

Metalation-induced formation of novel fused porphyrinoid dimers from tetrabromo-[36]octaphyrin *via* transannular bond formation

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Keywords: global aromaticity; N-confused porphyrin; octaphyrin; porphyrin(2.1.1.1); transannular reaction

Porphyrin tapes have been targets of extensive studies because of their remarkably red-shifted absorptions, multi-charge responsibility, and electric conductivity.¹ A variety of porphyrin tape variants have also been created to display perturbed photophysical properties being characteristic of constituent porphyrin(oid) units. Such tape-like porphyrinoid arrays are synthesized mostly by oxidative fusion of the corresponding singly-linked precursors.

Here we found that tetrabromo-[36]octaphyrin was transformed to novel fused porphyrin dimers such as porphyrin(2.1.1.1) dimer **2** and N-confused porphyrin dimer **3** through metalation-induced transannular C–C bond formation. Tetrabromo-[36]octaphyrin **1** was synthesized as a novel *meso*-free type octaphyrin. Zn^{II} complexation of **1** afforded bis-Zn(II) complex **2** through C_{meso}–C_{meso} bond formation. The complex **2** exhibits a diatropic ring-current effect due to its 36 π Möbius aromaticity.² On the other hand, Ni^{II} complexation of **1** caused C_{meso}–C β bond formation with concomitant debrominations. Bis-Ni^{II} complex **3** shows a paratropic ring-current effect due to its global 36 π antiaromaticity.

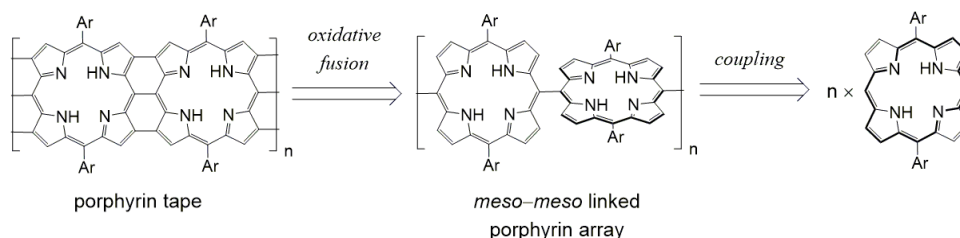
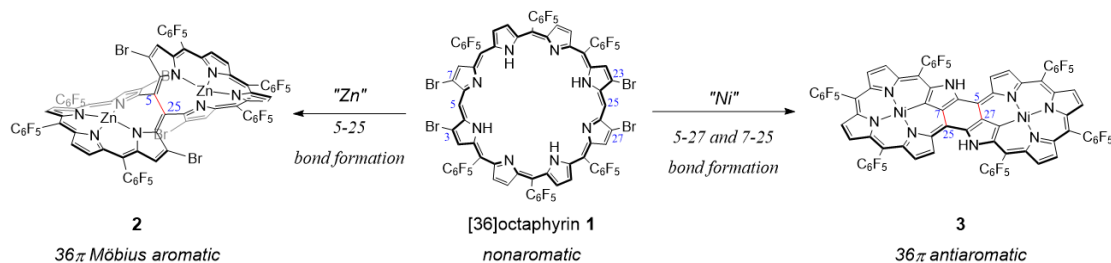


Figure 1. Typical synthetic route of porphyrin tape.



Scheme 1. Synthesis of **2** and **3**.

1) T. Tanaka, A. Osuka, *Chem. Soc. Rev.* **2015**, 44, 943. 2) T. Tanaka, A. Osuka, *Chem. Rev.* **2017**, 117, 2584; D. Kim, A. Osuka *et al. Angew. Chem. Int. Ed.* **2008**, 47, 681.