

Photoactive pyrene-containing receptors for transition-metal ions*

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Abstract: Photoresponsive molecular receptors based on the photophysical properties of the pyrene chromophore were designed to exhibit tunable fluorescence emission upon binding of transition-metal ions.

INTRODUCTION

The design of supramolecular systems operating signal transduction upon an external stimulus occupies a central place in the development of functional molecular-scale devices for information processing, storage, and transport [1]. Photosensitive receptors, combining an aromatic fluorophore moiety and a recognition site, were shown to act as tunable, fluorogenic multicomponent systems whose fluorescence output is highly sensitive to chemical inputs, such as proton or metal ion concentration jumps [2,3]. Of the many promising applications of these systems, chemosensing, optical switching, or molecular computation are among the most exciting, which motivates the tremendously increasing scientific activity in the field [1–4]. In this contribution, we report the approach we developed in our group concerning supramolecular receptors specifically designed to display fluorescence tunability upon binding of transition-metal ions. The first part of the paper is devoted to ligands based on the hydroxamic acid functionality, which were shown to act as siderophore-like chelators allowing the detection of trivalent metal ions such as iron(III). The second part of this account deals with pyrene-2,2'-bipyridine (bpy) systems, which are well suited for the complexation of divalent transition-metal ions. Interestingly, they enable the construction of polychromophoric pyrene-Ru(II) structures with outstanding photophysical properties. In this case, the presence of the pyrene chromophore allows a fine tuning of the emission features of the luminophoric metal center.

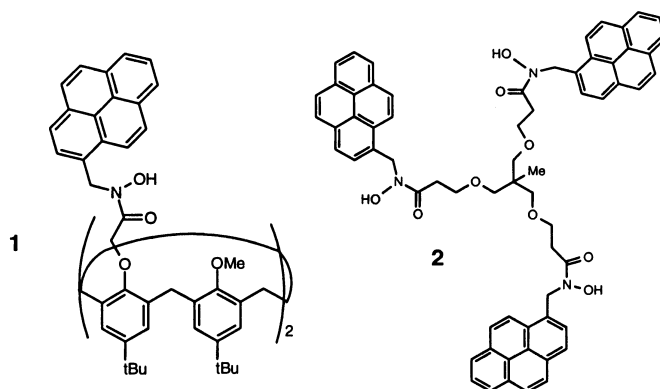
PYRENE-CONTAINING HYDROXAMIC ACID LIGANDS

Trishydroxamate siderophores are naturally occurring and synthetic ion chelators that exhibit a high affinity toward acidic metal cations, with a dramatically marked selectivity for Fe³⁺. As a design strategy based on a biomimetic approach, the incorporation of siderophore-like complexing scaffolds in light-sensitive molecular structures was anticipated to provide systems with improved sensitivity and selectivity. We focused our attention on bi- and trichromophoric systems in which two or three pyrene nuclei, respectively, were attached to a central core via conformationally flexible complexing arms. We thus envisaged the bispyrenyl calix[4]arene-based receptor, **1**, incorporating two hydroxamic acid functionalities, and the tripod-shaped trishydroxamate, **2**, as two interesting prototype structures [5–7]. Ligands **1** and **2** both exhibited in solution a dual fluorescence emission spectrum composed of

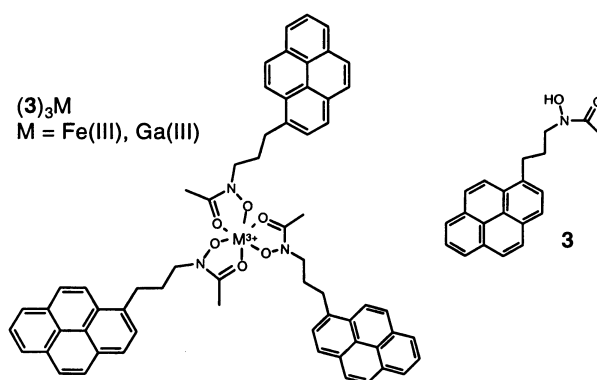
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monomer and excimer contributions, the latter resulting from intramolecular interactions between pyrene nuclei in the excited state. Particularly, ligand **1** was shown to exist in CDCl_3 solution at room temperature as a mixture of mainly two conformers, namely the cone and partial-cone species (partial-cone/cone ratio ca. 57/43). Addition of transition-metal ions (Fe^{3+} , Cu^{2+} , Ni^{2+}) induced a dramatic quenching of the fluorescence emission in **1** and **2**, which corresponds to a fluorescence ON/OFF switching transduction mechanism. Furthermore, selective optical discrimination between competing metals in aqueous methanol solution could be achieved by varying proton concentration, the proton-assisted metal decomplexation process being accompanied by a fluorescence intensity enhancement. Besides the effect of nonquenching metal ions such as Ga(III) cation on the fluorescence behavior of **2** was found to affect the value of the excimer-to-monomer fluorescence intensity ratio in the fluorescence spectrum of compound **2**.



Two trichromophoric systems, $(\mathbf{3})_3\text{Ga}$ and $(\mathbf{3})_3\text{Fe}$, were obtained by the self-assembly of a monohydroxamic pyrenyl derivative, **3**, using gallium(III) or iron(III) as metal templates, respectively [8,9].

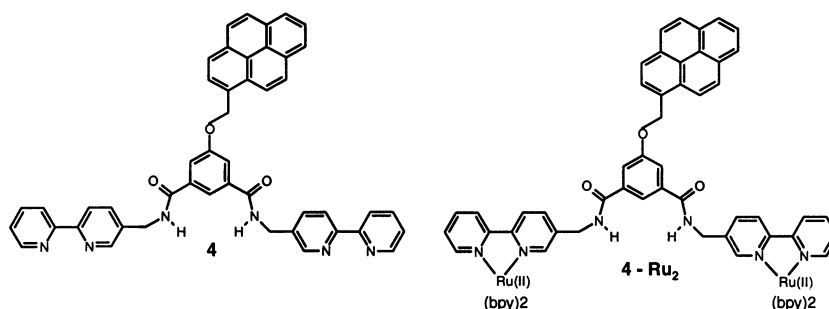


The trivalent gallium metal cation was demonstrated to play the role of an inert and transparent linker, whereas the ferric center acted additionally as an extra chromophore prone to deactivate the pyrene singlet state. As a result, $(\mathbf{3})_3\text{Ga}$ showed an intense pyrene excimer fluorescence emission in acetonitrile, while the fluorescence of the iron(III) analogue, $(\mathbf{3})_3\text{Fe}$, was subject to a nearly quantitative quenching. Interestingly, this effect was found to be strongly dependent on the nature of the solvent. Indeed, in methanol, both systems were observed to be highly fluorescent, their fluorescence spectrum being characteristic of the monomeric emission of the nonperturbed pyrene chromophore. Actually, it was found that the Fe(III)-induced quenching process was triggered by the solvent-dependent intramolecular dimerization state of the pyrene moieties, the pyrene-to-iron energy transfer taking place more readily from the excimer singlet state as donor than from the locally-excited state. This result illustrat-

ed the utilization of excimer formation (or disappearance) as a functional mechanism capable of switching photoinduced electron or electronic energy transfer processes prevailing in multicomponent systems, which could be of interest for the conception of supramolecular switching devices.

PYRENE-CONTAINING BIPYRIDINE LIGANDS

Bipyridyl ligands represent versatile building blocks on which to base the design of supramolecular architectures. They allow the formation of complexes with a wide range of metal ions leading to a variety of optical properties, such as the appearance of intense metal-to-ligand charge transfer (MLCT). Particularly, we were interested in systems combining ruthenium(II) tris(bpy) and pyrene chromophores. Indeed, recent work has shown that among the number of $\text{Ru}(\text{bpy})_3^{2+}$ -incorporating dyads bearing a pendant polycyclic aromatic moiety, those based on the pyrene chromophore were of particular interest due to the quasi isoenergetic position of the triplet excited state of the metal complex and the pyrene. This feature is unique as it allows reversible triplet electronic energy transfer to take place efficiently between the two partners, the result of which being an extraordinarily extension of the triplet lifetime of the $\text{Ru}(\text{bpy})_3^{2+}$ chromophore [10]. Such systems could be of great interest in many applications in which excited states with long-lived luminescence are desirable, such as solar energy conversion or oxygen sensing.



Among the series of molecules we synthesized and investigated, the triad ditopic ligand, **4**, consisted of a pyrene-labelled bis-2,2'-bipyridine molecular system in which the fluorophore and ligand components are held via the 5-hydroxy-isophthalic core [11]. Compound **4** allowed the preparation of the binuclear ruthenium complex **4-Ru₂**, which represents the first example of a trichromophoric system in which two Ru(II) tris(bpy) moieties are covalently linked to one pyrene chromophore [12]. The UV-visible spectrum of **4-Ru₂** was composed of the characteristic absorption bands of both the pyrene and coordination center, the molar absorption coefficient for the MLCT band being $20\,700\text{ M}^{-1}\text{ cm}^{-1}$ at 452 nm. Following excitation into either the $^1\text{L}_a$ band of pyrene or the MLCT band of the metallic part, the typical steady-state emission spectrum of the Ru(II) tris(bpy) chromophore was observed at 610 nm. However, the luminescence lifetime value for **4-Ru₂**, recorded at room temperature in degassed acetonitrile, was found to be about 8 μs , which dramatically exceeded that of the $\text{Ru}(\text{bpy})_3^{2+}$ species. Furthermore, the binuclear ruthenium complex of the reference ligand bearing a propyl substituent instead of the pyrenyl group was found to display a lifetime of 820 ns, which indicated the absence of interactions between the two metal centers in the excited state. Therefore, the 10-fold lifetime extension was attributed to reversible triplet energy transfer between the pyrene triplet state and the $^3\text{MLCT}$ state. Further investigation using time-resolved absorption and emission spectroscopies should provide valuable insights into the mechanism of excited-state energy redistribution in this trichromophoric assembly. The design of polymeric systems incorporating alternating pyrene and $\text{Ru}(\text{bpy})_3^{2+}$ components may lead to the generation of new light-harvesting materials.

CONCLUDING REMARKS

This account was intended to describe the behavior of a selected series of systems synthesized in our group and thereby to illustrate the versatility of pyrene-incorporating ligand structures. Indeed, they are shown to exhibit a variety of photophysical responses that could be exploited in many important applications. Future investigations are directed to further improve the performances of these systems. Particularly, special emphasis is given to the design of conjugated dyads in which the bpy and pyrene termini are connected by a conjugated bridge [13]. New systems have been synthesized, and they exhibit remarkable photophysical properties sensitive to the nature of the conjugated bridge. Particularly, some of these conjugated compounds appear as good candidates for tunable two-photon excited fluorescence emission.

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