

# Unravelling of Baird's Rule via Spectroscopic Analysis: Reversal of Hückel Aromaticity in the Excited Singlet and Triplet States of Hexaphyrins

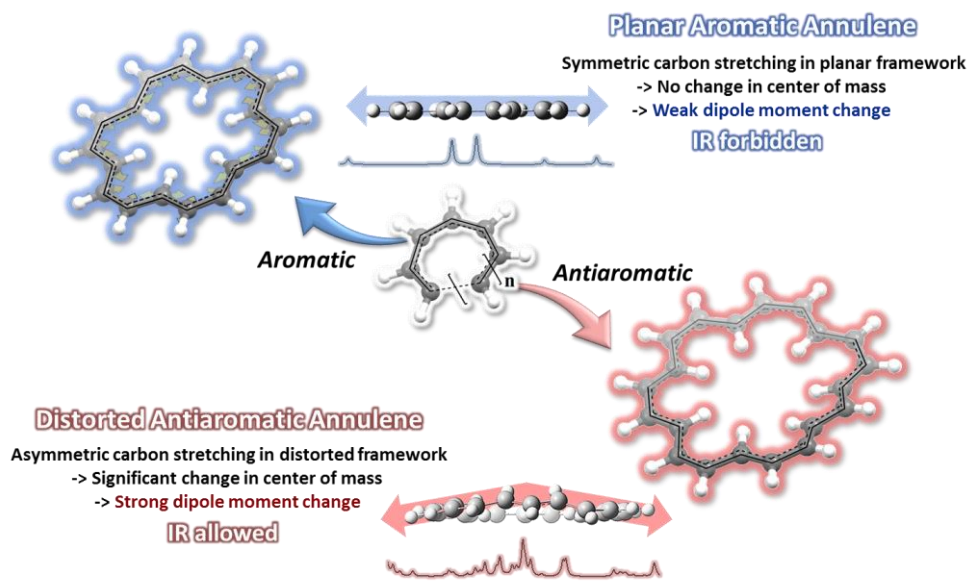
Dongho Kim\*

Department of Chemistry, Yonsei University, Seoul, South Korea, 03722

\*dongho@yonsei.ac.kr

Attention on the aromaticity in the ground state has been shifted to that in the excited state and its application because the determination of excited state aromaticity not only rationalizes the photostability and photoreactivity but also provides crucial insight into photosynthetic mechanisms and designing photoactive materials such as saturable absorbers. The excited state aromaticity was first described by Baird, where he proposed that Hückel aromatic and antiaromatic characters are reversed in the lowest excited triplet state into antiaromatic and aromatic ones, respectively (known as aromaticity reversal; Baird's rule).<sup>[1]</sup>

Here, we discuss the aromaticity reversal in the excited state of a comparable set of Hückel aromatic/antiaromatic hexaphyrin congeners by time-resolved infrared (TRIR) spectroscopy. Aromaticity is deeply related with molecular conformations;<sup>[2-6]</sup> electronically unstable antiaromatic molecules tend to become stable via structural distortions while aromatic ones exhibit planar and rigid geometries for more effective  $\pi$ -conjugation.<sup>[7-9]</sup> Judging from this aromaticity-dependent conformational differences, we investigate the aromaticity reversal in the excited state with the IR-activity of C=C stretching modes, which are sensitive to conformational distortions due to the vibrational selection rule for a change of the dipole moment.<sup>[5]</sup> The aromatic/antiaromatic hexaphyrin congeners showed the interconvertible IR spectral features between the ground and excited states arise from aromaticity-driven structural changes, which clearly demonstrates the



**Figure 1.** Aromaticity-dependence of molecular structures and IR-activities.

aromaticity reversal in the excited state. Our unconventional findings by the IR spectroscopy will provide deeper insight into the effect of aromaticity reversal on the photochemical synthesis as well as the photostability and photoreactivity for photoactive materials.

- [1] Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941–4948.
- [2] Sung, Y. M.; Yoon, M. C.; Lim, J. M.; Rath, H.; Naoda, K.; Osuka, A.; Kim, D. *Nat. Chem.* **2015**, *7*, 418–422.
- [3] Sung, Y. M.; Oh, J.; Kim, W.; Mori, H.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2015**, *137*, 11856–11859.
- [4] Oh, J.; Sung, Y. M.; Kim, W.; Mori, S.; Osuka, A.; Kim, D. *Angew. Chem. Int. Ed.* **2016**, *55*, 6487–6491.
- [5] Sung, Y. M.; Oh, J.; Naoda, K.; Lee, T.; Kim, W.; Lim, M.; Osuka, A.; Kim, D. *Angew. Chem. Int. Ed.* **2016**, *55*, 11930–11934.
- [6] Hong, Y.; Oh, J.; Sung, Y. M.; Tanaka, Y.; Osuka, A.; Kim, D. *Angew. Chem. Int. Ed.* **2017**, *56*, 2932–2936.
- [7] Sung, Y. M.; Oh, J.; Cha, W.; Kim, W.; Lim, J. M.; Yoon, M. C.; Kim, D. *Chem. Rev.* **2017**, *117*, 2257–2312.
- [8] Cha, W.; Kim, T.; Ghosh, A.; Zhang, Z.; Ke, X.; Ail, R.; Lynch, V. M.; Jung, J.; Kim, W.; Lee, S.; Fukuzumi, S.; Park, J. S.; Sessler, J.; Chandrashekar, T. K.; Kim, D. *Nat. Chem.* Under revision.
- [9] Ueda, M.; Jorner, K.; Sung, Y. M.; Mori, T.; Kim, D.; Ottosson, H.; Aida, T.; Itoh, Y. *Nat. Commun.* Under revision.