

The extension of Baird's rule to twisted heteroannulenes: the aromaticity reversal of singly-twisted and doubly-twisted molecular systems in the lowest triplet state

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We have investigated the lowest triplet state (T_1) aromaticity of singly-twisted Möbius aromatic and doubly-twisted Hückel antiaromatic bis(palladium(II)) [36]octaphyrins using spectroscopic measurements and quantum calculations (Fig. 1). The T_1 state of singly-twisted Möbius [36]octaphyrin shows broad and weak absorption spectral features that are analogous to those of antiaromatic expanded porphyrins, while the T_1 state of d Intriguingly, while these two twisted octaphyrins have the same molecular compositions and number of electrons along with π -conjugation pathways, they show different topologies and aromatic characters.^[1] This pair allows us to access a correlation between the molecular topology and the excited state aromaticity doubly-twisted Hückel [36]octaphyrin exhibits intense and distinct spectral features, representing aromatic nature. These results along with theoretical calculations support the aromaticity reversal in the T_1 state. Furthermore, we have revealed that the degree of structural smoothness affects the aromaticity reversal in the T_1 state.

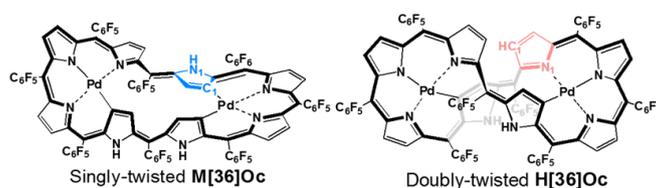


Figure 1. The molecular structures of **M[36]Oc** (left) and **H[36]Oc** (right). We highlighted the rotating pyrroles of **M[36]Oc** (blue) and **H[36]Oc** (red). The bold line denotes the representative π -electronic circuit.

The T_1 state of singly-twisted Möbius [36]octaphyrin shows broad and weak absorption spectral features that are analogous to those of antiaromatic expanded porphyrins, while the T_1 state of doubly-twisted Hückel [36]octaphyrin exhibits intense and distinct spectral features, representing aromatic nature (Fig. 2). The maximum extinction coefficient (ϵ_{\max}) of **M[36]Oc** in the T_1 absorption spectrum is 0.66 times smaller than that in the S_0 state ($\epsilon_{\max} = 220,000 \rightarrow 145,000 \text{ cm}^{-1}\text{M}^{-1}$ for the S_0 and T_1 state, respectively). The T_1 absorption spectrum of **M[36]Oc** shows ill-defined and relatively weak spectral features, which resembles those of antiaromatic expanded porphyrins. On the other hand, the ϵ_{\max} of **H[36]Oc** in the T_1 state absorption spectrum is 1.4 times larger than that in the S_0 state ($\epsilon_{\max} = 88,200 \rightarrow 120,300 \text{ cm}^{-1}\text{M}^{-1}$ for the S_0 and T_1 state, respectively). The T_1 absorption spectrum of **H[36]Oc** indicates relatively distinct and intense spectroscopic features, which are analogous to those of aromatic **M[36]Oc**.

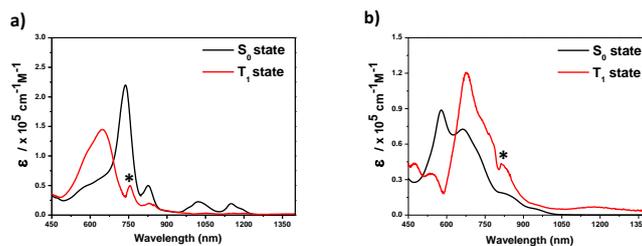


Figure 1. The S₀ and T₁ absorption spectra of a) M[36]Oc and b) H[36]Oc in toluene. The asterisks indicate experimental errors that are induced by different spectral resolutions between spectrometers used for ground-state absorption and TA measurement.

These results along with theoretical calculations support the aromaticity reversal in the T₁ state. Furthermore, we have revealed that the degree of structural smoothness affects the aromaticity reversal in the T₁ state.

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References:

- [1] Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shinata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.*, Wiley **2008**, 47, 681–684; *Angew. Chem.*, Wiley, **2008**, 120, 693–696.