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Designed Assembly and Structures and Photoluminescence of a New Class of Discrete Zn^{II} Complexes of 1*H*-1,10-Phenanthroline-2-one

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The hydrothermal reaction of 1*H*-1,10-phenanthroline-2-one (Hophen), zinc acetate, benzoic acid (Hba), and triethylamine (3.0 mL) yields the tetranuclear complex [$Zn_4(\mu_3\text{-}OH)_2(ophen)_4(ba)_2$] (**2**), which features a chair-like $Zn_4(\mu_3\text{-}OH)_2$ cluster with two ba ligands centrosymmetrically oriented. [(OAc){$Zn_3(\mu_3\text{-}OH)(ophen)_3$}(ox){$Zn_3(\mu_3\text{-}OH)(ophen)_3$}(OAc)] (**3**; ox = oxalate) was isolated when less triethylamine (1.0 mL) was used. Two $Zn_3(\mu_3\text{-}OH)(ophen)_3$ clusters in **3** are linked together by an oxalate to form a dumbbell-like structure in which the acetate and oxalate ligands point outward from the $Zn_3(\mu_3\text{-}OH)(ophen)_3$ cluster with an acute bending angle. A geometric analysis reveals that $Zn_3(\mu_3\text{-}OH)(ophen)_3$ and dicarboxylate with an obtuse bending angle cannot form an infinite zigzag chain, whereas the ring isomer can. With isophthalate (ipa), thiophene-2,5-dicarboxylate (tda), and 4,4′-oxybis(benzoate) (oba) instead of the acetate of **3** three new complexes, namely [{$Zn_3(\mu_3\text{-}OH)(ophen)_3$}(ipa)$_2${$Zn_3(\mu_3\text{-}OH)(ophen)_3$}]·$0.5H_2O$ (**4**), [{$Zn_3(\mu_3\text{-}OH)(ophen)_3$}(tda)$_2${$Zn_3(\mu_3\text{-}OH)(ophen)_3$}] (**5**), and [{$Zn_3(\mu_3\text{-}OH)(ophen)_3$}(oba)$_2${$Zn_3(\mu_3\text{-}OH)(ophen)_3$}] (**6**), were obtained in which two $Zn_3(\mu_3\text{-}OH)(ophen)_3$ clusters are linked by a pair of ipa, tda, or oba ligands to form isostructural, cluster-based 2:2 metallomacrocycles. Photoluminescence studies of **2**–**6** revealed that their luminescent properties are derived from ophen-based π-π* excited states.

Introduction

The rational design of supramolecular metal–organic compounds has received considerable attention. Due to the lack of control over the self-assembly of individual metal ions or ligands, chemists have introduced metal clusters as molecular building blocks as they offer greater structural rigidity and predictable coordination geometries.[1] This strategy has been successfully combined with net-based or reticular approaches to assemble many pre-designed cluster-based coordination polymers,[2] and has recently been extended to discrete metal–organic polyhedra.[3] Discrete metal–organic polygons and polyhedra have been widely studied[4] and continue to be one of the most interesting research topics.[3,5–9] Generally, the vertices or the edges of these polygons and polyhedra are occupied by single metal ions such as *cis*-protected Pt^{II} and Pd^{II},[4–7] while reported cluster-based polygons or polyhedra are rare.[3,8,9] Systematic studies of cluster-based polygons have mainly been concerned with *cis*-protected Mo_2^{4+} and Rh_2^{4+} dimetal units.[8] It should be noted that common metal clusters can possess more than two leaving groups, for example there are six substitutable acetates in [$Zn_4O(OAc)_6$], whereas a polygon requires uniquely two-connected building blocks. Therefore, known cluster-based metal–organic polygons are extremely rare, especially for trinuclear or larger metal clusters. In this context, the key strategy for the rational construction of cluster-based polygons is to select metal clusters with only two substitutable monotopic ligands.

Another problem in the controlled assembly of metal–organic polygons comes from the phenomenon of supramolecular isomerism. Both polygons and infinite zigzag chains as possible extended superstructures can be obtained for a given set of two-connected angular and/or linear molecular building blocks.[10] The kinetically favored infinite framework structures are usually the dominant species for highly insoluble metal–organic systems, especially those neutral ones such as metal polyazolates/polycarboxylates. Therefore, the reaction conditions should also be controlled to avoid the formation of infinite chain isomers.

Recently, we discovered a novel chelating/bridging ligand, namely 1*H*-1,10-phenanthroline-2-one (Hophen), which tends to form polynuclear metal clusters such as [$Cu_2(ophen)_2$],[11] [$Cd_3(ophen)_5Cl$], and [$Zn_4(\mu_4\text{-}O)(ophen)_4(OAc)_2$] (**1**).[12] Obviously, the two acetate ligands located on two opposite sides of the centrosymmetric cluster of **1** might be substituted by angular dicarboxylates to form infinite chains or finite rings. Unfortunately, our preliminary trials of substituting the acetates in **1** by dicarbox-

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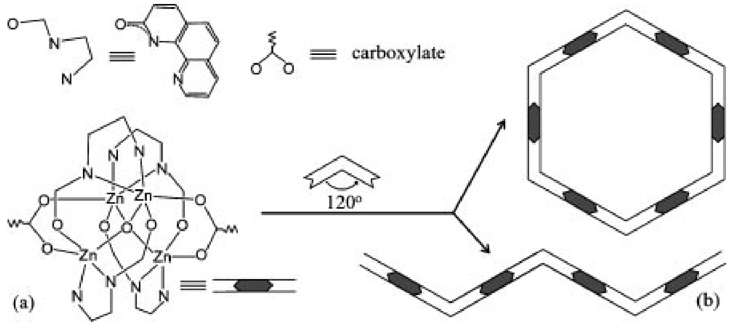


Scheme 1. Simplification of **1** as a linear two-connected building block (a) and two typical supramolecular isomers formed by using a bent dicarboxylate to substitute the two acetates of **1** (b).

ylates failed. From a geometrical point of view, centrosymmetric $Zn_4(\mu_4\text{-}O)(ophen)_4$ is a linear two-connector since the two acetates are located on two opposite sides of the $Zn_4(\mu_4\text{-}O)$ core. When a common rigid angular dicarboxylate such as isophthalate is used, the hypothetical cluster-based hexagonal ring of $Zn_4(\mu_4\text{-}O)(ophen)_4$ should be expected. Similar to the approaches for copper(I) imidazolate rings,[6a] the inner cavity of this hexagon is too large for common templates. Although we can use dicarboxylates with smaller bending angles (much smaller than 120°) to reduce the difficulty, such rigid angular dicarboxylates are not readily available. Alternatively, we can also shift our attention to reducing the bending angle by modifying the Zn^{II} cluster.

Since acidity can play an important role in controlling the degree of aggregation and the structure of oxo/hydroxo-bridged Zn^{II} clusters, we anticipated being able to synthesize new Zn^{II} clusters by varying the reaction conditions, especially the pH. Simple carboxylates like acetate and benzoate were used as the potential leaving groups. Herein, we report our step-by-step approach toward the rational design and synthesis of a new series of cluster-based metallacycles (Scheme 1).

Results and Discussion

Synthesis and Structure

We first obtained the discrete, tetranuclear cluster $[Zn_4(\mu_3\text{-}OH)_2(ophen)_4(ba)_2]$ (**2**; ba = benzoate) using triethylamine (3.0 mL) as base, while the oxo-bridged **1** was synthesized by using the very strong base $NaOCH_3$. The four Zn^{II} ions of **2** are bridged by two $\mu_3\text{-}OH^-$ groups [Zn–O1 1.932(2)–2.018(2) Å] to form a centrosymmetric, chair-like $Zn_4(\mu_3\text{-}OH)_2$ core. The Zn^{II} ions are also chelated by the bipyridyl fragments of ophen ligands [Zn–N 2.028(2)–2.127(2) Å] (Figure 1). The ketone oxygen atoms of the ophen ligands further bridge the $Zn_4(\mu_3\text{-}OH)_2$ core either by coordinating to Zn^{II} ions [Zn1–O3 2.018(2) Å] or by hydrogen bonding to the hydroxo groups (O1···O2 2.562(2) Å, O1–H···O2 166(3)°]. The outer Zn^{II} ions are further coordinated by ba ligands in a chelating mode [Zn2–O4 2.247(2), Zn2–O5 2.088(2) Å]. According to the above discussion, **2** is not a good candidate for the construction of cluster-based metallacycles as the ba ligands are oriented centrosymmetrically, as in **1**.

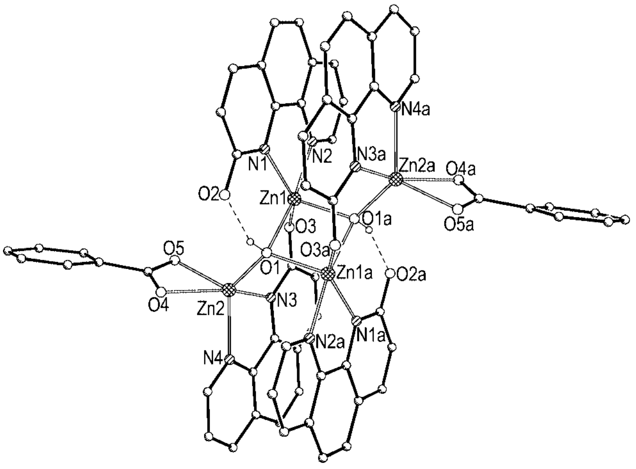


Figure 1. Perspective view of the molecular structure of **2** (a: –*x*, 1 – *y*, –*z*).

The chair-like $Zn_4(\mu_3\text{-}OH)_2$ cluster is composed of two edge-sharing triangular $Zn_3(\mu_3\text{-}OH)$ clusters. One may expect that changing the pH value would either prevent or promote the expansion of the $Zn_3(\mu_3\text{-}OH)$ cluster, and consequently modify the size and symmetry of the Zn^{II} cluster. For example, $Zn_4(\mu_4\text{-}O)$ or $Zn_5(\mu_3\text{-}OH)_2$ might be generated at higher pH, while $Zn_3(\mu_3\text{-}OH)$ might be generated at lower pH. When the experiments were carried out using less triethylamine (1.0 mL), we managed to isolate several new complexes with the expected $Zn_3(\mu_3\text{-}OH)(ophen)_3$ clusters. A discrete, hexanuclear complex $[(OAc)\{Zn_3(\mu_3\text{-}OH)(ophen)_3\}(ox)\{Zn_3(\mu_3\text{-}OH)(ophen)_3\}(OAc)]$ (**3**; ox = oxalate) was isolated in 20% yield by the solvothermal reaction of $Zn(OAc)_2$, Hophen, triethylamine, and benzoic acid in water. We subsequently found that **3** could also be synthesized in a higher yield (40%) in the absence of benzoic acid. The $Zn_3(\mu_3\text{-}OH)$ cluster in **3** [Zn–O1 1.983(2)–2.037(2) Å] replicates part of the $Zn_4(\mu_3\text{-}OH)_2$ core in **2**. Each of the three Zn^{II} ions is also chelated by a corresponding ophen ligand through its bipyridyl fragment [Zn–N 2.062(2)–2.193(2) Å]. Each ketone oxygen atom of the ophen ligands further ligates another Zn^{II} ion [Zn–O 1.962(2)–2.125(2) Å]. An acetate ligand coordinates to the outer sphere of $Zn_3(\mu_3\text{-}OH)(ophen)_3$ by ligation to the Zn^{II}

ion [Zn–O 2.053(2) Å] and hydrogen bonding to the hydroxy ion (O1···O8 2.594(3) Å, O1–H···O8 170(3)°]. Finally, two {Zn$_3$(μ_3-OH)(ophen)$_3$}(OAc) moieties are linked by a bis-chelating, *exo*-tetradentate oxalate ligand [Zn–O 2.011(2)–2.169(2) Å]. This unexpected oxalate ligand must be derived from an acetate since no oxalic acid or oxalate was added. An oxalate ligand can be generated by oxidation of ethanol or oxidative coupling of methanol under solvothermal conditions using nitrate as the oxidant.[13] It has also been reported that oxalate can be generated by the decarboxylative coupling of isonicotinates under solvothermal conditions.[14] Since no obvious oxidant was added in our experiment, we believe that the oxalate in **3** might be derived from the decarboxylative coupling of an acetate (Figure 2).

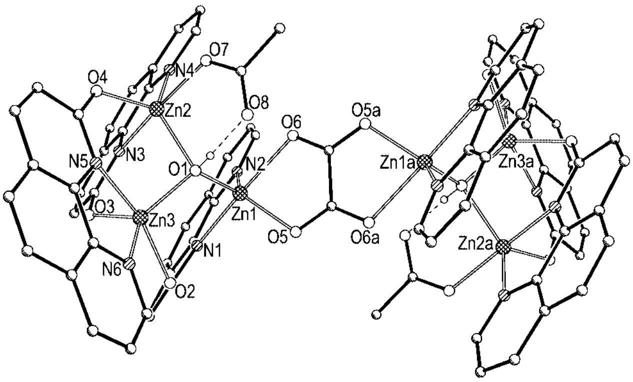
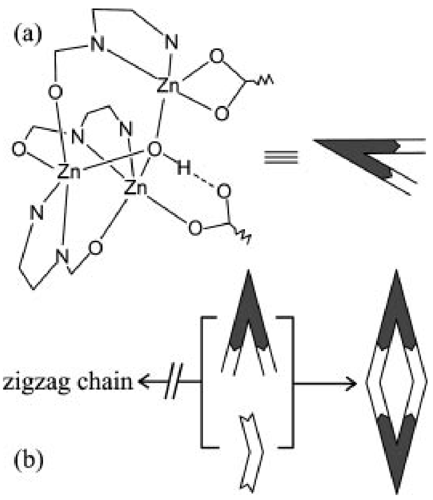


Figure 2. Perspective view of the molecular structure of **3** (a: –*x*, –*y*, 1 – *z*).

Two carboxylate vectors (OAc$^-$ and ox^{2-}) in **3** point outward from Zn$_3$(μ_3-OH)(ophen)$_3$ with a bending angle of around 30° (or turning angle of around 150°). Therefore, we can construct a 2:2 cluster-based metallacycle by substituting the carboxylates by dicarboxylates with a bending angle of about 150° (or turning angle of about 30°). Interestingly, these two types of two-connected molecular building blocks, which individually contain an acute or an obtuse bending angle, cannot be self-assembled into an infinite zigzag chain, as illustrated in Scheme 1. Geometrically, this phenomenon can be explained by considering the geometric criteria for these isomers. For the ring isomers, the overall turning angle is equal to $360° = n(x + y)$ ($x \geq 0$, $y \geq 0$, $x \neq y$, $n \geq 2$), whereas for the zigzag chain isomers the overall turning angle is equal to $0° \neq n(x - y)$ ($x \geq 0$, $y \geq 0$, $x \neq y$, $n \geq 2$), where x and y are the turning angles of the molecular building blocks and n is the number of repeat units. In other words, a finite ring-like structure would be much more easily obtained in such a self-assembly system because it does not contain infinite zigzag chain isomers (Scheme 2).

We therefore used isophthalate (ipa), thiophene-2,5-dicarboxylate (tda), and 4,4′-oxybis(benzoate) (oba) as the obtuse dicarboxylates to replace the acetate and oxalate. Three new, isostructural, centrosymmetric, cluster-based metallacycles, namely [{Zn$_3$(μ_3-OH)(ophen)$_3$}(ipa)$_2$-{Zn$_3$(μ_3-OH)(ophen)$_3$}]·0.5H$_2$O (**4**), [{Zn$_3$(μ_3-OH)(ophen)$_3$}(tda)$_2${Zn$_3$(μ_3-OH)(ophen)$_3$}] (**5**), and [{Zn$_3$(μ_3-OH)(ophen)$_3$}(oba)$_2${Zn$_3$(μ_3-OH)(ophen)$_3$}] (**6**), were obtained in high yields under solvothermal conditions similar to that of **3**. It should be noted that no zigzag chain isomer or other crystalline product was isolated in these experiments (Figure 3).



Scheme 2. Simplification of the Zn$_3$(μ_3-OH)(ophen)$_3$ cluster as an angular building block (a) and possible extended structures for combining two different types of angular building blocks (b).

The Zn$_3$(μ_3-OH)(ophen)$_3$ clusters in **4**–**6** are isostructural to that of **3** with similar structural parameters [Zn–OH 1.950(1)–2.059(1), Zn–N 2.022(2)–2.177(2), Zn–O$_{\text{ophen}}$ 1.968(2)–2.196(2) Å], while the acetate and oxalate ligands in **3** are now replaced by dicarboxylate ligands. The coordination/hydrogen-bonding mode of the carboxylate group of the acetate in **3** is retained in **4**–**6** [Zn2–O7a 2.042(2)–2.056(2), O1···O8a 2.613(2)–2.668(3) Å; O1–H···O8a 160(3)–168(3)°]. The stable five-membered chelating mode of the oxalate in **3** is not available for ipa, tda, or oba, and is replaced by four-membered chelating carboxylate groups in **4**–**6**. Two Zn–O bond lengths of the chelating carboxylate groups in **4**–**6** show remarkable structure-related differences. Two carboxylate groups in an ipa moiety are oriented with a bending angle of about 120°, which is significantly smaller than the required angle of 150°. This structural deviation is compensated for by distorting the very energetically stable, ideal chelating carboxylate to a quasi-monodentate one [Zn1–O5 1.946(2), Zn1–O6 2.560(2) Å]. On the other hand, two carboxylate groups in tda are oriented with a bending angle of about 140°, and the difference in the Zn–O bond lengths in **5** [Zn1–O5 2.039(2), Zn1–O6 2.283(2) Å] is much smaller than that in **4**. A short intramolecular S···S contact [3.461(2) Å] is also found in **5**. Furthermore, the bending angle of oba (ca. 130°) and the difference in Zn–O bond lengths in **6** [Zn1–O5 2.002(2), Zn1–O6 2.366(2) Å] lies between those of ipa and tba.

Two Zn$_3$(μ_3-OH)(ophen)$_3$ clusters are linked by different dicarboxylates to give nanosized supermolecules. According to the lengths of the dicarboxylates, the sizes of **3**–**6** vary from 1.76 to 2.15, 2.20, and 2.72 nm, respectively. Similar to **1**, intermolecular, head-to-tail π-π stacking interactions are the major supramolecular interactions between the dis-

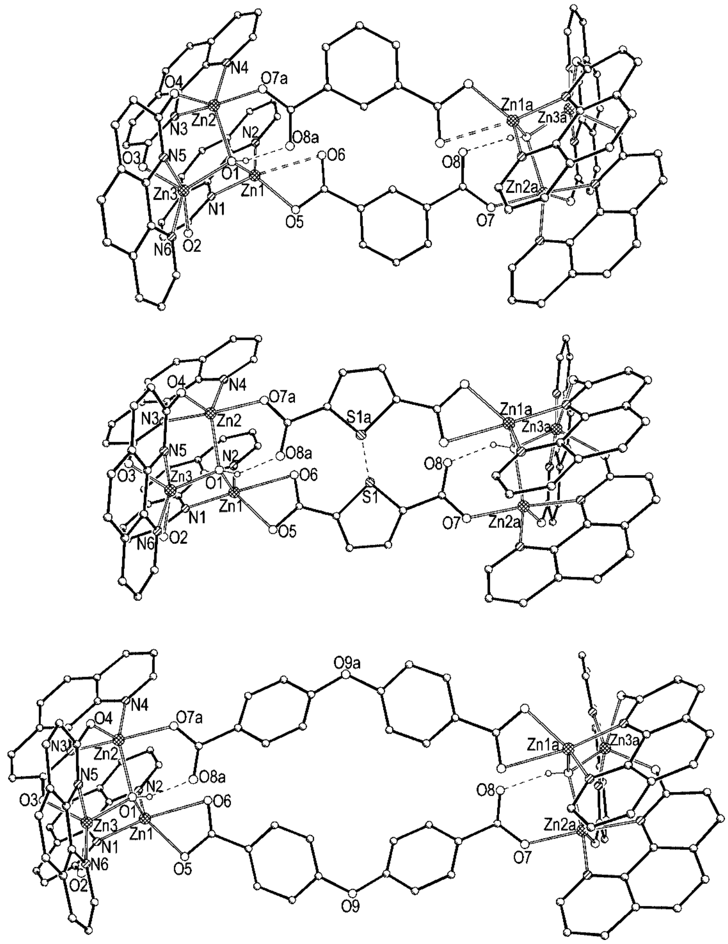


Figure 3. Perspective view of the molecular structures of **4** (a: –*x*, –*y*, 1 – *z*), **5** (a: 1 – *x*, –*y*, 1 – *z*), and **6** (a: –*x*, –*y*, –*z*).

crete molecules in **2**–**6**. Significant intramolecular, head-to-head π-π stacking interactions are also found in **1**–**6**. Although **2**–**6** are discrete, neutral molecules, they are barely soluble in common solvents. This interesting phenomenon has also been observed in other solvothermally synthesized discrete complexes and may be partially ascribed to the significant three-dimensional packing of the molecules (see Supporting Information).

Photoluminescence

Compounds **2**–**6** display bright blue to green photoluminescence upon UV irradiation. The photoluminescence parameters of **2**–**6** are summarized in Table 1 and the emission and excitation spectra of **2**–**6** are shown in Figure 4. The solid-state photoluminescent properties of **2**–**6** are very similar to those of **1**,[12] thus implying that the carboxylate ligands may not influence the nature or energy of the luminescence-related electronic ground state or excited state. The carboxylate ligands in **1**–**6** have much smaller π-conju-

Table 1. Photoluminescence properties of **2**–**6**.

	Excitation [nm]	Emission [nm]	Lifetime [ns]
2	383 sh, 402 sh, 418	487	3.43(5)
3	375, 404 sh	464	3.58(4)
4	383, 402 sh, 409 sh	468	6.97(1)
5	383, 401 sh, 413	469	7.70(2)
6	376, 393 sh, 406	477	7.57(4)

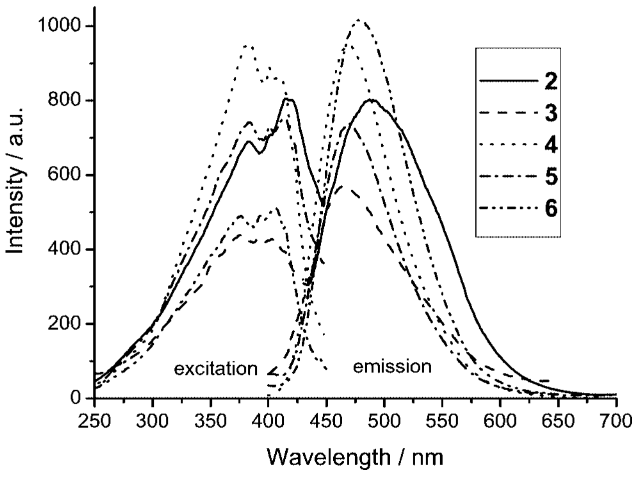


Figure 4. Photoluminescence spectra of **2**–**6**.

gated systems than that of the ophen ligand, therefore the lowest lying HOMO–LUMOs should be mainly localized on the ophen ligand, which results in an ophen-based π-π* excitation mechanism. Compared with that of oxo-bridged **1** (15 ns), the shorter luminescence lifetime of **2**–**6** (3.4–7.7 ns) may be attributed to the quenching effect of the OH stretch.

Conclusions

Based on geometrical considerations and a strategy of controlling the reaction condition, we have successfully synthesized a new series of cluster-based metallacycles. Our results demonstrate that the degree of aggregation of the hydroxy- or oxo-bridged Zn–ophen cluster can be simply controlled by varying the reaction conditions, generating $[Zn_4(\mu_4\text{-O})(ophen)_4]^{2+}$, $[Zn_4(\mu_3\text{-OH})_2(ophen)_4]^{2+}$, or $[Zn_3(\mu_3\text{-OH})(ophen)_3]^{2+}$ from very high (NaOMe) to relatively low basicity (triethylamine). Although the above Zn clusters are potential candidates for the construction of cluster-based metallacycles, we have demonstrated that $[Zn_3(\mu_3\text{-OH})(ophen)_3]^{2+}$, which binds two carboxylate groups in an acute angle, can easily form 2:2 metallacycles with different dicarboxylate ligands with obtuse bending angles. The self-assembly principle has been rationalized in the context of supramolecular isomerism, in which the infinite zigzag chain isomer is excluded by the geometrical requirements of the molecular building blocks. Owing to its tendency to form metal clusters, ophen may be an excellent ligand for paramagnetic transition metal ions to form metal clusters of significance in molecular magnetism.

Experimental Section

General Remarks: Commercially available reagents were used as received without further purification. Hophen was prepared by our previously reported method.[12] IR spectra were obtained from KBr pellets on a Bruker EQUINOX 55 FT IR spectrometer in the 400–4000 cm^{-1} region. Elemental analyses (C, H, N) were performed with a Perkin–Elmer 240 elemental analyzer. The steady-state fluorescent and fluorescence lifetimes were determined with an Edinburgh Instrument FLS920 fluorescence spectrophotometer. Single-crystal samples were used in photoluminescence analyses.

Synthesis of $[Zn_4(\mu_3\text{-OH})_2(ophen)_4(ba)_2]$ (2): Reaction of a mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.220 g, 1.0 mmol), Hophen (0.196 g, 1.0 mmol), benzoic acid (0.060 g, 0.5 mmol), triethylamine (3.0 mL), and water (10.0 mL) in a 23-mL Teflon-lined bomb at 160 °C for 80 h afforded yellow, block-like crystals (yield: 0.20 g, 60%). $C_{62}H_{40}N_8O_{10}Zn_4$ (1318.6): calcd. C 56.47, H 3.06, N 8.50; found C 56.34, H 3.09, N 8.39. IR: ṽ = 3059 cm^{-1} w, 1624 s, 1593 s, 1560 s, 1534 s, 1483 s, 1391 s, 1313 w, 1136 m, 845 s, 723 m, 657 m, 473 w.

Synthesis of $[(OAc)\{Zn_3(\mu_3\text{-OH})(ophen)_3\}(ox)\{Zn_3(\mu_3\text{-OH})(ophen)_3\}(OAc)]$ (3): Reaction of a mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.220 g, 1.0 mmol), Hophen (0.196 g, 1.0 mmol), triethylamine (1.0 mL), and water (10.0 mL) in a 23-mL Teflon-lined bomb at 160 °C for 80 h afforded yellow, block-like crystals (yield: 0.12 g, 40%). $C_{76}H_{44}N_{12}O_{16}Zn_6$ (1773.6): calcd. C 51.47, H 2.50, N 9.48; found C 51.36, H 2.54, N 9.40. IR: ṽ = 3409 cm^{-1} w, 3057 w, 2921 w, 1652 s, 1624 s, 1560 s, 1526 s, 1481 s, 1389 s, 1309 m, 1138 m, 943 w, 846 s, 734 m, 659 m, 496 m.

Synthesis of $[\{Zn_3(\mu_3\text{-OH})(ophen)_3\}(ipa)_2\{Zn_3(\mu_3\text{-OH})(ophen)_3\}]\cdot 0.5H_2O$ (4): Reaction of a mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.220 g, 1.0 mmol), Hophen (0.196 g, 1.0 mmol), isophthalic acid (0.041 g, 0.25 mmol), triethylamine (1.0 mL), and water (10.0 mL) in a 23-mL Teflon-lined bomb at 160 °C for 80 h afforded yellow, block-like crystals (yield: 0.19 g, 80%). $C_{88}H_{53}N_{12}O_{16.5}Zn_6$ (1934.8): calcd. C 54.63, H 2.76, N 8.69; found C 54.67, H 2.68, N 8.72. IR: ṽ = 3411 cm^{-1} w, 3057 w, 1624 s, 1561 s, 1528 s, 11484 s, 1388 s, 1307 w, 1140 w, 944 w, 846 s, 737 m, 657 m, 496 w.

Synthesis of $[\{Zn_3(\mu_3\text{-OH})(ophen)_3\}(tda)_2\{Zn_3(\mu_3\text{-OH})(ophen)_3\}]$ (5): Reaction of a mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.220 g, 1.0 mmol), Hophen (0.196 g, 1.0 mmol), thiophene-2,5-dicarboxylic acid (0.043 g, 0.25 mmol), triethylamine (1.0 mL), and water (10.0 mL) in a 23-mL Teflon-lined bomb at 160 °C for 80 h afforded yellow, block-like crystals (yield: 0.16 g, 65%). $C_{84}H_{48}N_{12}O_{16}S_2Zn_6$ (1937.8): calcd. C 52.06, H 2.50, N 8.67, S 3.31; found C 52.17, H 2.51, N 8.59; S 3.18. IR: ṽ = 3421 cm^{-1} w, 3059 w, 1624 s, 1563 s, 1526 s, 1482 s, 1391 s, 1141 w, 943 w, 846 s, 735 m, 656 w, 498 w.

Synthesis of $[\{Zn_3(\mu_3\text{-OH})(ophen)_3\}(oba)_2\{Zn_3(\mu_3\text{-OH})(ophen)_3\}]$ (6): Reaction of a mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.220 g, 1.0 mmol),

Table 2. Crystallographic data and structure refinement for **2**–**6**.

Compound	**2**	**3**	**4**	**5**	**6**
Formula	$C_{62}H_{40}N_8O_{10}Zn_4$	$C_{76}H_{44}N_{12}O_{16}Zn_6$	$C_{88}H_{53}N_{12}O_{16.5}Zn_6$	$C_{84}H_{48}N_{12}O_{16}S_2Zn_6$	$C_{100}H_{60}N_{12}O_{18}Zn_6$
Formula weight	1318.50	1803.52	1934.64	1937.68	2109.82
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	10.3041(6)	10.5382(6)	10.4276(5)	10.4076(5)	11.1842(5)
b [Å]	13.5436(8)	10.8562(6)	10.8019(6)	10.6861(5)	14.1429(6)
c [Å]	18.8727(11)	17.2856(10)	20.1650(10)	18.5376(9)	15.7344(8)
α [°]	90	81.156(1)	91.529(1)	98.675(1)	64.734(2)
β [°]	104.884(1)	76.051(1)	104.170(1)	96.148(1)	87.895(2)
γ [°]	90	61.021(1)	118.809(1)	116.608(1)	73.613(2)
V [Å^3]	2545.4(3)	1677.35(16)	1901.49(17)	1786.32(15)	2149.23(17)
Z	2	1	1	1	1
D_c [gcm^{-3}]	1.720	1.785	1.689	1.801	1.630
μ [mm^{-1}]	1.938	2.197	1.945	2.126	1.729
Final *R* indices[a]	$R_1 = 0.0492$	$R_1 = 0.0499$	$R_1 = 0.0346$	$R_1 = 0.0450$	$R_1 = 0.0395$
All data[a]	$wR_2 = 0.0917$	$wR_2 = 0.0938$	$wR_2 = 0.0795$	$wR_2 = 0.0955$	$wR_2 = 0.0938$
GooF	1.039	1.002	1.046	1.033	1.028

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Hophen (0.196 g, 1.0 mmol), 4,4′-oxybis(benzoic acid) (0.060 g, 0.25 mmol), triethylamine (1.0 mL), and water (10.0 mL) in a 23-mL Teflon-lined bomb at 160 °C for 80 h afforded yellow, block-like crystals (yield 0.18 g, 70%). $C_{100}H_{60}N_{12}O_{18}Zn_6$ (2110.0): calcd. C 56.92, H 2.87, N 7.97; found C 56.87, H 2.95, N 7.83. IR: $\tilde{\nu}$ = 3418 cm^{-1} w, 3051 w, 1625 s, 1595 s, 1559 s, 1534 s, 1484 s, 1390 s, 1243 s, 1161 m, 849 s, 781 m, 734 m, 704 m, 661 m, 496 w.

X-ray Crystallographic Study: Diffraction intensities were collected at 293(2) K on a Bruker Smart APEX CCD area-detector diffractometer (Mo-K_α, λ = 0.71073 Å). Absorption corrections were applied by using the multi-scan program SADABS.[15] The structures were solved by direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.[16] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H: 0.96 Å); hydroxy hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data as well as details of data collection and refinements for the complexes are summarized in Table 2.

CCDC-291301 to -291305 (for **2**–**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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