



**Intramolecular Strong Electronic Coupling in a Discretely H-Aggregated Phthalocyanine Dimer Connected with a Rigid Linker**

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## Intramolecular Strong Electronic Coupling in a Discretely *H*-Aggregated Phthalocyanine Dimer Connected with a Rigid Linker

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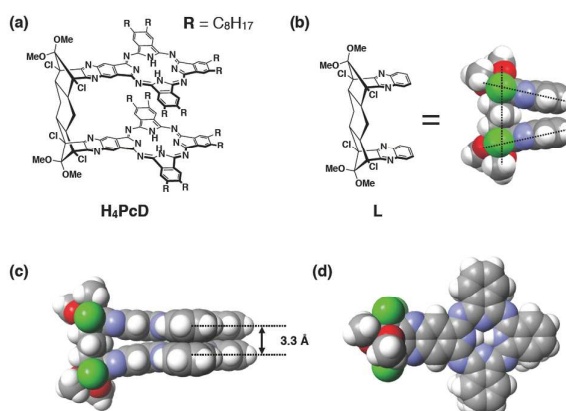
**Preparation of an accurate assembly of phthalocyanines is rather difficult because of the high aggregation property of phthalocyanines. In this study, a novel discrete phthalocyanine dimer was prepared in which the relative configuration of each component was tightly and accurately fixed in an *H*-aggregate 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.<sup>1–3</sup> Inspired by these phenomena occurring in the biological systems, considerable efforts have been made to create artificial photosystems based on cofacial assemblies of porphyrinoids.<sup>4,5</sup> While it is crucial to exert control over the special configuration of the components in order to generate effective electronic communication between them, synthesis of a conjugate with 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.<sup>6</sup> In particular, their strong and broad Q-bands in the visible light region are considered to be suitable for fabricating an artificial photoantenna.<sup>6b,7,8</sup> 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.<sup>8,9</sup> 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.<sup>7b,8b,10</sup> 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 **H<sub>4</sub>PcD** is shown in Figure 1a. In order to minimize the structural fluctuations of the relative configuration between



**Figure 1.** (a) Chemical structure of **H<sub>4</sub>PcD**. (b) Chemical and X-ray crystal structure of **L**.<sup>11</sup> (c) Side view and (d) top view of a CPK molecular model of **H<sub>4</sub>PcD** (MM3, SCIGRESS v.2.1.0 (Fujitsu), C<sub>8</sub>H<sub>17</sub> sidechains of the phthalocyanine units were omitted for clarity).

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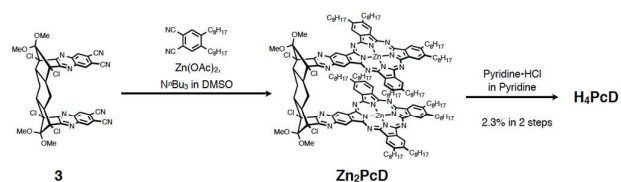
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Electronic Supplementary Information (ESI) available: Experimental section, detailed synthesis, characterization data, crystallographic data, UV-Vis spectra, CVs, and spectroelectrochemistry data. See DOI: 10.1039/x0xx00000x

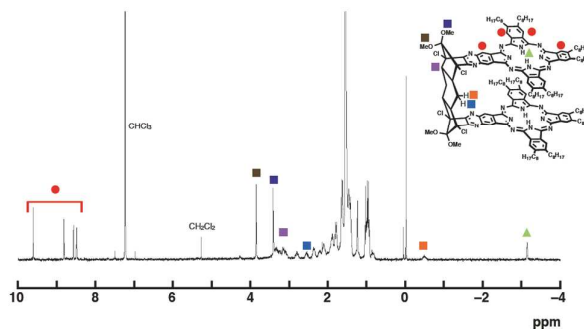
the phthalocyanines, the bridge should be robust. Hence, the *syn*-bis-quinoxaline-based U-shaped bridge **L** developed by Chou et al. was chosen.<sup>11</sup> This bridge is suitable for fixing the two planar components in a *H*-aggregate fashion because each planar molecule can stack on another without structural fluctuation supported by the  $\pi$ -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 (Figure 1b). Therefore, the phthalocyanine units in **H<sub>4</sub>PcD** are also expected to stack close to each other and form the *H*-aggregate, as revealed in the molecular model (Figures 1c and 1d).

The synthesis of **H<sub>4</sub>PcD** started from the formation of quinoxaline; the reaction between bis- $\alpha$ -diketone **1**<sup>11</sup> and 1,2-diamino-4,5-dibromobenzene gave **2**, and subsequent cyanation with CuCN afforded *syn*-bis-dicyanoquinoxaline **3** (Scheme S1 in the Supporting Information). Phthalocyanine formation by condensation of **3** with 4,5-dioctylphthalonitrile in DMSO in the presence of Zn(OAc)<sub>2</sub> and <sup>n</sup>Bu<sub>3</sub>N afforded the desired Zn(II)phthalocyanine dimer **Zn<sub>2</sub>PcD** (Scheme 1). After removal of zinc ion from **Zn<sub>2</sub>PcD** by heating with pyridine-HCl in pyridine,<sup>12</sup> the metal-free phthalocyanine dimer **H<sub>4</sub>PcD** was obtained. It should be noted that our attempt of phthalocyanine formation in the absence of Zn(OAc)<sub>2</sub> was not successful, implying that the template effect of zinc ion worked effectively. It was also found that zinc ion was a more suitable template than nickel ion 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. Attempt to introduce bulky *t*-butyl units instead of *n*-octyloxy groups proved unsuccessful, probably because of steric repulsion between the *t*-butyl units during the formation of the phthalocyanine dimer.



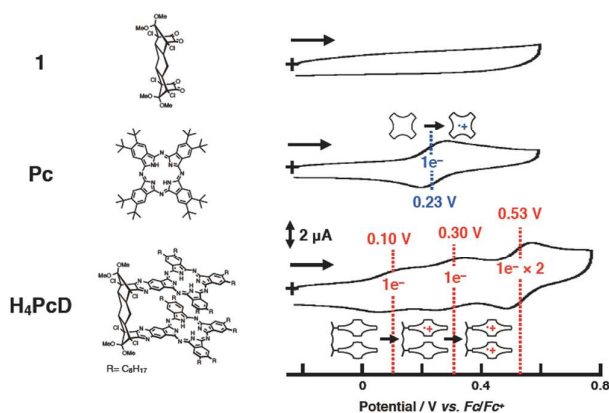
**Scheme 1.** Synthesis of **H<sub>4</sub>PcD**.

The structure of **H<sub>4</sub>PcD** was confirmed by elemental analysis, <sup>1</sup>H-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 [**H<sub>4</sub>PcD**+H]<sup>+</sup> (Figure S7 in the Supporting Information). In the <sup>1</sup>H-NMR spectrum (Figure 2), **H<sub>4</sub>PcD** showed four different singlets in the aromatic region. This clearly indicated that the two A<sub>3</sub>B-type phthalocyanine rings in **H<sub>4</sub>PcD** 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



**Figure 2.** <sup>1</sup>H-NMR spectrum of **H<sub>4</sub>PcD** in CDCl<sub>3</sub> at 293 K.

phthalocyanine rings.<sup>13</sup> UV-Vis spectrum showed broad bands from 550 to 800 nm, which were assigned as the Q-band of phthalocyanine (Figure S8). These were significantly broadened in comparison to those of typical A<sub>3</sub>B-type phthalocyanine monomers.<sup>14,6b,8b</sup> This might be a result of the  $\pi$ -expanded structure in conjunction with the quinoxaline unit.<sup>15</sup> Considering all of these results together, the spatial arrangements of the two phthalocyanines in **H<sub>4</sub>PcD** were successfully fixed in the *H*-aggregate form with the help of the robust bridging unit.



**Figure 3.** Cyclic voltammograms of **1**, **Pc**, and **H<sub>4</sub>PcD** in CH<sub>2</sub>Cl<sub>2</sub> containing 100 mM <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> at a scan rate of 100 mV/s at 298 K.

Cyclic voltammograms of **H<sub>4</sub>PcD** were measured in a CH<sub>2</sub>Cl<sub>2</sub> solution (200  $\mu$ M) containing 100 mM <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> to evaluate the electronic communication between the two phthalocyanines. Reversible 1e<sup>-</sup> redox waves were observed at 0.10 V and 0.30 V vs. Fc/Fc<sup>+</sup>, whereas two quasi-reversible 1e<sup>-</sup> oxidation waves overlapped each other at 0.53 V (Figure 3). By comparison with the redox waves of the reference compounds **1** and **Pc**<sup>16</sup>, 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<sup>-</sup> oxidations of the chemically identical phthalocyanines occurred at different redox potentials suggests that the phthalocyanine radical cation in **H<sub>4</sub>PcD**<sup>•+</sup> was significantly stabilized by the electronic interactions between the two cofacially stacked phthalocyanines. To evaluate the electronic

interaction, we calculated the comproportionation constant  $K_c$ <sup>17</sup>, 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 **H<sub>4</sub>PcD** was  $2.7 \times 10^3$ , which is one of the highest values among the discrete cofacial assemblies of phthalocyanines.<sup>10a,10c,13c</sup> This is apparently the benefit of the tightly fixed *H*-aggregate form of the two phthalocyanines in **H<sub>4</sub>PcD**.

## Conclusions

In summary, we synthesized a novel discrete *H*-dimer of phthalocyanines, **H<sub>4</sub>PcD**, 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 **H<sub>4</sub>PcD** 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.<sup>11</sup> Since phthalocyanines are an interesting building block to construct supramolecular stacked assemblies, we expect that **H<sub>4</sub>PcD** itself would also be a good building block for fabricating functional supramolecular assemblies.

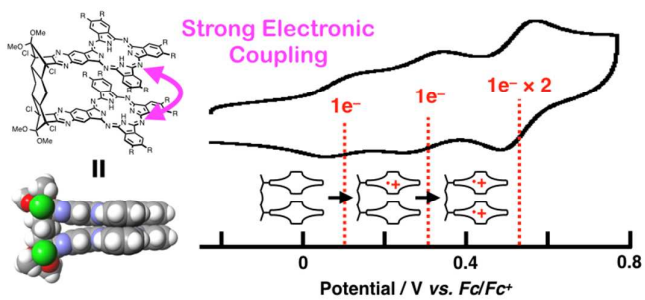
## Acknowledgements

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## Notes and references

- (a) P. Jordan, P. Fromme, H. T. Witt, O. Klukas, W. Saenger, N. Krauß, *Nature*, 2001, **411**, 909–917. (b) A. Ben-Shem, F. Frolow, N. Nelson, *Nature*, 2003, **426**, 630–635. (c) A. Amunts, O. Droy, N. Nelson, *Nature*, 2007, **447**, 58–63. (d) X. Qin, M. Suga, T. Kuang, J.-R. Shen, *Science*, 2015, **348**, 989–995.
- (a) D. M. Jonas, M. J. Lang, Y. Nagasawa, T. Joo, G. R. Fleming, *J. Phys. Chem.*, 1996, **100**, 12600–12673. (b) T. Renger, E. Schlodder, *ChemPhysChem*, 2010, **11**, 1141–1153.
- D. Gust, T. A. Moore, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guiard, Academic Press, New York, 2000, vol. 8, p153–202.
- (a) P. D. Harvey, C. Stern, R. Guillard, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith, R. Guiard, World Scientific, Singapore, 2011, vol. 11, p5–179. (b) S. Fukuzumi, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith, R. Guiard, World Scientific, Singapore, 2011, vol. 10, p183–243.
- (a) A. Satake, Y. Kobuke, *Org. Biomol. Chem.*, 2007, **5**, 1679–1691. (b) Y. Kobuke, *Eur. J. Org. Chem.*, 2006, 2333–2351.
- (a) D. Dini, M. Hanack, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guiard, Academic Press, New York, 2003, vol. 17, p1–36. (b) K. Ishii, N. Kobayashi, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guiard, Academic Press, New York, 2003, vol. 16, p1–42.
- (a) G. Bottari, O. Trukhina, M. Ince, T. Torres, *Coord. Chem. Rev.*, 2012, **256**, 2453–2477. (b) F. D'Souza, E. Maligaspe, K. Ohkubo, M. Zandler, N. K. Subbaiyan, S. Fukuzumi, *J. Am. Chem. Soc.*, 2009, **131**, 8787–8797.
- (a) A. W. Snow, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guiard, Academic Press, New York, 2003, vol. 17, p129–176. (b) T. Fukuda, N. Kobayashi, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith, R. Guiard, World Scientific, Singapore, 2011, vol. 9, p1–644.
- (a) M. S. Rodríguez-Morgade, G. de la Torre, T. Torres, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guiard, Academic Press, New York, 2003, vol. 15, p125–160. (b) W. M. Sharman, J. E. van Lier, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guiard, Academic Press, New York, 2003, vol. 15, p1–60.
- (a) Z. Odabas, F. Dumludağ, A. R. Özkaya, S. Yamauchi, N. Kobayashi, Ö. Bekaroğlu, *Dalton Trans.*, 2010, **39**, 8143–8152. (b) E. Ciliberto, K. A. Doris, W. J. Pietro, G. M. Reisner, D. E. Ellis, I. Fragalá, F. H. Herbstein, M. A. Ratner, T. J. Marks *J. Am. Chem. Soc.*, 1984, **106**, 7748–7761. (c) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, *Inorg. Chem.*, 1990, **29**, 3415–3425. (d) A. Lützen, S. D. Starnes, D. M. Rudkevich, J. Rebek Jr., *Tetrahedron Lett.*, 2000, **41**, 3777–3780. (e) K. Kameyama, M. Morisue, A. Satake, Y. Kobuke, *Angew. Chem. Int. Ed.*, 2005, **44**, 4763–4766.
- T.-C. Chou, K.-C. Liao, J.-J. Lin, *Org. Lett.*, 2005, **7**, 4843–4846.
- J. Alzeer, P. J. C. Roth, N. W. Luedtke, *Chem. Commun.*, 2009, **45**, 1970–1971.
- (a) Y. Yamada, M. Okamoto, K. Furukawa, T. Kato, K. Tanaka, *Angew. Chem. Int. Ed.*, 2012, **51**, 709–713. (b) Y. Yamada, N. Mihara, K. Tanaka, *Dalton Trans.*, 2013, **42**, 15873–15876. (c) Y. Yamada, T. Kato, K. Tanaka, *Chem. Eur. J.*, 2016, **22**, 12371–12380. (d) Y. Yamada, T. Kubota, M. Nishio, K. Tanaka, *J. Am. Chem. Soc.*, 2014, **136**, 6505–6509.
- N. Kobayashi, J. Mack, K. Ishii, M. J. Stillman, *Inorg. Chem.*, 2002, **41**, 5350–5363.
- We also checked the concentration dependence of the UV-Vis spectrum of **H<sub>4</sub>PcD** to conclude that **H<sub>4</sub>PcD** did not form aggregates at least at the concentration of 1  $\mu$ M (see Figure S9 in the Supporting Information).
- N. R. S. Gobo, T. J. Brocksom, J. Zukerman-Schpector, K. T. de Oliveira, *Eur. J. Org. Chem.*, 2013, 5028–5031.
- C. Creuz, *Prog. Inorg. Chem.* 1983, **30**, 1-73 and references therein.

## Graphical Abstract



This is the first example of a discrete dimer of phthalocyanines in a H-aggregated form. Intramolecular Strong Electronic Coupling was observed between the phthalocyanines electrochemically.