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Intramolecular strong electronic coupling in a discretely H-aggregated phthalocyanine dimer connected with a rigid linker†

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Preparation of an accurate assembly of phthalocyanines is rather difficult because of the high aggregation property of phthalocyanines. In this study, a novel discrete phthalocyanine dimer was prepared in which the relative configuration of each component was tightly and accurately fixed in an H-aggregate form by a rigid U-shaped linker. Electrochemical measurements showed that there were strong intramolecular electronic interactions between the two phthalocyanines.

Cofacial assemblies of porphyrinoids play central roles in natural photosystems for harvesting light energy and photo-induced charge separation.^{1–3} Inspired by these phenomena occurring in biological systems, considerable efforts have been made to create artificial photosystems based on cofacial assemblies of porphyrinoids.^{4,5} While it is crucial to exert control over the special configuration of the components in order to generate effective electronic communication between them, the synthesis of a conjugate with an accurate configuration in accordance with the design is very challenging because of the high aggregation property of porphyrinoids.

Phthalocyanines, a class of porphyrinoids, have generated considerable interest because of their unique physical and chemical properties.⁶ In particular, their strong and broad Q-bands in the visible light region are considered to be suitable for fabricating an artificial photoantenna.^{6b,7,8} Although various cofacial assemblies have been synthesized so far, the number of discrete cofacial assemblies of phthalocyanines is much less than that of porphyrins, presumably because of the limitation of the synthetic methods and their low solubility in various solvents.^{8,9} Furthermore, it is much more difficult to synthesize

a cofacial assembly in which the relative distances and angles of each component are perfectly defined. In fact, the discrete cofacial dimers of phthalocyanines reported so far include some regioisomers and/or flexible linkers of dimers that do not fix the components in the desired relative configuration.^{7b,8b,10} The electronic interaction between the components inside a cofacial phthalocyanine dimer is highly dependent on their relative configuration. Therefore, it is necessary to synthesize a cofacial phthalocyanine dimer with a well-defined structure to evaluate the electronic interactions accurately. Herein, we report the first electrochemical evaluation of the electronic coupling between two perfectly fixed phthalocyanines in a well-defined H-aggregated cofacial dimer.

The structure of the H-aggregated phthalocyanine dimer **H₄PcD** is shown in Fig. 1a. In order to minimize the structural fluctuations of the relative configuration between the phthalocyanines, the bridge should be robust. Hence, the *syn*-bis-quinoxaline-based U-shaped bridge **L** developed by Chou *et al.*

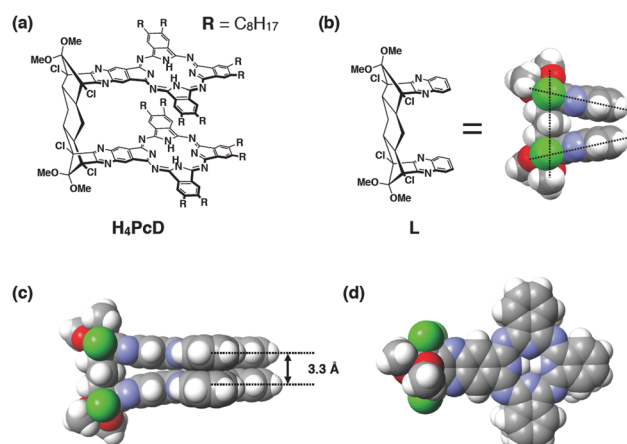


Fig. 1 (a) Chemical structure of **H₄PcD**. (b) Chemical and X-ray crystal structure of **L**.¹¹ (c) Side view and (d) top view of a CPK molecular model of **H₄PcD** (MM3, SCIGRESS v.2.1.0 (Fujitsu), C₈H₁₇ sidechains of the phthalocyanine units were omitted for clarity).

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was chosen.¹¹ This bridge is suitable for fixing the two planar components in an H-aggregate fashion because each planar molecule can stack on another without structural fluctuation supported by the π -conjugated anchors on the robust bridge. Moreover, according to the crystal structure of **L**, the two planar molecules are inclined inward, which effectively reinforced their stacking (Fig. 1b). Therefore, the phthalocyanine units in **H₄PcD** are also expected to stack close to each other and form the H-aggregate, as revealed in the molecular model (Fig. 1c and d).

The synthesis of **H₄PcD** started from the formation of quinoxaline; the reaction between bis- α -diketone **1**¹¹ and 1,2-diamino-4,5-dibromobenzene gave **2**, and the subsequent cyanation with CuCN afforded *syn*-bis-dicyanoquinoxaline **3** (Scheme S1 in the ESI†). Phthalocyanine formation by condensation of **3** with 4,5-diethylphthalonitrile in DMSO in the presence of Zn(OAc)₂ and ⁿBu₃N afforded the desired Zn(II) phthalocyanine dimer **Zn₂PcD** (Scheme 1). After the removal of zinc ions from **Zn₂PcD** by heating with pyridine-HCl in pyridine,¹² the metal-free phthalocyanine dimer **H₄PcD** was obtained. It should be noted that our attempt to form phthalocyanine in the absence of Zn(OAc)₂ was not successful, implying that the template effect of zinc ions worked effectively. It was also found that zinc ions were a more suitable template than nickel ions for this reaction. Another key point of this synthesis was the introduction of long *n*-octyl sidechains on the phthalocyanine cores to improve solubility in organic solvents. An attempt to introduce bulky *t*-butyl units instead of *n*-octyloxy groups proved unsuccessful, probably because of the steric repulsion between the *t*-butyl units during the formation of the phthalocyanine dimer.

The structure of **H₄PcD** was confirmed by elemental analysis, ¹H-NMR, MALDI-TOF MS, and UV-vis spectroscopies. MALDI-TOF MS showed clear signals at around *m/z* = 2891, which corresponded to the calculated isotopic distribution pattern of [**H₄PcD** + H]⁺ (Fig. S7 in the ESI†). In the ¹H-NMR spectrum (Fig. 2), **H₄PcD** showed four different singlets in the aromatic region. This clearly indicated that the two A₃B-type phthalocyanine rings in **H₄PcD** were identical, as expected. The signals in the aliphatic region corresponded to those of the rigid linker unit and the octyl sidechains of the phthalocyanines. The signals for pyrrolic NH protons were observed at −3.19 ppm. These protons were significantly shifted to higher field compared to those of the monomeric phthalocyanines. This suggested that two phthalocyanine units were closely stacked in the H-aggregate form such that the NH protons were situated in the shielded regions of the neighboring phthalocyanine rings.¹³ The UV-vis spectrum showed broad bands from 550 to 800 nm, which were assigned to the Q-band of phthalocyanine (Fig. S8, ESI†). These were

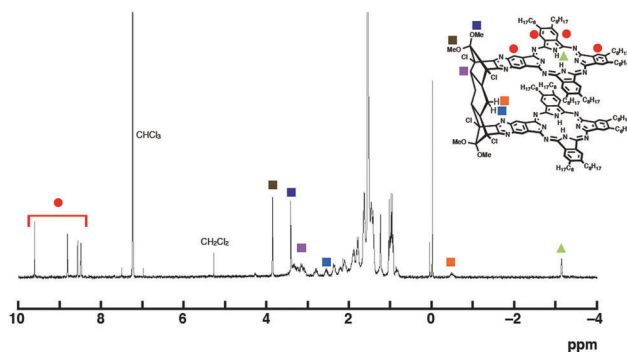
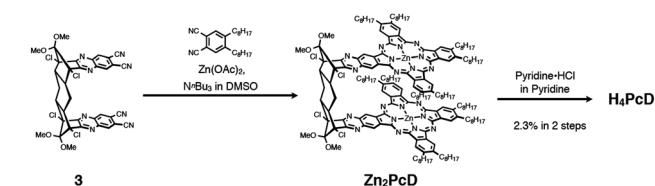


Fig. 2 ¹H-NMR spectrum of **H₄PcD** in CDCl₃ at 293 K.

significantly broadened in comparison to those of typical A₃B-type phthalocyanine monomers.^{6b,8b,14} This might be a result of the π -expanded structure in conjunction with the quinoxaline unit.¹⁵ Considering all of these results together, the spatial arrangements of the two phthalocyanines in **H₄PcD** were successfully fixed in the H-aggregate form with the help of the robust bridging unit.

The cyclic voltammograms of **H₄PcD** were measured in a CH₂Cl₂ solution (200 μ M) containing 100 mM ⁿBu₄N⁺PF₆[−] to evaluate the electronic communication between the two phthalocyanines. Reversible 1e[−] redox waves were observed at 0.10 V and 0.30 V vs. Fc/Fc⁺, whereas two quasi-reversible 1e[−] oxidation waves overlapped with each other at 0.53 V (Fig. 3). By comparison with the redox waves of the reference compounds **1** and **Pc**,¹⁶ the first two redox waves (0.10 V, 0.30 V) could be assigned to the oxidation of phthalocyanine rings. The fact that the 1e[−] oxidations of the chemically identical phthalocyanines occurred at different redox potentials suggests that the phthalocyanine radical cation in **H₄PcD**^{•+} was significantly stabilized by the electronic interactions between the two cofacially stacked phthalocyanines. To evaluate the electronic interaction, we calculated the comproportionation constant *K_c*,¹⁷ which is a typical indicator of electronic coupling and thermodynamic stability of the mixed valence state. It was found that the *K_c* value of **H₄PcD** was 2.7 \times 10³, which is one of the highest values among the



Scheme 1 Synthesis of **H₄PcD**.

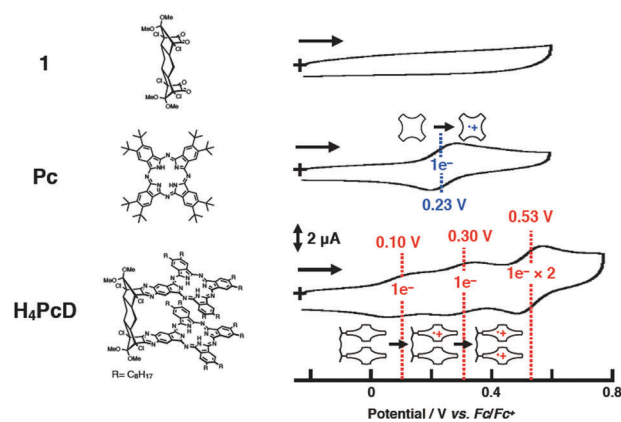


Fig. 3 Cyclic voltammograms of **1**, **Pc**, and **H₄PcD** in CH₂Cl₂ containing 100 mM ⁿBu₄N⁺PF₆[−] at a scan rate of 100 mV s^{−1} at 298 K.

discrete cofacial assemblies of phthalocyanines.^{10a,c,13c} This is apparently the advantage of the tightly fixed H-aggregate form of the two phthalocyanines in **H₄PcD**.

In summary, we synthesized a novel discrete H-dimer of phthalocyanines, **H₄PcD**, in which the spatial arrangements of each component were tightly fixed by a double cyclization reaction with asymmetric components. The *syn*-bis-quinoxaline-based U-shaped bridge was found to be suitable for this purpose. Evaluation of the electronic interactions between phthalocyanines by cyclic voltammetry indicated that **H₄PcD** showed one of the highest *K_c* values among the cofacial phthalocyanine dimers reported so far. Moreover, to the best of our knowledge, this is the first example of the evaluation of electronic interactions between two stacked phthalocyanines in a well-defined H-type dimer with no regioisomers. The strategy to construct a dimer of phthalocyanine with a rigid bridge could be expanded to have a series of dimers with a different stacking angle or a different stacking distance by using related bridges.¹¹ Since phthalocyanines are an interesting building block to construct supramolecular stacked assemblies, we expect that **H₄PcD** itself would also be a good building block for fabricating functional supramolecular assemblies.

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Conflicts of interest

There are no conflicts to declare.

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