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Synthesis, properties and crystal structures of rigid porphyrins fused with bicyclo[2.2.2]octene units

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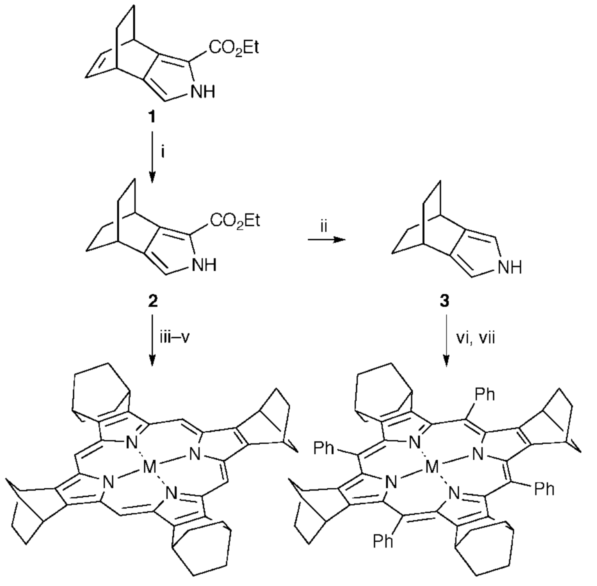
Porphyrins fused with bicyclo[2.2.2]octene frameworks are prepared; the bicyclo[2.2.2] units rigidify the porphyrin ring to maintain planar conformations in solution.

In order to develop new functions and properties of porphyrins, variously substituted porphyrins have been extensively studied. For example, electron withdrawing groups,[1] electron donating groups[2] and sterically hindered groups[3] have been introduced into the porphyrin periphery to control the redox, spectroscopic and catalytic properties of metalloporphyrins. However, porphyrin rings are flexible enough to adopt various distorted conformations such as saddle, wave, ruffle and dome conformations depending the size of periphery substituents and the central metal.[3,4] Furthermore, π–π stacking of porphyrin rings also affects their conformations and electronic properties.[4] Here we report a new type of porphyrin which has a more rigid core than octaethylporphyrin (OEP) and *meso*-tetraphenylporphyrins (TPPS). Our new strategy to control the structure and properties of porphyrins is based on the annelation of porphyrins with bicyclo[2.2.2]octene frameworks, such as **4** and **5** in Scheme 1.† Bicycloannelation of annulenes has been extensively used to control the structure and electronic properties of various aromatic and non-aromatic compounds.[5] Thus, various annulenes fused with bicyclo[5.4.0]octene frameworks give stable oxidized products such as cation radicals and dications.[5] In a similar way, porphyrins fused with bicyclo[2.2.2]octene units are expected to have raised HOMO energies and conformationally rigid structures due to the presence of the fused frameworks.



4 M = H_2, Zn **5** M = H_2, Zn

Scheme 1 *Reagents and conditions*: i, H_2, Pd/C, EtOH, room temp., 8 h, 95%; ii,KOH,$HOCH_2CH_2OH$, 160 °C, 2 h, 79%; iii, $LiAlH_4$, THF, 0 °C, 2 h; iv, TsOH, $CHCl_3$, room temp., 12 h; v, *p*-chloranil, room temp., 12 h, 34% (3 steps); vi, PhCHO, $BF_3{\cdot}OEt_2$, $Zn(OAc)_2$, $CHCl_3$, room temp., 12 h; vii, *p*-chloranil, room temp., 3 h, 32% (2 steps).

The key pyrroles **2** and **3** were prepared from **1**[6] by hydrogenation and deethoxycarbonylation. Pyrrole **2** was converted into porphyrin **4** in about 30% yield by reduction with $LiAlH_4$ and the subsequent treatment with acid and oxidation. Porphyrin **5** was prepared by the reaction of **3** with benzaldehyde in the presence of $BF_3{\cdot}OEt_2$ and $Zn(OAc)_2$ and subsequent oxidation.

Theoretical calculations and experimental data on the effects of non-planarity indicate that the HOMO energy should be destabilized with respect to the LUMO energy, resulting in a red shift of the first visible absorption band.[1c] The chemical shifts of NH and the red-shifts of the electronic absorption correlate with deviation from planarity of the porphyrin ring.[3b] So the spectroscopic data of porphyrins **4**, **5** and their Zn complexes were compared with those of other related porphyrins, 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP), 2,3,7,8,12,13,17,18-octamethoxyporphyrin (OMP), 5,10,15,20-tetraphenylporphyrin (TPP) and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin (OETPP). The electronic absorptions of **4** and Zn-**4** are blue shifted compared to the corresponding OEP and Zn-OEP, and such blue shifts are more enhanced in the Q (0,0) bands. The Q bands of **4** and Zn-**4** are at 610 and 558 nm, respectively, which are considerable blue-shifted compared to those of OEP (622 nm), Zn-OEP (569 nm), OMP (618 nm) and Zn-OMP (573 nm). The Q band of Ni-**4** is at 543 nm, which is also blue shifted compared to Ni-OEP (551 nm). Several factors are operative in the absorption spectra of porphyrins.[1–3] Recent studies show that the shifts of spectra originate from ring conformations and substituent effects.[1a,b] As the substituents of **4** and OEP consist of alkyl groups and have similar electronic properties, ring conformations should be the main factors controlling the blue shifts of **4**. The porphyrin cores are flexible and can adopt various conformations in solution. In fact, NiOEP, NiTPP, CuTPP and other related porphyrins are present as a mixture of both planar and nonplanar conformations in solution.[7] In particular, large deviations from planarity are observed in TTP derivatives.[7] Thus, the blue shifts of **4** and Zn-**4** shows quite clearly that they exist in planar conformations in solution. The ^1H NMR chemical shifts also support the planar conformation of **4**. The difference of the chemical shifts between the N-H and *meso*-H resonances of **4**, $\Delta\delta$ = 14.84 ppm, is larger than that of other porphyrins ($\Delta\delta$ of OEP is 13.92 and that of OMP is 14.47 ppm). The planar structure of **4** in solution leads to the large $\Delta\delta$ of **4**.[8]

Conformational distortions of porphyrin rings are enhanced by the introduction of substituents at the *meso* position. The introduction of alkyl, perfluoroalkyl, aryl and nitro groups at the *meso*-positions induces the distortion of porphyrin cores.[1,3] So, **5** and Zn-**5** were prepared, and their properties were compared with those of OETPP and Zn-OETPP. It is well-established that the red shift of absorptions observed for OETPP (686 nm) and Zn-OETPP (637 nm) is due to the non-planar distortions of their rings. On the other hand, the absorption λ_{max} values of **5** (665 nm) and Zn-**5** (551 nm) are not as red-shifted as OETPP and Zn-OETPP, when compared to those of TPP (645 nm) and Zn-TPP (552, 596 nm). The ^1H NMR chemical shift of NH in **5** appears at $\delta -3.10$, whereas those of TPP and OETPP appear at $\delta -2.78$ and -2.0, respectively. These results indicate that **5** and Zn-**5** have planar conformations, while OETPP derivatives adopt nonplanar conformations in solution.

The stereochemistry of the porphyrin macrocycles has been studied extensively by X-ray diffraction. Porphyrin cores are very flexible and most porphyrins adopt nonplanar shapes in the solid state. The shapes are readily changed by periphery substituents, central metals and their axial ligands.[4] For example, Zn-OETPP adopts a saddle conformation,[3a] where a maximum displacement of 1.18 Å (for C_β) from the porphyrin mean plane is observed. The dihedral angles of the phenyl rings with the nitrogen plane are about 45–47°. The structure of Zn-**5**, as shown in Fig. 1,‡ is different from that of Zn-OETPP. The porphyrin ring is fairly planar, exhibiting a mean plane deviation of only 0.06 Å for from the 24 core atoms. The reported mean plane deviation of distorted porphyrins is about 0.3–0.5 Å depending on steric crowding and the size of the central metal.[4] The angles between the phenyl rings and the porphyrin plane of Zn-**5** are 89 and 78°. The structure of Zn-**5** is very close to that of nickel(II) *meso*-tetrakis(2,6-dichlorophenyl)-β-tetranitroporphyrin,[1d] where steric crowding between the phenyl and nitro groups is minmized by adopting a near planar conformation. Nonplanar distortions of OEP and TPP derivatives are derived from ring contraction about the central metal ion or from steric crowding about the porphyrin periphery. On the other hand, steric interactions in porphyrins **4** and **5** shoud be at a minimum in planar or near-planar conformatons, as steric interactions between the bicyclo[2.2.2]octene units are increased by adopting nonplanar conformations. Simple calculations also suggest the planar structure as the most stable conformer for **4** and **5**.

The oxidation potentials were determined by cyclic voltammetry (CV) for Zn-**4** and Zn-**5** in 0.1 M Bu_4NClO_4 in CH_2Cl_2. The CVs of other related porphyrins were also measured under the same conditions. Although the CVs of Zn-**4**, Zn-OEP and Zn-**5** showed two reversible peaks, the highly distorted Zn-OETPP gave only one peak. The first oxidation potentials of Zn-**4** and Zn-**5** were +0.38 and +0.26 V (*vs.* Ag/Ag$^+$, Fc/Fc$^+$ = +0.19 V), respectively. They are a little higher than those of Zn-OEP (+0.35 V) and Zn-OETPP (+0.22 V). The second oxidation potential of Zn-**4** (0.74 V) is also a little higher than that of Zn-OEP (+0.68 V). The second oxidation potential of Zn-**5** is 0.43 V, but the CV of Zn-OETPP gives one peak at $E_{1/2} = +0.22$ V. It is reasonable to assume that the first and second oxidation of Zn-OETPP takes place at this potential. However, further studies are necessary to confirm this conclusion. Although the difference is very small, the HOMO energy levels of Zn-OEP and Zn-OETPP are a little higher than those of Zn-**4** and Zn-**5**, respectively. It is well-established that the distortion of nonplanarity on Zn-OETPP raises the HOMO enegy level.[3,4] The CV data suggest that the HOMO energy of Zn-OEP is also slightly raised by a contribution from nonplanar conformations of Zn-OEP in solution. As the LUMO energy levels are less sensitive to nonplanar distortion compared to the HOMO energy levels,[1] the energy difference between the HOMO and LUMO levels of **4** or Zn-**4** is larger than that of OEP or Zn-OEP. Thus, the absorption spectra of **4** and its metal complexes are blue shifted compared to OEP derivatives. It is noteworthy that the HOMO energy levels of porphyrin derivatives are sensitive to such small deviations from planarity of the porphyrin rings in cases such as OEP in solution. Considering the destabilization effect on the HOMO level of annulenes of the σ–π conjugation of fused bicyclo[2.2.2]octene units, which is general in the other macrocycles,[5] conformational distortions may be major factors in controlling the electronic properties of alkyl substituted porphyrins like **4** and OEP.

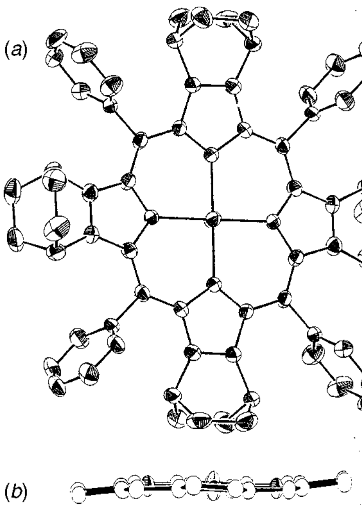


Fig. 1 (*a*) X-Ray crystal structure of Zn-**5**. Hydrogens and solvents are omitted for clarity. Average of bond distance (Å) and angles (°): N–C_α 1.383, Zn–N 2.067, C_α–C_β 1.454, C_β–C_β 1.351, C_α–C_m 1.403, C_m–C_Φ 1.498; NZnN 90.0, $C_\alpha NC_\alpha$ 107.3, $ZnNC_\alpha$ 126.1, $NC_\alpha C_m$ 125.3, $NC_\alpha C_\beta$ 108.9, $C_\beta C_\alpha C_m$ 125.9, $C_\alpha C_m C_\alpha$ 121.9, $C_\alpha C_\beta C_\beta$ 107.5. (*b*) Edge-on view of Zn-**5** (substituent groups are omitted for clarity).

In conclusion bicyclo[2.2.2]octene frameworks are useful to rigidify porphyrin rings in order to maintain planar conformations in solution. Although planar porphyrins have problems of solubility due to π–π stacking, porphyrins fused with bicyclo[2.2.2]octene units have good solubility in various organic solvents such as CH_2Cl_2, benzene and THF. Thus, porphyrin **4** and its derivatives may be useful as standards for planar porphyrins in solution.

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Notes and references

† *Selected data* for **4**: $\delta_H(CDCl_3)$ −4.43 (2H, br s), 1.94–1.98 (16H, m), 2.44–2.48 (16H, m), 4.91 (8H, m), 10.40 (4H, s); $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1}) 389 (162 000), 492 (15 100), 524 (6200), 558 (6200), 610 (2000). For **5**: $\delta_H(CDCl_3)$ −3.10 (2H, br s), 1.22–1.25 (16H, m), 1.54–1.57 (16H, m), 2.51 (8H, m), 7.70–7.77 (12H, m), 8.25–8.36 (8H, m); $\lambda_{max}(CHCl_3)$/nm (ε/dm^3 mol^{-1} cm^{-1} 434 (222 000), 528 (10 400), 568 (sh), 598 (1900), 665 (3000).

‡ *Crystal data* for Zn-**5**: $C_{68}H_{60}N_4Zn{\cdot}H_2O{\bullet}CHCl_3$, M = 1136.02, monoclinic, space group $P21/c$, a = 9.599 (2), b = 26.053 (7), c = 11.809 (2) Å, β = 104.21 (1)°, U = 2863 (1) Å^3, Z = 2, D_c = 1.318 g cm^{-3}, μ = 0.617 mm-1, Mo-Kα radiation, λ = 0.71073 Å, T = 298 K, 7114 determined 6734 independent, 3158 observed reflections [$I > 2\sigma(I)$], R = 0.080, Rw = 0.054. Non-hydrogen atoms were refined anisotropically except for the chloroform carbon atom. Hydrogen atoms were included but not refined. CCDC 182/1441. See http://www.rsc.org/suppdata/cc/1999/2275/ for crystallographic data in .cif format.

1 (*a*) J. Leroy, A. Bondon, L. Toupet and C. Rolando, *Chem. Eur. J.*, 1997; **3**, 1890; (*b*) S. G. DiMagno, A. K. Wertsching and C. R. Ross, II, *J. Am. Chem. Soc.*, 1995, **117**, 8279; (*c*) P. Ochsenbein, K. Ayougou, D. Mandon, R. Weiss, R. N. Astin, K. Jayaraj, A. Gold, J. Terner and J. Fajer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 348; (*d*) K. Ozette, P. Leduc, M. Palacio, J. F. Bartoli, K. M. Barkigia, J. Fajer, P. Battioni and D. Mansuy, *J. Am. Chem. Soc.*, 1997, **119**, 6442.
2 A. Merz, R. Schropp and J. Rex, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 291.
3 (*a*) K. M. Barkigia, M. D. Barber, J. Fajor, C. J. Medforth, M. W. Renner and K. M. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 8851; (*b*) J. Takeda and M. Sato, *Tetrahedron Lett.*, 1994, **35**, 3565.
4 D. J. Nurco, C. J., Medforth, T. P. Forsyth, M. M. Olmstead and K. M. Smith, *J. Am. Chem. Soc.*, 1996, **118**, 10918; T. D. Brennan, W. R. Scheidt and J. A. Schelnutt, *J. Am. Chem. Soc.*, 1988, **110**, 3919.
5 T. Nishinaga, T. Kawamura and K. Komatsu, *Chem. Commun.*, 1998, 2263 and references therein.
6 S. Ito, T. Murashima and N. Ono, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3161.
7 W. Jentzen, E. Unger, X. Z. Song, S. L. Jia, I. T. Tyrk, R. S. Stenner, W. Dreybrodt, W. R. Scheidt and J. A. Shelnutt, *J. Phys. Chem. A*, 1997, **101**, 5789 and references therein.
8 M. S. Somma, C. J. Medforth, N. Y. Nelson, M. M. Olmstead, R. G. Khoury and K. M. Smith, *Chem. Commun.*, 1999, 1221 and references therein.

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