doi:10.1246/cl.2012.168

Homohelical Porphyrin Analogue Embedded with Binaphthol Units

Jun-ichiro Setsune* and Shintaro Omae
Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501

(Received September 5, 2011; CL-110736; E-mail: setsunej@kobe-u.ac.jp)

An expanded porphyrin analogue embedded with binaphthol units provides unidirectional overall helical conformation with hexaanionic N_4O_4 coordination environment that is suited to support a linear array of three metals.

Combination of dipyrrin and 1,1′-binaphthyl unit is of considerable interest because metal complexes with unique chiroptical properties can be generated.[1] In fact, homochiral 1,1′-binaphthyl with dipyrrin boron complexes **1**[1a] and with bisdipyrrin zinc complex **2**[1b] have been reported (Chart 1). Highly diastereoselective (>99% d.r.) helicate formation was achieved in the latter and redox-induced switching of the chiroptical signal was demonstrated in the former. Macrocycle **3**[1c] where the chiral atropisomeric 1,1′-binaphthyl substructure is part of the ring system was formed by the condensation of tetrapyrrolic dialdehyde with 1,1′-binaphthyl-2,2′-diamine. However, extensive study has never been done for this macrocycle probably because of its tendency to undergo hydrolytic decomposition. It is also noteworthy that chiral porphyrin analogues bearing an (*R*)- or (*S*)-1,1′-binaphthyl unit were developed for enantioselective recognition of carboxylate anions.[2] We have been studying the helical chirality induction of expanded porphyrin analogues and their metal complexes by binding chiral amines,[3a] α-hydroxy acids,[3b,3c] and α-amino acids,[3c] which can be applied to chirality sensing. Here, we have developed expanded porphyrin analogues (*S*)-**5** and (*R*)-**5** having a unidirectional overall helical conformation in itself by embedding (*S*)- and (*R*)-1,1′-bi-2-naphthol, respectively, within the macrocycle.

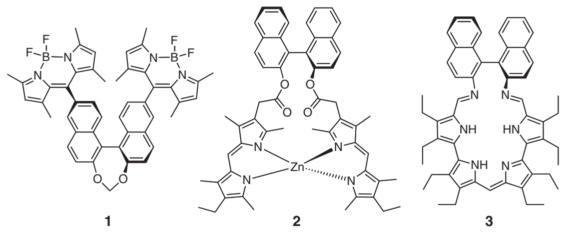
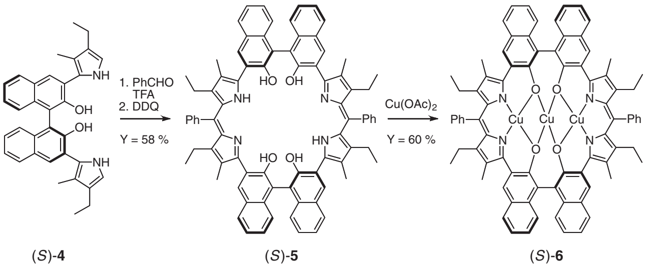


Chart 1.

A porphyrin analogue (*S*)-**5** was prepared in 58% yield through the acid-catalyzed condensation of (*S*)-3,3′-bis(4-ethyl-3-methylpyrrol-2-yl)-1,1′-bi-2-naphthol ((*S*)-**4**) and benzaldehyde followed by DDQ oxidation (Scheme 1).[4] (*S*)-**4** was prepared by using Pd-catalyzed cross-coupling reaction of 2-borylpyrrole and (*S*)-3,3′-diiodo-1,1′-bi-2-naphthol in 60% yield as a key transformation.[4,5] A modified protocol for unactivated substrates in the cross coupling using tris(dibenzylideneacetone)dipalladium ([$Pd_2(dba)_3$]), tricyclohexylphosphine ($P(Cy)_3$), and K_3PO_4 at 90 °C for 24 h worked well in this case.[6] Synthetic transformation to (*S*)-**5** and (*R*)-**5** starting from (*S*)- and (*R*)-1,1′-bi-2-naphthol, respectively, did not reduce the original optical purity, as evidenced by HPLC analysis of (*S*)-**5** and (*R*)-**5** on a chiral phase.[4]



Scheme 1. Synthesis of a hybrid macrocycle (*S*)-**5** and its trinuclear Cu complex (*S*)-**6**.

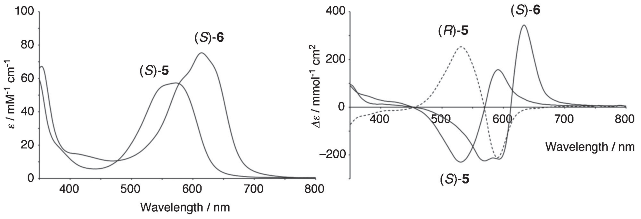


Figure 1. UV–vis (left) and CD (right) spectra of (*S*)-**5**, (*R*)-**5** (broken line), and (*S*)-**6** in CH_2Cl_2.

The CD spectrum of (*S*)-**5** shows a bisignate signal with a positive 1st Cotton effect at 591 nm and a negative 2nd Cotton effect at 530 nm in CH_2Cl_2. A mirror image CD couplet was observed for (*R*)-**5** (Figure 1). Metallation of (*S*)-**5** with $Cu^{II}(OAc)_2\cdot 2H_2O$ in CH_2Cl_2–MeOH containing triethylamine at room temperature for 5 h afforded a trinuclear Cu^{II} complex (*S*)-**6** in 60% yield.[4] The UV–vis absorption band of (*S*)-**6** at 614 nm is by 42 nm red shifted relative to that of (*S*)-**5** at 572 nm. The CD couplet of (*S*)-**6** showed a positive 1st Cotton effect at 634 nm and split negative peaks at 593 and 569 nm.

X-ray crystallography of (*S*)-**6** shows that three Cu^{II} ions are aligned linearly with the central Cu^{II} ion shared between two Cu_2O_2 diamond cores (Figure 2).[7] The Cu(1)Cu(2)Cu(1′) angle is 174.7° and two Cu_2O_2 planes make a plane-to-plane angle of 8.3°. The Cu_2O_2 diamond core of (*S*)-**6** is quite planar as seen from the deviation less than 0.012 Å of each atom from the Cu_2O_2 mean plane. The terminal Cu^{II} ions are in a distorted square-planar geometry where the angle between the N(1)Cu(1)N(2) plane and the O(1)Cu(1)O(2) plane is 30.7°. The central Cu^{II} ion is in a square-pyramidal geometry composed of four binaphthol oxygens as the basal plane and a weakly coordinating water oxygen in the apical position. The apical Cu–O distance (2.43 Å) is much longer than the equatorial Cu–O distances (1.922 and 1.949 Å). The Cu(1)–Cu(2) distance

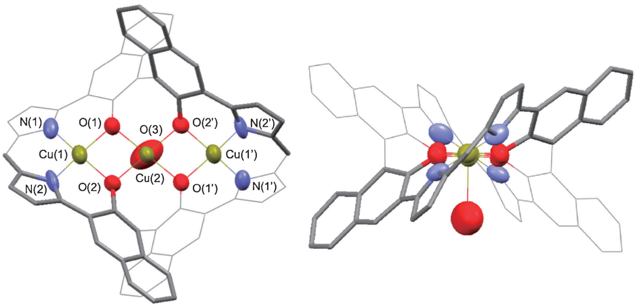


Figure 2. X-ray diagrams of (*S*)-**6**; a top view (left) and a side view (right) omitting peripheral alkyl groups and phenyl groups for clarity: Cu(1)–N(1) 1.851(8), Cu(1)–N(2) 1.809(8), Cu(1)–O(1) 1.877(6), Cu(1)–O(2) 1.893(5), Cu(2)–O(1) 1.922(5), Cu(2)–O(2) 1.949(6), Cu(2)–O(3) 2.43(2), Cu(1)–Cu(2) 2.9096(10) Å.

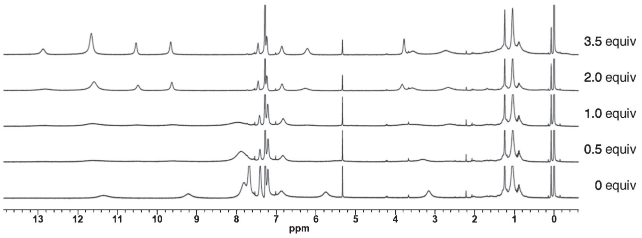


Figure 3. ^{1}H NMR titration of (*S*)-**6** with 0.5, 1.0, 2.0, and 3.5 equiv of butylamine at 253 K in $CDCl_3$.

(2.910 Å) of (*S*)-**6** is one of the shortest among linear trinuclear Cu^{II} complexes of the (L)Cu(μ-OR)$_2$Cu(μ-OR)$_2$Cu(L) form.[8]

The magnetic moment (3.2 μ_B) of (*S*)-**6** measured by the Evans method in $CDCl_3$ at 293 K is close to the spin only theoretical value (3.0 μ_B) for three noninteracting $S = 1/2$ electron spin system. It is noteworthy that all the proton signals of (*S*)-**6** are detected in the chemical shift range of 0–12 ppm in the ^{1}H NMR as a result of fast electron spin relaxation.[4] Addition of butylamine to (*S*)-**6** caused chemical shift changes without changing D_2 symmetric spectral pattern (Figure 3). The pyrrole β-methyl proton signal underwent high frequency shift from 7.81 to 11.66 ppm at 253 K. When 0.5 equiv of butylamine was added, signals of (*S*)-**6** shifted and got broader probably because of fast ligand exchange. Only a single set of signals due to the butylamine adduct appeared at the two equiv of butylamine. UV–vis binding study of (*S*)-**6** with butylamine in CH_2Cl_2 showed a parabolic titration curve that fits well with one-to-one binding isotherm of the association constant $K = 2200\,M^{-1}$.[4] Based on these observations in addition to the X-ray structure of (*S*)-**6** having one apical water ligand at the central Cu^{II} ion, it is reasonably considered that butylamine binds to the central Cu^{II} ion without decomposing the Cu_3O_4 core. Very fast binding equilibrium of one butylamine ligand between both apical sites accounts for the D_2 symmetric ^{1}H NMR spectral pattern of the monoamine adduct.

The macrocycle core of (*S*)-**6** is well preorganized for linear trinuclear complexes of the (L)M(μ-OR)$_2$M(μ-OR)$_2$M(L) form. Coordination chemistry of porphyrin analogues of large ring size has extensively been studied to generate a number of dinuclear metal complexes.[9] However, examples of trinuclear complexes have been still quite limited and (*S*)-**6** is the first example of linear trinuclear complex of porphyrin analogues.[10]

Detailed study of the structure and magnetic properties of linear trinuclear complexes is now ongoing. Application to chirality transfer or chirality sensing would be of interest on the basis of reversible coordination of ligands to the stable M_3O_4 core demonstrated here.

This work was supported by a Grant-in-Aid for Scientific Research (No. 21550045) from the MEXT Japan and a grant (No. 211068) from the Hyogo Science and Technology Association, Japan.

References and Notes

1 a) G. Beer, C. Niederalt, S. Grimme, J. Daub, *Angew. Chem., Int. Ed.* **2000**, *39*, 3252. b) A. A.-S. Ali, R. E. Benson, S. Blumentritt, T. S. Cameron, A. Linden, D. Wolstenholme, A. Thompson, *J. Org. Chem.* **2007**, *72*, 4947. c) K. Gunst, S. Seggewies, E. Breitmaier, *Synthesis* **2001**, 1856.

2 H. Miyaji, S.-J. Hong, S.-D. Jeong, D.-W. Yoon, H.-K. Na, J. Hong, S. Ham, J. L. Sessler, C.-H. Lee, *Angew. Chem., Int. Ed.* **2007**, *46*, 2508; J. L. Sessler, A. Andrievsky, V. Král, V. Lynch, *J. Am. Chem. Soc.* **1997**, *119*, 9385.

3 a) J.-i. Setsune, A. Tsukajima, N. Okazaki, J. M. Lintuluoto, M. Lintuluoto, *Angew. Chem., Int. Ed.* **2009**, *48*, 771. b) J. M. Lintuluoto, K. Nakayama, J.-i. Setsune, *Chem. Commun.* **2006**, 3492. c) J.-i. Setsune, M. Kawama, T. Nishinaka, *Tetrahedron Lett.* **2011**, *52*, 1773.

4 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

5 J.-i. Setsune, M. Toda, K. Watanabe, P. K. Panda, T. Yoshida, *Tetrahedron Lett.* **2006**, *47*, 7541; J.-i. Setsune, K. Watanabe, *J. Am. Chem. Soc.* **2008**, *130*, 2404.

6 N. Kudo, M. Perseghini, G. C. Fu, *Angew. Chem., Int. Ed.* **2006**, *45*, 1282; G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555.

7 Crystal data for (*S*)-**6**: Formula $C_{82}H_{62}Cu_3N_4O_4\cdot6H_2O$, $M_r = 1466.08$, hexagonal, space group $P3_221$, $a = b = 22.7984(16)$, $c = 15.2704(13)$ Å, $V = 6873.7(9)$ Å^3, $Z = 3$, $D_{calcd} = 1.063\,Mg\,m^{-3}$, μ(Mo K$\alpha$) = 0.739 mm^{-1}, $T = 299(2)$ K, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0952$, $wR_2 = 0.2267$, $GOF = 0.952$. CCDC-842598.

8 J. M. Epstein, B. N. Figgis, A. H. White, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **1974**, 1954; M. Ruf, C. G. Pierpont, *Angew. Chem., Int. Ed.* **1998**, *37*, 1736; L. Cronin, P. H. Walton, *Inorg. Chim. Acta* **1998**, *269*, 241; M. Du, X.-J. Zhao, J.-H. Guo, X.-H. Bu, J. Ribas, *Eur. J. Inorg. Chem.* **2005**, 294; G. Izzet, H. Akdas, N. Hucher, M. Giorgi, T. Prangé, O. Reinaud, *Inorg. Chem.* **2006**, *45*, 1069; R. Shakya, A. Jozwiuk, D. R. Powell, R. P. Houser, *Inorg. Chem.* **2009**, *48*, 4083; C. A. Barta, S. R. Bayly, P. W. Read, B. O. Patrick, R. C. Thompson, C. Orvig, *Inorg. Chem.* **2008**, *47*, 2294; S. Thakurta, J. Chakraborty, G. Rosair, J. Tercero, M. S. El Fallah, E. Garribba, S. Mitra, *Inorg. Chem.* **2008**, *47*, 6227; Y. Song, P. Gamez, O. Roubeau, M. Lutz, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **2003**, 2924; X.-H. Bu, M. Du, Z.-L. Shang, R.-H. Zhang, D.-Z. Liao, M. Shionoya, T. Clifford, *Inorg. Chem.* **2000**, *39*, 4190.

9 J. L. Sessler, E. Tomat, *Acc. Chem. Res.* **2007**, *40*, 371; S. Shimizu, A. Osuka, *Eur. J. Inorg. Chem.* **2006**, 1319; E. Vogel, *J. Heterocycl. Chem.* **1996**, *33*, 1461; S. J. Weghorn, J. L. Sessler, V. Lynch, T. F. Baumann, J. W. Sibert, *Inorg. Chem.* **1996**, *35*, 1089; S. Shimizu, V. G. Anand, R. Taniguchi, K. Furukawa, T. Kato, T. Yokoyama, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 12280; L. K. Frensch, K. Pröpper, M. John, S. Demeshko, C. Brückner, F. Meyer, *Angew. Chem., Int. Ed.* **2011**, *50*, 1420; G. Givaja, M. Volpe, J. W. Leeland, M. A. Edwards, T. K. Young, S. B. Darby, S. D. Reid, A. J. Blake, C. Wilson, J. Wolowska, E. J. L. McInnes, M. Schröder, J. B. Love, *Chem.—Eur. J.* **2007**, *13*, 3707; J. M. Veauthier, E. Tomat, V. M. Lynch, J. L. Sessler, U. Mirsaidov, J. T. Markert, *Inorg. Chem.* **2005**, *44*, 6736.

10 Y. Kamimura, S. Shimizu, A. Osuka, *Chem.—Eur. J.* **2007**, *13*, 1620; M. Inoue, C. Ikeda, Y. Kawata, S. Venkatraman, K. Furukawa, A. Osuka, *Angew. Chem., Int. Ed.* **2007**, *46*, 2306; J.-i. Setsune, M. Toda, T. Yoshida, *Chem. Commun.* **2008**, 1425.