Pergamon

Tetrahedron Letters 43 (2002) 4881–4884

TETRAHEDRON
LETTERS

Effective *face-to-face* dimerization of a crown ether appended *N*-confused porphyrin

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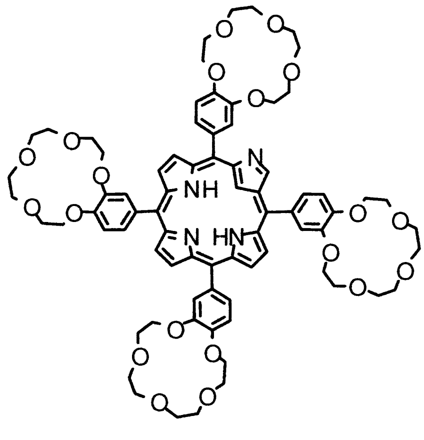
Received 4 April 2002; accepted 26 April 2002

Abstract—An *N*-confused porphyrin bearing four crown ethers attached at the *meso*-positions was synthesized and its *face-to-face* dimerization ability has been shown to be several orders larger than that of the corresponding porphyrin derivative. © 2002 Elsevier Science Ltd. All rights reserved.

Well-ordered architectures constructed by self-assembly of porphyrins have been attracting considerable interest in a view of their potential applications in material science,[1] template-directed synthesis,[2] enzyme-like catalysis,[3] and duplication of photosynthetic functions of light harvesting and charge separation.[4] On the other hand, only scattered attention has been paid to self-assembly of porphyrin analogs that have been actively studied in recent years. Self-assembly of porphyrin analogs would also be promising in light of their intriguing properties of metal coordination,[5] photochemistry,[4] molecular recognition,[6] etc., which differ largely from those of porphyrins. In recent years, we have been studying *N*-confused porphyrins (NCP),[7,8] a kind of porphyrin isomer which possesses a confused pyrrole ring with its nitrogen pointing outward, and revealing the uniqueness of this isomer. Here, we report the *face-to-face* dimerization of crown ether appended *N*-confused porphyrins (NCP, **1**), which is to the best of our knowledge the first example of designed self-assembly of porphyrin isomers.

Crown ether appended NCP **1** was prepared by Lindsey's method of NCP synthesis.[9] Thus, a solution of 4′-formyl-benzo-15-crown-5 and pyrrole in CH_2Cl_2 was treated with methanesulfonic acid and the resulting reaction mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to furnish **1** in 4% yield. Consistent with the structure, the ^1H NMR spectrum of **1** in $CDCl_3$ shows the inner NH and CH protons at −2.34 and −4.86 ppm, respectively, and the FAB mass spectrum reveals its molecular weight at $m/z=1375.3$ (calcd for $C_{76}H_{86}N_4O_{20}$, 1375.5).[10] The absorption spectrum of **1** in $CHCl_3$ is quite similar to that of usual NCP, featuring a Soert band at 448 nm ($\varepsilon=126000$) and Q-bands at 548 ($\varepsilon=7900$), 597 ($\varepsilon=12600$), and 738 ($\varepsilon=10000$) nm.[7]



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Addition of potassium ions to a solution of **1** in MeCN caused clean absorption spectral changes with several isosbectic points. The Soret band was blue-shifted from 443 to 428 nm with an isosbectic point at 435 nm (Fig. 1(a)) and the fluorescence intensity was decreased. These spectral changes are quite analogous to those found for *face-to-face* dimerization of crown ether appended porphyrin **3**,[11,12] and therefore strongly suggest the similar *face-to-face* dimerization through formation of four sandwich complexes between the crown ether moieties and potassium ion, also for **1**.[13] VPO (vapor pressure osmometry) measurement confirmed

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PII: S0040-4039(02)00832-8

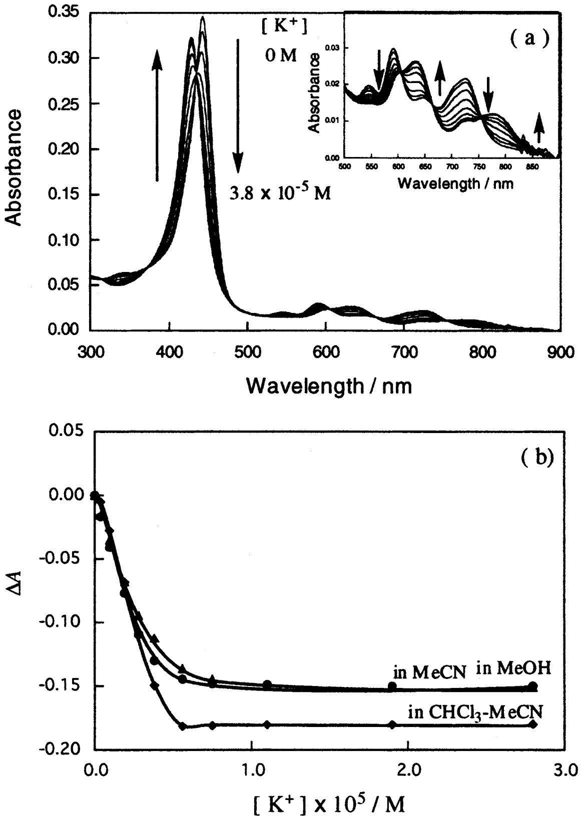
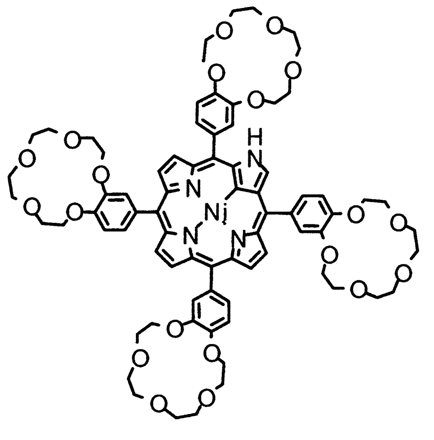


Figure 1. Absorption spectra of **1** plus $KClO_4$ in MeCN at 25°C (a) and plots of [K^+] versus ΔA for **1** (b); at 443 nm in MeCN, 448 nm in $CHCl_3$–MeCN (9:1), 447 nm in MeOH, [**1**] = 2.7×10^{-6} M.

the dimeric nature of the 2:4 complex between **1** and potassium perchlorate with an average molecular weight of 2910±410 g mol^{-1} (*M*w **1** = 1376). In contrast, the addition of sodium ions induced no significant spectral change. Decrease in an intensity of the original Soret band upon addition of potassium ions in the various solvents is depicted in Fig. 1(b). The profiles in the various solvents were almost identical. Interestingly, the plots of the titration featured a sigmoidal curve, suggesting homotropic, positive allosterism. The analysis of the cooperative guest binding process using the Hill equation,[14] $\log(y/(1-y)) = n \log[\text{guest}] + \log K$; where K, n and y are the stability constant, Hill coefficient and $K/([\text{guest}]^{-n}+K)$, gave the following stability constants, $\log K = 13.6$–15.1, and Hill coefficient, $n = 2.4$–2.6. These $\log K$ are several order of magnitude greater than those observed for the interaction between crown ether and potassium ion,[15] suggesting the cooperative binding of metal ions and π–π interaction of NCP macrocycles. Also n values indicate that the multipoint binding of potassium ions to **1** is cooperative.[5b,16,17]

The similar *face-to-face* dimerization was observed for the corresponding porphyrin **3** upon addition of potassium ions. The Soret band at 422 nm was blue-shifted to 410 nm with an isosbectic point at 415 nm. The analysis of the absorption spectra by using the Hill plots gave the stability constants, $\log K = 11.7$–12.1, and Hill coefficients, $n = 2.1$–2.3. The stability constants for *face-to-face* dimer of **3** are considerably smaller, ca. 100–1000 times, in comparison to those for **1**. The larger stability constants of dimer for **1** mean that NCP skeleton serves as a more effective subunit for the *face-to-face* dimerization.



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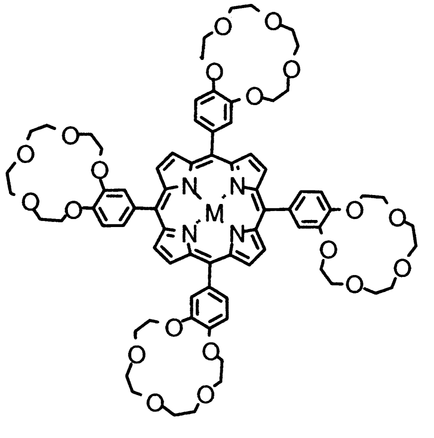

3: M = H_2
4: M = Ni

At the present stage, it is not clear what is the main factor for the observed stronger dimerization tendency of **1** in comparison to **3**. NCP structure leads to non-symmetrical electronic density, which may be suited for the dimerization through complementary association. Absence of the peripheral β-hydrogen at the outward pointing nitrogen may be suited for the dimerization owing to less steric demand. Alternatively, the outward pointing nitrogen may enhance the complexation tendency of the crown ether moiety with potassium ion.

In order to get more information, we prepared Ni(II)–NCP complex (**2**) as greenish solids using $Ni(acac)_2$ in 50% yield. The ^1H NMR spectrum of **2** exhibits the NH proton at 10.31 ppm, indicating the presence of the peripheral β-hydrogen.[10] The addition of potassium ions caused a blue shift of Soret band from 428 to 423 nm with an isosbectic point at 409 nm (Fig. 2), again

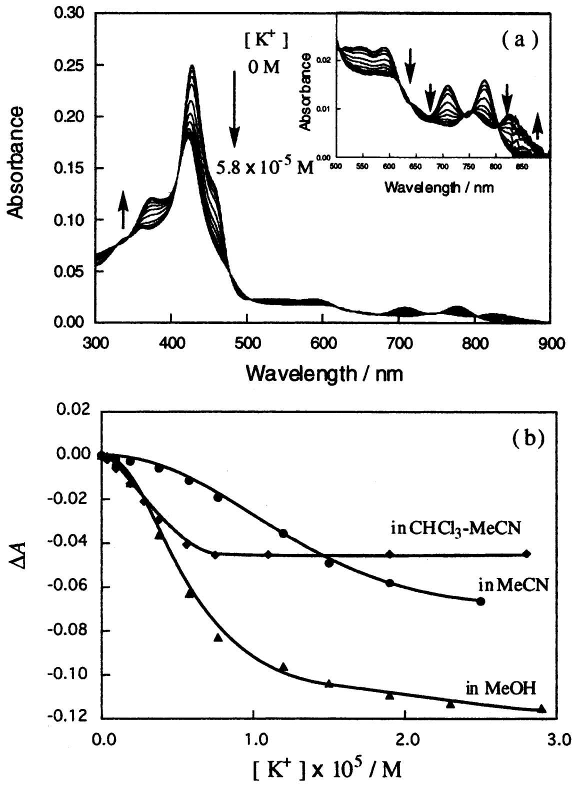

Figure 2. Absorption spectra of **2** plus $KClO_4$ in MeCN at 25°C (a) and plots of $[K^+]$ versus ΔA for **2** (b); at 428 nm in MeCN, 431 nm in $CHCl_3$–MeCN (9:1), 427 nm in MeOH, $[\mathbf{2}] = 2.7\times10^{-6}$ M.

indicating the formation of *face-to-face* dimer but the stability constants ($\log K = 11.0$–12.3, $n = 2.1$–2.4) are distinctly smaller than those of **1** and are roughly the same with those of **3** and **4**.[18] The dimerization profiles showed slight solvent dependencies. These results suggest that the presence of an imine group at the peripheral position play some roles either sterically or electronically.

In summary, the crown ether appended NCP was prepared and its dimerization upon addition of potassium ions has been demonstrated to be more effective in comparison to the corresponding porphyrin derivative, in which the peripheral β-hydrogen is suggested to play some role for the smaller stability constant of the dimer of **2**. Further detail characterizations of the structure of *face-to-face* NCP dimer are currently under way in our laboratory.

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10. Compound **1**: ^1H NMR (500 MHz, $CDCl_3$, TMS, rt): δ/ppm −4.86 (s, 1H), −2.34 (bs, 1H), 3.78–4.44 (m, 64H), 7.31–7.36 (m, 4H), 7.65–7.72 (m, 4H), 7.83–7.93 (m, 4H), 8.55–8.61 (m, 4H), 8.72 (s, 1H), 8.90 (d, $J = 5.0$ Hz, 1H), 8.96 (d, $J = 5.0$ Hz, 1H); FAB MS m/z 1375.3 (calcd for $C_{76}H_{86}N_4O_{20}$: 1375.5); UV–vis ($CHCl_3$): λ_{max} ($\log \varepsilon$) = 448 (5.1), 548 (3.9), 597 (4.1), 738 (4.0) nm. Compound **2**: ^1H

NMR (500 MHz, $CDCl_3$, TMS, rt): δ/ppm 3.82–4.33 (m, 64H), 7.05–7.11 (m, 4H), 7.29–7.40 (m, 8H), 7.80 (d, $J=5.0$ Hz, 1H), 7.85 (d, $J=5.0$ Hz, 1H), 7.91 (d, $J=5.0$ Hz, 1H), 7.94 (d, $J=5.5$ Hz, 1H), 8.07 (d, $J=5.0$ Hz, 1H), 8.09 (d, $J=5.5$ Hz, 1H), 8.56 (s, 1H), 10.31 (bs, 1H); MALDI-TOF MS, m/z 1429.3 (calcd for $C_{76}H_{84}N_4O_{20}Ni$: 1432.2); UV–vis ($CHCl_3$): λ_{max} ($\log \varepsilon$) = 367 (sh), 431 (4.9), 460 (sh), 522 (3.9), 553 (3.9), 596 (3.9), 715 (3.7), 785 (3.7) nm.

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18. The dimerization constant ($\log K$) was determined to be 11.8 ($n=2.3$) for **4** in MeCN.