ELSEVIER

Coordination Chemistry Reviews
160 (1997) 53–91

COORDINATION CHEMISTRY REVIEWS

Assemblies of phthalocyanines with porphyrins and porphyrazines: ground and excited state optical properties

T.-H. Tran-Thi

CEA/Saclay, DSM/DRECAM/SCM, URA 331 du CNRS, 91191 Gif-sur-Yvette Cedex, France

Received 3 January 1996

Contents

Abstract

This review describes the history, back ground and recent progress on mixed complexes of phthalocyanines and porphyrins from 1984 to the present time. The emphasis is mainly on the optical properties of the ground and excited states of three families of mixed complexes, either covalently-linked and linear or cofacial and columnar. Their properties are compared and discussed in relation to their potential as light harvesting systems. © 1997 Elsevier Science S.A.

PII S0010-8545(96)01341-0

Keywords: Optical properties; Phthalocyanines; Porphyrins; Ground state optical properties; Excited state optical properties

---

1. Introduction

Light collection, energy transport and charge separation in photosynthesis are very efficient energy conversion processes. The complexity of the primary photoprocesses in natural photosynthesis have prompted the search for model systems in which an initial photoexcited state produces a final long-lived separated state. Starting from the early seventies, a tremendous number of works have been devoted to the design and study of porphyrin-like systems, following two main strategies. Both strategies are essentially based on light harvesting process followed by electron transfer, but differ slightly on the molecular engineering.

The first route consisted in making porphyrin dimers or mixed porphyrin complexes linearly linked through peptide bond or long alkyl chains [1], self-assembled via ligands [2] or bound with rigid spacers [3]. Those mixed complexes were in most cases bridged to a good electron acceptor such as quinone [4] or methylviologen [5]. The idea was to separate the charges in the photoinduced ion pair over a large distance so as to retard the back transfer reaction. The second route exploited the properties of the special pair in the photosynthetic organism [6]. The energy conversion process begins with the excitation of the special pair of bacteriochlorophyll molecules, which are in van der Waals contact with one another [7] and the charge separation process proceeds with a quantum yield equal to unity. Based on the geometry of the special pair, numerous models of cofacial porphyrins were elaborated. They are either linked through multiple chains [8] or spacers [9], chelating a common metal ion [10], or self-assembled via axial ligands [11]a forming in some cases "shish-kebab" oligomers [11]b. They are also ion pairs formed from the coupling of two porphyrins bearing oppositely charged substituents [12].

Both strategies were fruitful. Over the last 25 years, the understanding of the multistep photoinitiated electron transfer has progressed tremendously. From the first porphyrin–quinone system synthesized and studied by Kong and Loach [13] to the pentad complex of the Tempe group [14], we have learned through the studies of hundreds of diad [15], triad [16] and tetrad [17] complexes how to engineer the charge separation and recombination processes. In both linear and cofacial systems, a gradation of the redox properties of the donor and acceptor compounds linked together is needed to achieve the best light to chemical potential conversion.

Systems of porphyrins capped by a quinone, which is more or less in close contact with the porphyrin plane, show a solvent dependence of the charge separation with time constants between 1 and 20 ps, whereas charge recombination proceeds on a slower time of 10–300 ps [18].

In the linear pentad [14] with the following sequence of molecules, carotene (Car), zinc porphyrin (ZnP), free base porphyrin (H_2P) and a diquinone (Q_a and Q_b), the photosensitizer, H_2P, triggered by light absorption, transfers an electron to Q_a. This primary reaction is followed by a cascade of hole transfer process from H_2P to ZnP to Car, and electron transfer from Q_a to Q_b. The resulting separated ion pair, Car^{+}–ZnP–H_2P–Q_a–Q_b^{-}, displays the record lifetime of 340 μs, which is five orders of magnitude longer than that of the first linear ZnP–Q diad studied by Kong and Loach [13]. It is, however, noteworthy that for the diads systems of P–Q studied in the literature, the charge recombination reaction is slower for the face-to-face complexes than for the linearly linked compounds.

In contrast to chlorophylls and bacteriopheophytins of the natural photosystem which absorb light over a wide range of wavelengths, from the UV to the near infrared [19], the spectra of porphyrin complexes are restricted to a strongly allowed transition in the UV region (Soret band, 400–450 nm) and much less intense ones over the visible region (500–650 nm) [20].

In order to enhance their potential as light harvesting systems, the idea was to couple the porphyrins with compounds displaying complementary absorption spectrum or redox properties. Some porphyrin–chlorophyll systems had been synthesized and investigated. However, because of their respective redox properties, the energy of the lowest charge transfer state obtained by varying the nature of the central metal ion was still very high (1.8 eV) with respect to the lowest singlet excited state of the free base chlorophyll (1.85 eV) [21] and therefore the electron transfer process was not thermodynamically favorable.

Among the macrocyclic complexes which exhibit the requisite properties, phthalocyanine (Pc) [22] and octaethylporphyrin (OEP) [23] derivatives, appear as the porphyrin ideal partners. OEP is more easily oxidized while P is more easily reducible. On the other hand, Pc derivatives are more easily oxidized and reduced [22,23] with respect to porphyrins and could therefore act as well as a donor or an acceptor. Their electronic transitions differ from that of the porphyrin; OEPs display an intense Soret band red-shifted from that of the porphyrin, while Pcs display very complementary transitions with an intense Q band in the red and a less intense Soret band blue-shifted with respect to the porphyrin (Fig. 1).

Surprisingly, very few studies reported such association in the literature, especially for P/OEP mixed complexes. More studies have been devoted to P/Pc systems; The first phthalocyanine was accidentally discovered in 1907 by Braun and Tcherniac [24], then by Diesbach in 1927 [25], and were characterised for the first time by Linstead [26], who gave them their present name, derived from the greek words naphta (rock oil) and cyano (dark blue). Since then, the chemistry of phthalocyanines has been widely developed in parallel to that of the porphyrins [22]. Thanks to their particularly high chemical and photochemical stability, phthalocyanines have been used as inks, laser dyes, photosensitizers in photovoltaic cells, molecular semiconductors, photosensitizers for dynamic phototherapy, etc. [27].

The chemistry of mixed porphyrin–phthalocyanine systems is very young. Gaspard introduced for the first time in 1984 the idea of pairing phthalocyanines with porphyrins [28], using the strategy developed by Shimidzu in 1981 for mixed systems of ionic porphyrins [12]. He also pioneered in 1986 the synthesis of covalently linked porphyrin–phthalocyanine systems [29]. His work triggered a new interest and, despite the difficulties of such synthesis, novel compounds appeared in the literature. Lashkar et al. were the first to report, in 1988, the synthesis and characterisation of

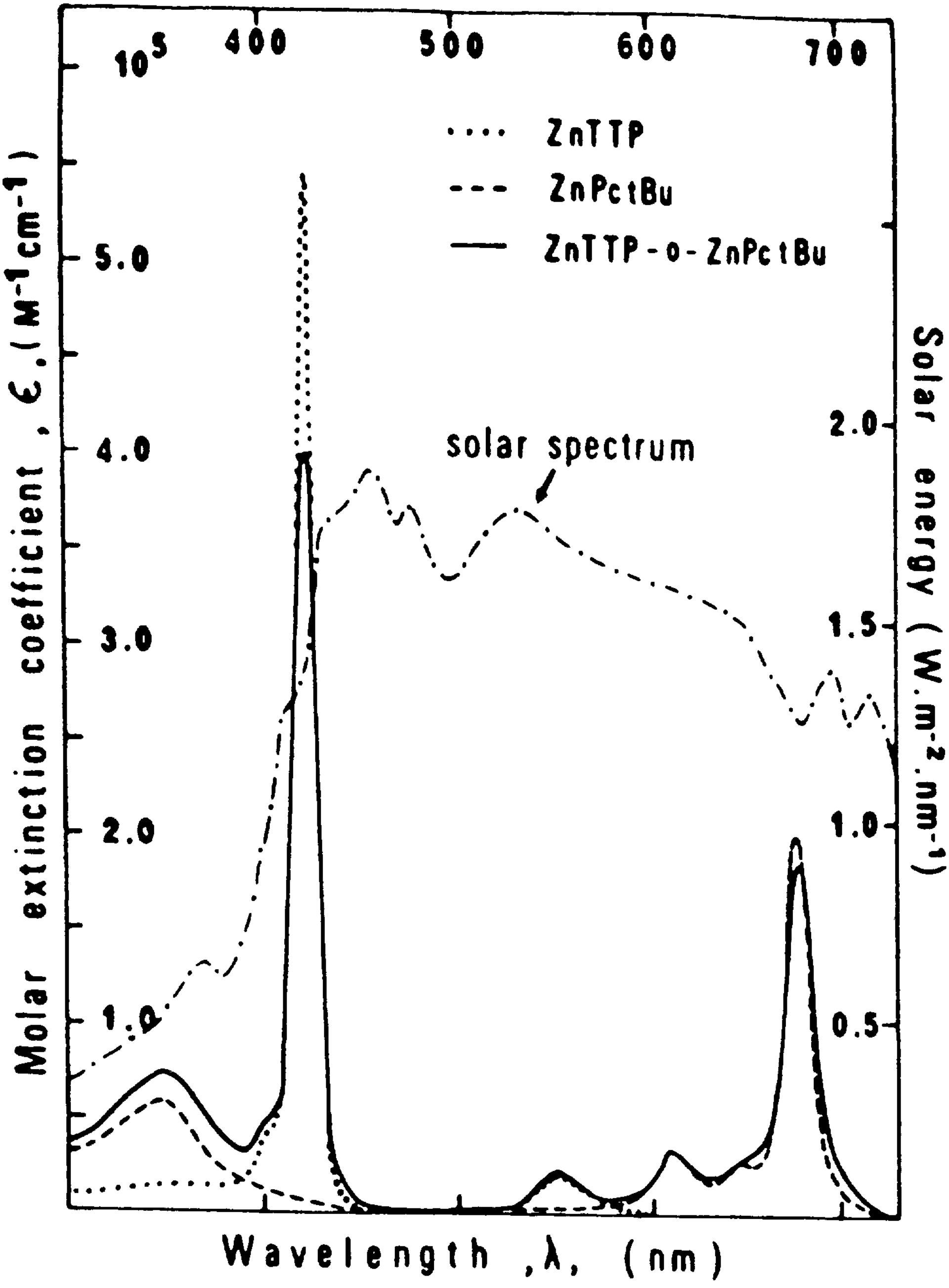


Fig. 1. Absorption spectra of the mixed complex and the corresponding monomers in toluene [34].

a double-decker mixed porphyrin and phthalocyanine of cerium [30]. Chabach et al. later developed a new route for the synthesis of lanthanide porphyrin–phthalocyanine triple-decker complexes [31]. Though only a small community has focused its effort on such systems, fast advances were realized over the subsequent 10-year period, which will be reviewed here. From the literature reports, one can divide the porphyrin–phthalocyanine area into the three following domains: covalently linked systems, multiple-decker mixed complexes and self-assembled ionic systems.

2. Covalently linked systems

2.1. *Ground state optical properties*

Very few covalently-linked and mixed porphyrin–phthalocyanine systems were reported in the literature. The first two complexes synthesized by Gaspard et al. were the zinc and free base tri(tolyl)porphyrin linked via an oxo-bridge to a zinc tri(*t*-butyl) phthalocyanine, ZnTTP–O–ZnPctBu and H_2TTP–O–ZnPctBu [29].

The spectrum of the mixed complexes are very similar to the sum of the spectra of the individual units. One can note a slight decrease of the oscillator strength corresponding to the most intense Soret band of the porphyrin in the mixed complexes, while the most intense Q band of the phthalocyanine moiety remains identical to that of the monomeric unit (Fig. 1 and Table 1). Similar optical properties were also observed for the peptide-linked tricarboxylated free base porphyrin and tri(amino)phthalocyanine [32] and the free base tritolylporphyrin linked via a di-oxy(*n*-alkyl) chain to the free base phthalocyanine [33] (Table 1). These absorption changes were ascribed to weak exciton coupling interactions between the two chromophores in the ground state [32–34].

The magnitude of such an interaction depends markedly upon the relative orientation of the two macrocycles. A more important decrease of the oscillator strength of the porphyrin Soret band was observed with increased solvent polarity and was attributed to a conformational change, which favors an overlap of the phenyl rings of the porphyrin and phthalocyanine (see Fig. 2).

2.2. *Excited states properties*

The photophysics of the covalently linked mixed complexes is governed by two main reactions: energy transfer (ET) and electron transfer (eT). As the energy levels of the $^1\pi$–π^* and $^3\pi$–π^* of phthalocyanines lie below the porphyrin ^1S and ^1T levels, the excitation energy can only be transferred from the porphyrin to the phthalocyanine moiety. For the eT reaction, however, as porphyrins and phthalocyanines can both act as donor or acceptor, the electron will be transferred in the most thermodynamically favored direction, determined by the redox potentials of the two sites.

When the exciton interaction between the two moieties is weak, the main deactivation pathway of the excited mixed complex is the ET process. This behavior was reported for three systems, ZnTTP–O–ZnPctBu in toluene [34], H_2TPP–O–H_2Pc in benzene [34] and H_2PCOOH–CONH–H_2PcNH_2 in chloroform [32]. In all cases,

Table 1
Ground state optical properties

Compound	Solvent	λ_{max}(nm)	$\epsilon(M^{-1} cm^{-1})$	f	Ref.
ZnTTP	toluene	424	5.4×10^5	1.59	[34]
		550	2.6×10^4		
	DMSO	428	6.9×10^5	1.94	
		560.5	2.7×10^4		
		600.5	1.7×10^4		
ZnPctBu	toluene	350	5.2×10^4		[34]
		610	3.1×10^4		
		677	2.0×10^5	0.36	
	DMSO	350	6.2×10^4		
		610	3.1×10^4		
		678	1.94×10^5	0.39	
ZnTTP–O–ZnPctBu	toluene	350	7.4×10^4		[34]
		425	4.0×10^5	1.29	
		550	2.4×10^4		
		612	3.2×10^4		
		679	1.8×10^5	0.38	
	DMSO	350	7.1×10^4		
		428	4.3×10^5		
		560	2.1×10^4		
		615	3.5×10^4		
		680	1.7×10^5	0.38	[32]
H_2TTPCOOH	$CHCl_3$	419.7	3.36×10^5	1.08	
		516	1.5×10^4		
		551.7	8.1×10^3		
		591.1	5.1×10^3		
		648.2	5.1×10^3		
ZnPcNH_2	$CHCl_3$	348	3.9×10^4		[32]
		616.1	1.5×10^4		
		684	7.4×10^4	0.19	
H_2TTPCOOH–CONH–ZnPcNH_2	$CHCl_3$	349	3.9×10^4		[32]
		420	2.0×10^4	0.71	
		516	8.4×10^3		
		551	6.0×10^3		
		682	7.9×104	0.19	

the fluorescence of the porphyrin moiety in the excited mixed complex is strongly quenched while the fluorescence quantum yield of the phthalocyanine moiety remains identical to that of its corresponding monomer. The ET reaction is very efficient and the quantum yield is close to one. This process is followed by the relaxation of the excited phthalocyanine to the ground state, by fluorescence and via intersystem crossing from singlet to triplet excited states. Increasing the solvent polarity with dimethylsulfoxide or dimethylacetamide favors the eT process on the expense of ET: the fluorescence of both chromophores is quenched and the lifetime of both singlets is shortened. Moreover, a new short component (0.33 ns) contributes to the fluorescence of the phthalocyanine moiety, which could be the fluorescence of a transient charge transfer (CT) state. This has been explained in terms of the conformational

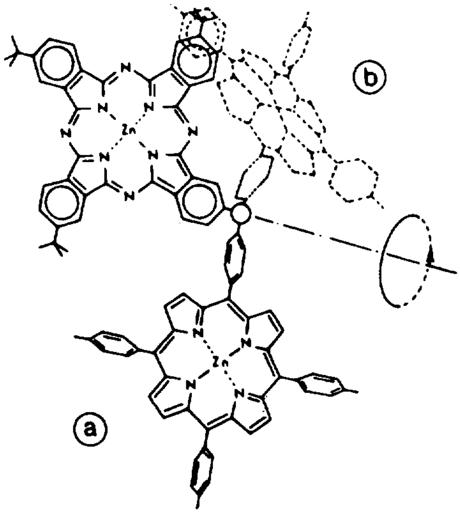


Fig. 2. Schematic representation of the ZnTTP–O–ZnPctBu mixed complex (a) conformation in toluene and (b) conformation in DMSO [34].

change in the ground state and stabilization of the CT excited state by the solvent [34].

In contrast to these three compounds, complexes linked by a di-oxy(*n*-alkyl) chain exhibit a different behavior: in polar as well as non-polar solvents, the fluorescence of the porphyrin and phthalocyanine is quenched and both singlet lifetimes are shortened, indicating that eT prevails [33]. The authors explained these results in terms of the flexibility of the chains, which allow the two moieties to adopt a conformation favouring the eT process. The process was optimized for $n=3$ and 4.

The photophysical properties of the different mixed complexes are summarized in Table 2. From these data, it seems clear that, when the mixed complexes adopted an extended conformation in solution, the ET process prevails; eT can efficiently compete with ET especially when the complexes adopt a folded conformation, which allow a larger interaction between the two moieties. However, when eT did occur in these systems, the CT states were too short lived to be detected on the nanosecond time scale. The lifetime of the CT states could be increased by adding extra constituents with the required gradient of redox properties.

A triad system, consisting of the ZnTTP–O–ZnPc complex with three anthraquinones (AQ), covalently linked to the ZnPc moiety through di-oxyphenyl chains, was reported in the literature [33].

The authors proposed, on the basis of redox potentials and analysis of the transient absorption spectra, the formation of the final ZnP^{+}–O–ZnPc–O–ϕ–O–AQ^{-} via a two-step reaction implying first an eT from ZnP to ZnPc, followed by a second transfer from $ZnPc^{-}$ to AQ. Their nanosecond time-resolved experiment did not allow them to directly follow the eT process, but the species formed immediately after the laser pulse decays within 50 ns. It was attributed to the charge separated

Table 2
Excited state properties of covalently linked mixed complexes

Compounds	Solvent	λ_{ex} (nm)	λ_f (nm)	Φ_f	τ_s (ns)	k_{eT} (s^{-1})	Φ_{eT}
ZnTTP	toluene	550	600	0.034			
			650				
		424	600		2.0		
	DMSO	550	610	0.035			
			663				
		580	610		1.75		
ZnPctBu	toluene	610	682	0.23			
			755				
		350	682		3.3		
	DMSO	610	685	0.18			
			755				
		350	685		3.1		
ZnTTP–O–ZnPctBu	toluene	424	600	0.004	0.26		
			685	0.24	3.3		
	DMSO	580	663		2.05		
			686	0.038	0.33		
					2.1		
			755		0.33		
					2.1		
H_2TTPCOOH	$CHCl_3$	515	650	0.053			
			720				
		575	665		7.7		
ZnPcNH_2	$CHCl_3$	330	696	0.103			
		575	696		3.0		
H_2TTPCOOH–CONH–ZnPcNH_2	$CHCl_3$	330	691	0.187			
		515	650	$<10^{-4}$			
			691	0.187			
		575	691		3.0		
			715				
H_2Pc	benzene	640	710		7.5		
	DMF	640	710		6.8		
H_2TTP–O–H_2Pc	benzene	515	650		5.1		
			710		7.2		
		640	710		7.5		
	DMF	640	710		7.3	1.7×10^8	0.531
H_2TTP–O–$(CH_2)_2$–O–H_2Pc	benzene	515	710		6.5		
		640	710		6.2	2.8×10^7	0.173
H_2TTP–O–$(CH_2)_3$–O–H_2Pc	benzene	515	710		5.8		
		640	710		5.8	3.9×10^7	0.226
H_2TTP–O–$(CH_2)_4$–O–H_2Pc	benzene	515	710		5.8		
		640	710		5.8	3.9×10^7	0.226
H_2TTP–O–$(CH_2)_5$–O–H_2Pc	benzene	515	710		6.1		
		640	710		6.0	3.4×10^7	0.204

radical ions, on the basis of the transient absorption spectrum, which display the photobleaching of both the ground state porphyrin Soret band and phthalocyanine Q band and new absorptions at 550, 580 and 630 corresponding to AQ^-, $ZnPc^-$

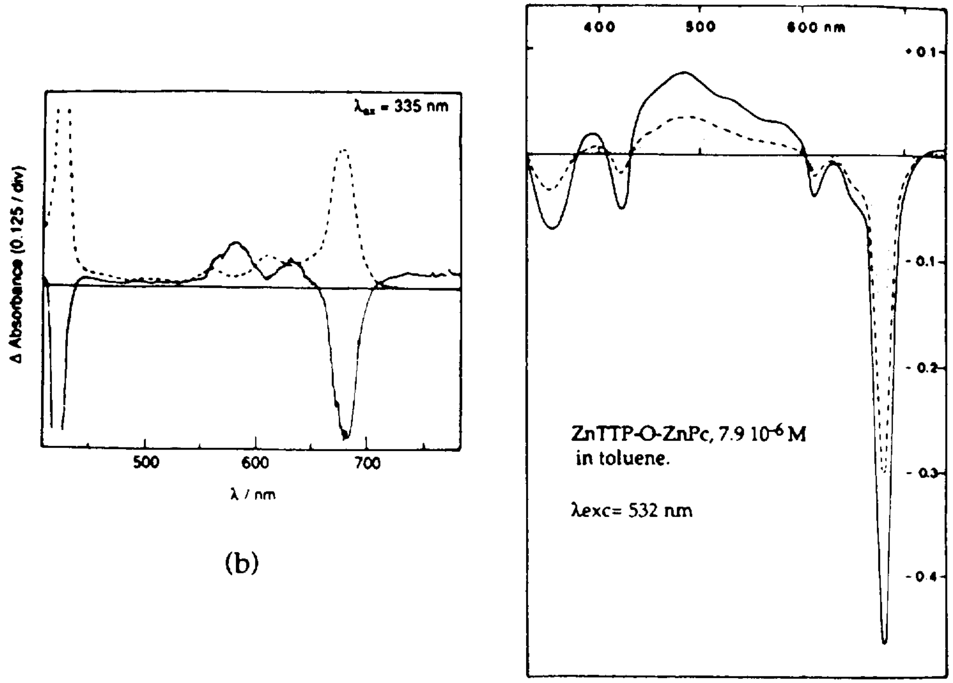


Fig. 3. Transient differential absorption spectrum of (a) ZnTTP–O–ZnPctBu in toluene [34] and (b) ZnTTP–O–ZnPc–O–ϕ–O–AQ in dimethylformamide [33].

and ZnP^+ respectively. Such a transient spectrum is very different from the one obtained for the diad ZnP–O–ZnPc, in which energy transfer occurred (see Fig. 3).

The lifetime of the CT species was effectively increased by adding a third component to the diad. In our view, it could be further improved by adding either a donor or an acceptor to the porphyrin moiety, rather than to the phthalocyanine one, to give D-ZnP-O–ZnPc or A-ZnP–O–ZnPc. In either case, the ZnP would be the photosensitizer and the eT reaction, which is thermodynamically much more favorable, would lead to D^+-ZnP–O–$ZnPc^-$ or A^--ZnP–O–$ZnPc^+$. One should also mention that the chemistry is much easier to handle: linking substituents to the phthalocyanine is much more difficult and time-consuming than linking substituents to the porphyrin.

3. Double- and triple-decker mixed complexes of lanthanides

3.1. History

Among all the bis-porphyrins, bis-phthalocyanines and mixed porphyrin–phthalocyanine systems reported in the literature, the double and triple-decker complexes are some of the most interesting systems, in many regards. First of all, their synthesis is much easier than that of covalently-linked complexes, and high product yield can be obtained. The first synthesis of a double-decker complex of stanum, $Sn(Pc)_2$, was reported in 1936 by Linstead [35]a, but the study of its optical properties was only reported a long time later by Whalley [35]a, who discovered an unusual absorption band red-shifted to the near IR at 900 nm [35]b. A few years later, in 1965, the synthesis of the double-decker bis-phthalocyanine of lutecium was reported by Kirin and Moskalev [36]a who proposed, on the basis of its redox properties, the $Lu(Pc)_2$ formulation. The nature of the complex, radicalar ($Lu^{III}(Pc)_2$) or neutral ($Lu^{III}H(Pc)_2$), was debated for years. A definite formulation was finally given 20 years later, in 1985, by Decian et al. [36]b with the first X-ray structure of the $(Pc^{-\circ})Lu^{III}(Pc^{-2})$.

The interest in porphyrin derivatives of this type came much later. Although a single sandwich-type complex of porphyrins of mercury, $Hg_3(OAc)_2(OEP)_2$, was reported by Hudson and Smith in 1975 [10]a, the chemistry of the double-decker complexes really started in 1983, with the first synthesis by Buchler's group of a cerium^{IV} bisporphyrinate, $Ce(TPP)_2$ and a hydrogen praseodynium^{III} bisporphyrinate, $PrH(TPP)_2$ [10]b. They discovered, 3 years later, a new synthetic route which allowed them to obtain the whole series of double- and triple-decker complexes of octaethylporphyrins of lanthanides [37]. Their work triggered a new interest, and many groups around the world [38,39], became very active in this area.

Five years later, in 1988, Lachkar et al. reported the synthesis and characterisation of the first double-decker mixed complex of porphyrin and phthalocyanine of cerium [30]. Weiss's group was also very prolific: they succeeded in synthesizing two new triple-decker complexes of cerium, with various relative position of the porphyrin and phthalocyanine chromophores [31]. They discovered a new synthesis route for double- and triple-decker mixed complexes of lanthanides with very high yield [40,41]. Moreover, their very recent work, showing the possibility of mixing lanthanide metal ions in the mixed complexes of porphyrin and phthalocyanine [42], opens up a new and unexplored area of research.

Unlike the covalently-linked complexes, monocrystals of these sandwich complexes could be obtained and therefore their structures are well established [30,31,36]b[37]. Moreover, they can display very different electronic properties, depending on the nature of the central metal ions.

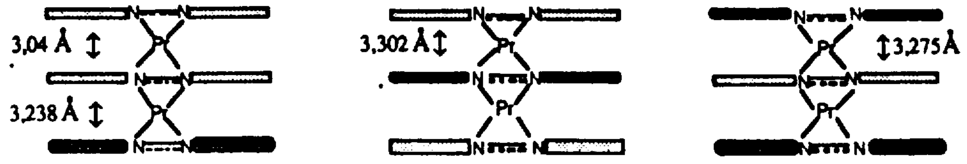
With tetravalent metal ions, such as Sn^{4+}, Hf^{4+}, Zr^{4+}, Ce^{4+}, Th^{4+} and U^{4+}, neutral double-decker complexes are formed. $Sn(Pc)_2$ [35]b, $Hf(TPP)_2$, $Zr(TPP)_2$ [43], $Ce(TPP)_2$ [10]b, Ce(TPP)(OEP) [44], Ce(TPP)(Pc), [31], $Th(OEP)_2$ [45] and $U(Pc)_2$ [46], which belong to this category, were reported in the literature. Similarly, with trivalent metal ions of the lanthanide series, neutral triple-decker complexes are formed. In contrast to these neutral complexes, lanthanides(III) metal ions form, with two tetrapyrrolic rings, a radical compound, the nature of which has been thoroughly discussed in the literature. In these radical compounds, one of the rings is a mono-ion and the other a di-anion. They display new near infrared absorption bands, which have been related to the electronic interaction between the two macrocycles. These near infrared absorption bands also appear when one of the rings of the neutral double- or triple-decker complexes is chemically oxidized.

From a fundamental point of view, the study of the mixed neutral complexes may provide new insights into the electronic interactions between porphyrin-like systems held in close proximity and how these interactions can influence the initial stages of the charge separation. The mixed systems provide model compounds for such studies, especially in the case of the triple-decker complexes; three types of triads can be obtained, with various relative positions of the porphyrins and phthalocyanines (see Fig. 4).

For each of the triads, the interchromophore distance can be varied by changing the metal ion. Very recently, mixed metal complexes have also been synthesized [42], which widens the field of investigation on the electronic, redox, magnetic and photophysical properties of these systems. Furthermore, another fundamental question which has also triggered numerous studies on bis-(porphyrin)s and bis-(phthalocyanine)s complexes, is to know to what extent a hole could be localized or delocalized in radical complexes. Such knowledge would provide further evidence for the electronic nature of the oxidized special pair in the photosystem I.

Numerous targeted aspects have also been investigated. Kirin and Moskalev, in the early seventies [47], discovered the electrochromic properties of thin films of sublimated bis-(phthalocyanine)s of lanthanides. Thus, a wide variety of electrochromic complexes can be obtained by molecular engineering [48]. Changing or mixing different metal ions and changing the relative positions of the chromophores in the triad systems will give different redox properties [31]. The change of colours can therefore be precisely tuned by applying the corresponding voltage. Semi-conduction properties have also been investigated by the group of Simon and collaborators [49], for a series of bis-(phthalocyanine)s of lanthanides but no comparable work was reported for the mixed complexes. The existence of near infrared absorption bands, with high oscillator strength and the position whose maxima can be controlled by molecular engineering, opens up a new and still unexplored field of investigation of those compounds as saturable absorbers for near infrared laser sources.

The bis-(porphyrin)s and bis-(phthalocyanine)s of lanthanides have been studied by many groups around the world. Like the covalently-linked systems, all these studies earlier focused either on pure porphyrin systems, or pure phthalocyanine ones. The mixed porphyrin–phthalocyanine systems were mainly studied by Weiss's group and his collaborators [30,31]. Their recent and comprehensive work with



Pc(Pr)Pc(Pr)TPP Pc(Pr)TPP(Pr)Pc TPP(Pr)Pc(Pr)TPP

Fig. 4. Typical triple-decker complexes avaible by molecular engineering.

Tran-Thi's group, reported the structural, electronic, vibrational, redox, electrochromic, magnetic and photophysical properties of the double-decker Ce^{IV}(TPP)(Pc) in solution and sublimated film [50,51]. Minor studies concerned some triple-decker cerium derivatives such as Ce^{III}(TPP)(Pc)$_2$ and Ce^{III}(Pc)(TPP)$_2$ and the corresponding triple-decker complexes of Gd^{III} [50].

3.2. Ground state electronic properties

3.2.1. Double-decker mixed complexes

The first porphyrin–phthalocyanine double-decker complex, reported by Lachkar et al. [30], was the neutral Ce^{IV}(TPP)(Pc), whose structure has been solved by X-ray diffraction. In this complex, the distance between the two rings, from the mean plane formed by the four pyrrole nitrogens of the porphyrin to the plane formed by the four isoindole nitrogens in the phthalocyanine, is 2.780 Å. For steric reasons (phenyl ring of the porphyrin) and also because of the repulsion of the π orbitals, the porphyrin ring is rotated with respect to the phthalocyanine ring by an angle of 43.4°. In such a system, the electronic interaction between the two π systems is important. As a consequence, the absorption of the double-decker complex is strongly modified, both in intensity (strong decrease) and position of the maxima, with respect to the individual chromophores. The attribution of the bands was therefore based, not only on the spectral changes in correlation with the oxidation and reduction sites, but also by analogy with the spectra of Ce^{IV}(TPP)$_2$ [10]b and Sn^{IV}(Pc)$_2$, [35]b previously reported.

Fig. 5 shows the ground state absorption spectra of the neutral, mono-oxidized and mono-reduced complexes. The neutral compound contains the features characteristic of the Soret and Q bands of the porphyrin, centered at 403 and over 540–650 nm, respectively. The bands peaking at 326, 735 and 817 nm were attributed to the phthalocyanine Soret and Q bands, respectively. As mentioned by the authors, it is clear that the absorption over 540–650 nm contains both phthalocyanine and porphyrin contributions, as it does not disappear completely when the phthalocyanine moiety is oxidized [50].

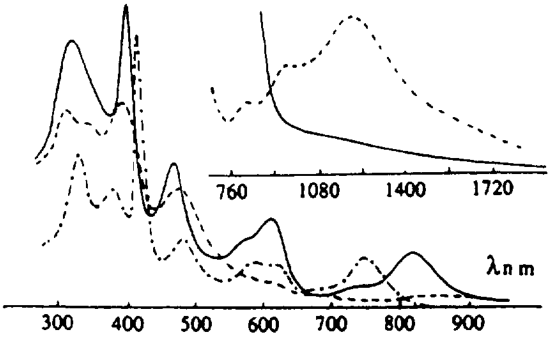


Fig. 5. Absorption spectra of (———) neutral Ce^{IV}(TPP^{2-})(Pc^{2-}) in DCM, (- - -) oxidized Ce^{IV}(TPP^{2-})(Pc$^{\circ -}$) in DCM, (- · -) Ce^{III}(TPP^{2-})(Pc^{2-}) in DMF [50].

A new and broad absorption, centered at 482 nm, was attributed to new π–π^* transitions arising from molecular orbitals delocalized over both macrocycles. Such transitions were found to become more strongly allowed as the radius of the metal ion diminished, i.e., in $Hf^{IV}(TPP)_2$ and $Zr^{IV}(TPP)_2$ complexes [43].

Like the radical Ln^{III} bis-(porphyrin)s and bis-(phthalocyanine)s, the oxidized $Ce^{IV}(TPP^{2-})(Pc^{\circ -})$ displays new near infrared transitions, which can be attributed to the electronic interaction between the two TPP and Pc rings. On the contrary, unlike the other Ln^{III} derivatives, the first reduction corresponds to $Ce^{IV} \rightarrow Ce^{III}$.

The spectra of the radical double-decker complex, $Gd^{III}(TPP^{2-})(Pc^{\circ -})$ and its reduced form $Gd^{III}(TPP^{2-})(Pc^{2-})$ (see Fig. 6) display the same features observed for the oxidized $Ce^{IV}(TPP^{2-})(Pc^{\circ -})$ and neutral $Ce^{IV}(TPP^{2-})(Pc^{2-})$, respectively. There is no clear influence of the metal ion, Gd^{III} or Ce^{IV} , but one can also note that Gd^{III} and Ce^{IV} have the same radius.

It would be interesting to compare the energy of the near infrared absorption band of the mixed porphyrin–phthalocyanine complexes with the corresponding bis-(porphyrin)s and bis-(phthalocyanine)s. In the latter cases, a linear relation between the energy of the maximum of the near IR band, E_{IR}, and the size of the metal ion, was established for the radical double-decker complexes, $(TPP^{2-})Ln^{III}(TPP^{\circ -})$, and their oxidized forms, $Ln^{III}(TPP^{\circ -})_2$. It is interesting to note that an increase of the radius of the metal ion of 0.1 Å results in a decrease of E_{IR} by values of 0.124, 0.110, and 0.030 eV for $(OEP^{2-})Ln^{III}(OEP^{\circ -})$ [37], $(TPP^{2-})Ln^{III}(TPP^{\circ -})$ [37] and $(Pc^{2-})Ln^{III}(Pc^{\circ -})$ [52], respectively. However, the literature data are still too scarce with respect to the mixed complexes to allow such a comparison.

3.2.2. *Triple-decker mixed complexes*

Only two types of triad, $(TPP)Ln^{III}(Pc)Ln^{III}(TPP)$ and $(Pc)Ln^{III}(TPP)Ln^{III}(Pc)$, were reported for Ce^{III} and Gd^{III}. The ground state electronic properties of their neutral forms are very similar, probably because Ce^{III} and Gd^{III} ions have the same radius. In the first triple-decker compound, the inner Pc ring is strongly interacting

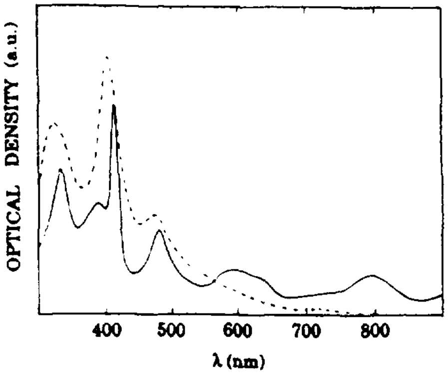


Fig. 6. Absorption spectra of (———) radical $Gd^{III}(TPP^{2-})(Pc^{\circ -})$ in DCE, (———) reduced $Gd^{III}(TPP^{2-})(Pc^{2-})$ in DMF [50].

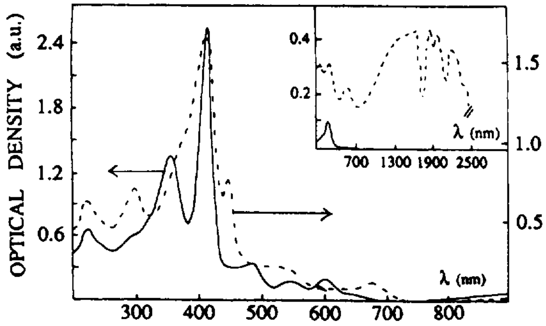


Fig. 7. Absorption spectra of (——) neutral (TPP)Ce^{III}(Pc)Ce^{III}(TPP), 1.2×10^{-5} M, and (— —) oxidized form, 10^{-4} M; solvent = DCM [50].

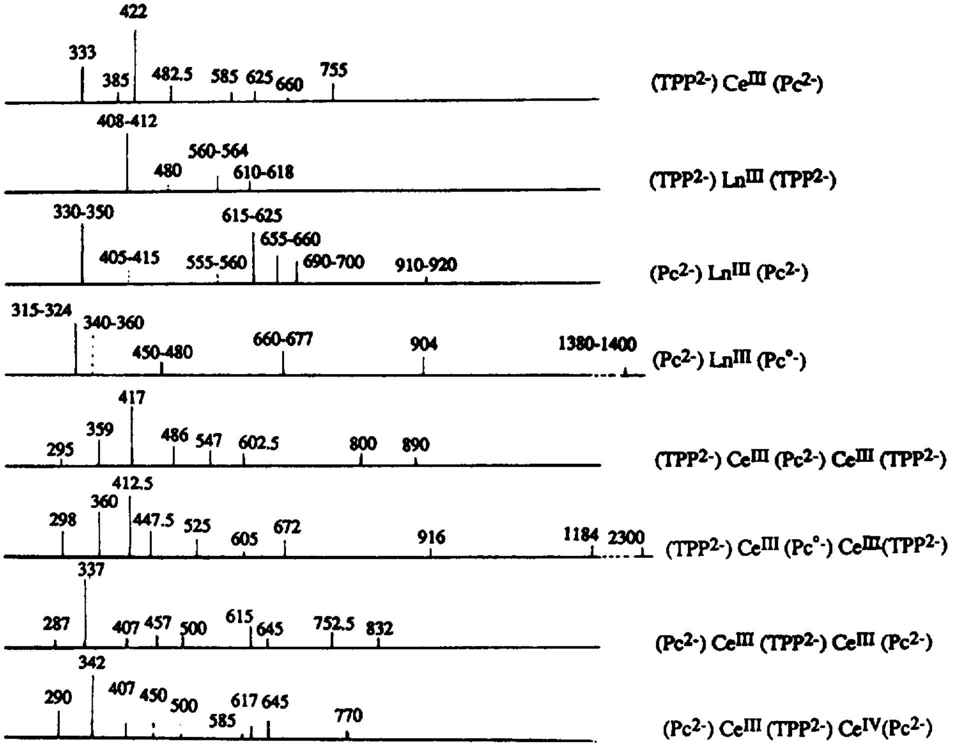


Fig. 8. Schematic representation of the electronic absorption bands for various double- and triple-decker complexes [50].

with the two outer TPP rings. As a consequence, the Pc Q band is strongly depleted and its position is strongly shifted to the red (890 nm), with respect to the Pc Q band in the reduced (TPP)Ce^{III}(Pc) form (755 nm) (see Fig. 7 and Fig. 8).

Similar features were observed in the second triad, where the inner ring is the porphyrin moiety. Here, the porphyrin Q band is strongly depleted and its position largely shifted to the red (832 nm) with respect to the TPP Q band in the (TPP)Ce^{III}(Pc) (625 nm).

When the two triple-decker complexes of Gd^{III} are oxidized, the authors could clearly attribute the site of the first oxidation to the phthalocyanine moiety. The case of the cerium derivatives, where the metal ion can also be oxidized, is more complex. However, by strategic modifications of the substituents on the Pc ring, and using complementary techniques such as electrochemistry, magnetism, X-ray photoelectron spectroscopy (XPS) and resonance Raman, the authors could conclude that the hole resides on one of the cerium ions in the oxidized (Pc)Ce^{IV}(TPP)Ce^{III}(Pc) complex. In the case of (TPP)Ce^{III}(Pc)Ce^{III}(TPP), a thermodynamic equilibrium

$$Ce^{IV}(Pc^{2-}) \rightleftarrows Ce^{III}(Pc^{\circ -})$$

was proposed to reconcile the liquid phase data and the solid state behavior. Interestingly, the authors proposed, for the first time, a new marker Raman band for the phthalocyanine, at 1500 cm^{-1}, which is redox-sensitive and significantly upshifts when the Pc ring is oxidized. They also noted in one singular system, corresponding to the oxidized (Pc)Ce^{IV}(TPP), that the hole is delocalized over the TPP and Pc moieties [50].

3.3. *Excited states properties*

Very few works have reported excited states properties of the double- and triple-decker complexes. The reasons are very simple: most of the complexes do not fluoresce or display very weak emission. Moreover, their excited states are very short-lived. Ultrafast laser sources coupled with transient absorption spectroscopy are therefore the tools needed and best-suited to probe the excited state properties of these complexes. Holten and colleagues were the first to report such studies on a series of lanthanide double-decker complexes of porphyrins.

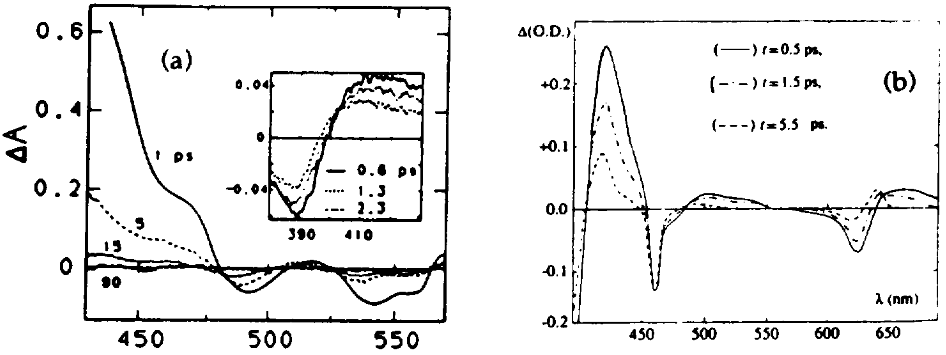


Fig. 9. Time-resolved absorption difference spectra of (a) Ce(TPP)(OEP) from Ref. [53]a; (b) of Ce(TPP)(Pc) from Ref. [51].

Table 3
Excited states properties of cerium complexes

Complex	Solvent	T (°K)	τ_1 (ps)	τ_2 (ps)	Ref.
$Ce(OEP)_2$	toluene	295	1.5 ± 0.2	6 ± 2	[53]a
	toluene	180	1.2 ± 0.5	7 ± 2	
	acetone	295	2.5 ± 0.6	14 ± 3	
	CH_2Cl_2	295	1.5 ± 0.5	7 ± 2	
$Ce(TTP)_2$	CH_2Cl_2	295	1.5 ± 0.2	9 ± 3	[53]a
Ce(TPP)(OEP)	toluene	295	1.8 ± 0.2	10 ± 3	[53]a
	toluene	180	2.0 ± 0.3	10 ± 3	
Ce(TPP)(Pc)	CH_2Cl_2	295	2.5 ± 0.5	33 ± 8	[51]
	thin film	295	0.9 ± 0.5	30 ± 7	

Their work, especially on the Ce derivatives [53]a, $Ce(TPP)_2$ and Ce(TPP)(OEP) was of particular interest, because of the similarity of the two Ce(TPP)(OEP) [53]a and Ce(TPP)(Pc) systems [1]. The data are compared in Fig. 9. and Table 3.

Similar difference absorption spectra and decay kinetics were established for the two systems. The two groups suggested the same mechanism of relaxation of the primary excited states:

$$(\pi,\pi^*)\text{ state} \xrightarrow{\tau_1} \text{RMCT state} \xrightarrow{\tau_2} \text{ground state}$$

where the ring to metal charge transfer state, RMCT, would correspond to $Ce^{III}(TPP^{2-})(OEP^{\circ -})$ for Holten's system and $Ce^{III}(TPP^{2-})(Pc^{\circ -})$ for Tran-Thi's system. This interpretation was based on the redox properties of the Ce^{IV} derivatives. A very low lying RMCT state, at 0.77 [53]a and 0.67 eV [50], was expected for both systems, from the redox potential values of $Ce^{IV}(TPP^{2-})(OEP^{2-})$ and $Ce^{IV}(TPP^{2-})(Pc^{2-})$, respectively.

Among the Ce^{IV} derivatives, the lifetime of the RMCT state in the Ce^{IV}(TPP)(Pc) complex is the largest. This is probably due to the re-distribution of the charge (hole) over the different, TTP, OEP and Pc rings, when they are oxidized. Such long lifetimes were reported for $Lu^{III}(Pc)_2$ systems [53]b, for which the authors also suggested a decay of the primary excited states to the ground state, via a low lying RRCT state (see Table 4).

Table 4
Excited states properties

Complex	Solvent	λ^F (nm)	λ^P (nm)	τ_S (ps)	$\tau_{(T\text{ or }CT)}$	Ref.
$Th^{IV}(OEP)_2$		790	960	10	50 µs	[45]
$Hf^{IV}(TPP)_2$	toluene	960		550	3 ns	[43]
$Zr^{IV}(TPP)_2$	toluene	960		1100	5.7 ns	[43]
$Lu^{III}(Pc)_2$	CH_2Cl_2			60		[53]b
$Lu^{III}(Pc)_2^+$	CH_2Cl_2/TBAP			60		[53]b
$Lu^{III}(Pc)_2^-$	CH_2Cl_2/TBAP			36		[53]b

In contrast to the systems described above, some other complexes such as $Th^{IV}(OEP)_2$ [45], $Hf^{IV}(TPP)_2$ and $Zr^{IV}(TPP)_2$ [43] display a very different behavior. Intersystem crossing from singlet excited state to the low lying triplet is the main deactivation pathway. The triplet lifetime was very long (see Table 4).

Though the literature data are very scarce especially on the excited state properties of double- and triple-decker complexes, it is interesting at this point to note the trends observed for these compounds. Two main processes exist which could compete with one another: intersystem crossing from singlets to triplets and charge transfer reaction (RMCT or RRCT). The heavy atom effect and paramagnetic properties of the metal ion favour the first process, while low values of reduction and oxidation potentials favour the second. The difference of energy between the two states, triplet and CT, is therefore crucial, as well as their position with respect to the first singlet state. One should also consider the possibility of the existence of CT reaction from the triplet excited states, especially when paramagnetic double- or triple-decker are excited. Such cases have not been reported in the literature up to now. Their study would allow a deeper understanding of the excited state properties in strongly coupled systems. Such problems are under consideration in Tran-Thi's group with ongoing work on double and triple-decker complexes of the paramagnetic Gd derivatives.

4. Self-assembled ionic systems

4.1. Formation of the ionic assemblies in solution

Inorganic coordination chemistry offers numerous examples of supramolecular assemblies bound by ion pair attraction in solution. In most cases, the properties of such complexes differ notably from those of the parent compounds. So-called ion pair charge transfer (IPCT), or outer sphere charge transfer (OSCT) transitions are frequently observed in these complexes [54] and have been successfully interpreted in the context of the Marcus and Hush theories [55]. Organic molecules, on the other hand, are usually stable in an electrically neutral state. Nevertheless, a number of organic ions form stable ion pairs in solution, and IPCT type transitions have been observed in some cases. In the last few years, the photochemical properties of pairs of organic ions with methylviologen, MV^{2+}, (dimethyl-1,1-bipyridinium-4,4′) as the cation, have been particularly studied. These complexes are usually highly photosensitive and yield the reduced radical cation $MV^{+\circ}$ upon light exposure. Ion pairs such as MV^{2+}/triphenylborate or MV^{2+}/benzylate have been used in photoelectrochemical cells [56]. The MV^{2+}/rose bengale couple has also been proposed as a photosensitizer for the photoreduction of water [57], and more recently MV^{2+} coupled with a series of tetrasulfonated porphyrins has been extensively studied [58].

Stable ion pairs can also be obtained with tetrapyrrole macrocycles such as porphyrins and phthalocyanines grafted with ionic substituents of opposite charges. In this case, both the coulombic attraction between the charged substituents and the hydrophobic interaction of the aromatic macrocycles act to hold the individual

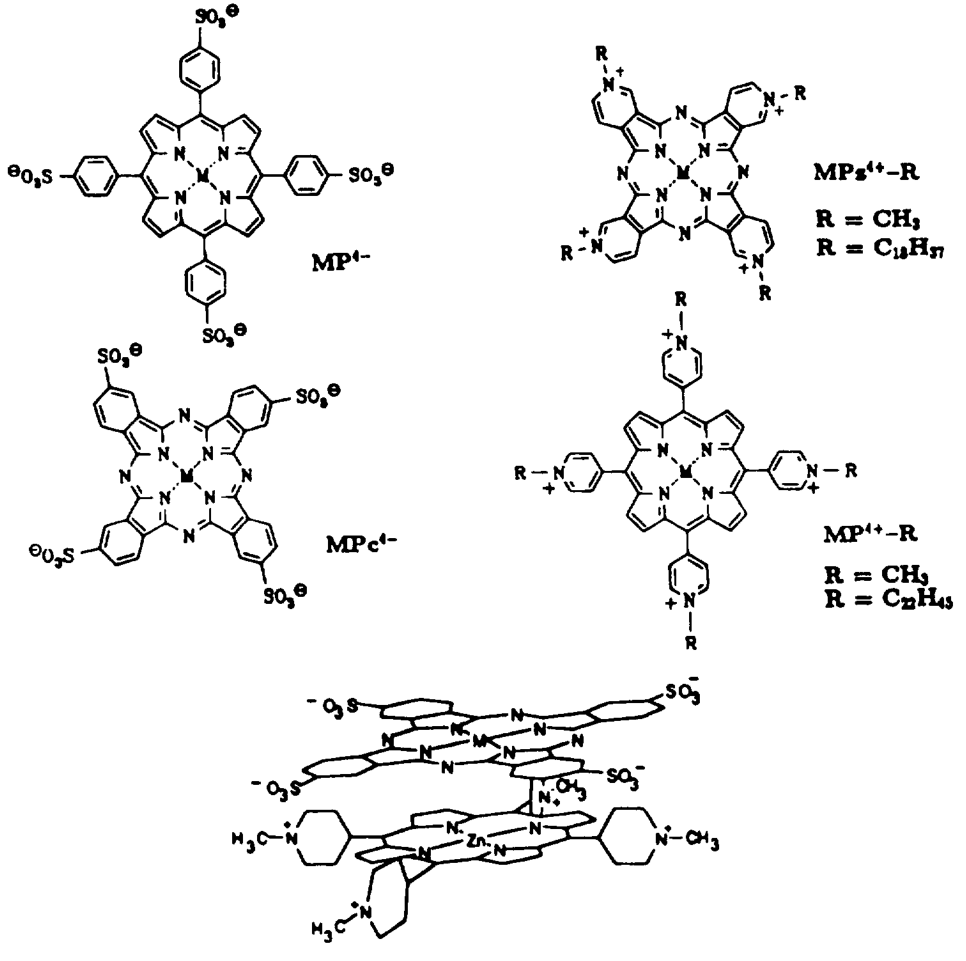


Fig. 10. Ionic porphyrins, phthalocyanines and porphyrazins used as starting materials for sel-assembled ionic systems. The counter ions are Na^+ and Cl^-.

components together. In addition, their planar geometry allows a close contact and therefore an extensive orbital overlap in the face-to-face configuration Fig. 10.

The formation of complexes of tetraanionic and tetracationic porphyrins with a 1:1 stoichiometry was first reported by Shimidzu [12] and then by Linschitz et al. [59] and Schaafsma et al. [60]. The existence of similar complexes obtained by pairing tetrasulfonated phthalocyanines with tetrakis (*N*-methylpyridinium-4-yl)porphyrins [28,61,62] or tetrasulfonated tetraphenylporphyrins with either tetrakis (3-methylpyridyloxy)phthalocyanine [63] or tetrakis (*N*-methylpyridinio) porphyrazines [64] has also been reported.

In contrast to the mixed porphyrin complexes, the parent constituents of the mixed porphyrin–phthalocyanine and porphyrin–porphyrazin complexes display very different and complementary absorption spectra, which allow the study of their aggregation properties using spectroscopic methods.

The method of Job has been commonly used to determine the stoichiometry of the mixed complexes and was successfully used for tetrapyrrole systems [12,23,58,61]. It relies on the fact that the optical density of a mixture of chromophores which do not interact with each other is the sum of the absorptions due to each chromophore separately. Conversely, departures from additivity, as the composition of the solution is continuously varied, can be interpreted as evidence of the formation of a complex. In the Job method, the stoichiometry of this complex can be deduced from the composition at which the deviation from additivity is a maximum.

Examples of titration methods of the $H_2P^{4+}/CuPc^{4-}$ system by absorption spectroscopy are shown in Figs. 11(a) and (b). The series of absorption spectra exhibit a first set of perfectly defined isobestic points up to 1:1 stoichiometry, which is replaced by a second one up to 1:2 stoichiometry. This clearly indicates the successive formation of the two complexes. The analysis of the data by the Job method (Fig. 12) clearly shows the formation of the complexes of different stoichiometries.

In addition to the Job method, Tran-Thi et al. proposed a second fluorimetric method of determination of the stoichiometry of the mixed complexes, which takes

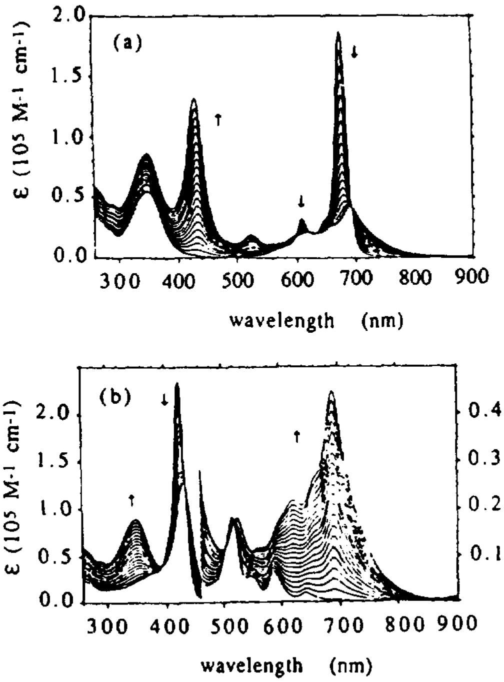


Fig. 11. (a) Spectral evolution of H_2P^{4+} 10^{-5} M in DMSO upon addition of small aliquots of $CuPc^{4-}$, 10^{-3} M [65]. (b) Spectral evolution of $CuPc^{4-}$, 10^{-5} M, in DMSO upon addition of small aliquots of H_2P^{4+}, 10^{-3} M [65].

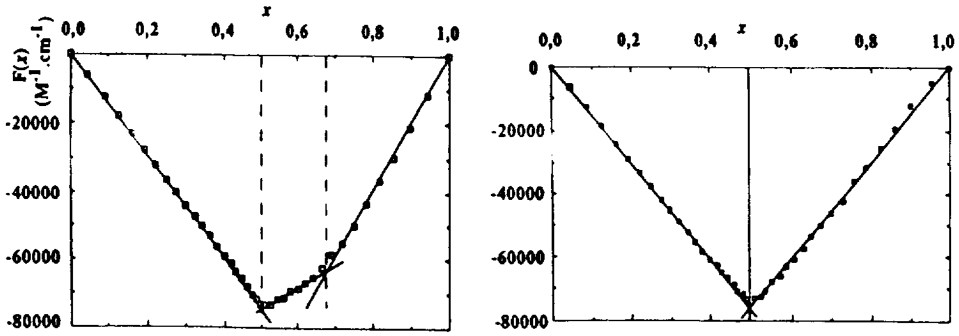


Fig. 12. Job diagram for (a) $H_2P^{4+}/CuPc^{4-}$ and (b) $ZnP^{4+}/CuPc^{4-}$ in DMSO: $\lambda = 680$ nm [65]. $F(x) = d(x) - (\epsilon_{Pc^{4-}} - \epsilon_{P^{4+}})x - \epsilon_{P^{4+}}$, where $x = [Pc]/([P] + [Pc])$ and $d(x)$ the absorbance of the solution.

advantage of the strongly fluorescent properties of the tetrapyrrole systems. They pointed out, for the first time, by using both methods, the existence of aggregates of high order, i.e., triads [65] and pentads [64].

Fig. 13 shows an example of the evolution of the fluorescence H_2P^{4+} upon addition of small aliquots of $CuPc^{4-}$. The fluorescence intensity decreases linearly as the amount of $CuPc^{4-}$ increases, until the 1:1 stoichiometry is reached. A second linear regime is observed up to 2 equivalents after which no further evolution occurs. Just as for the Job diagram, the equilibrium constants can be easily determined from the

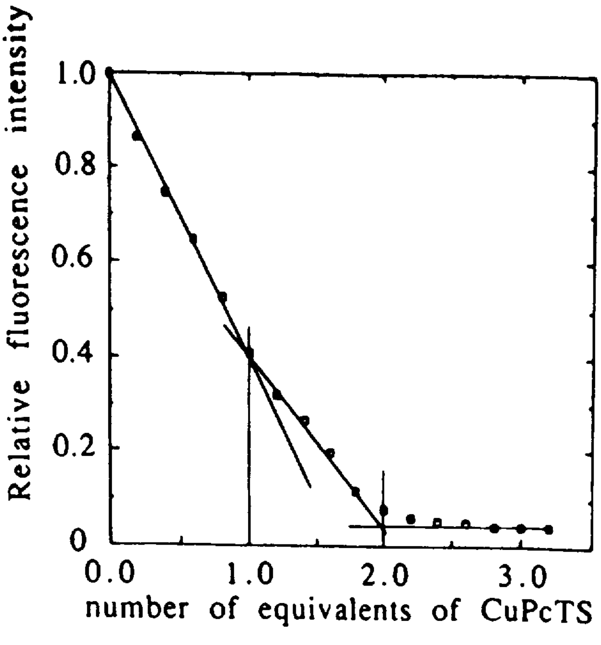


Fig. 13. Evolution of the H_2P^{4+} fluorescence in DMSO upon addition of small aliquots of $CuPc^{4-}$ [65].

difference between the experimental curve and the intersection of the lines extrapolated from the linear parts of the graph ([65], supplementary materials).

The fluorimetric method is very sensitive and reliable, but requires that the mixed complexes resulting from the self-aggregation are non-or poorly fluorescent over the spectral domain of fluorescence of the two parent compounds. This condition is fulfilled, not only when one of the parent compounds is non-fluorescent (as when it contains a paramagnetic or heavy metal ion), but also when both monomers fluoresce, as recently demonstrated by Tran-Thi et al. [66].

Tran-Thi et al demonstrated the crucial role of the solvent and metal ion in the formation of the self-assembled complexes [65]. Diads and triads were identified for the $H_2P^{4+}/CuPc^{4-}$ system in dimethylsulfoxide (DMSO), whereas only diads were observed for the $ZnP^{4+}/CuPc^{4-}$ in the same solvent. Changing DMSO to a mixture of water–dioxane (Fig. 14) allowed them to reveal the existence of the two triads, $ZnP^{4+}/CuPc^{4-}/ZnP^{4+}$ and $CuPc^{4-}/ZnP^{4+}/CuPc^{4-}$ stabilized by their counter ions Cl^- and Na^+, whereas only the diad $ZnP^{4+}/CuPc^{4-}$ was formed in aqueous solutions containing a small amount of pyridine.

An extensive survey of the literature, by Tran-Thi et al., of ionic complexes with various metal ions and solvents, summarized in Table 5, were rationalized as follows.

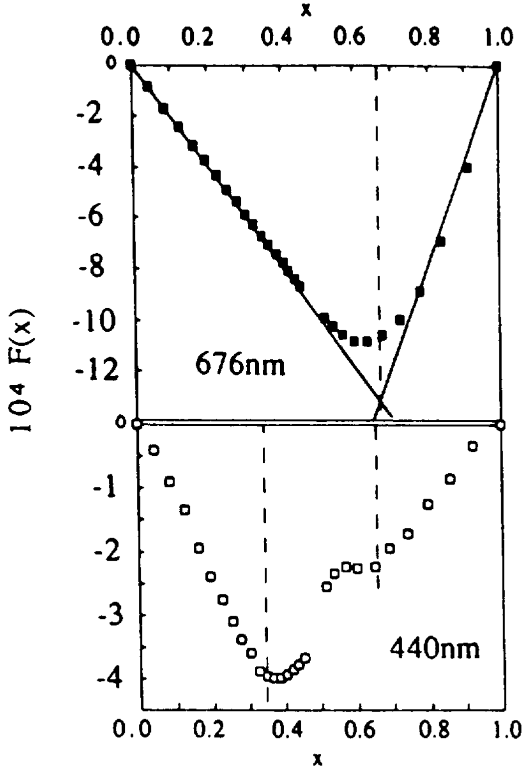


Fig. 14. Job diagram for $ZnP^{4+}/CuPc^{4-}$ in water/dioxane, 80/20 (v/v) [65].

Table 5
Association constant of the mixed complexes

Systems	Solvent	Job	Fluo	k_{ass} (Job)	k_{ass} (Fluo)	Ref.
$ZnP^{4+}/CuPc^{4-}$	DMSO	P/Pc	P/Pc	4.0×10^7 M^{-1}	3.6×10^7 M^{-1}	[65]
	H_2O	—	P/Pc			[65]
			P_2/Pc			
	H_2O/dioxane	P_2/Pc				[65]
		P/Pc		4.0×10^7 M^{-1}	3.6×10^7 M^{-1}	
		P/Pc_2				
	H_2O/pyridine	P/Pc				[65]
$H_2P^{4+}/CuPc^{4-}$	DMSO	P/Pc	P/Pc	2.3×10^{10} M^{-1}	2.3×10^{10} M^{-1}	[65]
		P/Pc_2	P/Pc_2	4.8×10^{17} M^{-2}	5.1×10^{17} M^{-2}	[65]
	DMSO	P/Pc		5.0×10^6 M^{-1}		[28]
ZnP^{4+}/H_2Pc^{4-}	DMSO	P_2/Pc		7.2×10^{17} M^{-2}	6.8×10^{17} M^{-2}	[65]
		P/Pc		4.0×10^{10} M^{-1}	3.8×10^{10} M^{-1}	
$ZnP^{4+}/NiPc^{4-}$	DMSO	P/Pc				[65]
$ZnP^{4+}/AlClPc^{4-}$	DMSO	P/Pc	P/Pc		2.3×10^7 M^{-1}	[65]
	H_2O		P_2/Pc			[65]
		P/Pc	P/Pc			
			P/Pc_2			
$ZnP^{4+}/GaClPc^{4-}$	DMSO	none	none			[66]
$H_2P^{4+}/NiPc^{4-}$	DMSO	P/Pc		1.2×10^{10} M^{-1}		[65]
		P/Pc_2		9.0×10^{16} M^{-2}		[65]
H_2P^{4+}/H_2Pc^{4-}	DMSO	P_2/Pc				
		P/Pc		2.0×10^{10} M^{-1}		[66]
		P/Pc_2		3.1×10^{17} M^{-2}		[66]
$H_2P^{4+}/ZnPc^{4-}$	DMSO	P/Pc		5.0×10^6 M^{-1}		[28]
$MgP^{4+}/CuPc^{4-}$	DMSO	P/Pc		7.8×10^8 M^{-1}		[66]
MgP^{4+}/H_2Pc^{4-}	DMSO	P_2/Pc		7.3×10^{16} M^{-2}		[66]
		P/Pc				
$MgP^{4+}/CoPc^{4-}$	H_2O/EtOH 50:50, V/V	P/Pc		1.3×10^5 M^{-1}		[66]
$MgP^{4+}/NiPc^{4-}$	H_2O/EtOH 50:50, V/V	P/Pc		2.0×10^5 M^{-1}		[62]
$MnClP^{4+}/NiPc^{4-}$	H_2O/EtOH 50:50, V/V	P/Pc		3.0×10^5 M^{-1}		[62]
$MnClP^{4+}/CoPc^{4-}$	H_2O/EtOH 50:50, V/V	P/Pc		2.1×10^5 M^{-1}		[62]
$MnClP^{4+}/MnPc^{4-}$	DMSO	P/Pc				[61]
$H_2P^{4-}/CoPz^{4+}$	H_2O	P_2/Pz				[64]
		P/Pz				
		P_2/Pz_3				
		P/Pz_2				

Self aggregation of the mixed complexes is governed by: (1) the ability of the metal ion to coordinate one or two axial ligands; (2) the donating power of the solvent; (3) the relative position of the oppositely charged substituents on the macrocycles.

Steric hindrance due to axial ligation has a dramatic effect on the nature of the complexes formed in solution. Five typical cases can be pointed out:

(1) combining metal ions such as Zn, Mg, Cu or Ni with strongly coordinating solvents such as DMSO, pyridine, or nitrogenous bases like pyrimidines, picoline and imidazole, will only give 1:1 complexes;
(2) combining the same metal ions, Zn, Mg, Cu or Ni with poorly coordinating solvent such as water, MeOH, EtOH or dioxane will give aggregates of high order;
(3) dissolving non-metallated (free base) complexes in any polar solvent will give complexes of high order;
(4) mixing Zn, Mg, Cu or Ni with a free base partner in strongly coordinating solvents will give the diad and one triad;
(5) combining free base compounds or metallated ones to some typical metal ions such as Al and Ga, which are pentacoordinated and able to become hexacoordinated in strongly coordinating solvents, will not give any mixed complexes in these solvents. However, in water, aggregates can be formed.

These five cases are summarized in Fig. 15.

The relative position of the charged substituents on the two macrocycles has also a strong influence on the formation of the complexes. Lipskier and Tran-Thi showed that heteroaggregation only occurs when the quaternary N^+–CH_3 substituents are in the *para* position of the phenyl ring of the porphyrin and the sulfonated ones in the 4,4′,4″,4‴ positions of the phthalocyanine ring [65]. Fig. 16 shows the hindrance effect observed on mixing a 3,3′,3″,3‴-tetrasulfonated phthalocyanine with the tetracationic porphyrin; no strongly coupled complexes can be obtained in such a case.

On the basis of these results [65], the authors suggested that the relative face-to-

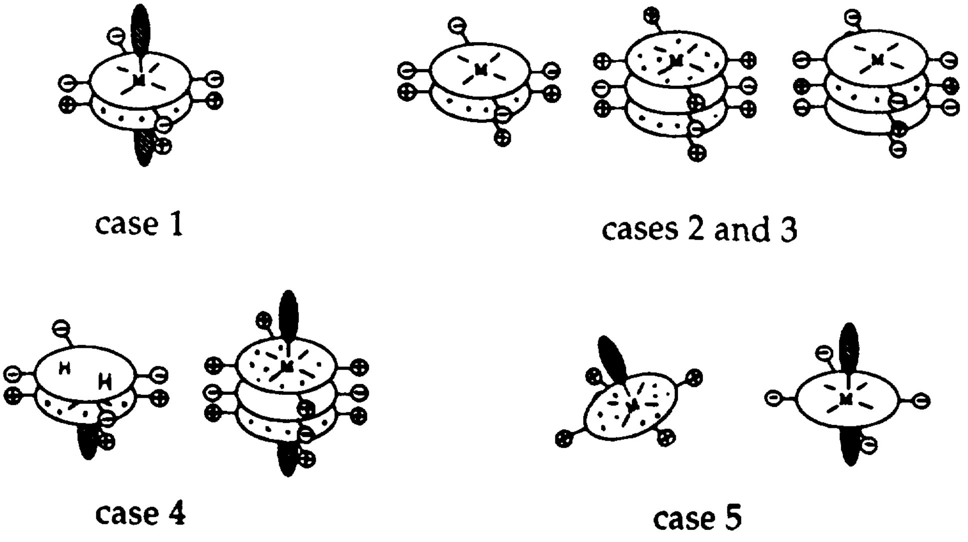


Fig. 15. Effect of axial ligation on the formation of diad and triads.

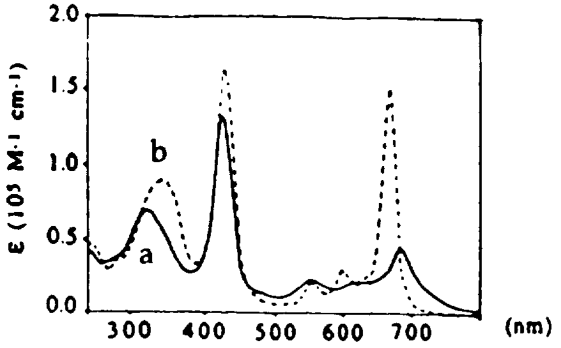


Fig. 16. Spectra of a 1/1 mixture of 10^{-5} M $ZnP^{4+}/AlClPc^{4-}$ in water. (a) with the 4,4′,4″,4‴ tetrasulfonated $AlClPc^{4-}$, (b) with a mixture (50/50) of 3,3′,3″,3‴ and 4,4′,4″,4‴ $AlClPc^{4-}$.

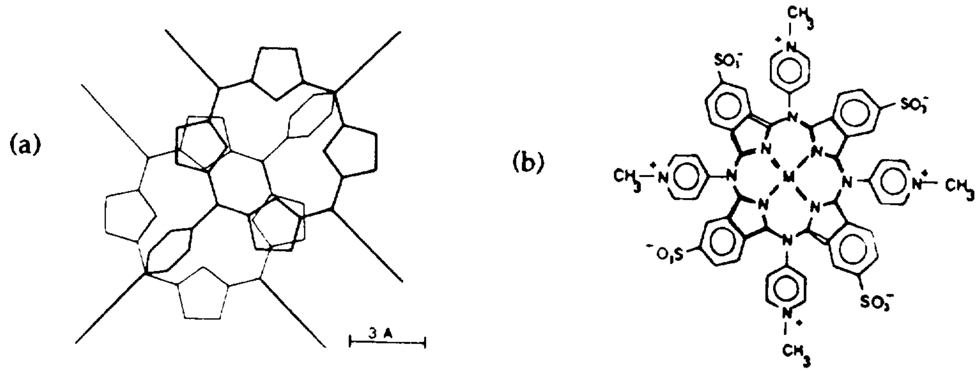


Fig. 17. Top views of (a) the ZnP^{4+}/ZnP^{4-} complex calculated from NMR data [60], (b) the $MP^{4+}/MTPc^{4-}$ complex derived from complexation studies [65].

face conformation of the heterocomplex must be very different from that found by Schaafma's group for the ionic porphyrin complexes [60] (see Fig. 17). Space filling molecular models show that there is practically no hindrance in the face-to-face porphyrin–phthalocyanine complex, when all the phthalocyanine substituents are on the 4,4′,4″,4‴ positions (see Fig. 17). In contrast, a large steric repulsion is to be expected when one or several substituents are in any of the 3,3′,3″,3‴ positions.

The conformation which seems to stabilize the 1/1 mixed and ionic complex is very reminiscent of the relative conformation adopted by the two moieties in the double-decker mixed porphyrin–phthalocyanine complexes [30].

The aggregation properties of the ionic porphyrin–phthalocyanine complexes reported in the literature are summarized on Table 5.

4.2. Ground state optical properties

The absorption spectra of the various mixed ionic diads display the same features, independent of the nature of the metal ions. In contrast to the covalently linked mixed porphyrin–phthalocyanine complexes, the interaction between the two moieties is much stronger, resulting in a drastic decrease of the intensities and a red shift of both the porphyrin Soret band and the phthalocyanine Q band (Fig. 18 and Fig. 19). New absorptions also appear in the 480–650-nm range, which are reminiscent of those observed in the closed packed, sandwich type double-decker complex of porphyrin and phthalocyanine of cerium (IV).

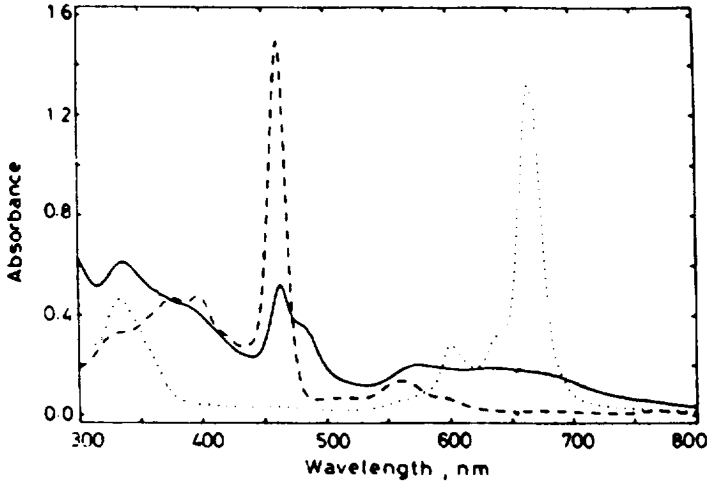


Fig. 18. Absorption spectra of (– · –) ZnP^{4+}, $4Cl^-$ (left ordinate), (– – –) $CuPc^{4-}$, $4Na^+$ (right ordinate), (- - -) 1/1 $ZnP^{4+}/CuPc^{4-}$, (right ordinate) in DMSO [65].

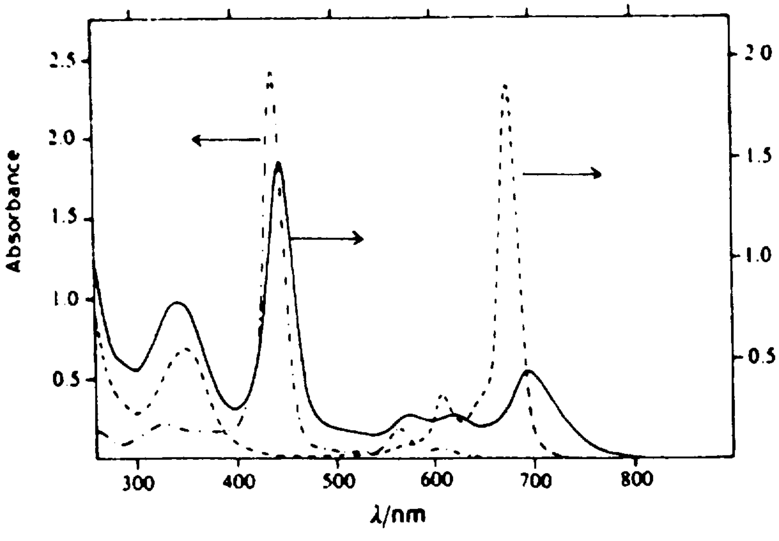


Fig. 19. Absorption spectra of: (————) $MnClP^{4+}$, $4Cl^-$; (· · ·) $NiPc^{4-}$, $4Na^+$; (- - -) 1/1 $MnClP^{4+}/NiPc^{4-}$, 10^{-5} M in 50% (v/v) water/EtOH [62].

Similar absorption spectra have also been established for diads and high order complexes composed of tetrasulfonated porphyrins, H_2P^{4-}, $4Na^+$, and cationic porphyrazins $CoPz^{4+}$, $2SO_4^{2-}$ (Fig. 20), thus indicating again the importance of the hydrophobic interaction between the macrocycles.

The first ionic triads were reported by Tran-Thi's group. The absorption spectra of the $H_2P^{4-}/2CoPz^{4+}$ [64] $H_2P^{4+}/2CuPc^{4-}$ [61] and $2MgP^{4+}/H_2Pc^{4-}$ [66] are shown in Fig. 20, Fig. 21 and Fig. 22, respectively.

Up to the present time, the geometry of the aggregates, diads, triads and pentads

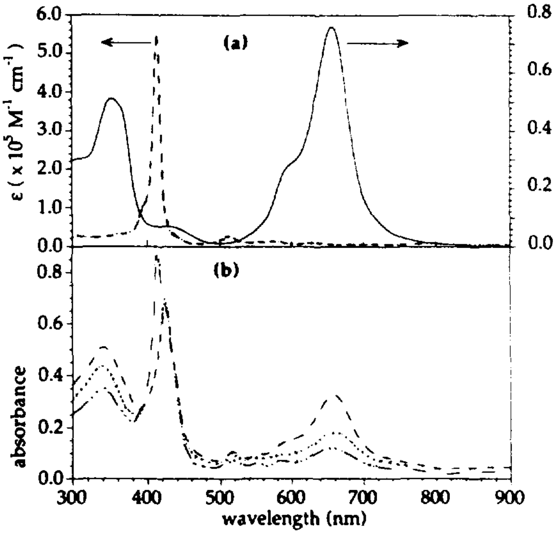


Fig. 20. Absorption spectra of aqueous solutions of (a) (· · ·) H_2P^{4-}, $4Na^+$ (left ordinate); (- - -) $CoPz^{4+}$, $2SO_4^{2-}$ (right ordinate). (b) Mixed complexes with different stoichiometry: (—· · ·—) diad, (– – –) $H_2P^{4-}/2CoPz^{4+}$ triad, (· · ·) $2H_2P^{4-}/3CoPz^{4+}$ pentad [64].

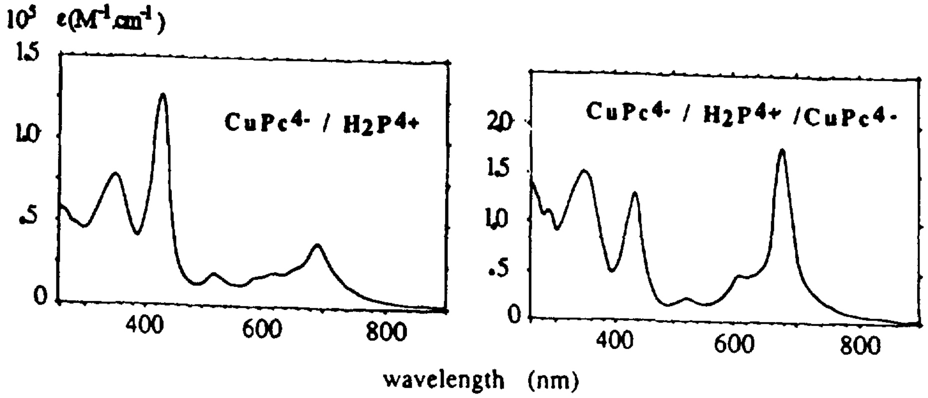


Fig. 21. Absorption spectra of the diad and triad, 10^{-5} M in DMSO [65].

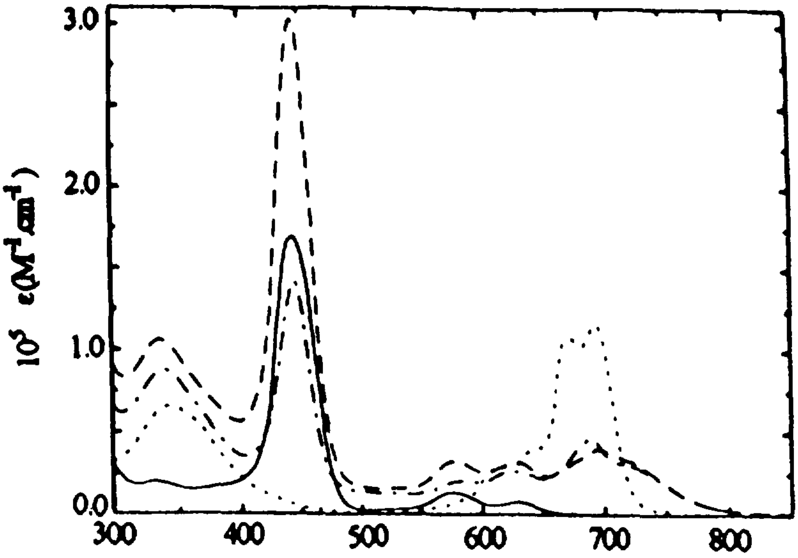


Fig. 22. Absorption spectra of (a) MgP^{4+}, (b) H_2Pc^{4-}, (c) MgP^{4+}/H_2Pc^{4-} and (d) $2MgP^{4+}/H_2Pc^{4-}$ in DMSO [66].

is not precisely known. NMR, static and dynamic light scattering and neutron scattering techniques applied to these systems, were unsuccessful, mainly because of concentration and precipitation problems. However, some clues have been shed with the study of the ionic diads in the solid state; Tran-Thi et al., by using the Langmuir-Blodgett technique (LB) and semi-amphiphilic heterocomplexes, formed with the same tetrasulfonated phthalocyanines coupled with cationic porphyrins bearing long alkyl chains, succeeded in transferring the mixed complex from the water subphase onto solid quartz substrates [67]. The spatial orientation and anisotropy of the self-assembled mixed complexes in LB films was probed with polarized light, using the UV and visible dichroism. The authors deduced that the mixed complex lies flat on the substrate and the tilted angle between the complex plane and the substrate plane is less than 15°. Moreover, the surface pressure vs. area isotherms, established for a series of mixed complexes, allowed the extraction of a molecular surface area of the mixed complex, 235 ± 10 Å^2, which is consistent with the proposed model [66,67].

In such face-to-face complexes, the two chromophores are expected to be held in close contact (3 Å), forming intimate ion pairs. Such complexes, because of the chemical versatility and variety of photophysical properties of each partner, display a variety of properties in the excited state.

4.3. Excited state properties

The photophysical properties of porphyrin and phthalocyanine monomers have been studied since the early sixties by numerous groups around the world. It is well known that, depending on the nature of the metal ions which can be diamagnetic or paramagnetic, oxidizable or reducible, the two monomers display a wide variety of properties in their excited states; intersystem crossing from singlet to triplet excited state (k_{isc}), fluorescence (k_{f}), internal conversion (k_{ic}), ligand to metal charge transfer (k_{LMCT}) and metal to ligand charge transfer (k_{MLCT}) are the main processes which govern the energy dissipation process of the excited state and compete with one another. In the mixed complexes, one should also consider interchromophore transfer reactions such as ligand to ligand charge transfer, metal to metal charge transfer, in addition to MLCT and LMCT.

From the excited state properties gathered in the literature, we can classify the mixed complexes into four distinct categories: (1) diamagnetic mixed complexes, resulting from the pairing of two metallated, diamagnetic monomers or metallated diamagnetic monomer with a free base partner; (2) paramagnetic mixed complexes, issued from the coupling a paramagnetic porphyrin (or phthalocyanine) with a diamagnetic phthalocyanine (or porphyrin); (3) mixed complexes with one oxidizable or reducible metal ion; (4) mixed complexes with one oxidizable and one reducible metal ion.

4.3.1. Mixed diamagnetic complexes

The photophysical properties of the diamagnetic complexes have been studied thoroughly by Tran-Thi's group, using time resolved techniques, such as femtosecond absorption spectroscopy, nanosecond flash photolysis, picosecond single photon counting and steady-state fluorimetry [65,68]. In both solutions and Langmuir-blodgett films of the same complexes, the relaxation processes of the first singlet state of the excited mixed complex are identical and can be summarized in the following scheme.

$$\mathrm{M_1P-M_2Pc} \xrightarrow{h\nu} {}^{1\mathrm{S}}(\mathrm{M_1P-M_2Pc})^*$$

$${}^{1\mathrm{S}}(\mathrm{M_1P-M_2Pc})^* \xrightarrow{{}^{1}k_{et}} {}^{2\mathrm{S}}(\mathrm{M_1P^{\circ +}-M_2Pc^{\circ -}})$$

$${}^{1\mathrm{S}}(\mathrm{M_1P-M_2Pc})^* \xrightarrow{k_{isc}} {}^{1\mathrm{T}}(\mathrm{M_1P-M_2Pc})^*$$

$${}^{2\mathrm{S}}(\mathrm{M_1P^{\circ +}-M_2Pc^{\circ -}}) \xrightarrow{\mathrm{k_f}} {}^{\mathrm{S}^{\circ}}(\mathrm{M_1P-M_2Pc})+\mathrm{h}\nu'$$

$${}^{2\mathrm{S}}(\mathrm{M_1P^{\circ +}-M_2Pc^{\circ -}}) \xrightarrow{{}_{1}k_{(-\mathrm{et})}} {}^{\mathrm{S}^{\circ}}(\mathrm{M_1P-M_2Pc})$$

$${}^{1\mathrm{T}}(\mathrm{M_1P-M_2Pc}) \xrightarrow{K_{\mathrm{T}}} {}^{2\mathrm{T}}(\mathrm{M_1P^{\circ +}-M_2Pc^{\circ -}}) \text{ and } {}^{\mathrm{S}^{\circ}}(\mathrm{M_1P-M_2Pc})$$

$${}^{2\mathrm{T}}(\mathrm{M_1P^{\circ +}-M_2Pc^{\circ -}}) \xrightarrow{{}_{3}k_{(-\mathrm{et})}} {}^{\mathrm{S}^{\circ}}(\mathrm{M_1P-M_2Pc})$$

(with $\mathrm{P=P^{4+}}$ and $\mathrm{Pc=Pc^{4-}}$)

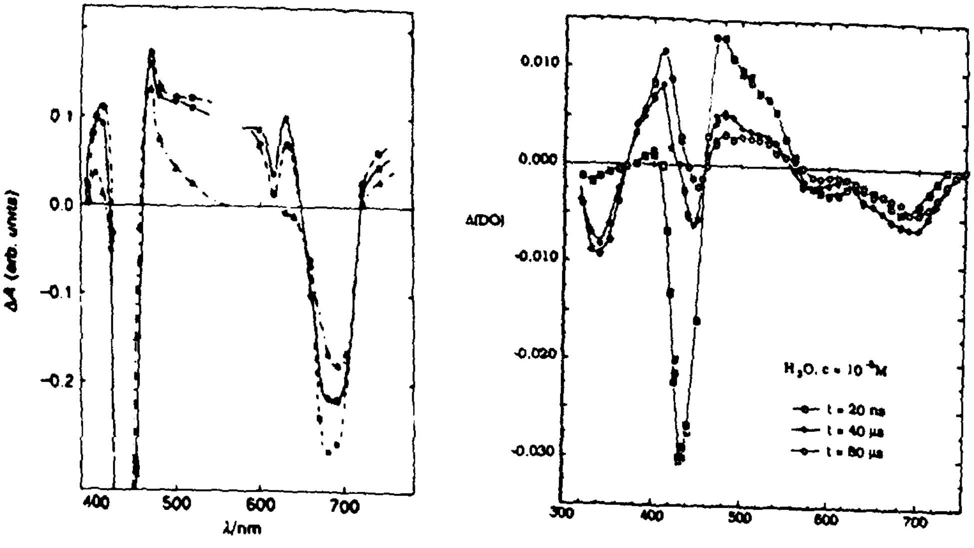
These authors found that ligand to ligand charge transfer (LLCT) in the singlet excited state was the most efficient deactivation pathway, with quantum yield values approaching unity ($\phi_{et}=0.95$–0.975). Intersystem crossing from singlet to triplet, which is the most important deactivation process within the respective monomers, is the main process competing with electron transfer within the mixed complex ($\phi_{isc}=0.025$–0.05).

When M_1 = Zn, Mg, H_2 and M_2 = AlCl, H_2, the CT states, resulting from charge transfer in the excited singlet or triplet states, correspond to the oxidized porphyrin and reduced phthalocyanine. The attribution of the LLCT species is based on the typical absorption displayed by the oxidized zinc porphyrin and reduced phthalocyanines, peaking at 410 [69] and at 550 and 650 nm [70], respectively.

This is clearly seen, for example, by the formation of the oxidized zinc porphyrin and reduced aluminum phthalocyanine shown in Fig. 23.

New emissions, attributed to the radiative decay of LLCT states, were observed for the $ZnP^{4+}-H_2Pc^{4-}$ and $MgP^{4+}-H_2Pc^{4-}$ systems, with maxima at 787 and 810 nm, respectively [66]. These maxima are both red-shifted with respect to the fluorescence of the corresponding monomers.

These authors profited from their complementary studies, covering liquid and organized solid media, by gauging the importance of the solvent effect on the forward



(a)

(b)

Fig. 23. difference absorption spectra of ZnP^{4+}-$AlClPc^{4-}$: (a) 10^{-4} M in water established at t=O, 1.8; ■, 8.0; and Δ=400 ps, λ_{exc}=565 nm; (b) 10^{-5} M in water established at t= ■, 20 ns; ◆, 40; and O, 80 µs, λ_{exc}=532 nm [67].

Table 6
Electron transfer rate constant and free energy

System	Medium	$-\Delta G^\circ_{et}$ (eV)	$-\Delta G^\circ_{-et}$ (eV)	k_{et} (s^{-1})	k_{-et} (s^{-1})	k_{isc} (s^{-1})
MgP^{4+}/H_2Pc^{4-}	DMSO	0.605	1.294	$3.1 \pm 0.9 \times 10^{12}$	$5.2 \pm 1.0 \times 10^{10}$	
ZnP^{4+}/H_2Pc^{4-}	DMSO	0.563	1.387	$2.1 \pm 0.4 \times 10^{12}$	$2.4 \pm 0.6 \times 10^{10}$	$9.0 \pm 2.0 \times 10^{10}$
$ZnP^{4+}/AlClPc^{4-}$	DMSO	0.450	1.500	$3.8 \pm 0.5 \times 10^{11}$	$1.4 \pm 0.2 \times 10^{10}$	$9.5 \pm 3.2 \times 10^{9}$
$ZnP^{4+}/CuPc^{4-}$	DMSO	0.303	1.647			$5.0 \pm 0.5 \times 10^{11}$
ZnP^{4+}/H_2Pc^{4-}	LB film	0.563	1.387	$2.7 \pm 0.7 \times 10^{12}$	$2.5 \pm 1.2 \times 10^{10}$	
$ZnP^{4+}/AlClPc^{4-}$	LB film	0.450	1.500	$5.0 \pm 0.5 \times 10^{11}$	$1.4 \pm 0.2 \times 10^{10}$	
$ZnP^{4+}/CuPc^{4-}$	LB film	0.303	1.647	$2.5 \pm 0.4 \times 10^{11}$	$6.7 \pm 0.5 \times 10^{9}$	

$E^{+}_{1/2}$ (ZnP^+/ZnP)$=0.94$ V/S.C.E in water [72]a; $E^{+}_{1/2}$ (MgP^+/ZnP)$=0.94$ V/S.C.E in DMF [72]b; $E^{-}_{1/2}$ ($AlClPc/AlClPc^-$)$=-0.656$ V/E.C.S. in DMF [70]; $E^{-}_{1/2}$ ($CuPc/CuPc^-$)$=-0.544$ V/S.C.E. in DMSO [70]; $E^{-}_{1/2}$ (H_2Pc/H_2Pc^-)$=-0.530$ V/S.C.E. in DMSO [70].

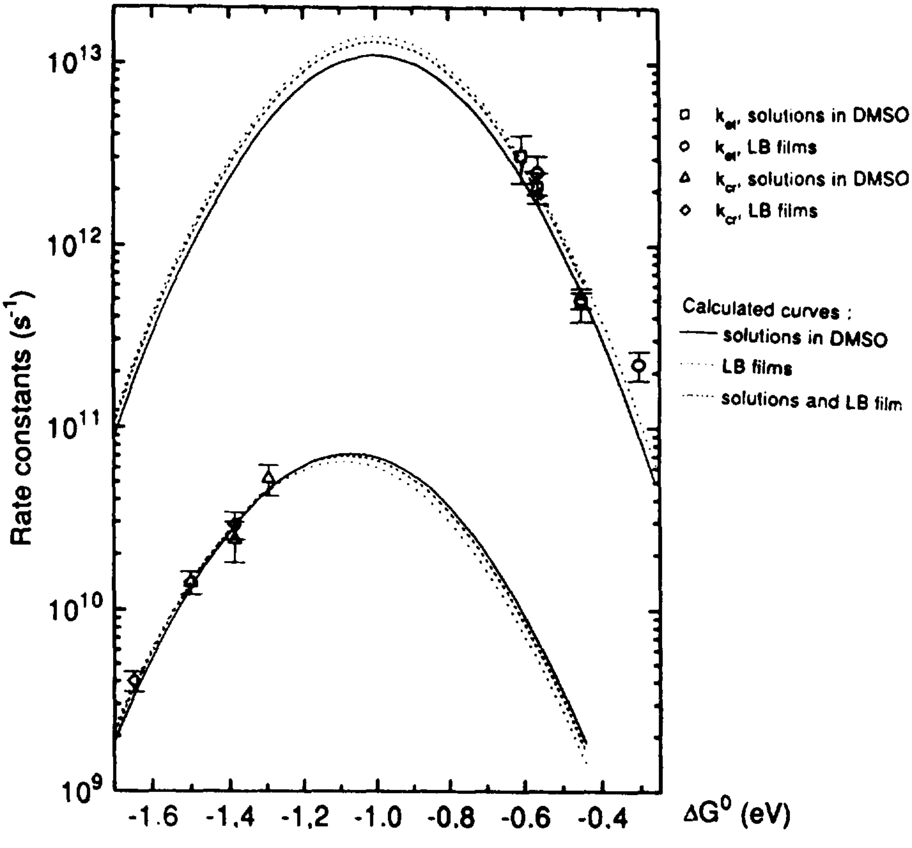


Fig. 24. Plots of k_{et} and k_{-et} as functions of the free energy.

and backward electron transfers. They successfully applied the Marcus theory to the diamagnetic systems. These data are summarized in Table 6.

Fig. 24 displays the plots of k_{et} as a function of ΔG°, following the relation established by Marcus for the non-adiabatic electron transfer [71]:

$$k_{\mathrm{et}} = V^2 (\pi/h^2 \lambda k_{\mathrm{B}} T) \, |V|^2 \exp[-(\Delta G^\circ + \lambda)^2 / 4\lambda k_{\mathrm{B}} T) \qquad (1)$$

where ΔG° is the standard free energy of the photoinduced transfer reaction and λ is the total reorganisation energy during the transfer, including an intramolecular vibrational energy term and a solvent contribution.

The standard free energy $(\Delta G^\circ)_x$, in a solvent x, can be approximated from the redox potentials of the monomers in a solvent m, using Weller's expression [73]

$$(\Delta G^\circ)_x = (E^+_{1/2} - E^-_{1/2})_m + [e^2/\epsilon_x(2r_+^{-1} + 2r_-^{-1} - r_{12}^{-1})] - [e^2/\epsilon_m(2r_+ + 2r_-) \qquad (2)$$

with $E^+_{1/2}$ and $E^-_{1/2}$ being, respectively, the half-wave potential of monoelectronic oxidation of the donor and reduction of the acceptor measured in a solvent m, r_+ and r_- are the ionic radii, r_{12} the distance between the two ions, e_x and ϵ_m the respective static dielectric constants of solvents x and m, and e the electron charge.

Values of $\Delta G^\circ{}_{\mathrm{et}}$ and $\Delta G^\circ{}_{-\mathrm{et}}$ were calculated taking r to be equal to the radius of the Onsager cavity for a porphyrin monomer (7.6 Å) [74], and $r_{12} = 3$ Å for the reactants being in close contact. The energy of the singlet excited state of the mixed complex was taken to be equal to that of the singlet excited state of the corresponding donor moiety (1.95 for $\mathrm{ZnP^{4+}}$ and 1.90 eV for $\mathrm{MgP^{4+}}$) (see Table 5).

The best fits were obtained with the pre-exponential factor and λ values equal to $(1.1 \pm 0.85) \times 10^{13}\ \mathrm{s^{-1}}$ and 1.05 ± 0.11 eV, and $(1.5 \pm 1.3) \times 10^{13}\ \mathrm{s^{-1}}$ and 0.99 ± 0.13 eV, for the forward electron transfer in the liquid and solid phases, respectively. For the much slower back reactions, the authors found the pre-exponential factor and λ values to be equal to $(4.8 \pm 1.2) \times 10^{10}\ \mathrm{s^{-1}}$ and 1.12 ± 0.04 eV, and $(3.3 \pm 0.9) \times 10^{10}\ \mathrm{s^{-1}}$ and 1.19 ± 0.04 eV for the liquid and solid state media, respectively.

Two important points were raised. First, the absence of any large difference between λ values for the forward and backward electron transfer reactions led the authors to conclude a minimal influence of the solvent on the electron transfer reaction. The reorganisation energy, in the present case, would then correspond to a rearrangement of the two moieties within the dimer. Second, in agreement with the first point, the observation of the very high rate constants for electron transfer in the mixed complexes suggests that the reaction may be controlled mainly by intramolecular nuclear vibrations along the coordinate that carries reactants into products. This seemed to be confirmed by the calculated values of V, the electronic coupling of the reactant state with the product, which are slightly higher than the thermal energy, ca. 208 and 240 $\mathrm{cm^{-1}}$ for the forward eT in solutions and LB films, respectively. The mixed ionic complexes fall into the limit of the non-adiabatic regime.

At first sight, this result was very surprising since one would expect, from the ground state absorption of the mixed complex, a strong interaction between the two chromophores and therefore an adiabatic regime with a strong electronic coupling in the excited state. However, a very recent study of the redox properties of some mixed complexes favour this hypothesis. The oxidation and reduction potential of each chromophore in a diamagnetic dimer is practically unchanged as compared to the corresponding monomer, while a very strong catalytic oxidation was found for the $CoP^{4+}/AlClPc^{4-}$ [66]. The Diamagnetic complexes described in [68] can therefore be considered as weakly coupled in the ground and excited states.

The studies on diamagnetic complexes had shown that eT occurred both in the singlet and triplet excited states of the mixed complexes. Very high quantum yields were found for the first process, but the charge separated ion pairs are short lived (few tens of picoseconds). On the other hand the CT states issued from eT occurring in the triplet excited state, are very long-lived (few to hundreds of microseconds), but their quantum yield of formation is rather low. Therefore, the strategy adopted by Tran-Thi's group was to enhance the intersystem crossing process by mixing paramagnetic and diamagnetic chromophores in the mixed complexes, or using diamagnetic metallated complexes with heavy metal ions.

4.3.2. Paramagnetic mixed complexes

Copper porphyrins and phthalocyanines are good candidates. Cu(II) has a d^9 electronic configuration and the unpaired electron in the d_{x2-y2} orbital can couple with the porphyrin (or phthalocyanine) singlet and triplet (π–π^*) excited states. As a consequence, the singlets (^1S) become doublets (^2S) and the triplets (^1T) split into tri-doublets (^2T) and quartets (^4T). The intersystem crossing process from ^2S to $^2T-{}^4T$ has been shown to be too fast to be resolved with ultrafast detection system with a time resolution of 300 fs [75].

Tran-Thi et al. investigated the excited state properties of the mixed complex, composed of the cationic ZnP^{4+} and anionic $CuPc^{4-}$ [68]. As they expected, the presence of a paramagnetic metal ion greatly enhanced the intersystem crossing decay pathway in the mixed complex. However, they observed a difference of properties when going from the solutions to the organized Langmuir-Blodgett films. Their findings can be summarized in the following scheme.

In solution,

$$^{S0}(ZnP-CuPc) \xrightarrow{h\nu} {}^{2S}(ZnP-CuPc)^*$$

$$^{2S}(ZnP-CuPc)^* \xrightarrow{k_{isc}=5\times10^{11}\,s^{-1}} {}^{S0}(ZnP)^{2T-4T}(CuPc)^*$$

$$^{S0}(ZnP)-{}^{2T-4T}(CuPc)^* \xrightarrow{k_T=3.2\times10^{7}\,s^{-1}} {}^{S0}(ZnP-CuPc)$$

while eT occured in the solid state,

$$^{S0}(ZnP-CuPc) \xrightarrow{h\nu} {}^{2S}(ZnP-CuPc)^*$$

$$^{2S}(ZnP-CuPc)^* \xrightarrow{k=2.5\times10^{11}\,s^{-1}} {}^{S0}(ZnP)^{2T-4T}(CuPc)^* \text{ and } {}^{2S}(ZnP^+-CuPc^-)^*$$

$$^{2S}(ZnP^+-CuPc^-)^* \xrightarrow{k_{-eT}=6.7\times10^{9}\,s^{-1}} {}^{S0}(ZnP-CuPc)$$

$$^{S0}(\mathrm{ZnP})-{}^{2T-4T}(\mathrm{CuPc})^{*} \xrightarrow{<20\ \mathrm{ns}} {}^{S0}(\mathrm{ZnP}-\mathrm{CuPc}) \text{ and } (\mathrm{ZnP}^{+}-\mathrm{CuPc}^{-})^{*}$$

$$(\mathrm{ZnP}^{+}-\mathrm{CuPc}^{-})^{*} \xrightarrow{k_{-eT}=5.0\times10^{5}\ \mathrm{s}^{-1}} {}^{S0}(\mathrm{ZnP}-\mathrm{CuPc})$$

The authors tentatively explained this difference in terms of a difference in the interplanar distance when the mixed complex is in solution or in the LB film. Another explanation was also proposed, which is based on the gradient of polarity of the local environment of the mixed complex in LB films.

The first strategy, consisting in mixing one paramagnetic chromophore with a diamagnetic one, was successful and an enhancement of the CT lifetime was observed in the mixed paramagnetic/diamagnetic dimer, ca. 150 ps for the CT state formed from the doublets. However, the CTs states, formed from tri-doublet and quartet states are short-lived, as compared to the ones resulting from the triplet states of diamagnetic complexes. The second strategy, which consists in chelating the porphyrin or the phthalocyanine with a heavy and diamagnetic ion, might be more rewarding, but up to the present time, no work has been reported on such systems.

4.3.3. *Mixed complexes with one oxidizable or reducible metal ion*

These complexes display very peculiar but also the most promising properties. The first system, reported by Tran-Thi and Gaspard [76], was a mixture of a chloromanganese(III) tetrakis-(sulfonatophenyl) porphyrin, MnClP^{4-}, and a cationic zinc tetrakis-(3-methylpyridiloxy) phthalocyanine, $\mathrm{ZnPc{-}O{-}TMPyr}^{4+}$ in DMSO.

In contrast to the cationic porphyrin or porphyrazin derivatives of Fig. 10, the four $\mathrm{N}^{+}{-}\mathrm{CH}_3$ of $\mathrm{ZnPc{-}O{-}TMPyr}^{4+}$ are situated far away from the macrocycle ring, on a flexible –O–phenyl substituent. Because of these long flexible chains, mixed diads and triads, able to bind axial ligands, can be formed, unlike in the previously described systems. A larger intermacrocycle distance was expected in these complexes, which can "accommodate" an axial ligand, thus explaining the weak interaction observed in their ground states.

On irradiating continuously solutions containing an excess of one of the components, the authors discovered the existence of mixed valence complexes, the nature of which depends drastically on the stoichiometry of the system [76]. Their data are summarized in Fig. 25.

Different triads are formed in the solution, depending on the presence of an excess of the porphyrin (Fig. 25(a)) or phthalocyanine (Fig. 25(b)). Upon irradiation, the former, $2\mathrm{Mn}^{\mathrm{III}}/1\mathrm{ZnPc}$, were transformed into very stable mixed valence complexes, $\mathrm{Mn}^{\mathrm{III}}/\mathrm{ZnPc}^{-}/\mathrm{Mn}^{\mathrm{IV}}$, while irradiation of the $1\mathrm{Mn}^{\mathrm{III}}/2\mathrm{ZnPc}$ led to the formation of $\mathrm{ZnPc}^{+}/\mathrm{Mn}^{\mathrm{II}}/\mathrm{ZnPc}$. Both processes are reversible in the dark. The surprisingly high stability of these zwitterionic triad complexes, as compared to the transient CT states of the diads, was tentatively explained in terms of the stabilization of the negative charge or hole by the third chromophore. The longer interchromophore distance (>3 Å) would also delay the back reaction transfer. Both effects can contribute to the stabilization of these peculiar CT states.

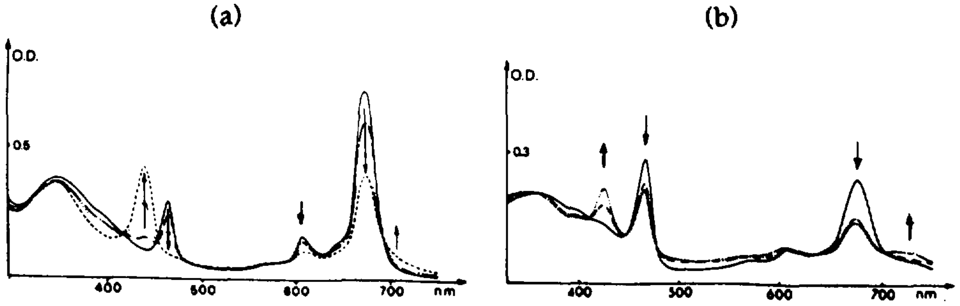


Fig. 25. Spectral variation upon irradiation of mixtures of $Mn^{III}/ZnPc$ containing (a) an excess of $Mn^{III}/$, (b) an excess of ZnPc [76]. $Mn^{III}=MnP^{4-}$ and $ZnPc=ZnPc-OTMPyr^{4+}$.

To test these two hypotheses, Tran-Thi's group investigated the excited state properties of diads and triads formed upon mixing free base tetrasulfonated porphyrins and tetracationic cobalt(II) porphyrazins. Like Mn(III), Co(II) can be reduced and oxidized, but in contrast to the former system, the aggregates formed in the second one are strongly coupled.

They found, for the diad system [64], the same sequence of reactions previously described for the mixed paramagnetic/diamagnetic complexes: an ultrafast (unresolved <120 fs) formation of the quartet states of the mixed $H_2P^{4-}/Co^{II}Pz^{4+}$, followed by a fast transfer (1.2 ± 0.2 ps) of an electron from H_2P^{4-} to $CoPz^{4+}$. The CT state is short-lived (few tens of picoseconds). Unlike the diads, but similar to the $2Mn^{III}/ZnPc$ triad, very stable products were formed upon steady state irradiation, which was attributed to the $CoH^{II}Pz^{4+}/(H_2P^{4-})^{+}/Co^{I}Pz^{4+}$. This last result strongly supports the hypothesis of the stabilization of the CT state, due to the presence of the third chromophore.

4.3.4. Mixed complexes with reducible and oxidizable metal ions

Metal to metal charge transfer in face-to-face self-assembled systems is very interesting in many respects. In a multi-component system, the electron will be able to migrate along the axis perpendicular to the stacked face-to-face macrocycles formed by the different oxidizable and reducible metal ions, if a gradient of redox properties could be established along the column. Although the applied aspect of such systems as molecular wires is attractive, their excited state properties have not been explored so far.

5. Conclusion

This review has summarized and discussed the optical properties of the ground and excited states of three different families of mixed complexes of porphyrin and phthalocyanine. Each section merits further development and critical comparison with the "all porphyrin" and "all phthalocyanine" systems. Such demanding but interesting work would be very valuable since a tremendous number of works has been developed in parallel in the three domains.

Very interesting points have been raised by the comparison of the properties of the three families of mixed complexes. In the ground state, the two porphyrin and phthalocyanine moieties interact weakly within the covalently-linked mixed complex. In contrast to these linear complexes, the co-facial sandwich-type and ionic-type complexes display new electronic transitions arising from the stronger interaction between the two moieties. The same contrast is observed for the excited state properties: energy transfer from the porphyrin to the phthalocyanine moiety is the dominant process in the covalently-linked and linear complexes and charge transfer is very dependent on the solvent polarity. In the co-facial complexes, intersystem conversion from singlet (or doublet) to triplet (or quartet) competes with electron transfer. The efficiency of both processes is only dependent on the properties of the metal ion (heavy, diamagnetic, paramagnetic, oxidizable or reducible) and the interplane distance.

In systems where electron transfer prevails, the electron back transfer reaction is still very fast, and no "stabilized" CT can exist. Such a result is perhaps not surprising as similar behavior was reported in the literature for the "all porphyrin" diad systems. However, a new and very unusual behavior has been discovered with the mixed triads formed with the self-assembled ionic monomers. Very stable CT states can be observed in two systems in which the nature of the charge separated species depends upon the stoichiometry of the triad (2/1 or 1/2). Such a peculiar behaviour is not clearly understood up to now. The comparison of the excited state properties of these complexes with those of the triple-decker complexes, in which the relative position of the porphyrin and phthalocyanine and the metal ion can be changed, might bring some light to that problem. Such an understanding, combined with the high chemical versatility of the co-facial complexes, will allow the engineering of the excited state properties of molecular systems for targeted applications.

Some targeted aspects, such as electrochromism or semi-conduction in thin films of sublimated bis-(phthalocyanine)s have only been briefly mentioned. Photoconduction and nonlinear optical properties of the mixed co-facial complexes are also under investigation in many laboratories, using either thin films of the sublimated double- and triple-decker complexes [77] or Langmuir-Blodgett technique [78] to self-assemble ionic complexes in the solid state. One should expect in the coming years rapid advances in these domains.

Acknowledgements

THTT addresses her special thanks to all the undergraduate, PhD students and post-doctoral collaborators who have worked with her and contributed to the progress of the work on the mixed complexes, during these past nine years. She is also indebted to Drs S. Gaspard, P. Maillard, De Cian, D. Chabach, H. Ali, R. Langlois, D. Lexa, S. Palacin, D. Markovitsi, Profs. R. Weiss, J. E. van-Lier, D.

Houde, for the continuing collaboration which has been so productive during these nine years. Warm thanks are also addressed to G. Derost, for her valuable help in keeping an up-to-date bibliography on porphyrins and phthalocyanines. THTT is also indebted to the Centre National de la Recherche Scientifique (CNRS), the Atomic Energy Commission, the Ministère de la Recherche et de l'Enseignement superieur (MRES), the Natural Science and Engineering Research Council (NSERC) of Canada and the European Committee HCM program, for their continuing financial supports.

References

[1] D. Gust, T.A. Moore, A.L. Moore, L. Leggett, S. Lin, J.M. DeGraziano, R.M. Hermant, D. Nicodem, P. Craig, G.R. Seely and R.A. Nieman, J. Phys. Chem., 97 (1993) 7926. F.P. Schwarz, M. Gouterman, Z. Muljiani and D.H. Dolphin, Bioinorg. Chem., 2 (1972) 1. J.A. Anton and P.A. Loach, Govindjee, Photochem. Photobiol., 28 (1978) 235. J.-C. Mialocq, C. Giannotti, P. Maillard and M. Momenteau, Chem. Phys. Lett., 112 (1984) 87. R.L. Brookfield, H. Ellul and A. Harriman, J. Chem. Soc., Faraday Trans., 2, 81 (1985) 1837. Y. Kaizu, H. Maekawa, H. Kobayashi, J. Phys. Chem., 90 (1986) 4234. O. Ohno, Y. Ogasawara, M. Asano, Y. Kajii, Y. Kaizu, K. Obi and H. Kobayashi, J. Phys. Chem., 91 (1987) 4269. H. Levanon, A. Regev and P.K. Das, J. Phys. Chem., 91 (1987) 14. N. Mataga, H. Yao, T. Okada, Y. Kanda and A. Harriman, Chem. Phys., 131 (1989) 473. D. Gust, T.A. Moore, H.-K. Kang, J.M. DeGraziano, P.A. Liddell and G.R. Seely, J. Phys. Chem., 97 (1993) 13637.

[2] K. Susumu, K. Kunimoto, H. Segawa and T. Shimidzu, J. Phys. Chem., 99 (1995) 29.

[3] G.P. Gurinovich, E.I. Zen'Kevich, A.M. Shul'ga, E.I. Sagun and A. Suisalu, Zh. Prikl. Spekt., 41 (1984) 446. D. Heiler, G. McLendon and P. Rogalskyj, J. Am. Chem. Soc., 109 (1987) 604. T. Nagata, A. Osuka and K. Maruyama, J. Am. Chem. Soc., 112 (1990) 3054. A. Osuka, T. Nagata, F. Kobayashi, R.P. Zhang, K. Maruyama, N. Mataga, T. Asahi, T. Ohno and K. Nozaki, Chem. Phys. Lett., 199 (1992) 302. T.-H. Tran-Thi, A. Dormond and R. Guilard, J. Phys. Chem., 96 (1992) 3139. J.C. Chambron, A. Harriman, V. Heitz and J.-P. Sauvage, J. Am. Chem. Soc., 115 (1993) 7419. A. Osuka, F. Kobayashi, K. Maruyama, N. Mataga, T. Asahi, T. Okada, I. Yamazaki and Y. Nishimura, Chem. Phys. Lett., 201 (1993) 223. A. Harriman, F. Odobel and J.-P. Sauvage, J. Am. Chem. Soc., 116 (1994) 5481.

[4] H.L. Anderson, C.A. Hunter and J.K.M. Sanders, J. Chem. Soc. Chem. commun., (1989) 226. C.A. Hunter, J.K.M. Sanders and G.S. Evans, J. Chem. Soc. Chem. Commun., (1989) 1765.

[5] U. Rempel, B. Von Maltzan and C. Von Borczyskowski, Chem. Phys. Lett., 169 (1990) 347. U. Rempel, B. Von Maltzan, C. Von Borczyskowski, M. Glasbeek, R.S. Meltzer and S. Volker, J. Lum., 53 (1992) 175. J.L. Sessler, V.L. Capuano and A. Harriman, J. Am. Chem. Soc., 115 (1993) 4618. A. Osuka, S. Marumo, S. Taniguchi, T. Okada and N. Mataga, Chem. Phys. Lett., 230 (1994) 144.

[6] M.R. Wasielewski, Chem. Rev., 92 (1992) 435 and references therein.

[7] J. Deinsenhofer, O. Epp, K. Miki, R. Huber and H. Michel, J. Mol. Biol., 180 (1984) 385. J. Deinsenhofer, O. Epp, K. Miki, R. Huber and H. Michel, Nature, 318 (1985) 618.

[8] C.K. Chang, M.S. Kuo and C.B. Wang, J. Heterocycl. Chem., 14 1977) 943. C.K. Chang and J. Heterocycl. Chem., 14 (1977) 1285. N.E. Kagan, D. Mauzerall and R.B. Merrifield, J. Am. Chem. Soc., 99 (1977) 5484. M.A. Bergkamp, C.-K. Chang and T.L. Netzel, J. Phys. Chem., 87 (1983) 4441. F. Gückel, D. Scheitzer, J.P. Collman, S. Bencosme, E. Evitt and J. Sessler, Chem. Phys. 86 (1984) 161. J.M. Zaleski, C.K. Chang and D.G. Nocera, J. Phys. Chem., 97 (1993) 13206. G.M. Dubowchick and A.D. Hamilton, J. Chem. Soc. Chem. Commun., (1986) 665. P. Seta, E. Bienvenue, P. Maillard and M. Momenteau, Photochem. Photobiol., 49 (1989) 537. T. Nataga, A. Osuka and K. Maruyama, J. Am. Chem. Soc., 112 (1990) 3054. H. Levanon, A. Regev, T. Galili, M. Hugerat, C.K. Chang and J. Fajer, J. Phys. Chem., 97 (1993) 13198.

[9] J.-C. Chambron, S. Chardon-Noblat, A. Harriman, V. Heitz and J.-P. Sauvage, Pure Appl. Chem., 65 (1993) 2343. A. Harriman, F. Odobel and J.-P. Sauvage, J. Am. Chem. Soc., 116 (1994) 5481. M. Momenteau, F. Le Bras and B. Loock, Tetrahedron Lett., 35 (1994) 3289.

[10] (a)M.F. Hudson and K.M. Smith, Tetrahedron, 31 (1975) 3077. (b) J.W. Buchler, H.G. Kapellmann, M. Knoff, K.L. Lay and S. Pfeifer, Z. Naturforsch. b: Anorg. Chem. Org. Chem., 38B (1983) 1339.

[11] (a)U. Rempel, B. Von Maltzan and C. Von Borczyskowski, Pure and Appl. Chem., 65 (1993) 1681. E. Zenkevich, A. Shulga, A. Chernook, U. Rempel and C. von Borczyskowski, Proceedings of SPIE, “Laser Application in Life Sciences”, Minsk, (1995). in press. (b) J.S. Lindsey and D.C. mauzerall, J. Am. Chem. Soc., 105 (1983) 6528. W. Kobel and M. Hanack, Inorg. Chem., 25 (1986) 103. J.P. Collman, J.T. McDevitt, C.R. Leidner, G.T. Yee, J.B. Torrance and W.A. Little, J. Am. Chem. Soc., 109 (1987) 4606. V. Marvaud and J.-P. Launay, Inorg. Chem., 32 (1993) 1376. C.A. Hunter, J.K.M. Sanders, G.S. Beddard and S. Evans, J. Chem. Soc., Chem. Commun, (1989) 1765. A. Kimura, K. Funatsu, T. Imamura, H. Kido and Y. Sasaki, Chem. Lett., (1995) 207.

[12] T. Shimidzu and T. Iyoda, Chem. Phys. Lett., (1981), 853. H. Segawa, H. Nishino, T. Kamikawa, K. Honda and T. Shimidzu, Chem. Lett., (1989), 1917.

[13] J.L.Y. Kong and P.A. Loach, in P.L. Dutton, J.S. Leigh, A. Scarpa (eds.), Frontiers of Biological Energetics: From Electron to Tissues, Academic Press, New York, Vol. 1, (1978) 73. J.L.Y. Kong, K.G. Spears and P.A. Loach, Photochem. Photobiol., 35 (1982) 545.

[14] D. Gust, T.A. Moore, A.L. Moore, S.-J. Lee, E. Bittersmann, D.K. Luttrull, A.A. Rehms, J.M. DeGraziano, X.C. Ma, F. Gao, R.E. Belford and T.T. Trier, Science, 248 (1990) 199.

[15] L.R. Milgrom, J. Chem. Soc. Perkin Trans., 1 (1983) 2535. B.A. Leland, A.D. Joran, P.M. Felker, J.J. Hopfield, A.H. Zewail and P.B. Dervan, J. Phys. Chem., 89 (1985) 5571. Y. Kanda, H. Sato and T. Okada, Chem. Phys. Lett., 129 (1986) 306. J.D. Batteas, A. Harriman, Y. Kanda, N. Mataga and A.K. Novak, J. Am. Chem. Soc., 112 (1990) 126. V.Ya. Shafirovich, E. Amouyal and J. Delaire, Chem. Phys. Lett., 178 (1991) 24. I. Okura and H. Hosono, Inorg. Chim. Acta, 201 (1992) 11. K. Kamioka, R.A. Cormier, T.W. Lutton and J.S. Connolly, J. Am. Chem. Soc., 114 (1992) 4414. T. Asaki, M. Ohkohchi, R. Matsusaka, N. Mataga, R.P. Zhang, A. Osuka and K. Maruyama, J. Am. Chem. Soc., 115 (1993) 5665. A.N. Macpherson, P.A. Liddell, S. Lin, L. Noss, G.R. Seely, J.M. DeGraziano, A.L. Moore, T. Moore and D. Gust, J. Am. Chem. Soc., 117 (1995) 7202.

[16] S. Nishitani, N. Kurata, Y. Sakata, S. Misumi, A. Karen, T. Okada and N. Mataga, J. Am. Chem. Soc., 105 (1983) 7771. T.A. Moore, D. Gust, P. Mathis, J.C. Mialocq, C. Chachaty, R.V. Bensasson, E.J. Land, D. Doizi, P.A. Liddell, W.R. Lehman, G.A. Nemeth and A.L. Moore, Nature, 307 (1984) 630. M.R. Wasielewski, M.P. Niemczyk, W.A. Svec and E.B. Pewitt, J. Am. Chem. Soc., 107 (1985) 5562. D. Gust and T.A. Moore, in D.H. Volman, G.S. Hammond and D.C. Neckers (eds.), Advances in Photochemistry, Vol. 16, John Wiley & Sons, (1991) 1. A. Osuka, T. Nagata, F. Kobayashi, R.P. Zhang, K. Maruyama, N. Mataga, T. Asahi, T. Ohno and K. Nozaki, Chem. Phys. Lett., 199 (1992) 302. Xiang Dong Wan, Bao Wen Zhan, Jian Wei Ba, Y. Cao, Xu Rui Xi and X. Jing Mei, J. Phys. Chem., 96 (1992) 2886. J. Hirota and I. Okura, J. Phys. Chem., 97 (1993) 6867.

[17] D. Gust, T.A. Moore, D. Barrett, L.O. Harding, L.R. Makings, P.A. Liddell, F.C. De Schryver, M. Van der Auweraer, R.V. Bensasson and M. Rougée, J. Am. Chem. Soc., 110 (1988) 321.

[18] R.J. Harrison, B. Pearce, G.S. Beddard, J.A. Cowan and J.K.M. Sanders, Chem. Phys., 116 (1987) 429. W. Frey, R. Kllann, F. Laermer, T. Elsaesser, E. Baumann, F. Futscher and H.A. Staab, Chem. Phys. Lett., 190 (1992) 567.

[19] W.W. Parson and R.J. Cogdell, Biochim. Biophys. Acta, 416 (1975) 105.

[20] M. Gouterman, in D. Dolphin (ed.), The Porphyrins, Vol. III, Academic Press, New York, (1978) 1.

[21] M.R. Wasielewski, D.G. Johnson, M.P. Niemczyk, G.L. Gaines III, M.P. O'Neil and W.A. Svec, J. Am. Chem. Soc., 112 (1990) 6482. D.G. Johnson, M.P. Niemczyk, D.W. Minsek, G.P. Wiederrecht, W.A. Svec, G.L. Gaines III and M.R. Wasielewski, J. Am. Chem. Soc., 115 (1993) 5692.

[22] M.J. Stillman and T. Nyokong, in C.C. Leznoff and A.B.P. Lever (eds.), Phthalocyanines, Properties and Applications, Vol. III, Absorption and Magnetic Circular Dichroism Spectral Properties of Phthalocyanines, (1991) 139.

[23] D.G. Davis in D. Dolphin (ed.), The Porphyrins, Vol. V, Electrochemistry of Porphyrins, Academic Press, New York (1978) 127.

[24] A. Braun and J. Tcherniac, J. Ber. Dtsch. Chem. Ges., 40 (1907) 2709.
[25] H. De Diesbach and E. von der Weid, Helv. Chem. Acta, 10 (1927) 886.
[26] R.P. Linstead, J. Chem. Soc., (1934) 1016.
[27] I. Rosenthal and E. Ben-Hur, in C.C. Leznoff and A.B.P. Lever (eds.), Phthalocyanines, Properties and Applications, Vol. III, Phthalocyanines in Photobiology, (1991) 397.
[28] S. Gaspard, C.R. Acad. Sci. Paris, 298 (1984) 379.
[29] S. Gaspard, C. Giannotti, P. Maillard, C. Schaeffer and T.-H. Tran-Thi, J. Chem. Soc. Chem. Commun., (1986) 1239.
[30] M. Lachkar, A. De Cian, J. Fischer and R. Weiss, New J. Chem., 16 (1988) 729.
[31] D. Chabach, M. Lachkar, A. De Cian, J. Fischer and R. Weiss, New J. Chem., 16 (1992) 431.
[32] T.-H. Tran-Thi, H. Ali, J.-F. Lipskier, S. Gaspard and J.E. van-Lier, J. Chim. Phys., 88 (1991) 1151.
[33] H.-J. Tian, Q.F. Zhou, S.-Y. Shen and H.-J. Xu, J. Photochem. Photobiol. A: Chem., 72 (1993) 163. L. Li, S. Shen, Q. Yu, Q. Zhou and H. Xu, J. Chem. Soc. Chem. Commun., (1991) 619.
[34] T.-H. Tran-Thi, C. Desforge, C. Thiec and S. Gaspard, J. Phys. Chem., 93 (1989) 1226.
[35] (a) P.A. Barret, C.E. Dent and R.P. Linstead, J. Chem. Soc., (1936) 1719. (b) M. Whalley, J. Chem. Soc., (1961) 866.
[36] (a) I.S. Kirin, P.N. Moskalev and Y.A. Makashev, Russ. J. Inorg. Chem., 10 (1965) 1065. I.S. Kirin, P.N. Moskalev and Y.A. Makashev, Russ. J. Inorg. Chem., 12 (1967) 369. (b) A. De Cian, M. Moussavi, J. Fischer and R. Weiss, Inorg. Chem., 24 (1985) 3162.
[37] J.W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus and R. Weiss, J. Am. Chem. Soc., 108 (1986) 3652–3659.
[38] R.J. Donohoe, J.K. Duchowski and D.F. Bocian, J. Am. Chem. Soc., 110 (1988) 6119. J.H. Perng, J.K. Duchowski and D.F. Bocian, J. Phys. Chem., 94 (1990) 6684. J.K. Duchowski and D.F. Bocian, Inorg. Chem., 29 (1990) 4158–4160. J.H. Perng, J.K. Duchowski and D.F. Bocian, J. Phys. Chem., 95 (1991) 1319.
[39] J.W. Buchler and P. Hammerschmitt, Liebigs Ann. Chem., (1991) 1177. J.W. Buchler and J. Löffler, Z. Naturforsch., 45b (1990) 531. M. kihn-Botulinski, Dissertation, TH Darmstadt (1986).
[40] M. Lashkar, Thesis, Université Louis Pasteur, Strasbourg, France (1988)
[41] D. Chabach, Thesis, Université Louis Pasteur, Strasbourg, France, (1994).
[42] D. Chabach, A. De Cian, J. Fischer, R. Weiss and M. El Malouli Bibout, Angew. Chem. Int. Ed. Engl., 35 (1996) 898.
[43] O. Bilsel, J.W. Buchler, P. Hammerschmitt, J. Rodriguez and D. Holten, Chem. Phys. Lett., 182 (1991) 415.
[44] (a) J.W. Buchler, A. De Cian, J. Fischer, J. Löffler and R. Weiss, Chem. Ber., 122 (1989) 2219. (b) M. Safarpour Haghighi, Chr.L. Teske and H. Homborg, Z. Anorg. Allg. Chem., 608 (1992) 73. M. Safarpour Haghighi and H. Homborg, Z. Naturforsch., 46B (1991) 641.
[45] O. Bilsel, D. Holten, G.S. Girolami, S.N. Milam and K.S. Suslick, J. Am. Chem. Soc., 112 (1990) 4075.
[46] F. Lux, D. Dempf and D. Gran, Angew. Chem., 80 (1968) 792. A. Gieren and W. Hoppe, J. Chem. Soc. Chem. Commun., (1971) 413. O. Bilsel, S.N. Milam, G.S. Girolami, K.S. Suslick and D. Holten, J. Phys. Chem., 97 (1993) 7216.
[47] P.N. Moskalev and I.S. Kirin, Russ. J. Inorg. Chem., 46 (1972) 1019.
[48] M. L'Her, Y. Cozien and J. Courtot-Coupez, J. Electroanal. Chem., 157 (1983) 183. M. L'Her, Y. Cozien and J. Courtot-Coupez, C.R. Acad. Sci. Paris, 300 (1985) 487. M. L'Her, Y. Cozien and J. Courtot-Coupez, C.R. Acad. Sci. Paris, 302 (1986) 9. M. M'Ksadak, J. Roncali and F. Garnier, J. Electroanal. Chem., 189 (1985) 99. M.L. Rodriguez-Mendez, J. Souto, J.A. Desaja and R. Aroca, J. Mater. Chem., 5 (1995) 639.
[49] R. Even, J. Simon and D. Markovitsi, Chem. Phys. Lett., 156 (1989) 609. J.-J. André, K. Holczer, P. Petit, M.-T. Riou, C. Clarisse, R. Even, M. Fourmigué and J. Simon, Chem. Phys. Lett., 115 (1985) 463. R. Even, Thesis, Université Pierre et Marie Curie, Paris VI, June 1987.
[50] T.-H. Tran-Thi, T.A. Mattioli, D. Chabach, A. De Cian and R. Weiss, J. Phys. Chem., 98 (1994) 8279.
[51] T.-H. Tran-Thi, T. Fournier, D. Chabach, A. De Cian, R. Weiss, D. Houde, C. Pépin and L. Dao, Chem. Phys. Lett., 213 (1993) 139.

[52] D. Markovitsi, T.-H. Tran-Thi, R. Even and J. Simon, Chem. Phys. Lett., 137 (1987) 107.
[53] (a) O. Bilsel, J. Rodriguez and D. Holten, J. Phys. Chem., 94 (1990) 3508. (b) A. Germain and T. Ebbesen, Chem. Phys. Lett., 199 (1992) 585.
[54] V. Balzani and F. Scandola, Photoinduced Electron Transfer, Part D, Elsevier, Amsterdam, (1988) 148.
[55] R.A. Marcus, Annu. Rev. Phys. Chem., 15 (1964), 155. N.S. Hush, Electrochim. Acta, 13 (1968) 1005. A. Haim, Commemts Inorg. Chem., 4 (1985) 113. N. Sabbatini and V. Balzani, Less Common Met., 112 (1985), 381.
[56] B.P. Sullivan, W. Dressick and T.J. Meyer, J. Phys. Chem., 86 (1982) 1473.
[57] A. Mills, C. Lawrence and P.J. Douglas, J. Chem. Soc., Faraday Trans., 2 (82) (1986) 2291.
[58] S.L. Logunov and M.A. Rodgers, J. Phys. Chem., 96 (1992) 8697.
[59] E. Ojadi, R. Selzen and H. Linschitz, J. Am. Chem. Soc., 107 (1985) 7783.
[60] U. Hofstra, R.B.M. Koehorst and T.J. Schaafsma, Chem. Phys. Lett., 130 (1986) 555. U. Hofstra, R.B.M. Koehorst and T.J. Schaafsma, Magn. Res. Chem., 25 (1987) 1069.
[61] S. Radzki, S. Gaspard and C. Giannotti, J. Chem. Res. M, (1986) 3101.
[62] D.K. Geiger and G.A. Kelly, Inorg. Chim. Acta, 154 (1988) 137. S.L. Povlock, L.A. Dennis and D.K. Geiger, Inorg. Chim. Acta, 176 (1990) 295.
[63] T.-H. Tran-Thi and S. Gaspard, J. Chem. Soc. Perkin Trans., 2 (1989) 383.
[64] I. Salabert, T.-H. Tran-Thi, H. Ali, J. van-Lier, D. Houde and E. Keszei, Chem. Phys. Lett., 223 (1994) 313.
[65] J.-F. Lipskier and T.-H. Tran-Thi, Inorg. Chem., 32 (1993) 722.
[66] T. Fournier, Thesis, (1994) University of Orsay, France.
[67] T.-H. Tran-Thi, J.-F. Lipskier, D. Houde, C. Pépin, R. Langlois and S. Palacin, J. Chem. Soc., Faraday Trans., 88 (1992) 2529.
[68] T.-H. Tran-Thi, J.-F. Lipskier, D. Houde, C. Pépin, E. Keszei and J.-P. Jay-Gerin, J. Chem. Soc., Faraday Trans., 88 (1992) 2129. T.-H. Tran-Thi, J.-F. Lipskier, D. Houde, C. Pépin, S. Palacin, in Y. Gauduel, P.J. Rossky (eds.), Ultrafast Reaction dynamics and Solvent Effect, AIP Press, New York (1993) 460.
[69] J. Fajer, D.C. Borg, A. Forman, D. Dolphin and R.H. Felton, J. Am. Chem. Soc., 92 (1970) 3451.
[70] L.D. Rollman and R.T. Iwamoto, J. Am. Chem. Soc., 90 (1968) 1455.
[71] R.A. Marcus, Discuss. Faraday Soc., 29 (1960) 21. R.A. Marcus and N. Sutin, Biochim. Biophys. Acta, 811 (1985) 265.
[72] (a) K. Kalyanamsundaram and M. Neumann-Spallart, J. Phys. Chem., 86 (1982) 5163. K. Kalyanamsundaram, J. Chem. Soc., Faraday Trans. 2, 79 (1983) 1365. (b) D. Lexa and M. Reix, J. Chem. Phys., 71 (1974) 517.
[73] A. Weller, Z. Physik. Chem., 133 (1982) 93.
[74] T.-H. Tran-Thi, J.-F. Lipskier, P. Maillard, M. Momenteau, J.-M. Lopez-Castillo and J.-P. Jay-Gerin, J. Phys. Chem., 96 (1992) 1073.
[75] X. Yan and D. Holten, J. Phys. Chem., 92 (1988) 409.
[76] T.-H. Tran-Thi and S. Gaspard, Chem. Phys. Lett., 148 (1988) 327.
[77] L. Pan, L.G. Caron, R. Loucif-Saòbi, D. Houde, L. Dao, D. Chabach, A. De Cian, R. Weiss and T.-H. Tran-Thi, Phys. Rev. B, accepted.
[78] T.-H. Tran-Thi, T. Fournier, A. Yu Sharonov, N. Tkachenko, H. Lemmetyinen, P. Grenier, K.-D. Truong and D. Houde, Thin Solid Films, 273 (1996) 8.