Supporting Information on

"Theoretical Study on Quasi-One-Dimensional Open-Shell Singlet Ladder Oligomers: Multi-Radical Nature,

Aromaticity and Second Hyperpolarizability"

Kotaro Fukuda¹, Jun-ya Fujiyoshi,¹ Hiroshi Matsui,¹ Takanori Nagami,¹ Shota Takamuku,¹ Yasutaka Kitagawa,^{1,2} Benoît Champagne³ and Masayoshi Nakano*,^{1,2} ¹Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan ²Center for Spintronics Research Network (CSRN), Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan ³Laboratoire de Chimie Théorique, University of Namur, rue de Bruxelles, 61, B-5000 Namur, Belgium

Corresponding Author

*Fax: +81-6-6850-6268. E-mail: mnaka@cheng.es.osaka-u.ac.jp

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1. Spin density distributions of ladder oligomers (Figure S1–S3)



Figure S1. Spin density distributions of the orbitals related to y_0 for the smallest systems and to y_0 and y_1 for second smallest systems of the series 2 and 3. Yellow and blue surfaces represent α and β spin densities with ±0.002 a.u. iso-surfaces, respectively.



Figure S2. Total spin density distributions of the two smallest systems of series 1–4 and PA(5) and PA(10). Yellow and blue surfaces represent α and β spin densities with ± 0.002 a.u. iso-surfaces, respectively.



Figure S3. Comparison between odd electron density and spin density distributions for the representative system 1(9). Contour values are 0.0008 a.u. for odd electron density and ± 0.002 a.u. for spin density.

2. Basics of the relationship between natural orbitals and corresponding orbitals (Figure S4)

Here, the basics of the relationship between the natural orbitals and corresponding orbitals are given. More details should be referred to the paper [A. T. Amos, G. G. Hall, *Proc. R. Soc. Lond. A* 1961, **263**, 483.]. Generally, the *n*-particle wavefunction, Ψ , with singlet spin state within the unrestricted singlet determinantal scheme is expressed as

$$\Psi = \frac{1}{\sqrt{n!}} \det \left\{ \varphi_1^{\alpha}(1)\alpha(1), \dots, \varphi_{n/2}^{\alpha}(n/2)\alpha(n/2), \varphi_1^{\beta}(1)\beta(1), \dots, \varphi_{n/2}^{\beta}(n/2)\beta(n/2) \right\},\$$

where φ^{α} and φ^{β} are the orthonormal spatial molecular orbitals. Using this wavefunction, the first-order density matrix $\Gamma(s,t)$ is expressed as

$$\Gamma(s,t) = \sum_{r}^{n/2} \varphi_r^{\alpha^*}(s) \varphi_r^{\alpha}(t) \alpha^*(s) \alpha(t) + \sum_{r}^{n/2} \varphi_r^{\beta^*}(s) \varphi_r^{\beta}(t) \beta^*(s) \beta(t).$$

By integrating $\Gamma(s,t)$ over spin, we obtain the reduced density matrix $\gamma(s,t)$ as

$$\gamma(s,t) = \sum_{r}^{n/2} \varphi_r^{\alpha^*}(s) \varphi_r^{\alpha}(t) + \sum_{r}^{n/2} \varphi_r^{\beta^*}(s) \varphi_r^{\beta}(t) \, .$$

Note that this is not generally diagonal since φ^{α} and φ^{β} are not necessarily spatially orthogonal each other. The unitary transformation of these sets of molecular orbitals offers the fully diagonalized spatial orbitals, χ^{α} and χ^{β} , of each spin except for the orbital pair with same index. This transformation attains the diagonalized overlap integral T_{rs} :

$$T_{rs} = \int \chi^{\alpha^*} \chi^{\beta} d\tau = T_r \delta_{rs}.$$

Again, these orbitals χ^{α} and χ^{β} are orthogonal each other except when r = s from definition. They are called corresponding orbitals (COs) because of the property. Using COs, the reduced density matrix is similarly expressed as

$$\gamma(s,t) = \sum_{r}^{n/2} \chi_r^{\alpha^*}(s) \chi_r^{\alpha}(t) + \sum_{r}^{n/2} \chi_r^{\beta^*}(s) \chi_r^{\beta}(t).$$

By combining the set of COs with same index, the natural orbitals (NOs) can be constructed

as

$$\psi_{\text{HONO}-i} = \frac{1}{\sqrt{2+2T_i}} \left(\chi^{\alpha}_{\text{HOCO}-i} + \chi^{\beta}_{\text{HOCO}-i} \right)$$

and

$$\psi_{\text{LUNO}+i} = \frac{1}{\sqrt{2 - 2T_i}} \left(\chi^{\alpha}_{\text{HOCO}-i} - \chi^{\beta}_{\text{HOCO}-i} \right)$$

Note that here the index is redefined. These NOs are fully orthonormal and the reduced density matrix becomes

$$\gamma(s,t) = \sum_{i=0}^{n/2-1} (1+T_i) \psi_{\text{HONO}-i}^*(s) \psi_{\text{HONO}-i}(t) + \sum_{i=0}^{n/2-1} (1-T_i) \psi_{\text{LUNO}+i}^*(s) \psi_{\text{LUNO}+i}(t).$$

This expression shows that $1+T_i$ and $1-T_i$ are the occupation numbers of the HONO-*i*-th and LUNO+*i*-th NOs.



Figure S4. Comparison between natural orbitals and corresponding orbitals related to y_0 and y_1 values for the representative system 1(9). Contour values are ±0.02 a.u. for both orbitals.



3. Comparison between NICS(1) and NICS(1)_{yy} values (Figure S5)

Figure S5. Comparison between $NICS(1)_{yy}$ and NICS(1) values for the representative system 1(49).

4. Resonance structures (Figure S6)



Figure S6. Resonance structures of 1(9).

5. Further discussion on the geometry optimization (Figure S7 and S8)

Here, we compare the optimized geometries calculated with the spin-restricted (R) (U) B3LYP/6-31G* methods. Since the and spin-unrestricted static second hyperpolarizability of polyacetylene series is largely affected by the BLA [1], it is expected that the choice of the optimization method would have a large effect on the NLO properties. Figure S7 and S8 show the absolute values of the bond-length alternation (BLA) of the zigzag edges of the inner and outer five-membered rings for series 1 and 4 evaluated with the unrestricted method, together with the BLA of the central and terminal vinylene units of polyacetylene series calculated at both spin-restricted and unrestricted levels. In series 1 and 4, the unrestricted method predicts the disappearance of the BLA in the central region. Since several studies have experimentally and theoretically (add references; later) shown that polyacetylene chains exhibit a finite BLA value, even in the infinite chain limit [2], the current UB3LYP results stem from spin contaminations [3]. This explains the choice of the spin-restricted B3LYP method for geometry optimizations.



Figure S7. Size dependence of the absolute BLA values for series 1 and 4 calculated using the spin-unrestricted method.



Figure S8. Size dependence of the absolute BLA values for polyacetylene series calculated using the spin-restricted and unrestricted method.

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6. Spin density distributions of polyacetylene(30) (Figure S9)



Figure S9. Total spin density distribution of polyacetylene(30). Yellow and blue surfaces represent α and β spin densities with ±0.002 a.u. iso-surfaces, respectively.