Dy(1). In the second mode (mode II, Scheme 2), the two phenoxide oxygen atoms and the imine nitrogen atom are chelated to the Dy^{III} centre, while the phenoxide oxygen atom (from the 2-aminophenol unit), is further bound to two Zn^{II} centres. One ethanol molecules is bound one to the Zn^{II} ion and two others are bound to the Dy^{III} ion. Each Zn^{II} centre coordinates to six atoms (O_5N) and displays an octahedral coordination, while each Dy^{III} centre coordinates to eight atoms (O_7N). Using Shape software,[68] the geometry of Dy(1) can be best described as biaugmented trigonal prismatic, with an S(P) value 1.415. There are two $Zn^{II}\cdots Dy^{III}$ distances at 3.5513(5)Å and 3.5329(5) Å and one $Zn^{II}\cdots Zn^{II}$ distance at 3.172(5)Å. Two coordinating ethanol molecules, one to Zn^{II} and one to Dy^{III} ion, form an H-bond (O8 – H8···O9) while the third coordinating ethanol molecule forms an H-bond with the lattice EtOH (O7 – H7···O10), which in turn is H-bonded to the uncoordinated methoxide oxygen atom (O10 – H10A··· O1) (Fig S1). No other intramolecular interactions (e.g H-bonds or stacking) can be found between neighbouring entities. According to our topological representation,[69,70] the main core of compound **1** can be described as **2,3M4-1**[70] and according to a literature survey[71] this topology can be found in Zn_2Eu_2[19] and Zn_2Yb_2[72] CCs and the recent examples reported by us.[17]

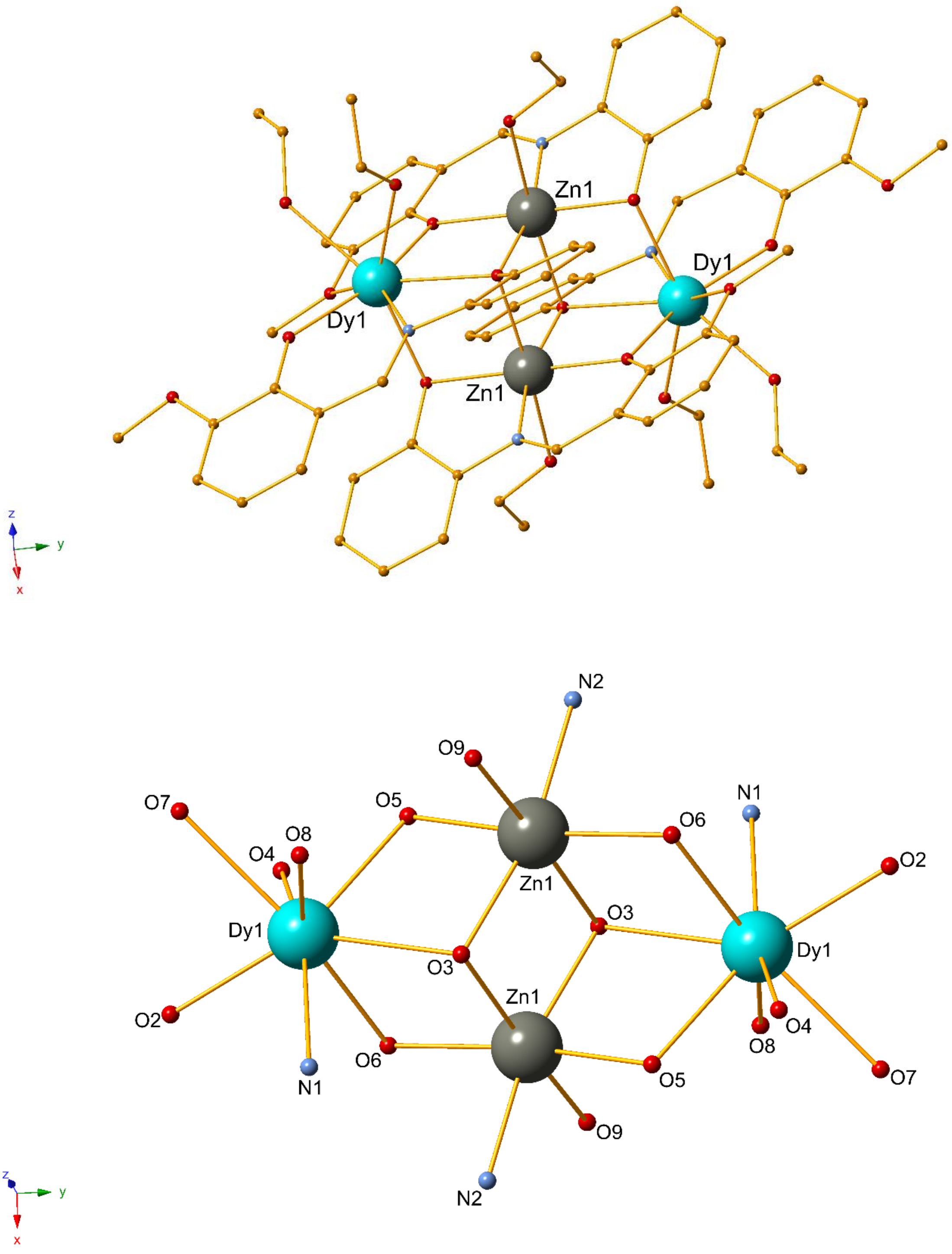
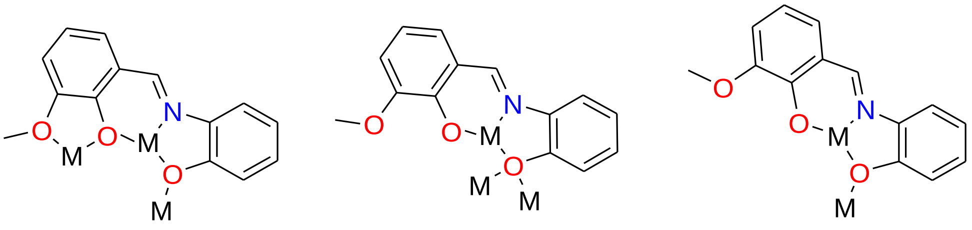


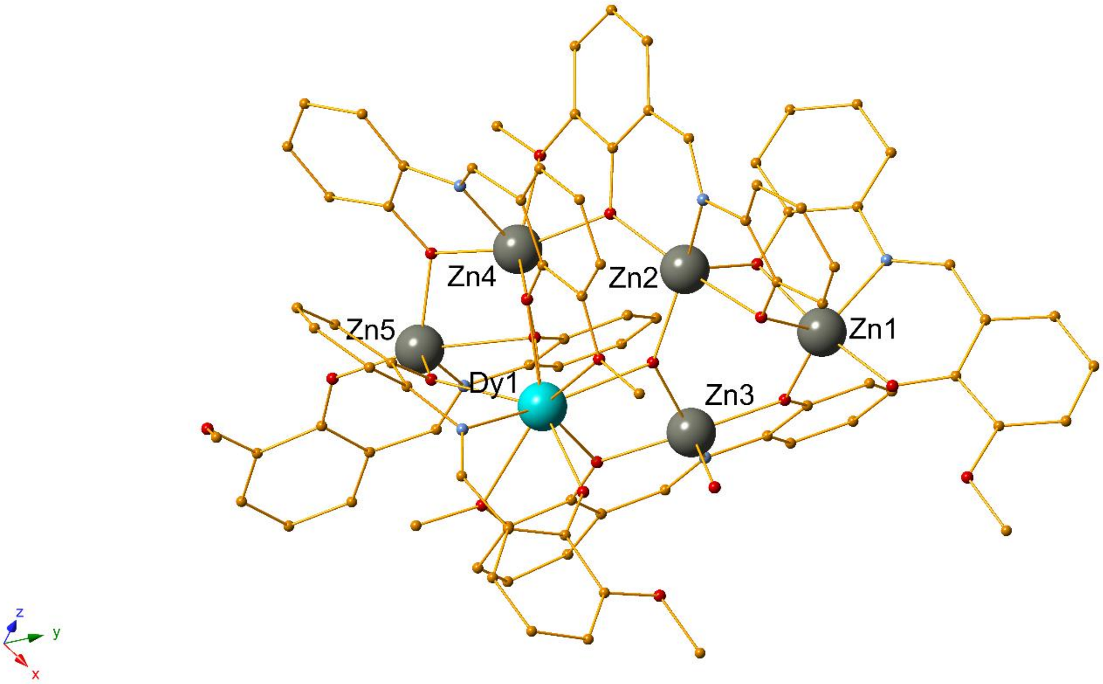
Figure 1. The structure of compound **1** (up) and its core (down). C, H atoms and lattice molecules are omitted for clarity. Colour code Zn (grey), Dy (light blue), O (red), N (blue).

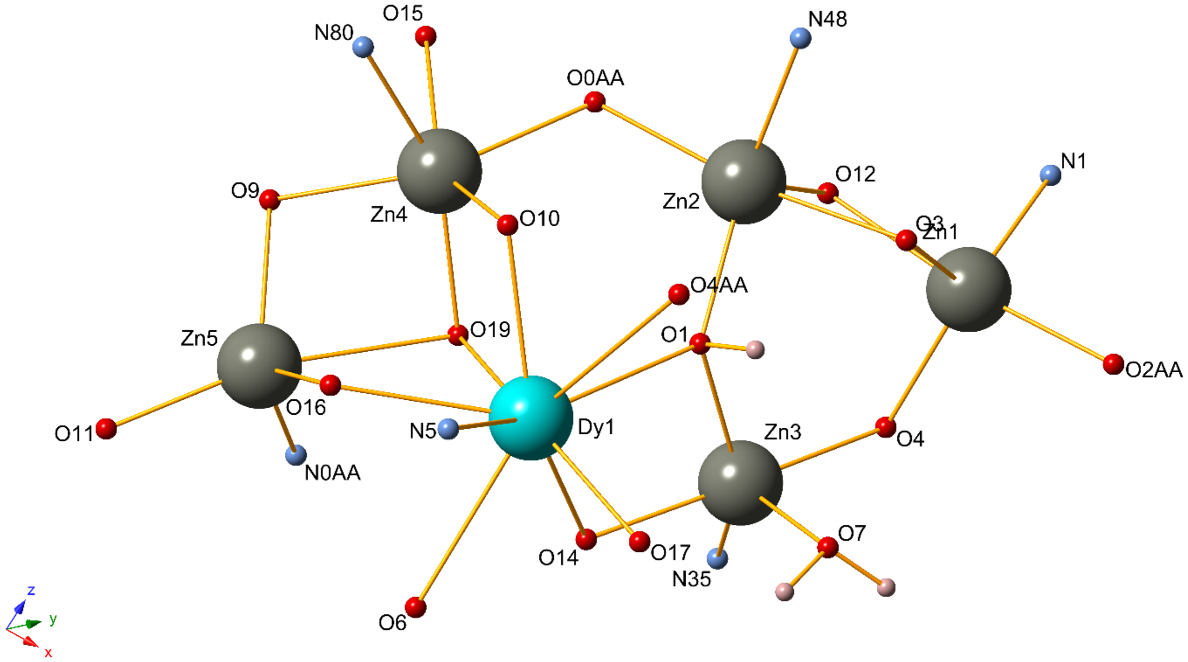


mode I mode II mode III

Scheme 3. The coordination modes found in **1** and **4**.

Compounds **4 – 6** crystallize in the triclinic *P*-1 space group and are isoskeletal, thus only **4** will be further described. The asymmetric unit of **1** contains five Zn^{II} ions, one Dy^{III} ion, six doubly deprotonated organic ligands (**L1**), one triply bridging hydroxyl group, one coordinated water molecule and two lattice molecules (one water and one acetonitrile). The main core of **1** can be considered as four fused triangles forming a distorted ‘‘chair’’ shaped core. The five Zn^{II} ions are situated in plane, while the Dy^{III} is situated 1.998Å above this plane. Each of the six organic ligands is chelated to one metal centre and further bridges other metal centres with the phenoxide and methoxide oxygen atoms. Three different coordination modes can found for the six organic ligands; 3, 1 and 2 for modes I, II and III, respectively (Scheme 3). The hydroxyl group bridges Zn2, Zn3 and Dy1 and is situated (0.311Å) above their plane. The coordination sphere of Zn3 is completed by one water molecule. Zn1 and Zn5 are five coordinated (O_4N) with trigonality index τ = 0.79 and 0.88, respectively, indicating that they adopt distorted trigonal bipyramidal coordination. Zn2 and Zn3 are five coordinated (O_4N) with trigonality index τ = 0.46 and 0.43, respectively, indicating that the coordination is between square pyramidal and trigonal bipyramidal [73] Zn4 is six coordinated (O_5N). From Shape software,[68] the geometry of Zn4 can be best described as trigonal prismatic, with S(P) value 5.126. The Dy^{III} centre coordinates to nine atoms (O_8N). From Shape software,[68] the coordination of Dy(1) can be best described as between a spherical tricapped trigonal prism and a spherical capped square antiprism [S(P) 1.606 and 1.656, respectively]. There are two Zn$^{II}\cdots$Dy^{III} distances of 3.4317(3) Å and 3.4452(3) Å and four Zn$^{II}\cdots$Zn^{II} distances at 3.0942(3) Å, 3.1296(3) Å, 3.527(3) Å and 3.626(3) Å. The coordinating water molecule forms two strong H-bonds, one with the methoxido oxygen atom (O7···O1AA) and the other with lattice water (O7···O3A). No other supramolecular interactions (H-bonds or stacking) can be found between neighbouring entities. According to our topological representation,[69,70] the main core of compound **4** can be described as **2,3,4M6-1**[70] and represents the first example of this configuration in Zn^{II}/Dy^{III} chemistry.





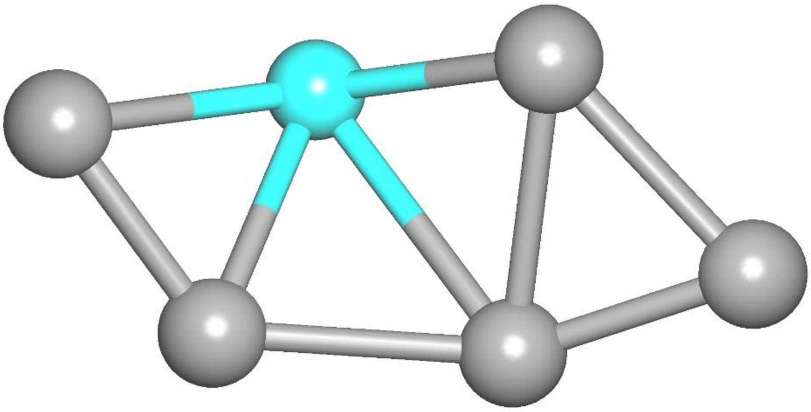
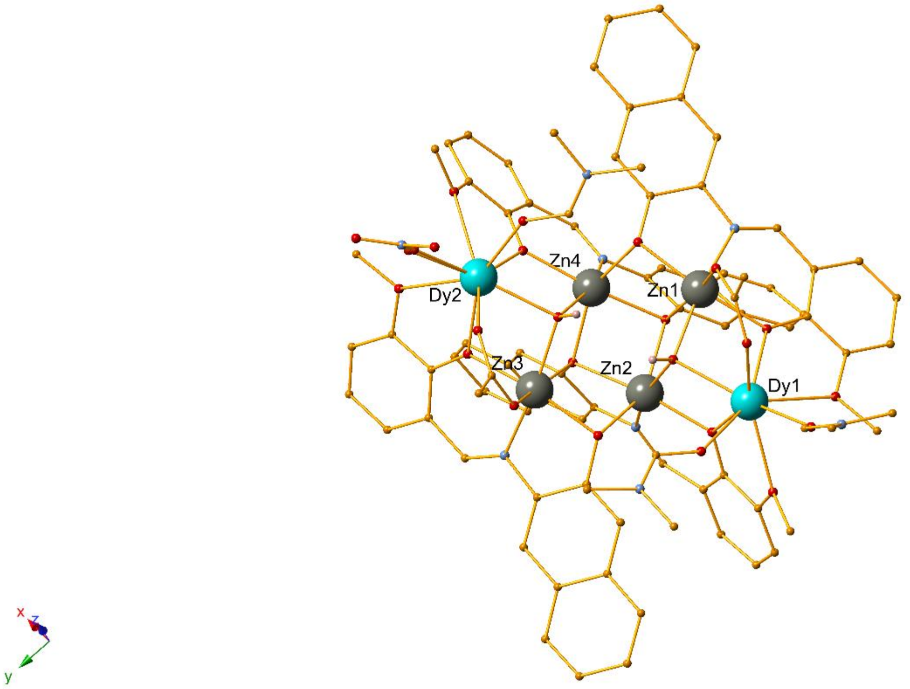
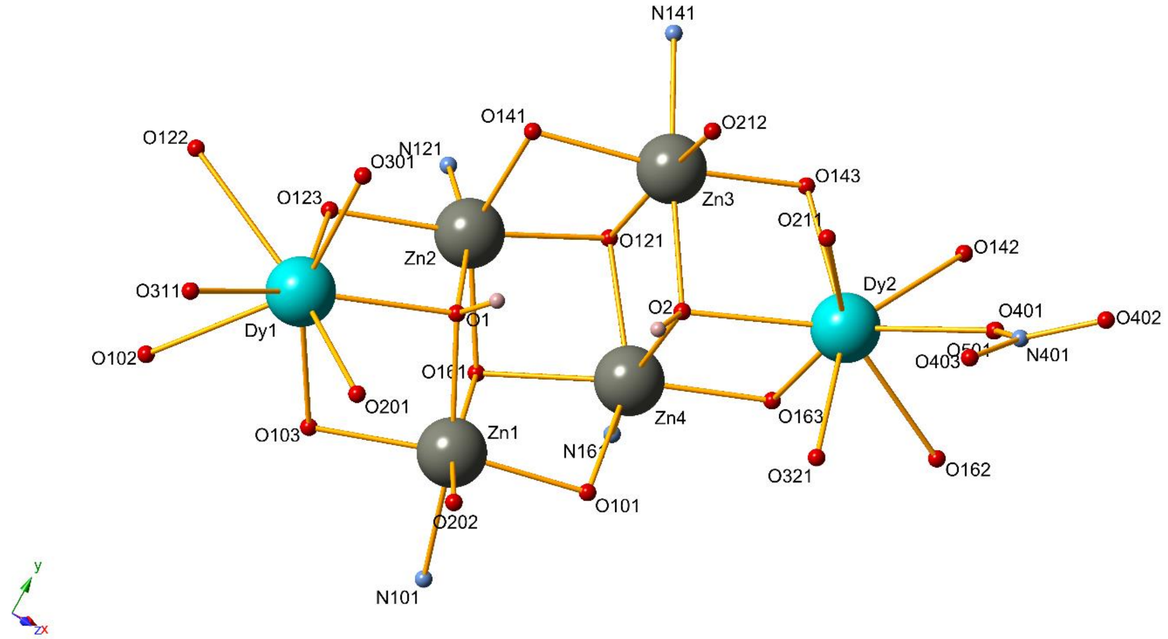


Figure 2. The structure of compound **4** (upper) and its core (middle). C, H atoms and lattice molecules are omitted for clarity. Colour code Zn (grey), Dy (light blue), O (red), N (blue), (Lower) The decorated **2,3,4M6-1** motif.

Compounds **7** –**9** crystallize in the monoclinic $P2_1/c$ space group and are isoskeletal, thus only **7** will be further described. The asymmetric unit of **7** contains four Zn^{II} ions, two Dy^{III} ions, four doubly deprotonated organic ligands (**L2**), two triply bridging hydroxyl groups, two acetates, , three coordinating and one lattice DMF molecules. One of the coordination sites of Dy is disordered with water and nitrate present. The core of **7** can be considered as four fused triangles. Dy2, Zn1, Zn2 and Zn3 are strictly coplanar, while Dy1, Zn4, Zn3 and Zn2 are nearly so. The distorted angle between the two mean planes is 62.39°. Alternatively, the core can be considered as a Zn^{II}_4 defect dicubane with each Dy^{III} ion attached in the wings. Each organic ligand is chelated to one Zn^{II} ion forming four neutral metalloligands (Zn**L2**) which are further bridged to neighbouring Zn^{II} and two Dy^{III} ions. In total each **L2** coordinates to three metal centres; two Zn^{II} and one Dy^{III}, exhibiting a coordination mode analogous to mode I (Scheme 3). Each hydroxyl group bridges three metal centres, O1 bridges Dy1, Zn2 and Zn4, and O2 bridges Dy2, Zn1 and Zn3, and O1 and O2 are 0.895 and 0.911Å, respectively above the plane. Each acetate group bridges two metal centres, Dy1 – Zn4 and Dy2, Zn1. Two DMF molecules coordinate to Dy1 and one N,N' – DMF and one nitrate complete the coordination geometry of Dy2. Each Zn^{II} ion has coordination number six (O_5N) albeit with a distorted octahedral coordination geometry. Each Dy^{III} ion coordinates to eight oxygen atoms. From Shape software,[68] the geometry of Dy(1) and Dy(2) can be best described as between biaugmented trigonal prismatic and triangular dodecahedral [S(P) values 1.763 and 1.868, respectively] and biaugmented trigonal prism [S(P) value 1.626], respectively. There are four Zn$^{II}\cdots$Dy^{III} distances between 3.3598(10) Å - 3.5333(10) Å and four Zn$^{II}\cdots$ Zn^{II} distances 3.1216(12) Å - 3.354(12) Å. The lattice N,N' – DMF molecule forms strong H-bonds with the two hydroxyl groups. No other supramolecular interactions (H-bonds or stacking) can be found between neighbouring entities. According to our topological representation,[69,70] the core of compound **7**, like the core of **4**, can be described as **2,3,4M6-1**[70]. A literature survey reveals that the same motif with the same M/Ln ratio can be seen in Ni/Ln[52] and Co/Ln[74] chemistry.


Dy2
Zn4
Zn1
Zn3
Zn2
Dy1
x
z
y


N141
O141
O212
N121
O143
O122
O301
Zn3
O123
O211
O142
O121
Zn2
Dy2
O311
O1
O2
O401
O402
O102
Dy1
O161
O501
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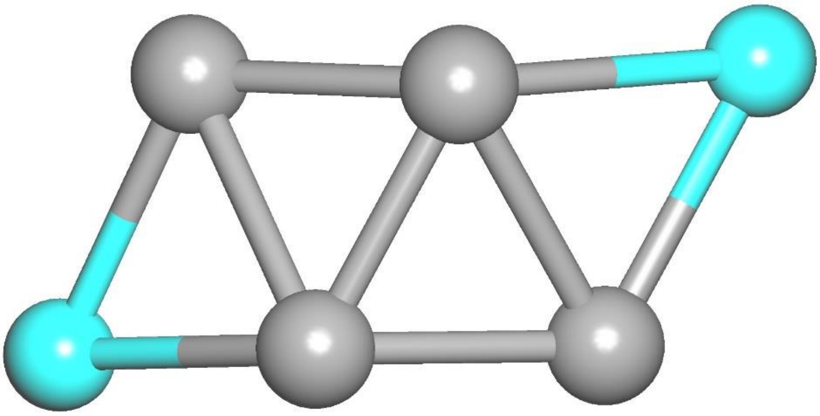
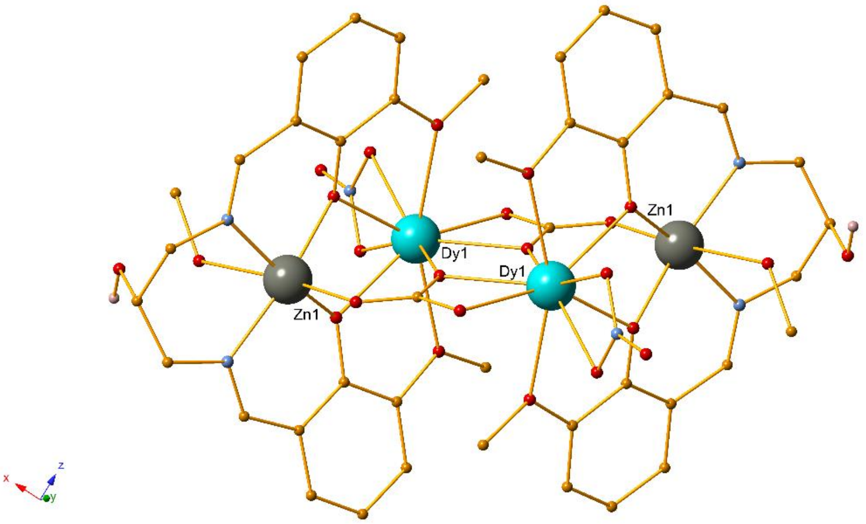
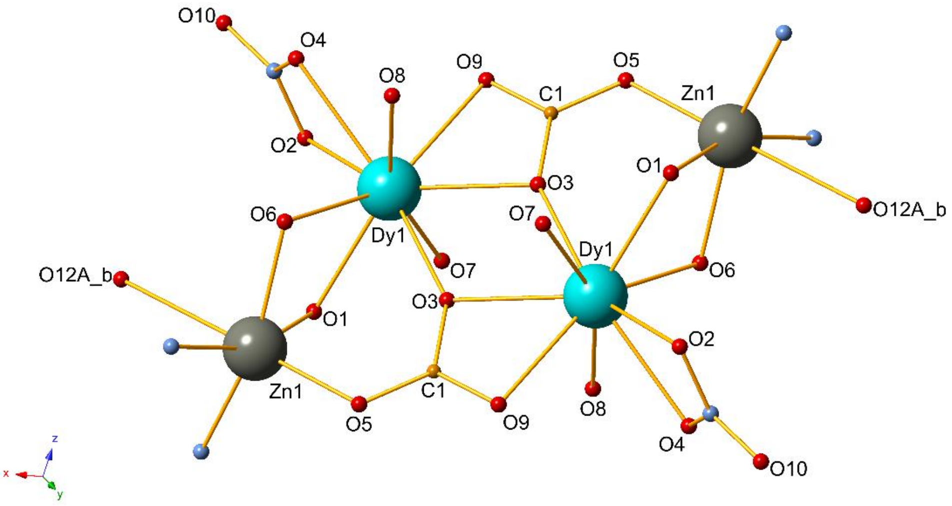


Figure 3. The structure of compound **7** (upper) and its core (middle). C, H atoms and lattice molecules are omitted for clarity. Colour code Zn (grey), Dy (light blue), O (red), N (blue), (Lower) The decorated **2,3,4M6-1** motif.

Compounds **10** – **12** are tetranuclear CCs synthesized from a mixture with a 2:1:1:4.5 Zn / Dy / ligand / base ratio in MeOH as solvent. All compounds crystallized in the monoclinic $P2_1/n$ space group and are isoskeletal, thus only **10** is further described. The asymmetric unit contains one Zn^{II} ion, one Dy^{III} ion, one doubly deprotonated organic ligand (H**L3**), one carbonate, one nitrate and one methanol molecule. The main core of **10** can be considered as two of Zn-Dy pairs bridged by two carbonate groups. The four metal centres are situated in a plane (Torsion angle Zn1 – Dy1 – Dy1 – Zn1 is 0). Each organic ligand is chelated to the Zn^{II} ion via the two imino N atoms and the two phenoxide O atoms and to the Dy^{III} ion via the two methoxido and two phenoxide O atoms (Scheme 3). The carbonate group bridges the two Dy^{III} ions via oxygen O3 and coordinates to Zn1 and the nitrate group is chelated to the Dy^{III} ion. The distorted octahedral geometry (O_4N_2) of the Zn^{II} ion is completed by the oxygen atom of a methanol molecule. The coordination number of the Dy^{III} ion is completed by one chelated nitrate. From Shape software,[68] the geometry of Dy(1) can be best described as spherical capped square antiprism [S(P) 2.489]. There is one $Zn^{II}\cdots Dy^{III}$ distance at 3.446(2) Å and one $Dy^{III}\cdots Dy^{III}$ distance at 4.007(2) Å. The central OH group of the organic ligand remains protonated and forms a strong H-bond with an oxygen atom of a carbonate group of a neighbouring $Zn^{II}_2Dy^{III}_2$ entity forming a two dimensional (2D) H-bonded framework, which extends perpendicular to the *ac* plane. According to our topological representation,[69,70] the main core of compound **10** can be described as **1,2M4-1**[70] and it is the fifth example of the motif in Zn^{II}/Dy^{III} chemistry.[32,34,39,41] A comparison between the H_3**L3** ligand used for the synthesis of **10** and the Schiff base ligands used in the previous reported the same **1,2M4-1** motif indicates that ,despite the existence of the central OH group, this type of ligand favours the formation of Zn-Ln[27] dimers which combine via the carbonate unit to the tetranuclear motif.





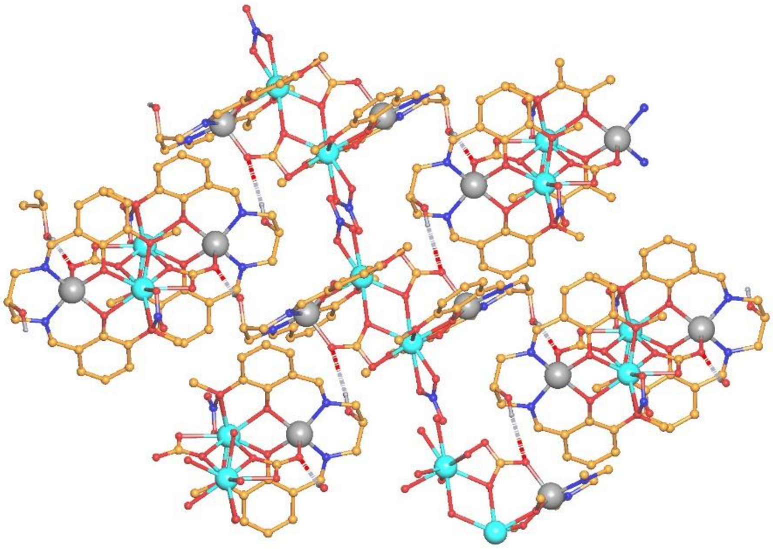


Figure 4. The structure of compound **10** (upper) and its core (middle).. C, H atoms and lattice molecules are omitted for clarity. Colour code Zn (grey), Dy (light blue), O (red), N (blue). (lower) The 2D H-bonded framework seen in the crystal structure of **10**.

Magnetic Properties. Magnetic measurements were made on selected powdered samples of compounds **1**, **7** and **10** to detect any SMM response. In preliminary AC measurements at zero field and two frequencies (10 and 1000 G) for the three compounds showed a similar response, was only observable by the tail of their AC signals. A series of new measurements under fields up to 3000 G showed a shift of the signals to higher temperature but AC peaks were not observable for **1** and **10**, (Figure S9). In contrast, well defined peaks were obtained for **7** for frequencies larger than 80 Hz and under a field of 3000 G, Figure S10. These measurements are evidence of strong tunnelling relaxation. Complementary susceptibility measurements were made for **7**. The $\chi_M T$ product at room temperature is 27.2 $cm^3mol^{-1}K$, slightly lower than the expected value of 28.3 for two Dy^{III} cations, (**Figure 5**, left). On cooling the $\chi_M T$ value decreases monotonically down to a final value of 20.7 $cm^3mol^{-1}K$ at 2 K. Magnetization experiments show a fast increase of the magnetization and a roughly linear dependence with the applied field in the 2 - 5 T field range. The final value of 9.4 $N\mu_\beta$ (for the two

Dy^{III} cations) under the maximum explored field of 5 T is lower than the expected suggesting a moderately high anisotropy.

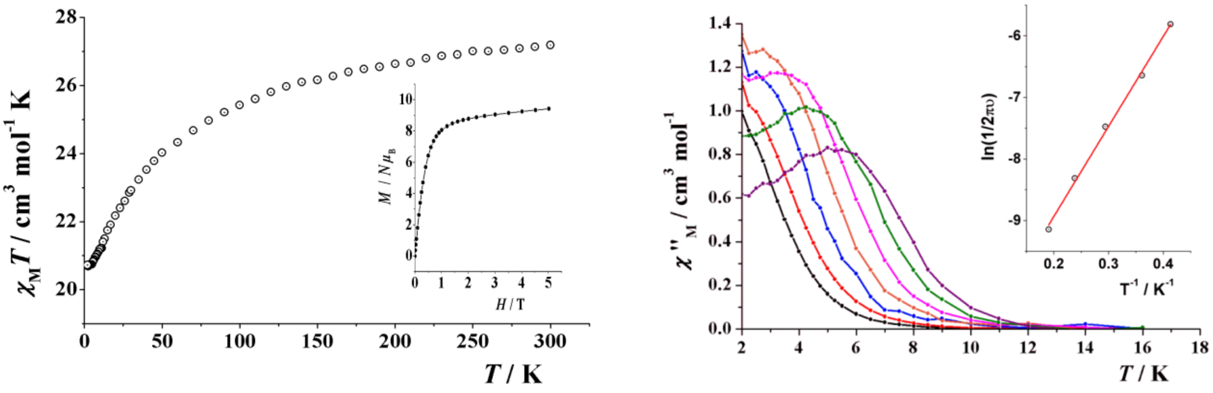


Figure 5. (left) $\chi_M T$ product vs. temperature for complex **7**. (right) AC susceptibility measurements for **7** at frequencies comprised between 23 and 1500 Hz.

The AC susceptibility measurement in the 80-1500 Hz frequency range show well defined frequency-dependent peaks. An Arrhenius fit of the maxima of the peaks for compound **7** gives an energy barrier of 10.2 cm^{-1} and $\tau_0 = 7.1 \cdot 10^{-6}$, (Figure 5, right). In the light of the structural data it shows that the two Dy^{III} cations are do not interact and are well isolated by the Zn_4 butterfly, compound **7** should be assumed as a Single-Ion-Magnet with a low barrier for the reversal of magnetization.

The magnitude of the barrier for systems of this kind is sensitive to multiple factors but the importance of the ligand field and the position of the charged or neutral donors around the lanthanide cation to determine the spatial arrangement of electronic density in the oblate-prolate model.[75–77] For the case of Dy^{III} its oblate electron density will generate larger barriers when negatively charged donors are above and below the radial plane of the cation. For **7** we are far from this situation because the O-phenoxo and O-carboxylate donors (with the shorter Dy-O distances) are placed on the same side of the coordination sphere whereas the other side is occupied by solvent molecules with two Dy-O distances larger than 2.5 Å. Calculation of the direction of the easy axis for the Dy^{III} cations, in low symmetry environments, such as that in of **7** can be performed with the MAGELLAN program.[78] The directions are similar, as can be expected from the similar (but not identical) coordination spheres around Dy1 and Dy2. The axes are directed towards the O-phenoxo donors and are inclined at 54.1° not parallel. Both factors in non-ideal arrangements of the charged O-donors around the Dy^{III} cations and the angle between the easy axes contribute to the low energy barrier of the system.

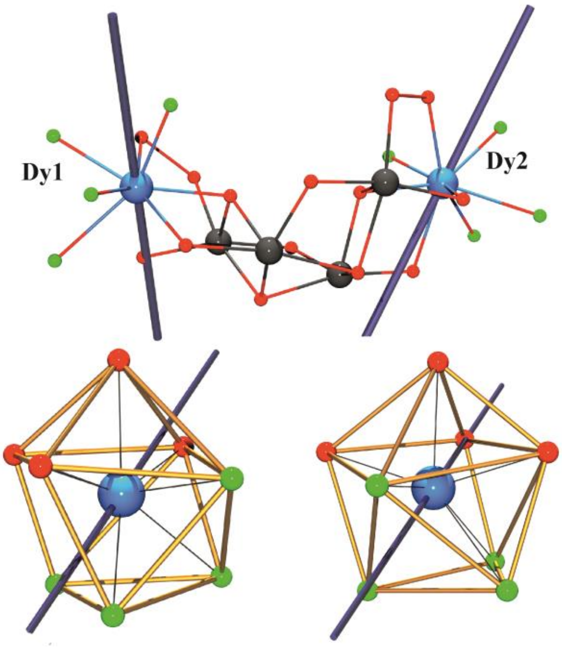


Figure 6. Relative position of the easy axis of the two Dy^{III} cations on the core of **7** (top) and in their DyO_8 coordination spheres (bottom). Red O-atoms corresponds to the O-phenoxo and O-carboxylate donors.

Photoluminescence. Solution luminescence measurements were made for nine of the CCs (**4-12**) in DMF and each of the three ligands (in MeCN). The spectra of the Dy^{III} containing species (Figure 7) show that broad ligand-based emission with some metal contribution (resulting in red-shift of the profile) dominates for each of the three compounds. Though each of these species have distinctly different absorption spectra, all three emit near 560 nm (**4**: λ_{em} = 560, 7: λ_{em} = 567, and **10**: λ_{em} = 555) correlating with the $^4F_{9/2}$ - $^6H_{13/2}$ transition that accompanies Dy^{III} emission. However, the broad nature of these signals indicates the significance of the ligand contribution to these emitters. Compounds **4 - 9** containing **L1** and **L2** exhibited similar behaviour (see Figure S11). However, Tb and Eu-containing complexes with **L3** (Figure S12-S13) displayed more typical emission spectra for lanthanide species with multiple narrow emission bands correlating to specific transitions within a broad ligand emission peak. In particular, **11** exhibits an emission spectrum centred at 550 nm comparable to that described by Murugesu and coworkers in 2009 with discrete $^5D_4 – ^7F_6$, $^5D_4 - ^7F_5$, $^5D_4 – ^7F_4$, $^5D_4 – ^7F_3$ transitions.[10] Emission in the NIR region was not observed below 1100 nm for any of the nine compounds tested.

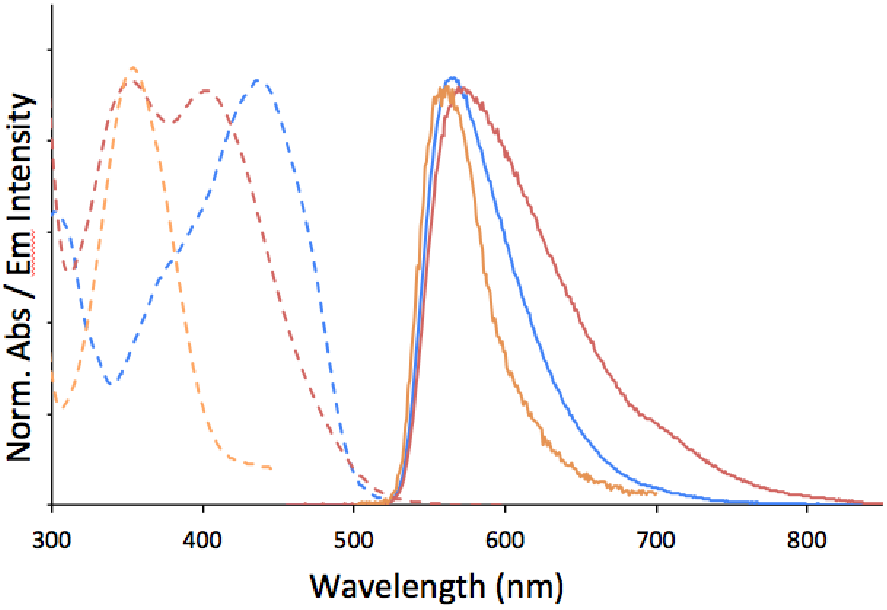
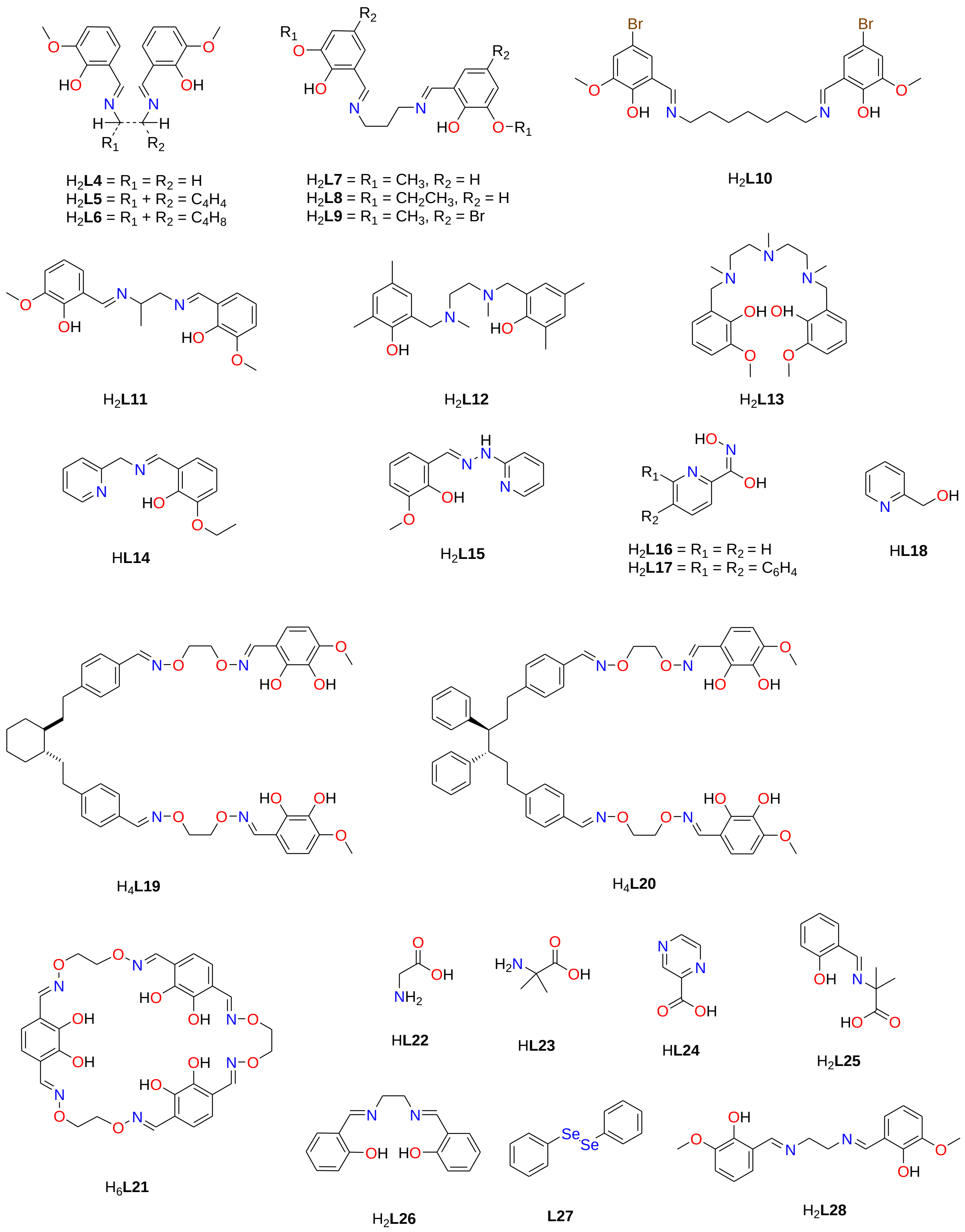


Figure 7. Normalised absorption (dashed line) and emission spectra (solid line) of compounds **4** (blue; λ_{ex} = 440), **7** (red; λ_{ex} = 400), and **10** (yellow; λ_{ex} = 355) recorded in DMF ($1x10^{-5}$M, 298 K).

Synthetic and Topological Aspects. Many polynuclear heterometallic Zn^{II}/Ln^{III} compounds have been reported in the literature, but a significant number of these are di or tri-nuclear species. There are fewer examples with a nuclearity above four, as above in Table 2 along with their core topology (**Figure 6**) and ligand (**Scheme 4**). Recently two Zn^{II}/Ln^{III} CC with nuclearity 30 were reported, showcasing the current interest in Zn^{II}/Ln^{III} chemistry.[79,80] Adopting our topological approach, all compounds can be presented by the NDK-symbol (Table 2). The most common nuclearity reported of the Zn^{II}/Ln^{III} clusters is four; it shows a number of topologies, which appear to be dependent on the structure of the ligand used for their synthesis.

The most common Zn^{II}/Ln^{III} CC topology, share a common ligand structure (Scheme 4-top Left). The **1,2M4-1** topology is formed in alcoholic solvents (MeOH, EtOH) (**Table 2** entries 1,4,9, 31); Zn^{II} ions are co-ordinated between the imine/secondary amine and deprotonated hydroxyl groups, while Ln^{III} ions are bound to the deprotonated hydroxyl and methoxy groups, forming a $[Zn^{II}Ln^{III}(L)]^{3-}$ unit. In these examples, counter-ions such as Cl or carbonate (from atmospheric CO_2) bridge between two $[Zn^{II}Ln^{III}(L)]^{3}$ units to form the **1,2M4-1** topology as a dimer. The coordination sphere is then completed by counter-ions such as NO_3 and solvent molecules for charge balance. Of the Schiff base ligands employed in polynuclear Zn/Ln CC synthesis, few demonstrate a nuclearity above five, tetranuclear compounds are the most frequently reported. This may be due to the many co-ordinating groups usually present and the ridged structural fragments. The **2,3M4-1** motif corresponding to a defect dicubane topology is very common motif in 3d/4f chemistry. We recently reported the first example of a family of Zn/Ln CCs that possess this motif,[17] and in this work we report another variation of this topology. The second most widespread motif in hexanuclear 3d/4f chemistry is **2,3,4M6-1** (Figures 2&3 lower). According to a survey in CSD,[71] 33 crystal structures[52,54,81–89] possess this motif that corresponds to four fused triangles aligned in a plane or forming a twisted boat. The first 3d/4f CCs with this topology can be found in a family of $Mn_4^{III}Ln_2^{III}$ compounds where Ln is Gd, Tb, Y, reported in 2008 by Oshi et al.[81] Other examples were reported in Mn/4f, [54,82,83] Ni/4f,[52,86] Co/4f,[74,84,85,87] and Fe/4f[88] chemistry.

The **2,4M6-1** motif, in comparison to the previously discussed examples, is less common in 3d/4f chemistry. This motif is best described as a single central triangle with 3 triangles fused side on to each side. Overall this forms a larger triangle, which can be planar or distorted. The first example of this topology was a heterometallic $Mn^{III}_3Li^{I}_3$ cluster[90] reported in 1991, until recently only homometallic clusters e.g. Co^{II}_3/Co^{III}_3[91] and Zn^{II}_6[92,93] have been reported. There are three examples of 3d/4f CCs with the **2,4M6-1** motif exist in the literature Cr^{III}_3 Ln^{III}_3 [94], $Co^{III}_3Ln^{III}_3$ [95] and $Ni^{II}_3Ln^{III}_3$[96] species. These examples show the same configuration of 3d and 4f ion nodes within the motif, with 4f ions occupying the vertices of the central triangle and 3d ions occupying the vertices of the larger triangle resulting in a core of Ln^{III} ions. Compounds **7-9** are the first examples of the **2,4M6-1** motif in Zn^{II}/Ln^{III} chemistry. In the present study, despite using organic ligands that offer similar pockets, a range of topologies was obtained and the unexpected involvement of the non-expected formed carbonate group, does not allow for a complete systematic study.



Scheme 4. The organic ligands used in the synthesis of Zn/Ln CCs.

Table 2. Reported Polynuclear Zn^{II}/Ln^{III} species with a nuclearity of 4 and above.

Entries	Complexes	Ligand	Nuclearity	Nuclearity	Topological Nomenclature	Reference
1	$[\mathrm{Nd_2(Zn}\mathbf{L5})_2\mathrm{Cl_6(MeOH)_2]\cdot MeOH}$ $[\mathrm{Dy_2Zn_2(}\mathbf{L6})_2\mathrm{(OAc)_2(CO_3)_2]\cdot 10CH_3OH}$	$\mathrm{H_2}\mathbf{L5}$ $\mathrm{H_2}\mathbf{L6}$	Zn_2Ln_2	4	**1,2M4-1**	34, 47
2	$[\mathrm{Zn_2Ln_3(}\mathbf{L4})_3\mathrm{(N_3)_5(OH)_2]}$ Ln = (Tb, Eu, Ho, Dy)	$\mathrm{H_2}\mathbf{L4}$	Zn_2Ln_3	5	**1,2,3M5-1**	10
3	$[\mathrm{Zn_2(}\mathbf{L6})_3\mathrm{Cl_2(OH)_3Ln_3(N_3)_2]}$; Ln=(La, Nd, Yb, Er)	$\mathrm{H_2}\mathbf{L6}$	Zn_2Ln_3	5	**1,2,3M5-1**	97
4	$[\mathrm{Zn^{II}{}_2Ln^{III}{}_2(}\mathbf{L7})_2\mathrm{(CO_3)_2(NO_3)_2]}$.solv Ln = Dy, Tb, Gd	$\mathrm{H_2}\mathbf{L7}$	Zn_2Ln_2	4	**1,2M4-1**	39
5	$[\mathrm{Zn^{II}{}_2Ln^{III}{}_2(}\mathbf{L8})_2\mathrm{(CO_3)_2(NO_3)_2]}$.solv Ln = Dy, Tb, Gd	$\mathrm{H_2}\mathbf{L8}$	Zn_2Ln_2	4	**1,2M4-1**	39
6	$[\mathrm{Zn_2Yb_2(}\mathbf{L6})_2\mathrm{(l\text{-}OH)2Cl4]\cdot 2MeCN}$	$\mathrm{H_2}\mathbf{L9}$	Zn_2Ln_2	4	**1,2M4-1**	98
7	$[\mathrm{Zn_8Ln_4\ (}\mathbf{L10})_2\mathrm{(OAc)_{20}(OH)_4]}$ Ln= Nd, Yb	$\mathrm{H_2}\mathbf{L10}$	Zn_8Ln_4	12	**2(1,2,3M6-1)**	99
8	$[\mathrm{Zn_4Eu_4(}\mathbf{L11})_4\mathrm{(CO_3)_6]\cdot EtOH}$	$\mathrm{H_2}\mathbf{L11}$	Zn_4Ln_4	8	**1,3M8-1**	35
9	$[\mathrm{Zn^{II}{}_2Eu^{III}{}_2(PhCOO)_2\ (}\mathbf{L12})_4]$ $[\mathrm{Zn^{II}{}_2Dy^{III}{}_2(PhCOO)_2(}\mathbf{L12})_4]$ $[\mathrm{Zn^{II}{}_2Tb^{III}{}_2(PhCOO)_2\ (}\mathbf{L12})_4]$	$\mathrm{H_2}\mathbf{L12}$	Zn_2Ln_2	4	**2M4-1**	100, 25, 101
10	$\mathrm{Zn_2Dy_2(}\mathbf{L12})_2\mathrm{(\mu_3\text{-}OH)_2(\mu_4\text{-}OH)(dbm)_2(MeOH)_2]X}$ (X = NO_3, ClO_4)	$\mathrm{H_2}\mathbf{L12}$	Zn_2Ln_2	4	**3M4-1**	40
11	$[\mathrm{Zn^{II}{}_2Ln^{III}{}_2(}\mathbf{L13})_2\mathrm{(CO_3)_2(NO_3)_2].4CH_3OH}$ Ln = Gd, Yb	$\mathrm{H_2}\mathbf{L13}$	Zn_2Ln_2	4	**1,2M4-1**	32
12	$[\mathrm{(Yb}\mathbf{L14})_2\mathrm{(H_2O)Cl(Oac)]_2\cdot[ZnCl_4]_2}$	$\mathrm{H}\mathbf{L14}$	Zn_2Ln_2	4	**3M4-1**	102
13	$[\mathrm{Zn_2Ln_2(OH)_2(}\mathbf{L15})_2\mathrm{(OAc)_5(EtOH)(H_2O)](ClO_4)\cdot\ 2EtOH\cdot 1.5H_2O}$ Ln= Gd, Dy	$\mathrm{H_2}\mathbf{L15}$	Zn_2Ln_2	4	**3M4-1**	33
14	$[\mathrm{Zn_3La}\mathbf{L19}\mathrm{(OAc)_3]}$	$\mathrm{H_4}\mathbf{L19}$	Zn_3Ln	4	**1,3M4-1**	103
15	$[\mathrm{Zn_3La}\mathbf{L20}\mathrm{(OAc)_3]}$	$\mathrm{H_4}\mathbf{L20}$	Zn_3Ln	4	**1,3M4-1**	104
16	$\mathrm{Zn_3La(}\mathbf{L21})\mathrm{(NO_3)_3(MeOH)_2]}$ / $\mathrm{Zn_3La(L}\mathbf{21})_3\mathrm{(NO_3)_2(MeOH)_6](NO_3)}$ .MeOH	$\mathrm{H_6}\mathbf{L21}$	Zn_3Ln	4	**1,3M4-1**	93
17	$\mathrm{Zn_4Dy(}\mathbf{L17}\mathrm{)4(DMF)_4(NO_3)_3}$ Ln=Dy, Tb, Y, Er	$\mathrm{H_2}\mathbf{L17}$	Zn_4Ln	5	**1,4M5-1**	38
18	$\mathrm{Zn_{16}Ln(}\mathbf{L17})_{16}\mathrm{(Py)_8(CF_3SO_4)}$ Ln= Tb, Dy, Yb, Er, Nd	$\mathrm{H_2}\mathbf{L17}$	$Zn_{16}Ln$	17	**2,3,8M17-1**	105

19	$Zn_9Ln_2(\mathbf{L17})_{10}(OH)(NO_3)_{2.25}Cl_{0.75}$; Ln=Dy, Tb, Eu	H2**L17**	Zn_9Dy_2	11	**1,1,2,2,5,7M11-2**	29
20	$[Zn_8Ln(\mathbf{L16})_8(OH)_3]$;Ln= Dy, Nd	$H_2\mathbf{L16}$	Zn_8Ln	9	**1,2,8M9-1**	29
21	$[Zn^{II}_8Gd^{III}_4(OH)_8(\mathbf{L18})_8(O_2CHMe_2)_8](ClO_4)_4$	H**L18**	Zn_8Gd_4	12	**3,6M12-1**	42
22	$[Zn_2Ln_2(L\mathbf{18})_4(PhCO_2)5(ROH)_2](ClO_4)$ (MeOH)2 Ln=Dy,Gd	H**L18**	Zn_2Ln_2	4	**3M4-1**	36
23	$[Zn_6Ln(OH)(\mathbf{L22})_6(NO_3)_3](OH)(NO_3)_2$. $8H_2O$ Ln = Er, Dy	H**L22**	Zn_6Ln	7	**2,6M7-1**	106
24	$[Zn_6Dy(\mathbf{L23})_6(OH)_3(Oac)_3(NO_3)_3]$	H**L23**	Zn_6Ln	7	**2,6M7-1**	107
25	$[Zn_6Ln_{24}(\mathbf{L24})_{24}(Oac)_{22}(\mu_3\text{-}OH)_{30}(H_2O)_{14}](ClO_4)_7(OAc)\cdot 2CH_3OH\cdot 26H_2O$ Ln = Gd, Tb, Dy	H**L24**	Zn_6Ln_{24}	30	**3(3,3,5M10-1)**	79
26	$[Zn^{II}_{12}Dy^{III}_{18}(OH)_{30}(\mathbf{L25})_{12}(sal)_6(OAc)_6(NO_3)_3(H_2O)_6](NO_3)_3$ 12MeOH $5H_2O$	$H_2\mathbf{L25}$	$Zn_{12}Ln_{18}$	30	**3,4,6,8M30-1**	80
27	$[Zn_2Ln(\mathbf{L26})_2(Py)_2(NO_3)_2][ZnLn(L)(Py)(NO_3)_3(H_2O)]$ (NO_3) (solv) Ln= Er, Gd	$H_2\mathbf{L26}$	Zn_3Ln_2	5	**(1,2M3-1)+(1M2-1)**	108
28	$[(THF)_8Ln_4Se(\mathbf{L27})_8][Zn_8Se(\mathbf{L27})_{16}]$.THF Ln=Sm, Nd	**L27**	Zn_8Ln_4	12	**(3,6M8-1)+(3M4-1)**	109
29	$[Zn_4Nd_2(\mathbf{L28})_4(1,4\text{-}BDC)_2][ZnNd(\mathbf{L28})(NO_3)_3(OAc)]_2$	$H_2\mathbf{L28}$	Zn_6Nd_4	10	**2(1,2M3-1)+2(1M2-1)**	110
30	$[Zn_2Ln_2(\mathbf{L1})_4(EtOH)_6].2(ClO_4)$	$H_2\mathbf{L1}$	Zn_2Ln_2	4	**2,3M4-1**	This work
31	$[Zn^{II}_5Ln(OH)(\mathbf{L1})_6(H_2O)]$	$H_2\mathbf{L1}$	Zn_5Ln	6	**2,3,4M6-1**	This work
32	$[Zn^{II}_4Dy^{III}_2(OH)_2(\mathbf{L2})_4(OAc)_2(NO_3)_2(DMF)_4]$	$H_2\mathbf{L_2}$	Zn_4Ln_2	6	**2,3,4M6-1**	This work
33	$[Zn^{II}_2Ln^{III}_2(\mathbf{L3})_2(CO_3)_2(NO_3)_2(CH_3OH)_2]$	$H_3\mathbf{L_3}$	Zn_2Ln_2	4	**1,2M4-1**	This work
34	$[Zn_2Ln_2(\mathbf{L1})_4(NO_3)_2(DMF)_2]$	$H_2\mathbf{L1}$	Zn_2Ln_2	4	**2,3M4-1**	17

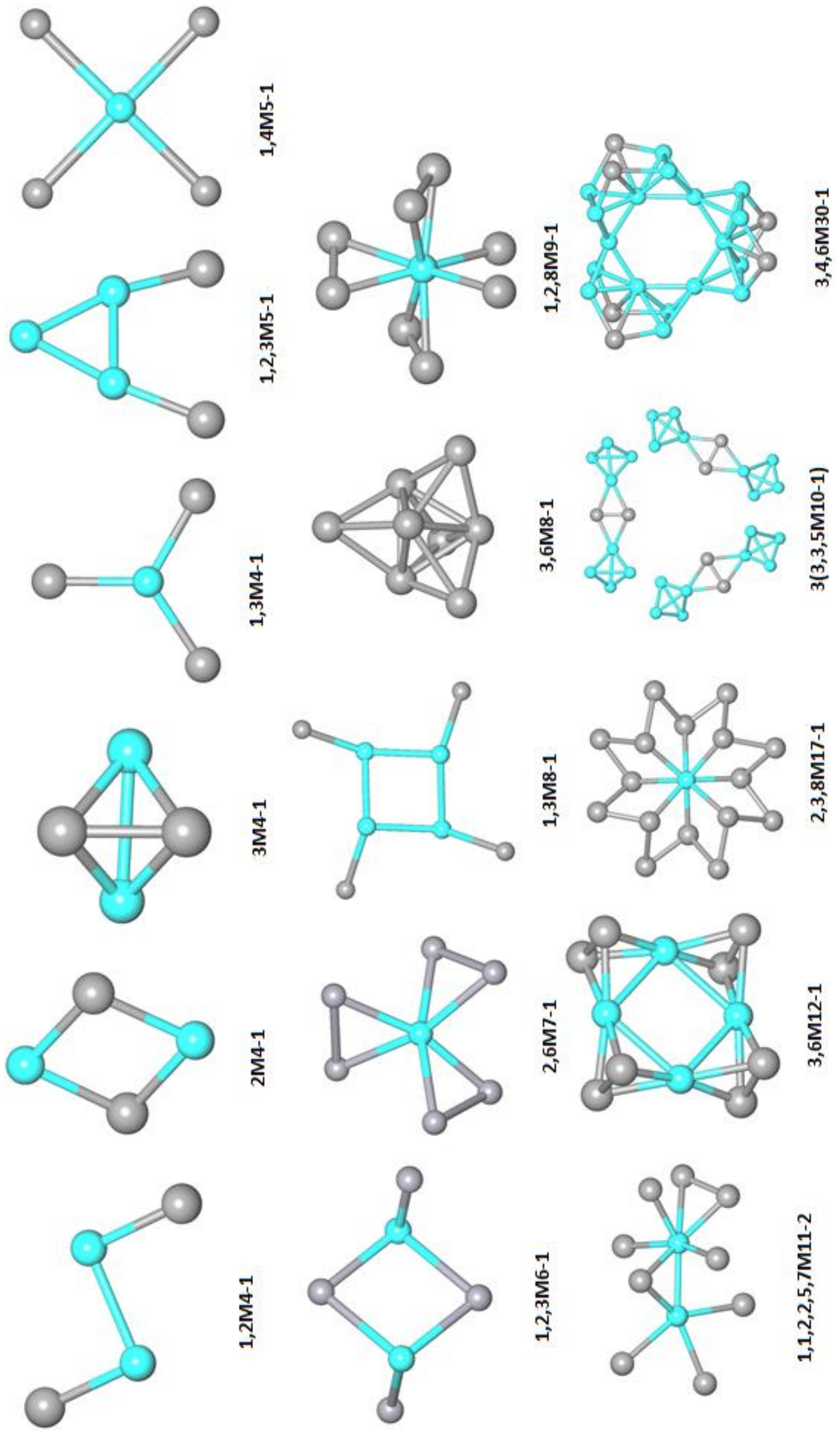


Figure 9. The topological representation of all known polynuclear Zn/Ln CCs

Conclusions

Reactions of zinc and lanthanide salts with various Schiff bases and a range of reaction conditions yielding four families of Zn/Ln CCs with robust and unseen topologies. Magnetic studies reveal the single ion magnet behavior of **7**, and luminescence studies indicate a significant ligand contribution to the emitters. Despite incorporating organic ligands, that offer similar coordination pockets, in similar synthetic ratios, products with a range of,nuclearities, motifs are obtained, showing that more systematic studies are required to fully understand the growth of such crystalline species and target the specific products. However, these structural studies should be carried out in a careful manner. When we studied the reaction that yielded **4** under reflux instead of room temperature, two different type of crystals were observed $[Zn_4Dy_7(OH)_4(O_2)_2(\mathbf{L1})_8Cl_4(H_2O)_4]Cl_5$ (**13**) and $[Zn_6Dy_4(OH)_2(\mathbf{L1})_{10}(MeOH)_2(H_2O)_4]Cl_2$ (**14**) and corresponding to **2,2,3,3M10-1** and **2,4,4,4M11-1** topologies, respectively (Fig S14). Our future studies will be focused as the following directions: a) to extend the synthetic study metal, ligand, co-ligands, ratios, aiming to obtain higher nuclearity Zn/Ln CCs and b) to test our ligand and coordination environment pockets selection in our topological approach to synthetic stratergy.[70,111]

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