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2,2′-Biphenyldiol-bridged bis(free base porphyrin): synthesis and chiroptical probing of asymmetric amino alcohols

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Abstract—A new type of bis(free base porphyrin) **1**, in which two porphyrin units are attached to the 5,5′-positions of the 2,2′-biphenyldiol group, has been synthesized. It exhibits exciton-coupled bisignate circular dichroism (CD) spectra upon interaction with chiral amino alcohols. The chiral information from the stereogenic center of amino alcohols is introduced as a twist of the porphyrin units in **1** via hydrogen bonding interactions, detectable by the signal in the CD spectrum. Based on these findings, it is proposed that **1** should serve as a reporter unit of chiral sensor systems.

Bisporphyrins with a well-defined spacer unit can serve as preorganized molecular systems. In biomimetics, there have been considerable efforts to develop covalently linked bisporphyrins as a catalytic model for the direct four-proton, four-electron reduction of O_2 to H_2O,[1] photosynthetic reaction center, and light-harvesting systems.[2] Metal-centers of the porphyrin units can form coordination bonds with guest Lewis bases, facilitating not only the assembly of supramolecular arrays[3] but also receptor systems for diamines[4] and fullerenes.[5] On another front, there is a growing interest in the interdisciplinary area of supramolecular chemistry and chirality in which bisporphyrins can act as chiral receptors and circular dichroism (CD) reporters.[6] If porphyrin bis-chromophore in the system, with known electric transitions, can be arranged in a clockwise or anticlockwise sense upon complexation with chiral guests, its behavior will allow us to determine the absolute configuration by means of CD spectroscopy.[7] Accordingly, the choice of linker unit between the porphyrins is significant; preorganized flexibility is required for a chiral screw conformation of porphyrin units upon interaction with asymmetric substrates. 2,2′-Biphenyldiols with C_2-symmetry can act as the simplest dynamically racemic linker parts. The atropisomeric biphenyl moiety appears particularly suitable for chirality control, promising not only supramolecular systems through intermolecular interaction[8] but also unique *tropos* ligands in asymmetric catalysis.[9] These facts indicate that 2,2′-biphenyldiol has a great promise in the development of supramolecular systems for chirality manipulation.[10]

We have synthesized the titled compound **1**, and investigated its fundamental properties. As described below in detail, the biphenyldiol unit in **1** binds to chiral amino alcohols in a nonpolar solvent such as CH_2Cl_2 to induce chirality through rotation along the phenyl–phenyl linkage. The information can be read out by CD spectra based on chirality-twisted free base porphyrins. We believe that **1** is the first prototype of chiral probes obtained by simply combining dynamically racemic biphenyldiol with bis(free base porphyrin) units.

The synthetic path for target **1** is shown in Scheme 1. 5,5′-Dibromo-2,2′-dimethoxy-1,1′-biphenyl[11] was allowed to react with KI in the presence of CuI to give **2** in a 64% yield, followed by a Pd-mediated coupling reaction using (trimethylsilyl)acetylene in the presence of CuI to give 5,5′-diethynyl derivative **3** in an 80% yield. The connection of 5-(4-iodophenyl)-10,15,20-triphenylporphyrin[12] to **3** by a copper-free cross-coupling reaction using $Pd(PPh_3)_4$ led to 2,2′-dimethoxy-1,1′-biphenyl-derived bis(free base porphyrin) **4** in a 53% yield. Finally, deprotection using BBr_3 gave the desired **1** in a 90% yield.

The structure was assigned by various spectroscopic data.[13] It was found that ^1H NMR spectra using CD_2Cl_2

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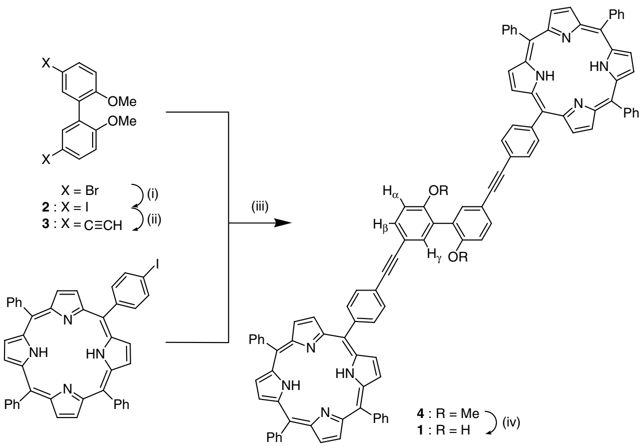


Scheme 1. Reagents and conditions: (i) KI, CuI, HMPA, 160 °C, 26 h, 64%; (ii) CuI, $(PPh_3)_2PdCl_2$, TMSA, dry $^iPr_2NH$, 70 °C, 3 h, and then 1 N KOHaq, MeOH–THF = 2:1(v/v), rt, 3 h, 80%; (iii) $(PPh_3)_4Pd$, dry DMF–dry NEt_3 5:1 (v/v), 50 °C, 65 h, 53%; (iv) BBr_3, dry CH_2Cl_2, −40 °C, 2.5 h, 90%.

show changes in the shift of protons in **1** with varying concentration from 0.48 mM to 9.7 mM (Fig. 1); the largest shift difference was obtained for the H_α proton, being the *ortho* position of phenol–OH, by 0.93 ppm. This is attributable to self-association of **1** via intermolecular hydrogen bonding interactions between the biphenyldiol units. Further, the chemical shift broadened with increasing concentration, suggesting that a conformational change occurs dynamically with the self-association. ^1H NMR dilution experiments in CD_2Cl_2 on **1** were then carried out; the shift of the most sensitive H_α upon changing the concentration was monitored to estimate the dimerization constant of K_d ($20 \pm 12\ M^{-1}$).[14] Based on this parameter, **1** exists mainly as a monomer (98%) at 0.48 mM, indicating that at a UV–vis or CD detectable concentration, **1** does not undergo the self-association.

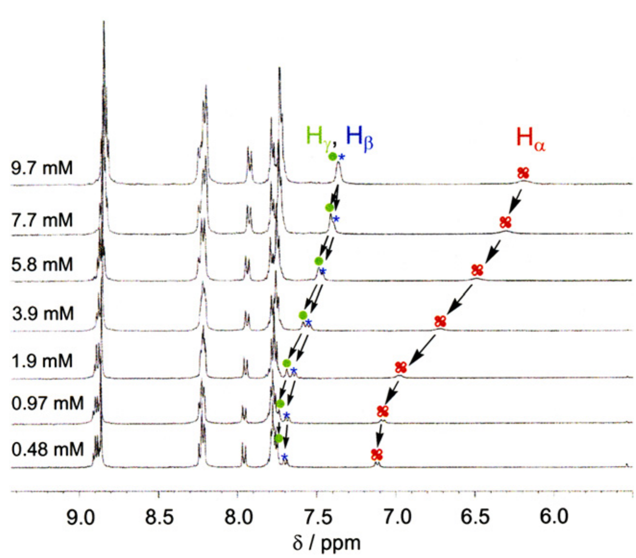
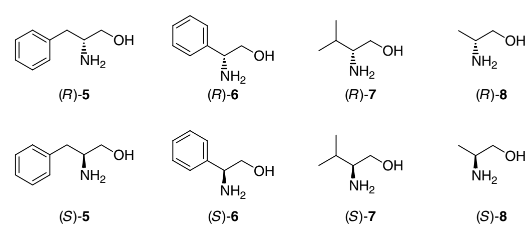


Figure 1. ^1H NMR spectra of **1** at several concentrations in CD_2Cl_2 at 23 °C.

Compound **1** consists of porphyrin units and a chirality-flexible (*tropos*) 2,2′-biphenyl linker. This combination leads us to investigate whether **1** is able to read out the chirality of any guest species, which interacts with the biphenyldiol linker. Figure 2a shows CD spectra of **1** (25 μM) in CH_2Cl_2 upon adding incremental amounts of (*R*)-phenylalaninol, (*R*)-**5**, at 25 °C; although **1** is inherently CD inactive, addition of the chiral guest gave bisignated Cotton effects at 425 nm and 415 nm, respectively. The λ_{CD} value is in good agreement with the λ value of the Soret band of porphyrin-chromophore, indicating that the corresponding negative exciton-coupled CD spectrum was obtained as a result of a chiral twist of the built-in porphyrins. Figure 2b shows the changes in CD amplitude as a function of the concentra-



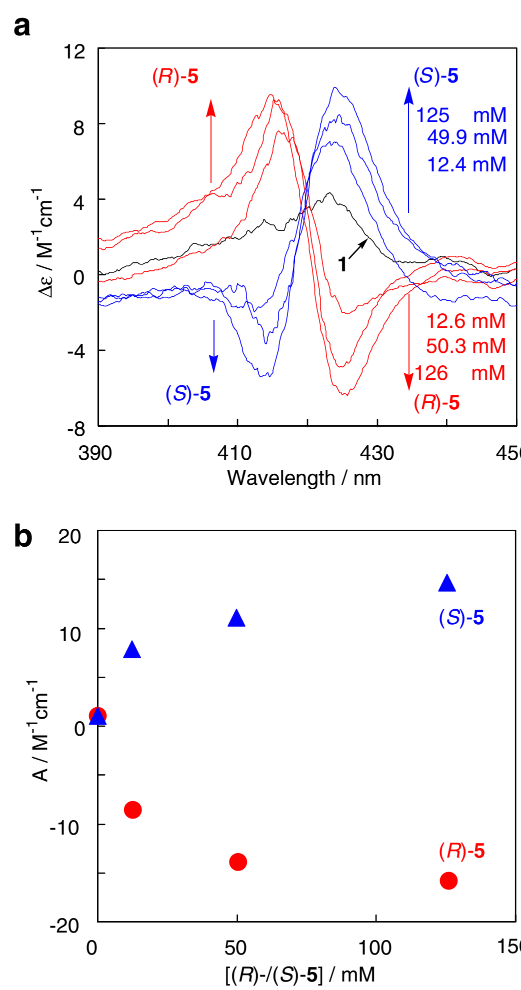


Figure 2. (a) CD spectra of **1** (25 μM) upon addition of incremental amounts of chiral **5**; (b) Changes in amplitude [A ($=\Delta\varepsilon_1 - \Delta\varepsilon_2$)] of **1** (25 μM) as a function of the concentration of chiral **5** in CH_2Cl_2 at 25 °C.

tions of (*R*)-**5** in CH_2Cl_2 at 25 °C, in which the CD amplitude virtually reached a plateau with 50 mM of (*R*)-**5**. It is noted that the presence of 12.6 mM of (*R*)-**5** allows us to detect a negative exciton-coupled CD spectrum ($\Delta\varepsilon - 1.98\ M^{-1}\ cm^{-1}$ (425 nm)/+6.57 $M^{-1}\ cm^{-1}$ (415 nm); entry 1 in Table 1), the total amplitude being $-8.55\ M^{-1}\ cm^{-1}$. By employing the chiral amino alcohol with concentrations in the order of 10^{-2} M, it is possible to elucidate the absolute configuration. Indeed, when (*S*)-**5** was added to the solution of **1**, we were able to read out the form of a positive exciton-coupled CD spectra (Table 1, entries 4–6). Table 1 also summarizes the induced CD spectra in **1** upon interaction with other chiral amino alcohols (**6**–**8**). Similar CD activity has been obtained in the enantiomers of both phenylglycinol **6** (Table 1, entries 7–10) and valinol **7** (Table 1, entries 11–14); in contrast, the use of chiral 2-amino-1-propanol **8** with a less bulky substituent (methyl group) gave only silence in the CD spectrum (Table 1, entries 15 and 16). Steric interaction between the chiral ligand's bulkiest substituent and the biphenyl unit may be essential for chirality induction in **1**.

Let us suppose that the chiral information on the amino alcohols is transferred in **1** via a noncovalent interaction. No interaction between the porphyrin unit and the guest was obtained using a UV–vis titration in CH_2Cl_2 (see Supplementary data; Fig. S1), making us assume hydrogen bonding interactions in which the biphenyldiol unit participates. This is supported by the fact that, when dimethoxy analogue **4** was used as a control instead of **1**, the solution upon addition of (*R*)-**5** (126 mM) under similar conditions induced no CD spectra (Table 1, entry 17). The direct evidence for the interaction comes from ^1H NMR titrations, where an aliquot solution of **1** was added to the solution of (*R*)-**5** in CD_2Cl_2 (Fig. 3). The guest, (*R*)-**5**, displays in the NMR four double doublets at 3.56 (dd, $J = 10.5$ and 4.0 Hz; H_a), 3.29 (dd, $J = 10.5$ and 7.3 Hz; H_b), 2.76 (dd, $J = 13.5$ and 5.3 Hz; H_d) and 2.50 (dd, $J = 13.5$ and 8.5 Hz; H_e) for the methylene protons as well as 3.09–3.02 ppm (m; H_c) for the methine proton. The addition of incremental amounts of **1** to the solution resulted in downfield shifts of the resonances, with broadening (Fig. 3); for example, the complexation-induced shifts ($\Delta\delta$) in H_a reached 0.069 ppm when [**1**]/[(*R*)-**5**] = 2.4, being attributable to an enhancement of the electronegativity of alcohol-O in (*R*)-**5**, which induces a downfield shift of H_a. This indicates that the OH-groups of the biphenyldiol unit can participate in hydrogen bonds with the chiral amino alcohol. We therefore further investigated the concentration-dependence of the chemical shifts of (*R*)-**5** in the presence of 1 equiv of **1** (see Supplementary data; Fig. S2). The decrease in the concentrations of the solution of **1** and (*R*)-**5** in a 1:1 molar ratio from 2.0 mM to 0.5 mM led to somewhat upfield shifts in the CH signals of (*R*)-**5** (for example, $\Delta\delta = 0.024$ ppm for H_a). This result supports the existence of hydrogen bonding interactions. On the other hand, when the ratio [**1**]/[(*R*)-**5**] exceeds 2.4, every chemical shift (H_a–H_e) moves slightly in the opposite direction, possibly due to self-association of **1** competitively affecting the binding phenomenon with (*R*)-**5**, as inferred from broadening in the spectra. The association constant between (*R*)-**5** and **1** could be apparently estimated by a nonlinear curve fitting plot, based on $\Delta\delta$ of Ha upon adding **1**, as $2010 \pm 200\ M^{-1}$.[15]

On the basis of our data, we display two possible diastereoisomers of the **1**-(*R*)-**5** complex, having either *P* or *M* torsion of the biphenyl (Fig. 4), where the porphyrin units are omitted for clarity. Since the interaction between **1** and (*R*)-**5** is not strong via hydrogen bonds, it is hypothesized that the optimized conformation of (*R*)-**5** would remain upon complexation. In the diastereoisomer having *P* torsion, the largest group (benzyl)

Table 1. CD spectral data for probe with chiral amino alcohols in CH_2Cl_2 at 25 °C[a]

Entry	Probe	Amino alcohol	(mM)[b]	First Cotton effect		Second Cotton effect	
				Sign	Δε (λ)	Sign	Δε (λ)
1	**1**	(*R*)-**5**	12.6	−	1.98 (425)	+	6.57 (415)
2	**1**	(*R*)-**5**	50.3	−	4.88 (425)	+	9.02 (415)
3	**1**	(*R*)-**5**	126	−	6.32 (425)	+	9.50 (415)
4	**1**	(*S*)-**5**	12.4	+	6.81 (425)	−	1.09 (415)
5	**1**	(*S*)-**5**	49.9	+	8.01 (425)	−	3.05 (415)
6	**1**	(*S*)-**5**	125	+	9.48 (425)	−	5.19 (415)
7	**1**	(*R*)-**6**	13.7	−	0.20 (424)	+	6.58 (415)
8	**1**	(*R*)-**6**	49.9	−	2.68 (424)	+	7.90 (415)
9	**1**	(*S*)-**6**	13.3	+	8.71 (424)	−	0.97 (415)
10	**1**	(*S*)-**6**	49.6	+	9.47 (424)	−	3.22 (415)
11	**1**	(*R*)-**7**	12.1	−	2.83 (424)	+	6.48 (414)
12	**1**	(*R*)-**7**	50.4	−	4.90 (424)	+	10.67 (414)
13	**1**	(*S*)-**7**	12.7	+	7.36 (424)	−	1.20 (414)
14	**1**	(*S*)-**7**	51.6	+	9.19 (424)	−	3.57 (414)
15	**1**	(*R*)-**8**	124	[c]	[c]	[c]	[c]
16	**1**	(*S*)-**8**	124	[c]	[c]	[c]	[c]
17	**4**	(*R*)-**5**	126	[c]	[c]	[c]	[c]

[a] Δε ($M^{-1}\ cm^{-1}$), λ (nm).
[b] [Amino alcohol].
[c] No CD spectrum was obtained.

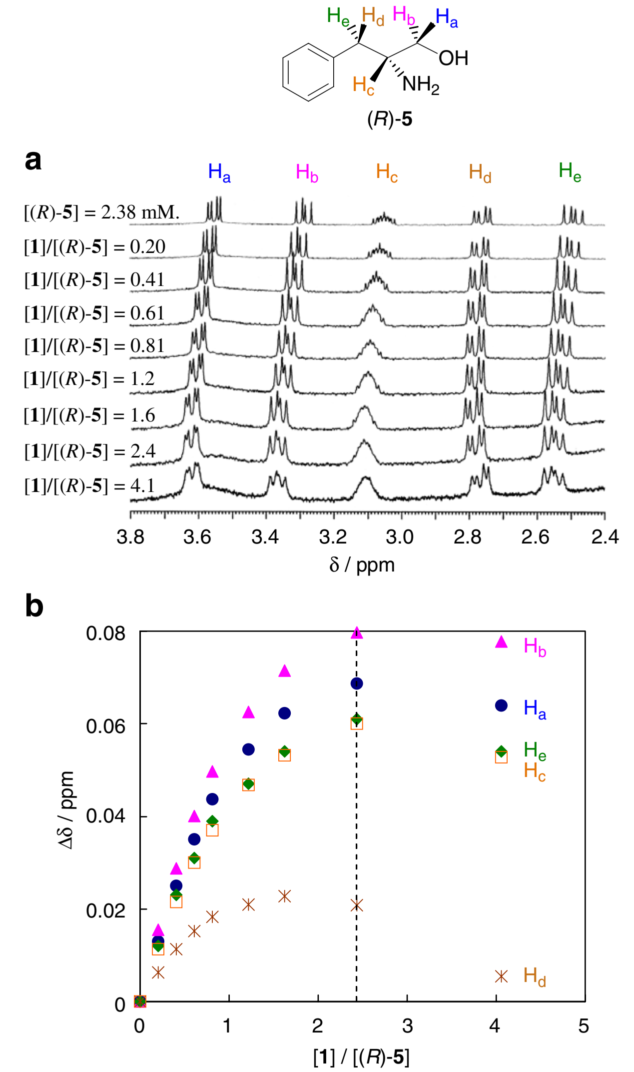


Figure 3. ^{1}H NMR titration of (R)-**5** with **1**. The titration was performed by adding **1** an aliquot solution for each point to the CD_2Cl_2 solution of (R)-**5** (2.38 mM) at 23 °C.

is closer to the biphenyl aromatic ring than the corresponding *M* torsion. Therefore, the *M* diastereoisomer gives rise to less steric interactions, being more stable than the *P* one. The *M* biphenyl torsion induces a negative exciton-coupled CD spectra. On the other hand, the use of chiral **8** with a less hindered group cannot give rise to a preferred diastereoisomer with the conformational equilibrium, resulting in CD silence (vide supra).

In summary, we present the newly synthesized 2,2′-biphenyldiol-bridged bis(free base porphyrin) **1**. This shows the CD activity which correlates with the chirality of amino alcohols, and is potentially useful in the determination of the absolute configuration. It is noteworthy to point out that our system **1** does not require the metal-center of the porphyrin unit, in contrast to 'porphyrin tweezers' reported to date as chiral probes containing metal-inserted porphyrin unit capable of binding guest analytes.[16] Therefore, the insight obtained here suggests that a well-tailored combination of chirality-flexible biphenyldiol and porphyrin units could be used to develop chiral probes. Further exploration of this strategy is under way in our laboratory.

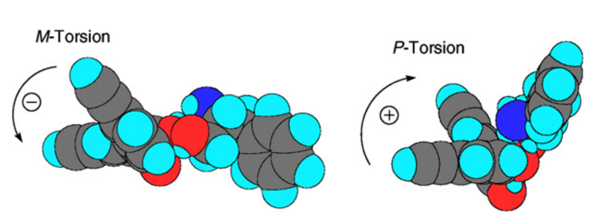


Figure 4. Plausible representation of the conformational equilibrium in biphenyldiol-amino alcohol complex.

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Supplementary data

Synthesis, UV–vis spectra of **1** upon adding (R)-**5** and ^{1}H NMR spectra of (R)-**5** in the presence of 1 equiv of **1** at several concentrations at 23 °C are provided in Supplementary data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.09.106.

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13. ^{1}H NMR (400 MHz, 0.48 mM in CD_2Cl_2) δ 8.91–8.86 (m, 16H), 8.25–8.21 (m, 16H), 7.96 (d, $J = 8.1$ Hz, 4H), 7.80–7.75 (m, 18H), 7.74 (d, $J = 2.0$ Hz, 2H), 7.70 (dd, $J = 8.4$ and 2.0 Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), −2.78 (br s, 4H); ^{13}C NMR (100.7 MHz, 9.7 mM in $CDCl_3$) δ 153.6, 146.8, 142.1, 141.8, 135.1, 135.0, 134.8, 132.4, 131.2, 130.9, 130.1, 128.0, 126.9, 124.8, 123.3, 120.6, 119.6, 117.0, 91.0, 88.4; *m/z* (FAB MS, NBA) 1459 (100%, $[M+H]^+$); Anal. Calcd for $C_{104}H_{66}N_8O_2 \cdot 0.5H_2O \cdot 0.5C_6H_{14}$: C, 85.01; H, 4.93; N, 7.41. Found: C, 84.99; H, 4.60; N, 7.14.
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