Theoretical Aspects on the Evaluation and Interpretation of the Third-Order Nonlinear Optical Properties of Diradical Compounds

Benoît Champagne,[1] Edith Botek,[1] Raphaël Carion,[1] Akihiro Shimizu,[2] Takashi Kubo,[2] Kenji Kamada,[3] Koji Ohta,[3] Ryohei Kishi,[4] Hitoshi Fukui,[4] Yasuteru Shigeta,[4] and Masayoshi Nakano[4]

[1] *Laboratoire de Chimie Théorique, UCPTS, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles, 61, B-5000 Namur, BELGIUM,* benoit.champagne@fundp.ac.be

[2]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, JAPAN;* [3] *Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, JAPAN;* [4] *Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, JAPAN*

I. Introduction

Over the last decades, scientists have designed molecules and materials with unique nonlinear optical (NLO) properties targeting the realization of all-optical computing and signal processing. For many reasons (large response, short response time) organic compounds are of considerable interest. However, suitable materials for practical applications are still missing because the third-order NLO responses and the related molecular second hyperpolarizability (γ) are still too small. Increasing the conjugation length was a first strategy to maximize γ while in subsequent approaches appropriate substituents with specific donor and acceptor strengths were selected. More recent strategies consist in varying the shape and dimensionality of the chromophore and of charging it, for instance by chemical doping.

II. Diradicals and multiradicals as third-order NLO compounds

Although most of these systems are closed-shell molecules, recent studies have demonstrated that open-shell species show potential as materials with high NLO efficiency and, in particular, singlet diradical systems with intermediate diradical character. For instance, *ab initio* molecular orbital and DFT calculations performed on the *p*-quinodimethane model showed that γ attains a maximum in the intermediate diradical character region and subsequently that π-conjugated diradical systems involving imidazole rings and compounds of the family of thermally stable diphenalenyl diradical systems display significant enhancements of γ with respect to their analogous closed-shell systems. Then, the dependence of γ on the spin states makes these compounds further attractive for designing multifunctional materials. In this presentation, theoretical aspects on the evaluation and interpretation of γ of diradical and multiradical species will be discussed.