

SOLVENT EFFECTS ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF Er(III) (AZO-DYES AND SCHIFF BASES) COMPLEXES: DETERMINATION OF GROUND AND EXCITED STATE DIPOLE MOMENT

I.C. VASILIU^{*}, C. CONSTANTINESCU^a, M. VOICESCU^b, A. EMANDI^c
*INOE 2000 - National Institute for Optoelectronics, 1 Atomistilor Blvd., PO Box
MG 5, RO-077125 Magurele, Bucharest, Romania*

^a*INFLPR - National Institute for Laser, Plasma and Radiation Physics, 409
Atomistilor Blvd, RO-077125 Magurele, Bucharest, Romania*

^b*Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202,
060021 Bucharest, Romania*

^c*University of Bucharest, Faculty of Chemistry, Department of Inorganic
Chemistry, 23 Dumbrova Rosie St., RO-010184 Bucharest, Romania*

Absorption and fluorescence emission spectra of some thermally stable Er(III) mononuclear complexes of azo dyes, namely *o, o'* - dihydroxy azobenzene (DAB), *o, o'* - dihydroxy 4-Cl-phenylazonaphthalene (P1) and Schiff bases *o, o'* - dihydroxy phenylazomethinnaphthalene (D2), *o*- hidroxy - *o'* - carboxy (D3), were recorded in solvents with different solvent dielectric constant ϵ and refractive index n . The solvatochromic shift method was used to determine the experimental ground and excited state dipole moments of the complexes. All the complexes were proved to be more polar in the excited state as compared with the ground state.

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1. Introduction

Organic molecules represent a great potential for applications in electro-optic devices and all optical devices. Incorporation of metals into organic NLO (Non-Linear Optical) system gives a new dimension of study and introduces many new variables. These coordinative compounds exhibit a real potential for applications in optical devices due to: optical absorption bands in the visible region as a consequence of charge transfer bands metal \rightarrow ligand (MLCT) and ligand \rightarrow metal (LMCT); availability of the metal centre to change the oxidation number behaving itself as an extreme strong donor or acceptor; low energy of excited states with providing significant differences between ground state dipole moment and excited state dipole moment with a substantial contribution to the first molecular hyperpolarizability β ; a large possibility for fine tuning and optimizing β by means of interactions among metal d orbital and π electron orbital of the conjugated ligand system. [1-2]

K. Sénéchal and al., mentioned lanthanide complexes as efficient NLO-phores, where NLO activity depends on the nature of the rare earth itself. [3] N. Tancrez, and al. showed that in the coordinative compounds of lanthanides f electrons directly participate to the first hyperpolarizability β . [4]

The effect of solvents on the absorption and fluorescence characteristics of organic compounds has been a subject of several investigations. Dipole moments of short-lived species are

^{*}Corresponding author: icvasiliu@inoe.inoe.ro

of considerable interest because, they provide information of electronic and geometrical structure of these transient. Knowledge of dipole moment of electronically excited species is often useful in the design of non-linear optical materials and elucidation of the nature of the excited state, as well as course of any photochemical transformation. The ground and excited state dipole moments were determined using different methods. [5-10].

This paper, as part of our systematic study presents the experimentally determined the ground and excited state dipole moments of four erbium azo compounds by solvent perturbation method [11] based on absorption and fluorescence shift in various solvents.

2. Theory

The following equations, that is $\tilde{\nu}_a - \tilde{\nu}_f = m_1 f(\epsilon, n) + \text{const}$ and $\tilde{\nu}_a + \tilde{\nu}_f = -m_2 [f(\epsilon, n) + 2g(n)] + \text{const}$, obtained based on quantum mechanical perturbation theory of absorption ($\tilde{\nu}_a$) and fluorescence ($\tilde{\nu}_f$) band shift in different solvent of varying permittivity (ϵ) and refractive index (n), were used [11].

where:

$$f(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (1)$$

and

$$g(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \quad (2)$$

The parameters m_1 and m_2 can be determined from absorption and fluorescence band shifts ($\tilde{\nu}_a - \tilde{\nu}_f$ and $\tilde{\nu}_a + \tilde{\nu}_f$) of equations:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (3)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (4)$$

where h is Planck's constant and c , is the velocity of light in vacuum. μ_g and μ_e are the dipole moments in the ground and excited states.

If the ground and excited states are parallel, the following expressions are obtained on the basis of equations (3) and (4) [11].

$$\mu_g = \frac{m_2 - m_1}{2} \left[\frac{hca^3}{2m_1} \right]^{1/2} \quad (5)$$

$$\mu_e = \frac{m_2 + m_1}{2} \left[\frac{hca^3}{2m_1} \right]^{1/2} \quad (6)$$

$$\mu_e = \frac{m_1 + m_2}{m_1 - m_2} \mu_g \quad (7)$$

The Onsager radius “ a ” of the solute molecule was evaluated by using atomic increment method [11]

3. Experimental

Er(III) mononuclear complexes of azo dyes *o*, *o*' - dihydroxi azobenzene (DAB), *o*, *o*' - dihydroxi 5-Cl-phenylazonaphatalene (P1) and schiff bases *o*, *o*' - dihydroxi phenylazomethinnaphatalene (D2), *o*- hidroxy - *o*' - carboxy (D3) were prepared and the synthesis was reported in our previous studies [12].

The solvatocromism behaviour was investigated for solution at concentration of 2.5×10^{-4} M in polar solvents: dimethylsulphoxide (DMSO), acetonitrile (AN), dimethylformamide (DMF), ethanol (EtOH), 1,4- dioxane (Diox).

Luminescent properties were evaluated using a Spectrofluorimeter Perkin Elmer 204. For UV-VIS spectra a UV-VIS Perkin Elmer Lambda 35 spectrophotometer was used.

Molar conductance of the complexes was measured in acetone at room temperature using systronic conductivity bridge type 305.

4. Results and discussion

Absorption and fluorescence emission spectra of Er(III) mononuclear complexes of azo dyes *o*, *o*' - dihydroxi azobenzene (DAB), *o*, *o*' - dihydroxi 4-Cl-phenylazonaphatalene (P1) and schiff bases *o*, *o*' - dihydroxi phenylazomethinnaphatalene (D2), *o*- hidroxy - *o*' - carboxy (D3), in solvents with different dielectric constant ϵ and refractive index n were recorded. The emission spectra were recorded by exciting the sample at its longest absorption maximum. Figure 1 presents as an example the emission spectra of D2 erbium complexes. The absorption and emission maxima, dielectric constant and refractive index of the erbium complexes in different solvents are given in Table 1.

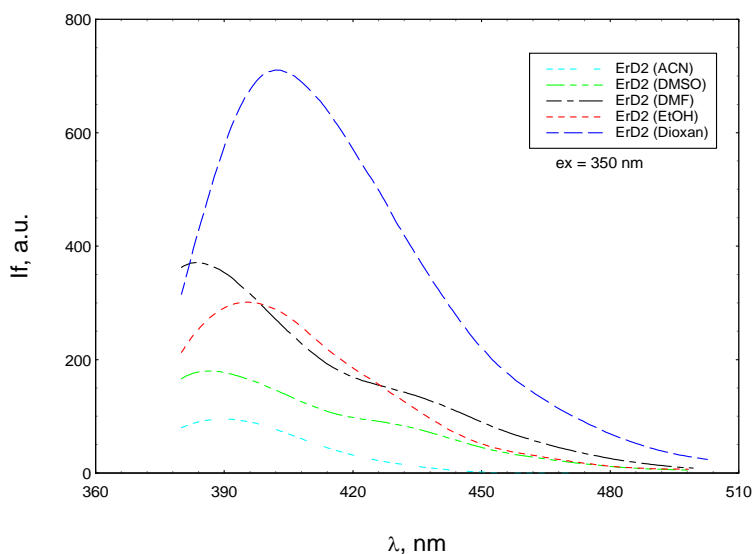


Fig. 1. Fluorescence emission spectra in different solvents of Er(III) complexes with ligand D2

Table 1 The maximum of the absorption and emission wavelength of Er(III) complexes in different solvents

Solvent	Er/DAB		Er/P1		Er/D2		Er/D3		ϵ^b	n^b
	λ_{abs} (nm) ^a	λ_{em} (nm) ^a	λ_{abs} (nm) ^a	λ_{em} (nm) ^a	λ_{abs} (nm) ^a	λ_{em} (nm) ^a	λ_{abs} (nm) ^a	λ_{em} (nm) ^a		
Diox	504.1	549.20	506.3	560.67	338.3	408	348.2	418.08	2.210	1.4210
Et-OH	509.2	549.38	508.4	561.5	340.6	400	350.1	504.25	24.550	1.3614
DMF	511.4	561.28	509.3	562.13;	343.3	380	353.4	510.12	38.3	1.4305
ACN	514.1	544.98	510.2	553.99;	344.2	390	355.6	493.61	38.80	1.3440
DMSO	516.4	566.07	513.5	563.26;	345.1	380	360.1	519.68	47.2	1.4793

^a λ_{abs} and λ_{em} are wavelengths of absorption and fluorescence maxima, (nm); ^b ϵ and n are dielectric constant and refractive index [13,14].

ν_a (cm^{-1}), ν_f (cm^{-1}), $f(\epsilon, n)$, $g(n)$ for each erbium complex in each solvent were calculated and presented in table 2

Table 2 ν_a (cm^{-1}), ν_f (cm^{-1}), $f(\epsilon, n)$, $g(n)$ for erbium complexes with DAB, P1, D2, D3 in solvents: dimethylsulphoxide (DMSO), acetonitrile (AN), dimethylformamide (DMF), ethanol (EtOH), 1,4- dioxane (Diox).

Er / DAB							
	ν_a (cm^{-1})	ν_f (cm^{-1})	$\nu_a - \nu_f$ (cm^{-1})	$\nu_a + \nu_f$ (cm^{-1})	$f(\epsilon, n)$	$g(n)$	$f(\epsilon, n) + 2 g(n)$
DIOX	19837	18208	1629	38046	0,042397067	0,285744	1,261436
EtOH	19639	18202	1436	37841	0,812932514	0,245993	1,998841
DMF	19554	17816	1738	37371	0,839441153	0,292021	2,063796
ACN	19451	18349	1102	37801	0,866017699	0,234279	2,042336
DMSO	19365	17666	1699	37030	0,841224962	0,323973	2,092998
Er / P1							
	ν_a (cm^{-1})	ν_{em} (cm^{-1})	$\nu_a - \nu_f$ (cm^{-1})	$\nu_a + \nu_f$ (cm^{-1})	$f(\epsilon, n)$	$g(n)$	$f(\epsilon, n) + 2 g(n)$
DIOX	19751	17836	1915	37587	0,042397067	0,285744	1,261436
EtOH	19670	17809	1860	37479	0,812932514	0,245993	1,998841
DMF	19635	17789	1845	37424	0,839441153	0,292021	2,063796
ACN	19600	18051	1549	37651	0,866017699	0,234279	2,042336
DMSO	19474	17754	1720	37228	0,841224962	0,323973	2,092998
Er / D2							
	ν_a (cm^{-1})	ν_{em} (cm^{-1})	$\nu_a - \nu_f$ (cm^{-1})	$\nu_a + \nu_f$ (cm^{-1})	$f(\epsilon, n)$	$g(n)$	$f(\epsilon, n) + 2 g(n)$
DIOX	29560	24510	5050	54069	0,042397067	0,285744	1,261436
EtOH	29360	25000	4360	54360	0,812932514	0,245993	1,998841
DMF	29129	26316	2813	55445	0,839441153	0,292021	2,063796
ACN	29053	25641	3412	54694	0,866017699	0,234279	2,042336
DMSO	28977	26316	2661	55293	0,841224962	0,323973	2,092998
Er / D3							
	ν_a (cm^{-1})	ν_{em} (cm^{-1})	$\nu_a - \nu_f$ (cm^{-1})	$\nu_a + \nu_f$ (cm^{-1})	$f(\epsilon, n)$	$g(n)$	$f(\epsilon, n) + 2 g(n)$
DIOX	28719	23919	4800	52638	0,042397067	0,285744	1,261436
EtOH	28563	19831	8732	48395	0,812932514	0,245993	1,998841
DMF	28297	19603	8693	47900	0,839441153	0,292021	2,063796
ACN	28121	20259	7863	48380	0,866017699	0,234279	2,042336
DMSO	27770	19243	8527	47013	0,841224962	0,323973	2,092998

The spectral shifts (in cm^{-1}) $\tilde{\nu}_a - \tilde{\nu}_f$ and $\tilde{\nu}_a + \tilde{\nu}_f$ of Er/DAB, Er/P1, Er/D2 and Er/D3C6 complexes in polarity functions $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ were represented. A linear progression was done by employing Origin 6.0 program and the data was fit to a straight line. The slopes m_1 and m_2 of the fitted lines are given in Table 3.

The Onsager radius of solute was calculated from the theoretical values of dipole momentum, using Hyperchem software.

The dipole moments in ground (μ_g) and excited states (μ_e), as well as the change in the dipole moments ($\Delta\mu$) were calculated using the equations (5) and (6) respectively, and the values are presented in table 3.

Table 3 Dipole moments and slopes of erbium complexes with DAB, P1, D2, D3

	Radius „a” (10^{-8} cm)	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_e / μ_g	m_1 (cm^{-1})	m_2 (cm^{-1})	Correlation factor (r)
Er/DAB	6.2	13,158	13,822	0.664	1.050	185.730	7555.600	0,065:0,426
Er/P1	6.5	3,102	3,895	0.793	1.255	230.770	2034.900	0,317:0,194
Er/D2	6.7	1,812	2,627	0.815	1.449	222.500	1211.400	0,602:0,528
Er/D3	6.8	7,371	8,559	1.242	1.169	452.350	6062.000	0,935:0,967

The solvatochromic shift observed and discussed as possible charge transfer and possible resonant structures presented in a previous paper [15] ordered the complexes Er/P1 > Er/DAB and Er/D3 > Er/D2.

The proposed order was verified in the investigations presented in this paper by the values reflecting the variation mode of the difference $\Delta\mu$, between the dipole moment in excited and fundamental state respectively.

It was noticed a non correlation namely:

- **The charge transfer order is** Er/P1 > Er/DAB > Er/D3 > Er/D2 [15]
- **The $\Delta\mu$ order is** Er/D3 > Er/D2 > Er/P1 > Er/DAB

This phenomenon can be explained as follows: When discussing the variation of the charge transfer from the solvatochromic shift, only the solvent polarity could stimulate the CT. The investigation of the solvatochromic behaviour as a function of the solvent polarity gave only qualitative previsions regarding the modification potential of the dipole momentum based on the resonant formula corresponding to the charge transfer.

Under the conditions used in this paper the charge transfer was stimulated by both solvent polarity and absorption light of the excitation source. As a consequence we have obtained direct information referring to the behaviour of dipole moments at the interaction with the excited factor (light irradiation).

5. Conclusions

The dipole moments of Er(III) mononuclear complexes of azo dyes o, o' - dihydroxi azobenzene (DAB), o, o' - dihydroxi 5-Cl-phenylazonaphatalene (P1) and schiff bases o, o' - dihydroxi phenylazomethinnaphatalene (D2), o- hidroxy - o' - carboxy (D3) in the ground and excited states were determined by using the fluorescence solvatochromic method.

All complex molecules in excited state are more polar than in the ground state. By estimating the surface area of the molecule, the Onsager radius was determined, assuming the molecule as spherical. Based on absorption and fluorescence band shifts in different solvents, the ratio of dipole moments (μ_e/μ_g) was measured.

The value of $\mu\epsilon$ was estimated using equation (7) by pre knowledge of the value of μg , without the necessity of knowing the radius of the molecule.

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