

### Synthesis and Reactivities of *meso*-Free and Core-Modified [14]Triphyrins(2.1.1)

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Triphyrins are porphyrin analogues that contain three pyrrole rings linked through *meso*-sp<sup>2</sup> carbon atoms. Triphyrins have been reported as dome-shaped boron complexes and 14 $\pi$ -electron aromatic system except subpyriporphyrins. In particular, subphthalocyanines<sup>[1]</sup> and subporphyrins<sup>[2]</sup> have demonstrated a variety of optoelectronic properties such as non-linear optical absorption and higher emission quantum yield. On the other hand, we have developed boron free [14]triphyrins(2.1.1) by modified Lindsey method<sup>[3]</sup> or intramolecular McMurry coupling of diformyltripyrrane<sup>[4]</sup>. They are centered on a 14 $\pi$ -electron aromatic system with nearly planer structure. They also can be act as a monovalent ligand. Moreover, McMurry coupling method was expected to realize the synthesis of heterocycles-included triphyrins because diformyltripyrrane units can control the replacement of one of the pyrrole rings to heterocycle. Here, we will report the synthesis and reactivity of *meso*-free triphyrin metal complexes and core-modified triphyrins.

Firstly, we investigated the metal complexes of triphyrins which have been prepared from free-base triphyrin with manganese (I), rhenium (I), ruthenium (II) and boron (III). They showed dome-shaped structure changed from the nearly planer structure of free-base triphyrin. In this presentation, we will discuss the optical and electrochemical properties and crystal structures of these triphyrin metal complexes.

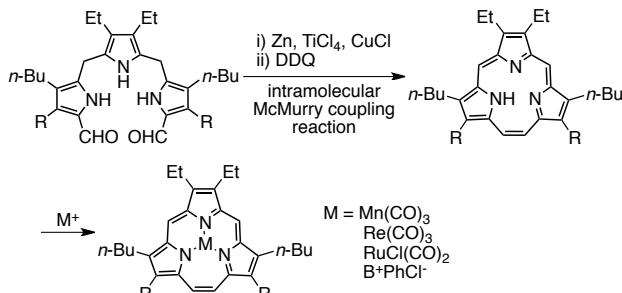


Figure 1 Synthesis of meso-free triphyrin and its metal complexes.

Secondly, we considered the thiophene ring included core-modified triphyrins (TTP). TTP has highly reactivity with alcohol to give alkoxy-substituted thiatriphyrin since the steric hindrance of inner cavity reduced the stability of 14 $\pi$ -aromaticity. Interestingly, the treatment of alkoxy-substituted thiatriphyrin with acid led to the elimination of the alkoxy group and generated the protonated thiatriphyrin. In this presentation, we will report the synthetic procedures as well as the reactivity, the crystal structures, and the optical properties of these thiatriphyrin derivatives.

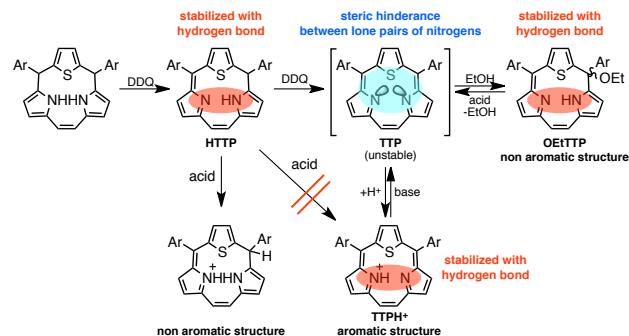


Figure 2. Reaction scheme of thiatriphyrins.

### References

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