

# Reversal of Hückel (anti)aromaticity in the lowest triplet states of hexaphyrins and spectroscopic evidence for Baird's rule

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## 1. Introduction

### 1-1. Aromaticity: Hückel's rule and Baird's rule

➤ Aromaticity is one of the most fundamental concepts in organic chemistry, which governs chemical properties and reactivities of molecules.

#### (a) Hückel's rule: aromaticity in ground state

➤ Planer cyclic systems with  $[4n+2]\pi$ -electron receive great stabilization effect (aromatic), whereas  $[4n]\pi$  systems are less stable (antiaromatic) in the ground state (Figure 1).

➤ Hückel's rule has been explicitly demonstrated through experiments.

#### (b) Baird's rule (prediction): aromaticity in lowest triplet state

➤ Baird expanded the concepts of aromaticity to the lowest triplet state.

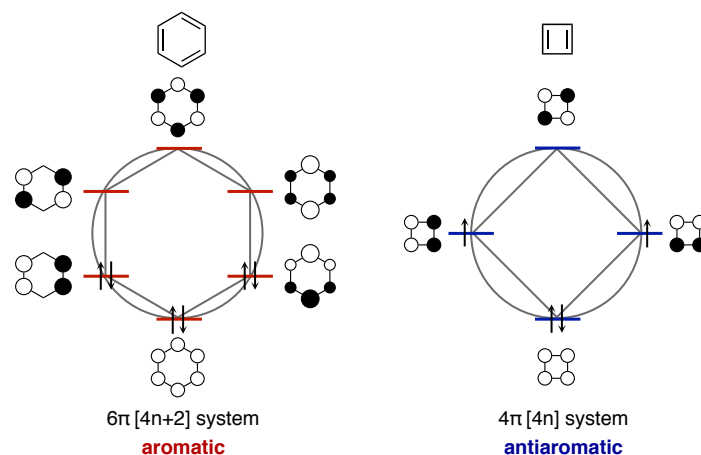
➤ Baird predicted that the Hückel aromaticity observed in ground-state systems would be reversed in the lowest triplet state.<sup>1</sup>

➔  $[4n+2]\pi$  cyclic systems would exhibit antiaromatic character, while  $[4n]\pi$  systems should show aromatic character in the lowest triplet state (Figure 2).

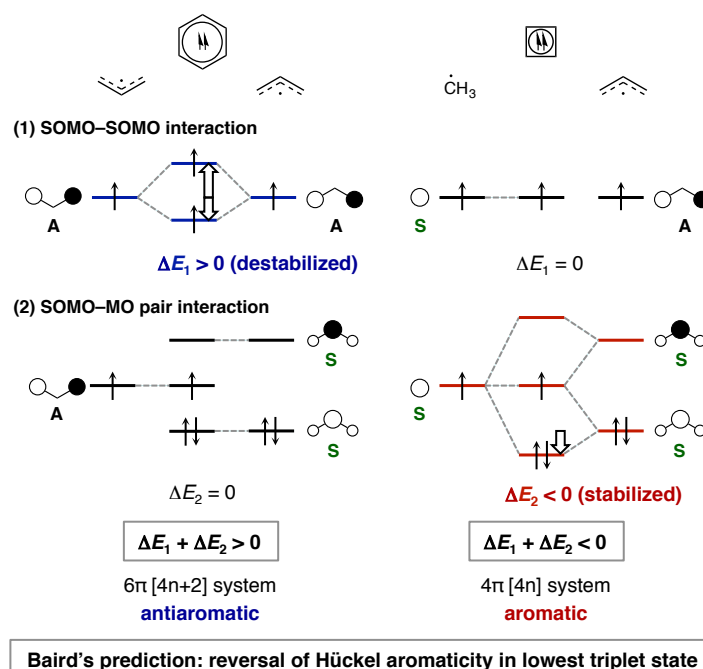
➤ The concept of excited-state aromaticity would have possibilities of predicting photochemical properties of molecules and understanding photochemical reactions (Figure 3).

➤ Baird's prediction has been supported by various theoretical calculations such as nucleus-independent chemical shifts (NICS) and harmonic oscillator model of aromaticity (HOMA).

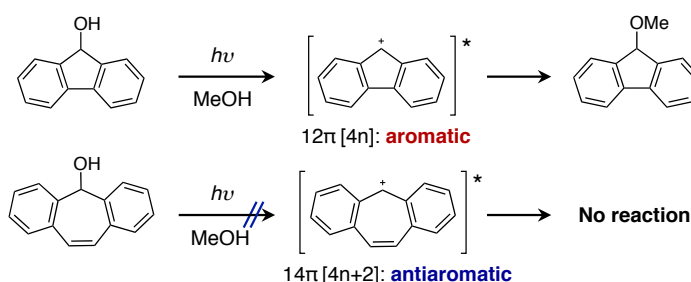
➤ However, **electronic structures of excited states of a pair of  $[4n+2]$  and  $[4n]$  systems have not been analyzed experimentally.**



**Figure 1.** Hückel aromaticity in the ground state.



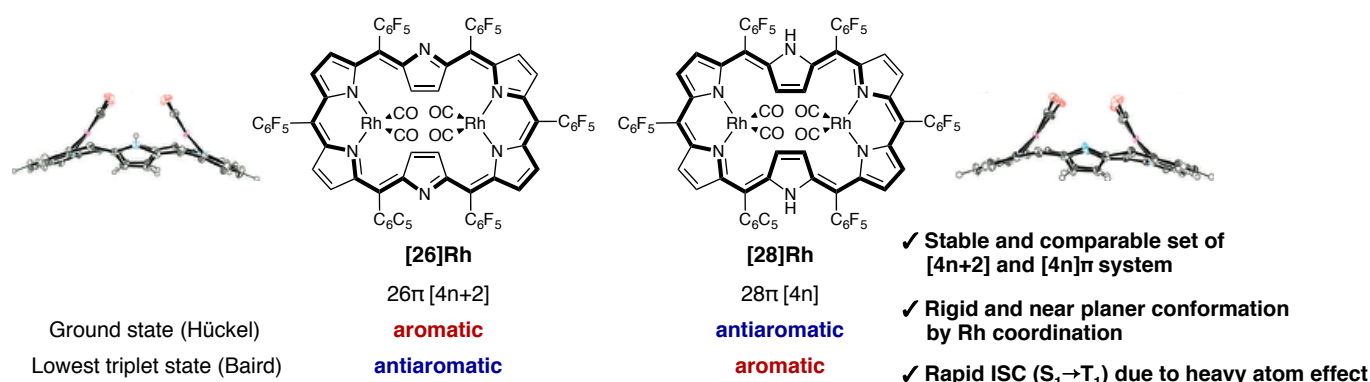
**Figure 2.** Baird aromaticity in the lowest triplet state.



**Figure 3.** Photosolvolytic reactions of fluorenol and suberenol.

## 1-2. This work: first direct confirmation of Baird's rule via experiment

- Generally, it is difficult to prepare a directly comparable set of stable  $[4n+2]$  and  $[4n]\pi$  cyclic systems.
- Expanded porphyrins can release or capture two pyrrolic protons following  $2e^-$  reduction or oxidation.  
➔  $[4n+2]$  and  $[4n]\pi$  expanded porphyrins as test beds for evaluation of molecular aromaticity
- It has been known that **antiaromatic expanded porphyrins have broad and weak absorption spectra compared to aromatic ones.**<sup>2</sup>
- In this work, the authors proposed bis-rhodium [26]- and [28]hexaphyrins as a stable and comparable set of  $[4n+2]$  and  $[4n]\pi$  cyclic systems for investigating aromaticity in the lowest triplet state (Figure 4).
- These hexaphyrins are ideal systems for testing Baird's prediction because coordinated rhodium metals could (i) rigidify the nearly planar conformations and (ii) accelerate the intersystem crossing processes needed to populate the excited triplet states.

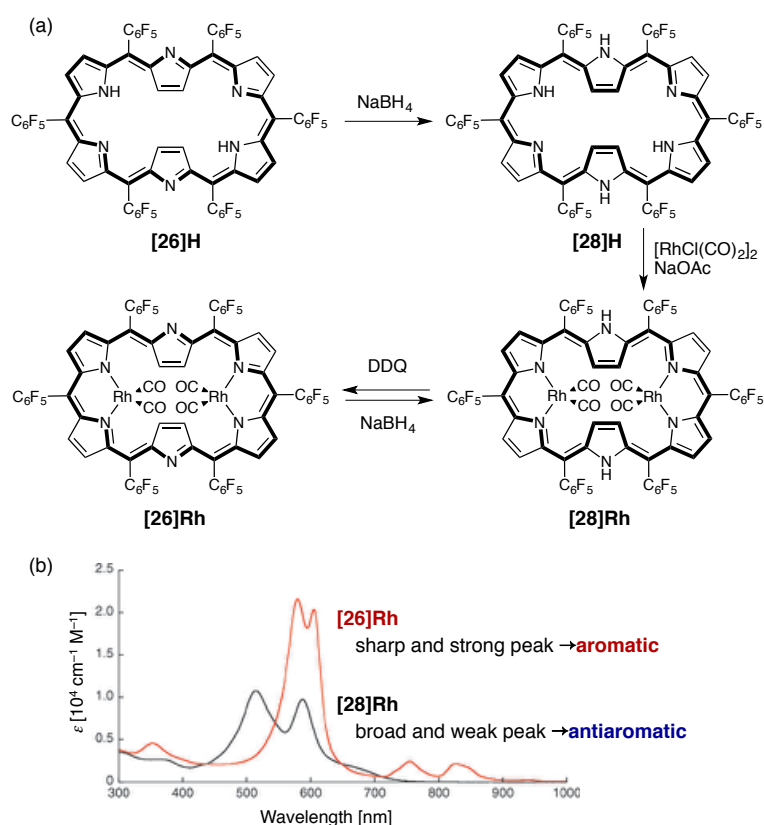


**Figure 4.** Molecular design of bis-rhodium hexaphyrins for testing Baird's prediction.

## 2. Results and discussion

### 2-1. Synthesis of bis-rhodium hexaphyrins

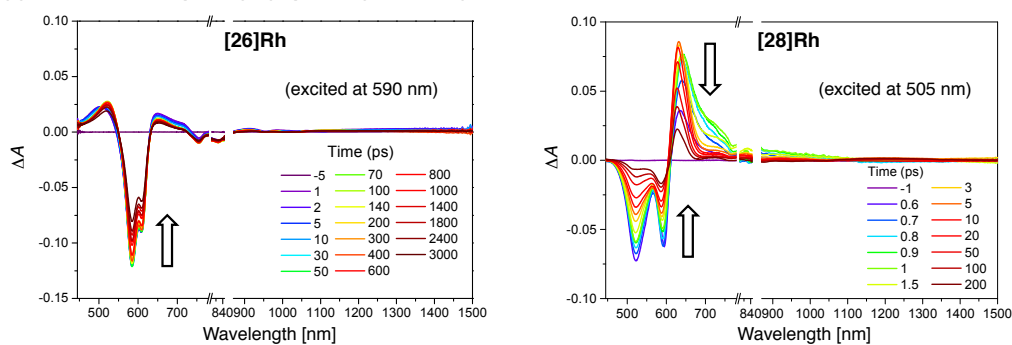
- Treatment of [28]hexaphyrine with  $[\text{RhCl}(\text{CO})_2]_2$  in the presence of sodium acetate gave the bis-rhodium [28]hexaphyrine ([28]Rh).
- [28]Rh was oxidized with DDQ to give [26]hexaphyrine ([26]Rh) and this step could be reversed by the reduction with  $\text{NaBH}_4$  (Figure 5).<sup>3</sup>
- Ground-state absorption spectrum of [26]Rh shows two intense Soret-like bands and several Q-like bands, which are characteristic of aromatic porphyrinoids.
- In contrast, absorption spectrum of [28]Rh shows relatively broad and weak peaks, which are indicative of antiaromatic nature.



**Figure 5.** (a) Synthesis of bis-rhodium hexaphyrins and (b) their ground-state absorption spectra.

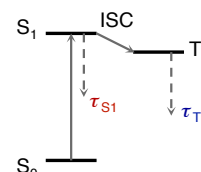
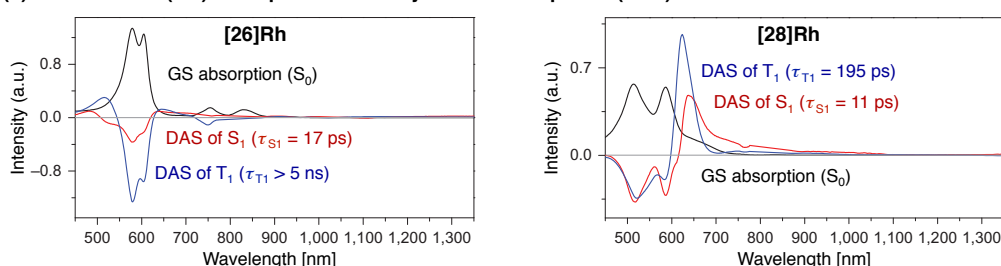
## 2-2. Spectroscopic analyses: confirmation of Baird's rule

### (a) Transient absorption (TA) spectra (in toluene)



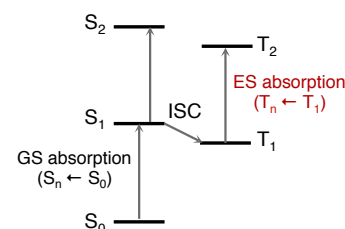
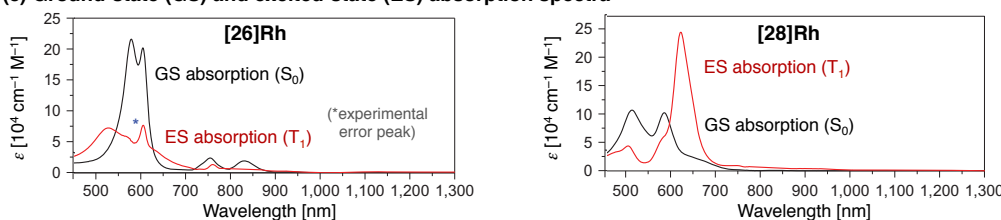
Double exponential decay:  $A_{S_1} \exp(-t/\tau_{S_1}) + A_{T_1} \exp(-t/\tau_{T_1})$   
 → corresponding to  $S_1$ - and  $T_1$ -state lifetime

### (b) Ground-state (GS) absorption and decay-associated spectra (DAS)



ES absorption ( $T_1$ ) = DAS of  $T_1$  – GS absorption ( $S_0$ )

### (c) Ground-state (GS) and excited-state (ES) absorption spectra



**GS absorption ( $S_0$ )**  
 sharp and strong peak ( $216,000 \text{ cm}^{-1} \text{ M}^{-1}$ ) → **aromatic**  
**ES absorption ( $T_1$ )**  
 broad and weak peak ( $72,500 \text{ cm}^{-1} \text{ M}^{-1}$ ) → **antiaromatic**

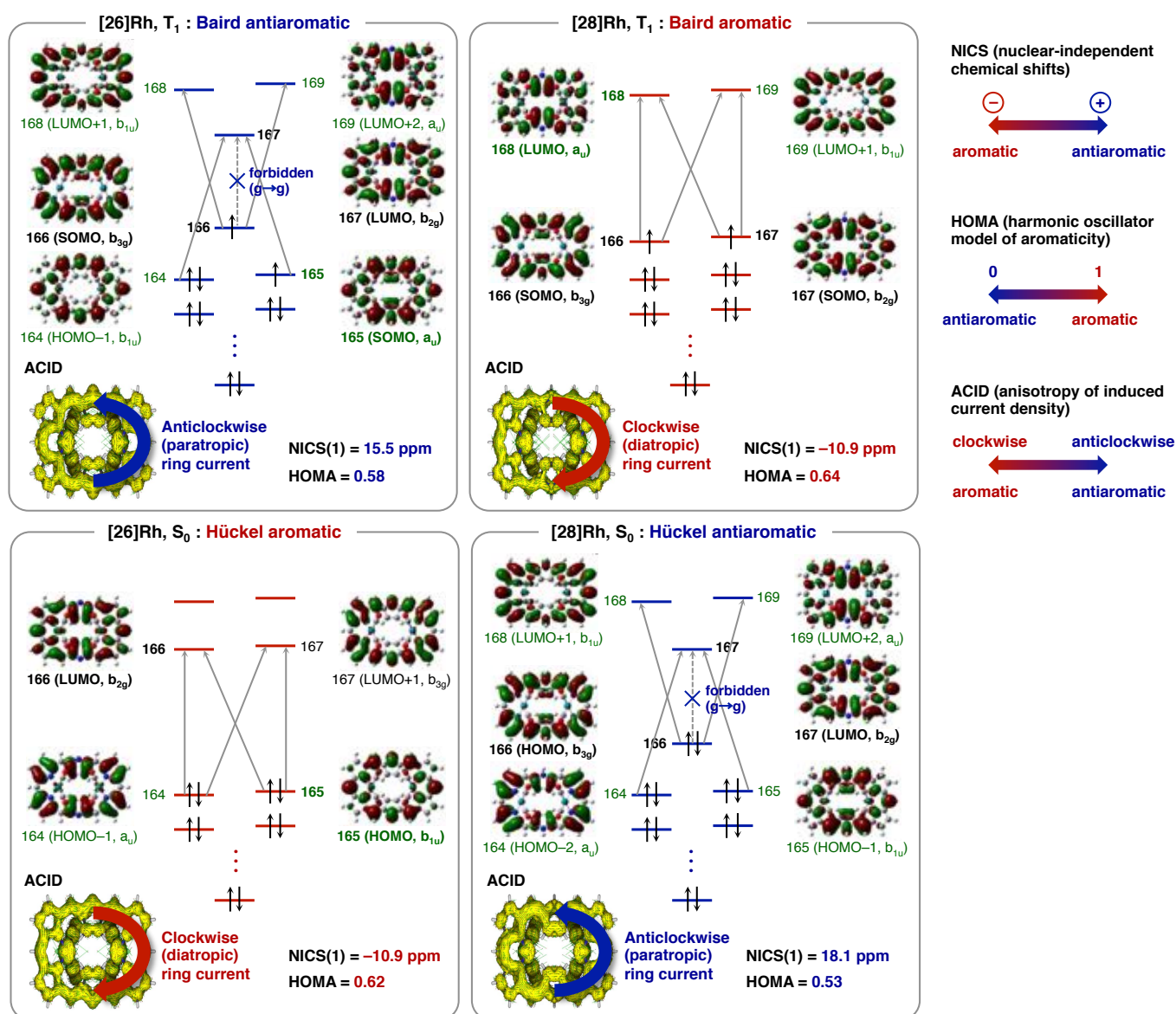
**GS absorption ( $S_0$ )**  
 broad and weak peak ( $108,000 \text{ cm}^{-1} \text{ M}^{-1}$ ) → **antiaromatic**  
**ES absorption ( $T_1$ )**  
 sharp and strong peak ( $246,500 \text{ cm}^{-1} \text{ M}^{-1}$ ) → **aromatic**

**Reversal of Hückel aromaticity in the lowest triplet state in accord with Baird's rule**

**Figure 6.** Spectroscopic analyses of **[26]Rh** and **[28]Rh** for testing Baird's rule.

- Femtosecond time-resolved transient absorption (TA) spectra exhibit double exponential decay features with two time constants, which correspond to the  $S_1$ -state and  $T_1$ -state lifetimes ( $\tau_{S_1}$  and  $\tau_{T_1}$ ; Figure 6(a)).
- Decay-associated spectra (DAS) of two transient species were obtained, which correspond to the  $S_1$  and  $T_1$  state, respectively (Figure 6(b)).
- Excited-state absorption of  $T_1$  state could be evaluated by subtracting the ground-state absorption from the decay-associated spectra of  $T_1$  state (Figure 6(c)).
- Broad and weak peaks in the obtained excited-state absorption of **[26]Rh** indicates its antiaromatic character compared to its aromatic character in the ground state. In contrast, sharp and strong peaks in the ES absorption of **[28]Rh** shows its aromatic feature compared to its antiaromatic feature in the ground state.
- **These results suggest the reversal of Hückel aromaticity in the lowest triplet state in accord with Baird's rule.**

### 2-3. Theoretical calculations



**Figure 7.** Theoretical calculations supporting the reversal of aromaticity in the lowest triplet state.

- The calculated energy level diagrams of the ground and  $T_1$  state exhibit contracting features.
- The substantial change in the NICS(1) and HOMA values and ACID plots further support the reversal of aromaticity in the lowest triplet state.

### 3. Conclusion

- The authors for the first time displayed experimental evidence for the reversal of Hückel aromaticity in  $T_1$  states compared to ground states by the spectroscopic analyses of  $[4n+2]$  and  $[4n]\pi$  hexaphyrines.

### 4. References

- (1) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941–4948.
- (2) Shin, J.-Y.; Kim, K. S.; Yoon, M.-C.; Lim, J. M.; Yoon, Z. S.; Osuka, A.; Kim, D. *Chem. Soc. Rev.* **2010**, *39*, 2751–2767.
- (3) Rath, H.; Aratani, N.; Lim, J. M.; Lee, J. S.; Kim, D.; Shinokubo, H.; Osuka, A. *Chem. Commun.* **2009**, 3762–3764.