

A Novel Porphycene Dimer with a Large Bathochromic Shift

Chihiro Sonoda and Takashi Hayashi

Department of Applied Chemistry, Osaka University, 2-1 Yamadaoka, Suita, 565-0871, Japan

Porphycene (**Pc**, Figure 1a), a constitutional isomer of porphyrin, possesses a symmetrically reduced porphyrinoid structure. A series of porphycene compounds are known to have remarkable photo- and physicochemical features such as stronger absorptions in the visible region and unique tautomerization behavior of the inner hydrogen atoms. These attractive properties have further motivated us to prepare novel porphycene derivatives with an extended π -electron system which modulate the electronic and structural properties of porphycene. Especially, it has been found that modifying the ethylene bridges (*meso*-positions) of porphycene (Figure 1b, 1c) may effectively extend the π -system.¹ Taking advantage of this effect, our group designed a bis-**Pc** framework (Figure 1d) with a benzene ring fused between the *meso*-positions of the two porphycene frameworks.

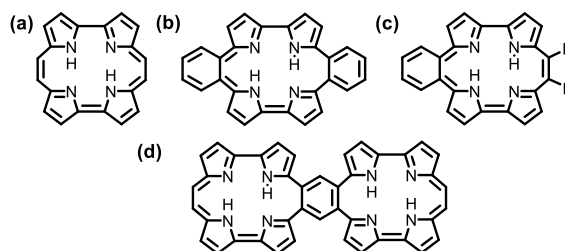
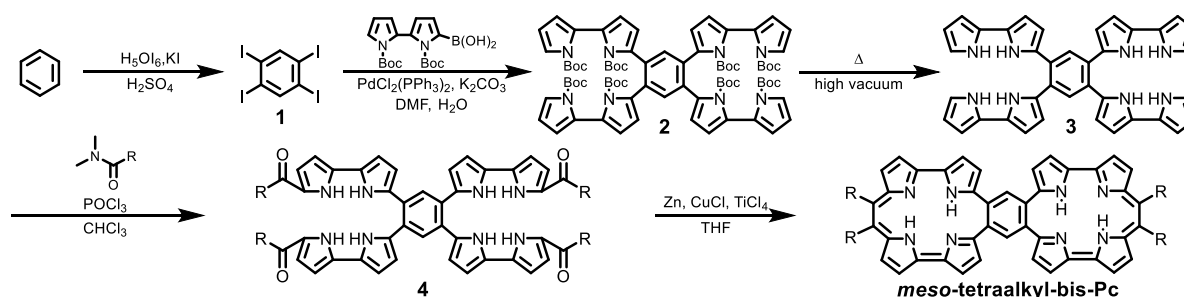


Figure 1. Molecular structure of (a) **Pc**, (b) *meso*-dibenzo-**Pc**, (c) *meso*-dialkyl-monobenzo-**Pc**, (c) bis-**Pc**.

In this study, a novel porphycene dimer, *meso*-tetraalkyl-bis-**Pc** in which two porphycene rings are constructs two porphycene rings via Suzuki-Miyaura coupling and intramolecular McMurry coupling.

In this study, a novel porphycene dimer, *meso*-tetraalkyl-bis-**Pc** in which two porphycene rings are constructs two porphycene rings via Suzuki-Miyaura coupling and intramolecular McMurry coupling.



Scheme 1. The synthesis of *meso*-tetraalkyl-bis-porphycene.

UV-Vis-NIR spectroscopic study suggests that the absorption bands of *meso*-tetraalkyl-bis-**Pc** are significantly red-shifted (shifted by approximately 400 nm in the Q bands) compared to those observed by **Pc** (Figure 1a) with Q bands at 558, 596 and 629 nm. In contrast, *meso*-dialkyl-monobenzo-**Pc** (Figure 1c), in which monobenzoporphycene with two alkyl moieties linked at the *meso*-positions, exhibited the Q bands at 634, 670 and 744 nm. A Comparison of the spectra of *meso*-dialkyl-monobenzo-**Pc** and *meso*-tetraalkyl-bis-**Pc** shows that the absorption of the latter is more red-shifted than that of the former. This finding suggests that the π -conjugated system of the bis-**Pc** compound is not independent in each ring (22π) and has a significantly extended 38π -conjugation system throughout the two porphycene rings.

¹H NMR spectroscopic study shows that the porphycene dimer exhibits unusual both *cis* and *trans* tautomeric forms, despite the fact that essentially most known porphycene derivatives adopt the *trans* tautomeric form. The dimerization of porphycene might have a significant effect on the tautomerism of the porphycene rings. The detailed investigation of the tautomerization is in progress.

REFERENCES

1. T. Hayashi *et al.*, *Angew. Chem. Int. Ed.* **2015**, *54*, 6227–6230.