Communication

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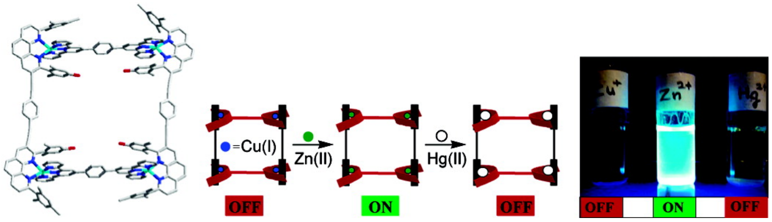

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Dynamic and Fluorescent Nanoscale Phenanthroline/Terpyridine Zinc(II) Ladders. Self-Recognition in *Unlike* Ligand/*Like* Metal Coordination Scenarios

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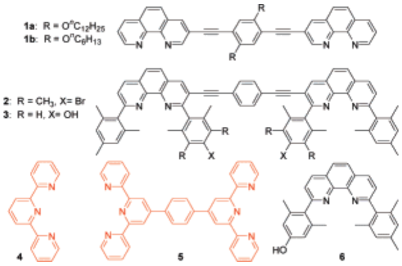
The availability of reliable metal−ligand combinations, such as Pt(Pd)−N(P), Pt−C≡C, etc., is a *conditio sine qua non* for the erection of intricate metallosupramolecular architectures.[1] While eye-catching but mostly single component aggregates have been widely prepared,[1] our tools to assemble well-defined and robust multicomponent structures are still limited. Thus, homoleptic assemblies, such as grids[1e] and squares,[1a−d,g] predominate in the literature,[1f] 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.[2]

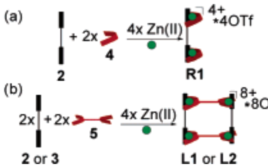
So far, five-coordinated metal centers with phenanthrolines (or 2,2′-bipyridines) and terpyridines as ligands have been of little utility in dynamic heteroleptic aggregation,[3] except in highly restricted topologies[4c] or cooperative helicates.[4a,b] Clearly, a quantitative yield can only be realized 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^{2+}, Hg^{2+}, and even Cu^{+}. 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[5] (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).[6] Thus, in combination with sterically innocent phenanthrolines, merely heteroleptic bisphenanthroline complexes form.[6] 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.[8] With **1a**, **5**, and zinc(II) ions, only homoleptic combinations were detected by ESI MS and ^{1}H NMR (see Supporting Information). Evidently, self-recognition is the dominating phenomenon, as also recognized by other authors.[3] In contrast, from the reaction of **2**, **4**, and $Zn(OTf)_2$, only the rack assembly **R1** = $[Zn_2(\mathbf{2})(\mathbf{4})_2]^{4+}$ emerged, as evidenced by ESI MS, ^{1}H NMR, ^{13}C NMR, and UV/vis (Scheme 1a). For example, the ^{1}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).

Chart 1. Ligands Used in This Study



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



Along the same strategy, ladders **L1** = $[Zn_4(\mathbf{2})_2(\mathbf{5})_2]^{8+}$ and **L2** = $[Zn_4(\mathbf{3})_2(\mathbf{5})_2]^{8+}$ were furnished upon reaction of **2** or **3** and **5** with $Zn(OTf)_2$ (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 [($\lambda_{exc} = 389$ nm)]) in acetonitrile at room temperature (Supporting Information). The ^{1}H NMR showed a single set of sharp signals, with the mesityl protons being high field shifted (in **2**,**3**: δ ~7 ppm; in **L1**,**L2**: δ ~6.1 ppm). Peak assignments were corroborated by COSY experiments. ^{13}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 $[Zn_4(\mathbf{2})_2(\mathbf{5})_2(OTf)_n]^{(8-n)+}$ 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 ± 500 Da (measured at 45 μg mL^{-1}) was detected in KOTF-saturated 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**.[10] **L2** possesses a nanoscale ladder structure, in which two **3** and **5** assemble about four Zn^{2+} 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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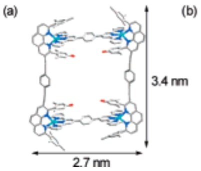
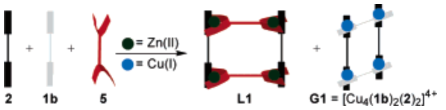


Figure 1. (a) Single-crystal structure stick representation of **L2**. (b) Space filling representation. For clarity, H atoms, solvent molecules, and anions are omitted.

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

M	log K^{M}_{ML}	log K^{M}_{MLT}	log β_{21}
Cu^+	5.0 ± 0.2	4.3 ± 0.9	9.3
Zn^{2+}	5.9 ± 0.6	6.5 ± 0.2	12.4[a]
Hg^{2+}	6.7 ± 0.6	8.0 ± 0.1	14.7[a]

[a] With 0.1 vol % of methanol.



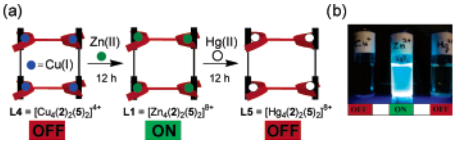
Scheme 2. Cartoon Representation of the *Like* Metal/*Unlike* Ligand Recognition Scenario

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_2Cl_2/CH_3OH (8:2). Within 5 min, the mixed species **L3** = $([Zn_4(\mathbf{2})(\mathbf{3})(\mathbf{5})_2]^{8+})$ built up beside **L1** and **L2**, as verified by ESI-MS and ^1H 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** = $[Cu_4(\mathbf{2})_2(\mathbf{5})_2]^{4+}$ and **L5** = $[Hg_4(\mathbf{2})_2(\mathbf{5})_2]^{8+}$. The low binding constant in Table 1 suggests that Cu^+ is only four-coordinated in $[Cu(\mathbf{4})(\mathbf{6})]^+$, while the five-coordinated complexes $[Zn(\mathbf{4})(\mathbf{6})]^{2+}$ and $[Hg(\mathbf{4})(\mathbf{6})]^{2+}$ 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.[11] Such phenomena had earlier been studied by Lehn,[11a] 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^{2+} and Cu^+ 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 **G1**[6c] (Scheme 2). Despite extensive ESI MS and ^1H 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 addition of Hg(II) (Scheme 3). The transmetalations were conveniently followed by ESI MS and fluorescence spectrometry (see Supporting Information).



Scheme 3. (a) A Two-Step Transmetalation off-on−off Fluorescence System. (B) Photo Taken under UV Lamp (254 nm)

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.

Acknowledgment. We are very much indebted to the DFG for continued financial support, and to Antje Völkel for experimental help with the analytical ultracentrifugation experiments.

Supporting Information Available: ^1H and ^{13}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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(10) The crystals were extremely solvent-sensitive and diffracted only poorly. Crystal data of **L2**: $C_{216}H_{156}F_{24}N_{20}O_{28}S_8Zn_4$, $M = 4453.57$, monoclinic, space group $P21/n$, $a = 21.715(6)$ Å, $b = 19.196(6)$ Å, and $c = 28.620(7)$ Å, $\beta = 94.851(17)°$, $V = 11887(5)$ A^3, $T = 157(2)$ K, $Z = 2$, $D_c = 1.244$ g/cm^3, λ(Mo Kα) = 0.71073 Å, 101 150 reflections measured, 17 215 unique ($R_{int} = 0.2147$) which were used in all calculations. $R_1 = 0.2315$ ($I > 2\theta(I)$) and $wR_2 = 0.4456$, GOF = 1.638; max/min residual density 1.272/−0.556 e Å^{-3}. See also Supporting Information.

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