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Symmetry-Lowering of the Phthalocyanine Chromophore by a C_2 Type Axial Ligand

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Symmetry-lowering is an important approach for controlling the properties of the phthalocyanine (Pc) chromophore such that research on symmetry-lowered Pcs has become popular in recent years.[1] Monosubstituted type C_{2v} Pc derivatives have been synthesized by mixed condensation,[2] a polymer support method,[3] or ring expansion of subPcs.[4] Opposite disubstituted Pcs have been prepared by either the trichloroisoindolenine method[3] or the use of steric hindrance.[5] In these cases, the lowest excited singlet (S_1) state becomes nondegenerate, although it is degenerate for normal metalloPcs (MPcs) with D_{4h} or approximate D_{4h} symmetry. These properties originate from the low symmetry of Pc ligands composed of four isoindoles fused with different π systems or having substituents. In this way, it is difficult in general to control the S_1 properties without modifying the Pc ligand (or periphery). In this communication, we have synthesized (2,2′-biphenyldioxy)-(tetra-*tert*-butylphthalocyaninato)titanium(IV), Ti(Pc)(BP) (Scheme 1), and succeeded in lowering the practical chromophore symmetry of a Pc ligand with approximate D_{4h} symmetry. The key feature is to attach a biphenyldioxy (BP) ligand just above the Pc plane so that the transition electric dipole moment of the BP ligand interacts with that of the Pc ligand.

Ti(Pc)(BP) was synthesized as shown in Scheme 1. Oxo(tetra-*tert*-butylphthalocyaninato)titanium(IV), TiO(Pc) (0.062 mmol), and 2,2′-biphenol (0.068 mmol) were dissolved in dichloromethane (2 mL), and the solution was stirred at room temperature.[6] After 2 h, the solvent was evaporated and the residue washed with acetonitrile and imposed on a gel permeation chromatography column using Bio-beads SX-2 (Bio-rad) to give the desired product in 64% yield.[7]

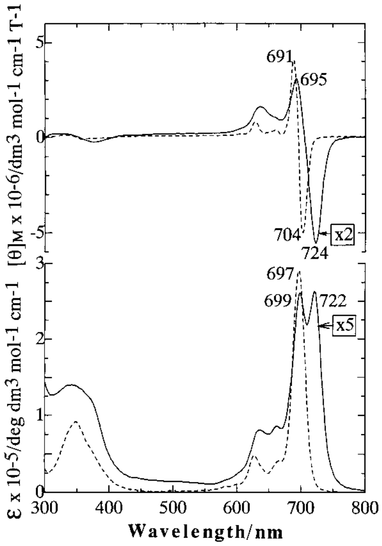

Figure 1. Electronic absorption (bottom) and MCD (top) spectra of TiO(Pc) (broken lines) and Ti(Pc)(BP) (solid lines) in dichloromethane.

Scheme 1

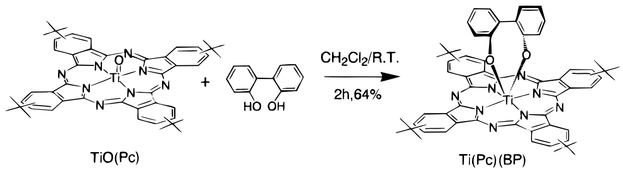

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of TiO(Pc) and Ti(Pc)(BP).[8] TiO(Pc) has a slightly square pyramidal structure,[9] but it shows an absorption spectrum characteristic of D_{4h} metalloPcs (the Q_{00} and Q_{01} bands appear at 697 and 627 nm, respectively), and its MCD spectrum has an intense Farady *A* term corresponding to the Q_{00} absorption peak at 697 nm, indicating that two excited states (E_x and E_y) are degenerate in the Q band. On the other hand, two split Q_{00} absorption bands (699 and 722 nm) are seen in the Q band region of the Ti(Pc)(BP) spectrum,[10] similar to D_{2h} Pc derivatives.[5] Further, the MCD spectrum of the Q band of this species is assigned to Faraday *B* terms, since the positive and negative peak positions (695 and 724 nm) are almost identical with the absorption peak positions (699 and 722 nm). These features reveal disruption of the degeneracy of the E_x and E_y states. Thus, lowering of the practical chromophore symmetry has been attained using a Pc ligand with approximate D_{4h} symmetry by attachment of the BP unit as an axial ligand.

The above splitting of the Q band may be explained as follows. First, since this kind of Q band splitting has not been observed

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(7) Anal. Calcd for $C_{60}H_{56}N_8O_2Ti$: C, 74.37; H, 5.82; N, 11.56%. Found: C, 73.47; H, 6.09; N, 11.68%. Mass (*m*/*z*): 969 (M + 1). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.42−9.67 (8H, m, Pc ring), 8.43−8.49 (4H, m, Pc ring), 1.83−1.85 (36H, m, *tert*-butyl), 4.63−4.68 (2H, dd, phenyl ring closest to the Pc core), 6.05−6.17 (6H, m, phenyl ring). The Ti═O stretching IR band seen for the starting TiO(Pc) at 972 cm^{-1} was absent in this compound.

(8) Electronic absorption spectra were measured with a Hitachi U-3410 spectrophotometer. MCD measurements were made with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.09 T with parallel and then antiparallel fields. Dichloromethane was used as solvent for all measurements.

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(10) The splitting of the Q band of this compound is not due to the aggregation, since the ^{1}H NMR measured at a concentration 10 times higher than that used in the absorption and MCD measurements (ca. 1 × 10^{-5} mol/L) in the same solvent still shows a spectrum ascribable only to monomeric species (above, ref 7).

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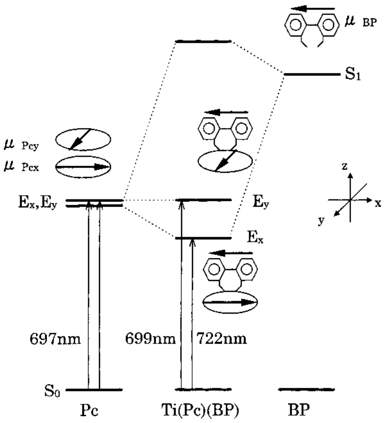

Figure 2. Exciton interaction between the Pc and BP ligands. The μ_{Pcx}, μ_{Pcy}, and μ_{BP} are the electric dipole moment of the Q_x transition, that of the Q_y transition, and the electric dipole moment of a transition to the S_1 BP, respectively.

when general axial ligands (hydroxide, acetate, halide, phenol, pyridine, etc.) are linked or coordinated to MtPcs,[11] the coordination of the BP ligand is considered to be of crucial importance. Then, as a plausible cause of this phenomenon, an exciton interaction between the Pc and BP ligands can be considered (Figure 2). In a transition to the S_1 state, the BP ligand has an electric transition dipole moment (μ_{BP}), which is parallel to the Pc plane. In the S_1 region of the Pc ligand, there are degenerate E_x and E_y states. The electric transition dipole moment (μ_{Pcx}) of a transition to the E_x state (Q_x) is parallel to the μ_{BP}, while that (μ_{Pcy}) of a transition to the E_y state (Q_y) is perpendicular to the μ_{BP}. In this case, only μ_{Pcx} can couple with μ_{BP}, and as a result, the E_x state shifts to lower energy without a change in the energy of the E_y state. In fact, it is seen in the absorption spectrum of Ti(Pc)(BP) that only the Q_x band (722 nm) is red-shifted, while the peak position (699 nm) of the Q_y band is almost identical with that (697 nm) of TiO(Pc). This feature strikingly supports our explanation.[12−14]

In summary, by synthesizing Ti(Pc)(BP), we have succeeded in lowering the practical symmetry of a D_{4h} type Pc chromophore by attaching an axial ligand with C_2 symmetry. The Q_x−Q_y splitting is reasonably interpreted by the exciton interaction between the Pc and BP ligand. In contrast to the cases reported to date in which the symmetry of the Pc ligand itself is lowered, our approach in this study is different in principle in that the Pc ligand is not peripherally modified. Therefore, the introduction of Ti(Pc)(BP) in the present study is not only interesting as a method leading to novel Pc derivatives but also important as a new concept for lowering the effective chromophore symmetry in the excited state of macrocycles.

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(12) To obtain further information, the exciton interaction between the Pc and BP ligands was evaluated[13] using the following equation.

$$\begin{aligned} W &= \langle \Psi_{\mathrm{Pc}*}\Psi_{\mathrm{BP}}|H|\Psi_{\mathrm{Pc}}\Psi_{\mathrm{BP}*}\rangle \\ &= 2\langle \phi_{\mathrm{HOMO}}{}^{\mathrm{Pc}}(1)\ \phi_{\mathrm{LUMO}}{}^{\mathrm{BP}}(2)\ |e^2/r_{12}|\ \phi_{\mathrm{LUMO}}{}^{\mathrm{Pc}}(1)\ \phi_{\mathrm{HOMO}}{}^{\mathrm{BP}}(2)\rangle \\ &= 2\sum_s\sum_t Cs_{\mathrm{HOMO}}{}^{\mathrm{Pc}}Cs_{\mathrm{LUMO}}{}^{\mathrm{Pc}}Ct_{\mathrm{HOMO}}{}^{\mathrm{BP}}Ct_{\mathrm{LUMO}}{}^{\mathrm{BP}}e^2/R_{\mathrm{st}} \end{aligned}$$

Here, ϕ_i^{Pc} ($=\sum_s Cs_i^{\mathrm{Pc}}\varphi s$) and $\phi_{\mathrm{j}}^{\mathrm{BP}}$ ($=\sum_t Ct_j^{\mathrm{BP}}\varphi t$) are the *i*th MO of the Pc ligand and the *j*th MO of the BP ligand, respectively. R_{st} denotes the distance between the *s* and *t* atoms. The optimum structure of Ti(Pc)(BP) was calculated using a PM3 Hamiltonian by means of the program *Hyperchem*, release 5.1. The MOs of the Pc and BP ligand were calculated using a ZINDO/S Hamiltonian. As a result, the $|W|$ was evaluated as 1.7×10^3 cm^{-1}, indicating the existence of a significant interaction between the Pc and BP ligands.

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(14) The naphthalene analogue of Ti(Pc)(BP), i.e., (2,2′-binaphthyldioxy)(tetra-*tert*-butylphthalocyaninato)titanium(IV), Ti(Pc)(BN), was similarly obtained using 2,2′-binaphthol in place of 2,2′-biphenol in the preparation of Ti(Pc)(BP). Ti(Pc)(BN) showed two intense absorption bands at 700 and 726 nm. The electronic and MCD spectral features of Ti(Pc)(BN) are similar to those of Ti(Pc)(BP).