Quantum chemical evaluation of the effect of radical substituents on molecular open-shell characters and associated physical properties

(*Graduate School of Engineering, Kyoto University*) Tomohito Shinozuka, Daiki Shimizu, Kenji Matsuda

Keywords: Open-shell character; Radical substituent; Quantum chemical calculation; Polycyclic aromatic hydrocarbon; Electron spin

Open-shell character *y* of a molecule correlates with its physical properties, such as singlet fission and nonlinear optical responses.[1] As guidelines for controlling *y*, donor-acceptor substitution, external electric field application, π-extension, and introduction of electron-rich heteroatoms have already been reported.[2,3] In this study, we investigated the effect of various radical substituents on *y*. We evaluated *y* by natural orbital occupation numbers of radical/non-radical substituted polycyclic aromatic hydrocarbons (PAHs) such as pentacene calculated at the LC-UBLYP/6-311G(d,p) level of theory. It was found that radical substituents significantly altered the *y* of PAHs compared to non-radical substituents. The calculated *y* of both radical/non-radical substituted PAHs was correlated to their HOMO–LUMO gaps. Non-radical substituents such as amino-, nitro-, and phenyl-substituted PAHs showed comparable H–L gaps. On the other hand, dicyanomethyl (DCM) substituted PAHs exhibited decreased *y* and increased H–L gap due to the interaction of the SOMO of the radical unit with the frontier orbitals of the PAHs. Contrarily, in the case of the nitronyl nitroxide (NN) substituted PAHs, the H–L gaps are narrowed by the interaction of the HOMO and LUMO of the radical (rather than SOMO) with the frontier orbitals of the PAHs, leading to the increased *y*. These results showcase the unique character of radical substituents for controlling the open-shell character *y* of PAHs. We will discuss the effect in detail from the viewpoint of the topology of molecular orbitals and also referring other properties, such as the spin-state energy gap.

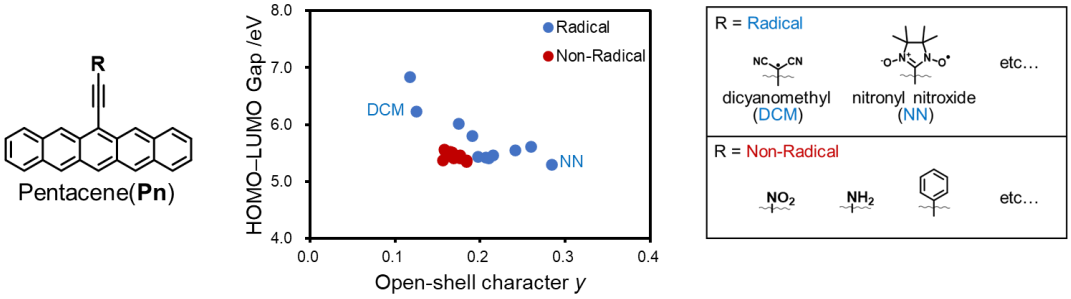

Fig. Correlation of open-shell character *y* and HOMO–LUMO gap of radical/non-radical substituted pentacenes (as an example of substituted PAHs)

1) M. Nakano *Chem. Rec.* **2017**, *17*, 27; 2) M. Nakano *et al. J. Phys. Chem. Lett.* **2011**, *2*, 1094;
3) M. M. Haley *et al. J. Phys. Org. Chem.* **2020**, *33*, 4114.

© The Chemical Society of Japan