

The Correlation Between $f-f$ Absorption and Sensitized Visible Light Emission of Luminescent Pr(III) Complexes: Role of Solvents and Ancillary Ligands on Sensitivity

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Abstract The electronic absorption, excitation and sensitized visible light emission studies of three praseodymium (III) complexes: $[\text{Pr}(\text{fod})_3(\text{bpy})]$, $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ (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) in a series of non-aqueous solvents is presented. The $f-f$ absorption transitions of Pr(III) are environment sensitive which is reflected by the change in the intensity (oscillator strength) and band shape (stark splitting) upon change in the solvent and/or the ligands. The sensitization of intense Pr(III) emission, in the visible region, of the complexes in solution upon excitation into the ligand centered $\pi \rightarrow \pi^*$ absorption band is remarkable. The planar phen has pronounced impact and increases considerably the emission intensity of Pr(III) luminescence than the flexible bpy while bpm has been found least effective in promoting the emission intensity. The intensity of the $f-f$ absorption and sensitized emission are correlated with the nature of the solvents. The donor solvent pyridine enhances the emission intensity of the $[\text{Pr}(\text{fod})_3(\text{phen})]$ drastically and of $[\text{Pr}(\text{fod})_3(\text{bpy})]$ marginally while the luminescent intensity of $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ is decreased. The combined photophysical studies demonstrate that entry of the solvent molecule(s) to inner coordination sphere (complex-solvent interaction) is governed by the structure and basicity of the ancillary heterocyclic ligand attached to the Pr(III) complex. The strong donor DMSO transforms the three

complexes into a similar species, $[\text{Ln}(\text{fod})_3(\text{DMSO})_2]$, which results in similar electronic absorption and emission properties of the complexes in this solvent. The results demonstrate that highly luminescent praseodymium chelates can be designed with ligands containing suitable energy levels and their emission properties can be further modulated through suitable ancillary ligands and donor solvents, thus opening perspectives for applications in electroluminescent devices and luminescent probes.

Keywords Praseodymium · Ancillary ligand · $f-f$ absorption · Luminescence · Solvent effect

Introduction

The design and synthesis of lanthanide complexes is a fascinating field of research due to the unique properties associated with Ln(III) ions [1–4]. The most striking feature of the lanthanide complexes is their line-like emission which results in a high colour purity of the emitted light. The luminescent lanthanide complexes find a variety of applications, particularly as luminescent probes [5], sensors [6] and emitting materials for LEDs [7]. The intra-configurational $f-f$ transitions are parity forbidden and these absorptions have low molar absorptivities ($\epsilon < 1 \text{ M}^{-1} \text{ cm}^{-1}$) making direct photo-excitation of the Ln(III) ions very inefficient, unless high power laser excitation is utilized. This problem is overcome by using a strongly absorbing chromophore, attached to the lanthanide, to sensitize Ln(III) emission in a process known as antenna effect [8, 9]. Initial excitation occurs via the chromophore, which transfers the energy to Ln(III), populating the lanthanide-centered excited state, which then emits. Given the short lifetimes of the excited singlet states for organic chromophores,

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energy transfer is usually discussed as proceeding from the excited triplet state. In terms of desired photophysical properties, the organic chromophore should possess a very high molar absorptivity (ϵ) and excitation wavelength, (λ_{ex}) should be above ca. 350 nm to facilitate use of inexpensive excitation source. The luminescence efficiency largely depends upon the choice of the organic ligands [8]. The β -diketone ligands possess a strong π - π^* absorption band in the UV region which is desired for efficient transfer of this absorbed energy to the emitting level of Ln(III) ion. Generally, complexes of Sm^{3+} , Eu^{3+} , Tb^{3+} , and Dy^{3+} are considered to have the brightest emission in the visible region and a large number of studies about the sensitization of luminescence of these lanthanides by different type of ligands including β -diketones have been reported [3–5, 10–14]. However, it is surprising that the emission properties of praseodymium complexes with β -diketonates and other ligands have received little attention and is least explored [15–19]. A recent study [16] has demonstrated that luminescence efficiency of praseodymium complexes could be greater than the Sm^{3+} , Eu^{3+} , Tb^{3+} and Dy^{3+} complexes provided a suitable chromophore is attached to Pr^{3+} ion. Iftikhar and his coworkers have recently reported the luminescence properties of mono- and dinuclear β -diketonate complexes of Pr(III), Sm(III), Eu(III) and Tb(III) and investigated the effect of environment (solvent/ligand) on the luminescence efficiency and band shape of the emission transitions [20–25]. It has been demonstrated that changing solvent or ligand environment around the Ln(III) ions has an impressive impact on the luminescence properties.

In the present paper, we extend our investigations on the synthesis and photophysical properties of three praseodymium complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$, $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ (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) at room temperature in a series of non-aqueous solvents. Of the three complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\text{phen})]$ are known and have been reported by Iftikhar et al. [26] while $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ is new and has not been reported so far. The $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ as well as its phen and bpy analogues were thoroughly characterized before investigating the photophysical properties. The complexes display remarkable luminescence in the visible region which is very sensitive to the environment around Pr(III) ion. The effect of change in the solvent and/or ancillary ligand around the praseodymium ion on the photophysical properties of these complexes is being investigated.

Experimental

Materials The commercially available chemicals that were used without further purification are: Pr_6O_{11} from Leico

Chem. This oxide was converted to praseodymium chloride 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, 2,2'-bipyridyl 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 RX1 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 were 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 $^\circ\text{C}/\text{min}$. 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. The concentration range was kept 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 in CDCl_3 . Steady state room temperature excitation and luminescence spectra of the solutions (2×10^{-3} M) were recorded on Horiba Jobin Yvon Fluorolog 3–22 spectrofluorometer using 450 W xenon lamp as the excitation source and Hamamatsu R928P PMT as detector.

Synthesis The $\text{Pr}(\text{fod})_3$ chelate was synthesized according to the published procedure [27] with the modification that praseodymium chloride was used instead of praseodymium nitrate. The $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\text{phen})]$ were isolated according to procedure given in ref. [26]. The chelate and the complexes were thoroughly characterized before use.

$[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ $\text{Pr}(\text{fod})_3$ (0.25 g, 0.243 mmol) was dissolved in 15 mL absolute ethanol. To this solution was slowly added an absolute ethanol solution of 2,2'-bipyrimidine (19.2 mg, 0.121 mmol bpm in 8 mL ethanol). The mixture was kept on hot plate at 40 $^\circ\text{C}$ and was continuously stirred for 4 h. The resulting solution (approx. 12 mL) was kept overnight at room temperature. Slow evaporation of the solvent resulted in the precipitation of very small needle light green crystals, which were filtered off and washed with cold ethanol and dried *in vacuo* over P_4O_{10} . The pure product was obtained by repeated recrystallization from ethanol and dried *in vacuo* (0.11 g, 40.86%). m.p. 161 $^\circ\text{C}$, Anal. Calc. for $[\text{Pr}(\text{fod})_3(\text{bpm})]$ ($\text{PrC}_{38}\text{H}_{36}\text{F}_{21}\text{O}_6\text{N}_4$): C, 38.52; H, 3.06; N, 4.73. Found: C, 38.73; H, 3.06; N, 4.73%. ^1H NMR (CDCl_3

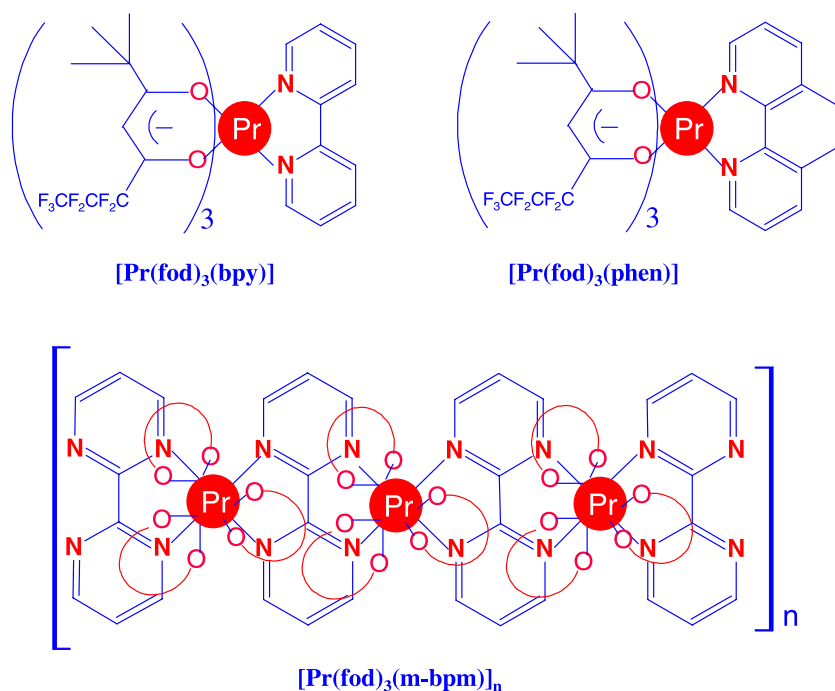
300 MHz): δ (ppm)=1.25 (tert-butyl, 27 H), 21.71 (methine, 3 H), -26.50 (H2 and H2', 4 H, very broad), -2.10 (H3, 2 H, broad), IR (cm^{-1}), 1,624 (vs) {C = O stretching}; 1,572 (s)/1,534 (w) {doublet, bpm ring stretching modes}; 1,507 (s) {C = C stretching}; 1,474 (s); 1,414 (m); 1,394 (w); 1,345 (vs); 1,276 (w); 1,227 (vs); 1,179 (m); 1,155 (m); 1,118 (s); 1,100 (m); 1,072 (w); 1,023 (w); 1,007 (w); 958 (m); 935 (w); 908 (s). ESI-MS (positive ion mode): $m/z=889.1$ {[Pr(fod)₂(bpm)]⁺}; $m/z=1049.2$ {[Pr(fod)₂(bpm)₂]⁺}.

Results and discussion

Synthesis The synthesis of the complexes is based on the well known fact that the Ln(β -diketonate)₃ chelates are coordinatively unsaturated and rapidly react with NN donor ligands such as phen and bpy, in solution, to form coordinatively saturated complexes [20, 26, 28, 29]. Therefore, the reaction of Pr(fod)₃ chelate with an equimolar amount of phen or bpy (diimine ligands) in ethanol yields air and moisture stable complexes of the type [Pr(fod)₃(phen)] and [Pr(fod)₃(bpy)] in high yield (Chart 1). The reaction of Ln(fod)₃ with potentially bridging bpm ligand was expected to yield the dinuclear complex of the form [Ln(fod)₃(μ -bpm)Ln(fod)₃] in line with their Nd, Eu, Tb and Lu analogues [21, 24, 25]. However, the reaction of Pr(fod)₃ chelate with bpm in 2:1 ratio did not yield the expected dinuclear complex. The isolated product, on the basis of elemental analysis, is identified as mononuclear bpm adduct of the type [Pr(fod)₃(bpm)]. Furthermore, the

complex was isolated in low yield (40%) as compared with its dinuclear Nd, Eu, Tb and Lu analogues [21, 24, 25] which were isolated in very high yields (~85%). This prompted us to believe that mono-nuclear species is formed instead of dinuclear complex. The IR spectrum of the complex displays bands at ca. 1,572 cm^{-1} (strong) and 1,534 cm^{-1} (weak) as an asymmetric doublet. These bands are due to ring stretching modes of bipyrimidine and the presence of an asymmetric doublet in this region is diagnostic of bis-chelating modes of bipyrimidine (i.e. bridging-bipyrimidine) [30, 31]. It is important to mention that IR results favour coordination of both sides bpm to Pr (III) while elemental analysis corresponds to mononuclear formula unit. Therefore, this complex is presumed to adopt a coordination polymeric structure of the form [Pr(fod)₃(μ -bpm)]_n as shown in Chart 1. This presumption is strongly supported by the recent report on [Nd(tta)₃(bpm)] [32] (tta is the anion of 2-thenoyltrifluoroacetone) where X-ray crystal structure of this complex has shown that it adopts a polymeric array of the type [Nd(tta)₃(μ -bpm)]_n and one-dimensional structure for the analogous bpm-bridged complexes [33, 34]. Hence, it is concluded that the present Pr complex forms one dimensional array structure in which both the ends of bpm are involved in coordination and each Pr(III) ion is attached to six O-atoms from three fod units and two NN donors from two bpm units as represented in Chart 1. Thus, each Pr(III) is ten-coordinate in the complex. The reason for the unusual reactivity of this Pr(III) compared with other Ln(III) in the series [21], which yielded bpm-bridged eight-coordinate dinuclear complexes, could be safely related to the larger size of the

Chart 1 Chemical structure of the complexes. The semicircles with O-atoms at the terminal represent β -diketonate (fod) moieties



former ion. The ten-coordinate praseodymium complex has recently been reported with hexafluoroacetylacetonate (hfaa) and phen by reacting with additional ancillary ligand [20, 29]. The larger size of Pr(III) and electron withdrawing fluorines present in β -diketonate moiety [20, 29] facilitate acquiring higher coordination number. In the present case, the lower basicity of bpm could also be helpful since it will facilitate the larger Pr(III) ion to coordinate with two NN donors of bpm instead of only one to attain greater electron affluence.

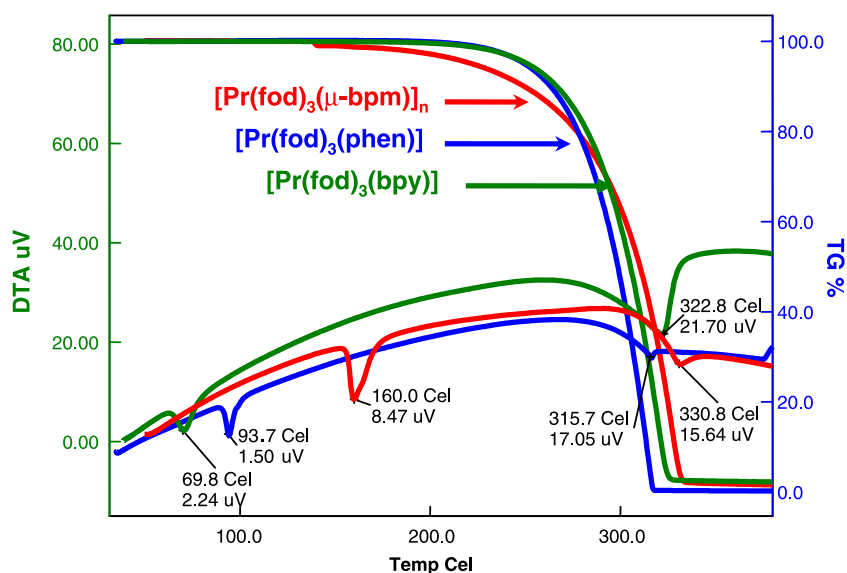
ESI-MS⁺ The electrospray mass spectra of $[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ in positive ion mode was studied in methanol solution. The spectrum is complicated possibly due to partially fragmented β -diketonate moieties as observed in lanthanide complexes with fluorinated β -diketonate [35]. Therefore, various peaks centered at higher mass distribution $m/z=1207.2$, 1223.2, 1367.2 and 1383.2 could not be identified. However, two peaks centered at $m/z=889.1$, 23.52% and 1049.2, 27.75% are easily assigned to the monomeric fragments, $[\text{Pr}(\text{fod})_2(\text{bpm})]^+$ and $[\text{Pr}(\text{fod})_2(\text{bpm})_2]^+$, respectively. It is important to mention that mass spectrum of this complex did not display any peak for the free bpm which indicates that bpm is tightly held with the metal ion in the fragments.

NMR One of us has discussed elsewhere [36] the NMR of $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpy})]$ complexes in detail thus we will limit, here, to the NMR of bpm complex only. The ^1H NMR spectrum of $[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ was recorded in CDCl_3 and covers a chemical shift range of about 49 ppm (from -26.5 to 21.70 ppm). We have also recorded the NMR spectrum of the chelate, $\text{Pr}(\text{fod})_3$ for comparison purpose. The spectrum of the bpm complex displays four

peaks in the intensity ratio of 27:3:4:2. A strong resonance at 1.25 ppm is assigned to *tert*-butyl protons while a relatively sharp resonance at 21.71 ppm is assigned to methine protons, of the coordinated fod moieties. The *tert*-butyl and methine resonances in the ^1H NMR of the Pr (fod)₃ chelate appear at 0.35 ppm and 19.60 ppm, respectively. Both the *tert*-butyl and methine resonances are significantly shifted to the downfield in the complex as compared with their position in the chelate which is consistent with the coordination of nitrogen base and reflects a change in geometry around Pr(III) ion after coordination [36]. Comparatively broad resonances observed at -26.50 ppm and -2.10 ppm (in the intensity ratio of 2:1) are assigned to H-2 and H-3 protons, respectively, of the coordinated bpm. These resonances are substantially shifted and appear to the high-field side of the TMS as compared to their position in free bpm. The broadening in these resonances is due to enhanced paramagnetic relaxation of these nuclei. The degree of broadening is more in H-2. The broadening is also associated with proton-metal distance, since H-2 protons are closer to the Pr(III) centre and therefore, are broader. The line widths decrease with the number of bonds separating the nucleus in question from the paramagnetic center.

Thermal studies The TGA/DTA plots of the three complexes are shown in Fig. 1. The thermograms of the complexes are similar in shape, therefore, thermal behavior of the complexes is similar. The one step weight loss is consistent with the complete evaporation without dissociation. The DTA curves of the complexes show two endothermic peaks; one sharp peak at lower temperatures (between 69 and 160 °C) corresponding to the melting and another peak at higher temperatures (between 315 and

Fig. 1 TGA/DTA plot of the complexes



330 °C), indicates volatilization of the complexes. It can be seen from Fig. 1 that melting point of bpm complex is much higher than the mononuclear bipyridine and phenanthroline analogues which reflects that the coordination polymer is thermally more stable over mononuclear discrete complexes. Among mononuclear complexes the phen complex is thermally more stable over bpy complex, due to rigidly planner structure of phen than flexible bpy.

4f–4f electronic absorption The absorption spectra of the complexes were recorded in series of non-aqueous solvents (chloroform, dichloromethane, carbon tetrachloride, pyridine and DMSO). The complexes display strong broad band in the UV region (240–400 nm) which is assigned to the ππ* transitions of coordinated β-diketone and ancillary heterocyclic ligands.

The absorption spectra of the complexes, in the visible region, display characteristic 4f–4f transitions of the Pr³⁺ ion. The f² configuration of Pr(III) ion involves thirteen energy levels above the ground state. Their location is found experimentally by analysis of the spectra for the gaseous Pr(III) ion [37, 38]. All the lines observed in the absorption spectra for the Pr(III) in solutions and crystals in the near infra-red and visible spectral regions correspond to the transitions from the ground state, ³H₄. The transitions between the levels of f² are assumed to occur by forced electric-dipole mechanism due to mixing of higher configuration of opposite-parity into the ground state (configuration interaction). This small mixing may increase on complexation, if the energy of the excited state is lowered. The Judd-Ofelt theory is totally inapplicable to Pr(III). The ground state configuration is very low lying and it has been suggested that [39] the approximation made in the theory [40, 41], that the energy difference between the perturbing configuration and the ground and excited states of the 4fⁿ configuration are equal, is not valid. In fact the perturbing configuration is of much higher energy than f-f transition.

Only four transitions ¹D₂ (593 nm, 16,840 cm⁻¹), ³P₀ (485 nm, 20,750 cm⁻¹), ³P₁+¹I₆ (472 nm, 21,300 cm⁻¹) and

³P₂ (444 nm, 22,520 cm⁻¹) have been observed for the three complexes under study. The energy given in the parenthesis are that of Pr(III) aqua ion. The ³F₂←³H₄ transition which appears in the near infra-red region~5,200 cm⁻¹ (1,923 nm), follows selection rules, ΔJ ≤ 2, ΔL ≤ 2 and ΔS=0 for electric quadrupolar transitions, and is classified as being hypersensitive [42]. This transition could not be observed in the present study due to inadequacy of the range of the spectrophotometer.

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 ε(ν) and the energy of the transition “ν” (cm⁻¹) as given in the equation (1) [39].

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

where η is the refractive index of the solution, ε(ν) is the molar extinction coefficient at wavelength ν.

The oscillator strength of the transitions of the complexes are calculated from the spectra and are collected in Tables 1, 2 and 3 along with the oscillator strength of hydrated PrCl₃ in water. Of the four transitions, the ³P₂ is the most intense followed by ³P₁ while ³P₀ is the least intense for any of the complexes in any given solvent. Only ³P₂ is sensitive to environment. Changing the solvent from CCl₄ to CHCl₃ does not bring any appreciable change in the oscillator strength of this transition in both [Pr(fod)₃(phen)] and [Pr(fod)₃(bpy)] complexes. However, dichloromethane increases the oscillator strength of all observed transitions for both the complexes. This reflects that the transitions of Pr(III) are sensitive to change in the environment around this ion, a phenomenon noted earlier in the case of [Pr(hfaa)₃(phen)₂] complex (hfaa is the anion of hexafluoroacetylacetone) [20]. Of the four, ³P₂ and ³P₁+¹I₆ are affected the most in dichloromethane. Among the three solvents (CCl₄, CHCl₃ and CH₂Cl₂) CH₂Cl₂ is most

Table 1 Oscillator strengths of the 4f-4f transitions of [Pr(fod)₃(bpy)] in different non-aqueous solvents

Transitions ³ H ₄ (G.S)	Spectral range (cm ⁻¹) ^a	Pr ³⁺ aqua ion P (×10 ⁶)	Solvents (P×10 ⁶) ^b				
			A	B	C	D	E
¹ D ₂	15,250–17,602	3.12	1.74	3.48	2.23	3.68	2.75
³ P ₀	19,801–20,737	2.25	0.40	1.16	0.61	0.74	1.08
³ P ₁ + ¹ I ₆	20,737–21,636	6.60	2.55	5.21	2.64	5.95	4.03
³ P ₂	21,598–23,108	14.60	5.78	11.90	6.02	12.54	9.53

^aThe 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

^bA = Carbon Tetrachloride; B = Dichloromethane; C = Chloroform; D = Pyridine; E = Dimethylsulphoxide

Table 2 Oscillator strengths of the 4*f*-4*f* transitions of [Pr(fod)₃(phen)] in different non-aqueous solvents

Transitions ³ H ₄ (G.S)	Spectral range (cm ⁻¹) ^a	Pr ³⁺ aqua ion P (×10 ⁶)	Solvents (P×10 ⁶) ^b				
			A	B	C	D	E
¹ D ₂	15,518–17,534	3.12	2.26	3.50	3.13	3.31	1.90
³ P ₀	19,862–20,739	2.25	0.56	0.86	0.68	0.99	0.57
³ P ₁ + ¹ I ₆	20,739–21,616	6.60	2.72	5.18	2.80	5.72	3.76
³ P ₂	21,616–22,991	14.60	6.09	11.75	6.44	12.35	8.10

^aThe 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

^bA = Carbon Tetrachloride; B = Dichloromethane; C = Chloroform; D = Pyridine; E = Dimethylsulphoxide

asymmetric (C_{2v}) with highest dielectric constant (9.10) as compared with CHCl₃ (C_{3v}) with lower dielectric constant (4.80). Thus, asymmetry of the dichloromethane along with high dielectric constant is responsible for producing more asymmetric field around Pr(III), in these two complexes, which could result in higher oscillator strength. Thus, the increasing asymmetry results in oscillator strength increase. It is to be noted that the largest increase in the oscillator strength of ³P₂ transition, in the cases of phen and bpy complexes, is observed in pyridine (Tables 1 and 2), with distinctively different band shape of ³P₂ transition, indicating that highly polarizable pyridine is especially effective in promoting 4*f*-4*f* electric-dipole intensity. It is reasonable to associate this change to the coordination of pyridine, which could change nature of the chemical environment and geometry around Pr (III). Pyridine coordination has been demonstrated in many lanthanide complexes from this laboratory [24, 25, 43–45]. It is further supported by the observation noted by Iftikhar et al. who have found proton resonances due to coordinated pyridine in the NMR spectra of nine-coordinate phen complexes of Eu and Yb, in Pyridine-*d*₅ and have confirmed that pyridine did coordinate without displacing any of the ligands already present, thus resulting in an increase in the number of coordinated ligands around the lanthanides [46].

As noted in the case of phen and bpy complexes the oscillator strength of the transitions of [Pr(fod)₃(bpm)]_n are higher in CH₂Cl₂ than CHCl₃. The reason could be the

same, as pointed out in the discussion of phen and bpy complexes, i.e. the difference in dielectric constant and asymmetry of the field, around Pr(III). The enhancement of the intensity of ³P₂ transition of this complex in pyridine, as compared to that in chloroform, could be related to the coordination of the pyridine. The coordination of further ligands (pyridine) to already too crowded (ten-coordinate) complex seems unlikely. Therefore, it is believed that pyridine being more basic (pK_a=5.9) and stronger donor replaces one of the weakly basic bpm (pK_a=0.6) leading to the formation of [Pr(fod)₃(bpm)(py)₂] species in solution. Replacement of even stronger basic diimine, phen, (pK_a=4.9) by pyridine has been demonstrated in a closely related ten-coordinate complex, [Sm(hfaa)₃(phen)₂] [47].

The foregoing discussion reveals that ³P₂←³H₄ and ³P₁+¹I₆←³H₄ transitions are sensitive to the environment but since these do not obey electric-quadrupole selection rules, they are not considered hypersensitive in the sense meant for hypersensitive transitions. The ³P₂←³H₄ and ¹D₂←³H₄ transitions have been reported [42] to exhibit hypersensitivity (although this word should really be reserved for transitions obeying quadrupole selection rule). We found the ¹D₂←³H₄ transition of the complexes quite insensitive to the environment.

Dissolving the complexes in any of the solvents decreases the oscillator strength of the ³P_j levels relative to the aqueous solution of hydrated PrCl₃ while the ¹D₂ transition is only

Table 3 Oscillator strengths of the 4*f*-4*f* transitions of [Pr(fod)₃(μ-bpm)]_n in different non-aqueous solvents

Transitions ³ H ₄ (G.S)	Spectral range (cm ⁻¹) ^a	Pr ³⁺ aqua ion P (×10 ⁶)	Solvents (P×10 ⁶) ^(b)			
			A	B	C	D
¹ D ₂	15,904–17,527	3.12	1.94	3.60	3.20	2.70
³ P ₀	20,131–20,744	2.25	0.85	1.25	0.83	1.35
³ P ₁ + ¹ I ₆	20,722–21,612	6.60	3.00	5.14	5.07	3.70
³ P ₂	21,678–23,050	14.60	6.65	11.35	11.73	8.35

^aThe 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

^bA = Chloroform; B = Dichloromethane; C = Pyridine; D = Dimethylsulphoxide

affected in CCl_4 and in CHCl_3 in the cases of bpy and bpm complexes; otherwise the oscillator strength of this transition remains unchanged in any of the solvents. None of the transitions show any intensification of the peak as compared with the Pr(III) aqua-ion. In the case of Pr(III), it appears that dielectric of the medium is playing influencing role and affects the oscillator strength. The dielectric constant of water is highest (80) and could be the reason for higher oscillator strength of the transitions of Pr(III) in this medium. There is no definite trend regarding intensification of the peaks. Marked sensitivity in the oscillator strength of ${}^3\text{P}_2 \leftarrow {}^3\text{H}_4$ and ${}^1\text{D}_2 \leftarrow {}^3\text{H}_4$ has been reported [42, 43, 48–51]. In the present complexes the oscillator strength of ${}^3\text{P}_2 \leftarrow {}^3\text{H}_4$ transition is about half of the Pr(III) aqua-ion.

Solvent effect on the band shapes

Much work on the relationship between the intensity, and more commonly the shape, of the hypersensitive bands of Nd(III), Ho(III) and Er(III) has been done. Reports on the band shape of the Pr(III) complexes are few [20, 43, 45, 49, 50, 52, 53]. We have studied the spectra of Pr(III) complexes in detail and have noted that the transitions ${}^3\text{P}_2$ and ${}^1\text{D}_2 \leftarrow {}^3\text{H}_4$ show variations in the bands shape with change in the environment [20, 46]. Dissolving the complexes in any of the solvents brings appreciable differences in the band shape of ${}^3\text{P}_2$ and ${}^1\text{D}_2$ transitions. The ${}^3\text{P}_2$ band of the $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpy})]$ (eight-coordinate complexes) show similar stark splitting pattern in these complexes in chloroform while the shape of ${}^3\text{P}_2$ band of $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ (ten-coordinate complex) is different from above two complexes (Fig. 2). However, the ${}^1\text{D}_2$ band of the three complexes in chloroform is similar in shape. Next we compare the band shape of the ${}^3\text{P}_2$ transition in pyridine (Fig. 3). The band shape are identical for $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ complexes in

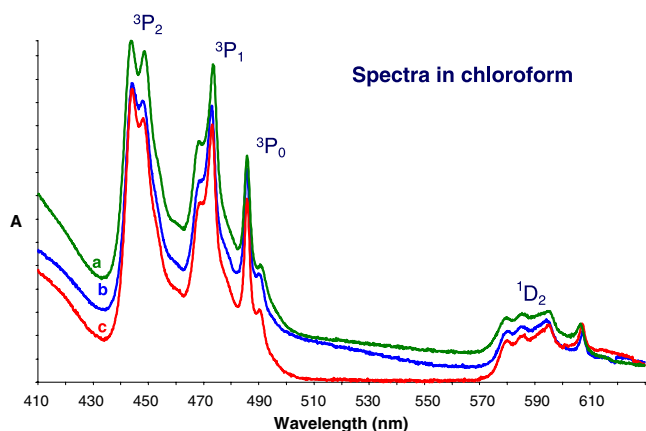


Fig. 2 $4f-4f$ absorption spectra of the complexes, (a) $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$, (b) $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and (c) $[\text{Pr}(\text{fod})_3(\text{phen})]$ in chloroform

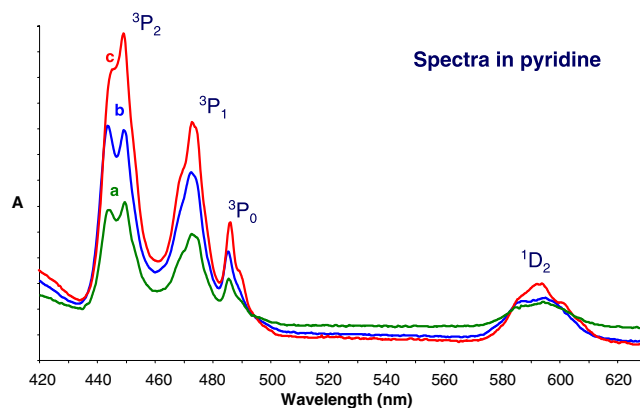


Fig. 3 $4f-4f$ absorption spectra of the complexes, (a) $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$, (b) $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and (c) $[\text{Pr}(\text{fod})_3(\text{phen})]$ in pyridine

pyridine and remarkably these are comparable with the band shape of this transition of the $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ in chloroform. Since the band shapes of the bpy and bpm complexes, in pyridine, are identical with the band shape of $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ in chloroform, the two complexes could be ten-coordinate in pyridine. This implies that two pyridine molecules coordinate with $[\text{Pr}(\text{fod})_3(\text{bpy})]$ making it ten-coordinate. Since increase in the oscillator strength of the ${}^3\text{P}_2$ band of $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ is substantial authenticates that one bpm ligand of this complex is replaced by two pyridine molecules (vide supra). The band shape of the $[\text{Pr}(\text{fod})_3(\text{phen})]$ in pyridine is different from the band shape of this transition in other two complexes and the band shape of any of the complexes in chloroform. The reasonable explanation is that only one pyridine molecule enters the inner coordination sphere and transforms it to nine-coordinate species (vide infra).

The splitting of the J levels into stark components by ligand field in the praseodymium complexes indicates larger probability of interaction between praseodymium $4f$ wave function and the ligand wave function, which leads to stronger praseodymium bonds with the surrounding ligands. Because of electronic configuration feature of the lanthanides (i.e. shielding of the ligands by $5s$ and $5p$ electrons) the spatial extension of $4f$ -orbitals is exceedingly small and, therefore, the Ln^{3+} ions are characterized by large spin-orbital coupling constants and small ligand field splitting. Due to this feature, the $4f-4f$ electronic transitions appear sharp lines. Any deviation from this feature i.e. broadening or splitting of the bands (lines) is taken as strong evidence of partaking of $4f$ -orbitals in bonding.

Comparison with other β -diketonate complexes

Finally, we compare the oscillator strength and band shape of the present phen and bpy complexes with those of other

similar phen and bpy β -diketone complexes of trivalent lanthanides. A comparison of the oscillator strength of the present complexes with those of $[\text{Pr}(\text{acac})_3(\text{phen})]$ and $[\text{Pr}(\text{acac})_3(\text{bpy})]$, in different solvents [45] reveals that the oscillator strength are generally higher, with the exception of chloroform where oscillator strengths are lower, for the present fod complexes (Tables 1 and 2). The seven electronegative fluorine atoms present in fod moieties of the complex would increase the residual acidity of Pr(III) making it a better complexing site for additional ligands (phen or bpy). This would lead to greater deal of covalency in is bonding and would result in some change in the extent of overlap and, therefore, in the degree of Ln-N(phen or bpy) bonds. This is clearly polarizability related effect rather than symmetry. The asymmetry of the fod ligand may also contribute in enhancing the intensity but this effect (low symmetry) is specific to the hypersensitive transitions. The oscillator strength of the transitions of the eight-coordinate $[\text{Pr}(\text{fod})_3(\text{phen})]$ are higher than the oscillator strength of the transitions of the ten-coordinate $[\text{Pr}(\text{hfaa})_3(\text{phen})_2]$ [20] in non-coordinating dichloromethane, while chloroform is again an exception where the values of the present phen complex are lower than the ten-coordinate hfaa complex. Both the diketones have electronegative fluorine atoms; fod is an asymmetric than the quite symmetric hfaa. The asymmetry of the fod ligand could be the case of the enhanced intensity since it would produce more asymmetric field around Pr(III) ion in this complex.

The band shapes of $^3\text{P}_2$ transition of the phen and bpy complexes are considerably different from the band shape of this transition of $[\text{Pr}(\text{acac})_3(\text{phen})]$ and $[\text{Pr}(\text{acac})_3(\text{bpy})]$ complexes, in any of the solvents investigated. This could be due to the different nature of the β -diketones present in the two complexes. The bands shape of $^3\text{P}_j$ and $^1\text{D}_2$ transitions of $[\text{Pr}(\text{acac})_3(\text{phen})]$ in both chloroform and CH_2Cl_2 , are entirely different from the bands shape observed for $[\text{Pr}(\text{hfaa})_3(\text{phen})_2]$ in these solvents. The bands of the present complex is comparatively sharp showing splitting of j levels which is due to asymmetry of fod ligand.

Absorption spectra in DMSO

The $4f-4f$ absorption spectra of the complexes in DMSO are shown Fig. 4 and the oscillator strength of the transitions in this solvent are given in Tables 1, 2 and 3. It is important to note that the oscillator strengths of the transitions of the three complexes in DMSO are similar in magnitude and the $4f-4f$ absorption bands are identical in shape. Appearance of identical band shape and virtually similar oscillator strength of the transitions of these complexes in this solvent reflects that structurally similar

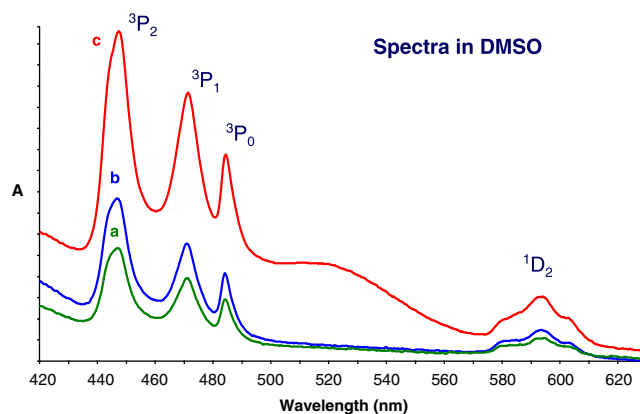
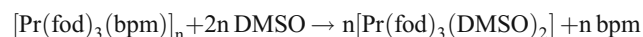
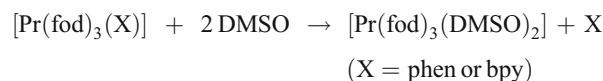


Fig. 4 $4f-4f$ absorption spectra of the complexes, (a) $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$, (b) $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and (c) $[\text{Pr}(\text{fod})_3(\text{phen})]$ in DMSO

species exist in solution. Among the solvents, in which the spectra of the complexes have been examined, DMSO is the strongest coordinating solvent with very high Gutmann donor number of 29.8 and it could invade the inner coordination sphere of the complexes, coordinates to the Pr(III), and replaces the heterocyclic ligands from the complexes, generating structurally similar species in solution. We believe that two DMSO units coordinate after replacing the heterocyclic ligand.



This gets support from our observation on holmium [24] and erbium [25] analogues; and $[\text{Ln}(\text{acac})_3(\text{phen})]$ and $[\text{Ln}(\text{acac})_3(\text{bpy})]$ complexes (where acac is anion of acetylacetonate and Ln is Pr and Nd) [44, 45]. To confirm displacement of the heterocyclic amine we have studied ^1H NMR of the lanthanum analogue, $[\text{Ln}(\text{fod})_3(\text{bpm})]_n$, in both CDCl_3 and $\text{DMSO}-d_6$. The CDCl_3 spectrum shows substantially downfield shifted resonances due to coordinated bpm while in $\text{DMSO}-d_6$ the spectrum displays sharp resonances with fine structures due to free bpm. This confirms displacement of bpm by DMSO. The number of DMSO molecules coordinated gets support from a recent report on the crystal structure of a closely related compound containing three β -diketonate like ligands and two DMSO molecules [54].

The difference between coordination of DMSO and pyridine is that DMSO replaces heterocyclic amine and two molecules acquire its position while pyridine attaches, without replacing the heterocyclic amine, leading to an increase in both the number of coordinated ligands and asymmetry of the field around Pr(III).

Photoluminescence properties

The sensitization of lanthanide luminescence by organic ligands is well documented [2–5, 9, 55]. It consists of (a) the absorption of light (usually UV light) by the coordinating ligands (antenna) into their excited singlet states; $S_0 \rightarrow S_1$ (b) an intersystem crossing from excited singlet state to a triplet state of the ligand; $S_1 \rightarrow T_1$ and (c) an intramolecular energy transfer from the triplet state of the antenna to the closest emitting level of the Ln^{III} ions; $T_1 \rightarrow \text{Ln}(\text{III})$. The excited levels of lanthanide(III) ions get deactivated either radiatively with the emission of light of the colour characteristic of a particular lanthanide (III) ion or non-radiatively by the energy degradation to the vibrations of the surrounding molecules. Moreover, if the energy gap between the ligand triplet state and the emitting level of the lanthanide (III) ion is less than the optimum energy gap required for the efficient energy transfer, the back energy transfer may also take place from Ln^{3+} ion to the triplet level of the sensitizing ligand, resulting into the quenching of lanthanide centered luminescence [8]. If the energy of the triplet level of the ligand is too high, it will not be able to overlap with the emitting level of $\text{Ln}(\text{III})$ ion and therefore, ineffective to sensitize the lanthanide luminescence. The quenching of lanthanide luminescence also occurs by the attachment of solvent molecules containing high energy oscillators such as C–H and O–H in the first coordination sphere [56]. To avoid the coordination of solvent molecules, the coordination sphere of lanthanide β -diketonate complexes is usually saturated with neutral ancillary ligands such as phen and bpy. The ancillary ligands can also take part in the sensitization process along with the primary antenna ligands [35].

The emission and excitation spectra of the complexes were recorded in a series of non-aqueous solvents. The complexes show intense 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 emission line at ~ 610 nm. The room-temperature excitation spectra of the complexes: $[\text{Pr}(\text{fod})_3(\text{phen})]$, $[\text{Pr}(\text{fod})_3(\text{bpy})]$, and $[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ in chloroform are shown in Fig. 5. They feature an intense broad band between 335 and 410 nm with maxima around 350 nm. This band is attributed to $S_0 \rightarrow S_1$ transitions of β -diketonate and heterocyclic ligands. The excitation spectra of the complexes also contain very weak $f-f$ transitions at 446, 470 and 485 nm which are due to ${}^3\text{P}_2$, ${}^3\text{P}_1 + {}^1\text{I}_6$ and ${}^3\text{P}_0$ transitions, respectively from ${}^3\text{H}_4$ ground-state of $\text{Pr}(\text{III})$. However, the $f-f$ transitions are very weak as compared to ligand centered $S_0 \rightarrow S_1$ band. This is strong evidence that Pr^{3+} luminescence is efficiently sensitized by the ligands [16].

The visible light emission spectra of the complexes in chloroform are shown in Fig. 6. The spectra mainly consist

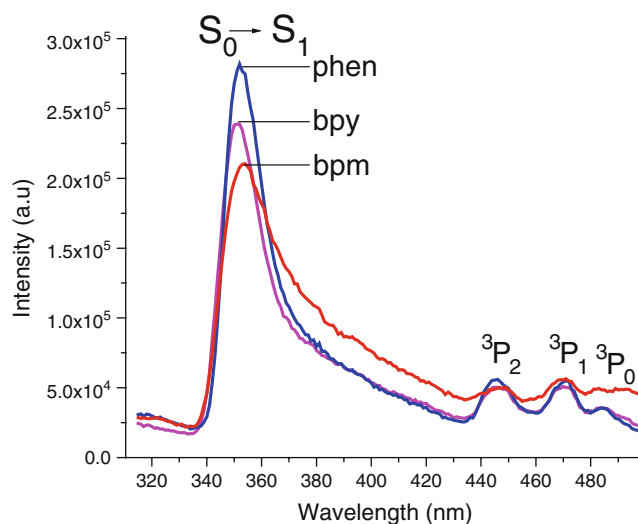


Fig. 5 Excitation spectra of the complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$, $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ in chloroform

of three peaks in the 525 to 680 nm range. The most intense peak centered at 610 nm is assigned to ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transition. This transition is also believed to be overlapped by a much weaker ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6$ transition [16, 57]. The other two emission transitions correspond to ${}^3\text{P}_0 \rightarrow {}^3\text{H}_5$ (543 nm) and ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ (648 nm). Since the luminescence intensity of the lanthanide complexes depends upon the effective overlap between the ligand triplet state (E_T) and the emitting level of the $\text{Ln}(\text{III})$ ion, the strong luminescence observed for the complexes reflects a good match between the ligand centered triplet state and ${}^1\text{D}_2$ emissive state of $\text{Pr}(\text{III})$. The triplet energy state of the main sensitizer (fod) lies near $22,500 \text{ cm}^{-1}$ [15] which is well above the ${}^1\text{D}_2$ emitting state ($\sim 16,500 \text{ cm}^{-1}$) of $\text{Pr}(\text{III})$. The energy gap between the two states ($\Delta E \sim 6,000 \text{ cm}^{-1}$) seems ideal for an efficient energy transfer to the $\text{Pr}(\text{III})$ emitting level (Fig. 7). The triplet state of fod is closer to the ${}^3\text{P}_0$ level ($\sim 20,600 \text{ cm}^{-1}$) and the energy difference, ΔE , between the two levels is $\sim 1,900 \text{ cm}^{-1}$. Therefore, emission originating from this level is weaker than ${}^1\text{D}_2$ level. There are two additional excited states above ${}^1\text{D}_2$ and ${}^3\text{P}_0$ states of $\text{Pr}(\text{III})$ and these are ${}^1\text{I}_6$ ($\sim 21,350 \text{ cm}^{-1}$) and ${}^3\text{P}_1$ ($\sim 21,150 \text{ cm}^{-1}$). These excited states are lower in energy than the triplet state of fod ($22,500 \text{ cm}^{-1}$) and can also receive energy from it; however, the luminescence is only observed from ${}^1\text{D}_2$ and ${}^3\text{P}_0$ levels since the other excited states are too close in energy to the ligand centered triplet state (Fig. 7). Since sensitization typically occurs via the excited triplet state, the antenna should possess a high inter-system crossing efficiency and the ligand triplet state should be at least $2,000 \text{ cm}^{-1}$ higher in energy than the $\text{Pr}(\text{III})$ emitting state to minimize thermal population of the triplet [8]. Therefore, it is postulated that ${}^1\text{I}_6$ and ${}^3\text{P}_1$ excited states after receiving energy from the

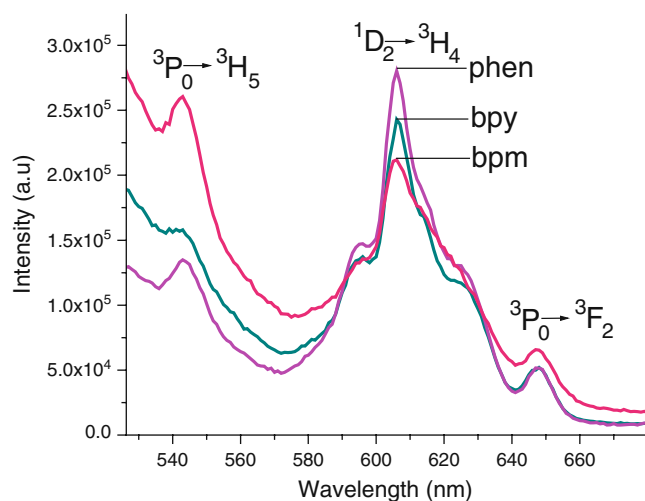


Fig. 6 Emission spectra of the complexes $[\text{Pr}(\text{fod})_3(\text{bpy})]$, $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ in chloroform

ligand centered triplet state rapidly transfer this energy to the $^1\text{D}_2$ emissive state of Pr(III) *via* non-radiative relaxation. Due to the presence of two emitting states, the Pr(III) emission can be controlled by tuning the triplet states of the antenna relative to the $^3\text{P}_0$ and $^1\text{D}_2$ levels.

Role of ancillary ligands

We compare the luminescence intensity and bands shape of the complexes: $[\text{Pr}(\text{fod})_3(\text{phen})]$, $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ in chloroform (Fig. 6). The most intense luminescence is from phen complex while the luminescent

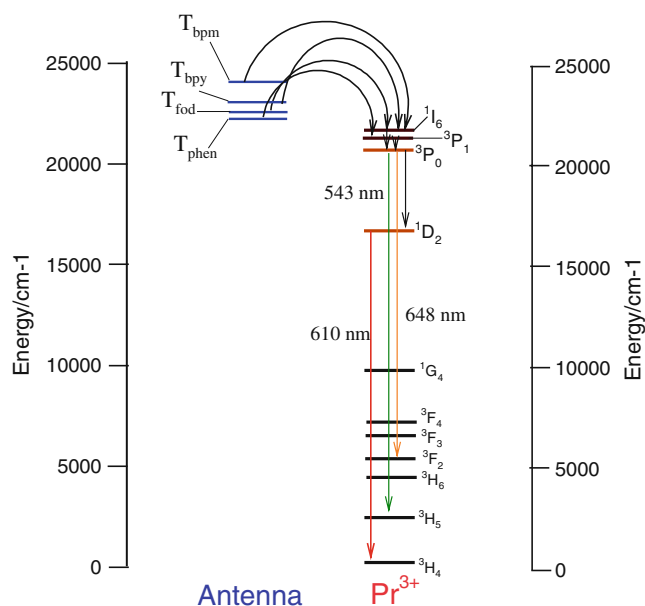


Fig. 7 Energy level diagram for the sensitized emission of Pr(III) complexes

intensity is lowest for the bpm complex. The excitation spectrum of the phen complex also displays higher intensity than bpy and bpm complexes (Fig. 5). Furthermore, the bands shape of the most intense $^1\text{D}_2 \rightarrow ^3\text{H}_4$ hypersensitive transition are similar for phen and bpy complexes while it is different in the case of bpm complex. The chloroform is non-coordinating, therefore, would not lead to change coordination geometry and effective symmetry of the complexes in solution. The only variable which could affect the luminescent intensity of these complexes is the nature of the ancillary ligands coordinated to Pr(III) ion since the number and nature of the other chromophore (β -diketone) is similar. The ancillary ligands are known to increase considerably the luminescence intensity either through the formation of intra-ligand excited state or intramolecular energy migration [24, 25, 35]. It could be seen from the Fig. 6 that the phen is especially effective in the overall sensitization process of Pr(III)-centered luminescence in $[\text{Pr}(\text{fod})_3(\text{phen})]$. The triplet energy state of phen, bpy and bpm are $\sim 22,200 \text{ cm}^{-1}$, $\sim 23,100 \text{ cm}^{-1}$ and $\sim 24,100 \text{ cm}^{-1}$, respectively while the energy of the $^1\text{D}_2$ emitting state of Pr(III) is $16,500 \text{ cm}^{-1}$. The energy difference (ΔE) between the E_T of the three aromatic ligands and the $^1\text{D}_2$ emitting level of Pr(III) are $\sim 5,700 \text{ cm}^{-1}$, $\sim 6,600 \text{ cm}^{-1}$ and $7,600 \text{ cm}^{-1}$, respectively. The best match is in the case of phen and, thus, the luminescence from this complex is most intense while the energy match in the case of bpm is poor which leads to lowest luminescent intensity. The bpy complex comes in between. The rigidly planar structure of phen is an additional feature of this in gaining more intensity. A rigidly planar ligand allows feasible energy transfer due to effective overlap leading to higher intensity of the sensitized luminescence. Although the match between energy of the triplet state of bpy and $^3\text{P}_0$ of Pr(III) is better than the energy match in the case of phen, the intensity of peaks originating from this level, are comparable in both the complexes. This indicates that rigid planar structure of phen contributing in gaining intensity due to more effective overlap.

Solvent effect on the emission properties

$[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpy})]$ The emission spectra of the $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpy})]$ in pyridine (with equal concentrations) are shown in Fig. 8. There is a distinctive change in the spectral shape and intensity of the bands in this solvent as compared with band shape and intensity in chloroform (non-coordinating solvent). Since The luminescence properties of the lanthanide complexes are very sensitive to (a) the variations in the symmetry of the coordination sphere around the Ln(III) ion and (b) polarizability of coordinated groups. The changes resulting

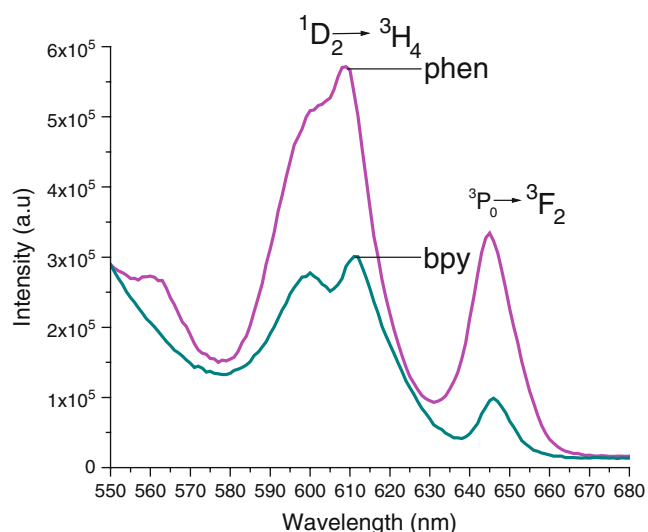


Fig. 8 Emission spectra of the complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\text{phen})]$ in pyridine

in the spectral shape and intensity of the emission transitions in pyridine could be related to change in the symmetry of the complex in this solvent, for which the reasonable explanation is the coordination of pyridine. We have discussed coordination of pyridine in the absorption section. It should be further pointed out that the enhancement in the luminescence intensity is much larger for the phen complex than the bpy complex. The two complexes display distinctively different bands shape of the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition in this solvent, a phenomenon observed on the $^3\text{P}_2$ band shape of the complexes under $4f-4f$ absorption section (Fig. 3). This transition of the bpy complex shows prominent stark splitting while in the case of phen complex the sign of stark component is seen. Both the complexes are expected to show similar luminescence behaviour in pyridine. The different luminescence behavior of the two complexes in this coordinating solvent could be explained by invoking the difference in the basicity of the two ligands; the phen is more basic ($\text{pK}_a=4.9$) than bpy ($\text{pK}_a=4.35$) and would be expected to contribute more electron density through Pr–N bonds making the Pr(III) ion more electron rich, the Pr(III) ion will show fewer attraction in acquiring additional electron density from the electron donating pyridine through coordination. Furthermore, phen has a rigidly planar structure which would be helpful in obstructing coordination of incoming solvent molecule to the inner coordination sphere of Pr(III) and would restrict the complex–solvent interaction. The bpy on the other hand is a flexible ligand and less basic than phen, thus strong donor like pyridine could find comparatively easy access to the inner coordination sphere of Pr(III) ion in this complex. Thus, it is believed that two pyridine molecules enter the inner-coordination sphere in bpy complex in solution and

the original eight-coordinate complex changes to a ten-coordinate complex while only one molecule of pyridine enters into the inner-coordination sphere Pr(III) in the phen complex and a nine-coordinate structure around Pr(III) ion results (vide supra). The nine-coordinate structure would be more asymmetric than the symmetric ten-coordinate environment around Pr(III). The low molecular symmetry (more asymmetry) of the phen complex results in larger enhancement of the intensity of the transitions ($^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$) in this complex.

The emission spectra of the phen and bpy complexes in acetonitrile are shown in Fig. 9. The $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of the phen complex is more intense in this solvent than in the chloroform while the emission intensity of this transition of the bpy complex is marginally increased in this solvent compared to chloroform. Similar result was observed in the pyridine. The band shape of $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition is distinctively different in acetonitrile and chloroform. These results indicate that acetonitrile also interact with the inner-coordination sphere of the complexes and changes both the number of coordinated ligands and symmetry around Pr(III) ion in the same manner as discussed in the case of pyridine. However, it should be pointed out that $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transition is weak with identical band shape for both the complexes in this solvent. This indicates that the triplet energy state of the antenna ligands are not perturbed in this solvent which is expected since acetonitrile is a weaker donor than pyridine. The emission spectra of the complexes in ethanol (Fig. 10) are similar to those in acetonitrile (Fig. 9). However, a close examination reveals that the emission intensity of both the transitions of the bpy complex is marginally decreased as compared to its intensity in chloroform and acetonitrile. The

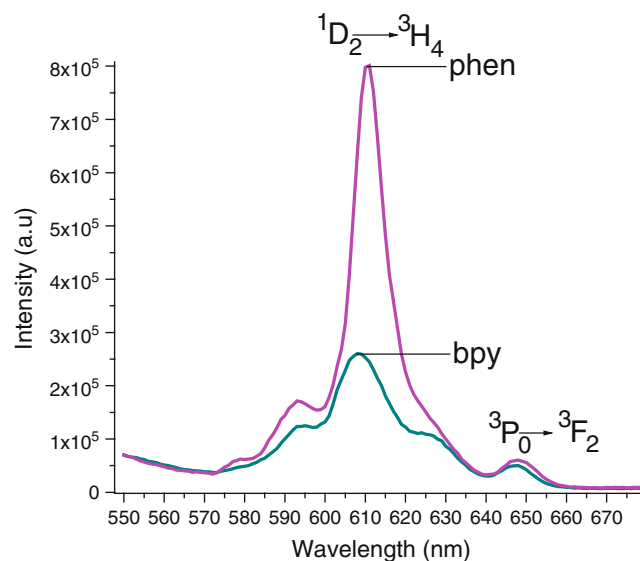


Fig. 9 Emission spectra of the complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\text{phen})]$ in acetonitrile

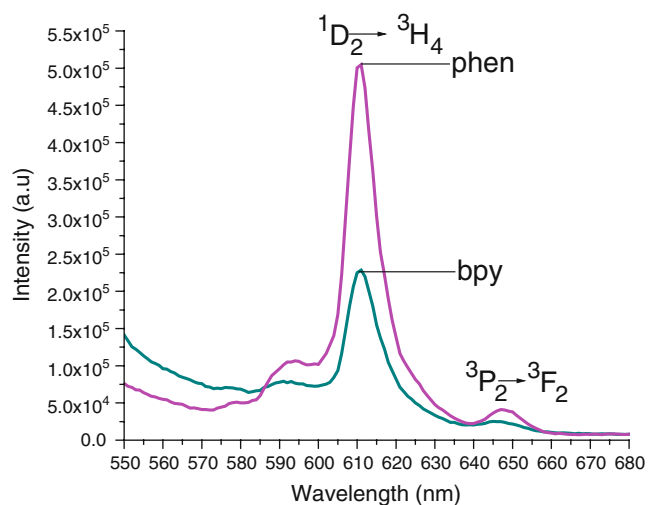


Fig. 10 Emission spectra of the complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$ and $[\text{Pr}(\text{fod})_3(\text{phen})]$ in ethanol

emission intensity of the transition ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ of the phen complex is considerably enhanced in ethanol than chloroform; however, it is lower than what is observed in acetonitrile. This is due to the presence of O–H oscillators in ethanol which would lead to partial quenching of the Pr(III) luminescence.

$[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ The complex, $[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ is insoluble in acetonitrile which could be due to its polymeric nature. The emission properties of this complex are, therefore, investigated in chloroform, benzene, acetone and pyridine and the spectra are shown in Figs. 6 and 11. The ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ emission transition of this complex displays almost similar spectral shape and intensity in chloroform and benzene (non-coordinating solvents) and acetone (coordinating solvent) while the intensity is drastically quenched, in pyridine, with different band shape. This

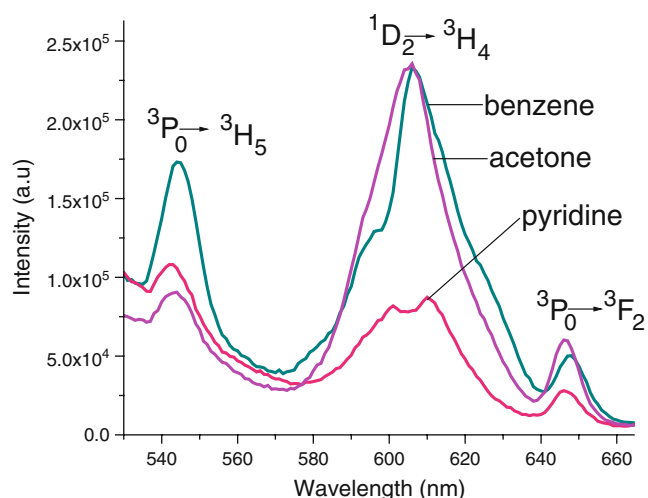


Fig. 11 Emission spectra of the complex, $[\text{Pr}(\text{fod})_3(\mu\text{-bpm})]_n$ in benzene, acetone and pyridine

transition shows stark splitting in pyridine similar to that observed in bpy complex. Similar reason, argued in the discussion of absorption spectrum of this complex in this solvent, could be assigned for this behaviour i.e. formation of $[\text{Pr}(\text{fod})_3(\text{bpm})(\text{py})_2]$ species in pyridine solution. Although the band shape of bpy and bpm complexes in pyridine is similar indicating a similar symmetry around Pr (III) in this solvent, but the intensity of bpy complex is larger than the bpm complex. This indicates the loss of one bpm unit (ancillary sensitizer) affects the luminescence intensity.

Luminescence properties in DMSO

Finally, the luminescence behaviour of these complexes is discussed in DMSO. The spectra are shown in Fig. 12. The three complexes remarkably display identical band shape with virtually similar luminescence intensity in this solvent. Furthermore, it is important to mention that ${}^3\text{P}_0 \rightarrow {}^3\text{H}_5$ transition is not detected in the DMSO spectra. As pointed out in the absorption section, these complexes lose the ancillary ligand (phen, bpy or bpm) by the invasion of stronger coordinating DMSO and form similar species, $[\text{Pr}(\text{fod})_3(\text{DMSO})_2]$ in this solvent. Since the band shape and the luminescence intensity of the emission transitions, besides E_T of the sensitizers, also depend upon the nature of ligands (antenna) around the metal, strongly reflects that species present in solution are similar. This strengthens our conclusion drawn in absorption section that two molecules of DMSO replace the heterocyclic ligand from complex and acquire its position.

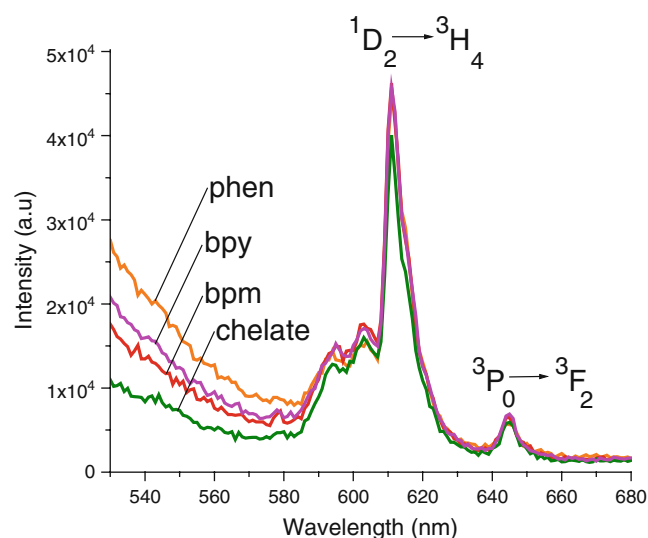


Fig. 12 Emission spectra of $\text{Pr}(\text{fod})_3$ and the complexes, $[\text{Pr}(\text{fod})_3(\text{bpy})]$, $[\text{Pr}(\text{fod})_3(\text{phen})]$ and $[\text{Pr}(\text{fod})_3(\text{bpm})]_n$ in DMSO

Conclusion

The visible light luminescence and absorption of the complexes [Pr(fod)₃(bpy)], [Pr(fod)₃(phen)] and [Pr(fod)₃(bpm)]_n in a series of non-aqueous solvents revealed that 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod) is a good sensitizer for Pr(III) luminescence. Among phen, bpy and bpm, luminescence is enhanced by introduction of the rigid planar more basic ancillary ligand, phen, and could be used in designing highly luminescent ternary lanthanide β-diketonate complexes for fabricating light emitting devices. The *f-f* transitions are remarkably sensitive to the environment (ligand/solvent) around Pr(III) ion and pyridine has been found most effective in promoting intensity. A good correlation of solvent effect exists between the directly excited *f-f* absorption transitions and sensitized emission transitions. The strong donor solvent DMSO invades the inner coordination sphere of the complexes and replaces the heterocyclic ligand attached to Pr(III) leading to the formation of similar species [Pr(fod)₃(DMSO)₂] in solution.

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