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# A Convergent Coordination Chemistry-Based Approach to Dissymmetric Macrocyclic Cofacial Porphyrin Complexes

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We report a highly convergent and modular approach for the synthesis of dissymmetric cofacial porphyrin complexes, which is based upon the weak-link approach to supramolecular coordination chemistry. Specifically, we have utilized a halide-induced ligand rearrangement reaction, which is capable of providing heteroligated mixed-metal porphyrin complexes in quantitative yield. Significantly, the adoption of a coordination chemistry based approach for the synthesis of these complexes allows for facile in situ regulation of the porphyrin–porphyrin interactions through the addition of external chemical stimuli.

For over 25 years, research focused on studying the synthesis and properties of cofacial porphyrin complexes[1] has generated many sophisticated and potentially useful species.[2−6] While these elegant structures have played a crucial role in elucidating many interesting physicochemical phenomena,[7] they are often synthesized using tedious multistep procedures, relying on rigid scaffolds that restrict the overall structural flexibility of the targeted complex. Therefore, it is difficult to carry out comprehensive studies addressing the consequences of changing the porphyrin−porphyrin distance, their orientation with respect to each other, and the metal centers that reside within them.[8,9] A significant advance would be the development of a synthetic methodology that allows for the rapid assembly of porphyrin building blocks into cofacial structures with control over the orientation and interfacial distances of the porphyrins. Herein, we report how the weak-link approach (WLA)[10,11] can be used to assemble porphyrins into multimetallic cofacial structures in a highly modular, convergent, and high-yielding manner. This approach not only enables the systematic placement of different metals within the cofacial assembly but also allows for significant control over the porphyrin orientation and interporphyrin distances. These capabilities will open many avenues for studying such structures in the context of catalysis and biomimetic systems, especially in the context of energy transfer.[12]

Recently, we reported the synthesis of *symmetric* supramolecular cofacial porphyrin assemblies that can be modified in situ to allosterically control a catalytic reaction.[13] The allosteric effect is made possible by linking porphyrins together through a working molecular hinge that operates by reaction with specific small-molecule effectors. While this system possesses several attributes, the synthetic methodology used to prepare such complexes does not allow one to selectively access multiple porphyrin−porphyrin orientations or dissymmetric mixed-metal complexes. To overcome this challenge, we have developed a halide-induced ligand rearrangement (HILR) reaction that enables the preparation

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of dissymmetric heteroligated coordination complexes.[14−16] This reaction employs simple $Rh^{I}$ precursors and a combination of phosphine−thioether (PS) and phosphine−ether (PO) hemilabile ligands to afford heteroligated $Rh^{I}$ macrocyclic,[14] tweezer,[15] and triple-decker[16] supramolecular complexes. Significantly, because this reaction relies on the use of two unique ligands, it can be easily extended to the synthesis of dissymmetric mixed-metal cofacial porphyrin assemblies. Owing to the (PS)(PO)$Rh^{I}$ coordination environment, such complexes can undergo significant structural modifications in situ through the manipulation of the ancillary ligands at each $Rh^{I}$ center.

To demonstrate the utility of the HILR approach in the synthesis of mixed-metal cofacial porphyrin assemblies, we synthesized a $Mg^{II}$ PO hemilabile porphyrin ligand. $Mg^{II}$ was inserted[17] into 5,15-bis{4-[2-(diphenylphosphinothioyl)ethoxy]-phenyl}-10,20-bis(mesityl)porphyrin,[13] which provided the corresponding $Mg^{II}$-metalated analogue (**1**) in 93% yield. Upon isolation of **1**, the sulfide protecting groups were easily removed from the phosphine moieties using $Cp_2ZrHCl$ to yield the ether-based hemilabile phosphine ligand **2** in 89% yield (see the Supporting Information).

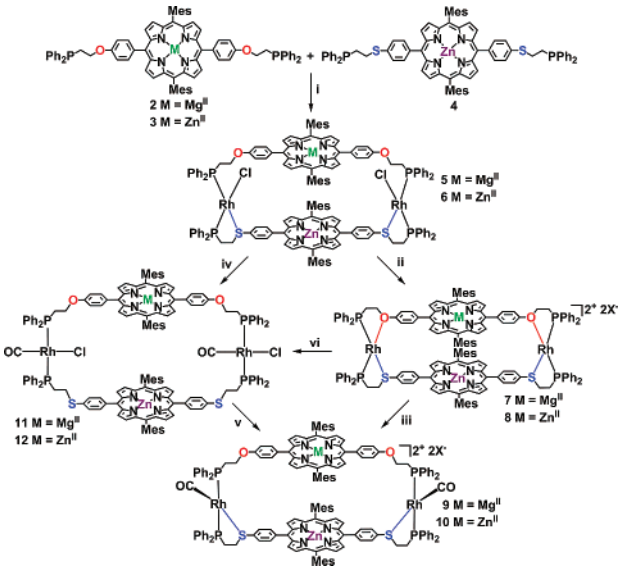
Hemilabile phosphine ligands **3** and **4** were prepared according to previously published methods.[13] Upon the addition of tetrahydrofuran (THF) to a mixture of PO ligand **2** (or **3**), PS ligand **4**, and $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) followed by sonication for 1 h, the semi-open complexes **5** and **6** form quantitatively according to $^{31}P\{^{1}H\}$ NMR spectroscopy and are isolated in 94% and 93% yield, respectively (Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectra of **5** and **6** in $CD_2Cl_2$ both show two distinct resonances at $\delta$ 72.5 (dd, $J_{Rh-P}$ = 182 Hz, $J_{P-P}$ = 40 Hz) and 32.7 (dd, $J_{Rh-P}$ = 170 Hz, $J_{P-P}$ = 41 Hz), which are highly diagnostic of the dimeric $Rh_2(Cl)_2(\kappa^2\text{-PS})(\kappa^1\text{-PO})$ heteroligated *cis*-P−Rh−P coordination environment.[14−16] Additionally, the electrospray ionization mass spectrometry (ESI-MS) spectra for **5** and **6** display $M^{2+}$ ion peaks at *m*/*z* 1351.7 and 1373.3, respectively.

Magenta single crystals of **5**, suitable for X-ray diffraction analysis, were grown by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of **5** with 1 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO). The DABCO guest acts as a bifunctional bridge between the $Mg^{II}$PO and $Zn^{II}$PS porphyrins (Figure 1). Additionally, each of the square-planar $Rh^{I}Cl$ sites exhibits *cis*-P−Rh−P coordination environments, with the PS and PO porphyrin ligands coordinated to $Rh^{I}$ in $\kappa^2$ and $\kappa^1$ fashions, respectively.

Upon sonication with 2 equiv of $Na[B(ArF)_4]$ in $CH_2Cl_2$, the semi-open assemblies **5** and **6** are quantitatively converted to the fully closed cationic macrocycles **7** and **8** (isolated yields >90%; Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectra for compounds **7** and **8** display two resonances at $\delta$ 72.5 (dd, $J_{Rh-P}$ = 198 Hz, $J_{P-P}$ = 40 Hz) and 51.6 (dd, $J_{Rh-P}$ = 167 Hz, $J_{P-P}$ = 41 Hz), indicating the formation of complexes with the desired closed geometries in which the phosphines have retained their *cis*-P−Rh−P orientation. The ESI-MS spectra of **7** and **8** exhibit $M^{2+}$ ion peaks at *m*/*z* 1316.8 and 1337.7, respectively.

Because the Rh−O bonds in macrocycles **7** and **8** are weaker than the Rh−S bonds, they can be quantitatively converted to the semi-open assemblies **9** and **10**, respectively, upon the addition of CO (1 atm) (Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectra for **9** and **10** display two resonances at $\delta$ 61.3 (dd, $J_{Rh-P}$ = 265 Hz, $J_{P-P}$ = 114 Hz) and 18.6 (dd, $J_{Rh-P}$ = 263 Hz, $J_{P-P}$ = 115 Hz), respectively, indicating complete

**Scheme 1.** In Situ Regulation of Heteroligated Supramolecular Cofacial Porphyrin Complexes[a]




[a] Mes = mesityl and $X^-$ = $[B(ArF)_4]^-$ = tetrakis(3,5-trifluoromethylphenyl)borate. (i) $[Rh(COD)Cl]_2$, THF; (ii) $Na[B(ArF)_4]$ (2 equiv), $CH_2Cl_2$; (iii) CO (1 atm), $CD_2Cl_2$; (iv) CO (1 atm), $CD_2Cl_2$; (v) $Na[B(ArF)_4]$ (2 equiv), $CD_2Cl_2$; (vi) $(n\text{-Bu})_4NCl$ (2 equiv), CO (1 atm), $CD_2Cl_2$.

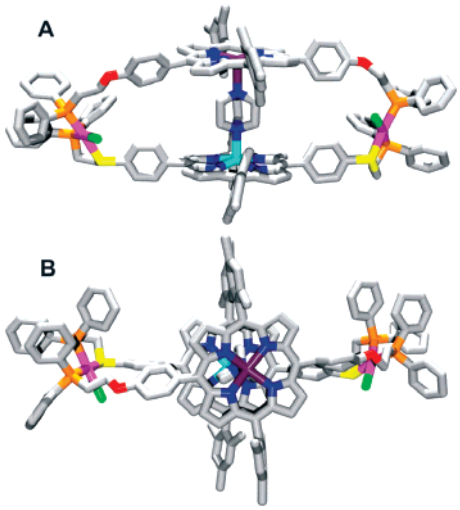



**Figure 1.** Molecular connectivity diagram obtained from the X-ray crystal structure of heteroligated host−guest complex **5**⊃**DABCO**. Views are shown from the side (A) and the top (B). All hydrogens and disordered atoms have been omitted for clarity. Selected distances: $Rh^{I}-Rh^{I}$ = 20.9 Å; $Zn^{II}-Mg^{II}$ = 7.12 Å. Color code: gray, C; pink, Rh; orange, P; yellow, S; red, O; green, Cl; blue, N; light blue, Zn; purple, Mg.

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conversion into complexes with *trans*-P−Rh−P coordination environments. The Fourier transform IR (FTIR) spectra for **9** and **10** exhibit a single $\nu_{C\equiv O}$ band at 1970 $cm^{-1}$, consistent with the proposed formulation of $[Rh_2(\kappa^2\text{-PS})(\kappa^1\text{-PO})(CO)_2]^{2+}$ adducts.[15] Consistent with the proposed formulations, the ESI-MS spectra of **9** and **10** display $M^{2+}$ peaks at *m/z* 1346.3 and 1365.3, respectively.

Adding 2 equiv of $(n\text{-Bu})_4NCl$ followed by the introduction of CO (1 atm) to solutions of **7** or **8** results in the quantitative formation of the fully open assemblies **11** or **12**, respectively (Scheme 1). Alternatively, **11** or **12** can be directly prepared via introduction of CO (1 atm) to solutions of the semi-open assemblies **5** or **6**. The $^{31}P\{^1H\}$ NMR spectra of **11** and **12** both exhibit a broad multiplet at $\delta \sim 23$, which arises as a result of the overlap of a pair of doublet of doublets. The presence of a CO-bound $Rh^I$ species was confirmed through FTIR spectroscopy, where **11** and **12** display a $\nu_{C\equiv O}$ stretch at 1968 and 1965 $cm^{-1}$, respectively.[15] Furthermore, the ESI-MS spectra of **11** and **12** contain peaks that correspond to the $M^{2+}$ ions at *m*/*z* 1345.5 and 1365.8, respectively, indicating the loss of the $Cl^-$ ligands bound to the $Rh^I$ metal centers.[15,16]

The transformations described in Scheme 1 demonstrate the power of the WLA as a highly convergent and modular synthetic methodology for the preparation of cofacial porphyrin structures in which the porphyrin−porphyrin distance and orientation can be selectively modulated in situ. Significantly, the $Rh^I$ heteroligated environment enables the user to selectively access four different cofacial assemblies from a single macrocycle that is synthesized in high yield from two unique hemilabile ligands and simple metal precursors. Additionally, through this approach one can easily prepare dissymmetric cofacial porphyrin systems in which each porphyrin ligand contains a different metal. Because porphyrins are abundant in nature and are highly functional building blocks involved in many important proteins and enzymes (such as cytochrome P-450,[18] cytochrome *c* oxidase,[19] and hemoglobin[20]), we anticipate that the ability to design dissymmetric, multimetallic cofacial porphyrin superstructures where the orientation of the porphyrins contained within such structures can be "fine-tuned" in situ will facilitate significant discoveries in the fields of energy transfer, host−guest chemistry, and supramolecular catalysis.

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**Supporting Information Available:** Experimental procedures for compounds **1**−**12** and X-ray crystallographic data for **5**⊃**DABCO** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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