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Hypersensitivity in the Luminescence and 4f–4f Absorption Properties of Mono- and Dinuclear Eu^III and Er^III Complexes Based on Fluorinated β-Diketone and Diimine/ Bis-Diimine Ligands

Mir Irfanullah · Khalid Iftikhar

Abstract The results of our investigation on the sensitized luminescence properties of three Eu(III) β-diketonate complexes of the form $[Eu_2(fod)_6(\mu\text{-bpm})]$, $[Eu(fod)_3(phen)]$ and $[Eu(fod)_3(bpy)]$ and 4f–4f absorption properties of their Er (III) analogues (fod = anion of 6,6,7,7,8,8,8- heptafluoro-2,2-dimethyl-3,5-octanedione, bpm = 2,2′-bipyrimidine, phen = 1,10-phenanthroline and bpy = 2,2′-bipyridyl) in a series of non-aqueous solvents are presented. The Eu(III) complexes are highly luminescent and their luminescence properties (intensity and band shape) are sensitive to the changes in the inner coordination sphere of the Eu(III) ion. The luminescence intensity of the mononuclear complexes in pyridine is drastically decreased. The coordination structure of the complexes in pyridine is transformed into a more symmetrical one which results into a slow radiative rate of the emission from the complexes. The ancillary ligands, phen and bpy are found better co-sensitizers as compared to the bpm to sensitize Eu(III)-luminescence. The 4f–4f absorption properties (oscillator strength and band shape) of the Er(III) complexes demonstrate that $^4G_{11/2} \leftarrow \, ^4I_{11/2}$ and $^2H_{11/2} \leftarrow \, ^4I_{15/2}$ hypersensitive transitions of Er(III) are very sensitive in some coordinating solvents which reflects complex–solvent interaction in solution. The hypersensitive transitions of $[Er(fod)_3(phen)]$ remain unaffected in any of the solvents and this complex retains its bulk composition in solution. The erbium complexes as well as the $Er(fod)_3$ chelate are invaded by DMSO. This solvent enters the inner coordination sphere by replacing heterocyclic ligand and the complexes acquire similar structure $[Er(fod)_3(DMSO)_2]$ in this solvent. The results reveal that the luminescence and absorption properties of lanthanide complexes in solution can be controlled by tuning the coordination structure through ancillary ligands and donor solvents. This work shall prove useful in designing new biological applications with such probes.

Introduction

The synthesis and study of lanthanide complexes continues to be an active area of research because of their unique absorption and luminescence properties [1, 2]. The luminescence from these complexes find many applications such as in light emitting devices [3], luminescent polymer films and active optical fibers for data transmission [4], sensors [2, 5] and as luminescent probes [6]. Since 4f–4f transitions are Laporte forbidden, the direct excitation of lanthanide luminescence is not possible. However, this problem is often overcome by use of organic ligands attached to the lanthanide ion. These ligands function like an antenna by absorbing light and transferring this energy to excited states of the central lanthanide ion [7]. The excited lanthanide ion then undergoes radiative transition to lower energy levels resulting in characteristic multiple narrow emission bands. The complexes of Eu(III), Tb(III), Sm(III) and Dy(III) are known to have brightest luminescence in the visible region but the luminescence intensity of these complexes depends largely on the choice of antenna ligand [8]. Although a large number of ligands have been

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developed and tested for their ability to sensitize lanthanide luminescence [4, 9], the β-diketones have received special attention as one of the most important antenna system which efficiently transfer the excited energy to the Ln(III) ion [10].

The optical absorption and luminescence spectra of the lanthanide complexes give very narrow and line like $4f$–$4f$ transitions which are very unique from other metal complexes and molecular species since the $4f$ electrons are shielded by the outer 5s and 5p shells. Some transitions of the lanthanides are very sensitive to the changes in the coordination sphere and symmetry around the metal ion. These are termed as hypersensitive transitions. The changes in the intensity and band shape of the hypersensitive transitions can be used to probe the changes in coordination sphere and complex–ligand/solvent interactions in solution [11–16].

The tris β-diketonate lanthanide complexes are coordinatively unsaturated and usually contain solvent molecules with high energy oscillators, such as C–H and O–H bonds. These high energy oscillators are able to quench the lanthanide excited states non-radiatively [17]. Therefore, the inner coordination sphere of tris β-diketonate lanthanide chelates are usually saturated by neutral ancillary ligands such as 2,2-bipyridine (bpy) or 1,10-phenanthroline (phen) to overcome the difficulty of solvent quenching. Furthermore, the ancillary ligand can also improve the sensitization of the lanthanide ion if it contains a suitable energy level to effectively transfer the energy to the emitting level of the Ln(III) ion [18, 19].

In this paper, we report the results of photoluminescence and $4f$–$4f$ absorption properties of three type of complexes, [Ln(fod)$_3$(bpy)], [Ln(fod)$_3$(phen)] and [Ln$_2$(fod)$_6$(μ-bpm)] { fod = anion of 6,6,7,7,8,8,8- heptafluoro-2,2-dimethyl-3,5-octanedione; bpy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, bpm = 2,2′-bipyrimidine; Ln = Eu(III) and Er(III)} at room temperature in a series of non-aqueous solvents. The effect of changing the environment (ligand/solvent) around the metal ions on the luminescence intensity and band shape of hypersensitive transition of Eu(III) complexes and on the oscillator strength and band shape of the $4f$–$4f$ hypersensitive as well as non-hypersensitive transitions of Er(III) complexes have been investigated.

Experimental

Materials

The commercially available chemicals that were used without further purification are: Ln$_2$O$_3$ (Ln =, Eu and Er 99.99%) from Aldrich. These oxides were converted to their corresponding chlorides by the standard procedure. 6,6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod) was purchased from Lancaster, 2,2′-bipyrimidine (bpm), 2,2′-bipyridyl (bpy) and 1,10-phenanthroline were purchased from Aldrich. The solvents used in this study were AR/spectroscopic grade.

Methods

Infrared spectra were recorded on a Perkin-Elmer spectrum RX 1 FT-IR spectrophotometer as KBr disc in the range 4,000–400 cm^{-1}. Elemental analyses were performed by sophisticated analytical instrumentation facility (SAIF), Punjab University, Chandigarh, India. Melting points were recorded by conventional capillary method and confirmed by the DSC 6220 Exstar 6000 instrument from SIINT, Japan. The thermograms were recorded on TG/DTA 6300 Exstar 6000 from SIINT, Japan, under N$_2$ atmosphere at a heating rate of 10 °C/min. The electronic absorption spectra of the complexes were recorded on a Perkin-Elmer Lambda-40 spectrophotometer, with the samples contained in 1 cm^3 stoppered quartz cell of 1 cm path length, in the range 200–1,100 nm, in the concentration range between 1×10^{-3} to 5×10^{-3} M. The NMR spectra were recorded either on a BRUKER AVANCE II 400 NMR spectrometer or BRUKER DPX-300 spectrometer. Steady state room temperature excitation and luminescence spectra of the solutions (2×10^{-3} M) were recorded on Jobin Yvon Flourolog 3-22 spectrofluorometer using 450 W xenon lamp as the excitation source and R928P PMT as detector.

Synthesis

The Eu(fod)$_3$ and Er(fod)$_3$ chelates were synthesized according to a published procedure [20] with slight modification. The complexes [Ln(fod)$_3$(bpy)] [21] and [Ln(fod)$_3$(phen)] [21] were synthesized by reacting Ln(fod)$_3$ chelates and heterocyclic ligands (phen or bpy) in 1:1 mole ratio in ethanol. The dinuclear complexes were synthesized according to the published method [22]. These complexes were fully characterized before their use.

Results and discussion

It has been known for many years that coordinatively unsaturated Ln(β-diketonate)$_3$ chelates rapidly react with NN donor heterocyclic ligands such as phen and bpy in solution to form coordinatively saturated complexes [21, 23–26]. Therefore, the reaction of Ln(fod)$_3$ chelate with an equimolar amount of phen or bpy (diimine ligands) in ethanol yields air and moisture stable complexes of the type [Ln(fod)$_3$(phen)] and [Ln(fod)$_3$(bpy)],

while the reaction of chelate with bpm (a bis-diimine ligand) in 2:1 molar ratio yields homodinuclear complexes of the type [Ln$_2$(fod)$_6$(μ-bpm)] {Ln = Eu(III), Er(III)}, as shown in Chart 1. The formation of these complexes was confirmed by melting points, elemental analysis, thermal analysis, IR, UV–Vis, and NMR studies. Earlier one of us has reported [Ln(fod)$_3$(bpy)] complexes as dihydrates [21], however, during the present synthesis, anhydrous eight-coordinate complexes have been isolated in line with [Ln(fod)$_3$(phen)].

Thermal studies

The TG/DTA of Eu(III) and Er(III) complexes are shown in Figs. 1 and 2. The complexes exhibit similar thermal behaviour with one step weight loss. The dinuclear bipyrimidine complexes melt at much higher temperature than the mononuclear bipyridine and phenanthroline analogues which reflects that the dinuclear complexes are thermally more stable than their mononuclear analogues. Among mononuclear complexes the phen complexes are thermally more stable over bpy complexes due to rigidly planar structure of the phen. The DTA curves of the complexes show two endothermic peaks; one sharp peak at lower temperatures corresponding to the melting of the complex and the other peak at higher temperatures, which is consistent with the volatilization of the complexes.

Photoluminescence properties of Eu(III) complexes

The luminescence spectra of the complexes were recorded in various non-aqueous solvents. The complexes show intense characteristic Eu(III) luminescence, upon excitation into the ligand centered absorption bands. The excitation spectra of all the complexes were obtained at room temperature and monitored around the most intense $^5D_0 \rightarrow {}^7F_2$ emission line at 610 nm. The spectra feature an intense broad band between 320 and 435 nm with maxima around 360 nm (Fig. 3). These bands are attributed to $S_0 \rightarrow S_1$ transitions of β-diketonate and heterocyclic ligands. The excitation spectra of the complexes, in pyridine, are broader than in other solvents with maxima shifted to lower wavelength. No f–f transitions were observed in the excitation spectra of the complexes, thus indicating an efficient sensitization of the Eu(III)-luminescence in these complexes through ligands.

All the complexes show a series of emission peaks in the 500–750 nm range. These are the transitions from $^5D_0$ excited state of Eu(III) to the ^7F_j (J=0–4) levels. The most intense transition in the emission spectra of the complexes is the induced electric-dipole, $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition. This transitions is notably much more intense than the magnetic-dipole, $^5D_0 \rightarrow {}^7F_1$ transition in all the complexes, which reflects a low symmetry of the Eu(III) site in these complexes. Furthermore, the emission spectra of the complexes show only one peak for $^5D_0 \rightarrow {}^7F_0$

Chart 1 Chemical structure of the complexes

[Ln(fod)$_3$(bpy)]

[Ln(fod)$_3$(phen)]

[Ln$_2$(fod)$_6$(μ–bpm)]
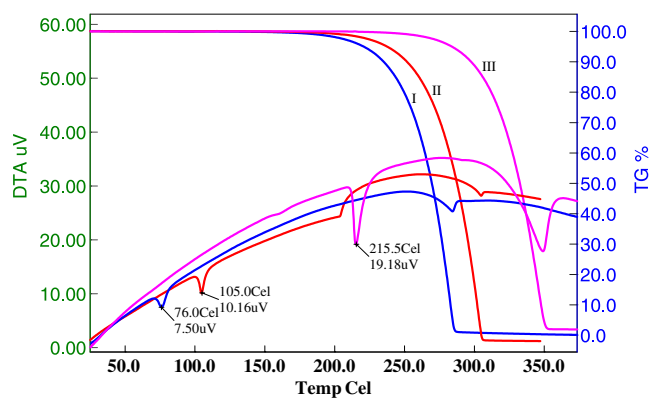
Ln = Eu(III) and Er(III)
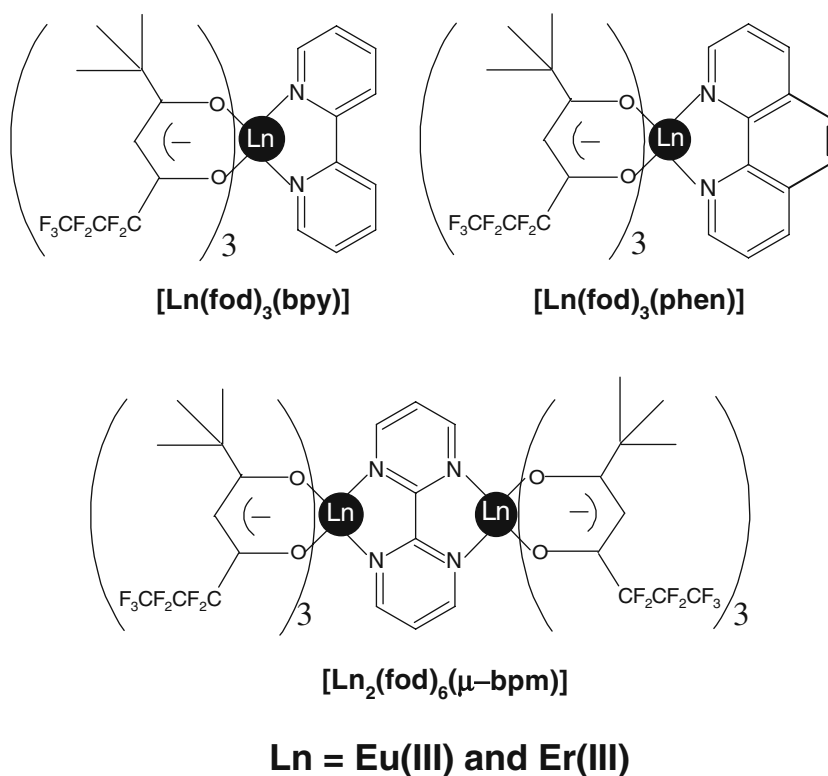
Fig. 1 TG/DTA plots of (I) [Eu(fod)₃(bpy)] (II) [Eu(fod)₃(phen)] and (III) [Eu₂(fod)₆(μ-bpm)]

transition indicating the presence of a single chemical environment around the Eu(III) ion.

Solvent effect on photoluminescence

The intensity and band shape of $^5D_0 \rightarrow {}^7F_2$ transition show interesting sensitivity to a change in the environment (solvents/ligand). The emission spectra of [Eu(fod)₃(phen)] in acetonitrile, ethanol and pyridine are shown in Fig. 4. The luminescence intensity of the transitions of this complex, in acetonitrile and ethanol, are equal while drastic decrease in intensity is noted in pyridine. The luminescence spectra of [Eu(fod)₃(bpy)] in acetonitrile, ethanol and pyridine are shown in Fig. 5. The luminescence intensity of the above transition of this complex, in acetonitrile is slightly higher than ethanol. However, the luminescence intensity decreases drastically in pyridine. The luminescence spectra of dinuclear [Eu₂(fod)₆(μ-bpm)] complex, recorded in acetone, benzene and pyridine are shown in Fig. 6. The acetone and benzene were employed because this complex has poor solubility in acetonitrile and ethanol. The complex shows largest luminescence intensity in non-

Fig. 2 TG/DTA plots of (I) [Er(fod)₃(bpy)] (II) [Er(fod)₃(phen)] and (III) [Er₂(fod)₆(μ-bpm)]

coordinating benzene followed by acetone and is least intense in pyridine. Therefore, it is a general observation that the luminescence intensity decreases in pyridine.

The luminescence of lanthanide complexes is very sensitive to the changes in the inner coordination sphere and the symmetry around the Ln(III) ion [27]. Generally a more asymmetric coordination environment around Ln(III) ion leads to enhanced luminescence due to faster radiative rate. It is noteworthy that in the cases of [Eu(fod)₃(phen)] and [Eu(fod)₃(bpy)] the luminescence intensities decrease in pyridine. This is attributed to the coordination of pyridine (py) molecule(s) to the inner coordination sphere of the Eu(III) ion which results into transformation of the eight-coordination structure to a more symmetric coordination structure around the Eu(III) ion. The Eu(III) center in the present complexes is coordinated to six O-atoms (from three fod moieties) and coordination structure is completed by association of two N atoms of the heterocyclic ligand (phen, bpy or bpm) and, thereby, eight-coordination is achieved. The coordination of one pyridine molecule would lead to nine-coordinate structure around the Eu(III) center leading to more asymmetric geometry and, therefore, enhanced luminescence would be expected [28]. The experimental observation is reverse of the expectation and the luminescence intensity decreases drastically, in pyridine, in the mononuclear complexes. Thus, it is believed that two pyridine molecules are coordinating in solution, since Eu(III) is reasonably larger, which results into a less asymmetric structure around the Eu(III). The transformation of eight-coordination sphere around Eu(III) in pyridine is also apparent from the change in the shape of $S_0 \rightarrow S_1$ excitation band of the mononuclear complexes in this solvent in comparison to the $S_0 \rightarrow S_1$ excitation band in other solvents (Fig. 3). Contrary to the results observed for the mononuclear phen and bpy complexes, luminescence intensity of the dinuclear bpm complex does not show drastic decrease, in pyridine, although it is lower than in the two solvents (Fig. 6). This is a surprising outcome considering the results observed in above two cases. Moreover, the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition of Eu(III) of dinuclear complex in pyridine shows a slight red shift from 610 nm in acetone and benzene to 614 nm in pyridine. The red shift of the $^5D_0 \rightarrow {}^7F_2$ transition indicates an increase in the nephelauxetic effect and also reflects an increase in the coordination number around each Eu(III) center from eight in the original complex to probably nine in pyridine due to the coordination of one pyridine molecules. The shape of $S_0 \rightarrow S_1$ excitation band of this complex in pyridine is also distinctive from the $S_0 \rightarrow S_1$ excitation of band of mononuclear complexes in pyridine. Thus, the supplementary coordination of pyridine molecules to inner coordination sphere of Eu(III) ions in dinuclear complex appears to have led to a lower symmetry
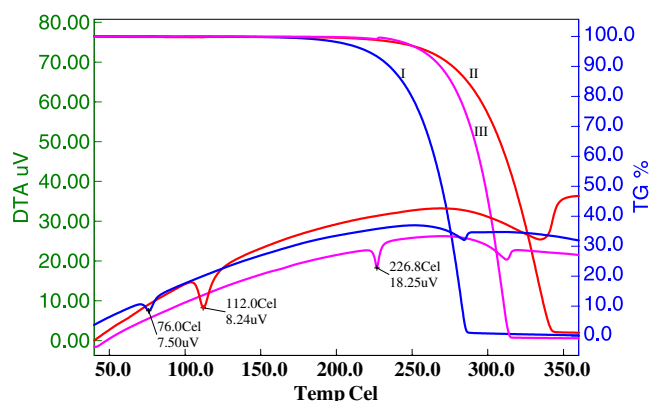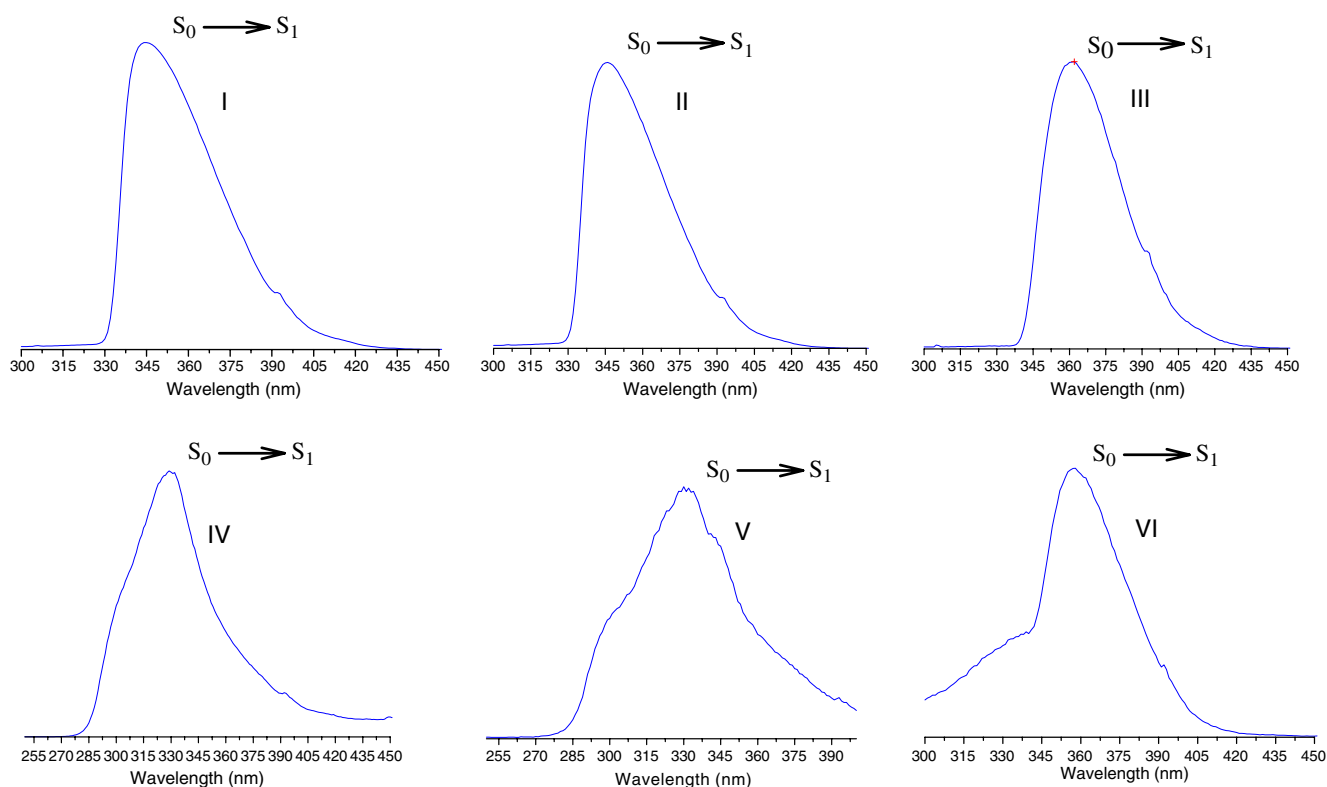
Fig. 3 Excitation spectra of the complexes in different solvents: (I) [Eu(fod)$_3$bpy] in acetonitrile (II) [Eu(fod)$_3$phen] in acetonitrile (III) [Eu$_2$(fod)$_6$(μ-bpm)] in acetone (IV) [Eu(fod)$_3$bpy] in pyridine (V) [Eu(fod)$_3$phen] in pyridine and (VI) [Eu$_2$(fod)$_6$(μ-bpm)] in pyridine

around metal ions and higher polarisability than in mononuclear bpy and phen complexes.

The change in the coordination structure around Eu(III) ion is also reflected by the disappearance of stark splitting from the hypersensitive transition in pyridine, while prominent ligand field splittings could be seen in the spectra of bpy and phen complexes in ethanol and

acetonitrile and of dinuclear complex in acetone and benzene. This is an additional evidence that these Eu(III) complexes of phen and bpy acquire more symmetric environment in pyridine. The luminescence spectra of these complexes are not much affected by other solvents. It is, therefore, concluded that these solvents (ethanol and acetonitrile or acetone and benzene) do not alter the
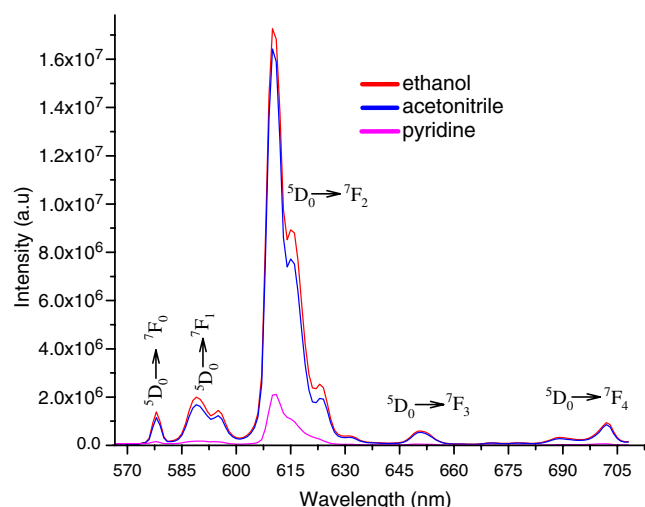

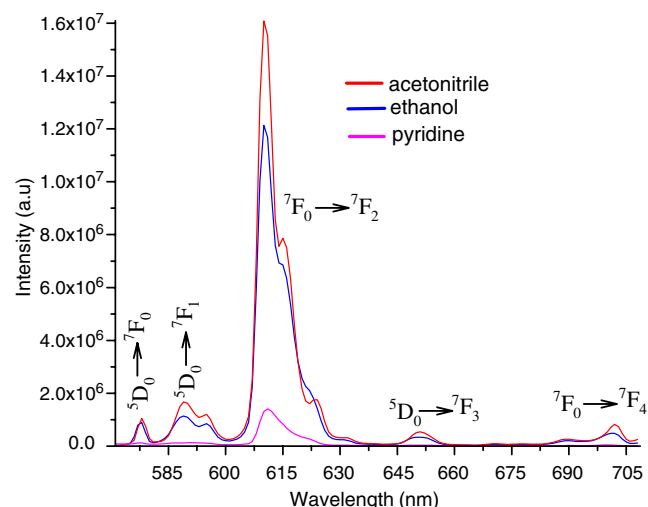**Fig. 4** Emission spectra of [Eu(fod)$_3$(phen)] complex in various solvents

Fig. 5 Emission spectra of [Eu(fod)$_3$(bpy)] complex in various solvents
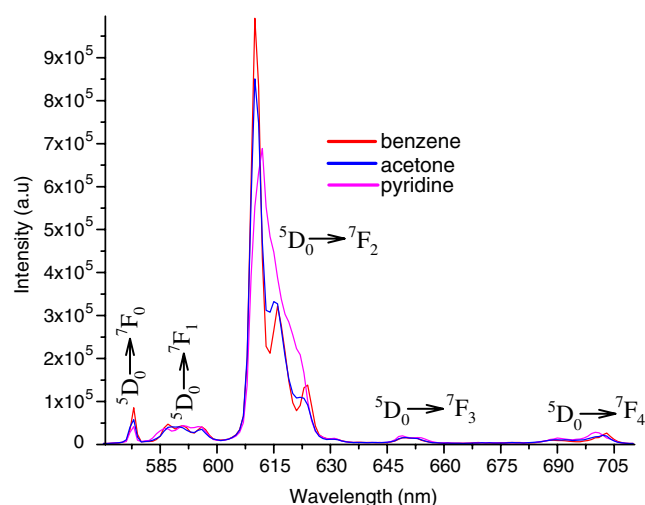
Fig. 6 Emission spectra of [$Eu_2(fod)_6(\mu$-bpm)] complex in various solvents

structure of these complexes in solution although ethanol and acetone are potentially coordinating ones. The small decrease observed in the luminescence intensity of [Eu(fod)$_3$(bpy)] in ethanol as compared to acetonitrile could be related to the quenching of Eu(III) emission by OH group of ethanol. The solvent molecules containing high energy oscillators play a significant role in quenching Eu(III) luminescence [10, 17].

Role of ancillary ligands

A comparison of the luminescence intensity of the three complexes in non-coordinating solvents reveals that the emission is most intense in the case of phen complex followed by bpy complex and least intense in dinuclear bpm complex. The luminescent intensity of lanthanides depends on the effective overlap between the ligand triplet state and the emitting level of the Ln(III) ion. For an effective ligand to metal energy transfer in Eu(III) complexes, the empirical rule suggests that $\Delta E(T_1 \rightarrow {}^5D_0)$ should be greater than 2,500 cm^{-1} [29]. The triplet energy state of fod [30] lies near 22,500 cm^{-1} which is well above the ${}^5D_0$ emitting state (17,500 cm^{-1}) of Eu(III). This energy gap between the two states ($\Delta E \sim 5,000$ cm^{-1}) is highly appropriate for an effective energy transfer to Eu(III) ion [9, 29, 31]. Therefore, the variation in the luminescence intensity, in these complexes, could be accounted to the co-sensitization of different heterocyclic (ancillary) ligands since the type and number of diketonate (fod) moieties, around the Eu(III) ions remains the same. The triplet states of bpy (22,900 cm^{-1}) and phen (22,200 cm^{-1}) [32] are higher than the ${}^5D_0$ level of Eu(III) and the energy differences between these triplet states and ${}^5D_0$ state are 5,400 and 4,700 cm^{-1}, respectively. Thus, phen and bpy ligands are also well suited for effective energy transfer to ${}^5D_0$ state Eu(III) ions. The higher luminescence of

phen complex than bpy complex could be related to the rigid planar structure of phen ligand than the flexible structure of bpy. The presence of a rigid planar structure in the complex causes a higher intensity of the sensitized luminescence, because such structure allows a better energy transfer [33]. In contrast, bpm has a high energy singlet state (S$_1$) at 265 nm (37,735 cm^{-1}), which is apparent from the high energy shoulder in the $\pi \rightarrow \pi^*$ transition of ligand centered absorption band (240–400 nm) of this complex. This large energy associated with the excited singlet state suggests that bpm has a high energy triplet state (T$_1$) which is also observed in other lanthanide tris β-diketonates [34]. Thus, bpm appears to play a minor role in the thermal population of ${}^5D_0$ emitting state of Eu(III). Therefore, it is inferred that phen is a better co-sensitizer followed by bpy while bpm, as ancillary ligand, is poor co-sensitizer. This is in agreement to our observation on Tb(III) complexes [35]. The lower luminescence intensity of dinuclear bpm complex as compared to mononuclear phen and bpy complexes could also be attributed to the intramolecular Eu(III)–Eu(III) energy transfer in this complex. It may be emphasized that the luminescence properties of dinuclear lanthanide complexes are affected by intramolecular intermetallic energy transfer since it is a nonradiative process and partially contributes to the quenching of Ln(III) emission [36, 37].

The 4f–4f absorption properties of Er(III) complexes

The intensity of the absorption band can be expressed in terms of a quantity called oscillator strength (P). Experimentally it is related to the integrated area of the absorption band and can be expressed in terms of absorption coefficient $\varepsilon(\nu)$ and the energy of the transition "ν" (cm^{-1}) as given in the Eq. 1 [38].

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + 2)^2} \right] \int \varepsilon(\nu) d\nu \qquad (1)$$

Where η is the refractive index of the solution, $\varepsilon(\upsilon)$ is the molar extinction coefficient at wavelength υ.

The electronic absorption spectra of the complexes have been recorded in a series of solvents (chloroform; dichloromethane; carbon tetrachloride; benzene; methanol; ethanol; acetonitrile; nitromethane; DMSO; pyridine; and acetone) and contain nine multiplet-to-multiplet transitions originating from ${}^4I_{15/2}$ ground state of Er(III) to various excited states. These are (i) ${}^4I_{11/2} \leftarrow {}^4I_{15/2}$ (ii) ${}^4I_{9/2} \leftarrow {}^4I_{15/2}$ (iii) ${}^4F_{9/2} \leftarrow {}^4I_{15/2}$ (iv) ${}^4S_{3/2} \leftarrow {}^4I_{15/2}$ (v) ${}^2H_{11/2} \leftarrow {}^4I_{15/2}$ (vi) ${}^4F_{7/2} \leftarrow {}^4I_{15/2}$ (vii) ${}^4F_{5/2}$, ${}^4F_{3/2}$, $\leftarrow {}^4I_{15/2}$ (viii) ${}^2H_{9/2} \leftarrow {}^4I_{15/2}$ and (ix) ${}^4G_{11/2} \leftarrow {}^4I_{15/2}$. The oscillator strength ($P \times 10^6$) of the complexes in different solvents along with the oscillator strength of ErCl$_3$ in water is given in Tables 1, 2 and 3.

Table 1 Oscillator strength of $[Er_2(fod)_6(\mu\text{-bpm})]$ in different non-aqueous solvents

Transitions $^4I_{15/2}$ (G.S)	Spectral Range (cm^{-1})[a]	Er aqua ion; P ($\times 10^6$)[b]	Solvents ($P \times 10^{-6}$)								
			A	B	C	D	E	F	G	H	I
$^4I_{11/2}$	9707–10496	0.19	1.32	1.15	1.63	–	1.55	1.33	1.33	–	1.32
$^4I_{9/2}$	12339–12596	0.13	0.56	0.33	0.51	0.62	0.16	0.35	0.47	–	–
$^4F_{9/2}$	14569–15597	1.94	3.82	3.40	3.37	4.29	2.99	3.59	3.54	4.63	4.52
$^4S_{3/2}$	17970–18613	0.41	1.07	1.14	0.86	1.14	0.82	0.79	1.05	0.96	0.92
$^2H_{11/2}$	18613–19556	2.91	43.79	43.62	50.92	56.41	43.56 (24.57)[d]	51.63	42.08	42.06	45.86
$^4F_{7/2}$	20028–20899	2.22	3.50	3.55	3.79	4.43	2.83	3.35	3.48	3.48	4.87
$^4F_{5/2}$, $^4F_{3/2}$	21482–22888	1.10	0.56	1.15	1.80	1.64	1.32	0.54	1.34	1.65	2.18
$^2H_{9/2}$	24037–24899	0.51	0.47	–	1.38	1.16	1.15	–	–	–	–
$^4G_{11/2}$	25759–26793	5.90	c	c	204.18	219.37	165.22	207.96	c	c	155.38

A Chloroform; *B* Dichlomethane; *C* Methanol; *D* Ethanol; *E* DMSO; *F* Pyridine; *G* Benzene; *H* Carbon tetrachloride; *I* Acetone

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate location of the bands

[b] Data taken from reference [15]

[c] These transitions are partially masked by strong ligand centered π–π* transitions in these solvents

[d] The values in parentheses are the due to Er(fod)$_3$ in DMSO

The transitions, $^2H_{11/2} \leftarrow {}^4I_{15/2}$, (19,240 cm^{-1}) and $^4G_{11/2} \leftarrow {}^4I_{11/2}$, (26,490 cm^{-1}) are very sensitive to the changes in environment around Er(III) ion. The oscillator strengths of these transitions of the complexes, in any given solvent, show pronounced increase as compared to Er(III) aqua-ion. These transitions follow the electric-quadrupole selection rules $\Delta J \leq 2$, $\Delta L \leq 2$ and $\Delta S = 0$ and have been classified as being hypersensitive by previous workers [15, 39–42]. Of

the two hypersensitive transitions, $^4G_{11/2} \leftarrow {}^4I_{11/2}$ is four times more intense than $^2H_{11/2} \leftarrow {}^4I_{15/2}$ for any of the given complexes and in any give solvent. The hypersensitive as well as non-hypersensitive transitions of the dinuclear complex, $[Er_2(fod)_6(\mu\text{-bpm})]$ are twice more intense than the mononuclear analogues, $[Er(fod)_3(bpy)]$ and $[Er(fod)_3(phen)]$ as revealed by the oscillator strengths (Tables 1, 2 and 3). This two fold increase in the oscillator

Table 2 Oscillator strength of $[Er(fod)_3(phen)]$ in different non-aqueous solvents

Transitions $^4I_{15/2}$ (G.S)	Spectral Range (cm^{-1})[a,b]	Solvents ($P \times 10^{-6}$)										
		A	B	C	D	E	F	G	H	I	J	K
$^4I_{11/2}$	9867–10484	0.77	0.65	0.88	1.37	0.62	0.81	0.62	0.64	1.52	0.63	–
$^4I_{9/2}$	12044–12897	0.24	0.32	0.38	0.31	0.35	1.42	0.40	0.22	–	–	–
$^4F_{9/2}$	14585–15728	1.73	1.69	1.77	1.86	1.84	–	1.61	1.90	1.90	1.54	–
$^4S_{3/2}$	17960–18558	0.59	0.53	0.58	0.62	0.61	0.60	0.55	0.50	0.64	0.47	–
$^2H_{11/2}$	18558–19701	20.46	18.02	20.87	21.80	21.19	17.92	18.37	20.22	21.96	19.41	23.50 (24.57)[d]
$^4F_{7/2}$	19919–20990	1.85	1.72	1.78	1.84	1.86	1.61	1.58	1.78	1.78	1.64	–
$^4F_{5/2}$, $^4F_{3/2}$	21516–22877	0.65	0.57	0.66	0.72	0.74	0.58	0.67	0.54	0.58	0.53	–
$^2H_{9/2}$	23947–25090	0.71	0.68	0.66	0.75	0.60	0.48	0.68	0.52	0.71	0.71	–
$^4G_{11/2}$	25680–26807	79.06	67.44	79.69	81.76	c	69.87	69.70	78.35	79.74	68.97	81.57

A Chloroform; *B* Dichlomethane; *C* Methanol; *D* Ethanol; *E* Nitromethane; *F* Acetonitrile; *G* Benzene; *H* Pyridine; *I* Carbon tetrachloride; *J* Acetone; *K* DMSO

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate location of the bands

[b] The oscillator strength of aqua ion are given in Table 1

[c] This transition was partially subtracted due to the absorption of solvent in this region

[d] The values in parentheses are the due to Er(fod)$_3$ in DMSO

Table 3 Oscillator strength of [Er(fod)$_3$(bpy)] in different non-aqueous solvents

Transitions $^4I_{15/2}$ (G.S)	Spectral Range (cm^{-1})^{a,b}	Solvents ($P \times 10^{-6}$)										
		A	B	C	D	E	F	G	H	I	J	K
$^4I_{11/2}$	9717–10540	–	0.74	0.42	1.38	0.64	0.60	0.67	–	0.77	0.57	0.57
$^4I_{9/2}$	12133–12849	–	0.33	0.25	0.31	0.25	0.23	0.17	–	–	–	0.29
$^4F_{9/2}$	14656–15730	1.98	1.72	1.88	1.81	1.61	1.62	1.65	–	1.95	2.18	1.81
$^4S_{3/2}$	17823–18557	0.65	0.55	0.55	0.55	0.55	0.55	0.64	–	0.43	0.58	0.61
$^2H_{11/2}$	18557–19738	21.07	20.26	23.40	21.69	19.67	19.22	18.84	24.05 (24.57)^d	28.41	20.95	23.06
$^4F_{7/2}$	19935–20972	1.89	1.83	1.86	1.90	1.84	1.71	1.69	–	1.86	1.76	1.99
$^4F_{5/2}$, $^4F_{3/2}$	21662–22942	2.40	0.71	0.75	0.62	0.82	0.63	0.61	–	0.58	0.61	0.80
$^2H_{9/2}$	24064–25128	–	0.72	0.72	0.70	0.73	0.61	0.74	–	0.98	0.91	0.84
$^4G_{11/2}$	25676–26820	81.12	77.22	91.56	83.23	75.04	c	72.05	97.68 (94.95)^d	111.56	80.12	87.34

A Chloroform; *B* Dichlomethane; *C* Methanol; *D* Ethanol; *E* Acetonitrile; *F* Nitromethane; *G* Benzene; *H* DMSO; *I* Pyridine; *J* Carbon tetrachloride; *K* Acetone

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate location of the bands

[b] The oscillator strength of aqua ion are given in Table 1

[c] This transition was partially subtracted due to the absorption of solvent in this region

[d] The values in parentheses are the due to Er(fod)$_3$ in DMSO

strengths of the transitions of the dinuclear complex is due to the presence of two Er(III) metal ions in [Er$_2$(fod)$_6$(μ-bpm)] and offers as a remarkable application of 4*f*–4*f* absorption spectroscopy in finding the number of lanthanide ions present in a complex.

Solvent effect on hypersensitive transitions

The solvents employed in this study can be broadly classified as (i) non-coordinating solvents (chloroform, dichloromethane, carbon tetrachloride, acetonitrile and benzene) and (ii) potentially coordinating solvents (methanol, ethanol, acetone, dimethylsulphoxide, nitromethane and pyridine). It is noted that the oscillator strengths of the hypersensitive transitions of the dinuclear complex, [Er$_2$(fod)$_6$(μ-bpm)], in non-coordinating solvents (chloroform; dichlomethane; carbon tetrachloride, benzene) and potentially coordinating solvents acetone and DMSO, are similar in magnitude (Table 1). However, the oscillator strength in methanol, ethanol and pyridine are larger than the values observed in the above mentioned solvents. We observe that the oscillator strengths of hypersensitive transitions, in the case of [Er(fod)$_3$(phen)], are not affected by any of the solvents (Table 2). The oscillator strengths observed for the hypersensitive transitions of [Er(fod)$_3$(bpy)] are similar in the various coordinating and non-coordinating solvents employed in this study (Table 3). However, the oscillator strengths of these transitions of this complex in pyridine are significantly enhanced while in methanol and acetone show a marginal increase as compared to the values in carbon tetrachloride and chloroform.

An increase in the oscillator strength of the hypersensitive transition in a coordinating solvent demonstrates complex–solvent interaction in solution [11, 12, 15, 43]. Thus, it is apparent, from these results, that potentially coordinating solvents which do not affect magnitude of the oscillator strength of the complexes do not enter the inner-coordination sphere of the Er(III) which indicates very stable nature of the complexes. They retain their bulk composition in solution, without any alteration in geometry. Therefore, it is concluded that phen complex is least affected by the solvents and is most stable in solution, followed by bpy complex, while dinuclear bpm complex shows interaction with many solvents. Given the complexities encountered in the structures in the solution, it is not possible to give a simple explanation for these results. However, if a solvent molecule enters the coordination sphere of Er(III) in [Er(fod)$_3$(bpy)] or [Er$_2$(fod)$_6$(μ-bpm)], the species in the solution will have a significantly different coordination geometry and "effective" symmetry of the ligand field about the Er(III) ion. Although many theories to explain hypersensitivity in lanthanide complexes have been proposed [44] but the present result is clearly a geometry-related effect rather than a polarizability effect [15] and an explanation of this can be found in the inhomogeneous dielectric theory (static coupling) of *hypersensitivity* proposed by Jørgensen and Judd [45]. Since these are eight-coordinate complexes, the coordination of a solvent molecule will transform them into nine-coordinate complexes which seem to have less effective symmetry of the field around Er(III) than the original eight-coordinate complexes. This accepts the premise that hypersensitivity depends on the asymmetry of the field on the ion [45].

Fig. 7 Band shapes of hypersensitive transitions ($^4G_{11/2} \leftarrow {}^4I_{15/2}$ and $^2H_{11/2} \leftarrow {}^4I_{15/2}$) of [Er(fod)$_3$(phen)] in various coordinating and non-coordinating (CH$_2$Cl$_2$) solvents
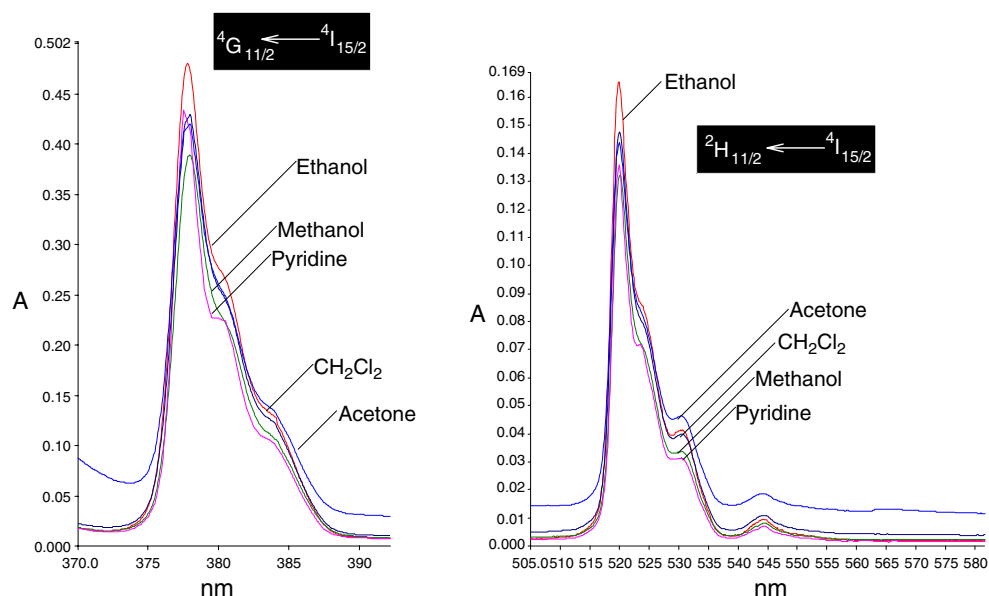
Effect of ancillary ligands

Although these complexes are eight-coordinate, the solvent effect on the hypersensitive transitions are dissimilar. It is interesting to associate these results with the basicity of the heterocyclic ligands (bpm, bpy and phen). The phen is more basic (pKa=4.9) than bpy (pKa=4.35) while bpm has lowest basicity (pKa=0.6). Being most basic, phen would be expected to contribute more electron density through Er–N bond making the Er(III) ion more electron rich. As a result, the

Er(III) will show less attraction for electron donor solvents. The rigidly planar structure of phen would also be helpful in obstructing the coordination of solvent molecules to inner coordination sphere of Er(III) and prevent the complex–solvent interaction. The bpy is flexible and a less basic ligand than phen, thus strongly basic molecules like pyridine would easily find their way to enter the coordination sphere of Er(III) ion. Contrary to above two cases, the bpm is much weaker base and after coordination, the Er(III) ion would seek more electron richness and therefore, electron donor solvents like

Fig. 8 Band shape of hypersensitive transitions ($^4G_{11/2} \leftarrow {}^4I_{15/2}$ and $^2H_{11/2} \leftarrow {}^4I_{15/2}$) of [Er$_2(fod)_6$(μ-bpm)] in various coordinating and non-coordinating (CCl$_4$) solvents
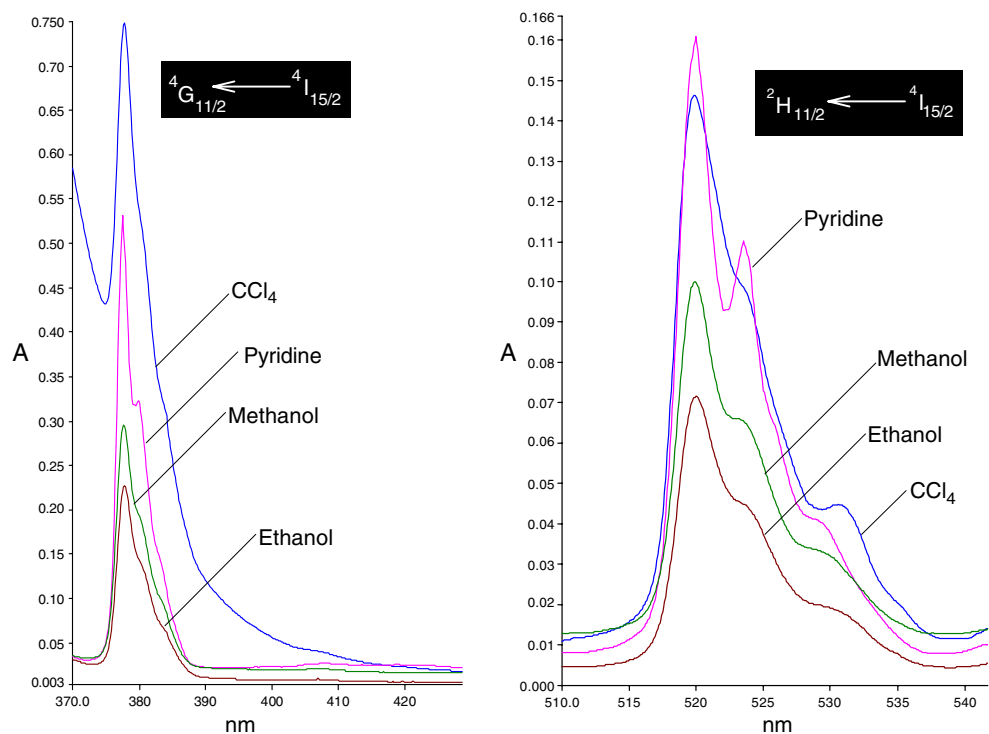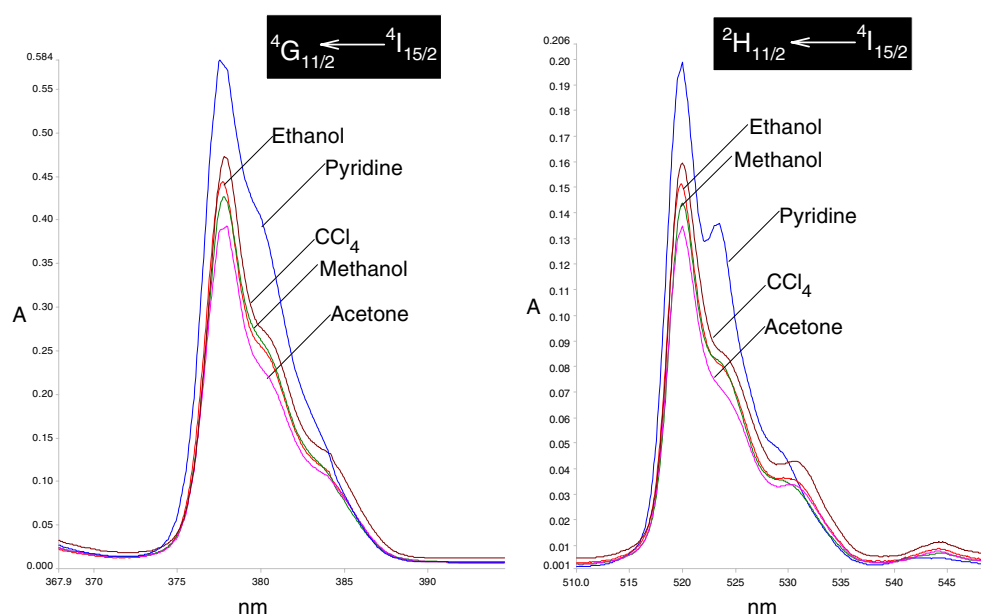
Fig. 9 Band shapes of hypersensitive transitions ($^4G_{11/2} \leftarrow$ $^4I_{15/2}$ and $^2H_{11/2} \leftarrow$ $^4I_{15/2}$) of [Er(fod)$_3$(bpy)] in various CCl$_4$ and various coordinating solvents

methanol, ethanol and pyridine would be encouraged to enter the coordination sphere of the metal ion. The coordination of the solvent changes the symmetry of the complex which results into a change in (i) the oscillator strength of 4f–4f hypersensitive transitions in the absorption spectra of Er(III) complexes and (ii) the luminescence intensity of its Eu(III) analogues (vide supra). However, it is remarkable that the coordination of pyridine decreases the luminescence intensity of Eu(III) complexes while oscillator strength of the hypersensitive transitions of Er(III) increased in this solvent. This irregularity could be attributed to the difference in the size between two metal ions (the ionic radii of Eu(III) and Er(III) are 0.950 and 0.881 Å, respectively). The significantly larger size of Eu(III) would be helpful in accommodating more than one pyridine molecules. The smaller size Er(III) would lead to acquire closely packed coordination sphere around it. Thus, it would be difficult for more than one pyridine molecules to enter the packed coordination sphere of Er(III). Consequently, the complexes of these two metal ions attain different symmetry in pyridine.

Solvent effect on band shape

The changes in band shape of the hypersensitive transitions have been used as qualitative indication of symmetry and have been correlated with a change in the coordination geometry and symmetry of the complex [10–12, 42]. It is observed, in the present study, that change in oscillator strength is accompanied by a change in the band shape of the hypersensitive transitions. The band shape of the two transitions in [Er(fod)$_3$(phen)] in all solvents remain similar and does not show any appreciable modification upon changing the solvent (Fig. 7). This is in agreement with

the observation that oscillator strengths of these transitions, of this complex, also do not show any appreciable increase or decrease. This indicates that the complex is inert towards the solvents and this may be due to very close packing of the ligands around Er(III) and rigidly planar structure of phen would be helpful in achieving this. The band shape of these transitions in the case of [Er$_2$(fod)$_6$(μ-bpm)] in non-coordinating solvents are similar, while the band shapes are distinctively different in the coordinating solvents; ethanol, methanol and pyridine (Fig. 8) and show splittings. The splitting is more prominent
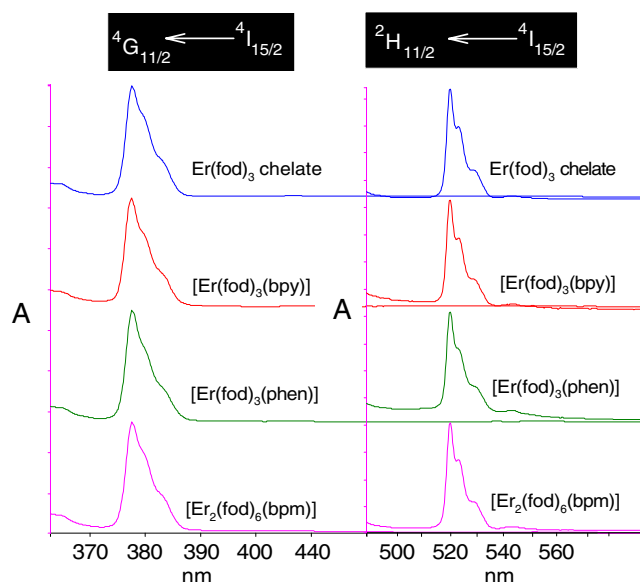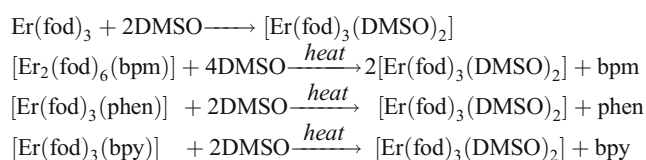

Fig. 10 Band shape of hypersensitive transitions of Eu(fod)$_3$ and its complexes in DMSO

in pyridine than methanol and ethanol. The band shapes of these transitions in [Er(fod)$_3$(bpy)] in different solvents (Fig. 9) reveals that only pyridine brings out a change in shape while rest of the solvents remains ineffective. Pyridine coordination has been demonstrated in many lanthanide complexes [12, 15, 28, 46]. Since the largest increase in the oscillator strength for [Er(fod)$_3$(bpy)] is noted in pyridine (Table 3) with distinctively different band shape, it is reasonable to associate this with a change in geometry due to coordination of pyridine.

Spectra in DMSO

We have also investigated the absorption spectrum of Er(fod)$_3$ chelate in DMSO and the oscillator strength is calculated. The chelate is soluble in this solvent but the complexes were insoluble. However, upon heating the complexes on gas burner in DMSO solvent, they become soluble in this solvent and do not reappear. It is interesting to compare the oscillator strength and band shape of the hypersensitive transitions of three erbium complexes and Er(fod)$_3$ in DMSO. The band shapes of these transitions in this solvent are identical (Fig. 10). The oscillator strength of the hypersensitive transitions of Er(fod)$_3$, [Er(fod)$_3$(phen)] and [Er(fod)$_3$(bpy)] are similar in magnitude (Tables 2 and 3) while the oscillator strength of these transitions for the dinuclear complex is double of those observed for the mononuclear complexes (Tables 1). This is because the mononuclear complexes have only one Er(III) centre and two Er(III) centres are present in the dinuclear complex. Thus, we believe that DMSO, being a very strong coordinating solvent (Gutmann number = 29.8) [47] invades the complexes and enters the inner-coordination sphere of Er(III) by replacing the heterocyclic ligand to give [Er(fod)$_3$(DMSO)$_2$] species as shown below.

$$Er(fod)_3 + 2DMSO \longrightarrow [Er(fod)_3(DMSO)_2]$$
$$[Er_2(fod)_6(bpm)] + 4DMSO \xrightarrow{heat} 2[Er(fod)_3(DMSO)_2] + bpm$$
$$[Er(fod)_3(phen)] + 2DMSO \xrightarrow{heat} [Er(fod)_3(DMSO)_2] + phen$$
$$[Er(fod)_3(bpy)] + 2DMSO \xrightarrow{heat} [Er(fod)_3(DMSO)_2] + bpy$$

The [Ln(β-diketonate)$_3$(DMSO)$_2$] species have been reported in the literature [35, 48]. These results also corroborate with our earlier observation [12] on [Nd(acac)$_3$(phen)] and [Nd(acac)$_3$(bpy)] complexes. By replacing the heterocyclic ligand structurally similar species exist in solution. This is why the oscillator strength is similar in magnitude and bands are identical. The two fold larger oscillator strength in case of dinuclear complex is due to the formation of two units of [Er(fod)$_3$(DMSO)$_2$] species by one unit of [Er$_2$(fod)$_6$(μ-bpm)]. We also studied the NMR of [Nd(fod)$_3$(phen)] and [La(fod)$_3$(bpm)] complexes in DMSO-d$_6$, in order to confirm dissociation of the aromatic ligands. The NMR spectra of the two complexes show

resonances due to free phen and bpm while no signal due to dissociated (free) fod was observed. This confirms the formation of kinetically stable [Ln(fod)$_3$(DMSO)$_2$] species in DMSO. Thus, these complexes, which have different structure in the solid state, acquire similar structure in this solvent.

Conclusion

The present investigations reveal that the photoluminescence properties of eight-coordinate Eu(III) β-diketonate complexes with various diimine ligands in solution are sensitive towards; (i) donor solvents due to changes in the inner coordination sphere around Eu(III) ion and (ii) the sensitizing ability of the ancillary ligands. It is also observed that some coordinating solvents (methanol, ethanol and pyridine) have a great impact on the oscillator strength and band shape of the 4f–4f hypersensitive transitions of Er(III). However, the [Er(fod)$_3$(phen)] has been found inert toward any of the solvents and retains its bulk composition in solution. Therefore, ancillary ligands with higher basicity and rigidly planar structure are effective for the design of solution stable Ln(β-diketonate)$_3$ adducts. Pyridine has been found most effective in promoting 4f–4f intensity in case of bpy and bpm complexes. The transformation of the erbium complexes in DMSO into [Er(fod)$_3$(DMSO)$_2$] species is found. The results give a direction for controlling the luminescence and absorption properties of lanthanide complexes in solution by tuning the coordination structure through ancillary ligands and donor solvents. This work shall prove useful in designing new biological applications with such probes.

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