

smaller than that of the A-term; however, in this case, the B-terms gain their intensity from the small energy gap between the two states.¹⁵ Thus, even though the molecular symmetry is lower,¹⁶ *pseudo*-A terms can be observed in MCD spectra when the magnitude of the splitting between the LUMO and the next LUMO is sufficiently small.

3.2.4 Interaction Between Chromophores

When two or more macrocycles are close to each other, regardless of whether they are chemically bonded or not, the observed optical absorption spectra, particularly in the Q-band region, are generally different from the superposition of the spectra of the monomers. The spectral changes can be due to the interaction between the transition dipole moments of each chromophore (when the distance between the macrocycles is larger than the van der Waals distance of 3.4 Å) or due to the overlapping of their π -conjugation systems (when the distance < 3.4 Å).

3.2.4.1 Spectral Changes Associated with Molecular Aggregation

Before discussing the interaction between chromophores, it should first be noted that the optical absorption spectrum of phthalocyanines can be dependent on their concentration. Chemists working with phthalocyanines may often encounter such a phenomenon in their laboratories. The deviation of the spectrum from the “prototypical” monomer spectrum significantly depends on how the macrocycles are aligned, as described in the next subsection (Sect. 3.2.4.2). Figure 3.14 shows the optical absorption spectra of the Co^{II} complex of octakis(3,3-dimethyl-1-butynyl) phthalocyanine (Fig. 3.14 right), which is highly soluble in common organic solvents, in dichloromethane solutions at various concentrations [101]. Although this compound shows a prototypical Q-band in a very dilute solution (ca. 10^{-6} M), the apparent Q-band intensity decreases with increasing concentration, and a new absorption band appears at the blue flank of the Q-band. The inset of Fig. 3.14 clearly indicates that the Q-band intensity does not obey Lambert-Beer’s law. Such a phenomenon is common in the solution chemistry of phthalocyanines [101, 117, 131–133] and has been interpreted in terms of molecular aggregation, that is, the formation of dimers, trimers, or aggregates of higher order.¹⁷ Some

¹⁵As mentioned in Sect. 2.2.8, the intensity of B-terms is larger as the two excited states are closer in energy.

¹⁶States can be degenerate when the molecular symmetry is not lower than C_3 .

¹⁷Only monomers and dimers contribute to the absorption spectra (Fig. 3.14) within this concentration range because sharp isosbestic points are seen in the spectral changes; hence, the two species are in equilibrium.

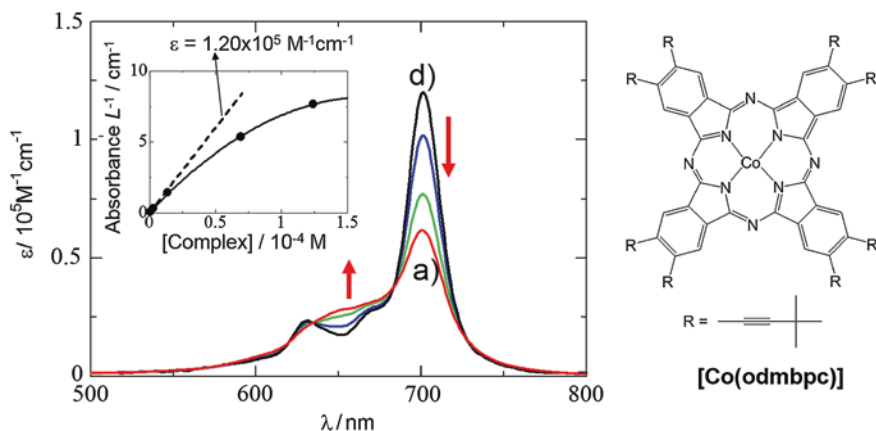


Fig. 3.14 Optical absorption spectra of Co^{II} complex of octakis(3,3-dimethyl-1-butynyl)-substituted phthalocyanine in dichloromethane at various concentrations (a $1.24 \times 10^{-4} \text{ M}$; b $6.93 \times 10^{-5} \text{ M}$; c $1.39 \times 10^{-5} \text{ M}$; d $2.77 \times 10^{-6} \text{ M}$). The inset shows Beer's plots (absorbance at the monomer Q-band maximum wavelength), in which the slope of the broken line exhibits the molar extinction constant of the complex monomer. The red arrows indicate the changes in molar absorptivity with increasing concentration. Reprinted from Ref. [101], Copyright 1998, with permission from the Chemical Society of Japan

types of solvent can effectively induce aggregation even at very low concentrations ($\sim 10^{-6} \text{ M}$).¹⁸ In this case, the absorption band appears at the higher-energy side of the Q-band, and this manner of aggregation is referred to as “H-aggregation”. In H-aggregates, the macrocycles are aligned in a face-to-face manner (Fig. 3.15b) similarly to a pile of saucers. With respect to phthalocyanines, we most often encounter this type of aggregation because of their planar molecular structure.

In contrast, aggregates of some phthalocyanines show their absorption band on both sides of their Q-band (Fig. 3.16) [134] or occasionally, on the lower-energy side of their Q-band alone (Fig. 3.17) [6]. In these cases, the macrocycles are aligned in a “slipped face-to-face” manner (Fig. 3.15b, c). Such aggregates are

¹⁸The author has learned through his activities as a scientist and an article reviewer that a considerable number of people (including experts) believe that highly aggregating phthalocyanines are poorly soluble in common solvents or that highly soluble phthalocyanines are nonaggregating. However, this is not always true. For example, the octa(alkynyl)-substituted derivative in Fig. 3.14 is highly soluble (its solubility reaches almost 10^{-2} M) but it also aggregates even in dilute solutions (ca. 10^{-5} M) as illustrated above. On the other hand, the Sb^{V} complex of unsubstituted Pc is not very soluble (at most, 10^{-4} M) whereas its aggregation could not be detected by optical absorption spectroscopy using an optical cell of 1 mm path length up to the upper limit of the concentration range studied. Thus, having good solubility is one thing and being nonaggregating is another, at least with respect to phthalocyanines.

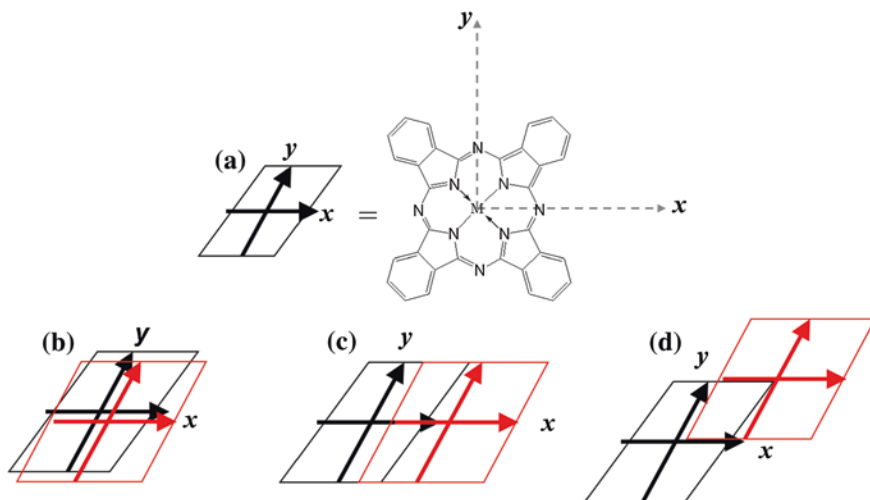


Fig. 3.15 Some common stacking manners observed for phthalocyanine derivatives: **a** monomer; **b** face-to-face stacking; **c** slipped face-to-face stacking (along x-axis); **d** slipped face-to-face stacking (along both axes). The two crossing arrows represent two orthogonal transition dipole moments

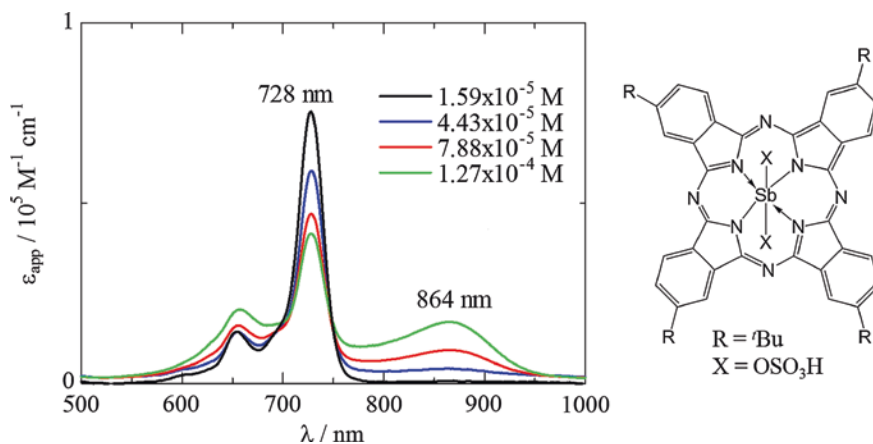


Fig. 3.16 Optical absorption spectra of $[\text{Sb}(\text{tbp})(\text{SO}_4\text{H})_2]^+$ at various concentrations in water solutions containing Triton X-100 (2 % w/v). Below $1.59 \times 10^{-5} \text{ M}$, the complex is free from aggregation under these conditions. Reprinted from Ref. [134], Copyright 2012, with permission from Elsevier

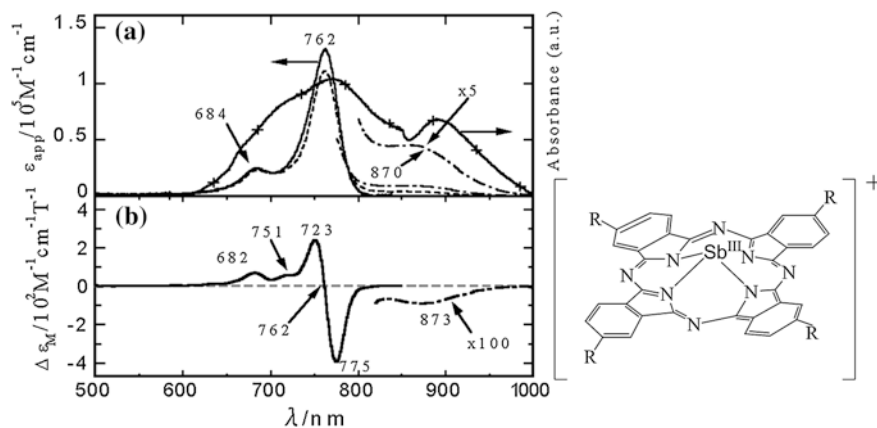


Fig. 3.17 Optical absorption (*top*) and MCD (*bottom*) spectra of Sb^{III} complex of tetra-*tert*-butyl phthalocyanine in dichloromethane at various concentrations. Reproduced from Ref. [6] with permission from The Royal Society of Chemistry

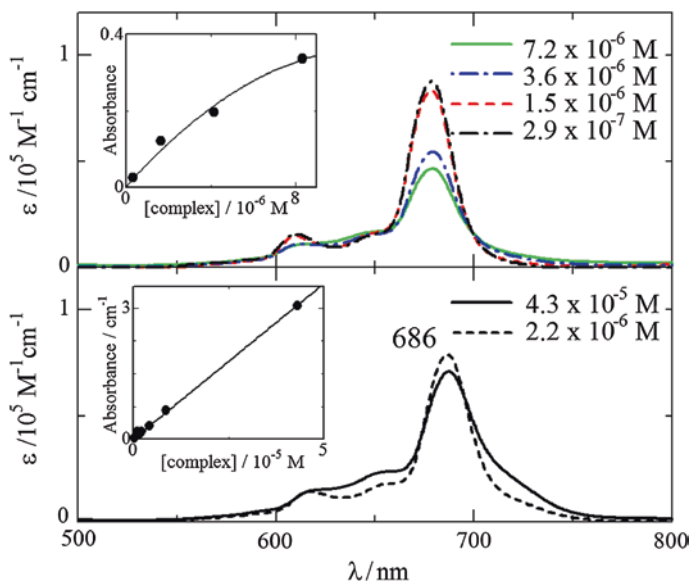


Fig. 3.18 Optical absorption spectra of $[\text{P}(\text{tppc})(\text{O})(\text{OH})]$ in acetonitrile (*top*), and dichloromethane solutions at various concentrations. The insets depict plots of absorbance at the Q-band maximum wavelength versus concentration. Reproduced from Ref. [59], Copyright 2013, with permission from World Scientific Publishing Company

referred to as J-aggregation.¹⁹ We have much less opportunity to observe this type of aggregation unless the metal ion of the macrocyclic ligand has axial ligands to sterically prevent H-aggregation or the peripheral substituents are capable of coordination to the central metal ion in the cavity of another macrocycle.

The relationship between the spectra of the aggregates and the alignment of the chromophores can be understood in terms of exciton coupling theory [135], as described in the next subsection (Sect. 3.2.4.2).

Note that the linear concentration dependence of the Q-band intensity is not necessarily sufficient to show that a given compound is free from aggregation in the solvent. The author has reviewed articles for a number of journals and has seen many researchers concluding that their compounds were free from aggregation in some specific solvents on the basis of a linear Lambert-Beer plot alone.²⁰ This may be true for some cases because the linear dependence indicates an insignificant contribution from aggregated species in the concentration range studied. Here, an example is given of a case where a linear Lambert-Beer plot was obtained for a specific phthalocyanine dye, even though it aggregates in the same solvent. Figure 3.18 shows the optical absorption spectra of a P^V complex (the same compound as that shown in Fig. 3.3) in acetonitrile and dichloromethane solutions at various concentrations. In acetonitrile, clear spectral changes are observed in a narrow concentration range, and the absorbance-concentration correlation gives a convex curve (top inset of Fig. 3.18). Therefore, one can easily conclude that the compound aggregates in the solvent. On the other hand, in dichloromethane, the Lambert-Beer plot appears linear up to 4.3×10^{-5} M (bottom inset of Fig. 3.18). Nevertheless, a careful comparison of the absorption spectra at 4.3×10^{-5} M and a much more dilute solution shows a clear spectral difference: i.e., the apparent Q-band intensity decreases and the absorbances at both flanks of the Q-band intensify [59], as is the case for J-aggregation. Thus, it is risky to exclude the possibility of aggregation on the basis of the linear Lambert-Beer plots alone. This can happen when the dimerization constant of the dye of interest is relatively small because the deviation from the linear regression line due to aggregation is comparable to the scatter deviation of the data owing to experimental errors generated during the preparation of the solutions. Even if a linear correlation is obtained, a few (several, if possible) spectra should be compared with each other in terms of molar absorptivity, as shown in Figs. 3.14, 3.16, 3.17,

¹⁹J-aggregates show their main band at a red flank of the monomer band, but the converse is not necessarily true. A number of phthalocyanines show an additional band at a wavelength longer than that of the monomer Q-band owing to acid-base equilibria involving the macrocycle (Sect. 3.2.5.2), electron transfer (Sect. 3.2.6.1), etc. Special care has to be taken when assigning such extra bands at longer wavelengths as “J-aggregates” particularly in the case of nondonor solvents (Sect. 3.2.5.2).

²⁰Readers are reminded that the Lambert-Beer plot must include the zero point because the absorbance attributed to the compound must be zero when its concentration is zero. Nevertheless, a number of authors have concluded a lack of aggregation of their compounds on the basis of the linear Lambert-Beer plot within a narrow concentration range excluding the zero point. The same plot including the zero point could be nonlinear.

and 3.18, but not in terms of absorbance (those of the highest and lowest concentrations inclusive). In addition, the concentration range to be studied should be as wide as possible (two orders of magnitude if the other conditions allow).

3.2.4.2 Exciton Coupling of Nondegenerate Transitions

First of all, we consider the interaction between two rodlike dye molecules in close proximity ($>3.4 \text{ \AA}$ so that the effects of the overlap of π -clouds between the two molecules are negligible) for simplicity. We assume that the transition dipole is generated along the long axis of the molecule [recall that an optically excited molecule has a vector (Sect. 2.2.1)]. In this model, we do not need to consider the degeneracy of their transitions. Figure 3.19 shows a schematic diagram of exciton coupling between the two excited molecules aligned in various manners. When the two rods are parallel to each other, the two transition dipoles can be parallel or antiparallel (Fig. 3.19a). In this arrangement, the parallel configuration gives rise to the destabilization of the excited state (S_2') relative to that of the monomer (S_1) owing to the repulsion between the dipoles (similarly to that between two magnets). This excited state is allowed because the dipole moment is nonzero (in fact, it is doubled); hence, intense optical absorption is expected to be observed on the higher-energy side of the monomer band. In contrast, the antiparallel configuration leads to a forbidden excited state because the two dipoles offset each other. This state is stabilized (S_1') relative to that of the monomer because of the attractive interaction between the two dipoles. Hence, no intense absorption band is expected to be observed on the red side of the monomer band. Thus, two chromophores in this arrangement show their new absorption band only on the blue flank of their monomer band. This type of assembly is referred to as the H-aggregate (Cf. Sect. 3.2.4.1).

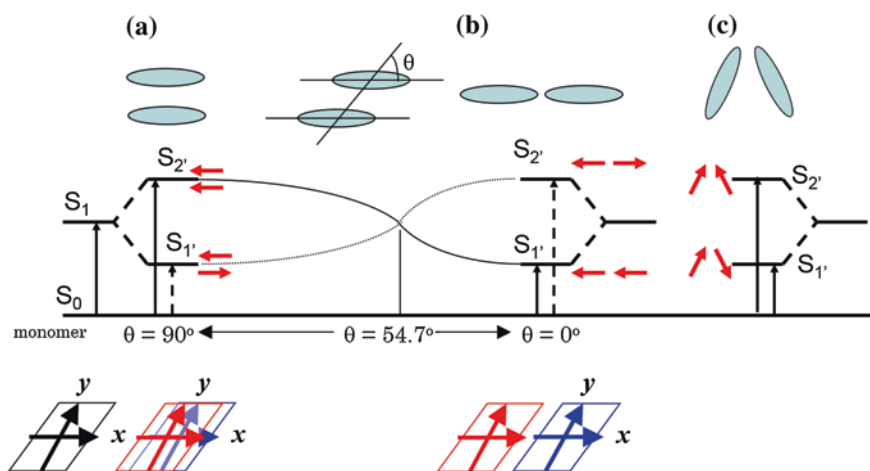


Fig. 3.19 Schematic diagram of exciton coupling between two chromophores stacked in various manners. *Source* NIMS eSciDoc—IMEJI. © Hiroaki Isago with CC-BY-NC 3.0 license

When two dye molecules are aligned in a head-to-tail manner (Fig. 3.19b), parallel and antiparallel configurations likewise generate dipole-allowed and dipole-forbidden excited states, respectively. However, in this case, the parallel and antiparallel configurations give rise to stabilization ($S_{1'}$, due to their attractive interaction) and destabilization ($S_{2'}$, due to repulsion) of the excited states, respectively, relative to that of the monomer. Consequently, only the $S_{1'}$ state is allowed; hence, the absorption band of the aggregated species appears at the red flank of the monomer band. This type of assembly is referred to as the J-aggregate.

Coplanar inclined transition dipoles lead to the exciton energy diagram shown between Fig. 3.19a, b, which continuously covers the variation of angle θ between the polarization axis and the line passing through the molecule centers from $\theta = 0^\circ$ (corresponding to Fig. 3.19b) to $\theta = 90^\circ$ (corresponding to Fig. 3.19a). The exciton band splitting ΔE in this case is given by the formula

$$\Delta E = \frac{2M^2(1 - 3\cos^2\theta)}{r^3} \quad (3.1)$$

M and r denote the magnitude of the transition moment for the singlet-singlet transition in the monomer (i.e., S_0 – S_1) and the center-to-center distance between the molecules, respectively. ΔE becomes zero for $\theta = 54.7^\circ$, where $\cos^2\theta = 0$, i.e., the dipole-dipole interaction is zero for this orientation of transition moments in the aggregate, regardless of the intermolecular distance. That is, the two molecules behave as an H-aggregate above 54.7° and as a J-aggregate below this angle.

Oblique transition dipoles in a dimer lead to the energy diagram shown in Fig. 3.19c. In this case, the antiparallel (along the vertical direction) arrangement of transition dipoles for the monomer is attractive and leads to the stabilization of the excited state ($S_{1'}$) relative to that of the monomer, and the parallel arrangement is repulsive and causes the destabilization of the excited state ($S_{2'}$). The transition moments from the ground state to the excited states of the dimer are both non-vanishing: their moments are nonzero along the vertical direction in the $S_{2'}$ state and along the horizontal direction in the $S_{1'}$ state.

As the description of exciton coupling theory in this monograph is superficial, readers who are interested in this theory should refer to Kasha's original paper [135].

3.2.4.3 Cofacial Dimers of Phthalocyanine and Degeneracy of Their Transitions

In the previous subsection, the interaction between nondegenerate electronic transitions was described. However, the transitions of interest in phthalocyanines or porphyrins (Q and Soret bands) are doubly degenerate. Therefore, we need to consider two orthogonal dipole moments instead of a single dipole moment. Here again, we take the C_4 axis as the z-axis and hence the molecular plane as the xy plane. With this convention, the optical absorption around the Q-band (as well as the Soret band) leads to x- and y-polarized dipoles in the S_1 state (Fig. 3.15a) in the monomer.

When two macrocycles aggregate in a face-to-face manner (i.e., H-aggregation), both the x- and y-polarized dipoles are aligned in a parallel arrangement (Fig. 3.15b). Consequently, both the allowed excited states are destabilized; hence, the Q-band of the dimer is blue-shifted, in common with the case for the nondegenerate transition. Although many phthalocyanines are known to form H-aggregates, probably because of their planar structure [40, 117, 131–133, 136], only a limited number of examples of phthalocyanine H-aggregates, in which the relative conformation is known, have been reported. Kobayashi and Lever have revealed that the species exhibiting the blue-shifted Q-band are composed of two macrocycles stacked in a cofacial manner through elegant experiments using phthalocyanines bearing crown ethers as peripheral substituents (Fig. 3.20a) [136]. Figure 3.20b shows the optical absorption spectra of the Co^{II} complex of the crown-ether-substituted phthalocyanine in the presence of various concentrations of CH_3COOK . In the absence of the K^+ ion, the spectrum is characteristic of the monomer, but the Q-band apparent intensity decreased with increasing $[\text{K}^+]$ until two equivalents of K^+ (i.e., four K^+ ions for two macrocycles) were added and a new band appeared at the blue flank of the Q-band. This clearly indicates that the two macrocycles cofacially stacked via the four K^+ ions in the cavity of the crown-ether substituents. This has further been evidenced by ESR works on the Cu^{II} analogue [136].

As discussed in Sect. 2.2.9, the Q-band transition for metal complexes of the normal phthalocyanine monomer is doubly degenerate. When two molecules form a cofacial dimer, both the x- and y-polarized dipoles are parallel (or antiparallel) as mentioned above (Fig. 3.15b); hence, the excited state of the dimer is also doubly degenerate. This has been exemplified by Gasyna et al. [137] on the basis of the

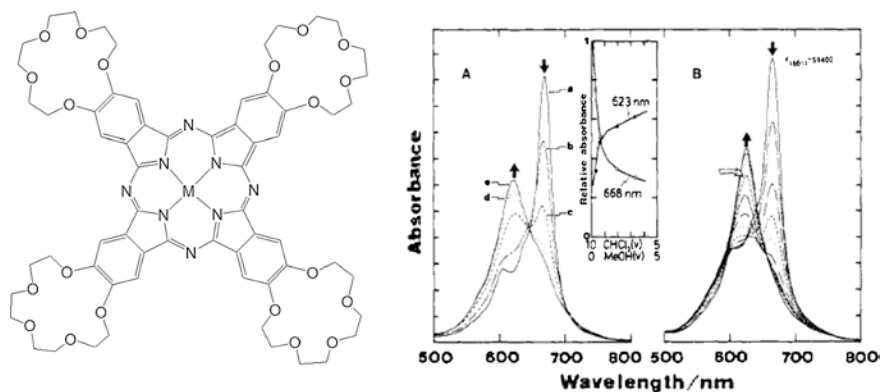
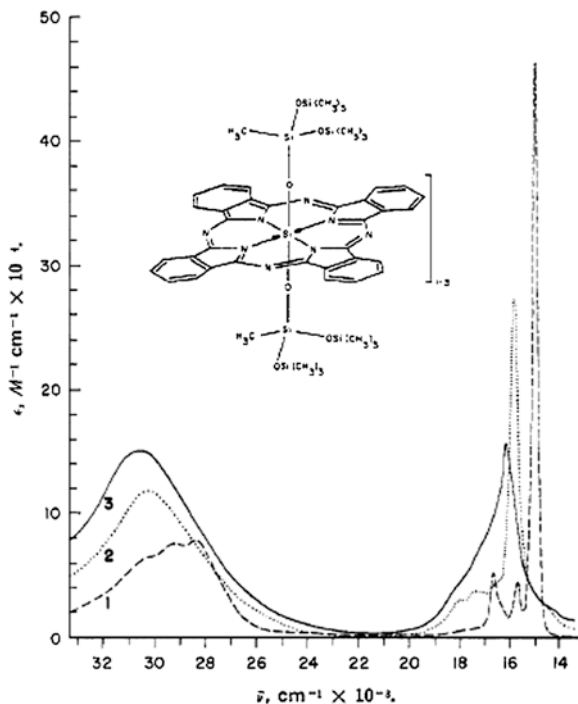


Fig. 3.20 Crown-ether-substituted phthalocyanines (*left*) and optical absorption spectra of Co^{II} complex ($\text{M} = \text{Co}^{\text{II}}$) in chloroform/methanol mixed solvent systems at various mixing ratios (A) and in chloroform solutions containing various concentrations of CH_3COOK dissolved in chloroform/methanol (95:5 v/v). Reprinted from Ref. [136], Copyright 1987, with permission from the American Chemical Society

Fig. 3.21 Optical absorption spectra of monomeric Si^{IV} phthalocyanine and μ -oxo oligomers (1 one macrocyclic ring, 2 two rings, and 3 three rings in cyclohexane. Reprinted from Ref. [34], Copyright 1970, with permission from the American Chemical Society



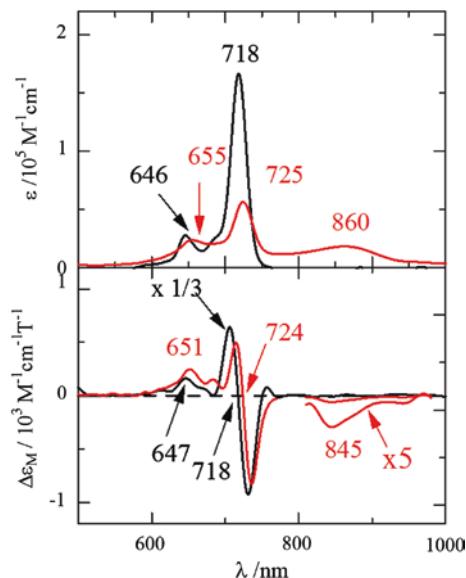
appearance of the Faraday A-term in the MCD spectra associated with the blue-shifted Q-band of the aforementioned crown-ether-substituted phthalocyanines.

The optical absorption spectra of μ -oxo dimers of the Si^{IV} complex of phthalocyanine derivatives in cyclohexane (Fig. 3.21) also show that both the Q- and Soret bands blue-shift with an increase in the number of stacked macrocycles [34, 138]. A similar blue shift of the Q-band has also been reported for Al^{III} [47, 139], Ge^{IV} [34], Fe^{III} [140], Mn^{III} [49], and Cr^{III} [141] derivatives. The degeneracy of the Q-transition has been evidenced by MCD spectroscopy for the μ -oxo dimer of the Si^{IV} complex of the phthalocyanine derivative [142]. A similar blue shift of the Q-band and the appearance of the Faraday A-term in the spectral range have been reported for a μ -oxo Si^{IV} complex heterodimer composed of phthalocyanine and naphthalocyanine [143].

3.2.4.4 J-Aggregation of Phthalocyanines and Degeneracy of Their Transitions

J-aggregates of phthalocyanines are much less common. Many of them have been reported for water-soluble derivatives [134, 143, 144], such as cationic porphyrin derivatives that are relatively well known [145]. In the last decade, J-aggregation in nonaqueous media has been reported [6, 146]. This type of aggregate has a

Fig. 3.22 Optical absorption (top) and MCD (bottom) spectra of [Sb(tbpc)(SO₄H)₂]⁺ (the compound shown in Fig. 3.16) in ethanol (black solid lines) and water containing surfactant (2 % w/v Triton X-100) (red solid lines). Reprinted from Ref. [134], Copyright 2013, with permission from Elsevier



slipped cofacial conformation between macrocycles, as shown in Fig. 3.15c, d. In the former case, one macrocycle has slipped relative to another one along only the *x*-axis. Hence, with respect to dipole-allowed excited states, *y*-polarized dipoles are parallel to each other, while *x*-polarized dipoles are aligned in a head-to-tail manner. Therefore, the *x*-polarized excited state is stabilized relative to that of the monomer (redshifted) whereas the *y*-polarized excited state is destabilized (blue-shifted). Consequently, two bands are observed (e.g., Fig. 3.16). In another case, one macrocycle has slipped along both axes. Hence, both the *x*- and *y*-polarized dipoles are aligned in a head-to-tail manner. Therefore, as both the *x*- and *y*-polarized excited states are stabilized, only the redshift of the Q-band is observed (Fig. 3.17) [6]. Unlike cofacial dimers, the new chromophore loses the C₄ symmetry upon J-aggregation that the monomers used to have. As the excited states are no longer degenerate, the observed MCD spectra are dominated by Faraday B-terms (Figs. 3.17 and 3.22).

3.2.4.5 Oblique Dimer of Phthalocyanines

Split Q-bands have been observed in the optical absorption spectra (Fig. 3.23a) of clamshell-type phthalocyanine dimers that are bridged via a peripheral substituent (Fig. 3.23b) [131, 147–149]. Some absorption bands are concentration-dependent owing to intermolecular aggregation, whereas others are unchanged regardless of concentration and hence are attributed to intramolecular exciton coupling [147–149]. As the split Q-bands are observed even in sufficiently dilute solutions, the

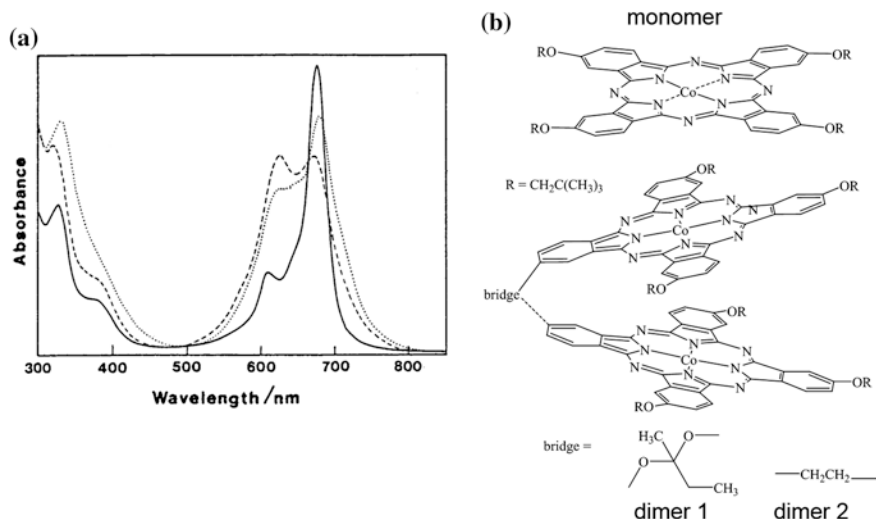


Fig. 3.23 Optical absorption spectra of Co^{II} complex of monomer (*solid line*) and bridged-dimer phthalocyanines 1 (*dashed line*) and 2 (*dotted line*) in 1,2-dichlorobenzene. Reprinted from Ref. [147], Copyright 1987, with permission from the American Chemical Society

splitting has been attributed to exciton coupling between macrocycles aligned in an oblique arrangement, as shown in Fig. 3.19c [149]. Similar splitting of Q-bands has also been reported for phthalocyanine dimers bridged via a more rigid aromatic ring such as 1,8-naphthyl groups as a spacer [150].

3.2.4.6 π – π Interaction Between Macrocycles

When two macrocycles in a cofacial dimer are much closer (<3.4 Å), their π -clouds can overlap with each other; hence, the ground-state electronic structure of individual macrocycles can no longer be considered independently. The molecular structure of the Sn^{IV} complex of the double-decker phthalocyanine in a cofacial manner, [Sn(pc)₂], has been crystallographically determined (Fig. 3.24a), and the distance between the two macrocyclic ligands²¹ (2.61 Å) has been found to be shorter than the sum of the van der Waals distances (3.4 Å) [151]. Therefore, the π – π interaction between the two macrocycles needs to be taken into consideration [152]. Its optical absorption spectrum in solution shows split Q-bands and a single Soret band (Fig. 3.24b) [153]. The appearance of Faraday A-terms in the MCD spectra for both the split Q-bands indicates that both transitions are degenerate. Similar split Q-bands have been reported for derivatives of lanthanoids (III/IV)

²¹Actually, this is the distance between the planes composed of the four pyrrole nitrogen atoms in each macrocyclic ligand.

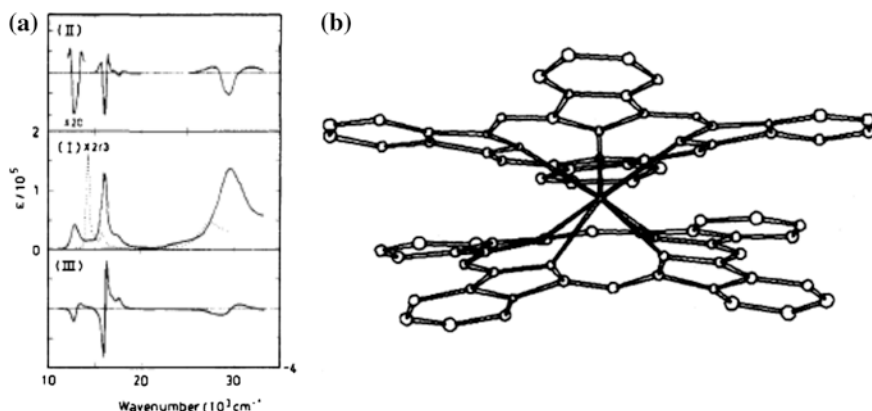


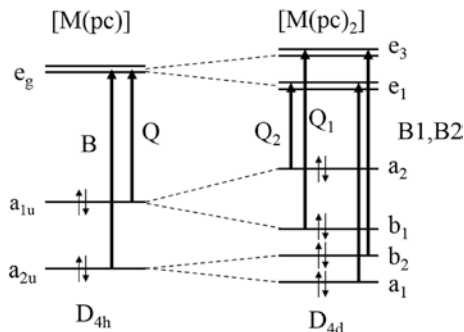
Fig. 3.24 **a** Optical absorption (*middle*), second-derivative absorption (*top*), and MCD (*bottom*) spectra of double-decker Sn^{IV} -diphthalocyanine $[\text{Sn}(\text{pc})_2]$ in toluene (Reprinted from Ref. [152], Copyright 1989, with permission from the American Chemical Society) and **b** crystal structure of $[\text{Sn}(\text{pc})_2]$ (Reprinted from Ref. [151], Copyright 1973, with permission from the American Chemical Society)

[154–156], actinoids (III/IV) [157–160], Zr^{IV} and Hf^{IV} [161–164], In^{III} [165], Bi^{III} [166], and Sb^{III} [167]. In particular, in the series of double-decker rare-earth (III) derivatives, $[\text{M}(\text{pc})_2]^-$ (where $\text{M} = \text{Sc}^{\text{III}}$, Y^{III} , and lanthanoid (III)), the magnitude of the splitting significantly increases with decreasing ionic radius of the central metal ion [154], indicating that the π – π interaction between the macrocycles becomes stronger with decreasing interplanar distance. Similar split Q-bands have been reported for triple-decker $[\text{M}_2(\text{pc})_3]$ (where $\text{M} = \text{lanthanoid (III)}$) [168] and quadruple-decker derivatives (two double deckers bridged via a Hg^{II} ion) [169].

To explain the splitting of the Q-band and the strong effect of the ionic radius of the central elements on the magnitude of the splitting,²² the overlapping of π -conjugation systems between the two macrocycles has been proposed [170]. As shown in Fig. 3.24a, the two macrocycles in double-decker phthalocyanine dimers are cofacial but staggered by ca. 45° . Konami et al. have reported that the overlapping of the following four frontier orbitals (LUMO (doubly degenerate), HOMO, and next-HOMO) between the two macrocycles is important for understanding the properties of double-decker phthalocyanine dimers and, in particular, that the overlap integral between HOMOs ($\pi(a_{1u})$ in monomer) is much larger than those between next-HOMO ($\pi(a_{2u})$) and LUMO ($\pi(e_g)$) [170]. Therefore, their MOs should be considered not in D_{4h} symmetry for two independent monomers, but in D_{4d} for one conjugation system composed of two macrocycles (Fig. 3.25).

²²The splitting of the Q-band can be explained by exciton coupling (one is assigned as an allowed transition and the other weaker one is due to the forbidden transition that borrowed intensity from vibronic transition). However, the increase in the magnitude of the splitting with decreasing ionic radius is much steeper than expected from the change in the interplanar distance (Eq. 3.1).

Fig. 3.25 Schematic diagrams of frontier orbitals in single-decker (left) and double-decker phthalocyanines (right). The large and small arrows denote dipole-allowed electronic transitions and electrons, respectively



Because of the overlap of π -clouds, each of the MOs in a single-decker macrocycle will be split in the new conjugation system owing to bonding and antibonding interactions. The magnitude of the splitting becomes larger with a decrease in distance between the two macrocycles because the magnitude of the overlap integral of their π -clouds decreases with increasing distance [170]. The $\pi(a_{1u})$ HOMO in a single-decker phthalocyanine will be split into antibonding $\pi(a_2)$ and bonding $\pi(b_1)$ orbitals in the new MOs [153]. Likewise, the $\pi(a_{2u})$ and $\pi(e_g)$ in a monomer will be reorganized to a set of bonding $\pi(a_1)$ and antibonding $\pi(b_2)$ orbitals and a set of bonding $\pi(e_1)$ and antibonding $\pi(e_3)$ orbitals, respectively [153], although the magnitude of splitting between these MOs is much smaller than that between the MOs derived from the monomer HOMOs. Therefore, it is easily understood that the Q-band for the monomer will be split into two bands, which are both degenerate, in the double-decker dimer: That is, of the four possible transitions derived from a_{1u} -to- e_g (Q-band) transitions, $a_2 \rightarrow e_1$ and $b_1 \rightarrow e_3$ transitions are dipole-allowed. Furthermore, as the π - π interaction becomes stronger with decreasing interplanar distance, the energy gap between the b_1 and a_2 MOs increases; hence, the magnitude of the Q-band splitting becomes larger. In contrast, as the overlapping between $\pi(a_{2u})$ MOs and that between $\pi(e_g)$ MOs are small, the Soret band is observed as a single band. Thus, this MO model successfully explains the optical absorption spectra of double-decker phthalocyanines and the effects of ionic radius of the central metal on the splitting of the Q-band.²³

Optical absorption spectra of metal complex dimers linked by a direct M-M bond, i.e., $(pc)M-M(pc)$, ($d(M-M \text{ distance}) = 2.89 \text{ \AA}$ for $M = Ir$ [171], $d = 2.827 \text{ \AA}$ for $M = Rh$ [172], and $d = 3.14 \text{ \AA}$ for $M = Re$ [173]) also show split Q-bands²⁴ of essentially the same intensity. Interestingly, those of Si^{IV} -

²³This model also successfully explains the spectral properties of a series of lanthanoid(III) derivatives of neutral double-decker phthalocyanines $[M(pc^{2-})(pc^-)]$ and $[M(pc^-)]_2^+$ as well as their redox potentials.

²⁴In these works, the authors have tried to explain the splitting on the basis of the exciton coupling alone.

phthalocyanine cofacial dimers linked by a direct Si–Si bond show a single Q-band despite the much shorter Si–Si distance (2.576 Å)²⁵ [138].

Readers who are interested in syntheses, structures, and other properties as well as spectral properties of phthalocyanine dimers should refer to Kobayashi's excellent review paper [154].

3.2.5 Effects of Acid-Base Equilibria Involving Phthalocyanine Macrocycle

As one phthalocyanine molecule has a nitrogen atom in each of the four pyrrole units and four aza nitrogen atoms bridging the units, each of them can be involved in an acid-base reaction (as a base). In addition, metal-free phthalocyanines, such as H₂pc, can dissociate one or two of the pyrrole N–H protons under appropriate conditions. Therefore, they can act as acids. Since these nitrogen atoms are members of the innermost 16-membered ring that dictates the spectral properties of the macrocycle (Sect. 2.2.6), any small changes may give rise to a significant spectral change.

3.2.5.1 Metal-Free Phthalocyanines as Acids

Figure 3.26a shows the optical absorption spectra of a water-soluble metal-free phthalocyanine in ethanolic solutions at various NaOH concentrations [174]. In ethanol alone, its spectrum shows twin Q-bands, which are characteristic of metal-free phthalocyanines (Sect. 2.1.1), but they coalesce with increasing [NaOH] and only one peak appears in the final solution. Quantitative analyses of the Q-band intensity as a function of [NaOH] have revealed that the spectral changes involve two Na⁺ ions per chromophore [174]; hence, the final product is the doubly deprotonated species Pc^{2−}. The final spectrum is very close to those of metal complexes of phthalocyanine, which is understandable because their spectra have been successfully interpreted by employing the dianion of phthalocyanine as a model (Chap. 2). Similar spectral changes have been observed in aqueous solutions containing the same compound (Fig. 3.26b) and surfactant to prevent molecular aggregation. However, the dissociation of only one of the two protons (pK_a = 12.5) has been found to be involved in this spectral change on the basis of quantitative analyses of the Q-band intensity as a function of pH [174]. It is noteworthy that a tetraazaporphyrin that has eight *N*-methyl-pyridinium groups, which are strongly electron-withdrawing, on its periphery releases its imino protons more easily in water (pK_{a1} = 6.3 and pK_{a2} = 8.8) and shows a single Q-band [175]. These findings clearly indicate that the spectra of Pc^{2−} and HPc[−] are close to each other.

²⁵The authors reported that the absorption spectra of the Si–Si dimers are very similar to those of tetrabenzotriazacorroles (Sect. 3.3.3).