Synthesis and characterization of novel chiral diporphyrins and their dimetal complexes

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Reaction of chiral 2,2'-biamino-1,1'-binaphthalene (R or S) with monosubstituted porphyrin 1b and 2b—c afforded novel chiral diporphyrins 3a—c and 4a—c. Their dimetal complexes [(M)₂DiPor] have also been prepared. Both structures have been identified by MS, IR, UV-visible, ¹H NMR spectra and elemental analysis. These novel chiral compounds show very high optical activities.

Introduction

The metal complexes of diporphyrin have been used as molecular catalysts for the multielectron redox transformation of small molecules (*e. g.* , O_2, N_2, and H_2).[1] Collman and co-workers have developed several metallodiporphyrins that show very efficient behavior in catalyzing multielectron redox reactions.[2,3] These metallodiporphyrins can also be utilized in molecular recognition. Sessler has reported that several open-chain and cyclic diporphyrins, as receptor, display excellent recognition properties for various dicarboxylate anions.[4] Crossley has reported that the Tröger's base dizinc(II) diporphyrin strongly binds ditopic diamino ligands.[5] In most cases the chirality of receptors plays an important role in recognition for donors. On the other hand, the distance and orientation between the two porphyrin rings is another important factor for the selective recognition abilities of these diporphyrin-based receptors.[3,6] In this paper, we provide a new approach for the synthesis of diporphyrins, which allows changing the length of the linker between the chiral diaminobinaphthalene and porphyrin ring. This makes the distance and orientation between the two porphyrin rings different. The target diporphyrin receptors have more selective properties.

Experimental

Microanalyses were performed by MHW laboratory (Phoenix, AZ, U.S.A) and Carlo-Erba 1106 Elemental Analyzer. Infrared spectra were measured with a Perkin-Elmer 1600 spectrometer (as KBr disc, values in cm^{-1}) . Mass spectra were obtained on a Finnigan TSQ 7000 spectrometer. ¹H NMR spectra were collected on a Bruker ARX-300 MHz spectrometer. ¹H chemical shifts (δ) were reported relative to tetramethyl-silane (TMS). UV-visible spectra were measured with Milton Roy 3000 Array spectrophotometer. The optical rotation values were measured by a Perkin-Elmer 241 Polarimeter.
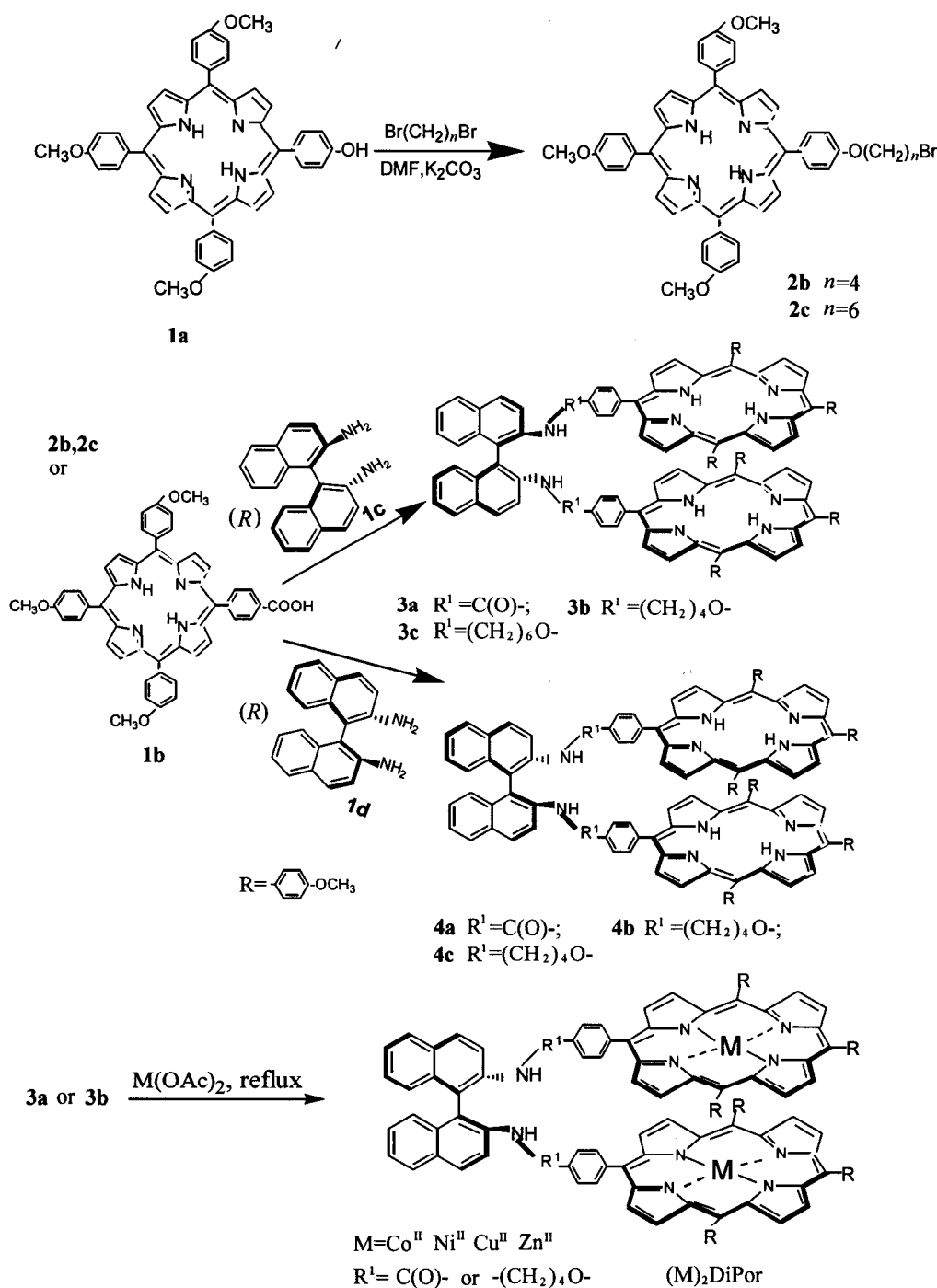
5-(4-Hydroxyphenyl)-10,15,20-tris(4-methoxyphenyl)porphyrin and 5-(4-carbonoxyphenyl)-10,15,20-tris(4-methoxyphenyl)porphyrin were respectively prepared according to modified procedures of Ref. 7 and 8. 1,3-Dicyclohexylcarbodiimide (DCC) and chiral 2,2'-diamino-1,1'-binaphthalene(R or S) were used as received.

The synthetic routes into new diporphyrins and their metal complexes are summarized in Scheme 1.

Scheme 1

1a   → $Br(CH_2)_nBr$ / DMF, K_2CO_3 → $-O(CH_2)_nBr$

2b $n=4$
2c $n=6$

2b,2c or **1b**   -COOH

(R) **1c**

3a $R^1 = C(O)-$;   **3b** $R^1 = (CH_2)_4O-$
3c $R^1 = (CH_2)_6O-$

(R) **1d**

$R = $ ⬡$-OCH_3$

4a $R^1 = C(O)-$;   **4b** $R^1 = (CH_2)_4O-$;
4c $R^1 = (CH_2)_4O-$

3a or 3b $\xrightarrow{M(OAc)_2, \text{ reflux}}$

$M = Co^{II}\ Ni^{II}\ Cu^{II}\ Zn^{II}$
$R^1 = C(O)-$ or $-(CH_2)_4O-$ (M)$_2$DiPor

Compound **2b**   To a solution of compound **1a** (110 mg, 0.15 mmol) in dry DMF (10 mL), K_2CO_3 (550 mg, 4 mmol) was added. The mixture was stirred for 0.5 h at 60℃, and then $Br(CH_2)_4Br$ (650 mg, 3 mmol) was added and stirring was kept for 4 h at 60℃. The mixture was cooled, washed with water (30 mL) and methanol (10 mL) respectively, and filtered. The filtrate was chromatographed on silica gel with $CHCl_3$ as eluent, and the first band was collected. Removal of the solvent yielded a violet solid (120 mg, 93%). δ_H(CD-Cl_3): -2.65(s, 2H, NH), 2.26—2.28(m, 2H, CH_2CH_2Br), 2.34—2.37(m, 2H, OCH_2CH_2), 3.74

(t, $J = 6.0$ Hz, 2H, $BrCH_2$), 4.21(s, 9H, OCH_3), 4.41(t, $J = 6.0$ Hz,2H,CH_2O), 7.40(dd,$J = 6.6$, 4.5 Hz, 8H, PhH_m), 8.22(dd, $J = 2.7$, 3.0 Hz, 8H, PhH_o), 8.97(s, 8H, H_β). ν_{max}: 1606, 1508 (Ph), 1248(OCH_3) cm^{-1}. λ_{max}($CHCl_3$): 423, 522, 556, 594 and 650 nm. Anal. $C_{51}H_{43}N_4O_4Br$. Calcd: C, 71.57; H, 5.06; N, 6.55. Found: C, 71.86; H, 5.42; N, 6.03. FAB MS m/z: 855.3(M^+).

Compound **2c** was prepared by the same method of **2b**, and the yield was 93%. δ_H($CDCl_3$): -2.64(s, 2H, NH), 1.85—2.08(m, 4H, (CH_2)$_2CH_2$-(CH_2)$_2Br$),2.22—2.26(m,2H,CH_2CH_2Br),2.35 —2.41(m, 2H, OCH_2CH_2), 3.72(t, $J = 6.0$ Hz, 2H, $BrCH_2$), 4.19(s, 9H, OCH_3), 4.40(t, $J = 6.0$ Hz, 2H, CH_2O), 7.41(dd, $J = 6.6$, 4.5 Hz, 8H, PhH_m), 8.22(dd, $J = 2.7$, 3.0 Hz, 8H, PhH_o), 8.93 (s, 8H, H_β). ν_{max}: 1605, 1506 (Ph), 1245 (OCH_3) cm^{-1}. λ_{max}($CHCl_3$): 424, 518, 556 and 650 nm. Anal. $C_{53}H_{47}N_4O_4Br$. Calcd: C,71.02; H,5.36; N, 6.34. Found: C, 71.12; H, 5.42; N, 6.33.

Compound **3a**   Compound **1b** (120 mg, 0.16 mmol), (R)-2, 2′-diamino-1, 1′-binaphthalene (20 mg, 0.07 mmol), and DCC (140 mg, 0.7 mmol) were dissolved in 20 mL of anhydrous DMF under N_2. Then dry pyridine (0.1 mL) and HOBu-t (13.5 mg, 0.1 mmol) were added. The mixture was stirred for 3 days at room temperature under N_2. The second portion of DCC (140 mg, 0.7 mmol) was added, and the reaction mixture was stirred for additional 3 days. Trifluoroacetic acid (TFA) (0.1 mL) was then added, the solvent evaporated, and the solid dried *in vacuo*. The resulting product was purified with column chromatography on silica gel and $CHCl_3$:MeOH = 30:1 as the eluent, and the second band was collected. Removal of solvent gave red solid (TFA salt, 128 mg, 93%). $[\alpha]_D^{20} = -3462°$ (see Table 3). δ_H($CDCl_3$): -2.65(s, 4H, NH), 4.21(s, 18H, OCH_3), 7.41(d, $J = 8.4$ Hz, 16H, PhH_m), 8.08(d, $J = 8.1$ Hz, 4H, binaphthalene H), 8.23(d, $J = 8.4$ Hz, 16H, PhH_o), 8.38(d, $J = 8.1$ Hz, 4H, binaphthalene H), 8.87(d, $J = 4.8$ Hz, 4H, binaphthalene H), 8.98 (s, 16H, H_β). ν_{max}: 2930, 2852 (CONH · TFA), 1702, 1654 (C = O), 1606, 1508 (Ph), 1290, 1174 (N—C), 1248 (O—CH_3) cm^{-1}. λ_{max}($CHCl_3$): 423, 522, 556, 594 and 650 nm. Anal. $C_{116}H_{84}N_{10}O_8$.2TFA. Calcd: C, 73.01; H, 4.39; N, 7.10. Found: C, 74.48; H, 4.39; N,

7.52. ESI MS m/z: 1773.7(M^+·2TFA).

Compound **3b**   The compound **2b** (80 mg, 0.093 mmol) and K_2CO_3 (300 mg, 2 mmol) were dissolved in 15 mL of anhydrous DMF under N_2. The solution was heated to 100℃, and a solution of (R)-2,2′-diamino-1, 1′-binaphthalene (11 mg, 0.04 mmol) in DMF (5 mL) was dropped in slowly (about 1.5 h). The reaction mixture was kept stirring for 24 h at 100℃ under N_2. The solution was then cooled to room temperature, and water (30 mL) added. The resulting crude product was purified with column chromatography using silica gel as solid support, and 3% methanol in $CHCl_3$ as eluent. Removal of the solvent yielded violet solid compound **3b** (40 mg, 54%). $[\alpha]_D^{20} = -2278°$ (in $CHCl_3$). δ_H($CDCl_3$): -2.62(s, 4H, NH), 2.01—2.07(m, 4H, CH_2CH_2NH), 2.14—2.21(m, 4H, H_2CH_2),3.95(t, $J = 6.2$Hz,4H,$NHCH_2$),4.20 (s, 18H, OCH_3), 4.39(t, $J = 6.0$ Hz, 4H, CH_2O), 7.39(m, 24H, PhH_m and binaphthalene H), 8.21—8.25(m, 20H, PhH_o and binaphthalene H), 8.98 (s, 16H, H_β). ν_{max}: 3316(N—H), 1606, 1508(Ph), 1290, 1174(N—C), 1248(O—CH_3) cm^{-1}. λ_{max} ($CHCl_3$): 424, 518, 556, 594 and 650 nm. Anal. $C_{122}H_{100}N_{10}O_8$. Calcd: C, 79.89; H, 5.49; N, 7.64. Found: C, 79.84; H, 5.44; N, 8.03.

The compound **3c** was obtained by the similar method of the synthesis of **3b**.

Compound **3c**   Yield was 30%. δ_H($CDCl_3$): -2.64(s, 4H, NH), 1.77—1.84(m, 8H, (CH_2)$_2$-CH_2NH), 2.07—2.14 (m, 8H, OCH_2CH_2 and CH_2CH_2NH), 3.85(t, $J = 6.3$ Hz, 4H, $NHCH_2$), 4.21(s, 18H, OCH_3), 4.37(t, $J = 6.4$ Hz, 4H, CH_2O), 7.34—7.41(m, 24H, 16 PhH_m and 8 binaphthalene H), 8.13—8.25(m, 20H, 16 PhH_o and 4 bianphthlene H), 8.98(s, 16H, H_β). ν_{max}: 3316(N—H), 1606, 1508(Ph—H), 1290, 1174 (N—C), 1248(O—CH_3) cm^{-1}. λ_{max}($CHCl_3$): 423, 522, 556, 594, 650 nm. Anal. $C_{118}H_{92}N_{10}O_8$. Calcd: C, 80.06; H, 5.76; N, 7.41. Found: C, 79.56; H, 5.38; N, 6.86. ESI MS m/z: 1890.9(M^+).

Compounds **4a**, **4b** and **4c** were prepared by the same method of compounds **3a**—c from (S)-2, 2′-diamino-1, 1′-binaphthalene reacting with **1a**, **2b** and **2c** respectively. Their ^1H NMR, MS, UV-vis and IR spectral data are also the same as those of **3a**—c.

Complex **(Zn)$_2$(3a)**   20 mg of **3a** and 50 mg

of Zn(OAc)$_2$ were added into a solution of chloroform (20 mL) with 5% methanol. The mixture was refluxed for 2 h. The crude product was purified with column chromatography using silica gel as solid support, and CHCl$_3$ as eluent. Removal of solvent yielded purple-red solid (Zn)$_2$(3a) (18 mg).

Complexes (Co)$_2$(3a), (Ni)$_2$(3a), (Cu)$_2$(3a), (Co)$_2$(3b), (Ni)$_2$(3b), (Cu)$_2$(3b) and (Zn)$_2$(3b) were prepared by the same method of the complex (Zn)$_2$(3a). Their yields were around 50—70%, and state and color were brown-red solid for (Co)$_2$(3a) and (Co)$_2$(3b), brown solid for (Ni)$_2$(3a) and (Ni)$_2$-(3b); red solid for (Cu)$_2$(3a) and (Cu)$_2$(3b), purple-red solid for (Zn)$_2$(3a) and (Zn)$_2$(3b) respectively. Anal. [(Co)$_2$(3a)], Co$_2$C$_{116}$H$_{80}$N$_{10}$O$_8$. Calcd: C, 74.91; H, 4.34; N, 7.53. Found: C, 75.26; H, 4.48; N, 7.65. (Ni)$_2$(3a), Ni$_2$C$_{116}$H$_{80}$N$_{10}$O$_8$. Calcd: C, 74.93; H, 4.34; N, 7.53. Found: C, 75.36; H, 4.45; N, 7.55. (Cu)$_2$(3a), Cu$_2$C$_{116}$H$_{80}$N$_{10}$O$_8$. Calcd: C, 74.54; H, 4.31; N, 7.50. Found: C, 74.06; H, 4.41; N, 7.95. (Zn)$_2$(3a), Zn$_2$C$_{116}$H$_{80}$N$_{10}$O$_8$. Calcd: C, 74.40; H, 4.31; N, 7.48. Found: C, 74.56; H, 4.49; N, 7.77. (Co)$_2$(3b), Co$_2$C$_{122}$H$_{96}$N$_{10}$O$_8$. Calcd: C, 75.22; H, 4.97; N, 7.19. Found: C, 74.11; H, 4.48; N, 7.35. (Ni)$_2$(3b), Ni$_2$C$_{122}$H$_{96}$-N$_{10}$O$_8$. Calcd: C, 75.24; H, 4.97; N, 7.19. Found: C, 75.44; H, 4.48; N, 7.35. (Cu)$_2$(3b), Cu$_2$C$_{122}$-H$_{96}$N$_{10}$O$_8$. Calcd: C, 74.87; H, 4.94; N, 7.16. Found: C, 74.56; H, 4.68; N, 7.25. (Zn)$_2$(3b), Zn$_2$C$_{122}$H$_{96}$N$_{10}$O$_8$. Calcd: C, 74.73; H, 4.93; N, 7.14. Found: C, 74.66; H, 4.48; N, 7.65. The spectral data are described in the following.

Results and discussion

Synthesis of compound 3a

Compound 3a was synthesized by a method similar to that described in Ref. 4. Some modifications were also made to improve the yield. DCC was used as a coupling reagent instead of DIC.[4] DCC was used in a large excess, and the proportion of DCC to 2,2'-diamino-1,1'-binaphthalene was 20 : 1. With these modifications, diporphyrin 3a was obtained in good yield (93%). Alternatively, compound 3a could be also prepared on treatment of porphyrin acid chloride (obtained

from 1a) and 2, 2'-diamino-1, 1'-binaphthalene. The latter method needed two steps, but the final yield was lower (72%) than that of the former method.

^{1}H NMR spectra

The ^{1}H NMR signals have been well assigned (see experimental section). Chemical shifts from 7 to 9 of 3a are shown in Fig. 1, where there are five doublets located at 7.40, 8.08, 8.23, 8.38, 8.87 respectively. The coupling constants: $J = 8.4$ Hz for δ 7.40; $J = 8.1$ Hz for δ 8.08; $J = 8.4$ Hz for δ 8.23; $J = 8.1$ Hz for δ 8.38; $J = 4.8$ Hz for δ 8.87. Therefore two doublets located at 7.40 and 8.23 belong to the same system and can be assigned to phenyl proton resonances because of their similar coupling constants. The other two doublets located at 8.08 and 8.38 belong to the same system and should be assigned to binaphthalene proton resonances.
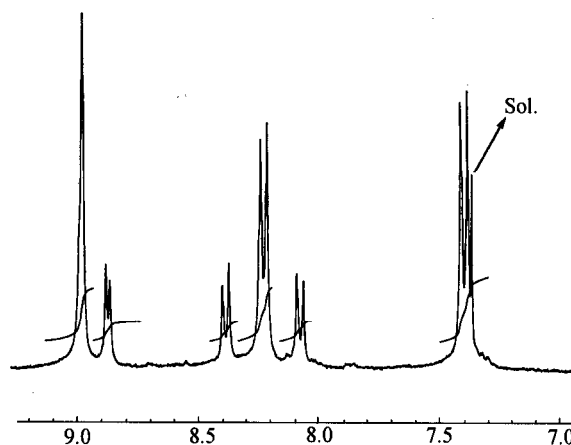

Fig. 1 300 MHz ^{1}H NMR spectrum of the diporphyrin 3a in CDCl$_3$.

The chemical shift data of ligand 3a and its Co^{II} and Zn^{II} complexes are listed in Table 1. It can be seen that cobalt insertion results in proton resonance on porphyrin and benzene rings exhibiting a large downfield chemical shift, while zinc insertion results in very little change, as compared with the free-base porphyrin proton resonances. The large downfield chemical shift of cobalt complexes is attributed to the back bonding between Co^{II} and the porphyrin ring.[9] For Co^{II}, the outer electron arrangement is d^7 and the cobalt ion has empty d-orbitals which overlap with the porphyrin π* -orbital. This leads to a decrease in the ring current shielding. Therefore the resonances of protons on porphyrin and benzene rings are

downfield.

Table 1   Proton chemical shifts (δ) of compound **3a** and its complexes

	3a	**(Co)TPP**[10a]	**(Co)₂3a**	$\Delta\delta^a$	**(Zn)₂3a**	$\Delta\delta^a$
H_β	8.98	15.98	16.04	7.06	9.08	0.10
H_o	8.23	13.16	13.25	5.02	8.23	0.00
H_m	7.40	9.96	9.59	2.19	7.38	-0.02
$H_p OCH_3$	4.21	—	5.41	1.20	4.21	0.00

^{a} $\Delta\delta$ is the chemical shift change between metal complex and ligand **3a**. The data of (Co)TPP are taken from Ref. 10a.

This is fairly typical for a low-spin Co^{II} porphyrin complex.[10] But for Zn^{II}, the outer d-orbitals are filled, and there is very little interaction between its d-orbitals and the porphyrin π^*-orbital. So the spectra of zinc complex are similar to those of ligand **3a**.

The chemical shift changes ($\Delta\delta$) between the cobalt complex and ligand **3a** are different. For β and *ortho* protons, which are near the metal center, $\Delta\delta$ is bigger than that of protons on *meta*- and *para*-OCH₃ positions. Therefore, $\Delta\delta$ decreases as the distance between proton and metal center is increased.

IR spectra

In the IR spectra of these dimetallic complexes, as compared with free-base porphyrin, the N—H streching band located at about 3300 cm⁻¹ disappeared. A strong and sharp peak located at about 1000 cm⁻¹, which was the oxidation state marker band (OSMB), appeared. The frequencies of OSMB are listed in Table 2. The OSMB frequencies of Co^{II} and Ni^{II} complexes are higher than those of Cu^{II} and Zn^{II} complexes.

UV-vis spectra

The UV-vis spectra of the dimetallic porphyrins are dominated by the Soret band near 410 nm and the α and β bands. The data are described in Table 2.

Table 2   UV-vis and IR(OSMB) spectral data of dimetallic complexes (in CHCl₃)

Complex	Wavelengths (nm)			Frequencies (cm⁻¹)	Complex	Wavelengths(nm)			Frequencies (cm⁻¹)
	Soret band	β-band	α-band	OSMB^a		Soret band	β-band	α-band	OSMB
(Co)₂3a	414	536	—	1002	(Co)₂3b	418	538	—	1003
(Ni)₂3a	420	530	590	1003	(Ni)₂3b	422	524	592	1003
(Cu)₂3a	420	540	—	999	(Cu)₂3b	420	542	—	999
(Zn)₂3a	426	558	600	996	(Zn)₂3b	426	554	598	995

^{a} OSMB = Oxidation State Marker Band.

Optical properties

The optical properties of the novel diporphyrins were tested, and the results shown in Table 3, showing that they possess exceptionally high optical activities, which are much bigger than those of the starting materials, (R) or (S) 2,2'-diamino-1,1'-binaphthlene (**1c** and **1d**), due to their helicity.[11] The attachment of two porphyrin macrocycles to chiral 2,2'-diamino-1,1'-binaphthlene generates a chiral molecular cleft[5a] and the new diporphyrin is helical. From **3a** to **3b** and **3c**, the

linker between the binaphthlene and the porphyrin ring increases, but the optical rotation value decreases. This is because the rotation between two porphyrin rings in molecular **3b** and **3c** is easier than that in **3a**. The same conclusion could be obtained from **4a—c**. The different optical notation values show that these novel diporphyrins have different molecular clefts, which demonstrate that the distances and orientations between the two porphyrin rings are different. Therefore a family of receptors which display assorted selective properties have been obtained.

Table 3   Optical rotation values of materials and novel diporphyrins in $CHCl_3$

Compounds	1c	3a	3b	3c	1d	4a	4b	4c
c (g/100 mL)	0.246	0.146	0.257	0.158	0.253	0.106	0.265	0.143
$[\alpha]_D^{20}$	152°	− 3462°	− 2278°	− 2044°	− 153°	− 1671°	− 1333°	− 1037°

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