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# Theoretical investigation of the effect of radical substituents on the open-shell character of polycyclic aromatic hydrocarbons†

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The open-shell character $y$ of a molecule correlates with its physical properties, such as singlet fission and nonlinear optical responses. In this study, we investigated the effect of various radical substituents on the $y$ of polyaromatic hydrocarbons (PAHs) using occupation numbers of natural orbitals calculated at the LC-UBLYP($\mu$=0.33)/6-311G(d,p) level of theory. It was found that radical substituents significantly altered the $y$ of PAHs compared to non-radical substituents. Specifically, substituting methyl-type radicals such as the dicyanomethyl radical decreased the $y$ value, while substituting allyl-2-yl-type radicals such as nitronyl nitroxide increased it. In addition, we also evaluated the correlation between the $y$ and the HOMO−LUMO gaps and between the $y$ and the spin-state energy gaps.

## 1. Introduction

For closed-shell molecules, the ground electronic state can be described by a single electronic configuration in which two electrons occupy the orbitals up to the HOMO, and none of the electrons occupy the orbitals starting from the LUMO. However, for open-shell molecules with quasi-degenerate frontier orbitals, it is necessary to consider additional electronic configurations with excited electrons in the LUMO or orbitals above it. Dissociation of a hydrogen molecule is the simplest example to show how to describe the partially-bond-dissociated state (Fig. 1). The electronic state $\Psi$ of a hydrogen molecule with arbitrary bond lengths can be described using two electronic configurations with minimal basis: the ground state configuration $\phi_g$ and doubly excited configuration $\phi_e$.[1]

$$\Psi = c_1\phi_g - c_2\phi_e \quad \text{where } c_1{}^2 + c_2{}^2 = 1 \qquad (1)$$

The weight of the doubly excited configuration $(c_2{}^2)$ corresponds to the open-shell character $y = 2c_2{}^2$.[2,3] For example, $y \approx 0$ corresponds to a closed-shell state with almost no contribution of the excited configuration $(c_1{}^2 \approx 1, c_2{}^2 \approx 0)$, while $y \approx 1$ corresponds to an open-shell state where the excited configuration is mixed with the ground configuration to the same extent $(c_1{}^2 \approx 1/2, c_2{}^2 \approx 1/2)$. Open-shell character $y$

also correlates with the degree of chemical bonding, as $y \approx 1$ indicates that the bond is almost dissociated.

Nakano *et al.* have revealed the correlation between the open-shell character $y$ and molecular properties such as singlet fission[4] and nonlinear optical responses,[5] providing a guideline for designing functional molecules. The $y$ strongly depends on the size and shape of molecules.[6] The $y$ values have been reported for a variety of polycyclic aromatic hydrocarbons (PAHs) such as oligoacenes,[7] bisphenalenyls,[8] zethrenes,[9] anthenes,[10] and rylene ribbons.[11]

It has also been reported that $y$ can be controlled without significantly changing the molecular framework (Fig. 2). For example, introducing donor/acceptor substituents or placing the molecule in an external electric field can reduce $y$ values.[12] Haley *et al.* have reported that $y$ can be increased by introducing electron-rich thiophene moieties or by extending the conjugation system.[13]
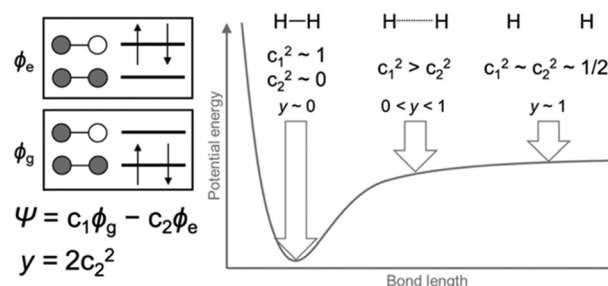
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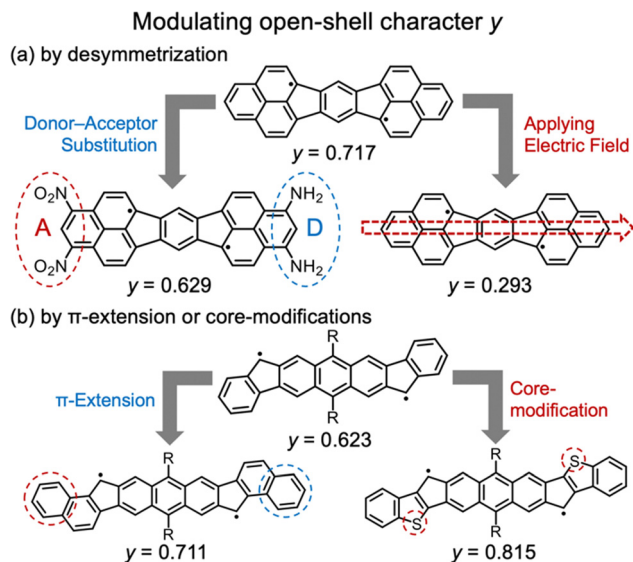† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4nj00555d



Fig. 1 Dissociation of a hydrogen molecule and open-shell character $y$.

Fig. 2 Reported guidelines for modulating $y$ values: (a) desymmetrization[12] and (b) $\pi$-extension or core-modification.[13]

In this study, we focused on the introduction of radical substituents with unpaired electrons as a new attempt to control $y$ and evaluated their effects using computational chemistry. We found that the radical substitution can significantly change $y$ compared to conventional closed-shell structural modifications, such as donor–acceptor substitution. It has been reported that conjugated radical substituents affect the excited-state dynamics of acene derivatives,[14–20] which have been utilized for enhancing the photostability of pentacene.[17–20] We have also reported that a radical substituent significantly enhances the conductance of a molecular wire, which was proved by single molecular measurements.[21]

In this work, PAHs with various open-shell characters were selected as model molecules. The $y$ of a molecule is generally evaluated by computational means. Although an experimental method for assessing $y$ has been proposed,[22] it is not widely applied at present due to practical difficulties. In addition to the estimation of $y$, we also evaluated HOMO–LUMO gaps and the energy differences between spin states, which are generally considered to correlate with $y$.

## 2. Computational methodology

### 2.1 Model structures

We examined the $y$ of various molecules by combinations of core structures and substituents linked by saturated ($-CH_2CH_2-$) or conjugated ($-C\equiv C-$) linkers. These linkers were selected to make the PAH and substituent coplanar as much as possible. The core structures are PAHs with a wide range of open-shell characters from $y_0 = 0.000$ (anthracene) to $y_0 = 1.000$ (triangulene). We surveyed various substituents on them, such as spin-localized/delocalized radical substituents and donor/acceptor or $\pi$-conjugated non-radical substituents.
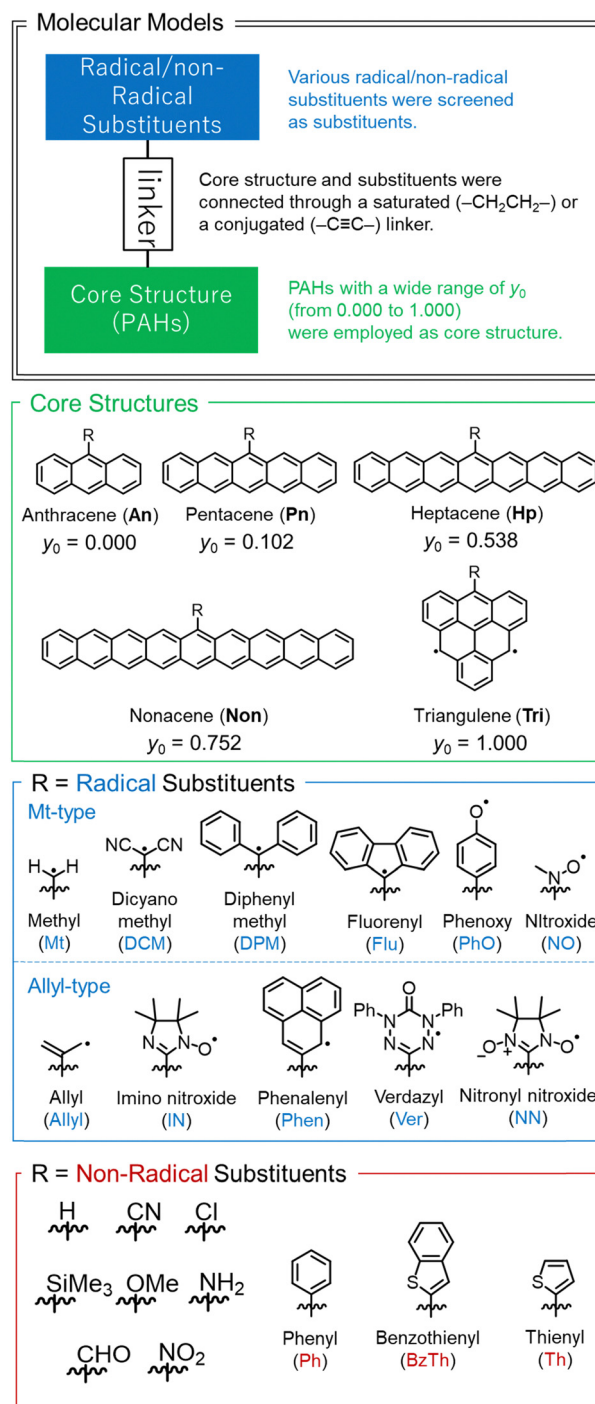


Fig. 3 Summary of molecules examined in this work. The values of $y_0$ shown in the 2nd panel are for PAHs with "R = H" listed in the 4th panel.

Core structures and substituents reported in this work are summarized in Fig. 3.

### 2.2 Calculation methods

In this study, we examined the diradical character of an even-electron system without radical substituents. For an odd-electron system with one radical substituent, we analyzed the

triradical character to evaluate the effect of radical substituents on inducing an extra open-shell character.

Open-shell character $y$ was evaluated using occupation numbers $n$ of natural orbitals of the LUMO or orbitals above it (LUMO+$i$; $i$ = 0, 1, 2…).[23]

$$y_i = n_{LUMO+i} \qquad (2)$$

The first open-shell character, $y_0$, represents the diradical character of an even-electron system and the triradical character of an odd-electron system. Therefore, we explored $y_0$ for both even- and odd-electron systems. The higher $y$ correlates to a multi-radical character: *e.g.* the second open-shell character, $y_1$, corresponds to tetraradical (pentaradical) characters of an even-electron (odd-electron) system. The LC-UBLYP[24] functional with the range-separating parameter $\mu$ = 0.33 and the 6-311G(d,p)[25] basis set were employed for the natural orbital analysis to evaluate $y$. The LC-UBLYP functional is commonly used for this purpose.[26] The calculation was performed by specifying a charge of 0 and multiplicity of 1 for even-electron systems with one non-radical substituent, and a charge of 0 and multiplicity of 2 for odd-electron systems with one radical substituent. Molecular geometries were based on the energy-minimized structures calculated at the UB3LYP[27–30]/6-311G(d,p) level. DFT calculations were carried out using the Gaussian16 package.[31]

We also evaluated the HOMO–LUMO gap of even-electron systems without radical substituents at the LC-RBLYP($\mu$=0.33)/6-311G(d,p) level and those of radical mono-substituted systems at the LC-ROBLYP($\mu$=0.33)/6-311G(d,p) level. Not only the HOMO–LUMO gap, but the singlet–triplet energy gap ($\Delta E_{ST}$) is also known to correlate with open-shell character $y$. The relationship between the $\Delta E_{ST}$ and $y$ is expressed by the following equation:[32]

$$\Delta E_{ST} = \frac{U}{2}\left[1 - \frac{1}{\sqrt{y(2-y)}}\right] + 2K_{ab} \quad \text{with } y = 1 - \frac{1}{\sqrt{1+\left(\frac{U}{4t_{ab}}\right)^2}} \qquad (3)$$

where $U$ is the effective Coulomb integral, $K_{ab}$ is the exchange integral, and $t_{ab}$ is the transfer integral. Eqn (3) indicates that $y$ and $\Delta E_{ST}$ do not correlate linearly. However, in the case that $U$ and $K_{ab}$ do not change significantly, $\Delta E_{ST}$ is solely dependent on $y$.

To evaluate the energy difference between the spin states, the $\Delta E_{ST}$ of even-electron systems with non-radical substituents and the doublet–quartet gap ($\Delta E_{DQ}$) of radical substituted systems were calculated. The energy gaps between spin states were estimated by the RAS-SF[33] method using the cc-pVTZ[34] basis set (RAS-SF/cc-pVTZ) implemented in the Q-Chem 5.4 package.[35]

# 3. Results and discussion

## 3.1 Effect of radical substituents on the open-shell character $y$ of the pentacene

First, we discuss the substituent effect on the pentacene core, which has a non-zero diradical character ($y_0$ = 0.102). In Fig. 4, substituents are classified into three groups: the ''Sat-Radical'' group with radical substituents *via* saturated hydrocarbon linkers, the ''Non-Radical'' group with non-radical substituents *via* conjugated linkers, and the ''Radical'' group with radical substituents *via* conjugated linkers.

For the Sat-Radical group, the triradical character $y_0$ was not affected by the substituents ($y_0$ = 0.1268 ± 0.008) as expected from the non-conjugated nature (Fig. 4 top and Table S8, ESI†). Importantly, the triradical character is comparable to the diradical character of pristine pentacene ($y_0$ = 0.102, Fig. 3). The triradical character can be divided into one pure radical of the substituents and diradical character of the core. Therefore, triradical character of radical-substituted species can be interpreted as the induced diradical character of the core unit.

For the Non-Radical group, the effect of substituents on the open-shell (diradical) character $y_0$ is also small regardless of whether the substituent is electron donating/withdrawing,
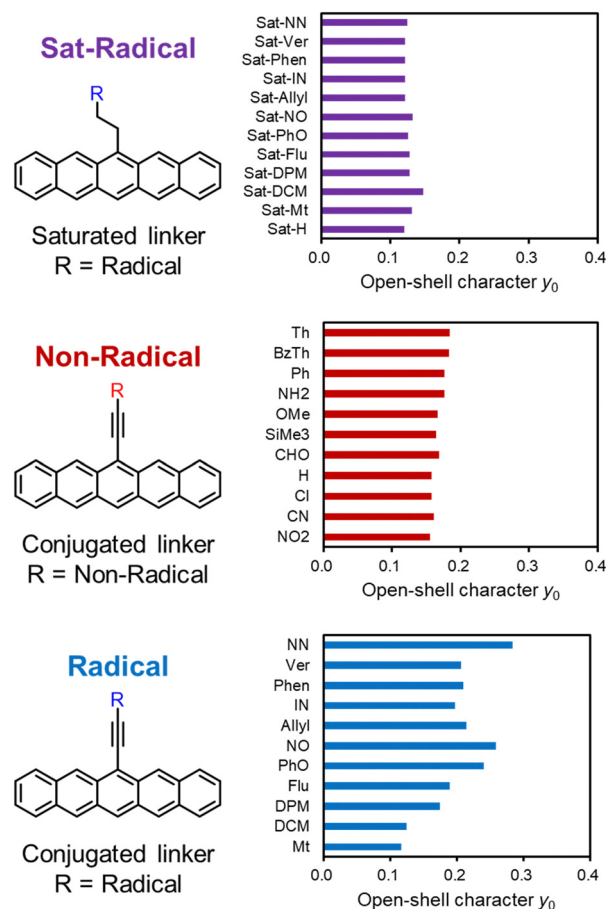


**Fig. 4** Calculated structures and $y_0$ values of pentacene derivatives with Sat-Radical (purple bars), Non-Radical (red bars), and Radical (blue bars) substituents.

$\pi$-conjugated, or heteroatoms ($y_0 = 0.1683 \pm 0.010$, Fig. 4 middle and Table S6, ESI†). The minor substitution effect will be discussed later.

Non-conjugated radical substituents and conjugated non-radical substituents do not affect the open-shell character. In the case of the conjugated radical substituents, however, we found that the $y_0$ value widely ranges from 0.117 to 0.284, unlike the other two groups (Fig. 4 bottom, Table S7, ESI†). The radical substituents have a significant effect on the open-shell properties of PAHs when they interact with the PAH $\pi$-conjugation.

## 3.2  Relationship between $y_0$ and HOMO–LUMO gap in substituted pentacene

The open-shell character $y_0$ is generally correlated with the HOMO–LUMO (H–L) gaps of molecules, and this was also observed in this study. Fig. 5 shows the scatter plots of $y_0$ and H–L gaps for the three groups of pentacene derivatives (see Tables S6–S8 for details, ESI†). It should be noted that the restricted methods (RDFT or RODFT) were used to qualitatively evaluate the HOMO–LUMO gaps free from spin polarization.[36] As shown in Fig. 5, the H–L gaps and $y_0$ are well-correlated; the Sat-Radical and Non-Radical groups do not change the H–L gaps, and substituents in the conjugated Radical group significantly alter the H–L gap.

To disclose how the radical substituents change the H–L gap of PAHs, the radical substituents are divided into two types in terms of conjugational topology: methyl-type (squares) and allyl-2-ly-type (triangles, hereafter called allyl-type), shown in Fig. 5. The plot shows a trend that the methyl-type radicals tend to decrease $y_0$ and the allyl-type radicals tend to increase $y_0$.

## 3.3  Interpretation of the effects of radicals based on Hückel molecular orbitals

We examined the effects of the two types of radical substituents (methyl-type and allyl-type) based on the simple Hückel molecular orbitals. Fig. 6 shows the orbital interactions between methyl/allyl radical substituents and pentacene (see Table S1 for
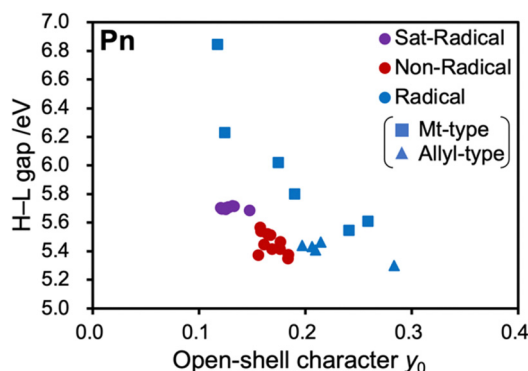


Fig. 5 Scatter plot of HOMO–LUMO gaps and $y_0$ of the three groups of pentacene derivatives shown in Fig. 4. The plots of the Radical groups are distinguished by square and triangle icons, which indicate methyl-type radical substituted pentacenes and allyl-type radical substituted pentacenes, respectively.
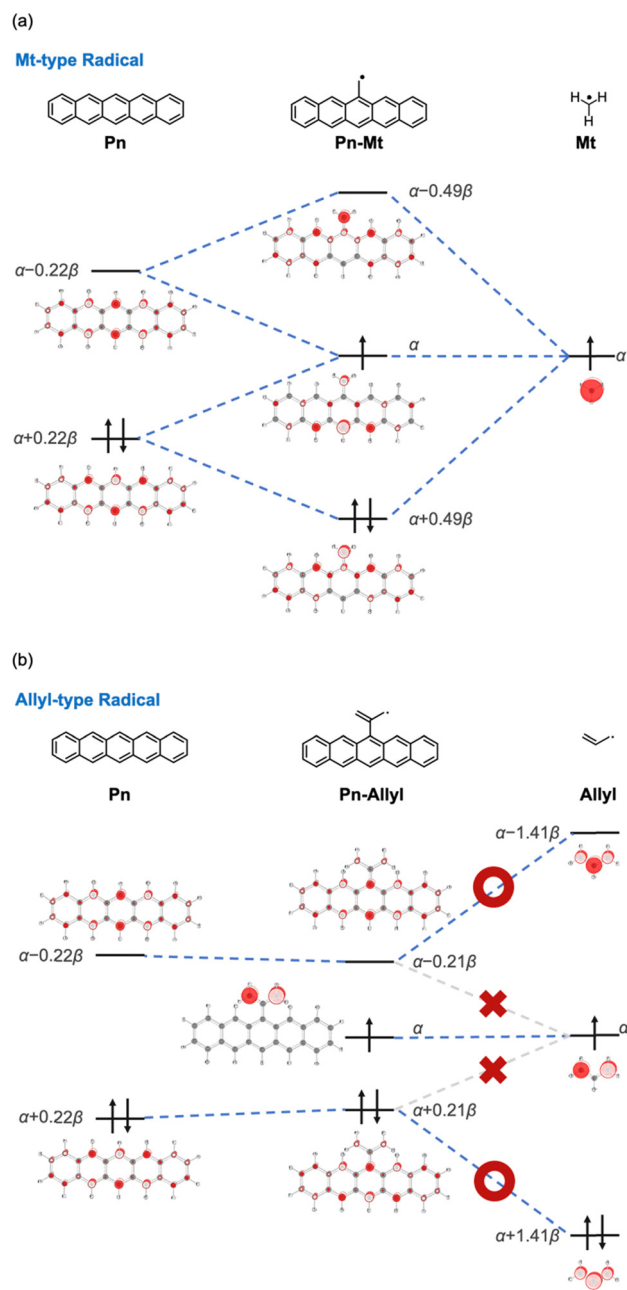


Fig. 6 Orbital interactions between PAHs and (a) methyl radicals or (b) allyl-2-yl radicals expressed by simple Hückel molecular orbitals ($\alpha$ represents the Coulomb integral and $\beta$ represents the resonance integral).

details, ESI†).[37] First, the SOMO of the methyl radical strongly interacts with both frontier orbitals of pentacene, resulting in an expansion of the H–L gap. On the other hand, in the case of the allyl radical, the SOMO of the radical moiety cannot interact with the frontier orbitals of pentacene because the orbital coefficient on the carbon atom directly bonding to pentacene is zero. Instead, the HOMO and LUMO of the radical moiety have significant orbital coefficients on the carbon atom. These orbitals interact with the frontier orbitals of the pentacene moiety, leading to the narrower H–L gap and larger $y_0$. In

summary, the increase or decrease in $y_0$ observed for the radical substituents can be understood from the conjugational topology of the radical moiety, and it is a fundamental property of radical substituents. The same trend was observed for the molecular orbitals obtained by DFT calculations (Fig. S1 and Table S2, ESI†).

### 3.4 Influence of radical substituents on different PAHs

To discuss the generality of the substituent effect, we move on to the calculation results of other core structures (Fig. 7 and Tables S3–S17, ESI†). Similar to pentacene, non-conjugated radical and conjugated non-radical substituents have a negligible impact, but the conjugated radical substituents significantly alter the open-shell character except for anthracene. The sensitivity of $y_0$ differs from anthracene ($y_0 = 0.012$–$0.083$) to triangulene ($y_0 = 0.143$–$1.000$), suggesting a trend that a more prominent open-shell character leads to higher sensitivity of $y_0$ to substitution. Other than anthracene, the methyl radical (Mt) substituent gives the smallest $y_0$, and the nitronyl nitroxide (NN) substituent gives the largest $y_0$ among all examined substituents.

The larger the $y_0$ value of the original PAH, the larger the decrease in $y_0$ due to Mt, and the smaller the $y_0$ value of the original PAH, the larger the increase in $y_0$ due to NN. This is also interpreted by the orbital interaction between PAHs and radicals. The methyl-type radicals cause orbital interactions

with their SOMO. Hence, a larger $y_0$ of PAH (with a smaller H–L gap or energetically close frontier orbitals to the SOMO of radical units) is more favorable for orbital interaction. On the other hand, the allyl-type substituents interact with the HOMO and LUMO of the radical moiety, and so a smaller $y_0$ of PAH (with larger H–L gaps or energetically close frontier orbitals to the HOMO and LUMO of radical units) is favorable for orbital interaction. These trends are also found in the simple Hückel calculation results (Table S1, ESI†).

### 3.5 Effect of radical substituents on the magnetic properties of molecules

Finally, Fig. 8 shows the correlation between $y_0$ and the singlet–triplet (S–T) gap for the Non-Radical groups and the doublet–quartet (D–Q) gap for the Radical group for each PAH as a measurable relationship of molecular properties and $y_0$. Fig. 8 reveals the correlation between the H–L gap and $y_0$ shown in Fig. 7, indicating that radical substituents can significantly change the magnetic properties of open-shell molecules. Correlated with $y_0$, the Mt substituted PAHs show the largest D–Q gap, and the NN substituted counterparts show the smallest D–Q gap. The D–Q gaps of the Mt- and NN-substituted PAHs are at least different by 1 eV, including the case of anthracene. The 1 eV change corresponds to a difference of more than $10^4$ K in thermal energy, clearly showing how significant the effect of radical substituents is on the magnetic properties of molecules.
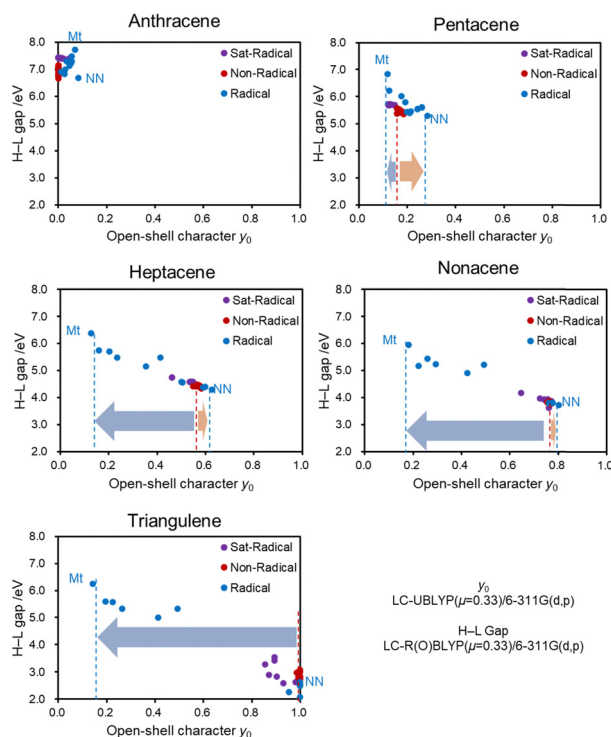


**Fig. 7** Relationship of HOMO−LUMO gaps and $y_0$ of the Sat-Radical/Non-Radical/Radical groups of the PAHs shown in Fig. 3. Horizontal blue and orange arrows represent the decrease and increase in $y_0$ induced by introducing Mt and NN radical substituents, respectively. All calculated data in these plots are summarized in Tables S3–S17 (ESI†).
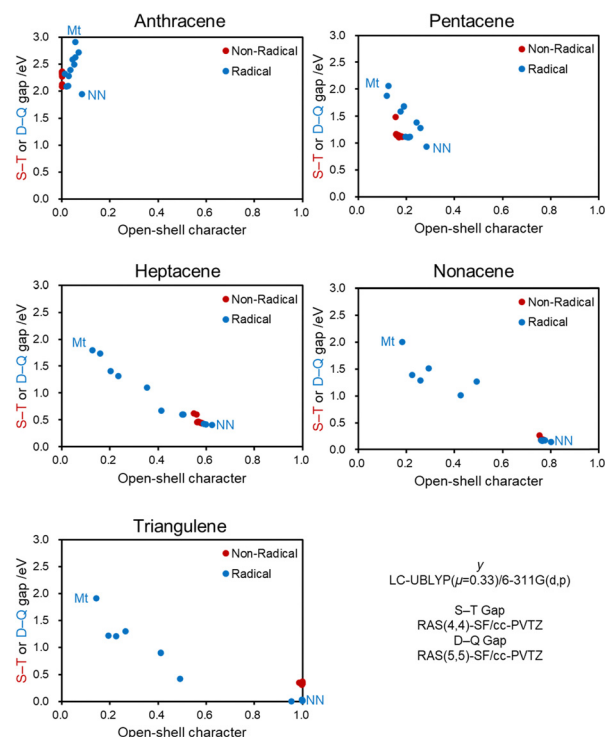


**Fig. 8** Relationship between the singlet−triplet (S−T)/doublet−quartet (D−Q) gaps and $y_0$ of the Non-Radical/Radical groups of the PAHs shown in Fig. 3. All calculated data in these plots are summarized in Tables S3–S17 (ESI†).

## 4. Conclusions

In summary, we have evaluated the effect of radical substituents on the open-shell character $y_0$, which correlates with various molecular properties. We found that radical substituents change the $y_0$ more significantly than non-radical substituents and that the influence of the radical substituents can be understood in terms of orbital interactions. Finally, we also predicted the significant substitution effect on measurable magnetic properties.

This study demonstrated the power of radical substituents in controlling the open-shell character and related properties of a molecule. We are also working on the correlation between open-shell character and nonlinear optical response, which is not well understood for three-spin systems.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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