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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. A detailed comparison of the physical properties of a series of fused 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 a high tendency to form intermolecular π - π stacking structures have attracted considerable attention due to their potential for application in organic semiconductors and organic photovoltaic cells.¹⁻³ Tetraphenylporphyrin (TPP),⁴ a representative of synthetic porphyrins,⁵ and its derivatives are promising candidates as functional dyes for the purpose mentioned above, because of the highly-extended π -conjugation, facileness of the synthesis and 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 stacked one-dimensional molecular wires, which are very important to construct molecule-based optoelectronic materials.⁷

On the other hand, modification of porphyrins by introduction of fused rings on the periphery of the porphyrin aromatic circuit has been intensively studied recently,⁸⁻¹⁴ 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 1400 nm based on one porphyrin unit,¹² and by increasing the number of porphyrin units fused, the 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-fusion reactions reported so far are highly limited and the synthetic procedures for the precursors are time-consuming.

Herein, we report a facile and efficient procedure for the preparation of a quadruply ring-fused porphyrin (4 in Fig. 1), in which the four *meso*-phenyl groups are covalently bonded to the 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 (ZnTPPBr₄), was easily prepared with a two-step procedure from TPP¹⁵ and thus can be easily modified by changing tetraarylporphyrin precursors. In addition, the ring-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-fusion reactions of ZnTPPBr₄ were conducted by direct C–H activation in the presence of a Pd catalyst.¹⁶ The key factor of the reaction is the selection of the Pd catalyst. The usual molecular Pd catalysts, such as Pd(PPh₃)₄, did not afford the fully fused product 4, but the partially fused products, 1 and 2 (Table S1 in the ESI†).^{14c} In sharp contrast, when Pd-nanoclusters derived from [Pd(η^3 -C₃H₅)Cl]₂ 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 was very easily performed by virtue of its low solubility in organic solvents. The reaction mixture was filtered to remove the Pd catalyst and other 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



Fig. 1 Structures of fused porphyrins 1-4.

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Scheme 1 Synthetic route to quadruply-fused porphyrin **4**.

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 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 using preparative-scale thin-layer chromatography on silica gel followed by recrystallization 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 the ESI†).^{17,19}

Characterization of the ring-fused porphyrins was performed using ¹H NMR spectroscopy, MALDI-TOF-MS spectrometry, elemental analysis¹⁹ and X-ray crystallography (*vide infra*). The 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 molecule²⁰ were observed (Fig. S2 in the ESI[†]). Each signal of **4** was assigned on the basis of the ¹H-¹H COSY spectrum (Fig. S3 in the ESI[†]). The ¹H NMR spectrum of **3** showed a relatively complicated pattern due to the low-symmetric structure (Fig. S2b in the 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 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 nitrogen atoms of the pyrrole rings involved in the ringfused structures were much shortened than those for the ${\rm Zn}^{\rm II}$ and the nitrogen atoms of non-fused pyrrole rings (Table S2 in the ESI⁺): for instance, in 4-py, the bond distances of Zn-N2 and Zn-N4 were found to be 1.894(2) Å and 1.900(2) Å, respectively, involving 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 is probably caused by the 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 (Fig. S4 in the 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 (Cipso) of the fused phenyl groups and the ortho-carbon (Co(fus)) of the same



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

phenyl group in the ring-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 *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 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 phenyl rings in the fused porphyrins are recognized in the crystal structures.

The fused porphyrins obviously showed intermolecular π - π stacking in the crystal packing and the π - π stacking distances gradually shortened as the number of the fused rings increased. The THF-ligated 1 formed π - π stacked dimers, in which the interplanar distance of the two porphyrins was 3.46 Å (Fig. S5 in the ESI[†]). On the other hand, compounds 2 and 3 having no axial ligands formed π -stacked one-dimensional (1D) supramolecular arrays in the crystals (Fig. S6 and S7 in the ESI⁺). Both the 1D arrays with 2 and with 3 exhibit two interplanar distances of 3.43 and 3.58 Å for 2, and 3.28 and 3.36 Å for 3, respectively. With respect to 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 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 the ESI⁺).

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 the ESI†). Due to the low solubility of **3** and **4**, we employed dimethylformamide (DMF) as the solvent for absorption spectroscopy and electrochemical measurements. In the absorption spectra, both the



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

Soret- and Q-like bands gradually red-shifted upon increasing the number of the fused rings (Fig. 3). The lowest energy of the Q-like band was observed for 4, reaching over 1000 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 and first-reduction waves in DMF, and reversible or pseudo-reversible second-oxidation and second-reduction waves (Fig. S9 in the ESI[†]). HOMO-LUMO gaps obtained from the firstoxidation and the first-reduction potentials become narrower with increasing the number of fused rings. It should be noted that the 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 the 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 the ESI[†]). Therefore, the energy level of 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 a 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-fusion 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 onedimensional molecular wires with intermolecular π - π stacking.

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- 18 The doubly-fused porphyrin contains three isomers, 7,22;18,40-fused, 2, 7,22;17,34-fused, 2', as well as 7,22;8,28-fused, 2" (Fig. S1 in the ESI[†]). 2 was the major product and could be easily isolated by column chromatography (see ref. 14).
- 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. 14*c*).