Magnetic Circular Dichroism of 1,8-Naphthalene and 1,8-Anthracene-Linked Cofacial Binuclear Phthalocyanines

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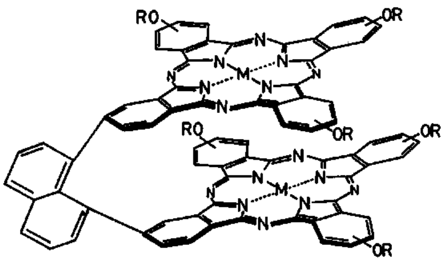
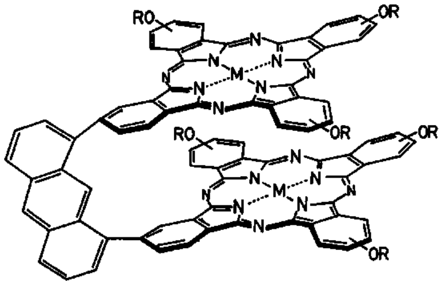
Magnetic circular dichroism (MCD) spectroscopy of non-metallated, dizinc, dicopper and dicobalt derivatives of 1,8-naphthalene and 1,8-anthracene-linked cofacial binuclear phthalocyanines is reported. Not only the spectra of neutral species, but also the spectrum of the mixed valence Co(II)Co(I) species have been recorded. These MCD spectra are, especially in the Q band region, similar in shape to those so far reported for aggregated phthalocyanines. Very intense intramolecular interaction between two phthalocyanine cores is observed in all compounds except cobalt-reduced Co(I)Co(I) species.

Keywords Magnetic circular dichroism, cofacial phthalocyanine, naphthalene, anthracene, absorption spectrum

Magnetic circular dichroism (MCD) spectroscopy has been successfully applied for porphyrin[1] and phthalocyanine[2] compounds. MCD is not only sensitive to the spin and the oxidation state of the central metals but also to changes in the porphyrin or phthalocyanine cores, so that it was once used to give "fingerprints" of various porphyrin species.[3] Phthalocyanines in the title (Scheme 1) are composed of mixtures of several positional isomers, the major ones being the *syn* and *anti* isomers on the pillared naphthalene and anthracene molecules.[4] Nevertheless, these compounds are relatively well defined rigid binuclear phthalocyanines. For example, a large splitting of Co$^{II/I}$ couple which was caused by rigid cofaciality has been reported recently.[5] Thus, it is significant to report MCD spectra of the title compounds as "fingerprints" of cofacial binuclear phthalocyanines. In addition, absorption and MCD spectra of such compounds are important from the standpoint of aggregation of phthalocyanines. Phthalocyanines, especially water-soluble phthalocyanines, are known to aggregate easily in solution in a card-pack fashion.[6] However, the relationship between the shape and position of MCD or absorption spectrum and the mutual distance of constituent phthalocyanines is not known because of the lack of appropriate model compounds. In this respect, the cofacial binuclear phthalocyanines in this study can be good models since two phthalocyanine units are rigidly constrained to 1 and 8 positions of naphthalene and anthracene. As shown below, the difference of the distance between 1 and 8 positions of naphthalene and anthracene is indeed well reflected in both absorption and MCD spectra.



Nap[ZnTrNPc]$_2$: M=Zn, R=CH$_2$C(CH$_3$)$_3$
Nap[CoTrNPc]$_2$: M=Co, R=CH$_2$C(CH$_3$)$_3$
Nap[CuTrNPc]$_2$: M=Cu, R=CH$_2$C(CH$_3$)$_3$
Nap[H$_2$TrNPc]$_2$: M=H$_2$, R=CH$_2$C(CH$_3$)$_3$



Ant[ZnTrNPc]$_2$: M=Zn, R=CH$_2$C(CH$_3$)$_3$
Ant[CoTrNPc]$_2$: M=Co, R=CH$_2$C(CH$_3$)$_3$
Ant[H$_2$TrNPc]$_2$: M=H$_2$, R=CH$_2$C(CH$_3$)$_3$

Scheme 1

A Brief Explanation of MCD and the Spectra of Phthalocyanines, and the Significance of This Study in Analytical Science

In order to assist the understanding of this paper, we first explain the essentials of MCD[7], spectra of phthalocyanines[2] and their interrelation.

All chromophore molecules in a longitudinal magnetic field are optically active, *i.e.* there is a difference in the absorption coefficients for left and right circularly polarized light for some regions of the spectrum. In MCD this difference is measured as a function of frequency (or wavelength) and is often expressed in terms of molar ellipticity per unit magnetic field, $[\theta]_M$. For an isotropic molecule, the experimental band shape would be written as $[\theta]_M \propto [f_1 A + f_2(B + C/kT)]$, the (Faraday) A, B and C terms each giving its own molecular properties (f_1 and f_2 are wave shape functions). An MCD band shape which changes sign at the absorption maximum is sometimes called a Faraday A term and arises when the system possesses a degenerate ground or excited state. An MCD band shape which peaks nearly at the absorption maximum and whose magnitude is temperature-dependent is generally called a Faraday C term, and its sign and magnitude are related to the sign and magnitude of splitting of the ground state. Thus a non-zero C term requires the presence of a degenerate ground state and a non-zero A term requires either a degenerate ground or excited state. It is known, however, that a ground state degeneracy usually ensures that the chief contribution is the C term, the A and B terms generally being much smaller. If the ground state is non-degenerate, the presence of an A term indicates that the excited state is degenerate. The B term arises from the mixing of the states due to the magnetic field, and the band shape is similar to that of the C term but is temperature-independent. All chromophore molecules show the B terms.

The spectra of phthalocyanines[7] consist generally of two regions. The one in the 600 - 750 nm region is called the Q band and the other in the 300 - 450 nm is called the Soret band. In the case of methallophthalocyanines (MtPcs) with D_{4h} symmetry, the intense Q band is related to a single transition from a non-degenerate ground state to a doubly-degenerate excited state, while the Soret band contains a set of transitions of less intensity. The Soret band of MtPcs includes at least one transition from a non-degenerate ground state to a doubly-degenerate excited state. Thus, MtPcs show Faraday A terms at both the Soret and Q bands. In contrast, non-metallated phthalocyanines exhibit only Faraday B terms through all regions since there is no degeneracy at either ground or excited states.

As mentioned here, MCD curves can have both plus and minus signs. Accordingly, seemingly broad absorption bands may be resolved into several components in MCD spectra to give more information. Indeed as this article will describe, MCD spectroscopy coupled with absorption spectroscopy can discriminate two compounds which have two phthalocyanine units at the 1 and 8 positions of naphthalene and anthracene. This implies that other compounds which have cofacial arrangements can be distinguished from each other if there are slight differences in the structure (for example, in mutual distances of two chromophore units). This is important from an analytical viewpoint since such a subtle difference in molecules is not always easily detectable by other methods. In addition, cofacial arrangement is quite common, as seen in aggregation phenomena of dyes.

Experimental

Materials

Synthesis and purification procedures of the pillared phthalocyanines employed in the present study have been published elsewhere.[4] They will be expressed by abbreviated notations in the scheme. *o*-Dichlorobenzene for rapid liquid chromatography (Nakarai) was used as received as solvent for MCD and UV-visible absorption spectroscopy. Tetrabutylammonium perchlorate (TBAP, an electrolyte) was twice recrystallized from absolute ethanol and dried *in vacuo* at *ca.* 50°C.

Measurements

UV-visible absorption spectra were run on a Shimadzu UV-250 spectrophotometer, while MCD spectra were recorded on a Jasco J-400X spectrodichrometer equipped with a Jasco electromagnet to produce longitudinal magnetic fields up to 1.17 T. Each MCD measurement was made with both parallel and antiparallel fields. Measurements of electrolyzed species were performed using an optically transparent thin layer electrode cell (OTTLE) which could fit into the cell holders of the absorption and MCD apparatus.[8] The path length of OTTLE was 1 mm and the solution contained *ca.* 0.3 M (1 M=1 mol dm^{-3}) TBAP as an electrolyte. Spectra for unelectrolyzed species were recorded using solutions of (6 - 8)$\times 10^{-6}$ M in a 10 mm cell at 20°C, while those of electrochemically generated species were obtained using solutions of *ca.* 8×10^{-5} M in the OTTLE. Potentials were controlled by a potentiostat which was built by the method reported in the literature.[9]

Results and Discussion

Figures 1 and 2 show the spectra of non-metallated and dizinc derivatives, respectively. In both cases, absorption coefficients of anthracene pillared derivatives are slightly larger than those of naphthalene pillared ones over a wide range of wavelengths, and Q bandwidths of these molecules (2350 - 2620 cm^{-1} at half-height) are obviously much wider than those of mononuclear species (*ca.* 350 - 750 cm^{-1})[10], reflecting the

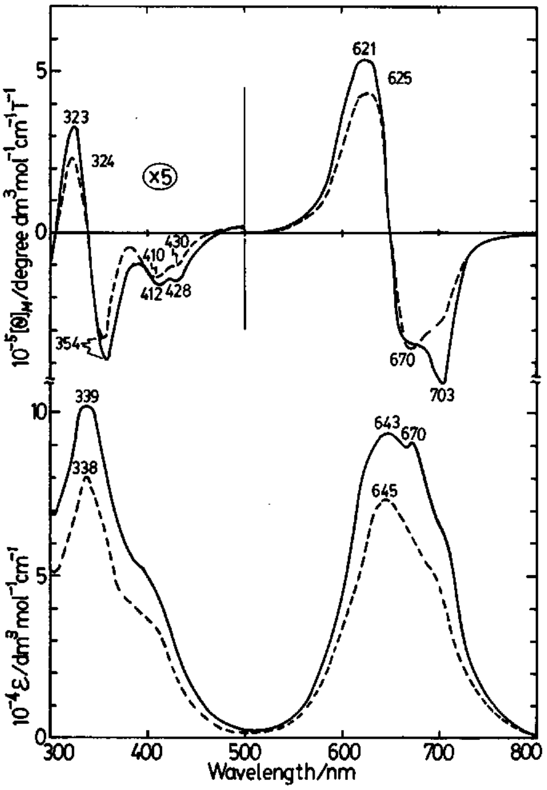


Fig. 1 Absorption (bottom) and MCD (top) spectra of Ant[H_2TrNPc]$_2$ (solid lines) and Nap[H_2TrNPc]$_2$ (broken lines) in *o*-dichlorobenzene.

presence of both the *syn* and *anti* isomers and the relatively low symmetry of the *syn* isomer. In the symmetry of the *syn* isomer, a broad absorption is predicted[11], shifted to the blue of the mononuclear absorption and possessing a broad weak tail to the red, while the *anti* isomer may add complexity on this envelope by superimposing more monomer-like absorption peaks (the inset in Fig. 2 shows the qualitative energy diagram for exciton coupling in the D_{4h} *syn* isomers). This overall appearance is in fact observed, but with peaks observed rather prominently to the shorter wavelength of mononuclear absorption (the absorption spectra of mononuclear control molecules, *i.e.* neopentoxyphthalocyanine and its zinc derivative, were already reported[12] and the redmost Q bands exist at 705 and 685 nm, respectively). Thus, as the inset shows, the prominent blue-shifted Q bands are indications of strong intramolecular coupling in these molecules.

MCD spectra of these compounds are relatively similar in shape in the Q region. They have S-shaped patterns with crossover points at *ca.* 650 nm, which is close to the position of the blue-shifted prominent absorption peak, reflecting cofacial arrangement of the binuclears. However, the contents of the spectra between the dizinc derivatives and non-metallated ones appear at least theoretically[7] different from each other.

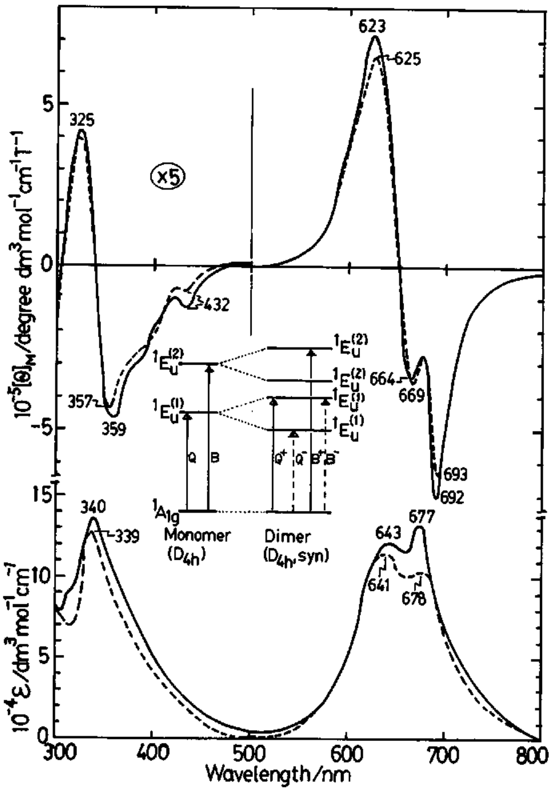


Fig. 2 Absorption (bottom) and MCD (top) spectra of Ant[ZnTrNPc]$_2$ (solid lines) and Nap[ZnTrNPc]$_2$ (broken lines) in *o*-dichlorobenzene. The inset shows orbital diagram for exciton coupling in a phthalocyanine dimer with D_{4h} geometry. The solid line and broken line arrows mark allowed and forbidden transitions, respectively (diagram taken from ref. 11). In this figure Q^+ and Q^- bands are in *ca.* 600 - 650 nm and 700 - 750 nm region, respectively.

Namely, the Q band MCD of the dizinc derivatives seems to be formed largely by the superimposition of two Faraday *A* terms, since each phthalocyanine unit has approximate D_{4h} symmetry. The small dispersion curves at around 660 - 710 nm would be attributed to the *anti* isomer or the lower out-of-phase transition of the *syn* isomer. In contrast, the Q band MCD trough in the longest wavelength of non-metallated compounds is obviously attributed to Faraday *B* term, since no degeneracy exists in either the ground or the excited states. Almost all mononuclear phthalocyanines with D_{2h} symmetry so far reported produced negative MCD troughs associated with the Q band absorption peaks in the longest wavelength.[13] And, since neopentoxyphthalocyanine shows an intense absorption at around 700 - 710 nm[12], a negative MCD trough is expected in this region if the present system contains monomer-like species in solution. Comparing the MCD spectrum of Nap[H_2TrNPc]$_2$ with that of Ant[H_2TrNPc]$_2$, keeping these facts in mind, we notice that the content of "monomer-like" species is larger for the latter system, since the MCD trough for the latter is more intense. This would be further related to the difference of the distance between 1 and 8 positions of naphthalene and anthracene. In anthracene pillared compounds, both the *syn* and *anti* isomers may behave as more "monomer-like" species than in the naphthalene pillared ones, since the distance of two phthalocyanine units is larger.

The interpretation of the main Q band MCD of non-metallated compounds is more complicated. Originally, this should be the superimposition of Faraday *B* terms (dispersion type MCD can be explained as superimposition of *B* terms[7,13]). However, the possibility of Faraday *A* terms is not completely ruled out. The *A* term is expected if the molecule has D_{4h} symmetry, *i.e.* if two protons in each phthalocyanine core are shared equally among four nitrogens. In fact, this was recently experimentally substantiated using a perfectly eclipsed cofacial dimeric phthalocyanine.[14]

The MCD curves of non-metallated and dizinc derivatives in the 300 - 500 nm are similar in appearance. In the case of several metallophthalocyanines, Faraday *A* terms have been detected in the longer wavelength of what we believed to be the Soret bands.[15] From the band shape, the curvature between *ca.* 420 and 440 nm of dizinc derivatives would correspond to this Faraday *A* term. Then the curvature in *ca.* 380 - 400 nm may correspond to another *A* term caused by intramolecular coupling of two phthalocyanine units. If this is the case, its energy difference (*ca.* 2000 cm^{-1}) is roughly the same as that of a cofacial phthalocyanine dimer.[10,14] In contrast, MCD curves in non-methallated derivatives should be Faraday *B* terms in nature. Although not well discernible in the absorption spectra, two absorption peaks are considered to exist associated with the two MCD troughs between *ca.* 400 and 440 nm.

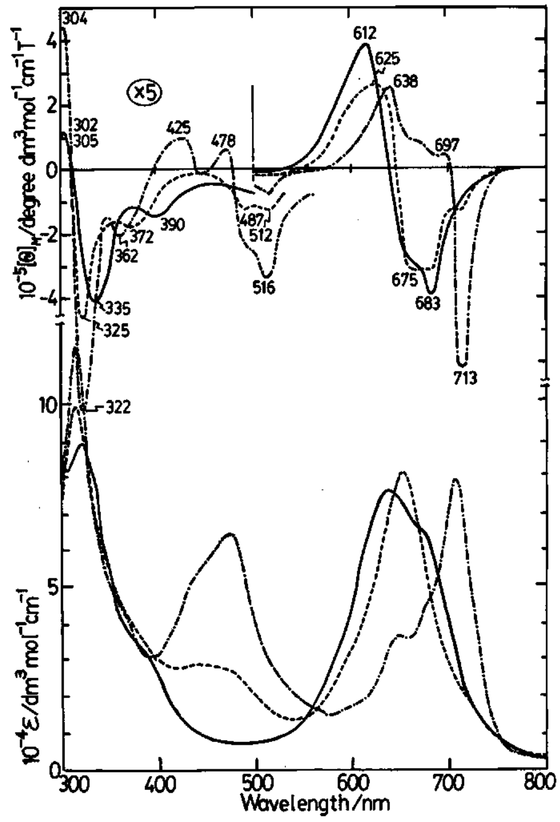


Fig. 3 Absorption (bottom) and MCD (top) spectra of Nap[CoTrNPc]$_2$ in the Co(II)Co(II) state (solid lines), Co(II)Co(I) mixed valent state (broken lines), and Co(I)Co(I) state (dotted broken lines) in *o*-dichlorobenzene containing 0.3 M TBAP.

Figure 3 shows the spectra of Nap[CoTrNPc]$_2$ and its one- and two-electron reduced species. In *o*-dichlorobenzene, the one-electron reduced species is a Co(II)-Co(I) mixed valence species, while the two-electron reduced species is a Co(I)Co(I) species.[4a] As for the spectra for non-metallated and dizinc derivatives in Figs. 1 and 2, the Q band of the unelectrolyzed Co(II)Co(II) species lies at shorter wavelength than that of mononuclear tetraneopentoxyphthalocyaninatocobalt-(II) (680 nm[12]), and the Q bandwidth (2700 cm^{-1} at half-height) is very wide, suggesting intensive intramolecular exciton interaction of the two phthalocyanine units. With a reduction of cobalt(II), the Q band shifts to a longer wavelength and becomes sharper, and a new peak and shoulder develop in the 400 - 550 nm region, while the Soret region becomes sharper and intensifies with a slight blue-shift. The absorption spectroscopic shape of Co(I)Co(I) species resembles that of general mononuclear Co(I) phthalocyanines[2,16], suggesting the presence of electrostatic repulsion between the two Co(I) phthalocyanines.

The Q band MCD spectra of the Co(II)Co(II) and Co(II)Co(I) species are similar, having broad S-shape curvature at around the peak position of the absorption spectra. These MCD spectra are considered to be caused by the superimposition of Faraday *A* terms, since each phthalocyanine unit in Nap[CoTrNPc]$_2$ has approximate D_{4h} symmetry. The Q band MCD of Co(I)Co(I) species is, however, unique in that the shape is seemingly that of the Faraday *B* term. Since the band especially that at the longest wavelength is sharp (or narrow) enough to be judged as that of monomeric phthalocyanines, this uniqueness may be an indication of perturbation of the Co(I) ion to π ring systems rather than the intramolecular interaction of the two Co(I) phthalocyanines. The spectra of Co(I) phthalocyanines in the 400 - 500 nm range have been assigned to charge-transfer transitions from Co(I)$e_g(d\pi)$ to ligand b_{1u} and b_{2u} (π) orbitals.[16,17] The Co(I)Co(I) species alone exhibited clear Faraday *A* terms corresponding to an absorption spectroscopic peak and shoulder in this region. Since the b_{2u} orbital lies at higher energy than b_{1u} orbital[17], the Faraday *A* term in the longer wavelength (*ca.* 470 - 500 nm) may correspond to an $e_g \longrightarrow b_{1u}$ transition. Strangely, the mixed valence Co(II)Co(I) species showed a Faraday *A* term only in this longer wavelength region. Although peaks are not clear in the absorption spectra, several MCD troughs seen in the 350 - 400 nm range may indicate the position of the true Soret bands.[15] These troughs shift to a shorter wave-

Table 1 Positions and magnitudes of main MCD peaks and troughs of 1,8-naphthalene- and 1,8-anthracene-linked cofacial binuclear phthalocyanines in *o*-dichlorobenzene

Pc	$[\theta]_M$ max or min/nm ($10^{-5}[\theta]_M$/degree $dm^3\ mol^{-1}\ cm^{-1}\ T^{-1}$)						
Ant$[H_2TrNPc]_2$	323(0.56)	354(−0.76)	412(−0.34)	428(−0.31)	621(5.40)		703(−4.59)
Nap$[H_2TrNPc]_2$	324(0.51)	354(−0.60)	410(−0.28)	430(−0.21)	625(4.41)	670(−3.57)	
Ant$[ZnTrNPc]_2$	325(0.81)	359(−0.93)	432(−0.25)		623(7.24)	664(−3.01)	693(−7.30)
Nap$[ZnTrNPc]_2$	325(0.74)	357(−0.90)	432(−0.16)		625(6.93)	669(−2.85)	692(−6.05)
Ant$[CoTrNPc]_2$	312(0.22)	338(−0.79)	385(−0.39)	431(−0.13)	611(3.17)		688(−3.51)
Nap$[CoTrNPc]_2$	312(0.17)	348(−0.55)	400(−0.19)	431(−0.05)	615(3.71)		689(−3.33)
Nap$[CuTrNPc]_2$	322(0.38)	351(−0.54)	401(−0.15)	431(−0.09)	620(3.07)		691(−2.78)

length with the progress of reduction of cobalt(II), in contrast to the shift of the Q band to a longer wavelength. This opposite shift can reasonably be explained if we take configuration interaction between the Soret and Q states into account, albeit it is generally known to be much smaller in phthalocyanine systems than in porphyrin systems.[18]

The Table 1 summarizes the MCD data in the present study. Compared with the MCD spectra of monomeric phthalocyanines[2], all unelectrolyzed compounds show relatively structureless, blue-shifted, weaker Q band MCD values.

Phthalocyanines are prone to aggregation in a card-pack fashion in solution.[6] For example, tetracarboxylated metallophthalocyanines aggregate in water, and exhibit MCD spectra similar to those in the present study.[8] Although their mutual distance has not been determined to date, this spectroscopic similarity suggests that phthalocyanine–phthalocyanine distance in the carboxylated phthalocyanine is not greatly different from the distance between the 1 and 8 positions of, say, the anthracene molecule (4.9 – 5.0 Å).[19] Thus, the present study may be useful as a model of MCD of aggregated phthalocyanines.

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(Received June 23, 1990)
(Accepted October 16, 1990)