# Intermolecular quenching of excited singlet states by ferrocenyl derivatives: study with ketocyanine dyes

Suzanne Fery-Forgues [a,*], Béatrice Delavaux-Nicot [b],
Dominique Lavabre [a], Knut Rurack [c]

[a] *Laboratoire des Interactions Moléculaires Réactivité Chimique et Photochimique, UMR CNRS 5623,*
*Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex, France*
[b] *Laboratoire de Chimie de Coordination, UPR 8241 liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse,*
*205 route de Narbonne, F-31077 Toulouse Cedex 04, France*
[c] *Department I.3902, Federal Institute for Materials Research and Testing (BAM), Richard-Willstaetter Street 11, D-12489 Berlin, Germany*

## Abstract

The fluorescence quenching of 1,5-bis[4-(diethylamino)phenyl]penta-1,4-dien-3-one (**1**), 1-[4-(diethylamino)phenyl]-5-phenylpenta-1, 4-dien-3-one (**2**) and chalcone **3** (1-[4-(diethylamino)phenyl]but-1-en-3-one) was studied in acetonitrile using ferrocene and three commercially available derivatives, 1,1′-diacetylferrocene, acetylferrocene and 1,1′-dimethylferrocene. The spectroscopic and electrochemical characteristics of all the compounds were investigated. The feasibility of the quenching process was calculated, showing in particular that electron transfer was thermodynamically possible in every case. The steady-state fluorescence of the three organic dyes was then measured in the presence and in the absence of the ferrocenyl derivatives and the data were corrected for inner-filter effects. 1,1′-Diacetylferrocene and acetylferrocene proved to be the most efficient quenchers, and among the three dyes investigated, chalcone **3** was the most sensitive to the presence of the ferrocenyl derivatives. However, the fluorescence decay times of the ketocyanines were not affected by the presence of the ferrocene derivatives, indicating that quenching was not diffusion-controlled but rather the consequence of the formation of a ground state complex.
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## 1. Introduction

The study of triplet state quenching by ferrocene and ferrocenyl derivatives has for long been the object of considerable attention [1–4]. Ferrocenyl derivatives are very efficient triplet state quenchers. They react with a large number of organic, organometallic and inorganic compounds, and the quenching rate constant is often close to the diffusion constant. This efficiency has been attributed to the geometry of ferrocene, which allows good spatial overlap between the metal-centered $d$ orbitals and the $\pi$ orbitals of the excited molecule [5].

However, as we reported in a recent review, intermolecular quenching of singlet states by ferrocenyl compounds is poorly documented in the literature [6]. On the other hand, this photophysical process is increasingly involved and relied upon in numerous applications such as the study of

electron transfer [7–9] and mass transfer [10] in various systems, artificial photosynthesis [11–13], photocurrent generation [14,15] and biology [16,17].

This prompted us to study intermolecular quenching reactions between fluorescent dyes and ferrocene. In the present work, symmetrical ketocyanine dye **1**, asymmetrical compound **2** and chalcone **3** were used as fluorophores (Scheme 1). These dyes offer the distinct advantage that their spectroscopic behavior is well known. They were studied elsewhere for their solvatochromic properties [18] and a bis-crowned derivative of **1** proved to be useful in the study of rotamerism [19] and ion-recognition by fluorescence spectroscopy [20]. Moreover, a fragment of **3** was recently included in a ferrocenyl derivative, introducing a new generation of redox-active fluorescent compounds [21,22]. To get more information on quenching energetics and dynamics, we employed commercially available ferrocenyl derivatives, differing in their optical and electrochemical properties, and analyzed the spectroscopic features of every pair of dye and quencher.

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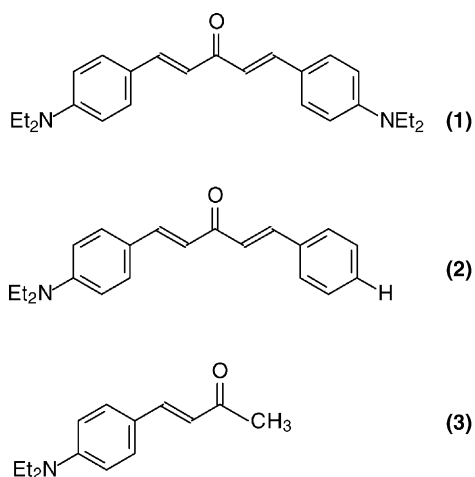
Scheme 1. Chemical structures of compounds **1**–**3**.

## 2. Experimental details

### 2.1. Materials

Spectroscopic grade solvents (Merck, SDS, and Aldrich) were used for spectrophotometric measurements. Dyes **1**–**3** were prepared according to the general procedure of Olomucki and Le Gall [23] and recrystallized in carbon tetrachloride, petroleum ether 40–65° and hexane, respectively. 1,1′-Diacetylferrocene, acetylferrocene and ferrocene purchased from Acros, and 1,1′-dimethylferrocene from Aldrich, were used as received.

### 2.2. Measurements

All the spectroscopic measurements were conducted at 25 °C in a thermostatted cell under normal air atmosphere. For steady-state fluorescence quenching experiments, a Hewlett-Packard 8452 A diode array spectrophotometer was used for measuring absorbance. The estimated experimental error was 2 nm for the band position and 15% for the molar extinction coefficient. Steady-state fluorescence spectra were recorded on a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer and were corrected. The excitation wavelength was 400 nm for all three dyes. Emission was recorded at 572, 615 and 472 nm for dyes **1**, **2** and **3**, respectively. Requiring a wavelength-to-wavenumber transformation of the band maxima for the energetic analyses, an additional correction term was applied in the subsequent conversion of the emission spectra to the energy scale. This procedure is necessary to take into account the changing bandpass in $cm^{-1}$ when scanning with an emission monochromator with constant wavelength resolution [24], but does not apply to absorption spectra, which are obtained from a relative measurement. For the features discussed in Section 3.5, the absorption titration spectra were analyzed with in house-developed software packages [25].

For the time-resolved fluorescence quenching experiments, the absorbance of the solutions was adjusted with a Perkin-Elmer Lambda 9 spectrophotometer, and the steady-state quenching was checked on a LS50B spectrofluorometer (Perkin-Elmer). Fluorescence lifetimes were measured using a set-up very similar to that described in [26]. The samples were excited by the frequency-doubled output of a femtosecond Ti:sapphire laser, pumped by a diode-pumped and frequency-doubled $NdYVO_4$ laser. The excitation wavelength was set at 416 nm for **1** and **2** as well as 384 nm for **3**. To check the uniformity of the decays of the dyes in the absence of quenchers over the whole emission band, eight decays were recorded between 500 and 640 nm for **1**, between 540 and 680 nm for **2**, and between 420 and 560 nm for **3**, in steps of 20 nm. The spectral bandwidth in emission was 10 nm. The instrumental response function was 27 ps (full width at half maximum). The accuracy of the measurements was estimated to be ±3 ps.

Electrochemical measurements were performed by cyclic voltammetry and linear voltammetry using a Au electrode (2 mm) in 0.1 M solution of $Bu_4NPF_6$ in $CH_3CN$, with a compound concentration of $10^{-3}$ M, in experimental conditions already described [27]. NMR spectra were recorded on an ARX 400 MHz Bruker spectrometer, with TMS as external reference.

## 3. Results

### 3.1. Spectroscopic characteristics of the compounds

In order to estimate the thermodynamic feasibility of the quenching process, the spectroscopic and electrochemical characteristics of the compounds involved must be known. As far as the organic dyes are concerned, the absorption spectrum in acetonitrile displays an intense low-energy band, assigned to a charge-transfer transition from the electron-donating amino group to the withdrawing carbonyl group [28]. The emission spectrum is a single, broad, structureless, and largely Stokes-shifted band, typical for a charge-transfer type fluorescence (Fig. 1).

From the frequency of the absorption ($\nu_a$) and fluorescence ($\nu_f$) maxima, the position of the 0,0 band was calculated to $\nu_{0,0} = (\nu_a + \nu_f)/2$. The corresponding energy is considered to be the gap between the two first singlet states $S_0$ and $S_1$, at their lower vibrational level. It increases in the order of **2** < **1** < **3** (Table 1).

Regarding ferrocene and its derivatives, the absorption spectrum in acetonitrile displays intense bands above 33 300 $cm^{-1}$, and two weak bands at lower energy (with a maximum at 30 300 and 22 100 $cm^{-1}$ in Fig. 1) which are due to metal-centered transitions [29–31]. The band at the smallest wavenumber is of interest here, since it corresponds to the $S_0 \rightarrow S_1$ transition of lowest energy. Its position ranges from 22 880 $cm^{-1}$ for 1,1′-dimethylferrocene to 21 740 $cm^{-1}$ for 1,1′-diacetylferrocene (Table 2), a shift
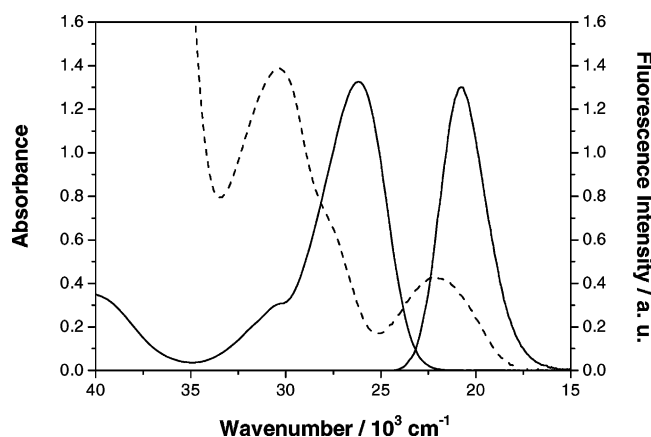
Fig. 1. Absorption (solid line, left) and emission (solid line, right) spectrum of **3**, $4 \times 10^{-5}$ M, $\nu_{ex} = 25\,000$ cm$^{-1}$ (400 nm); absorption spectrum of acetylferrocene, $2.9 \times 10^{-3}$ M (dotted line). The dye concentration is approximately 15 times higher than that used for the quenching experiments.

towards lower energy being observable with increase in the electron-withdrawing nature of the substituent, as already reported in the literature [32]. The intensity of this band, measured by the molar extinction coefficient $\varepsilon_M$, increases in the same way, except that very close values were obtained for ferrocene and dimethylferrocene. These ferrocenyl derivatives are not fluorescent, so that the position of the 0,0 band could not be calculated from the spectroscopic data.

### 3.2. Electrochemical characteristics of the compounds

The electrochemical properties of the dyes and the ferrocenyl derivatives were investigated in acetonitrile (see Section 2). The reduction potential of the organic molecules

was measured by linear voltammetry and found to range from $-1.44$ V for **2** to $-1.84$ V for **3** versus SCE (Table 1). The values obtained compare well with those measured in dichloromethane by Harvey et al. for closely related structures [33]. The oxidation potentials of the ferrocenes increase, as expected [34], with the strength of the electron-withdrawing substituent (Table 2).

### 3.3. Quenching feasibility

Among the different quenching processes known, energy transfer and electron transfer [35,36] are the most commonly invoked as far as ferrocene is concerned.

The excitation energy can be transferred according to $^1$A$^* +$ Fc $\rightarrow$ A $+^1$Fc$^*$, where A is the organic molecule and Fc the ferrocenyl derivative. This process is usually followed by the thermal relaxation of the excited ferrocenyl derivative. Whatever mechanism of energy transfer is involved, the first requirement for the occurrence of such a process is that the dye's excited state $^1$A$^*$ is energetically higher lying than the excited state $^1$Fc$^*$ of the ferrocenyl derivative. It is assumed, following the usual representation, that the ground states of both partners are approximately at the same level. For the organic dye, the energy of the excited state, with respect to the ground state, is given by the 0,0 band. For the ferrocenyl derivatives, the exact value of the 0,0 band is unknown, but it is reasonable to assume that it lies at a lower frequency than the absorption maximum of the lowest energy band. Therefore, at least for **3**, energy transfer should be possible, the 0,0 band being situated at a higher frequency than the absorption maximum of the ferrocenyl derivatives.

Regarding the photoinduced electron transfer (PET) process, ferrocene is well known to act as an electron donor: A$^* +$ Fc $\rightarrow$ A$^- +$ Fc$^+$ [6]. Generally, the charges recombine

**Table 1**
Maximum absorption wavenumber $\nu_a$, molar absorption coefficient $\varepsilon_M$ at the absorption maximum, maximum emission wavenumber $\nu_f$, wavenumber of the 0,0 band $\nu_{0,0}$, energy of the 0,0 band $E_{0,0}$ and reduction potential $E_{1/2}$ of the organic dyes in acetonitrile

| | $\nu_a$ (cm$^{-1}$)[a] | $\varepsilon_M$ (M$^{-1}$ cm$^{-1}$) | $\nu_f$ (cm$^{-1}$) | $\nu_{0,0}$ (cm$^{-1}$) | $E_{0,0}$ (kJ mol$^{-1}$) | $E_{1/2}$ (V vs. SCE) |
|---|---|---|---|---|---|---|
| **1** | 22 520 | 50 000[b] | 17 215 | 19 870 | 237.6 | −1.54 |
| **2** | 23 360 | 32 200 | 15 946 | 19 650 | 234.9 | −1.44 |
| **3** | 26 320 | 33 600 | 20 772 | 23 550 | 281.9 | −1.84 |

[a] From [18].
[b] At 22 420 cm$^{-1}$, from [20].

**Table 2**
Maximum absorption wavenumber $\nu_a$ of the low-energy band, molar absorption coefficient $\varepsilon_M$ at the absorption maximum and at $25\,000$ cm$^{-1}$ (400 nm), oxidation potential $E_{1/2}$ in acetonitrile for the ferrocenyl derivatives and free energy variation $\Delta G^0$ calculated for **1**, **2** and **3**, respectively

| | $\nu_a$ (cm$^{-1}$) | $\varepsilon_M$ (M$^{-1}$ cm$^{-1}$) at $\nu_a$ | $\varepsilon_M$ (M$^{-1}$ cm$^{-1}$) at $25\,000$ cm$^{-1}$ | $E_{1/2}$ (V vs. SCE) | $-\Delta G^0$ (kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | | | | **1** | **2** | **3** |
| 1,1′-Diacetylferrocene | 21 740 | 479 | 232 | 0.87 | 5.0 | 12.0 | 20.4 |
| Acetylferrocene | 22 120 | 365 | 149 | 0.65 | 26.3 | 33.2 | 41.6 |
| Ferrocene | 22 620 | 93 | 58 | 0.40 | 50.4 | 57.3 | 65.8 |
| 1,1′-Dimethylferrocene | 22 880 | 109 | 72 | 0.30 | 60.0 | 67.0 | 75.4 |

to restore both neutral species in the ground state, A + Fc, with an output of thermal energy. The thermodynamic feasibility of the initial step depends on the variation of the PET free energy, according to the Rehm–Weller equation [37,38] that can be transposed as follows:

$$\Delta G^0 = -96.49[E^0(A/A^-) - E^0(Fc^+/Fc)] - \frac{e_0^2}{a\varepsilon - E_{0,0}}$$
(1)

In this equation, the factor 96.49 allows $\Delta G^0$ to be expressed in kJ mol$^{-1}$. $E^0(A/A^-)$ is the organic dye's reduction potential (in V) and $E^0(Fc^+/Fc)$ is the ferrocenyl derivative's oxidation potential ($E_{1/2}$, although approximated, is used in practice). $E_{0,0}$ is the energy of the excited singlet state of A, and $e_0^2/a\varepsilon$ is the energy gained by bringing the reactants or products together from an infinite distance to their separation distance $a$ in the activated complex, in a solvent of dielectric constant $\varepsilon$ (Coulomb attraction). For polar solvents with a high dielectric constant, this term is usually small (<0.1 eV) and can be neglected [8,39].

The free energy variation $\Delta G^0$ has been calculated for each couple of ferrocenyl derivative and organic dye (Table 2). This value was found to be negative, indicating that the potential energy of the products is lower than the energy of the reactants and that thus the PET mechanism is thermodynamically feasible in every case. However, the $\Delta G^0$ value is most negative for the chalcone dye and the dimethylferrocene quencher, suggesting that the electron transfer process should be most efficient in this particular case.

### 3.4. Steady-state fluorescence quenching

Dyes 1–3 in acetonitrile were used at concentrations ranging from $1 \times 10^{-6}$ to $5 \times 10^{-6}$ M, according to the compound, so that the absorbance was ca. 0.05 at 400 nm. This wavelength is suitable to excite all three dyes in their CT band, and it also corresponds to a minimum in the absorption spectrum of the ferrocenyl derivatives that display the highest molar absorption coefficient (diacetylferrocene and acetylferrocene). Then, ferrocenyl derivatives were added to the solutions. It must be noted that diacetylferrocene is not very soluble in acetonitrile, so it was not used above a concentration of $5 \times 10^{-4}$ M. No solubility problems were encountered for the other ferrocenyl derivatives at the concentrations used. The fluorescence spectra were recorded. Upon titration with the ferrocenyl compounds, the fluorescence intensity strongly decreased as a function of the added quencher. For 1 and 2, no shift of the fluorescence spectrum was observed. However, for 3, the emission maximum was slightly red-shifted, for instance, from 472 nm in the absence to 480 nm in the presence of $2.15 \times 10^{-3}$ M acetylferrocene (Fig. 2).

For the analysis of the quenching data, it was necessary to correct the data for inner filter effects [23,40–43]. There are
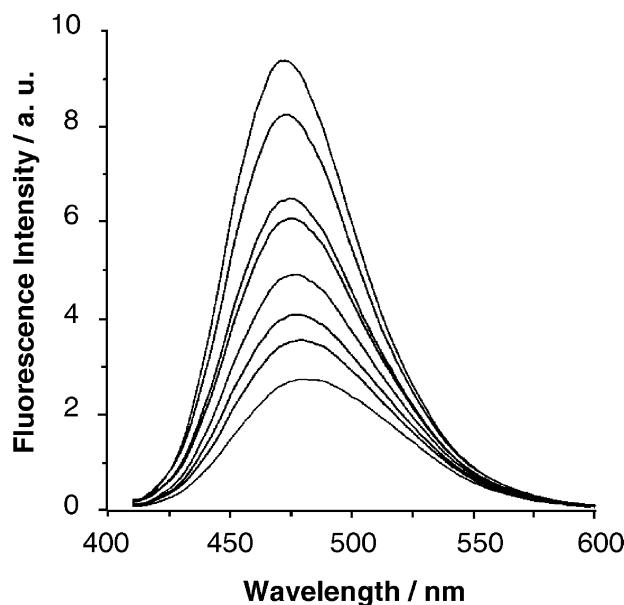


Fig. 2. Emission spectrum of 3 ($2 \times 10^{-6}$ M) in the absence and in the presence of acetylferrocene. From top to bottom, acetylferrocene: 0, $1.8 \times 10^{-4}$, $5.4 \times 10^{-4}$, $7.2 \times 10^{-4}$, $1.1 \times 10^{-3}$, $1.4 \times 10^{-3}$, $1.6 \times 10^{-3}$, $2.2 \times 10^{-3}$ M; $\nu_{ex} = 25\,000$ cm$^{-1}$ (400 nm).

two reasons for this. First, the organic dyes were excited at wavelengths where the absorbance of the ferrocenyl derivatives is not negligible (Fig. 1). The amount of light actually absorbed by the dye was therefore much lower than that absorbed by the mixture (pre-filter effect). Secondly, the ferrocenyl derivatives also absorb within the spectral range of the dye's emission, so that the intensity of the emitted light is reduced by reabsorption (post-filter effect). This effect could be neglected for 1 and 2, the fluorescence of which was collected at higher wavelengths (572 and 615 nm). In contrast, the fluorescence of dye 3 was monitored at 473 nm, where interferences by absorbing ferrocenyl derivatives can occur (Fig. 1). The distortion of the fluorescence spectrum noted for dye 3 (Fig. 2) can be attributed to the reabsorption of the emitted light by the ferrocenyl derivative. Both pre- and post-filter effects result in a decrease of the emitted light. The proper corrections were applied as explained in the Appendix A.

The first correction yields a value $F_0'$ that corresponds to the intensity of fluorescence *actually* emitted at the center of the cell, in the presence of a pre-filter effect. The second correction leads to a value $F_{em}$, which is the fluorescence intensity that would be measured in the absence of reabsorption. Note that for 1 and 2, the measured fluorescence intensity, $F_{meas}$, was directly used instead of $F_{em}$. The quenching effect can then be determined from the ratio $F_0'/F_{em}$. In the absence of any quenching effect, $F_0'$ equals $F_{em}$, and the ratio $F_0'/F_{em}$ is equal to 1. This ratio is identical to the classical $F_0/F$ ratio of the Stern–Volmer equation

$$\frac{F_0'}{F_{em}} = \frac{F_0}{F} = 1 + k_q \tau_0 [Q]$$
(2)

Table 3
Slope of the Stern–Volmer plot ($k_q \tau_0$) and quenching constant $k_q$

| | 1,1′-Diacetylferrocene | | Acetylferrocene | | Ferrocene | | 1,1′-Dimethylferrocene | |
|---|---|---|---|---|---|---|---|---|
| | $k_q \tau_0$ ($M^{-1}$) | $k_q$ ($M^{-1} s^{-1}$) | $k_q \tau_0$ ($M^{-1}$) | $k_q$ ($M^{-1} s^{-1}$) | $k_q \tau_0$ ($M^{-1}$) | $k_q$ ($M^{-1} s^{-1}$) | $k_q \tau_0$ ($M^{-1}$) | $k_q$ ($M^{-1} s^{-1}$) |
| **1** | 310 | $4.43 \times 10^{11}$ | 183 | $2.61 \times 10^{11}$ | 83 | $1.18 \times 10^{11}$ | 92 | $1.31 \times 10^{11}$ |
| **2** | 356 | $1.56 \times 10^{12}$ | 161 | $7.09 \times 10^{11}$ | 59 | $2.60 \times 10^{11}$ | 70 | $3.08 \times 10^{11}$ |
| **3** | 311 | $3.66 \times 10^{12}$ | 157 | $1.84 \times 10^{12}$ | 61 | $7.17 \times 10^{11}$ | 63 | $7.41 \times 10^{11}$ |

The correlation coefficient $r^2$ was higher than 0.99 for the experiments done with acetylferrocene, ferrocene and dimethylferrocene with dyes **1** and **2**. It was higher than 0.97 for the other pairs of dyes and quenchers, except for diacetylferrocene with chalcone **3**.

where $F_0$ and $F$ are the fluorescence intensity in the absence and presence of a quencher $Q$, and $k_q$ is the quenching constant. The latter can be obtained when the lifetime in the absence of quencher, $\tau_0$, is known. The ratios $F_0'/F_{em}$ were calculated for all three organic dyes in the presence of each ferrocenyl derivative, and plotted versus the quencher concentration. Straight lines were obtained in every case, as illustrated in Fig. 3 for chalcone **3**. The corresponding slopes are summarized in Table 3.

The $k_q$ value was calculated from the slope $k_q \tau_0$. The fluorescence lifetimes of the three dyes in acetonitrile are monoexponential, show no dependence on the emission wavelength, and were determined to 785, 227 and 85 ps for **1**, **2** and **3**, respectively. The value measured for **1** is in good agreement with that reported in a previous work [20]. Accordingly, the $k_q$ values lie in the $10^{11}$ to $10^{12}$ $M^{-1} s^{-1}$ range. It is interesting to note that this value increases in the order of 1,1′-dimethylferrocene $\cong$ ferrocene $<$ acetylferrocene $<$ 1, 1′-diacetylferrocene. Additionally, the $k_q$ values increases when going from dye **1** to dye **2**, and then to chalcone **3**.

### 3.5. Search for the formation of a ground state complex by steady-state methods

Taking into account the high quenching constants obtained, such a behavior can arise from the formation of a ground state complex. To evaluate the features of a
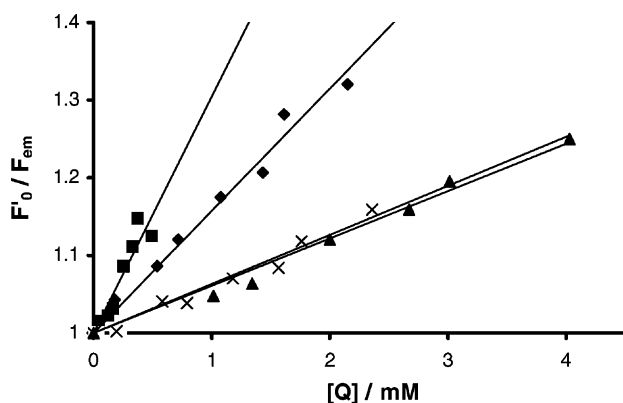


Fig. 3. Stern–Volmer plots for **3** after correction of inner-filter effects. Quenchers [$Q$]: diacetylferrocene (squares), acetylferrocene (diamonds), ferrocene (triangles) and dimethylferrocene (crosses).

representative combination of dye and quencher in this respect, the $^1$H NMR spectrum of an equimolecular mixture ($8.7 \times 10^{-3}$ M) of chalcone **3** and acetylferrocene in $CD_3CN$ was recorded. No shifts were observed compared to the position of the signals recorded for the pure compounds. Additionally, the UV-Vis absorption spectrum of a mixture of **3** ($2 \times 10^{-5}$ M) and acetylferrocene (up to $5 \times 10^{-3}$ M) in acetonitrile was found to be a linear combination of the spectra of each component. Consequently, no evidence for the formation of a complex in the ground state was obtained from these measurements.

### 3.6. Fluorescence lifetime and quenching

Monitoring the fluorescence lifetime during a titration with the quencher allows to obtain valuable information on the nature of the quenching process(es) involved from a different methodological point of view. Qualitatively, the procedure is similar to the study of triplet quenching by ferrocenyl compounds [44,45]. In the present case, solutions of the ketocyanine dyes **1–3** in acetonitrile ($1 \times 10^{-5}$ M) were titrated with stock solutions of the four ferrocenyl derivatives at steps of $5 \times 10^{-5}$, $9 \times 10^{-5}$, $1.8 \times 10^{-4}$, $4.5 \times 10^{-4}$, $8.1 \times 10^{-4}$ and $1.9 \times 10^{-3}$ M of the quencher in the cuvette. The dye concentration was different for lifetime quenching and steady-state fluorescence measurements. Therefore, control experiments by steady-state fluorescence spectroscopy were additionally carried out at the concentrations used for dynamic measurements. However, in contrast to the similarly occurring decrease in the overall fluorescence intensity, virtually no changes were registered in the fluorescence decay times. Only at the highest quencher concentrations employed, slight reductions of ca. 2% were found. For example, the end-point lifetimes obtained in the presence of the strongest quencher 1,1′-diacetylferrocene were 774, 223 and 82 ps for dyes **1–3**, respectively. Thus, dynamic quenching does not occur in any case.

## 4. Discussion

In contrast to what a preliminary study seemed to reveal [46], the present experiments show that ferrocene and its derivatives display a strong quenching effect upon the

fluorescence properties of the organic dyes investigated. The $k_q$ constant was found to be higher than the diffusion rate constant, which is around $10^{10} \, M^{-1} \, s^{-1}$. This means that the quenching step exceeds that expected for a diffusion-controlled process. This situation is generally attributed either to the formation of a ground state complex, or to long-range interactions, the encounter radius between the dye molecule and the quencher being greater than predicted by collision theory [36].

Discussing the results of a case of bimolecular interaction, the second hypothesis seems to be very attractive. Energy transfer based on dipole–dipole interactions (Förster's mechanism) is often assumed to take place in long-range quenching [36,47,48]. It is known that singlet–singlet energy transfer is generally so efficient, and can occur over such long distances, that diffusion is unimportant. As early as 1954, Bowen and Livingston have studied the transfer of excitation energy between aromatic hydrocarbons, and have obtained a quenching rate at least 10 times faster than a diffusion-controlled process [49]. This mechanism is favored when the emission spectrum of the energy donor overlaps with the absorption spectrum of the quencher, that is when the transitions $A^* \rightarrow A$ and $Q \rightarrow Q^*$ are isoenergetic. This condition is well fulfilled here in the case of chalcone **3**, the emission spectrum of which is virtually superimposed with the absorption spectrum of the ferrocenyl derivatives (Fig. 1). Actually, the most efficient quenching process was encountered here for **3**, and the $k_q$ constant increased with increasing spectral overlap. However, the fluorescence lifetimes were not affected by the presence of the quencher, as it is the case when long-range energy transfer is involved [50]. This mechanism can therefore be ruled out.

Despite the calculated rates in Table 2 indicating that a photoinduced electron transfer should be thermodynamically allowed in every case, the possibility of quenching via such a collisional process is also disfavored by our experimental results. The fluorescence decay profiles were unchanged. Moreover, a comparison of the data in Tables 2 and 3 reveals a significantly different variation of $k_q$ and $\Delta G^0$ with the combinations of dye and quencher. These are clear evidence against an occurrence of PET. On such a basis, the quenching process would be expected to be much more efficient for ferrocene and dimethylferrocene than for the two other derivatives. Actually, just the opposite was observed. Based on the background of electron-transfer theory [51,52], inefficient photoinduced electron transfer for systems with a calculated positive driving force, i.e. a negative value for $\Delta G^0$, can be caused by an overall negative activation energy or positive value for the ET energy barrier $\Delta G^{\#}$. This parameter depends not only on $\Delta G^0$ but also on the 'reorganization energy', that is a complex parameter which takes into account the modifications of the molecular geometry and of the solvent shell during the reaction. Most probably, in the present case, unfavorable steric and geometrical effects can cancel out the initial driving force.

The most probable explanation for the observed quenching features thus is that static quenching occurs. With $k_q$ rates being partly much faster than for a diffusion-controlled process, the present bimolecular interaction would involve ground state association between the fluorophore and the quencher. Such an association was not observed here by UV-Vis absorption spectroscopy and NMR spectroscopy, but such loose complexes are frequently found to escape straightforward detection [53]. The complex formed is thought to be entirely non-fluorescent, since it did not influence the lifetime or the decay profiles of the residual free fluorophores. However, concerning the actual quenching mechanism, static quenching in non-fluorescent complexes where easily oxidizable or reducible partners are involved often relies on very efficient intracomplex (short-range or contact-pair) electron or energy transfer [54].

## 5. Conclusions

This work sheds new light on the reactivity of ferrocenyl derivatives with respect to organic singlet states. According to the literature, the bimolecular quenching of organic singlet states is mostly attributed either to long-range energy transfer [55,56] or electron transfer [11,14,57,58]. In the present case, static quenching as a result of ultrafast electron or energy transfer between the loosely associated partners seems to be the predominant process being responsible for the loss of fluorescence of the ketocyanine dyes. With our present studies, we could underline the fact that ferrocenyl derivatives are efficient but versatile quenchers of the excited singlet state, and that the mode of quenching critically depends on the nature of the excited species.

## Appendix A. Correction of the inner-filter effect

### A.1. Pre-filter effect

When a dye is present in a solution containing another species and they both absorb at the same wavelength, the intensity of light $I_a$ actually absorbed by the dye is given by

$$I_a = I_0(1 - 10^{-A_{tot}}) \frac{A_D}{A_{tot}} \qquad (3)$$

In this expression, $I_0$ is the intensity of the incident light, $A_{tot}$ and $A_D$ stands for the total absorbance of the solution and for the absorbance of the dye, respectively, at the excitation wavelength.

Table 4

Experimental data and correction of inner-filter effects for chalcone **3** in the presence of acetylferrocene

| $[Q]$ | $A_F$ | $A_{tot}$ | $F_{meas}$ | $F_0'$ | $F_{em}$ | $F_0'/F_{em}$ |
|---|---|---|---|---|---|---|
| 0 | – | 0.04988 | 941 442 | – | – | – |
| $1.79 \times 10^{-4}$ | 0.05817 | 0.08553 | 827 833 | 922 564 | 885 172 | 1.042 |
| $5.37 \times 10^{-4}$ | 0.17452 | 0.13305 | 676 784 | 898 185 | 827 390 | 1.086 |
| $7.16 \times 10^{-4}$ | 0.23270 | 0.15568 | 605 657 | 886 880 | 791 729 | 1.120 |
| $1.07 \times 10^{-3}$ | 0.34775 | 0.21553 | 488 740 | 857 897 | 729 378 | 1.176 |
| $1.43 \times 10^{-3}$ | 0.46475 | 0.27144 | 403 754 | 831 974 | 689 432 | 1.206 |
| $1.61 \times 10^{-3}$ | 0.52325 | 0.29924 | 349 722 | 819 482 | 638 775 | 1.283 |
| $2.15 \times 10^{-3}$ | 0.69875 | 0.37978 | 265 938 | 784 716 | 594 504 | 1.320 |

Now, the fluorescence intensity $F$ varies linearly with the absorbed intensity $I_a$ according to

$$F = kI_a \tag{4}$$

In the absence of a pre-filter effect and quenching effect, $A_{tot}$ equals $A_D$, hence the measured fluorescence intensity is

$$F_0 = k I_0 (1 - 10^{-A_D/2}) \tag{5}$$

The absorbance is divided by 2 since it is considered that emission arises from the center of the cell, which halves the optical path-length. This approximation is generally accepted when using the usual right angle geometry.

In the presence of pre-filter effect, $F$ becomes

$$F_0' = kI_0(1 - 10^{-A_{tot}/2}) \frac{A_D}{A_{tot}} \tag{6}$$

Combining (5) and (6) gives

$$F_0' = F_0 \left[ \frac{(1 - 10^{-A_{tot}/2})}{(1 - 10^{-A_D/2})} \right] \frac{A_D}{A_{tot}} \tag{7}$$

$F_0'$ is the fluorescence intensity measured in the absence of quenching effect, but in the presence of pre-filter effect. It corresponds to the $F_0$ value of a classical quenching experiment, that is the fluorescence intensity determined in the absence of quencher.

### A.2. Post-filter effect

The ferrocenyl derivatives absorb at the emission wavelength of the dye, according to the equation

$$F_{abs} = F_{em}(1 - 10^{-A_F/2}) \tag{8}$$

where $F_{em}$ is the intensity of the fluorescence emitted by the dye, $F_{abs}$ is the amount of reabsorbed fluorescent light, and $A_F$ is the absorbance of the ferrocenyl derivative at the *emission* wavelength. The intensity of the emitted light is reduced by reabsorption, and the intensity of the measured signal $F_{meas}$ can be expressed as

$$F_{meas} = F_{em} - F_{abs} = F_{em} \times 10^{-A_F/2} \tag{9}$$

So, the fluorescence intensity actually emitted by the dye is

$$F_{em} = F_{meas} \times 10^{A_F/2} \tag{10}$$

Consequently, the real quenching effect, after correction of inner-filter effects can be expressed by the ratio $F_0'/F_{em}$.

### A.3. Example: calculation of the quenching effect for chalcone **3** in the presence of acetylferrocene

The absorbance of the dye at the excitation wavelength (400 nm) was invariant throughout the experiment, and was measured in the absence of quencher. The absorbance $A_F$ of the ferrocenyl derivative at the emission wavelength (472 nm) was calculated from the molar absorption coefficient previously measured. The values of $\varepsilon$ at this wavelength were found to be 428, 325, 75, and 81 $M^{-1} cm^{-1}$ for 1,1'-diacetylferrocene, acetylferrocene, ferrocene and 1,1'-dimethylferrocene, respectively. The results are given in Table 4.

After correction, it appears that the whole fluorescence decrease cannot be explained only by an inner-filter effect, but that an actual quenching effect is taking place.

### References

[1] W.G. Herkstroeter, J. Am. Chem. Soc. 97 (1975) 4161–4167.
[2] A. Farmilo, F. Wilkinson, Chem. Phys. Lett. 34 (1975) 575–580.
[3] A. Gilbert, J.M. Kelly, E. Koerner von Gustorf, Mol. Photochem. 6 (1974) 225–230.
[4] M. Kikuchi, K. Kikuchi, H. Kokubun, Bull. Chem. Soc. Jpn. 47 (1974) 1331–1333.
[5] A.J. Fry, R.S.H. Liu, G.S. Hammond, J. Am. Chem. Soc. 88 (1966) 4781–4782.
[6] S. Fery-Forgues, B. Delavaux-Nicot, J. Photochem. Photobiol., A: Chem. 132 (2000) 137–159.
[7] Y. Hsu, T.L. Penner, D.G. Whitten, J. Phys. Chem. 96 (1992) 2790–2795.
[8] N.B. Thornton, H. Wojtowicz, T. Netzel, D.W. Dixon, J. Phys. Chem. B 102 (1998) 2101–2110.
[9] J.-L. Shi, J.-Y. Xu, X.-K. Jiang, Chin. J. Chem. 19 (2001) 481–487.
[10] K. Nakatani, T. Uchida, H. Misawa, N. Kitamura, H. Masuhara, J. Phys. Chem. 97 (1993) 5197–5199.
[11] D.M. Guldi, M. Maggini, G. Scorrano, M. Prato, J. Am. Chem. Soc. 119 (1997) 974–980.
[12] V. Biju, S. Barazzouk, K.G. Thomas, M.V. George, P.V. Kamat, Langmuir 17 (2001) 2930–2936.
[13] M. Even, B. Heinrich, D. Guillon, D.M. Guldi, M. Prato, R. Deschenaux, Chem. Eur. J. 7 (2001) 2595–2604.
[14] J.W. Choi, G.Y. Jung, S.Y. Oh, W.H. Lee, D.M. Shin, Thin Solid Films 284–285 (1996) 876–878.

[15] T. Kondo, T. Kanai, K. Isoo, K. Uosaki, Z. Phys. Chem. 212 (1999) 23–30.

[16] S.E. Gasanov, B.A. Salakhutdinov, T.F. Aripov, Biofizika 35 (1990) 879–880.

[17] V.M. Mekler, A.I. Kotel'nikov, G.I. Likhtenshtein, R.A. Kotel'nikova, L.V. Tatyanenko, V.I. Shvets, A.P. Kaplun, Biofizika 29 (1984) 809–813.

[18] N. Marcotte, S. Fery-Forgues, J. Chem. Soc., Perkin Trans. 2 (2000) 1711–1716.

[19] N. Marcotte, S. Fery-Forgues, J. Photochem. Photobiol., A: Chem. 130 (2000) 133–138.

[20] N. Marcotte, S. Fery-Forgues, D. Lavabre, S. Marguet, V.G. Pivovarenko, J. Phys. Chem. 103 (1999) 3163–3170.

[21] B. Delavaux-Nicot, S. Fery-Forgues, Eur. J. Inorg. Chem. 10 (1999) 1821–1825.

[22] J. Maynadié, B. Delavaux-Nicot, S. Fery-Forgues, D. Lavabre, R. Mathieu, Inorg. Chem. 41 (2002) 5002–5004.

[23] M. Olomucki, J.Y. Le Gall, Bull. Soc. Chim. Fr. 9–10 (1976) 1467–1468.

[24] J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Plenum Press, New York, 1983, pp. 42–43.

[25] K. Rurack, U. Resch-Genger, W. Rettig, J. Photochem. Photobiol., A: Chem. 118 (1998) 143–149.

[26] K. Rurack, J.L. Bricks, B. Schulz, M. Maus, G. Reck, U. Resch-Genger, J. Phys. Chem. A 104 (2000) 6171–6188.

[27] B. Delavaux-Nicot, A. Bigeard, A. Bousseksou, B. Donnadieu, G. Commenges, Inorg. Chem. 36 (1997) 4789–4797.

[28] A.A. Khalaf, S.H. Etaiw, R.M. Issa, A.K. El-Shafei, Rev. Roum. Chim. 22 (1977) 1251–1259.

[29] D.R. Scott, R.S. Becker, J. Chem. Phys. 35 (1961) 516–531.

[30] A.T. Armstrong, F.J. Smith, E. Elder, S.P. McGlynn, J. Chem. Phys. 46 (1967) 4321–4328.

[31] Y.S. Sohn, D.N. Hendrickson, H.B. Gray, J. Am. Chem. Soc. 93 (1971) 3603–3612, and references cited therein.

[32] A.M. Tarr, D.M. Wiles, Can. J. Chem. 46 (1968) 2725–2731.

[33] P.D. Harvey, L. Gan, C. Aubry, Can. J. Chem. 68 (1990) 2278–2288.

[34] K.L. Cunningham, D.R. McMillin, Inorg. Chem. 37 (1998) 4114–4119.

[35] P. Suppan, Chemistry and Light, Royal Society of Chemistry, Cambridge, 1994, pp. 66–68.

[36] K.K. Rohatgi-Mukherjee, Fundamentals of Photochemistry, Wiley Eastern Ltd., New Delhi, 1978, pp. 183–201.

[37] M. Chanon, M.D. Hawley, M.A. Fox, in: M.A. Fox, M. Chanon (Eds.), Photoinduced Electron Transfer, Pt. A: Conceptual Basis, Elsevier, Amsterdam, 1998, pp. 8–13.

[38] D. Rehm, A. Weller, Isr. J. Chem. 8 (1970) 259–271.

[39] K.-W. Poon, Y. Yan, X.-Y. Li, D.K.P. Ng, Organometallics 18 (1999) 3528–3533.

[40] I. Lopez Arbeloa, J. Photochem. 14 (1980) 97–105.

[41] V.A. Mode, D.H. Sisson, Anal. Chem. 46 (1974) 200–203.

[42] H.-P. Lutz, P.L. Luisi, Helv. Chim. Acta 66 (1983) 1929–1935.

[43] S. Fery-Forgues, D. Lavabre, J. Chem. Educ. 76 (1999) 1260–1264.

[44] J.M. Bevilacqua, R. Eisenberg, Inorg. Chem. 33 (1994) 1886–1890.

[45] M. Ollino, W.R. Cherry, Inorg. Chem. 24 (1985) 1417–1418.

[46] B. Delavaux-Nicot, S. Fery-Forgues, N. Marcotte, Luminescence 15 (2000) 60–61.

[47] M.J. Pilling, S.A. Rice, J. Chem. Soc., Faraday Trans. 2 72 (1976) 792–801.

[48] J.G. Calvert, J.N. Pitts, Photochemistry, Wiley, New York, 1966, pp. 336–339.

[49] E.J. Bowen, R. Livingston, J. Am. Chem. Soc. 76 (1954) 6300–6304.

[50] W.R. Ware, J. Am. Chem. Soc. 83 (1961) 4374–4377.

[51] G.J. Kavarnos, Top. Curr. Chem. 156 (1990) 21–58.

[52] R.A. Marcus, Rev. Mod. Phys. 65 (1993) 599–610.

[53] G. Beer, K. Rurack, J. Daub, J. Chem. Commun. (2001) 1138–1139.

[54] L. Fabbrizzi, M. Licchelli, P. Pallavicini, A. Perotti, A. Taglietti, D. Sacchi, Chem. Eur. J. 2 (1996) 75–82.

[55] E. Pénigault, A.M. Braun, J. Faure, C. R. Acad. Sci. Paris, Ser. C 283 (1976) 655–658.

[56] O. Traverso, F. Scandola, V. Carassati, Inorg. Chem. Acta 6 (1972) 471–474.

[57] T.A. Wells, A. Losi, R. Dai, P. Scott, M. Anderson, J. Redepenning, S.-M. Park, J. Golbeck, P.-S. Song, J. Phys. Chem. A 101 (1997) 366–372.

[58] D.G. Whitten, S.P. Spooner, Y. Hsu, T.L. Penner, React. Polym. 15 (1991) 37–48.