Metal-Induced Self-Assembly of a Pyrene-Tethered Hydroxamate Ligand for the Generation of Multichromophoric Supramolecular Systems. The Pyrene Excimer as Switch for Iron(III)-Driven Intramolecular Fluorescence Quenching

Bruno Bodenant,[†] **Frédéric Fages,***[,†] **and Marie-Héléne Delville**[‡]

Contribution from the Laboratoire de Chimie Organique et Organométallique, CNRS UMR 5802, Université Bordeaux I, 351 Cours de La Libération, 33405 Talence Cedex, France, and Institut de Chimie de la Matière Condensée de Bordeaux, CNRS UPR 9048, Château Brivazac, Avenue du Dr Schweitzer, 33608 Pessac Cedex, France

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Abstract: We report the first example of intramolecular excimer formation in supramolecular trichromophoric systems resulting from the metal-directed self-assembly of chromophore-labeled ligand molecules. The trichromophoric gallium(III) chelate, (**1**)$_3$Ga, shows an intense pyrene excimer fluorescence emission in acetonitrile, while the iron(III) analogue, (**1**)$_3$Fe, exhibits a fluorescence of very low intensity compared to that of the free hydroxamate ligand **1**. The trivalent gallium metal cation is demonstrated to play the role of an inert and transparent linker, whereas the ferric center acts additionally as an extra chromophore that quenches the pyrene singlet state. On the basis of low-temperature fluorescence measurements, the mechanism of quenching within (**1**)$_3$Fe is attributed to a pyrene-to-iron electronic energy transfer process. ^{1}H NMR and electronic absorption spectroscopies show that intramolecular interactions between pyrene chromophores prevail in the ground state, which leads to the formation of preassociated excimers for both chelates. From the dependence of the solvent on the photophysical properties of (**1**)$_3$Ga and (**1**)$_3$Fe, it is inferred that the Fe(III)-induced quenching process is triggered by the ground-state and excited-state intramolecular dimerization of the pyrene moieties, with the pyrene-to-iron energy transfer taking place more readily from the excimer singlet state as donor than from the locally excited state.

Introduction

The quenching of singlet and triplet excited states of aromatic hydrocarbons by transition-metal ions and their coordination complexes is a process which has been known for a long time and is still the subject of intense investigations.[1−4] It is now well recognized that photoinduced electron transfer and electronic energy transfer are to be considered as the two main deactivation pathways responsible for efficient fluorescence or phosphorescence inhibition. In that connection, a great deal of attention has been devoted to the design and the synthesis of transition-metal complexes of chromophore-tethered ligands in which the metallic and aromatic components are held in a defined spatial arrangement.[5] This approach has led to the generation of a variety of chromophore−quencher complexes, which have provided outstanding information concerning the factors that influence photoinduced charge separation and antenna effects within these entities.[5−10] Moreover, these molecular and supramolecular metallosystems have found applications of paramount interest in many areas such as metal ion sensing,[11,12] artificial photosynthesis and photocatalysis,[13] information processing,[10,14] DNA cleavage,[15] or optical sensing of DNA[16]

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* Corresponding author. E-mail: f.fages@lcoo.u-bordeaux.fr.

[†] Laboratoire de Chimie Organique et Organométallique.

[‡] Institut de Chimie de la Matière Condensée de Bordeaux.

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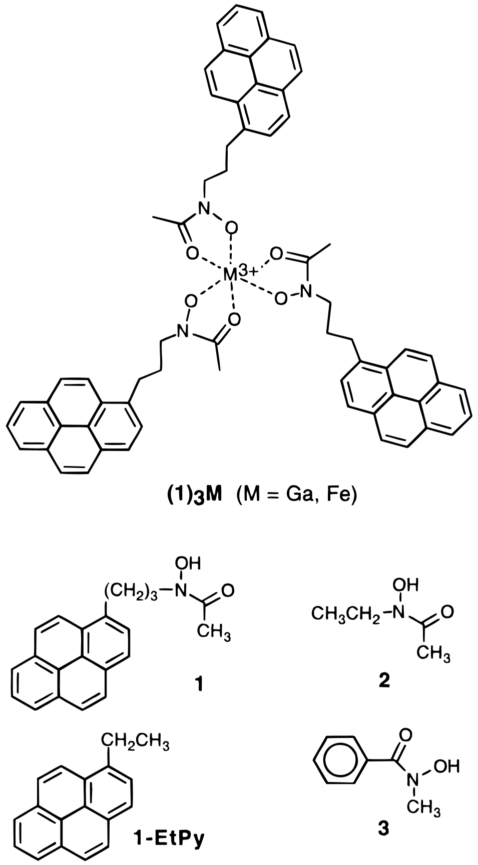
Most of these studies have focused on aromatic hydrocarbon−transition-metal systems which contain a *single* organic chromophore as light-absorbing moiety. It occurred to us that some attractive properties could be expected from coordination complexes in which an *array* of aromatic nuclei would be properly assembled around a metal center, including (i) the occurrence of excited-state interactions between aromatic moieties leading to excimer formation, provided the latter is geometrically allowed and can compete very efficiently with quenching of excited monomer species and (ii) locally excited (monomer) and excimer emissions being affected to different extents by the presence of the bound quenching metal, for example, a quenching efficiency sensitive to the nature of the excited state.[17,18] Considering also that excimer formation (or disappearance) in solution is known to be modulated by structural and environmental factors,[19] excimerization might then prove to be a functional mechanism capable of switching on/off the flow of charge or electronic excitation within multicomponent supramolecular systems.

Recently, we reported[20] the synthesis and preliminary fluorescence emission properties of two self-assembling trichromophoric systems, (**1**)$_3$Ga and (**1**)$_3$Fe (Scheme 1). Ligand **1** was synthesized as a model compound for the study of a series of fluorescent hydroxamate chelators designed for the detection of transition-metal ions.[12f,21] A three-methylene chain was chosen to tether the pyrene chromophore to the bidentate hydroxamate binding unit in order to provide conformational flexibility. Actually, we envisioned that the electroneutral metal trischelates, (**1**)$_3$Ga and (**1**)$_3$Fe, could be seen as fluxional bunches of chromophores featuring monomer/excimer interconversion and displaying geometrical properties characteristic of the octahedral arrangement of the chelating sites around the metal. The gallium(III) metal ion was expected to play the role of a transparent and inert linker from the photophysical standpoint, whereas the iron(III) metal cation was anticipated to act additionally as a fluorescence quencher owing to the optical properties and redox activity of tris(hydroxamato)iron(III) centers.[22] Excimer fluorescence emission of (**1**)$_3$Ga and fluorescence quenching within (**1**)$_3$Fe were indeed observed in acetonitrile.[20] Furthermore, the pyrene nucleus appeared to be attractive aromatic hydrocarbon for the conception of polychromophoric systems in view of the aforementioned objectives due to not only its well-known ability to generate intramolecular excimers (“dynamic excimers”)[23−27] but also a marked propensity to associate intramolecularly in the ground state, leading to the kinetically favored formation of preformed excimers (“static excimers”).[25−27] Moreover, Caldwell et al. have shown[28] that the pyrene excimer was less sensitive to electron-transfer quenching than the pyrene singlet monomer.

Scheme 1. Free Ligand **1**, Its Electroneutral Metal Complexes, and the Reference Compounds



This paper describes the structural characterizations and the electrochemical and spectroscopic properties of (**1**)$_3$Ga and (**1**)$_3$Fe in solution (^{1}H NMR, cyclic voltammetry, electronic absorption, and fluorescence and phosphorescence emission spectra). It is shown that the molecular dynamics of the three hydroxamic acid ligands chelated to a trivalent metal ion such as Ga^{3+} can be probed by excimer formation between pyrenes. The ground-state conformer distribution and specific, solvent−

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Table 1. Chemical Shifts, δ (in ppm),[a] for 1-Ethylpyrene (1-EtPy), Free Ligand **1**, and Its Gallium Complex ((**1**)$_3$Ga)

	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	1a	1b	1c	CH_3
1-EtPy[b]	7.896	8.136	8.034	8.011	8.163	7.985	8.156	8.110	8.301	3.372	1.527		
(**1**)$_3$Ga	7.695	8.075	*d*	*d*	*d*	*d*	7.995	*d*	8.168	3.297	2.307	3.729	2.023
	(−0.20)	(−0.06)	(−0.10)	(−0.08)	(−0.23)	(−0.06)	(−0.16)	(−0.18)	(−0.13)				
1[c]	7.929	8.137	8.056	8.020	8.188	7.991	8.177	8.141	8.341	3.371	2.180	3.791	2.150

[a] $CDCl_3$ as solvent unless otherwise stated, 250 MHz, 25 °C, ca. 2×10^{-3} M; $\Delta\delta$, the chemical shift difference, is given in parentheses ($\Delta\delta = \delta((\mathbf{1})_3\mathrm{Ga}) - \delta(\text{1-EtPy})$). [b] Values taken from ref 26. [c] MeOH-d$_4$ as solvent. [d] Not assigned. $\Delta\delta$ was estimated.

metallic center interactions are features that strongly influence the fluorescence emission properties of the coordination compound, (**1**)$_3$Ga. Furthermore, the results support that the formation of an intramolecular excimer species is a prerequisite to the quenching of the pyrene excited singlet state by iron(III) in (**1**)$_3$Fe. The mechanism of quenching is discussed.

Experimental Section

Materials and Methods. Solvents for spectroscopic measurements (methylcyclohexane, $CHCl_3$, acetonitrile and methanol) were of spectrometric grade and were used as received. All 250-MHz proton NMR spectra were recorded on Bruker AC 250 and DPX 200 instruments. Chemical shifts are reported in ppm vs Me_4Si. FAB mass spectra were obtained with a Fisons-Instruments AutoSpec-EQ spectrometer. FT-IR spectra were recorded with a Perkin-Eltrans Paragon 1000PC apparatus. UV−vis spectra were obtained using a Hitachi U3300 spectrophotometer. Fluorescence and phosphorescence emission spectra were recorded using a Hitachi F4500 or a Spex Fluorolog spectrofluorimeter. Fluorescence decays were obtained using a single-photon timing apparatus as described elsewhere.[29] Fluorescence emission measurements were carried out in degassed solvents, and fluorescence quantum yields were obtained by comparison with quinine sulfate as a standard ($\Phi_f = 0.55$ at 25 °C in 1 N H_2SO_4). Cyclic voltammetry data were recorded as previously described[30] using 0.1 M $^nBu_4NBF_4$ as electrolyte in acetonitrile. The counter electrode was a Pt wire, and the working electrode was a hanging mercury drop electrode. Thermodynamic potentials were recorded with reference to SCE.

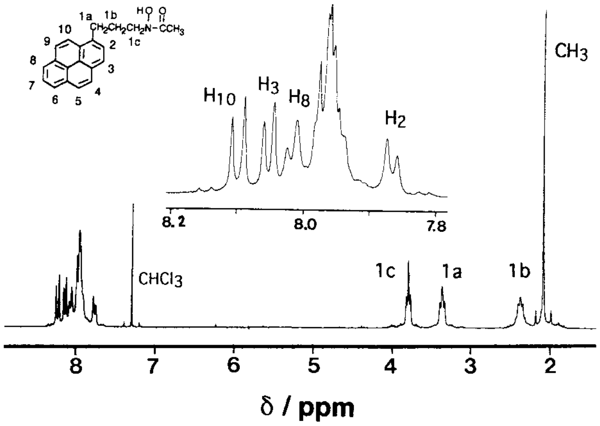
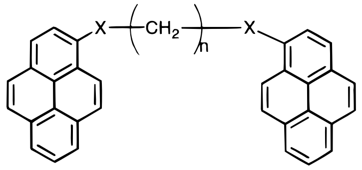


Figure 1. 250-MHz ^1H NMR spectrum of (**1**)$_3$Ga in $CDCl_3$ (25 °C, 2×10^{-3} M).

Scheme 2. Selected Examples of Excimer-Forming Bis-Pyrenyl Molecules[a]



X = -CH_2- 1,*n*-di(1-pyrenyl) alkanes

X = -C(=O)O- 1,*n*-di(1-pyrenylcarboxy) alkanes

[a] From refs 26 and 27.

Preparation of the Neutral Complexes. The synthesis of the free ligand, **1**, has been reported elsewhere.[20] The neutral complexes were obtained by reacting free **1** with 1/3 molar equiv of the corresponding metal(III) nitrate in the methanol/THF (50/50 v/v) solvent system, followed by the addition of water. The resulting precipitates were removed by filtration, washed with water, and vacuum dried for 1 week over P_2O_5 at room temperature. (**1**)$_3$Fe(III) and (**1**)$_3$Ga(III) were purified by dissolution in CH_2Cl_2 and reprecipitation with *n*-heptane. Several attempts of the slow evaporation of solutions of (**1**)$_3$Fe(III) in CH_2Cl_2/*n*-heptane solvent mixtures afforded orange-red needles which were not of satisfactory quality for X-ray measurements. The isolated neutral complexes were white (gallium) and orange (iron) in color and were very soluble in dichloromethane, acetonitrile, and DMSO. The free ligand and its complexes gave satisfactory elemental analyses.[20] Positive ion fast-atom bombardment (FAB) mass spectra showed the molecular ion peaks of the mononuclear 1:3 neutral chelates with the characteristic isotope distribution patterns. The infrared spectra (KBr pellets) showed a decrease in the C═O infrared stretching frequency on going from the free ligand (1630 cm^{-1}) to the complexes (**1**)$_3$Ga (1600 cm^{-1}) and (**1**)$_3$Fe (1580 cm^{-1}), consistent with earlier data obtained on hydroxamate ligands and their complexes.[31] The hydroxyl peaks were absent in the IR spectra of the complexes. The absence of free ligand in both complexes was further confirmed by thin-layer chromatography and, in the case of (**1**)$_3$Ga, by 250-MHz ^1H NMR. The synthesis of the reference ligands, *N*-ethyl-acethydroxamic acid, **2**, and *N*-methyl-benzohydroxamic acid, **3**, and their iron(III) neutral complexes were performed according to known procedures.[32,33]

Results

^{1}H NMR. The structure of the diamagnetic complex (**1**)$_3$Ga was examined at room temperature by 250-MHz ^1H NMR spectroscopy using $CDCl_3$ as solvent (1−5 mM). Its ^1H NMR spectrum showed an upfield shift of the resonances of all the aromatic protons (Figure 1and Table 1) compared to those of 1-ethylpyrene[26,27] (1-EtPy) in chloroform.[34] This feature is consistent with previous observations reported for 1,*n*-bis(2-pyrenylcarboxy)- and 1,*n*-bis(1-pyrenylcarboxy) alkanes (Scheme 2).[26] In these compounds, the aromatic parts were demonstrated to exert a ring current effect on each other, due to a decrease of the end-to-end separation induced by the bending and folding motions of the hydrocarbon chain in solution. The amplitude of the shielding was thus directly related to the length and the

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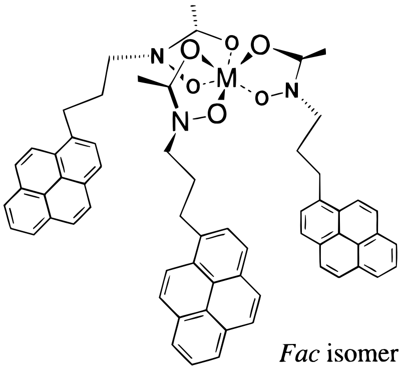
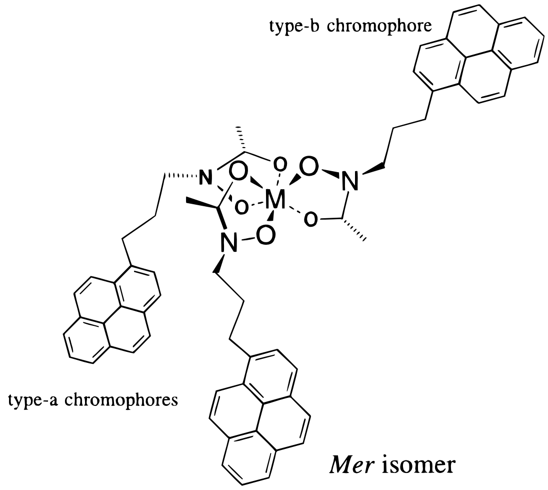
[34] Comparison with free compound **1** was not possible due to aggregation through hydrogen bonding in chloroform as mentioned for other *N*-methyl-substituted hydroxamic acids,[32] which in our case induced the splitting of aliphatic and aromatic proton resonances. However, compound **1** gave a spectrum in methanol-*d*$_4$ solution quite similar to that of 1-EtPy, indicating no detectable perturbation of the resonances of the aromatic protons by the hydroxamic acid moiety (Table 1).

Scheme 3. Cis and Trans Geometric Isomers of $(\mathbf{1})_3M$ (M = Ga, Fe)



Fac isomer



Mer isomer

conformational properties of the chain. In some cases, intramolecular dimerization in the ground state was invoked.[26,35] A similar behavior is postulated to account for the up-shielding of the aromatic H-atom resonances of $(\mathbf{1})_3$Ga. The chemical shift differences, $\Delta\delta$ (Table 1), obtained for the aromatic protons of this complex with respect to the model compound, 1-EtPy, were compared to those given for 1,*n*-bis(pyrenylcarboxy) alkanes.[26] Noticeably, $(\mathbf{1})_3$Ga, containing an 11-atom (including the gallium metal ion) interchromophore linker, gave rise to $\Delta\delta$ values much higher than those of literature compounds of similar length ($n \geq 10$) and of the same order of magnitude as those corresponding to the shorter bichromophoric compounds, for example, having $n = 3-8$.[26] This indicated that pyrene nuclei could experience particularly favored intramolecular interactions in $(\mathbf{1})_3$Ga, likely due to the peculiar geometrical features of the coordination-center-containing spacer. Indeed the latter, in contrast to linear hydrocarbon chains of similar length, is expected to adopt a preferential bent shape arising from the octahedral arrangement of the ligands around the metal, which would tend to reduce the average separation between the ligand termini.

Octahedral, tris(hydroxamato) complexes of gallium(III) and high-spin iron(III) are likely to exist as two geometric isomers, namely the fac and mer forms with C_3 and C_1 symmetry, respectively (Scheme 3). It is worth noting that the fac isomer of Ga(III) and Fe(III) complexes of N-substituted hydroxamates has been preferentially isolated in the solid state[36] under experimental conditions similar to those we used in this study. The ^{1}H NMR spectrum of $(\mathbf{1})_3$Ga clearly showed one set of signals for the aromatic and the aliphatic protons of the ligand (Figure 1). The ^{13}C NMR spectrum of the Ga(III) complex of **1** in chloroform (50 mM) also indicated the occurrence in solution of a symmetrical species on the NMR timescale at room temperature. These observations may suggest the presence in solution of either the single fac isomeric complex of C_3 symmetry, or more likely, a fast interconverting mixture of octahedral species giving rise to a symmetrical ^{1}H NMR spectrum due to time averaging. Low-temperature proton NMR spectroscopy confirmed the latter possibility. At −40 °C in $CDCl_3$, an intermediate-exchange spectrum was obtained and was clearly indicative of an interconversion between species with different symmetries. Particularly, the methyl resonance was exchange broadened and began to resolve into a set of single resonance lines, which is expected for a mixture of fac and mer isomers.[37c,d] Tris(hydroxamato) complexes of iron(III) and gallium(III) are well-known to be kinetically labile. For such "fast" complexes, rapid intramolecular rearrangements on the NMR timescale were also observed in the nonprotic solvent chloroform.[37]

At this stage, it is worth pointing out a particular feature. In the mer stereoisomer, two pendant pyrene units experience a cis relationship (chromophores of type a in Scheme 3) and are located close to each other, whereas the third one is insulated (chromophore of type b). In contrast, the fac chelates only contain three type a chromophores as the three pyrenes are constrained in a cis relationship. Examination of molecular models indicated that intramolecular dimer formation was geometrically allowed only for two type a pyrene moieties and could lead to significant overlap between aromatic π clouds, whereas trimer formation was precluded even in the fac and, a fortiori, in the mer isomer.

UV−Vis Absorption Spectroscopy. The electronic absorption spectra of the free ligand and its metal complexes were recorded in solution at room temperature. They were compared to those of the reference compounds, for example, 1-EtPy and the tris(*N*-ethyl-acethydroxamato)iron(III) model complex, $(\mathbf{2})_3$Fe.

The spectroscopic data (λ_{max} and ϵ_{max}) for the first vibronic band of the ^1L_a electronic transition of the pyrene chromophore are collected in Table 2. The UV−vis spectrum of $(\mathbf{1})_3$Fe was given in ref 20. The monohydroxamic acid ligand, **1**, displayed in acetonitrile and methanol UV-vis absorption spectral data characteristic of 1-substituted pyrene derivatives, similar to that of 1-ethylpyrene. In the gallium and iron complexes, the absorption features of the pyrene nucleus were significantly modified relative to those of the free compound. Indeed, the spectrum of these trichromophoric assemblies in acetonitrile displayed a strong hypochromic effect and a bathochromic shift ($\Delta\lambda$ ca. +1 nm), whereas in methanol, only a hypochromic effect of weaker amplitude was noticed. These features, in agreement with our NMR observations, supported the existence of ground-state intramolecular interactions between pyrene chromophores[25] that would be more pronounced in acetonitrile than in methanol.

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Table 2. Electronic Absorption Spectral Data[a] for 1-EtPy, free **1**, (**1**)$_3$Ga, (**1**)$_3$Fe, and (**2**)$_3$Fe

	λ_{max} (ϵ_{max})	
	methanol	acetonitrile
1-EtPy	341 (43800)	342 (43400)
1	342 (53000)	342 (48300)
(**1**)$_3$Ga	342 (133200)	343 (117800)
(**1**)$_3$Fe	342 (127000)	343 (107800)
	419 (2870)[b]	430 (3100)[b]
(**2**)$_3$Fe	*c*	432 (3200)[b]

[a] λ_{max} (nm) and ϵ_{max} (M^{-1} cm^{-1}) are respectively the maximum wavelength and the intensity of the lowest-energy vibronic band of the ^1L_a electronic transition of the pyrene chromophore (25 °C, ca. 5×10^{-6} M). [b] Data for the LMCT absorption band of the tris(hydroxamato)ferric moiety recorded at ca. 5×10^{-5} M. [c] Not measured.

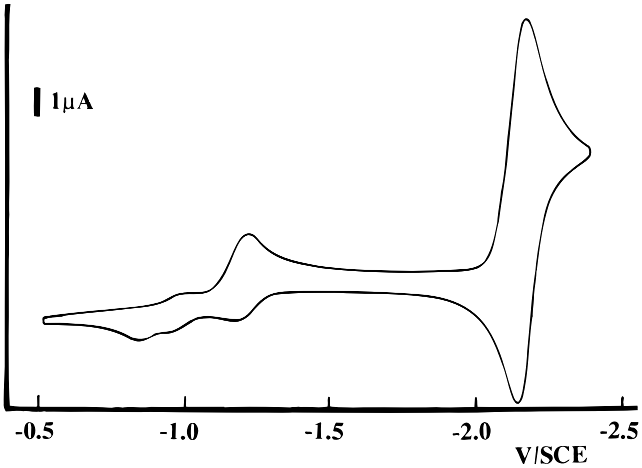

Figure 2. Cyclic voltammogram of (**1**)$_3$Ga in CH_3CN (0.1 M ^{n}Bu$_4$NBF$_4$, at hanging Hg electrode, scan rate = 0.4 V/s, 25 °C, ca. 9×10^{-4} M).

In contrast to the case of the gallium(III) complex, the lowest energy band in the iron(III) complex does not arise from the pyrene-based transitions but from the ligand-to-metal charge transfer (LMCT) transition characteristic of the tris(hydroxamato)Fe(III) center (Table 2). The values of the maximum wavelength and molar absorption coefficient of the LMCT absorption band correlated well with those of (**2**)$_3$Fe (Table 2) and those reported for related complexes.[22,38] Upon addition of an excess of a strong competing ligand (desferrioxamine B) to the methanolic solutions of the complexes, the spectral features of the pyrene chromophore became identical to those of the free ligand for both complexes, and in the case of the iron chelate, the disappearance of the LMCT band was noticed.

Electrochemistry. Ligand **1** and its complexes were investigated by cyclic voltammetry in acetonitrile at room temperature (Figure 2). Their potential, electrochemical, and chemical reversibilities are listed in Table 3, together with data obtained for a series of reference compounds. The electrochemical reduction of the (*N*-methylbenzohydroxamato)iron(III) complex, (**3**)$_3$Fe, has already been examined by Raymond et al., to our knowledge the only example in the literature of a cyclic voltammetry study of hydroxamato ferric complexes in *acetonitrile*.[39]

The cyclic voltammogram of (**1**)$_3$Ga exhibited a single reduction wave at around −2.1 V characterized by a Nernstian behavior (electrochemical reversibility) and a good chemical reversibility at 25 °C. It was found to be quite similar to those displayed by 1-EtPy and free **1** and was ascribed to the reduction of the pyrene moiety.[40]

Table 3. Redox Potentials[a] Measured by Cyclic Voltammetry for Ligand **1** and Its Complexes, (**1**)$_3$Ga and (**1**)$_3$Fe, and for the Reference Compounds 1-EtPy, (**2**)$_3$Fe, and (**3**)$_3$Fe in Acetonitrile

	ferric center			pyrene moiety			
	E_{Red}	ΔE_p	i_a/i_c	E_{ox}	E_{red}	ΔE_p	i_a/i_c
1-EtPy				+1.22[b]	−2.14	60	0.70
free **1**				*c*	−2.12	60	0.85
(**1**)$_3$Ga				*c*	−2.11	60	0.75
(**1**)$_3$Fe	−1.19	60	0.52	+1.22[b]	−2.145	60	0.87
(**2**)$_3$Fe	−1.16	*c*	*c*				
(**3**)$_3$Fe	−1.03[d]	*c*	*c*				
	−1.025[e]						

[a] Values quoted were at 400 mV/s in ca. 10^{-3} M solutions of the compounds in 0.1 M ^{n}Bu$_4$NBF$_4$−CH_3CN (hanging Hg electrode, 25 °C). The redox potential values are given in V vs SCE. ΔE_p (in mV) and i_a/i_c are the electrochemical and chemical reversibilities, respectively. [b] Irreversible. E_{ox} were determined using a Pt electrode as working electrode. [c] Not determined. [d] This work. [e] From ref 39.

The cyclic voltammogram of (**1**)$_3$Fe exhibited the reduction peak of pyrene similar to that mentioned above. Another reduction wave was present in the spectrum and was assigned to the iron-centered redox couple by analogy with data obtained for other tris(hydroxamato) iron complexes bearing no chromophore, particularly (**3**)$_3$Fe.[39] The latter Nernstian one-electron reduction wave at $E_{1/2} = -1.19$ V displayed a peak-to-peak separation of 60 mV (Table 3) and presented only a partial chemical reversibility between −0.4 and −2.4 V. The latter feature is consistent with the lower thermodynamic stability of the Fe(II) species at the electrode.[39] Actually, the ratio between the anodic and cathodic currents for the iron(III) reduction wave could be raised to unity upon addition of increasing amounts of free ligand into the solution, which indicated that partial decoordination of the ligand at the Fe(II) state was inhibited under these conditions.[39] Chemical reversibility was also observed to increase when the switching potential was located between the waves corresponding to the pyrene and iron redox couples. Furthermore, (**1**)$_3$Fe exhibited the nonreversible oxidation peak characteristic of the pyrene nucleus at around +1.20 V, which is consistent with literature data.[41]

Steady-State Fluorescence Emission. The corrected fluorescence emission spectra of **1** and its metal chelates were recorded in diluted solutions ($<10^{-6}$ M, methanol or acetonitrile) to determine their fluorescence quantum yields, the results of which are collected in Table 4. The spectrum of the free ligand was found to be quite similar to that of 1-EtPy. In contrast, the pyrene fluorescence emission was observed to undergo profound changes in intensity and wavelength upon metal complexation, and the effect was strongly dependent not only on the nature of the chelated metal but also, for a given metal, on the nature of the solvent (Figure 3).[20]

(a) In Acetonitrile. In the case of the nonquenching gallium(III) metal cation, the trichromophoric complex, (**1**)$_3$Ga, exhibited in acetonitrile a dual spectrum (Figure 3a), the monomer-like emission and a new broad, red-shifted band which was attributed to the emission of an intramolecular excimer. Consistently, increasing solvent polarity, from methylcyclohexane to $CHCl_3$, CH_2Cl_2, and CH_3CN, had no effect on the

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(39) Abu-Dari, K.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1978**, *17*, 3394−3397.

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Table 4. Fluorescence Emission Data[a] for 1-EtPy, Free Ligand **1**, and Its Metal Complexes

	MeOH	CH_3CN		CH_3CN/MeOH 90/10 (v/v)	
	Φ_f	Φ_f	I_E/I_M	I_E/I_M	$\Phi_f(\lambda_{exc})/\Phi_{f(340)}$
1-EtPy	0.65	0.64			
1	0.61	0.61			
(**1**)$_3$Ga	0.55	0.38	2.5 2.2(335) 4.5(350)	1.2 1.2(335) 1.5(345) 2(350)	*d*
(**1**)$_3$Fe	0.48	0.05	*b*	*c*	1(335) 0.86(345) 0.65(350)

[a] Values of the fluorescence quantum yields (Φ_f) and excimer-to-monomer fluorescence intensity ratio (I_E/I_M) were determined at 25 °C for degassed solutions ($<10^{-6}$ M). The excitation wavelength is set at 340 nm unless otherwise stated, the value being then indicated in parentheses. [b] Dual emission (monomer + excimer). [c] Monomer emission only. [d] Not determined.

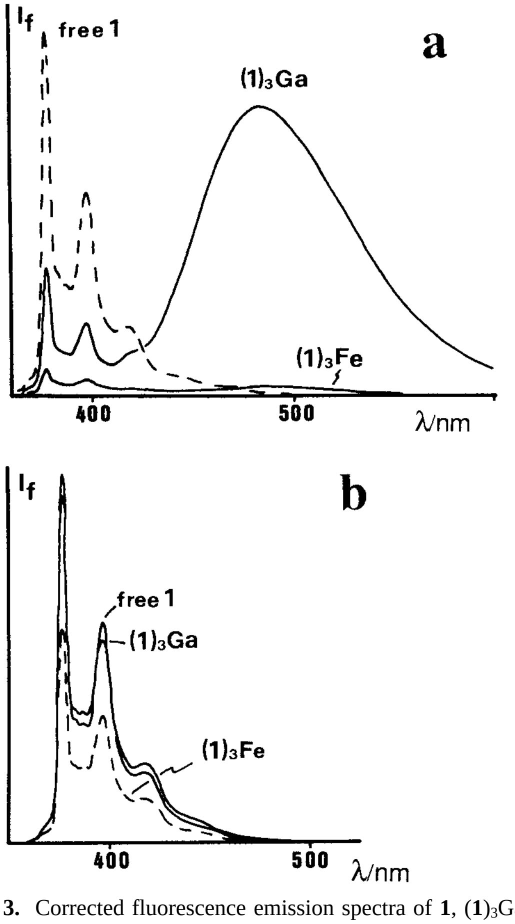

Figure 3. Corrected fluorescence emission spectra of **1**, (**1**)$_3$Ga, and (**1**)$_3$Fe in (a) acetonitrile and (b) methanol (25 °C, $\lambda_{exc} = 340$ nm, $<10^{-6}$ M).

maximum emission wavelength of this emission band, indicating that the excited state did not possess any charge transfer character.[29,42] For (**1**)$_3$Ga in acetonitrile, the spectrum showed a high value of the excimer-to-monomer fluorescence intensity ratio ($I_E/I_M = 2.5$, Table 4), which was indicative of the formation of a quasisandwich excimer ($\lambda_{max} = 480$ nm).[19] According to our comment on the structure of the chelates, excimer formation is believed to result from the stacking of two type a pyrene chromophores (Scheme 3), that is, ones experiencing a cis relationship. In the fac complex, the formation of a triple excimer (exterplexe) is quite unlikely for geometrical reasons.

The fluorescence excitation spectra of (**1**)$_3$Ga were monitored at the monomer-like and the excimer emissions. The lowest energy band of the spectrum monitored for the monomer ($\lambda_{obs} = 380$ nm) pointed at 342 nm, which matched the lowest energy band (^1L_a transition) of the monochromophoric ligand **1**. In contrast, the excitation spectrum obtained at the excimer emission band ($\lambda_{obs} = 500$ nm) gave absorbances exactly similar to the UV-vis absorption data obtained for the trichromophoric complex (Table 2). In connection with these experiments, we observed that the value of the I_E/I_M ratio depended on the excitation wavelength, I_E/I_M increasing gradually from 2 to 4.5 when the excitation monochromator was scanned from 335 to 350 nm. The latter data, together with the fluorescence excitation results, provided further compelling evidence for the existence of ground-state intramolecular interactions between pyrene nuclei in the metal tris(chelate), in agreement with UV absorption and NMR results. Furthermore, these fluorescence experiments showed that the intramolecular excimer emission originated to a large extent from a population of chelates bearing intramolecularly preassociated pyrenes in the ground state.[25] These features are in total agreement with those reported for bis(pyrenyl) molecules.[26]

As reported previously,[20] the iron(III) complex exhibited a fluorescence emission of very weak intensity, reaching nearly baseline level (Figure 3a). This behavior is consistent with that related for other ferric hydroxamates labeled with fluorescent aromatic groups.[12c,f] It is noteworthy that the fluorescence spectrum of (**1**)$_3$Fe exhibited both monomer and excimer contributions.

(b) In Methanol. Strikingly, the fluorescence spectra of the two complexes in methanol became close in intensity and shape to that of the free ligand (Figure 3b, Table 4), that is, the two complexes exhibited an intense monomer-like emission. With (**1**)$_3$Fe, a partial quenching (ca. 15%) was noticed relative to (**1**)$_3$Ga. By using a 10-cm pathway cell, the LMCT transition band in the UV-vis absorption spectrum of (**1**)$_3$Fe could be recorded at a concentration of about 5×10^{-7} M and its spectroscopic features were found to be identical to those recorded in more concentrated solutions (ca. 5×10^{-5} M, Table 2). This permitted the conclusion that the iron complex did not undergo any dissociation at very low concentration in the protic methanol solvent. Reasonably, it was assumed that the gallium complex was also stable under these conditions.

To get a better insight into the effect of the solvent on the fluorescence emission of the complexes, the photophysical properties of the two chelates, (**1**)$_3$Fe and (**1**)$_3$Ga, were investigated in various solvent mixtures. We observed that the addition of 10% (v/v) of n-hexanol into a solution of (**1**)$_3$Ga in acetonitrile caused a slight increase of the monomer emission at the expense of the excimer emission ($I_E/I_M = 1.9$) as compared to neat acetonitrile, while this effect was more pronounced in the case of the addition of the same amount of methanol ($I_E/I_M = 1.2$) (Table 4). In the same way, a significant enhancement of the fluorescence quantum yield of (**1**)$_3$Fe was observed upon addition of 10% of either of these two alcohols, with the methanol being here again the most effective. In the presence of 10% (v/v) of 2-chloroethanol, the total disappearance of the excimer emission band in the spectrum of (**1**)$_3$Ga and the quantitative revival of the fluorescence emission of (**1**)$_3$Fe were noticed. But in this case, electronic absorption spectroscopy showed that metal decomplexation did occur. Finally, it

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(42) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2, p 159.

Table 5. Fluorescence Decay Parameters[a] of 1-EtPy, Free Ligand **1**, and Its Gallium Complex (**1**)$_3$Ga

	solvent	λ_{em} (nm)	a$_1$	1/λ_1 (ns)	a$_2$	1/λ_2 (ns)	a$_3$	1/λ_3 (ns)	χ^2	D.W.
1-EtPy	CH_3CN	390	0.18	193					1.040	1.901
1	CH_3CN	390	0.20	216					1.000	1.880
(**1**)$_3$Ga	CH_3CN	380	0.25	2.8	0.05	45.3	0.18	238	1.088	2.030
		520	−0.17	2.2	0.25	48.2	0.03	93	1.044	2.010
(**1**)$_3$Ga	MeOH	380	0.28	237					1.050	2.020

[a] A sum of exponentials $\sum_i (a_i \exp(-\lambda_i t))$ was used for fitting the fluorescence decays. The values for χ^2 and the Durbin−Watson parameter are also indicated. All decays gave satisfactory weighted deviation curves and autocorrelation functions.

was observed that the value of I_E/I_M for (**1**)$_3$Ga gradually decreased when the volume amount of methanol was incremented in acetonitrile, an isoemissive point being observed at ca. 420 nm.

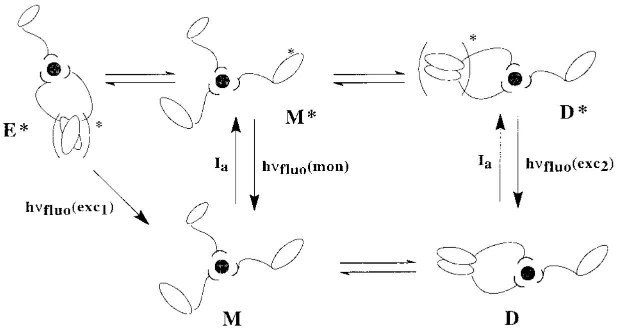
The dependence of the fluorescence spectrum on excitation wavelength was also observed in the CH_3CN/CH_3OH (90/10 v/v) solvent system as in neat acetonitrile, with an increase of the value of I_E/I_M for (**1**)$_3$Ga being recorded when the excitation wavelength was increased from 335 to 350 nm. The response qualitatively matched that previously reported for (**1**)$_3$Ga in acetonitrile solution (Table 4). In the mixed solvent system, the extent of pyrene fluorescence quenching in (**1**)$_3$Fe was intermediate between methanol and acetonitrile, which allowed us to appreciate the effect of varying the excitation wavelength as for (**1**)$_3$Ga. Notably, the fluorescence quantum yield of (**1**)$_3$Fe was observed to decrease significantly when the excitation wavelength was scanned from 335 to 350 nm. Indeed, when the excitation wavelength was set at 350 nm, the Φ_F value was about 65% of that obtained at 340 nm.

(c) Low-Temperature Luminescence Spectroscopy. Fluorescence and phosphorescence spectra were performed in a methylcyclohexane glass at 77 K. Freezing of a methylcyclohexane solution of (**1**)$_3$Ga did not lead to a significant modification of the shape of the fluorescence emission spectrum relative to the fluid solution; an intense excimer emission was still detected. The typical phosphorescence emission of the pyrene chromophore in this chelate was detected at lower energies (0−0 transition at ca. 598 nm) similar to those of 1-EtPy and free **1**. Noticeably, the phosphorescence lifetime of (**1**)$_3$Ga (ca. 370 ms) was found to be of the same order of magnitude as that measured for free **1**.

In the case of the iron complexes, neither fluorescence nor phosphorescence were detected under the same conditions.

Single-Photon Counting Experiments. Fluorescence emission decays were recorded for 1-EtPy, **1**, and (**1**)$_3$Ga in acetonitrile at room temperature. Pure monoexponential decays giving a lifetime of about 200 ns were obtained for both monochromophoric compounds. With (**1**)$_3$Ga, the decays on both monomer and excimer parts were deconvoluted by a sum of three exponential terms (Table 5), indicating the occurrence of several kinetically distinguishable species in the excited state. The values of the decay times in the excimer fluorescence response function of (**1**)$_3$Ga were in agreement with those determined for other bispyrenyl compounds.[26,27,43] Specifically, a short, rising component, corresponding to the growth of excimer emission, and two longer decay parameters, corresponding to the emission of two sets of excimers,[44] were observed in the excimer time-resolved profile.[23,25] The sum of the exponential prefactors deviated from zero, which also corroborated our previous observation that the excimer-like emission in (**1**)$_3$Ga originated from ground-state preassociated pyrenes.

Scheme 4. Kinetic Scheme Proposed for (**1**)$_3$Ga in Acetonitrile[a]



[a] M and D represent the ground-state conformers of the complex, with D corresponding to those species in which two pyrene nuclei are preassociated. M* and D* are the corresponding excited species and E* represents the pool of excimers that are not preformed in the ground state. For the sake of clarity, the involvement of fac and trans isomeric species is not taken in account (see text).

In contrast to literature data on classical bispyrenes,[26,27,43] the monomer and the excimer response functions for (**1**)$_3$Ga were not exactly described by the same set of decay parameters. A long-lived component (238 ns), resembling that of the reference compound, was present in the monomer function but not in the excimer function. This overlapping emissive contribution from a nonperturbed chromophore to the monomer-like fluorescence emission was attributed to an excited mer isomeric form in which the electronic excitation would be located on the type b pyrene moiety (Scheme 3). This excited monomeric pyrene would remain insulated during its lifetime. In methanol, consistent with the steady-state fluorescence behavior, the kinetics is switched toward a single-exponential function (ca. 237 ns) similar to that of the reference compound, 1-EtPy.

Discussion

These results, taken together, lead to some important conclusions concerning the photophysical behavior of both gallium and iron complexes of ligand **1**.

The comparison of our spectroscopic results with literature data led us to propose a kinetic scheme (Scheme 4) that outlines the photophysics of (**1**)$_3$Ga in acetonitrile solution. This complex exists as two interconverting geometric isomers in solution (Scheme 3). For the sake of simplicity, they are represented by a single entity, M or D, depending on the intramoleculer aggregation state of the pyrene chromophores in the ground state. D represents those complexes that bear two intramolecularly preassociated pyrene moieties. Moreover, we have only considered the sets of compounds in which the primarily excited pyrene chromophore experiences a cis rela-

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(43) Reynders, P.; Dreeskamp, H.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1987**, *91*, 3982−3992. Zachariasse, K. A.; Busse, R.; Duveneck, G.; Kühnle, W. *J. Photochem.* **1985**, *28*, 237−253.

(44) This feature is typical of 1,*n*-bis(1-pyrenyl)alkanes, which are known to give rise to symmetrical and asymmetrical excimer geometries with respect to the relative orientation of the pyrene moieties. The symmetrical excimer, characterized by a full overlap, is usually long-lived relative to the asymmetrical one.[23,43]

tionship with another pyrene moiety (type a chromophore). From fluorescence decay measurements, electronic excitation of a type b pyrene (in the mer isomer) gives rise to monomer-like emission only. Consistent with the behavior of published bichromophoric systems,[23,25−27] excimer emission in (**1**)$_3$Ga was observed to originate to a great extent from direct excitation of the preassociated species, D. Furthermore, as typically observed with bichromophoric compounds that incorporate nonsymmetrically substituted pyrenes halves, that is, 1-substituted pyrenes, single photon counting data for (**1**)$_3$Ga indicate the formation of two sets of excimers,[23,25,43,44] represented by E* ("dynamic excimer") and D* ("static excimer"), irrespective of their symmetrical or asymmetrical structure (Scheme 4).[44]

In the presence of methanol, the steady-state and time-dependent fluorescence emission properties of (**1**)$_3$Ga are considerably altered, indicating a simplification of the kinetics toward the occurrence of a single excited monomer-like species, M*. Actually, it has been proposed that solvation of electrically neutral complexes with H-donor organic solvents could lead to the formation of outer-sphere complexes, which as a result would considerably affect the structure and physicochemical properties of coordination complexes in solution.[45]

The addition of methanol molecules to the outer sphere of (**1**)$_3$Ga through hydrogen bond formation with the tris(hydroxamato) units in the ground state can modify the conformational properties of the complex in mainly two ways: (i) ground-state intramolecular interactions between pyrene chromophores could be hindered and (ii) excited-state conformational dynamics of the pendant ligand chains could be less favorable for excimer formation. The former point is supported by the fact that no bathochromic shift of the pyrene absorption bands was noted in methanol relative to acetonitrile. On these bases, M would no longer give rise to D in the ground state, and additionally, the formation of D* and E* would not be detected in the excited state. Finally, the trichromophoric system would behave in methanol as a set of three independent, nonperturbed pyrene nuclei whose photophysical properties would tend toward that of a single chromophore such as 1-EtPy. In that connection, it should be mentioned that the excimer emission intensity in *N*-acetyl-bis(pyrenylalanine)-methylester was found to be very dependent on the tendency of protic solvents to interact with the peptide functions through hydrogen bonding.[46] Similarly, we also reported the quenching of the amine−anthracene exciplex emission in an anthraceno-cryptand due to the ground-state interaction of methanol molecules with the nitrogen sites.[47] Also, the fluorescence spectrum of the europium(III) complex of a tetranaphthylamide ligand was found to be solvent dependent.[18]

A question arises as to whether the kinetic scheme proposed for (**1**)$_3$Ga can also account for the photophysical properties of the iron complex, (**1**)$_3$Fe. Ga^{3+} and Fe^{3+} metal cations are known to present a similar chemistry, with Ga^{3+} ($3d^{10}$) often being used instead of Fe^{3+} (high-spin $3d^5$) in siderophore studies.[48] Indeed, these cations have the same charge and are within 0.025 Å in ionic radius. They are structurally very close and give isomorphous complexes, especially with hydroxamate ligands.[36] Moreover, both cations lack ligand field stabilization and were shown to form kinetically labile chelates with respect to isomerization and racemization processes.[37] From these considerations, it is reasonable to assume that both chelates, (**1**)$_3$Ga and (**1**)$_3$Fe, display very close stereochemical characteristics and conformational dynamics. In other words, (**1**)$_3$Fe is postulated to exhibit the same capability as (**1**)$_3$Ga to form both monomer and excimer species in the excited state. In the fluorescence emission spectrum of (**1**)$_3$Fe in acetonitrile, an excimer contribution has effectively been detected. Particularly, intramolecular preassociation of pyrene dimers in the ground state is also to be invoked in the case of (**1**)$_3$Fe, according to similar UV-vis absorption features noticed for both chelates (Table 2). These observations lead us to propose that (**1**)$_3$Fe, similarly to (**1**)$_3$Ga, occurs in the excited state as an interconverting mixture of species M*, E*, and D*. Once formed, the last two would be more sensitive to the quenching effect of iron(III) than is the pyrene monomer M*. In the presence of methanol, the fluorescence intensity of (**1**)$_3$Fe was indeed observed to increase under the conditions where the excimer emission in (**1**)$_3$Ga decreased. Furthermore, excitation at 350 nm of the red-absorbing preassociated D species resulted in a higher quenching efficiency than excitation at $\lambda_{exc} < 340$ nm, where M entities predominantly absorb.

These considerations now lead us to examine an important point, the mechanism of the quenching process. Quenching of the pyrene excited singlet state by transition-metal ions has been the subject of several investigations.[1−3,9] It seems from these studies that paramagnetically induced and heavy-atom-assisted intersystem crossing due to the presence of the metal does not contribute significantly to the quenching of the pyrene fluorescence. The latter effect can be ruled out since it is not observed in the case of (**1**)$_3$Ga, the gallium element being heavier than iron. This is confirmed by phosphorescence emission spectroscopy. Photoinduced electron transfer (PET) and/or electronic energy transfer (EET) should therefore be considered as the most probable mechanisms.

Pyrene-to-iron(III) PET is thermodynamically favorable whether it is considered to take place from the monomer or the excimer-like excited singlet state.[49] Yet, the fluorescence of the pyrene monomer is not readily quenched in the case of (**1**)$_3$Fe in methanol solution. Moreover, quenching of the pyrene excimer by donors or acceptors has been shown to proceed less efficiently than that of the pyrene monomer.[28] Finally, spectrofluorimetric experiments carried out in frozen glass solution at low temperature (77 K) showed the absence of any emission from a solution of (**1**)$_3$Fe, which would suggest the occurrence of an EET process[12b,50] to account for the observed pyrene fluorescence quenching.[51] In (**1**)$_3$Fe, both monomer and excimer excited singlet states of the pyrene chromophore, on one hand, and the ligand-to-metal charge-transfer states, on the other hand, are likely to act as energy donors and acceptors, respectively.

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(45) For a review, see: Zamaraev, K. *New J. Chem.* **1994**, *18*, 3−18.

(46) Goedeweeck, R.; De Schryver, F. C. *Photochem. Photobiol.* **1984**, *39*, 515−520.

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(49) $\Delta G_{PET} = -E_{0-0} - (E^0_{red}(Fe^{III}/Fe^{II}) - E^0_{ox}(pyrene^{\bullet+}/pyrene)) = -0.92$ eV, where E_{0-0} corresponds to the energy of the monomer emission band ($E_{0-0} = 3.30$ eV). $E^0_{red}(Fe^{III}/Fe^{II})$ and $E^0_{ox}(pyrene^{\bullet+}/pyrene)$ have been determined from the voltammetric measurements in acetonitrile solution. ΔG_{PET} should be less negative in the case of the pyrene excimer owing to the lower value of E_{0-0} (the electronic stabilization of the pyrene excimer[25] is ca. $\Delta H = 10$ kcal mol^{-1}) and to less facile[28] electron transfer from the excimer singlet state than from the monomer.

(50) Chen, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 5520−5524.

(51) In recent studies (see refs 5−7 in ref 50), donor−acceptor systems have been designed which possess large driving forces (typically much larger than 1 eV) for PET. As a result, the inhibition to electron transfer in a rigid medium caused by the loss of solvent dipole reorientation can be overcome. This might not be the case for (**1**)$_3$Fe, as the PET reaction is anticipated to not be as favored thermodynamically.[49]

Our experimental results indicate that electronic energy transfer could occur from excimer species preferentially. It should be mentioned that, whatever the kind of EET mechanism (Förster's dipole−dipole or Dexter's exchange mechanism), theory predicts proportionality of the energy transfer rate and the spectral overlap between donor emission and acceptor absorption. In both cases, the value of the spectral overlap was estimated to be higher in the case of the pyrene excimer than in the case of the monomer as donor. Similar conclusions were drawn from the study of multichromophoric cyclodextrins that form inclusion complexes with a merocyanine dye.[52]

Finally, the presence of the iron(III)-centered low-energy levels, $^4T_{1g}$ and $^4T_{2g}$, which were shown to play an important role in the deactivation of the pyrene triplet state through electronic energy transfer, could account for the quenching of the pyrene phosphorescence in (**1**)$_3$Fe at low temperature.[53]

Conclusion

To our knowledge, (**1**)$_3$Ga represents the first example of an excimer-forming trichromophoric system based on the metal-assisted self-assembly of pyrene-appended ligand molecules. In this compound, the gallium(III) center plays the role of an inert and transparent linker from the electrochemical and photophysical standpoints. Excimer formation between pyrene termini emerges as a versatile means to investigate the conformational dynamics of the chelate. In the case of (**1**)$_3$Fe, the ferric tether acts as an extra chromophore that quenches the pyrene singlet state likely via electronic energy transfer (EET). From the solvent-dependent fluorescence studies, it is inferred that the efficiency of iron(III)-induced quenching is triggered by ground-state and excited-state intramolecular dimerization of the pyrene nuclei. This work could open the way toward the utilization of excimer formation (or disappearance) as a functional mechanism capable of switching on/off photoinduced electron or electronic energy transfer processes prevailing in multicomponent systems, which could be of interest for the conception of supramolecular switching devices. Moreover, fluorescently labeled ferric complexes whose photophysical properties are modulated by specific ground-state interactions between the environmental medium and the metallic center are desirable as valuable sensitive probes to investigate the mechanisms of iron transport and release by siderophores in biological media.

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