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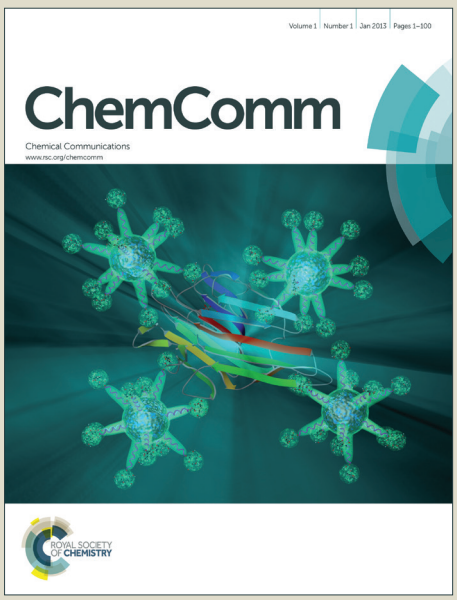

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Bis(zinc porphyrin) as a CD-sensitive bidentate host molecule: direct determination of absolute configuration of mono-alcohols†

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A facile, direct protocol to determine the absolute configurations of chiral mono-alcohols without analyte derivatization can now be realized utilizing a novel circular dichroic (CD)-sensitive bis(zinc porphyrin) BP1 host system. Binding of mono-alcohols to BP1 should be greatly enhanced by the simultaneous double coordination of the hydroxyl group to the two central metals of the porphyrin subunits.

Determining the absolute configuration of chiral organic molecules remains an important and challenging task in materials and life sciences. Recently, supramolecular chirality induction (supramolecular chirogenesis) with a circular dichroic (CD)-sensitive host molecule possessing two or more chromophores with known electronic transitions has attracted interest for the sensitive, non-empirical, microscale determination of the absolute configuration of chiral organic molecules. Upon complexation with chiral substrates, the host systems yield the corresponding host-guest complexes with one favored conformation, which exhibits exciton-coupled bisignate CD (ECCD) spectra that reflect the absolute configuration of the substrates.[1] Several elaborate CD-sensitive host systems, including bis(metalloporphyrin) derivatives,[2] have been developed as chirality probes[3] for determining the absolute stereochemistry of chiral amines,[2a,3a-f,m,n] diamines,[2b,e,g-i,3a,b] amino acids,[2c,3b,g,h,j,k] carboxylates,[2c,j,k,3b,i-l] and hydroxyl-containing bifunctional substrates, such as 1,2-aminoalcohols,[2b,3n] vicinal diols,[2b,d] 1,*n*-glycols,[2l] and epoxy alcohols.[2f] Apart from the synthetic difficulty in obtaining these host systems, another major problem is their insufficient binding affinity for weakly ligating substrates, particularly simple chiral mono-alcohols. Indeed, there is almost no precedent for sensing the absolute configuration of chiral mono-alcohols at low concentrations and ambient temperature without chemical modifications. To the best of our knowledge, there is only one example of a highly Lewis acidic porphyrin tweezer system; ethane-bridged bis(magnesium porphyrin), developed by Inoue and Borovkov, has overcome the disadvantages of the method.[4] This elegant host system shows strong ECCD signals above 400 nm,

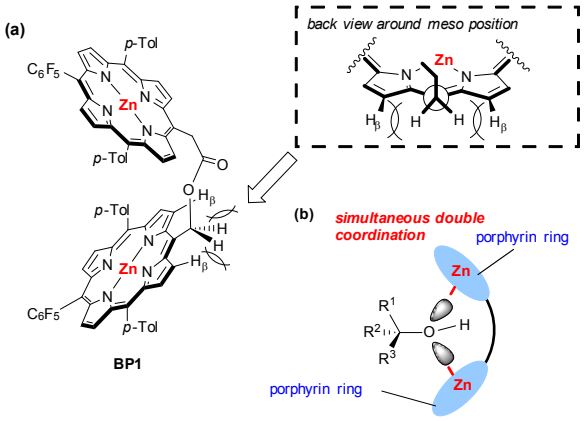

Fig. 1 (a) Structure of bis(zinc porphyrin) **BP1** and (b) schematic of its simultaneous double coordination with mono-alcohols.

where the potential for sample interference from other absorbing species is minimized, and there is broad scope for sensing chiral mono-alcohols. However, this bis(magnesium porphyrin) is moisture sensitive owing to the highly oxophilic central magnesium ion. As is the often the case with magnesium-based porphyrin derivatives,[5] the bis(magnesium porphyrin) gradually decomposes into the demetallated free base, even in neutral solution, which could be problematic for the chiral sensing of target substrates. Therefore, developing efficient, robust CD-sensitive host systems with a strong binding affinity for weakly ligating substrates, such as chiral mono-alcohols, still remains a highly desirable target in supramolecular chirogenesis.[6,7]

Herein, we report the design and synthesis of bis(zinc porphyrin) **BP1** bearing a splayed cofacial structural motif as a CD-sensitive host molecule, which can be used as an efficient, chemically robust chirality probe for direct determination of absolute configuration of mono-alcohols at ambient temperature without chemical modifications (Fig. 1). In the complexation with mono-alcohols, the host molecule **BP1** can capture both hydroxyl lone pairs through simultaneous coordination with the two central metals of the porphyrin subunits, thereby exhibiting high affinity for weakly ligating mono-alcohols despite the lower oxophilicity of its central zinc ions.

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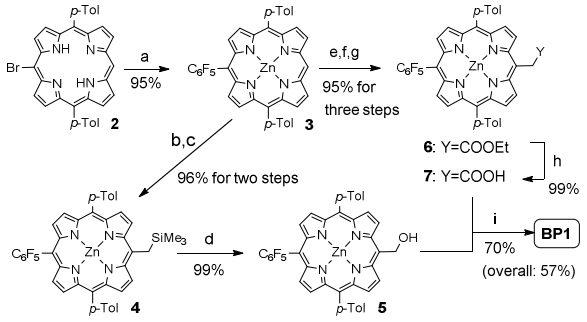
The design of bidentate host system **BP1** stems from following considerations. (1) Zinc is the central metal of choice for bidentate bis(metalloporphyrin) compounds because of its excellent moisture resistance. (2) An alkyl substituent directly attached at the *meso* position of the porphyrin ring points upward from the π plane owing to the steric repulsion between the hydrogen atoms on the benzylic carbon of the alkyl group and those at the β positions of the porphyrin ring close to the meso substituent (Fig. 1). Hence, when two porphyrin units are linked by an alkyl chain spacer between the *meso* carbons, these porphyrin units are arranged in a splayed cofacial structural motif, which should allow simultaneous double coordination of the hydroxyl group with the central zinc ions of bis(zinc porphyrin) compounds. (3) Incorporating an ester moiety into the alkyl spacer would provide bis(zinc porphyrin) derivatives with significant lateral flexibility, which is required for effective CD-sensitive host molecules in the ECCD protocol. (4) The CH_2COOCH_2 linkage is the shortest ester-containing alkyl chain spacer, which minimizes the interplanar distance between the porphyrin subunits, and thus may provide a suitable cleft in the host molecule for its simultaneous coordination to the hydroxyl group. Finally, (5) appending C_6F_5 substituents to the porphyrin periphery would enhance the Lewis acidity of the zinc porphyrin subunits, strengthening the binding affinity of the host molecules for hydroxyl groups.

The bidentate bis(zinc porphyrin) **BP1** was constructed from *meso* brominated porphyrin starting material **2** as outlined in Scheme 1. This convergent route involves Pd-catalyzed pentafluorophenylation,[8a] silylmethylation,[8b] and ethoxycarbonylmethylation of porphyrins,[8c] which we have recently developed.[8d] Each synthetic step of the procedure could be carried out over a 0.1 mmol scale to afford the corresponding functionalized porphyrin derivatives in good to high yields, and **BP1** was obtained in 57% overall isolated yield based on starting *meso*-bromoporphyrin **2**.

The cofacial arrangement of porphyrin rings in **BP1** was identified by ^{1}H NMR and UV-vis spectroscopy. In the ^{1}H NMR spectrum of **BP1**, the proton signals of the β-pyrrolic positions of the porphyrin units exhibited significant upfield shifts compared with those of its monomeric counterparts, **5** and **6** (Fig. S1, ESI†). These upfield signal shifts can be explained by the shielding effect caused by ring current interactions between the closely associated porphyrin moieties. The absorption spectrum of **BP1** in hexane at 25 °C showed that the Soret band was broadened with a shoulder at a longer wave length (419 nm) to the absorption maximum (410 nm), probably because of excitonic dipole-dipole coupling by the slipped-cofacial coordination (Fig. S2 and S3, ESI†).[9] These observations also support the cofacial disposition of rings in **BP1**.[10]



Scheme 1 Synthesis of bis(zinc porphyrin) **BP1**. Reagents and conditions: (a) $(C_6F_5)_2Zn$ (5 equiv), $Pd(OAc)_2$ (5 mol %), *t*-$Bu_3P{\cdot}HBF_4$ (10 mol %), THF, 65 °C; (b) NBS, $CHCl_3$, 0 °C; (c) Me_3SiCH_2MgCl (3 equiv), PEPPSI (4 mol %), THF, 60 °C; (d) DDQ, THF-H_2O (10:1), 25 °C; (e) NBS, $CHCl_3$, 0 °C; (f) HCl aq; (g) $BrZnCH_2COOEt$ (20 equiv), $Pd(OAc)_2$ (5 mol %), Cy_3P (10 mol %), THF, 65 °C; (h) NaOH aq; (i) EDC (3 equiv), DMAP (1 equiv), THF, 25 °C.

Next, we focused on the binding between mono-alcohols and **BP1**. ^{1}H NMR binding experiments[11] and UV-vis titrations confirmed the enhanced binding affinity of **BP1**, confining the mono-alcoholic guest within the cleft between the two porphyrin units. In the ^{1}H NMR analysis (Fig. S4, ESI†), adding ethanol to a $CDCl_3$ solution of monomeric zincated porphyrin **6** caused a 0.2 ppm upfield shift of the methylene protons of ethanol compared with the free alcohol. In contrast, ethanol bound to **BP1** showed a larger upfield shift (0.4 ppm) of the methylene protons because of the stronger ring current of the two porphyrins. These observations are consistent with the coordination of the mono-alcoholic guest in the cleft of the host. This binding was also observed through the UV-vis titration of **BP1** with ethanol in hexane at 25 °C. The titration of ethanol (1-600 equiv) complexed with **BP1** exhibited a small bathochromic shift (~3 nm) in the absorption maximum from 410 to 413 nm (Fig. S5, ESI†),[12] whereas a larger bathochromic shift (~15 nm) was present upon ethanol binding with monomeric counterpart **6** (Fig. S6, ESI†). These observations indicate that the slipped-cofacial arrangement of the two porphyrins in **BP1** was well preserved upon binding the host molecule binding the mono-alcoholic guest. A Job plot reveals a 1:1 stoichiometry for the binding between **BP1** and the mono-alcoholic guest (Fig. S7, ESI†). **BP1** bound more strongly to ethanol than to its monomeric counterpart **6**; the binding constants increased by more than one order of magnitude for the complex of ethanol with **BP1** (K_{assoc} = 2960 M^{-1}) compared with that with **6** (K_{assoc} = 150 M^{-1}) (Fig. S5 and S6, ESI†).[13] These data indicate the formation of a 1:1 complex of **BP1** and ethanol, in which the mono-alcoholic guest is strongly bound inside the cleft between the two porphyrins of the host molecule.

This sandwich binding mode led us to suspect that the exceptionally strong binding affinity of **BP1** toward mono-alcohols would probably arise from the simultaneous double coordination of the hydroxyl group with two central zinc ions in the host-guest complexation. This simultaneous double coordination could be observed through the CD analysis of chiral mono-alcohols bound to **BP1**. Fig. 2a illustrates a working model that would predict the ECCD spectra for a chiral mono-alcohol with an *R* configuration complexed with **BP1**. The alcohol is represented by the Newman projection with the oxygen atom of its hydroxyl group in front and the stereogenic center at the back. We proposed that the bidentate host **BP1** approaches the hydroxyl group of the *R* alcohol from the side of its smallest group (S) to capture both the hydroxyl lone pairs (Fig. 2a, dashed box). Porphyrin ring **P1** would rise above porphyrin ring **P2** because of the steric repulsion between **P1** and the largest substituent (L) on the left side. As a result, **P1** adopts a counter clockwise helicity relative to **P2**, which would produce a negative ECCD spectrum.[14] Fig. 2b shows the complexation of chiral alcohol (*R*)-**8** with **BP1** in hexane at 25 °C that leads to the anticipated negative spectrum in the Soret region, where the hydrogen atom, methyl, and phenyl moieties on the stereogenic carbon correspond to the smallest (S), medium (M), and largest (L) groups in the working model. As expected, enantiomer (*S*)-**8** yields the opposite

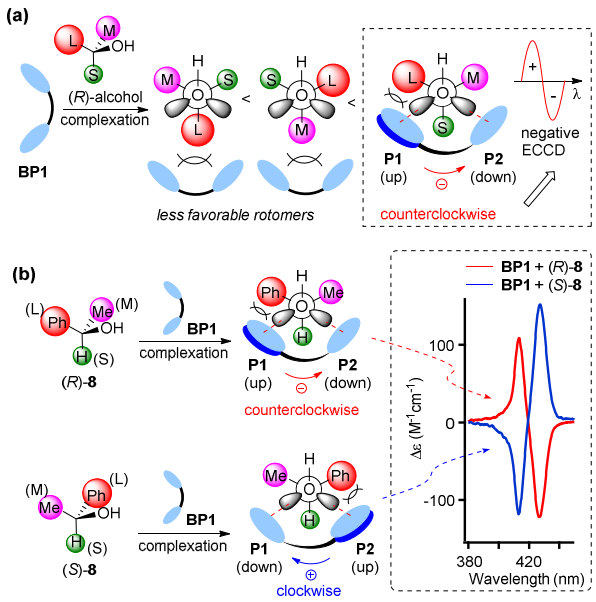


Fig. 2 (a) Complexation of bidentate host molecule **BP1** with chiral mono-alcohols, and proposed working model for assigning the absolute configuration of the chiral guest. (b) Left: Proposed working model for predicting the helicity in complexes of **BP1** and chiral mono-alcohols (*R*)-**8** and (*S*)-**8**. Right (dashed box): CD spectra of **BP1** (1.7 μM) in the presence (1000 equiv) of chiral mono-alcohols (*R*)-**8** (red line) and (*S*)-**8** (blue line) in 1% CH_2Cl_2/*n*-hexane at 25 °C.

ECCD spectrum.

To test the scope of the supramolecular chirogenesis using **BP1** as a CD-sensitive bidentate host molecule, a variety of chiral mono-alcohols with different substituents were investigated. As shown in Fig. 3, Table 1 and Fig. S9-S17 in ESI,† all the mono-alcoholic substrates examined upon complexation with bidentate host **BP1** exhibited the corresponding ECCD signals with acceptable to fairly high amplitude in hexane at 25 °C. In all cases, the predicted ECCD sign based on the binding mode in Fig. 2 agreed with the observed ECCD couplet of the mono-alcohol-**BP1** complex. The method showed promising functional group compatibility; the substrates bearing aryl, alkenyl, alkynyl, and halogenic moieties and simple alkyl chains were tolerated well, producing the expected results. Remarkably, even the differences in the steric bulk of the methyl and ethyl groups in (*S*)-**12** and (*R*)-**12** could be distinguished. The presence of ether functionalities in **13**, which could coordinate to zinc porphyrins, did not interfere with the chiral sensing. Furthermore, much less nucleophilic substrates (*S*)-**14** and (*R*)-**14** that bear highly electrophilic CF_3 groups could participate as guests in the complexation under similar conditions, producing ECCD spectra with acceptable amplitude. Cyclic alcohols **15** and **16** were also compatible with the chiral sensing, and furnished the expected ECCD signals with medium amplitude. Interestingly, bidentate host **BP1** could bind cyclic alcohols **16** bearing a tertiary carbinol carbon and it produced the expected ECCD spectra. The CD amplitude intensities obtained from the host-gust complexes of 2-butanol **12** and menthol **15** with **BP1** were roughly similar to those with ethane-bridged bis(magnesium porphyrin) developed by Inoue and Borovkov.[4] These observations should indicate that the binding affinity of **BP1** for mono-alcohols is almost comparable to the bis(magnesium porphyrin), although its binding constants for mono-alcohols have not been reported. Quite large CD amplitude were

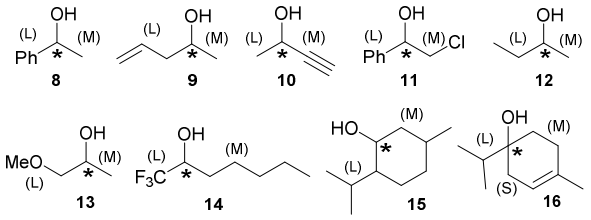


Fig. 3 Structures of chiral mono-alcohols **8**-**16**; assignments of the S, M, and L groups are based on either their conformational energies (*A* values), or the Taft's steric substituent constants (E_s), see, Fig. S9-S17 in ESI†.

Table 1 ECCD data for chiral mono-alcohols with **BP1**.[a]

Chiral alcohol[b]	Predicted sign	1st λ nm (Δε)	2nd λ nm (Δε)	A[c]
(*R*)-**8**	neg	427 (-122)	413 (+108)	-230
(*S*)-**8**	pos	427 (+151)	413 (-115)	+266
(*R*)-**9**	neg	428 (-7)	416 (+9)	-16
(*S*)-**9**	pos	430 (+10)	411 (-8)	+18
(*R*)-**10**[d]	pos	428 (+41)	415 (-24)	+65
(*S*)-**10**[d]	neg	428 (-49)	414 (+32)	-81
(*R*)-**11**[d]	pos	429 (+21)	413 (-17)	+38
(*S*)-**11**[d]	neg	430 (-14)	413 (+19)	-33
(*R*)-**12**	neg	426 (-9)	415 (+7)	-16
(*S*)-**12**	pos	426 (+9)	413 (-9)	+18
(*R*)-**13**	neg	427 (-252)	412 (+137)	-389
(*S*)-**13**	pos	427 (+311)	412 (-161)	+472
(*R*)-**14**	neg	427 (-6)	416 (+5)	-11
(*S*)-**14**	pos	428 (+7)	415 (-4)	+11
(*R*)-**15**	neg	426 (-46)	414 (+25)	-71
(*S*)-**15**	pos	426 (+48)	415 (-35)	+83
(*R*)-**16**	neg	427(-54)	415(+39)	-93
(*S*)-**16**	pos	427 (+56)	414 (-34)	+90

[a] All CD measurements were performed with 1.5-1.7 μM **BP1** in 1% CH_2Cl_2/*n*-hexane at 25 °C; 1000 equiv of chiral mono-alcohol was used to obtain the data. [b] All substrates were >95% ee. [c] $A = \Delta\varepsilon_{1st} - \Delta\varepsilon_{2nd}$. [d] The substituent's bulkiness order differs from the priority rules.

observed for substrates **8** and **13** compared with other substrates examined. For these substrates, additional other interactions (e.g. π-π or CH-π interactions in **8** and coordination by both oxygen in **13**) might concurrently occur along with the simultaneous double coordination in the complexation with **BP1**. Further experiments are currently underway to elucidate the mechanism and geometries for the present host-guest complexation in more detail.

In summary, we have developed a facile, fast method for determining the absolute configurations of chiral mono-alcohols based on the supramolecular ECCD protocol at ambient

temperature with no chemical derivatization. The success of this method relies on our splayed cofacial bis(zinc porphyrin) **BP1**, which functions as a bidentate CD-sensitive host molecule. **BP1** exhibits high affinity for weakly ligating mono-alcohols through the simultaneous double coordination of the hydroxyl group to the two central metals of the porphyrin subunits. The combination of **BP1** as a chirality probe and the simple working model in Fig. 2 is effective for determining the absolute configuration of chiral mono-alcohols non-empirically. Moreover, **BP1** can be synthesized easily in high yields, and it is robust and does not require special handling. Elucidation of the precise mechanism and detailed geometries for the complexation of the bis(zinc porphyrin) **BP1** with mono-alcohols and applying the host molecule for other functional groups are now under active investigation.

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10 Approximate 60° dihedral angle of the two porphyrin planes and an 8.9 Å metal-metal distance are estimated by the DFT calculation for **BP1**, see Fig. S8, ESI†.

11 Studies on ^{1}H-NMR spectroscopic properties of a series of supramolecular chiral 1:1 bis(porphyrin)-chiral diamine complexes have been reported by Rath and co-workers, see refs 2e, 2g-i.

12 This small bathochromic shift observed upon binding of ethanol with **BP1** should be the result of two opposite effects: a ~10 nm bathochromic shift as a result of the alcohol binding with the zincated porphyrin, and the hypso-chromic shift caused by bringing the two porphyrin rings close to each other. For a leading discussion, see ref 2b.

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