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Theoretical Study on Third-Order Nonlinear Optical Property of One-Dimensional Cyclic Thiazyl Radical Aggregates: Intermolecular Distance, Open-Shell Nature, and Spin State Dependences

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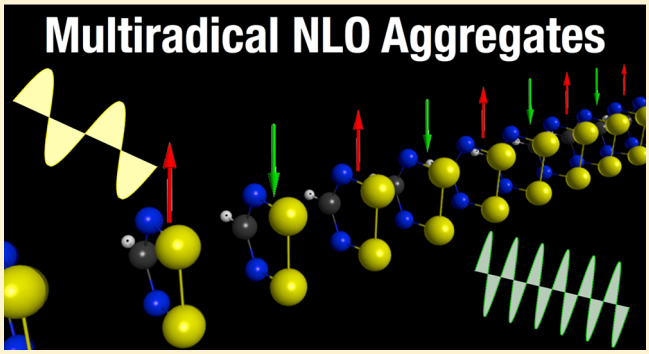
Supporting Information

ABSTRACT: Using the spin-unrestricted density functional theory method, we investigate the relationship between structure, spin state, and second hyperpolarizability (γ) of the finite and infinite one-dimensional open-shell aggregates composed of cyclic thiazyl radicals, that is, 1,2,3,5-dithiadiazolyl (DTDA) radicals. The DTDA aggregates with antiferromagnetic spin-alignment exhibit much greater enhancement of γ than the aggregates with ferromagnetic spin-alignment and the closed-shell benzene aggregates due to the intermediate open-shell singlet nature of the antiferromagnetic DTDA aggregate. It is found that this enhancement shows strong intermolecular distance dependences: the intermolecular distance giving the largest enhancement of γ decreases with increasing the number of molecules, and intermolecular distance alternation reduces the γ. For the infinite antiferromagnetic DTDA aggregate with a realistic intermolecular distance d = 3.1 Å, the γ per monomer reaches 1.9×10^6 au, which is comparable to that of the infinite open-shell singlet aggregate of phenalenyl radicals, and exhibits ~2400 times enhancement as compared to that of the closed-shell benzene aggregate. This feature indicates the high-potential application of open-shell singlet cyclic thiazyl radical aggregates to outstanding third-order NLO materials.



1. INTRODUCTION

Since the first synthesis by Markovski and co-workers,[1] a number of cyclic thiazyl radical compounds have been synthesized and crystallized.[2−4] These compounds are remarkable owing to their stability (low reactivity of the unpaired electron), their electron donor character, and their ability to form covalent-like intermolecular interactions, which make them candidates as organic molecular conductors.[3,5] In fact, Oakley and co-workers reported that a single crystal of an *N*-methyl bisdithiazolyl radical exhibits high conductivity reaching nearly 10^{-3} S/cm at room temperature,[5] which is comparable to nickel bisdithiolato-complex $[Ni(dmit)_2](NBu_4)_{0.29}$, a typical high-conductive molecular crystal.[6]

Cyclic thiazyl compounds have also been investigated from the viewpoint of organic molecular magnets.[3,7,8] For example, Rawson and co-workers disclosed that the β-phase of the dithiadiazolyl radical p-$NCC_6F_4CN_2S_2^{\bullet}$ exhibits weak spin-canted antiferromagnetism at 36 K.[7] Moreover, Fujita and Awaga reported that the benzo-bis(dithiazole)1,3,2-benzodithiazolyl radical cation salt $[BBDTA][GaCl_4]$ exhibits a ferromagnetism at 6.7 K.[8] These systems have higher ferromagnetic transition temperatures than a typical organic ferromagnetic molecule like nitroxide biradical *N*,*N*′-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane (1.48 K).[9]

On the other hand, recent computational chemistry investigations have predicted that the electronic structure of thiazyl radical compounds is favorable for realizing third-order nonlinear optical (NLO) materials. There are several molecular design guidelines for enhancing and controlling the second hyperpolarizability γ (the third-order NLO property at the molecular scale): extending the π-conjugated backbone,[10−13] substituting this backbone at appropriate position by donors/acceptors,[10−14] changing the charge states,[10,15,16] and as suggested more recently, tuning the diradical character, y,[17,18]

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of open-shell singlet compounds.[19−22] In the latter case, the γ-values can be much larger than for traditional closed-shell NLO systems. y, which quantifies the open-shell character of those systems, is a quantum chemical index describing the "chemical bond instability". Our previous theoretical studies have unveiled the relationship between y and the static γ by analyzing the dependences of the excitation energies and transition moments on y: systems with intermediate y $(0 < y < 1)$ exhibit larger γ-values than closed-shell $(y = 0)$ and pure open-shell $(y = 1)$ systems of similar size. This molecular design guideline has been elucidated by analyzing the analytical solutions for two-site diradical model as well as using highly accurate *ab intio* and density functional theory (DFT) calculations for a variety of open-shell singlet systems.[19−22] Furthermore, this guideline has been extended to dynamic NLO response properties, third-harmonic generation[23] and two-photon absorption cross section.[24] Utilizing covalent-like intermolecular interactions between π-systems, known as "pancake bond",[25] is one of the prospective ways to achieve intermediate y-values and therefore to enhance γ as evidenced in a recent study on phenalenyl radical dimers and multimers.[26] This was later corroborated by periodic boundary conditions calculations due to Salustro et al.[27] on an infinite singlet linear chain of phenalenyl radicals that exhibits γ as large as to that of polyacetylene. Still, structure−property relationships in these one-dimensional open-shell singlet aggregates have not yet been fully characterized. To tackle these relationships, thiazyl compounds are good candidates because they can form a variety of pancake-bonded π−π stacked one-dimensional aggregates and stable electronic structure with intermediate diradical characters. In this regard, the quantum chemical predictions that cyclic thiazyl diradical compounds present large γ-values owing to an intermediate diradical character,[28] was experimentally verified by Takauji et al.[29] for films of naphtho[2,1-d:6,5-d′]bis([1,2,3]-dithiazole). Moreover, thiazyl derivatives present the advantage over phenalenyls that they can easily be synthesized and that their aggregate structures are fairly controllable by modifying the substituents as well as by electron/hole doping. In fact, the pancake-bond intradimer distance of 1,2,3,5-dithiazolyl (DTDA) derivatives varies from 2.93 to 3.30 Å depending on the substituents,[30] while the interdimer distance changes by iodine doping[31] and phase transition of the crystal structure.[32,33]

As a consequence, the goals of this paper are first to characterize the pancake bonds and the π-stacking interactions in open-shell singlet DTDA aggregates and then to analyze their impact on the diradical character and second hyperpolarizability to derive structure-NLO property relationships. Moreover, these investigations will further help in understanding electric conductive and magnetic properties of these thiazyl radical aggregates. The properties of both finite and infinite aggregates will be investigated since these pancake-bonded π−π stacking appears in crystals. The paper is organized as follows. Section 2 summarizes the methodology for obtaining the geometries, the second hyperpolarizabilities and their infinite aggregate values. Section 3 presents the main results and their analysis before conclusions are drawn in Section 4.

2. METHODOLOGY

2.1. Model Systems and Geometries. Figure 1 shows the structures of the one-dimensional DTDA aggregates. Geometrical structure optimization of DTDA was conducted only

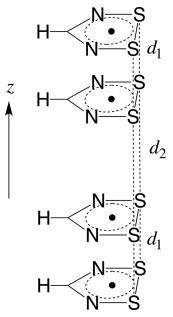

Figure 1. Structure of one-dimensional DTDA aggregates (tetramer in this case). d_1 and d_2 indicate the intradimer and interdimer distances, respectively. The direction of z-axis is also shown.

for the monomer using the UMP2/6-311+G* method under the C_{2v} symmetry constraint. As a closed-shell reference, benzene was also selected for examination. Its optimization was also conducted using the same UMP2/6-311+G* method under the D_{6h} symmetry constraint but, as expected, the closed-shell solution was obtained. These structures were confirmed as stable local minima by vibrational analysis. The geometries of the corresponding one-dimensional aggregates were not optimized but were built as π−π stacked columnar structures of monomers with different intradimer (d_1) and interdimer (d_2) distances (see Figure 1). Using d_1 and d_2 values ranging from 2.8 to 4.0 Å enables to vary the intermolecular distance alternation (IDA). This range of interplanar distances covers the intradimer and interdimer distances observed in real crystal structures, as reported by Cordes et al., which amount to 3.04−3.13 Å and 3.73−3.82 Å, respectively.[34]

2.2. Calculation Method. Aggregate systems of radical compounds present a variety of multiradical nature. To quantitatively characterize this nature, we employed the diradical characters y_i, which are defined as the occupation numbers of the corresponding lowest unoccupied natural orbitals, (LUNO) + i $(i = 0, 1, ...)$[35−37]

$$y_i = n_{\mathrm{LUNO}+i} \tag{1}$$

The average diradical character y_{av} is given by the arithmetic mean[38]

$$y_{\mathrm{av}} = \frac{1}{k}\sum_{i=0}^{k-1} y_i \tag{2}$$

Because a one-dimensional DTDA aggregate that is composed of N monomers contains N unpaired electrons, k is equal to $N/2$ in such system. The y_i values were calculated using the LC-UBLYP (μ = 0.33 bohr^{-1}) method.

Because we focus on the effects of π−π intermolecular interactions (i.e., pancake bond), which determine the diradical character on γ, only the longitudinal components of γ (γ_{zzzz}) in the stacking direction (z) (referred to as γ hereafter) were evaluated for finite aggregates and then extrapolated to the infinite limit. In these one-dimensional systems, this longitudinal γ-component per unit is known to saturate when increasing the number of units.[35] The extrapolated γ-value per monomer (γ_∞) is obtained using

$$\gamma_\infty = \lim_{N\to\infty} \Delta\gamma(N) \equiv \lim_{N\to\infty} \frac{\gamma(N+2) - \gamma(N)}{2} \tag{3}$$

where N and $\gamma(N)$ denote the number of monomers and γ-value of the N-mer, respectively.[39] The reason why we

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extrapolate $\Delta\gamma(N)$ instead of $\gamma(N)$ originates from the faster saturation of $\Delta\gamma(N)$ with respect to N. The extrapolations were carried out using the following fitting function

$$\Delta\gamma(N) = a - b\exp(-cN) \quad (4)$$

and the stability of the extrapolated value (given by a) is assessed by changing the data range. In this study, N is set to be an even number ranging from 2 to 28.

The γ-values were evaluated using LC-UBLYP (μ = 0.33), a long-range corrected exchange functional that avoids the catastrophic increase of (nonlinear) electric field response properties in large π-conjugated closed-shell systems as seen in pure and global hybrid DFT methods.[40−42] In addition, the LC-UBLYP (μ = 0.33) method was found to semiquantitatively reproduce the γ-values for open-shell singlet systems calculated by the UCCSD(T) method.[43] This agreement between UCCSD(T) and LC-UBLYP (μ = 0.33) results was here confirmed in the case of the DTDA dimer (see the Supporting Information). The γ-values were calculated by using the finite field (FF) approach combined with the Romberg procedure[44] because highly precise γ-values are needed for extrapolation. In the Romberg procedure, the number of electric field amplitudes, the smallest field amplitude, and the common ratio were set to 4, 0.0002 au, and $\sqrt{2}$, respectively. Field-dependent longitudinal first hyperpolarizabilities were calculated and differentiated once with respect to the external electric field. The effects of basis set superposition error (BSSE) on γ were ignored because they are negligible even for the dimer (see the Supporting Information). For all the calculations, the 6-31G* basis set was adopted. Still, the effect of including diffuse functions has been addressed by performing additional calculations with the 6-31+G* (Table S2 in the Supporting Information). It was demonstrated that the 6-31G* basis set underestimates the 6-31+G* γ-values by less than 10% and that this underestimation is stable with the number of DTDA monomers (N = 2−8). This comparison therefore substantiates the choice of using the 6-31G* basis set. All the calculations were performed using the Gaussian 09 program package.[45] The automatic Romberg differentiations were performed using the T-REX program.[44] All γ-values are given within the B convention.

3. RESULTS AND DISCUSSION

3.1. Geometric Structures. Figure 2a,b shows the optimized (in gas at UMP2/6-311+G* level of approximation)

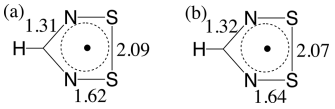

Figure 2. UMP2/6-311+G* optimized structure (a) and the crystal structure (b) of the DTDA unit. The crystal structure is obtained from ref 34.

and experimental (in crystal) geometric structures of the DTDA monomer, respectively. The UMP2/6-311+G* method well reproduces the crystal structure,[34] which substantiates the use of this optimized structure to build the model one-dimensional systems. The singly occupied molecular orbital (SOMO) of DTDA is delocalized on the N and S atoms (Figure 3a). The length of N—S bond (1.62 Å) is close to that of poly(thiazyl) ((SN)$_x$, 1.59 and 1.63 Å), which is known to

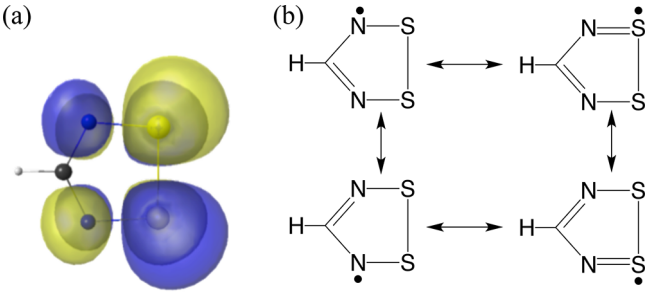

Figure 3. Singly occupied molecular orbital (SOMO) calculated by the UMP2/6-311+G* method (a) and resonance structures of the DTDA monomer (b).

present delocalized π-bonding.[2] The S—S bond length (2.09 Å) is typical of a disulfide bond. This implies little contribution of S—S double bond in the resonance structures and leads to the primary contributing resonance structures sketched in Figure 3b.

3.2. Effects of the Intermolecular Distance and of the Open-Shell Nature on the Second Hyperpolarizability of DTDA Dimer. When increasing d_1, the y_0 value of the singlet DTDA dimer increases from the nearly closed-shell region (y_0 = 0.091 at d_1 = 2.8 Å) to the pure open-shell region (y_0 = 0.892 at d_1 = 4.0 Å) (Figure 4). This originates from the decrease of

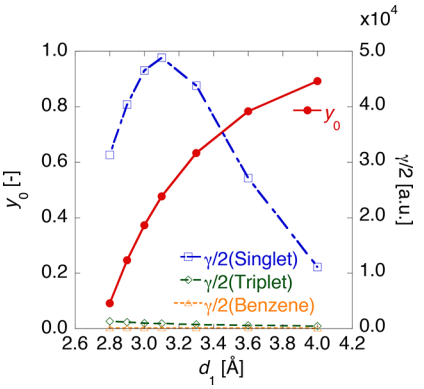

Figure 4. Intradimer distance d_1 dependences of diradical character y_0 and second hyperpolarizability γ per monomer (γ/2) of singlet DTDA dimer. The results for triplet DTDA dimer and benzene dimer are also shown.

the SOMO−SOMO overlap and thereof of pancake-bonding stabilization when d_1 increases. Concomitantly, the γ/2 versus d_1 curve shows a maximum at $d_1 \sim$ 3.1 Å, which is close to the intradimer distance in the crystal structure.[34] This confirms that the γ/2 maximum is caused by the intermediate y_0 nature.

In contrast, the triplet DTDA dimer and the closed-shell benzene dimer do not show any γ enhancement in the whole d_1 region. The corresponding γ/2 amplitudes are also small, 53.3 times smaller than in the DTDA singlet dimer for the triplet DTDA dimer and up to 310 times smaller for the benzene dimer, for d_1 = 3.1 Å. These results are in agreement with the "y−γ correlation" in our previous studies.[26,46,47]

3.3. Size Dependence of the Open-Shell Nature in One-Dimensional DTDA Aggregates. Figure 5 shows the evolution of the average diradical character y_{av} as a function of the intermolecular distance d (= d_1 = d_2) for different N-mers (N = 2−8). Increasing N has little impact on the d dependence of y_{av}. In the case of d_1 = d_2 = 3.1 Å (Figure 6a), y_i has a

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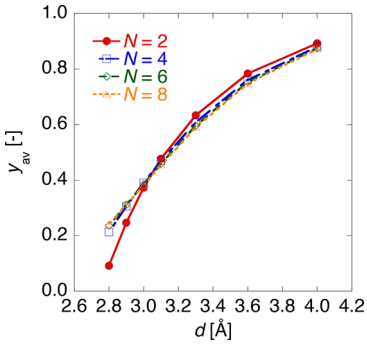

Figure 5. Intermolecular distance d (= d_1 = d_2) dependences of average diradical character y_{av} for DTDA N-mers. N denotes the number of monomers.

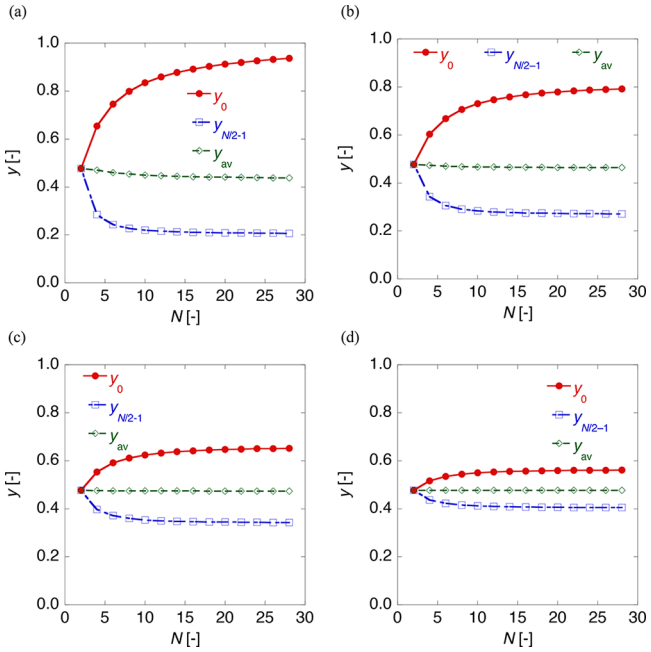

Figure 6. Monomer number (N) dependences of y_0, $y_{N/2-1}$, and y_{av} for different intra-(d_1)/inter-(d_2) dimer distances for DTDA N-mers: (d_1, d_2) = (3.1 Å, 3.1 Å) (a), (3.1 Å, 3.3 Å) (b), (3.1 Å, 3.6 Å) (c), and (3.1 Å, 4.0 Å) (d).

dominant value for i = 0 − N/2−1 in N-mer, it ranges from 0.2 to 1.0. Then, upon increasing N, y_0 increases from 0.5 from 1.0 while $y_{N/2-1}$ decreases from 0.5 to 0.2, resulting in negligible variations in y_{av}.

Moreover, introducing an intermolecular distance alternation (IDA) does not change this tendency but simply narrows y_i range while y_{av} is almost kept constant (Figure 6a−d). This is attributed to the decrease of the interaction between the dimers with increasing IDA, which highlights the character of each dimer rather than that of multimer. These tendencies are consistent with the results on the H_{2n} model chains.[38]

3.4. Second Hyperpolarizability of DTDA One-Dimensional Aggregates. Figure 7 shows the effects of the intermolecular distance d (= d_1 = d_2) on γ/N for different N-mers (N = 2−8). It highlights that the intermolecular distance giving the largest γ-value depends on N: the maximum γ/N value moves toward smaller d region with N, that is, toward smaller y_{av} region. This tendency is also in agreement with that in H_{2n} chain model,[38] though the latter are much simpler

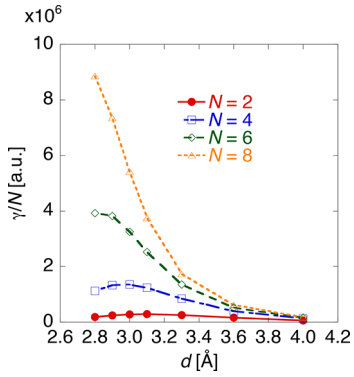

Figure 7. Effect of the Intermolecular Distance d (= d_1 = d_2) on the second hyperpolarizability per monomer γ/N for DTDA N-mers.

compounds. In the infinite aggregate systems, γ_∞ is also enhanced when decreasing the intermolecular distance (Table 1). These results are attributed to the increasing electron

Table 1. Effect of the Intermolecular Distance d on the Second Hyperpolarizability per Monomer for the DTDA Dimer ($\gamma(2)/2$) in Comparison to the Infinite One-Dimensional DTDA Aggregate (γ_∞)

d [Å]	$\gamma(2)/2$ [× 10^5 au]	γ_∞ [× 10^5 au]
2.9	0.40	90
3.0	0.46	39
3.1	0.49	19
3.3	0.44	5.7
3.6	0.27	1.5
4.0	0.11	0.39

delocalization length along monomer stacks. In general, when elongating the system the (hyper)polarizabilities per unit are expected to increase and then to reach a plateau due to the existence of an upper limit of electron delocalization length. So, when many units are interacting the electron delocalization length is increasing, and the hyperpolarizabilities are enhanced. In DTDA aggregates, for d = 4.0 Å, γ_∞ is only a factor of 3−4 larger than the dimer response [$\gamma(2)/2$], highlighting weak interactions between the units. On the other hand, for smaller d values, the interactions are much stronger, leading to enhanced γ_∞ responses (by 2 orders of magnitude from d = 4.0 Å to d = 3.0 Å). Moreover, Figure 8 shows that for small intermolecular distances, $\Delta\gamma$ saturates slowly as a function of the number of units whereas saturation appears faster for larger intermolecular distances.

Then, as seen from Table 2, the IDA diminishes γ_∞. Indeed, as compared to the aggregate with (d_1, d_2) = (3.1 Å, 3.1 Å) (d_2/d_1 = 1.0), the aggregate with (d_1, d_2) = (3.1 Å, 3.3 Å) (d_2/d_1 = 1.065) exhibits a reduction of γ_∞ by about a factor of 2 (95.7 × 10^4 a.u.), and the aggregate with (d_1, d_2) = (3.1 Å, 4.0 Å) (d_2/d_1 = 1.290) exhibits a reduction by 1 order of magnitude (γ_∞ = 20.4 × 10^4 a.u.). This tendency is also observed in the case of polyacetylene: the smaller the bond length alternation, the larger γ.[48,49] Still, the γ-variations with IDA/BLA are larger in polyacetylene than in DTDA aggregates, which results from different types of interactions between the π-orbitals. Indeed, varying the IDA of DTDA from 1.00 to 1.16 causes a 80% decrease of γ, whereas in the $C_{20}H_{22}$ polyacetylene oligomer γ decreases by as much as 95%.[49] In the DTDA aggregates, the π-orbitals give rise to σ-bonding interactions in the stacking

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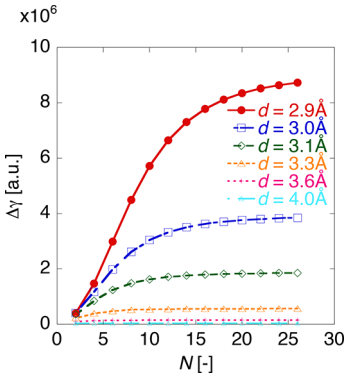

Figure 8. Evolution of the second hyperpolarizability per monomer ($\Delta\gamma$) as a function of the number of monomer units in the DTDA *N*-mers for different intermolecular distances d (= d_1 = d_2).

Table 2. Effect of the Intermolecular Distance Alternation on the Second Hyperpolarizability per Monomer of Infinite One-Dimensional Singlet DTDA Aggregates (γ_∞)

d_1 [Å]	d_2 [Å]	d_2/d_1	γ_∞ [× 10^4 au]
3.1	3.1	1.000	187
3.1	3.3	1.065	95.7
3.1	3.6	1.161	42.1
3.1	4.0	1.290	20.4

direction, so that the interaction can be maintained for larger distances than in the case of polyacetylene chains where the π-orbitals overlap in the chain length direction.

Furthermore, as seen from Table 3, the fact that the open-shell singlet DTDA dimers exhibit much larger γ-values than the closed-shell benzene dimers and the triplet DTDA dimers is intensified in the infinite one-dimensional aggregates. The γ_∞ of open-shell singlet DTDA aggregate with antiferromagnetic spin-alignment (DTDA(AFM)) is 280 times larger than the analogous DTDA aggregate with ferromagnetic spin-alignment (DTDA(FM)). It is also 2400 times larger than closed-shell benzene aggregate. This results from the much larger enhancement ratio [39 with respect to 7.4 and 4.9 for DTDA(FM) and benzene, respectively], which finds its source in the stronger interactions between units owing to their intermediate diradical character and optimal intermolecular distance.

Table 3. Second Hyperpolarizability per Monomer for Dimers ($\gamma(2)/2$) and for Infinite One-Dimensional Aggregates (γ_∞)[a] Together with That for Singlet (Antiferromagnetic), Highest Spin (Ferromagnetic) DTDA, and for Closed-Shell Benzene Aggregates

	$\gamma(2)/2$ [au]	γ_∞ [au]
DTDA (antiferromagnetic)	4.89×10^4	1.9×10^6
DTDA (ferromagnetic)	9.15×10^2	6.8×10^3
benzene	1.58×10^2	7.8×10^2

[a]The same intermolecular distance d (= d_1 = d_2) = 3.1 Å was used for all systems.

Finally, it is important to point out that the DTDA γ_∞ values and their enhancement ratio are comparable to those observed in infinite one-dimensional aggregates of phenalenyl radicals with similar intermolecular distance (d_1 = 3.111 Å, d_2 = 3.119 Å) that exhibit γ_∞ = 2.5678 × 10^6 au and a 38 times enhancement of γ/N as compared to the dimer at LC-UBLYP (μ = 0.33)/6-31G* level of approximation.[27]

4. CONCLUSION

Using the spin-unrestricted DFT method, the relationship between structure, spin state and γ of the finite and infinite one-dimensional 1,2,3,5-dithiadiazolyl (DTDA) radical aggregates has been investigated. It is found that DTDA(AFM) aggregates exhibit much larger enhancement of γ than DTDA(FM) aggregates and the benzene aggregates due to its intermediate open-shell singlet nature. The γ-value of the DTDA(AFM) aggregates turns out to have significant dependences on the intermolecular distance d. For example, it shows the peak at $d \sim$ 3.1 Å for the dimer, while for the infinite aggregates it is found that the closer d is, the larger γ is. The intermolecular distance alternation (IDA) is also found to diminish the γ-values. As a realistic case, DTDA(AFM) aggregate with d = 3.1 Å gives a γ_∞ value of 1.9 × 10^6 au, which is found to be 39 times as large as that of the dimer and is comparable to that of the open-shell singlet one-dimensional phenalenyl radical aggregates.[27] Moreover, considering the strong stability and easy preparation of DTDA aggregates as compared to phenalenyl radical aggregates, cyclic thiazyl radical aggregates appear as very promising NLO open-shell candidates as well as to display NLO-switching behavior as a function of the spin state or aggregate structure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11319.

Comparison of intradimer distance d_1 dependences of $\gamma/2$ for open-shell singlet DTDA dimers calculated by the LC-UBLYP(μ = 0.33) and UCCSD(T) methods using the 6-311+G* basis set; effect of basis set superposition error (BSSE) on $\gamma/2$ of DTDA dimers; effect of diffuse function in basis set on γ; Cartesian coordinates of the DTDA monomer and benzene monomer optimized using the UMP2/6-311+G* method(PDF)

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Notes

The authors declare no competing financial interest.

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