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Excited state properties of $Ir^{III}(phpy)_2$(naphthylalaninate) with phpyH = 2-phenylpyridine Energy transfer and luminescence

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Abstract

The complex $Ir^{III}(phpy)_2$(nala) with phpyH = 2-phenylpyridine and nalaH = 3-(2-naphthyl)alanine was prepared and characterized. The electronic spectrum of the complex shows long-wavelength absorptions which are attributed to the $Ir^{III}(phpy)_2$ chromophore. The lowest-energy excited state is a metal-to-ligand charge transfer (MLCT) triplet which is emissive under ambient conditions. Excitation of the naphthyl chromophore at shorter wavelength is followed by an efficient energy transfer to the $Ir^{III}(phpy)_2$ fragment.

Keywords: Electronic spectra; Luminescence; Iridium complexes; Amino acids

1. Introduction

Nonnatural amino acids have attracted much recent attention. They are used for the de novo design of proteins and as probes for the structure and function of proteins in general [1–3]. Suitable labels can be incorporated in such unnatural amino acids in order to provide a simple analytical access. In particular, fluorophores are useful probes for the examination of the environment of labeled amino acids [4–6]. This concept may be extended to metallo proteins. As a suitable model we selected the complex $Ir^{III}(phpy)_2$(nala) with phpyH = 2-phenylpyridine and nalaH = 3-(2-naphthyl)alanine for the present study.

This choice was based on the following considerations. The nonnatural amino acid nalaH contains the naphthyl substituent as well-known fluorophore. Moreover, in analogy to various other complexes of the type $Ir^{III}(phpy)_2$(aa) [7] with aaH = amino acid, our target compound should be easily synthesized. These complexes show a luminescence [7] which certainly originates from a $Ir^{III} \rightarrow phpy^-$ metal-to-ligand charge transfer (MLCT) state [8–10]. Accordingly, the complex $Ir(phpy)_2$(nala) has available two emissive excited states, the naphthyl intraligand (IL) state and the MLCT state. However, both luminophores are separated by electronically insulating methylene spacers. The consequences are not obvious. Both excited states could show independent emissions. As an alternative only the lower-energy state may be emissive while the higher-energy state could undergo energy transfer to the emissive state. Irrespective of the outcome, the observations of the present study should be of general interest in the area of metallo protein chemistry.

2. Experimental

2.1. Materials

Solvents used for spectroscopic measurements were of spectrograde quality. The amino acids 3-(2-naphthyl)alanine (nalaH) and glycine (glyH) were commercially available from Acros and used without further purification. $Ir(phpy)_2$(gly) [7] and $[Ir(phpy)_2Cl]_2$ [11] were prepared according to literature procedures.

$Ir(phpy)_2$(nala) was obtained by the following procedure: nalaH (0.108 g, 0.5 mmol) and potassium *t*-butoxide (0.056 g, 0.5 mmol) were dissolved in 50 ml of warm ethanol. This solution was added to a solution of $[Ir(phpy)_2Cl]_2$ (0.268 g, 0.25 mmol) in 50 ml of acetonitrile. This mixture was heated under reflux for 10 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2/CH_3CN (1:1) and the solution filtered. Upon addition of ether to the filtrate a yellow powder precipitated. It was collected by filtration, washed with ether and dried over

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silica gel. Yield of Ir(phpy)$_2$(nala)·2H$_2$O: 0.330 g (87%). Anal. Calcd (Found): C, 55.99 (56.52); H, 4.03 (4.24); N, 5.60 (5.63). MS(CH$_2$Cl$_2$/CH$_3$OH), +ESI, *m*/*z*: 716; −ESI *m*/*z*: 714.

2.2. Instrumentation

Absorption spectra were measured with a Shimadzu UV-2100 spectrometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. Absolute emission quantum yields were determined by comparison of the integrated emission intensity with that of fluorescein in 0.1 M NaOH [12] under identical conditions such as exciting wavelength, optical density and apparatus parameters. Mass spectra were obtained using a TSQ 7000 Finnigan Thermoquest mass spectrometer.

3. Results

The desired compound was prepared according to the synthesis of other complexes of the same type [7]:

$$\tfrac{1}{2}[\mathrm{Ir(phpy)_2Cl}]_2 + \mathrm{K(nala)} \rightarrow \mathrm{Ir(phpy)_2(nala)} + \mathrm{KCl} \quad (1)$$

The composition of Ir(phpy)$_2$(nala) was confirmed by elemental analysis and mass spectroscopy. The +ESI spectrum shows a peak which corresponds to the addition of one proton to the complex. Moreover, [Ir(phpy)$_2$]$^+$ was observed as a fragmentation product. The −ESI spectrum displays a peak of the deprotonated complex. As a reference compound Ir(phpy)$_2$(gly) [7] was also prepared.

The absorption and emission spectra of nala (Fig. 1) were measured in CH$_3$CN/C$_2$H$_5$OH (1:1) as the solvent which contained a small amount of ammonia to increase the solubility of nala. The spectra were not affected by the presence of ammonia. The absorption spectrum shows a maximum

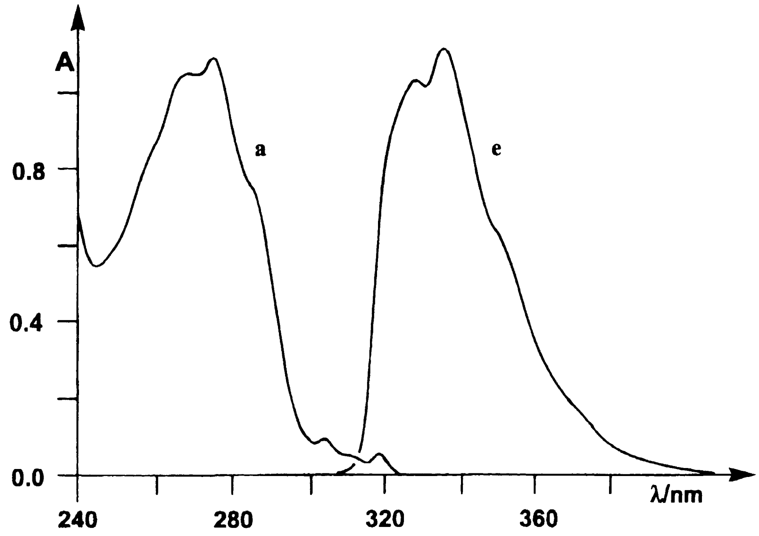

Fig. 1. Electronic absorption (a) and emission (e) spectrum of 2.34 × 10^{-4} M nala in a mixture of CH$_3$CN/C$_2$H$_5$OH (1:1) at room temperature, 1 cm cell. Emission: λ_{exc} = 275 nm, intensity in arbitrary units.

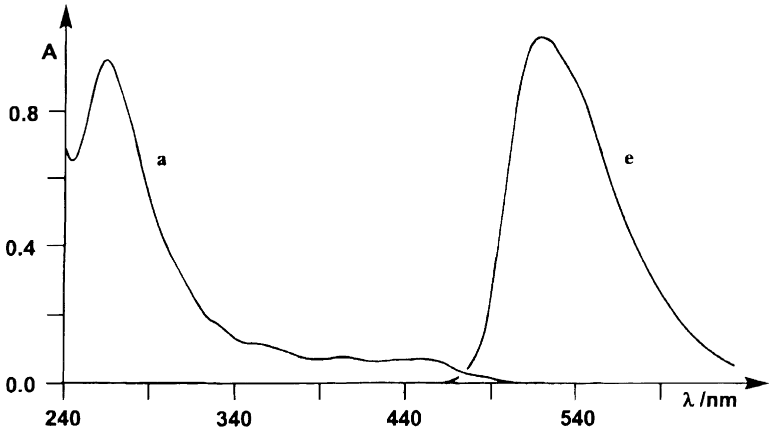

Fig. 2. Electronic absorption (a) and emission (e) spectrum of 2.23 × 10^{-5} M Ir(phpy)$_2$(nala) in CH$_2$Cl$_2$ at room temperature, 1 cm cell. Emission: λ_{exc} = 400 nm, intensity in arbitrary units.

at $\lambda = 275\,\text{nm}$ ($\varepsilon = 4680\,\text{M}^{-1}\,\text{cm}^{-1}$) while the emission appears at $\lambda_{\text{max}} = 336\,\text{nm}$.

The absorption spectrum of Ir(phpy)$_2$(nala) (Fig. 2) exhibits bands at $\lambda_{\text{max}} = 449\,\text{nm}$ (3270), 402 (3740), 350 (sh, 5490), and 265 (42 860). The emission spectrum shows a single band (Fig. 2) at $\lambda_{\text{max}} = 517\,\text{nm}$. The quantum yield of emission is $\phi = 0.09$ at $\lambda_{\text{exc}} = 400\,\text{nm}$ in argon-saturated solutions. The emission is partially quenched by oxygen.

The absorption spectrum of Ir(phpy)$_2$(gly) is very similar to that of Ir(phpy)$_2$(nala). However, the 265 nm absorption of Ir(phpy)$_2$(gly) is less intense ($\varepsilon = 37720$) since the naphthyl chromophore is missing. The emission quantum yield of Ir(phpy)$_2$(gly) is the same as that of Ir(phpy)$_2$(nala) irrespective of the exciting wavelength ($\lambda_{\text{exc}} = 400$ and 275 nm). The emission of Ir(phpy)$_2$(gly) is not quenched upon addition of naphthaline to solutions of the complex.

4. Discussion

The electronic spectra of nalaH resemble those of β-methylnaphthaline [13]. Since the amino and carboxyl substituents of nala are connected to the naphthyl chromophore by electronically insulating methylene groups, it is not surprising that the electronic spectrum of the naphthyl group is not affected by the amino and carboxylic substituents. The lowest-energy transitions are all of the $\pi\pi^*$ type. The emission is a fluorescence [13].

The longest-wavelength absorptions of Ir(phpy)$_2$(gly) and Ir(phpy)$_2$(nala) are nearly identical and similar to those of Ir(phpy)$_3$ [14,15] and Ir(phpy)$_2$(acetylacetonate) [16] and other Ir$^{\text{III}}$(phpy) complexes [8–10]. It follows that the spectra of Ir(phpy)$_2$(aa) are determined by the Ir$^{\text{III}}$(phpy) chromophore while the deprotonated amino acids are only spectator ligands. The lowest-energy transitions are then of the MLCT type [8–10]. The emission of Ir(phpy)$_2$(aa) originates also from the lowest-energy MLCT triplet in analogy to other Ir$^{\text{III}}$(phpy) complexes which display this phosphorescence at comparable energies [8–10].

Although the naphthyl group of Ir(phpy)$_2$(nala) is a separate chromophore of the complex, excited state interactions with the Ir(phpy)$_2$ moiety might take place. Since the phosphorescence quantum yield of Ir(phpy)$_2$(aa) does not decrease if gly is replaced by nala, the naphthyl group is apparently not able to quench the emission of the MLCT triplet by energy or electron transfer. However, this may not be caused the insulating effect of the spacer, but could simply be prevented for thermodynamic reasons. This assumption is supported by the observation that the emission of Ir(phpy)$_2$(gly) is also not quenched by naphthaline in an intermolecular energy or electron transfer process. The energy of the emitting triplet of Ir$^{\text{III}}$(phpy) complexes amounts approximately to 2.5 eV [8,14,17] while the $\pi\pi^*$ triplet of the naphthaline chromophore requires 2.64 eV [18]. Energy transfer from Ir(phpy)$_2$(nala) to naphthaline is thus not favored. Moreover, while Ir$^{\text{III}}$(phpy) complexes are strong excited state reductants (−1.7 V) [8,14,17] their potential is not sufficient to reduce naphthalene (−2.53 V) [19].

On the other hand, light absorption by the naphthalene chromophore of Ir(phpy)$_2$(nala) is apparently followed by efficient energy transfer to the Ir(phpy)$_2$ moiety. At $\lambda_{\text{exc}} = 275\,\text{nm}$ at least 10% of the light is absorbed by the naphthalene chromophore. However, its fluorescence is absent. In addition, the luminescence quantum yields of Ir(phpy)$_2$(nala) and Ir(phpy)$_2$(gly) at $\lambda_{\text{exc}} = 275\,\text{nm}$ are the same. Accordingly, the light absorbed by the naphthalene substituent appears as emission of the Ir(phpy)$_2$ fragment.

In summary, in the complex Ir$^{\text{III}}$(phpy)$_2$(nala) the excitation of the naphthalene substituent which is an independent chromophore of the complex leads to a subsequent energy transfer to the emitting MLCT triplet of the Ir(phpy)$_2$ moiety.

Acknowledgements

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