Strong Aggregation Properties of Novel Naphthalocyanines

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The aggregation properties of naphthalocyanines having different ring substituents have been studied in solution. MNc(Bu^t)$_4$ and MNc(OBu^n)$_4$ showed moderate tendencies for aggregation (M = Cu^{II}, Ni^{II}, Pd^{II} and V^{IV}=O). However, novel naphthalocyanines such as MNc(CO_2R)$_4$ induced marked aggregation. Especially, MNc(CO_2R)$_4$ complexes (M = Cu, Pd and Ni) were found to exist exclusively in aggregated states without monomers even in highly diluted solutions.

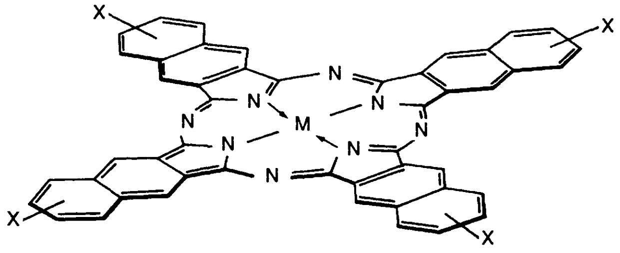
Metal complexes of tetrapyrroles such as chlorophyll and pheophytin are important compounds constituting the photosynthetic reaction centre in plants, inducing highly efficient charge separation *via* photoinduced electron-transfer processes and various subsequent intermolecular interactions.[1] Since a recent X-ray analysis of a bacterial photosynthetic reaction centre from *Rhodopseudomonas viridis* showed the critical arrangement of tetrapyrroles at the active site,[1a] studies on photoinduced electron-transfer reactions and various intermolecular interactions relating to metalloporphyrins have been accelerated.[2] Many fundamental studies with respect to the development of biomimetic photosynthetic systems,[3] organic semiconductors[4] and organic photoconductors[5] have been performed by using synthetic porphyrins. However, the chemical instability of porphyrins is an obstacle to carrying out this kind of research using porphyrins. On the other hand, phthalocyanines, one group of porphyrin derivatives, seem to be suitable for this purpose and also for the purposes of application, which requires durability, because of their high chemical stability. However, it is well known that phthalocyanines, even in dilute solution, tend to form molecular aggregates such as dimers, trimers and oligomers.[6] This is in contrast to porphyrins, which show sharp ^1H NMR signals and fluorescence emission spectra suggesting a tendency to dissociate into monomeric states in solution.[2f,g,j] The aggregated states have very different characteristics when compared with the monomers. Hence, studies on phthalocyanine derivatives are complicated because of the presence of aggregates. For a detailed study of these compounds it is desirable to obtain the monomer and each aggregate separately. Recently, a naphthalocyanine which is monomeric in solution was synthesized[7a] and its photochemistry was examined.[7b,c]

In this study we have investigated the aggregation characteristics of both metallonaphthalocyanine complexes having different ring substituents and novel organic-soluble naphthalocyanines which have a strong tendency to form aggregates and where no monomer is present, even in dilute solution.

Results and Discussion

Naphthalocyanine derivatives such as MNc(Bu^t)$_4$ and MNc(OBu^n)$_4$ (Fig. 1) were prepared by a slight modification of the method described in the literature from the reaction of 6-substituted 2,3-dicyanonaphthalenes with a metal halide.[8] MNc(CO_2R)$_4$ complexes (Fig. 1) were synthesized according to the method[9] mentioned in the Experimental section. Purification of all of these compounds was performed by Soxhlet extraction followed by recrystallisation. Purification by column chromatography over silica gel or alumina[8] was not suitable because these compounds were all strongly adsorbed onto the column packing material and could not be eluted.

The electronic spectrum of CuNc(Bu^t)$_4$ exhibits absorption maxima at 770 nm and ~700 nm, corresponding to monomeric and aggregated forms, respectively, in 1.28×10^{-4} mol dm^{-3} toluene solution as shown in Fig. 2(a). When this solution was diluted gradually to 2.56×10^{-7} mol dm^{-3}, the monomeric absorption maximum increased and the aggregate absorption maximum disappeared as shown in Fig. 2(*d*). Further spectral change was not observed at concentrations less than 2.56×10^{-7} mol dm^{-3}. Therefore, the spectrum observed in the 2.56×10^{-7} mol dm^{-3} solution was confirmed



MNcX$_4$
Napthalocyanine

MNc(Bu^t)$_4$ X = Bu^t	MNc(CO_2R)$_4$ X = CO_2R	MNc(OBu^n)$_4$ X = OBu
CuNc(Bu^t)$_4$ M = Cu	OVNc($CO_2C_8H_{17}$)$_4$ M = OV, R = C_8H_{17}	OVNc(OBu^n)$_4$ M = OV
NiNc(Bu^t)$_4$ M = Ni	OVNc($CO_2C_{18}H_{37}$)$_4$ M = OV, R = $C_{18}H_{37}$	
OVNc(Bu^t)$_4$ M = OV	CuNc($CO_2C_8H_{17}$)$_4$ M = Cu, R = C_8H_{17}	
	CuNc($CO_2C_{18}H_{37}$)$_4$ M = Cu, R = $C_{18}H_{37}$	
	NiNc(CO_2R)$_4$ M = Ni	
	PdNc(CO_2R)$_4$ M = Pd	

Fig. 1 Molecular structure of metallonaphthalocyanines (MNcX$_4$)

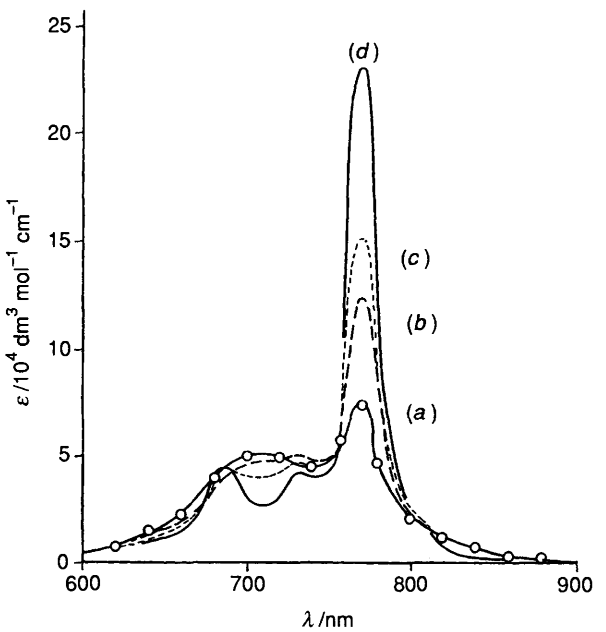


Fig. 2 Concentration dependence of electronic absorption spectra of $\mathrm{CuNc(Bu^t)_4}$ in toluene solution: (a) (—o—o—), 1.28×10^{-4} mol dm^{-3}; (b) (– – – –), 3.20×10^{-5} mol dm^{-3}; (c) (· · · ·), 1.28×10^{-5} mol dm^{-3}; (d) (——), 2.56×10^{-7} mol dm^{-3}

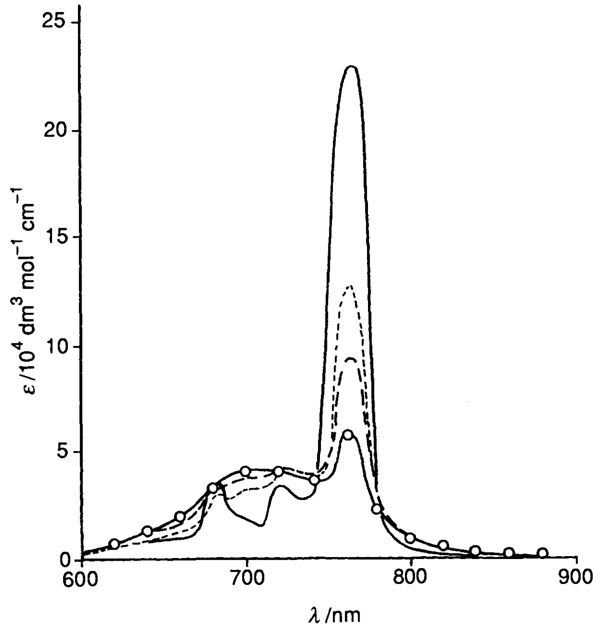


Fig. 3 Concentration dependence of electronic absorption spectra of $\mathrm{NiNc(Bu^t)_4}$ in toluene solution: (—o—o—), 1.08×10^{-4} mol dm^{-3}; (– – – –), 2.71×10^{-5} mol dm^{-3}; (· · · ·), 1.08×10^{-5} mol dm^{-3}; (——), 5.42×10^{-8} mol dm^{-3}

to be the absorption spectrum of purely monomeric $\mathrm{CuNc(Bu^t)_4}$. $\mathrm{NiNc(Bu^t)_4}$ showed similar spectral changes in toluene as shown in Fig. 3 and the absorption spectrum of purely monomeric $\mathrm{NiNc(Bu^t)_4}$ were observed at concentrations below 5.42×10^{-8} mol dm^{-3}. However, $\mathrm{OVNc(Bu^t)_4}$ did not show a significant change in the absorption maximum under our experimental conditions as depicted in Fig. 4, and the absorption spectrum of purely monomeric $\mathrm{OVNc(Bu^t)_4}$ was observed in solutions of concentration 5.88×10^{-7} mol dm^{-3}.

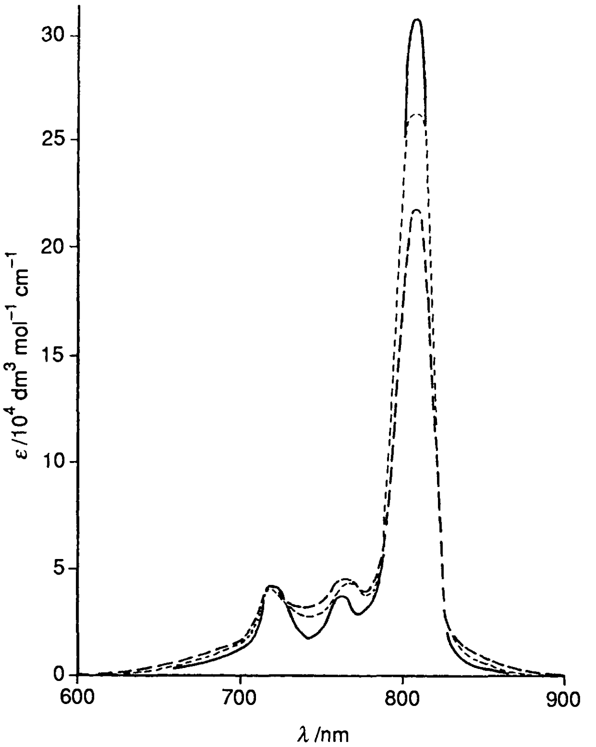


Fig. 4 Concentration dependence of electronic absorption spectra of $\mathrm{OVNc(Bu^t)_4}$ in toluene solution: (– – – –), 5.88×10^{-5} mol dm^{-3}; (· · · ·), 2.94×10^{-5} mol dm^{-3}; (——), 5.88×10^{-7} mol dm^{-3}

Therefore, with these $\mathrm{MNc(Bu^t)_4}$ complexes, when the absorption spectrum of the pure monomer can be observed under highly dilute conditions, the aggregated forms and the aggregation number can be estimated on the basis of these results and the method described previously.[10] Assuming a one-step equilibrium between naphthalocyanine monomer (Nc) and aggregated naphthalocyanine (Nc_n) the equilibrium by eqn. (1), where K is the aggregation constant and n is the aggregation number. K is given by eqn. (2), where x represents the ratio of monomer concentration to the total concentration of naphthalocyanine, C_t.

$$n{\cdot}\mathrm{Nc} \overset{K}{\rightleftharpoons} \mathrm{Nc}_n \qquad (1)$$

$$K = x/[n{\cdot}C_t^{\,n-1}{\cdot}(1 - x)^n] \qquad (2)$$

Observed extinction coefficient (ε) at a certain wavelength (λ) is represented by eqn. (3), where ε_m and ε_n are extinction coefficients for pure monomer and n-aggregate at λ, respectively.

$$\varepsilon = x{\cdot}\varepsilon_n/n + (1 - x){\cdot}\varepsilon_m \qquad (3)$$

From eqns. (2) and (3), eqn. (4) is obtained, where $C = n^n/(n - \varepsilon/\varepsilon_m)^{n-1}$.

$$\log[C_t(1 - \varepsilon/\varepsilon_m)] = \log(C{\cdot}K) + n{\cdot}\log[C_t\{\varepsilon/\varepsilon_m - \varepsilon_n/(n{\cdot}\varepsilon_m)\}] \qquad (4)$$

If the extinction of n-aggregate, ε_n, is very small relative to ε_m at the absorption maximum of the monomer, eqn. (4) is simplified to eqn. (5) at the absorption maximum by assuming $\varepsilon/\varepsilon_m \gg \varepsilon_n/(n{\cdot}\varepsilon_m)$ and $n \gg \varepsilon_n/\varepsilon_m$.

$$\log[C_t{\cdot}(1 - \varepsilon/\varepsilon_m)] = \log(n{\cdot}K) + n{\cdot}\log[C_t{\cdot}(\varepsilon/\varepsilon_m)] \qquad (5)$$

Plots of $\log[C_t{\cdot}(1 - \varepsilon/\varepsilon_m)]$ *vs.* $\log[C_t{\cdot}(\varepsilon/\varepsilon_m]$ for each $\mathrm{MNc(Bu^t)_4}$ gave straight lines as depicted in Fig. 5. The slope of the lines represents the aggregation number (n). From the intercept [$\log(n{\cdot}K)$] and the n-value, the aggregation constant

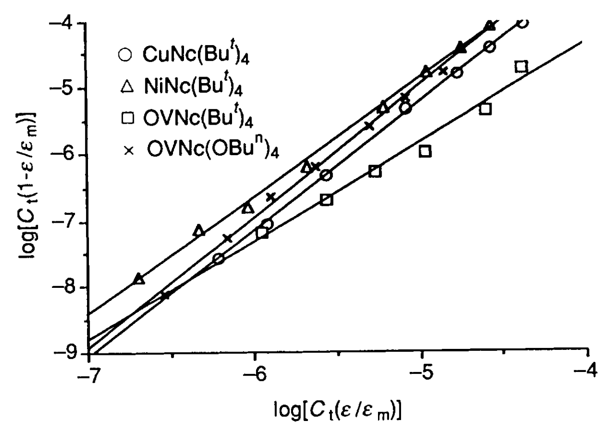


Fig. 5 Plot of $\log[C_t(1 - \varepsilon/\varepsilon_m)]$ *vs.* $\log[C_t(\varepsilon/\varepsilon_m)]$ for the spectral changes of naphthalocyanines

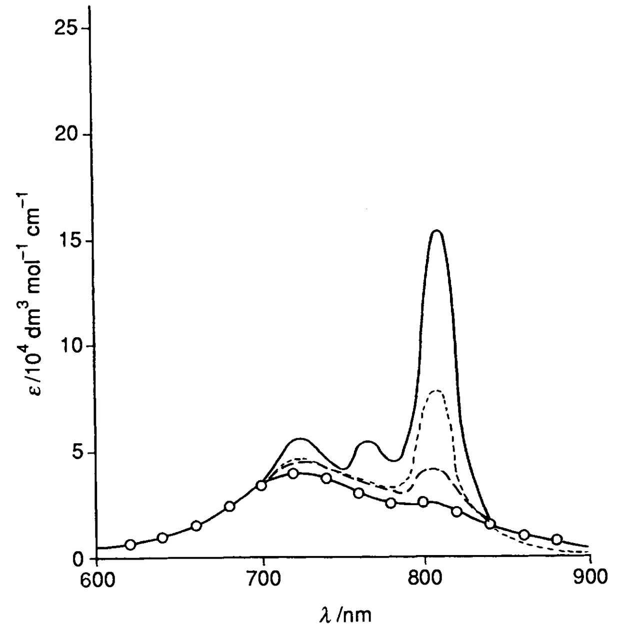


Fig. 6 Concentration dependence of electronic absorption spectra of $OVNc(CO_2C_8H_{17})_4$ in toluene solution: (—o—o—), 7.55×10^{-5} mol dm^{-3}; (– – – –), 7.55×10^{-6} mol dm^{-3}; (· · · ·), 7.55×10^{-7} mol dm^{-3}; (——), 7.55×10^{-8} mol dm^{-3}

Table 1 The aggregation constants (*K*), the aggregation numbers (*n*) and extinction coefficients (ε_m) at the monomeric absorption maximum for naphthalocyanines

	n	*K*	ε_m [a]
$CuNc(Bu^t)_4$	1.91	1.03×10^4	2.32×10^5 (770 nm)
$NiNc(Bu^t)_4$	1.76	4.67×10^3	2.29×10^5 (764 nm)
$OVNc(Bu^t)_4$	1.48	2.24×10	3.10×10^5 (807 nm)
$OVNc(OBu^n)_4$	1.96	3.08×10^4	2.18×10^5 (810 nm)

[a] Numbers in parentheses are wavelengths of the monomeric absorption maxima for each complex.

(*K*) was obtained. The *K*-value for each $MNc(Bu^t)_4$ is shown in Table 1 together with values for *n* and ε_m.

Aggregation numbers between 1.4 and 2 suggest that $MNc(Bu^t)_4$ prefers to form the dimer in solution. The aggregation constant for $OVNc(Bu^t)_4$ was extremely low compared with those for $CuNc(Bu^t)_4$ and $NiNc(Bu^t)_4$. This low aggregating tendency of $OVNc(Bu^t)_4$ seems to result from steric hindrance of the oxygen atom on the central vanadium atom.

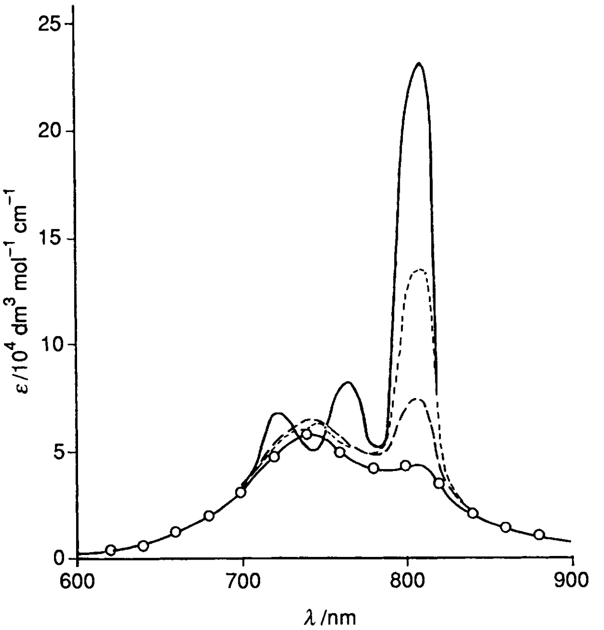


Fig. 7 Concentration dependence of electronic absorption spectra of $OVNc(CO_2C_{18}H_{37})_4$ in toluene solution: (—o—o—), 9.16×10^{-5} mol dm^{-3}; (– – – –), 9.16×10^{-6} mol dm^{-3}; (· · · ·), 9.16×10^{-7} mol dm^{-3}; (——), 6.36×10^{-8} mol dm^{-3}

On the other hand, the electronic spectrum of $OVNc(CO_2C_8H_{17})_4$ in toluene exhibits significant decreases in the monomeric absorption (809 nm) and increases in the aggregate absorption (725 nm) compared with those of $OVNc(Bu^t)_4$ under similar conditions, as shown in Fig. 6. Since, with the concentration range of $OVNc(CO_2C_8H_{17})_4$ solutions we used, it was not possible to attain a sufficiently dilute solution to acquire purely monomeric species, the aggregation number and the aggregation constant for $OVNc(CO_2C_8H_{17})_4$ could not be estimated. In other words, high dilution of the solution below 7.55×10^{-8} mol dm^{-3} was necessary to obtain an absorption spectrum of the $OVNc(CO_2C_8H_{17})_4$ pure monomer. Similarly, results for $OVNc(CO_2C_{18}H_{37})_4$ are shown in Fig. 7; the absorption spectrum indicating purely monomeric $OVNc(CO_2C_{18}H_{37})_4$ could not be obtained at concentrations higher than 6.36×10^{-8} mol dm^{-3}. The alkyl-chain length of R in $OVNc(CO_2R)_4$ exhibited no significant effect on the aggregation of $OVNc(CO_2R)_4$. These results reveal that $OVNc(CO_2R)_4$ generally has a high tendency for aggregation compared with $OVNc(Bu^t)_4$ having the same central metal.

Electronic spectra of $OVNc(Bu^t)_4$ and $OVNc(CO_2C_8H_{17})_4$ were examined in other solvents such as benzene, tetrahydrofuran and chloroform. The electronic spectrum of $OVNc(Bu^t)_4$ in chloroform (Fig. 8) was different from that in toluene (Fig. 4), which was closely related to those in benzene and tetrahydrofuran. However, the electronic spectra of $OVNc(CO_2C_8H_{17})_4$ in these solvents at similar concentrations were similar. The low solvent-dependency of the aggregation ability for $OVNc(CO_2C_8H_{17})_4$ seems to arise from its strong aggregation ability. Consequently, the introduction of four alkoxycarbonyl groups into the naphthalocyanine ring instead of t-butyl groups generates a strong aggregation ability. This may result from a steric effect of the substituents' binding to the naphthalocyanine ring or from an electronic inductive effect of the substituent. To clarify this substituent effect, spectra of $OVNc(OBu^n)_4$ were measured under similar experimental conditions as shown in Fig. 9. $OVNc(OBu^n)_4$ had an intermediate tendency of aggregation between those of $OVNc(Bu^t)_4$ and $OVNc(CO_2R)_4$,

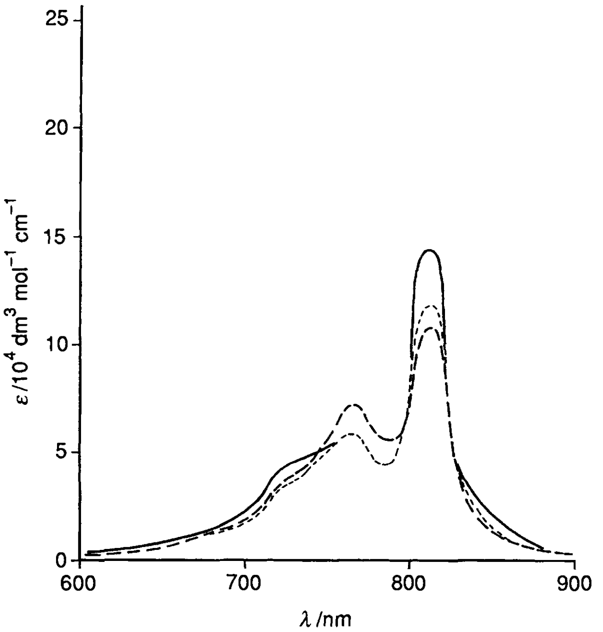


Fig. 8 Concentration of electronic absorption spectra of OVNc(Bu^t)$_4$ in chloroform solution: (– – – –), 5.85 × 10^{-5} mol dm^{-3}; (· · · ·), 2.11 × 10^{-5} mol dm^{-3}; (——), 1.06 × 10^{-5} mol dm^{-3}

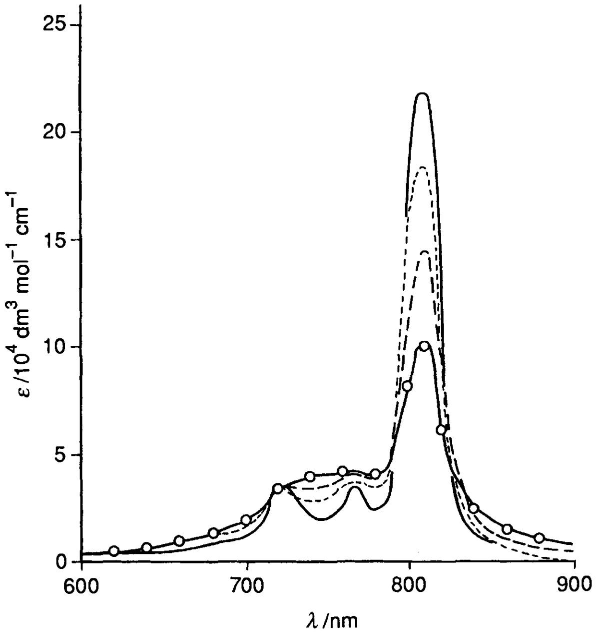


Fig. 9 Concentration dependence of electronic absorption spectra of OVNc(OBu^n)$_4$ in toluene solution: (—o—o—), 3.00 × 10^{-5} mol dm^{-3}; (– – – –), 7.49 × 10^{-6} mol dm^{-3}; (· · · ·), 1.50 × 10^{-6} mol dm^{-3}; (——), 1.50 × 10^{-7} mol dm^{-3}

and the absorption spectrum of purely monomeric OVNc(OBu^n)$_4$ was observed at concentrations below 1.50 × 10^{-7} mol dm^{-3}. The *K*- and *n*-values for OVNc(OBu^n)$_4$ in toluene were estimated as shown in Fig. 5 and Table 1. The results suggest that the strong aggregation ability of OVNc(CO$_2$R)$_4$ arises from both the steric and the electronic effect of the alkoxycarbonyl group.

The strongest aggregation tendency was observed with CuNc(CO$_2$C$_8$H$_{17}$)$_4$, the electronic absorption spectrum of which showed no monomeric absorption maximum even in dilute solution (1 × 10^{-6} mol dm^{-3}). At concentrations greater than 1 × 10^{-6} mol dm^{-3}, no spectral change was observed. A typical example is shown in Fig. 10. A small degree of monomeric absorption around 775 nm and a slight red shift of the aggregate absorption were observed by further dilution to a concentration of less than 1 × 10^{-6} mol dm^{-3}. It is believed that these observations arose from a slight dissociation of the aggregate. Similar spectra were observed for CuNc(CO$_2$C$_{18}$H$_{37}$)$_4$, suggesting that the alkyl-chain length of the alkoxycarbonyl group contributes to the aggregation. Even in other solvents, such as chloroform, tetrahydrofuran and benzene, CuNc(CO$_2$R)$_4$ revealed no monomeric absorption maximum in similar concentration ranges. Their ^{1}H NMR spectra showed broadening of all signals and they exhibited no fluorescence emission. These observations suggest that most CuNc(CO$_2$R)$_4$ molecules do not exist in a monomeric state but in an aggregated state in solution because of their high aggregation tendency. Similar aggregation properties were observed for NiNc(CO$_2$R)$_4$ and PdNc(CO$_2$R)$_4$. The electronic spectrum of CuNc(CO$_2$C$_8$H$_{17}$)$_4$, thin-film spin-coated on a glass plate, as shown in Fig. 11, was very close to that in solution. This observation indicates that the aggregation state of CuNc(CO$_2$C$_8$H$_{17}$)$_4$ in solution is similar to that in a thin-film state. Therefore the introduction of alkoxycarbonyl groups into the naphthalocyanine ring instead of other substituents, such as alkyl and alkoxy groups, causes the strong aggregation property of metallonaphthalocyanines.

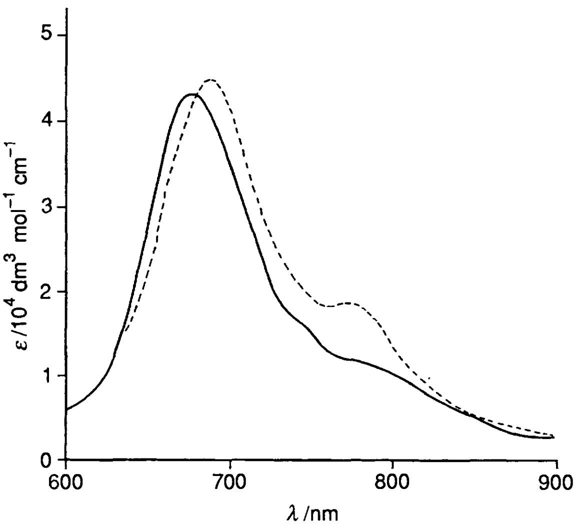


Fig. 10 Electronic absorption spectrum of CuNc(CO$_2$C$_8$H$_{17}$)$_4$ in toluene solution: (——), 6.85 × 10^{-5} mol dm^{-3}; (· · · ·), 3.43 × 10^{-7} mol dm^{-3}

Conclusions.—Studies on the aggregation properties of naphthalocyanines having different ring substituents were performed. Generally, MNc(Bu^t)$_4$ and MNc(OBu^n)$_4$ had showed aggregation tendencies. However, novel naphthalocyanines such as MNc(CO$_2$R)$_4$ showed much stronger aggregation properties compared with those of MNc(Bu^t)$_4$ and MNc(OBu^n)$_4$. Especially, MNc(CO$_2$R)$_4$ complexes (M = Cu, Ni, Pd) exist only in aggregated forms, since monomers were not detected even in dilute solutions. MNc(CO$_2$R)$_4$ complexes (M = Cu, Ni, Pd) in solution can be acceptable models of their states as thin solid films.

Experimental

Apparatus.—All m.p.s were determined with a Yanagimoto micro melting point apparatus and were uncorrected. Electronic spectra were obtained at 25 °C on a Hitachi 150-20 spectrometer and a Hitachi U3410 spectrometer. Fluorescence emission spectra were observed using a Hitachi 850 fluorescence spectrometer. ^{1}H NMR spectra were taken on a Hitachi R-250 spectrometer and chemical shifts were recorded downfield from

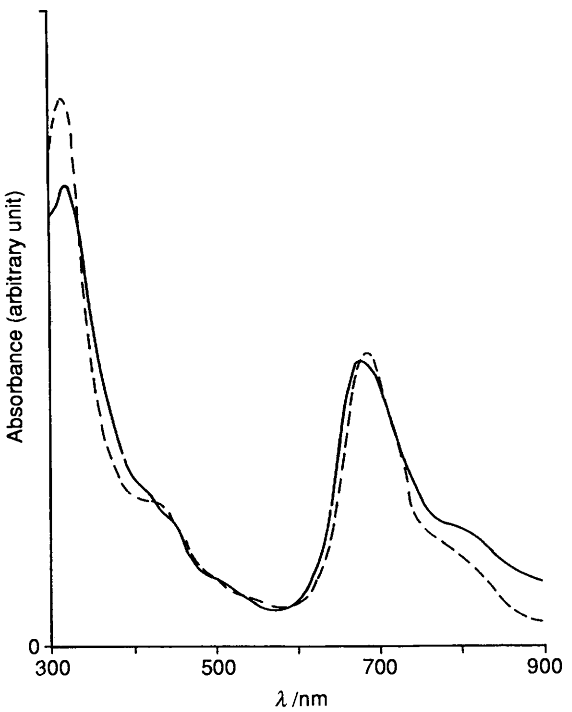


Fig. 11 Electronic absorption spectra of $\mathrm{CuNc(CO_2C_8H_{17})_4}$: (——), thin solid film; (– – – –), chloroform solution [1.62×10^{-5} mol dm^{-3}]

tetramethylsilane as internal standard (δ-scale). Elemental analyses were performed at the microanalytical laboratory of Sagamihara Chemical Research Center.

Materials.—$\mathrm{MNc(Bu^t)_4}$ and $\mathrm{OVNc(OBu^n)_4}$ were synthesized as described previously.[8] Purification was performed by use of a Soxhlet apparatus as mentioned below. All $\mathrm{MNc(CO_2R)_4}$ were prepared according to the following general procedure.

General Procedure for Preparation of Compounds $\mathrm{MNc(CO_2R)_4}$.—Metal halide (1.6 mmol), 6-alkoxycarbonyl-2,3-dicyanonaphthalene[9] (5 mmol), ammonium molybdate (10 mg) and urea (5 g) were heated at ~220 °C for 2.5 h with initial thorough stirring of the mixture. After cooling, the reaction mixture in solid form was mixed with 5% hydrochloric acid (40 cm^3). This mixture was stirred vigorously at ~50 °C for 30 min and then the insoluble material was collected by filtration and washed successively with water, methanol and acetone. The resulting solid was extracted with a mixed solvent consisting of methanol–acetone (1:1) in a Soxhlet apparatus for ~50 h. Soxhlet extraction was then continued with chloroform for 20 h. The resulting deep green chloroform solution was filtered and concentrated to dryness to obtain $\mathrm{MNc(CO_2R)_4}$ as greenish black crystals. All ^{1}H NMR signals of $\mathrm{MNc(CO_2R)_4}$ showed broadening.

Physical Properties of Species $\mathrm{MNc(CO_2R)_4}$.—$\mathrm{OVNc(CO_2C_8H_{17})_4}$ *from* $\mathrm{VCl_3}$. Yield 76%, m.p. > 300 °C (Found: C, 72.0; H, 6.2; N, 8.3. $\mathrm{C_{84}H_{88}N_8O_9V}$ requires C, 71.83; H, 6.33; N, 8.00%); ν_{max}(KBr)/cm^{-1} 1700, 1250, 1240 and 1065; electronic spectrum in toluene is shown in Fig. 6.

$\mathrm{CuNc(CO_2C_8H_{17})_4}$ *from* $\mathrm{CuCl_2{\cdot}2H_2O}$. Yield 79%, m.p. >300 °C (Found: C, 71.95; H, 6.1; N, 8.1. $\mathrm{C_{84}H_{88}CuN_8O_8}$ requires C, 72.00; H, 6.33; N, 8.00%); ν_{max}(KBr)/cm^{-1} 1700, 1255, 1240 and 1080; electronic spectrum in toluene is shown in Fig. 10.

$\mathrm{OVNc(CO_2C_{18}H_{37})_4}$ *from* $\mathrm{VCl_3}$. Yield 83%, m.p. (softening point) 135–138 °C (Found: C, 75.25; H, 8.5; N, 6.2. $\mathrm{C_{124}H_{168}N_8O_9V}$ requires C, 75.55; H, 8.61; N, 5.70%); ν_{max}(KBr)/cm^{-1} 2900, 2820, 1700, 1240 and 1065; electronic spectra in toluene are shown in Fig. 7.

$\mathrm{CuNc(CO_2C_{18}H_{37})_4}$ *from* $\mathrm{CuCl_2{\cdot}2H_2O}$. Yield 77%, m.p. (softening point) 119–121 °C (Found: C, 75.6; H, 8.5; N, 5.7. $\mathrm{C_{124}H_{168}CuN_8O_8}$ requires C, 75.90; H, 8.63; N, 5.71%); ν_{max}(KBr)/cm^{-1} 2920, 2850, 1720, 1265, 1255 and 1095; λ_{max}(toluene)/nm 673 (log ε 4.27).

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