ARTICLE TYPE

Multiply-Fused Porphyrins—Effects of Extended π-Conjugation on the Optical and Electrochemical Properties

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A novel quadruply-fused porphyrin has been synthesized with a facilely prepared precursor in a high yield. Detailed comparison of the physical properties for a series of fused
10 porphyrins revealed remarkable effects of the ring fusion on lowering LUMO levels rather than HOMO levels.

π-Conjugated organic molecules exhibiting long-wavelength absorption and high tendency to form intermolecular π-π stacking structures have attracted considerable attention due to interests
15 for the application to organic semiconductors and organic photovoltaic cells.[1-3] Tetraphenylporphyrin (TPP),[4] a representative of synthetic porphyrins,[5] and the derivatives are promising candidates as functional dyes for the purpose mentioned above, because of the highly-extended π-conjugation,
20 facileness of the synthesis and of introduction of functional groups, and the robustness among the organic dyes.[4] TPP, however, cannot form strong intermolecular π-π stacking with the porphyrin core due to the steric repulsion of the *meso*-phenyl groups,[6] and thus, it cannot be directly used to construct π-π
25 stacked one-dimensional molecular wires, which are very important to construct molecule-based optoelectronic materials.[7]

On the other hand, modification of porphyrins with introduction of fused rings on the periphery of the porphryin aromatic circuit have been intensively studied recently,[8-14]
30 because of the merits of the unique physical properties derived from the narrowed HOMO-LUMO gaps. The ring-fusion strategy has been successfully applied to obtain a chromophore showing an absorption band over 1,400 nm based on one porphyrin unit,[12] and by increasing the number of porphyrin units fused, the
35 longest absorption band can reach the infrared region.[13] In particular, *meso*-β-arene-fused derivatives[10-14] exhibit larger red-shifts of the optical absorption bands and smaller HOMO-LUMO gaps, compared to β-β-arene fused derivatives.[9] However, the ring-fusing reactions reported so far are highly limited and the
40 synthetic procedures for the precursors are time-consuming.

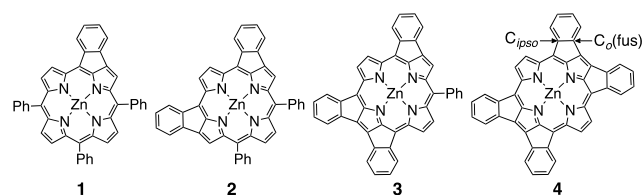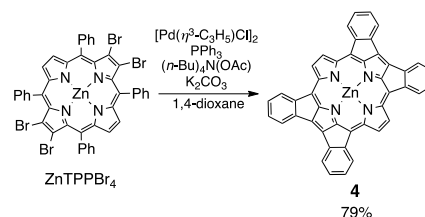Herein, we report the facile and efficient procedure for the

Fig. 1 Structures of fused porphyrins **1**–**4**.

45 **Scheme. 1** Synthetic route of quadruply-fused porphyrin **4**.

preparation of a quadruply ring-fused porphyrin (**4** in Fig. 1), in which the four *meso*-phenyl groups are covalently bonded to the
50 β-carbons of the pyrrole rings at the *ortho*-positions. The precursor of the fused porphyrin, zinc(II) 2,3,12,13-tetrabromo-tetraphenyl-porphyrinate (ZnTPPBr$_4$), was easily prepared with two-step procedure from TPP[15] and thus can be easily modified by changing tetraarylporphyrin precursors. In addition, the ring-
55 fused porphyrins are highly planar with extended π-conjugation, showing strong π-π stacking tendency and physical properties based on the narrowed HOMO-LUMO gaps.

The ring-fusing reactions of ZnTPPBr$_4$ were conducted by direct C-H activation in the presence of a Pd catalyst.[16] The key
60 factor of the reaction is the selection of the Pd catalyst. The usual molecular Pd catalysts, such as Pd(PPh$_3$)$_4$, did not afford the fully fused product **4**, but the partially fused products, **1** and **2** (Table S1 in Electronic Supplementary Information (ESI)).[14c] In sharp contrast, when Pd-nanoclusters derived from [Pd(η^3-C$_3$H$_5$)Cl]$_2$
65 were employed as the catalyst (Scheme 1),[17] the quadruply fused **4** was obtained in 79% yield accompanying the triply fused **3** as a minor product in 11% yield. The isolation of **4** is very easily performed by virtue of the low solubility to organic solvents. The reaction mixture was filtered to remove the Pd catalyst and other
70 insoluble materials, and then the solvent of the filtrate was evaporated under vacuum. The residual solid was dissolved in THF and the remaining violet solid was filtered to give a red-brown filtrate. The solid obtained mainly included **4** and the recrystallization from THF-EtOH in the presence of 1 drop of
75 pyridine to increase the solubility gave **4** with a pyridine molecule as an axial ligand (**4**-py) in the pure form. In addition, the major component of the red-brown filtrate in THF was the triply fused **3** and further purification by preparative-scale thin-layer chromatography on silica gel followed by recrystallization
80 from THF/hexane gave violet crystals of **3**. The singly-fused **1** and doubly-fused **2**[18] were also obtained from the reactions under different conditions using Pd-nanoclusters derived from

Pd(OAc)₂ as catalysts (entry 2 in Table S1 in ESI).[17, 19]

Characterization of the ring-fused porphyrins was performed by ¹H NMR spectroscopy, MALDI-TOF-MS spectrometry, elemental analysis[19] and X-ray crystallography (*vide infra*). The ⁵ ¹H NMR spectrum of **4** in DMSO-d_6 displayed a simple signal pattern reflecting the symmetric structure and eight ¹H NMR signals including three signals due to a free pyridine molecule[20] were observed (Fig. S2 in ESI). Each signal of **4** was assigned on the basis of the ¹H-¹H COSY spectrum (Fig. S3 in ESI). The ¹H ¹⁰ NMR spectrum of **3** showed relatively complicated pattern due to the low-symmetric structure (Fig. S2b in ESI).

Recrystallization of **1**–**4** gave single crystals appropriate for X-ray diffraction analysis.[21] The ORTEP drawings of **1**-THF, **2**, **3**, and **4**-py are shown in Fig. 2. Compounds **1** and **4** took a THF ¹⁵ and a pyridine (py) molecule, respectively, from the recrystallization solvents as axial ligands on the central Zn^II ions, whereas **2** and **3** did not have any axial ligand. As one of the characteristics of the ring-fused porphyrins in the crystal structures, the bond lengths between the central Zn^II ion and the ²⁰ nitrogen atoms of the pyrrole rings involved in the ring-fused structures were much shortened than those for the Zn^II and the nitrogen atoms of non-fused pyrrole rings (Table S2 in ESI): For instance, in **4**-py, the bond distance of Zn-N2 and Zn-N4 were found to be 1.894(2) Å and 1.900(2) Å, respectively, involving ²⁵ the fused-ring nitrogens, whereas those of Zn-N1 and Zn-N3 were 2.196(5) Å and 2.126(5) Å, respectively, involving the non-fused pyrrole nitrogens. On the other hand, the Zn-N bond lengths in ZnTPP were almost identical.[6] The difference in the Zn-N bond lengths observed for the fused and non-fused pyrroles ³⁰ is probably caused by rigidity of the fused ring structure, which results in shrinkage of the N2···N4 distance and elongation of the N1···N3 distance. The rhombic deformation of the porphyrin core by the ring fusion is confirmed by the density-functional-theory (DFT)-optimized structure of the free-base porphyrin of **4** ³⁵ (Fig. S4 in ESI), where the N1···N3 distance is 4.59 Å and the N2···N4 distance is 3.43 Å. Another feature found in the crystal structures of the fused porphyrins was the long bond lengths between the *ipso*-carbon (C$_{ipso}$) of the fused phenyl groups and the *ortho*-carbon (C$_o$(fus)) of the same phenyl group in the ring-⁴⁰ fused moieties (see Fig. 1). The C-C bond lengths of non-fused phenyl groups and the C-C bond lengths except the C$_{ipso}$-C$_o$(fus) bond in the fused phenyl rings were almost equal to be *ca.* 1.39 Å, whereas the C$_{ipso}$-C$_o$(fus) bond lengths were *ca.* 1.44 Å in common to all the crystal structures of the fused porphyrins. The ⁴⁵ elongation of the C$_{ipso}$-C$_o$(fus) bond by *ca.* 0.05 Å indicates that a single bond is localized between C$_{ipso}$ and C$_o$(fus), and thus the π-conjugation circuit always avoids the C$_{ipso}$-C$_o$(fus) bond and the isolated aromaticity of the *meso*-phenyl groups is almost lost. Therefore, the larger aromatic circuits soaking into the fused ⁵⁰ phenyl rings in the fused porphyrins are recognized in the crystal structures.

The fused porphyrins obviously showed intermolecular π-π stacking structures in the crystal packing and the π-π stacking distances gradually shortened as the number of the fused rings ⁵⁵ increased. The THF-ligated **1** formed π-π stacking dimers, in which the interplane distance of the two porphyrins was 3.46 Å (Fig. S5 in SI). On the other hand, compounds **2** and **3** having no axial ligands formed π-stacked one-dimensional (1D)
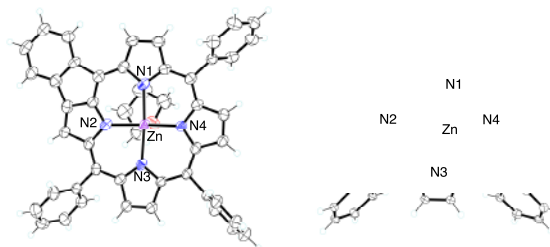

⁶⁰ **Fig. 2** Crystal Structures of **1**-THF (a), **2** (b), **3** (c), and **4**-py (d). The thermal ellipsoids are drawn with 50% probability.

supramolecular arrays in the crystals (Fig. S6 and Fig. S7 in ESI). Both the 1D arrays with **2** and with **3** exhibit two interplane ⁶⁵ distances of 3.43 and 3.58 Å for **2**, and of 3.28 and 3.36 Å for **3**, respectively. Concerning the π-π stacking distances of the three crystal structures, the order is **1**-THF (3.46 Å) > **2** (3.43 Å) > **3** (3.28 Å). This order indicates that increasing the number of the fused rings enhances the planarity of the molecule and ⁷⁰ simultaneously increases the number of the π-electrons involved in the π-conjugation. Due to the axial pyridine ligand, **4**-py showed a doming distortion of the fully fused porphyrin ligand in the crystal structure and the porphyrin core did not exhibit any intermolecular π-π stacking (Fig. S8 in ESI).

⁷⁵ To confirm the electronic effects of the ring-fusion on the porphyrin π-conjugation, we have measured the electronic absorption spectra and cyclic and differential-pulse voltammograms (CV and DPV) of the fused porphyrins (Table S3 in ESI). Due to the low solubility of **3** and **4**, we employed ⁸⁰ dimethylformamide (DMF) as the solvent for the absorption spectroscopy and electrochemical measurements. In the absorption spectra, both the Soret- and Q-like bands gradually red-shifted as increasing the number of the fused rings (Fig. 3). The lowest energy of the Q-like band was observed for **4**, ⁸⁵ reaching over 1,000 nm and the bathochromic shift was 420 nm relative to the longest Q-band of ZnTPP in DMF. In addition, the fused porphyrins absorb almost whole visible light and consequently, for example, the solution color of **4** in DMF is dark blue. All the fused porphyrins exhibited reversible first-oxidation ⁹⁰ and first-reduction waves in DMF, and reversible or pseudo-reversible second-oxidation and second-reduction waves (Fig. S9 in ESI). HOMO-LUMO gaps obtained from the first-oxidation and the first-reduction potentials become narrower with increasing the number of fused rings. It should be noted that the ⁹⁵ lowering of the LUMO level by ring-fusion was more remarkable than the rise of the HOMO level: For instance, the difference of the first reduction potentials between **4** (–0.67 V) and ZnTPP (–1.36 V) was 0.69 V, whereas that of the first oxidation potentials of **4** (+0.65 V) and ZnTPP (+0.83 V) was 0.18 V (Table S4 in ¹⁰⁰ ESI). To confirm the large effect of the ring-fusion on the LUMO level, we conducted DFT calculations on **4**. As a result, it was indicated that the HOMO was delocalized mainly on the porphyrin core, whereas the LUMO was expanded to the ring-

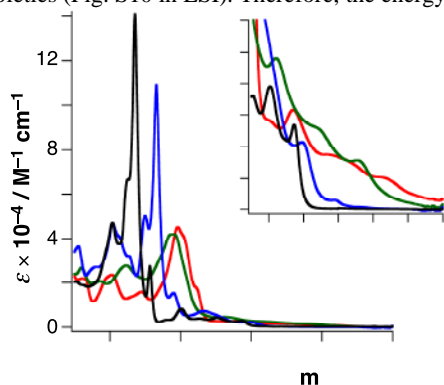fused moieties (Fig. S10 in ESI). Therefore, the energy level of

Fig 3. UV-Vis absorption spectra of fused porphyrins in DMF. **1** (black), **2** (blue), **3** (green), and **4** (red).

LUMO is strongly affected by the degree of ring-fusion, compared to that of HOMO.

In summary, we have synthesized a novel quadruply-fused porphyrin with an facilely prepared precursor in a high yield. In addition, we have isolated and fully characterized partly-ring-fused porphyrin derivatives. The crystal structures revealed the extension of the π-conjugation circuits to the fused *meso*-phenyl groups by the bond lengths between the *ipso*-carbon and the *ortho*-carbon bonded to the *β*-pyrrole carbon. In the crystal packing, the fused porphyrins exhibited strong intermolecular π-π stacking, reflecting the highly planar structures. The UV-Vis spectra and the electrochemical studies of the fused porphyrins indicate the narrowing of the HOMO-LUMO gaps by the extension of the ring-fusing reactions. The planar and π-extended porphyrins developed here would be applicable to various optoelectronic materials on the basis of the highly red-shifted absorption bands covering the entire visible wavelength region and the strong tendency to form one-dimensional molecular wires with intermolecular π-π stacking.

Notes and references

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† Electronic Supplementary Information (ESI) available: Complete experimental details of syntheses, compound characterization, summary for optical absorption and redox potentials, details for crystal structural analyses, DFT-optimized structures and cyclic and differential-pulse voltammograms. CCDC-929175, -929176, -929177 and -929178 contain the supplementary crystallographic data. See DOI: 10.1039/b000000x/
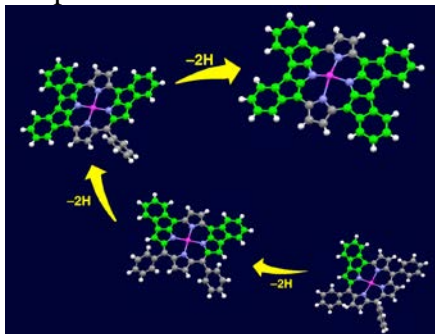
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18 The doubly-fused porphyrin contains three isomers; 7,22-&18,40-fused, **2**, 7,22-&17,34-fused, **2'**, and 7,22-&8,28-fused, **2"** (Figure S1 in ESI). **2** was the major product and easily isolated by column chromatography (see ref. 14). In this manuscript, the properties of **2** were used as the representative for the doubly-fused porphyrins.

19 See ESI.

20 The pyridine molecule was originally ligated on the central Zn^II of **4** during the recrystallization. Judging from the chemical shifts

observed, the pyridine molecule dissociates from the Zn^{II} upon dissolving in DMSO-d_6.

21 The crystal structure of **2** having THF as an axial ligand has been reported by Shen *et al.* (ref 14c).

Graphics for Table of Contents

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