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Optically Active Oxo(phthalocyaninato)vanadium(IV) with Geometric Asymmetry: Synthesis and Correlation between the Circular Dichroism Sign and Conformation

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Abstract: Oxovanadium(IV) phthalocyanines (VOPcs) with a single-handed rotation have been prepared, and their right- and left-handed enantiomers resolved on a chiral HPLC column. These enantiomers gave circular dichroism (CD) spectra of opposite signs; the correlation between the CD sign and conformation was obtained by time-dependent density functional theory (TDDFT) calculations: an enantiomer showing a negative sign in the Q band was suggested to be the right-handed conformer viewing from the axial oxygen side, whereas that giving a positive CD sign was assigned to the left-handed conformer. Although silicon phthalocyanines (SiPcs) with two different alkoxy axial ligands have been resolved similarly, the absence of a meaningful CD difference probably reflects the flat character of the SiPc plane compared to the VOPc plane. Changes in the Q-band CD, depending on the relative orientation of the peripheral substituents, have been worked out theoretically and the origin of the chiroptical properties is discussed.

Keywords: circular dichroism · configuration determination · density functional calculations · phthalocyanines · UV/Vis spectroscopy

Introduction

Various types of optically active phthalocyanines (Pcs) have been reported to date.[1,2] In most cases, Pcs are optically active because they contain optically active side chains[1] or chromophores.[2] Metal Pcs (MtPcs) are essentially almost planar D_{4h}- or C_{4v}-type molecules, so they are achiral when unsubstituted. However, by considering the position of peripheral substituent groups and deformation of the Pc skeleton, we can realize optically active Pcs, even if the substituent groups are not optically active. Such Pcs are said to be intrinsically optically active.[3] We report here MtPcs containing VO and Si(OH)(OR) (R = alkyl), of which the former is CD-active and the latter CD-inactive. The correlation between the CD sign of VOPcs and their conformation is elucidated, and the reason for the CD inactivity of Si(OH)(OR)Pcs is elucidated. We presented some of the results on VOPc in this study in 1999,[4] but at that time the method for calculating CD spectra had not been developed. Quantum chemical CD calculation became possible recently, and here we include consideration of CD calculations in our results. Since the optical activity of a molecule consisting of an achiral Pc chromophore with achiral substituents originates from the inherent chirality of the molecule, the present system has the potential to facilitate the CD analyses. This is in contrast to the previous systems in which a coupled-oscillator (coupled-dipole, $\boldsymbol{\mu}\cdot\boldsymbol{\mu}$) mechanism and a dynamic ($\boldsymbol{\mu}\cdot\mathbf{m}$) ($\mathbf{m}$ = magnetic dipole transition moment) mechanism play a vital role in their optical activities.[1,2] However, by utilizing chiral SiPcs containing oxygen as the two coordinating axial atoms (Figure 1) we also show that the present method is not applicable to macrocycles having a small degree of "geometric asymmetry."

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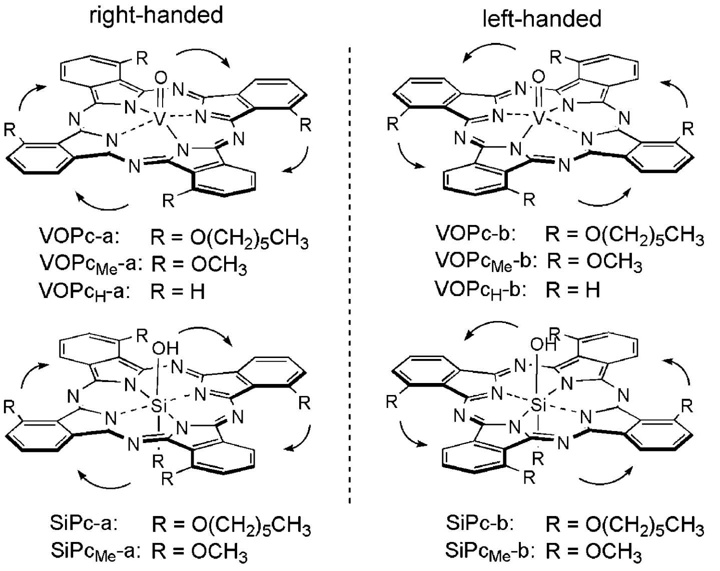

Figure 1. Structures and abbreviations of the Pc compounds in this study.

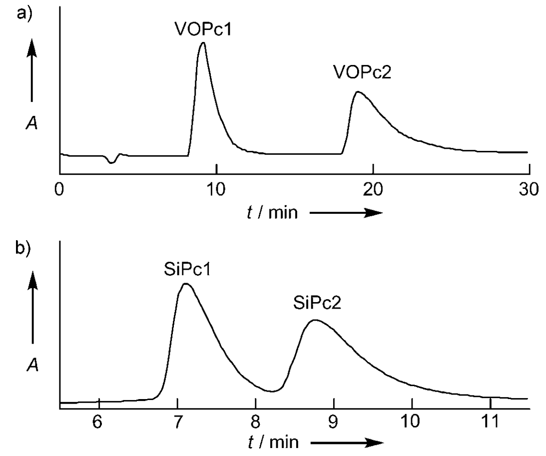

Figure 2. HPLC chromatograms of a) VOPc ($CHCl_3$/hexane 1:6 v/v, flow rate = 1 mL min^{-1}, l = 350 nm); b) SiPc ($CHCl_3/CCl_4$ 1:6 v/v, flow rate = 0.7 mL min^{-1}, l = 350 nm).

Results and Discussion

Synthesis and resolution of Pc samples

VOPc: Following the method reported by Leznoff et al.[5] and Kasuga et al.,[6] cyclic tetramerization of 3-hexyloxyphthalonitrile at room temperature gave almost exclusively 1,8,15,22-tetrahexyloxylated metal-free Pc in a high yield (41.6%). Accordingly, a metal insertion reaction with V_2O_5 in molten urea gave C_4-type VOPc with single-handed rotation quite easily. In order to separate two-enantiomeric VOPc, we had to use a mixed solvent containing a large volumetric percentage of hexane, because otherwise the cellulose tris(3,5-dimethylphenyl carbamate) used to modify the surface of silica gel tended to dissolve. However, this simultaneously made it difficult to dissolve VOPc. We found that hexane/chloroform (6:1 v/v) was a reasonable solvent (Figure 2a), but as the solubility of VOPc was insufficient, we had to use a dilute VOPc solution and repeat the chromatography several times.

SiPc: For synthesis of SiPc, no metal insertion reaction is yet known. Accordingly, 4-*n*-hexyloxy-1*H*-isoindole-1,3(2*H*)-diimine was condensed in the presence of $SiCl_4$ at 180 °C,[7] similarly to the preparation of normal SiPcs. The area under the peak in the ^{1}H NMR spectrum revealed that approximately 20–25% of the total SiPc was not the desired isomer. Complete separation of the desired isomer was not attained when the two axial ligands were OH groups. Replacement of one OH group by a hexyloxy group enabled separation of the two enantiomers (Figure 2b). However, in this case, it required $CCl_4/CHCl_3$ (6:1 v/v) as an eluting solvent, although there was a danger that the surface-modified cellulose tris(3,5-dimethylphenylcarbamate) might be washed out. The chromatographic separation of the two enantiomers was not good (Figure 2b) compared with that of VOPc (Figure 2a), although it was possible.

Electronic absorption, CD, and magnetic CD spectra: The spectra of VOPc in chloroform is shown in Figure 3. The absorption spectrum is characteristic of MtPcs, although its Q band (λ = 733 nm) lies at a slightly longer wavelength than

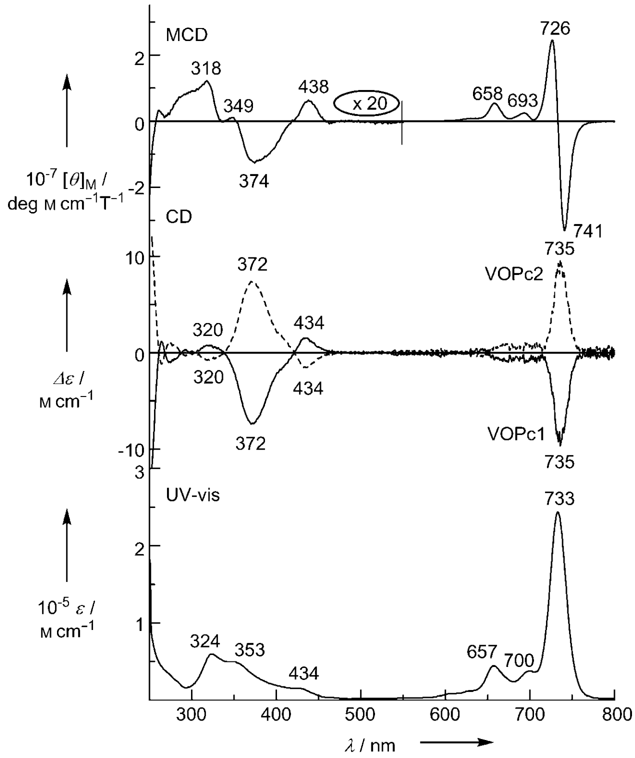

Figure 3. MCD, CD, and electronic absorption spectra of VOPc measured in $CHCl_3$ at RT: [VOPc1] = 3×10^{-6} M (solid line), [VOPc2] = 3×10^{-6} M (broken line). $[\theta]_M$ can be converted to $\Delta\varepsilon_M$ by dividing it by 3300.

those of normal VOPcs without substituent groups ($\lambda = 695$ nm in chlorobenzene).[8] This is due to the alkoxy group being attached to benzene carbon atoms closest to the Pc core.[9] In the Soret band region, three peaks were observed at $\lambda = 324$, 353, and 434 nm. Of these, the band at 434 nm can be assigned to a transition involving the ether oxygen lone pairs (plausibly n-π* transitions).[10] The magnetic CD (MCD) spectrum is also typical of MtPcs,[11] showing a clear Faraday *A*-term type of curve associated with the Q_{00} absorption peak at $\lambda = 733$ nm.

Band deconvolution of the Q band and experimental rotational strength: To estimate the rotational strength as correctly as possible, we adopted the band deconvolution technique[12] for the Q band (Figure 4). Deconvolution of the spectroscopic envelope can give reliable results if more than two types of spectra obtained from the same solution are fitted with the same or very similar band center and bandwidth parameters.

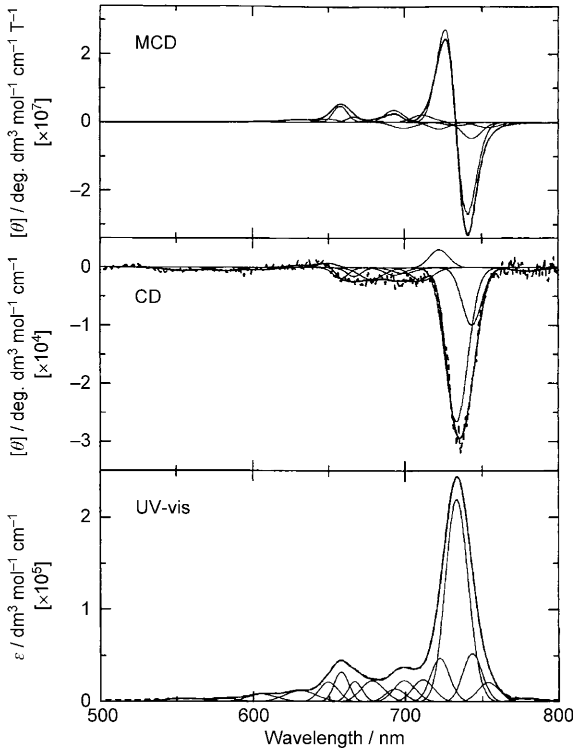

Figure 4. Spectral deconvolution analysis of the Q-band region of the absorption, CD, and MCD spectra of VOPc1. Identical bandwidths and centers are used to fit the spectra. Broken lines: experimental data, bold solid lines: fitted data, thin solid lines: individual bands. $[\theta]_M$ and $[\theta]$ can be converted to $\Delta\varepsilon_M$ and $\Delta\varepsilon$ respectively by dividing them by 3300.

Many absorption and MCD spectra of porphyrins and Pcs have been analyzed by band deconvolution,[13] which has been successful in analyzing transitions which had been postulated by MO calculations or in finding new degenerate excited states. The CD intensity in Figure 4 is weak, so this technique was first applied to both the electronic absorption and MCD spectra, and then the CD spectrum was deconvoluted using the parameters obtained. Seventeen components, approximately the same number as in previous studies,[11,13] were required to fit the $\lambda = 500$–800 nm region From the component corresponding to the Q_{00} band, the experimental oscillator strength, *f*, was found to be 0.33 by applying Equation (1),[14,15] in which $\boldsymbol{\mu}$, *h*, *m*, and *ν* are the electric transition dipole moment, Planck's constant, the electron mass, and the frequency at which a transition occurs, respectively.

$$f_{\mathrm{obsd}} = \frac{8\pi^2 m\nu}{3he^2}|\mu|^2 = 0.476 \times 10^{30}\nu|\mu|^2 \tag{1}$$

Similarly, the experimental rotational strength, *R*, of the Q_{00} band was estimated to be -0.46×10^{-40} cgs and $+0.46\times10^{-40}$ cgs for VOPc1 and VOPc2, respectively, by using Equation (2),[14,15] in which *N* and *c* are Avogadro's number and the speed of light in vacuum, respectively.

$$R_{\mathrm{obsd}} = \frac{hc}{48\pi^2 N}\int\frac{\theta(\lambda)}{\lambda}\mathrm{d}\lambda \approx 0.696 \times 10^{-42}\int\frac{\theta(\lambda)}{\lambda}\mathrm{d}\lambda \tag{2}$$

Calculation of rotational strength: We have analyzed contributions to the rotational strengths of VOPc, and assigned the absolute configuration. The present system consists of an achiral Pc chromophore with four achiral hexyloxy substituents, so the optical activity originates from the inherent chirality of the molecule (geometric chirality). The peripheral alkoxy substituent has so small an electric dipole transition moment that the contribution, if any, due to the coupled-oscillator (coupled-dipole, $\boldsymbol{\mu}\cdot\boldsymbol{\mu}$) and dynamic ($\boldsymbol{\mu}\cdot\mathbf{m}$) mechanisms to the observed CD signals would be negligible or very small,[16] making the system suitable for analysis of its inherent chirality. In this kind of system, the CD analysis method is limited to direct calculation from the Rosenfeld equation[17] by using the complete molecular wavefunctions. In this study, we have carried out time-dependent DFT (TDDFT) calculations of C_4-type oxovanadium(IV) 1,8,15,22-tetamethoxyphthalocyanine ($\mathrm{VOPc_{Me}}$) as a model system, to obtain theoretical absorption and CD spectra.[18] TDDFT combines computational efficiency with often quite reliable accuracy, and has been applied successfully to optically active porphyrinoid systems.[19] We have also studied in detail the effect of the relative orientation of the peripheral substituents on the Q-band CD of the present system .

Optimized structure of $VOPc_{Me}$: The ground-state geometry of a model right-handed isomer, $\mathrm{VOPc_{Me}}$-a, was calculated under C_4 symmetry restriction using the B3LYP functional in conjunction with the 6-31G* basis set.[20] The geometry of the alkoxy groups in the initial structure was referred to the geometric arrangement for the crystal structure of nickel(II) 1,8,5,22-tetra(3′-pentoxy)phthalocyanine.[21] The optimized structure (Figure 5) exhibits a doming of the Pc macrocycle,

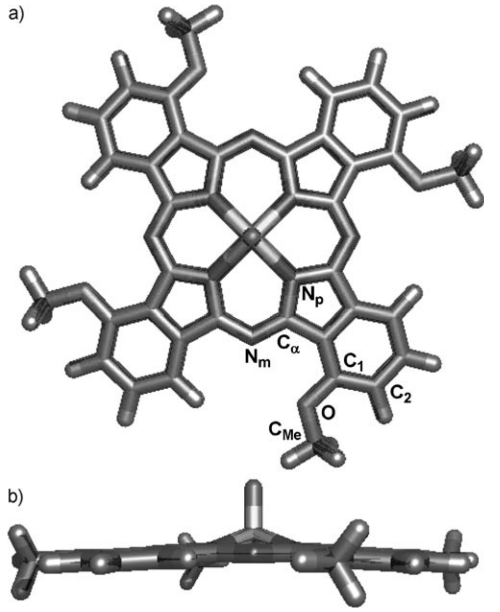

Figure 5. Optimized structure of oxovanadium 1,8,15,22-tetramethoxyphthalocyanine (VOPc$_{Me}$) with right-handed geometry (B3LYP/6-31G*): a) top view; b) side view.

as observed in the X-ray structure of oxovanadium(IV) phthalocyanine without peripheral substituents.[22] The geometric parameters for VOPc$_{Me}$ are nearly identical to those for the crystal structure (see Table 1). The distance between the vanadium ion and the four-nitrogen plane was calculated to be 0.598 Å (0.575(1) Å for the X-ray structure). Distinct distortion of the Pc ring due to the peripheral substituents was not seen in the optimized structure. The dihedral angle, θ, which is defined by the angle C$_2$-C$_1$-O-C$_{Me}$, is 0.35°, so the peripheral methoxy group lies almost parallel to the benzo ring.

Table 1. Comparison between the selected structural parameters (in Å or deg) in the optimized geometry of VOPc$_{Me}$ and those in the crystal structure of oxovanadium(IV) phthalocyanine without peripheral substituents (ref. [21]).

Parameter[a]	DFT structure	X-ray structure[b]
V=O	1.573	1.580(3)
V–N$_p$	2.053	2.026(7)
N$_p$–N$_p$	2.777	2.748(2)
N$_p$–C$_\alpha$	1.379	1.386(3)
C$_\alpha$–N$_m$	1.324	1.324(4)
N$_p$-V-N$_p$	85.13	85.4(2)

[a] C$_\alpha$, N$_p$, and N$_m$ indicate the pyrrole α-carbon, pyrrole nitrogen, and *meso* nitrogen. N$_p$–N$_p$ corresponds to the averaged distance between adjacent pyrrole nitrogen atoms. [b] The numbers in parentheses are the estimated standard deviations.

Calculated spectra of VOPc$_{Me}$ and origin of optical activity: To relate the observed spectroscopic properties to the molecular geometry, 60 excitation energies, oscillator strengths, and rotatory strengths for the optimized structure of VOPc$_{Me}$-a were calculated at the B3LYP/6-31G* level. All the main features in the spectra observed for the first eluted enantiomer (VOPc-1) (Figure 6) are well reproduced by the computations for the right-handed isomer. The calculations predict three absorption bands at $\lambda = 646$, 413, and approximately 360 nm, which can be associated with the observed bands at $\lambda = 733$, 434, and 353 nm, respectively. The lowest-energy absorption band consists of a doubly degenerate transition with a negative CD sign, which agrees with the dispersion-type MCD signal (Faraday A term) and negative Gaussian-type CD signal observed for VOPc-1, although the calculated rotatory strength for the Q transition (-3.751×10^{-40} cgs) overestimated the experimental value ($\pm 0.46 \times 10^{-40}$ cgs). Positive and negative CD signals were predicted corresponding to the 413 and 355 nm transitions respectively, which are in accordance with the observed positive and negative CD at $\lambda = 434$ and 372 nm. Comparison of various functionals and basis sets for calculating the Q-band CD of VOPc$_{Me}$-a (Table 2) shows that the CD sign for the Q band was independent of the level of theory, as far as was examined. From these results, we conclude that the first eluted enantiomer (VOPc1) has a right-handed geometry (VOPc-a), and the geometry of the second one eluted is left-handed (VOPc-b).

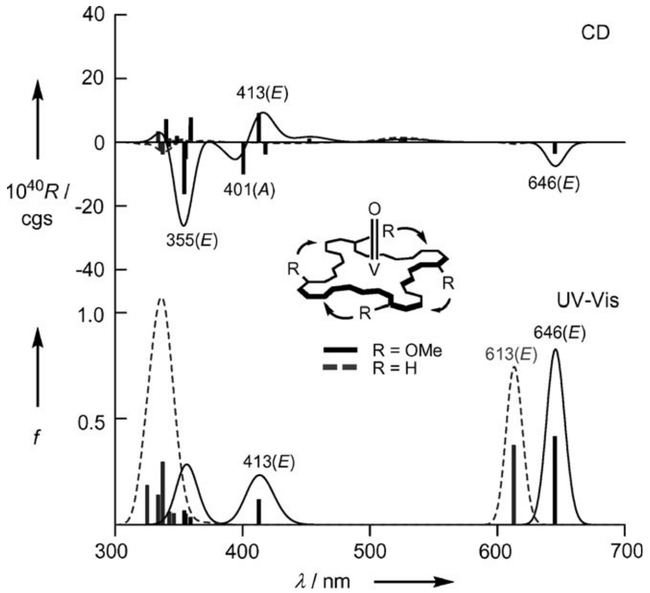

Figure 6. Simulated UV/Vis and CD spectra of VOPc$_{Me}$-a (B3LYP/6-31G*). Gray lines indicate simulated spectra of VOPc$_H$-a in which four methoxy groups were replaced by hydrogen atoms. Gaussian bands with a half-bandwidth of 400 cm^{-1} (Q region) or 1500 cm^{-1} (Soret region) were used.

To investigate the spectroscopic properties further, we have calculated the spectra of VOPc$_H$-a, in which four methoxy substituents in the optimized structure were replaced by hydrogen atoms, that is, normal VOPc without peripheral

Table 2. Dependence of functional and basis set on the Q-band CD of $VOPc_{Me}$-a.[a,b]

Functional	Basis set	λ [nm]	f	R(velocity)[c]	R(length)[c]
B3LYP	3-21G	617.1	0.421	−2.441	−2.911
	6-31G*	645.6	0.413	−3.751	−3.684
	6-31+G*	654.6	0.422	−3.148	−3.162
	6-31++G*	654.6	0.421	−3.237	−3.241
BLYP	3-21G	687.8	0.272	−1.107	−1.140
	6-31G*	705.9	0.267	−3.425	−3.294
B3P86	3-21G	616.0	0.400	−10.550	−13.635
	6-31G*	644.0	0.418	−3.710	−3.654
BP86	3-21G	686.6	0.276	−1.266	−1.331
	6-31G*	704.8	0.282	−3.518	−3.395
SVWN	3-21G	693.0	0.264	−1.230	−1.253
	6-31G*	709.6	0.271	−3.592	−3.455
Experimental		735	0.33	±0.46	

[a] The B3LYP/6-31G* optimized structure was used for these calculations. [b] The Q transition is doubly degenerate due to the C_4 symmetry of the molecule. [c] Rotational strength in 10^{-40} cgs.

substituents. $VOPc_H$-a exhibits almost silent CD in both the Q and the Soret regions (Figure 6). This result clearly indicates that the Pc skeleton itself does not contribute to the CD of the present Pc system: the peripheral alkoxy groups play an important role in their optical activities. The predicted Q band for $VOPc_H$-a ($\lambda = 613$ nm) lies at a shorter wavelength than that of $VOPc_{Me}$-a ($\lambda = 646$ nm), reproducing well the spectroscopic properties observed. The $\lambda = 413$ nm absorption band predicted for $VOPc_{Me}$-a was not seen in the calculated spectra of $VOPc_H$-a (the Q band of our VOPc is at $\lambda = 733$ nm (Figure 3), whereas that of VOPc without substituents is at $\lambda = 695$ nm in chlorobenzene[8]). From a comparison of the frontier molecular orbitals of $VOPc_{Me}$-a and those of $VOPc_H$-a, the 413 nm absorption can be assigned to a transition with n–π* character, since it is a transition from the occupied orbitals involving the ether oxygen orbitals to the doubly degenerate LUMO. The occupied orbitals are destabilized significantly due to the antibonding interaction between the oxygen orbitals and the π orbitals of the Pc skeleton (see the Supporting Information).

Dependence of the Q-band CD on the conformation of substituents: It is known that CD signals are sensitive to slight conformational changes of molecules.[14,15,23] We therefore explored the dependence of the Q-band CD on the relative orientation of substituents to highlight the important features of peripheral substituents. We have also carried out TDDFT calculations of the SiPc system to account for the experimental observation that our chiral SiPcs did not exhibit meaningful CD signals.

Figure 7a shows the relationship between the Q-band CD and the conformation of methoxy groups in $VOPc_{Me}$-a. Interestingly, a sigmoidal pattern was predicted for the Q-band CD by changing the dihedral (C_2-C_1-O-C_{Me}) angle θ in the optimized geometry. The CD sign becomes positive when the methoxy groups are located below the Pc plane (negative θ value), whereas a negative CD is calculated when the methoxy groups are located above the Pc plane

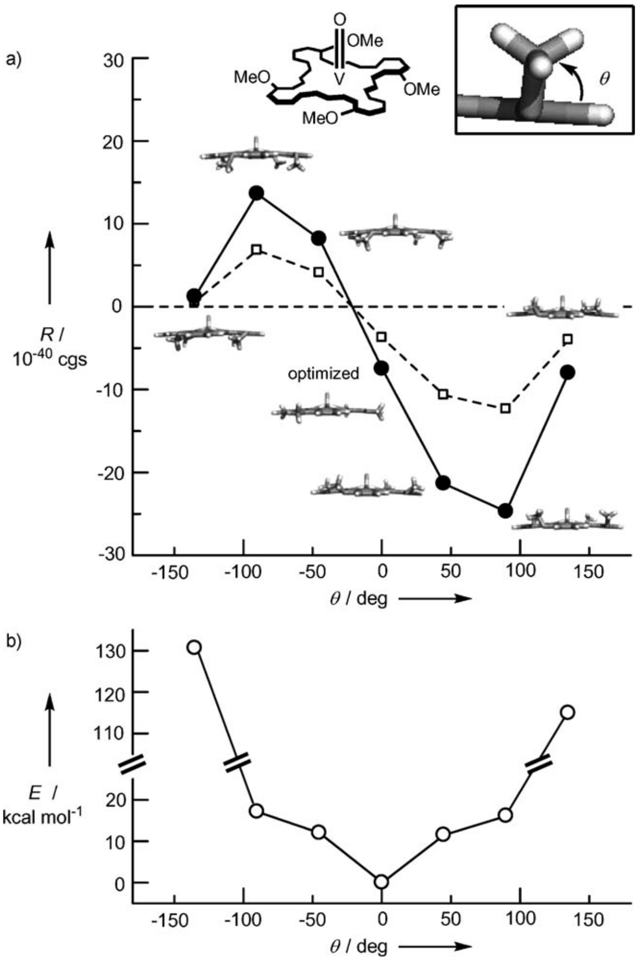

Figure 7. a) Relationship between the Q-band CD and the conformation of the methoxy groups (dihedral angle θ) in $VOPc_{Me}$-a: rotatory strength for the lowest-energy Q transitions (white squares) and sum of the degenerate CD intensities (black circles); b) variation of dihedral angle θ with relative energy. All calculations were carried out at the B3LYP/6-31G* level.

(positive θ value; direction toward axial oxygen). The relative energy of the conformer with the large absolute value of θ is quite high (Figure 7b), indicating that the geometry in which the peripheral methoxy group lies parallel to the benzo ring is strongly favored energetically. The average rotatory strength is still negative ($R = -2.75 \times 10^{-40}$ cgs) for the right-handed enantiomer, which strongly supports our absolute configuration assignment. It should be noted that the calculated CD became positive ($R = 4.645 \times 10^{-40}$ cgs) when a TDDFT calculation was performed for a right-handed $VOPc_{Me}$ system in which both the Pc skeleton and the methoxy groups were kept flat, that is, a nondomed structure system in which the vanadium atom lies in the center of the Pc ligand, just as a nickel atom lies in NiPc (not shown). This implies that the geometry of a Pc chromophore plays an additional role in the chiroptical properties, although theoretically the Pc skeleton itself does not exhibit a CD signal in the Q region (see Figure 6).

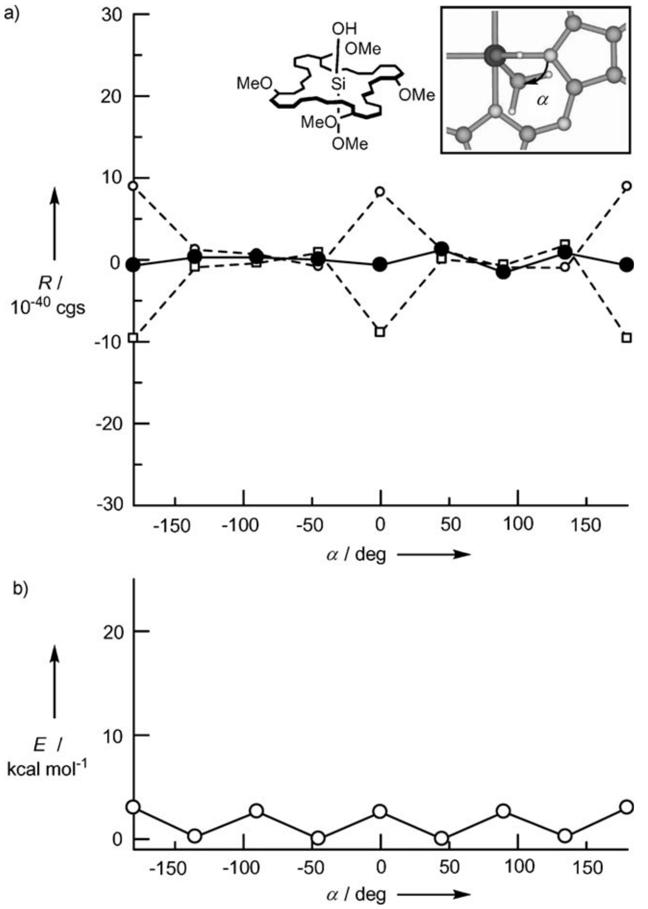

Figure 8. a) Relationship between the Q-band CD and conformation of an axial methoxy group (angle N_p-Si-O-C_{Me}, α) in $SiPc_{Me}$-a. The white circles and white squares indicate the rotatory strength for the lowest- and second-lowest-energy Q transitions, respectively. The black circles indicate the sum of the two CD intensities. b) Variation of dihedral angle α with relative energy. All calculations were carried out at the B3LYP/6-31G* level.

We have also calculated the rotatory strengths for the Q band of the SiPc system. In contrast to the vanadium complexes, our SiPc is complicated because it has two flexible axial ligands (OH and hexyloxy). Figure 8a shows the calculated rotatory strengths of a right-handed enantiomer of $SiPc_{Me}$ upon rotating the position of the axial methoxy group. Because of the low symmetry of the molecule, the Q transition is not degenerate. Two closely lying transitions with opposite CD sign were calculated for all the conformations, so the sum of the two CD intensities was always close to zero. Although the relative energy of the staggered conformations (with respect to the axial ligands) is lower than that of the eclipsed conformation (Figure 8b), the energy difference is quite small (approximately 3 $kcal\,mol^{-1}$), thus indicative of free rotation of axial ligands under the experimental conditions.

Figure 9 shows the relationship between the Q-band CD and the conformation of the methoxy groups in $SiPc_{Me}$-a with $a=0°$. A sigmoidal pattern was predicted for the sum of the rotatory strengths for the two Q-band CD signals when the dihedral (C_2-C_1-O-C_{Me}) angle θ was changed, a result similar to those for the VOPc system. Because the relative energy of the conformer with the large absolute value of θ was quite high, CD signals for the Q transition of the SiPc system in equilibrium are predicted to be nearly zero. Consequently, the computational results can account for the experimental observation that the chiral SiPc system did not exhibit a meaningful CD sign.

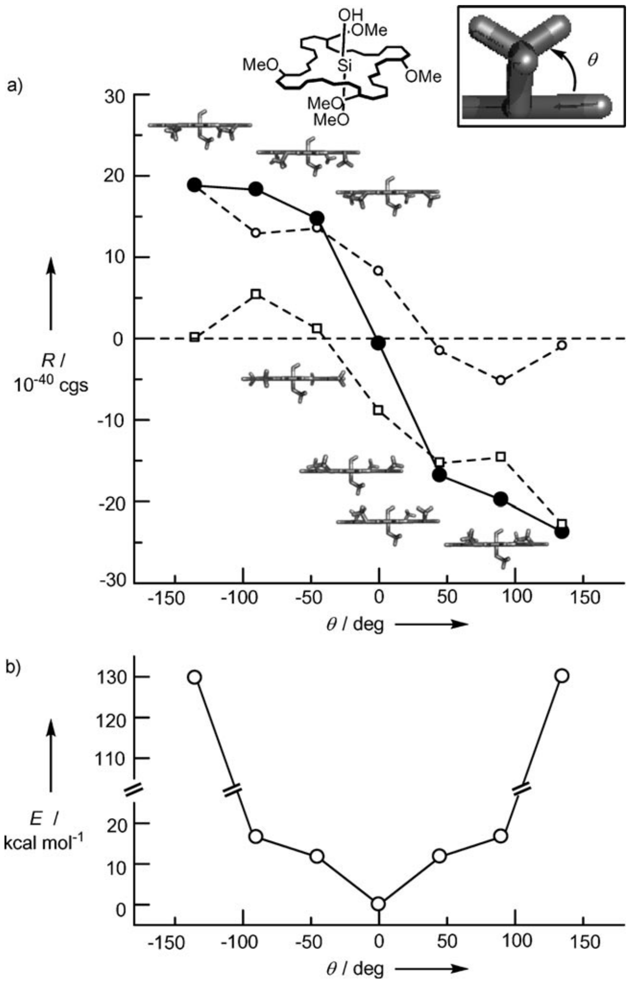

Figure 9. a) Relationship between Q-band CD and conformation of methoxy groups (dihedral angle θ) in $SiPc_{Me}$-a with $\alpha=0°$. The white circles and white squares indicate the rotatory strength for the lowest- and second-lowest-energy Q transitions, respectively. The black circles indicate the sum of the two CD intensities. b) Variation of dihedral angle θ with relative energy. All calculations were carried out at the B3LYP/6-31G* level.

Conclusions

VOPcs and SiPcs with single-handed rotation have been prepared, and were resolved successfullly into optically active enantiomers by cellulose tris(3,5-dimethylphenylcarbamate)-modified reversed-phase HPLC. Two enantiomeric VOPcs exhibited CD spectra of opposite signs, whereas chiral SiPcs coordinated by axial OH and hexyloxy ligands did not exhibit a meaningful CD sign.

Comparison of the experimental data with those calculated by using TDDFT indicates that the first-eluted VOPc1, which shows a negative CD sign associated with the Q_{00} band, is a right-handed conformer (VOPc-a). Thus, our present data suggest that, in alkoxy-substituted Pcs with a domed π skeleton, the right-handed conformer shows a negative CD sign in the Q band and a positive CD sign in the n–π^* transition band. The left-handed conformer exhibits the opposite CD sign in both the Q and n–π^* bands. It has been further demonstrated that the calculated CD sign in the Q region is sensitive to the relative orientation of the peripheral alkoxy groups. The relationship between the Q-band CD and the dihedral angle (θ) was sigmoidal for the vanadium complexes, and the averaged CD sign was found to be negative for the right-handed conformer. In contrast, the Q-band CD of SiPcs was predicted to be almost silent due to the cancellation of two Q-band CD signals of opposite sign, regardless of the relative orientation of the axial group. It should be noted that the Q-band CD sign would be inverted even in a chiral Pc with single-handed orientation when the position of peripheral substituents is flipped with respect to the Pc plane. (In the present system, however, it appears energetically highly unfavorable for substituents to tilt significantly from the macrocyclic plane (see Figures 7 and 9).) Although, at present, it might be difficult to confirm the above prediction experimentally, we believe that the correlation found between the CD sign in the Q region and the relative orientation of the peripheral groups has implications not only in the present system but also in many different chiral Pc and porphyrin systems.

Experimental Section

General: Electronic absorption spectra were measured by using a Hitachi U-3410 spectrophotometer. CD and MCD measurements were performed by using a JASCO J-720 spectrodichrometer with a chloroform solution (10^{-6} mol L^{-1}), without and with a JASCO electromagnet that produced magnetic fields of up to 1.09 T. CD curves shown here were obtained by accumulation of more than 8 h.

Synthesis

3-Hexyloxyphthalonitrile: In a minor modification of Leznoff's procedure,[5,24] 3-nitrophthalonitrile (2.0 g, 11.6 mmol), hexanol (2.5 mL, 20.0 mmol), and anhydrous potassium carbonate (1.2 g, 8.7 mmol) were stirred at room temperature under a nitrogen atmosphere in dry DMF (12 mL). Potassium carbonate (1.2 g in each portion) was added to the system after 24 and 48 h and the stirring was continued for three days in total. The crude reaction mixture was poured into water (400 mL). The precipitate was collected by filtration, washed thoroughly with water, and dried. The crude product was purified by silica gel column chromatography with chloroform as the eluting solvent. Off-white needles of 3-hexyloxyphthalonitrile (2.00 g, 76 %), mp 110–111 °C, were recrystallized from a chloroform/hexane mixture.[6]

1,8,15,22-Tetrahexyloxyphthalocyanine, H_2Pc:[6] Lithium (1.1 g, 158 mmol) was dissolved in anhydrous hexanol under reflux and a nitrogen atmosphere. After cooling, 3-hexyloxyphthalonitrile (630 mg, 2.76 mmol) was added and the mixture was stirred at room temperature for three days.[5] The solvent was removed in a rotatory evaporator and the residue was collected, washed with water, and after drying it was purified by silica gel chromatography with chloroform as eluent, then recrystallized from a chloroform/hexane mixture, to give 263 mg (41.6 %) of the dark blue shiny solid, H_2Pc. Elemental analysis (%): calcd for $C_{56}H_{66}N_8O_4$: C 73.50, H 7.27, N 12.24; found: C 73.86, H 7.29, N 12.15; ^{1}H NMR ($CDCl_3$): $\delta=$ 8.88 (d, 4H, $J=6.85$ Hz), 7.99 (t, 4H, $J=7.33$ Hz), 7.54 (d, 4H, $J=$ 7.33 Hz), 4.66 (t, 8H, $J=6.36$ Hz), 2.46 (m, 8H), 2.08 (m, 8H), 1.72 (m, 8H), 1.57 (m, 8H), 1.06 (t, 12H, $J=7.33$ Hz), −0.66 ppm (s, 2H); UV/Vis ($CHCl_3$): λ_{max} ($10^{-4}\varepsilon$) = 728 (18.2), 694 (16.3), 678 (5.00), 628 (3.56), 353 (4.76), 322 nm (6.72 mol^{-1} dm^3 cm^{-1}). The above NMR data clearly indicate that the hexyloxy groups are attached to the phthalocyanine periphery in a single-handed rotation.[5,6]

1,8,15,22-Tetrahexyloxyphthalocyaninatovanadium(IV) oxide, VOPc: A mixture of the single-handed H_2Pc (40.7 mg, 0.045 mmol) described above, vanadium(V) pentoxide (99 mg, 5.44 mmol), and dried urea (547 mg, 9.1 mmol) was stirred at 140 °C for ≈1 h, and after addition of DMF (1 mL) the reaction was continued for further 17.5 h. After removal of the solvent by an evaporator, the residue was washed with water, dried, and purified by column chromatography over alumina with carbon tetrachloride/methanol (10:1 v/v) as the eluting solvent. Recrystallization from chloroform/methanol gave the desired VOPc (29.2 mg (66 %). Elemental analysis (%): calcd for $C_{56}H_{64}N_8O_5V$: C 68.62, H 6.58, N 11.43; found: C 69.98, H 6.75, N 11.73; UV/Vis ($CHCl_3$): λ_{max} ($10^{-4}\varepsilon$): 733 (24.4), 700 (3.82), 657 (4.39), 434 (1.48), 353 (4.96), 324 nm (5.91 mol^{-1} dm^3 cm^{-1}).

1,8,15,22-Tetrahexyloxyphthalocyaninatosilicon hydroxide hexyl oxide, SiPc. In freshly distilled dry quinoline (9.3 mL), 4-*n*-hexyloxy-1*H*-isoindole-1,3(2*H*)-diimine (1.51 g, 6.16 mmol), prepared from 3-hexyloxyphthalonitrile and ammonia gas by a general procedure,[25] and silicon tetrachloride (2.3 mL, 20 mmol) were stirred at 180 °C under nitrogen for 18 h. After the system had been cooled, chloroform and water were added to it, the chloroform layer was collected, and the solvents were removed as much as possible by an evaporator. The residue was subjected to alumina chromatography (Act. IV) with first hexane (to remove the residual quinoline) and then chloroform as the eluting solvents. The mixtures of $Si(OH)_2Pc$ isomers obtained were separated on an HPLC (Ultron VX-ODS) column using methanol/chloroform (7:2 v/v) as the eluting solvent (flow rate = 9 mL min^{-1}, detection wavelengths = 220, 350, 600, 700 nm).

A portion of the separated 1,8,15,22-tetrahexyloxyphthalocyaninatosilicon dihydroxide, $Si(OH)_2Pc$ (6 mg, 6.15×10^{-3} mmol) and hexanol (400 mL, 3.20×10^{-3} mmol) were heated at reflux in toluene (75 mL) for 1.5 h in the presence of dried calcium dichloride (2.5 g).[26] The solvent was removed by a vacuum evaporator and the residue was placed on an alumina column (Act. V) with first hexane and then chloroform as eluents, and further on an alumina TLC plate with chloroform as eluent, to give the desired SiPc (ca. 3.4 mg, 52 % from $Si(OH)_2Pc$) as a green powder; ^{1}H NMR ($CDCl_3$): $\delta=9.16$ (d, 4H), 8.17 (t, 4H), 7.70 (d, 4H), 4.75 (m, 8H), 2.52 (m, 8H), 2.15 (m, 8H), 1.75 (m. 8H), 1.21 (m, 8H), 1.05 (t, 12H), 0.27 (m, 2H), 0.23 (t, 3H), −0.39 (m, 2H), −1.32 (m, 2H), −1.57 (m, 2H), −1.94 (m, 2H), −5.50 ppm (s, 1H); UV/Vis ($CHCl_3$): λ_{max} ($10^{-4}\varepsilon$) 712 (18.0), 678 (2.73), 636 (3.03), 322 nm (4.38 mol^{-1} dm^3 cm^{-1}); FABMS $[M]^+$: calcd for $C_{62}H_{78}N_8O_6Si$: 1058.6; found: 1058.6. These NMR data confirm that SiPc is indeed a Pc with a single-handed rotation.

Separation of VOPc and SiPc into two enantiomers: Single-handed VOPc and SiPc were separated into two enantiomers on a reversed-phase silica gel HPLC column ($0.46\phi\times25$ cm) coated with cellulose tris(3,5-dimethylphenylcarbamate) by using mixtures of hexane/chloroform (6:1 v/v) for VOPc (flow rate = 1 mL min^{-1}, detection wavelength = 350 nm) and carbon tetrachloride/chloroform (6:1 v/v) for SiPc (flow rate = 0.7 mL min^{-1}, detection wavelengths = 210, 350, 600, 700 nm). In the case of VOPc, two fractions were eluted at 9 min (VOPc-1) and 19 min (VOPc-2) in areal ratio 49:51 (Figure 2a); for SiPc two fractions were eluted at 7 min (SiPc-1) and 9 min (SiPc-2) in areal ratio 49:51 (Figure 2b). The electronic absorption spectra of VOPc-1 and VOPc-2 were exactly the same, and for SiPc-1 and SiPc-2 not only the electronic spectra but also the ^{1}H NMR spectra were found to be the same.

Band deconvolution analysis: To analyze the experimental spectra, band deconvolution analysis was carried out by using SIMPFIT, developed by Stillman et al.[12]

Computational details: All calculations were done by using a Gaussian 03 program package.[27] The geometry optimization of VOPc with four methoxy groups (VOPc$_{Me}$-a) was performed at the UB3LYP/6-31G* level,[19] using C_4 symmetry restriction. Sixty excitation energies, oscillator strengths, and rotatory strengths for the optimized structure were calculated by TDDFT. We mostly used the B3LYP functional and 6-31G* basis sets for CD calculations. Rotatory strengths reported here are based on the dipole–velocity expression. The CD spectrum of VOPc without peripheral substituents was calculated from the optimized geometry of VOPc$_{Me}$-a by removing peripheral methoxy groups. The rotatory strength for the Q transition of VOPc$_{Me}$-a with a flat π skeleton was calculated using the optimized geometry of C_{4h} vanadium(IV) phthalocyanine with an additional oxygen atom as an axial ligand. The V=O distance was set to 1.58 Å. To estimate the geometric parameters of SiPc$_{Me}$-a, geometric optimization of silicon phthalocyanine dichloride (SiPcCl$_2$) with C_{4h} symmetry was first performed at the B3LYP/6-31G* level.[20] The dihedral angle, θ, which is defined by the angle C$_2$-C$_1$-O-C$_{Me}$, was 0°. Two chlorine atoms were removed from the resulting structure and then methoxy and hydroxy units were added to construct SiPc$_{Me}$-a. Each Si–O distance was set to 1.72 Å. The direction of the O–H bond was kept parallel to the Si–N$_p$ direction.

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