

Exotic Aromaticity in Porphyrinoids

Hiroshi Shinokubo

Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University,
 Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
 hshino@chembio.nagoya-u.ac.jp

Norcorrole is a ring-contracted antiaromatic porphyrin, which lacks two *meso*-carbons from porphyrin. We have synthesized stable norcorrole Ni(II) complexes and investigated their reactivities, optical properties, and electrochemical properties, which are markedly different from aromatic porphyrins. We have also reported that norcorrole dimers **1** and **2** exhibit closely stacked orientation.^[1] The remarkable proximity of the two norcorrole units is rationalized by the emergence of the stacked-ring aromaticity owing to intermolecular orbital interactions between two antiaromatic systems.^[2]

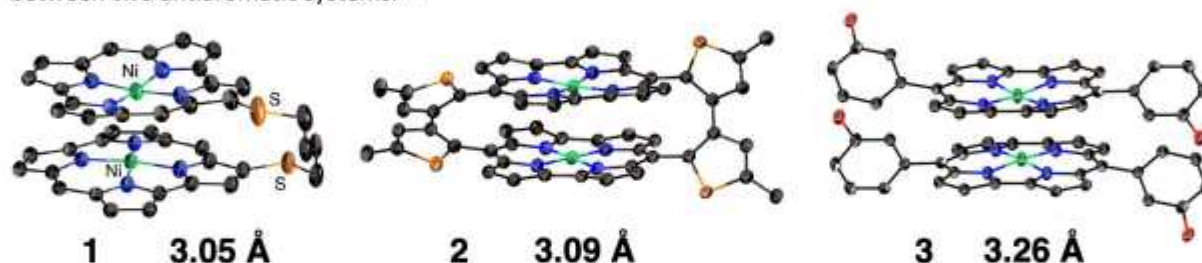


Figure: Stacked norcorrole Ni(II) complexes. Alkyl linkers are omitted in **3**.

Recently, we have prepared norcorrole cyclophane **3** tethered with two flexible alkyl chains.^[3] Interestingly, norcorrole cyclophane **3** exhibited crystal polymorphism leading to three different solid-state structures, in which the orientation of the two norcorrole units is substantially different. The stacked-ring aromaticity of **3** depends on the twist angle between two stacking norcorrole units.

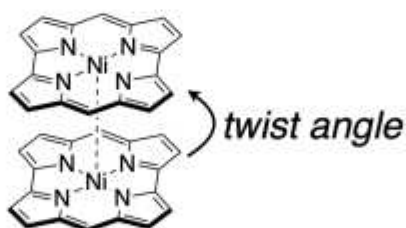


Figure: Twist angle between two Ni(II) norcorrole units.

I would also like to discuss the metalloaromaticity of a new porphyrinoid, which we have recently prepared.

REFERENCES

- (a) R. Nozawa, H. Tanaka, W.-Y. Cha, Y. Hong, I. Hisaki, S. Shimizu, J.-Y. Shin, T. Kowalczyk, S. Irle, D. Kim, H. Shinokubo, *Nat. Commun.* **2016**, *7*, 13620. (b) R. Nozawa, J. Kim, J. Oh, A. Lamping, Y. Wang, S. Shimizu, I. Hisaki, T. Kowalczyk, H. Fliegl, D. Kim, H. Shinokubo, *Nat. Commun.* **2019**, *10*, 3576.
- (a) C. Corminboeuf, P. v. R. Schleyer, P. Warner, *Org. Lett.* **2007**, *9*, 3263. (b) D. E. Bean, P. W. Fowler, *Org. Lett.* **2008**, *10*, 5573.
- H. Kawashima, S. Ukai, R. Nozawa, N. Fukui, G. Fitzsimmons, T. Kowalczyk, H. Fliegl, H. Shinokubo, *J. Am. Chem. Soc.* **2021**, *143*, 10676.