

Cyclo[4]pyrrole: Structural Analysis and Redox Property

(¹ Grad. Sch. Eng., Hokkaido University, ² Grad. Sch. Eng., Kyushu University, ³WPI-ICReDD, Hokkaido University, ⁴ Grad. Sch. Eng., Kyoto University) ○Yuhua Sun,¹ Soji Shimizu,² Yuki Ide,³ Hisanori Senboku,¹ Takayuki Tanaka,⁴ Yasuhide Inokuma^{1,3}

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Cyclo[*n*]pyrroles are porphyrinoids in which all pyrrole units are connected directly. Several cyclo[*n*]pyrroles congeners have been reported with concern on their optoelectronic properties. While the ring-contraction effect is expected to grant certain special properties to the system, the contracted analogues of cyclo[*n*]pyrrole have been less explored. We successfully synthesized α - β directly linked cyclo[4]pyrrole (**3**) as a novel contracted macrocycle for investigating the effect of structure on the electronic properties.¹⁾

The construction of cyclo[4]pyrrole (**3**) was achieved via terpyrrole precursor **2** which was obtained from tetraacetylene (**1**) with a five-step synthesis (**Figure 1a**). Suzuki-Miyaura cross-coupling between **2** and 2,5-diborylpyrrole furnished target compound **3** in 25% yield. X-ray crystallographic and StrainViz analyses revealed a highly strained structure of **3** with a total strain of 20.8 kcal/mol.

Two reversible oxidation waves were observed for **3** by cyclic voltammetry measurement. We further performed spectroelectrochemical analysis of **3** (**Figure 1b**). Theoretical calculation indicated the spin density of radical cation **3**^{•+} was localized on the 3,2':5',3''-terpyrrole moiety. In contrast, in the triplet diradical dication state **3**²⁺ the spin density was delocalized on the whole four pyrrole units.

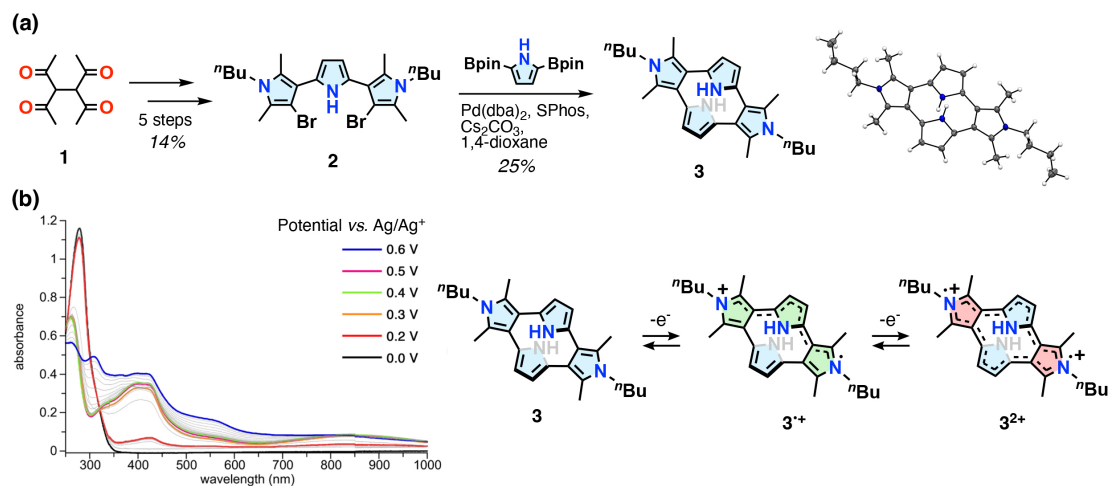


Figure 1. (a) Synthetic route for cyclo[4]pyrrole (**3**) with its X-ray structure in the right. (b) Absorption spectral change during the electrochemical oxidation process of **3** in dichloromethane (left) and possible redox states of **3** (right).

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