

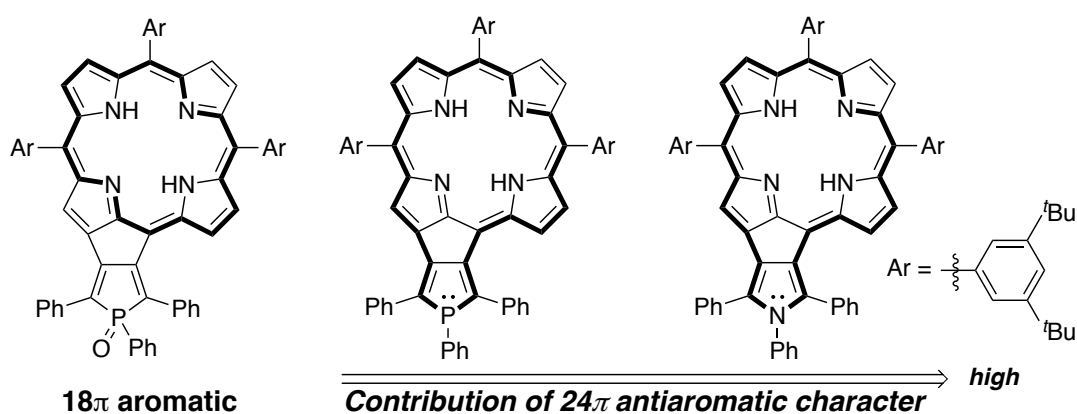
## Modulation of Aromaticity and Properties of Porphyrins by Peripheral Heterole-fused Structures

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Porphyrins are macrocyclic  $18\pi$  aromatic molecules that have been actively studied in various fields owing to their intriguing properties for diverse applications. Introducing peripheral fused structures is quite effective for electronic perturbations (i.e., red-shift in absorption) because of their expanded  $\pi$ -conjugated networks. Among various fused porphyrins, heteroatom-embedded fused-porphyrins have attracted much attention because of their unique optical and electrochemical properties derived from effective interaction between porphyrins and main group elements. However, the introduction of fused heterole structures into peripheral regions is still a challenge. Considering the properties of heterole derivatives can be modulated by main group elements and their oxidation states, we envisioned that the properties of fused porphyrins would also be tuned by peripheral heterole-fused structures.

Herein, we established a new synthetic strategy for heterole-fused porphyrins using [2+2+1] cyclization of bis(alkynyl)porphyrin and succeeded in the synthesis of phosphole-fused<sup>[1]</sup> and pyrrole-fused<sup>[2]</sup> porphyrins. The difference of main group elements (i.e., nitrogen or phosphorus) as well as oxidation states of the phosphorus atom have a clear influence on the whole aromatic character and the resultant electronic properties of porphyrins. Therefore, we demonstrated the modulation of aromaticity and properties of heterole-fused porphyrins by control of main group elements and their oxidation states.



[1] I. Nishimura, T. Higashino, H. Imahori, *Chem. Eur. J.* **2019**, *25*, 13816.

[2] I. Nishimura, T. Higashino, H. Imahori, *Chem. Eur. J.* **2020**, *26*, 12043.