

## Assembly of Dynamic Heterometallic Oligoporphyrins Using Cooperative Zinc–Nitrogen, Ruthenium–Nitrogen, and Tin–Oxygen Coordination

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The construction of supramolecular architectures<sup>1</sup> through noncovalent self-assembly has led to a resurgence of interest in coordination chemistry. For example, the ligand coordination properties of metalloporphyrins have resulted in a vast array of supramolecular systems, such as, cyclic oligomers,<sup>2</sup> linear oligomers<sup>3</sup> and polymers,<sup>4</sup> squares,<sup>5</sup> tapes,<sup>6</sup> and other geometries.<sup>7</sup> However, each of these constructions has employed only a single type of metal–ligand interaction. This report describes what we believe to be the first association under conditions of thermodynamic reversibility of heterometallic porphyrin oligomers driven by the synergistic coordination of at least two different metalloporphyrin building blocks designed to exhibit complementary geometries and cooperative binding properties.

To achieve our goal, we chose Zn(II), Ru(II), and Sn(IV) porphyrins for the contrast in their coordination chemistry. Zn porphyrins prefer nitrogen donor ligands, adopt 5-coordinate square pyramidal geometry, and are kinetically very labile, while Ru(CO) porphyrins form stable and inert complexes with nitrogen donor ligands and adopt 6-coordinate geometry. Sn(IV) porphyrins, on the other hand, prefer oxygen donor ligands, adopt 6-coordinate octahedral geometry, and exchange carboxylate ligands rather slowly.<sup>8</sup> When complementary binding functions are introduced into appropriately designed Zn(II), Ru(II), and Sn(IV) porphyrins, it becomes possible to assemble multiple components in a controlled manner.

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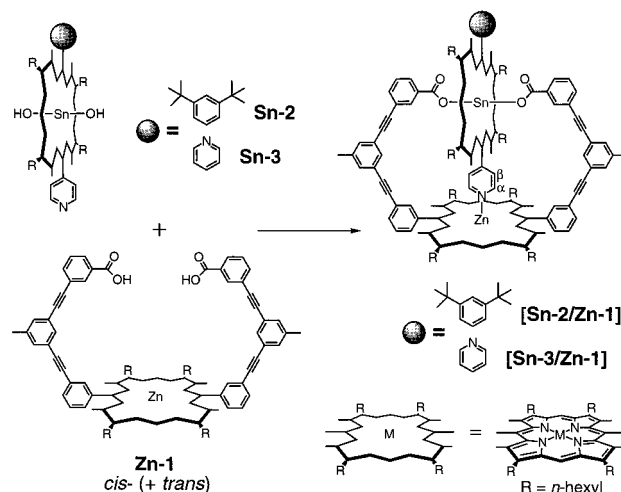
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### Scheme 1



For example, a two-component system can be readily envisaged: Zn porphyrin **Zn-1** was designed with two carboxylic acid groups for recognizing Sn(IV), while Sn(IV) porphyrin **Sn-2** possesses a single pyridyl group for recognizing Zn, as shown in Scheme 1.<sup>9</sup> **Zn-1** is obtained as a highly insoluble mixture of interconverting cis and trans atropisomers, which, upon addition of 1 equiv of **Sn-2**,<sup>10</sup> are converted quantitatively (over 24 h due to the insolubility) to the heterodimer [**Sn-2/Zn-1**] (Scheme 1). The resonances of [**Sn-2/Zn-1**] are sharp and well resolved in the <sup>1</sup>H NMR spectrum, allowing assignment and characterization by 2D NMR techniques (COSY, NOESY). The most diagnostic signals are the pyridyl resonances which are sharp and shifted significantly to higher field ( $\Delta\delta H_{\alpha} -6.23$  and  $H_{\beta} -1.44$  ppm). Usually, resonances of pyridyl ligands bound to simple Zn porphyrins are difficult to detect at room temperature as the ligand undergoes fast exchange on the NMR time scale; however, for [**Sn-2/Zn-1**] in the presence of excess **Sn-2**, slow exchange between free and bound ligands on the NMR chemical shift time scale allows observation of sharp coordinated ligand resonances. Structurally diagnostic nOe connectivities between the sharp pyridine ligand resonances of **Sn-2** and the meso and the aryl protons of the Zn porphyrin (pointing into the cavity) are also observed in the NOESY spectrum of [**Sn-2/Zn-1**], confirming the integrity of the Zn–pyridyl bond. These spectroscopic features provide strong evidence for the intramolecular interaction between the Zn porphyrin and the pyridine of the Sn porphyrin in [**Sn-2/Zn-1**]. Furthermore, in a 2 mM solution of [**Sn-2/Zn-1**], displacement of the intramolecularly bound Sn pyridine requires the addition of more than 1000 equiv of neat pyridine. This suggests that the effective molarity for the intramolecular Zn–N binding event is more than 2 M.<sup>11</sup> The Sn porphyrin unit becomes free to rotate about the Sn–carboxylate bond, as indicated by the disappearance of the upfield shifted  $\alpha$  and  $\beta$  resonances of the pyridine unit of [**Sn-2/Zn-1**]. When the solvent is removed by evaporation and the residue reconstituted in pyridine-free CDCl<sub>3</sub>, the original conformation of [**Sn-2/Zn-1**] is restored as confirmed by <sup>1</sup>H NMR spectroscopy, with the intramolecular Zn–pyridyl bond intact.

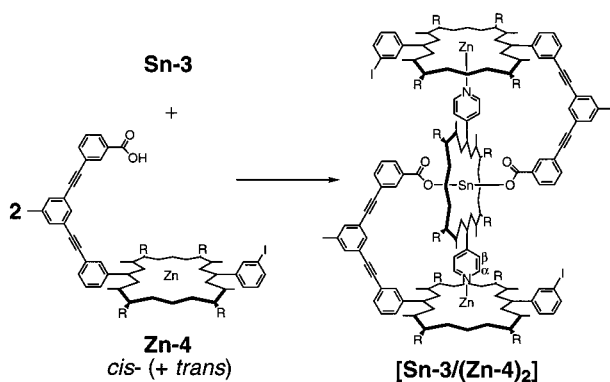
Recognition of the pyridyl group of **Sn-2** by the Zn center of **Zn-1** is kinetically the first event in the assembly process, even though the Zn–pyridyl binding affinity is significantly weaker than that between the Sn porphyrin of **Sn-2** and the carboxylate component of **Zn-1**. The evidence for this is the observation that

(9) The synthesis of **Zn-1** and **Sn-2** will be described elsewhere.

(10) All NMR experiments were performed at 2–5 mM concentration.

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Scheme 2



a mixture of oligomers is obtained in the reaction of the free-base analogue **H<sub>2</sub>-1**, which lacks the recognition site for the pyridyl group, with **Sn-2**. The poor solubility of **Zn-1** in CDCl<sub>3</sub>, resulting in a lack of signals in its <sup>1</sup>H NMR spectrum, ensures that the molarity of **Sn-2** is in effect much higher than that of **Zn-1** during the early stages of the reaction period (about 24 h), over which no intermediate species were detected, implying that the assembly of [Sn-2/Zn-1] is rapid. It has been established previously that addition of 2 equiv of benzoic acid to Sn(TPP)-(OH)<sub>2</sub> results in the complete formation of Sn(TPP)(benzoate)<sub>2</sub> in about 30 min via Sn(TPP)(OH)(benzoate).<sup>8</sup> In sharp contrast, while a combination of complex oligomers can be envisaged for the reaction in Scheme 1 where the carboxylate can bind intermolecularly to other Sn units, the accelerated rate and exclusive formation of the Sn-carboxylate component of [Sn-2/Zn-1] is driven by the intramolecular recognition of the pyridine group of **Sn-2** by the Zn ion of **Zn-1**.

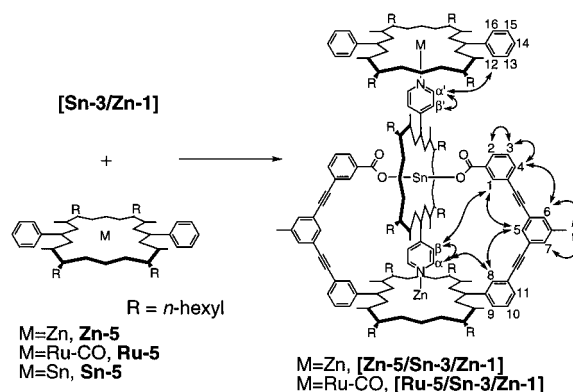
By exploiting the binding affinities resulting in the cooperative construction of [Sn-2/Zn-1], it has been possible to specifically design the structure of the building blocks to construct structurally diverse but well-defined assemblies. For example, the heterotrimer [Sn-3/(Zn-4)<sub>2</sub>] is quantitatively prepared from the combination of 2 equiv of **Zn-4** and 1 equiv of **Sn-3**, Scheme 2. While the heterodimer [Sn-2/Zn-1] is remarkably robust, [Sn-3/(Zn-4)<sub>2</sub>] is coordinatively saturated at each site but is less robust overall, as it lacks the cooperativity inherent in [Sn-2/Zn-1]; as a result [Sn-3/(Zn-4)<sub>2</sub>] displays dynamic NMR behavior analogous to that of the [Sn-2/Zn-1] complex only at low temperatures.

In a series of experiments designed to investigate the cooperative Sn-carboxylate binding, treatment of the dichloroacetate derivative of **Sn-3** with **Zn-4** yields [Sn-3/(Zn-4)<sub>2</sub>] in a matter of minutes, while treatment of the analogous dichloroacetate derivative of **Sn-5** with benzoic acid fails to produce any of the dibenzoate product, as expected from the relative pK<sub>a</sub> values. These competition experiments demonstrate that coordination of the Zn-pyridyl and Sn-carboxylate components is highly synergistic, resulting in a dramatic increase in the effective concentration of carboxylate at the Sn center.

The heterodimer [Sn-3/Zn-1] is obtained quantitatively from the addition of the Zn-diacid porphyrin **Zn-1** to the Sn di-pyridyl porphyrin **Sn-3** (1:1 mixture, Scheme 1). Complex [Sn-3/Zn-1] possesses both Zn-bound and uncoordinated pyridyl groups, prompting us to investigate the time scale of the "spinning" Sn-porphyrin and the ability to use the free pyridine to construct a trimetallic assembly. The structure of [Sn-3/Zn-1] in solution was confirmed by its <sup>1</sup>H NMR spectrum: diagnostic signals (H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>, and H<sub>δ</sub>) for both the Zn-bound pyridine and the unbound-pyridine are observed only at temperatures below 250 K, suggesting a temperature-dependent rotation of the Sn-porphyrin component of [Sn-3/Zn-1]. We exclude intermolecular competition on the basis that we failed to detect a concentration dependence on the appearance of the pyridyl signals of [Sn-3/Zn-1].

To further probe these interactions, we added 1 equiv of a simple Zn porphyrin **Zn-5** to a solution of [Sn-3/Zn-1]<sup>10</sup> (Scheme

Scheme 3



3). In the resulting <sup>1</sup>H NMR spectrum, the meso proton of the Sn-porphyrin and the α-protons of the coordinated carboxylate (H<sub>2</sub> in Scheme 3) of [Zn-5/Sn-3/Zn-1] were shifted upfield relative to the case of [Sn-3/Zn-1] in the absence of **Zn-5**, while the diagnostic pyridyl protons were difficult to identify due to exchange. This observation at 300 K implies a weak contribution from the ring current of coordinated **Zn-5**. The pyridyl signals of [Sn-3/Zn-1] sharpen (at 245 K) in the presence of **Zn-5** at a temperature which is higher than when **Zn-5** is absent (at 220K), suggesting that the spinning motion of the Sn-porphyrin can be retarded by the cooperativity of the intra- and intermolecular coordination of two Zn porphyrins. In effect, the weak binding of **Zn-5** converts [Sn-3/Zn-1] into a complex with dynamic properties resembling those of the monopyrindyl analogue [Sn-2/Zn-1].

We also assembled a trinuclear heterometallic oligoporphyrin [Ru-5/Sn-3/Zn-1] consisting of Zn, Sn, and Ru porphyrins. [Ru-5/Sn-3/Zn-1] is quantitatively prepared by the addition of 1 equiv of the Ru porphyrin **Ru-5** to [Sn-3/Zn-1] (Scheme 3). Ru porphyrins exhibit a significantly larger association constant than Zn porphyrins, so that in [Ru-5/Sn-3/Zn-1] all binding interactions are amplified relative to [Zn-5/Sn-3/Zn-1], effectively "locking" the whole structure into a rigid conformation. Most remarkably, the same heterotrimer assembles when the three individual components **Zn-1**, **Sn-3**, and **Ru-5** are simply mixed in solution. To the best of our knowledge, [Ru-5/Sn-3/Zn-1] represents the first example of a thermodynamically constructed heterometallic oligoporphyrin containing three different metals.<sup>12</sup> The rigidity of the structure and the favorable geometry of [Ru-5/Sn-3/Zn-1] make this molecule ideal for characterization by 2D NMR techniques; nOe cross peaks (NOESY) were identified throughout the molecule, linking the three porphyrins of the assembly (represented by double-headed arrows in Scheme 3).

In summary, we have prepared the heterometallic dynamic oligoporphyrins which possess a noncoordinated pyridine and have shown that competition experiments are able to provide new insights into the intramolecular and intermolecular coordination processes. We also report the first thermodynamically driven trinuclear heterometallic oligoporphyrin assembly, based on a combination of covalent and noncovalent interactions which may provide a new approach for the preparation of complex porphyrin assemblies such as catenanes and rotaxanes.

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**Supporting Information Available:** Synthetic procedure and spectroscopic characterization of [Sn-2/Zn-1], [Sn-3/(Zn-4)<sub>2</sub>], [Sn-3/Zn-1], and [Ru-5/Sn-3/Zn-1]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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