

## ポルフィリン分子ワイヤーの効率的電子状態計算と

### 伝導性・磁性・NLO 特性

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We present a quantum-chemical analysis of the central metal effect on the (hyper)polarizabilities of *meso-meso* linked metal porphyrin oligomers using elongation finite-field (elongation-FF) method. Three *meso-meso* linked metal porphyrins are selected and shown in Figure 1. The molecular structures are optimized at B3LYP/6-31G using GAUSSIAN 03. Here, the porphyrins are connected directly at the *meso* position of the porphyrin ring. The NLO properties of metal porphyrins, where M=Mg, Zn, and Ni, are investigated using Hartree-Fock elongation method. The starting cluster for elongation-FF contained 2 units, and the chain was elongated by one unit at a time up to  $N = 20$ . HF/STO-3G basis set at *ab initio* level is employed for C, N, H and Mg atoms, Zn and Ni metals are described by model core potentials (MCP) which are included in GAMESS. The magnitude of the external field is fixed to  $E=0.001$  a.u. The discrepancy in total energy between the elongation method and a conventional calculation was negligibly small in the order of  $10^{-7}$  hartree/atom for *meso-meso* linked metal porphyrins (metal=Mg, Zn, and Ni).

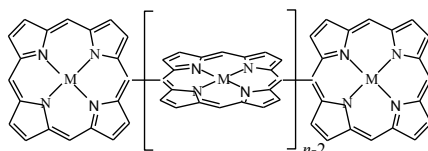


Figure 1 Structure of *meso-meso* linked metal porphyrin (M=Mg, Zn, and Ni)

The LUMO and HOMO energies, as well as energy gap between HOMO and LUMO are shown in Table 1. It can be noticed that the HOMO energy down shifts moving from Mg to Ni for dimer, trimer and tetramer, while the LUMO energy is increased from Mg to Ni. So the HOMO and LUMO energy gap increases from Mg to Ni. It suggests that the HOMO and LUMO energies as well as energy gap are sensitive to the metal, which might influence the NLO properties of *meso-meso* linked metal porphyrins. Plots of  $\alpha$  and  $\gamma$  values versus chain length ( $N$ ) are shown for metal porphyrin oligomers in Figure 2. It is found that *meso-meso* linked metal porphyrins exhibit remarkable evolution of  $\alpha$  and  $\gamma$  along with an increasing number of porphyrin units  $N$ . For *meso-meso* linked Mg-porphyrin, the  $\gamma$  value is increased from  $3.140 \times 10^5$  a.u. in two units to  $1.522 \times 10^7$  a.u. in 20 units, while for Zn-porphyrin, the  $\gamma$  value is increased from  $2.569 \times 10^5$  a.u. in two units to  $1.311 \times 10^7$  a.u. in 20 units. At the same unit, the values of  $\gamma$  are as following:  $\gamma_{\text{Mg}} > \gamma_{\text{Zn}} > \gamma_{\text{Ni}}$ . Comparing with linear polarizability, the second order NLO properties of *meso-meso* linked metal porphyrin are sensitive to the metals, that is, the nature of the metal can influence the second order NLO response of metal porphyrins. On the basis of these results, the *meso-meso* linked metal porphyrins are promising candidates for NLO materials. Further investigations with different transition metals are required for quantitative analysis of the metal porphyrins.

Table 1 The LUMO, HOMO energies and the energy gap between HOMO and LUMO for dimer, trimer and tetramer of metal porphyrins (metal=Mg, Zn, Ni) (eV)

	Dimer			Trimer			Tetramer		
	Mg	Zn	Ni	Mg	Zn	Ni	Mg	Zn	Ni
$E_{LUMO}$	-2.300	-2.297	-2.246	-2.343	-2.351	-2.333	-2.380	-2.383	-2.349
$E_{HOMO}$	-5.178	-5.216	-5.238	-5.149	-5.181	-5.219	-5.143	-5.168	-5.205
$\Delta E$	2.877	2.919	2.993	2.807	2.830	2.887	2.763	2.785	2.855

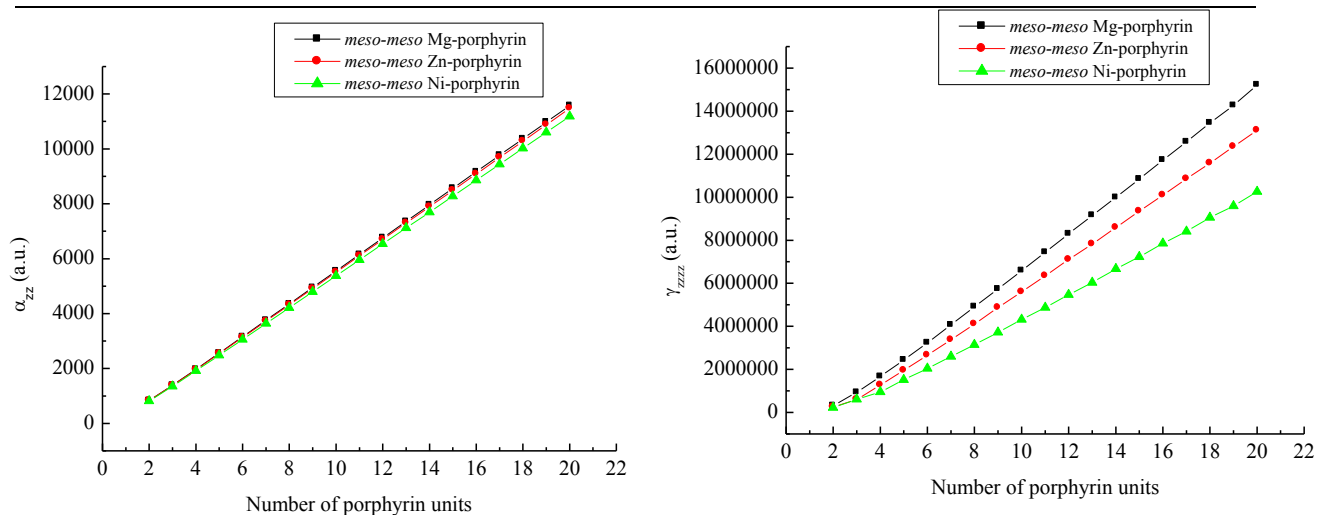


Figure 2 Dependence of (hyper) polarizabilities on the number of porphyrin units for *meso-meso* linked metal porphyrin

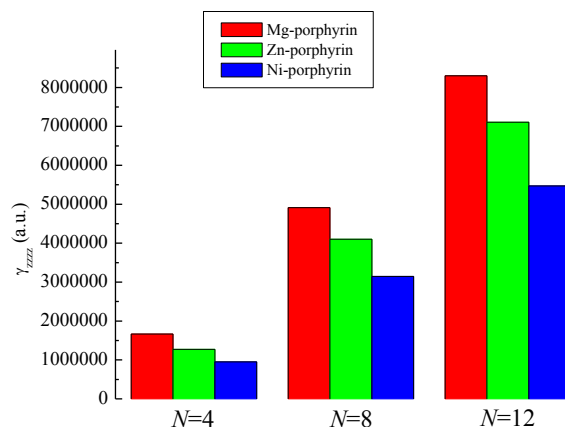


Figure 3 The  $\gamma$  values for *meso-meso* linked metal porphyrins (metal=Mg, Zn, and Ni) in the  $N = 4, 8, 12$

## References

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