開殻性を持つ光機能性分子系の理論設計

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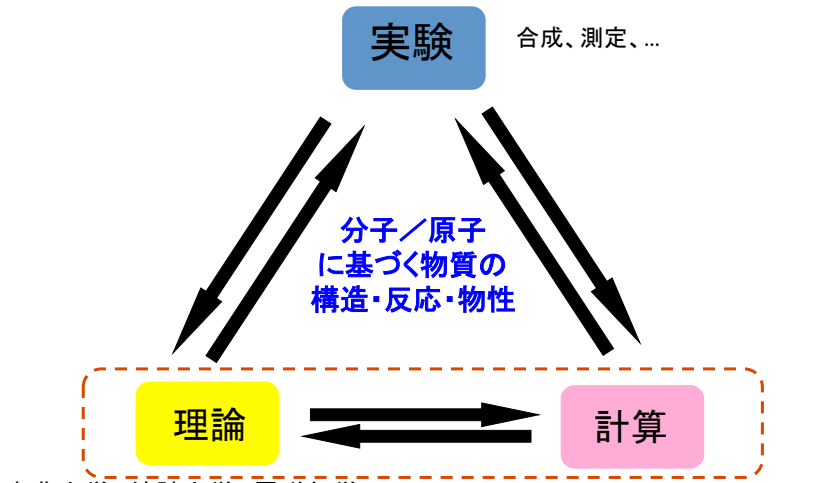
統計数理研究所　数学協働プログラム　ワークショップ工学と現代数学の接点を求めて(1)

化学における研究



理論化学、計算化学とは？

理論化学、計算化学：

理論（モデルや概念）の構築やその適用（計算手法の開発、数値計算、紙と鉛筆）
⇄ 既知の実験事実を説明、未知の物質の性質などを予言

実験化学：

多数の実験 ⇄ その背後にある普遍的な理論を導く

対象： 物質の構造、物質の性質、物質の反応

小サイズの単分子	→	巨大分子、分子集合系
弱電子相関系	→	電子相関系
基底状態	→	励起状態
時間無依存	→	時間発展（ダイナミクス）
量子系、古典系	→	量子-古典ハイブッリド
定常、平衡状態	→	非定常、非平衡状態
均一系	→	不均一系
温度無依存	→	温度効果
古典場	→	量子場

. . .

内容

0. 開殻分子系とは？

1. 非線形光学（NLO）効果

2. 開殻分子系の電子状態とNLO効果

3. 様々な開殻分子系のNLO効果

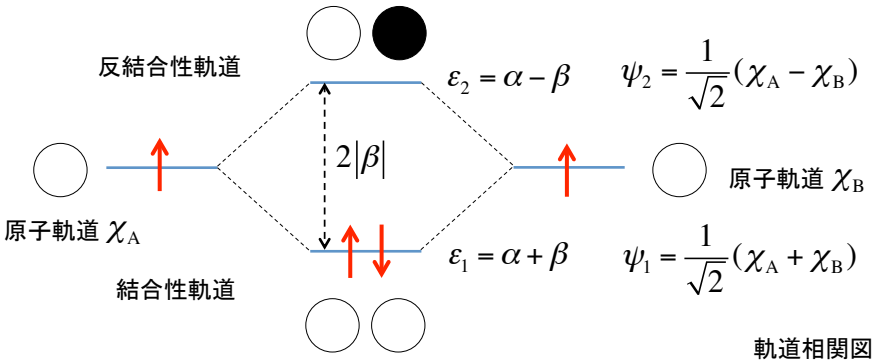
4. まとめと今後の展望

化学結合: 2原子分子

$h\psi_i = \varepsilon_i \psi_i$　　1電子についてのSchrödinger 波動方程式

$\psi_i = c_{Ai}\chi_A + c_{Bi}\chi_B$　分子軌道

$$\begin{pmatrix} h_{AA}-\varepsilon & h_{AB}-\varepsilon S_{AB} \\ h_{BA}-\varepsilon S_{BA} & h_{BB}-\varepsilon \end{pmatrix}\begin{pmatrix} c_A \\ c_B \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix} \qquad \begin{pmatrix} \alpha-\varepsilon & \beta \\ \beta & \alpha-\varepsilon \end{pmatrix}\begin{pmatrix} c_A \\ c_B \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix}$$



軌道相関図

開殻性とは？: 例として二原子分子の解離過程

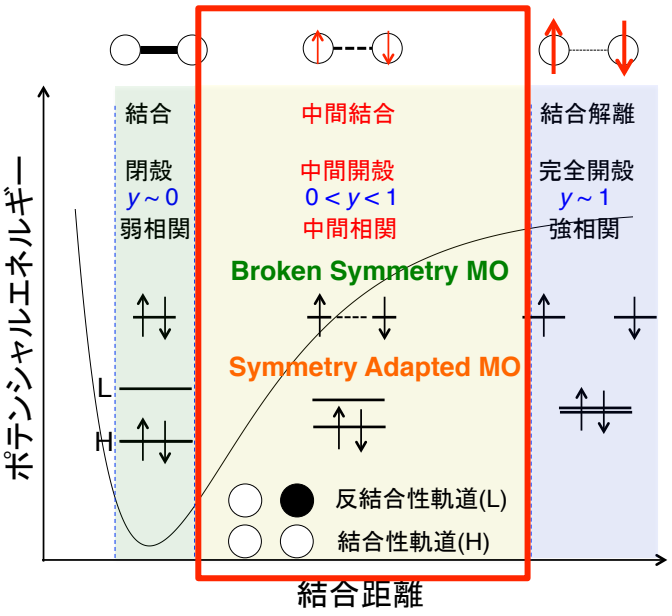
開殻因子
（ジラジカル因子）
y ($0 \le y \le 1$)

中間ジラジカル領域

中間的な強さの結合
電子状態が揺らぎやすい

物理的・化学的な弱い外部摂動により容易に電子状態や物理化学的性質を変化させることが可能

特異な物理化学的性質、高い機能性、. . .



Open-Shell Singlet Molecular Systems

Diradical / Diradicaloid (= Diradical-like):

Two weakly interacting electrons with similar energy

L. Salem, C. Rowland, *Angew. Chem. Int. Ed.* **11**, 92 (1972).
W. T. Borden (Ed.), Diradicals, Wiely, New York, 1982.

➔ **Molecules with two nearly degenerate bonding and anti-bonding MOs**

ex. H_2 molecule (with different bond lengths),
Twisted ethylene (with different twisted angles)

➔ **Recent development in synthesis realizes various types of stable singlet diradicaloids/multi-radicaloids**

ex. Diphenalenyl compounds, Transition metal compounds,
Polycyclic aromatic hydrocarbons (PAHs), etc.

C. Lambert, *Angew. Chem. Int. Ed.* **50**, 1756 (2011).
Z. Sun, J. Wu, *J. Mater. Chem.* **22**, 4151 (2012).

Unique Properties of Open-Shell Singlet Molecular Systems

- **Longer acenes possess a nonzero bandgap with a singlet open-shell ground state followed by a triplet state a few kcal/mol higher in energy.**

  M. Bendikov et al. *J. Am. Chem. Soc.* **126**, 7416 (2004).

- **High reactivity of the zigzag edges of the longer oligoacenes.**

- **High charge carrier mobilities in the solid state.**

- **Electronic states are characterized by "diradical character".**

  K. Yamaguchi, T. Fueno, H. Fukutome, *Chem. Phys. Lett.* 22, 461 (1973); in, *Self-Consistent Field: Theory and Applications*, R. Carbo et al. Eds.; Elsevier: Amsterdam, pp. 727 (1990).

- **Excitation energies and properties are strongly correlated to the diradcial character in the ground state.**

  M. Nakano et al. *Phys. Rev. Lett.* **99**, 033001 (2007)

- **Diradcial character control of optical properties, e.g., nonlinear optical responses, optical absorption, singlet fission, etc.**

  M. Nakano et al., *J. Phys. Chem. A* **109**, 885 (2005); *J. Chem. Phys.* **133**, 154302 (2010);
  T. Minami, M. Nakano, *J. Phys. Chem. Lett.* **3**, 145 (2012).

開殻因子に基づいた理論分子設計

開殻因子（ジラジカル因子 y）

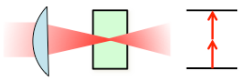
$y = 0$ (閉殻)　　$0 < y < 1$ (中間開殻)　　$y = 1$ (完全開殻)

構造、物性、反応性

新奇光機能性物質の理論先行型分子設計
実験より先に、望みの機能をもつ物質の設計を行う！

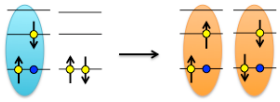
開殻性に基づく機能性物質の理論設計

光応答物性



Ex. Two-photon absorption (TPA)

一重項分裂

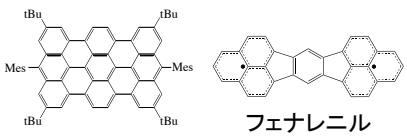


S_1S_0　　T_1T_1

設計原理の構築　*Phys. Rev. Lett.* 99, 033001 (2007); *J. Phys. Chem. Lett.* 3, 145 (2012)

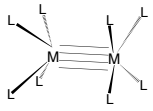
- 中間ジラジカル性をもつ系における光非線形応答物性の著しい増大
- Singlet Fission実現条件：小さなジラジカル性とずっと小さなテトラジカル性

量子化学計算による分子設計と実験による検証

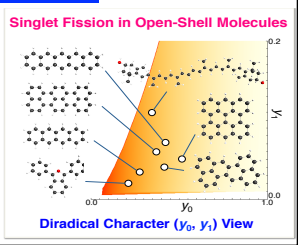


グラフェンナノフレーク

フェナレニル



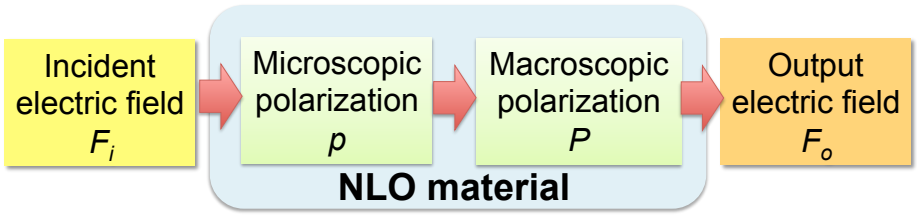
金属-金属多重結合



Angew. Chem. Int. Ed., 46, 3544 (2007)

非線形光学効果

Nonlinear optical (NLO) process



Frequency of F_i ≠ Frequency of F_o

Macroscopic polarization P and microscopic polarization p

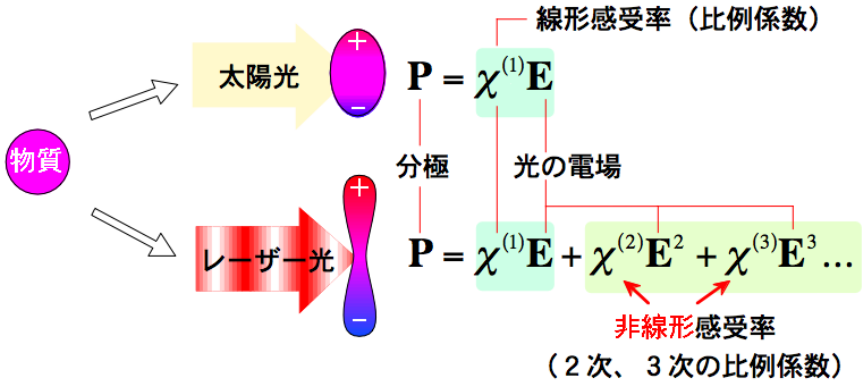
$$P = \chi^{(1)}F + \chi^{(2)}F^2 + \chi^{(3)}F^3 \cdots$$
$$p = \alpha F + \beta F^2 + \gamma F^3 \cdots$$

$\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$: linear, second-order and third order nonlinear susceptibilities

α, β, γ: polarizability, first hyperpolarizability, second hyperpolarizability

Fundamental factors for description and applications of NLO

Nonlinear optical (NLO) polarization



ミクロ（原子・分子）レベル

$$p = \alpha E + \beta EE + \gamma EEE + \ldots$$

α：分極率、β：第一超分極率、γ：第二超分極率

Nonlinear optical (NLO) effect

光高調波発生、光混合、光パラメトリック効果
. . . 入射光と異なる周波数の出力光
レーザー光の波長変換
例. THG, SHG, 和周波発生

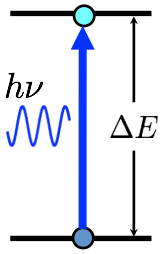
非線形屈折率変化（電場依存屈折率変化（電気光学効果））
. . . 媒質の屈折率が電場強度により変化
自己収束、自己位相変調（情報通信、
超高速スイッチ）、光双安定性（超高速スイッチ）

多光子吸収，多光子放出
. . . 複数のフォトンを吸収、放出するコヒーレントな過程、
3次元メモリー、非線形分光、超微細加工技術、フォトダイナミック
セラピーなど応用は幅広い。

外場（光）との相互作用によりあらゆる物質に現れる現象。科学と工学のテーマ
- 基底及び励起電子状態間の諸物性量（励起エネルギー、遷移モーメント）と環境との相互作用による緩和により支配。
- 分子物性、分子間相互作用効果
- 外場の高次に比例する応答量

多光子吸収

吸収
（一光子）



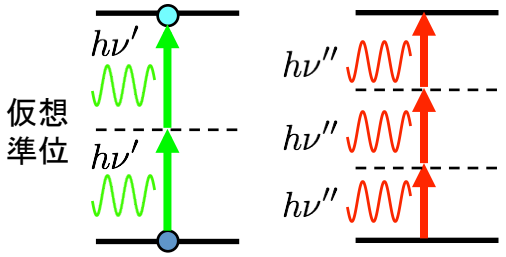
$h\nu = \Delta E$

準位差に一致するエネルギーを持つ光子のみが吸収
光化学等量の法則
(Stark-Einstein則)

多光子吸収

二光子

三光子

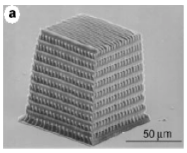


$2h\nu' = \Delta E$　　$3h\nu'' = \Delta E$

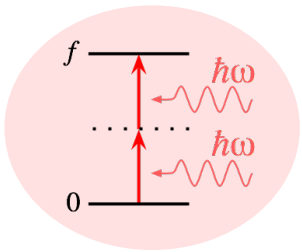
励起エネルギーΔE＝光子n個のエネルギー
仮想準位を経た遷移

Applications (Third-Order NLO; TPA)

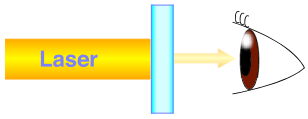
3D microfabrication



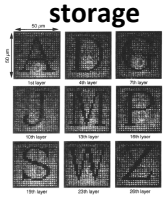
B.H. Cumpston *et al.*, *Nature 1999*, **398**, 53.



Optical limiting

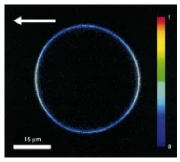


3D optical data storage



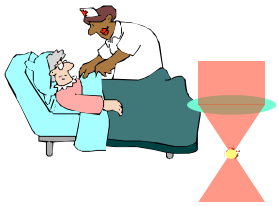
S. Kawata *et al.*, *Chem. Rev.* 2000, **100**, 1777.

3D fluorescence microscopy



L. Ventelon *et al.*, *Angew. Chem. Int. Ed.*, 2001, **40**, 2098.

Photodynamic therapy



and new applications...

時間依存摂動論による超分極率の定式化

時間依存摂動論による応答量の解析式

分極とは？

$$p^i \equiv \mu^i_{\mathrm{tot}} - \mu^i_0 = \sum_j \alpha_{ij} F^j + \sum_{jk} \beta_{ijk} F^j F^k + \sum_{jkl} \gamma_{ijk} F^j F^k F^l + \ldots \quad (1)$$

分極率　第一超分極率　第二超分極率

時間に依存したSchrödinger方程式

$$H\Psi = i\hbar \frac{\partial}{\partial t}\Psi \quad (2)$$

$H = H_0 + H_1(t)$ ここで、摂動ハミルトニアン $H_1(t) = \sum_j e\boldsymbol{r}_j \cdot \boldsymbol{F}\cos\omega t = -\boldsymbol{\mu}\cdot\boldsymbol{F}\cos\omega t$ (3)

無摂動系でのSchrödinger方程式 → 解けているとする

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad (4)$$

式(2)の解

$$\Psi(t) = \sum_n c_n(t)\psi_n^{(0)}(t)e^{-iE_n^{(0)}t/\hbar} \quad (5)$$

この展開係数を求める

時間依存摂動論による応答量の解析式

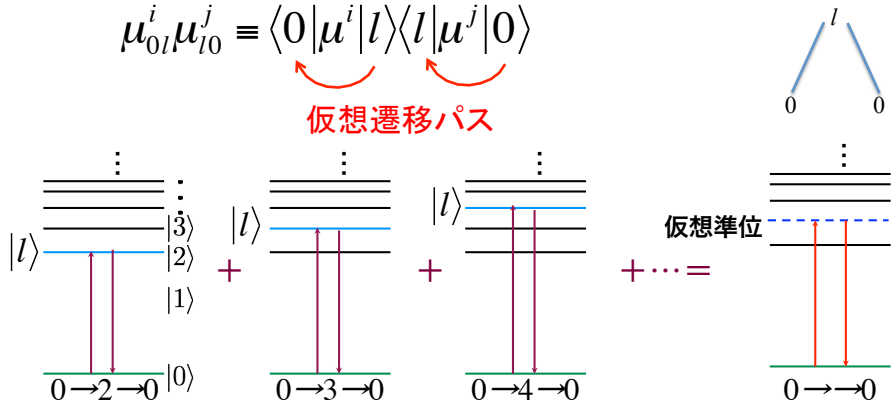
仮想遷移

$$\alpha_{ij}(-\omega;\omega) = 2\sum_{l\neq 0} \mu^i_{0l}\mu^j_{l0} \frac{E_{l0}}{[E^2_{l0} - (\hbar\omega)^2]}$$

遷移双極子項　　共鳴項（重み）

$$\mu^i_{0l}\mu^j_{l0} \equiv \langle 0|\mu^i|l\rangle\langle l|\mu^j|0\rangle$$

仮想遷移パス

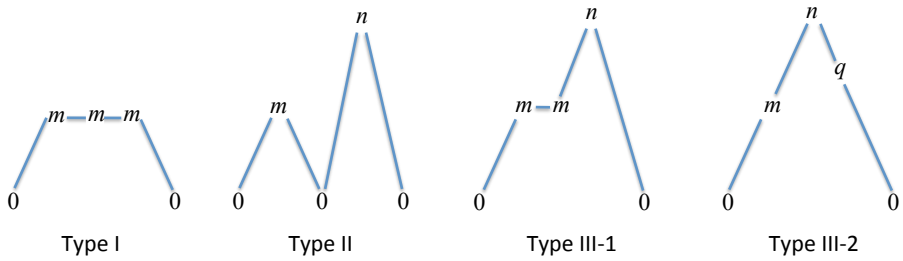


時間依存摂動論による応答量の解析式

第二超分極率

$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{6}P(i,j,k,l;-\omega_\sigma;\omega_1,\omega_2,\omega_3)\left\{\sum\sum\sum_{m\neq 0 n\neq 0 q\neq 0} \frac{\mu^i_{0m}\bar{\mu}^j_{mn}\mu^k_{nq}\mu^l_{q0}}{(E_{m0}-\hbar\omega_\sigma)(E_{n0}-\hbar\omega_2-\hbar\omega_3)(E_{q0}-\hbar\omega_3)} - \sum\sum_{m\neq 0 n\neq 0} \frac{\mu^i_{0m}\bar{\mu}^j_{m0}\mu^k_{0n}\mu^l_{n0}}{(E_{m0}-\hbar\omega_\sigma)(E_{n0}-\hbar\omega_3)(E_{n0}+\hbar\omega_2)}\right\}$$

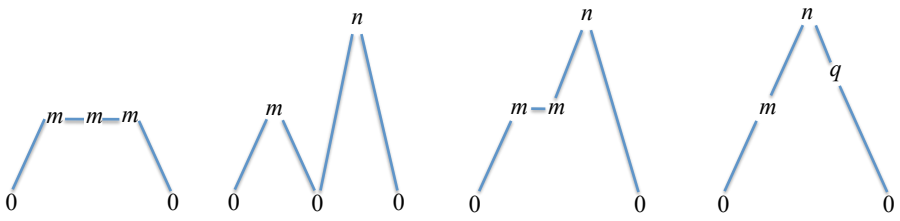
$P(i,j,k,l;-\omega_\sigma;\omega_1,\omega_2,\omega_3)$　置換演算子　すべてで24項　(10)



応答量の仮想遷移過程解析

静的第二超分極率

$$\gamma_{iiii}(0) = 4\left\{\sum_{n\neq 0}\frac{(\mu^i_{0m})^2(\bar{\mu}^i_{mm})^2}{E^3_{m0}} - \sum_{n,m\neq 0}\frac{(\mu^i_{0m})^2(\mu^i_{n0})^2}{E_{m0}E^2_{n0}} + 2\sum_{m\neq n}\frac{\mu^i_{0m}\bar{\mu}^i_{mm}\mu^i_{mn}\mu^i_{n0}}{E^2_{m0}E_{n0}} + \sum_{m\neq n}\frac{\mu^i_{0m}\mu^i_{mn}\mu^i_{nq}\mu^i_{q0}}{E^2_{m0}E_{n0}}\right\} \quad (13)$$



Type I　Type II　Type III-1　Type III-2

非対称系のみ　非対称系のみ

正の寄与　負の寄与　～正の寄与　～正の寄与

対称系ではType I, III-1の寄与が消え、正と負の寄与のバランスで全体の大きさと符号が決まる

非共鳴で負の系は稀である（かけた電場の向きと逆向きに三次分極が生じる）

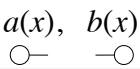
開殻分子系の電子状態と非線形光学効果

VBおよびMO描像と対称性の破れた方法

Symmetry adapted MOs … $g(x)$(bonding), $u(x)$(antibonding)

$$g(x) \equiv \frac{1}{\sqrt{2(1+S_{AB})}}[\varphi_A(x)+\varphi_B(x)] \qquad u(x) \equiv \frac{1}{\sqrt{2(1-S_{AB})}}[\varphi_A(x)-\varphi_B(x)]$$

Localized natural orbitals (LNOs) … $a(x)$, $b(x)$ $\langle a|b\rangle = 0$



$$a(x) \equiv \frac{1}{\sqrt{2}}[g(x)+u(x)] \approx \varphi_A(x) \qquad b(x) \equiv \frac{1}{\sqrt{2}}[g(x)-u(x)] \approx \varphi_B(x)$$

Singlet spin-unrestricted (broken symmetry) MO … $\chi(x)$, $\eta(x)$

$$\chi(x) = \cos(\theta/2)g(x) + \sin(\theta/2)u(x), \qquad \eta(x) = \cos(\theta/2)g(x) - \sin(\theta/2)u(x)$$

$$\chi(x) = \cos(\omega/2)a(x) + \sin(\omega/2)b(x), \qquad \eta(x) = \cos(\omega/2)b(x) + \sin(\omega/2)a(x)$$

(i) Weak correlation limit (MO limit) at $\theta = 0$ ($\omega = \pi/2$): $\chi = \eta = g$
(ii)Strong correlation limit (VB limit) at $\theta = \pi/2$ ($\omega = 0$): $\chi = a$, $\eta = b$

UMOs can describe both weak and strong correlation limits (MO and VB limits) as well as intermediate correlation regime.

Diradical character *y*

UHF wavefunction $\Psi_{UHF}(\chi\bar{\eta}) = \frac{1}{\sqrt{2}}\begin{vmatrix}\chi(1) & \chi(2)\\ \bar{\eta}(1) & \bar{\eta}(2)\end{vmatrix}$

a, b : magnetic orbitals,
$\phi_1(\mathrm{HOMO}-i)$, $\phi_2(\mathrm{LUMO}+i)$: symmetry adapted MOs

$$\chi = \cos\frac{\theta}{2}\phi_1 + \sin\frac{\theta}{2}\phi_2, \quad \eta = \cos\frac{\theta}{2}\phi_1 - \sin\frac{\theta}{2}\phi_2$$

θ : mixing angle
$0 \le \theta \le \pi/2$

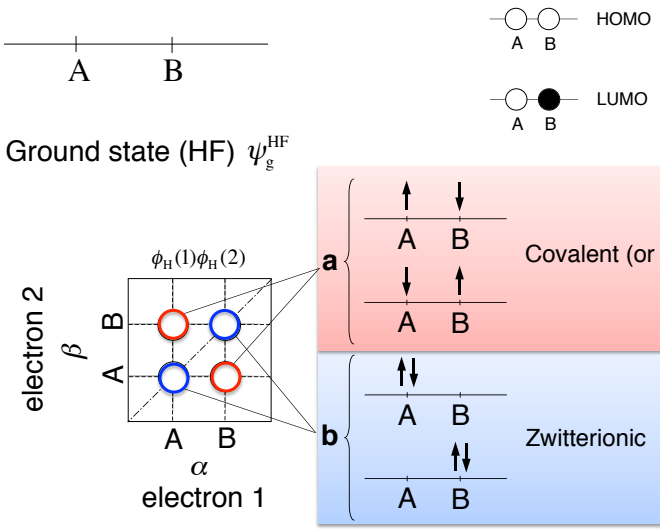
$$\Psi_{UHF}(\chi\bar{\eta}) = \cos^2\frac{\theta}{2}\Psi(1\bar{1}) + \sqrt{2}\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left[\frac{1}{\sqrt{2}}(\Psi(2\bar{1}) - \Psi(1\bar{2}))\right] - \sin^2\frac{\theta}{2}\Psi(2\bar{2})$$

Singlet HF | **Triplet** Spin contamination | **Singlet double excitation**

The diradical character is defined by twice the weight of double excitation configuration of CASCI(2,2) (~ spin-projected UHF (PUHF)).

Electronic structure of two-electron system

Two-dimensional coordinate for one-dimensional two-electron system

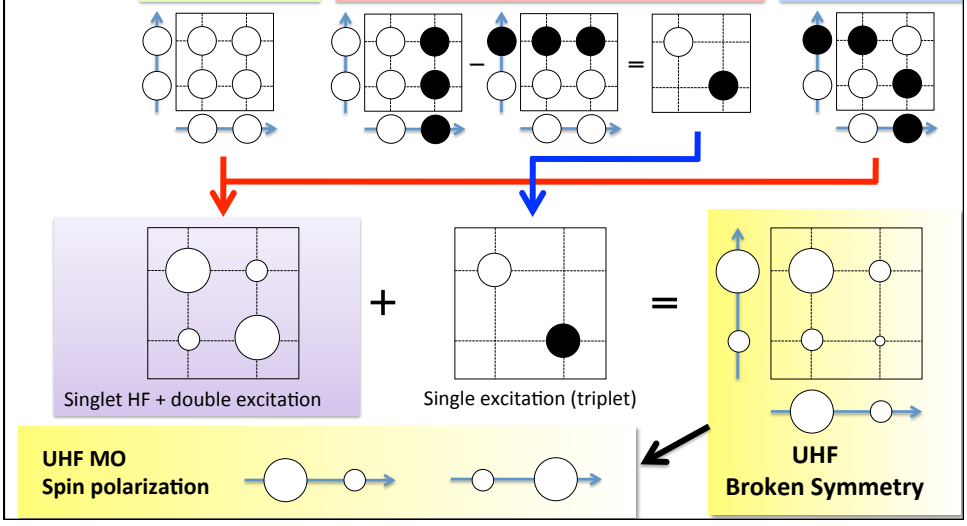


Nakano *et al*. *J*. *Chem*. *Phys*. **125**, 074113 (2006)

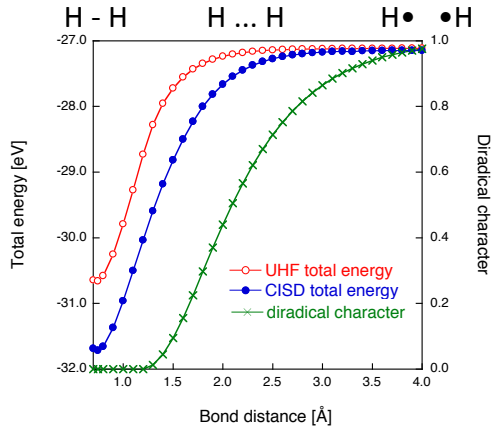
UHF wavefunction

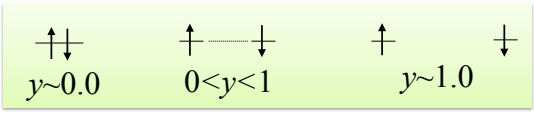
$$\Psi_{UHF}(\chi\overline{\eta}) = \cos^2\frac{\theta}{2}\Psi(1\overline{1}) + \sqrt{2}\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left[\frac{1}{\sqrt{2}}(\Psi(2\overline{1}) - \Psi(1\overline{2}))\right] - \sin^2\frac{\theta}{2}\Psi(2\overline{2})$$

Singlet HF | **Triplet (Spin contamination)** | **Singlet double excitation**



Variation in diradical character (y) for the dissociation of H_2





Diradical character $0 \le y \le 1$

$$y_i = 1 - \frac{2T_i}{1+T_i^2}$$

T_i :overlap between

$$\chi_{\mathrm{H}-i} = \left(\cos\frac{\theta}{2}\right)\phi_{\mathrm{H}-i} + \left(\sin\frac{\theta}{2}\right)\phi_{\mathrm{L}+i}$$

and

$$\eta_{\mathrm{H}-i} = \left(\cos\frac{\theta}{2}\right)\phi_{\mathrm{H}-i} - \left(\sin\frac{\theta}{2}\right)\phi_{\mathrm{L}+i}$$

ϕ :UNOs

$$T_i = \cos\theta = \frac{n_{\mathrm{H}-i} - n_{\mathrm{L}+i}}{2}$$

n :occupation number of UNO

(Yamaguchi et al. 1975)

Two-site model A˙–B˙ with two electrons in two orbitals: Valence configuration interaction (VCI) approach

Symmetry adapted MOs … $g(x), u(x)$

Localized natural orbitals (LNOs) … $a(x), b(x)$ $\langle a|b\rangle = 0$

$$a(x) \equiv \frac{1}{\sqrt{2}}[g(x)+u(x)] \qquad b(x) \equiv \frac{1}{\sqrt{2}}[g(x)-u(x)]$$

Basis sets for $M_s = 0$ (singlet and triplet) states

$$\left\{\left|a\bar{b}\right\rangle, \left|b\bar{a}\right\rangle, \left|a\bar{a}\right\rangle, \left|b\bar{b}\right\rangle\right\}, \quad \text{where} \quad \left|a\bar{b}\right\rangle (\equiv \left|\text{core}\ a\bar{b}\right\rangle), \ \ldots$$

CI matrix using LNOs

$$\begin{pmatrix} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{pmatrix}$$

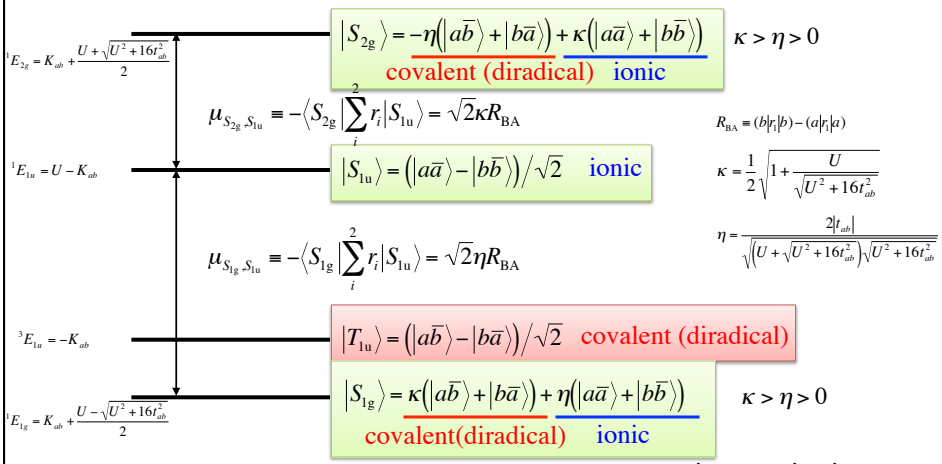
$$U \equiv U_{aa} - U_{ab}$$

$$K_{ab} \equiv \left\langle a\bar{b}\middle|1/r_{12}\middle|b\bar{a}\right\rangle \ge 0$$

$$t_{ab} \equiv \langle a|F|b\rangle \quad F\text{: Fock operator}$$

Electronic states of two-site model A·–B· (VCI)

Using **localized natural orbitals (LNOs)**

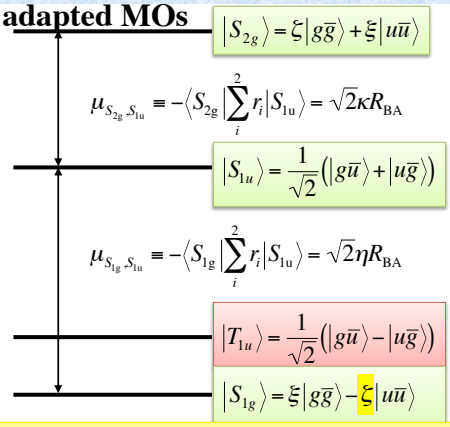


Effective exchange integral J of Heisenberg Hamiltonian $\hat{H}_{HB} = -2J\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$

$$2J = {}^1E_{1g} - {}^3E_{1u} = 2K_{ab} + \frac{U-\sqrt{U^2+16t_{ab}^2}}{2}$$

Two-site model A·–B· with two electrons in two orbitals: Molecular orbital configuration interaction (MOCI) approach

Using **symmetry adapted MOs**



$$\xi = \kappa + \eta = \frac{1}{2}\left(\sqrt{1+\frac{U}{\sqrt{U^2+16t_{ab}^2}}} + \frac{4|t_{ab}|}{\sqrt{(U+\sqrt{U^2+16t_{ab}^2})\sqrt{U^2+16t_{ab}^2}}}\right)$$

$$\zeta = \kappa - \eta = \frac{1}{2}\left(\sqrt{1+\frac{U}{\sqrt{U^2+16t_{ab}^2}}} - \frac{4|t_{ab}|}{\sqrt{(U+\sqrt{U^2+16t_{ab}^2})\sqrt{U^2+16t_{ab}^2}}}\right)$$

Diradical characters of two-site model A˙–B˙

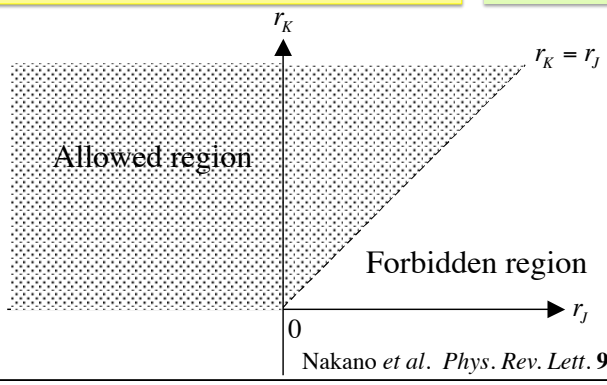
Diradical character (0≤ y ≤1)

$$y \equiv 2\zeta^2 = 1 - \frac{4|t_{ab}|}{\sqrt{U^2 + 16t_{ab}^2}} = 1 - \frac{4r_t}{\sqrt{1+16r_t^2}} = 1 - \frac{2\sqrt{(r_K - r_J)(r_K - r_J + 1)}}{1 + 2(r_K - r_J)}$$

Here

$$r_J \equiv \frac{2J}{U}, \quad r_K \equiv \frac{2K_{ab}}{U} (\geq 0), \quad r_t \equiv \frac{|t_{ab}|}{U} (\geq 0)$$

$$r_J = r_K + \frac{1}{2}\left(1 - \sqrt{1+16r_t^2}\right)$$



Nakano *et al*. *Phys. Rev. Lett*. **99**, 033001 (2007)

Diradical characters of two-site model A˙–B˙

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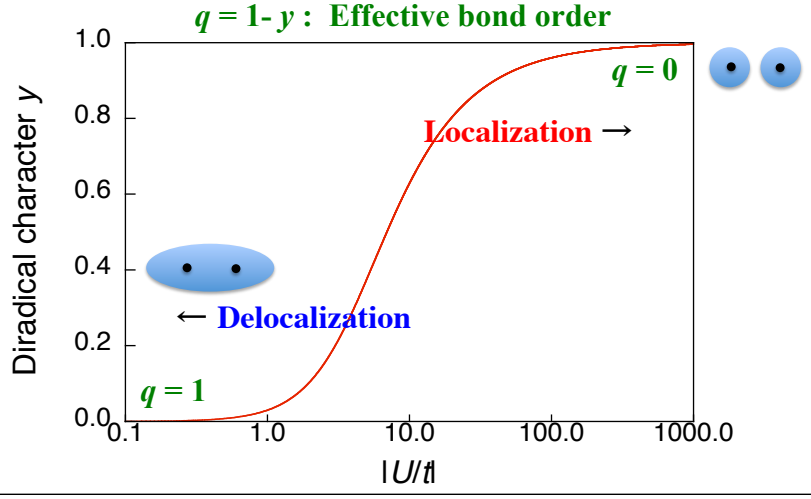
q = 1- y : Effective bond order



Relationships between transition properties and diradical character

Transition properties

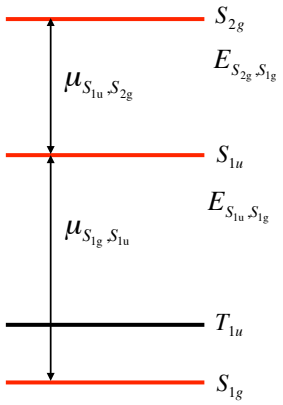
$$(\mu_{S_{1g},S_{1u}})^2 = R_{BA}^2 \frac{r_K - r_J}{1+2(r_K - r_J)} = R_{BA}^2 \frac{1-\sqrt{1-q^2}}{2}$$

$$(\mu_{S_{1u},S_{2g}})^2 = \frac{R_{BA}^2}{2}\left(1+\frac{1}{1+2(r_K - r_J)}\right) = R_{BA}^2 \frac{1+\sqrt{1-q^2}}{2}$$

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

$$E_{S_{2g},S_{1g}} \equiv {}^1E_{2g} - {}^1E_{1g} = U\left[1+2(r_K - r_J)\right] = \frac{U}{\sqrt{1-q^2}}$$

$q \equiv 1-y$ **: effective bond order**

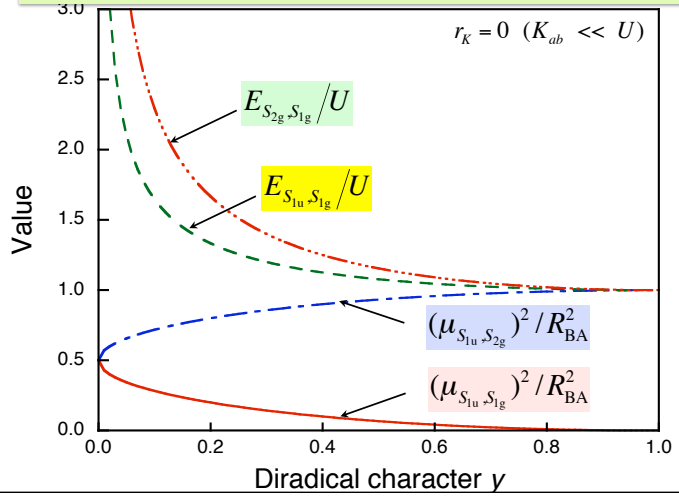


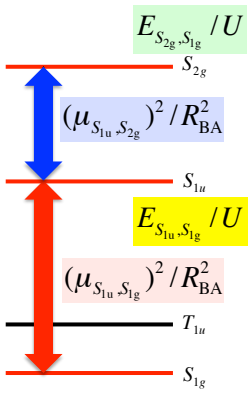
Static second hyperpolarizability

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

Diradical Character Dependences of Excitation Energies and Transition Properties

Increase of y (Ground-state diradical character)
First singlet excited state : Pure ionic
Second singlet excited state : Increase of ionic character





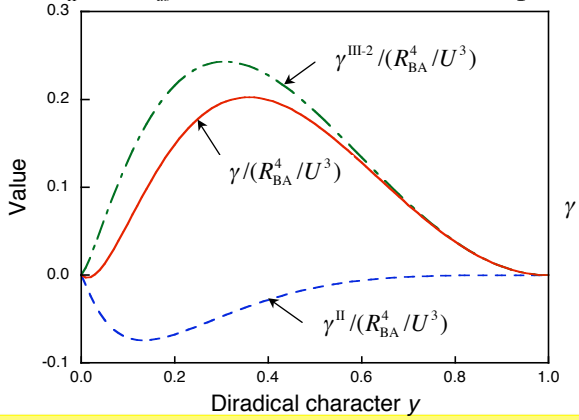
開殻分子系の静的第二超分極率

Relationships between second hyperpolarizability and diradical character

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

Case $r_K = 0$ $(K_{ab} << U)$

$q \equiv 1-y$: effectctive bond order



$y_{\max} \approx 1-0.6414 = 0.3586$

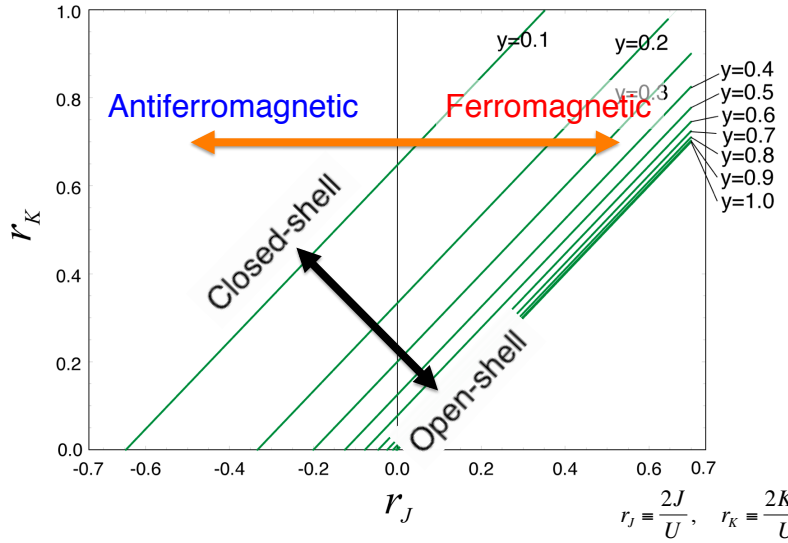
$\gamma_{\max}/\left(R_{\mathrm{BA}}^4/U^3\right) \approx 0.2025$

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

Keeping y constant, $\gamma^{\mathrm{III\text{-}2}}/\left(R_{\mathrm{BA}}^4/U^3\right)$ increases with r_K as a function of $1/(const-2r_K)^2$.

Diradical character on r_J- r_K plane

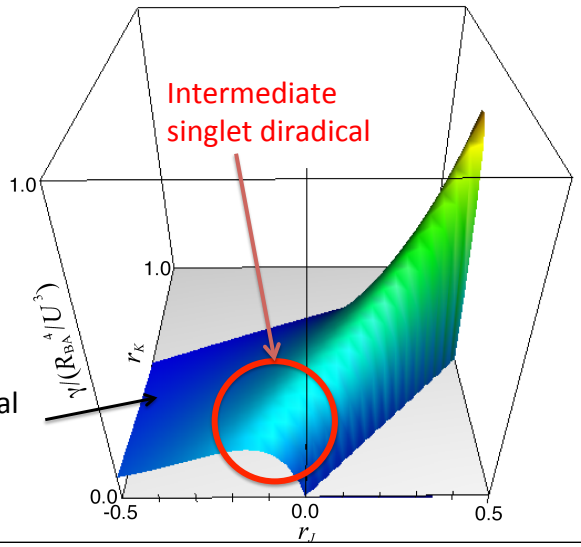
$$y = 1 - \frac{2\sqrt{(r_K - r_J)(r_K - r_J + 1)}}{1 + 2(r_K - r_J)}$$



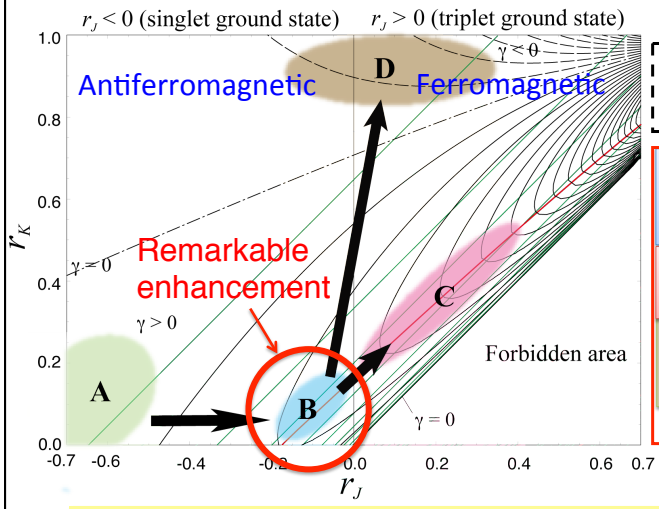
$$r_J \equiv \frac{2J}{U}, \quad r_K \equiv \frac{2K_{ab}}{U} (\geq 0)$$

(Anti)ferromagnetic interaction and second hyperpolarizability

$$\frac{\gamma}{\left(R_{BA}^4/U^3\right)} = -\frac{4(r_K - r_J)^2}{\left[1 + 2(r_K - r_J)\right]^2 (1 - r_J)^3} + \frac{4(1 + r_K - r_J)(r_K - r_J)}{\left[1 + 2(r_K - r_J)\right]^3 (1 - r_J)^2}$$



Off-resonant open-shell NLO: Static γ on r_J- r_K plane



Closed shell

A: conventional systems (ground state) γ > 0

B: Singlet diradical (ground state) γ > 0

C: Singlet diradical (excited state) γ > 0

D: Singlet diradical (ground/excited state) Small U γ < 0

Open shell

$r_J \equiv 2J/U, \quad r_K \equiv 2K_{ab}/U$

$$\frac{\gamma}{\left(R_{\mathrm{BA}}^4/U^3\right)} = -\frac{4\left(r_K - r_J\right)^2}{\left[1+2\left(r_K - r_J\right)\right]^2\left(1-r_J\right)^3} + \frac{4\left(1+r_K - r_J\right)\left(r_K - r_J\right)}{\left[1+2\left(r_K - r_J\right)\right]^3\left(1-r_J\right)^2}$$

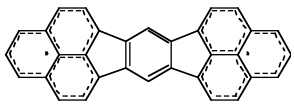
Nakano *et al*. *Phys*. *Rev*. *Lett*. **99**, 033001 (2007)

UNOCASCI(2,2)/6-31G* calculations for two polycyclic diphenalenyl radicals, IDPL and *as*-IDPL

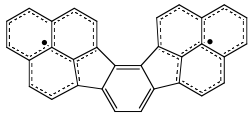
	IDPL	*as*-IDPL
r_J	-0.061	-0.001
r_K	0.004	0.007
r_t	0.131	0.043
y	0.537	0.830
y (UNO)	0.770	0.923
$\gamma/(R^4/U^3)$	0.158	0.028
γ (x 10^4 a.u.)	399	55
γ (x 10^4 a.u.)	228	47

by UBHandHLYP

IDPL



as-IDPL



一重項開殻性を持つ系の探索とその構造ー特性相関

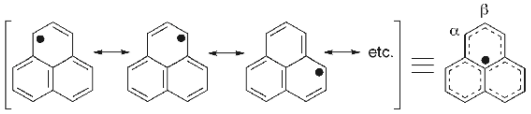
基底状態で一重項ジラジカル性をもつ分子系の探索

- フェナレニルジラジカル分子
  π-共役リンカー
  ⇒ 芳香族性の制御 ⇒ ジラジカル因子の制御
- ナノグラフェン
- 遷移金属含有系
  周期、族、配位子によるジラジカル性制御
- 高周期典型元素含有系　etc.

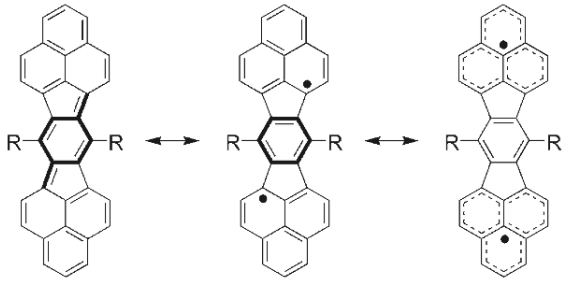
分子の幾何構造・サイズ・置換基、芳香族性、元素の種類の変化

ジラジカル因子の制御 ⇒ 非線形光学特性の制御

ジフェナレニル化合物



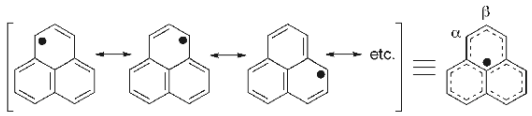
Phenalenyl group



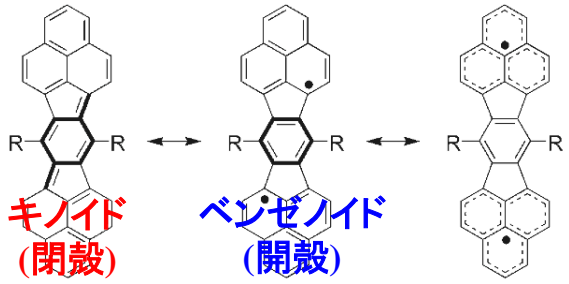
Singlet diradical

T. Kubo et al., *Angew. Chem. Int. Ed.* **2005**, 44, 6564.

ジフェナレニル化合物



Phenalenyl group



キノイド (閉殻)　ベンゼノイド (開殻)

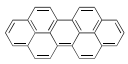
Singlet diradical

T. Kubo et al., *Angew. Chem. Int. Ed.* **2005**, 44, 6564.

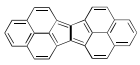
→ 中間ジラジカル性が期待

Polycyclic diphenalenyl radicals: control of diradical character

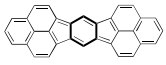
PERO　$y = 0.2620$　$\alpha = 605$ a.u.　$\gamma = 51 \times 10^3$ a.u.



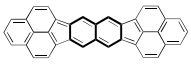
PDPL　$y = 0.5833$　$\alpha = 744$ a.u.　$\gamma = 1255 \times 10^3$ a.u.



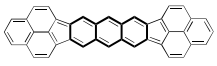
IDPL　$y = 0.7461$　$\alpha = 896$ a.u.　$\gamma = 2383 \times 10^3$ a.u.



NDPL　$y = 0.8317$　$\alpha = 1115$ a.u.　$\gamma = 3803 \times 10^3$ a.u.



ADPL　$y = 0.8821$　$\alpha = 1380$ a.u.　$\gamma = 5935 \times 10^3$ a.u.



UBHandHLYP/6-31G*

Aromaticity of middle rings

Small

Large

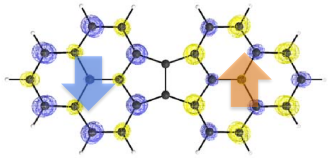
Diradical character

Small

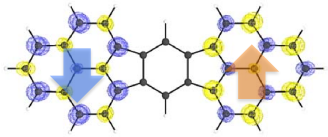
Large

ジフェナレニル化合物

PDPL $y = 0.5833$ $\gamma = 1255 \times 10^3$ a.u.



IDPL $y = 0.7461$ $\gamma = 2383 \times 10^3$ a.u.



Yellow: α spin
Blue: β spin

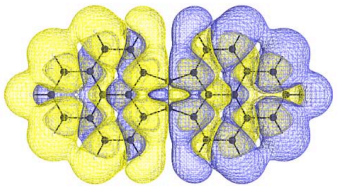
主要なスピン分極が両端のフェナレニル環の間で生じる

Iso-surface with 0.01 a.u. (UBHandHLYP/6-31G*)

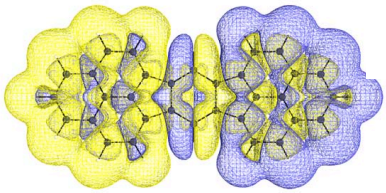
ジフェナレニル化合物：第二超分極率γへの電子の空間的寄与

中間ジラジカル系

PDPL $y = 0.5833$ $\gamma = 1255 \times 10^3$ a.u.



IDPL $y = 0.7461$ $\gamma = 2383 \times 10^3$ a.u.

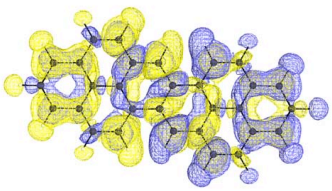


$$\gamma_{ijkl} = -\frac{1}{3!}\int r^i \rho^{(3)}_{jkl}(\boldsymbol{r}) d\boldsymbol{r}$$

Third derivative of density with respect to F
Second hyperpolarizability (γ) density

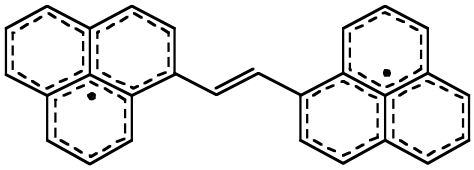
閉殻系

PY2 $y = 0$ $\gamma = 194 \times 10^3$ a.u.



Field

Spin state dependence of γ for intermediate diradical molecules



BPLA1

Singlet state $\gamma = 1889\ [\times 10^3\ \text{a.u.}]$ $y = 0.518$

$\times \frac{1}{3}$

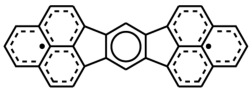
Triplet state $\gamma = 687\ [\times 10^3\ \text{a.u.}]$

UBHandHLYP/6-31G*

フェナレニル骨格をもつ分子系

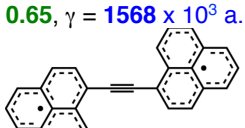
高精度量子化学計算による予測

IDPL (y = 0.77, γ = 2284 x 10^3 a.u.)



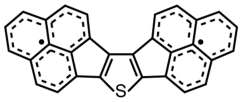
Chem. Phys. Lett., 418, 142 (2006)

BPLE (y = 0.65, γ = 1568 x 10^3 a.u.)



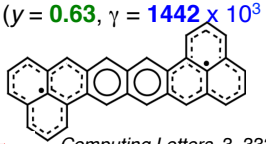
J. Phys. Chem. A 111, 3633 (2007)

TDPL (y = 0.77, γ = 1375 x 10^3 a.u.)



J. Phys. Chem. A, 111, 9102 (2007)

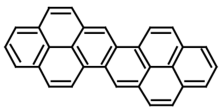
Zethrene (y = 0.63, γ = 1442 x 10^3 a.u.)



Computing Letters, 3, 333 (2007)

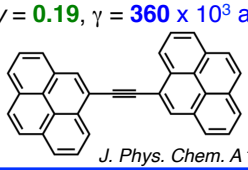
一重項ジラジカロイド分子

PY2 (y = 0.0, γ = 194 x 10^3 a.u.)



Chem. Phys. Lett., 418, 142 (2006)

BPRY (y = 0.19, γ = 360 x 10^3 a.u.)



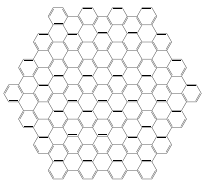
J. Phys. Chem. A 111, 3633 (2007)

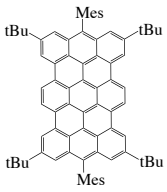
閉殻分子

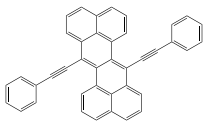
UBHandHLYP/6-31G*

Graphene Nanoflakes

Graphene Nanoflakes (GNFs)





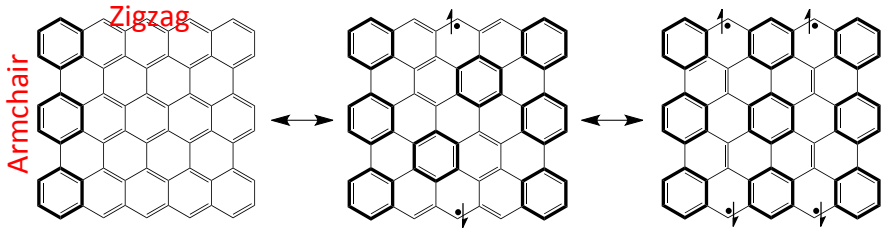


C. D. Simpson et al., *Chem.–Eur. J.* (2002)

A. Konishi et al., *JACS* (2010)

R. Umeda et al., *Org. Lett.* (2009)

Resonance structure



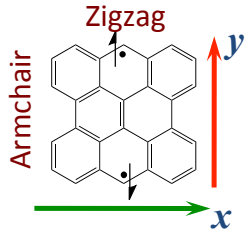
M. Fujita et al., *JPSJ* (1996), J. Hachmann et al., *JCP* (2007), D.-E. Jiang et al., *JCP* (2008)

Localized radical on the zigzag edges → Open-shell singlet

Square GNFs (γ_{xxxx}, γ_{yyyy}): Edge Dependence

Intermediate diradical (y = 0.510)

Chem. Phys. Lett. **467**, 120 (2008)



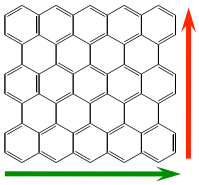
γ_{yyyy} =14.45×10^4 a.u.

×4.2

Enhance γ along the spin polarization axis

γ_{xxxx} = 3.412×10^4 a.u.

Pure diradical (y = 0.989)



γ_{yyyy} = 40.54×10^4 a.u.

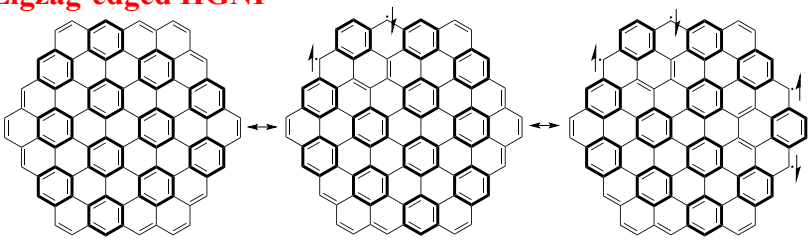
Similar

γ_{xxxx} = 49.95×10^4 a.u.

Intermediate diradical character → Enhancement of γ

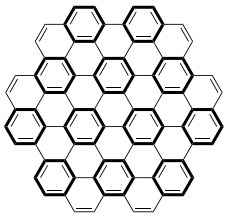
Diradical Characters and γ of HGNFs

Zigzag-edged HGNF



Closed-shell form | Diradical form | Tetraradical form

Armchair-edged HGNF



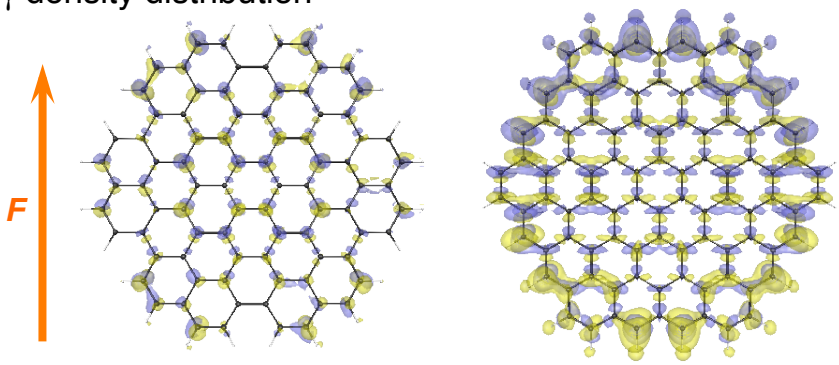
Closed-shell form

The relative contribution of each resonance form is qualitatively predicted based on the Clar's sextet rule, where the most important resonance structure has the most disjoint aromatic π-sextets, i.e., benzene-like moieties.

Diradical Characters and γ of HGNFs

γ density distribution

Chem. Phys. Lett. **477**, 355 (2009)



Armchair-edged-HGNF

$y_0 = 0.0$

Closed-shell

$\gamma = 41.7 \times 10^4$ a.u.

× 3.3

Zigzag-edged-HGNF

$y_0 = y_1 = 0.410$

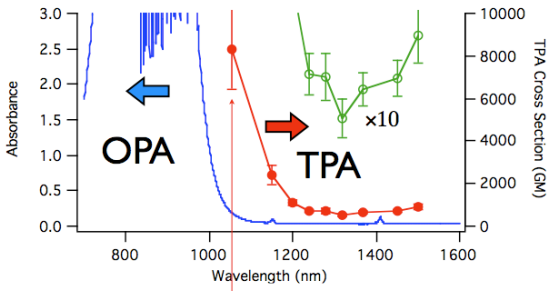
Intermediate tetraradical

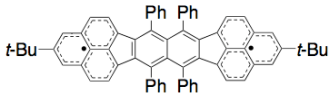
$\gamma = 139 \times 10^4$ a.u.

Contour value = ±500 a.u.

Experiments
based on our theoretical prediction

Measurement of two-photon absorption (TPA) of diphenalenyl radicals (Kamada *et al. Angew. Chem. Int. Ed.*, 2007)





Kubo *et al.*

NDPL

(*t*-Bu$_2$, Ph$_4$)

>8000GM@1040nm

TPA+SA

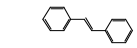
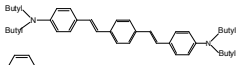
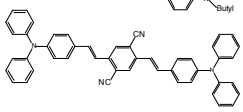
One of the largest TPA cross section in pure hydrocarbon systems !

c.f. TIPS-Pentacene (closed-shell) ~ 10 - 30 GM

Experiment: two-photon absorption (TPA) spectrum

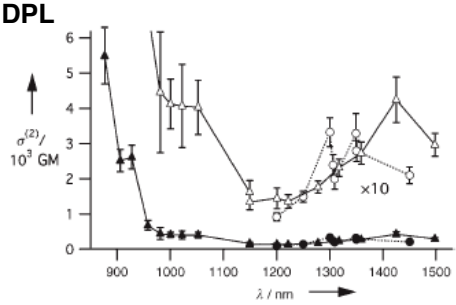
Closed-shell systems

$\sigma^{(2)}$: TPA cross section

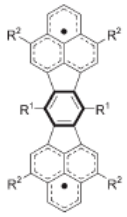
compound	TPA λ_{max} [nm]	$\sigma^{(2)}$ [GM]
	514	12
	730	995
	835	1940

M. Albota et al., *Science vol 281 (1998)*

IDPL



● : IDPL a ▲ : IDPL b ○,△ : x 10



a : R^1 = H
R^2 = *t*Bu

b : R^1 = Ph
R^2 = H

$\sigma^{(2)} > 5450$GM

1GM = 10^{-50}cm^{4}sphoton^{-1}molecule^{-1}

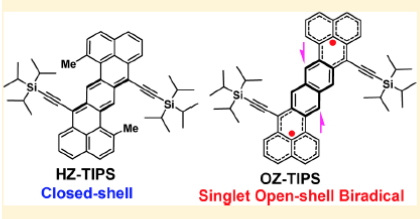
K. Kamada et al., *Angew. Chem. Int. Ed.* (2007).

Experiments

M. Ishida et al. *J. Am. Chem. Soc.* **2011**, 133, 15533

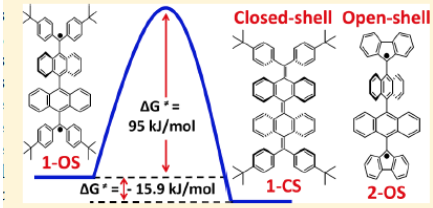
Hexaphyrins

Y. Li et al. *J. Am. Chem. Soc.* **2012**, 134, 14913



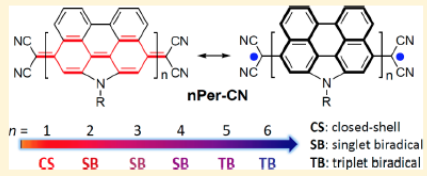
Zethrenes

Z. Zeng et al., *J. Am. Chem. Soc.* **2012**, 134, 14513



Tetrabenzo-Chichibabin's hydrocarobons

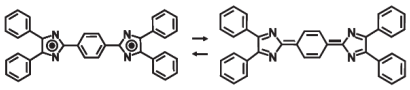
Z. Zeng et al., *J. Am. Chem. Soc.* **2013**, 135, 6363



Tetracyano-oligo(N-annulated perylene)quinodimethane

Experiments

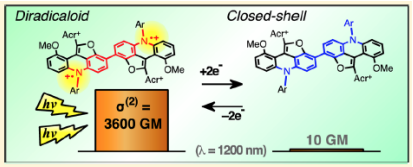
H. Kishida et al. *This Solid Films* **2010**, 1028-2030



BDPI-2Y $\chi^{(3)} = 3.0 \times 10^{-11}$ esu

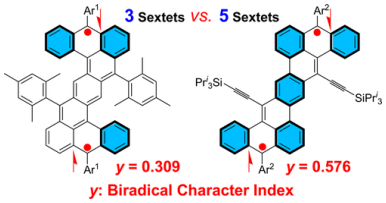
Comparable to those of π-conjugated polymer

K. Kamada et al. *J. Am. Chem. Soc.* **2013**, 135, 232-241



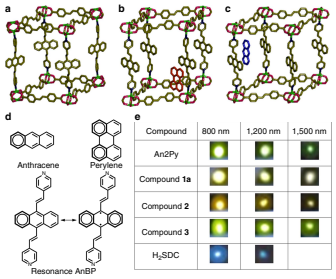
Redox change control of diradical character

Z. Sun et al., *J. Am. Chem. Soc.* **2012**, 134, 14513



Dibenzoheptazethrene isomers

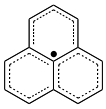
H. S. Quah et al., *Nature Communications* **2015**, 6, 7954



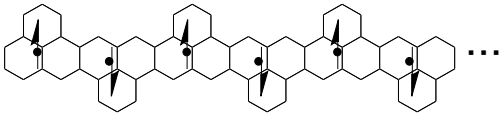
Multi-photon harvesting MOFs

Multiradical Systems

One-Dimensional GNFs: Multiradical Effect on Size Dependence of γ



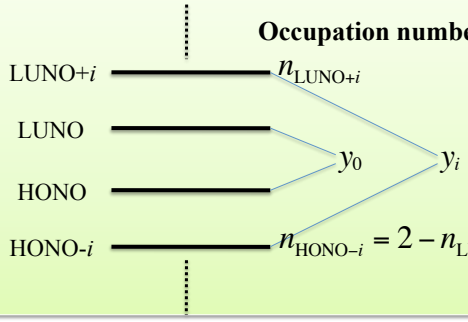
Trigonal GNF unit
(phenalenyl radical)



One-dimensional GNF

Multiradical character → **Multiple diradical characters y_i**

Occupation number $0 \le n_i \le 2$

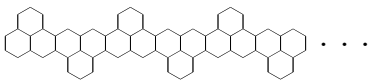


$$y_i = n_{\mathrm{LUNO}+i} = 2 - n_{\mathrm{HONO}-i}$$

Theoret. Chem. Acc. **130**, 711 (2011)

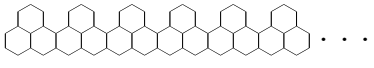
Size Dependences of Diradical Characters

Alternately-linked (AL) systems

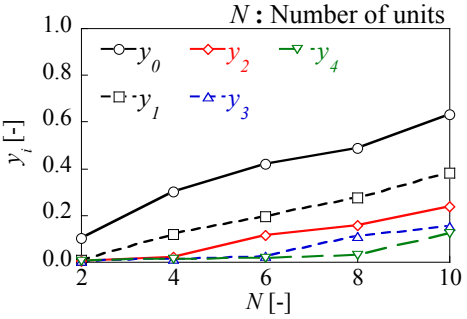


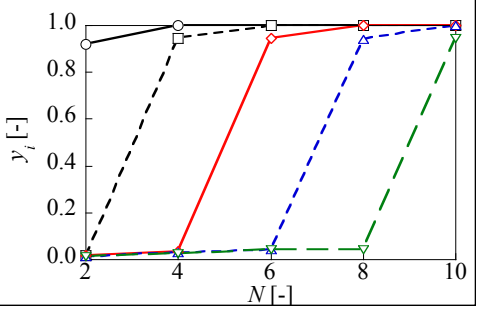
Intermediate multiradical character

Non-alternately-linked (NAL) systems



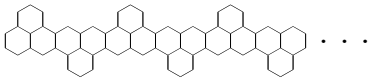
Pure multiradical character





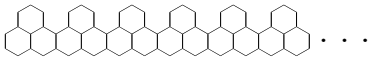
Size Dependences of Diradical Characters

Alternately-linked (AL) systems



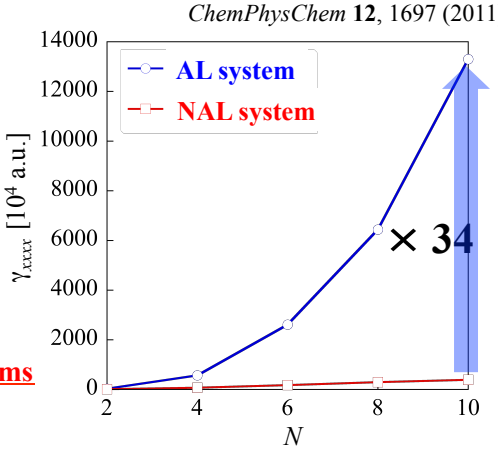
Intermediate multiradical character

Non-alternately-linked (NAL) systems



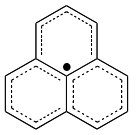
Pure multiradical character

ChemPhysChem **12**, 1697 (2011)

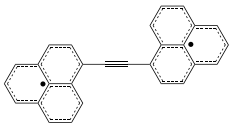


With increasing the number of units, **AL systems having intermediate open-shell characters** show more striking enhancement of γ than NAL systems.

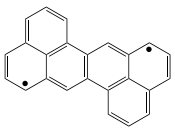
One-Dimensional Open-Shell Aggregates



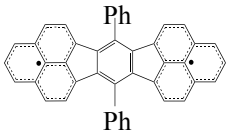
Phenalenyl radical



K. Nakasuji et al., *JACS* (1982)



R. Umeda et al., *Org. Lett.* (2009)

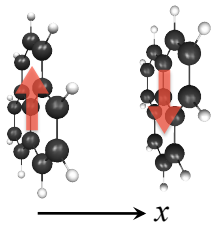


T. Kubo et al., *Org. Lett.* (2007)

Several dicadicaloids have been synthesized

Phenalenyl radical is a good building block for open-shell molecular systems.

K. Yoneda, M. Nakano et al., *Chem. Eur. J.* **20**, 11129 (2014).



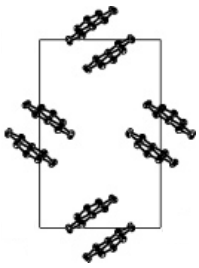
We investigate the variation of open-shell natures and third-order NLO properties for **phenalenyl aggregates with several interplanar distances**.

Open-shell nature ➡ Diradical character *y*

3rd order NLO property ➡ Second hyperpolarizability γ (= γ_{xxxx})

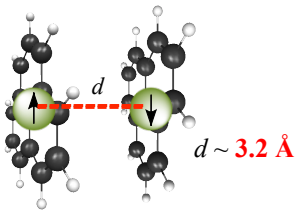
One-Dimensional Open-Shell Aggregates

K. Goto, T. Kubo et al., *J. Am. Chem. Soc.* **121**, 1619 (1999)



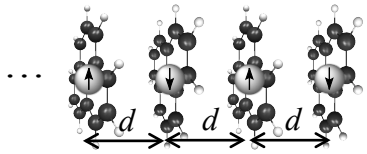
Dimerize in crystal

Short intermolecular distance ***d*~ 3.2 Å**



Covalent-like strong intermolecular interaction

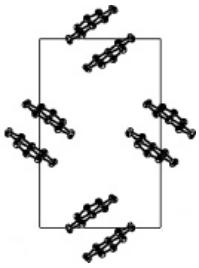
Realistic one-dimensional multiradical GNF system



Intermolecular distance (d) dependences of y_i and γ for dimer and tetramer models

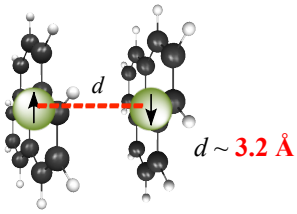
One-Dimensional Open-Shell Aggregates

K. Goto, T. Kubo et al., *J. Am. Chem. Soc.* **121**, 1619 (1999)



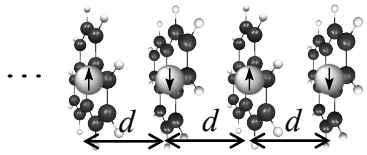
Dimerize in crystal

Short intermolecular distance ***d*~ 3.2 Å**



Covalent-like strong intermolecular interaction

Realistic one-dimensional multiradical GNF system



Intermolecular distance (d) dependences of y_i and γ for dimer and tetramer models

Recently, this type of crystal has been made !

K. Uchida et al. *Chem. Asian J.* **9**, 1823 (2014)

CHEMISTRY AN ASIAN JOURNAL — ACES — FULL PAPER

DOI: 10.1002/asia.201402187

Dual Association Modes of the 2,5,8-Tris(pentafluorophenyl)phenalenyl Radical

Kazuyuki Uchida,[a] Yasukazu Hirao,[a] Hiroyuki Kurata,[b] Takashi Kubo,*[a] Sayaka Hatano,[c] and Katsuya Inoue[c]

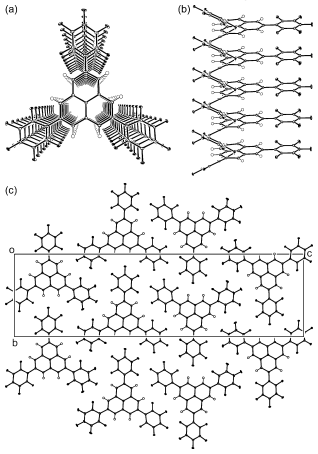
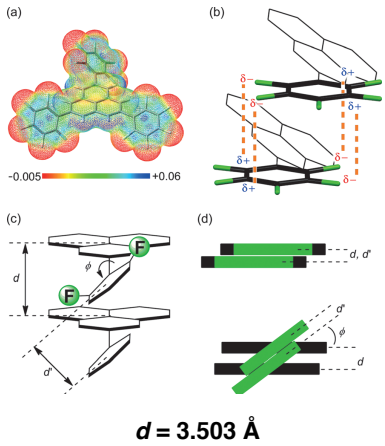


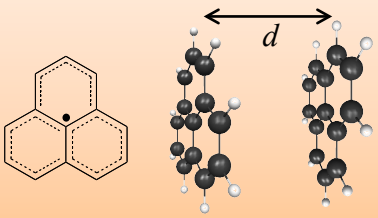
Figure 5. a,b) Two orthogonal views of the 1D chain of compound **1c**. c) Packing diagram of compound **1c** in the (100) (*bc*) plane. All of the molecules were crystallographically equivalent and stacked along the [100] direction (*a* axis).



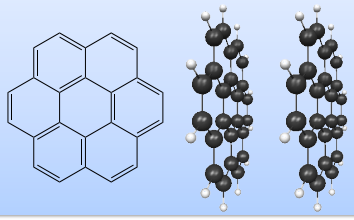
***d* = 3.503 Å**

Model Systems and Methodology

Phenalenyl dimer (open-shell singlet)



Coronene dimer (closed-shell)



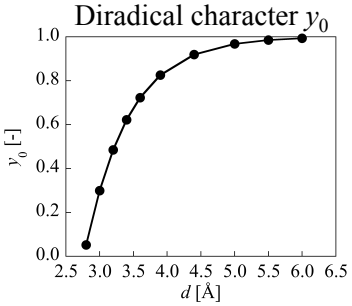
Geometry Optimization : UB3LYP/6-31G* for monomer

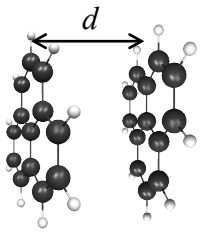
Diradical character
Second hyperpolarizability : LC-UBLYP (μ = 0.33)/6-31+G*

One-Dimensional Open-Shell Aggregates

Chem. Eur. J. **20**, 11129 (2014)

Diradical character y_0





Diradical model

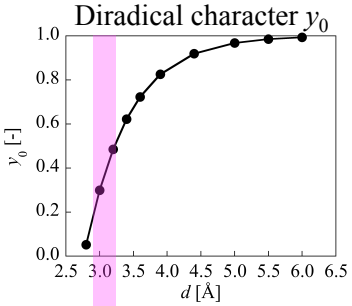
A wide range variation of y_0

y , γ : LC-UBLYP/6-31G*

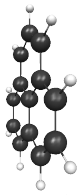
One-Dimensional Open-Shell Aggregates

Chem. Eur. J. **20**, 11129 (2014)

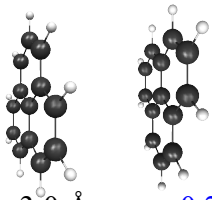
Diradical character y_0



Monomer

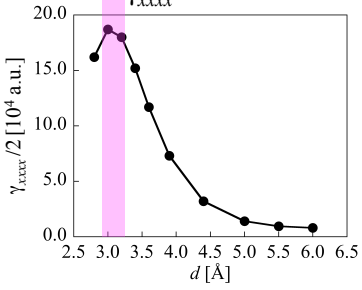


Dimer



d = 3.0 Å, y_0 = 0.299

γ_{xxxx}/monomer



γ_{xxxx} = 2980 a.u. → $\gamma_{xxxx}/2 = 9.30\times10^4$ a.u.

× 30

A wide range variation of y_0

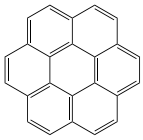
Intermediate y region

→ Significant enhancement of γ

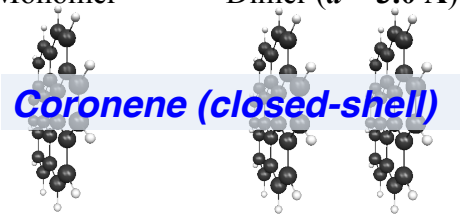
y , γ : LC-UBLYP/6-31G*

Closed-Shell (Coronene) vs. Open-Shell (Phenalenyl)

Coronene

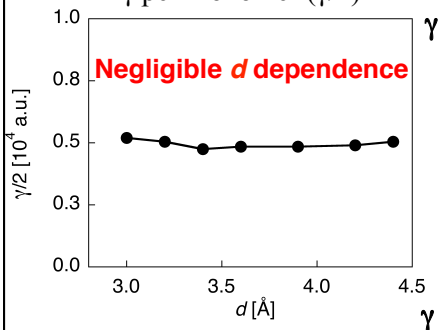


Monomer Dimer (d = 3.0 Å)



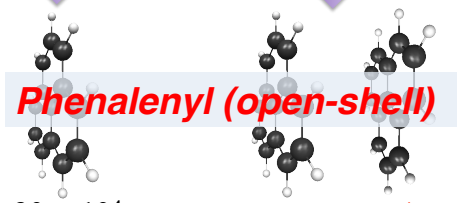
Coronene (closed-shell)

γ per monomer (γ/2)



γ = 0.40 × 10⁴ a.u. γ/2 = 0.52 × 10⁴ a.u.

× 0.75 × 18



Phenalenyl (open-shell)

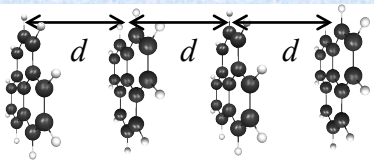
γ = 0.30 × 10⁴ a.u. γ/2 = 9.35 × 10⁴ a.u.

The γ enhancement is not observed in the closed-shell aggregate.

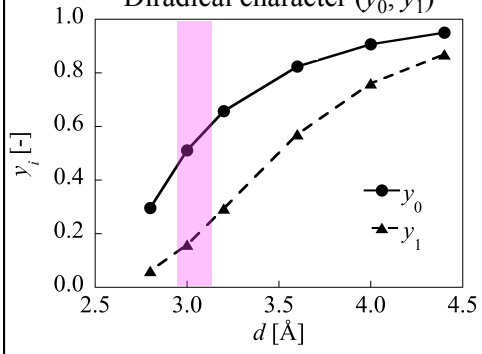
One-Dimensional Open-Shell Aggregate: Tetramer model

Chem. Eur. J. **20**, 11129 (2014)

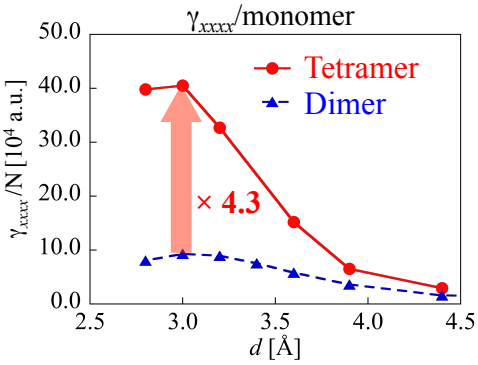
Tetraradical model



Diradical character (y_0, y_1)



γ_{xxxx}/monomer



Intermediate **tetraradical** character ➡ Further enhancement of γ

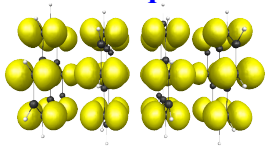
Spin and Charge State Dependences

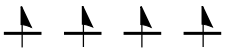
Chem. Eur. J. **20**, 11129 (2014)

Stacking distance
$d = 3.2$ Å

Odd electron densities (Contour: 0.002 a.u.)

Neutral quintet

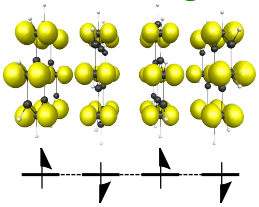




Pure tetraradical

$\gamma = 2.96 \times 10^4$ a.u.
Significant reduction

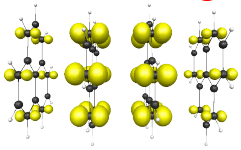
Neutral singlet



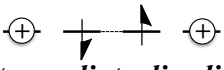
$y_0 = 0.657$
$y_1 = 0.294$

$\gamma = 131 \times 10^4$ a.u.
Intermediate tetraradical

Dicationic singlet



$y_0 = 0.597$
$y_1 = 0.012$



Intermediate diradical *sandwiched between two holes*

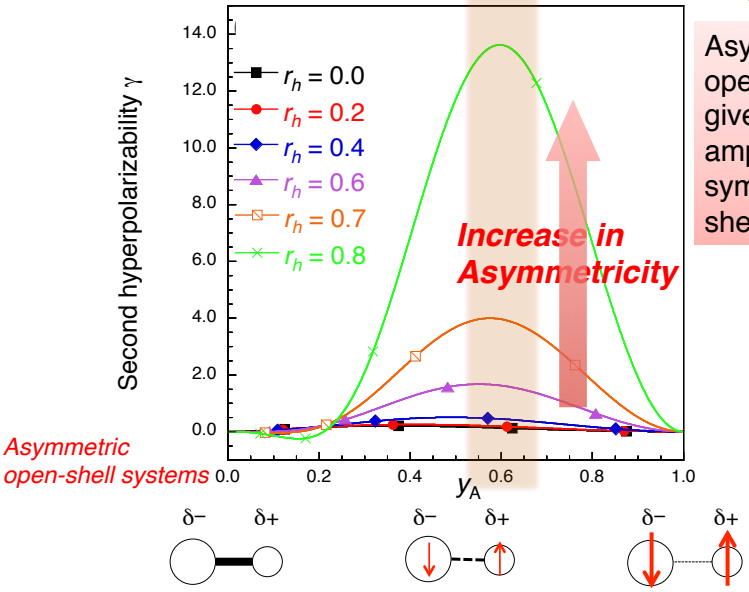
$\gamma = 1730 \times 10^4$ a.u.
Large enhancement

Asymmetric Open-Shell Systems

Asymmetric Open-Shell Systems

J. Chem. Phys. **138**, 244306 (2013)

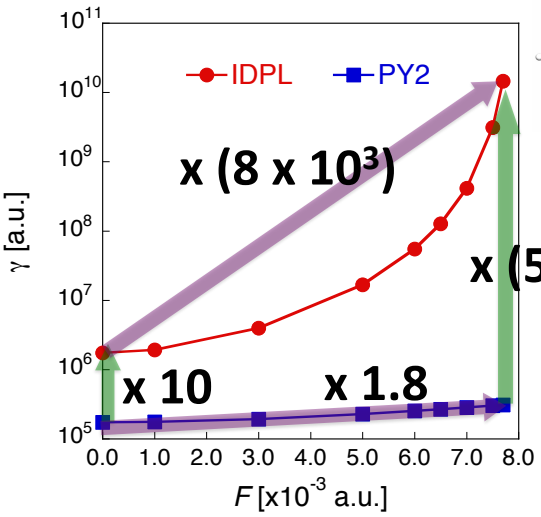
Enhanced in the intermediate diradical character (y_A) region

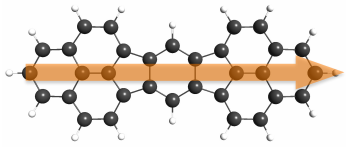


Asymmetric open-shell singlet gives larger γ amplitude than symmetric open-shell system

Asymmetric Open-Shell Systems: Giant Field Application Effect on γ

J. Phys. Chem. Lett. **2**, 1094 (2011)

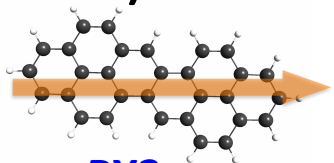




IDPL ($y_{F=0}$ = 0.717)

γ = 1.746 x 10^6 a.u. (F = 0.0 a.u.)

γ = 1.456 x 10^{10} a.u. (F = 0.0077 a.u.)



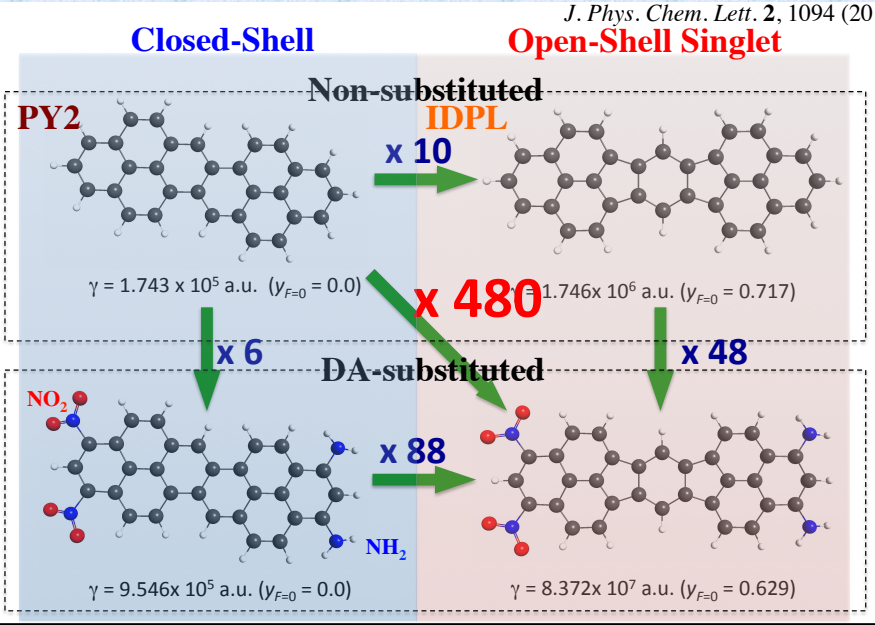
PY2 ($y_{F=0}$=0)

γ = 1.743 x 10^5 a.u. (F = 0.0 a.u.)

γ = 3.107 x 10^5 a.u. (F = 0.0077 a.u.)

Asymmetric Open-Shell Systems: Donor-Acceptor Substitution Effect on γ

J. Phys. Chem. Lett. **2**, 1094 (2011)



Summary

- **Diradical character** *y* (= **Bond weakness** = **Electron correlation**) is correlated with the excitation energies and properties.
- **Open-shell singlet systems with intermediate diradical charcater exhibit enhanced second hyperpolarizaibilities (γ)** as compared to conventional closed-shell and pure diradical systems.
- **Control of diradical character (in the ground state)**:
  Relation to conventional chemical concepts and indices
  - Edge shape, size, and architecture of graphene nanoflakes
  - Quinoid (closed-shell) and benzenoid (open-shell) resonance structures
  - Aromaticity, Multiple bond, Main group elements, …
- Examples of **diradical**/**multiradical**
  Diphenalenyl compounds, Geaphene nanoflakes,
  Open-shell aggregates, etc.

These results demonstrate the **high potential of open-shell singlet molecular systems for third-order NLO applications**.

A New Types of Open-Shell Systems

• **Asymmetric open-shell systems**

Extraordinary enhancement of hyperpolarizabilities and reduction of diradical character M. Nakano et al. *J. Chem. Phys.* **138**, 244306 (2013)

– **External field application** → NLO switch
– **Donor/acceptor substitution** to open-shell symmetric systems
– **Asymmetric fused-ring** systems such as azulene-like molecules

• **Open-shell aggregates → Open-shell NLO materials**

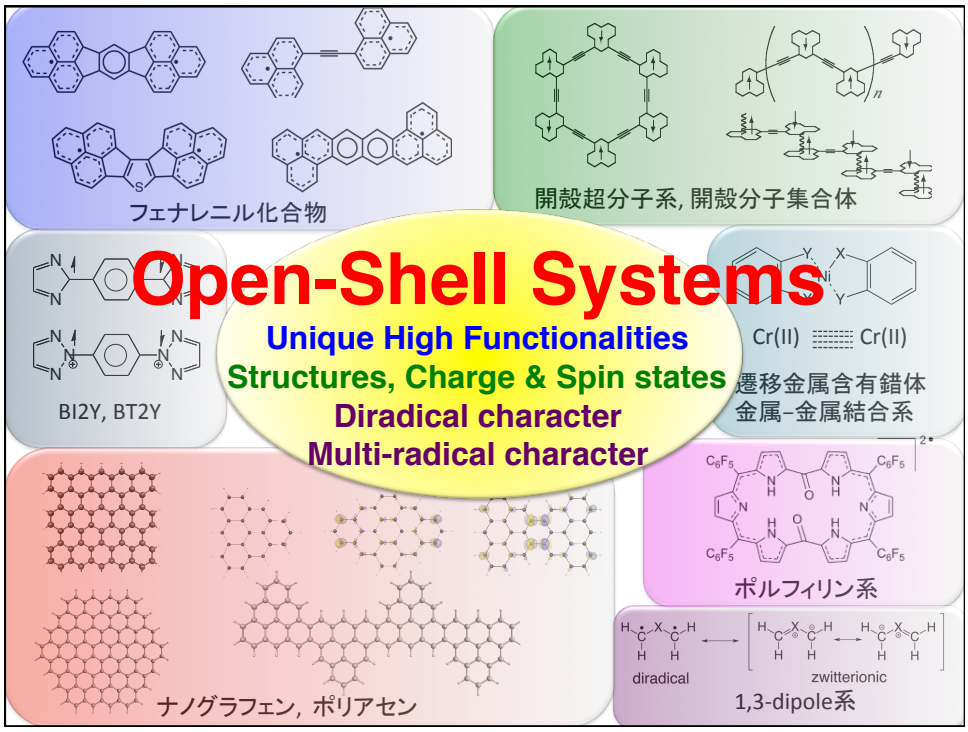
– **Equilibrium intermolecular distance = intermediate y_i region**
– **Multi-radical** character dependences
– **Charge and spin-multiplicity** dependences → Multifunctionality

References
1. M. Nakano, *Excitation Energies and Properties of Open-Shell Singlet Molecules Applications to a New Class of Molecules for Nonlinear Optics and Singlet Fission.* Springer, **2014**.
2. M. Nakano* and B. Champagne, Theoretical Design of Open-Shell Singlet Molecular Systems for Nonlinear Optics. *J. Phys. Chem. Lett.* (Perspective) **2015**, *6*, 3236−3256.
3. M. Nakano* and B. Champagne, Nonlinear Optical Properties in Open-Shell Molecular Systems, *WIREs Comput Mol Sci,* in press **2015**

まとめと今後の展望

1. 開殻性に基づく高機能、物性の発現機構の提案と具体的な分子設計
2. 分子間相互作用によるマルチラジカル性の制御： 開殻性を持つ凝縮系
3. 開殻性のダイナミクス：動的物性との関係
4. 緩和過程の及ぼす効果

- 高周期典型元素や遷移金属からなる開殻系への展開
- 開殻分子集合系、開殻超分子系
- 外部レーザー場による系の開殻性の制御 –動的開殻因子の定義–
- 一重項分裂(SF)： 分子間相互作用およびエキシトンダイナミクスの解明
- 三重項–三重項消滅(TTA)とSFの制御： 新しいエキシトン移動・貯蔵・変換系の提案



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Theory and Computation

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Mr. Kotaro Fukuda (Osaka Univ.)
Mr. Soichi Ito (Osaka Univ.)
Mr. Hiroshi Matsui (Osaka Univ.)
Mr. Shota Takamuku (Osaka Univ.)
Dr. Masato Kobayashi (Hokkaido Univ) …

Triangle approach

Synthesis

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Prof. Yoshito Tobe (Osaka Univ.)
Dr. Akihiro Shimizu (Kyoto Univ.)
Prof. Yosuke Yamamoto (Hiroshima Univ.)
Prof. Manabu Abe (Hiroshima Univ.)
Prof. Akira Sekiguchi (Univ. Tsukuba)
Prof. Hiroshi Ikeda (Osaka Pref. Univ.)
Prof. Jishan Wu (NUS)
Prof. Michael Haley (Univ Oregon) …

Measurement

Dr. Kenji Kamada (AIST) …

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