Adaptive Aromaticity : From Fundamental to Application

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According to Hückel's and Baird's rules, cyclic conjugated species with 4*n*+2 π-electrons are aromatic in the singlet electronic ground state (S_0) and antiaromatic in the lowest triplet state (T_1), and vice versa. Thus, species with aromaticity in both states (S_0 and T_1), termed as adpative aromaticity, are particularly rare.[1-2] Here we carry out density functional theory calculations to probe the origin of adaptive aromaticity in metallapyridiniums.[3] Specifically, rhenapyridiniums and osmapyridiniums both exhibit adaptive aromaticity whereas iridapyridiniums do not. Further analysis reveals that the strength of metal-carbon and metal-nitrogen bonds in metallapyridiniums is the key factor to achieve aromaticity in the lowest triplet state. Blocking the spin delocalization in the six-membered ring of metallapyridiniums also help the persistence of aromaticity in the lowest triplet state. In addition, such a concept in the applicaiton of singlet fission will be discussed briefly.[4-5] In most cases, species with adaptive aromaticity not only satisfy the thermodynamic requirements of the singlet fission process ($2E(T_1) < E(S_1)$ and $2E(T_1) < E(T_2)$) but also usually generate an intermediate $E(T_1)$ value (the energy gap of the singlet-triplet state). Thus, adaptive aromaticity could be an alternative strategy for experimentalists and theoreticians to design singlet fission materials.

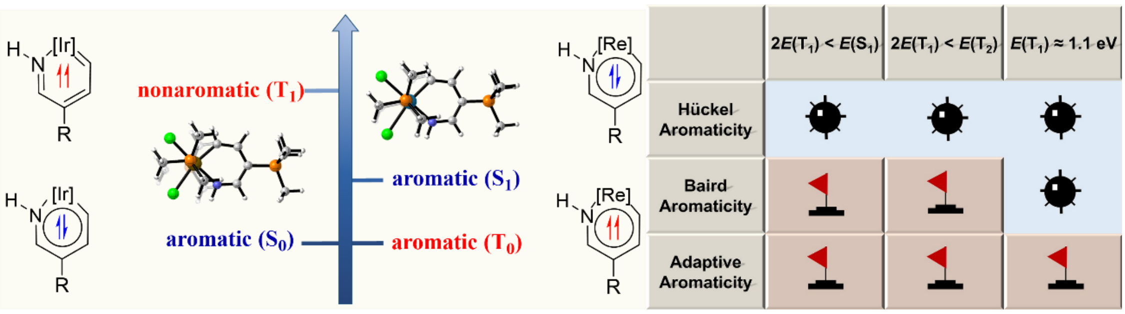

Figure 1. Schematic illustration of adaptive aromaticity in metallapyridiniums (left) and application in singlet fission (right)

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