

Supplementary Material on “Theoretical study on gigantic effect of external static electric field application on nonlinear optical properties of 1,2,3,5-dithiadiazolyl π -radical dimer”

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1. Brief outline of the theory for the asymmetric two-site diradical model

Let us consider the asymmetric model with two-radical sites $A\bullet - B\bullet$ and two atomic orbitals χ_a and χ_b ^{S1}. We can define bonding and antibonding molecular orbitals (MOs), g and u , as follows:

$$g(\mathbf{x}) = \frac{1}{\sqrt{2(1+S_{AB})}} [\chi_A(\mathbf{x}) + \chi_B(\mathbf{x})] \text{ and } u(\mathbf{x}) = \frac{1}{\sqrt{2(1-S_{AB})}} [\chi_A(\mathbf{x}) - \chi_B(\mathbf{x})], \quad (\text{S1})$$

where $S_{AB} = \langle \chi_A | \chi_B \rangle$. From these MOs, we can define the localized natural orbitals (LNOs) a and b ^{S2}:

$$a(\mathbf{x}) = \frac{1}{\sqrt{2}} [g(\mathbf{x}) + u(\mathbf{x})] \text{ and } b(\mathbf{x}) = \frac{1}{\sqrt{2}} [g(\mathbf{x}) - u(\mathbf{x})], \quad (\text{S2})$$

which are mainly localized on one site (A or B) and satisfy the orthogonal condition, $\langle a | b \rangle = 0$. The corresponding electronic Hamiltonian H for N -electron system is

$$\begin{aligned} H &= -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{X=A}^B \frac{Z_X}{r_{iX}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \\ &= \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}. \end{aligned} \quad (\text{S3})$$

Using the LNOs as the basis set, the valence configuration interaction (VCI) matrix corresponding to $M_s = 0$ is expressed as:

$$\begin{aligned} &\begin{pmatrix} \langle a\bar{b} | H | a\bar{b} \rangle & \langle a\bar{b} | H | b\bar{a} \rangle & \langle a\bar{b} | H | a\bar{a} \rangle & \langle a\bar{b} | H | b\bar{b} \rangle \\ \langle b\bar{a} | H | a\bar{b} \rangle & \langle b\bar{a} | H | b\bar{a} \rangle & \langle b\bar{a} | H | a\bar{a} \rangle & \langle b\bar{a} | H | b\bar{b} \rangle \\ \langle a\bar{a} | H | a\bar{b} \rangle & \langle a\bar{a} | H | b\bar{a} \rangle & \langle a\bar{a} | H | a\bar{a} \rangle & \langle a\bar{a} | H | b\bar{b} \rangle \\ \langle b\bar{b} | H | a\bar{b} \rangle & \langle b\bar{b} | H | b\bar{a} \rangle & \langle b\bar{b} | H | a\bar{a} \rangle & \langle b\bar{b} | H | b\bar{b} \rangle \end{pmatrix} \\ &= \begin{pmatrix} 0 & K_{ab} & t_{ab(aa)} & t_{ab(bb)} \\ K_{ab} & 0 & t_{ab(aa)} & t_{ab(bb)} \\ t_{ab(aa)} & t_{ab(aa)} & -h + U_a & K_{ab} \\ t_{ab(bb)} & t_{ab(bb)} & K_{ab} & h + U_b \end{pmatrix}, \end{aligned} \quad (\text{S4})$$

where the energy of the neutral determinants is set as the energy origin, and h is defined as the one-electron core Hamiltonian difference $h = \langle b | h(1) | b \rangle - \langle a | h(1) | a \rangle \geq 0$. In the above matrix, K_{ab} denotes exchange integral, and $t_{ab(aa)}$ and $t_{ab(bb)}$ denote two types of transfer integrals as $t_{ab(aa)} = \langle a\bar{b} | H | a\bar{a} \rangle$ and $t_{ab(bb)} = \langle a\bar{b} | H | b\bar{b} \rangle$, respectively. The average transfer

integral t_{ab} is introduced as $t_{ab} = (t_{ab(aa)} + t_{ab(bb)})/2$. Then, U_a and U_b are respectively defined as

$$U_a = U_{aa} - U_{ab} + X \quad \text{and} \quad U_b = U_{bb} - U_{ab} - X, \quad (\text{S5})$$

where $X = \sum_c^{\text{core}} \{2(U_{ac} - U_{bc}) - (K_{ac} - K_{bc})\}$. Here, U_{pq} and K_{pq} denote the Coulomb integral and exchange integral between LNOs $\{a, b, \text{core}\}$, respectively. When the system is symmetric, $U_a (= U_b)$ indicates the effective Coulomb repulsion defined by the difference between the on-site ($U_{aa} = U_{bb}$) and inter-site (U_{ab}) Coulomb integrals. For nondimensionalization, we introduce the average effective Coulomb repulsion $U = (U_a + U_b)/2$, and the dimensionless quantities are defined as follows:

$$r_t = \frac{|t_{ab}|}{U} (\geq 0), r_K = \frac{2K_{ab}}{U} (\geq 0), r_h = \frac{h}{U} (\geq 0), r_U = \frac{U_a}{U_b} (\geq 0), \text{ and } r_{tab} = \left| \frac{t_{ab(aa)}}{t_{ab(bb)}} \right| (\geq 0). \quad (\text{S6})$$

To describe open-shell nature, we introduce the parameter y_S as an alternative to r_t ,

$$y_S = 1 - \frac{4r_t}{\sqrt{1+16r_t^2}}, \quad (\text{S7})$$

which is the diradical character for the symmetric two-site diradical system^{S3}. Note that y_S is not for the asymmetric system but is referred to as ‘‘pseudo diradical character’’. As seen from Eq. S6, the asymmetric electron distribution occurs with more population on A than on B with the increase of r_h and/or decrease of r_U and/or decrease of r_{tab} . Since the LNOs are well localized in each site, it is estimated that the difference between $t_{ab(aa)}$ and $t_{ab(bb)}$ is negligible compared to the difference between h_{aa} and h_{bb} . Thus, r_h is the main source of asymmetry. Then, the VCI eigenvalue equation is expressed as:

$$HC = CE \quad (\text{S8})$$

or by using the dimensionless quantities

$$H_{\text{ND}}C = CE_{\text{ND}}, \quad (\text{S9})$$

where H_{ND} denotes dimensionless energy matrix. Keeping $(r_U, r_{tab}) = (1, 1)$ for simplicity, which corresponds to the situation where the asymmetry dominantly derives from the difference of ionization energies of the radical sites A and B, the dimensionless energy matrix H_{ND} is expressed as:

$$\begin{pmatrix} 0 & \frac{r_K}{2} & -r_t & -r_t \\ \frac{r_K}{2} & 0 & -r_t & -r_t \\ -r_t & -r_t & 1-r_h & \frac{r_K}{2} \\ -r_t & -r_t & \frac{r_K}{2} & 1+r_h \end{pmatrix}. \quad (\text{S8})$$

Using this Hamiltonian matrix, excitation energies and transition moments can be obtained. Under the condition of $r_K = 0$, which is satisfied in usual non-magnetic molecular systems, the relationship between r_h, y_S and NLO properties (β and γ) are obtained as shown in Figure 1. More details are described in ref. S1.

2. Optimized structures

Table S1. Optimized Structure of DTDA Calculated Using the UMP2/6-311+G* Method

Atom	$x/\text{\AA}$	$y/\text{\AA}$	$z/\text{\AA}$
C	0.00000000	0.00000000	0.59711897
N	1.16931701	0.00000000	0.00000000
N	-1.16931701	0.00000000	0.00000000
H	0.00000000	0.00000000	1.68290699
S	1.04492199	0.00000000	-1.61802197
S	-1.04492199	0.00000000	-1.61802197

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