FROM MESO-MESO COUPLED DIPORPHYRIN TO A MOLECULAR WIRE

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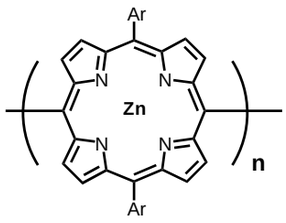
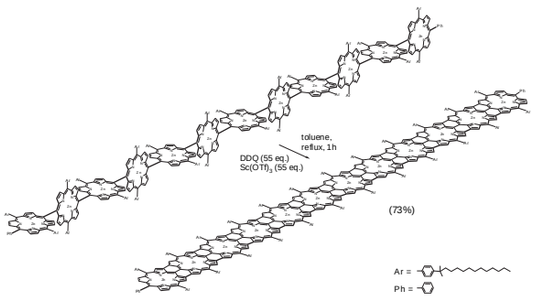
Treatment of Zn(II) 5,15-diarylporphyrin with Ag(I) salt in $CHCl_3$ led to the formation of *meso-meso* coupled diporphyrin.[1] In contrast, *meso-β* coupled diporphyrins were formed from the electrochemical oxidation of Ni(II) and Pd(II) 5,15-diarylporphyrins.[2] The coupling regioselectivities can be understood in terms of the HOMO orbital characteristics; probably A_{2u} for Zn(II) porphyrin and A_{1u} for Ni(II) and Pd(II) porphyrins. Interestingly, oxidation of Ni(II) and Pd(II) porphyrins with $(BrC_6H_4)_3NSbCl_6$ gave doubly *meso-β*-linked diporphyrins by way of singly *meso-β* linked diporphyrin.[3,5] These fused diporphyrins have enforced planar structures and display red-shifted absorption bands and lowered oxidation potentials. Oxidation of a singly *meso-meso* linked Cu(II) diporphyrin with $(BrC_6H_4)_3NSbCl_6$, afforded a triply *meso-meso*, *β-β*, *β-β* linked symmetric diporphyrin in good yield, which displays extensively red-shifted absorption band and a lowered oxidation potential.[4,5]

Synthesis of discrete long *meso-meso* coupled porphyrin arrays has been attempted by repeated doubling reactions, leading to the synthesis of 128-mer whose molecular length exceeds 0.1 μm in its linear form.[6] When end-phenyl capped *meso-meso* coupled porphyrin arrays were oxidized with DDQ and $Sc(OTf)_3$, completely planar porphyrin tapes were obtained, which displayed the extremely red-shifted absorption bands which reach in the infrared.[7] The porphyrin tapes prepared are interesting in light of their extremely extending π-conjugated systems.





1 A. Osuka, H. Shimidzu, *Angew. Chem., Int. Ed.* **1997**, *36*, 135.

2 T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Angew. Chem. Int. Ed.* **1999**, *38*, 176.

3 A. Tsuda, T.; Nakano, A.; Furuta, H.; Yamochi, H.; Osuka A. *Angew. Chem, Int. Ed*. **2000**, *39*, 558.

4 A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem. Int. Ed.* **2000**, *39*, 2549.

5 A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304.

6 N. Aratani, Osuka, et al., *Angew. Chem, Int. Ed.* **2000**, *39*, 1458.

7 A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79.