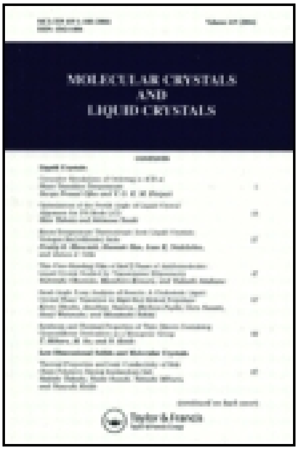


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Enhanced Fluorescence of Ni(II) Complex Compounds in the Presence of DNA Components

Laura Bancu [a], Nicoleta Badea [a], Rodica Nita [a] & Aurelia Meghea [a]

[a] Faculty of Applied Chemistry and Material Science, Department of Applied Physical Chemistry, 'Politehnica' University of Bucharest, Bucharest, Romania

To cite this article: Laura Bancu, Nicoleta Badea, Rodica Nita & Aurelia Meghea (2008): Enhanced Fluorescence of Ni(II) Complex Compounds in the Presence of DNA Components, Molecular Crystals and Liquid Crystals, 486:1, 230/[1272]-238/[1280]

To link to this article: http://dx.doi.org/10.1080/15421400801921595

Mol. Cryst. Liq. Cryst., Vol. 486, pp. 230/[1272]–238/[1280], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801921595

Enhanced Fluorescence of Ni(II) Complex Compounds in the Presence of DNA Components

Laura Bancu, Nicoleta Badea, Rodica Nita, and Aurelia Meghea
Faculty of Applied Chemistry and Material Science, Department of Applied Physical Chemistry, 'Politehnica' University of Bucharest, Bucharest, Romania

DNA-mediated charge transfer currently attracts considerable interest because of its relevance for molecular electronics. In this work the fluorescence behavior of the ligand-ligand charge transfer complexes Ni(diimine)(thiol)$_2$, where diimine = 2,2′-bipiridine and its 4,4′ derivatives and thiol = thioaminoacid cisteine and its methyl esther were studied in the presence of DNA components. Substitution of an electron withdrawing group in 4,4′ position of 2′2′-bipiridine causes red shift in the absorption spectrum. For all synthesized complex compounds it has been observed a significant increase of fluorescence emission intensity in the presence of DNA nucleobases.

Keywords: bipiridine; charge transfer; DNA nucleobases; fluorescence; Ni(II) complex compounds

INTRODUCTION

Within the research field of molecular and hybrid NLO materials, increasing attention have been paid to metal complexes, mostly of the *d*-transition elements, which offer possibilities for combination of NLO effects with other molecular electronic properties [1–4]. Since the preparation of metal complexes with NLO activity mainly depends on ligand design, the studies classify metal complexes according to their ligands, rather than their metal ions or their specific NLO properties. Compared to organic molecules, metal complexes offer a

Address correspondence to Laura Bancu, Faculty of Applied Chemistry and Material Science, Department of Applied Physical Chemistry, 'Politehnica' University of Bucharest, Polizu Str., no. 1, 011061, Bucharest, Romania. E-mail: laurabancu@yahoo.com

larger variety of structures, the possibility of high environmental stability, and a diversity of electronic properties tunable by means of the coordinated metal center. Complex compound metal centers are often engaged in π-bonding, both with organic ligating groups and (if it is the case) with other metallic centers, and they can be involved in various strongly intramolecular charge transfer processes, i.e., charge transfer metal-ligand (MLCT), ligand-metal (LMCT), ligand-ligand (LLCT) or metal-metal (MMCT). They can also participate in $\pi \rightarrow \pi^*$ electronic excitation processes.

Complex compounds of [M(diimine)(dithiol)] type, where M is a d^8 metal with a square planar geometry are known for their nonlinear optic properties [3].

Aromatic diimines, such as 2,2′-bypiridine provide a ligand-ligand charge-transfer absorption with particularly large solvatochromic shifts of complexes [5]. A wide variety of thiolates and dithiolates are known to coordinate to transition metals and several have been utilized for square-planar mixed-ligand systems [6].

In case of [M(diimine)(thiolate)$_2$] complex compounds thiolate acts as an electron donor, contributing to the HOMO orbital. Structural variations can be obtained by using various monodentate thiolates. A low-energy π^* orbital of the diimine serves as the electron-accepting orbital. Because the LUMO is localized on the diimine charge transfer may be increased by extending the conjugation length and by placing electron-withdrawing substituents further from metal center. Since the charge transfer in case of [M(diimine)(thiolate)$_2$] complex compounds is from thiolate to diimine ligand, electron accepting substituents on the diimine ligand will lower the energy of transition.

Amongst essential aminoacids, cysteine is the most frequently occurring ligand of metals in biological environment. Sulphur coordination is an important feature in metalloenzymes and the covalency and soft environment are possible prerequisites for efficient charge transfer.

Most DNA research has concentrated on gene technology, not on the novel properties such as molecular weights of over 1 billion, semiconductivity, enhancement fluorescence, and self-assembled supramolecular structure, which make DNA complexes suitable for the construction of molecular, optical, photoelectric, and electronic devices.

The aim of this article is to study the fluorescence behavior of the ligand-ligand charge transfer complexes Ni(diimine)(thiol)$_2$, where diimine = 2,2′-bipiridine and its 4,4′ derivatives and thiol = thioaminoacid cisteine and its methyl esther in the presence of DNA nucleobases.

EXPERIMENTAL

UV-VIS-NIR spectra have been recorded with a Jasco V570 spectrophotometer with reflexion device ILN-472.

For solvatochromic studies, 10^{-2} g/L DMF, CH_3CN, MeOH and H_2O solution of complex compounds have been prepared.

Fluorescence spectra have been recorded with a Jasco FP 6500 spectrofluorimeter in 200–900 nm range.

For complex compounds [M(diimine)(thiolate)$_2$], where M is Ni(II) and Zn(II), diimine is 2,2′-bypiridine (bpy), 4,4′-dicarboxilic acid 2,2′-bypiridine (dabpy), 4,4′-dimethyl 2,2′-bypiridine (Mebpy) and thiolate is cysteine (cys) or cysteine methyl ester (cysMe) the synthesis is presented elsewhere [7]. The synthesized complex compounds have been characterized by means of elemental analysis, molar conductivity and magnetic susceptibility measurements, DTA and FT-IR and UV-Vis spectrometry and a square planar coordination have been assigned.

RESULTS AND DISCUSSION

There are several factors determining the intensity of thiol → diimine charge transfer (CT). Among these, we have studied the influence of the following factors:

- metallic ion nature;
- acceptor strength;
- donor strength.

Influence of Metallic Ion

The UV-Vis spectra recorded for Zn(II) complexes present an absorption band in visible range, between 500–550 nm. As Zn(II) is a fully shielded d^{10} ion with no *d*-*d* bands or possibility of ligand to metal or metal to ligand CT bands, this band should be assigned to an intramolecular ligand to ligand CT. Zn(II) ion has a very small electron donor capacity, while Ni(II) ion has a greater oxidizing capacity, so an increasing of both the wavelength and the intensity of the charge transfer to diimine absorption band from Zn(II) complexes to Ni(II) complexes is observed (Fig. 1). This trend in wavelength follows the tendency in the second ionization potentials of metals.

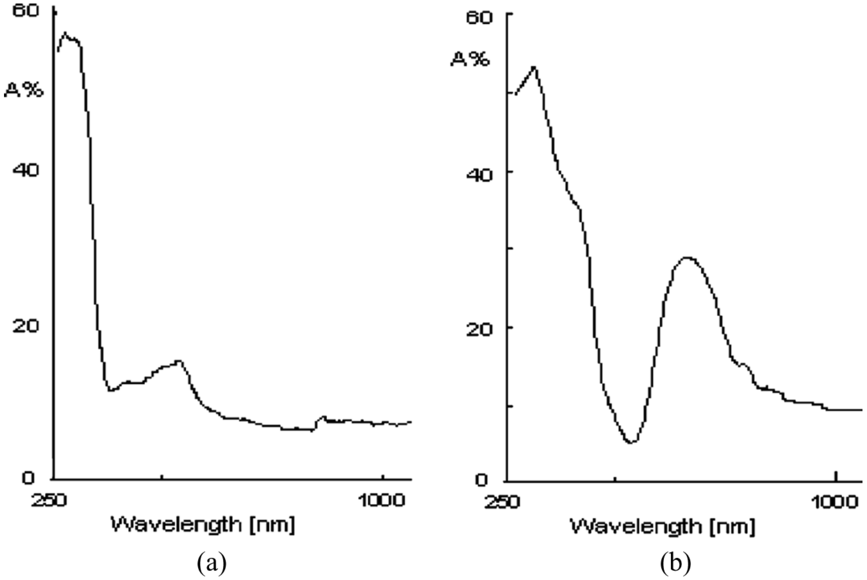


FIGURE 1 Electronic spectra of (a) [Zn(dpy)(cys)$_2$] and (b) [Ni(dpy)(cys)$_2$].

Influence of Donor

The thiolate group of thioaminoacid cysteine represents the electron donor group in these complex compounds, with a high participation to HOMO orbitals formation. By using a thiolat derivative with an electron donating group CH_3 (cysteine methyl ester) a small shift of absorption maximum to a higher wavelength is observed by comparison to complex compound with cysteine (Fig. 2).

Influence of Acceptor

The diimine represents the electron acceptor in π^* LUMO orbitals. The synthesis of a large number of substituted derivates of 2,2′-bypiridine has led to the discovery that substitution in the 4,4′-positions has a profound effect upon the stabilities, oxidation reduction potentials and color intensities of the metal complexes. The synthesis pathways of the new or already known symmetric or asymmetric derivatives of 2,2′-bipiridine, are not very facile and present low yields. The derivatization of a 2,2′-bipyridyl ligand with electron donating/withdrawing groups in the 4,4′-positions has been popular means of controlling the redox potential of transition metal bipyridil complexes. The 4,4′

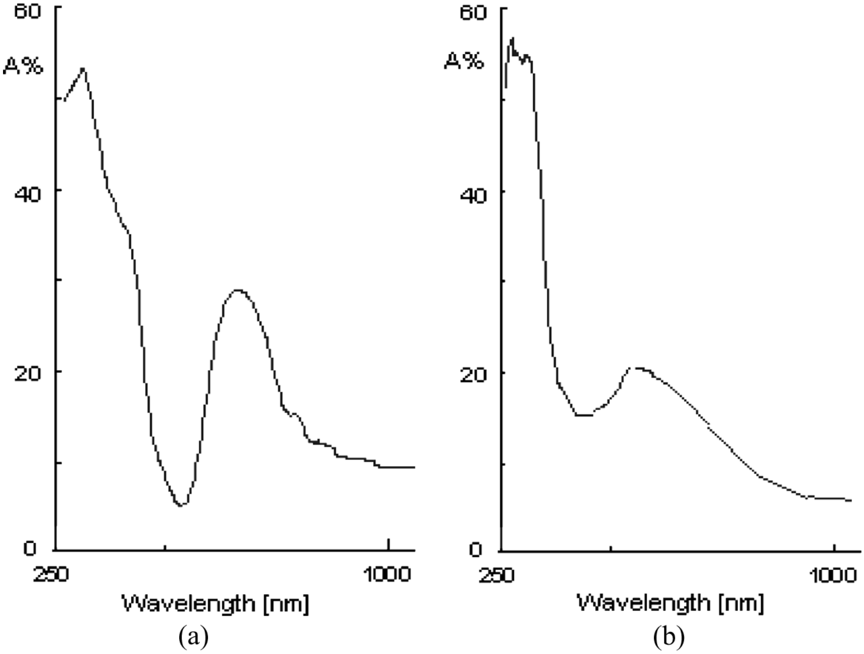


FIGURE 2 Electronic spectra of (a) [Ni(dpy)(cys)$_2$] and (b) [Ni(dpy)(cysMe)$_2$].

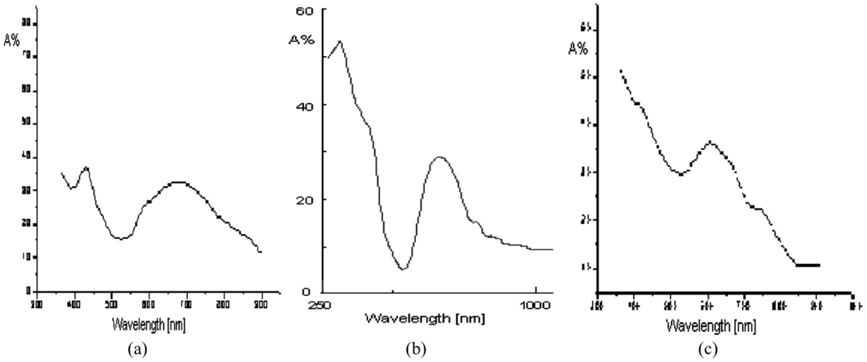
disubstitution pattern is desirable, not only because it is the synthetically simplest to prepare but also because substitution at these positions offers no steric complications on complexation.

Derivatives containing withdrawing groups (COOH) in 4,4′ position lower redox potential of 2,2′-bypiridine, becoming better electron acceptor, which lead to a shift to a higher wavelength of CT band by comparison to complex compound containing 2,2′-bypiridine (Fig. 3a).

In case of derivatives containing donating group (CH_3) is observed a decreasing of wavelength and intensity of CT band from spectrum of complexes containing 2,2′-bypiridine to complexes containing 4,4′-dimethyl 2,2′-bypiridine (Fig. 3c).

Solvatochromic Studies

Solvatochromic effect or solvatochromic shift refers to a strong dependence of *absorption* and emission spectra with the *solvent polarity*. A pronounced solvatochromic effect is, usually, associated with considerable changes of electron density in molecule. The molecule with solvatochromism also presents NLO properties.



(a) (b) (c)

FIGURE 3 Electronic spectra of (a) [Ni(dabpy)(cys)$_2$], (b) [Ni(bpy)(cys)$_2$] and (c) [Ni(Mebpy)(cys)$_2$].

A correct study of solvatochromism can be performed only if the complex compound is soluble and stable in solvents with different polarities.

Stability in time in 5–60 min range of complex compounds in organic solvents solutions have been analyzed by means of spectrophotometry. It can be observed that absorption maximum in UV-Vis spectra remains at the same wavelength in case of organic solvents for the same complex compound even after 60 min, while in aqueous solution it can be observed a decomposition of complex compound after 30 min.

Spectra have been recorded in less than 30 min after solution preparation. These complex compounds have a low solubility in a limited number of polar solvents. Even though only spectra of polar solvent solutions have been recorded, it can be observed an absorption maximum shift to a higher wavelength as the solvent polarity increases (Fig. 4).

The UV bands ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) assigned to both organic ligands suffer small solvent shifts, a behavior which is characteristic of these types of electronic transitions. The visible band is more sensitive towards the nature of the organic solvent, a behavior that can be considered as further evidence for the CT nature of this band.

Fluorescence Studies

Though there are no magnetic interactions in the ground state owing to the diamagnetic low spin Ni(II) complexes and, usually, 3*d* metals do not exhibit fluorescence emission, it is well known that CT complex compounds might present fluorescence emission by excitation at wavelength of maximum absorption. Although the absorption maximum for

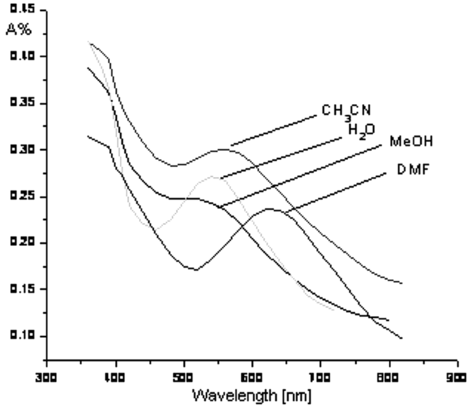


FIGURE 4 Electronic spectra of [Ni(bpy)(cys)$_2$] in different solvents.

all Ni(II) and Zn(II) complex compounds is over 500 nm, fluorescence emission maximum has been obtained at 460 nm, by excitation at 440 nm.

In Table 1 fluorescence emission intensities for Ni(II) and Zn(II) complexes are presented.

It can be observed that in case of Zn(II) complexes fluorescence emission intensity increase by comparison to the fluorescence emission intensity of the corresponding Ni(II) complexes, probably due to Zn(II) ion and its tetrahedral environment.

Nucleobases also present fluorescence emission at 460 nm by excitation at 440 nm. Fluorescence emission intensity for adenosine, guanidine, thymine and cytosine is 351, 441, 406 and 183 respectively.

In order to study the complex compounds behavior in the presence of nucleobases, mixtures of 1:1, 1:2, 1:4 and 1:10 of complex compound: nucleobase (molar ratio) have been prepared. In all cases, for 1:1 molar

TABLE 1 Complex Compounds Fluorescence Emission Intensity at 460 nm by Excitation at 440 nm

Complex compound	Fluorescence intensity	Complex compound	Fluorescence intensity
[Ni(bpy)(cys)$_2$]	60	[Zn(bpy)(cys)$_2$]	128
[Ni(bpy)(cysMe)$_2$]	63	[Zn(bpy)(cysMe)$_2$]	147
[Ni(Mebpy)(cys)$_2$]	58.4	[Zn(Mebpy)(cys)$_2$]	115
[Ni(Mebpy)(cysMe)$_2$]	65	[Zn(Mebpy)(cysMe)$_2$]	122
[Ni(dabpy)(cys)$_2$]	78	[Zn(dabpy)(cys)$_2$]	130
[Ni(dabpy)(cysMe)$_2$]	84	[Zn(dabpy)(cysMe)$_2$]	148

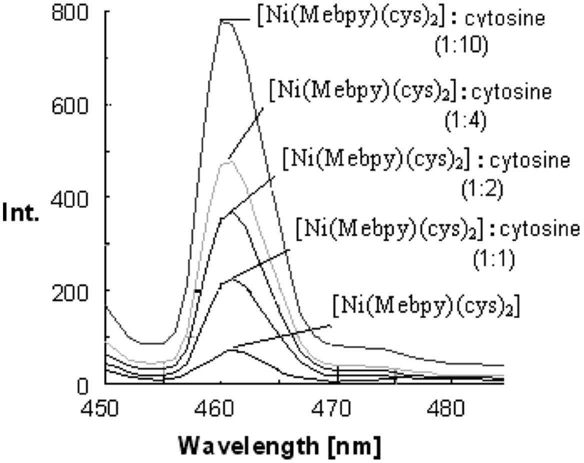


FIGURE 5 Fluorescence emission intensity for [Ni(Mebpy)(cys)$_2$] and cytosine mixture.

ratio fluorescence emission intensity is less than a simple sum of complex compound and nucleobase fluorescence emission intensity. For higher molar ratio, especially 1:4 and 1:10 a dramatic increase of the fluorescence emission intensity has been observed. The best values have been obtained for cytosine and thymine, where the fluorescence emission intensity of the 1:10 mixture was higher than ten times initial complex compound value. In Figure 5 the fluorescence emission intensity for the less fluorescent complex compound, [Ni(Mebpy)(cys)$_2$] and the less fluorescent nucleobase, cytosine mixtures is presented.

This tendency is probably due to an interaction between pyridine ring and nucleobases heterocyclic aromatic rings, and similar values for cytosine and thymine and adenosine and guanidine respectively is due to their similar structure. A coordination bond formation is not assumed because a complex compound of Ni(II) in which cytosine is coordinated presents a much lower fluorescence emission (around 80).

CONCLUSION

Due to the fact that performance of optoelectronic devices materials depends on the emission fluorescence of species included, this research intended to amplify the complex compounds fluorescence effect by bonding them to biorelevant molecules, such as DNA components.

Based on their enhanced fluorescence emission, mixture of nucleobases and complex compounds of [Ni(diimine)(thiolate)$_2$] type might be used as optical nonlinear materials.

REFERENCES

[1] Ciurli, S. (1999). *Coord. Chem. Rev.,190*, 331.

[2] Mashin, N. I., Tumanova, A. N. & Rudnevskii, N. K. (2001). *J. Anal. Chem.*, *56*, 6581.

[3] Kwong, R. C., Nugent, M. R., Michalski, L., Ngo, T., Rajan, K., Tung, Y.-J., Weaver, M. S., Zhou, T. X., Hack, M., Thompson, M. E., Forrest, S. R., & Brown, J. J. (2002). *Appl. Phys. Lett.*, *8*, 62.

[4] Ikai, M., Tokito, S., Sakamoto, Y., Suzuki, T., & Taga, Y. (2001). *Appl. Phys. Lett.*, *79*, 156.

[5] Adachi, C., Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2001). *J. Appl. Phys.*, *90*, 5048.

[6] Li, F., Zhang, M., Cheng, G., Feng, J., Zhao, Y., Ma, Y. G., Lui, S. Y., & Shen, J. C. (2004). *Appl. Phys. Lett.*, *84*, 148.

[7] Bancu, L., Carp, O., Stanica, N., & Jitaru, I. (2006). *Rev. Roum. Chim.*, *51*(6), 497.