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Coordination Chemistry Reviews 227 (2002) 129–152

COORDINATION
CHEMISTRY REVIEWS

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Dimers, trimers and oligomers of phthalocyanines and related compounds

Nagao Kobayashi *

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received 8 August 2001; accepted 1 September 2001

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* Tel./fax: +81-22-217-7719.
E-mail address: nagaok@mail.cc.tohoku.ac.jp (N. Kobayashi).

PII: S0010-8545(02)00010-3

Abstract

Cofacial and planar homo- and heteroleptic dimers and oligomers of phthalocyanine (Pc) and its analogues reported to date have been reviewed.

Keywords: Phthalocyanine; Dimer; Oligomer; Naphthalocyanine; Tetraazaporphyrin; Porphyrin

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1. Introduction

Phthalocyanine (Pc) was synthesized by chance approximately one century ago [1] and its structure was confirmed by X-ray analysis about 65–70 years ago [2]. Since then, Pcs have long been used as blue and green dyestuffs and pigments, and nowadays their use as photoconducting agents in photocopying machines has stimulated research in various fields, including chemical sensors, electrochromism, photodynamic reagents for cancer therapy and other medical applications, computer read/write discs, low dimensional metals, deodorants, non-linear optics, electrocatalysis, liquid crystals, and germicides [3–7]. For these purposes, more than 50 000 tons of monomeric Pcs have been used per year. On the other hand, however, a variety of Pc dimers and oligomers have been known since only ca. 30 years ago. In this review, homo- and heterodimers and oligomers of Pcs, tetraazaporphyrins (TAPs), naphthalocyanines (Ncs), subphthalocyanines (SubPcs), and pyrazinoporphyrazines (PyZs) are reviewed. TAPs are compounds lying structurally in-between normal porphyrins and Pcs, while Ncs, PyZs, and SubPcs are considered to be relatives of Pcs. Since there have been many papers published on these compounds, only representative synthetic procedures and properties are introduced in each case. Although these compounds are interesting in applied fields such as sensors, these applications are omitted in this review.

2. Metal-(X)1 or 2-metal dimers

2.1. μ-Oxo phthalocyanines, tetraazaporphyrins and subphthalocynines

The most well known μ-oxo Pc dimers are those of SiPc. These are easily obtained, for example, by refluxing $SiPc(OH)_2$ and $CaCl_2$ in toluene for several hours, and have been intensively studied by the many spectroscopic methods available. In electronic absorption spectroscopy [8], the Q band was shifted towards shorter wavelength compared with monomers, and hence this became a good example to confirm the exciton model. ^{1}H-NMR [9] and redox potentials were also measured, and in particular, all redox couples seen in monomeric SiPc split into two couples [10]. In a He(I) photoelectron spectroscopy study of the SiPc monomer and μ-oxo dimer [11], the lowest ionization of the monomer, which yields a π-cation radical with calculated $^2A_{1g}$ ground state symmetry, occurred at 6.42 eV, while this band in the dimer split into two bands of roughly equal intensity at 6.19 and 6.51 eV, the transannular interaction energy thus being 0.32 eV.

μ-Oxo dimers of AlPc, TiOPc, MnPc, FePc and CrPc are known. $(AlPc)_2O$ was formed during sublimation of AlPc(OH) at higher temperature [12]. An interesting and characteristic feature of this dimer is that the two Pc rings take an eclipsed structure with a ring-ring separation of 4.27 Å, compared with 3.32 Å in $(SiPc)_2O$ [11]. The Al–O–Al angle is exactly 180°. Surface enhanced Raman spectroscopic studies have allowed identification of the Al–O–Al asymmetric vibration at 1050 cm^{-1}[13]. The μ-oxo dimer of TiPc was isolated as a perchlorate salt $[(TiPc)_2O](ClO4)_2$ by suspending TiOPc in the presence of HClO4 in CH_2Cl_2–CH_3CN [14]. This shows an IR absorption peak at 820 cm^{-1}, tentatively assigned to the antisymmetric Ti–O–Ti stretch. In the presence of amines, the dimer generates TiOPc. $(MnPc)_2O$ can be prepared from $[(pyridine)MnPc]_2O$ obtained by reaction of MnPc with oxygen in pyridine [15], by eliminating the pyridine molecule at higher temperature in vacuo. Although the X-ray data of $(MnPc)_2O$ is not reported, that of $[(pyridine)MnPc]_2O$ with λ_{max} at 620 nm in pyridine is known [16]. This molecule consists of two approximately flat and parallel MnPc ring systems, with staggering of the two Pc rings by 49 rather than 45°. Both the Mn–O–Mn and N(pyridine)–Mn–O angles are 178°. $(MnPc)_2O$ undergoes a reversible one-electron oxidation at 0.35 V versus SCE in pyridine to the mixed-valence cationic Mn(IV)Pc–O–Mn(III)Pc. In handling well-characterized MnPcs, we have to be careful to purify the solvent, since it may take various oxidation states and axial ligands [17].

In contrast, $(FePc)_2O$ is formed very easily. For example, suspension of FePc in DMF, THF, dioxane, kept in an air atmosphere under stirring, gives quantitatively $(FePc)_2O$ which is unique in the field of μ-oxo dimers in that it has been isolated and characterized in two distinct isomeric forms having a bent and a linear Fe–O–Fe moiety [18]. The bent isomer obtained by the above procedure is stable to ca. 300°, and has IR absorptions at 852 and 824 cm^{-1}, assigned as the antisymmetric stretching vibration. The linear isomer can be prepared in two ways. By adding 2-propylamine to a bent isomer suspended in chloronaphthalene, the linear isomer is precipitated out. In another method, oxygen is bubbled into a solution of FePc in concentrated (96%) H_2SO_4 for ca. 20 min, and this solution is then poured into cold water. The resulting precipitate is the desired linear isomer, which does not show any IR absorption at ca. 850 cm^{-1}. Although the X-ray structure of the bent isomer has not been obtained, the structure of a linear isomer [19] is thought to be similar to that of the above $[(pyridine)MnPc]_2O$ [16]. Mossbauer spectroscopic and magnetic susceptibility (μ) data indicate the presence of antiferromagnetically interacting couples of high-spin (5/2, 5/2) Fe(III) for the both isomers [18,20,21]. The isomer shift and quadrupole splitting values for the bent $(FePc)_2O$ are 0.36 and 0.44 mm s^{-1}, and for the linear $(FePc)_2O$ are 0.26 and 1.26 mm s^{-1}, respectively. The antiferromagnetic constants J, obtained from measurements in the range 300–304 K, are -120 and -195 cm^{-1} for the bent and linear isomers, respectively. In voltammetry carried out in pyridine (so that the species is actually $[(pyridine)FePc]_2O$), oxidation couples occurred at 0.47 (removal of an electron from Fe) and 0.87 V, and two reductions were seen at -0.59 and -0.95 V [22].

By heating CrPc(OH) in pyridine, $[(pyridine)CrPc]_2O$ with $\mu = 1.24$ μ_B was obtained [23]. This compound shows a single Q band at 633 nm in pyridine and an antisymmetric stretching vibration (Cr–O–Cr) band at 870 cm^{-1} in IR spectroscopy, and a symmetric Cr–O–Cr stretching band at 426 cm^{-1} in resonance Raman (RR) spectroscopy.

μ-Oxo dimers of phenyl-substituted TAP were reported recently [24]. Octa- and tetra-phenylated species showed antisymmetric stretching vibrations at 826 and 841 cm^{-1}, respectively. These species show a broad Q band peak in the range of 610–650 nm, depending on the axial ligand and solvent.

SubPc is an analogue of Pc, consisting of three isoindoline units and boron [25]. Two μ-oxo dimers of SubPc have been reported to date [26,27]. Dimerization of SubPc containing an OH group was carried out either in toluene containing $CaCl_2$ [26] or under vacuum at ca. 200 °C [27]. A broad Q band appears at ca. 500–600 nm, with a main peak at ca. 540 nm, which is shorter than that of the starting SubPc (ca. 560–570 nm). Although IR data were reported [26], no assignments were given.

2.2. *μ-Nitrido phthalocyanines and tetraazaporphyrins*

$(FePc)_2N$ is readily obtained by heating FePc or $(FePc)_2O$ with NaN_3 in boiling chloronaphthalene [28] as a paramagnetic species with one unpaired electron per dimer unit. It shows ESR signals at $g = 2.03$ and 2.13, consistent with an A_1 ground state and indicative of extensive charge delocalization over the two iron centers. In pyridine, it has a Q band peak at 625 nm and its IR spectrum showed an antisymmetric Fe–N–Fe stretching vibration at 910–915 cm^{-1}. In the Mossbauer spectrum, the isomer shift and quadruple splitting values were 0.06 and 1.76 mm s^{-1}, respectively at 77 K. Although $(FePc)_2N$ reacts with amines and anions to form derivatives [28b,29], all the deta support the iron being in a tetravalent state. X-ray data are reported for $(BrFePc)_2N$ [30]. The Fe atoms are located at the center of the Pc rings, which are rigorously planar, parallel (3.278 Å apart) and staggered by an angle of 39°. The Fe–(μ)N distance is 1.639 Å.

$(RuPc)_2N$ was similarly easily synthesized, by heating RuPc or $RuPc(pyridine)_2$ and NaN_3 at 280–290 °C for 20 min [31]. This shows an IR band at 1040 cm^{-1}, which is assignable as a Ru–N–Ru antisymmetric vibration, a Q band at ca. 600 nm in pyridine, and a room temperature (r.t.) magnetic susceptibility of 1.8 ± 0.15 μ_B, consistent with the presence of one unpaired electron per dimer. Since neither electronic absorption nor IR spectroscopy suggested the presence of a Pc anion, it was concluded that the positive charge is entirely localized on the Ru atoms. Thus, $(RuPc)_2N$ was identified to be a mixed valence Ru(III)–Ru(IV) dimer.

The μ-nitrido dimer of octaphenyl FeTAP is also known [32]. A benzene solution of monomeric FeTAP was reacted with concentrated NH_4OH, and the benzene layer purified using a silica gel column and benzene (34%). The dimer is paramagnetic, with one unpaired electron per dimer unit, and showed a typical axially symmetric EPR signal ($g = 2.126$, $g// = 2.001$) in toluene at liquid N_2 temperature, with well-resolved superhyperfine splitting from the m-nitrido bridge. The antisymmetric Fe–N–Fe stretching vibration appeared at 913 cm^{-1}.

2.3. *μ-Carbido phthalocyanines*

Most known m-carbido Pcs contain iron, except for an example containing ruthenium. $(FePc)_2C$ is obtained in chloronaphthalene, by reacting FePc with CI_4 at 140–150 °C for 30 min in the presence of reducing reagents such as sodium dithionite or iron powder[33,34]. In general, it was obtained as a mixture of two forms, where one form showed an antisymmetric Fe–C–Fe stretching vibration at 990 cm^{-1}, a Q band peak at 620 nm in pyridine, and isomer shift and quadruple splitting values of -0.16 and 2.69 mm s^{-1} at 77 K. The value of the isomer shift clearly indicates that the Fe is in a tetravalent state, while the largest quadruple splitting value seen among the N_4 macrocycles [35] suggests the presence of a high degree of π-bond conjugation in the Fe–C–Fe moiety. X-ray data are reported for $[(1\text{-methylimidazole})FePc]_2C$, where the two Pc planes are rotated by ca. 45°, the Fe–(μ)C distance is 1.70 Å, and the Fe–C–Fe angle is 178° [33]. Detailed data on derivatives of $(FePc)_2C$ are found in [36–38].

$[(pyridine)RuPc]_2C$ was prepared by reacting RuPc and $CHCl_3$ in boiling 2-propanol, and subsequent treatment with pyridine at 60 °C [37,38]. The Ru–(μ)C distance and the center–center distance of the N_4(pyrrole) are 1.77 and 3.65 Å, respectively, and an Ru–C–Ru antisymmetric IR vibration was observed at 974 cm^{-1}. The two Pc planes are slightly inwardly doming [37]. The oxidation state of Ru is assigned as tetravalent.

2.4. *Di-μ-iodo phthalocyanines*

Bismuth and antimony Pcs form di-μ-iodo Pcs in the crystalline state. In order to synthesize $(BiPc)_2I_2$, Bi_2Se_3 and *o*-dichlorobenzene were mixed at a molar ratio of 1:8, and this was inserted into an evacuated glass ampoule, together with an adequate quantity of iodine. The ampoule was kept at 200 °C for 1 day, and after cooling, the desired $(BiPc)_2I_2$ was obtained as black–violet crystals [39]. In the dimer, the Bi–I–Bi–I forms a rectangle of dimensions 3.343 and 3.362 Å and I–Bi–I angles of 85.98 and 94.02°. The interatomic distance of the bismuth atoms is 4.904 Å, and that between iodine atoms 4.571 Å. In the BiPc unit, the Bi atom is 1.177 Å out of the plane defined by the four isoindole nitrogens (the N_4 plane). Since the Pc plane assumes a domed conformation, the outermost carbon of the Pc ring is ca. 1.2 Å out of the N_4 plane.

$(SbPc)_2I_2$ was obtained by the reaction of antimony with phthalonitrile under I_2 vapor [40,41]. The Sb–I distances are 3.438 and 3.474 Å, while those between Sb and the pyrrole nitrogens are in the range of 2.202 and 2.236 Å. Thus, the molecular symmetry of the Sb–N core is close to C_s.

2.5. *μ-Oxo silicon phthalocyanine oligomers*

μ-Oxo SiPc trimers and tetramers were reported long ago [8,10]. These were separated from the condensation products of $SiPc(OH)_2$. Nowadays, separation of these species is relatively easy because of the development of gel permeation chromatography. With increasing number of Pc layers from 1 to 4 in a series of μ-oxo SiPcs, the Q band shifted to shorter wavelength (665, 630, 618, and 615 nm, respectively) [8a], while the number of redox couples of the Pc ligand increases. Thus, one oxidation couple seen in the SiPc monomer between 0 and 1 V versus Ag–AgCl increases to four couples in the μ-oxo tetramer [10].

3. Lanthanoid and actinoid sandwich dimers and oligomers

3.1. *Homodimers*

3.1.1. *Tetraazaporphyrins*

Lutetium TAP sandwich dimers substituted by 16 alkylthio- [42], eight *tert*-butyl- [43] or 16 ethyl groups [44] have been reported to date. Octabutylthio H_2TAP and $Lu(OAc)_3$ (2:1 molar ratio) were refluxed in *n*-hexanol for 1 week, and the product was purified by chromatography. In $CHCl_3$, it showed Q and Soret peaks at 670 and 354 nm, respectively, together with a small broad band at ca. 510 nm, which may be assigned to an $n-\pi^*$ transition of sulfur. Both the $CHCl_3$ solution and powder sample showed a single line at $g = 2.0037$ in the EPR spectra, manifesting the presence of an unpaired electron. *Tert*-butylated TAP dimer was obtained similarly from *tert*-butylated H_2TAP and $Lu(acac)_3$ in refluxing 1,3-dimethylamino-2-imidazolidinone. This shows Q and Soret bands at 586 and 315 nm in CCl_4, respectively, while the band lying in between these two bands, which is typical for this type of radical Pc analogue, is weak. The time-resolved EPR spectra of the chemically one-electron reduced and oxidized species were recorded, and their zero-field splitting values compared (0.48, and 0.41 GHz, respectively). From these values, with respect to the decrease in D in the reduced form, the contribution of the charge–resonance character was calculated to be 42%.

Octaethyl H_2TAP was refluxed with $Lu(OAc)_3$ in *n*-hexanol for 3 days to give the corresponding dimer in 45% yield, but prolonging the reaction to 1 week increased the yield to ca. 90% without the formation of trimers [44]. Very dilute $CHCl_3$ solution showed a Soret band at 342 nm, and Q bands at 640 and 599 nm, with shoulders at 534 and 575 nm. However, the spectroscopic shape changed markedly with increasing concentration. The Soret band split into two components, and the band at 640 nm disappeared, while the shoulders at 534 and 575 nm gained intensity. Since a set of isosbestic points was detected during this change, the change was thought to correspond to a cofacial dimerization process.

3.1.2. *Phthalocyanines*

There are ample reports in the literature dealing with Pc compounds classified in this category [45,46]. Historically, these compounds were first synthesized in the mid 1960s, and although there are several ways to synthesize them, a common feature is that relatively higher temperatures and longer reaction times are required compared with monomeric Pcs. The simplest way is to heat a mixture of a metal salt and phthalonitrile to 280–290 °C, until solidification of the melt occurs (ca. 0.5–4 h), followed by chromatographic

Table 1
Comparison of ionic radius, d_N,[a] d_{int},[b] and Twist(skew) values in MPc_2 and $MPcPc_{ox}$[c] structures (from [53])

Complex	Ionic radius (Å)	d_N (Å)	d_{int} (Å)	Skew angle (°)
$[Ti^{IV}Pc_2]^{0.66+}$	0.88	2.42	[d]	41.1
$Y^{III}PcPc_{ox}$	1.159	2.760	3.07	45
$Zr^{IV}Pc_2$	0.98	2.52	3.10	39.7
$Sn^{IV}Pc_2$	0.95	2.61	3.01	42
$Ce^{IV}Pc_2$	1.11	2.79	3.27	38.8
$Pr^{III}PcPc_{ox}$	1.266	3.0	3.25	42
$Pr^{III}Pc_{ox2}$	1.266	3.08	3.21	41
$Nd^{III}PcPc_{ox}$	1.249	2.96	3.29	38
$Nd^{III}Pc_2$	1.249	3.0	[d]	42.3
$[Nd^{III}Pc_2]^-$	1.249	3.08	3.59	6.2
$[Gd^{III}Pc_2]^-$	1.193	2.89	3.48	34.5
$[Ho^{III}Pc_2]^-$	1.155	2.76	3.30	43.2
$Er^{III}PcPc_{ox}$	1.144	2.74	3.06	41.4
$[Lu^{III}Pc_2]^-$	1.117	2.701	3.21	43
$Lu^{III}HPc_2$	1.117	2.676	3.05	41
$Lu^{III}PcPc_{ox}$	1.117	2.69	3.06	45
$Lu^{III}PcPc_{ox}$	1.117	2.68	3.08	41
$[Lu^{III}Pc_2]^-$	1.117	2.67	3.24	45
$Th^{IV}Pc_2$	1.19	2.87	3.32	39.8
$Th^{IV}Pc_2$	1.19	2.98	3.30	38
$Th^{IV}Pc_2$	1.19	2.96	3.39	37.4
$U^{IV}Pc_2$	1.14	2.81	[d]	37
$U^{IV}Pc_2$	1.14	2.84	3.28	39.1

[a] Distance between the upper and lower planes composed of four N_{iso} atoms.
[b] Distance between the upper and lower average planes of Pc ligands.
[c] Phthalocyaninato anion, $C_{32}H_{16}N_8^-$.
[d] Not calculated owing to the lack of the atomic parameters.

separation of the product [47,48]. The use of a high-boiling solvent such as chloronaphthalene is also beneficial. Thus, $Lu(Pc)_2$ was obtained by reacting $LuCl_3$ and phthalonitrile at 290° for a few hour [49]. Nowadays, for the preparation of lanthanoid sandwich dimers, hexanol and diazabicycloundecene (DBU) are intensively used, particularly for soluble dimers, since the chromatographic purification process is easier [50]. In general, if the reaction is carried out in the absence of a base or non-coordinating solvent, the isolated sandwich dimer contains a radical and this species was, in the old days, called 'the Green form'. By adding alkalis such as KOH or NaOMe, the corresponding reduced form, formally called 'the Blue form' is obtained [51–53].

Many X-ray crystallographic studies have shown that the two Pcs are mainly saucer-shaped, forming a biconcave lens structure. The so-called twist angle of the two Pc planes often depends on the size of the central metal. Among some lanthanide metals, the smaller the size, the larger the twist angle. For example, in the tetrabutylammonium salts of Nd, Gd, Ho, and Lu Pc dimers, the angles are 6, 34.4, 43.2 and 45°, while their ionic radii are 1.249, 1.193, 1.155, and 1.117 Å, respectively [53]. However, if we compare the data of a larger number of samples, this relationship does not necessarily hold (see Table 1). The twist angles of almost all sandwich Pcs reported to date lie between 37 and 45° (Fig. 1). The distances between the upper and lower planes composed of four isoindole nitrogen atoms in lanthanoid and actinoid sandwich Pc dimers lie mostly between 2.8 and 3.0 Å. For readers who are interested in this field, many X-ray data introduced in [45] and in particular, those published by Homborg's group over the last decade would be helpful [54].

The IR specra of these double decker complexes have also been intensively studied. Arnold et al. recently summarized IR data appearing in ca. 70 papers [55]. The characteristics of the IR spectra for both lanthanoid sandwich Pcs and Ncs are the occurrence of bands at around 1450 (isoindole stretching), 1310–1330 and 1370 (pyrrole C=C stretching), and at 1110 and 710–760 cm^{-1} (C–H bending and wagging vibration of the Pc rings). Of these, the band at 1310–1330 cm^{-1} may be assigned to two species: that appearing between 1310 and ca. 1320 cm^{-1} is characteristic of a $Pc^{\bullet -}$ π radical, while that at ca. 1330 cm^{-1} can be assigned to a normal Pc^{2-} dianion. Concomitant with the increase of the lanthanoid ionic radius, the radical marker band shifts from ca. 1310 to 1320 cm^{-1}. Jiang et al. very recently summarized the Raman spectroscopic characteristics of about 50 lanthanoid Pc dimers [56]. They concluded that when the laser excitation is in close resonance with the Q band absorption of Pc-containing sandwich lanthanoids, the band at ca. 1500 cm^{-1}, with contributions from both C=C (pyrrole) and C=N (aza group) stretches, is a good marker band for the Pc dianion, Pc^{2-}, in double-deckers and even triple-deckers. In $Pc^{\bullet -}$ radicals containing double-deckers, this band blue-shifts to ca. 1515 cm^{-1}.

The electronic spectra of these lanthanide sandwiches have been collected and interpreted by many researchers. The so-called blue-form spectra consist of a single Soret band and one or two split Q bands. The extent of the Q band splitting of the lanthanoid(III) complexes increases with decreasing ionic radius of the Ln(III) ions (Fig. 2; Table 2), reflecting the extent of the π–π interaction between the two Pc rings. This splitting can be explained by excitonic interaction. However, to explain the splitting which increases much more rapidly than anticipated from the change of the radius, a rapid increase of electronic interactions via overlapping orbitals with decreasing distance was proposed [57]. The absorption spectra of radical-containing species (the green form) are different from those of normal species in several respects. They have a peak of medium intensity at ca. 500 nm, a weak near-IR peak at ca. 900 nm, and broad near-IR absorption comprising one- or two-peaks in the 1100–1800 nm region. It is found that this near-IR band at around 1100–1800 nm, the main Q band at ca. 670–700 nm, and a band with intermediate intensity at around 460–520 nm, all shift to shorter wavelength with decreasing radius of lanthanoi-

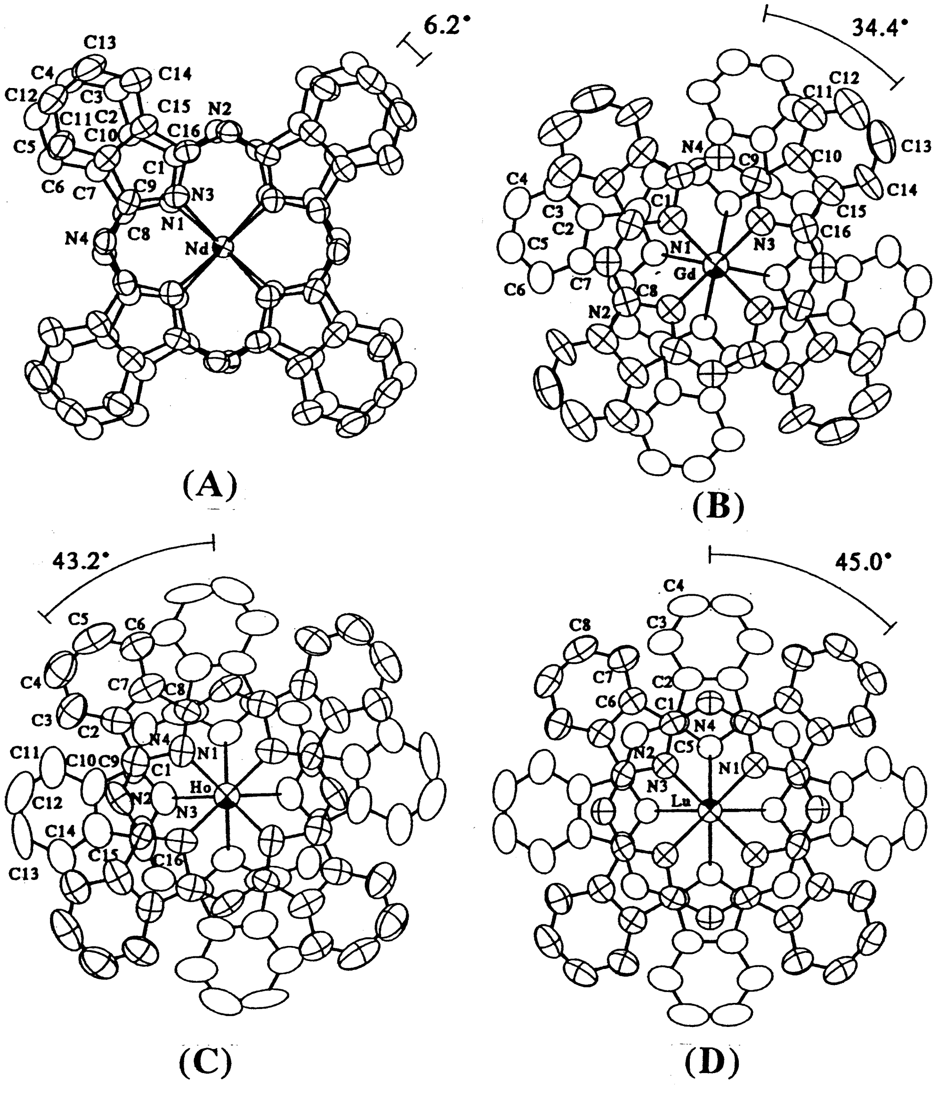


Fig. 1. Molecular structure of (A) $[Nd(III)Pc_2]^-$, (B) $[Gd(III)Pc_2]^-$, (C) $[Ho(III)Pc_2]^-$, and (D) $[Lu(III)Pc_2]^-$. The skew angles between the upper and lower Pc rings are shown (reprinted from [53] with permission of the authors).

d(III) ions (Table 3). The longest wavelength band was previously assigned as an intramolecular charge transfer from one Pc ligand to another radical-containing Pc ligand, assuming that the hole is localized on one of the Pc rings [58]. However, since it was found that the hole is delocalized over both Pc rings [59], this band is now being assigned to an electronic transition from a bonding orbital constructed from the HOMO of each Pc ring to a half-occupied antibonding orbital (intervalence, IV, band). Assignments of other bands have been the subject of intensive study. However, this appears to have been now settled by the accumulation of magnetic circular dichroism (MCD) data [60] and theoretical calculation [61] results, which support the experiments. According to these, Fig. 3 may best show the correct assignments. The 900 nm band corresponds to the RV ('red valence') transition in this Figure. The Q band corresponds to the $e_1(\pi^*) \leftarrow a_2(\pi)$, $e_3(\pi^*) \leftarrow b_1(\pi)$ excitation. The model in [61] predicts two further weak transitions of $e_g(\pi^*) \leftarrow a_{2u}(\pi)$ origin to the blue of the Q band (at ca. 570 nm, the charge resonance transition). However, this appears to be different from the above 500 nm band.

With respect to other spectroscopic information, a time-resolved EPR study [62] showed that the zero-field splitting of the sandwich dimer is smaller than that of the monomer, indicating a larger charge–resonance character for the dimer, while a magnetic susceptibility study on a series of lanthanoid (III) sandwiches showed that there is a strong magnetic interaction between the lanthanide f electrons and the Pc radical [63]. Both antiferro- and ferromagnetic ground states have been observed, depending on the symmetry and occupancy of the magnetic orbitals on the lanthanide ion. The excited-state properties of $Lu(Pc)_2$ in neutral radical, oxidized and reduced states in CH_2Cl_2-based solution have been

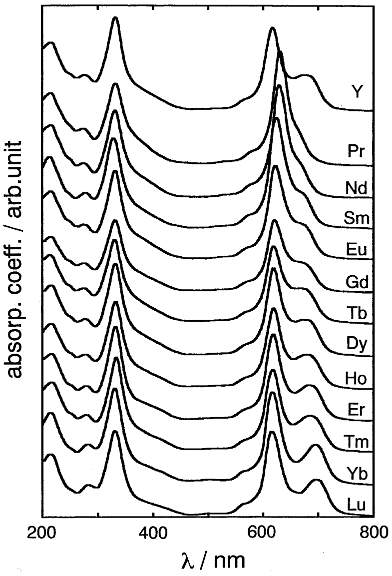


Fig. 2. Electronic absorption spectra of $[NBu_4][LanthanoidPc_2]$ in $CHCl_3$.

Table 3
Absorption data for neutral radical $M[Pc(OC_8H_{17})_8]_2$ ('green-form') (M = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm) in $CHCl_3$–EtOH (1:1) ([74]).

Cpd	M	λ_{max}							
(1)	La	343	374	513	630	699	900		2250
(3)	Pr	341	373	505	622	690	902		1950
(4)	Nd	340	373	503	620	688	905		1897
(5)	Sm	339	372	498	617	683	906		1730
(6)	Eu	338	372	495	616	681	907		1701
(7)	Gd	338	371	493	614	679	910	1421	1650
(8)	Tb	338	370	490	613	677	912	1435	1604
(9)	Dy	337	370	489	611	676	910	1430	1580
(10)	Y	335	369	486	610	675	915	1426	1580
(11)	Ho	337	370	488	610	674	910	1413	1564
(12)	Er	336	370	485	609	673	912	1414	1555
(13)	Tm	335	369	485	608	672	915	1416	1548

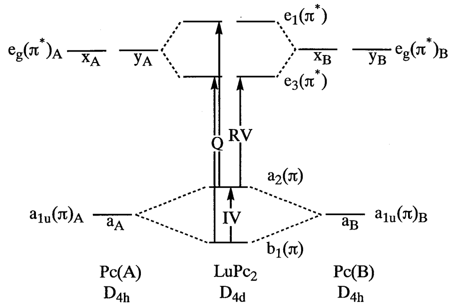


Fig. 3. Frontier MOs for the $Lu(III)Pc_2$ radical species, indicating ligand parentage and excitations assigned to the Q, RV (red valence), and IV (intervalence) bands (from [60]).

examined [64]. Upon excitation at either 354, 532, or 1064 nm, $Lu(Pc)_2^-$ deactivates through a low-lying doublet excited state of charge-transfer nature with a 60 ps lifetime. No evidence for charge hopping between the two Pc rings was observed. The lifetimes of the oxidized and reduced $Lu(Pc)_2$ were 60 and 36 ps, respectively.

The redox data of a series of tetrabutylammonium salts of lanthanide sandwiches in a single solvent were reported [65,66]. All the redox couples are Pc ligand-centered, those seen in the Pc monomer split into two couples, and the first and second reduction potentials do not differ from species to species while the first and second oxidation couples shift to more positive potential with increasing ionic radius of the Ln(III) ions (Fig. 4). The gradient of these oxidation potentials are more positive than for the octaethylporphyrin (OEP) Ln(III) sandwiches [67]. The potential difference between the first oxidation and reduction couples is 1.1–1.3 V.

Table 2
Absorption and MCD spectral data for $[Nbu_4]$ $[LnPc_2]$ ('blue-form') in $CHCl_3$

	Q band				Q′ band				
Ln	λ_{max}[a]	D_0	A_1/D_0	10^2B_0	λ_{max}	D_0	A_1/D_0	10^2B_0	$\Delta\varepsilon$
Pr	15 860	41.3	1.01	2.36	15 100	3.3	−0.14	−21.97	750
Nd	15 810	41.7	1.12	1.59	14 970	4.9	0.74	−11.68	850
Sm	15 910	44.8	1.08	1.42	14 880	11.5	0.94	−7.08	1020
Eu	15 970	37.1	1.23	1.77	14 870	13.3	1.11	−6.91	1100
Gd	16 010	28.5	1.55	2.32	14 860	12.0	1.40	−7.46	1150
Tb	16 070	29.1	1.47	1.39	14 830	15.7	1.31	−5.39	1250
Dy	16 100	31.5	1.44	1.78	14 740	17.1	1.11	−4.70	1350
Y	16 140	31.9	1.34	1.74	14 710	17.7	1.28	−4.86	1420
Ho	16 110	29.6	1.44	0.60	14 680	16.7	1.32	−4.96	1430
Er	16 170	33.0	1.14	1.03	14 640	18.5	1.06	−3.72	1530
Tm	16 180	32.3	1.26	0.66	14 570	17.9	1.28	−4.42	1620
Yb	16 220	37.1	1.17	0.96	14 530	21.8	1.13	−3.67	1690
Lu	16 320	32.5	1.43	2.06	14 510	18.1	1.42	−4.44	1810

[a] Energy of the band maxima. Units for the parameters λ_{max}, D_0, A_1, and B_0 are cm^{-1}, Debye, hDebye^2, and hDebye^2 per cm^{-1}, respectively.

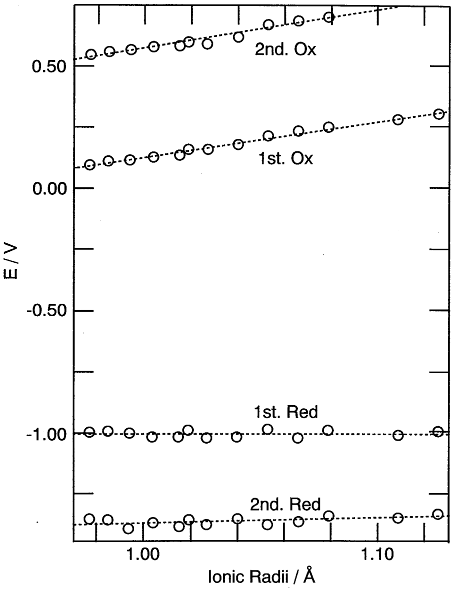


Fig. 4. Redox potentials of $[LnPc_2]^-$ (non-radical species) as a function of the ionic radii of tervalent lanthanides (redrawn from [65]).

3.1.3. Naphthalocyanines

There are two types of completely different Nc, depending on the starting naphthalonitrile. If 1,2-naphthalonitrile is used, the resultant Nc is called 1,2-Nc, while 2,3-dicyanonaphthalene gives 2,3-Nc [68]. Only a few papers have been published in the past [59,69–73], and no actinoid-containing Nc sandwiches have been reported. A series of tetra-*tert*-butylated 2,3-Nc Ln(III) sandwich dimers have been reported [71,73]. Similarly to the Pc series, both radical and reduced forms have been prepared. The main Q bands of the radical form lie between 765 and 790 nm, which is at longer wavelength than the Pc analogues [74] by ca. 90–100 nm. The 900 and 1100–1900 nm bands in the Pc series shift to ca. 1060–1085 nm and 1300–2200 nm, respectively, while the band with intermediate intensity lying in between the Q and Soret bands (ca. 460–520 nm for Pc series) appears at ca. 570–640 nm. The latter band shifts to longer wavelength while the other bands shift to shorter wavelength with decreasing Ln(III) ion radius, similarly to the Pc series. The band assignments appear to be the same as for the Pcs. In the reduced form, the Q band generally splits into two, but the relative intensity of the longer wavelength component of the split Q band appears smaller compared with the corresponding Pc system. The Q band of alkylthio-substituted 2,3-Nc differs from that of *tert*-butylated 2,3-Nc in shape, but the spectral shape is similar in other regions [71].

In the case of the 2,3-Nc dimer, the first oxidation couples in the monomer split into two, and as a result, one couple appears in the positive potential region while the other couple appears at a negative potential [73]. Accordingly, the meaning of the first oxidation and reduction is different from Pcs. The potential difference of the first oxidation and reduction in the normal sense is ca. 0.9–1.1 V, slightly smaller than in the Pc system, reflecting a larger π system.

The properties of 1,2-Nc sandwich dimers [70] are somehow closer to those of Pcs. The Q band does not shift to the red as much from that of Pcs, while the redox potentials are also close to Pcs. This was previously predicted by symmetry adapted perturbation theory and supported by molecular orbital (MO) calculations [75].

3.1.4. Pyrazinoporphyrazines

PyZ is a Pc analogue prepared from 2,3-dicyanopyrazine or its isoindoline derivative. Due to the electron-withdrawing property of the nitrogens in the pyrazine ring, macrocyclic formation is easier than for Pcs. However, because of this property, the sandwich dimers are unstable (low bond order between central metal and pyrrole nitrogens). Only two papers have been published on $Ln(PyZ)_2$. The non-radical form of $Lu(PyZ)_2$ was obtained similarly to $Lu(Pc)_2$ [76,76a]. The Q bands occurred at 681 and 573 nm, which are blue shifted by about 20 and 40–50 nm, respectively. The splitting of the Q band is more obvious than in the Pc systems, and the MCD spectrum showed dispersion type (Faraday *A* terms) curves corresponding to these bands, indicating that the Q1 state is orbitally degenerate. Compared with Pc systems, all the redox couples are shifted anodically by 0.4–0.7 V, thus indicating that this is a π acceptor molecule (accordingly, even the fourth reduction couple could be obtained). The potential difference between the first oxidation and -reduction is close to 1.3 V. $Yb(PyZ)_2$ was obtained by heating 2,3-dicyanopyrazine with $Yb(OAc)_3 \cdot 3H_2O$ at 170 °C for 5 h, and sublimation of the product [76b]. Y, Dy, Er, Gd, Nd and La complexes were also prepared in a similar manner. $Yb(PyZ)_2$ showed a single Q band at 680 nm in DMF, and when reduced by $Na_2S_2O_4$ this shifted to ca. 480 nm. It was concluded that the Q band shifts to shorter wavelength with decreasing radius of the central metal ion.

3.2. Heterodimers

The properties of heteroleptic sandwiches are not very different from homoleptic sandwiches when the two macrocycles belong to the same family. For example, when the two macrocycles are tetraphenylporphyrin (TPP) and ocataethylporphyrin (OEP), their properties are close to $Ln(TPP)_2$ or $Ln(OEP)_2$. In a similar manner, when the two macrocycles are Pc and alkylated Pc, the resultant $Ln(Pc)_2$ shows similar properties to the homoleptic $Ln(Pc)_2$. However, when the two macrocycles have different sizes of π system, their properties differ markedly from those of homoleptic dimers.

3.2.1. Phthalocyanine–porphyrin dimers

The first heteroleptic dimer of Pc and porphyrin (Por) was reported at the end of the 1980s as a cerium complex [77], but most of work has been done over the last 10 years [45,46]. Although a mixed condensation method using H_2Por, H_2Pc, and metal salt is possible [78], these compounds are often obtained by the raise-by-another-story method. Namely, for example, metallated porphyrin is reacted with H_2Pc, Na_2Pc, or Li_2Pc in a high-boiling solvent, such as chloronaphthalene or trichlorobenzene for several hours and the products are separated by column chromatography.

Due to the presence of a radical and counter macrocycle, the ^{1}H-NMR signals shift upfield in this type of double decker. For example, in U(OEP)(Pc) [79], the methyl protons appear at −2.80 ppm as a triplet and the methylene protons at −2.20 and −3.60 ppm, respectively, while the *meso*-protons of the OEP unit, which is generally detectable at 10–11 ppm, appear at −6.30 ppm.

The localization of a hole in the Pc moiety has been confirmed by several methods, the simplest of which is IR spectroscopy. For example, it was known previously that an OEP π radical absorbs between 1520 and 1570 cm^{-1} [80] while a Pc π radical displays this band at 1310 cm^{-1} [79]. When the IR spectrum of the oxidized Ln(TPP)(Pc) π radical was recorded, no vibration attributable to an OEP radical was recognized, but instead a very strong IR band was observed at 1317 cm^{-1}. Accordingly, it was concluded that the hole is mainly localized on the Pc ring [81]. The same conclusion was obtained from a significant (>15 cm^{-1}) upshift of a redox-sensitive Raman band at ca. 1500 cm^{-1} on going from the neutral radical Ln(TPP)(Pc) to the oxidized Ln(TPP)(Pc) π radical [82].

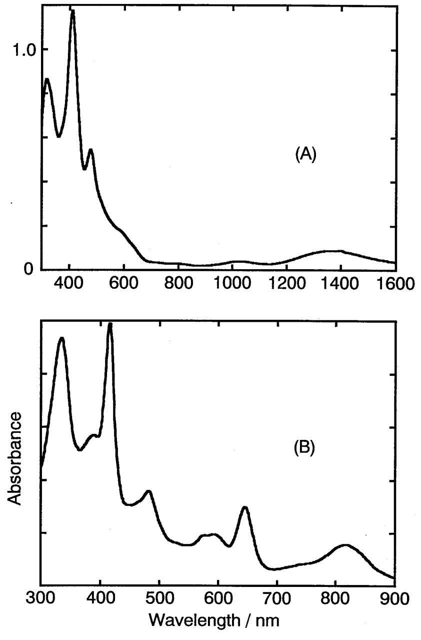


Fig. 5. (A) Electronic absorption spectra of the Eu(TPP)(Pc) radical species in CH_2Cl_2 (redrawn from [81]) and non-radical Li[Eu(T-PyP)(Pc)] in MeOH (redrawn from [78]) (TPyP: tetrapyridylporphynato).

X-ray crystallographic data were also collected for a few complexes [81,83]. These take a staggered conformation (twist angles of 45.7 and 37.1° are reported for Ln and Gd complexes, respectively), and one of the most marked features is that the metals are closer to the OEP plane than to the Pc plane by more than ca. 0.2 Å, plausibly because of the larger cavity of the OEP skeleton. Both the OEP and Pc ligands are domed, but the extent of doming of the OEP ring is much greater than that of the Pc ring.

The electronic absorption spectral features of radical and reduced non-radical forms are summarized in [81], with examples shown in Fig. 5(A and B). In the near-IR region of the radical species, a weak band is observed at around 960–1070 nm, depending on the compound, while another, slightly more intense, band appears at ca. 1600–1100 nm. These two bands may correspond to the 900 and 1100–1800 nm bands in $Ln(Pc)_2$ radical species, since they also disappear in the reduced form, as is observed for $Ln(Pc)_2$. Three intense peaks appear in the Soret band region (Fig. 5(A)). Of these, the peaks at ca. 325–330 nm and 395–415 nm are assigned to the Soret band of the Pc and OEP moieties, respectively. The assignment of the third band at ca. 470–485 nm has not been firmly established. With decreasing ionic radius, the band at ca. 325–330 nm shifts slightly to longer wavelength, the band at 960–1070 shifts markedly to longer wavelength, while the other bands move to shorter wavelength. Thus, although the Soret band of the Pc and porphyrin moieties appear at the positions of the respective monomeric species, π–π interactions are considered to be present, since there is a systematic shift of the absorption band with the ionic radius.

A subpicosecond time-resolved absorption study has been carried out on a Ce(TPP)(Pc) [84]. Following excitation, two relaxation processes, having time constants of ca. 1 and 40 ps, were observed. These processes were attributed to a relaxation of the excited state of the dimer to a low-lying charge-transfer state and a relaxation of the charge-transfer state back to the ground state, respectively.

Redox potentials are also collected for lanthanoid(III) complexes [81]. In general, two oxidation and two reduction couples are seen in the potential window. With decreasing ionic radius, the second oxidation potentials do not change, but the first oxidation and first and second reduction potentials shift cathodically, while the color of the solution changes dramatically. This behavior is different from that seen for $[NBu_4][Ln(Pc)_2]$, in that the second, radius-independent, reduction process in $[NBu_4][Ln(Pc)_2]$, which corresponds to the first reduction process in Ln(TPP)(Pc), is radius-dependent in Ln(TPP)(Pc).

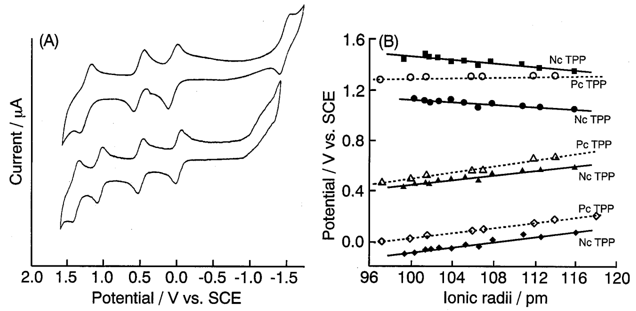


Fig. 7. (A) Cyclic voltammograms of Gd(TPP)(Pc) (top) and Sm(TPP)(Nc) (bottom) in CH_2Cl_2 containing 0.1 M NBu_4PF_6 (replotted from [81,85]). (B) Redox potentials of Lanthanoid(TPP)(Nc) (solid lines) and Lanthanoid(TPP)(Pc) (broken lines) as a function of the ionic radii of the lanthanoid(III) ions (collected from [81,85]).

3.2.2. *Naphthalocyanine–porphyrin dimers*

In this type of compound, the number of benzene units in the constituting monomers differs by eight. These compounds have been obtained by refluxing an *n*-octanol solution of metal-free porphyrin, naphthalonitrile, and lanthanide metal salt in the presence of DBU overnight under nitrogen, and subsequent chromatography [85]. In the IR spectra of a series of compounds, two bands were observed at ca.1320–1325 and 1520–1525 cm^{-1}, which are diagnostic for 2,3-Nc and a Por π radical monoanion, respectively. Accordingly, the coexistence of these two bands was taken to suggest that a hole or unpaired electron resides on a delocalised orbital over the two ligands.

X-ray data were collected for Eu(OEP)(2,3-Nc) [86]. The two macrocycles form a twist angle of 44.88°, and are domed outwards, the extent, of which is larger for the OEP ring. The Eu atom lies closer to the OEP ring because of its larger central cavity size, by ca. 0.24 Å. In this molecule, the inner benzene and outer benzene of Nc are different (the inner benzene is more ‘compressed’ than the outer benzene), and the naphthalene moiety is bent.

The absorption and MCD spectra of reduced, neutral radical, and oxidized forms are shown in Fig. 6. The Q band region of the radical form has many structures and is more complex than the corresponding Eu(Por)(Pc) complexes (Fig. 5). Although assignment of the bands has not been made in detail, the peaks at ca. 325–330 and 400 nm may be the Soret band of the Nc and OEP moieties, respectively. In the Q band region, the peak at ca. 600 nm appears to correspond to the main Q band, judging also from the size of the MCD spectrum. Absorption spectroscopic data for a series of Ln(TPP)(Nc) radical forms are collected in [85]. In these cases, intense bands occur at 1025–1150, 635–612 (Q band), 424–414, and 323–330 nm. With decreasing ionic radius, the Q band shifts to shorter wavelength, the near-IR band moves markedly to longer wavelength, while the Soret band does not shift systematically. Compared with the spectra of Ln(TPP)(Pc) complexes [81], the position of the Soret band is similar, that of the Q band is at ca. 140–150 nm to longer wavelength, and that of the shortest-wavelength near-IR bands is ca. 100–400 nm to shorter wavelength. In addition, interestingly, the shift of the shortest-wavelength near-IR bands is opposite between Ln(TPP)(Pc) and Ln(TPP)(Nc). Namely, with decreasing ionic radius, the shortest-wavelength near-IR bands shift to shorter wavelength for Ln(TPP)(Pc) [81], but to longer wavelength for Ln(TPP)(Nc) [85].

Redox data are collected in [85], where five couples were detected for each compound, but only four couples were tabulated, since the most negative couple was close to the solvent limit. In the case of Ln(TPP)(Pc) [81], the two most positive couples in Ln(TPP)(Nc) [84] appear as a single redox couple. The first reduction and oxidation couples occur at ca. 0.05 to −0.1 and 0.55–0.42 V,

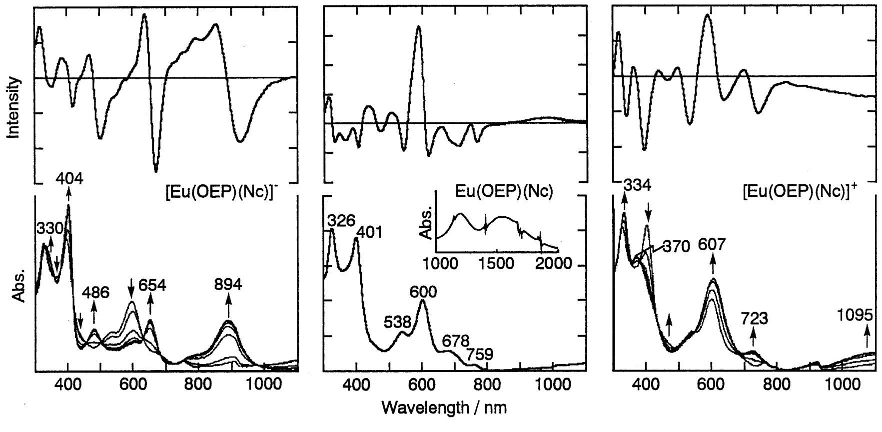


Fig. 6. Electronic absorption (bottom) and MCD spectra (top) of reduced, neutral radical, and oxidized forms of Eu(OEP)(Nc) (from [86]). The spectrum of the neutral species was collected in $CHCl_3$, while other species were generated and recorded in *o*-dichlorobenzene containing 0.1 M TBAP.

respectively, are ca. 0.5 and 0.2–0.4 V to more cathodic potential than the corresponding Ln(TPP)(Pc) [81], and shift to more cathodic potential with decreasing ionic radius (Fig. 7).

3.2.3. *Phthalocyanine–naphthalocyanine dimers*

Four papers have been published on the compound in this category [59,61,69,87]. Na_2Nc and LuPc(OAc) were refluxed in chloronaphthalene and the desired Lu(Pc)(Nc) radical form was separated using alumina chromatography. Similarly to $Ln(Pc)_2$ and $Ln(Nc)_2$ radical species, the absorption band appeared in the UV–vis to near-IR region. In the Q and near-IR band regions, the bands of Lu(Pc)(Nc) appeared in-between those of $Ln(Pc)_2$ and $Ln(Nc)_2$ radical species, confirming that a hole is delocalized over the Pc and Nc ligands. The lowest three bands of the $Ln(Pc)_2$ and $Ln(Nc)_2$ radical species are B_1, E_1, and E_1, respectively (for configuration and other details, see [61]). It was found that the Lu(Pc)(Nc) radical form has a hole which occupies the Nc ring more than the Pc ring, and that the population shifts toward Pc in the $^2A_2$ excited states.

3.3. *Homo- and heteroleptic trimers*

3.3.1. *Phthalocyanine trimers*

Although not well characterized, the first lanthanoid Pc trimer was reported in 1986 [88]. The first well-characterized trimers in this category appeared much later, in 1993 as $Yb_2(Pc)_3$ and $Dy_2(Pc)_3$ [89]. In the preparation, alkylated H_2Pc and lanthanoid salts in a molar ratio of 4:1 were refluxed in octanol for 4 h, and the separation was carried out using both adsorption and gel-permeation chromatography. In the cyclic voltammogram, four quasi-reversible one-electron oxidation and three quasi-reversible reduction couples were observed. By conducting spectroelectrochemistry, they succeeded in recording the spectra of four oxidation states. The neutral species displayed small and intense Q band peaks at ca. 635–645 and 695–710 nm, respectively, while a single Soret band appeared at ca. 360–365 nm. Theoretical interpretation of neutral [90] and oxidized [91] $Lu_2(Pc)_3$ has been attempted. The most intense band in the Q band region of the neutral species was assigned to an excited state of mainly exciton coupling character. The second intense band, which lies at longer wavelength to the most intense band could be assigned to a charge resonance state between the two outermost Pcs, which gains spectral intensity from the exciton component. The near-IR bands found by the authors of [90] were also characterized as combinations of excitations from the highest occupied localized orbitals (LOs) to the lowest unoccupied LOs. In the MO treatment, the leading configurations of the states corresponding to the most intense (E_u state) and the second intense Q bands (E_u state) are LUMO-third HOMO and second LUMO-second HOMO, respectively (see Fig. 8). The near-IR bands appear theoretically when the two outer Pc rings rotate in the opposite direction.

The first oxidation product, $[Lu_2(Pc)_3]^+$, showed a relatively intense band in the near-IR region (2150 nm), which was assigned to the LUMO-to-SOMO (singly occupied orbital) transition. This band has a transition moment perpendicular to the Pc planes. In addition to a single Q band, a characteristic band for Pc π radicals was seen between the Q and Soret band (Fig. 9(a); surprisingly, a negative MCD Faraday *A*-term was observed corresponding to this band!). The second oxidation product, $[Lu_2(Pc)_3]^{2+}$, displayed an intense

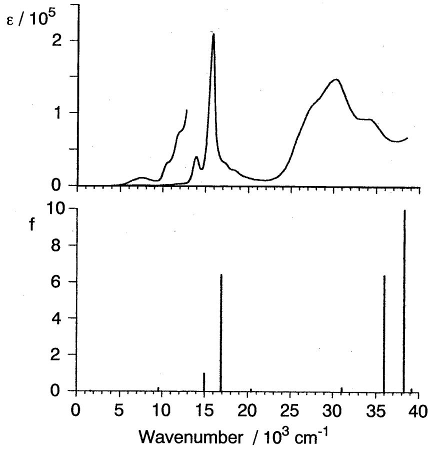


Fig. 8. Electronic absorption spectrum of (Pc)Lu(crowned Pc)Lu(Pc) in $CHCl_3$ (top), and calculated excitation energies and oscillator strengths (bottom) of $[Lu_2(Pc)_3]$ (redrawn from [90b]).

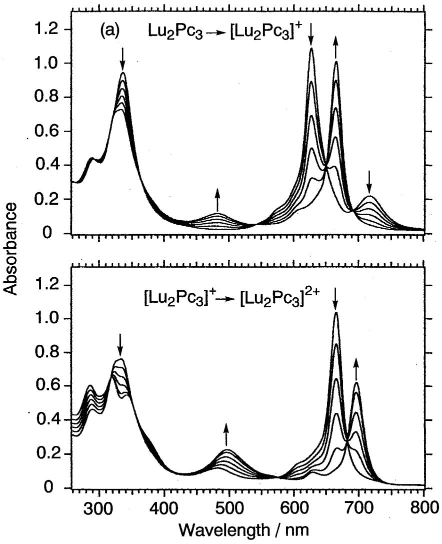


Fig. 9. Electronic absorption spectra for (a) the oxidation of $Lu_2(Pc)_3$ to $[Lu_2(Pc)_3]^+$ and (b) the oxidation of $[Lu_2(Pc)_3]^+$ to $[Lu_2(Pc)_3]^{2+}$ in CH_2Cl_2 by addition of phenoxathiin hexachloroantimonate solution in the same solvent (redrawn from [91b]).

band (at 1560 nm) with two distinct vibronic bands in the near-IR region. Compared with the spectra of $[Lu_2(Pc)_3]^+$, the Q band shifted to longer wavelength, while the radical band also shifted to the red but with increasing intensity (Fig. 9(b)).

Recently, soluble, well-characterized $La_2(Pc)_3$ and $Lu_2(Pc)_3$ complexes have been reported [92], where the assignment of the ^{1}H-NMR has been properly carried out. It was found that both alkyl and aromatic protons on the outer Pc ring appear at higher fields. These trimers show single Q bands in benzene similarly to normal monomeric Pcs, but the amount of structure in the Q_{0-1} vibrational region is lower.

3.3.2. Naphthalocyanine trimers

Only $Lu_2(1,2\text{-}Nc)_3$ is known to date [93]. $Li_2(1,2\text{-}Nc)$ was refluxed with $Lu(OAc)_2$ in chloronaphthalene overnight, and from the product, $Lu_2(1,2\text{-}Nc)_3$ was isolated chromatographycally, as a mixture of many isomers. Its absorption spectrum is close to that of $Lu_2(Pc)_3$, just as the spectrum of monomeric Mt(1,2-Nc) is close to that of MtPc rather than Mt(2,3-Nc) [68,75]. In voltammetry carried out in benzonitrile, five reduction couples and four oxidation couples were detected. The potential difference between the first oxidation and reduction was found to change from 1.64 to 1.12 V and further to 0.86 V on going from Lu(1,2-Nc)(OAc) to $Lu(1,2\text{-}Nc)_2$ and further to $Lu_2(1,2\text{-}Nc)_3$.

3.3.3. Phthalocyanine–porphyrin mixed trimers

In this case, four combinations of porphyrins (Por) and Pcs are possible, three of which have already been reported: Por–Pc–Por [94], Pc–Pc–Por [94b,95], and Pc–Por–Pc [94a,95b]. In synthesizing these compounds, MtPor was reacted with Li_2Pc in trichlorobenzene under an inert atmosphere, and the desired compounds were separated from the reaction mixture by chromatography and crystallization. These compounds show characteristic absorption bands dependent on the composition and order of the Pors and Pcs, since most of the transitions in the usual absorption spectral region are π–π^* type. Fig. 10 shows an example of Por–Pc–Pc and Por–Pc–Por type spectra [94b].

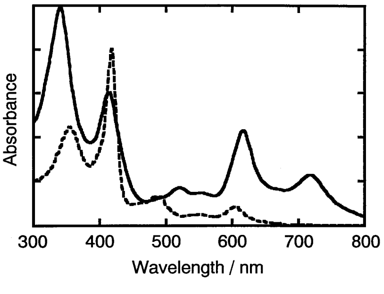


Fig. 10. Electronic absorption spectra of $Sm_2(TPP)_2(Pc)$ (broken line) and $Sm_2(TPP)(Pc)_2$ (solid line) in CH_2Cl_2 (redrawn from [94b]).

X-ray data [94a,94c,95a] indicate that the mean planes of the three rings are precisely parallel and exactly perpendicular to the Mt–Mt axis. The outer Por and Pc rings bend outwards.

4. Yttrium, zirconium, hafnium, tin, indium, titanium, mercury and bismuth sandwich dimers and oligomers

4.1. Tetraazaporphyrin dimer

Alkylthio-substituted $Zr(TAP)_2$ is the only compound [96] of this type so far reported. H_2TAP and $Zr(NEt_2)_4$ were dissolved in toluene–dioxane (4:1 v/v), refluxed for only 10 min, and the product purified by chromatography. In the ^{1}H-NMR spectrum, the $-CH_2-$ protons appeared at 4.00 and 4.21 ppm as double-quartets, while the CH_3- protons were seen at 1.46 ppm as a triplet. In the cyclic voltammogram, performed in CH_2Cl_2, an oxidation and two reduction couples were detected at 0.89, −0.33, and −0.65 V, respectively, versus Ag–AgCl. These values were compared with those of the corresponding Zr octaethylporphyrin dimer (0.06, −1.40, and −1.70 V, respectively), in the same solvent. The Q and Soret bands appear at around 675 and 385 nm, respectively, in acetonitrile.

4.2. Phthalocyanine dimers

$Y(Pc)_2$ was first synthesized from phthalonitrile and $Y(OAc)_3$ by heating at ca. 300 °C [97] (lower temperatures lead to monomeric YPc [98]), but it was later prepared by boiling the above two materials in 1-hexanol for 3 h in the presence of DBU [99]. The crystals of $[Y(Pc)_2]\cdot CH_2Cl_2$ were isostructural with those of $[Lu(Pc)_2\cdot CH_2Cl_2]$ [45]. The twist angle between the two Pc planes is 45°, the separation between two N_4(isoindole) planes is 2.760 Å, and the two Pc planes have a domed structure (the extent of which is, however, different). Magnetic properties down to 0.8 K of solvated and non-solvated forms were discussed from measurements of magnetic susceptibility. Red–brown poly-bromide, $[Y(Pc^-)_2]Br_x$ was also prepared [100]. Redox couples were observed at 0.47, 0.09, −1.04 and −1.25 V versus Ag–AgCl in CH_2Cl_2 containing 0.1 M TBAP. This compound shows absorption peaks at 6.50, 7.11, 10.95, 15.08, 21.81, and 31.26 kcm^{-1} in CH_2Cl_2, similar to the radical forms of $Ln(Pc)_2$ described above in Section 3.1.2. The neutral $Y(Pc)_2$ shows a two-peak Q band at 14.47 and 16.05 kcm^{-1} and a Soret band at 30.02 kcm^{-1}.

Unsubstituted $Zr(Pc)_2$ and $Hf(Pc)_2$ were synthesized by melting phthalonitrile and the respective metal trichlorides at 310–315 °C for 4–5 h [101,101a], while the *tert*-butylated compounds were obtained by reacting only at 220 °C for 2–3 h [101b]. These compounds correspond to the reduced form of lanthanoid sandwich complexes, so that the absorption spectroscopic behavior is very similar. *Tert*-butylated Hf(Pc)$_2$ shows absorption peaks at 332, 574, and 810 nm, and Zr(Pc)$_2$ at 336, 576, and 812 nm in *o*-dichlorobenzene. The former gave redox couples at -0.97, -0.70, 0.44, and 1.00 V, and the latter at -1.11, -0.74, 0.40, and 0.95 V versus Ag–AgCl in *o*-dichlorobenzene containing 0.2 M TBAP. They both show reversible electrochromic behavior. Zr(Pc)$_2$ prepared from isoindolediimine and ZrCl$_4$ in quinoline under an N$_2$ atmosphere for 2 h was crystallized, but its detailed structure was not described [102]. It has a staggered conformation as in the case of most of the lanthanoid sandwich complexes [45].

Linstead observed as early as 1936 that two Pc rings formed a sandwich-type compound with a tin atom in the center [103]. An X-ray study on Sn(Pc)$_2$, which was prepared from SnPcCl$_2$ and Na$_2$Pc in refluxing 1-chloronaphthalene for 90 min, was reported [104]. The cores of the Pc moieties are separated from each other by 2.70 ± 0.04 Å, and are rotated by 42° with respect to each other. Each Pc ring system bends away from the other, resulting in saucer-shaped ring. The electronic absorption spectrum is similar to the other Mt(IV)(Pc)$_2$ derivatives. Corresponding to two Q-band peaks at 699 and 671 nm in toluene, Faraday *A*-terms were detected in the MCD spectrum [105]. The spectra were interpreted with the aid of MO calculations. It was found that exciton coupling in the Pc dimer of a face-to-face stacking conformation yields a remarkable splitting of the Q band and also an increase in the total intensity of the Soret band. The lowest charge-resonance excitation was predicted at a lower energy than that of the lowest excited singlet state observed as the Q band. By irradiating at ca. 640 nm, the lowest lying triplet state, with a half-life of ca. 40 μs, was observed at ca. 500 nm [106].

In(Pc)$_2$ was prepared from InCl$_3$ and phthalonitrile at 140 °C in the presence of excess CH$_3$OMe, and isolated as (Bu$_4$N)In(Pc)$_2$ [100]. It shows five redox couples at 0.49, 0.32, -0.07, -1.08, and -1.37 V versus Ag–AgCl in CH$_2$Cl$_2$ containing 0.1 M TBAP. This compound has absorption peaks at 13.65, 16.34, and 29.79 kcm^{-1} in CH$_2$Cl$_2$. IR and RR spectra are reported in [100].

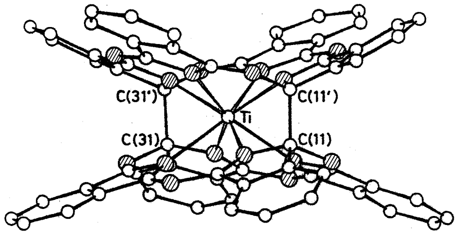


Fig. 11. Side view of TiPc stapled by two interring C–C σ bonds (redrawn from [107]). Hatched circles are nitrogen atoms.

Ti(Pc)$_2$ is an unique example in this group [107]. Two Pc planes are 'stapled' by two carbon-carbon σ bonds, and accordingly in the resultant compounds, the Pc chromophore no longer exists (no absorption above 500 nm). TiPcCl$_2$ and Na$_2$Pc were heated under vacuum at 150 °C for 3 h, and then in chloronaphthalene at 190 °C for 90 min. The desired Ti(Pc)$_2$ was finally purified by sublimation of the product. The two Pc units, rotated by 45° with respect to each other, were stapled by two interring C–C σ bonds of length 1.556 and 1.575 Å (Fig. 11). The average N$_4$ plane distance is 2.32 Å which is much shorter than that found in unstapled complexes.

Bi(Pc)$_2$ are known in two forms; Trivalent (Bu$_4$N)[Bi(Pc)$_2$] [108] and [Bi(Pc)$_2$]I$_{1.5}$ [109]. The former was first synthesized as K[Bi(Pc)$_2$] from phthalonitrile and BiO(NO$_3$) in the presence of MeOK, and its K was changed during the recrystalization process to (Bu$_4$N). Anodic oxidation of (Bu$_4$N)[Bi(Pc)$_2$] produced crystals of Bi(Pc)$_2$·CH$_2$Cl$_2$. The Bi(III) ion is eightfold coordinated by the $2 \times$ N$_4$ atoms of the slightly distorted Pc ligands in a square antiprismastic manner. The separation between the two N$_4$ planes is 2.98 Å. The latter [Bi(Pc)$_2$]I$_{1.5}$ was prepared by making a pellet from Bi powder, phthalonitrile, and iodine (in a portion 1:4:2), and heating this in an evacuated ampoule at 200 °C for 1 day [109]. The two Pc groups in the Bi(Pc)$_2$ unit are staggered at an angle of 39.4° and are 3.275 Å apart (this is the largest distance for this type of complex). The Bi(III) ion, eight-coordinated by N(isoindole) atoms, does not lie between the Pc rings at the center, since one Pc ring is Pc(2−) while the other is Pc(−).

4.3. Tetraazaporphyrin–porphyrin dimer

A Zr sandwich dimer of OEP and octaethylTAP was reported in 1997 [110]. Zr(OEP)(OTf)$_2$ converted from Zr(OEP)Cl$_2$ was combined with octaethylated Li$_2$TAP under reflux for 36 h in toluene. In the ^{1}H-NMR spectrum in C$_6$D$_6$, all signals of OEP appeared at higher field compared with the monomeric OEP, but since the shift of the *meso*-protons was much smaller than in the corresponding Zr(OEP)$_2$, the authors concluded that the ring current of TAP is presumably smaller than OEP. Cyclic voltammetry results indicated that Zr(TAP)$_2$ is more difficult to oxidize by about 600 mV, and easier to reduce by about 600 mV, compared with Zr(OEP)$_2$, while the mixed sandwich Zr(OEP)(TAP) exhibits intermediate redox potentials. The potential differences between the first oxidation and reduction couples were 1.66, 1.52, and 1.62 V respectively, in the order Zr(OEP)$_2$, Zr(OEP)(TAP), and Zr(TAP)$_2$. Zr(OEP)(TAP) showed absorption peaks at 336 (Soret of TAP), 378 (Soret of OEP), 430 (Q″), 598 (Q), and 922 (Q′) nm in CH$_2$Cl$_2$.

4.4. Oligomers

Two trimers, $In_2(Pc)_3$ [111] and $Bi_2(Pc)_3$ [112] are known to date. $In_2(Pc)_3$ was obtained by reacting $InSn_4$ and phthalonitrile in 1:2 weight proportion in an evacuated glass ampoule at 207 °C for 2 days. The two outer Pc planes are parallel to each other, while the central and outer Pc rings are rotated by about 37.5°. The mean intramolecular distance between the Pc planes is 2.954 Å, and the angle of inclination of the central Pc plane to the outer Pc plane is 5.2°. Two indium atoms are located between the Pc planes and have six-coordinate symmetry. $Bi_2(Pc)_3$ was prepared by heating pellets from Bi_2Se_3 and phthalonitrile in a molar ratio of 1:12 in a sealed and evacuated glass ampoule at 220 °C for 1 day. This molecule is centrosymmetric with the bismuth atoms located closer to the outer Pc rings than to the central Pc ring. Each Bi(III) ion is connected by four N(isoindole) atoms to the outer Pc rings and by four N(isoindole) to the central Pc ring, with average distances of 2.333 and 2.747 Å, respectively. The central Pc is rotated by 36.4° with respect to the outer Pcs. The average distance for α-pyrrole carbon atoms between neighboring Pc planes is 3.24 Å (3.05 Å for $In_2(Pc)_3$).

An oligomeric mercury-bridged phthalocyanine was reported in 1992 [113]. A mixture of oligomers was obtained by the addition of H_2Pc to a stirred THF solution of $Hg(OAc)_2$ or CH_3HgOAc at 23 °C, followed by refluxing for 4 h. Compared with the Q band of typical HgPc monomers at 721 nm, an oligomer (11 mer) showed a Q band at 618 nm without vibrational structure in THF.

5. Metal–metal directly linked dimers

A few metal–metal directly linked dimers have been reported over the last few years mostly from Homborg's group. $[Ir(Pc)]_2$ was prepared in two ways. In one method, IrPcCl was heated with $NaBH_4$ in boiling THF for 12 h and poured into water, to give the desired dimer [114,114a]. In another method, IrPcCl was thermally decomposed in an inert, high-boiling solvent such as 1-chloronaphthalene, or under reduced pressure at temperatures lower than 350 °C [114b]. Crystals for X-ray analysis were obtained as $[Ir(Pc)(Py)]_2$. The Ir–Ir distance is 2.707 Å, the Ir atoms are virtually in the center of the Pc ring, and the two Pc ligands are staggered by 43°. In spite of the short interplanar distance (center-to-center = 2.827 Å), the Pc ligands are only slightly distorted; one wagging, one doming. The N(Py)–Ir–Ir–N(Py) configuration is almost linear (177.2°). Four quasi-reversible redox couples were detected at 0.82, 0.55, −0.82, and −1.34 V versus Ag–AgCl in CH_2Cl_2 containing 10% pyridine and 0.1 M TBAP. In CH_2Cl_2, two Q bands of equal intensity were seen at 14970 and 17300 cm^{-1}, while a Soret band was observed at 30000 cm^{-1}. The Ir–Ir stretching vibration at 135 cm^{-1} was selectively enhanced in the RR spectrum.

$[Rh(Pc)]_2$ was prepared by keeping $H[RhPcCl_2]$ or $H[RhPcBr_2]$ under reduced pressure at 300 °C for 1 day, or refluxing them in 1-chloronaphthalene for 12 h [115]. Diamagnetic $[Rh(Pc)(Py)]_2$ suitable for X-ray analysis was obtained. The Rh–Rh distance is 2.741 Å, and the Rh atoms are virtually in the Pc center. The Pc ligands are staggered, with a skew angle of 42°. The center-to-center interplanar distance is 2.89 Å. Two quasi-reversible anodic and four cathodic processes were observed at 0.81, 0.55, −0.33, −0.50, −0.75, and −1.33 V versus Ag–AgCl in pyridine containing 0.1 M TBAP. Split Q bands of almost comparable intensity were observed at 15 440 and 16 890 cm^{-1} in pyridine. The Rh–Rh stretching vibration at 176 cm^{-1} was selectively enhanced in the RR spectrum.

Blue diamagnetic $[MoPc]_2$ was synthesized by the reduction of Mo=OPc with boiling triphenylphosphine [116]. The Mo–Mo stretching vibration was observed in the RR spectrum at 374 cm^{-1}. The complex is chemically inert and dissolves in concentrated H_2SO_4 without decomposition. In H_2SO_4, absorption peaks were detected at 12 000, 22 100, 31 600, 39 300 and 43 400 cm^{-1} (however, another set of values are reported in the same paper at 13 700, 24 600, 33 600 and 35 400 cm^{-1}).

Although X-ray analysis was not performed on single crystals, a RuPc obtained by thermal treatment (330 °C, 10^{-2} mmHg) of $[Ru(Pc)(DMSO)_2]\cdot 2DMSO$ appears to be $(RuPc)_2$, with a short Ru(II)-Ru(II) contact (2.40 Å) [117]. This compound, stable in air as a solid, is paramagnetic, with a r.t. magnetic moment of 2.54 μ_B, which is strongly temperature dependent in the range of 300–306 K.

$(SiPc)_2$ which was obtained using isoindolediimine and Cl_3–Si–Si–Cl_3 as a template is believed to be a Si–Si directly-linked dimer [118], although X-ray crystals suitable for analysis have not been obtained. Mass, gel-permeation, and electrochemical data support the structure. Interestingly, these dimers show a very strong

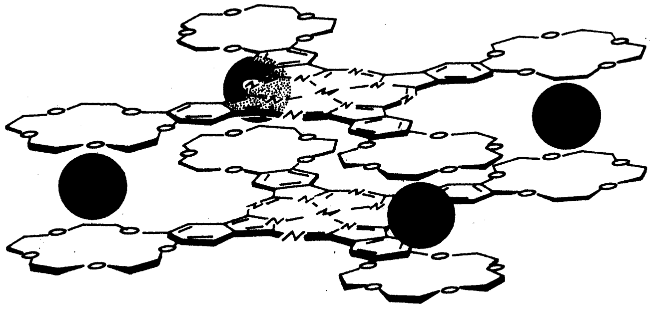


Fig. 12. Proposed structure for the cation-induced dimer of crowned MtPc. Solid circles indicate cations such as K^+ and Ca^{2+} (redrawn from [120a]).

electronic absorption band at ca. 445 nm which has been assigned to charge-transfer transitions from a Si–Si σ orbital to ligands [118b].

6. Cofacially assembled homo- and heterodimers

6.1. Crown phthalocyanines

CuPc substituted by four 15-crown-5 was published independently by three groups at approximately the same time [119], and other metalloPcs were reported subsequently [120]. By the addition of cations such as K^+ and Ca^{2+}, these Pcs form cofacial dimers via a two-step-three stage process. Cofacial structures (Fig. 12) were supported by many types of spectroscopy: ^{1}H-NMR, electronic absorption, MCD [121], EPR of the copper complex, and fluorescence emission of the Zn complex. In the ^{1}H-NMR spectrum, for example, the pyrrole proton signals shifted from −3.41 ppm for the monomer to −8.09 ppm, while analysis of the triplet EPR signal of the copper complex suggested a Cu–Cu distance of 4.1 Å. The Q band shifted to shorter wavelength, as expected from the exciton model [122]. Time-resolved EPR revealed the charge–resonance contribution in the excited triplet states to be 7 and 9.3% for the metal-free and Zn complexes, respectively [123]. Pc analogues containing three 15-crown-5 U have also been reported, and C_{2v} type cofacial dimers of these have been examined spectroscopically [124]. In particular, interestingly, it was found that the absorption spectra of the cofacial dimers do not reflect the molecular symmetry of the constituting monomers.

6.2. Porphyrin–phthalocyanine dimers

Cationic (anionic) porphyrins often form 1:1 cofacial complexes with anionic (cationic) Pcs. A 1:1 cofacial arrangement was generally confirmed by ^{1}H-NMR and Jobs continuous variation method [125]. The interaction depends significantly on the central metal, symmetry of the molecule, and solvent [126]. An example of a very strong interaction is reported for H_2- and ZnPors plus H_2Pcs in [126c], where the absorption spectroscopic shape differs greatly from the sum of the two monomer spectra. The results were interpreted as the formation of charge-separated $(Por)^-(Pc)^+$ species. Generation of transient charge carriers in LB films of these heterodimers has been discussed in [126d,126e].

7. Covalently linked cofacial dimers

1,8-Naphthalene- and -anthracene-pillared Pc dimers (Fig. 13) have been prepared from precursors obtained by the coupling of 4-iodophthalonitrile and 1,8-diiodo-

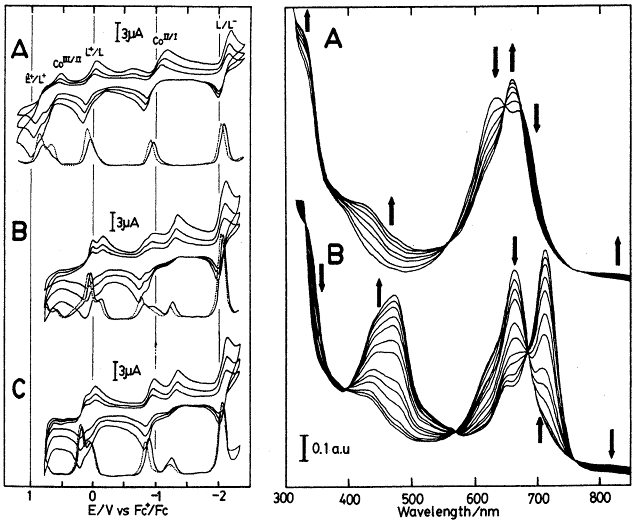
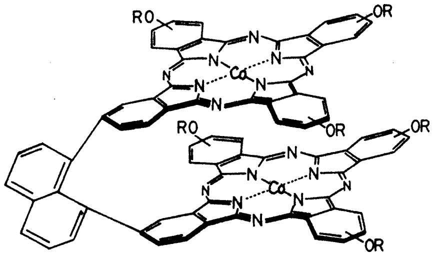
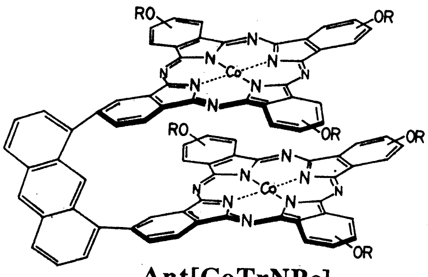


Fig. 14. (Left) Cyclic and differential pulse voltammograms of (A) cobalt neopentoxyPc monomer, (B) Nap$[CoTrNPc]_2$ and (C) Ant$[CoTrNPc]_2$ in *o*-dichlorobenzene containing 0.1 M TBAP. Assignments of redox couples are shown for cobalt neopentoxyPc. (Right) Development of the electronic absorption spectra of Ant$[CoTrNPc]_2$ in *o*-dichlorobenzene with time, showing the formation of (A) the mixed-valence $[Co(II)TrNPcCo(I)TrNPc]^-$ and (B) the doubly reduced $[Co(I)TrNPcCo(I)TrNPc]^{2-}$ species, obtained by reduction at potentials between −0.8 and −1.2 V, and −1.3 and −1.6 V, respectively (redrawn from [129]).



Nap[CoTrNPc]$_2$



Ant[CoTrNPc]$_2$

Fig. 13. '*Syn*' structures of naphthalene- and anthracene-linked cofacial binuclear Pcs (redrawn from [129]). Nap$[CoTrNPc]_2$ and Ant$[CoTrNPc]_2$ were used in the measurements of Fig. 14.

naphthalene or 1,8-dichloroanthracene, respectively [127].

A strong interaction between the halves of the molecule was detected in electronic absorption and MCD spectroscopy [128] and electrochemistry [129]. Due to the exciton coupling and a mixture of many *syn* and *anti* isomers, the Q bands were much broader than in the monomers, and the EPR spectra of the Co(I) species in the presence of 1-methylimidazole and the Cu complexes were composed of monomeric metal spectra and interacting metal–metal spectra. In the cyclic voltammetry, the first oxidation couple of the ligand split by about 250–330 mV, while two-electron ligand reductions occurred at approximately the same potential as those of monomers. In the case of the Co species, both the Co(II/I) and Co(III/II) couples split by ca. 250–480 mV, depending on the solvent (Fig. 14, left). Since the 1,8-anthracene linked CoPor dimer did not show such a splitting of redox couples [130], it was suggested that electron cloud overlap is important for strong interaction. Since some redox couples seen as single redox couples in monomeric species split into two couples, the spectra of mixed valence species have been recorded. For example, in the case of Co(I)–Co(II) mixed valence species (Fig. 14, right), it was concluded from the magnitude of spectroscopic change that a negative charge was delocalized over the two Pc rings [129]. In addition, it was found that when surface-adsorbed, these species acted as electrocatalysts for the reduction of dioxygen more effectively than the corresponding monomeric CoPcs.

8. Planar homo- and heterodimers and homotrimers

8.1. Homodimers sharing a common aromatic ring

Planar homodimers of Pc sharing benzene (Fig. 15(A)) [131–135] or naphthalene [135] have been reported. In synthesizing the former compounds, 1,2,4,5-tetracyanobenzene (or its isoindoline analogue) was reacted with excess phthalonitrile (or isoindoline) analogues, and the dimers were separated by chromatography. The yield of the metal-free dimer was ca. 6%, and several kinds of metal were inserted. The compounds showed broad Q bands extending from ca. 500 to 1000 nm, which were explained by excitonic interaction. The first oxidation and the first and second reduction couples observed in the constituting Pc monomer split into two couples each, and comproportionation data for each couple were collected [132]. Although the quantum yields (ϕ) of the S1 emission of H_4- and Zn_2-dimers were smaller than those of the monomers, the yields of S2 emission were larger than the corresponding monomers. The reason for this has not been elucidated to date. Simultaneous band deconvolution of the electronic absorption and MCD spectra succeeded in identifying the split Q and Soret band positions and intensity. In the MO calculations, the dimer MOs were expressed as a linear combination of monomers, supporting the electrochemical results. In addition, the results of the MO calculations reproduced experimental absorption and MCD spectra almost perfectly [133]. LB film behavior [132] and liquid crystalline behavior [134] have also been examined.

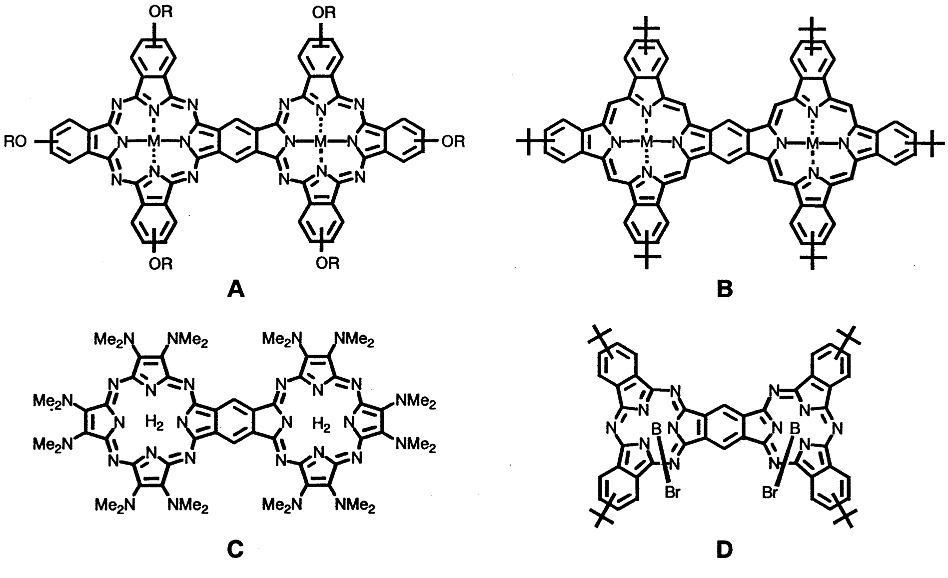


Fig. 15. Structures of planar (A) Pc, (B) tetrabenzoporphyrin, (C) TAP, and (D) SubPc sharing a common benzene ring, from [131], [136–138], respectively.

Planar tetrabenzoporphyrin dimers sharing a common benzene ring are also known (Fig. 15(B)) [136]. In this case, the interaction between the halves of the units appears smaller than in the Pc analogue, since the spectroscopic changes from the monomer are not marked, while the splitting of the redox couples is much less.

Hoffman's group recently reported the synthesis, spectra and redox potentials of a planar dimer of TAP substituted with 12 dimethylamino groups (Fig. 15(C)) [137]. The synthesis is straightforward: benzobis(1,3-diiminopyrroline) and an excess dimethylaminomaleonitrile were heated to reflux in the presence of Mg in BuOH for 2 days, and after treatment with acid, the residue was chromatographed to yield the desired dimer in 15% yield. This compound showed split Q bands at 839 and 548 nm and a single Soret band at 346 nm in CH_2Cl_2. An oxidation and three reduction couples were recorded at 0.099, −0.18, −1.44, and −1.56 V, respectively, versus the ferrocene–ferrocenium couple in CH_2Cl_2.

A planar SubPc sharing a common benzene was reported in 1991 (Fig. 15(D)) [138]. Although the Q band of the corresponding control monomer occurred at 567 nm, it split into two peaks in the dimer at 596 and 537 nm with concomitant decrease in the absorption coefficient, as a result of dipole–dipole interaction. This dimer showed fluorescence, as seen for the above planar Pc dimer [132].

8.2. Heterodimers sharing a common benzene ring

Pc–PyZ (Fig. 16A) [139,140], Pc–Nc [141] and Pc–triazolehemiporphyrazine dimers (Fig. 16B) [142] are the only compounds grouped into this category. In synthesizing Pc–PyZ and Pc–Nc, first a Pc containing *ortho*-dinitrile was prepared by mixed condensation of 5,6-dicyano-isoindolediimine and alkylated isoindolediimine. The nitrile moiety of the Pc was changed to isoindolediimine by bubbling ammonia, and this compound was then reacted with excess isoindolediimine derivative prepared from either 5-*tert*-butyl-2,3-dicyanopyrazine or 6-*tert*-butyl-2,3-dicyanonaphthalene. These compounds, commonly show broad Q absorption bands between ca. 500 and 1000 nm. In Pc–PyZ, no fluorescence was observed, plausibly because of intramolecular charge-transfer character, since Pc donates while the PyZ moiety withdraws electrons. Redox couples were detected at 1.36, 0.76, 0.50, −0.96, −1.34, −1.82, and −2.2 V, and were explained by dipole–dipole interaction of the two moieties. A charge-transfer character of Pc–PyZ in the lowest excited triplet state was confirmed by using a time-resolved EPR method [140]. In the case of Pc–Nc, the fluorescence spectrum was recorded, and its ϕ was two orders of magnitude lower than those of the constituting mononuclear control Pc and Nc.

Pc–triazolehemiporphyrazine dimers were prepared by the pathway shown in Scheme 1 [142]. What we call a hemiporphyrazine with an *ortho*-dicyano group was first synthesized in a stepwise manner, and this was heated with excess phthalonitrile derivative in the presence of a metal salt as a template. In a typical procedure, the yield of the final step was 10%. The spectrum of the dimer differs from the sum of the spectra of the constituting monomers, suggesting non-negligible intramolecular interactions.

8.3. Homodimers and homotrimers linked by other units

Cook [143] and Torres [144] independently and almost simultaneously published planar Pc dimers and trimers connected by several bis(acetylene) bridges (Fig. 17(A and B)). These compounds were obtained by the coupling of Pc derivatives having two acetylene units in the presence of a copper salt in pyridine or a solvent containing pyridine. Cook's and Torres's compounds differ from each other in the number, type and positions of substituents. In Cook's compounds, the dimer showed a well-split Q band at 823 and 691 nm, while the trimer showed these at 780 and 698 nm in toluene, consistent with the exciton coupling model. Cook's compounds showed mesophase behavior, since they contained many long alkyl chains.

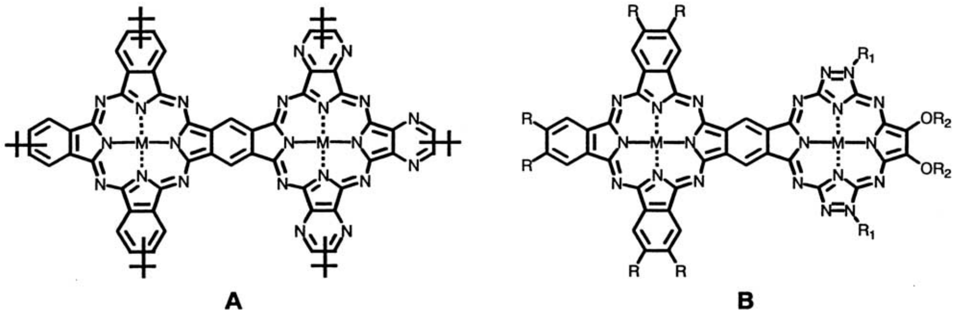
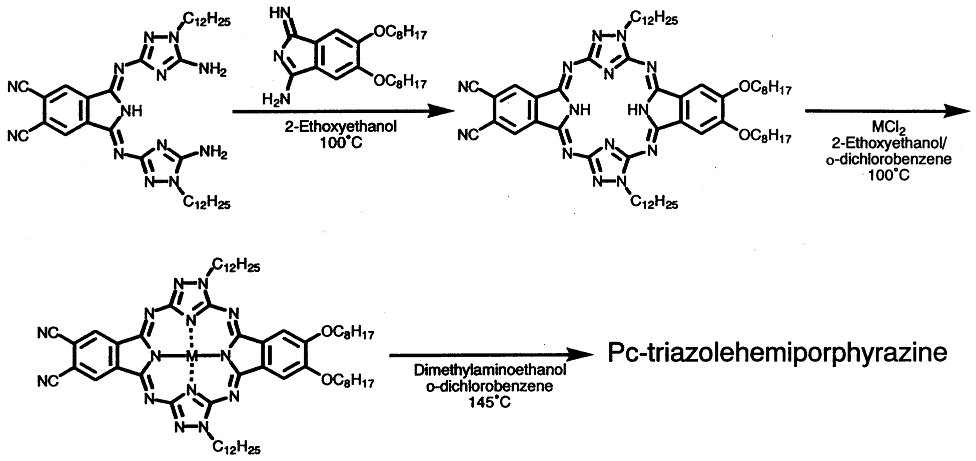


Fig. 16. Structures of heterodinuclear (A) Pc–PyZ and (B) Pc–triazolehemiporpyrazine, from [139,140] and [142], respectively.



Scheme 1.

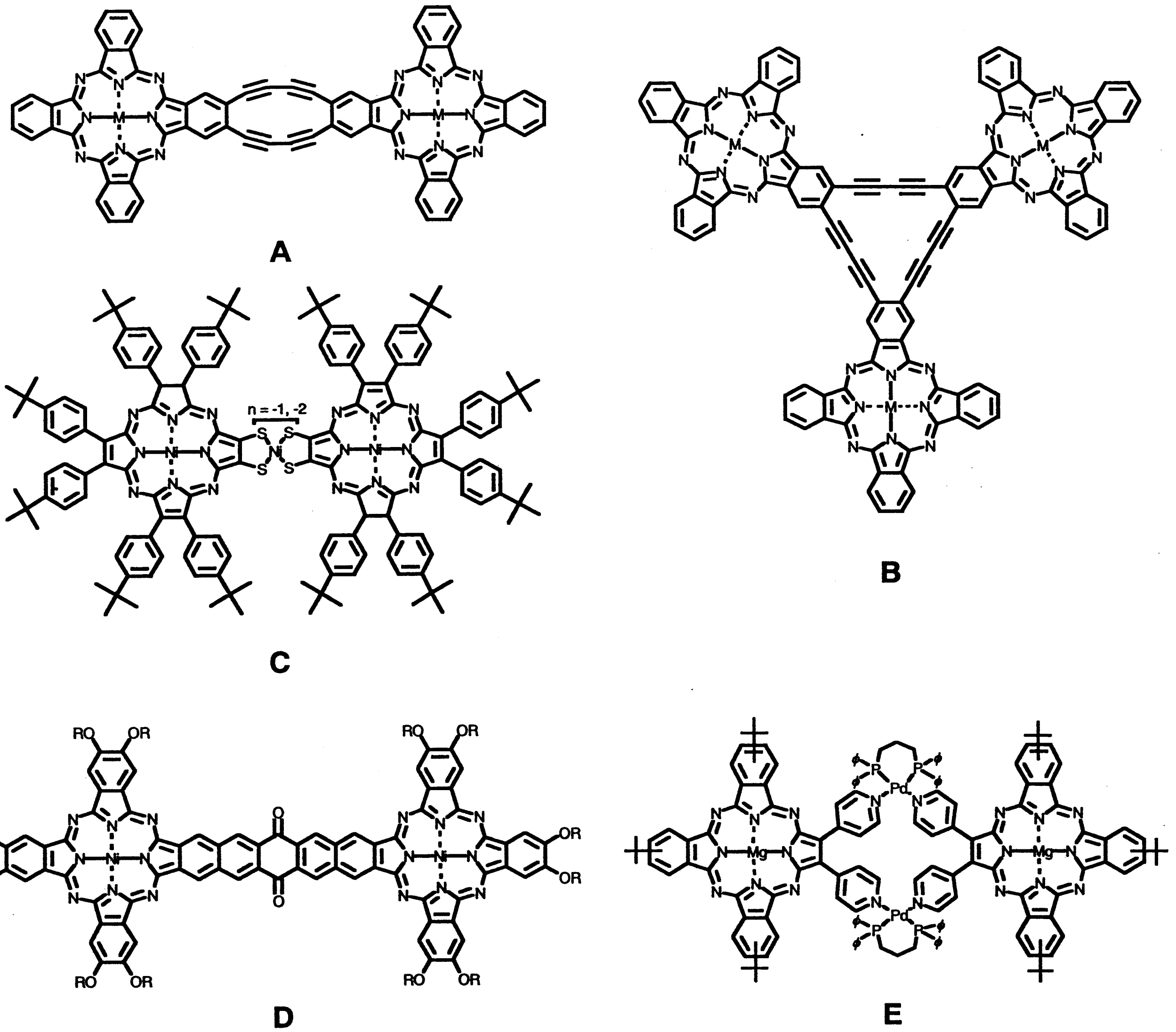


Fig. 17. π-Structures of the planar (A) Pc dimer and (B) Pc trimer of [143,144], (C) TAP dimer linked by Ni of ref. [145b], (D) anthraquinone-linked Pc dimer of ref. [146], and (E) palladium-bridged Pc analogue of [147].

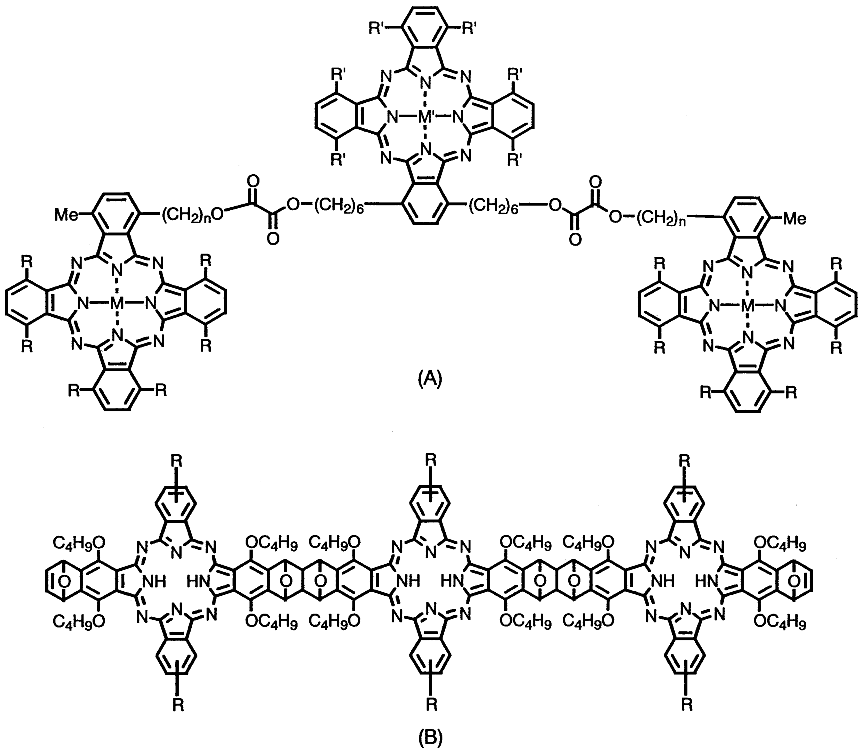


Fig. 18. (A) Linear Pc trimers used for a liquid crystal study [151]). (B) Linear ladder trimers from [152].

Hoffman's group has published near-planar TAP dimers connected by a benzene and two metals or just by a metal (Fig. 17(C)) [145]. In the former case, a TAP which has an adjacent bis(dimethylamino) group was prepared by a mixed condensation of 1,2-dialkylated maleonitrile and 1,2-bis(dimethylamino)maleonitrile. This was reacted with 1,2,4,5-benzenetetrathiolate and Pd under an inert atmosphere. Its NMR and mass spectra were collected, but the dimer was not stable enough for further characterization. In the latter case, a TAP, which has adjacent dithiolates was first prepared, and two molecules of this compound were then connected by a Ni atom using an indirect method [145b]. A split Q band with a splitting energy of ca. 790 cm^{-1} was observed at ca. 550–710 nm.

The synthesis of a planar Pc dimer fused with anthraquinone was reported 2 years ago (Fig. 17(D)) [146]. The first precursor was a Pc prepared from three phthalonitrile units and one 6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene. To this epoxy unit, tetraphenylcyclone was fused by a Diels–Alder reaction, and the resultant Pc derivative was reacted with π-benzoquinone in refluxing toluene. Judging from the position of the absorption peaks in CH_2Cl_2 (660, 629, 392, and 288 nm), the interaction of the two halves appears not to be significant.

We have recently reported a Pc dimer assembled by two Pd atoms (Fig. 17(E)) [147]. Although the dimer is not completely planar, molecular models suggested that it is almost planar. Due to the shape of the π system of the constituting monomer, two Q bands were observed even in the monomer. After formation of the dimer, the Q band shifted slightly to the red and intensified.

9. Linear dimers and oligomers

9.1. Linear dimers

There are several dimers linked by flexible alkyl chains, but in this section, I will describe only relatively rigidly linked Pc dimers. Pc dimers connected by one C–C bond [127b] and one ethylene or acetylene bond [148] were first reported by Leznoff's group. In all these cases, the connecting units containing two isoindolediimine units at both ends were first prepared, and then excess isoindolediimine was reacted. Since then, several groups have synthesized Pc dimers linked by bridges containing acetylene and/or ethylene unit(s) [149]. In [149], however, two mono-functionalized Pc units were linked by coupling reactions. From the shape of the absorption spectra, strong intramolecular interaction between the two Pc units is observed when the bridge contains less than two acetylene or ethylene units.

Lindsey's group has published several Pc–Por dimers connected by an acetylene bridge [150]. In these cases, monoacetylated Pc and mono-iodinated Por were linked by Pd-coupling reactions, and mainly the excited state

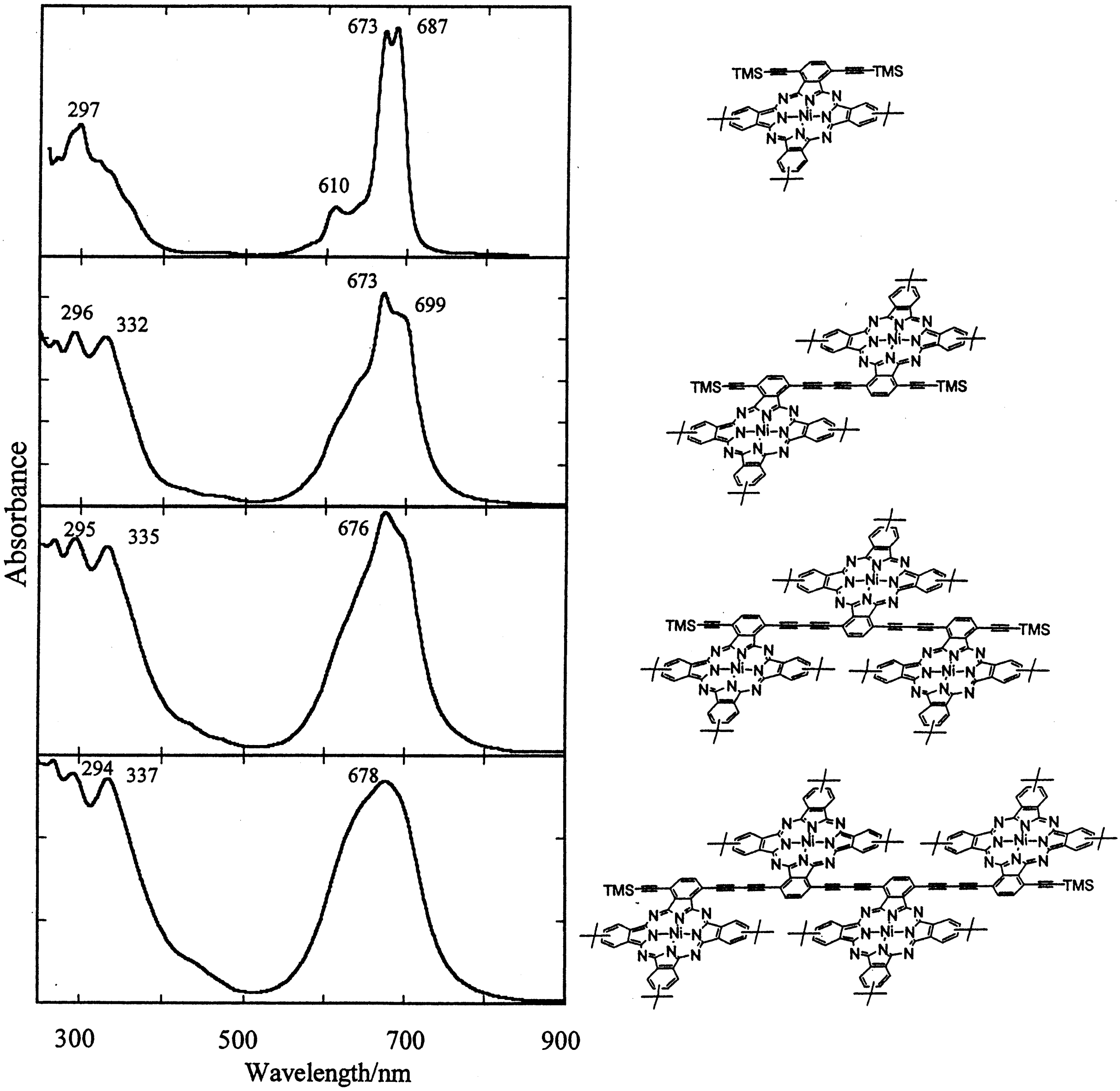


Fig. 19. Structures of rigid linear oligmers and their absorption spectra in $CHCl_3$ [153]).

properties were examined. They found the following: (i) Excited singlet-state intramolecular energy transfer from the Por to the Pc moiety occurs in less than 10 ps, with very high efficiency (typically more than 90%). (ii) Charge-transfer involving the excited Pc and the Por occurs to a limited degree (less than 10%, depending on the redox characteristics of the chromophores). (iii) The strong emission properties of monomeric Pcs were retained ($\phi = 0.37$–0.75).

9.2. Linear oligomers

Cook et al. obtained Pc trimers linked by flexible alkyl chains for a liquid crystal study (Fig. 18(A)) [151]. A Pc having OH groups at the end of long alkyl chains connected to two α-positions of one benzene ring of Pc were coupled by the action of oxalyl chloride, and the desired trimer was separated by chromatography. The phase-transition temperatures were dependent on the length of the linkages and whether or not copper was inserted into the Pc. A linear ladder-type Pc trimer (Fig. 18(B)) was synthesized from Pcs substituted with two 1,4-epoxy units at opposite positions by the use of a Diels–Alder reaction. Since the arrangement of adjacent oxygen bridges is either *exo*/*exo* or *exo*/*endo*, this trimer is not flat, and indeed is a mixture of several isomers [152].

We have recently synthesized a series of rigid, linear oligomers, as shown in Fig. 19. This was achieved by the coupling of Pcs having two acetylene units at two α-positions of one Pc benzene ring, and subsequent chromatographic separation [153]. As can be judged

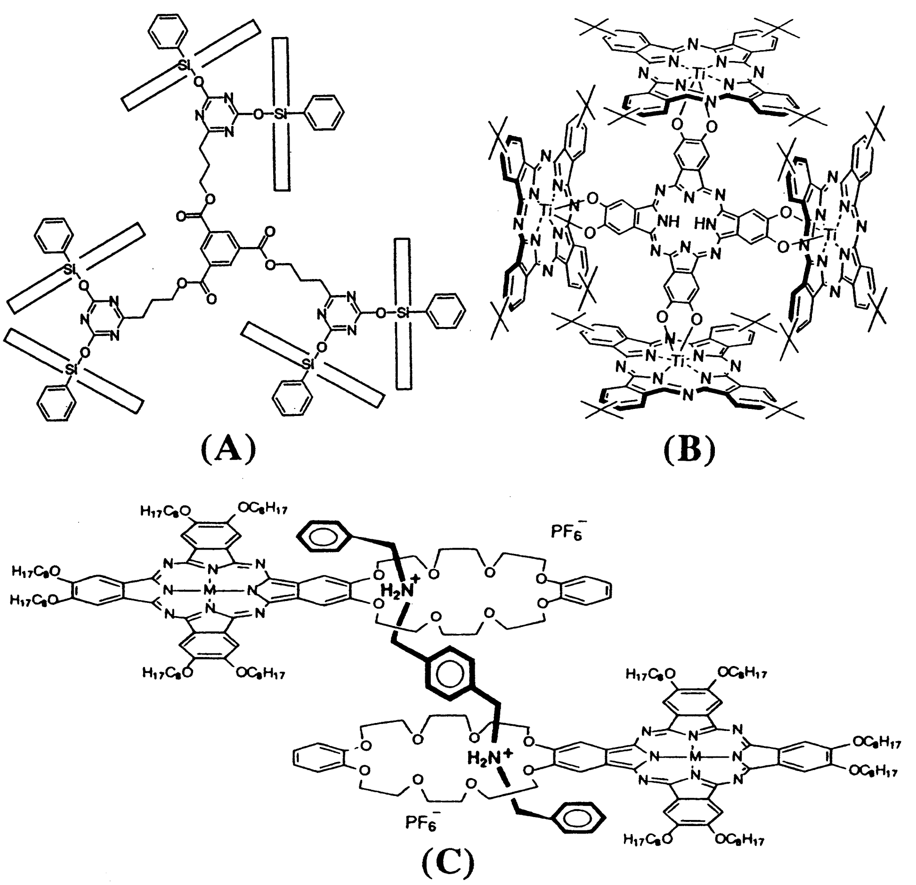


Fig. 20. Structures of (A) dendrimer type Pc hexamer, (B) mutually perpendicular Pc pentamer, and (C) supramolecular Pc dimer with pseudorotaxane geometry (from [154,155,158], respectively). In (A), the hollow rectangles indicate Pcs.

from the shape of this Figure, the interaction between the Pc units does not appear to be large.

10. Other homo- and hetero oligomers

A flexible, dendrimer type Pc hexamer has been reported (Fig. 20(A)) [154]. 1,3,5-Tribenzoic acid was treated with three equivalents of alcohol linked to two Pc units, giving a reported yield of 81%. Although the elemental analysis was satisfactory, the authors did not afford mass data nor gel permeation data. Accordingly, at least the yield value is fairly doubtful.

A mutually perpendicular Pc pentamer (Fig. 20B) was synthesized by a one-step, r.t. reaction [155]. In synthesizing this compound, the reactivity of the axial oxygen in TiOPc, which is readily displaced by *ortho*-phenolic OH groups to produce two ether linkages, was utilized. Due to the perpendicular arrangement, the interaction of the constituting Pc units does not appear to be large. Pc compounds where one Pc unit is surrounded by four or eight Por units have been reported by us [156] and Lindsey [150]. Leznoff's group has reported Pc tetramers and pentamers linked by flexible alkoxy chains [157]. In Leznoff's compounds, some intramolecular interactions were recognized spectroscopically and electrochemically, since the linkages were relatively short. Recently, a supramolecular Pc dimer, which may have a pseudorotaxane geometry (Fig. 20(C)), has been prepared [158].

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