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## Dynamic and Fluorescent Nanoscale Phenanthroline/Terpyridine Zinc(II) Ladders. Self-Recognition in *Unlike* Ligand/*Like* Metal Coordination Scenarios

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The availability of reliable metal-ligand combinations, such as Pt(Pd)-N(P),  $Pt-C\equiv C$ , etc., is a *conditio sine qua non* for the erection of intricate metallosupramolecular architectures.<sup>1</sup> While eye-catching but mostly single component aggregates have been widely prepared,<sup>1</sup> our tools to assemble well-defined and robust multicomponent structures are still limited. Thus, homoleptic assemblies, such as grids<sup>1e</sup> and squares,<sup>1a-d,g</sup> predominate in the literature,<sup>1f</sup> while ladder motifs, due to the lack of heteroleptic metal ligand combinations and thus of control in dynamic multicomponent aggregation, are restricted to a few reports.<sup>2</sup>

So far, five-coordinated metal centers with phenanthrolines (or 2,2'-bipyridines) and terpyridines as ligands have been of little utility in dynamic heteroleptic aggregation,<sup>3</sup> except in highly restricted topologies<sup>4c</sup> or cooperative helicates.<sup>4a,b</sup> Clearly, a quantitative yield can only be realized if the formation of four- and six-coordinated complexes is suppressed. Herein, we show that properly designed phenanthrolines can be instructed for quantitative heteroleptic complexation with terpyridine ligands in the presence of Zn<sup>2+</sup>, Hg<sup>2+</sup>, and even Cu<sup>+</sup>. Their superior value is illustrated by the synthesis of dynamic and fluorescent nanoscale ladders, by facile metal exchange escorted by OFF–ON–OFF fluorescence signaling, and by the realization of an unprecedented *like* metal/*unlike* ligand recognition scenario.

Phenanthrolines designed with steric stoppers according to the HETPHEN concept<sup>5</sup> (e.g., with 2,9-dimesityl/2,9-diduryl; cf. 2, 3) are instructed to avoid self-association in the presence of many metal ions, such as Cu(I), Ag(I), and Zn(II) ions (Chart 1).<sup>6</sup> Thus, in combination with sterically innocent phenanthrolines, merely heteroleptic bisphenanthroline complexes form.<sup>6</sup> A like protocol was now evaluated with terpyridines as partners for HETPHEN ligands. Hence,  $1-3^7$  were tested for their ability to recognize ligands 4-5 in the presence of zinc(II) ions.<sup>8</sup> With 1a, 5, and zinc-(II) ions, only homoleptic combinations were detected by ESI MS and <sup>1</sup>H NMR (see Supporting Information). Evidently, selfrecognition is the dominating phenomenon, as also recognized by other authors.<sup>3</sup> In contrast, from the reaction of **2**, **4**, and Zn(OTf)<sub>2</sub>, only the rack assembly  $\mathbf{R1} = [Zn_2(2)(4)_2]^{4+}$  emerged, as evidenced by ESI MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and UV/vis (Scheme 1a). For example, the <sup>1</sup>H NMR showed the expected high field shift ( $\Delta \delta =$ 0.8 ppm) for the mesityl protons of 2.6 Rack R1 proved to be fluorescent ( $\lambda_{em} = 456$  nm) upon excitation at 389 nm (see Supporting Information).

Along the same strategy, ladders  $L1 = [Zn_4(2)_2(5)_2]^{8+}$  and  $L2 = [Zn_4(3)_2(5)_2]^{8+}$  were furnished upon reaction of 2 or 3 and 5

Chart 1. Ligands Used in This Study



Scheme 1. Multicomponent Self-Assembly of Rack R1 and Ladders L1,L2 (cartoon representation)



with Zn(OTf)<sub>2</sub> (1:1:2 equiv, Scheme 1b). All spectroscopic data confirmed the clean formation and integrity of the ladders L1,L2 that exhibited a distinct fluorescence ( $\lambda_{em} = 463$  and 468 nm, respectively [( $\lambda_{exc} = 389 \text{ nm}$ ]) in acetonitrile at room temperature (Supporting Information). The <sup>1</sup>H NMR showed a single set of sharp signals, with the mesityl protons being high field shifted (in 2,3:  $\delta$  $\sim$ 7 ppm; in L1,L2:  $\delta \sim$ 6.1 ppm). Peak assignments were corroborated by COSY experiments. <sup>13</sup>C NMR showed single sets of the expected signals. ESI MS analysis of L1,L2 further substantiated the proposed structures by showing isotopically resolved signals, for example, for ladder L1 at m/z = 485.1, 539.2, 653.9, 814.4, 1055.3, 1455.8, corresponding to [Zn<sub>4</sub>(2)<sub>2</sub>(5)<sub>2</sub>- $(OTf)_n$ <sup>[8-n)+</sup> with n = 0, 1, ...5 (see Supporting Information). Strong confirmation for the integrity of L1,L2 in solution was obtained using analytical ultracentrifugation.9 Through sedimentation velocity experiments of L1, a single species with a molecular weight of  $5020 \pm 500$  Da (measured at 45  $\mu$ g mL<sup>-1</sup>) was detected in KOTFsaturated acetone in good agreement with the expected weight of L1 (4817.5 Da; see Supporting Information).

Ultimate structural proof was acquired by a single-crystal X-ray analysis of L2.<sup>10</sup> L2 possesses a nanoscale ladder structure, in which two **3** and **5** assemble about four Zn<sup>2+</sup> ions (Zn–Zn diagonals are 2.2 and 2.5 nm; Figure 1). The terpyridine units of **5** are sandwiched between the 2,9-aryl groups of the phenanthrolines of **3**, allowing for stabilizing  $\pi-\pi$  interactions (d = 3.4 Å). Hence, presence of the 2,9-steric stoppers in **3** forces Zn(II) ions to adapt a heavily distorted trigonal bipyramidal pentacoordination, with three positions being filled from the terpyridine unit and two from the

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*Figure 1.* (a) Single-crystal structure stick representation of L2. (b) Space filling representation. For clarity, H atoms, solvent molecules, and anions are omitted.

**Table 1.** Binding Constants for Various Heteroleptic Metal Phenanthroline (L) Terpyridine (T) Complexes  $[M(4)(6)]^{n+}$  in Dichloromethane

М	$\log K^{\rm M}{}_{\rm ML}$	$\log K^{\rm M}{}_{\rm MLT}$	$\log\beta_{\rm 21}$
Cu <sup>+</sup> Zn <sup>2+</sup>	$5.0 \pm 0.2$ $5.9 \pm 0.6$	$\begin{array}{c} 4.3 \pm 0.9 \\ 6.5 \pm 0.2 \end{array}$	9.3 12.4 <sup><i>a</i></sup>
$Hg^{2+}$	$6.7 \pm 0.6$	$8.0 \pm 0.1$	$14.7^{a}$

<sup>a</sup> With 0.1 vol % of methanol.

*Scheme 2.* Cartoon Representation of the *Like* Metal/*Unlike* Ligand Recognition Scenario



phenanthroline ligand. To our knowledge, this is the first structurally characterized nanoscale multicomponent ladder assembly combining both bi- (2 or 3) and tridentate ligands (5).

The dynamic nature of these aggregates was proven by mixing L1 and L2 in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (8:2). Within 5 min, the mixed species L3 = ([Zn<sub>4</sub>(2)(3)(5)<sub>2</sub>]<sup>8+</sup>) built up beside L1 and L2, as verified by ESI-MS and <sup>1</sup>H NMR (see Supporting Information). Hence, the above results demonstrate that a robust and reliable approach to *dynamic* heteroleptic terpyridine and phenanthroline (HETTAP) complexation has been developed. Analogously, we prepared other metal ladders, such as L4 = [Cu<sub>4</sub>(2)<sub>2</sub>(5)<sub>2</sub>]<sup>4+</sup> and L5 = [Hg<sub>4</sub>(2)<sub>2</sub>(5)<sub>2</sub>]<sup>8+</sup>. The low binding constant in Table 1 suggests that Cu<sup>+</sup> is only four-coordinated in [Cu(4)(6)]<sup>+</sup>, while the five-coordinated complexes [Zn(4)(6)]<sup>2+</sup> and [Hg(4)(6)]<sup>2+</sup> exhibit higher binding constants.

Combination of the structural robustness of L1,L2 with its dynamic nature allows one to conceive experiments with an unprecedented level of recognition.<sup>11</sup> Such phenomena had earlier been studied by Lehn,<sup>11a</sup> who was able to demonstrate that from a mixture of oligobipyridine strands and a mixture of metal ions [Cu-(I) and Ni(II)] only helicates composed of like ligands and like metal ions were afforded. In contrast, the combination of unlike ligands and like metal ions had not been realized. Using the conceptual insight gained from the HETPHEN and HETTAP strategies, we interrogated the reaction of ligands 1b, 2, and 5 in the presence of metal ions Zn<sup>2+</sup> and Cu<sup>+</sup> in a 1:2:1:2:2 stoichiometry. As conceived, only two discrete multicomponent nanostructures formed selectively from this cocktail of ligands and metal ions, that is, Zn-ladder L1 and Cu-grid G16c (Scheme 2). Despite extensive ESI MS and <sup>1</sup>H NMR checks, no other aggregates were detectable. Hence, this reaction is a unique example of a 2-fold like metal + unlike ligand recognition scenario that leads to the clean formation of two dynamic nanoaggregates.

L4 and L5 did not fluoresce quite in contrast to L1 (see Supporting Information). On the basis of the binding constants (see Table 1), a two-step double-transmetalation off-on-off fluorescence system was designed. Upon addition of Zn(II) salt to L4 (nonfluorescent; OFF), L1 was afforded (fluorescent; ON) that could be further transformed to L5 (nonfluorescent; OFF) upon the  $\it Scheme 3.$  (a) A Two-Step Transmetalation off-on-off Fluorescence System. (B) Photo Taken under UV Lamp (254 nm)



addition of Hg(II) (Scheme 3). The transmetalations were conveniently followed by ESI MS and fluorescence spectrometry (see Supporting Information).

In conclusion, a new coordination toolkit, the HETTAP approach, was developed. It allows one to prepare heteroleptic metal phenanthroline/terpyridine aggregates in basically quantitative yield. Due to the dynamic nature of the nanoladder structures, a two-step double-transmetalation and a *like* metal/*unlike* ligand recognition scenario were realized. Further studies are in progress to study host—guest complexation and photophysical properties of these unique multicomponent structures.

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**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C spectra for all compounds and crystallographic data for L2 (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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