Endocyclic extension of porphyrin π-system in etheno-bridged N-confused tetraphenylporphyrin†

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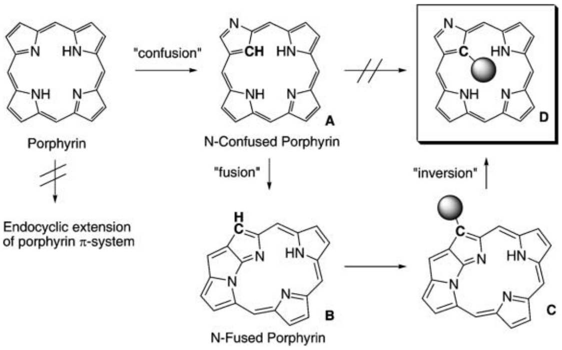
Etheno-bridged N-confused tetraphenylporphyrin was synthesized through flipping of the confused pyrrole ring and endocyclic extension of [18]annulenic π-conjugated system was exemplified by the absorption spectra as well as the calculated Kohn–Sham orbitals.

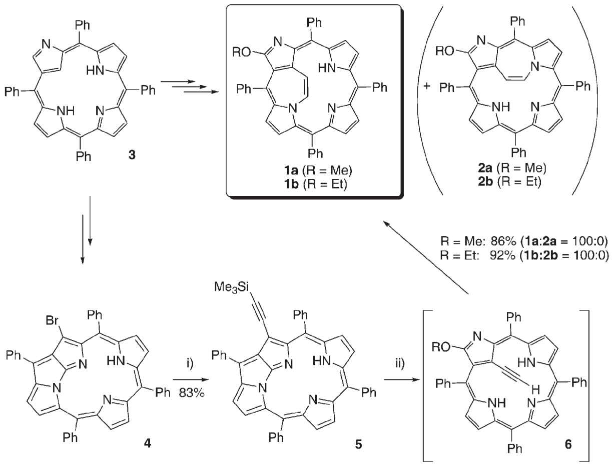
Extension of π-conjugated systems has continued to gain considerable attention, since it often leads to interesting physical properties, which would open up a new area of research in physical organic chemistry and materials science.[1] In most cases, the π-system extension in the cyclic compounds is achieved at the periphery of the molecules and examples of endocyclic extension are quite limited, probably due to the difficulty in regioselective chemical functionalization inside the macrocycles.

Porphyrins are well-known π-conjugated macrocyclic compounds and the exocyclic extension of the [18]annulenic π-system has been extensively studied.[2,3] Contrastingly, the endocyclic extension is usually considered to be impossible, since no accessible sp^2 carbon atoms are left inside the macrocyclic core. Meanwhile, a porphyrin analogue, carbaporphyrin, has a free sp^2 carbon atom in its core, and therefore, endocyclic π-system extension is essentially possible.[4] Nevertheless, a lack of a general method to introduce substituents into the inner sp^2 carbon atom, certainly due to the steric problem, has hindered the progress of research. One fascinating remedy against such a difficulty could be a *confusion* approach which utilizes the inversion of pyrrole rings.[5] In N-confused porphyrins,[6] the regioselective introduction of a bulky substituent into the inner sp^2 carbon atom was achieved by using the ring flip of the confused pyrrole (Scheme 1).[7,8] Through the transformation from N-confused porphyrin (**A**) to N-fused porphyrin (**B**), the carbon atom originally placed inside the core moves to the peripheral position. Chemical functionalization of the exposed sp^2 carbon atom in **B** would be easily accomplished to give the functionalized N-fused porphyrin (**C**) and a further treatment with a nucleophile causes the regeneration of N-confused porphyrin (**D**), where the functional group is located inside the core. This time, the endocyclic extension of the porphyrin π-system has been achieved by the *confusion* approach and etheno-bridged N-confused tetraphenylporphyrins (**1a** and **1b**) are successfully synthesized, where the extension of the porphyrin π-system is confirmed by the absorption spectra as well as the calculated Kohn–Sham orbitals.[9]



Scheme 1 *Confusion* approach to endocyclic chemical functionalization of porphyrins.

The preparation of the etheno-bridged N-confused tetraphenylporphyrins was carried out as shown in Scheme 2. Starting from N-confused tetraphenylporphyrin (**3**), the brominated N-fused tetraphenylporphyrin (**4**) was synthesized in two steps as reported previously.[10,11] Then, a trimethylsilylethynyl group was introduced by Pd-catalyzed Stille coupling reaction of **4** with the corresponding tin reagent to give the alkynylated product (**5**) in 83% yield. Finally, the inversion of the confused pyrrole ring was examined by treatment of **5** with NaOMe or NaOEt in THF. Surprisingly, the isolated product was not the expected N-confused porphyrin having an alkynyl group at the core but the etheno-bridged N-confused tetraphenylporphyrins. While no direct evidence is obtained yet, **1** would be produced by the intramolecular addition reaction of the pyrrolic nitrogen to the alkyne moiety *via* the



i) Bu_3Sn—≡—$SiMe_3$ (5 equiv), $Pd(PPh_3)_4$ (30 mol %), THF, 23 °C, 12 h.
ii) NaOMe (12 equiv), THF, 23 °C, 4 h or NaOEt (9 equiv), THF, 60 °C, 12 h.

Scheme 2 Synthesis of etheno-bridged N-confused porphyrins.

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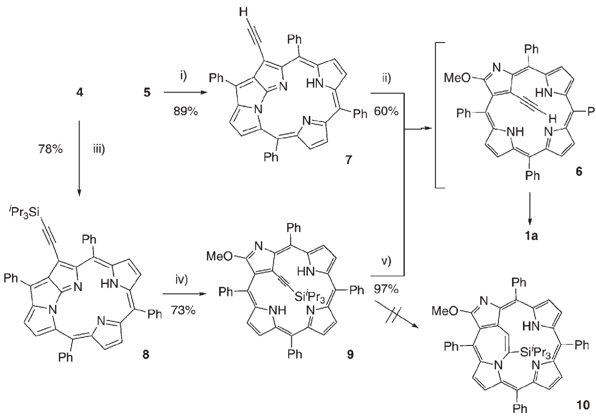

i) TBAF (1.5 equiv), CH_2Cl_2, 23 °C, 1.5 h. ii) NaOMe (12 equiv), THF, 23 °C, 30 min.
iii) Bu_3Sn—≡—Si^iPr_3 (5 equiv), $Pd(PPh_3)_4$ (15 mol%), THF, 60 °C, 18 h.
iv) NaOMe (9 equiv), THF, 23 °C, 4 h. v) TBAF (2 equiv), CH_2Cl_2, 23 °C, 72 h.

Scheme 3 Stepwise preparation of **1a**.

ethynylated N-confused tetraphenylporphyrin (**6**), which is supported by the further experiments described below. Interestingly, the reaction afforded only one type of product (**1a** or **1b**) in good yields and the isomer (**2a** or **2b**) was not detected at all.

Remarkable selectivity in the production of **1a** is commonly observed regardless of the starting compounds (Scheme 3). First, the conversion from **5** to **1a** was achieved in a stepwise manner. Deprotection of **5** with tetrabutylammonium fluoride (TBAF) afforded 21-ethynyl N-fused tetraphenylporphyrin (**7**) in 89% yield. Treatment of **7** with NaOMe gave **1a** in 60% yield. While the yield became lower than that of one-pot reaction, the isomer **2a** was never detected by TLC and ^1H NMR analyses. The plausible intermediate **6** was not obtained. Then, the deprotection was performed after the inversion from N-fused porphyrin to N-confused porphyrin. The triisopropylsilyl derivative **8** was prepared in 78% yield by the Stille coupling reaction of **4** in the same manner as the preparation of **5**. Next, **8** was reacted with NaOMe, which gave the interiorly ethynylated N-confused tetraphenylporphyrin (**9**) in 73% yield. The intramolecular addition reaction from **9** to **10** does not proceed at ambient temperature and thus **9** is stable enough to be isolated. Finally, deprotection of the triisopropylsilyl group was performed with TBAF. In this reaction, similar to the one-pot reaction from **5**, only the single isomer (**1a**) was isolated in 97% yield and **6** was never obtained.

The structural assignment of the etheno-bridged N-confused porphyrins rests on X-ray crystallographic analysis on a single crystal of **1b**.[12] The ORTEP drawing of **1b** is shown in Fig. 1. The etheno-bridged structure between the inner carbon atom of the confused pyrrole and the adjacent pyrrole nitrogen atom, which lies 1.271 Å above the porphyrin mean plane composed of the 24 heavy atoms, is clearly observed. The C1–C2 bond length is 1.337(6) Å, which is a typical length for carbon–carbon double bonds. This bond length indicates that the strain present in the unique [5.7.5] tricyclic ring system is modest.

All the spectroscopic data of **1a** and **1b** are fully consistent with the assigned structures. The MALDI-TOF mass analysis affords the expected values for M^+ (**1a**: *m*/*z* 668.2, **1b**: *m*/*z* 682.0). The signals due to the two olefinic protons inside the macrocycle of **1a** appear at δ −0.78 and −0.47 ppm, which couple with each other ($^3J_{HH}$ = 7.3 Hz) in the ^1H NMR spectrum. Corresponding signals for **1b** appear in the same way as those of **1a**.

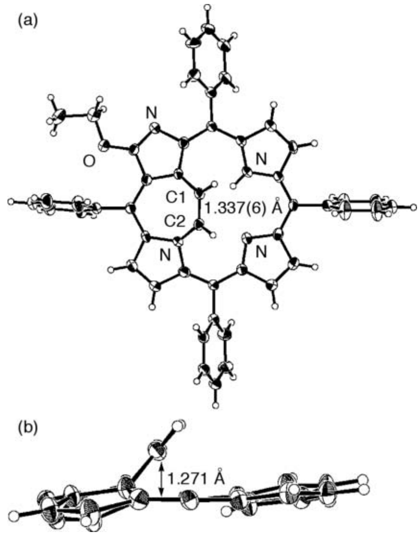

Fig. 1 The ORTEP drawing of **1b** at the 30% probability level: (a) top view, (b) side view. The phenyl and ethoxy groups are omitted for clarity in (b).

While the reason for the exclusive formation of **1** over **2** is unclear yet, it would be due to a kinetic reason since **2a** is suggested to be more stable than **1a** by 2.66 kcal mol^{-1} according to B3LYP/6-311++G**//B3LYP/6-31G** level calculations (Fig. 2). In the optimized structures, no prominent difference is observed between **1a** and **2a** except for the positions of the inner olefin moiety. For example, the lengths of the inner olefins are 1.336 Å for **1a** and 1.341 Å for **2a**. Unlike the imino-fused N-confused porphyrin having a similar [5.7.5] tricyclic ring structure,[13] the thermal isomerization from **1a** to **2a** has not been observed yet. When **1a** was heated to 180 °C in 1,2-$Cl_2C_6H_4$ under Ar, only slight decomposition was observed by ^1H NMR analysis. Thus, the isomer (**2a**) is not obtained in spite of its stability inferred from the calculations.

The endocyclic extension of the porphyrin π-system can be illustrated by photophysical measurements. The absorption spectrum of **1a** in CH_2Cl_2 is shown in Fig. 3 together with that of 3-methoxy N-confused tetraphenylporphyrin (**11**)[10] for comparison. The severe deformation of the Soret band of **1a** would imply the unique π-delocalization in the new π-conjugated system. The longest λ_{max} in the Q-band region for **1a** appears at 775 nm and that of **11** appears at 706 nm. The observed large red-shift of nearly 70 nm suggests the smaller HOMO–LUMO gap of

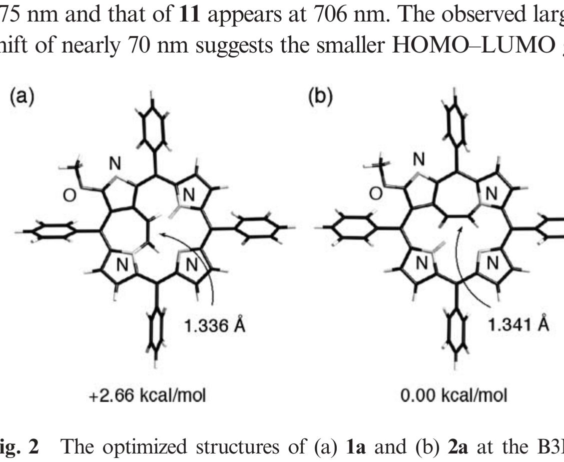

Fig. 2 The optimized structures of (a) **1a** and (b) **2a** at the B3LYP/6-31G** level.

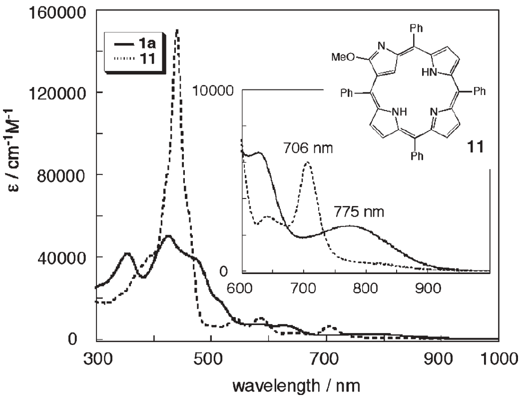

Fig. 3 Absorption spectra of **1a** and **11** in CH_2Cl_2.

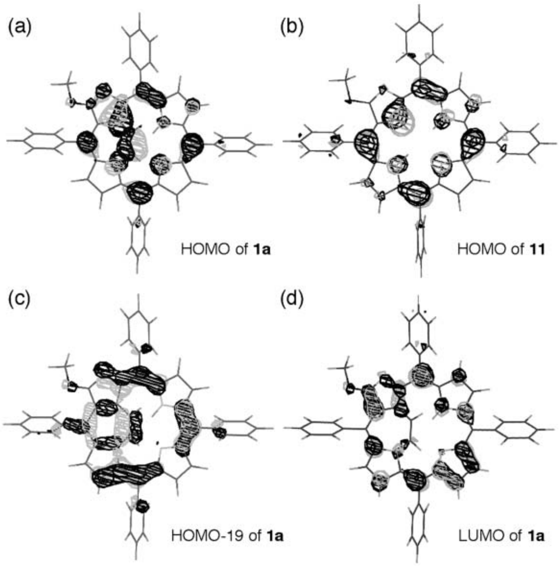

Fig. 4 Kohn–Sham orbitals calculated at the B3LYP/6-31G** level. (a) HOMO of **1a**, (b) HOMO of **11**, (c) HOMO−19 of **1a**, and (d) LUMO of **1a**.

the etheno-bridged N-confused porphyrins.[14] No significant difference from **1a** is recognized in the absorption spectrum of **1b** (see ESI†).

Further evidence of the endocyclic extension of the porphyrin π-system is obtained by theoretical calculations. The calculated orbitals for **1a** at the B3LYP/6-31G** level are shown in Fig. 4 together with the calculated HOMO of **11** at the same level. In the HOMO of **1a**, a significant contribution of the π-orbital of the etheno-bridge moiety is observed (Fig. 4(a)) and the remaining orbitals are quite similar to those of **11** (Fig. 4(b)). The relationship between the porphyrin π-orbital and the etheno π-orbital is out-of-phase in the HOMO, and one of the in-phase interactions is observed in HOMO−19 (Fig. 4(c)). Contrastingly, no contribution of the etheno part is observed in the LUMO of **1a** (Fig. 4(d)). The energy values of HOMO (LUMO) level for **1a** and **11** are −0.16647 (−0.8396) and −0.17419 (−0.08318) Hartree, respectively. Hence, the observed smaller HOMO–LUMO gap of **1a** than **11** would be attributable to the raising of the HOMO energy level.

In conclusion, we have succeeded in extending the porphyrin π-system inside the core using the *confusion* strategy and the etheno-bridged N-confused porphyrins are synthesized for the first time. The introduction of an etheno-bridge in the N-confused porphyrin would cause the rise of the HOMO energy level, which is illustrated by the absorption spectra and the DFT calculated orbitals. The strategy developed here seems useful for the construction of unique π-conjugated systems and further application is now under investigation.

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12 *Crystal data*: **1b**, Violet plate, $C_{48}H_{34}N_4O$, $M_r = 682.79$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.648(3)$, $b = 13.477(4)$, $c = 15.109(4)$ Å, $\alpha = 82.536(6)$, $\beta = 74.261(6)$, $\gamma = 82.981(6)^\circ$, $V = 1867.2(9)$ Å^3, $Z = 2$, $T = 223(2)$ K, $R = 0.0866$ ($I > 2\sigma(I)$), $R_w = 0.2415$ (all data), GOF = 0.929. CCDC 636924. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713845h.

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