



A note on second-order nonlinear optical response of high-spin bis-TEMPO diradicals with possible application



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ABSTRACT

In this note, we have theoretically evaluated second-order nonlinear optical (NLO) responses of two structural isomeric forms of three different green fluorescent protein chromophores (*viz.* cyan fluorescent protein (CFP), orange variant of *Discosoma coral* (DsRed) and *Zoanthus sp.* (zFP)) coupled bis-TEMPO based photomagnetic high-spin diradicals by measuring the second-order effect of first molecular hyperpolarizabilities. The magnetic character and certain biological applicabilities of these diradicals are investigated theoretically in one of our recent papers (Bhattacharya et al., 2013). The second-order total molecular hyperpolarizabilities of these molecules are correlated with their respective HOMO–LUMO energy gaps (ΔE_{H-L}) and also with the extent of the π -network of the couplers. Relations between ΔE_{H-L} , chemical hardness, NLO response and exchange energy (Bhattacharya et al., 2013) are made. The applicability of these diradicals in the light of NLO properties are also highlighted in this note. Here these resulting fluoroprotein coupled diradicals can switch back and forth between two isomeric states of different colors upon irradiation by light of appropriate wavelength. Nonetheless, the magnitude of second-order NLO responses is different for different isomeric forms; hence we made a correlation between the color codes with the magnitude of second-order NLO responses. Thence with just simple visual inspection one can understand the extent of second-order of NLO response for these diradicals.

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1. Introduction

The study of π -conjugated organic based nonlinear optical (NLO) processes has greatly accelerated in the last two to three decades, as is evident from the number of peer reviewed articles that one fetches from a simple Google search with the development of various technological (to replace electronics by photonics) as well as chemical and biological applications [1]. The interaction of an applied electromagnetic field with matter gives a new electromagnetic field having different, phase and other physical properties. NLO deals with this area of science and has potential in the field of optical switching, optical computing, dynamic image processing, *etc.* [2]. The wave of developing second-order NLO properties of different materials started from 1998 onward for the photonics and biological investigations [1]. In molecular level, it is to be noted that, the second-order nonlinear images depend on the second-order effect of total first molecular hyperpolarizability (β) values [3]. On the other hand, green fluorescent proteins (GFPs) are used as nonlinear contrast agents [4]. This property of the very

chromophore and their homologues helps for nonlinear microscopy. GFP-like chromophores which are bound to a cell membrane can change their second harmonic generation (SHG) image response with the change of membrane potential [5]. The NLO responses of these photochromic chromophores are differ from ordinary organic π -conjugated molecules as they change their NLO responses upon irradiation of light by proper frequencies. Moreover, the NLO responses also depend on the length of the π -conjugation of the concerned molecules. These GFP-like chromophores of organic origin give very high second-order molecular nonlinearity [6] which gives a future direction to design more effective NLO materials for bio-imaging.

Photochromic molecules show reversible photoinduced transformations between two structural states in which one can find significantly different molecular spectral character indicating definite color changes in these two different structural isomers. Such photochromic molecules play an important role in reaching the highest peak of merit as compared to different other materials, *e.g.*, having larger hyperpolarizabilities or a combination of photochromism with NLO properties to bring forth special features [7]. Note that GFP-chromophore-based high-spin systems can undergo photomagnetic changes upon irradiation by appropriate wave

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length of light [8,9]. Nonetheless, only by visual inspection one can evaluate the structural changes of these chromophores [9].

In 1961, Franken et al. [10] first observed SHG in a single quartz crystal. SHG is very simple example of a nonlinear optical phenomenon although with a centrosymmetrical molecule it is forbidden. The area of optical microscopy of biological systems starts its journey towards ultrahigh detection sensitivity with spectroscopic contrasts. Image contrasts for non-fluorescent species can be generated through coherent nonlinear optical imaging, dissipation microscopy and pump–probe microscopy [11]. Second harmonic imaging microscopy (SHIM) is a new nonlinear optical (NLO) imaging technique which is attracting greater attention of biologists day by day. The second harmonic signal in endogenous proteins originates because of their dipolar and chiral non-centrosymmetric nature [12]. There are several reports about the qualitative use of second-harmonic imaging from GFP [5,6,13]. The nonlinear optical phenomenon of SHG is an efficient monitor of membrane potential [14]. Pulse of laser light induces a dipolarity in chromophores which are asymmetrically associated with a membrane potential to thereby help in selective observations of chromophores in SH imaging [15]. The changes in membrane potential alter the magnitude of the induced dipole which in turn generates the SH signal. The SH signal provides specific information on the non-centrosymmetric arrangements of the chromophores [3]. The different variants of GFP have long been used as probes in SH imaging technique. A recent example experimentally and theoretically demonstrates the use of enhanced-GFP and one of its variants in SHIM to generate an appreciable second harmonic signal for second-order NLO properties [3].

Ray [1] has pointed out that during the last three decades a large class of organic chromophore families have been found with very large hyperpolarizabilities. These extreme special structural features seem to be necessary for the production of high second-order NLO responses. Still the challenge of finding efficient arrangements of naturally occurring NLO chromophores with large hyperpolarizability (β) responses is fascinating. Logically the aim of this note is to estimate and predict the uses of the previously designed bis-TEMPO-based high-spin diradicals as potential candidates for second-order NLO responses. In this work, we have chosen 3 bis-TEMPO-based GFP-coupled diradical systems (Scheme 1) in both *cis* and *trans* isomeric forms such as also considered in earlier work [8c].

2. Theoretical background

In the presence of a homogeneous weak electric field, the coefficients of the cubic term of the Taylor series expansion give the hyperpolarizability tensor (β) of an isolated species. The energy expression is

$$E = E^0 - \mu_x F_x - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots, \quad (1)$$

where E and E^0 are the energies of the perturbed and zero-field unperturbed states, the F_x 's are the field strength along a particular direction, μ_x , $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the components of the dipole moment, the linear polarizability, and the first or quadratic hyperpolarizability respectively. In general, the field as well as polarizability and hyperpolarizability terms of the above eqn. are frequency dependent. One point to be noted here is that the fluoro-protein chromophores of our designed diradicals are noncentrosymmetric in nature. Consequently in this study, our interest is to evaluate the total first static hyperpolarizability or intrinsic quadratic hyperpolarizability or mean first hyperpolarizability (β_{TOTAL}) [16], which is expressed by using x , y , z components as follows,

$$\beta_{TOTAL} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (2)$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz},$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yyz},$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}.$$

As all of these molecules are optimized at the UB3LYP/6-31G(d,p) level of theory in our previous work [8c], we have done all the NLO calculations for this note at the same level of theory using those optimized geometries. All the calculations of this note have been carried out using Gaussian 09W quantum chemical software [17].

3. Results and discussion

All the GFP-like chromophores taken for this study viz. CFP, DsRed, zFP [8c] are formed by the autocatalytic modification of the relevant tripeptide [9]. These chromophores have a phenol group conjugated with an imidazolone group with highly polarizable electrons. Among theoretical and experimental scientists, static first total hyperpolarizability (β_{TOTAL}) is recognized as a key factor to design species of high second-order NLO response. Length, planarity, etc. of a conjugated π -system are other guiding factors for the design of molecules with desired NLO properties, as NLO response largely depends on these properties. On the other hand, all these fluorescent protein chromophores (FPCs) have the ability to photo-switch reversibly between bright fluorescent *cis* (*c*) form to a dark *trans* (*t*) state. Since FPC's structures are noncentrosymmetric in both of these two isomeric forms [9], it is especially interesting to evaluate their first hyperpolarizability response. We theoretically investigate here the first static hyperpolarizability for both *cis* and *trans* isomers of three different diradicals with three different FPCs, keeping in mind their capability of generating second harmonic light. Table 1 shows the static first hyperpolarizabilities (β_{TOTAL}), the coupling constant (J) values, the highest occupied- and lowest unoccupied-MO energy gaps (ΔE_{H-L}), and the corresponding chemical hardness (η) of these molecules. The chemical hardness is calculated from the formula, $\eta = -\Delta E_{H-L}/2$ [18]. It is found that the lower energy band gap (ΔE_{H-L}) corresponds to the larger intrinsic first hyperpolarizabilities [19]. It is also interesting to note that with the increase of π -conjugation, organic polymers show higher second-order NLO responses [20]. Here, from Table 1 it is found that the highest value of β_{TOTAL} is obtained for diradical (2*t*) among all of our investigated molecules along with the corresponding lowest HOMO–LUMO energy gap. The enhanced nonlinear optical property of diradical (2*t*) is attributed to the planarity [8c] of the *trans*-DsRed (2*t*) chromophore resulting in an extended π -conjugation. As we go down in Table 1 from diradical (1*t*) to diradical (3*c*) we see that with the increase of total first hyperpolarizability, the band gap decreases. The highest and lowest β_{TOTAL} values are found for DsRed and CFP chromophore containing diradicals in two isomeric forms if we compare these values taking one of the structural isomers (either *cis* or *trans*) separately in each case. However, the intermediary β_{TOTAL} values are obtained for the zFP-chromophore containing diradicals with intermediate band gaps when we compare each of one isomeric form separately. Nonetheless, for the CFP chromophore based diradicals the β_{TOTAL} values are marginally similar. Now we are intending to discuss about the extent of π -conjugation through the couplers of these species. As the TEMPO radical moiety contains only a σ -network in its own structure, we do not look at this radical moiety for this purpose. From Scheme 1 it is clear that DsRed chromophore contains 8 π -bonds in its structure, whereas the other two chromophores contain just 7 π -bonds in their

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