Synthesis and Properties of Triply Fused N-Confused Porphyrin Dimer

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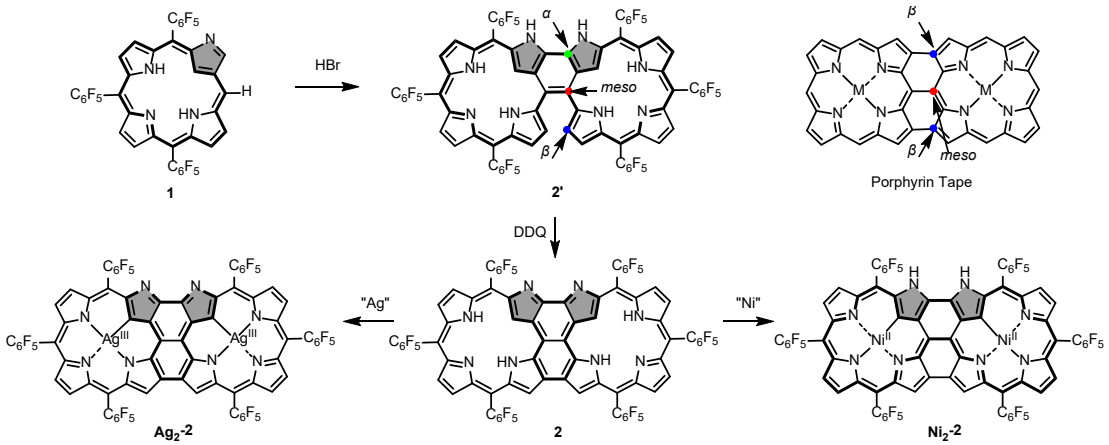
meso-meso, *β-β*, *β'-β'* Triply linked porphyrin arrays, namely porphyrin tapes, have been extensively investigated on their remarkable electron-transporting capabilities and the nonlinear optical properties caused by the unique laterally π-conjugated structure.[1,2] To gain further insight into the aromaticity effect of the porphyrin tapes, we have synthesized a novel *α-α'*, *meso-meso*, *β-β'* triply linked dimeric porphyrin isomer (**2**) via the stepwise oxidative dimerization of 5-unsubstituted N-confused porphyrin (**1**) in this work.



Treatment of **1** with hydrogen bromide in toluene under reflux afforded *α-α'*, *meso-meso* doubly linked porphyrin dimer (**2'**) with global Hückel 38π aromaticity. Subsequently, the doubly fused **2'** was oxidized with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to furnish the triply linked porphyrin dimer **2**. Consistent with the NH tautomeric feature (2H vs. 3H forms in the core) of the N-confused porphyrins, coordination of silver(III) and nickel(II) ions yielded the bis-metal complexes, **Ag_2-2** and **Ni_2-2**, respectively, with distinct electronic features. Exclusively, a local paratropic ring-current was realized on the benzo[*e*]pyrrolo[3,2-*g*]indole moiety in **Ag_2-2**. In contrast, a strong paratropic ring current was emerged in **Ni_2-2** along with the distinct global Hückel antiaromaticity as inferred from the study on the NMR spectroscopy and the DFT calculations. The unique complexation-induced aromaticity switching is characteristic for the isomeric N-confused porphyrin tape **2**. The optical and electrochemical properties of these complexes will be presented in detail.

1) T. Tanaka, A. Osuka, *Chem. Eur. J.* **2018**, *24*, 17188.

2) A. Nakai, J. Kim, T. Tanaka, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2021**, *60*, 26540.