ChemComm

A porphyrin square: synthesis of a square-shaped π-conjugated porphyrin tetramer connected by diacetylene linkages

Ken-ichi Sugiura, Yoshinobu Fujimoto and Yoshiteru Sakata*

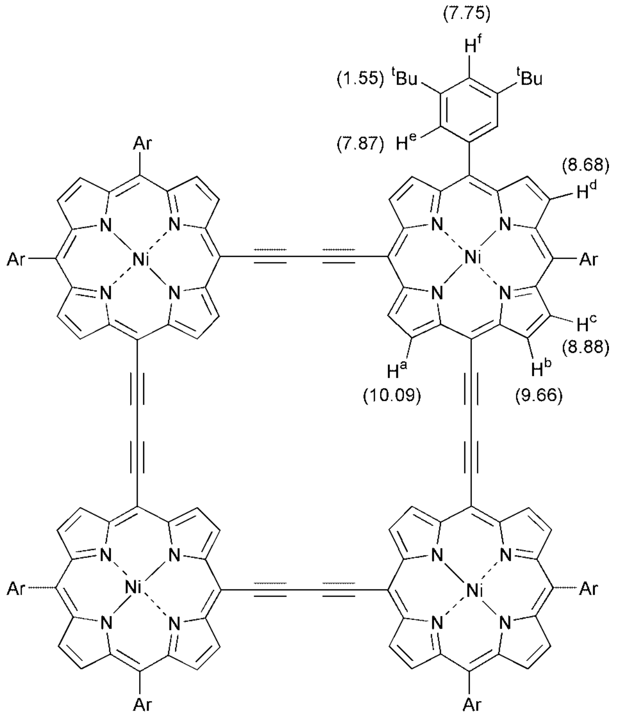
The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan. E-mail: sakata@sanken.osaka-u.ac.jp

Received (in Cambridge, UK) 5th April 2000, Accepted 9th May 2000
Published on the Web 8th June 2000

A square-shaped π-conjugated porphyrin tetramer has prepared: the excitation energies of both the Soret and Q bands, 19 880 (503) and 15 180 cm^{-1} (659 nm), respectively, are quite low compared with those for the monomer and reported cyclic porphyrin oligomers.

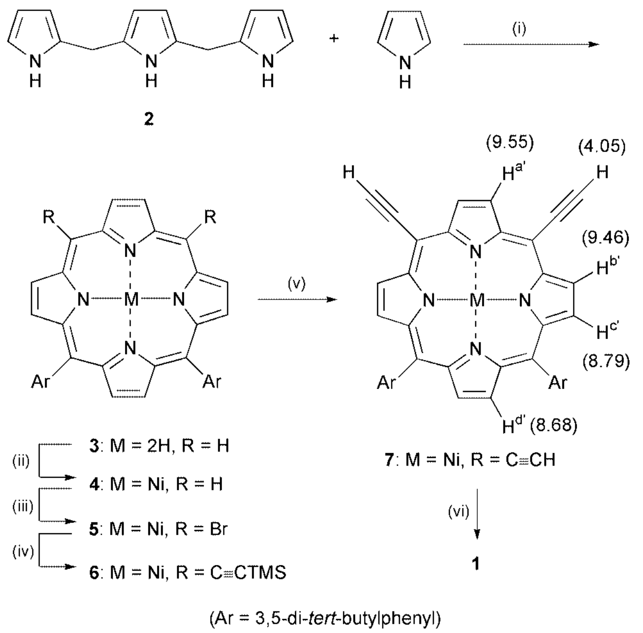
Interdisciplinary research on porphyrin oligomers (POs) has been attracting much attention over the last two decades.[1] Studies are focused on the elucidation of the function of naturally occurring POs, such as the cyclophane-like dimeric *special pair* in the photosynthetic reaction center,[1] as well as the creation of component molecules for novel advanced materials.[2–8] Recently, many efforts have been made to prepare cyclic porphyrin oligomers (CPOs) motivated by the wheel-shaped oligomeric porphyrinoid architecture found in the light harvesting proteins.[9] After the pioneering work of Sanders and Anderson in 1989,[10] several CPOs have been reported, in which each porphyrin is connected by covalent[11–13] or coordination bonds.[14] However, the linkages are only limited to aryl-based *meso*-groups in which the porphyrin and linker π-systems are orthogonal. Therefore, the electronic interaction between the neighbouring chromophores in the ground state remains small.[7] With the aim of creating a highly conjugated CPO, we chose a diacetylene unit to connect porphyrins directly at the *meso*-position.[4–8, 15] Here we report the synthesis and some basic properties of a new cyclic π-conjugated porphyrin tetramer **1** (Fig. 1).

The synthetic route to **1** is shown in Scheme 1. An important key intermediate, 5,10-bis(3,5-di-*tert*-butylphenyl)porphyrin **3**, which acts as the corners of the square **1** was prepared in 3% yield by the coupling reaction of 3,5-di-*tert*-butylphenylbenzaldehyde and pyrrole with tripyrrane **2**, as reported by Taniguchi and coworkers,[16] in the presence of powdered NaCl.[17] After metallation of **3**, functionalization reactions were performed at the *meso*-positions, *i.e.* bromination (affording **5**), introduction of acetylene groups (to give **6**), and the removal of the TMS groups (providing **7**).† Glaser–Hay coupling[4] of **7** at a 2.6 mM concentration gave moderately soluble, brown coloured crude products. The resulting reaction mixture was analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry to give a main peak for M$^+$ at *m/z* 3160, along with a weak one at *m/z* 2371. This clearly indicates the tetramer was formed exclusively (*m/z* calc. for M$^+$ of the cyclic tetramer, $C_{208}H_{200}N_{16}Ni_4$: 3159; *m/z* calc. for M$^+$ of the acyclic trimer, $C_{156}H_{152}N_{12}Ni_3$: 2371). Separation of the tetramer was successfully achieved using preparative gel permeation chromatography. The absence of C≡C–H and asymmetric C≡C stretching bands in the IR spectrum of **1**, characteristically observed for **7** at 3310s and 2106m cm^{-1}, respectively, suggest the tetramer to be cyclic. The simple pattern of ^{1}H-NMR peaks† also supports the cyclic structure having D_{4h} symmetry (*vide infra*). In a



1
(Ar = 3,5-di-*tert*-butylphenyl)

Fig. 1 Compound **1** along with ^{1}H-NMR assignments.



Scheme 1 *Reagents and conditions*: (i) 2.0 eq. 3,5-di-*tert*-butylphenylbenzaldehyde, TFA, NaCl, CH_2Cl_2; (ii) excess $Ni(CH_3CO_2)_2{\cdot}4H_2O$, $(CH_2Cl)_2$, reflux; (iii) 2.05 eq. NBS, CH_2Cl_2, −20 °C, (iv) 3.0 eq. TMS–C≡CH, Cu_2Cl_2, $Pd(PPh_3)_4$, NEt_2H, (v) $^nBu_4NF$, CH_2Cl_2 (vi) Cu_2Cl_2, TMEDA, CH_2Cl_2. The values in parentheses for **7** are ^{1}H-NMR assignments.

DOI: 10.1039/b002699i

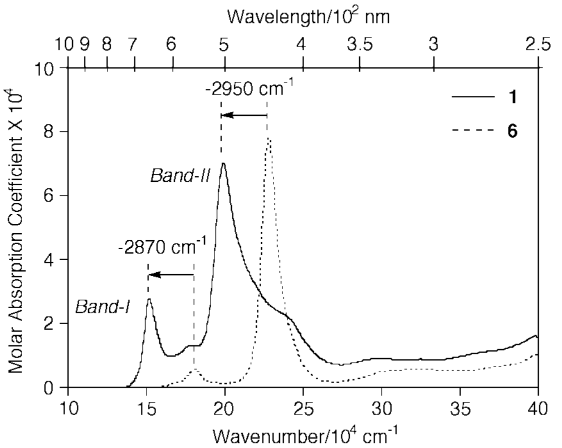


Fig. 2 Absorption spectra of **1** (solid line) and **6** (dotted line) in $CHCl_3$.

typical reaction, 41.3 mg of **7**, 400.0 mg of Cu_2Cl_2, 0.55 mL of TMEDA, and 50 mL of dry CH_2Cl_2 gave 8.9 mg of the tetramer **1** as a lustrous dark-green solid (22% yield). It should be emphasised that this relatively high yielding formation of cyclic **1** occurred in the absence of template;[12] the isolated yield of the structurally similar square was 7% at most.[11]

The ^{1}H-NMR chemical shift of the internal protons (H^a: 10.09 ppm) is informative about the structure of **1** from the following two view points. First, compared to the corresponding protons of **7** ($H^{a'}$: 9.55 ppm), H^a is shifted to low field by +0.54 ppm. Although a similar downfield shift was observed for the linear porphyrin oligomers connected by the diacetylene linkages, *e.g.* +0.22 ppm for the dimer,[8] the shift for **1** is more than double this value. Second, the difference in the chemical shifts of the internal (H^a) and the external protons (H^b: 9.66 ppm) adjacent to the diacetylene units of **1** is +0.43 ppm. This value is also larger than that observed for **7** (+0.09 ppm: 9.55 ppm for $H^{a'}$ and 9.46 ppm for $H^{b'}$). These results suggest that the H^a-protons of **1** are affected by the ring current, not only of the two adjacent porphyrin rings, but also of the diagonal porphyrin in the square and also clearly suggests **1** to be cyclic.

The electronic spectra of **1** and **6** are shown in Fig. 2. The spectrum of **1** is composed of two main bands: Q-band-like band I and Soret-band-like band II.† Reflecting the highly conjugated structure, band I and band II appear at 15 180 (659) and 19 880 cm^{-1} (503 nm), respectively. Both band I and band II are shifted to lower energy compared with those of the monomer **6** by about 2900 cm^{-1}. Although these bands appear at much longer wavelengths than those of the porphyrin square connected by *meso*-aryl-based linkages reported by Lindsey and coworkers (λ_{max} = 23 260 cm^{-1}; 430 nm),[11] these wavelengths are similar to the corresponding linear tetramer.[6] The intensity of band I normalized per chromophore was increased compared with that of **6**. Conversely, the intensity of band II was decreased. This phenomenon suggests that the degeneracy of the a_{1u} and a_{2u} orbitals of the porphyrins is lifted[7] and that a new π-electronic system in the square is formed.

In conclusion, a novel and highly conjugated porphyrin square was prepared. In addition to the expanded π-system of the molecule, our square has a central cavity corresponding to the size of molecules such as hexamethylbenzene.[18] These characteristics will allow us to use the square as an advanced host molecule. We are currently investigating the photochemistry of the corresponding free base and zinc complex, as well as contraction and expansion of the square by replacing the diacetylene units with –C≡C– and –(C≡C–)$_n$ (n > 3) linkers, respectively, keeping the π-conjugation between the four porphyrins.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (no. 11136222 'Metal-assembled Complexes' to K-i. S., no. 11166238 'Molecular Physical Chemistry' to K-i. S., and no. 10146103 'Creation of Characteristic Delocalized Electronic Systems' to Y. S.) from the Ministry of Education, Science, Sports and Culture, Japan. We appreciate the technical assistance provided by the Materials Analysis Centre of ISIR, Osaka University as well as helpful discussions with Professor S. Taniguchi, Ibaraki National College of Technology, Japan.

Notes and references

† *Data*: **3**: ^{1}H-NMR ($CDCl_3$) δ 10.21 (s, 2H), 9.44 (s, 2H), 9.33 (d, J = 5, 2H), 9.06 (d, J = 5, 2H), 8.97 (s, 2H), 8.09 (d, J = 2, 4H), 7.81 (t, J = 2 Hz, 2H), 1.54 (s, 36H), −3.27 (bs, 2H). **4**: ^{1}H-NMR ($CDCl_3$) δ 9.88 (s, 2H), 9.23 (s, 2H), 9.17 (d, J = 5, 2H), 8.98 (d, J = 5, 2H), 8.90 (s, 2H), 7.92 (d, J = 2, 4H), 7.76 (t, J = 2 Hz, 2H), 1.50 (s, 36H). **5**: ^{1}H-NMR ($CDCl_3$) δ 9.39 (s, 2H), 9.34 (d, J = 5, 2H), 8.69 (d, J = 5, 2H), 8.62 (s, 2H), 7.72 (d, J = 2, 4H), 7.64 (t, J = 2 Hz, 2H), 1.39 (s, 36H). **6**: ^{1}H-NMR ($CDCl_3$) δ 9.50 (s, 2H), 9.41 (d, J = 5, 2H), 8.75 (d, J = 5, 2H), 8.64 (s, 2H), 7.79 (d, J = 2, 4H), 7.70 (t, J = 2, 2H), 1.45 (s, 36H), 0.54 (s, 18H). UV–vis λ_{max} ($CHCl_3$): 310 (log ε = 3.77), 438 (4.89), 554 (3.76) nm. **7**: ^{1}H-NMR ($CDCl_3$) δ 9.55 (s, 2H), 9.46 (d, J = 5, 2H), 8.79 (d, J = 5, 2H), 8.68 (s, 2H), 7.81 (d, J = 2, 4H), 7.72 (t, J = 2, 2H), 4.05 (s, 2H), 1.46 (s, 36H) ppm. **1**: ^{1}H-NMR ($CDCl_3$) δ 10.09 (s, 8H), 9.66 (d, J = 5, 8H), 8.88 (d, J = 5, 8H), 8.68 (s, 8H), 7.87 (d, J = 2, 16H), 7.75 (t, J = 2, 8H), 1.55 (s, 144H). UV–vis λ_{max} ($CHCl_3$): 324 (log ε = 3.94), 423 (sh, 4.37), 503 (4.85), 562 (4.12), 659 (4.44) nm.

1 Reviews: M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435; H. Kurreck and M. Huber, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 849.
2 J. D. Spence and T. D. Lash, *J. Org. Chem.*, 2000, **65**, 1530.
3 K.-i. Sugiura, H. Tanaka, T. Matsumoto, T. Kawai and Y. Sakata, *Chem. Lett.*, 1999, 1193.
4 H. L. Anderson, S. J. Martin and D. D. C. Bradley, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 655.
5 H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972.
6 P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams and H. L. Anderson, *Chem. Commun.*, 1998, 909.
7 H. L. Anderson, *Chem. Commun.*, 1999, 2323.
8 V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105; V. S.-Y. Lin and M. J. Therien, *Chem. Eur. J.*, 1995, **1**, 645.
9 T. Pullerits and V. Sundström, *Acc. Chem. Res.*, 1996, **29**, 381.
10 H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1989, 1714.
11 R. W. Wagner, J. Seth, S. I. Yang, D. Kim, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 1998, **63**, 5042.
12 S. Anderson, H. L. Anderson and J. K. M. Sanders, *Acc. Chem. Res.*, 1993, **26**, 469.
13 J. Li, A. Ambroise, S. I. Yang, J. R. Diers, J. Seth, C. R. Wack, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 1999, **121**, 8927; O. Mongin, A. Schuwey, M.-A. Vallot and A. Gossauer, *Tetrahedron Lett.*, 1999, **40**, 8347.
14 C. M. Drain and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1994, 2313 (corrigendum: *J. Chem. Soc., Chem. Commun.*, 1995, 503); K. Funatsu, A. Kimura, T. Imamura and Y. Sasaki, *Chem. Lett.*, 1995, 765.
15 To the best of our knowledge, the introduction of the acetylene group on the *meso*-position was first proposed by Arnold and coworkers in 1978. D. P. Arnold, A. W. Johnson and M. Mahendran, *J. Chem. Soc., Perkin Trans. 1*, 1978, 366; D. P. Arnold and L. J. Nitschinsk, *Tetrahedron*, 1992, **48**, 8781; D. P. Arnold and D. A. James, *J. Org. Chem.*, 1997, **62**, 3460; D. P. Arnold, G. A. Heath and D. A. James, *J. Porphyrins Phthalocyanines*, 1999, **3**, 5.
16 S. Taniguchi, H. Hasegawa, M. Nishimura and M. Takahashi, *Synlett*, 1999, 73.
17 F. Li, K. Yang, J. S. Tyhonas, K. A. MacCrum and J. S. Lindsey, *Tetrahedron*, 1997, **53**, 12 339.
18 J. D. Ferrara, C. Tessier-Youngs and W. J. Youngs, *J. Am. Chem. Soc.*, 1985, **107**, 6719.