

Giant enhancement of the second hyperpolarizabilities of open-shell singlet molecular systems by an external electric field and donor-acceptor substitution

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We have theoretically found an external field (F) induced giant enhancement of the second hyperpolarizability γ of open-shell singlet systems with intermediate diradical characters [1]. As realistic examples, we examine the field effects on the γ of polyaromatic diradicaloid having intermediate diradical character, *s*-indaceno[1,2,3-*cd*;5,6,7-*c'd'*]diphenalene (IDPL), in comparison to a closed-shell analogue of similar size composed of two pyrene moieties (PY2) by carrying out spin-unrestricted density functional theory, LC-UBLYP, calculations (see Figure 1) [2]. For IDPL, the field-induced enhancement ratio is estimated to reach 4 orders of magnitude for an electric field of 0.0077 a.u., whereas it is less than a factor of 2 for PY2. Moreover, an enhancement is also observed by substituting both-end phenalenyl rings of IDPL by donor (NH_2)/acceptor (NO_2) groups but this enhancement is limited to about two orders of magnitude. These enhancements are associated with a reduction of the diradical character – and therefore an improved thermal stability – as well as with the appearance of substantial Type-I contributions to γ .

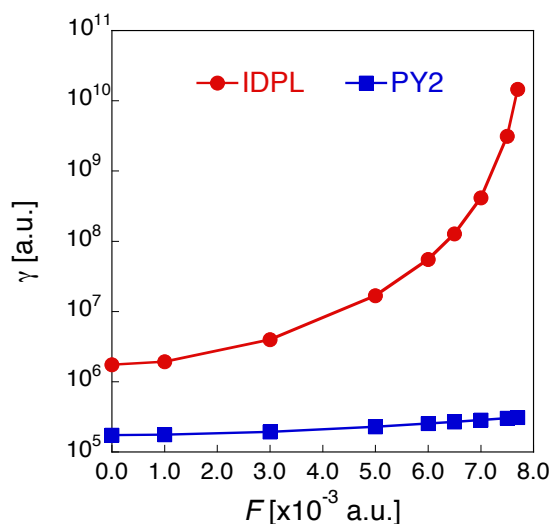


Figure 1. Static electric field (F) effect on γ [a.u.] of IDPL and PY2 calculated by the LC-UBLYP/6-31G* method.

[1] (a) M. Nakano et al. *Phys. Rev. Lett.* **99**, 033001 (2007); *J. Chem. Phys.* **133**, 154302 (2010). (b) K. Kamada et al. *J. Phys. Chem. Lett.* **1**, 937 (2010) [2] M. Nakano et al. *J. Phys. Chem. Lett.* **2**, 1094 (2011).