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Electronic Spectra of the Aluminum(III) Complexes of 5,10,15,20-Tetraphenylporphin and 2,3,7,8,12,13,17,18-Octaethylporphin

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Absorption, magnetic circular dichroism (MCD) and emission spectra as well as preparations of the aluminum(III) complexes of 5,10,15,20-tetraphenylporphin (TPP) and 2,3,7,8,12,13,17,18-octaethylporphin (OEP) are presented. On the basis of the spectral observations, the molecular parameters to describe the lowest (π,π^*) excited states of a typical metal porphyrin with only minor perturbation by the incorporated tervalent metal ion were determined. The orbital angular momenta in the excited states were evaluated from the MCD spectra as follows: TPPAlCl, $\Lambda_z=\pm3.0\hbar$ in Q_{00} band, $\Lambda_z=\pm0.61\hbar$ in B band and OEPAlCl, $\Lambda_z=\pm3.4\hbar$ in Q_{00} band, $\Lambda_z=\pm0.55\hbar$ in B band. A Davydov splitting of the Soret band observed for the μ-oxo dimer was interpreted in terms of the exciton coupling between two parallel porphyrin chromophores.

Aluminum(III) porphyrin is a typical porphyrin incorporated with a tervalent metal ion; characteristic Q and B bands in the visible and near-ultraviolet region, respectively, arise from the (π,π^*) excitations in the porphyrin ring with only minor perturbation from the outer-shell electrons of the central metal ion. On the other hand, the iron(III) porphyrins found in the heme proteins exhibit rather complicated spectral profiles attributable to the configuration-interaction admixtures of the porphyrin (π,π^*) excited states and the "porphyrin-to-iron" charge-transfer excited states.[1–4] Preparations of some aluminum(III) porphyrins have been reported,[5,6] however, the spectra of aluminum(III) porphyrins have received little attention until very recently.[7] A recent notable finding is that aluminum(III) porphyrin alkoxide behaves as the propagating end of the living polymerization of epoxide.[8]

In this paper, absorption and emission spectra as well as preparations of the aluminum(III) complexes of 5,10,15,20-tetraphenylporphin(TPP) and 2,3,7,8,12,13,17,18-octaethylporphin(OEP) are presented, since the spectra measured on the well-characterized samples of this particular reference porphyrin have never been reported. The spectra of the μ-oxo dimer, $(TPPAl)_2O$, which was prepared first in the present work, are also reported. The spectral character of the dimer is interpreted in terms of the exciton coupling model.

Experimental

Synthesis of Chloro(tetraphenylporphinato)aluminum(III) (TPPAlCl). The metal-free base ($TPPH_2$) was prepared from pyrrole and benzaldehyde by the method of Adler, *et al.*[9] A contamination of tetraphenylchlorin was oxidized by use of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.[10] $TPPH_2$(0.5 g) was vigorously refluxed for 1—2 h with anhydrous aluminum chloride(0.5 g) in dry benzonitrile (80 ml). The reflux was continued until no further change of the absorption spectrum was detected. If the metal insertion was incomplete, the mixture was refluxed again after addition of some anhydrous aluminum chloride. After cooled, the mixture was filtered and then excess hexane was added to the filtrate for completion of precipitation. (A trace of methanol facilitated precipitation of TPPAlCl from oily solutions which often appeared upon addition of hexane). The precipitates were collected by filtration, washed with hexane, and then dissolved in methanol (30—40 ml). After filtration of the methanol solution, 3 M HCl (1 M=1 mol dm^{-3}) was added for precipitation of the complex. The precipitates were collected on a filter, washed with 3 M HCl, dissolved in a smallest amount of acetone, and then recrystallized from the solution by addition of hexane. Reddish purple crystals thus obtained were $TPPAlCl\cdot4H_2O$. More reddish crystals of $TPPAlCl\cdot H_2O$ were obtained by drying $TPPAlCl\cdot4H_2O$ at 110—120 °C for 2 h.

Found: C, 76.12; H, 4.28; N, 7.98; Cl, 5.03%. Calcd for $C_{44}H_{30}N_4OAlCl(TPPAlCl\cdot H_2O)$: C, 76.24; H, 4.36; N, 8.08; Cl, 5.12%.

An effective metal insertion could not be achieved in pyridine, although the metal insertion in refluxing pyridine was reported in the case of meso- and etioporphin.[11]

Synthesis of Chloro(octaethylporphinato)aluminum(III) (OEPAlCl). The metal-free base ($OEPH_2$) was prepared by the method of Paine, *et al.*[12] from 3,4-diethyl-2-ethoxycarbonyl-5-methyl-pyrrole.[13]

Found: C, 80.87; H, 8.55; N, 10.38%. Calcd for $C_{36}H_{46}N_4$: C, 80.85; H, 8.67; N, 10.48%.

OEPAlCl was prepared in the similar way as described for preparation of TPPAlCl.

Found: C, 72.14; H, 7.52; N, 9.28; Cl, 5.42%. Calcd for $C_{36}H_{44}N_4AlCl(OEPAlCl)$: C, 72.65; H, 7.45; N, 9.41; Cl, 5.96%.

The reaction of $OEPH_2$ and tris(acetylacetonato)aluminum(III) in phenol was reported.[5,6] However, $OEPH_2$ as well as $TPPH_2$ showed no significant reaction with tris(acetylacetonato)aluminum(III) in boiling benzonitrile.

Synthesis of Hydroxo(tetraphenylporphinato)aluminum(III) (TPPAlOH). By shaking of porphinatoaluminum(III)-chloride dissolved in a mixture of chloroform and methanol with an aqueous solution of $AgNO_3$, porphinatoaluminum(III) hydroxide was obtained in the chloroform layer. The reaction of conc H_2SO_4, which had been applied to the preparation of phthalocyaninatoaluminum(III)hydroxide,[14,15] resulted in elimination of the central metal ion.

TPPAlCl·H_2O (300 mg) was dissolved in a mixture of chloroform (300 ml) and methanol (30 ml). The solution was shaken with 100 ml of 0.1% aqueous solution of $AgNO_3$ and the chloroform layer was separated. To the chloroform layer, 20 ml methanol and 30 ml chloroform were added. The mixture was again shaken with 100 ml of 0.1% aqueous solution of $AgNO_3$. This procedure was repeated until no AgCl precipitated. The chloroform layer was thoroughly washed with water, being added an amount of chloroform and methanol to keep solubility of the complex. The chloroform solution thus obtained was concentrated up to a volume of 150 ml, and then 300 ml hexane was added for precipitation of the complex. The precipitate was dissolved in a smallest amount of methanol, concentrated by distillation of methanol and recrystallized by adding water. The crystals were thoroughly washed with 0.5 M aqueous ammonia and then water and recrystallized from a mixture of methanol and water. Purple crystals thus obtained were dried at 110—120 °C for 3 h.

Found: C, 78.29; H, 4.44; N, 8.37; Cl, 0.00%. Calcd for $C_{44}H_{31}N_4O_2Al$(TPPAlOH·H_2O): C, 78.33; H, 4.63; N, 8.30; Cl, 0.00%.

Synthesis of Hydroxo(octaethylporphinato)aluminum(III) (OEPAlOH). OEPAlOH was prepared by reaction of aqueous $AgNO_3$ with OEPAlCl in a similar way as described for preparation of TPPAlOH.

Found: C, 72.05; H, 7.83; N, 9.45%. Calcd for $C_{36}H_{47}N_4O_2Al$(OEPAlOH·H_2O): C, 72.70; H, 7.97; N, 9.42%.

Synthesis of μ-Oxo-bis[(tetraphenylporphinato)aluminum(III)]. $(TPPAl)_2O$ was obtained by heating TPPAlOH·H_2O at 300—340 °C for 10 h under reduced pressure (10^{-2}—10^{-3} mmHg).

Found: C, 81.65; H, 4.29; N, 7.98%. Calcd for $C_{88}H_{58}N_8OAl_2$ ($(TPPAl)_2O$): C, 81.59; H, 4.36; N, 8.65%.

A trace of TPPAlOH contamination in $(TPPAl)_2O$ could not be eliminated by further purification because $(TPPAl)_2O$ was not so stable in solution and not sublimable. The μ-oxo dimer exhibits a characteristic IR band of Al-O-Al at 1050 cm^{-1} (Fig. 1), which conforms to the band found in the μ-oxo dimer of aluminum phthalocyanine.[15]

The corresponding band of $(OEPAl)_2O$, however, could not be detected after heating OEPAlOH for several hours under reduced pressure in a variety of temperatures around the melting point of OEPAlOH. Preparation of $(OEPAl)_2O$ by heating under reduced pressure has been reported, however, the reported IR spectrum lacks the characteristic Al-O-Al band.[16]

All other reagents and solvents used for preparations and measurements were commercially available. Benzonitrile was distilled under reduced pressure after dried over anhydrous sodium sulfate more than one night. Dichloromethane(CH_2Cl_2), chloroform($CHCl_3$) and carbon tetrachloride(CCl_4) were shaken with conc H_2SO_4 and then aqueous sodium hydrogencarbonate, washed with water, dried over anhydrous calcium chloride more than one night and then distilled. For further dehydration, CCl_4 was refluxed over phosphorus pentaoxide, distilled and then kept over sodium hydroxide. Methanol was purified by distillation after dried over $CaSO_4$.

Measurements. Electronic absorption spectra were taken on a Hitachi 220 A spectrophotometer. Since $(TPPAl)_2O$ was stable only in concentrated solution, the intense absorption band was measured using a cell of 0.3 mm path length. On the other hand, the routine spectral measurements were carried out with solutions in quartz cuvetts of 1 cm path length. Emission and excitation spectra were recorded on a Hitachi MPF-2A fluorescence spectrophotometer equipped with a Hamamatsu Photonics photomultiplier R-928. Fluorescence intensity was corrected by the method of Lippert, *et al.*[17] Phosphorescence was detected on the fluorescence spectrophotometer attached with its phosphorescence device.

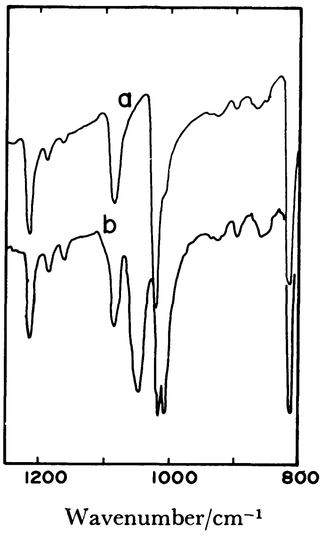

Fig. 1. IR spectra of TPPAlCl and $(TPPAl)_2O$ in KBr disks.
a: TPPAlCl, b: $(TPPAl)_2O$.

Magnetic circular dichroism was measured on a JASCO J-500C spectropolarimeter with an electromagnet. The magnetic field was set at 1T.

Infrared spectra of TPPAlCl and $(TPPAl)_2O$ in KBr disks were taken on a Hitachi 260-10 infrared spectrophotometer.

Results and Discussion

Absorption and fluorescence spectra of TPPAlCl and OEPAlCl in CCl_4 containing 2.5% methanol are shown in Fig. 2. The spectra of TPPAlOH and OEPAlOH were actually coincident with the spectra of the corresponding chloro complexes. In polar solvents such as methanol, ethanol, acetone, and acetonitrile, the complexes were stable. In non-polar solvents such as benzene and toluene, however, the complexes usually displayed a spectral drift for a period of time. A small amount of methanol added to the non-polar solvents stabilized the spectra and an increase in the concentration of methanol gives rise to a slight blue shift of each band. TPPAlOH and OEPAlOH in CH_2Cl_2 were rather stable and exhibited the spectral profiles given in Fig. 3. Absorption and fluorescence spectra of $(TPPAl)_2O$ in CCl_4 are illustrated in Fig. 4. The spectra were rather stable only when the dimer was dissolved in CCl_4 which was treated with NaOH just before use.

The fluorescence spectra given in Figs. 2, 3, and 4 are

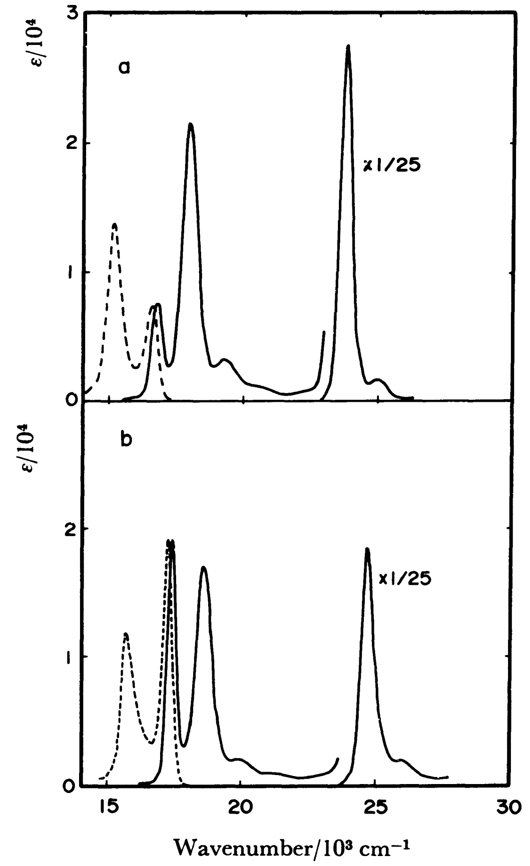

Fig. 2. Absorption and fluorescence spectra of TPPAlCl (a) and OEPAlCl (b) in methanol/CCl_4. (methanol: CCl_4=2.5: 97.5).
——: absorption, ----: emission.

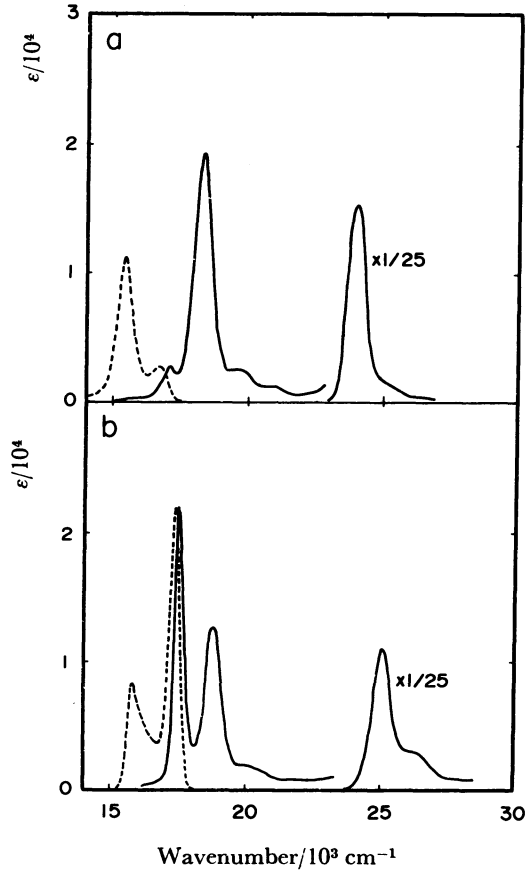

Fig. 3. Absorption and fluorescence spectra of TPPAlOH (a) and OEPAlOH (b) in CH_2Cl_2.
——: absorption, ----: emission.

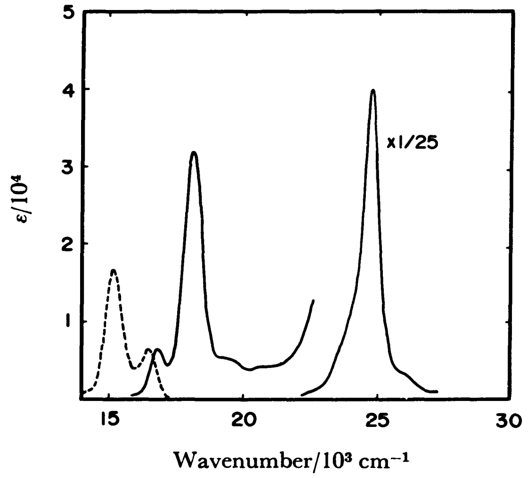

Fig. 4. Absorption and fluorescence spectra of $(TPPAl)_2O$ in CCl_4.

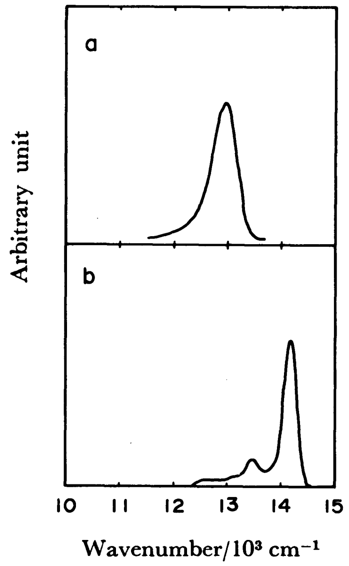

Fig. 5. Phosphorescence spectra of TPPAlCl (a) and OEPAlCl (b) in methanol glass at 77 K (uncorrected).

in a mirror image of the corresponding absorption spectra. The excitation spectra of fluorescence as well as phosphorescence were in good agreement with the absorption spectra. Figure 5 shows the phosphorescence spectra of the chloro complexes in ethanol at 77 K. Figure 6 shows the MCD spectra of TPPAlCl and OEPAlCl in methanol. The MCD spectra display a positive A term dispersion in each band. The ob-

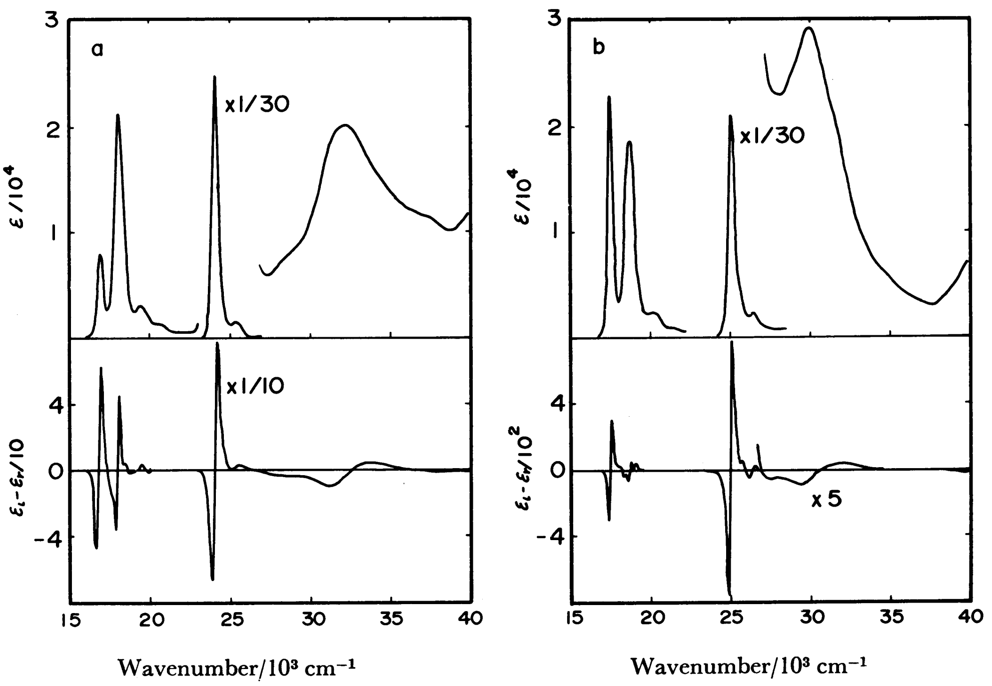

Fig. 6. MCD spectra of TPPAlCl (a) and OEPAlCl (b) in methanol.

served spectral characters are very similar to those of the typical (π,π^*) transition observed for the D_{4h} metalloporphins incorporated with a divalent metal ion such as Mg^{2+} and Zn^{2+}.

The lowest (π,π^*) excited states of metalloporphins are well described as a 50–50 admixture of the lowest excited configurations $(a_2)^2a_1e$ and $(a_1)^2a_2e$, where a_2 and a_1 are the highest filled orbital pair and e are the lowest vacant degenerate orbitals. Since the top filled orbitals are accidentally degenerate, their 50–50 admixtures $(a_2 \pm ia_1)/\sqrt{2}$ are taken instead of individual a_2 and a_1 orbitals. The highest occupied orbital pair correspond to the degenerate orbital pair of the circular box model

$$|\pm 4) = f(\mathbf{r})\exp[\pm 4i\theta], \tag{1}$$

where ±4 denote the z components of orbital angular momentum $\lambda = 4\hbar$, while the lowest vacant degenerate e orbitals are denoted as

$$|\pm 5) = f(\mathbf{r})\exp[\pm 5i\theta]. \tag{2}$$

The one-electron excitations $|\pm 4) \rightarrow |\pm 5)$ and $|\mp 4) \rightarrow |\pm 5)$ give rise to two degenerate excited states with different total angular momenta $\Lambda_z = \pm 1\hbar$ and $\Lambda_z = \pm 9\hbar$, respectively. The ground state has zero angular momentum $\Lambda_z = 0\hbar$. Thus the selection rule allows a pair of transitions of $\Delta\Lambda_z = \pm 1\hbar$, in which the angular momentum of the photons is conserved. The intense near-ultraviolet B(Soret) band is identified with the allowed transition pair $\Delta\Lambda_z = \pm 1\hbar$, whereas the weak Q band is characterized with the forbidden but vibronically allowed transition pair $\Delta\Lambda_z = \pm 9\hbar$. Table 1 shows the diagonal energies of the lowest excited states in terms of the exchange integrals

$$K_1 \equiv (4^*5|5^*4) = e^2\iint \frac{f^2(\mathbf{r}_1)f^2(\mathbf{r}_2)}{\mathbf{r}_{12}}\exp[i(\theta_1-\theta_2)]d\tau_1 d\tau_2, \tag{3}$$

$$K_9 \equiv (-4^*5|5^*-4) = e^2\iint \frac{f^2(\mathbf{r}_1)f^2(\mathbf{r}_2)}{\mathbf{r}_{12}}\exp[9i(\theta_1-\theta_2)]d\tau_1 d\tau_2, \tag{4}$$

and the off-diagonal one-electron term

$$\varepsilon \equiv -(4^*|\hat{\mathbf{h}}|-4) = \frac{1}{2}\{(a_1|\hat{\mathbf{h}}|a_1)-(a_2|\hat{\mathbf{h}}|a_2)\} \tag{5}$$

which arises from the fact that the a_2 and a_1 orbitals are not exactly degenerate in metalloporphins.

In the case of TPPAlCl in methanol, the Q band is observed at 16900 cm^{-1}($\varepsilon_{Q_{0,0}}$(max)=0.765×10^4 M^{-1} cm^{-1}), and the B band at 24100 cm^{-1}(ε_B(max)=73.3 ×10^4 M^{-1} cm^{-1}); the phosphorescence appears at 12900 cm^{-1}. The transitions to $^1(\pm 4 \rightarrow \pm 5)$ are exclusively allowed. However, the off-diagonal element ε carries the spectral intensity from the allowed B transition to the forbidden Q counterpart. Assuming a Gaussian shape function with half-width $\tilde{\Gamma}$, the transition moment is evaluated from the observed absorption intensity,

$$|\mathbf{m}|^2 = 1.514\times 10^{-3}\{(\tilde{\Gamma}/\tilde{\nu})\varepsilon(\max)/g\}\ (\text{a.u.}^2), \tag{6}$$

TABLE 1. THE LOWEST (π,π^*) EXCITED SINGLET AND TRIPLET STATES OF THE METALLOPORPHIN

$\lvert{}^{1,3}(-4\rightarrow+5)\rangle$	$\lvert{}^{1,3}(+4\rightarrow-5)\rangle$	$\lvert{}^{1,3}(+4\rightarrow+5)\rangle$	$\lvert{}^{1,3}(-4\rightarrow-5)\rangle$
$\Delta(4,5)+\binom{2}{0}K_9$	0	ε	0
	$\Delta(4,5)+\binom{2}{0}K_9$	0	ε
		$\Delta(4,5)+\binom{2}{0}K_1$	0
			$\Delta(4,5)+\binom{2}{0}K_1$

The top integer in ( ) stands for the excited singlet, while the bottom, for the excited triplet.
The excited states $\lvert Q\rangle$ and $\lvert B\rangle$ are described by

$$\lvert Q\rangle=-\sin\nu\lvert{}^1(\pm4\rightarrow\pm5)\rangle+\cos\nu\lvert{}^1(\mp4\rightarrow\pm5)\rangle$$
$$\lvert B\rangle=\cos\nu\lvert{}^1(\pm4\rightarrow\pm5)\rangle+\sin\nu\lvert{}^1(\mp4\rightarrow\pm5)\rangle,$$

where $\nu=\frac{1}{2}\tan^{-1}(\varepsilon/K_1-K_9)$.

where g is the degeneracy of excited state, $g=2$ in this particular case, ε(max), and $\tilde{\nu}$ are molar absorption coefficient and wavenumber at the absorption maximum, respectively. The observed intensity ratio yields $|\mathbf{m}(Q)|^2/|\mathbf{m}(B)|^2=0.016$, where the values of $\tilde{\Gamma}(Q)$ and $\tilde{\Gamma}(B)$ are 520 cm^{-1} and 490 cm^{-1} respectively. Provided that $\Delta(4,5)=13800$ cm^{-1}, $K_1=5100$ cm^{-1}, $K_9=1600$ cm^{-1}, and $\varepsilon=-900$ cm^{-1}, not only the observed transition energies of the lowest triplet and singlet excited states but also the ratio $|\mathbf{m}(Q)|^2/|\mathbf{m}(B)|^2$ are well reproduced.

The corresponding values of OEPAlCl in methanol are as follows:

$$\Delta(4,5)=15800\ \mathrm{cm}^{-1},\ K_1=4400\ \mathrm{cm}^{-1},\ K_9=1000\ \mathrm{cm}^{-1}$$
$$\varepsilon=1600\ \mathrm{cm}^{-1}.$$

Here it is assumed that the a_1 orbital is higher than the a_2 orbital in OEPAlCl while it is reversed in TPPAlCl.[18]

The *ab initio* molecular orbital calculations even at the recent stage provide only poor predictions on the electronic excited states. However the screened potential molecular orbital approach yields a reasonable picture of the porphin excited states.[19,20] Theoretically evaluated values for metalloporphin are as follows;[20]

$$\Delta(4,5)=13400\ \mathrm{cm}^{-1},\ K_1=6600\ \mathrm{cm}^{-1},\ K_9=1600\ \mathrm{cm}^{-1}$$
$$\varepsilon=1200\ \mathrm{cm}^{-1}.$$

These results seem reasonable but still far from the observation.

The orbital angular momenta in the excited states were determined by computer simulations of the positive A term dispersions observed in the MCD spectra assuming Gaussian shape functions for the corresponding absorption bands.[21] The orbital angular momenta of TPPAlCl were obtained as $\Lambda_z=\pm3.0\hbar$ and $\Lambda_z=\pm0.61\hbar$ in the excited states of Q_{00} and B band, respectively. This implies that the angular momenta of the highest occupied and the lowest vacant orbitals are $\lambda_4=1.2\hbar$ and $\lambda_5=1.8\hbar$, respectively. The corresponding values of OEPAlCl are as follows; $\Lambda_z=\pm3.4\hbar$ in Q_{00} band, $\Lambda_z=\pm0.55\hbar$ in B band, $\lambda_4=1.6\hbar$ and $\lambda_5=2.0\hbar$.

The absorption spectrum of the μ-oxo dimer as seen in Fig. 4 exhibits a remarkable blue shift of the B band with lower wavenumber tail extending to about 22000 cm^{-1} which is attributable to an exciton coupling in the B band. The dimer Q band is also blue-shifted but to a lesser extent. A similar spectral behavior has been found with the μ-oxo dimer $(\mathrm{TPPSc})_2\mathrm{O}$, while the red shift of the dimer Q band was observed in the case of $(\mathrm{OEPSc})_2\mathrm{O}$.[22]

The geometry of the μ-oxo dimer is assumed in D_{4d} symmetry. As revealed by X-ray analysis, the interplanar distance is greater than anticipated by the intermetal distance.[23,24] An extreme short intermetal distance has been found for the linear Al–O–Al bridge between two trigonal-bipyramidal pentacoordinated aluminum atoms.[25] In the case of $(\mathrm{TPPAl})_2\mathrm{O}$, Al^{3+} ion can not displace much more than 0.5 Å out of the porphin plane, however, a doming distortion in two porphin skeletons results in an interplanar distance as high as 4.8 Å. Because of the small overlap between the π orbitals of two component porphins in such a distance, K_{AB}, an electrostatic interaction between the overlap charges $(j_A j_B)$ and $(a_A a_B)$, can be ignored. The exciton coupling arises only from the Coulomb interaction J_{AB} between two transition charges $(j_A a_A)$ and $(j_B a_B)$, which are often approximated by the interaction between two transition dipoles $\mathbf{m}_A$ and $\mathbf{m}_B$ on the counterparts A and B.

The basis sets of the exciton states are given by 50-50 admixtures of the local excited states; $\lvert Q^+\rangle=(\lvert Q_A\rangle+\lvert Q_B\rangle)/\sqrt{2}$, $\lvert Q^-\rangle=(\lvert Q_A\rangle-\lvert Q_B\rangle)/\sqrt{2}$, $\lvert B^+\rangle=(\lvert B_A\rangle+\lvert B_B\rangle)/\sqrt{2}$, $\lvert B^-\rangle=(\lvert B_A\rangle-\lvert B_B\rangle)/\sqrt{2}$. The interactions between these states are shown in Table 2, where

Table 2. The interaction between the lowest (π,π^*) excited singlets of the μ-oxo metalloporphin dimer

$\lvert Q^+>$	$\lvert Q^->$	$\lvert B^+>$	$\lvert B^->$
$E(Q)+\sin^2\nu J$	0	$-\sin\nu\cos\nu J$	
	$E(Q)-\sin^2\nu J$		$\sin\nu\cos\nu J$
		$E(B)+\cos^2\nu J$	
			$E(B)-\cos^2\nu J$

The exciton states are given by

$$|Q> = -\sin\phi|B^\pm> + \cos\phi|Q^\pm>$$

$$|B> = \cos\phi|B^\pm> + \sin\phi|Q^\pm>$$

where $\phi = \frac{1}{2}\tan^{-1}\{\mp\sin 2\nu/[E(B)-E(Q)\pm\cos 2\nu J]\}$.

$E(Q)$ and $E(B)$ are the energies of the component Q and B states in the μ-oxo dimer, which might be different from the monomer values and the interaction terms are given in units of $J=2(4_A{}^*5_A|5_B{}^*4_B)$.

Absorption spectrum of $(TPPAl)_2O$ exhibits the $Q_{0,0}$ band at 16900 cm^{-1} ($\varepsilon_{Q_{0,0}}(\max)=0.650\times10^4$ M^{-1} cm^{-1}, $\Gamma=700$ cm^{-1}) and the B band at 24800 cm^{-1} ($\varepsilon_B(\max)=100\times10^4$ M^{-1} cm^{-1}, $\Gamma=550$ cm^{-1}), respectively. Assuming the monomer values for $E(B)$ and $E(Q)$, the absorption spectrum of the μ-oxo dimer was reproduced for $J=1000$ cm^{-1}. The theory predicts that the allowed B state is in 25100 cm^{-1} and the forbidden one in 23100 cm^{-1} and thus the Davydov splitting is 2000 cm^{-1} in the B band while that of the Q band is less than 50 cm^{-1}. Conserving the monomer values only for two-electron terms K_1 and K_9, $E(Q)=16900$ cm^{-1}, $E(B)=24100$ cm^{-1} and $J=700$ cm^{-1} are evaluated from the transition energies and the intensity ratio observed for the μ-oxo dimer spectrum. On the other hand, the values, $E(Q)=16800$ cm^{-1}, $E(B)=23300$ cm^{-1} and $J=1500$ cm^{-1}, yield the forbidden and allowed B states in 21800 cm^{-1} and 24800 cm^{-1} respectively, and the corresponding Q states in 16800 cm^{-1} and 16900 cm^{-1}. The observed Davydov splitting in the B band is less than 3000 cm^{-1}.

The transition dipole $\mathbf{m}\equiv\sqrt{2}(5|\mathbf{m}|4)$ is estimated as 3.4 a.u. from the parameter values determined for TPPAlCl in methanol and thus J is evaluated as 3400 cm^{-1} for the parallel stacking by the approximation of dipole-dipole interaction $\mathbf{m}^2/r_{AB}{}^3$ in a distance $r_{AB}=4.8$ Å. The diagonalization of the interactions using the parameters for TPPAlCl predicts a rather big splitting (≈ 6800 cm^{-1}) in the B band. The value of J can be calculated by use of the wavefunctions obtained by molecular orbital calculations.[20] For $r_{AB}=4.8$ Å is obtained $J=4400$ cm^{-1}, which predicts a much greater splitting.

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