Porphyrinoids

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Synthesis, Characterization, and Chirality of Dimeric N-Confused Porphyrin–Zinc Complexes: Toward the Enantioselective Synthesis of Bis(porphyrinoid) Systems**

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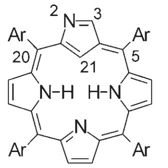

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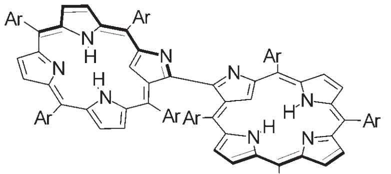

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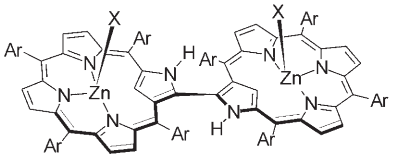
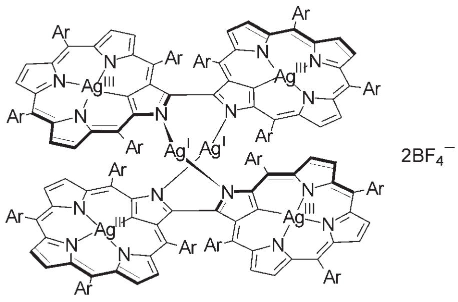


3-X_2

$2X = 2AcO^-, 2Cl^-, tart^{2-}, mal^{2-}$

Ar = *p*-Tol



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Oligoporphyrins have attracted much attention as a result of their properties related to the interaction between the aromatic subunits, and may find potential application in molecular electronics, nonlinear optics, and catalysis.[1] Directly linked porphyrin oligomers are of special interest as the interaction between chromophores in these systems is expected to be particularly strong and tunable.[2] Bis(porphyrins) in which a pyrrole carbon atom is directly linked to the other subunit display intrinsic axial chirality as a consequence of the restricted rotation around the β–β′ bond.[3] This restriction is imposed by the meso substituents, which preserve the axial chirality of the system by preventing the interconversion of the rotamers. Although some efforts have been made to resolve the racemic mixture, no enantioselective synthesis of a directly linked bis(porphyrin) system has been reported to date.[4]

The unique property of N-confused porphyrin[5] (NCP) **1** is its multimodal coordination to metal ions.[5a,6] The coordination core of NCP can be mono-, di-, or trianionic depending on the protonation status on the "internal" carbon atom (C21) and the "external" nitrogen atom (N2) of the confused pyrrole ring.[7] The variety of coordination modes is preserved in the directly linked 3,3′-bis(N-confused porphyrin) **2**, which allows further modification of the geometry of the system to control its stereochemistry.[8] Herein we describe the synthesis and characterization of bis(zinc) complexes of **2**, the supramolecular binding of alcohols by **3**-Cl_2, as well as an attempt at preparative resolution of the enantiomers.

The synthesis of bis(zinc) adducts **3**-X_2 was carried out by mixing a solution of **2** in chloroform with an excess of zinc acetate in methanol; the insertion of two metal ions was as confirmed by the ^{1}H NMR and ESI mass spectra. The two anionic acetate ligands, the presence of which was established by ^{1}H NMR spectroscopy, could be replaced by other anions by mixing **3**-$(AcO)_2$ in chloroform with an aqueous solution of the appropriate sodium salt. The single-crystal X-ray diffraction analysis of bis(N-confused porphyrinatozinc chloride) revealed (Figure 1) that the spatial arrangement of subunits in **3**-Cl_2 is quite different from that of the parent bis-NCP free base **2** or the assembly **4**, where the NCPAg^{III} subunits are essentially planar. In the present system the molecule adopts the shape of an open shell of a bivalve. A water molecule additionally bridges the subunits through the formation of two hydrogen bonds: one where it acts as an H acceptor with the external nitrogen atom of one of the subunits (N26-H26···O1, 176(3)°; N26–H26, 0.87(4) Å; H26–O1, 1.86(4) Å) and the other where it acts as an H donor with the chloride ligand bound to the zinc atom in the other subunit (O1-H1W···Cl1, 170(4)°; O1–H22, 0.99(5) Å; H22–Cl1, 2.13(5) Å). The zinc ion and the internal carbon atom of the confused pyrrole ring are separated by about 2.6 Å, which is out of the bonding distance range for these atoms.[7b,d,9] The external nitrogen atoms are *trans* to each other, with an N2-C3-C27-N26 torsion angle of 120.6(3)°, which contrasts the

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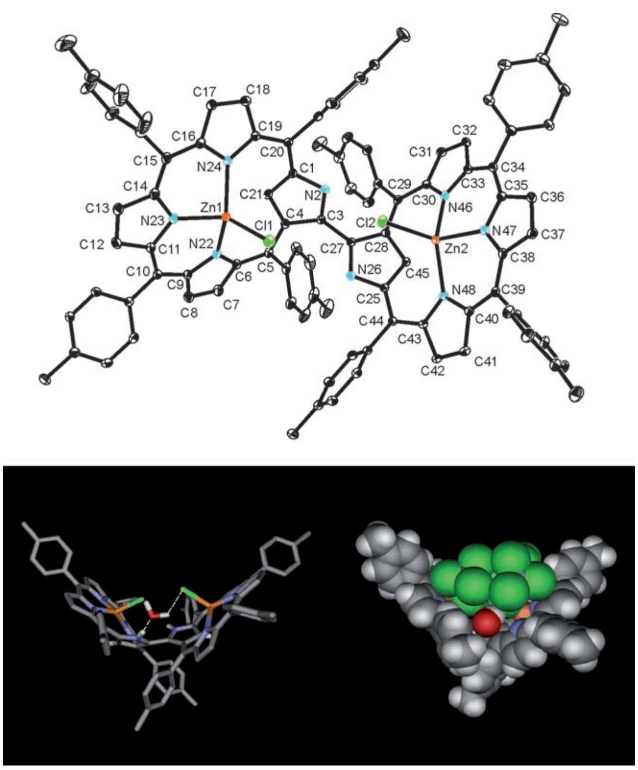

Figure 1. Molecular structure of **3**-Cl_2. Top: an ORTEP projection with thermal ellipsoids set at the 30% probability level. All hydrogen atoms and solvent molecules are removed. Bottom left: a side view with a wire-frame representation showing the position and hydrogen bonds of the water molecule inside **3**-Cl_2. Bottom right: a space-filling representation showing the water and three chloroform molecules localized within **3**-Cl_2. Color code: gray: carbon, white: hydrogen, blue: nitrogen, red: oxygen, green: chlorine, orange: zinc.

situation in **2** or **4** where these nitrogen atoms adopt a *cis* orientation (66° and 64°, respectively).[10] The unit cell of **3**-Cl_2 consists of a symmetry-dependent pair of enantiomers. The overall chirality of the molecule can be described as axial (*M*-*P*) and may be attributed to the lack of rotational freedom of the bipyrrole fragment. However, each subunit possesses its own chirality (defined by a chirality plane or asymmetric pseudotetrahedral environment of the metal ion), and the configuration of both subunits is the same in the dimer.[11] Thus, interconversion of the enantiomers cannot be accomplished merely by rotation around the C3–C27 bond.

Despite a considerable distortion of the macrocyclic rings, a strong interaction between the delocalized π-electron systems of the subunits in **3** can be inferred from its optical spectra, where the Soret-type band is split into two components, unlike in a monomeric chloride complex (Figure 2A).[7f]

The ^{1}H NMR spectrum of **3**-Cl_2 reflects the alteration in the geometry of the bis(porphyrinoid) system which arises upon coordination of the zinc atom and results in a lack of spectral features typical for **2**, its nickel(II) or silver(III) complexes, and **4**.[8] The NMR spectra reveal twofold symmetry of the dimer as well as the presence of only one type of stereoisomer of a defined spectral characteristic nature.

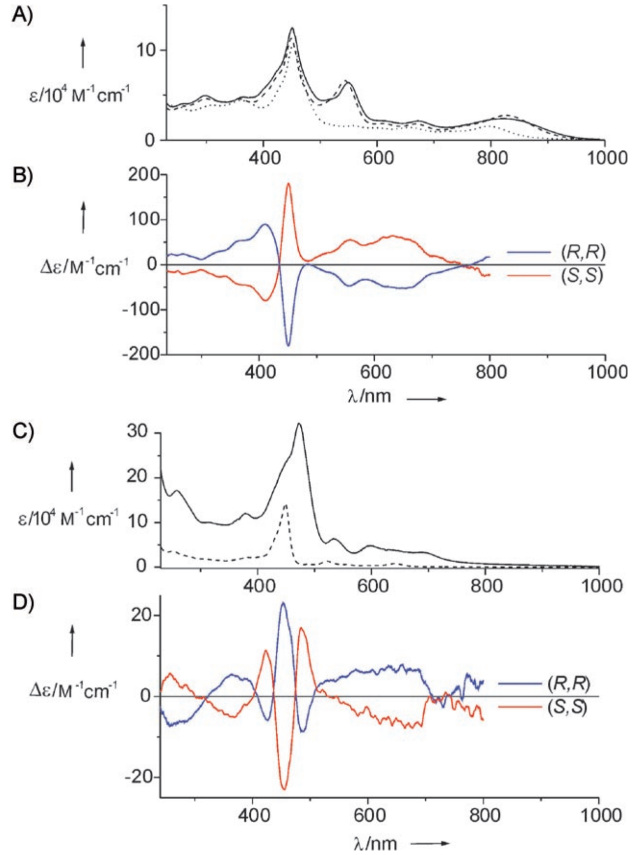

Figure 2. A) Optical spectra of **3**-Cl_2 (——), **3**-tart (-----), and monomeric tetraphenyl-2-aza-21-carbaporphyrinatozinc chloride (•••••); B) CD spectra of **3**-tart; C) optical spectra of **4** (——) and monomeric tetratolyl-2-aza-21-carbaporphyrinatosilver(III) (-----); D) CD spectra of **4** obtained from **3**-tart. The CD spectrum of **3**-(*R*,*R*)-tart and **4** obtained from this enantiomer by transmetalation are drawn in blue and marked (*R*,*R*); the spectra drawn in red and marked (*S*,*S*) were recorded for **3**-(*S*,*S*)-tart or for the assembly **4** synthesized from this enantiomer. All spectra were recorded in dichloromethane.

The association of water with **3**-Cl_2 in solution can be deduced from an upfield position of the H_2O signal ($\delta =$ 0.9 ppm) in the ^{1}H NMR spectrum ($CDCl_3$, 213 K) and from a strong through-space interaction with some of the meso-aryl and pyrrole protons (NOESY, $CDCl_3$, 213 K). The water molecule can be replaced by an alcohol, addition of which considerably affects the ^{1}H NMR spectrum of **3**-Cl_2 and shifts the H_2O resonance downfield. The ^{1}H NMR titrations indicate a 1:1 stoichiometry of adducts for all the alcohols studied (ethanol, *sec*-butanol, borneol, and menthol). In the case of ethanol, the association constant of which is the highest ($K \approx 100\,\text{M}^{-1}$), the composition of (EtOH)-**3**-Cl_2 was confirmed by a Job plot experiment (^{1}H NMR, $CDCl_3$, 213 K). For (*S*)-*sec*-BuOH and (*S*)-*endo*-borneol, association with **3**-Cl_2 results in the formation of *S*-*M* and *S*-*P* diastereomers which can be observed by a doubling of certain signals of the chiral host in the ^{1}H NMR spectrum at sufficiently high concentration of the guest (32- and 180-fold molar excess, respectively). No signal splitting was observed when racemic *sec*-BuOH was used as the titrant, which indicates the formation of an enantiomeric instead of diastereomeric mixture in this case. Upon titration of **3**-Cl_2 with (1*R*,2*S*,5*R*)-menthol, increasing the separation of a pair of signals of equal intensity is caused by changes in the resonance frequency of only one of the components. The resonance position of the other component can be changed by addition of enantiomeric (1*S*,2*R*,5*S*)-menthol. Again, no splitting was observed for racemic menthol (see the Supporting Information). Evidently, each enantiomer of the host discriminates between enantiomers of the guest.[12]

For a racemic mixture of **3**-X_2, it seemed rational to anticipate the formation of NMR-distinguishable (*M*)-(*R*,*R*) and (*P*)-(*R*,*R*) diastereomers upon substitution of the acetate or chloride ligands with L-(+)-(2*R*,3*R*)-tartrate. Instead, only one stereoisomer is formed for the tartrate complex, as inferred from the ^{1}H NMR spectrum, which displayed one set of signals both at room temperature and at 213 K.[13] A similar results are obtained for D-(−)-(2*S*,3*S*)-tartrate and D-(−)-(2*S*)-malate as the incoming ligands. The 1:1 stoichiometry and internally bridging function of the dianionic ligand can be established for both **3**-tart and **3**-mal (tart = tartrate dianion, mal = malate dianion) on the basis of the relative intensity of the CH or OH resonances and their upfield shift in the ^{1}H NMR spectra. From the NOESY spectrum of **3**-(*R*,*R*)-tart ($CDCl_3$, 213 K), which shows through-space interactions between the tartrate OH and *ortho* protons of a meso-tolyl substituent and the lack of such interactions for the tartrate CH group, formation of the (*M*)-(*R*,*R*) stereoisomer could be deduced by means of molecular modeling studies (see the Supporting Information). The CD spectra of **3**-tart or **3**-mal solutions show strong Cotton effects at wavelengths characteristic of the porphyrinoid absorption (Figure 2B). The sign of the effect depends on the enantiomer actually present in the complex being opposite for the antipodes of tartrate, and the same for **3**-(*S*,*S*)-tart and **3**-(*S*)-mal. The exciton coupling of two rigidly oriented and closely spaced chromophores of porphyrinoid subunits when there is an excess of one enantiomer is responsible for the observed bisignate CD signal at 450 nm, that is, in the region of the Soret (B) transition of the porphyrinoid.[3,14] The negative sign of the amplitude of this couplet for **3**-(*R*,*R*)-tart indicates a negative sense of chirality or an *M* configuration for this system, which is in line with the conclusions derived from the NOESY experiment. The optical activity induced by the coordination of a chiral guest has been reported for some achiral bis(porphyrin) systems consisting of subunits flexibly linked by an alkyl chain[15] and for a chiral, yet easily interconvertible, cyclooctapyrrole.[16] In the case of **3**, the process of induction of any enantiomeric excess is not confined to the conformational adaptation of the host to the steric factors imposed by a chiral guest but must involve concurrent changes in the environment of the tetrahedral metal ion. That may suggest a demetalation/inversion/remetalation sequence that selectively affects the fraction of molecules for which the configuration is changed upon ligand exchange, and constitutes the enantiomeric excess.

Demetalation of **3**-tart by acidification or by addition of an excess of a chelating ligand (1,2-ethylenediamine) leads to the optically inactive free base **2**. Conversion of the tartrate complex into **3**-Cl_2 by the addition of aqueous NaCl also resulted in racemization. To check if the system can resist racemization upon removal of the chiral dianion, we converted **3**-tart and **3**-mal complexes into **4** by reaction with $AgBF_4$ in THF.[8b] The resulting product of transmetalation, confirmed to be identical with **4** by UV/Vis and ^{1}H NMR spectroscopic measurements, does not contain a tartrate or malate dianion associated with the complex, but nevertheless exhibits optical activity as revealed by the CD spectra (Figure 2D).[17] Apparently, the chiral information introduced by the optically active ligand is transferred to the axially chiral bis(porphyrin) system. However, to maintain a persistent enantiomeric excess, the inversion of the configuration of the subunits should be prevented by coordination of the internal carbon atom (C21) to the inert metal ion.

In conclusion, we have shown that the bipyrrole moiety in the bis(N-confused porphyrin) system adopts a transoid configuration upon zinc coordination and its transition from the cisoid arrangement of the free base is combined with an unprecedented alteration of the whole structure of the macrobicyclic molecule. The bis(zinc) complex **3**-Cl_2, with its bivalve shape and polar interior, constitutes a new type of multifunctional chiral host suitable for anionic or neutral guests. The labile properties of the zinc ion and adaptability of the ligand skeleton allow generation of enantiopure bis(porphyrin) systems by substitution of the achiral ligand with an anion of defined chirality.

Experimental Section

3-Cl_2: A sample of **2** (20 mg, 0.015 mmol) was dissolved in chloroform (20 mL) and a solution of zinc acetate dihydrate in methanol (33 mg, 0.15 mmol in 10 mL) added. The mixture was then stirred at room temperature for 1 h. The solvents were then removed by evaporation at room temperature and the solid residue dissolved in dichloromethane (15 mL) and filtered. The filtrate volume was reduced to 5 mL and the solution was vigorously stirred for 1 h with an aqueous solution of NaCl (1 M, 2 mL), after which the organic phase was isolated and washed with three portions of water (10 mL each). After separation of the organic phase, the solution was filtered and the solvent evaporated to dryness. The solid residue was dissolved in chloroform and the dark red product **3**-Cl_2 was crystallized slowly after addition of hexane. Yield 20 mg (87 %). A similar procedure was applied to obtain **3**-tart or **3**-mal, using disodium tartrate or disodium malate instead of NaCl at the stage of substitution of the acetate ligands. The NMR data are presented in the Supporting Information.

3-Cl_2: UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 259 (sh), 299 (4.63), 360 (4.62), 403 (sh), 422(sh), 449 (11.30), 543 (6.60), 609 (1.86), 669 (1.81), 753 (sh), 829 (2.76). HRMS (ESI+) for $C_{96}H_{72}N_8ClZn_2$: *m*/*z* calcd: 1499.4150 ([*M*−Cl]$^+$); found: 1499.4154. Elemental analysis calcd for $C_{96}H_{72}Cl_2N_8Zn_2 \cdot 2\,CHCl_3 \cdot 2\,H_2O$: C 64.82, H 4.29, N 6.17; found: C 64.97, H 4.56, N 6.12.

3-tart: Yield of isolated product (crystallized from benzene/chloroform/hexane): 80 %. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 256 (sh), 298 (4.94), 365 (4.80), 404 (sh), 423(sh), 451 (12.51), 550 (6.42), 615 (sh), 672 (2.14), 829 (2.39). MS (FD+) for $C_{100}H_{75}N_8O_6Zn_2$: *m*/*z* calcd: 1615.5 ([*M*−H]$^+$); found: 1615.0. Elemental analysis calcd for $C_{100}H_{76}N_8O_6Zn_2 \cdot 2\,C_6H_6 \cdot CHCl_3$: C 71.73, H 4.74, N 5.92; found: C 71.99, H 4.15, N 5.70.

3-mal: Yield of isolated product (crystallized from dichloromethane/hexane): 85 %. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 256 (sh), 299 (4.00), 363 (3.89), 424 (sh), 450 (10.30), 547 (5.80), 610 (1.66), 671 (1.63), 750 (sh), 827 (2.13). HRMS (ESI+) for $C_{100}H_{77}N_8O_5Zn_2$: *m*/*z* calcd: 1597.4600 ([*M*+H]$^+$); found: 1597.4655. Elemental analysis calcd for $C_{100}H_{76}N_8O_5Zn_2{\cdot}CH_2Cl_2{\cdot}C_6H_{14}{\cdot}H_2O$: C 71.81, H 5.29, N 6.26; found: C 72.09, H 5.28, N 6.01.

X-ray quality crystals of **3**-Cl_2 were obtained by slow diffusion of a solution of **3**-Cl_2 in chloroform into hexane. Crystal data for **3**-Cl_2: $C_{100}H_{77}Cl_{14}N_8OZn_2$, $M_r = 2033.00$, $T = 100$ K, $Mo_{K\alpha}$ radiation, triclinic, space group $P\bar{1}$, $a = 14.740(4)$, $b = 16.973(4)$, $c = 20.161(5)$ Å, $\alpha = 95.59(2)$, $\beta = 101.56(3)$, $\gamma = 94.06(2)°$, $V = 4897(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.380$ Mg m^{-3}, $\lambda = 0.71073$ Å, $\mu = 0.923$ mm^{-1}, $F(000) = 2080$, diffractometer Oxford Diffraction Xcalibur PX with a KM4CCD Sapphire detector, $0.96 \leq \theta \leq 33.08°$, 86106 collected reflections, 35627 independent reflections with $I > 2\sigma(I)$, 1176 parameters, $R_1(F) = 0.0776$, $wR_2(F^2) = 0.2534$, $S = 1.000$, max./min. electron density 2.97/-0.93 e Å^{-3}. All non-H atoms were refined with anisotropic displacement parameters except for those of the disordered solvent. Hydrogen atoms involved in the formation of hydrogen bonds were localized on the differential electron density map. The other hydrogen atoms were included from the geometry of the molecules and refined isotropically. The asymmetric unit consists of a **3**-Cl_2 molecule, one water molecule, and four chloroform molecules, one of which is disordered over three sites. Data for the crystal obtained from a benzene solution can be found in the Supporting Information. CCDC-643818 and CCDC-643819 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conversion of **3**-tart or **3**-mal into **4** was carried out by dissolution of the zinc complex (10 mg) in freshly distilled THF (10 mL). $AgBF_4$ (10 mg) was added to the solution and the mixture was stirred at room temperature for 2 h. The solvent was then evaporated at room temperature and the solid residue was dissolved in dichloromethane (5 mL). The solution was then filtered and washed with water (10 mL × 3). After isolation of the crude product, it was crystallized from CH_2Cl_2/hexane to give **4** in quantitative yield.

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[10] Similar structural features, except solvent molecules inside the cleft, but including the association of one H_2O molecule, were observed for the crystals grown from a benzene/heptane mixture; see the Supporting Information for details.

[11] In this regard, the topology of **3**-X_2 differs from that of bivalves, in which the valves are hetoerochiral and the shell is effectively achiral.

[12] The PM3 energy-optimized modeling of (*M*)-**3**-Cl_2-(1*R*,2*S*,5*R*)-menthol and (*P*)-**3**-Cl_2-(1*R*,2*S*,5*R*)-menthol adducts comprising hydrogen-bonding systems analogous to that observed for the water molecule is inconclusive in regard to distinguishing the stability of the diastereomers; see the Supporting Information for details.

[13] A progress of the conversion of **3**-Cl_2 into **3**-tart was monitored by ^{1}H NMR spectroscopy. The crude reaction mixture contained **3**-tart and less than 10 % of the demetalation product **2**.

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[17] Although estimation of the enantiomeric excess is not feasible for this system, the *ee* value is probably lower for **4** than for its precursors, that is, **3**-tart or **3**-mal, as can be inferred on the basis

of the considerably lower molar amplitudes of the CD signals. The simplified interpretation of the signs of the amplitude of the Cotton effect in the Soret region indicates an *M* configuration of the bis(2-aza-21-carbaporphyrinatosilver(III)) units in **4** obtained from **3**-(*R*,*R*)-tart (negative sign) and a *P* configuration for the assembly obtained by transmetalation of **3**-(*S*,*S*)-tart and **3**-(*S*)-mal (positive sign).[14] The shape of the CD couplets in the Soret region of **4** closely resembles those observed for chiral directly β,β- or *meso*,*meso*-linked bis(porphyrinatozinc).[3,4] Since the orientation of the planar subunits in the X-ray structure of **4**[8b] is similar to that determined by DFT calculations for the free base of the β,β-dimer of a typical porphyrin,[3] the analogous exciton coupling mechanism can be adopted for both systems. The electrostatic interaction between the subunits in **4** has been demonstrated previously by electrochemical studies.[8b] Also comparison of the optical spectrum of **4** with that of the monomeric silver(III) complex[7a] indicates that the interaction removes the degeneracy of the electronic exited state (Figure 2C). It is noteworthy that the signs of the Cotton effects calculated for the *M* enantiomer of the regular β,β-bis(porphyrin)[3] are the same as those observed for **4** obtained from **3**-(*R*,*R*)-tart for which we propose an *M* configuration on the basis of NMR data analysis.