

Supporting Information of

“Theoretical Study on Second Hyperpolarizabilities of Intramolecular Pancake-Bonded Diradicaloids with Helical Scaffolds”

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1. Details of Romberg Differentiation Procedure

We evaluate the second hyperpolarizability (γ_{ijkl}) by using the numerical differential of energy (E) with respect to the electric field as follows:

$$\gamma_{ijkl} = -\frac{1}{6} \frac{\partial^4 E}{\partial F_i \partial F_j \partial F_k \partial F_l}, \quad i, j, k, l = x, y, z, \quad (\text{S1})$$

where F_i indicates the electric field component in the i direction. We calculate each component of second hyperpolarizability γ by using the Romberg differentiation procedure, which can eliminate the numerical differentiation error.^{S1,S2} We carry out ‘‘Romberg iterations’’ to obtain a more precise value by using a recurrence relation,

$$\gamma_{ijkl}(k, n) = \frac{a^{2n} \gamma_{ijkl}(k, n-1) - \gamma_{ijkl}(k+1, n-1)}{a^{2n} - 1}, \quad (\text{S2})$$

where n indicates the iteration step. The initial value $\gamma_{ijkl}(k, 0)$ of the iteration in this recurrence relation is defined by the numerical differentiation as follows:^{S1,3,4}

$$\gamma_{iiii}(k, 0) = \frac{\{E(F_{-i}(k+1)) - E(F_i(k+1))\} + a^2 \{E(F_{-i}(k)) - E(F_i(k))\} - (a^2 - 1)E(0)}{2a^2(a^2 - 1)(a^k F_0)^4}, \quad (\text{S3})$$

and,

$$\gamma_{iijj}(k, 0) = \frac{\{E(F_{i,j}(k)) + E(F_{-i,-j}(k))\} + 2\{E(F_{-i}(k)) + E(F_i(k)) + E(F_{-j}(k)) + E(F_j(k))\} - 4E(0)}{(a^k F_0)^4}. \quad (\text{S4})$$

Here, $F_i(k) = a^k F_0$, where F_0 is the smallest field value and a is the common ratio; i and s are the directions of electric field; $E(F_i(k))$ is the energy under the electric field in the i direction; $E(F_{i,j}(k))$ is the energy under the electric field in the i and j direction. In this study, we have used the $F_0 = 0.0004$ a.u., $a = 2$ and $k = 0 - 3$. Using the Romberg differentiation procedure, the errors of all components in all systems became smaller than 0.5 %.

2. γ - γ Correlation in Two-Site Diradical Model^{S5}

We discuss the nature of electronic structures of open-shell singlet systems with the simplest symmetric diradical model.^{S6} When the diradical model is composed of the two electrons in two orbitals (AO: atomic orbital χ_A and χ_B), the molecular orbitals (MO) with bonding (g : gerade) and anti-bonding (u : ungerade) can be described as follows,

$$g(\mathbf{r}) = \frac{1}{\sqrt{2(1+S_{AB})}} [\chi_A(\mathbf{r}) + \chi_B(\mathbf{r})], \quad (\text{S5})$$

$$u(\mathbf{r}) = \frac{1}{\sqrt{2(1-S_{AB})}} [\chi_A(\mathbf{r}) - \chi_B(\mathbf{r})], \quad (\text{S6})$$

where S_{AB} is an overlap integral between the χ_A and χ_B . If two electrons with up and down spin occupy the spatial orbital g , the electronic state is represented as the Slater determinant $|g\bar{g}\rangle$. The localized natural orbitals (LNOs) a and b are defined as follows:

$$a(\mathbf{r}) = \frac{1}{\sqrt{2}} [g(\mathbf{r}) + u(\mathbf{r})], \quad (\text{S7})$$

$$b(\mathbf{r}) = \frac{1}{\sqrt{2}} [g(\mathbf{r}) - u(\mathbf{r})]. \quad (\text{S8})$$

The LNOs satisfy the orthogonal condition, $\langle a|b\rangle = 0$. As will be discussed later, we can describe the electronic structure with a simple formalism by using LNO. For $M_s = 0$ (singlet or triplet), there are two neutral determinants,

$$|a\bar{b} \text{ core}\rangle \equiv |a\bar{b}\rangle, \quad |b\bar{a} \text{ core}\rangle \equiv |b\bar{a}\rangle, \quad (\text{S9})$$

and two ionic determinants,

$$|a\bar{a} \text{ core}\rangle \equiv |a\bar{a}\rangle, \quad |b\bar{b} \text{ core}\rangle \equiv |b\bar{b}\rangle. \quad (\text{S10})$$

Here, “core” means the orthogonal closed-shell core orbitals and the upper bar (nonbar) indicates the α (β) spin. The exact Hamiltonian for the electron is given by

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^2 \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{i>j}^N \frac{1}{r_{ij}}, \quad (\text{S11})$$

where the first term is the kinetic energies of electrons, the second term is the interaction between the nuclei and the electrons and, the final term is the interaction between the electrons. The first and the second terms in eq S11 are related with the one electron, then the one electron part is defined as $h(i)$ and eq S11 is rewritten as

$$\hat{H} = \sum_{i=1}^N h(i) - \sum_{i=1}^N \sum_{i>j}^N \frac{1}{r_{ij}}. \quad (\text{S12})$$

The CI matrix from the determinants of eqs S9 and S10 and the Hamiltonian (eq S12) is described by

$$\begin{pmatrix} \langle a\bar{b}|\hat{H}|a\bar{b}\rangle & \langle a\bar{b}|\hat{H}|b\bar{a}\rangle & \langle a\bar{b}|\hat{H}|a\bar{a}\rangle & \langle a\bar{b}|\hat{H}|b\bar{b}\rangle \\ \langle b\bar{a}|\hat{H}|a\bar{b}\rangle & \langle b\bar{a}|\hat{H}|b\bar{a}\rangle & \langle b\bar{a}|\hat{H}|a\bar{a}\rangle & \langle b\bar{a}|\hat{H}|b\bar{b}\rangle \\ \langle a\bar{a}|\hat{H}|a\bar{b}\rangle & \langle a\bar{a}|\hat{H}|b\bar{a}\rangle & \langle a\bar{a}|\hat{H}|a\bar{a}\rangle & \langle a\bar{a}|\hat{H}|b\bar{b}\rangle \\ \langle b\bar{b}|\hat{H}|a\bar{b}\rangle & \langle b\bar{b}|\hat{H}|b\bar{a}\rangle & \langle b\bar{b}|\hat{H}|a\bar{a}\rangle & \langle b\bar{b}|\hat{H}|b\bar{b}\rangle \end{pmatrix}. \quad (\text{S13})$$

The energy of neutral determinants, $\langle a\bar{b}|\hat{H}|a\bar{b}\rangle = \langle b\bar{a}|\hat{H}|b\bar{a}\rangle$, are taken as the energy origin. Before the discussion of the CI matrix, the following variables are introduced:

$$\text{On-site Coulomb repulsion: } U_{aa} = U_{bb} \equiv (aa|aa) = (bb|bb), \quad (\text{S14})$$

$$\text{Inter-site Coulomb repulsion: } U_{ab} = U_{ba} \equiv (aa|bb) = (bb|aa), \quad (\text{S15})$$

$$\text{Exchange integral: } K_{ab} = K_{ba} \equiv (ab|ba) = (ba|ab) = (ab|ab) = (ba|ba), \quad (\text{S16})$$

$$\text{Transfer integral: } t_{ab} = t_{ba} \equiv \langle a|f|b\rangle = \langle b|f|a\rangle = \langle \bar{a}|f|\bar{b}\rangle = \langle \bar{b}|f|\bar{a}\rangle \quad (\text{S17})$$

The matrix element of one electron operator is defined as

$$h_{aa} = \langle a|h|a\rangle = \langle b|h|b\rangle = \langle \bar{a}|h|\bar{a}\rangle = \langle \bar{b}|h|\bar{b}\rangle. \quad (\text{S18})$$

The CI matrix eq S13 can be described as,

$$\begin{pmatrix} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{pmatrix}. \quad (\text{S19})$$

By diagonalizing CI matrix eq S19, we obtain three singlet states (ionic state $|S_{1u}\rangle$, the ground state $|S_{1g}\rangle$ and higher-lying g symmetry state $|S_{2g}\rangle$) and one triplet state ($|T_{1u}\rangle$). The energies of states and the transition moments between the states can be described by using the VCI parameters.

Next, we introduce diradical character y to identify the electronic structure. Let us consider a simple two-electron two-orbital model in MO picture. In this picture, there are four configurations as follows.

RHF(restricted Hatree-Fock) ground state configuration:

$$|g\bar{g}\rangle. \quad (\text{S20})$$

Singly excited configuration:

$$|g\bar{u}\rangle, |u\bar{g}\rangle. \quad (\text{S21})$$

Doubly excited configuration:

$$|u\bar{u}\rangle. \quad (\text{S22})$$

The doubly excited configuration ($|u\bar{u}\rangle$) is needed to describe the exact ground state wavefunction as follows:

$$|\Psi_G\rangle = C_G|g\bar{g}\rangle - C_D|u\bar{u}\rangle, \quad (\text{S23})$$

where C_G and C_D represent the coefficient of the each configuration and they satisfy the relationship:

$$C_G^2 + C_D^2 = 1. \quad (S24)$$

In this formalism, the diradical character (y) is defined by^{S7}

$$y = 2C_D^2. \quad (S25)$$

In the closed-shell systems, $C_D \sim 0$, the diradical character y vanishes ($y \sim 0$). The diradical character increases with increasing C_D^2 , which weakens the bonding interaction. Finally, the bond is completely dissociated when the weight of each configuration becomes equal ($C_G^2 = C_D^2$), resulting in $y = 1$. In more general, the diradical character can be defined by the occupation number of the lowest unoccupied natural orbital (LUNO).

Next, we move on to the relationship between the diradical character and the VCI parameters. The coefficients C_G and C_D can be described by^{S5}

$$C_G = \frac{1}{2} \left(\sqrt{1 + \frac{U}{\sqrt{U^2 + 16t_{ab}^2}}} + \frac{4|t_{ab}|}{\sqrt{(U + \sqrt{U^2 + 16t_{ab}^2})\sqrt{U^2 + 16t_{ab}^2}}} \right), \quad (S26)$$

$$C_D = \frac{1}{2} \left(\sqrt{1 + \frac{U}{\sqrt{U^2 + 16t_{ab}^2}}} - \frac{4|t_{ab}|}{\sqrt{(U + \sqrt{U^2 + 16t_{ab}^2})\sqrt{U^2 + 16t_{ab}^2}}} \right). \quad (S27)$$

Then, the diradical character y is expressed by

$$y = 2C_D^2 = 1 - \frac{4|t_{ab}|}{\sqrt{U^2 + 16t_{ab}^2}}. \quad (S28)$$

This indicates that the y is the function of t_{ab} and U . If we define r_t as the ratio of transfer integral and effective Coulomb repulsion ($r_t = \frac{|t_{ab}|}{U}$), the diradical character becomes a function of r_t :

$$y = 1 - \frac{4r_t}{\sqrt{1 + 16r_t^2}}. \quad (S29)$$

If the transfer integral is much smaller than the effective Coulomb repulsion ($r_t \rightarrow 0$), which means that the electrons are localized at each site, the diradical character becomes 1 (pure diradical). If the transfer integral is almost the same as the effective Coulomb repulsion ($r_t \rightarrow 1$), which means that the electrons are delocalized over the two sites, the diradical character becomes 0 (closed-shell).

The static electronic γ of symmetric model is obtained by using perturbation theory as:^{S5}

$$\gamma = \gamma^{\text{II}} + \gamma^{\text{III-2}} = -4 \frac{(\mu_{S_{1g}, S_{1u}})^4}{(E_{S_{1u}, S_{1g}})^3} + 4 \frac{(\mu_{S_{1g}, S_{1u}})^2 (\mu_{S_{1u}, S_{2g}})^2}{(E_{S_{1u}, S_{1g}})^2 E_{S_{2g}, S_{1g}}}, \quad (\text{S30})$$

where type II and type III-2 terms indicate the class of the virtual excitations contributing to γ and $E_{S_{1u}, S_{1g}}$ and $E_{S_{2g}, S_{1g}}$ are the excitation energies defined by the difference between S_{1u} and S_{1g} , and that between S_{1u} and S_{2g} , respectively.^{S8} In summary, the transition moments squared and excitation energies can be expressed as

$$(\mu_{S_{1g}, S_{1u}})^2 = R_{\text{BA}}^2 \frac{1 - \sqrt{1 - q^2}}{2}, \quad (\text{S31})$$

$$(\mu_{S_{1g}, S_{2g}})^2 = R_{\text{BA}}^2 \frac{1 + \sqrt{1 - q^2}}{2}, \quad (\text{S32})$$

$$E_{S_{1u}, S_{1g}} = \frac{U}{2} \left(1 - 2r_K + \frac{1}{\sqrt{1 - q^2}} \right), \quad (\text{S33})$$

$$E_{S_{2g}, S_{1g}} = \frac{U}{\sqrt{1 - q^2}}, \quad (\text{S34})$$

where q is the effective bond order ($q \equiv 1 - y$) and r_K is the ratio between the exchange integral and effective Coulomb repulsion ($r_K \equiv \frac{K_{ab}}{U}$). Then, the variations in the excitation energies and transition moments squared as a function of y are shown in Figure S1. For $y = 0$, the dimensionless transition moments squared, $(\mu_{S_{1g}, S_{1u}})^2 / R_{\text{BA}}^2$ and $(\mu_{S_{1u}, S_{2g}})^2 / R_{\text{BA}}^2$, are equal to 0.5. As increasing y from 0 to 1, it is found that $(\mu_{S_{1g}, S_{1u}})^2 / R_{\text{BA}}^2$ decreases toward 0, while $(\mu_{S_{1u}, S_{2g}})^2 / R_{\text{BA}}^2$ increases toward 1. On the other hand, it is found that the dimensionless excitation energies, $E_{S_{1u}, S_{1g}} / U$ and $E_{S_{2g}, S_{1g}} / U$, gradually increase in the large y region ($y > \sim 0.2$) and then rapidly increase in the small y region ($y < \sim 0.2$) with decreasing y , while the both energies converge to 1 at $y \rightarrow 1$. These variations cause strong correlation between the diradical character and γ values.

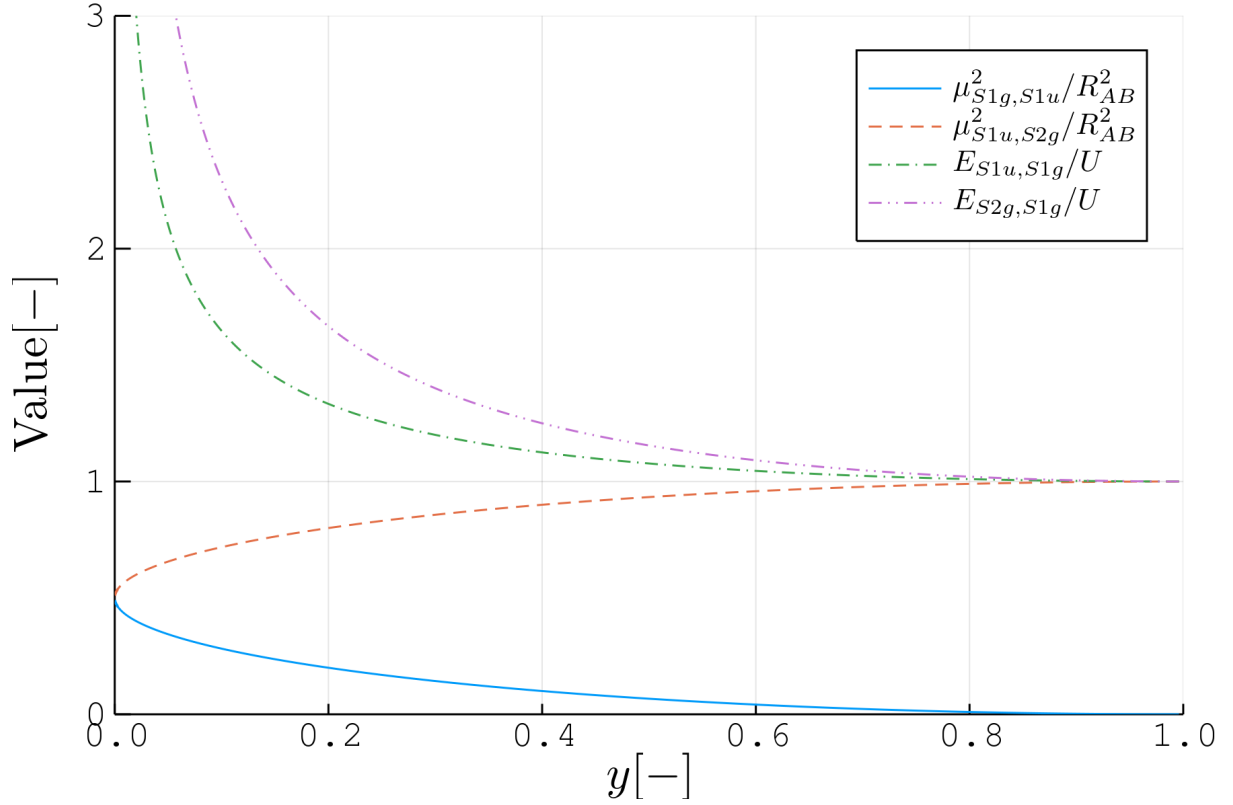


Figure S1. Diradical character dependences of dimensionless excitation energies $E_{S_{1u},S_{1g}}/U$ and $E_{S_{2g},S_{1g}}/U$, and squared transition moments, $(\mu_{S_{1g},S_{1u}})^2/R_{BA}^2$ and $(\mu_{S_{1u},S_{2g}})^2/R_{BA}^2$, for $r_K = 0$.

By using eqs S31–S34, second hyperpolarizability γ is expressed as

$$\frac{\gamma}{\left(\frac{R_{BA}^4}{U^3}\right)} = -\frac{8q^4}{(1 + \sqrt{1 - q^2})^2 \left(1 - 2r_K + \frac{1}{\sqrt{1 - q^2}}\right)^3} + \frac{4q^4}{\left(1 - 2r_K + \frac{1}{\sqrt{1 - q^2}}\right)^2 \left(\frac{1}{\sqrt{1 - q^2}}\right)}. \quad (\text{S35})$$

The variation of γ as a function of y is shown in Figure S2. For $r_K = 0$, the maximum dimensionless $\gamma_{\max} / \left(\frac{R_{BA}^4}{U^3}\right) \sim 0.2025$ is shown to be taken at $y_{\max} = 0.3586$. This result indicates that the second hyperpolarizability γ is maximized at an intermediate diradical character.

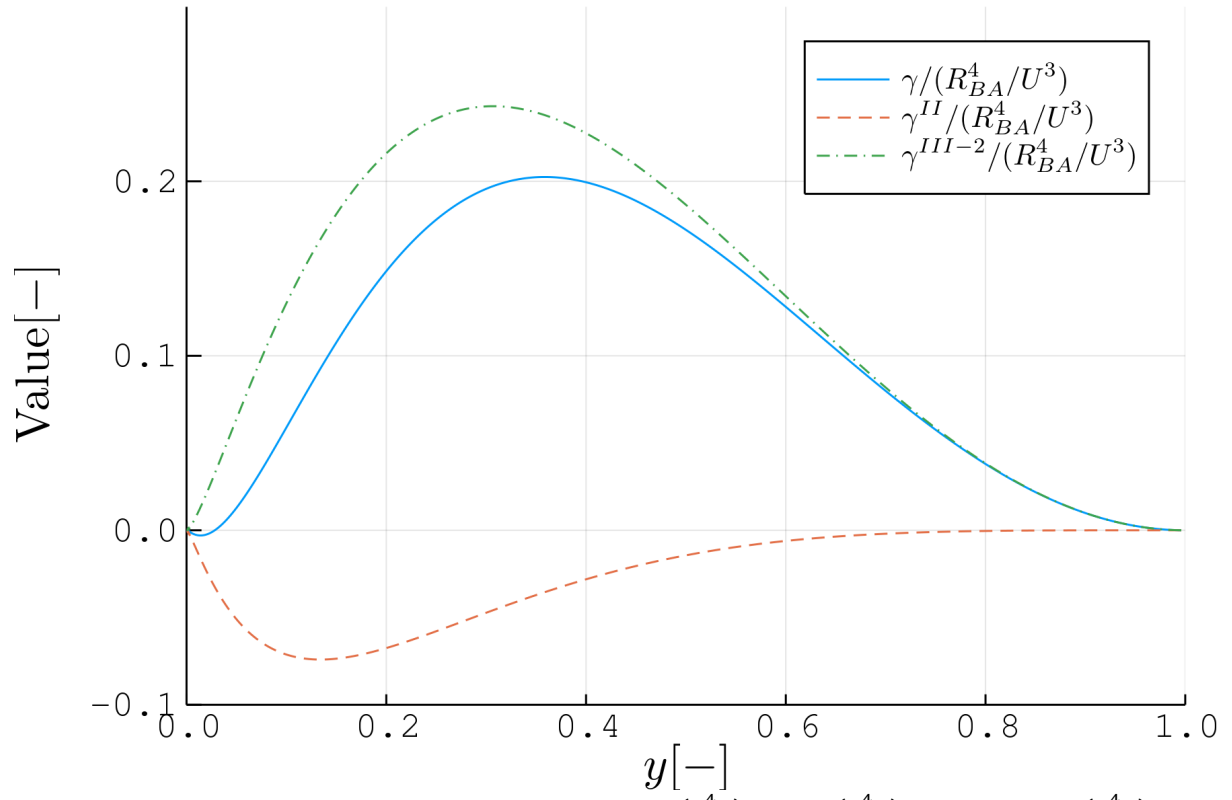


Figure S2. Diradical character dependences of $\gamma/\left(\frac{R_{BA}^4}{U^3}\right)$, $\gamma^{II}/\left(\frac{R_{BA}^4}{U^3}\right)$ and $\gamma^{III-2}/\left(\frac{R_{BA}^4}{U^3}\right)$, for $r_K = 0$.

3. Excitation Energies and Oscillator Strengths of Calculated Systems

Table S1. Excitation Energy E [eV], Oscillator Strength f and Main Configurations at TD-LC-(U)BLYP($\mu = 0.33 \text{ bohr}^{-1}$)/6-31+G(d) Level of Approximation

System	E [eV]	f [-]	Main configurations
10helicene	3.61	0.0866	H-1 -> L+1 : 0.44649
			H-2 -> L : -0.32899
			H -> L : 0.32097
8CTR	2.36	0.0160	α H -> L : 0.66231
			β H -> L : -0.64921
7helicene	3.87	0.0317	H-1 -> L : 0.65190
7AZ	1.35	0.0311	α H -> L : 0.92218
			α H -> L+1 : -0.30335
			H-5 -> L+28 : 0.13709
13C₂NH	5.46	0.0085	H-1 -> L+25 : 0.11524
			H -> L+29 : 0.11052
			H-1 -> L+37 : -0.10197
13C₂NHTCN	2.26	0.0626	α H-2 -> L: 0.53621
			β H-1 -> L: -0.39919
			β H-2 -> L: -0.39275

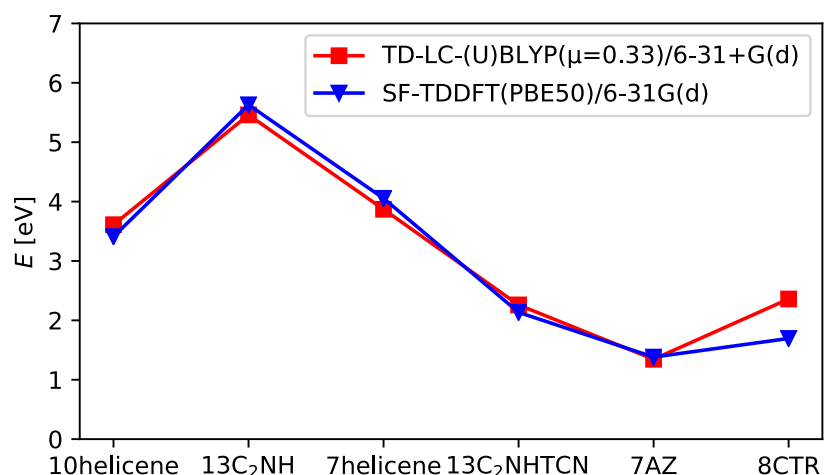


Figure S3. Excitation Energies E for the Present Systems at TD-LC-(U)BLYP($\mu = 0.33 \text{ bohr}^{-1}$)/6-31+G(d) and SF-TDDFT(PBE50)/6-31G(d) levels of approximation.

It is found that the excitation energies at the TD-LC-(U)BLYP/6-31+G(d) level of approximation quantitatively well reproduce those at the SF-TDDFT (PBE50 with 6-31G(d)) level of approximation except for **8CTR** system with the largest y value among the present systems, which gives $\sim 0.7 \text{ eV}$ higher excitation energy at the TD-LCUBLYP/6-31+G(d) level than that at the SF-TDDFT/6-31G(d) level. This may suggest that the TD-LC-(U)BLYP method tends to somewhat overshoot the first excitation energies for open-shell singlet systems with large diradical character. Here, we used a smaller basis set for SF-TDDFT (6-31G(d)) than that for TD-LC-(U)BLYP (6-31+G(d)) due to reducing the computational costs. However, the effect of diffuse function seems to be small for the first excitation energies of the present systems, for example, the difference of excitation energies of **7AZ** between these two methods is shown to be 0.1 eV , which is small enough to discuss the semi-quantitative trend of excitation energies in this study.

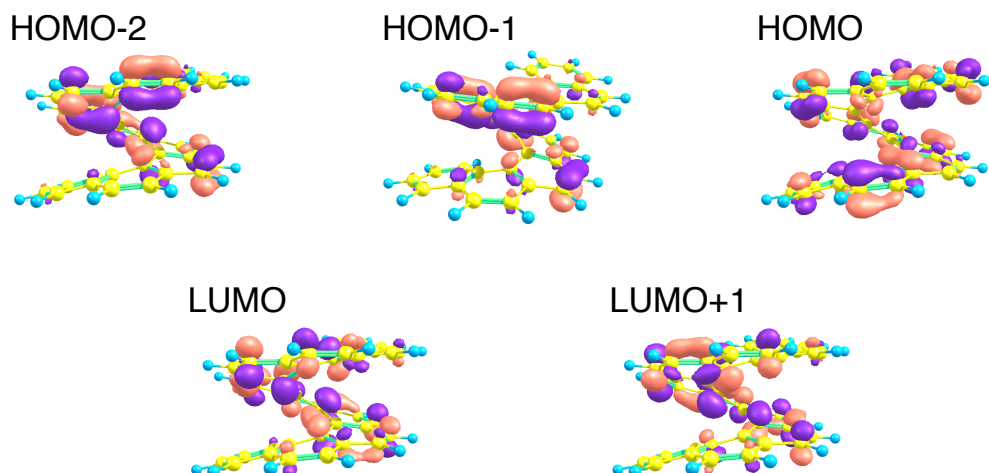


Figure S4. Molecular orbitals (MOs) with contour value of ± 0.04 a.u. related with the excitation (Table S1) in **10helicene** at TD-LC-RBLYP($\mu = 0.33$ bohr⁻¹)/6-31+G(d) level of approximation.

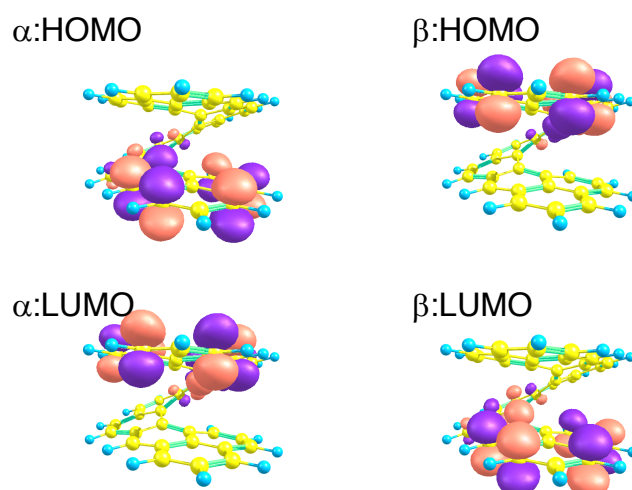


Figure S5. Molecular orbitals (MOs) with contour value of ± 0.04 a.u. related with the excitation (Table S1) in **8CTR** at TD-LC-UBLYP($\mu = 0.33$ bohr⁻¹)/6-31+G(d) level of approximation.

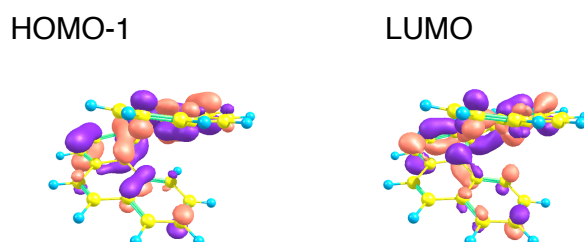


Figure S6. Molecular orbitals (MOs) with contour value of ± 0.04 a.u. related with the excitation (Table S1) in **7helicene** at TD-LC-RBLYP($\mu = 0.33$ bohr⁻¹)/6-31+G(d) level of approximation.

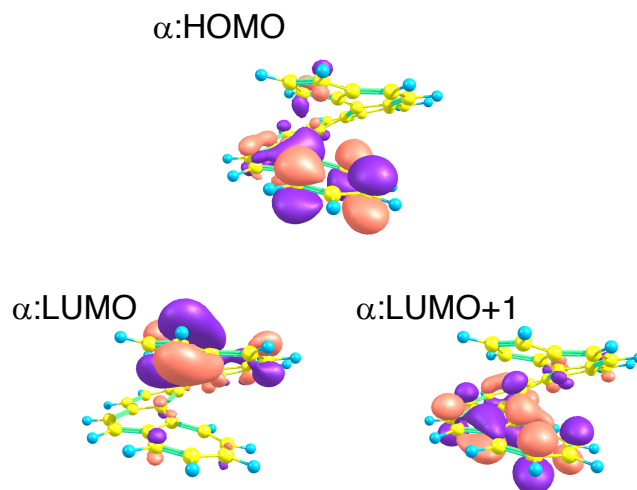


Figure S7. Molecular orbitals (MOs) with contour value of ± 0.04 a.u. related with the excitation (Table S1) in **7AZ** at TD-LC-UBLYP($\mu = 0.33$ bohr⁻¹)/6-31+G(d) level of approximation.

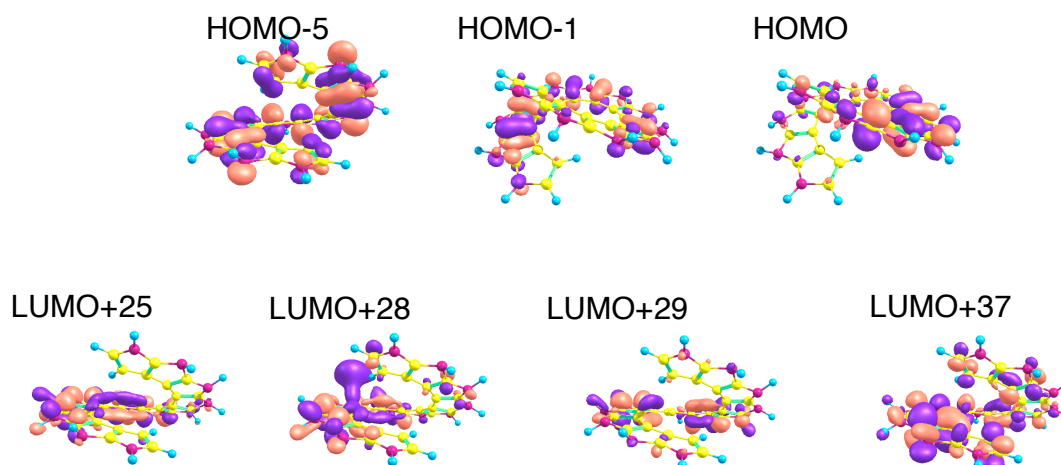


Figure S8. Molecular orbitals (MOs) with contour value of ± 0.04 a.u. related with the excitation (Table S1) in **13C₂NH** at TD-LC-RBLYP($\mu = 0.33$ bohr⁻¹)/6-31+G(d) level of approximation. Since there are a lot of low lying excited states composed of diffuse orbitals, we took the 38th excited state which has the transition moments large transition moment for the z direction and the contribution of LUMOs with not so large components of the diffuse orbitals.

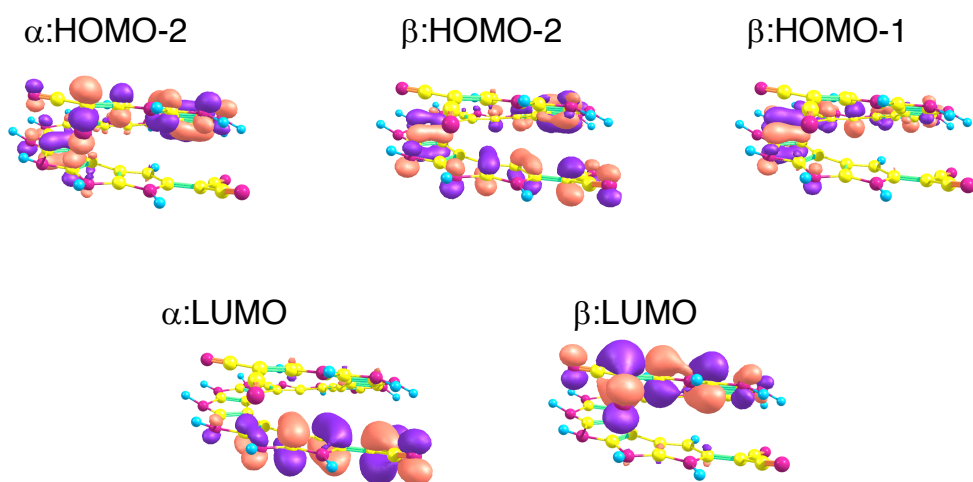


Figure S9. Molecular orbitals (MOs) with contour value of ± 0.04 a.u. related with the excitation (Table S1) in **13C₂NHTCN** at TD-LC-UBLYP($\mu = 0.33$ bohr⁻¹)/6-31+G(d) level of approximation.

4. Cartesian Coordinates of Calculated Systems

Cartesian coordinates [Å] of the optimized geometries and the corresponding total energies (in hartree) at the (U)M052x/6-31G(d) level of approximation.

8CTR: UM052x/6-31G(d), -1537.45402314 hartree

	x	y	z
6	-0.000580000	-2.421285000	1.717550000
6	2.372330000	-1.014495000	1.125840000
6	-1.140850000	1.040335000	-0.592470000
6	2.395210000	-2.407525000	1.305630000
1	3.346620000	-2.924815000	1.267830000
6	2.358370000	1.754495000	0.641840000
6	-1.203100000	-0.336165000	1.980750000
6	-2.368280000	3.167445000	-0.465850000
1	-3.310710000	3.693695000	-0.559870000
6	1.139350000	-0.316775000	1.083960000
6	1.201320000	-0.334465000	-1.984130000
1	1.215110000	0.745345000	-1.991860000
6	-2.373020000	-1.012475000	-1.127760000
6	0.035770000	-1.007795000	-1.577560000
6	-2.338280000	-1.034165000	2.383310000
6	-2.359020000	1.755315000	-0.641680000
6	1.220470000	-3.140965000	1.519470000
6	1.140420000	1.039445000	0.591320000
6	0.000580000	-2.420185000	-1.717550000
6	2.367960000	3.166645000	0.467120000
1	3.310490000	3.692665000	0.562130000
6	-0.000140000	1.714165000	-0.000030000
6	-0.036640000	-1.008985000	1.575660000
6	2.337450000	-1.032425000	-2.384320000
1	3.222460000	-0.480535000	-2.674150000
6	-1.140190000	-0.315215000	-1.086480000
6	3.599920000	-0.292215000	0.985510000
1	4.531940000	-0.840135000	1.055300000
6	-1.174440000	-3.137075000	2.088850000
6	2.347520000	-2.416195000	-2.394050000
1	3.240930000	-2.961025000	-2.674800000
6	1.175150000	-3.135905000	-2.085990000
6	-3.588960000	1.058365000	-0.848740000
1	-4.511310000	1.627025000	-0.835030000
6	-1.220830000	-3.139225000	-1.517980000
6	-1.206750000	3.841975000	-0.250220000
1	-1.186940000	4.924215000	-0.206920000
6	0.000140000	3.127305000	0.000030000
6	-3.600440000	-0.290735000	-0.986480000
1	-4.532140000	-0.839425000	-1.055470000
6	1.206780000	3.841765000	0.250990000
1	1.187120000	4.924075000	0.208260000
6	-2.395700000	-2.405625000	-1.306970000

1	-3.346890000	-2.923235000	-1.267880000
6	-2.346880000	-2.417895000	2.397130000
1	-3.239400000	-2.962785000	2.680600000
6	3.588310000	1.057095000	0.848780000
1	4.510460000	1.626015000	0.836340000
6	-1.129910000	-4.552705000	2.153360000
6	1.217550000	-4.549435000	1.611100000
6	0.047880000	-5.239785000	1.908890000
6	1.131120000	-4.551955000	-2.146350000
6	-1.216970000	-4.548285000	-1.605000000
6	-0.046790000	-5.238675000	-1.900150000
1	2.035720000	-5.088945000	-2.403920000
1	-0.060200000	-6.320035000	-1.952060000
1	-2.144240000	-5.083455000	-1.443500000
1	-2.034310000	-5.089005000	2.413040000
1	0.061960000	-6.320955000	1.964390000
1	2.145280000	-5.084415000	1.451120000
1	-3.223610000	-0.482435000	2.672350000
1	-1.217870000	0.743735000	1.986150000

7AZ: UM052x/6-31G(d), -1153.88385133 hartree

	x	y	z
6	-0.550400040	1.153480088	-1.257620096
6	0.819100065	0.959420075	-1.685700128
6	0.968560072	-0.371690028	-2.110220161
6	-0.247060019	-1.025950080	-1.972160150
6	-1.221010096	-0.072810006	-1.473200113
6	-2.595850197	-0.192390015	-1.257320095
6	-3.309150251	0.937860071	-0.902040068
6	-2.659910204	2.166910163	-0.659200052
6	-3.424110262	3.360410254	-0.433770033
6	-2.815000213	4.565960347	-0.316070024
6	-1.385770104	4.656590354	-0.214620017
6	-0.746490057	5.915670456	-0.055630004
6	0.610900044	5.993860469	0.067190005
6	1.385680107	4.813280367	0.223090017
6	2.809210215	4.884990372	0.364570028
6	3.549150269	3.752980285	0.479820037
6	2.911340222	2.483740192	0.650450048
6	3.661620278	1.297950097	0.809780063
6	3.023210230	0.102110008	0.998150076
6	1.623670124	0.029670002	1.239830094
6	1.094160086	-1.294100100	1.467940112
6	-1.362320106	0.441570033	2.205820169
6	-0.442060034	1.376940104	1.807490139
6	0.874130064	1.225110092	1.211630090
6	1.500700116	2.405830183	0.685630053
6	0.747400056	3.556750270	0.220360017
6	-0.611730048	3.482120265	-0.240390018
6	-1.239690095	2.256410170	-0.709790053

1	1.575930118	1.723720132	-1.741640132
1	1.882460146	-0.802950062	-2.489480188
1	-0.457770035	-2.055760154	-2.219010171
1	-3.102600237	-1.135730086	-1.421110106
1	-4.389150337	0.900750067	-0.820490060
1	-4.505300346	3.284840251	-0.433890033
1	-3.394370257	5.478190416	-0.239050018
1	-1.353500103	6.812910537	-0.080360006
1	1.112170083	6.953800540	0.100070008
1	3.283140253	5.858180428	0.319160025
1	4.631620353	3.793070288	0.501910038
1	4.742400361	1.344740103	0.747980056
1	3.596650277	-0.815560060	1.044290078
1	1.823550139	-2.080950161	1.314250100
1	-2.283720172	0.852310065	2.604700200
1	-0.722700057	2.404900185	1.988860154
6	-1.296260101	-0.960800074	2.153000162
6	-0.168190013	-1.717810132	1.812750140
1	-2.184070169	-1.505370116	2.445800189
1	-0.291800023	-2.794550211	1.864450143

13C₂NHTCN: UM052x/6-31G(d), -2234.96521640 hartree

	x	y	z
7	-2.407370000	-0.703020000	-1.425860000
7	-4.237160000	1.043970000	-1.017660000
7	-4.909150000	3.449690000	-0.500530000
7	-4.248480000	5.867860000	-0.048650000
7	-2.457060000	7.674010000	-0.008240000
7	0.004690000	8.325330000	-0.061420000
7	2.459950000	7.664520000	-0.064990000
7	4.247990000	5.853660000	0.035050000
7	4.921280000	3.433650000	0.441490000
7	4.236170000	1.045330000	1.002360000
6	-0.754880000	0.920780000	-1.430390000
6	-1.073900000	-0.465910000	-1.499410000
6	-2.002410000	1.573340000	-1.132240000
6	-2.955020000	0.569230000	-1.163390000
6	-2.712790000	2.774250000	-0.769480000
6	-4.041640000	2.389880000	-0.720660000
6	-2.699900000	4.179030000	-0.417060000
6	-4.034150000	4.511820000	-0.283130000
6	-1.974280000	5.421180000	-0.210180000
6	-2.959560000	6.388730000	-0.111610000
6	-0.728750000	6.128630000	0.016140000
6	-1.083690000	7.467570000	0.112410000
6	0.724180000	6.118560000	0.000220000
6	1.083570000	7.447970000	-0.067350000
6	1.985090000	5.395780000	0.073160000
6	2.965670000	6.364400000	-0.080790000

6	2.709680000	4.170130000	0.329970000
6	4.051400000	4.496270000	0.190430000
6	2.718590000	2.776530000	0.733680000
6	4.045410000	2.387660000	0.693510000
6	2.004130000	1.581280000	1.109670000
6	2.954360000	0.574550000	1.153340000
6	-2.446250000	-0.760820000	1.759630000
6	-2.682690000	-2.124300000	1.461400000
6	-3.559880000	0.100820000	1.905760000
7	-2.794670000	-3.233580000	1.130290000
7	-4.501900000	0.774650000	1.994820000
6	2.447420000	-0.773420000	-1.751790000
6	2.690130000	-2.131400000	-1.434920000
6	3.555450000	0.093110000	-1.912400000
7	2.807330000	-3.235390000	-1.088270000
7	4.490650000	0.774610000	-2.014250000
6	0.620600000	1.017420000	-1.605130000
6	1.124500000	-0.304990000	-1.697220000
7	0.051160000	-1.203570000	-1.636780000
6	0.755420000	0.933620000	1.417960000
6	1.073560000	-0.452290000	1.507570000
7	2.406490000	-0.692850000	1.437870000
6	-0.620600000	1.032110000	1.589850000
6	-1.124770000	-0.289120000	1.700130000
7	-0.051100000	-1.188050000	1.653440000
1	-0.133820000	-2.182960000	1.784240000
1	2.815310000	-1.574980000	1.165990000
1	4.971170000	0.505640000	0.570710000
1	5.735600000	3.284430000	-0.136570000
1	5.074360000	6.279460000	-0.346970000
1	2.851370000	8.391910000	-0.643970000
1	0.076800000	9.200190000	0.435040000
1	-2.941300000	8.397490000	0.498080000
1	-5.024520000	6.338140000	-0.487820000
1	-5.728000000	3.335570000	0.078610000
1	-4.963330000	0.511810000	-0.561070000
1	-2.820410000	-1.582040000	-1.151050000
1	0.134130000	-2.200340000	-1.752290000
1	-1.245320000	1.909780000	1.558360000
1	1.245160000	1.895600000	-1.585610000

10helicne: UM052x/6-31G(d), -1614.89284351 hartree

	x	y	z
6	0.999760077	2.784850212	4.358990335
6	-3.618560279	2.612460198	2.227790169
6	-2.408620185	4.760130365	1.917150149
6	-1.239140094	5.450160427	1.823390137
6	1.239140094	5.450160427	1.576580122
6	2.408620185	4.760130365	1.482830112

6	3.618560279	2.612460198	1.172190092
6	3.589590274	1.263740095	0.999790076
6	2.345660179	-0.812790060	0.493170038
6	1.177480092	-1.449540111	0.212080016
6	-1.205950092	-1.383550105	-0.431740033
6	2.068220157	3.440990265	4.923920376
6	-2.322300178	-0.695890054	-0.775060061
6	-3.374400256	1.428160107	-1.455590110
6	-3.285390251	2.768750211	-1.741190135
6	-2.068220157	3.440990265	-1.523940115
6	-0.999760077	2.784850212	-0.959010074
6	-1.091880083	1.427520109	-0.567350043
6	-2.276790173	0.727880057	-0.905910069
6	0.007700001	0.701570052	0.046810004
6	-0.007690001	-0.701560056	-0.046800004
6	1.158180087	1.326880101	0.659860052
6	3.285390251	2.768750211	5.141170391
6	2.361230182	0.592960046	0.720820054
6	1.172840091	2.663380205	1.210850094
6	2.400830182	3.345610257	1.285720096
6	0.000000000	3.345560255	1.699990131
6	0.000000000	4.751810365	1.699990131
6	-1.172840091	2.663380205	2.189130168
6	-2.400830182	3.345610257	2.114250163
6	-1.158180087	1.326880101	2.740120209
6	-2.361230182	0.592960046	2.679160207
6	-0.007700001	0.701570052	3.353170258
6	3.374400256	1.428160107	4.855560370
6	0.007690001	-0.701560056	3.446770262
6	1.091880083	1.427520109	3.967320302
6	2.276790173	0.727880057	4.305880328
6	2.322300178	-0.695890054	4.175040317
6	1.205950092	-1.383550105	3.831710292
6	-1.177480092	-1.449540111	3.187900244
6	-2.345660179	-0.812790060	2.906800220
6	-3.589590274	1.263740095	2.400180183
1	0.064160005	3.309050253	4.236530322
1	-4.556600349	3.141460241	2.110500159
1	-3.361780257	5.275110402	1.907530146
1	-1.232230093	6.532780506	1.776630136
1	1.232230093	6.532780506	1.623340124
1	3.361780257	5.275110402	1.492450116
1	4.556600349	3.141460241	1.289470100
1	4.503270343	0.681360053	1.010710077
1	3.272410248	-1.364230103	0.597250044
1	1.140610085	-2.528020194	0.111560008
1	-1.202040091	-2.467300190	-0.419070032
1	1.964790151	4.479820340	5.210410398
1	-3.239830249	-1.212310094	-1.031930080
1	-4.280910327	0.875610067	-1.674930127

1	-4.129020317	3.294780253	-2.170100165
1	-1.964790151	4.479820340	-1.810440138
1	-0.064160005	3.309050253	-0.836560062
1	4.129020317	3.294780253	5.570080405
1	4.280910327	0.875610067	5.074910388
1	3.239830249	-1.212310094	4.431900339
1	1.202040091	-2.467300190	3.819040291
1	-1.140610085	-2.528020194	3.288410250
1	-3.272410248	-1.364230103	2.802730212
1	-4.503270343	0.681360053	2.389260182

7helicne: UM052x/6-31G(d), -1154.00141860 hartree

	x	y	z
6	2.735000000	-2.373150000	0.907240000
6	1.371880000	-0.000500000	0.294390000
6	-0.639530000	-3.545400000	-1.370500000
6	2.780080000	0.008730000	0.511150000
1	3.304440000	0.955630000	0.465200000
6	-1.371880000	-0.000500000	-0.294390000
6	0.639530000	-3.545400000	1.370500000
6	-0.720460000	-3.524080000	1.758690000
1	-1.270980000	-2.596410000	1.712120000
6	-2.792450000	-4.738140000	-1.441810000
1	-3.333050000	-5.661820000	-1.610730000
6	0.667290000	-1.225020000	0.285060000
6	1.348140000	-4.657480000	-2.221380000
6	1.370690000	-4.737930000	1.595490000
6	-1.370690000	-4.737930000	-1.595490000
6	3.450940000	-1.156740000	0.712650000
1	4.530960000	-1.171280000	0.799020000
6	-0.667290000	-1.225020000	-0.285060000
6	-2.780080000	0.008730000	-0.511150000
1	-3.304440000	0.955630000	-0.465200000
6	-1.329710000	-2.384090000	-0.840430000
6	1.329710000	-2.384090000	0.840430000
6	0.720460000	-3.524080000	-1.758690000
6	0.700500000	-5.897930000	2.043240000
1	1.275270000	-6.806740000	2.178920000
6	0.673310000	1.225520000	0.092160000
1	1.229990000	2.153140000	0.149380000
6	3.450680000	-3.581570000	1.183100000
1	4.533620000	-3.550680000	1.158260000
6	-0.700500000	-5.897930000	-2.043240000
1	-1.275270000	-6.806740000	-2.178920000
6	-1.348140000	-4.657480000	2.221380000
6	-3.450680000	-3.581580000	-1.183100000
1	-4.533620000	-3.550690000	-1.158260000
6	-2.735000000	-2.373150000	-0.907240000
6	0.642120000	-5.869600000	-2.332470000
1	1.145990000	-6.762370000	-2.680250000

6	-3.450940000	-1.156740000	-0.712650000
1	-4.530960000	-1.171290000	-0.799020000
6	2.792450000	-4.738140000	1.441810000
1	3.333050000	-5.661820000	1.610730000
6	-0.642120000	-5.869600000	2.332470000
1	-1.145990000	-6.762370000	2.680250000
6	-0.673310000	1.225520000	-0.092160000
1	-1.229990000	2.153140000	-0.149380000
1	1.270980000	-2.596410000	-1.712120000
1	2.390580000	-4.610370000	-2.509540000
1	-2.390580000	-4.610370000	2.509540000

13C₂NH: UM052x/6-31G(d), -1788.60498266 hartree

	x	y	z
7	2.390600000	-0.716470000	1.971890000
7	4.201610000	0.857430000	1.074340000
7	4.901730000	3.216610000	0.393830000
7	4.258040000	5.638760000	-0.059960000
7	2.454110000	7.434440000	-0.222520000
7	-0.000190000	8.097500000	0.047350000
7	-2.464810000	7.425320000	0.110740000
7	-4.247730000	5.595830000	0.117510000
7	-4.896040000	3.189730000	-0.440060000
7	-4.195700000	0.821060000	-1.097080000
6	0.695860000	0.847780000	1.591300000
6	1.015490000	-0.432970000	2.002780000
6	1.956430000	1.435690000	1.175470000
6	2.899980000	0.461450000	1.398410000
6	2.696570000	2.579430000	0.685310000
6	4.023180000	2.193670000	0.723530000
6	2.710080000	3.931310000	0.172770000
6	4.049790000	4.253420000	-0.004010000
6	1.984520000	5.177940000	0.044550000
6	2.960840000	6.145390000	-0.073630000
6	0.727010000	5.894710000	-0.035770000
6	1.078860000	7.228750000	-0.111730000
6	-0.722150000	5.887770000	0.012670000
6	-1.083530000	7.216410000	0.087490000
6	-1.975730000	5.159620000	-0.048080000
6	-2.958340000	6.120010000	0.099750000
6	-2.691220000	3.920370000	-0.276100000
6	-4.026840000	4.246600000	-0.153420000
6	-2.681210000	2.527160000	-0.685240000
6	-4.007380000	2.140720000	-0.692250000
6	-1.953680000	1.393080000	-1.210430000
6	-2.905750000	0.428220000	-1.449380000
6	-0.702900000	1.006010000	1.824800000
6	-1.154380000	-0.179740000	2.350270000
7	-0.094330000	-1.070780000	2.468420000

6	-0.692290000	0.786660000	-1.597690000
6	-1.017610000	-0.496300000	-1.998160000
7	-2.395900000	-0.766480000	-1.987360000
6	0.707790000	0.935730000	-1.829910000
6	1.153610000	-0.255620000	-2.347920000
7	0.088760000	-1.140780000	-2.463890000
1	0.132340000	-2.059190000	-2.862570000
1	-2.715100000	-1.634950000	-1.581850000
1	-4.983350000	0.571160000	-1.673460000
1	-5.705370000	3.038420000	0.143670000
1	-5.011410000	6.083290000	-0.322750000
1	-2.853680000	8.114480000	0.736640000
1	-0.068930000	8.940270000	-0.502280000
1	2.897720000	8.210020000	0.243430000
1	4.958110000	6.044080000	-0.662510000
1	5.770820000	3.027440000	-0.079620000
1	4.966790000	0.590420000	1.674210000
1	2.691400000	-1.596550000	1.577000000
1	-0.141150000	-1.983370000	2.880090000
1	1.324110000	1.795260000	-1.625190000
1	2.147980000	-0.563750000	-2.622600000
1	-1.315110000	1.867000000	1.615000000
1	-2.148650000	-0.478840000	2.635000000

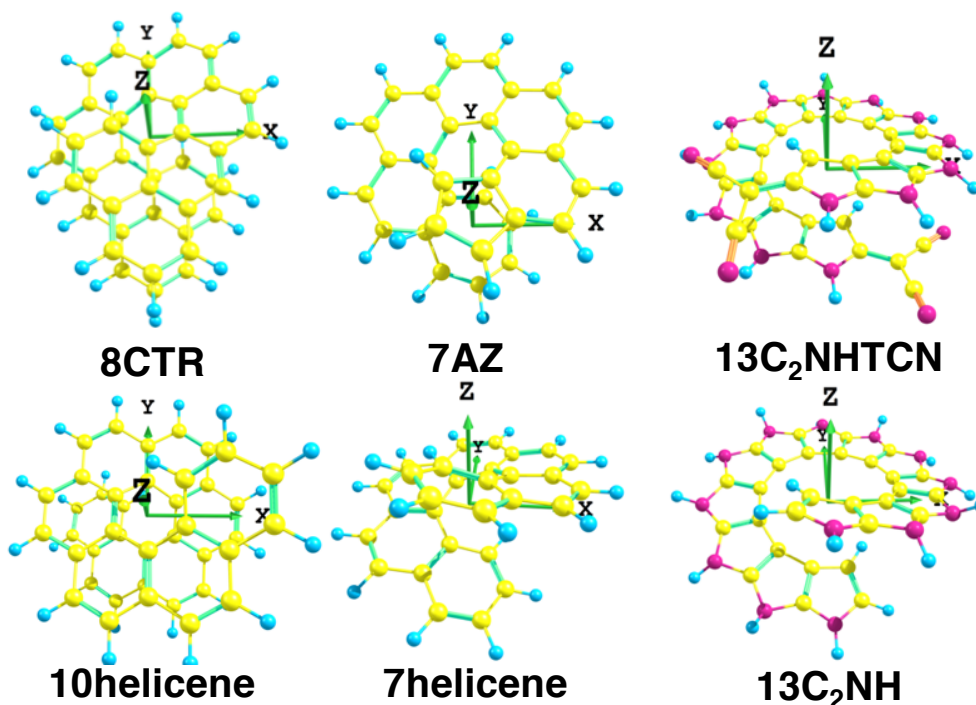


Figure S10. Molecular structures of the model systems optimized using the (U)M052x/6-31G(d) method.

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