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Ditopic Hexadentate Ligands with a Central Dihydrobenzodiimidazole Unit Forming a [2x2] Zn_4 Grid Complex

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A family of ditopic hexadentate ligands based on the parent compound 2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole (**L**) was developed and synthesized by using a straightforward condensation reaction, which forms the interlinking central benzo[1,2-d:4,5-d']diimidazole bridge in the ligand backbone. The two secondary amine groups of the benzodiimidazole unit tautomerize and allow the formation of two tauto-conformers, which upon treatment with metal salts forms different isomeric coordination complexes. Here we report six new derivatives (**1**–**6**) that can tautomerize (varying the pyrazolylpyridine part) and 14 derivatives (**7**–**13**) with different alkyl and benzyl substitution on secondary amino groups (of **L**) that prevent the tautomerization. This way, it is possible to study the properties of isomeric coordination complexes and their intrinsic cooperativity by the example of [2x2] grid complexes in the future. A [2x2] Zn_4 complex of the ligand **L** was synthesized and structurally characterized.

Introduction

Ditopic ligands are of continuing interest to the covalent integration of metal ions into molecular metal complexes.[1] Such ligands with at least two metal-binding domains can be used to synthesize homo and hetero multi-metallic complexes such as metal-containing supramolecular and macromolecular species (polymers, dendrimers, molecular wires) and oligonuclear grid type metal complexes.[2–5] If the coordination sites of ditopic ligands differ in their metal-chelating properties, discrimination by means of optimized synthetic protocols can yield hetero-metallic complexes.[6,7] The resulting complexes feature different catalytic, magnetic, and photophysical properties and may enable new cooperative functionality.[8–12] In this context, a number of bimetallic complex catalysts have been reported, e.g., in asymmetric allylic alkylation,[13] water oxidation,[14–18] epoxidation,[19] and transfer hydrogenation of ketones.[20] The probably most adaptable and established ligands for this purpose are derivatives of 2,2':6',2"-terpyridine (terpy) type containing, inter alia, pyrazole, tetrazole, and imidazole subunits.[21–29]

Whereas a number of ligands with tridentate chelates and tautomeric subunits have been described previously,[25,30,31,32,33] we are not aware of any examples that describe the presence of different tauto-conformers and the parallel formation of isomeric reaction products upon coordination to transition metal ions.

Recently, we reported on a homoditopic ligand **L**, which consists of two tridentate 2-(1H-imidazol-2-yl)-6-(pyrazol-1-yl) pyridine units interlinked via a central benzo[1,2-d:4,5-d'] diimidazole bridge (red, Figure 1a).[34] This bridging unit can simultaneously undergo two tautomerization processes between a secondary amine and imine functional groups. Besides, conformational isomers can be formed by rotation about the single bonds between the aromatic ring systems in the backbone of the ligand (Figure 1a). The rotational barriers of the single bonds connecting the pyridine and imidazole subunits enable two in-plane conformations, so-called S and C conformations (this denomination arises from their apparent shape, see Figure 1c). These two conformations are stabilized by the interaction between the N-based lone pair electrons and the H atoms of the neighboring aromatic rings (see Figure 1b).

The investigation of a solution sample of **L** by ^{1}H NMR spectroscopy revealed that both tauto-conformers are present in the solution and the $\mathbf{L_S}$:$\mathbf{L_C}$ ratio of one was estimated from ^{1}H

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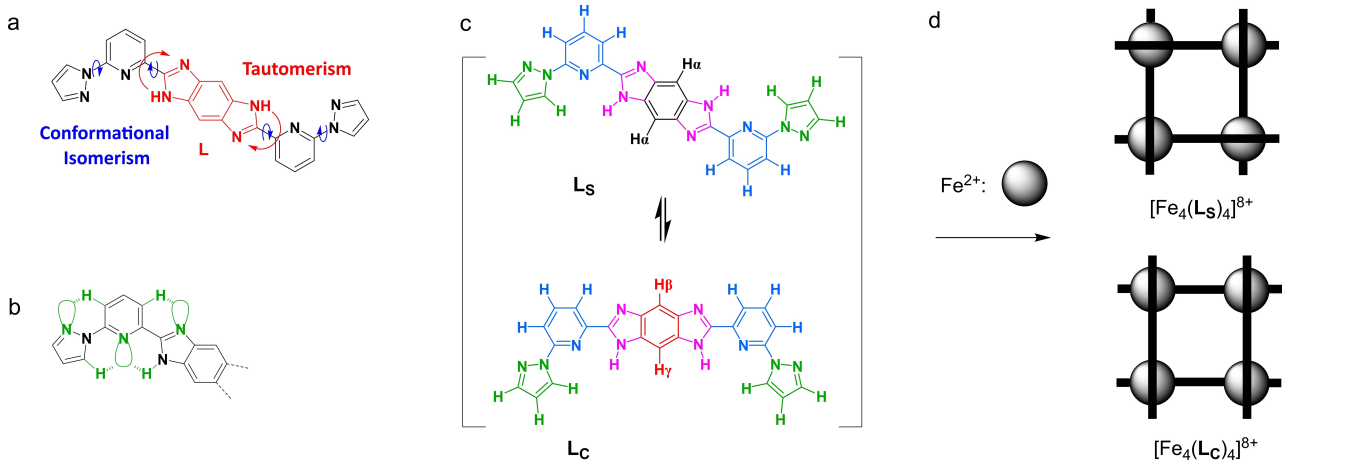


Figure 1. a) The conformational isomerism and tautomerism of **L**, b) stabilization of the planar ligand configuration by hydrogen contacts in the depicted conformation, c) the L_S and L_C conformers of **L** as found in solution,[34] d) the coordination of **L** to metal ions (e.g., Fe^{II}) develops the tautomerism-driven emergence of complexity (schematic representation of the cationic moieties of the isolated isomers of the [2x2] Fe^{II}_4 grid complexes, consisting of **L** (black bars) and Fe^{II} ions (grey spheres)).

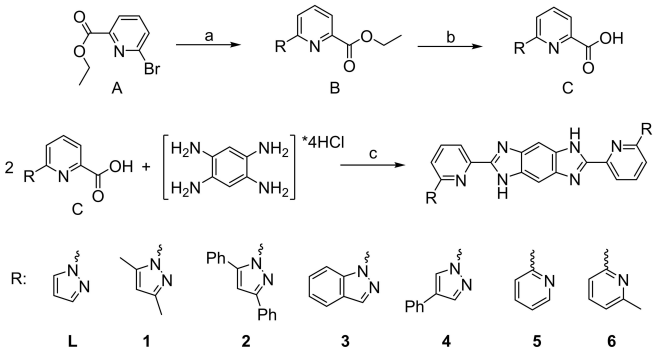
NMR studies in (deuterated) DMSO. Both tauto-conformers, L_S and L_C, can coordinate with metal ions in two tridentate binding pockets.

The different chelating modes of the homoditopic ligand **L** were read out by coordination with Fe^{II} ions. This read-out took place in parallel, and multiple coordination products differing in their structures and properties have been observed.[34] Among them, the two dominant, isomeric tauto-conformers $[Fe_4(L_S)_4]^{8+}$ and $[Fe_4(L_C)4]^{8+}$ of the [2x2] Fe^{II}_4 grid-type complexes were isolated as crystals by several steps of fractional crystallization.[34,35,36]

In the present work, we describe the synthesis, structures, and properties of some members of this new ligand family with respect to the substitution at the periphery and also to the central part of the ligand backbone, so that the ligands could not tautomerize; thus parallel product formation can be avoided. Here, we also present a coordination complex with Zn^{2+} metal ions and describe its properties.

Results and Discussion

The tauto-isomerization processes of the ligands and the formed complexes are interesting in themselves and may give insights regarding the general mechanisms of such tauto-isomerization processes. In the following, we will discuss the synthesis of six new ligands with a free NH group at the imidazole subunit but differing in their aromatic backbone. The intrinsic electronic and steric properties of ligand **L** can be easily adapted, which is apparent from the synthetic procedure shown in Scheme 1. The last step in the ligand synthesis is the condensation reaction of a carboxylic acid derivative (**C**) and a half equivalent of 1,2,4,5-benzenetetramine tetrahydrochloride in polyphosphoric acid (PPA). The character of the peripheral aromatic rings in the ligand can be determined in the synthetic step (a), where a suitable pyrazole derivative can be chosen



Scheme 1. Synthesis of the ligands **1** to **6** and the mother compound **L** (the first line is only for R = pyrazole derivative; in case of R being a pyridine, refer to Experimental section), a) K(pyrazolate), diglyme, 110 °C b) NaOH, EtOH/H_2O, 55 °C c) polyphosphoric acid (PPA), 200 °C.

(see R: **1**–**4** in Scheme 1). In the case of a peripheral pyridine substitution, as shown for **5** and **6**, we employed the respective [2,2′-bipyridine]-6-carboxylic acid, which was prepared either from 2,2′-bipyridine or 6′-methyl-[2,2′-bipyridine]-6-carboxylic acid in two steps. The final condensation reaction between the carboxylic acid derivative and benzene tetraamine in polyphosphoric acid (PPA) forms the respective ligand (**1**–**6**) in good yields.

The synthesized ligands **1** to **6** were entirely characterized by standard methods like ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. It was possible to determine the molecular structure of **3** and **5** by X-ray diffraction of single crystals crystallized from deuterated DMSO with a drop of CF_3COOD. Therefore, we found the compounds in the form of their dicationic triflate salts, showing a twofold protonation of each imidazole moiety (Figure 2). For comparison, Figure 2 also shows the reported compound **L**, which was crystallized as a neutral ligand from the DMF solution. All three

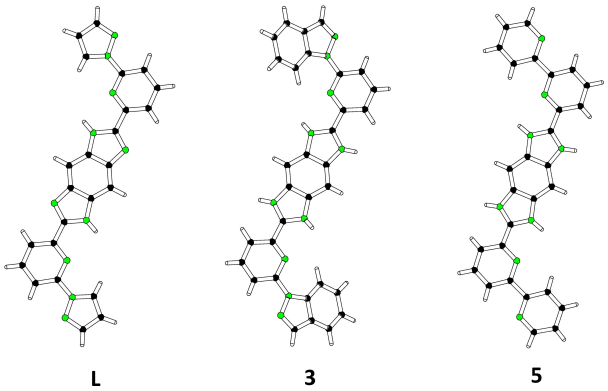


Figure 2. Molecular structure of **L**,[34] **3**, and **5** (C black, N green) obtained from single crystal XRD; the steric repulsion between H atoms of the imidazole and the indazole subunits in **3** is the reason for the larger torsion of the aromatic subunits with respect to the other two derivatives **L** and **5** (see text).

structures in Figure 2 show the molecules are in the S configuration (as depicted in Figure 1c).

A detailed examination of the X-ray data shows that the ligand **3** with indazole derivative is not in planar configuration in the crystal lattice. The torsion angles are 18° and 24°, respectively, between the imidazole/pyridine and the pyridine/indazole subunits. The reason for this torsion is the steric stress caused by the interaction between the hydrogen atoms of two opposite aromatic rings, namely the NH hydrogen of the imidazole and the hydrogen in the 7th position of the indazole ring. On the other hand, the ligand **5** has a near planar configuration in the crystal lattice. We calculated a plane out of all C and N atoms of the ligand backbone. Then we measured the distance between each carbon and nitrogen atom of the ligand **5** to this plane, calculating an average distance of 0.05 Å. The ligands are arranged in layers, and the distance between two adjacent layers is 3.36 Å. There are also small torsion angles found for **L** (13° pyrazole/pyridine and 1° pyridine/imidazole) and **5** (1° pyridine/pyridine and 6° pyridine/imidazole), but these are not caused by steric repulsion between H atoms.

We noticed that the protonation state of the ligand has to be carefully controlled during the workup. Otherwise, hydrochloride or phosphate adducts can form depending on the workup procedure. Since these ligands are hardly soluble in organic solvents that are not miscible with water, it is difficult to adjust the pH as quickly as could be done easily in a biphasic system. We suspended the compounds in aqueous/alcoholic media and changed the pH to the sufficient value (see experimental section for the preparation of **1·2HCl** and **1**), which is time-consuming since it requires time to work with such an inhomogeneous system. The protonation state of the final product was assessed by elemental analysis. Furthermore, the ^{1}H NMR spectroscopic investigations revealed that the hydrochloride adducts of these ligands **1** to **6** behave slightly different in solution compared to the free ligands.

As mentioned above, both tauto-conformers of **L** are present in solution, and their ratios could be determined by the integration of the singlet resonances of the central benzene moieties, H_α, H_β, and H_γ. In the case of DMSO (deuterated), we found an equimolar concentration of $\mathbf{L_S}$ and $\mathbf{L_C}$, both in dilute and concentrated solutions. This is different for the HCl adducts of such ligands **L**, **1**, **2**, **3**, and **4**, which were precipitated during the workup under acidic conditions. The ^{1}H NMR spectrum of **1·2HCl** adducts (with a concentration of 10 to 20 mM dissolved in deuterated DMSO) shows just one single resonance for the central benzene moiety corresponding to H_α. Furthermore, there is no (or only a very broad) signal for the secondary NH group at about 12.5 ppm. Apparently, we just found the S form of the compound from the NMR experiment. A successive dilution of the sample in 3 steps of one order of magnitude each is shown in Figure 3 for **1**·2HCl. The relatively sharp H**α** resonance (Figure 3a) becomes broader after dilution of one magnitude (Figure 3b) and is almost not visible after the next dilution step (Figure 3c). At a concentration of about 0.015 mM, the signals of H_α, H_β, and H_γ re-appear as it was observed for the free ligand. This phenomenon was also observed for the hydrochloride adducts of **L**, **2**, **3**, and **4** (see ESI, Figures S2-6). The coordination reaction of the presented ligands with transition metal ions such as Fe^{2+}, Co^{2+}, Zn^{2+} is generally carried out in solvents like acetonitrile, nitromethane, or methanol. The solubility of the ligands in these solvents is very low. Therefore, we can conclude from the ^{1}H NMR spectroscopic investigation that even for the HCl adducts, both tauto-conformers are present in solution and a divergent coordination[34] reaction takes place with at least two main coordination products. The tautomerization of the ligand is interesting and gives access to different coordination modes and products. It is possible to investigate the factors that

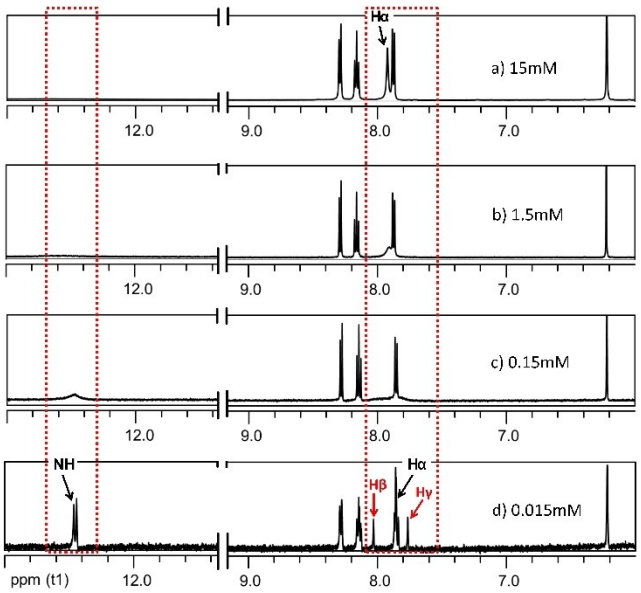
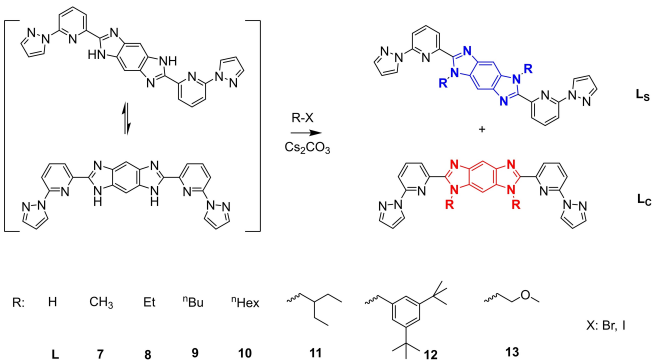


Figure 3. Concentration-dependent ^{1}H NMR spectra of **1·2HCl** in deuterated DMSO, at (a) a higher concentration of 15 mM, only the S-conformer is present, (d) a lower concentration of 0.015 mM, both the C- and S-conformers are present.

influence the isomerization of the formed grid complexes, such as temperature, solvent polarity, or pH.

However, if we want to study, in detail, the influence of the different coordination modes on the properties of the coordination products in the future, it may be advantageous to block the occurring tautomerization equilibrium of the two different tauto-conformers of **L** by chemical substitution at the secondary amine functionalities forming tertiary amines. The resulting ligands are either in a C- or S-type conformation which are unable to tautomerize and can be separated easily by column chromatography; thus, any parallel product formation is avoided during divergent coordination protocols. So to block the interconversion in ligand **L**, we treated it with alkyl or benzyl bromides or iodides either in DMF or DMSO as a solvent in the presence of Cs_2CO_3 as a base, as depicted in Scheme 2.



Scheme 2. Synthesis of the ligand pairs of **7** to **13** starting from the mother compound **L** (using either DMSO or DMF as a solvent and Cs_2CO_3 as a base for the reaction with the respective haloalkane or benzyl halide, see also the Experimental Section) different tautomers are chemically stabilized in this way so that an interconversion is not possible anymore.

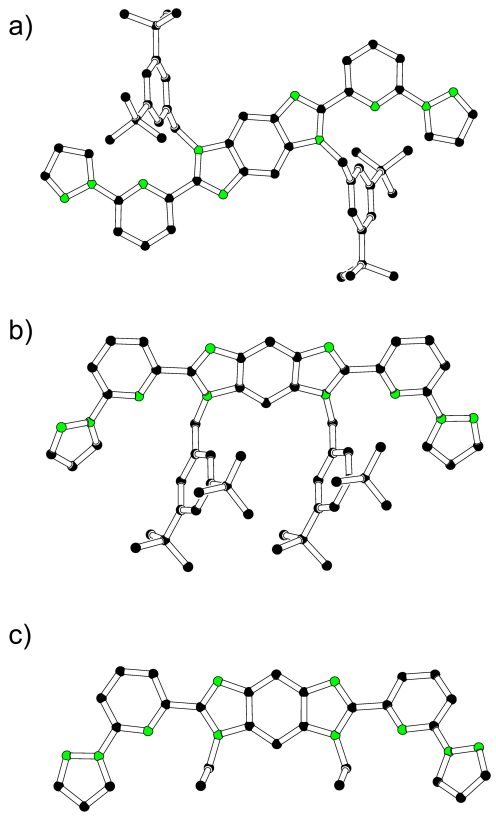


Figure 4. X-ray structures of a) $\mathbf{12_S}$, b) $\mathbf{12_C}$, and c) $\mathbf{8_C}$ (C black, N green, hydrogen atoms were omitted for clarity).

The seven pairs of prepared derivatives differ in the steric demand of the introduced substituents. Increasing the chain length of the alkyl substituent may influence the crystal packing of the resulting [2x2] Fe^{II} grid complexes in the solid-state and, therefore, also plays a role in the Spin Crossover (SCO) property of these compounds as seen before in mononuclear compounds.[37,38] The synthesized ligands $\mathbf{7_C}$/$\mathbf{7_S}$ to $\mathbf{13_C}$/$\mathbf{13_S}$ were characterized entirely by standard methods like ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis (see Experimental Section and ESI). It was possible to determine the molecular structure of $\mathbf{8_C}$, $\mathbf{12_C}$, and $\mathbf{12_S}$ by X-ray diffraction of single crystals (see Figure 4 and Table S2). The substitution of the secondary amine group of imidazole ring with alkyl and tert-butylbenzene moieties has improved the solubility of the ligands in solvents like chloroform/methanol, and even in diethyl ether in case of **12**.

The diverse nature of the prepared derivatives of **L** will allow in future a detailed study of different metal complexes prepared from these structurally related ligands and may uncover resulting structure-property relationships. As one first example, we want to report on a Zn_4 grid complex prepared from the reaction of equimolar amounts of **L** with the metal salt $Zn(ClO_4)_2 \cdot 6H_2O$ in acetonitrile. The complex formation leads to a clear yellow solution of a metal complex $[Zn_4(\mathbf{L})_4](ClO_4)_8$. The ^1H-NMR spectroscopic investigation of a sample of the reaction mixture showed 84% of the $[Zn_4(\mathbf{L_S})_4]^{8+}$ and 16% of a second complex, $[Zn_4(\mathbf{L_C})_4]^{8+}$ isomer, comparing the NMR data with the data of the Fe^{II} grid derivatives described elsewhere.[34] The second data set of the $[Zn_4(\mathbf{L_C})_4](ClO_4)_8$ isomer disappeared after recrystallization. The major fraction of the reaction product was isolated by slow diffusion of diisopropyl ether into the concentrated acetonitrile solution of the complex. The molecular structure of $[Zn_4(\mathbf{L_S})_4](ClO_4)_8$ could be determined by X-ray diffraction of single crystals obtained during this recrystallization process (Figure 5b).

So far, it was not possible to isolate the pure $[Zn_4(\mathbf{L_C})_4][ClO_4]_8$ isomer since both complexes (C and S) are of same color whereas in case of the Fe^{II} grid complexes, they show differences in their spin states. Figure 6 shows the ^1H NMR spectrum of the ligand **L** for comparison, where the **C** and the **S** conformation are in equilibrium, giving, therefore, three signals for the singlet resonances of the central benzene moieties, H_α, H_β, and H_γ.[34] (see Figure 1c and Figure 6) and the spectrum of $[Zn_4(\mathbf{L_S})_4][ClO_4]_8$ showing only one resonance H_α for this moiety. Besides NMR spectroscopy in solution and X-ray diffraction of single crystals, we also investigated the properties of $[Zn_4(\mathbf{L_S})_4][ClO_4]_8$ in the gas phase by high-resolution ESI-TOF mass spectrometry as shown in Figure 7. The mass spectrum of the reaction mixture following the coordination reaction is shown in the supporting information but has not such a high resolution as the one shown in Figure 7.

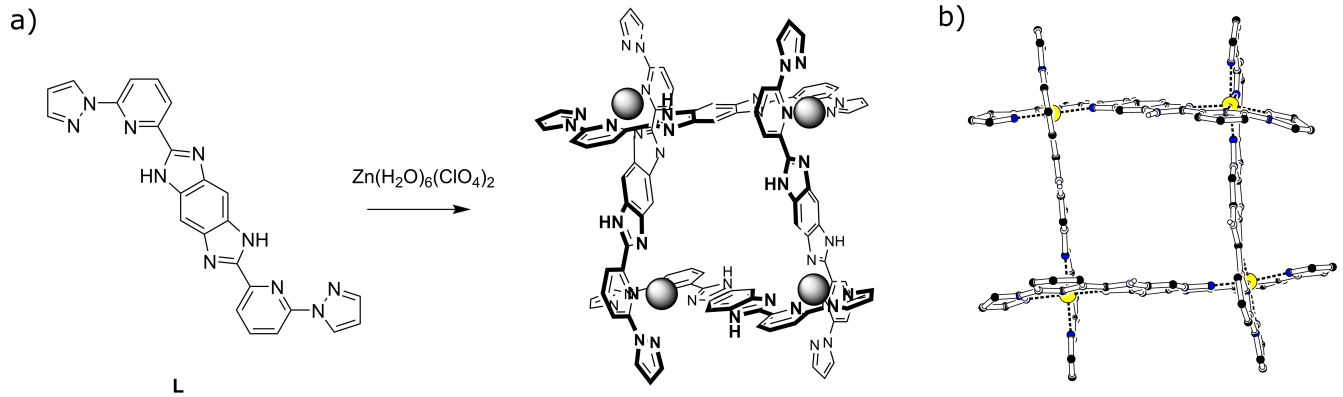


Figure 5. a) Schematic representation of the self-assembly process of **L** and octahedrally coordinating Zn^{II} ions leading to a [2x2] grid-type $[Zn_4(\mathbf{L})_4]^{8+}$ complex (Zn^{II} ions: gray spheres), b) Molecular structure of the $[Zn_4(\mathbf{L_S})_4]^{8+}$ tauto-conformer was determined by X-ray diffraction (top view, C black, Zn yellow, N blue).

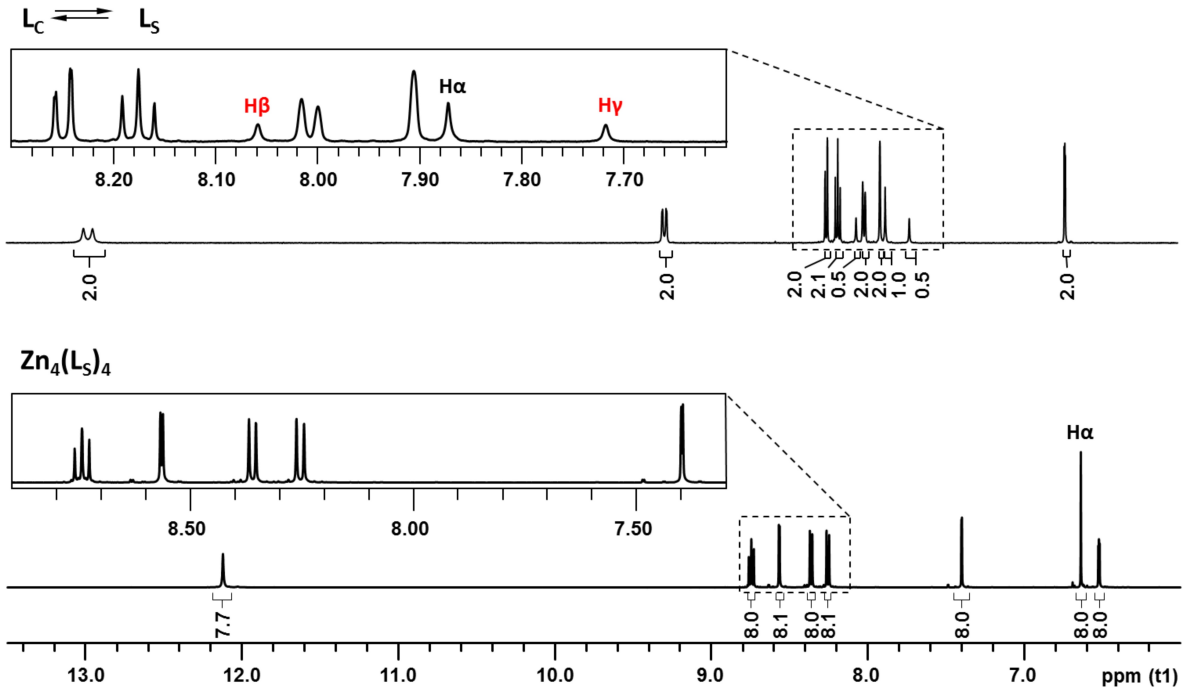


Figure 6. ^{1}H NMR spectra of $[Zn_4(\mathbf{L_S})_4][ClO_4]_8$ (bottom) in CD_3CN and **L** (top) in D_6-DMSO.

The absorption spectrum of $[Zn_4(\mathbf{L_S})_4][ClO_4]_8$ in acetonitrile is depicted in Figure 8, the absorption maxima (λ_{max}), and extinction coefficients (ε) for the complex are listed in the supporting information. The UV region of the absorption spectrum shows strong bands with maxima at 258 nm, 377 nm, and 394 nm, which corresponds to ligand-centered (LC) π-π^* transition bands. In the free ligand **L**, these bands are slightly higher in energy (see SI-Figure S33).

Conclusion

A family of ditopic hexadentate ligands with a central dihydrobenzo-diimidazole unit based on the mother compound 2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole (**L**) were successfully synthesized by condensation reactions. The two tautomerizing secondary amine functions of the benzodiimidazole unit are the origin of two tauto-conformers, which can translate into two different isomeric coordination complexes. We reported on six tautomerizing derivatives with different nitrogen containing aromatic subunits with different electronic and steric properties. The resulting [2x2] grid complexes of transition metals, e.g., Fe^{II}, Co^{II}, and the prepared ligands are interesting in themselves, regarding the structure-property relationship of the isomeric complexes and their isomerization equilibrium. The 14 derivatives with different alkyl and benzyl substitution on secondary amino groups do not tautomerize and can give access to only one [2x2] grid

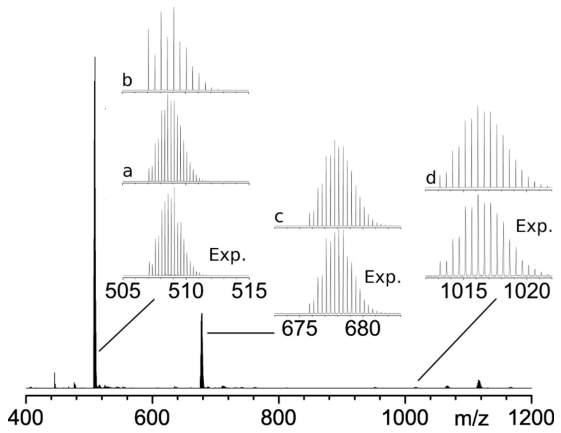


Figure 7. Mass spectrum of $[Zn_4(\mathbf{L_S})_4][ClO_4]_8$. The inset figures respectively correspond to (a) $[(C_{24}N_{10}H_{15}Zn)_4]^{4+}$ with a small contribution of (b) $[(C_{24}N_{10}H_{15}Zn)_2]^{2+}$, (c) $[(C_{24}N_{10}H_{15}Zn)_4\text{-}H]^{3+}$ and (d) $[(C_{24}N_{10}H_{15}Zn)^4 - 2H]^{2+}$. Some peaks corresponding to ClO_4^- adducts can also be observed at higher m/z.

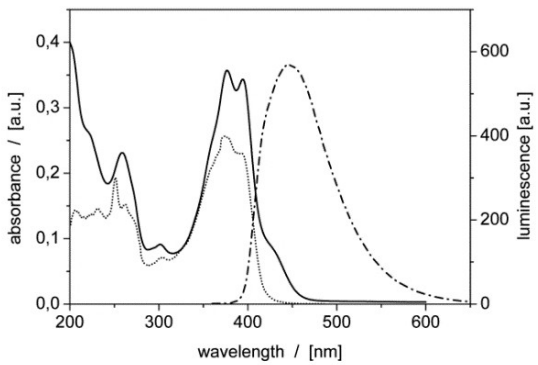


Figure 8. Electronic absorption (solid), excitation (dotted), and luminescence (dashed-dotted, $\lambda^{exc} = 340$ nm) spectra of the $[Zn_4(\mathbf{L_S})_4][ClO_4]_8$ complex in spectroscopic grade CH_3CN ($c = 2.1$ μM).

complex tauto-isomer. In this way, it will be possible to study the properties of isomeric coordination complexes and their intrinsic cooperativity on the models of [2x2] grid complexes in the future. Furthermore, we note that grid complexes built from the S form of such ligands show two chiral enantiomers. In the future, we will focus on the deconvolution/separation of these enantiomers and hope to study their properties in detail.

Experimental Section

General Methods: All the reactions were performed under Argon atmosphere using standard Schlenk techniques unless specified. All starting materials were purchased from commercial sources and were used as received. Solvents were freshly distilled over appropriate drying reagents. ^1H and ^{13}C NMR, COSY, HMQC correlation measurements were recorded using a Bruker Ultrashield plus 500 spectrometer with solvent-proton as an internal standard. Elemental analyses were carried out on a Vario Micro Cube. Infrared spectra were recorded using KBr-pressed pellets with a Perkin-Elmer Spectrum GX FT-IR spectrometer in the region of 4000–400 cm^{-1}. Mass spectrometric data were acquired with a MicroTOF-Q II Bruker for ESI-TOF. Electronic absorption and fluorescence spectra were acquired at room temperature for diluted solutions (e.g., 2×10^{-6} M) on a Cary 500 Scan UV-VIS-NIR spectrophotometer and a Cary Eclipse fluorescence spectrophotometer, respectively using a 1 cm quartz cell. For Zinc complex, Mass-spectrometric measurements we performed on a SYNAPT G2S-HDMS (Waters, Manchester, UK) using electrospray ionization.

X-Ray Crystallographic Data: Single crystal X-ray diffraction data were collected on a STOE IPDS II or IPDS2T diffractometer with monochromated Mo Kα radiation (0.71073 Å) at low temperatures. Using Olex2,[39] the structure was solved with the ShelXS[40] structure solution program using Direct Methods and refined with the ShelXL[41] refinement package using Least Squares minimization. Refinement was performed with anisotropic temperature factors for all non-hydrogen atoms (disordered atoms were refined isotopically); hydrogen atoms were calculated on idealized positions. Crystal data and structure refinement parameters are summarized in Tables S1–S3 in ESI.

Deposition Numbers 1436806 (for **L**), 1576574 (for **3**), 1576575 (for **5**), 1576576 (for **8c**), 1576577 (for **12c**), 1576578 (for **12s**), and 1576579 (for $\mathbf{[Zn_4(L_S)_4][ClO_4]_8}$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis of Ligands and Complex

Ligand L: (6-(pyrazol-1-yl)picolinic acid, 4.13 g, 21.8 mmol, 2.1 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (3.00 g, 10.6 mmol, 1 eq), and polyphosphoric acid (20 mL) were gently heated at 130 °C until the polyphosphoric acid got viscous enough to allow the stirring with a magnetic stirrer bar. Then the temperature was set to 200 °C. Caution: gas evolution leads to foam-formation. After 4 h at 200 °C, the reaction was stopped, allowed to cool below 100 °C and poured into crushed ice (100 g). The flask was rinsed with water. The aqueous suspensions were combined. The precipitate was filtered off. The solid was suspended in water, and the pH value was altered to 10 using NaOH (3 M). After the suspension was stirred for 1 h, the precipitate was collected again. Afterwards, it was suspended again in water, stirred, the pH was set to about 4 using HCl (1 mol/L). The precipitate was washed with MeOH (125 mL). Finally, the precipitate was suspended in MeOH (100 mL), stirred overnight, collected by filtration, dried in an oven at 120 °C for 3 h and then at vacuo (T = 90 °C). **Yield**: 4.27 g, 73 %. **^{1}H NMR** (500 MHz, $(CD_3)_2SO$, $c = 1.3$ mM): $\delta = 13.22$ (s, very broad, NH), 9.30 (d, $^3J = 2.3$ Hz, 2H, H5), 8.28 (d, $^3J = 7.1$ Hz, 2H, H7), 8.22 (dd (visual triplet), $^3J = 7.8$ Hz, $^3J = 7.8$ Hz, 2H, H8), 8.05 (d, $J = 8.0$ Hz, 2H, H9), 7.94 (s, very broad, 2H, Hα), 7.93 (d, $J = 0.9$ Hz, 2H, H3), 6.75 (dd, $^3J = 2.4$ Hz, $^3J = 1.7$ Hz, 2H, H4) ppm. **Elemental analysis (EA)** [**L***1.5H_2O*1.5HCl*0.5CH_3OH with $0.5(C_{49}H_{45}N_{20}O_4Cl_3)_{0.5}$ (542.2)]: calc. C 54.27, H 4.18, N 25.83; found C 54.58, H 4.45, N 25.45. **ES-MS** (in DMSO): m/z = 467.18 (100 %, $[M+Na]^+$). **IR** (KBr): $\tilde{\nu} = 3439, 3099.12, 1641, 1600, 1575, 1521, 1472, 1394, 1339, 1291, 1251,1239, 1203, 1170, 1150, 1137, 1040, 992, 973, 937, 915, 882, 811, 762, 739, 711, 651, 624, 593, 521, 418$ cm^{-1}.

Ligand 1·2HCl: (6-(3,5-dimethyl-pyrazol-1-yl)picolinic acid), 3.00 g, 13.8 mmol, 2 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (1.82 g, 6.42 mmol, 0.93 eq) and polyphosphoric acid (16 mL) were gently heated at 120 °C until the polyphosphoric acid got viscous enough to allow the stirring with a magnetic stirrer bar. Then the temperature was changed gradually to 200 °C (Caution: gas

evolution leads to foam-formation). After 4 hours at 200 °C, the reaction was stopped, allowed to cool below 100 °C and poured into crushed ice/water mixture (250 mL). The flask was rinsed with water. The aqueous suspensions were combined. The grey precipitate was slowly filtered off. The solid chunks were suspended in water by sonication and using a spatula while the pH value was altered to 9 using NaOH (1 M). After the suspension was stirred for 1.5 h the precipitate was collected again. Afterward, it was resuspended in water, stirred, the pH was set to about 3 using HCl (1 mol/L). The compound was suspended in MeOH (V = 100 mL), stirred for 2 h, and collected by filtration. Then the precipitate was suspended in DMSO (25 mL), stirred for 0.5 h, and collected by filtration. **Yield**: 3.14 g, 83 %.**^{1}H NMR** (500 MHz, $(CD_3)_2SO$): δ = 12.6 (s, 1.4H, NH, broad), 8.28 (d, ^3J = 7.5 Hz, 2H, H4), 8.15 (dd, ^3J = 7.8, ^3J = 7.8 Hz, 2H, H5), 7.90 (s, 2H, Hα), 7.86 (d,^3J = 8.0 Hz, 2H, H6), 6.21 (s, 2H, H1), 2.78 (s, 6H, H3), 2.25 (s, 6H, H2) ppm. **EA** [**1***H_2O*2HCl with ($C_{28}H_{28}N_{10}OCl_2$) (591.5)]: calc. C 56.86, H 4.77, N 23.68; found C 56.94, H 5.01, N 23.69. **ES-MS** (in DMSO): m/z = 523.198 (100 %, $[M+Na]^+ = [(C_{28}H_{24}N_{10})Na]^+$). **IR** (KBr): $\tilde{\nu}$ = 121, 2985, 2925, 1596, 1579, 1523, 1457, 1409, 1387, 1362, 1290, 1239, 1140, 1121, 1060, 1026, 993, 970, 884, 838, 812, 789, 733, 722, 654, 548, 492, 410 cm^{-1}.

Ligand 1: Ligand **1**·2HCl (2.88 g) was pestled and suspended in H_2O (30 mL) and MeOH (10 mL). The suspension was stirred and the pH was adjusted to 7 by using aqueous NaOH (1 mol/L). The pH value was controlled again after stirring overnight. Finally, the volume was reduced to 30 mL by rotary evaporation; the precipitate was collected by filtration, dried in an oven (at 120 °C) over the weekend. **Yield**: 2.37 g, 74 %. **1: ^{1}H NMR** (500 MHz, $(CD_3)_2SO$): δ = 12.46 (s, 2H, NH), 12.45 (s, 2H, NH), 8.28 (d, J = 7.5 Hz, 4H, H4), 8.14 (dd, ^3J = 7.8 Hz, 7.8 Hz, 4H, H5), 8.03 (s, 1H, Hβ), 7.85 (s, 4H, H6), 7.83 (s, 2H, Hα), 7.76 (s, 1H, Hγ), 6.21 (s, 4H), 2.77 (s, 12H, CH_3, H3), 2.25 (s, 12H, CH_3, H2) ppm. **EA** [**1***H_2O with ($C_{28}H_{26}N_{10}O$) (518.58)]: calc. C 64.85, H 5.05, N 27.01; found C 64.57, H 4.64, N 26.78. **ES-MS** (in DMSO): m/z = 501.218 (100 %, $[M+H]^+ = [(C_{28}H_{24}N_{10})H]^+$), m/z = 523.200 (100 %, $[M+Na]^+ = [(C_{28}H_{24}N_{10})Na]^+$). **IR** (KBr): $\tilde{\nu}$ = 3379, 3121, 2984, 2924, 1648, 1596, 1582, 1559, 1481, 1464, 1446, 1409, 1381, 1363, 1292, 1241, 1140, 1115, 1061, 1030, 989, 971, 886, 849, 812, 774, 723, 656, 632, 591, 497, 419 cm^{-1}.

Ligand 2·HCl: (6-(3,5-diphenyl-pyrazol-1-yl)picolinic acid), 0.763 g, 2.23 mmol, 2 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (0.284 g, 1.00 mmol, 0.9 eq) and polyphosphoric acid (5 mL) were used with procedure and workup same as that of synthesis of **Ligand 1·2HCl. Yield**: 0.641 g, 80 %. **^{1}H NMR** (500 MHz, $(CD_3)_2SO$, c = 15 mM): δ = 12.02 (s, 1.8 H, broad, NH), 8.38 (d, ^3J = 7.7 Hz, 2H, py-H4), 8.18 (dd, ^3J = 7.8, ^3J = 7.8 Hz, 2H, py-H5), 8.01 (d, ^3J = 7.2 Hz, 4H, Ph), 7.75 (s, 2H, broad, Hα), 7.68 (d, ^3J = 7.8 Hz, 2H, py-H6), 7.51 (dd, ^3J = 7.6, ^3J = 7.6 Hz, 4H, Ph), 7.41 (m, 12H, Ph), 7.31 (s, 2H, pz) ppm. **^{13}C-NMR** (126 MHz, $(CD_3)_2SO$): δ = 152.32, 151.99, 150.72, 148.00, 145.68, 141.00, 132.87, 130.78, 129.32, 129.01, 128.94, 128.85, 126.08, 121.48, 121.32, 106.25 ppm. **ES-MS** (in DMSO): m/z = 771.25 (100 %, $[M+Na]^+ = [(C_{48}H_{32}N_{10})Na]^+$). **EA** [**2***$H_2O$*HCl with ($C_{48}H_{35}N_{10}OCl$) (803.3)]: calc. C 71.77, H 4.39, N 17.44; found C 71.81, H 4.32, N 17.27. **IR** (KBr): $\tilde{\nu}$ = 3402, 3059,2968, 1643, 1597, 1577, 1471, 1443, 1424, 1404, 1377, 1361, 1299, 1237, 1198, 1147, 1078, 127, 992, 954, 913, 808, 768, 740, 698, 603, 561, 547, 518 cm[1].

Ligand 3·2HCl: (6-(indazol-1-yl)picolinic acid), 1.57 g, 6.61 mmol, 2 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (0.932 g, 3.28 mmol, 2.02 eq), and polyphosphoric acid (8 mL) were used with procedure and workup same as that of synthesis of **Ligand 1·HCl. Yield**: 1.51 g, 82 %.**^{1}H NMR** (500 MHz, $(CD_3)_2SO$): δ = 12.90 (s, 1.8 H, broad, NH), 9.05 (d, ^3J = 8.5 Hz, 2H, inda), 8.56 (s, 2H, H), 8.32 (d, ^3J = 7.8 Hz, 2H, pyH8), 8.24 (dd, ^3J = 7.8, ^3J = 7.8 Hz, 2H, pyH7), 8.15 (d, ^3J = 7.8 Hz, 2H, pyH6), 8.02 (s, 2H, bz), 7.98 (d, ^3J = 8.01 Hz, 2H, inda), 7.74 (dd, ^3J = 7.25, 7.3 Hz, 1H, inda), 7.44 (dd, ^3J = 7.3, ^3J = 7.3 Hz, 2H, inda) ppm. **^{13}C-NMR** (126 MHz, $(CD_3)_2SO$): δ = 153.97, 151.25, 147.07, 140.87, 138.60, 138.40, 129.04, 126.28, 123.43, 121.74, 119.41, 115.76, 115.35 ppm. **ES-MS** (in DMSO): m/z = 567.18 (100 %, $[M+Na]^+ = [(C_{32}H_{20}N_{10})Na]^+$), 545.17 (20 %, $[M+H]^+ = [(C_{32}H_{21}N_{10})]^+$). **EA** [**3***$H_2O$*0.5HCl*0.5$CH_3OH$ with 1/2($C_{65}H_{49}N_{20}O_3Cl$) (596.8)]: calc. C 65.40, H 4.14, N 23.47; found C 65.44, H 3.80, N 23.57. **IR** (KBr): $\tilde{\nu}$ = 3402, 3064, 2603, 1598, 1579, 1459, 1424, 1370, 1351, 1300, 1239, 1197, 1141, 1109, 1073, 1011, 968, 874, 843, 805, 749, 732, 632, 583, 525, 484 cm^{-1}.

Ligand 4·HCl: 6-(4-(4-(tert-butyl)phenyl)-pyrazol-1-yl)picolinic acid (2.90 g, 9.02 mmol, 2 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (1.19 g, 4.19 mmol, 0.93 eq) and polyphosphoric acid (20 mL) were used with procedure and workup same as that of synthesis of **Ligand 1·2HCl. Yield**: 2.36 g, 83 %. **^{1}H NMR** (500 MHz, $(CD_3)_2SO$, c = 21 mM): δ = 13.01 (s (broad), 2H, NH), 9.65 (s, 2H, H2), 8.41 (s, 2H, H1), 8.30 (d, J = 7.5 Hz, 2H, H3), 8.20 (t, J = 7.7 Hz, 2H, H4), 8.05 (d, J = 8.0 Hz, 2H, H5), 7.97 (s (broad), 2H, Hα), 7.85 (d, J = 7.4 Hz, 4H, H6), 7.53 (t, J = 7.6 Hz, 4H, H7), 7.36 (t, J = 7.3 Hz, 2H, H8) ppm. **^{13}C-NMR** (126 MHz, $(CD_3)_2SO$): δ = 151.30, 150.81, 147.46, 141.33 (C3), 140.86 (C1), 132.03, 129.52 (C7), 127.57 (C8), 126.04 (C6), 124.97 (C2), 124.91, 119.34 (C3), 112.57 (C5). **ES-MS** (in DMSO): m/z = 619.19 (50 %, $[M+Na]^+ = [(C_{36}H_{24}N_{10})Na]^+$), (100 %, $[2\,M+Na]^+ = [(C_{36}H_{24}N_{10})_2Na]^+$). **EA** [**4***$H_2O$*$CH_3OH$*HCl with ($C_{37}H_{31}ClN_{10}O_2$) (683.17)]: calc. C 65.05, H 4.57, N 20.50; found C 65.02, H 4.65, N 20.12. **IR** (KBr): $\tilde{\nu}$ = 3112, 1599, 1575, 1473, 1388, 1291, 1234, 1197, 1151, 1103, 1073, 1054, 992, 979, 953, 864, 835, 810, 763, 736, 694, 661, 595, 508 cm^{-1}.

Ligand 5: [2,2′-bipyridine]-6-carboxylic acid (0.703 g, 3.50 mmol, 2 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (0.447 g, 1.57 mmol, 0.9 eq) and polyphosphoric acid (5 mL) were gently heated to 195 °C (Caution: gas evolution leads to foam-formation). After 4 h at 195 °C, the reaction was stopped, allowed to cool below 100 °C and poured into 120 mL of water. The resulting melt was transformed to a powder by sonication and later by stirring. The precipitate was filtered off. The solid was suspended in water and the pH value was altered to about 9 using aqueous NH_3 (25 %). The product was collected by filtration, washed with water and MeOH. Finally, it was recrystallized from EtOH. **Yield**: 0.462 g, 56 %. **^{1}H NMR** (500 MHz, $(CD_3)_2SO$): δ = 13.00 (s, 2H, NH), 12.94 (s, 2H, NH), 9.02 (dd, ^3J = 13.7 Hz, ^3J = 7.9 Hz, 4H, H4), 8.8 (d, 4H, H1), 8.52 (dd, ^3J = 7.8, ^3J = 2.1 Hz, 4H, H5), 8.41 (d, ^3J = 7.4 Hz, 4H, H7), 8.16 (dd, ^3J = 11.1, ^3J = 11.1, ^4J = 4.5 Hz, 4H, H6), 8.11 (t, ^3J = 7.6 Hz, 4H, H3), 8.06 (s, 1H, Hβ), 7.91 (s, 2H, Hα), 7.81 (s, 1H, Hγ), 7.56 (dd, ^3J = 6.8, ^3J = 5.4 Hz, 4H, H2) ppm. **^{13}C-NMR** (126 MHz, $(CD_3)_2SO$): δ = 155.11, 155.06, 154.69, 151.55, 151.07, 149.33, 148.10, 142.49, 141.65, 138.65, 137.28, 133.58, 132.73, 124.61, 121.48, 121.38, 121.30, 120.86, 107.85, 99.76 ppm. **ES-MS** (in DMSO): m/z = 467.17 (8 %, $[M+H]^+$), m/z = 489.16 (100 %, $[M+Na]^+$), m/z = 955.32 (27 %, $[2\,M+Na]^+$); **A** [**5***3H_2O with ($C_{28}H_{24}N_8O_3$) (520.6)]: calc. C 64.61, H 4.65, N 21.53; found C 64.82, H 4.84, N 21.27. **IR** (KBr): $\tilde{\nu}$ = 3203, 3056,1641, 1583, 1566, 1462, 1428, 1391, 1294, 1277, 1240, 1153, 1119, 1052, 994, 968, 884, 827, 783, 745, 710, 686, 635, 622 cm^{-1}.

Ligand 6: 6′-methyl-[2,2′-bipyridine]-6-carboxylic acid (1.00 g, 4.67 mmol, 2.15 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (0.616 g, 2.17 mmol, 1 eq) and polyphosphoric acid (16 mL) were used with procedure and workup same as that of synthesis of **Ligand 5. Yield**: 0.657 g, 56 %. **^{1}H NMR** (500 MHz, $(CD_3)_2SO$): δ = 12.97 (s, 2H, NH), 12.91 (s, 2H, NH), 8.81 (dd, ^3J = 13.4, 7.8 Hz, 4H, H3), 8.51 (dd, J = 7.7, 2.3 Hz, 4H, H9), 8.39 (d, J = 7.7 Hz, 4H, H11), 8.15 (t, J = 7.8 Hz, 4H, H10), 8.05 (s, 1H, Hβ), 7.98 (dd, J = 7.7, 7.7 Hz, 4H, H4), 7.89 (s, 2H, Hα), 7.80 (s, 1H, Hγ), 7.42 (d, J = 7.6 Hz, 4H, H5), 4.37 (s, 6H, H7) ppm. **ES-MS** (in DMSO): m/z = 517.18 (100 %, $M+Na]^+ = [C_{30}H_{22}N_8Na]^+$), m/z = 1011.36 (40 %, $[2\,M+Na]^+ = [(C_{30}H_{22}N_8)_2Na]^+$). **EA** [**6***$^7/_3$ H_2O (536.6)]: calc. C 67.15, H 5.01, N 20.88; found C 67.28, H 4.73, N 20.80. **IR** (KBr): $\tilde{\nu}$ = 3191, 2250, 1636,

1571, 1452, 1432, 1385, 1315, 1283, 1239, 1167, 1152, 1077, 993, 972, 828, 794, 745, 716, 667, 633, 527, 420 cm^{-1}.

Ligand 7: An oven-dried Schlenk-flask was equipped with a magnetic stirrer bar and evacuated by three argon-vacuum cycles. **L** (0.895 g, 2.02 mmol, 1 eq) and Cs_2CO_3 (2.64 g, 8.10 mmol, 4 eq) were added and dried under vacuum at 100 °C overnight. The flask was flushed with Ar and DMF (40 mL, distilled from CaH_2) was added. After 30 min, the suspension was allowed to cool to ambient temperature. The iodomethane (0.855 g, 6.06 mmol, 3 eq, V = 0.375 mL) was added using a syringe. After the addition of the iodomethane the reaction was stopped after 24 h. The DMF was removed by distillation. The residue was taken into a mixture of $CHCl_3$/EtOAc and H_2O. After phase separation, the aqueous layer was extracted twice with $CHCl_3$. The organic layer was dried over Na_2SO_4, filtered, and reduced to dryness. Then the products were purified by column chromatography on silica as a stationary phase and a gradient of CH_2Cl_2 and MeOH as a liquid phase. **Yield**: **7S**: 0.254 g, 26 %, **7 C**: 0.221 g, 23 %.

Ligand 7S : ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.50 (d, ^3J = 2.4 Hz, 2H, H5), 8.26 (d, ^3J = 7.0 Hz, 2H, H7), 8.13 (s, 2H, Hα), 8.09 (d, ^3J = 7.9 Hz, 2H, H9), 8.05 (t, J = 8.0 Hz, 2H, H8), 7.70 (d, ^3J = 1 Hz, 2H, H3), 6.48 (dd, ^3J = 2.2 Hz, ^3J = 1.8 Hz, 2H), 4.41 (s, 6H, H14) ppm. A better resolution is observed in $CDCl_3$/CD_3OD [5 : 1]: ^{1}**H NMR** (500 MHz, $CDCl_3$/CD_3OD [5 : 1], $\delta(CDCl_3)$ = 7.26 ppm): δ = 8.52 (d, ^3J = 2.3 Hz, 2H, H5), 8.13 (t, ^3J = 4.2 Hz, 2H, H8), 7.97 (d, ^3J = 4.2 Hz, 4H, H7, H9), 7.74 (s, 2H, Hα), 7.70 (s, 2H, H3), 6.47 (s, 2H, H4), 4.30 (s, 6H, H14) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$/CD_3OD [5 : 1], $\delta(CDCl_3)$ = 77.16 ppm): δ = 150.70, 150.39, 147.92, 142.34 (C3), 140.07, 139.95 (C7), 135.43, 127.03 (C5), 122.15 (C8), 112.65 (C9), 108.17 (C4), 98.42 (Cα), 32.81 (C14) ppm. **EA** [**7S***H_2O with ($C_{26}H_{22}N_{10}O$) 490.5 g/mol]: calc. C 63.66, H 4.52, N 28.55; found C 63.91, H 4.47, N 28.84. **ES-MS** (in DMSO, DMF, $CHCl_3$): m/z = 605.088 (100 %, $[M+Cs]^+ = [(C_{26}H_{20}N_{10})Cs]^+$ = 605.092). **IR** (KBr): $\tilde{\nu}$ = 3403, 3060, 2924, 2849, 1692, 1593, 1577, 1514, 1475, 1453, 1393, 1368, 1280, 1231, 1201, 1147, 1073, 1034, 948, 896, 763, 810, 752, 653,622, 591 cm^{-1}.

Ligand 7 C: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.54 (d, J = 2 Hz, 2H, H5), 8.24 (d, ^3J = 7.5 Hz, 2H, H7), 8.15 (s, 1H, Hβ), 7.91 (d, J = 8.2 Hz, 2H, H9), 7.83 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, H8), 7.77 (s, 2H H3), 7.59 (s, 1H, Hγ), 6.55 (m, 2H, H4), 4.41 (s, 6H, H14) ppm. ^{1}**H NMR** (500 MHz, $CDCl_3$:CD_3OD [5 : 1], $\delta(CDCl_3)$ = 7.26 ppm): 8.45 (d, ^3J = 2.5 Hz, 2H, H5), 8.10 (dd, ^3J = 4.9, ^3J = 3.7 Hz, 2H, H8), 8.04 (s, 1H, Hβ), 7.88 (d, ^3J = 4.9 Hz, 2H, H7), 7.87 (d,^3J = 3.6 Hz, 2H, H9), 7.67 (d, ^3J = 1.5 Hz, 2H, H3), 7.24 (s, 1H, Hγ), 6.44 (dd, ^3J = 2.5, ^3J = 1.7 Hz, 2H, H4), 4.24 (s, 6H, H14) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 150.42, 150.36, 148.04, 142.45 (C3), 140.07 (C7), 139.74, 135.92, 127.16 (C5), 122.29 (C8), 112.71 (C9), 108.45(Cβ), 108.27 (C4), 89.25 (Cγ), 33.00 (C14) ppm. **EA** [**7 C***$^1/_3H_2O$ with $^1/_3$($C_{78}H_{62}N_{30}O$) 478.5 g/mol]: calc. C 65.26, H 4.35, N 29.27; found C 65.01, H 4.47, N 29.16. **ES-MS** (in DMSO, DMF, $CHCl_3$): m/z = 495.173 (100 %, $[M+Na]^+ = [(C_{26}H_{20}N_{10})Na]^+$ = 495.177). **IR** (KBr): $\tilde{\nu}$ = 3395, 3147, 3088, 2942, 1632, 1594, 1575, 1516, 1472, 1456, 1396, 1367, 1337, 1280, 1235, 1202, 1152, 1076, 1037, 950, 899, 842, 810, 773, 619, 592 cm^{-1}.

Ligand 8: The procedure used to prepare **ligand 7** was employed with **L** (0.895 g, 2.02 mmol, 1 eq), Cs_2CO_3 (2.64 g, 8.10 mmol, 4 eq), DMF (30 mL) and bromoethane (0.658 g, 6.06 mmol, 3 eq, V = 0.45 mL) **Yield**: **8S**: 357 mg, 35 %, **8 C**: 385 mg, 38 %.

Ligand 8S: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.51 (d, ^3J = 2.5 Hz, 2H, H5), 8.25 (d, ^3J = 7.2 Hz, ^{4}J = 1.0 Hz, 2H, H7), 8.05 (d, ^3J = 8.1 Hz, 2H, H9), 8.02 (t, ^3J = 7.4 Hz, 2H, H8), 7.82 (s, 2H, Hα), 7.76 (d, ^3J = 1.2 Hz, 2H, H3), 6.52 (m, 2H, H4), 4.91 (q, ^3J = 7.1 Hz, 4H, H14), 1.65 (t, J = 7.1 Hz, 6H, H15) ppm. ^{1}**H NMR** (500 MHz, $CDCl_3$/CD_3OD [5 : 1], $\delta(CDCl_3)$ = 7.26 ppm): δ = 8.44 (2H, H5), 8.13 (2H, H7), 7.96 (4H, H8, H9), 7.75 (2H, Hα), 7.68 (2H, H3), 6.45 (2H, H4), 4.82 (4H, H14), 1.58 (6H, H15) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$/CD_3OD [5 : 1], $\delta(CDCl_3)$ = 77.16 ppm): δ = 150.79, 150.25, 148.18, 142.48 (C3), 140.46, 140.09 (C8), 134.46, 127.04 (C5), 122.47 (C7), 112.98 (C9), 108.43 (C4), 98.71 (Cα), 40.81 (C14), 15.09 (C15) ppm. **EA** [**8S***$^1/_2H_2O$ with 1/2($C_{56}H_{50}N_{20}O$) 509.6 g/mol]: calc. C 66.00, H 4.95, N 27.49; found C 66.23, H 4.98, N 27.11. **ES-MS** (in DMSO): m/z = 633.1 (100 %, $[M+Cs]^+ = [(C_{28}H_{24}N_{10})Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3425, 3159, 3100, 2956, 1670, 1596, 1576, 1518, 1473, 1455, 1397, 1374, 1278, 1260, 1200, 1149, 1074, 1042, 994, 947, 906, 834, 807, 770, 732, 653, 423 cm^{-1}.

Ligand 8 C: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.50 (d, ^3J = 2.5 Hz, 2H, H5), 8.37 (d, J = 7.6 Hz, 2H, H7), 8.27 (s, 1H, Hβ), 8.03 (d, ^3J = 8.0 Hz, 2H, H9), 7.93 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, H8), 7.79 (d, ^3J = 1.0 Hz, 2H, H3), 7.25 (s, 1H, Hγ), 6.54 (dd, 2H, H4), 4.90 (q, ^3J = 7.1 Hz, 4H, H14), 1.67 (t, ^3J = 7.1 Hz, 6H, H15) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 150.70, 149.50, 148.71, 142.26 (C3), 140.43, 139.63(C8), 135.14, 126.67 (C5), 122.37 (C7), 112.59(C9), 109.78(Cβ), 108.21(C4), 88.28(Cγ), 40.71 (C14), 15.22 (C15) ppm. **EA** [**8 C***1/3 H_2O with 1/3($C_{84}H_{74}N_{30}O$) 506.6 g/mol]: calc. C 66.39, H 4.91, N 27.65; found C 66.41, H 4.93, N 27.39. **ES-MS** (in DMSO): m/z = 633.1 (100 %, $[M+Cs]^+ = [(C_{28}H_{24}N_{10})Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3430, 3156, 3100, 2956, 1669, 1596, 1576, 1518, 1473, 1456, 1397, 1374, 1278, 1259, 1200, 1149, 1074, 1042, 995, 947, 906, 834, 807, 770, 733, 652 cm^{-1}.

Ligand 9: The reaction was carried out as described for compound **8** using: **L** (0.895 g, 2.02 mmol, 1 eq), Cs_2CO_3 (2.65 g, 8.10 mmol, 4 eq), DMSO (20 mL, dried over mole sieves), 1-iodobutane (0.817 g, 4.42 mmol, 2.2 eq, V = 0.5 mL). After the addition of the 1-iodobutane, the reaction was stopped after 21 hours. **Yield**: **9S**: 184 mg, 16 %, **9 C**: 478 mg, 42 %.

Ligand 9S: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.54 (d, ^3J = 2.4 Hz, 2H, H5), 8.38 (d, ^3J = 7.6 Hz, 2H, H7), 8.10 (d, ^3J = 8.1 Hz, 2H, H9), 8.02 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, H8), 7.86 (s, 2H, Hα), 7.81 (d, ^3J = 1.0 Hz, 2H, H3), 6.55 (dd, ^3J = 2.4 Hz, ^3J = 1.7 Hz, 2H, H4), 4.93 (t, ^3J = 7.6 Hz, 4H, H14), 2.04 (visual quintet, 4H, H15), 1.47 (visual sextet, 4H, H16), 0.97 (t, J = 7.4 Hz, 6H, H17) ppm. ^{1}**H NMR** (500 MHz, $CDCl_3$/CD_3OD [5 : 1], $\delta(CDCl_3)$ = 7.26 ppm): δ = 8.46 (d, J = 2.54 Hz, 2H, H5), 8.18 (dd, ^3J = 6.4, ^3J = 2.2 Hz, 2H, H7), 7.99 (m, 4H, H8, H9), 7.78 (s, 2H, Hα), 7.73 (d, J = 1.6 Hz, 2H, H3), 6.48 (dd, ^3J = 2.5 Hz, ^3J = 1.7 Hz, 2H, H4), 4.82 (t, 4H, H14), 1.94 (q, 4H, H15), 1.36 (q, 4H, H16), 0.86 (t, ^3J = 7.4, ^3J = 7.4 Hz, 6H, H17) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$/CD_3OD, 5 : 1): δ = 150.74, 150.46, 148.27, 142.50 (C3), 140.23, 140.09 (C8), 134.84, 126.95 (C5), 122.62 (C7), 113.06 (C9), 108.31 (C4), 98.94 (Cα), 45.61 (C14), 32.05 (C15), 20.20 (C16), 13.71 (C17) ppm. **EA** [**9S***1/2 CH_2Cl_2 *1/2CH_3OH with [1/2($C_{66}H_{70}N_{20}Cl_2O$)], 615.2 g/mol]: calc. C 64.43, H 5.74, N 22.77; found C 64.46, H 6.21, N 22.46. **ES-MS** (in DMSO): m/z = 579.26 (100 %, $[M+Na]^+ = [(C_{32}H_{32}N_{10})Na]^+$), m/z = 689.16 (100 %, $[M+Cs]^+ = [(C_{32}H_{32}N_{10})Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3366, 3206, 2955, 2924, 2866, 1688, 1595, 1578, 1520, 1474, 1453, 1395,1324, 1272,1239, 1204, 1154, 1080, 1034, 942, 900, 850, 810, 752 cm^{-1}.

Ligand 9 C: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.53 (d, ^3J = 2.4 Hz, 2H, H5), 8.38 (d, ^3J = 7.6 Hz, 2H, H7), 8.29 (s, 1H, Hβ), 8.08 (d, ^3J = 8.1 Hz, 2H, H9), 8.01 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, H8), 7.81 (d, ^3J = 1.1 Hz, 2H, H3), 7.32 (s, 1H, Hγ), 6.55 (dd, ^3J = 2.4 Hz, ^3J = 1.8 Hz, 2H, H4), 4.93 (t, ^3J = 7.5 Hz, 4H, H14), 2.04 (visual quintet, 4H, H15), 1.46 (m, 4H, H16), 0.99 (t, J = 7.4 Hz, 6H, H17) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 150.76, 149.88, 148.87, 142.39 (C3), 140.32, 139.75 (C8), 135.61, 126.75 (C5), 122.65 (C7), 112.80 (C9), 109.69 (Cβ), 108.20 (C4), 89.06 (Cγ), 45.59 (C14), 32.21 (C15), 20.42 (C16), 14.03 (C17) ppm. **EA** [**9 C*** H_2O with [$C_{32}H_{34}N_{10}O$], 574 g/mol]: calc. C 66.88, H 5.96, N 24.37; found C 67.19, H 5.79, N 24.84. **ES-MS** (in DMSO): m/z = 557.277 (20 %, $[M+H]^+ = [(C_{32}H_{32}N_{10})H]^+$), m/z = 579.259 (100 %, $[M+Na]^+ = [(C_{32}H_{32}N_{10})Na]^+$). **IR** (KBr): $\tilde{\nu}$ = 3392, 3154, 3102, 2956, 2929, 2868, 1633, 1596, 1574, 1519, 1470, 1456, 1395, 1338, 1323, 1273, 1202, 1150, 1077, 1038, 994, 942 897, 859, 811, 756, 657 cm^{-1}.

Ligand 10: The reaction was carried out as described for compound **8** using: **L** (0.895 g, 2.02 mmol, 1 eq), Cs_2CO_3 (2.65 g, 8.10 mmol, 4 eq), DMSO (20 mL) and 1-iodohexan (0.856 g, 4.04 mmol, 2 eq, V = 0.528 mL). **Yield**: **10S**: 0.186 g, 16%, **10 C**: 0.469 g, 38%.

Ligand 10S: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.54 (d, ^3J = 2.5 Hz, 2H, H5), 8.38 (d, ^3J = 7.5 Hz, 2H, H7), 8.10 (d, ^3J = 8.1 Hz, 2H, H9), 8.02 (dd, ^3J = 7.9, ^3J = 7.9 Hz, 2H, H8), 7.86 (s, 2H, Hα), 7.81 (d, ^3J = 1.4 Hz, 2H, H3), 6.54 (dd, ^3J = 2.4 Hz, ^3J = 1.8 Hz, 2H, H4), 4.92 (t, ^3J = 7.7 Hz, 4H, H14), 2.06 (q, 4H, H15), 1.45 (q, 4H, H16), 1.31 (m, 8H, H17/H18), 0.85 (t, ^3J = 7.1 Hz, 6H, H19) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$/CD_3OD, 5:1): δ = 150.71, 150.45, 148.33, 142.47, 140.32, 140.05 (C8), 134.79, 126.98 (C5), 122.56 (C7), 112.97 (H9), 108.25(C4), 98.88 (Cα), 45.75 (C14), 31.48 (C17), 29.91 (C15), 26.56 (C16), 22.44 (C18), 13.73 (C19) ppm. **EA**[**10S** with [$C_{36}H_{40}N_{10}$], 612.8 g/mol]: calc. C 70.56, H 6.58, N 22.86; found C 70.42, H 6.72, N 22.81. **ES-MS** (in DMSO): m/z = 745.25 (100%, $[M+Cs]^+ = [(C_{36}H_{40}N_{10})Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3379, 3221, 3165, 2952, 2926, 2857, 1671, 1594, 1574, 1521, 1475, 1394, 1339, 1274, 1222, 1202, 1152, 1077, 1041, 992, 950, 917, 851, 813, 752, 654, 422 cm^{-1}.

Ligand 10 C: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.56 (d, ^3J = 2.5 Hz, 2H, H5), 8.41 (d, ^3J = 7.6, 2H, H7), 8.32 (s, 1H, Hβ), 8.11 (d, ^3J = 8.14 Hz, 2H, H9), 8.03 (dd, ^3J = 7.9 Hz, ^{3}J = 7.9 Hz, 2H, H8), 7.83 (d, ^3J = 1.1 Hz, 2H, H3), 7.33 (s, 1H, Hγ), 6.57 (dd, ^3J = 2.5 Hz, ^{3}J = 1.7 Hz, 2H, H4), 4.95 (t, ^3J = 7.5 Hz, 4H, H14), 2.07 (m, 4H, H15), 1.47 (q, 4H, H16), 1.27-1.40 (m, 8H, H17/H18), 0.88 (t, ^3J = 7.1 Hz, 6H, H19) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 150.72, 149.91, 148.97, 142.30 (H3), 140.40, 139.71 (C8), 135.57, 126.69 (C5), 122.62 (C7), 112.71 (C9), 109.84 (Cβ), 108.08 (C4), 88.87 (Hγ), 45.72 (C14), 31.60 (C17), 29.97 (C15), 26.75 (C16), 22.57 (C18), 13.97 (C19) ppm. **EA** [**10 C** with [$C_{36}H_{40}N_{10}$], 612.8 g/mol]: calc. C 70.56, H 6.58, N 22.86; found C 70.40, H 6.68, N 22.85. **ES-MS** (in DMSO): m/z = 745.24 (100%, $[M+Cs]^+ = I[(C_{36}H_{40}N_{10})Cs]^+$), 1357.59 (19%, $[2M+Cs]^+ = [(C_{36}H_{40}N_{10})_2Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3408, 3153, 3078, 2953, 2926, 2856, 1631, 1596, 1573, 1519, 1469, 1394, 1338, 1272, 1222, 1202, 1161, 1081, 1042, 992, 948, 913, 874, 817, 753, 784, 753, 657, 420 cm^{-1}.

Ligand 11: The reaction was carried out as described for compound **12** below. **L** (1.00 g, 2.25 mmol, 1 eq), Cs_2CO_3 (2.94 g, 9.00 mmol, 4 eq), DMSO (V = 8.5 mL), 3-(bromomethyl)pentane (1.11 g, 6.75 mmol, 3 eq, V = 0.944 mL). **Yield**: **11 C**: 0.386 g, 28%, **11S**: 0.596 g, 43%.

Ligand 11S: ^{1}**H NMR** (500 MHz, CD_2Cl_2): δ = 8.63 (d, ^3J = 2.4 Hz, 2H, H5), 8.33 (d,^3J = 7.5 Hz, ^4J = 1 Hz, 2H, H7), 8.12 (d, ^3J = 8.2 Hz, ^4J = 1 Hz, 2H, H9), 8.06 (dd,^{3} J = 7.6 Hz, ^{3} J = 8.1 Hz, 2H, H8), 7.86 (s, 2H, bz, Hα), 7.82 (d, J = 2 Hz, 2H, H3), 6.59 (dd, ^3J = 2.5 Hz, ^3J = 1.7 Hz, 2H, H4), 5.01 (d, ^3J = 7.7 Hz, 4H, H14), 2.00 (ttt, 2H, H15), 1.32 (m, 8H, H16), 0.82 (t, ^3J = 7.5 Hz, 12H, H17) ppm. ^{13}**C NMR** (126 MHz, CD_2Cl_2): δ = 150.85, 150.68, 149.52, 142.16 (C3), 140.94, 139.70 (C8), 135.31, 126.83(C5), 122.59(C7), 112.53 (C9), 108.00 (C4), 99.54 (Cα), 48.90 (C14), 40.91 (C15), 23.33 (C16), 10.45 (C17) ppm. **EA** [**11S***1/3 H_2O with [1/3($C_{108}H_{122}N_{30}O$)], 618.34 g/mol]: calc. C 69.88, H 6.62, N 22.64; found C 69.93, H 6.54, N 22.48. **ES-MS** (in DMSO): m/z = 745.22 (100%, $[M+Cs]^+ = [(C_{36}H_{40}N_{10})Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3415, 3103, 2960, 2931, 2873, 1592, 1573, 1520, 1469, 1396, 1337, 1273, 1248, 1203, 1177, 1153, 1076, 1040, 946, 880, 809, 753, 654 cm^{-1}.

Ligand 11 C: ^{1}**H NMR** (500 MHz, CD_2Cl_2): δ = 8.63 (d, ^3J = 2.4 Hz, 2H, H5), 8.34 (d, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 2H, H7), 8.17 (s, 1H, Hβ), 8.11 (d, ^3J = 8.2, ^4J = 1.0 Hz, 2H, H9), 8.06 (dd, ^3J = 7.7 Hz, ^3J = 8.0 Hz, 2H, H8), 7.82 (d, ^3J = 1.2 Hz, 2H, H3), 7.42 (s, 1H, Hγ), 6.59 (dd,^3J = 2.4, 1.8 Hz, 2H, H4), 5.01 (d,^3J = 7.6 Hz, 4H, H14), 1.96 (ttt, 2H, H15), 1.33 (m, 8H, H16), 0.82 (t, ^3J = 7.5 Hz, 12H, H17) ppm. ^{13}**C NMR** (126 MHz, CD_2Cl_2): δ = 150.65, 150.44, 149.50, 142.14 (C3), 140.35, 139.72 (C8), 135.79, 126.79 (C5), 122.60(C7), 112.51 (C9), 109.20 (Cβ), 107.95 (C4), 90.25 (Cγ), 48.77(C14), 41.14(C15), 23.40(C16), 10.53(C17) ppm. **EA** [**11 C** with ($C_{36}H_{40}N_{10}$) 612.79 g/mol]: calc. C 70.56, H 6.58, N 22.86; found C 22.61, H 6.61, N 22.61. **ES-MS** (in DMSO): m/z = 745.22 (100%, $[M+Cs]^+ = [(C_{36}H_{40}N_{10})Cs]^+$). **IR** (KBr): $\tilde{\nu}$ = 3430, 3104, 2961, 2931, 2874, 1594, 1574, 1519, 146, 1394, 1338, 1273, 1250, 1201, 1181, 1150, 1077, 1037, 944, 881, 811, 752, 662.

Ligand 12: The reaction was carried out as described for compound 8 using: L (0.895 g, 2.02 mmol, 1 eq), Cs_2CO_3 (2.65 g, 8.10 mmol, 4 eq), DMSO (20 mL, dried over mole sieves), 1-(bromomethyl)-3,5-di-tert-butylbenzene (1.73 g, 6.06 mmol, 3 eq). **Yield**: **12 C** 0.752 g, 42%, **12S** 0.782 g, 46%.

Ligand 12 C: ^{1}**H NMR** (500 MHz, CD_2Cl_2): δ = 8.40 (d, ^3J = 6.2, ^4J = 2.43 Hz, 2H, py), 8.29 (s, 1H, bz), 8.02 (m, 2H + 2H, py), 7.67 (d, ^3J = 1.6 Hz, 2H, pz), 7.52 (d, ^3J = 2.5, 2H, pz), 7.36 (s, 2H, dtbb), 7.33 (s, 1H, bz), 7.08 (s, ^4J = 1.7 Hz, 4H, dtbb), 6.23 (dd, ^3J = 2.5, ^3J = 1.7 Hz, 2H, pz), 6.03 (s, 4H, CH_2), 1.20 (s, 36H, tb-CH_3) ppm. ^{13}**C NMR** (126 MHz, CD_2Cl_2): δ = 151.69, 151.04, 149.05, 142.25, 141.06, 140.02, 136.70, 136.52, 127.50, 122.51, 121.64, 120.76, 112.69, 109.90, 108.09, 90.07, 49.99, 35.04, 31.48 ppm. **EA** [**12 C** with ($C_{54}H_{60}N_{10}$), 849.14 g/mol]: calc. C 76.38, H 7.12, N 16.50; found C 76.54, H 7.33, N 16.81. **ES-MS** (in DMSO): m/z = 871.479 (100%, $[M+Na]^+ = [(C_{54}H_{60}N_{10})Na]^+$). **IR** (KBr): $\tilde{\nu}$ = 3417, 3102, 2961, 2867, 1596, 1574, 1520, 1469, 1394, 1372, 1275, 1250, 1201, 1164, 1074, 1038, 994, 943, 885, 810, 751, 711, 662 cm^{-1}.

Ligand 12S: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.30 (d, ^3J = 7.4 Hz, 2H, py, H7), 8.04 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, py, H9), 8.00 (dd, ^3J = 7.8, ^3J = 7.8 Hz, 2H, py, H8), 7.83 (s, 2H, bz, Hα), 7.69 (d, 2H, pz, H5), 7.68 (d, J = 2.5 Hz, 2H, pz, H3), 7.33 (s, 2H, dtbb, H17), 7.05 (s, 4H, dtbb, H15), 6.22 (m, 2H, pz, H4), 6.09 (s, 4H, CH_2, H14), 1.19 (s, 36H, tb-CH_3, H19) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 151.29, 151.18, 150.66, 148.50, 142.10 (pz), 141.11, 139.74 (py), 135.95, 135.34, 127.26 (pz), 122.07 (py), 121.33 (dtbb), 120.28 (dtbb), 112.48 (py), 107.84 (pz-9), 99.85 (bz), 49.72 (***C***H_2), 34.76(^{t}bu-***C***(CH_3)), 31.36(^{t}bu-***C***H_3) ppm. **EA** [**12S***1/3 H_2O with [1/3($C_{162}H_{182}N_{30}O$)], 855.15 g/mol]: calc. C 75.85, H 7.15, N 16.38; found C 75.96, H 6.87, N 16.55. **ES-MS** (in DMSO): m/z = 871.478 (100%, $[M+Na]^+ = [(C_{54}H_{60}N_{10})Na]^+$). **IR** (KBr): $\tilde{\nu}$ = 3425, 3088, 3954, 2866, 1596, 1574, 1518, 1470, 1417, 1396, 1372, 1276, 1250, 1201,1162, 1077, 1040, 995, 945, 885, 832, 810, 759, 712 cm^{-1}.

Ligand 12: The reaction was carried out as described for compound 8 using: L (0.895 g, 2.02 mmol, 1 eq), Cs_2CO_3 (2.65 g, 8.10 mmol, 4 eq), DMF (30 mL), 1-bromo-2-methoxyethane (0.838 g, 6.06 mmol, 3 eq, V = 0.566 mL). **Yield**: **12 C** 0.752 g, 42%, **12S** 0.782 g, 46%.

Ligand 13 C: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.56 (d, ^3J = 2.5 Hz, 2H, H5),8.40 (d, ^3J = 7.7, 2H, H7), 8.22 (s, 1H, Hβ), 8.02 (d, J = 8.1 Hz, 2H, H9), 7.92 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, H8), 7.79 (d, J = 1.1 Hz, 2H, H3), 7.48 (s, 1H, γ), 6.54 (dd, ^3J = 2.5 Hz, ^3J = 1.6 Hz, 2H, H4), 5.05 (t, ^3J = 6.6 Hz, 4H, H14, CH_2), 3.96 (t, ^3J = 6.6 Hz, 4H, H15, CH_2), 3.38 (s, 6H, H16, CH_3) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 150.68, 149.54, 148.61, 142.41 (C3), 140.32, 139.80 (C8), 136.15, 126.99 (C5), 122.43 (C7), 112.81 (C9), 109.48 (Cβ), 108.39 (C4), 89.91 (Cγ), 71.53 (C15), 59.27 (C16), 45.59 (C14) ppm. **EA** [**13 C***1/3EtOAc with [1/3($C_{94}H_{92}N_{30}O_8$) 589.99 g/mol]]: calc. C 63.79, H 5.24, N 23.74; found C 64.02, H 5.62, N 23.34. **ES-MS** (in DMSO): m/z = 561.237 (55%, $[M+H]^+ = [(C_{30}H_{28}N_{10}O_2)H]^+$), 583.219 (100%, $[M+Na]^+ = [(C_{30}H_{28}N_{10}O_2)Na$. **IR** (KBr): $\tilde{\nu}$ = 3375, 3413, 3104, 2986, 2897, 1729, 1628, 1595, 1573, 1521, 1470, 1395, 1374, 1338, 1327, 1277, 1202, 1150, 1114, 1077, 1042, 994, 946, 906, 869, 811, 754, 660 cm^{-1}.

Ligand 13S: ^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 8.63 (d, ^3J = 2.5 Hz, 2H, H5), 8.42 (d, ^3J = 7.40 Hz, 2H, H7), 8.10 (d, ^3J = 8.13 Hz, 2H, H9), 8.02 (dd, ^3J = 7.9 Hz, ^3J = 7.9 Hz, 2H, H8), 7.94 (s, 2H, Hα), 7.80 (d, ^3J = 1.2 Hz, 2H, H3), 6.55 (dd, ^3J = 2.5, ^3J = 1.7 Hz, 2H, H4), 5.12 (t, ^3J = 6.6 Hz, 4H, H14, CH_2), 3.99 (t, ^3J = 6.6 Hz, 4H, H15, CH_2), 3.37 (s, 6H, H16, CH_3) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 150.86, 150.26,

148.40, 142.38 (C3), 140.63, 139.83 (C8), 135.46, 127.02 (C5), 122.50 (C7), 112.95 (C9), 108.36 (C4), 99.33 (Cα), 71.13 (C15), 59.15 (C16), 45.44 (C14) ppm. **EA** [13S *1/3EtOAc with [1/3($C_{94}H_{92}N_{30}O_8$) 589.99 g/mol)]: calc. C 63.79, H 5.24, N 23.74; found C 63.97, H 5.63, N 23.44. **ES-MS** (in DMSO): m/z = 561.236 (55%, $[M+H]^+ = [(C_{30}H_{28}N_{10}O_2)H]^+$), 583.219 (100%, $[M+Na]^+ = [(C_{30}H_{28}N_{10}O_2)Na]^+$). **IR** (KBr): $\tilde{\nu}$ = 3422, 3140, 3108, 2925, 289, 1742, 1594, 1574, 1510, 1471, 1455, 1395, 1372, 1338, 1279, 1248, 1200, 1150, 1118, 1074, 1040, 948, 906, 812, 754, 656 cm^{-1}.

$[Zn_4(L)_4](ClO_4)_8$: The ligand **L** (0.050 g, 0.11 mmol, 1 eq.) was suspended in CH_3CN (50 mL). Afterwards, a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.042 g, 0.11 mmol, 1 eq.) dissolved in CH_3CN (10 mL) was added. The reaction was heated at 70 °C for 48 h. It was allowed to cool to room temperature and filtered. The filtrate was reduced to about 15 mL. Diisopropyl ether (DIPE) diffused into the acetonitrile solution which led to yellow crystals. **Yield**: 0.059 g, 74%. **^{1}H-NMR** (500 MHz, CD_3CN): δ = 12.12 (2H, s, NH), 8.74 (2H, dd, ^3J = 8.1, ^3J = 8.2, pyridine), 8.57 (2H, d, J = 2.7 Hz, pyrazole), 8.36 (2H, d, J = 7.8 Hz, pyridine), 8.25 (2H, d, J = 8.5 Hz, pyridine), 7.40 (2H, d, J = 1.9 Hz, pyrazole), 6.64 (s, 2H, benzimidazole), 6.52 (dd, 2H, J = 2.1 Hz, J = 2.6 Hz, pyrazole) ppm. **^{13}C-NMR** (126 MHz, CD_3CN) δ = 150.2, 147.9, 147.4 (pyridine), 143.8 (pyrazole), 141.4, 138.3, 134.4, 130.8 (pyrazole), 121.4 (pyridine), 115.7 (pyridine), 112.1 (pyrazole), 100.9 (benzimidazole) ppm. High-resolution **ES-MS**: m/z = 507.081 (100%, [M-4H-8 ClO_4]$^{4+}$ = $[(C_{24}N_{10}H_{15}Zn)_4]^{4+}$), 675.766 (73.7%, [M-5H-8 ClO_4]$^{3+}$ = $[(C_{24}N_{10}H_{15}Zn)_4\text{-}H]^{3+}$), 1013.140(8.9%, [M-6H-8 ClO_4]$^{2+}$ = $[(C_{24}N_{10}H_{15}Zn)_4\text{-}2H]^{2+}$. **EA** [**1***2$HClO_4$*2$(C_3H_7)_2O$ with $C_{108}H_{94}Cl_{10}N_{40}O_{42}Zn_4$ (3240.20)]: calc. C 40.03, H 2.92, N 17.29; found C 40.00, H 2.62, N 17.01. **UV/Vis**: $\lambda(\varepsilon_{max}/10^{-3}\ M^{-1}\ cm^{-1})$ = 200 (188), 222 (sh 122), 258 (108), 301 (44), 377 (167), 394 (162), 432 (sh 35) nm. **IR** (KBr): $\tilde{\nu}$ = 1617, 1588, 1530, 1496, 1452, 1398, 1317, 1246, 1106, 1052, 986, 806, 764, 624 cm^{-1}.

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Conflict of Interest

The authors declare no conflict of interest.

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