

Pseudo-Jahn-Teller Effect in Deprotonated Dimethyl Amino Phenyl Substituted Phthalocyanine

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Breloy *et al.* [1] synthesized a new dimethyl amino phenyl substituted phthalocyanine (dmaphPcH₂) and its Ag(II) complex ([dmaphPcAg]⁰, see Fig. 1) used as a visible light-absorbing photoinitiator for free-radical and cationic polymerizations. Irradiation of the [dmaphPcAg]⁰ solution led to the reduction of Ag(II) to Ag(I) and simultaneously generated the nitrogen-centered radical. In the next step, Ag nanoparticles and aromatic carbon-centered radicals were formed. The proposed photoinitiation mechanisms under light irradiation suppose the existence of [dmaphPc]⁰, Ag⁰ and [dmaphPcAg]^q, q = -1, 0 and + 1, entities. DFT calculations indicate a D₄ → D₂ symmetry descent due to the Jahn-Teller effect in Ag complexes.

The aim of our recent study is to extend the DFT studies to free ligands. We have optimized the geometries of the [dmaphPc]^q species, q = -2 → 0, and performed TD-DFT calculations within the D₄ symmetry group and its subgroups. Using a group-theoretical treatment, the consequences of a pseudo-Jahn-Teller effect in these systems were explained in terms of the epikernel principle method [2, 3].

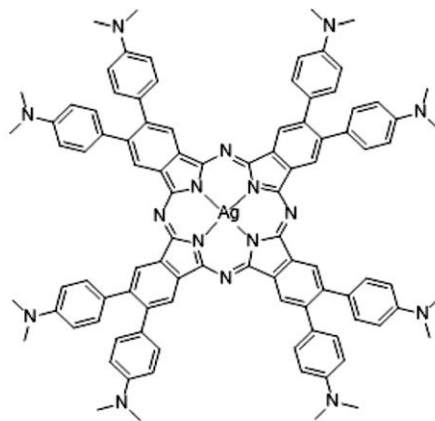


Figure 1. Structure of [dmaphPcAg]⁰ [1].

[1] L. Breloy, et al.; *Polym. Chem.* **12**, 1273 (2021).

[2] A. Ceulemans; L.G. Vanquickenborne; *Struct. Bonding* **71**, 125 (1989).

[3] M. Breza; *Progr. Theor. Chem. Phys.* **23**, 59 (2012).