

## Ferrocene and ferrocenyl derivatives in luminescent systems

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### Abstract

Owing to their fairly high stability under visible irradiation, ferrocene and ferrocenyl derivatives are widely used in luminescent systems. They are classical quenchers of excited states. Both energy and electron transfer may be involved, depending on the nature of the excited species. Inter- or intramolecular quenching are encountered. Applications span from the study of reaction mechanisms to that of organized or biological media. Recently, dyads and polyads designed for their ability to mimic photosynthetic centers or for their photodiode properties have also been obtained. Finally, the incorporation of a ferrocenyl derivative in a luminescent system does not necessarily lead to luminescence quenching. New applications are emerging, in which advantage is taken of the presence of ferrocene acting as a redox center: this gives optically and electrochemically active sensors. The present review encompasses the literature up to November 1999. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Ferrocene; Luminescence; Fluorescence; Phosphorescence; Emission; Quenching; Excited state; Energy transfer; Photoinduced electron transfer; Singlet; Triplet

**Abbreviations:** PET, photoinduced electron transfer; py, pyridine; bpy, 2,2'-bipyridine; bpz, 2,2'-bipyrazine; CTAC, cetyltrimethylammonium chloride; CTAB, cetyltrimethylammonium bromide; LB, Langmuir–Blodgett; TCNQ, tetracyanoquinodimethane; ITO, indium tin oxide; GOx, glucose oxidase; dba, dibenzylideneacetone; diphos, bis-1,2-diphenylphosphinomethane; diphos-FeCp<sub>2</sub>, 1,1'-bis-diphenylphosphinoferrrocene

### 1. Introduction

Ferrocene (dicyclopentadienyliron) has been called the benzene of modern organometallic chemistry, not only because it was the first pure hydrocarbon derivative of iron to be prepared, but also because it is indissociably linked to the development of organometallic chemistry. Since its accidental discovery in 1951, many derivatives have been synthesized and characterized. Their chemistry is now well known and they are often appreciated for their outstanding stability. They are of considerable interest in various areas [1], like asymmetric catalysis, non-linear optics [2] and electrochemistry [3] due to the quasi-reversible oxidation of iron II. In many cases, their photochemical behaviour has also been

investigated. Although they often are photochemically inert, ferrocene and ferrocenyl derivatives may undergo chemical modifications in the presence of light, or may be used as excited state quenchers or photosensitizers, that is as catalysts of photochemical reactions (they, therefore, find interesting applications in photography and in photoresists). Ferrocene photochemistry has been the topic of abundant literature and excellent reviews (see for example [4–7]). It is beyond the scope of the present review, which only deals with the use of ferrocenes in photophysics, and more particularly in luminescent systems. However, it will be seen that some properties of these compounds, which are profitably used in photochemistry, also are of major interest for photophysics.

Ferrocene has been widely used as a luminescence quencher in intermolecular processes taking place in solution. From a fundamental viewpoint, these quenching studies mainly allowed the nature of the excited states to be characterized. Luminescence quenching led to numerous applications in the areas of analytical chemistry, molecular organized systems and biology. Recently, new compounds have appeared, in which the ferrocenyl derivative is

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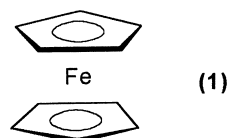


Fig. 1. Chemical structure of ferrocene ( $\text{FeCp}_2$ ).

covalently linked to a luminescent molecule. Interaction is, therefore, of the intramolecular type. A good illustration is provided by the dyads and polyads used to mimic photosynthetic centers and to prepare photodiodes. Finally, it will be seen that incorporating a ferrocenyl derivative into a luminescent system does not necessarily extinguish the luminescence. Ferrocene may then be advantageously used as a redox center to provide multiresponsive, photo- and electrochemically active compounds.

## 2. Structure and first energy levels of ferrocene

### 2.1. Basic description of the structure and molecular frontier orbitals

The cyclopentadienyl ligand  $\text{C}_5\text{H}_5$  (Cp) is derived from cyclopentadiene  $\text{C}_5\text{H}_6$  by abstraction of a hydrogen atom. In ferrocene (molecule 1,  $\text{FeCp}_2$ ), two  $\text{C}_5\text{H}_5$  ligands lie one on top of each other, with the iron atom sandwiched in the middle (Fig. 1). The plane of each ring is perpendicular to the metal–ligand bond with all five carbon atoms roughly equidistant from the metal<sup>2</sup>. Both metal–ring plane distances are 1.674 Å [8,9].

The electronic structure of metallocenes gave rise to a large number of publications which were often highly controversial. According to the type of calculation used, large variations were reported in the order and energy levels of the orbitals. The reader can refer to some essential publications (for example [8,10]) which give a chronological account of the debate. A simplified description of the orbitals is merely given here, in order to provide a convenient basic knowledge. We refer to the work of Sohn et al. [10] which is often quoted, although that of Rohmer et al. [11] could have been equally appropriate.

The  $\pi$ -orbitals of the Cp rings and the metal d-orbitals are responsible for coordination [8] and chemical reactivity. They also control the photochemical and photophysical properties. Fig. 2 displays their relative energies [4,9,10,12]. In the ground state, the frontier orbital electronic structure is generally accepted as being  $(3e_{2g})^4(5a_{1g})^2$ . It should be noted that these orbitals are essentially metal-centered. The lowest lying empty orbital is the antibonding d-orbital  $4e_{1g}$ . It is formally metal-centered, but in reality, there is substantial mixing with ligand orbitals [12,13]. This level is widely

<sup>2</sup> Ferrocene is often denoted by  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ . The Greek letter  $\eta$  designates ligands bound in this fashion and the superscript indicates the exact number of carbon atoms equidistant from the metal.

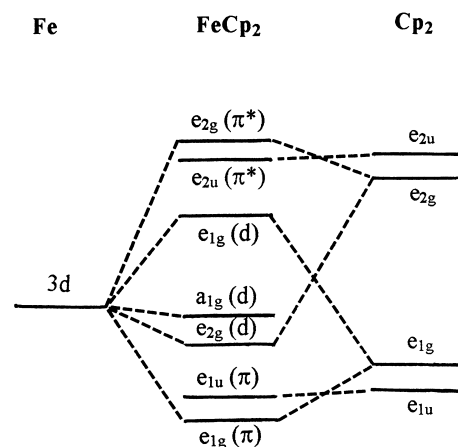


Fig. 2. Qualitative molecular orbital diagram for ferrocene complexes (from [9,10]).

involved in the formation of the first excited states which are of interest here. It is important to know the energy of these excited states as it is a key factor to explain the photo-physical behaviour of ferrocene with respect to luminescent compounds.

### 2.2. Spin-allowed transitions

The ground state of ferrocene is a singlet state  $S_0$  with a  $^1A_{1g}$  geometry. Consequently, the one-electron transitions which are allowed, i.e. those which are the most probable because they involve states of the same multiplicity, result in singlet excited states. The lower energy transitions are of the type  $5a_{1g} \rightarrow 4e_{1g}$  and  $3e_{2g} \rightarrow 4e_{1g}$ . They are responsible for two weak absorption bands situated at  $22\,700\text{ cm}^{-1}$  ( $\epsilon=91\text{ M}^{-1}\text{ cm}^{-1}$ ) and  $30\,800\text{ cm}^{-1}$  ( $\epsilon=49\text{ M}^{-1}\text{ cm}^{-1}$ ), respectively, in isopentane. It is considered that these transitions are metal-centered. They are the ones involved in most of the photophysical processes. The first singlet excited state  $S_1$  has been calculated to be around  $21\,800\text{ cm}^{-1}$ .

Since significant stabilization occurs when the complex is formed, the  $\pi$ -bonding orbitals lie at low energies. Consequently,  $\pi^*$  antibonding orbitals are found at high energies. Possible transitions towards these antibonding orbitals are not the concern of usual photophysical and photochemical processes. However, the intense charge transfer band from ligand to metal observed in the ultra-violet (UV) part of the absorption spectrum at  $50\,000\text{ cm}^{-1}$  ( $\epsilon=51\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) has been assigned to a transition from a  $\pi$ -orbital towards the  $4e_{1g}$  level [10,14,15].

### 2.3. Spin-forbidden transitions and energy of the lowest triplet excited state

The intersystem crossing  $S_1 \rightarrow T_1$  which populates the first triplet excited state  $T_1$  occurs with a quantum yield of 0.66 [16]. A major difficulty was the determination of the effective energy position of the lowest triplet excited state. For

more details, one may refer for example to Herkstroeter's publication [17]. Many attempts have been made to estimate this value from spectroscopic data. Scott and Becker [14] in 1964, and later Armstrong et al. [15], reported three long-wavelength transitions attributed to the forbidden absorption  $S_0 \rightarrow T_1$ , though Sohn et al. [10] considered that only the lowest was observable in the UV spectrum, giving a very weak band at  $18\,900\text{ cm}^{-1}$ . Additionally, the authenticity of the reported phosphorescence spectra was heatedly questioned (*vide infra*). In these conditions, estimating the position of the lowest vibrational states with accuracy was a very hard task. It was necessary to wait for the quenching experiments performed independently by Herkstroeter [17] and by Kikuchi et al. [18] before the lowest 'vertical' absorption of ferrocene could be placed around  $15\,000 \pm 1000\text{ cm}^{-1}$ , as predicted by Rohmer et al. [11].

#### 2.4. About ferrocene luminescence

The phosphorescence spectrum of ferrocene, which should correspond to the radiative deactivation of the excited triplet state  $T_1$ , has been the object of most detailed studies. As early as 1961, Scott and Becker reported that ferrocene was phosphorescent when excited to the  $S_2$  or  $S_3$  state [14]. The spectrum displayed a wide band centered at  $20\,000\text{ cm}^{-1}$ . In 1968, Smith and Meyer observed an emission at the same frequencies in various matrices at low temperature [19]. However, in the meantime, Armstrong et al. [15] as well as Tarr and Wiles [20] were simply unable to obtain a spectrum. Neither could Schandry and Voigtländer repeat the experiment [21]. They tried to excite ferrocene directly in its triplet state, although their choice of excitation wavelength has been discussed [22]. Finally, Müller-Goldegg and Voigtländer attributed these phosphorescence reports from the early literature to photolysis products of ferrocene [23]. It is now generally accepted that, unlike other metallocenes, ferrocene is not phosphorescent at all.

Regarding fluorescence, which should be the radiative deactivation of the singlet excited state, only Schandry and Voigtländer assigned an emission observed between  $24\,900$  and  $17\,400\text{ cm}^{-1}$  to this phenomenon [21]. To our knowledge, no other observations of this type have been reported until now, and it is highly probable that ferrocene is not fluorescent.

All the energy absorbed is thus converted into thermal energy. The absence of any luminescence is a great asset to the use of ferrocene in calibration experiments for photothermal spectroscopy [24,25].

### 3. The ferrocenium ion

It may be considered that the ferrocenium ion is a chemical species different from ferrocene and so deserves to be dealt with separately. The orbital structure is  $(3e_{2g})^4(5a_{1g})^1$ .

The ferrocenium ion and its derivatives are strong electron acceptors. The first excited state, obtained by the spin-allowed transition  $D_0 \rightarrow D_1$ , is a doublet<sup>3</sup> state  $D_1$ . It is interesting to note that it has been produced by a ligand-to-metal charge transfer (LMCT) [4,10]. The energy of this doublet excited state has been estimated to be  $14\,800\text{ cm}^{-1}$  for  $\text{Fc}^+$ ,  $13\,600\text{ cm}^{-1}$  for  $\text{Me}_2\text{Fc}^+$  and  $12\,000\text{ cm}^{-1}$  for  $\text{Me}_{10}\text{Fc}^+$  [26]. It is lower than the energy of the first singlet state in the corresponding ferrocene derivative. Consequently, the UV-Vis spectrum of ferrocenium ions shows a low-frequency absorption band [10].

### 4. Feasibility of excited state quenching

Ferrocene and its derivatives proved to be effective quenchers of excited states. More particularly, they have long been known for their capacity to inhibit the lowest energy excited states, generally the triplet state, of a number of molecules commonly used as photosensitizers. The mechanism is very efficient. The quenching rate constants often are at the diffusion-controlled limit or very close to it. They are much higher than those obtained with transition metals or organic quenchers. Among the different quenching processes known, *energy transfer* and *electron transfer* are the most commonly evoked as far as ferrocene is concerned.

The excitation energy can be transferred according to  $A^* + \text{FcCp}_2 \rightarrow A + \text{FcCp}_2^*$ , which may be followed by the thermal relaxation of the excited state, giving  $A + \text{FcCp}_2 + \text{thermal energy}$ . The first requirement for the energy transfer to take place is that the ferrocene molecule  $\text{FcCp}_2$  has an excited state  $\text{FcCp}_2^*$  lower than that of the excited molecule  $A^*$ . So ferrocene could logically accept energy from excited states higher than  $21\,800\text{ cm}^{-1}$ , in order to populate its excited singlet state, and from excited states higher than  $15\,000\text{ cm}^{-1}$  if its excited triplet state is to be populated. Remember that there are two major energy transfer processes: the Dexter mechanism by electron exchange, and the Förster mechanism by dipole-dipole interaction [27]. The ferrocenium ion can also inhibit excited states via an energy transfer pathway.

In the photoinduced electron transfer (PET) mechanism:  $A^* + \text{FcCp}_2 \rightarrow A^- + \text{FcCp}_2^+$ , ferrocene acts as an electron donor. The ferrocenium ion is temporarily formed. Then, charges recombine to restore both neutral species to the ground state  $A + \text{FcCp}_2$  with an output of thermal energy. The thermodynamic feasibility of the initial step depends on the variation of the free energy of the PET:  $\Delta G_{\text{ET}}^0 = E_{1/2}(A/A^-) - E_{1/2}(\text{FcCp}_2^+/\text{FcCp}_2) - E_{0-0} + W_p - W_r$  where  $E_{1/2}(\text{FcCp}_2^+/\text{FcCp}_2)$  is the donor oxidation potential,  $E_{1/2}(A/A^-)$  is the acceptor reduction potential,  $E_{0-0}$  is the energy of the excited state of A, and  $W_p$  and  $W_r$  are the so-called work terms, i.e., the energy required to bring the

<sup>3</sup> Doublet states are frequently encountered in organometallic compounds which bear unpaired electrons.

reactants or products together from an infinite distance apart to their separation distance in the activated complex [28]. The feasibility of the first step being conditioned by the oxidation potential of the ferrocenyl derivative, it can easily be modulated by varying the substitution of the latter. With the range of substituents used, the electrode potential shifts by more than a volt. Substitution by an electron-withdrawing group, such as *p*-nitrophenyl or acetyl, shifts the potential in the positive direction. In contrast, the addition of each methyl group causes a cathodic shift of ca. 50–55 mV [29–31].

The ferrocenium ion and its derivatives may also quench the excited states through an electron transfer mechanism. However, unlike ferrocenes, they act as electron acceptors, and therefore, extinguish, by electron transfer, the luminescence of compounds which are weaker oxidizing agents than themselves:  $A^* + \text{FeCp}_2^+ \rightarrow A^+ + \text{FeCp}_2 + \Delta$ .

### 5. A cursory glance at the techniques used to monitor excited state quenching

Monitoring photoluminescence is one of the most direct means to study an excited state. The emission variable can be either the intensity *I* or the radiative lifetime  $\tau$ . This variable is monitored depending on the quencher concentration [Q], and the data are analyzed using the classical Stern–Volmer equation:  $F_0/F = 1 + k_q \tau_0 [Q]$ , where *F* and *F*<sub>0</sub> are the emission variables measured in the presence and in the absence of quencher, *k*<sub>q</sub> is the quenching constant and  $\tau$  is the lifetime in the absence of quencher. Note that, when ferrocene is used as a quencher, internal filter effect problems may appear, due to the fact that ferrocene absorbs in the same absorption and/or emission range as the studied molecule. Corrections are often necessary when monitoring the luminescence intensity, but this drawback may be overcome by measuring the lifetimes [31,32].

However, all the excited states are not luminescent, and are even far from it. Flash-photolysis is an alternative way to study them. The technique consists of using a short and intense flash of light in order to generate ‘transient species’, that is atoms, molecules and fragments of molecules which have very short lifetimes. These transient species may include excited states. Detection may be achieved by different means, the most commonly encountered being monitoring of the transient absorbance changes. So the question is essentially one of absorption spectroscopy, but it must be mentioned here because it has been widely used in triplet states studies, and the results obtained by this technique are indissociable from those obtained from luminescence quenching experiments.

### 6. Triplet state quenching

The quenching of triplet states by ferrocene has been the object of considerable attention. The systems concerned

span from organic molecules, known to be phosphorescent, to organometallic complexes, the lowest excited states of which are often highly luminescent in fluid solution at room temperature. As for the results obtained, knowing whether the quenching is due to energy transfer or due to electron transfer has until now been extremely puzzling. In an attempt to clarify this situation, we propose to make a distinction between the triplet states of purely organic substances, and the others.

#### 6.1. Organic triplets

Regarding organic compounds, it has been shown by flash-photolysis that ferrocene is a very efficient triplet state quencher, as long as the triplet energy is in the range 15 000–24 000 cm<sup>-1</sup> [17,33,34]. Detailed investigations like that of Farmilo and Wilkinson [33], Gilbert et al. [35], and Herkstroeter [17] have shown that quenching efficiency decreases for lower energy triplets. This observation allowed them to establish that energy transfer is involved in the quenching of organic triplet states, ferrocene behaving as a ‘non-vertical’ energy acceptor [33,36], at least when the triplet energy level is higher than 15 000 cm<sup>-1</sup>. For triplet states with an energy lower than 13 000 cm<sup>-1</sup>, Kikuchi et al. suggested that electron transfer could take over from the energy transfer mechanism [18]. In contrast, Herkstroeter proposed that quenching proceeds by energy transfer, via a very distorted triplet [17].

The experiments based on phosphorescence quenching are in the same line. Biacetyl(2,3-butanedione) has been well studied because of its relatively unique property of exhibiting phosphorescence in degassed fluid solution at room temperature. Turro and Engel observed that the phosphorescence of biacetyl was non-linearly quenched by ferrocene [37], and Scandola’s group showed that an energy transfer mechanism was involved [38,39]. This was confirmed by Wrighton et al. [40]. The latter authors also showed that energy transfer took place when several metallocenes were used to quench the phosphorescence of benzil, which has a triplet energy nearly isoenergetic with biacetyl. To do so, they made a correlation between the quenching efficiency, on the one hand, and the relative position of the metallocene and the donor excited state, on the other hand. However, it must be noted that quenching was found to be linear and attributed to an electron transfer when biacetyl was caged in a hemispherical [41].

In fluid solution, the most plausible mechanism is energy transfer by electron exchange. Wilkinson emphasized that the efficiency of this process critically depends on orbital factors [42]. Using several coordination complexes as quenchers, he showed that, when energy transfer produces ligand-field states, i.e. those centered on the metal and hardly at all on the ligands, the quenching behaviour was different from that expected for a typical organic triplet state quencher. Actually, it seems that, for ferrocene, orbital factors are often favourable. This may be partly explained by the geometry

of this compound, which could allow good spatial overlap between the metal-localized d-orbitals and the  $\pi$ -orbitals of the excited organic molecules during collision [34]. A weak quenching efficiency has indeed been noticed when the approach of ferrocene was hindered by the geometrical distortion of the organic triplets [43,44].

## 6.2. Non-organic triplets

Let us now turn our attention towards the quenching of non-organic triplet states. Ruthenium derivatives have been the basis for numerous studies, although the various authors seem to have drawn contradictory conclusions. Firstly, Wrighton et al. suggested that the luminescence quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by ferrocene was achieved via energy transfer [40]. In contrast, the groups of Xia and Duan studied the same interaction using many ferrocenyl derivatives, and they concluded that electron transfer is involved [45–50]. The same may also explain the luminescence quenching of  $\text{Ru}(\text{Phen})_3^{2+}$  [51]. Some years later, Lee and Wrighton took up this work again using flash-photolysis [52]. They compared the quenching efficiency of ferrocene and several methyl derivatives. The methyl substituents were thought to have a minor influence on the energy levels, since these authors considered that the d–d excitation bands occur at similar energies for  $\text{FeCp}_2$  and  $\text{Fe}(\text{CpMe}_5)_2$  [53]. In contrast, the oxidation potential varied from one derivative to another. Consequently, the differences found in the quenching efficiency of the ferrocenyl derivatives investigated were attributed to variations of the driving force for electron transfer. It was, therefore, shown that the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{bpz})_3^{2+}$  luminescence by ferrocene derivatives actually occurs competitively by both energy transfer and electron transfer. The relative fraction of electron transfer to total quenching was estimated, and was even experimentally controllable.

The duality of this mechanism also emerges from the luminescence quenching study of copper(I)phenanthrolines, sterically hindered to varying degrees, and copper(I)tetraazaphenanthrene, reported by Cunningham et al. [29,54]. Working with a platinum complex, Bevilacqua and Eisenberg showed that the quenching rate constant decreased only slightly as the metallocene became more difficult to oxidize [31]. They also deduced that the quenching could not be explained by electron transfer alone, but by a combination of electron and energy transfer.

Finally, concerning the rare earths, Hall and Sharpe observed that the luminescence of terbium and dysprosium ions was strongly quenched by the presence of a ferrocene group in the cryptand (**2**, Fig. 3). The mechanism was not explained, but it was noted that an intimate interaction was necessary for the phenomenon to appear, since solutions of lanthanide acetate with ferrocene resulted in no quenching of the lanthanide excited state [55]. In addition, electron transfer was clearly demonstrated in the luminescence

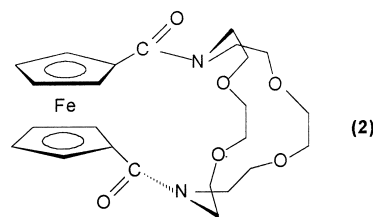


Fig. 3. Chemical structure of compound cryptand (**2**).

quenching of hydrated europium(III) [56] and uranyl ions [57]. Traverso et al. followed the variation of the luminescence intensity and lifetime of  $[\text{UO}_2]^{2+}$  in the presence of various metallocenes with known oxidation potential, and obtained an excellent linear free-energy relationship between the bimolecular quenching rate constant and the oxidation potential of the metallocene [57].

Analysis of the literature is made difficult by the fact that use is sometimes made of one or two organometallic or inorganic substances among organic triplets, which confuses the situation [17,33]. However, it seems that the distinction made here between organic and non-organic triplets allowed the main lines of the problem to be identified. Actually, the involvement of an energy transfer process has been clearly shown as far as organic triplets are considered. There are some exceptions, such as for biacetyl incorporated in a hemiacarcerand [41], but they may be explained by orbital factors. In contrast, for non-organic triplets, an electron transfer mechanism can take place even when energy transfer is energetically possible. This can essentially be assigned to the large driving force of electron transfer. In non-organic triplets, therefore, both mechanisms could compete. Since stereochemical and orbital factors are involved, it is possible, for example, that small variations can cause the mechanism to swing in one direction or the other.

Far less data are available regarding the luminescence quenching of triplet states by ferrocenium ions. Emission from the 'cluster centered' excited state of  $\text{Cu}_4\text{I}_4(\text{py})_4$  is reported to be quenched by electron transfer [30], which also seems to be the case for the luminescence quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  [58].

## 7. Doublet state quenching

The ground state of  $\text{Cr}(\text{bpy})_3^{3+}$  is a quartet. Light absorption induces the formation of an excited quartet state, which then gives an excited doublet state by intersystem crossing [59]. There are large similarities between the behaviour of this doublet state and that of non-organic triplet states. The quenching of the doublet excited state of  $\text{Cr}(\text{bpy})_3^{3+}$  by ferrocene has been attributed to electron transfer [60], but Lee et al. have shown that it could be partitioned into energy and electron transfer components [61]. The ferrocenium ions have also been used to quench the emission of  $\text{Cr}(\text{bpy})_3^{3+}$ ,

which is a more powerful oxidative agent than them, and a very poor reductant. Quenching was assigned to an energy transfer process because, thermodynamically speaking, electron transfer was very unlikely to occur [61].

## 8. Singlet state quenching

Quite surprisingly, not much work has been devoted to the study of singlet states quenching by ferrocene. It seems that, in this case, a linear dependence between the fluorescence decrease and the quencher concentration was obtained. Ferrocene quenched the fluorescence of quaternary salts of styrylquinolinium [62], as well as that of *trans*-4-nitro-4'-methoxystilbene [63], *trans*-cyanostilbenes [64] and biacetyl [37]. According to Wells et al., ferrocene interacts with ground-state hypericin [65]. After formation of the hypericin excited state, ferrocene quenches the fluorescence, probably via an electron transfer mechanism. Pénigault et al. observed the fluorescence quenching of some polyaromatic hydrocarbons in cyclohexane [66]. A mechanism based on singlet–singlet energy transfer was proposed, essentially because the hydrocarbon emission spectrum overlapped the ferrocene absorption spectrum. According to Traverso et al., energy transfer was also involved when ferrocene quenched the fluorescence of naphthalene in a chloroform–ethanol solution [67]. It will be seen below that fluorescence quenching by ferrocene and ferrocenyl derivatives is advantageously used in many systems, the energy and electron transfer mechanisms being postulated alternately. Evidence for this duality was provided by Giasson et al. with organometallic derivatives, i.e. porphyrins, the singlet state of which was inhibited by some ferrocenyl derivatives [68]. It has also been underlined by the group of Morlet-Savary and Fouassier who used a three-component system, made of a coumarin derivative, an iron arene and a phenylglycine, as a polymerization photoinitiator for imaging applications [69–71]. Note that the compounds under study were no longer ferrocenyl derivatives but ( $\eta^6$ -arenyl)( $\eta^5$ -cyclopentadienyl)iron(II) complexes. The first step of the photochemical reaction was the quenching of the coumarin excited state by iron arenes. The fluorescence quenching study revealed that this first step either involved electron transfer or energy transfer, depending on the structure of the iron arene. Finally, mention must be made of the work of Hrdlovic et al. which was aimed at estimating the quenching rate constant of singlet oxygen by various quenchers, including ferrocene [72]. These authors used rubrene, which generates singlet oxygen ( $^1\text{O}_2$ ) under light irradiation and undergoes photo-oxidation. The rubrene fluorescence was measured under continuous excitation and found to decrease with time, proportionally to the amount of  $^1\text{O}_2$  produced. In the presence of a  $^1\text{O}_2$  quencher, the decrease in fluorescence intensity was slowed by an increase in the efficiency of the quencher. It appeared that ferrocene is a very ineffective quencher of singlet oxygen.

## 9. Applications of intermolecular luminescence quenching in solution

Excited states are responsible for both luminescence and photochemical reactions. This is why luminescence quenching investigations often allow the mechanism of a photochemical reaction to be better understood. Fasano and Hoggard tried to elucidate the mechanism of the photochemical transformation of  $\text{Ru}(\text{bpy})_3^{2+}$  into  $[\text{Ru}(\text{bpy})_2(\text{DMF})\text{Br}]^+$ , with tetrabutylammonium bromide in DMF [73]. This reaction is a photoanation, that is a photochemical substitution of an organic ligand by an anion. For this, the quenching of the phosphorescence of  $\text{Ru}(\text{bpy})_3^{2+}$  by ferrocene was compared with the quenching of the photochemical reaction by the same compound. The quenching rate constant was found to be three times higher for photoanation, which suggested that the excited states involved in the reaction were not in equilibrium with the triplet state responsible for luminescence. Ollino and Cherry took up this study, monitoring the phosphorescence lifetimes, and found that, on the contrary, the quenching of both luminescence and photosubstitution were very similar [32]. Roundhill et al. used ferrocene, among other quenchers, in order to compare the photochemical reactivity of two platinum(II) complexes [74]. Görner and Schulte-Frohlinde measured the quantum yield of fluorescence and of *trans*-, *cis*-photoisomerization for quaternary salts of styrylquinolinium as a function of ferrocene concentration. The influence of the latter on the absorption of the transient triplet state was also studied. These comparisons allowed the excited state involved in photodimerization to be identified [62]. Finally, Traverso et al. tried to understand the mechanism of photo-oxidation of ferrocene sensitized by naphthalene in a chloroform–ethanol mixture [67]. A parallel was drawn between the photoreaction and the quenching of naphthalene fluorescence by ferrocene. It was concluded that sensitization occurred by means of an energy transfer process from naphthalene to the ferrocene– $\text{CHCl}_3$  complex.

From a more quantitative viewpoint, luminescence quenching or the absence of it may be useful to situate the energy level of an excited state. The estimation of the triplet state level of tungsten complexes [75] and that of aromatic thioketones [76] has been achieved this way. In the latter case, Mahaney and Huber showed that the triplet state was responsible for the red light emission detected, though there was an uncertainty about whether this emission was phosphorescence or fluorescence.

One of the most interesting applications of intermolecular quenching is met in the field of molecular recognition and analytical chemistry. In molecule **3** (Fig. 4), introduced by De Santis et al., anthracene was the fluorescent unit [77]. This anthracenyl group was linked to a chelating polyamine moiety, which complexed a zinc(II) ion. Owing to the Lewis acid character of the zinc cation, this structure recognized the carboxylate anion, and more particularly ferrocenecarboxylate, which is quite a strong electron donor. The presence

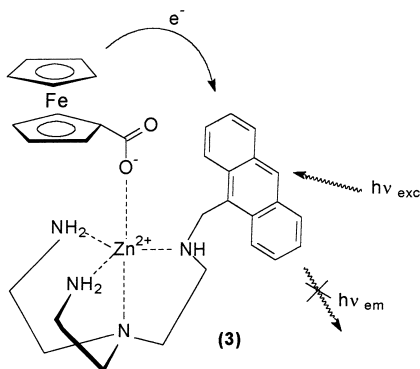


Fig. 4. Representation of the PET mechanism responsible for the fluorescence quenching of the excited anthracene unit, after binding of the ferrocenecarboxylate anion by the  $Zn^{2+}$  center (from [77]).

of the anion was indicated through fluorescence extinction involving PET.

## 10. Intramolecular luminescence quenching

In the systems described above, the ferrocenyl derivative and the fluorescent molecule were brought together in solution. Quenching was, therefore, of the intermolecular type. Recently, some new compounds have appeared in which the ferrocenyl derivative is covalently linked to a luminescent moiety. Luminescence quenching, if any, is then achieved intramolecularly. Applications range from artificial photosynthesis aiming at light energy storage, to the design of photodiodes, potentially useful for molecular electronics.

### 10.1. Artificial photosynthesis

The use of light energy requires this energy to be collected, converted and stored to make it permanently available. Nature has been the first source of inspiration since, starting from light energy, it succeeds in generating charges and separating them via multistep electron transfer reactions far apart across the thylakoid lipid bilayer membrane. The result is that energy is stored as reduced products on one side of the membrane, while oxygen appears on the other side. In order to simulate the primary process, that is the absorption of light energy and its use to create charges, some simple systems have been imagined. They comprise a photosensitive site (PS) covalently linked to an electron acceptor (A) or donor (D) site. These two-component systems are called dyads. The following sequence is, therefore, obtained:  $PS-A \rightarrow PS^*-A \rightarrow PS^+-A^-$  or  $PS-D \rightarrow PS^*-D \rightarrow PS^-D^+$ . One of the factors which limits the use of dyads is fast charge recombination. So a great deal of research has been devoted to reproducing the way that charges separate during the first steps of natural photosynthesis. To achieve that aim, multicomponent assemblies, called polyads, have been developed in order to move the

charges away from each other, and to model the cascade of electron transfer which happens in naturally-occurring reaction centers. For instance, the following sequence may be encountered:  $D-PS-A \rightarrow D-PS^*-A \rightarrow D-PS^+-A^- \rightarrow D^+-PS-A^-$ . With two electron donor groups in series, it becomes  $PS-D_1-D_2 \rightarrow PS^*-D_1-D_2 \rightarrow PS^-D_1^+-D_2 \rightarrow PS^-D_1-D_2^+$ . The ferrocene derivative is expected to act as an electron donor. An increase in the stability of the luminescent excited state, i.e. its lifetime, is not sought after.

Porphyrins have been widely used as PSs because they offer the advantage of absorbing over most of the solar spectrum and mimic the natural reaction center. The porphyrin absorption spectrum displays Q bands situated at much higher wavelengths than the absorption bands of ferrocene, ruling out efficient singlet energy transfer from the excited porphyrin to the ferrocene. However, other mechanisms remain possible. Actually, in molecule **4** reported by Giasson et al. (Fig. 5), the ferrocenyl center reduced the singlet excited state of porphyrin, via an electron transfer process, to lead to a strong decrease in the fluorescence efficiency [68]. Intramolecular quenching of porphyrin fluorescence was also observed by Beer and Kurek [78] in a porphyrin-ferrocene-quinone triad, **5**. In that particu-

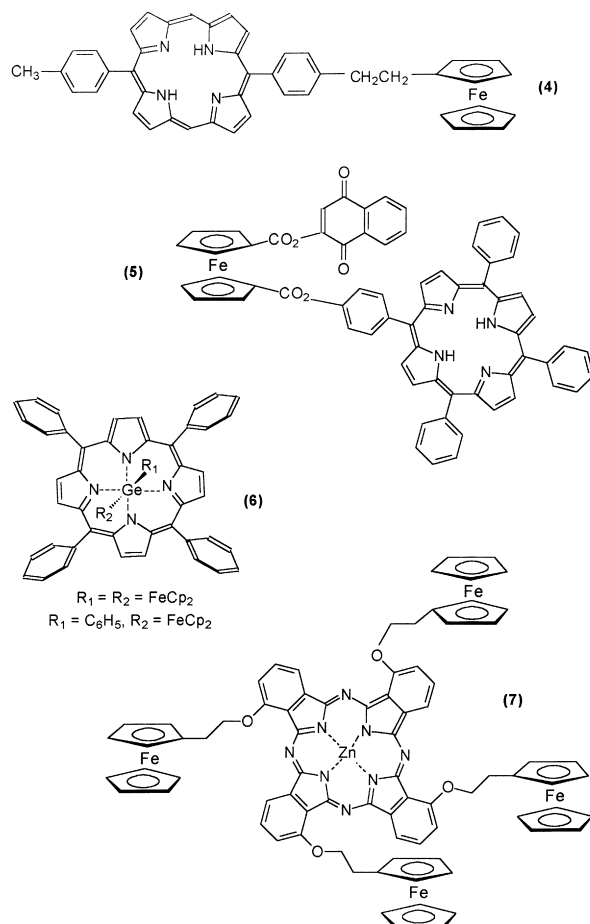


Fig. 5. Chemical structure of compounds **4-7**.

lar case, quenching was attributed to fast electron transfer between the excited electron-donor porphyrin and the electron-acceptor quinone, since the ferrocenyl moiety employed was thermodynamically unable to reduce the excited singlet state of the porphyrin. It has also been observed that ferrocene quenched the triplet excited state of a germanium porphyrin, **6**, probably via energy transfer, which led to the photochemical stabilization of this molecule [79].

Phthalocyanines, the properties of which closely resemble those of porphyrins, are also used as photosensitizer sites. With the triad system zinc-phthalocyanine–viologen–ferrocene, where viologen is an electron acceptor, long-lived states with separated charges were claimed to be obtained [80,81]. Poon et al. [82] presented a tetraferrocenylphthalocyanine, **7**. The electronic interaction between the ferrocenyl units and the macrocycle was reported to be insignificant in the ground state. However, very efficient fluorescence quenching was observed, and assigned to a PET mechanism.

Transition metal complexes are particularly versatile, and subtle modifications of both the metal and the ligand are enough to modulate their photophysical properties [83–90]. The geometry of these systems offers the possibility to design multicomponent molecular devices (see for example structures **8–12** in Fig. 6). Ruthenium(II) and osmium(II) complexes, which bear a reducing ferrocenyl center on a derivatized bi- or tridentate ligand, have been the most widely studied. The spacer size and chemical nature are variable. In every case, the presence of the ferrocene units quenched the luminescence properties of the complexes.

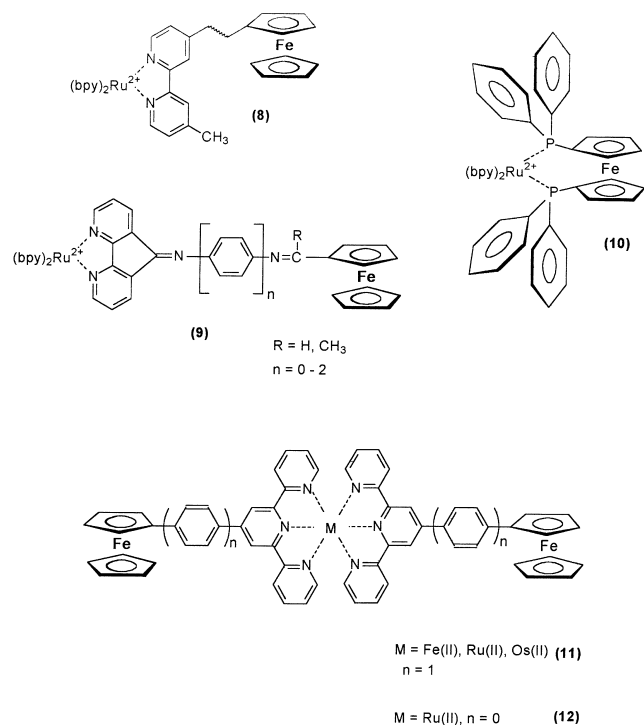


Fig. 6. Chemical structure of compounds **8–12**. The counteranions are PF<sub>6</sub><sup>-</sup>.

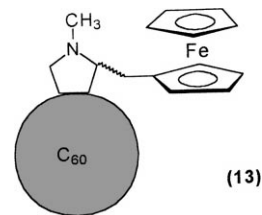


Fig. 7. Fullerene based dyad.

The quenching mechanism was sometimes difficult to characterize [83–89]. Note that Hutchinson et al. proposed an interesting energy level diagram to discuss the quenching effect due to the ferrocenyl sites [90]. For the dyad of Yam et al. (**10**), the luminescence quenching was mainly attributed to the presence of phosphine ligands, with ferrocene only contributing to the quenching process [86]. It is interesting to note that the work from Chambron et al. (compound **11**) is the only one in which ferrocene is described as an electron acceptor [87].

Dyads and polyads can also be built from organic chromophores. Then, there is a drift from the natural model, but the building blocks used may display very appealing photophysical properties. Dyads of the PS–D type have been synthesized by Guldi et al. [91,92] with fullerene C<sub>60</sub> as photosensitizer and ferrocene as electron donor (**13**, Fig. 7). Ground-state C<sub>60</sub> displays remarkable electron acceptor properties, since in solution, it is able to accommodate as many as six electrons. The fluorescence detected between 14 300 and 12 500 cm<sup>-1</sup> was strongly quenched in the presence of ferrocene. For energetic considerations, energy transfer from the fullerene excited state towards ferrocene was impossible. It was shown that the fluorescence quenching mechanism varied with the spacer. In the case of an unsaturated spacer, the decrease in the fluorescence intensity originated in electron transfer from ferrocene to fullerene, via the double bonds. With a saturated spacer, the electron-donating effect of ferrocene was felt through up to seven  $\sigma$  bonds. The formation of an intramolecular exciplex was proposed. A ferrocene–porphyrin–C<sub>60</sub> triad was prepared by Fujitsuka et al. and shown to produce a long-lived charge-separated state [93].

The goal of artificial photosynthesis is of course the production of photocurrents. It will be seen below how interesting results were obtained using these molecules in organized media, and particularly in Langmuir–Blodgett (LB) films.

## 10.2. From photocurrent generation to molecular photodiodes

Generating photocurrents is of major interest for molecular electronics too, where the limitations due to the size of present electronic micro-devices and micro-wiring must be eliminated. To do so, information should be processed using single molecules which display the properties of



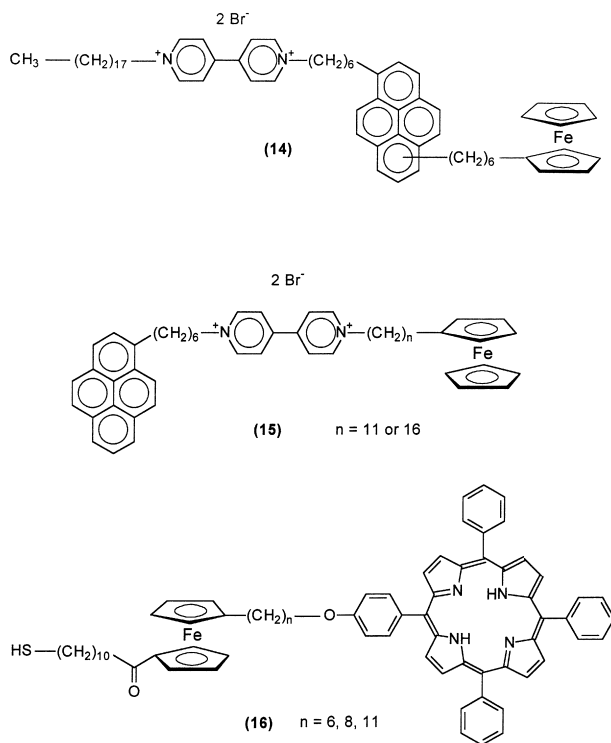


Fig. 8. Triads of D-PS-A type (**14**), D-A-PS type (**15**) and PS-D-A type (**16**).

electronic components, at the monomolecular scale. Inducing one-directional PET, subsequently leading to vectorial separation of the charges, would generate a molecular photodiode. It is clear that the polyads described above to simulate photosynthesis are good potential candidates for monomolecular photodiodes. Triads **14** and **15**, designed by Fujihira et al., can be added to this list [94,95]. Triad **14** is of the D-PS-A type, with ferrocene, pyrene and viologen units in the respective roles (Fig. 8). In triad **15**, the order of the building blocks was modified (D-A-PS). Compound **15** was deposited on a semitransparent gold electrode in order to test its efficiency [94]. The molecules formed a monolayer, in which they were oriented perpendicularly to the electrode surface. A vectorial photocurrent was detected.

Kondo et al. recently examined a (PS-D-A)-type triad, **16**, composed of porphyrin, ferrocene and thiol units, separated from each other by alkyl chains [96]. These triads formed LB films at the surface of the gold electrodes. They were soaked in a solution of methylviologen, which was expected to act as an additional electron acceptor, and thus, reduce reverse electron transfer. It was shown that the longer the alkyl chain between porphyrin and ferrocene, the higher the photocurrent. This suggests that inhibition of energy transfer and reverse electron transfer are key factors for the efficient generation of photocurrents. It may be considered that these two examples belong to organized systems, like those reviewed below.

## 11. Applications in organized media

### 11.1. Membranes, micelles and emulsions

Ferrocenyl derivatives find numerous applications in organized media, whatever the complexity of the media. Owing to their hydrophobic character, they are mainly encountered in lipid phases or incorporated into membranes and films. They can be used in luminescent systems for reasons other than the classical quenching effect. For instance, a ferrocenyl group linked to a hydrophobic alkyl chain (**17**), to the head-group of an amphiphile [97], or to polypeptides [98], has been incorporated into artificial membranes, with the aim that the ferrocene redox state controls the permeability of the membranes (Fig. 9). The membranes were placed on a platinum minigrad and were initially not permeable to a fluorescent probe. When an electric potential was applied, the ferrocenyl units were oxidized and they drifted apart because of charge repulsion. This caused a change in the membrane permeability. The fluorescent probe then passed through the membrane and was detected. This system aims at mimicking certain biological processes occurring in the synapses, where a potential variation induces the release of transmitter metabolites.

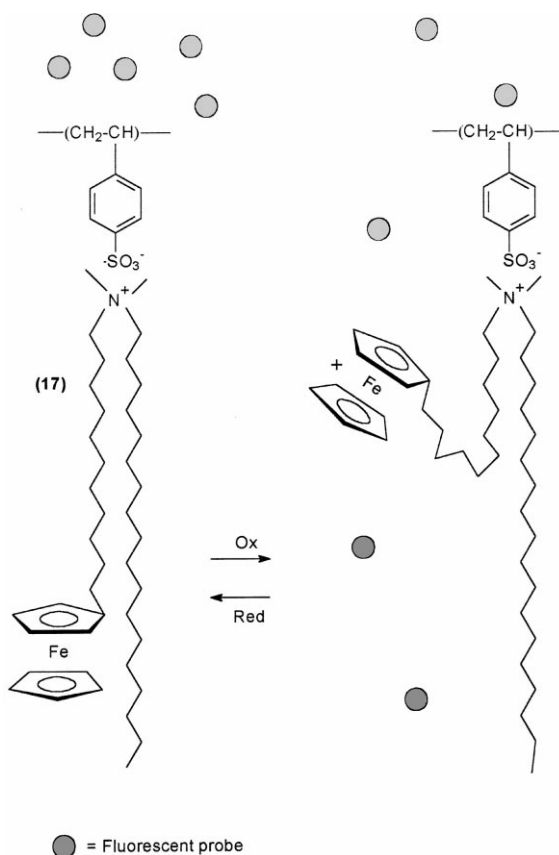


Fig. 9. Schematic representation of the permeation of a fluorescent probe through a redox-sensitive film (from [97]).

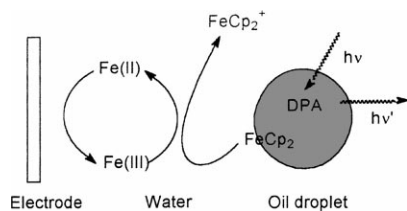


Fig. 10. Representation of the electron transfer and mass transfer mechanism in a microemulsion, responsible for 9,10-diphenylanthracene fluorescence recovery (from [101]).

However, the fluorescence quenching properties of ferrocene are advantageously used in most cases. They can help in understanding mass transfer within a complex medium, i.e. microemulsions [99–101]. These data are essential for studies on solvent extraction and on distribution dynamics of solutes in emulsion systems. Ferrocene was dissolved in tri-*n*-butyl phosphate droplets, in the presence of 9,10-diphenylanthracene (DPA), the fluorescence of which was inhibited (Fig. 10). The aqueous phase contained Fe(II) ions (as  $\text{Fe}(\text{CN})_6^{4-}$ ), which were oxidized at the electrode to give Fe(III) ions. The latter oxidized the ferrocene molecules present in the oil droplet. The ferrocenium ions, which are not hydrophobic like ferrocene, were ejected into the aqueous phase, and the DPA fluorescence in the oil droplet was restored. This fluorescence recovery allowed the mass transfer of  $\text{FeCp}/\text{FeCp}^+$  across the droplet–water interface to be monitored. The same observation was made in a single micrometer-sized droplet, dispersed in water and immobilized with the laser-trapping technique [102]. The accuracy of the measurement was, therefore, increased compared to that obtained with a dispersion of droplets.

Luminescence quenching also allowed PET in organized media to be investigated. The aim is often the photoelectric conversion of solar energy. It has been seen that light absorption allows charges to be generated, but one of the major subsequent problems is to keep them separate so that they cannot recombine. An electric gradient at the micelle surface is one of the best ways to prevent recombination. This is the reason why PET has been studied in cetyltrimethylammonium chloride (CTAC) micelles containing pyrene and butyl ferrocene [103]. The pyrene fluorescence is quenched by butyl ferrocene, and it has been shown that the diffusion rate of both molecules in the micelles determines the quenching rate constant. This quenching was 20 times more efficient for compound **18** (Fig. 11), where pyrene and ferrocene were linked by an alkyl chain, than for the mixture pyrene plus ferrocene. It was suggested that a large frac-

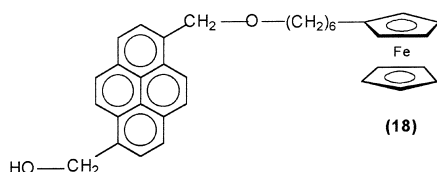


Fig. 11. Pyrene and ferrocene linked by alkyl chain (**18**).

tion of the molecules have conformations for which the distances between the functional moieties are sufficiently small to permit direct intramolecular electron transfer.

The quenching of DPA fluorescence by ferrocene in CTAC micelles was also observed by Papsun et al. in their study of ferrocene oxidation by organic oxidants and carbon tetrachloride [104]. D'souza and Krishnan investigated the quenching of tetraphenylporphyrin fluorescence by the ferrocenium ion in various micellar media. Their aim was to compare the quenching efficiency of several iron(III) coordination compounds in these media, and they showed that the quenching constants depend on the nature of the ligating atoms around iron(III) and on the extent of  $\pi$ -conjugation of the ligands. Evidence for electron transfer was obtained [105]. To the best of our knowledge, this is the only study dealing with singlet quenching by ferrocenium ions.

Finally, the goal may simply be to measure the ferrocene content in a solution. To do so, it has been shown that the ferrocene concentration was proportional to the luminescence decrease of a europium complex in cetyltrimethylammonium bromide (CTAB) micelles [106].

## 11.2. Interfaces

Photoluminescence can be a powerful tool for examining surface modifications. For instance, the influence of adsorbates on the luminescence of porous silicon, n-Si, has been studied by Lauerhaas et al. Many solvents led to a moderate quenching of luminescence, which was totally extinguished by a ferrocene solution in toluene. The mechanism was attributed to electron transfer. The effect on luminescence was partially reversible when ferrocene was rinsed out [107].

Regarding semiconductors, when such compounds are irradiated with light, electrons are promoted from the valence band to the conduction band, and positive holes are left in the valence band. The electron–hole pairs may subsequently recombine radiatively or non-radiatively. Photoluminescence depends on the electric field in the semiconductor. It mainly arises from the bulk material, since at the surface, there exists a region called the ‘dead layer’, where few radiative recombinations occur, and which is roughly related to the semiconductor depletion region.

For instance, Van Ryswyk and Ellis [108] studied the effect of the chemical modification of the surface of gallium arsenide, an excellent semiconductor which displays the property of emitting luminescence in the infra-red region, around  $11\,560\text{ cm}^{-1}$ . Samples of n-GaAs were derivatized with (1,1'-ferrocenediyl)dichlorosilane to yield at least one monolayer of a redox-active film (Fig. 12).

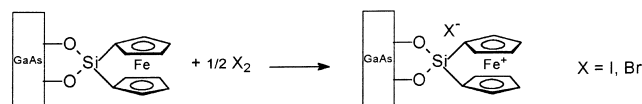


Fig. 12. Oxidation of the derivatized gallium arsenide surface (from [108]).

After reacting with oxidants like iodine or gaseous bromine, ferrocene was oxidized, and photoluminescence decreased. Treatment of the oxidized film with a volatile reductant restored the original photoluminescence signal. It was shown that the chemical modification of the surface modulated the electric field thickness of the underlying semiconductor by several hundred Angströms, hence the observed variations of photoluminescence. The system was proposed as a prototype optical sensor with chemical specificity.

For the quantum-confined semiconductor cadmium sulfide, a lower energy trap emission (peaking between 18 900 and 16 700  $\text{cm}^{-1}$ ) is related to the presence of defect sites at the material surface. Chandler et al. focused on the possibility of altering the photophysics of CdS particles via surface coordination, according to the hypothesis that the presence of an adsorbate may remove or enhance the defect sites responsible for emission [109]. Cadmium sulphide clusters were formed in inverse micelles and various ferrocenyl derivatives were added to the solution. The ferrocenyl derivatives were chosen for their capacity to bind to Lewis acid sites present at the surface and they also had the potential for future modification of the metal center after chemisorption. Photoluminescence enhancement was observed with addition of amino-substituted ferrocene, and attributed to adduct formation between the amino group and defect sites present at the cluster surface. Unsubstituted ferrocene, hydroxymethylferrocene and ferrocenecarboxaldehyde had no effect, whereas carboxylic-acid-substituted ferrocene, which bears a negative charge, totally quenched the luminescence. The latter effect was explained by the acid being ionized in the micelle water pool. The protons bind predominantly to negatively charged defect sites and act as electron traps.

Rosenwaks et al. showed that the quenching capacity generally associated with ferrocenes may also be of use to study the electron transfer kinetics at the interfaces [110]. These authors investigated the photoluminescence decay of illuminated GaAs semiconductor in the presence of ferrocenium ions contained in an acetonitrile solution. The luminescence quenching was attributed to electron transfer. This study was aimed at determining the rate at which photoinduced electrons are transferred at the interface, which plays an essential role in electrochemistry.

When luminescence is not naturally associated with the material, fluorescent probes may be used. This is what Marro and Thomas [111] did in order to investigate the movement of small molecules at the surface of porous silica,  $\text{SiO}_2$ . In this system, pyrene and its derivative 1-pyrene-butyric acid were adsorbed at the silica surface. Their singlet excited state was inhibited by ferrocene. This quenching study provided evidence for the probes being immobilized on silanol groups, whereas ferrocene moves at the silica surface. This is a good illustration of the advantages that can be taken from PET: the charged species are generated in a very short time, so that the rapid kinetics can be studied conveniently.

Finally, interesting photoeffects can also be encountered at liquid–liquid interfaces. It has been mentioned above (Section 10, second paragraph) that photodiodes may be obtained by linking a photosensitizer group with an electron-donor or -acceptor group. Photocurrent generation can be achieved more simply by bringing these molecules side to side. In the work, reported by Dvorak et al., the electron photoacceptor dye,  $\text{Ru}(\text{bpz})_3^{2+}$ , and ferrocene were placed in two immiscible electrolyte solutions [112]. The photoprocess then took place at the liquid–liquid interface and the current produced was measured. Luminescence was used to estimate the quenching rate constant.

### 11.3. LB films

The LB films are an almost perfect medium to study PET occurring between two entities separated by a fixed distance. Applications range from the fundamental study of electron transfer to the generation of photocurrents. These films are fatty acid multilayers, prepared by sequential transfer of compressed monolayer films formed at the air–water interface. Between two layers, the interfaces are of the hydrophilic–hydrophilic or hydrophobic–hydrophobic type. The nature of the different layers may be varied, in order to obtain a heterogeneous film. In the simplest systems, a ferrocene derivative is introduced into one of the layers, which thus acquires electron-donating properties. A second layer contains a light-absorbing dye, able to accept an electron in the excited state. The system is, therefore, of the D–PS type, and gives  $\text{D}^+\text{-PS}^-$  after excitation and charge separation. For Zhang et al., the electron-donating layer was obtained using fatty acids, the hydrophobic part of which bears a ferrocenyl group [113]. The electron-acceptor layer was made of rare-earth complexes solubilized in fatty acids.

Of most frequent use are modified fatty acids, labelled with dye molecules. In the following examples, the fluorescent dye was incorporated in the hydrophilic portion of fatty acids. The layer which bears ferrocene and that which bears thiocyanine are separated by a monomolecular spacer layer (Fig. 13). The group of Whitten and Hsu allowed the

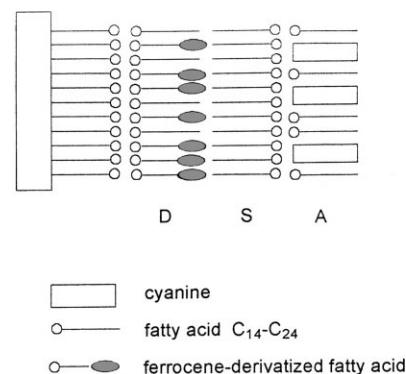


Fig. 13. Structure of Langmuir–Blodgett films containing monolayers of thiocyanine dye and ferrocene derivative separated by a single spacer monolayer of fatty acid (from [115]).

chemical nature and the thickness of this spacer layer to vary, and measured the influence of the variations on the quenching of the thiocyanine fluorescence [114,115]. They showed that the rate of electron transfer decreased with increasing separation distance of donor and acceptor, but the rate of attenuation was greater for saturated fatty acids than for *trans*-stilbene spacers.

Kondo et al. used amphiphiles with a  $\text{Ru}(\text{bpy})_3^{2+}$  head as dyes, while ferrocenes are inserted on alkyl chains bearing different charges (+1, 0, -1) at the hydrophilic head group. It was shown that the efficiency of the fluorescence quenching process depends on the sign borne by the polar head groups, hence on the internal potential difference across the bilayer [116–118]. According to the same principle, the value of the inner potential difference of the electrical double layer might be estimated, even though this cannot be directly measured by electrochemistry [118]. The electron transfer kinetics has also been studied with amphiphilic ferrocenyl derivatives which differed by their standard redox potential [119]. This allowed the importance of local electric fields in LB films to be underlined. The influence of other experimental parameters (photo-oxidation, dilution, inorganic salt addition, emission wavelength) has also been studied [120]. Finally, the dye which absorbs the excitation light and the electron acceptor can be two distinct species. This amounts to incorporating a third layer in the hetero-LB film. In the system reported by Choi et al. [121], tetracyanoquinodimethane (TCNQ), pyrene and ferrocene derivatives act as electron acceptor, photosensitizer and electron donor, respectively (Fig. 14). The system may be complicated once again by introducing of a fourth active layer, which contains an additional electron acceptor. Such an assembly of the  $A_2-A_1-PS-D$  type has been reported, where the respective roles were played by TCNQ, viologen, flavin and ferrocene derivatives [122,123]. The PET from excited PS layers to A layers was evaluated by measuring steady-state fluorescence quenching. These hetero-LB films were fixed to a quartz substrate [123] or arranged on indium tin oxide (ITO) glass normal to an electrode surface. In the latter case, aluminium was deposited at the film surface, constituting a metal/insulator/metal device. Photocurrents were detected upon irradiation.

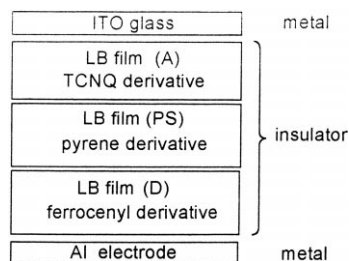


Fig. 14. Schematic representation of a metal-insulator-metal (MIM) device (from [121]).

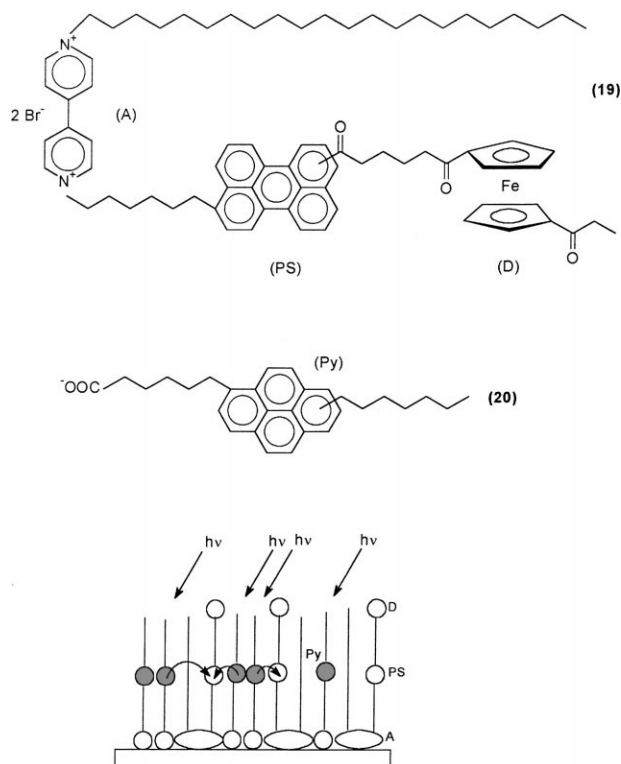


Fig. 15. Chemical structures (top) and schematic representation of the antenna effect in a Langmuir-Blodgett film made of compounds **19** and **20** (bottom). Light is absorbed by pyrene (py) in molecules **20**, which subsequently transfer the excitation energy to the perylene moiety of molecules **19** (from [124]).

So monomolecular layer assemblies succeed in simulating the first step of natural photosynthesis. Fujihira et al. modified the system by adding an antenna effect [124]. This consists of using molecules which absorb at different wavelengths, one of them being able to transfer its excitation energy to the other. The system is then effective over a large range of wavelengths. The linear molecule **19** contains perylene (PS), viologen (A) and ferrocene (D) derivatives, linked by normal hydrocarbon chain. The antenna is made with a fatty acid bearing a pyrene moiety in the middle of the chain, **20**. These molecules are mixed and they form a monolayer. The emission spectrum of the pyrene antenna overlaps the absorption spectrum of the sensitizer perylene moiety of the triad. So light energies harvested by the pyrene antenna molecules were efficiently transferred to the perylene sensitizer moiety of the triad and finally used for charge separation (Fig. 15). The monolayers exhibited anodic photocurrents upon excitation corresponding to the absorption maxima of the pyrene and the perylene moieties. This indicates that the photoprocess was initiated by light absorption, either by the photosensitizer or by the antenna molecule.

There are many other examples where ferrocene acts as an electron donor and is associated with luminescent dyes used as electron acceptors (see for example [118,125]), but the only ones mentioned here are those where the lumines-

cence properties are used to investigate the electron transfer involved in the primary step of the photogeneration process. Unfortunately, the quantum efficiency of most of these systems is very low. However, it is possible to have it improved markedly by using LB films made from polymers, as illustrated in the following section.

#### 11.4. Polymers

In this context, the aim is to study the polymer structure, its photostabilization, or the migration of the photonic excitation energy within the polymer until a point for useful energy conversion. Three situations are encountered. Firstly, the organic polymer contains a chromophore, the luminescence of which is quenched by ferrocene in solution. This is the case for homopolymers bearing 1,2-diketone chromophores [126]. The quenching effect was not as strong as that observed with monomers in solution, which suggested a steric effect altering accessibility of the quenched group. Secondly, the organic polymer is used as a solid matrix for both the electron donor and the electron acceptor, which may thus be regarded as solutes in a constrained medium. A good example is the study of the quenching of triphenylene phosphorescence by ferrocene in poly(methyl methacrylate) [127]. Vikesland and Wilkinson showed that, in this case, energy transfer involved a dipole–dipole mechanism. Thirdly, the donor and the acceptor are covalently grafted to the polymer [128]. In vinylferrocene-2-vinylnaphthalene copolymers, the naphthalene emission decreased when increased the ferrocenyl derivative content of the polymer. This effect was attributed to intramolecular energy transfer [129]. In the work reported by Albagli et al. [130], several ferrocene units are distributed within a polymer, which was end-capped with a pyrene derivative, **21** (Fig. 16). They observed that the pyrene emission was 30 times lower than in the ferrocene-free polymer. Regarding the quenching mechanism, both electron transfer and energy transfer were thermodynamically feasible.

The latter polymers are very close to the ‘spatially controlled’ LB films, used by Aoki et al. [131] to simulate photosynthesis. These authors consider that the spatial arrangement of the functional groups is a key factor in the inhibition of the reverse electron process. LB films consisting of low-molecular weight compounds are generally unstable

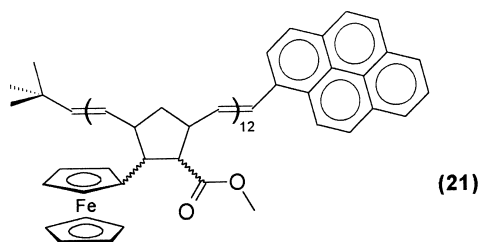


Fig. 16. Distribution of ferrocene units within a polymer, end-capped with a pyrene derivative.

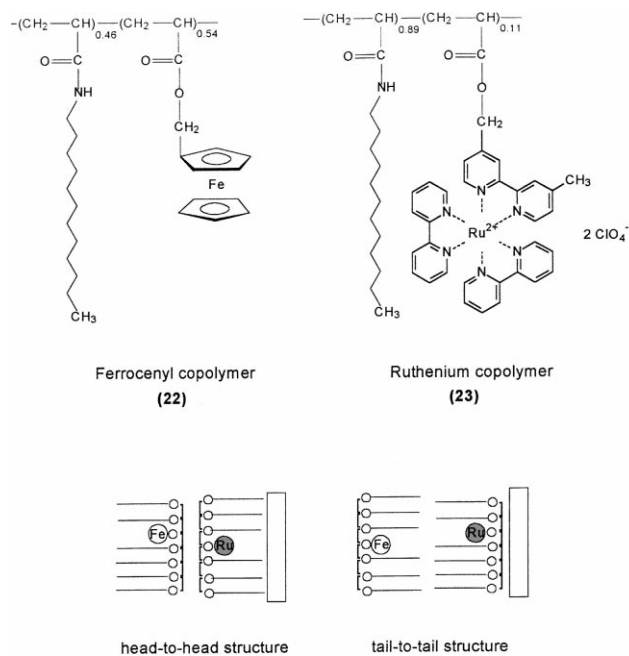


Fig. 17. Chemical structures of the amphiphilic redox copolymers and their arrangement in Langmuir–Blodgett films (from [131]).

because of the aggregation and crystallization of the active groups and flip-flop motion of amphiphiles. Therefore, instead of using free amphiphiles to form the layers of the LB film, they used copolymers which allow a better control of the molecular arrangement. The monolayers were made either from ferrocene-bearing polymers (**22**), or from polymers which contained some Ru(bpy)<sub>3</sub><sup>2+</sup> derivatives (**23**) (Fig. 17). It was shown by a fluorescence study that the electron transfer was particularly intense when these complexes were close to each other, that is in the head-to-head structure. As shown previously by Fujihira, the direction of photocurrent flow was controlled by the deposition order of the monolayers on the ITO electrode. A photocurrent quantum efficiency of almost 6% was achieved.

## 12. Biological applications

### 12.1. Lipids

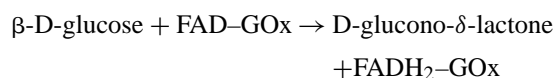
Biological applications are principally based on the luminescence quenching properties of ferrocene. Owing to its hydrophobic character, ferrocene can be used as a membrane probe to monitor the dynamic properties of lipids. In the work of Gasanov et al., ferrocene-containing liposomes were placed in the presence of other liposomes loaded with erythrosine [132,133]. When two neighbouring liposomes merged, lipid material was exchanged. Ferrocene and erythrosine came into contact. This results in quenching of the erythrosine fluorescence, which allowed the kinetics of this process to be visualized. The presence of calcium ions or

cobra venom cytotoxin favoured this probe exchange [132]. The same type of experiment has been applied to membrane models [133].

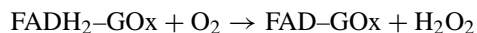
Mekler et al. introduced polyaromatic hydrocarbons into model or biological membranes and measured the annihilated delayed fluorescence. Upon addition of ferrocene, which becomes incorporated into the membrane, the decrease in the emission intensity was found to be stronger for liposomes than for sarcoplasmic reticulum membranes. Information was obtained concerning the organization of endoplasmic reticulum [134] and other biological membranes [135].

### 12.2. Proteins

There is presently a great deal of interest for glucose oxidase (GOx) covalently modified with electroactive groups (for a review, see [136]). Native GOx is a dimeric glycoprotein containing two flavin adenine dinucleotide (FAD) cofactors that are essential for glucose oxidation:



In the natural process, FADH<sub>2</sub> is reoxidized by oxygen:



It could also be oxidized at the electrode if it was not so deeply buried below the surface of GOx. For this reason, experiments have been conducted introducing electroactive groups which may act as electron transfer mediators into the protein. In the absence of oxygen, the enzyme reaction results in a current detected at the electrode, so that modified GOx may be used as reagentless biosensor or in electrochemical enzyme immunoassays for glucose detection. Badia et al. have examined a GOx derivatized by several units of ferrocene [137]. At the protein surface lie the residues of a basic amino acid, i.e. lysine, to which the ferrocenyl derivatives are coupled. This protein contains some residues of tryptophan, a naturally occurring fluorescent amino acid. Evidence was obtained for the covalent binding of ferrocene from the quenching of the endogenous tryptophan fluorescence. Such an effect was not observed when native GOx was in the presence of free ferrocene in solution.

Franz and Scheuner developed new dyes for electron microscopic immunohistochemistry [138]. 3-Carboxy-4-ferrocenylphenylisothiocyanate (**24**, Fig. 18) which reacted with the lysine residues of proteins seemed to be a good candidate and allowed labelled antibodies to be obtained. The covalent binding of **24** to human placental fibrin was shown by fluorescence microscopy. According to whether the biological sample has been treated with a solution of 4-ferrocenylphenylisothiocyanate, that is the carboxy group-free analogue, or with a solution of **24**, the fluorescence of acridine orange added to the sample was very differently affected.

### 12.3. Nucleic acids

Ferrocene has been linked to many molecules classically used as fluorescent probes for nucleic acids. This has been the case for aminoacridine, which was derivatized by Chen with the aim to obtain a dye suitable for cell imaging [139]. Compound **25** (Fig. 18) still strongly interacted with DNA. Its molar absorption coefficient and its fluorescence intensity were much lower than those of non-substituted 9-aminoacridine, but still high enough for this compound to be suitable for use in both fluorescence and electron microscopy observations.

The aim of Thornton et al. was to clarify vectorial electron transfer in biological systems and to design new molecular electron-transfer devices [140]. They used DNA as a matrix for controlling intramolecular long-distance electron transfer in a donor–spacer–acceptor assembly, one component of which was intercalated in the DNA duplex. The alteration of PET could arise from geometrical constraints undergone by the D–S–A assembly, changes in the redox potential of the intercalated, or groove-bound, portion of the molecule, and changes in the reorganization energy for electron transfer. In this work, an electron-donating ferrocenyl derivative was linked to electron-acceptor cationic porphyrins (**26**). The affinity for DNA was preserved and it depended on the solvent ionic strength: the intercalation of the porphyrin moiety between two base pairs occurred at low salt concentration, whereas binding in the grooves was favoured at

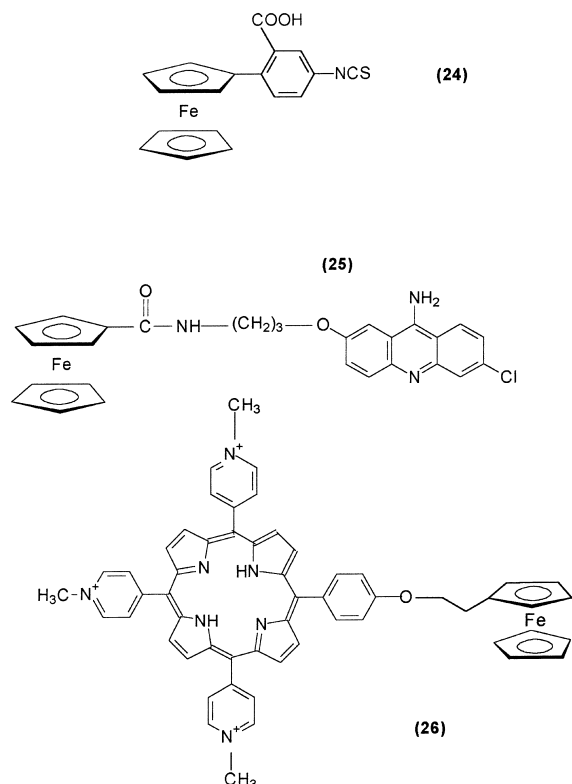


Fig. 18. Chemical structure of compounds **24**–**26**.

increased ionic strengths. The fluorescence study showed that binding to DNA did not reduce the intramolecular PET, since porphyrin fluorescence was very efficiently quenched by ferrocene. It seemed that changes in redox potential and reorganization energy had negligible consequences.

### 13. When luminescence properties must be preserved

In most of the previous examples, it has been seen that the quenching of excited states by ferrocene was often observed and has led to numerous applications. However, new molecules have recently appeared in which the aim is to have the properties of the luminescent system preserved, while taking advantage of the electroactive properties of ferrocene.

#### 13.1. Luminescent electroactive probes

Theoretically, the linkage of a pendant redox-active ligand to a conjugated system could allow the optical or photochemical properties of the molecule to be modulated via changes of the oxidation state, without altering the coordination sphere. In fact, swapping an electron-donating substituent, i.e. ferrocene, for an electron-withdrawing group, i.e. the ferrocenium ion, could induce significant changes in the conjugated system which bears these substituents. Harvey et al. have tackled this problem, using ligands based on diarylideneacetone. The luminescence study allowed them to understand how the energy transfer took place within the molecule and which excited states were involved. For instance, they showed that the luminescence of the ferrocenyl compounds **27** (Fig. 19) and **28** was strongly decreased in the solid state with respect to that of dibenzylideneacetone (dba) [141,142], and totally quenched in solution [143]. Moreover, for dba-FeCp<sub>2</sub>, the luminescence quenching was accompanied by photoisomerization quenching. It was deduced that luminescence and photoreactivity originated from the same excited state [141]. The quenching by ferrocene could involve energy transfer. The ligands of this series are known to give palladium(0) and platinum(0) complexes. It is interesting to see that the Pd<sub>2</sub>(dba-FeCp<sub>2</sub>)<sub>3</sub> complex was luminescent at 77 K, although much less emissive than the ferrocene-free analogue, Pd<sub>2</sub>(dba)<sub>3</sub> [144]. It is shown that, upon oxidation of the ferrocenyl residue, disturbances are felt along the whole molecule and the spectroscopic properties are affected. Unfortunately, the effect on the fluorescence spectrum was not reported. Actually, very few studies have been devoted to luminescent electroactive systems which include ferrocene, probably because the commonly encountered luminescence quenching has deterred numerous attempts. However, some encouraging results can be mentioned. Schmidt et al. [145] examined free-base porphyrins and metalloporphyrins substituted by four ferrocenyl groups, **29**. It is reported that the fluorescence of the free-base porphyrin increased when the ferrocene pendant group was oxidized as a ferrocenium ion, which strongly

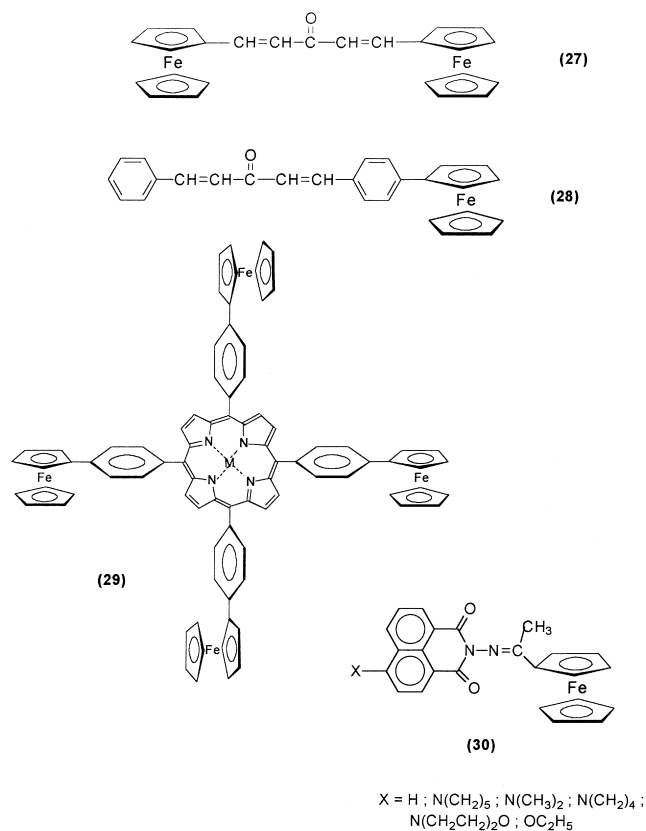


Fig. 19. Chemical structure of compounds **27–30**.

suggests that the ferrocenyl site exerted a quenching effect. The moderate magnitude of this effect was attributed to poor electron interactions between the ferrocene groups and the porphyrin  $\pi$ -system. Actually, the ferrocenyl residues are borne by phenyl groups which are situated out of the porphyrin plane, and essentially act as rigid spacers. Wang et al. [146] synthesized a ferrocene-naphthalimide dyad (**30**). The absorption spectrum of this compound was very similar to that of unsubstituted naphthalimide, and that of the mixture naphthalimide plus ferrocene (1:1 molar ratio), indicating little interaction in the ground state between the two moieties. In contrast, a large decrease was observed in the fluorescence intensity for **30**. Energy transfer and electron transfer were both plausible to explain the quenching mechanism, but the authors preferred the second hypothesis. When ferrocene was chemically oxidized, emission recovered.

#### 13.2. Luminescent sensors for molecular recognition

The molecular recognition of ions is an area of increasing research activity since ions play fundamental roles in biology, in chemical processes and for environmental pollution. Sensing systems usually comprise a signalling unit linked to a receptor so that ion binding is read out by a measurable physical change. It can be thought that adding a complexing moiety to a luminescent ferrocenyl molecule would

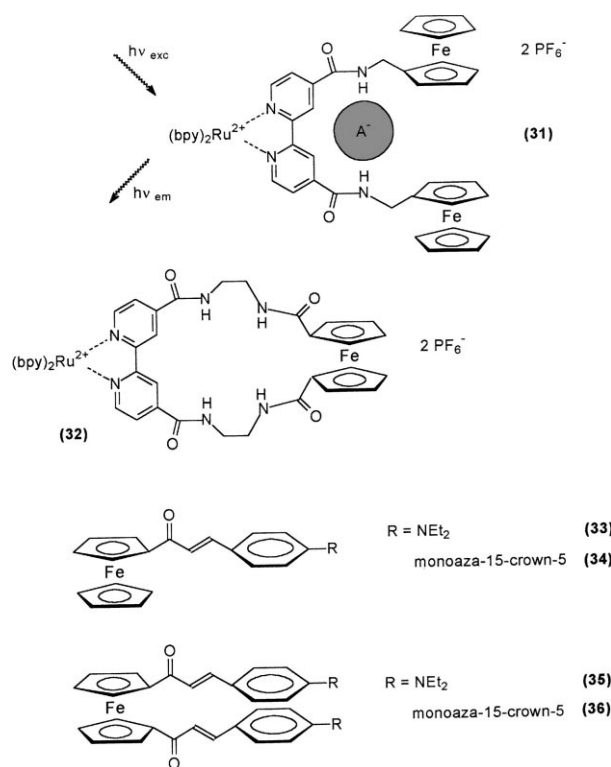


Fig. 20. Illustration of the luminescence mechanism of compound **31** after anion binding (from [147]), and other chemical structures.

lead to a sensor, the response of which would be detectable by both optical spectroscopy and electrochemistry. Actually, such molecules have recently been designed.

The two systems imagined by Beer et al. are principally meant for anion recognition, which is particularly difficult to achieve due to the lack of anion specific ligands. They are based on the luminescence properties of the organometallic compound,  $Ru(bpy)_3^{2+}$ . In the first system (**31**, Fig. 20), substituting the molecule by ferrocenyl units led to an almost total quenching of the initial luminescence [147]. Upon addition of chloride or hydrogensulphate anions, the luminescence signal of the ferrocenyl ligand was increased 20 times. The luminescence quantum yield of the complexed species was not given, but the observed switching on of emission is very interesting per se.

In the second system (**32**), ferrocene is an integral part of the macrocycle which contains the ionophore units [148]. The luminescence of this species was about five times lower than that of the analogue non-substituted by ferrocene, and the quenching was attributed to energy transfer. The sensing was based on a revival of luminescence, the intensity of which increased slightly upon anion complexation. The receptor selectivity was not enhanced by the presence of ferrocene. Cyclic voltammetry allowed the anion to be localized within the macrocycle. Cathodic perturbations of the metallocene redox complexes of up to 110 mV were observed in the presence of chloride anion. This suggests that ion detection could be concurrently achieved by electrochemistry.

Ligands **33–36** were designed so that cation or ion-pair recognition could be carried out by both fluorimetry and electrochemistry [149]. In contrast to compounds **27** and **28** synthesized by Harvey et al. [141–143], these ligands bear a terminal amino group which increases intramolecular charge transfer and is liable to be involved in interactions with ions or formation of complexes. Very weak emission was detected with the monosubstituted ferrocenyl ligand **33**. In contrast, the 1,1'-disubstituted ligand **35** was much more fluorescent than chalcone  $CH_3-CO-CH=CH-C_6H_4-NEt_2$ , in which ferrocene was replaced by a methyl group, and almost half as emissive as bis(diethylamino-benzylideneacetone). In this case, ferrocene was far from being a luminescence quencher and acted as an auxochrome. Fluorescence emission was also observed for **36**, where the nitrogen atom belongs to a crown-ether group. Upon addition of alkaline-earth cations in acetonitrile, the intensity of this signal was markedly decreased. Additionally, a preliminary electrochemical study of ligand **33** revealed that electron communication could occur through the fluoroionophore link between the complexing site and the redox center.

This field of research is obviously in its infancy and further developments are necessary. However, compounds **31**, **32**, **35** and **36** may already be considered as the first ferrocenyl derivatives potentially usable for ion recognition in solution, by both fluorescence spectroscopy and electrochemistry.

### 13.3. Fluorescence brighteners and scintillation agents

The literature reports an unexpected application of ferrocenyl derivatives [150]. 3-(2-Benzothiazolyl)propylferrocene (**37**, Fig. 21) and 1,1'-bis(2-benzothiazolyl)ferrocene (**38**) were proposed as fluorescence brighteners in textiles washing compounds and plastics. They are also presented as scintillation agents, that is molecules having the capacity to emit light flashes after excitation by high-energy radiation (such as  $\alpha$ -,  $\beta$ - or  $\gamma$ -radiation) and useful to measure radioactivity. It seems, therefore, that the presence of ferrocene on the thiazole derivative does not affect, or at least not too seriously, the fluorescence properties of the latter.

### 13.4. From electrochemiluminescence to immunoassay systems

Electrochemiluminescence (ECL) is a form of chemiluminescence in which the chemiluminescent reaction is preceded by an electrochemical redox reaction. Reactants are

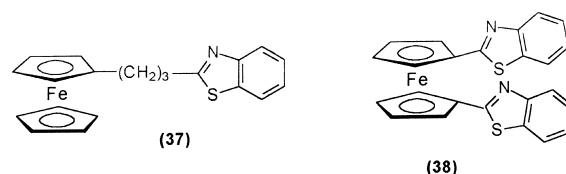


Fig. 21. Ferrocenyl derivative of benzothiazole (**37**, **38**).



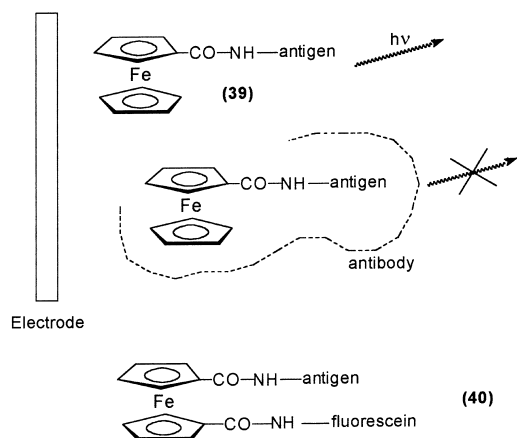
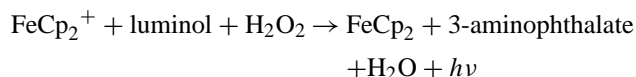
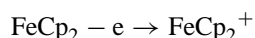


Fig. 22. Chemical structures and schematic representation of the ECL sensing mechanism. Reaction of the free compound **39** at the electrode results in an ECL emission (top). When **39** is buried within an antibody, no ECL is detected (middle) (from [151]).

generated at the electrode, and the recombination of the charges leads to an excited species which deactivates with light emission. The formation of ferrocenium ions is often a key step in this process.

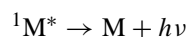
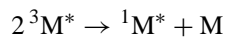
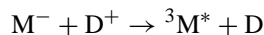
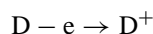
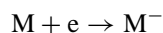
It is known that some Fe(III)-containing proteins (for example horseradish peroxidase) catalyze the chemiluminescent reaction between luminol and hydrogen peroxide. The invention of Schiffrin and Wilson derives from two observations [151]. Firstly, the addition of ferrocenyl derivatives increases the yield of these enzymatic reactions. Secondly, electrochemically oxidized ferrocene may catalyze the reaction in the absence of enzyme:



The reaction is accompanied by emission of light. This luminescent reaction may be used profitably to detect the presence of analytes such as narcotics, hormones or pesticides in solution, from a change in the emission intensity. For example, a bis-cyclopentadienyl mono or 1,1'-disubstituted metal complex was covalently grafted onto an antigen (**39**, Fig. 22). These compounds may be used in solution, or fixed on ITO-coated electrodes. As long as the labelled antigen is free, luminol oxidation is catalyzed. When antibodies bind to the antigen, ferrocene becomes electroinactive. This ferrocene 'switch off' results from two phenomena. On the one hand, ferrocene is deeply buried in the antibody, which therefore acts as a screen, and on the other hand, owing to its volume, the macromolecule slowly diffuses towards the electrode. Ferrocene is thus prevented from catalyzing the electroluminescent reaction. For instance, ferrocene attached to bovine serum albumin labelled with digoxin becomes electroinactive in the presence of antibodies to digoxin. The analyte presence is revealed by decrease in the

chemiluminescence intensity. The detection wavelength may be changed by simply linking a fluorophore like fluorescein to the ferrocenyl derivative (**40**). The fluorophore acts as an energy acceptor from the chemiluminescence reaction by resonance energy transfer. The luminescence was detected at  $19\,050\text{ cm}^{-1}$  for **40** instead of  $23\,530\text{ cm}^{-1}$  for **39**. Finally, a similar type of reaction based on electrochemifluorescence, that is the electrochemical generation of a fluorescent compound from a precursor oxidation, was imagined by the authors. The advantage of this mode of detection is to have the high degree of specificity of biological systems coupled with the sensitivity of luminometric detection.

The intensity of the ECL phenomenon can be enhanced with the use of external redox reagents that can serve as either oxidants or reductants. Pragst et al. [152] have studied the cathodic reduction and the ECL of rubicene and fluoranthene derivatives (M) in the presence of tertiary aromatic amines (D) in DMF. In these systems, two charged species are generated at the electrodes and they then recombine by electron transfer. This recombination produces an excited species which is responsible for emission of light. The following mechanism was presented:



It must be noted that, when the amine was replaced by ferrocene, ECL was no longer observed due to the quenching of the  ${}^1\text{M}^*$  luminescence by ferrocenium ions. The quenching mechanism was assumed to be an electron transfer.

As already mentioned, ECL is generally believed to arise from the intermolecular electron transfer recombination of electrogenerated reactants. According to Abruña, the fact that external redox agents could be used to obtain intense ECL spectra suggested that it might be possible

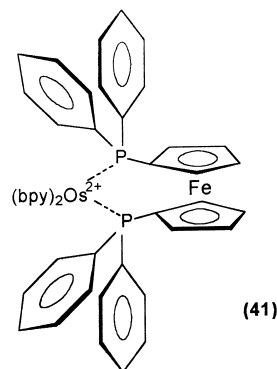


Fig. 23. Organometallic compound with two redox centers  $[\text{Os}(\text{bpy})_2\text{diphos}-\text{Fe}(\text{Cp}_2)]^{2+}$  (**41**).

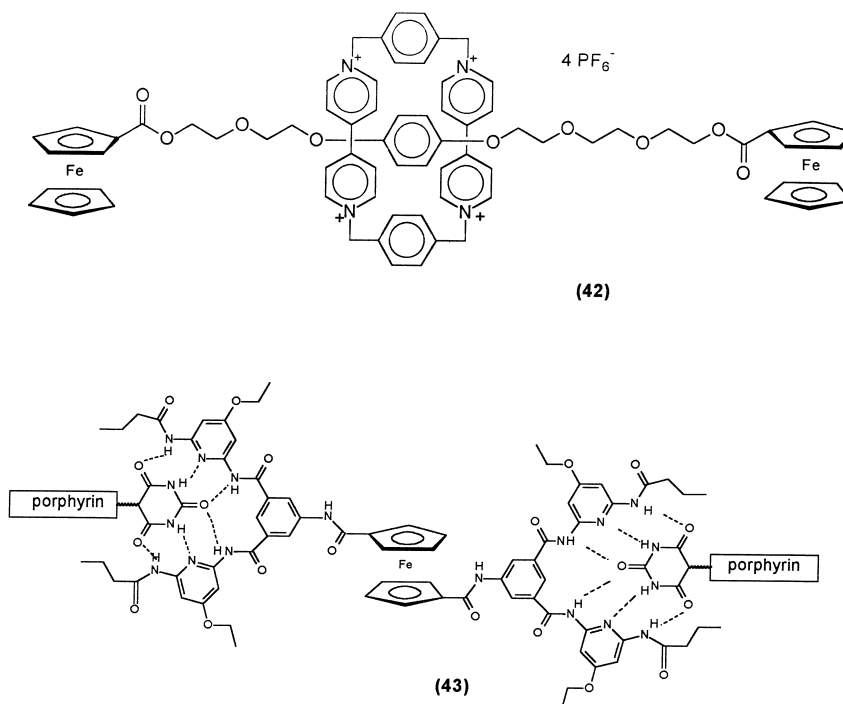


Fig. 24. Ferrocenyl derivatives in rotamer and in self-organised system.

to achieve this in an intramolecular fashion [153]. Consequently, he studied an organometallic compound bearing two redox centers,  $[\text{Os}(\text{bpy})_2\text{diphos}-\text{FeCp}_2]^{2+}$  (**41**, Fig. 23), and made a comparison with the analogue deprived of ferrocene,  $[\text{Os}(\text{bpy})_2\text{diphos}]^{2+}$ . Both compounds emitted phosphorescence in solution, with quite similar quantum yields. Upon pulsing the potential of an electrode, an ECL spectrum was observed for  $[\text{Os}(\text{bpy})_2\text{diphos}]^{2+}$ , which was very similar to the phosphorescence spectrum of this compound in solution. However, in the same conditions, only a very weakly intense ECL spectrum was obtained with  $[\text{Os}(\text{bpy})_2\text{diphos}-\text{FeCp}_2]^{2+}$ . The quenching of luminescence by electrogenerated  $\text{FeCp}_2^+$  was thus suspected. In order to test this hypothesis, diacetylferrocene<sup>4</sup> was added to a solution of the pure osmium compound. (i) The ECL intensity was then very close to that of  $[\text{Os}(\text{bpy})_2\text{diphos}-\text{FeCp}_2]^{2+}$ . (ii) The luminescence spectrum of  $[\text{Os}(\text{bpy})_2\text{diphos}]^{2+}$  in the presence or absence of diacetylferrocene in its reduced form was found to be the same, but addition of the ferrocenyl derivative in its oxidized form totally quenched the luminescence. According to the author, these results pointed out that what was taking place was not intramolecular ECL but rather a very effective quenching of the excited state by the Fe(III) center.

<sup>4</sup> Diacetylferrocene was chosen because its formal potential for oxidation is nearly identical to that of the first oxidation of  $[\text{Os}(\text{bpy})_2\text{diphos}-\text{FeCp}_2]^{2+}$ .

## 14. Conclusions and prospects

The studies reviewed here cover a wide range of perspectives concerning the use of ferrocenyl derivatives in luminescent systems. It has been seen that ferrocene gives rise to multifaceted applications. This has been allowed by the easiness of using commercially available products which are stable, handy, and soluble in various solvents. In the simplest cases, ferrocene and ferrocenyl derivatives were placed in the presence of a luminescent molecule in solution, and were expected to act as quenchers. From some angles, intermolecular luminescence quenching has been a much debated question. This is the case, for example, for triplet state quenching. However, other aspects, like singlet state quenching, deserve an in-depth analysis. At the same time, it is possible to use ferrocene in very sophisticated systems, and promising applications have appeared in the areas of photosynthesis simulation and photodiodes. Ferrocene has already been successfully used in organized media, though many systems have not been explored yet. Nevertheless, it is well known that ferrocene incorporates well in cyclodextrins, zeolites etc. and coupling with fluorescence techniques could bring extensive information. Ferrocenyl derivatives are increasingly present in supramolecular systems like rotamers (**42**, Fig. 24), where they are helpful for charge delocalization after PET [154]. Introducing an efficient luminophore in this system would not be a very complicated task. Presently, a new trend towards self-organized systems is also beginning to take shape. For instance,

Tecilla et al. [155] propose a novel noncovalent approach based on hydrogen-bonding self-assembly of chromophores rather than covalent linkages for diode preparation (**43**). The ferrocene-containing molecule was designed with the aim to recognize two porphyrins substituted by a barbiturate derivative. The spectroscopic characteristics were not reported, but it can be imagined that the presence of ferrocene induced an interesting effect on the porphyrin luminescence properties.

Numerous applications can also be expected to emerge at the frontiers of biology and photophysics. For example, ferrocene can be incorporated into amino acids. These could be used as building blocks in modified peptides, which can also bear photosensitizing chromophores and electron acceptors. Such peptides could be potentially useful for photoharvesting, because the spatial arrangement of the reactive units should prolong the lifetime of the photoinduced charge-separated state [156]. Finally, since ferrocene can be introduced in a molecule without destroying the fluorescence properties, the door is now open on a new generation of compounds, both photo- and electrochemically active.

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