

A porphyrin nanochannel: formation of cationic channels by a protonated saddle-distorted porphyrin and its inclusion behavior†

Ryosuke Harada and Takahiko Kojima*

Received (in Cambridge, UK) 21st September 2004, Accepted 5th November 2004

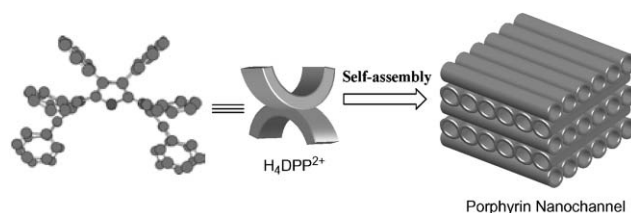
First published as an Advance Article on the web 15th December 2004

DOI: 10.1039/b414483j

A highly saddle-distorted dodecaphenylporphyrin dication ($\text{H}_4\text{DPP}^{2+}$) was revealed by X-ray crystallography to form positively charged porphyrin nanochannels which were 1 nm in diameter; chloride anion and redox-active hydroquinone could be incorporated in the channels.

Porphyrins are promising building blocks for constructing and creating a variety of functional materials, which can be responsible for photo-induced energy and electron transfer reactions,^{1,2} formation of specific environments for performing chemical reactions³ and molecular recognition.⁴ Aggregation of porphyrin arrays has been extensively studied and developed in terms of specific properties and reactivities. As can be found in Nature, porphyrin aggregation is known to be involved in the light-harvesting complex of bacteriochlorophylls to perform photo-induced energy transfer followed by electron transfer from water to plastoquinone to generate dioxygen for ATP and NADPH production.⁵

Nanomaterials based on porphyrin scaffolds have received much attention due to the scientific and technological benefits derived from the spectrum of chemical and physical properties mentioned above. In addition, preparation and functions of porous materials based on porphyrin complexes as building blocks have also been developed.^{6,7} Among those, porphyrin-based channel structures have been attractive objectives due to their potentials toward functional materials.⁸ We have focused on developing new functional materials on the basis of distorted porphyrins, which can construct unique curved surfaces in place of normal planar structures.⁹ Those porphyrins will afford unusual aggregation patterns, which cannot be achieved by planar porphyrin scaffolds. Recently, we reported a metalloporphyrin nanotube to include fairly large molecules such as tetranuclear molybdenum-oxo clusters.⁹ We have demonstrated that reactive and unstable substances are protected in the inner space of the nanotube from external lethal attack to undergo degradation. To construct redox-active functional materials based on porphyrin nanostructures, we took advantage of the curved surface(s) of saddle-distorted porphyrin and adopted dodecaphenylporphyrin dication ($\text{H}_4\text{DPP}^{2+}$)¹⁰ as a building block for novel nanochannels as shown in Scheme 1. We describe herein the first example of the preparation and the crystal structure of a protonated porphyrin nanochannel, which is reminiscent of zeolites, including *p*-hydroquinone (H_2Q) as a redox-active substance inside the channels.



Scheme 1

Co-crystallization of $[\text{H}_4\text{DPP}^{2+}]\text{Cl}_2 \cdot 4\text{CH}_3\text{CN}$ and an excess amount of H_2Q in $\text{CHCl}_3/\text{CH}_3\text{CN}$ afforded a cationic nanochannel including H_2Q ($[\text{H}_4\text{DPP}^{2+}]\text{Cl}_2 \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{Q}$; **1**).[†] Fig. 1 shows a side-view of the nanochannel of **1**. The $\text{H}_4\text{DPP}^{2+}$ unit showed larger distortion compared to that in $[\text{Mo}(\text{DPP})(\text{O})(\text{H}_2\text{O})]^{+}$ consisting of the porphyrin nanotube.⁹ Two porphyrin dications create a ring having 1 nm diameter with intermolecular π - π interactions between peripheral phenyl groups with 3.46 Å separation. The rings are connected together by weak π - π interactions with distances ranging from 3.56 to 3.71 Å to form the channels. The channels run below and above the individual porphyrin mean plane with an angle of 71° in the directions of [1 1 0] and [1 -1 0] in the crystal,¹¹ as can be seen in the crystal packing of **1** depicted in Fig. 2. The chloride anion was found to form hydrogen bonding with the pyrrole N-H proton with a distance of 3.22 Å. Also, H_2Q was found to interact weakly with porphyrin pyrrole rings *via* π - π interactions with a distance of 3.73 Å, and also with the DPP-phenyl groups showing 3.74 Å separation. Those π - π interactions operated in a T-shape (edge-to-face) orientation, not in a face-to-face fashion. The π - π interactions are thought to be the driving force to include aromatic substrates in the inner space as shown in Fig. 3.

The mechanism of inclusion of H_2Q was considered for a mixture of $[\text{H}_4\text{DPP}]\text{Cl}_2 \cdot 4\text{CH}_3\text{CN}$ and H_2Q by using VT-NMR spectroscopy in a $\text{CDCl}_3/\text{CD}_3\text{CN}$ mixed solution. A singlet

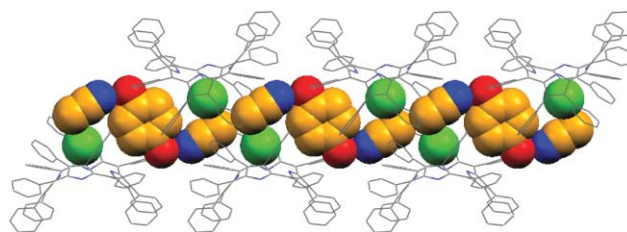


Fig. 1 A side view of the crystal structure of **1**. The $\text{H}_4\text{DPP}^{2+}$ unit is represented by gray wires. Orange, carbon; blue, nitrogen; red, oxygen; green, chloride.

† Electronic supplementary information (ESI) available: experimental section. See <http://www.rsc.org/suppdata/cc/b4/b414483j/>
*cosyscc@mbox.nc.kyushu-u.ac.jp

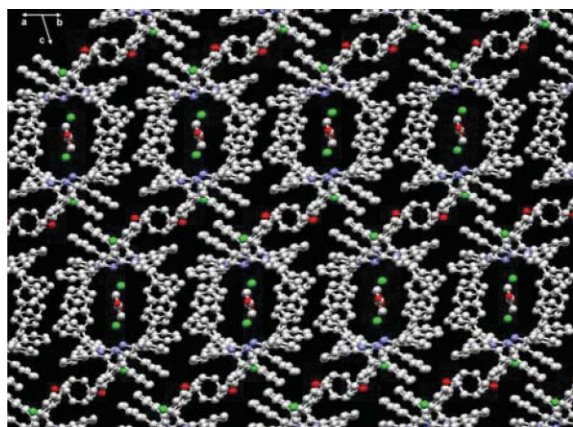


Fig. 2 A packing diagram of **1** (CH_3CN molecules are omitted for clarity). White, carbon; blue, nitrogen; green, chloride; red, oxygen.

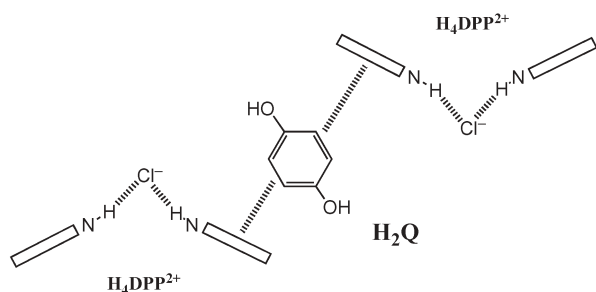


Fig. 3 Schematic description of non-covalent interactions around H_2Q in **1**.

assigned to the OH group of H_2Q exhibited a downfield shift and a broad singlet ascribed to porphyrin N–H protons showed an upfield shift (Fig. 4). These observations indicate the formation of hydrogen bonding between the OH group of H_2Q and Cl^- and this renders the polarization of OH and NH groups more positive and less negative, respectively. Thus, intermolecular hydrogen bonding is thought to be a dominant driving force to include H_2Q .

Redox potentials of $[\text{H}_4\text{DPP}]\text{Cl}_2 \cdot 4\text{CH}_3\text{CN}$ and H_2Q were determined in CH_2Cl_2 and CH_3CN , respectively. The porphyrin dication showed a reversible one-electron redox couple at $E_{1/2} = +1.26$ V (vs. SCE) in the presence of 0.1 M $\text{CH}_3\text{SO}_3\text{H}$. H_2Q exhibited a redox wave at +1.27 V (vs. SCE) due to a two-electron oxidation process (Figure S1, ESI). These results suggest that photoinduced electron transfer could occur from H_2Q to a photoexcited porphyrin dication and this may provide a novel pathway of photoinduced electron transfer performed by porphyrin systems.

In summary, we have demonstrated the first example of “porphyrin nanochannel” by using curved surfaces derived from dicationic $\text{H}_4\text{DPP}^{2+}$ to form cationic channels with π – π interactions. Due to the di-protonation to form hydrogen bonding receptor sites, this type of cationic porphyrin channels could use hydrophilic hydrogen bonding concomitant with hydrophobic π – π interactions. Thus, functional molecules such as quinones can be included by non-covalent interactions into the channels. This discovery of the porphyrin nanochannels can provide a new strategy for porphyrin-based functional nanomaterials to target

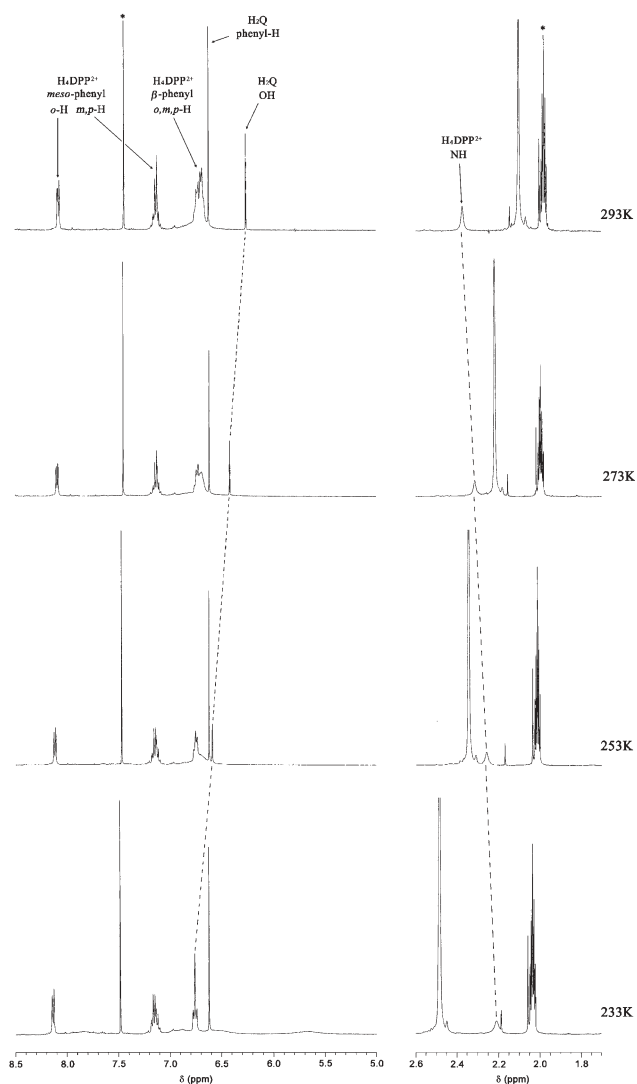


Fig. 4 VT-NMR of the mixture of $[\text{H}_4\text{DPP}]\text{Cl}_2 \cdot 4\text{CH}_3\text{CN}$ and *p*-hydroquinone in $\text{CDCl}_3/\text{CD}_3\text{CN}$.

novel photochemical devices in view of photoinduced electron and energy transfer.

Ryosuke Harada and Takahiko Kojima*

Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Higashi-Ku, Fukuoka 812-8581, Japan.

E-mail: cosyscc@mbox.nc.kyushu-u.ac.jp; Fax: +81-92-642-2570;

Tel: +81-92-642-4179

Notes and references

‡ Crystal data for **1**: $\text{C}_{102}\text{H}_{68}\text{N}_6\text{O}_2\text{Cl}_2$; monoclinic, $C2/c$, $a = 17.510(5)$, $b = 24.761(6)$, $c = 19.587(5)$ Å, $\beta = 108.711(4)^\circ$, $V = 8043.7$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.223$ g cm⁻³, 9102 unique reflections ($R_{\text{int}} = 0.051$), $R1 = 0.082$ ($I > 2\sigma(I)$), $Rw = 0.238$, GOF = 1.33. CCDC 247692. See <http://www.rsc.org/suppdata/cc/b4/b414483j/> for crystallographic data in .cif or other electronic format.

- M.-S. Choi, T. Aida, M. Yamazaki and I. Yamazaki, *Chem.-Eur. J.*, 2002, **8**, 2668; T. Konishi, A. Ikeda, M. Asai, T. Hatano, S. Shinkai, M. Fujitsuka, O. Ito, Y. Tsuchiya and J. Kikuchi, *J. Phys. Chem. B*, 2003, **107**, 11261; N. Eugster, D. J. Fermín and H. H. Girrault, *J. Am. Chem. Soc.*, 2003, **125**, 4862; M.-S. Choi, T. Aida, H. Luo, Y. Araki and

- O. Ito, *Angew. Chem., Int. Ed.*, 2003, **42**, 4060; K. Okamoto, Y. Mori, Y. Yamada, H. Imahori and S. Fukuzumi, *Chem.-Eur. J.*, 2004, **10**, 474; K. Ogawa, A. Ohashi, Y. Kobuke, K. Kamada and K. Ohta, *J. Am. Chem. Soc.*, 2003, **125**, 13356; D. Gust, T. A. Moore, A. L. Moore, X. C. Ma, R. A. Nieman, G. R. Seely, R. E. Belford and J. E. Lewis, *J. Phys. Chem.*, 1991, **95**, 4442.
- 2 S. Furu, T. Isobe, S. Takagi, D. A. Tryk and H. Inoue, *J. Am. Chem. Soc.*, 2003, **125**, 5734.
- 3 Y. Aoyama, M. Asakawa, Y. Matsui and H. Ogoshi, *J. Am. Chem. Soc.*, 1991, **113**, 6233; Y. Aoyama, M. Asakawa, A. Yamagishi, H. Toi and H. Ogoshi, *J. Am. Chem. Soc.*, 1990, **112**, 3145.
- 4 B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts and J. D. Watson, *Molecular Biology of the Cell*, 3rd Edn.; Garland Publishing: New York, 1994; pp. 691–695.
- 5 K. Yamaguchi, N. Ishii, K. Tashiro and T. Aida, *J. Am. Chem. Soc.*, 2003, **125**, 13934.
- 6 M. P. Bryn, C. J. Curtis, Y. Hsiou, S. I. Khan, P. A. Sawin, S. K. Tendick, A. Terzis and C. E. Strouse, *J. Am. Chem. Soc.*, 1993, **115**, 9480; M. P. Bryn, C. J. Curtis, I. Goldberg, Y. Hsiou, S. I. Khan, P. A. Sawin, S. K. Tendick and C. E. Strouse, *J. Am. Chem. Soc.*, 1991, **113**, 6549; M. P. Bryn and C. E. Strouse, *J. Am. Chem. Soc.*, 1991, **113**, 2501; M. P. Bryn, C. J. Curtis, S. I. Khan, P. A. Sawin, R. Tsurumi and C. E. Strouse, *J. Am. Chem. Soc.*, 1990, **112**, 1865.
- 7 Y. Diskin-Posner, G. K. Patra and I. Goldberg, *Eur. J. Inorg. Chem.*, 2001, 2515; Y. Diskin-Posner, S. Dahal and I. Goldberg, *Angew. Chem., Int. Ed.*, 2000, **39**, 1288.
- 8 B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727; P. Bhyrappa, S. R. Wilson and K. S. Suslick, *J. Am. Chem. Soc.*, 1997, **119**, 8492; C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger and R. D. Rogers, *J. Am. Chem. Soc.*, 1999, **121**, 1137; K.-J. Lin, *Angew. Chem., Int. Ed.*, 1999, **38**, 2730; M. E. Kosal, J.-H. Chou, S. R. Wilson and K. S. Suslick, *Nat. Mater.*, 2002, **1**, 118.
- 9 R. Harada, Y. Matsuda, H. Okawa and T. Kojima, *Angew. Chem., Int. Ed.*, 2004, **43**, 1825.
- 10 Structure of H₂DPP: C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1992, **114**, 9859.
- 11 The angle (θ) between channels was estimated as follows: $\tan((\pi - \theta)/2) = |b|/|a|$.