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π -Conjugated Polymer-Eu³⁺ Complexes: A Versatile Luminescent Molecular Probe for Temperature Sensing

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Polymer-Eu³⁺ Thermosesntive Probe: New carboxylic functionalized π -conjugated polymer-Eu³⁺ ion complexes were designed for turn "On-Off" thermosensitive luminescent switches in solution and solid state

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Abstract: We report π -conjugated polymer-Eu³⁺ ion complexes as new potential luminescent thermo-sensitive molecular probes. Carboxylic functionalized segmented π conjugated polymers having oligophenylenevinylene (OPV) chromophores in the poly(ethyleneoxide) or polymethylene backbones were custom designed, synthesized and utilized as efficient photosensitizer for Eu^{3+} ion. These π -conjugated polymer- Eu^{3+} ion complexes were found to be thermo-sensitive and behaved as reversible 'turn-On' or 'turn-Off' luminescent switches in solution and in solid state. Luminescent decay studies revealed that the red-emission from the Eu³⁺ ion excited state was highly sensitive to temperature which drove the functioning of optical switches. The decay rate constants followed typical Arrhenius trend over wide temperature range having similar activation energies. Both the nature as well as length of the segmented polymer chain that tied the OPV optical chromophores in the backbone determines the temperature range of the luminescent on-off process. The emission characteristics of the oligomer-Eu³⁺ ion complex was found to be non thermosensitive which emphasized the need for the segmented π -conjugated polymer ligand structure for the probes based on Eu^{3+} ion complexes. The present strategy opens up new concept and molecular design principles for π -conjugated polymer-lanthanide ion complexes as potential candidates for temperature sensitive luminescent molecular probes.

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Introduction

Thermo-sensitive polymers are emerging as important classes of sensing materials for accurate measurement of temperature in material science and in biological processes.¹ These classes of materials are typically made by blending or anchoring thermo-sensitive dye molecules such as benzofuran, BODIPY, benzoxazole and pyridinyl on polyacrylic or polystyrene backbone and the temperature dependent structural changes in the dyes were read as sensing out-put signals.² Poly(N-isopropylacryamide) is another example for temperaturesensitive polymer based on lower critical solution temperature (LCST) as a probe by the selective precipitation of polymer chains in the heating/coolong cycles.³ π -Conjugated polymers (or oligomers) based on diacetylene linkages were also reported as thermoresponsive probes due to their ability to change optical properties from blue to red depending upon the temperature, pH and mechanical stress and so on.⁴ Both the phase separations of dye molecules from the polymer support and broad spectral width (absorbance or fluorescence, larger half-width at maxima) of these dyes or π -conjugated polymer chains were found to be some of the inherent limitations in these materials for the sharp detection of temperature changes.^{4h,4i} Lanthanide metal ion complexes are important classes of inorganic luminescent materials as they possessed unique optical properties such as strong and sharp emissions, large stoke shifts, long lived excited states and so on.⁵ Typically, small organic or macromolecular ligands are coordinated with lanthanide ions and the photoemission are occurred via excitation energy transfer from ligand to metal core.⁶ The photophysical characteristic and energy transfer pathways are completely different in lanthanide metal complexes compared to other dye based systems like BODIPY (or poly(Nisopropylacryamide)). Recent studies revealed that the excited state energy levels of Ln³⁺ ions were highly sensitive to the temperature and this property was exploited for temperature sensing applications in Tb³⁺ and Eu³⁺ complexes.⁷ However, the disassociation of metalligand interaction of small molecular ligand- Ln³⁺complexes at the high temperature restricted their thermal reversibility.⁸ We have recently reported functionalized π -conjugated polymers such as poly(phenylenevinylene) and poly(m-phenylene) as photosensitizers for Tb³⁺ and Eu³⁺ ions to produce white light generation, selective red light emission and so on.⁹ The utilization of π -conjugated polymer backbone as photosensitizer ligand provided many advantages including mechanical stability and film forming ability for polymer-lanthanide metal ion complexes which are completely lacking in the small molecular ligand based approaches.¹⁰ Hybrid blends of non-luminescent polymer-lanthanide complexes were also

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reported and here the polymers typically employed to enhance the processability of the lanthanides.¹¹ Rybaltovskii et al. reported the doping of Eu(fod)₃ molecules (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadione) with polymers such as polypropylene and oligo(urethane methacrylate) by soaking in a supercritical CO₂ solution.¹¹ⁱ These blends were tested for temperature sensor, however, the polymer chains did not participate in the energy transfer mechanism and they were just used as mechanical support. Up to our knowledge, there is no report known till date for utilizing the π -conjugated polymer-lanthanide ion complexes as temperature-sensitive sources in the literature. This is partially associated with the non-availability of suitable π -conjugated polymer with appropriate energy levels for photoexcitation to lanthanide ions; as a result, both the materials development and the thermo-sensitive mechanistic pathways were understood only at the premature level. Hence, the development of new thermo-sensitive π -conjugated polymer-lanthanide ion complexes are one of the very important research activity for both fundamental understanding as well as developing new materials for innovative temperature sensing applications in the



polymer-inorganic chemistry interface.

Figure 1. Approach for thermo-sensitive π -conjugated polymer-Eu³⁺ ion complexes and their turn-on and turn-off switching pathways

Herein, we report a unique carboxylic acid functionalized π -conjugated polymer- Eu³⁺ ion complexes as thermo-sensitive luminescent molecular probes in both solution and in solid

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state (see figure 1). Blue light emitting oligophenylenevinylene (OPV) unit was chosen as optical chromophore and new series of main chain segmented polymers containing polymethylene or polyethylene oxides were prepared. These polymers were named as "segmented polymers" because the polymer chains were segmented by OPV units at the regular interval. The newly designed segmented OPV polymers were found to be efficient photosensitizers for Eu³⁺ ions to produce strong red emission from the metal center. The polymer-Eu³⁺ complexes were also found to show sharp changes in their emission characteristics with respect to temperature changes in solution and in thin film. Depending on the structure of the segmented polymer backbone, their temperature sensing ability 'turn-on' or 'turn-off'^{9c} varied from 20 to 100 °C (see figure 1). Photophysical experiments based on absorbance, emission, and luminescent decay time measurements were carried out to trace the mechanistic aspects of the luminescent pathways. The decay process was further investigated using Arrhenius equation which suggested that the kinetic rate constants of the polymer complexes followed typical linear relationship over a wide range of temperature in which the probes were active. The nature as well as length of the segmented chain (hydrophilic or hydrophobic) was found to be very crucial factor in determining their temperature sensing ability. Thus, the present approach opens up new molecular design for π -conjugated polymer-Eu³⁺ ions complexes for temperature sensors application based on luminescent molecular probes.

Results and Discussion

The carboxylic acid functionalized π -conjugated segmented polymers were synthesized by A-A + B-B polycondensation approach via Wittig-Horner route as shown in scheme-1. 4-Hydroxyphenylpropionc acid was converted into its methyl ester by acid catalysed esterification to get methyl 3-(4-hydroxyphenyl)propanoate (1). The compound 1 was substituted with 2-ethylhexylbromide in the presence of K₂CO₃ to give methyl 3-(4-((2ethylhexyl)oxy)phenyl)propanoate (2). It was treated with HBr/acetic acid in presence of pformaldehyde to yield the 3-(3,5-bis(bromomethyl)-4-(2-ethylhexyloxy)phenyl)propanoic acid (3). The compound 3 was converted into its corresponding bis-phoponate ester (4) by reacting with triethyl phosphite at 120° C. Oligo-ethyleneoxy substituted bis-benzaldehyde derivatives were synthesized by two step processes: (i) triethyleneglycol, hexaethyleneglycol and polyethylene glycol (PEG-400) were reacted with p-toluenesulfonylchloride in the

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presence of sodium hydroxide to get their corresponding tosylates (5a-5c) and (ii) they were further reacted with 4-hydroxybenzaldehyde in acetonitrile in the presence of K_2CO_3 to yield 4,4'-(((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))dibenzaldehyde (**6a-6c**). The reaction of 1, 12-dibromododecane with 4-hydroxybenzaldehyde produced the alkylated bisbenzaldehyde derivative (7). The segmented polymers were synthesised by reacting equimolar amounts of dialdehyde (6 and 7) with bisphosphonate ester (4) in the presence of potassium tertiarybutoxide as base in dry-THF. The polymerization reaction produced two kinds of carboxylic functionalized oligophenyelenvinylene (OPV) containing segmented polymers with either polyethyleneoxy chain or polymethylene chain segmented backbones. These polymers were referred as Poly(OPV-X): Poly(OPV-TEG), Poly(OPV-HEG), **Poly(OPV-PEG400)** and **Poly(OPV-DD)**, where x represent the nature of the segments TEG, HEG, PEG-400 and 1,12-dibromododecane, respectively. Similarly, structurally identical model compound OPV-TEG was also synthesized by reacting bisphosphonate ester 4 with two equivalents benzaldehyde derivative (8) having triethyleneglycol monomethyl as terminal units (see scheme SS1).



Scheme-1. Synthesis of Segmented π -conjugated polymer having OPV units

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The structures of the monomers, oligomer and polymers were characterized by ¹H-NMR, ¹³C-NMR, FT-IR, and MALDI-TOF analysis (see supporting information). The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran using polystyrene as standard (GPC chromatograms are provided in figure SF1). The molecular weights M_n , M_w and polydispersity are given in table ST-1 in the supporting information. The molecular weights of the polymers were obtained in the range of $M_w = 18,000 - 37,000$ with polydispersity of 1.9 - 3.0.¹³ Thermogravimetric analysis showed that the polymers were thermally stable up to 250 °C (see table ST-1 for values, TGA plots are shown in figure-SF2). DSC analysis of the polymers did not show any melting or crystallization peaks in the heating /cooling cycles indicating that they were highly amorphous in nature (see figure SF3 and ST-1). With increase in the PEG chain length, the glass transition temperature (T_g) of the segmented polymers decreased from 70 °C to 8 °C. This confirmed that rigidity of the polymeric backbone decreased with increase in the PEG chain length. The Tg of the rigid hydrophobic segmented polymer Poly(OPV-DD) was 84 °C, which was much higher compared to PEG-segmented polymers. The photophysical properties of the polymers and oligomer were studied in solutions and drop cast films (see figure SF4). In the solution, the absorption and emission spectra of the polymers were found to be almost identical and their maxima were observed at 310 and 405 nm, respectively. The absorption spectra of the polymers did not show any change in the solid state, however, their emission maxima (at 410 nm) showed slight red shifted (10- 50 nm) with respect to the difference in their polymer structures. The absorption and emission maxima of the OPV-TEG were found identical to that of its polymer. The quantum yields of the polymers (also oligomer) were determined using quinine sulfate ($\phi_r = 0.53$, in 0.1N Conc. H₂SO₄) as a standard (see table ST1).¹² The quantum yields of polymers (also oligomers) were obtained in the range of 0.13-0.27 in chlorobenzene (table ST1) which is in accordance with earlier reports. 12c

Newly synthesized carboxylic acid functionalized polymers were complexed with Eu³⁺ ions using theonyl acetylacetone (TTA) as co-ligand in the polymer-Eu complex. FT-IR spectra of these complexes showed peaks corresponding to the carbonyl stretching frequency at 1615 cm⁻¹ with respect to C=O...Eu³⁺ complex and confirmed the formation of the expected complex (see figure SF5).¹⁴ In order to prove the binding of TTA and OPV carboxylic acid functionality in the Eu³⁺ ion complex, MALDI-TOF-MS analysis of the OPV-Eu complex was carried out (see supporting information SF6). MALDI-TOF-MS

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spectra of the complex showed a mass peak at 1434.21amu with respect to (OPVTEG)(TTA)₂ $Eu^{3+}(H_2O)_2$. The Eu^{3+} ion complex was constituted by two TTA carboxylic units and one OPV carboxylic unit for the charge neutralization at the metal center. Further, the eight coordination of the Eu³⁺ ion was satisfied by the coordination of two water molecules from the solvent. Hence, both the carboxylic acid units from TTA and OPV units indeed participated in the Eu³⁺ ion complex formation. A similar MALDI-TOF-MS analysis for polymer complex was found to be not successful due to the large polydispersity of the samples. In order to confirm the formation of polymer-(TTA)-Eu³⁺ ion complex (TTA was used as co-ligand), the X-ray photoelectron spectroscopy (XPS) technique was employed. The XPS measurements were carried out for Poly(TEG-OPV) (TTA) Eu³⁺ complex and the details are provided in the supporting information in figure SF7. The Eu3d and Eu4d core level XPS spectra of the complex showed two doublets with binding energies at 1136.4 to 1166.2 eV and 139.3 to 144.6 eV, respectively. These energy values were exactly matched with earlier literature reports for Eu³⁺ ion coordinated with oxygen atom. ^{15a} The binding energy of C1s photoelectrons were appeared as broad peak in the range of 283-292 eV which was further fitted with multiple-Guassian programme as reported by others. ^{15b} The first major peak 287.2 eV was assigned to C1s electron from C-C and C-H groups. The second broad peak at 289.9 eV was assigned to the carbon atoms bonded to oxygen. The third high energy peak at 291.1 eV was assigned to the carboxylic group carbon atom coordinated to Eu^{3+} ion. The actual binding energies of the present complex were almost similar to the polyacrylic systems which was attributed to aliphatic COOH group in the conjugated OPV chromophore.^{15c,15d} Similarly O1s electron binding energies of the Eu³⁺ complex matched with the expected values (see supporting information).^{15e} These results clearly confirmed that the Eu³⁺ metal ion was coordinated by the carboxylate unit of the OPV chromophore in the polymeric chain.

Absorption, emission and excitation spectra of the polymer-Eu³⁺ complexes were recorded in solution (chlorobenzene) and in film (solid state). In figure 2a, the solution excitation spectra of all Eu³⁺ complexes showed broad absorption from 260 to 430 nm with peak maxima at 350 nm corresponding to π - π^* transition of the aromatic OPV chromophore (see also figure SF-8 and SF-9). The emission spectra of the polymer- Eu³⁺ complexes in solution (figure 2b) and film (figure 2c) showed characteristic Eu³⁺ strong metal centered sharp emission peaks at 580, 593, 614, 650 and 702 nm corresponding to the ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_3$ (weak emission), and ${}^5D_0 \rightarrow {}^7F_4$ transitions, respectively.⁵ In

both solution as well as in the solid state, the emission spectra of the polymeric Eu³⁺ complexes did not show polymer self-emission (at 410 nm) from the π -conjugated backbone. This confirmed that the excitation energy of the π -conjugated OPV chromophore in the polymer backbone was completely transferred to the Eu^{3+} ion during the photoexcitation process. The photographs of polymer-Eu³⁺ complexes showed homogeneous red emission in solution and in film (see figure 2). Interestingly, the photosensitizing ability of the polymer-Eu³⁺ ion complexes was found to be almost same irrespective of the nature of the segmented chains (hydrophilic PEG chain or hydrophobic dodecyl chain). Hence, it may be concluded that the custom designed carboxylic functionalized OPV segmented polymers were efficient photosensitizer for Eu³⁺ ion in solution and in solid state. The absorption spectrum of OPV-TEG-Eu $^{3+}$ and polymer- Eu $^{3+}$ complexes were almost same in solution (see figure SF8). However, the solid state exciattion spectra of Polymer-Eu³⁺ complexes were blue-shifted comapred to their oligomer complex (see figure 2a). The reason for the blue-shift in the polymer was attributed to the close packing of OPV chrmophores in the polymer chains which was completely lacking in the oligomer species. The photoexcitation spectra of structurally identical oligomer OPV-TEG-Eu³⁺ complex are shown along with the polymers in figure 2b and 2c. Both in solution (chlorobenzene) and in solid state, this oligomer complex showed only weak emission from Eu^{3+} ion (at 615 nm). Additionally, a strong selfemission at 410 nm was clearly visible which suggested that the excitation energy from the ligand to metal ions was not complete. The comparison of the emission spectra of the Poly(TEG-OPV)-Eu³⁺ and OPV-TEG-Eu³⁺ complexes indicated that for a given identical chromophore structure, the polymeric ligand was efficient photosensitizer for complete excitation energy transfer from the ligand to the metal center compared to that of small molecular systems.

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Figure 2. Excitation spectra (a) of the polymer and oligomer complex in chlorobenzene (emission $\lambda = 615$ nm). Emission spectra of polymer and oligomer complex in chlorobenzene solution (b) and in solid state (film)(c) (excitation $\lambda = 360$ nm). Luminescent decay profiles of polymer and oligomer complex in chlorobenzene (d) (excitation source $\lambda = 360$ nm).

To further understand the the energy transfer mechanism and trace the role TTA moiety in the complexes, singlet and triplet energy levels of polymeric and oligomeric ligands were determined. The schematic energy transfer diagrams for polymers and oligomer are shown in the supporting information (see figure SF10 and SF11). According to Latva's empirical rule, energy transfer from ligand to excited state of Eu³⁺ metal ion was more effective when ΔE (${}^{3}\pi\pi^{*}$ - ${}^{5}D_{0}$) was equal to 2500 - 4000 cm⁻¹.^{16a} As shown in figure SF11, energy gap ΔE (${}^{3}\pi\pi^{*}$ - ${}^{5}D_{0}$) between the triplet excited state of the polymer (or oligomer) ligand to the excited state of Eu³⁺ ion is obtained as 5755-5880 cm⁻¹. Therefore, according to Latva's rule, the direct energy transfer from the polymer ligand to Eu³⁺ ion is not possible. The triplet state energy level of TTA was much lower than that of the triplet state of polymer (or oligomer) and the same time the difference in the energy levels of TTA to the excited state of Eu³⁺ ion was only 2910 cm⁻¹. Hence, it may be postulated that during the

photoexcitation process, the energy was initially transferred from triplet state of polymers (or oligomer) to triplet state of the TTA and subsequently it was transferred to Eu³⁺ ion metal centre for the luminescence.^{16b} In order to confirm this hypothesis, controlled experiments were carried out by varying the amounts of TTA in the Poly(TEG-OPV)(TTA)-Eu³⁺ ion complex. The Poly(TEG-OPV) polymer was complexed with Eu³⁺ ion using various equivalents of TTA (zero, one, two and three mole equivalents) and further these complexes were subjected for excitation and emission studies (see supporting information for detailed characterization, figure SF12 and SF13). In the absence of the TTA, the emission spectrum of the Eu³⁺ complexes showed a large amount of self-emission from the OPV polymer backbone indicating the incomplete photoexcitation energy transfer to the metal centre. With further increase in the TTA in the complex, the self-emission of OPV was vanished and complete photoexcitation energy transfer from the polymer chromophores occurred. Further to confirm the enhanced photosensitizing ability of the polymer, luminescent decay lifetime measurements were carried out and their decay profiles are given in figure 2d. The lifetime decay profiles of the Eu³⁺ complexes were fitted with first order decay (see figure SF14 for other polymer complexes, see table ST2). The ${}^{5}D_{0}$ excited state lifetime of the polymer-Eu³⁺ complexes was obtained as 270 µs whereas the lifetime of OPV-TEG/Eu³⁺ complex was found much lower (180 µs) due to partial self-emission. Hence, the photosensitizing ability of the macromolecular ligand was much more robust and superior compared to small organic ligands.

The temperature dependent luminescent studies were carried out for the polymer (alone) and its Eu³⁺ ion complexes in chlorobenzene and the photographs are shown in figure 3. The photographs of the vials showed a strong blue emission from the OPV chromophores in the polymer backbone and their luminescent intensity was less influenced by the temperature changes from 20-100 °C (see emission spectra in the figure SF15 and SF16). Interestingly, the polymer- Eu³⁺ion complex showed a large variation in their red color luminescence depending upon their temperature of the solution. For instance, the strong and sharp red-emission at 20 °C was gradually reduced while heating up to 100 °C and their luminescent behavior was found to be completely reversible in the subsequent cooling cycles from 100 to 20 °C. The emission spectra of Poly (OPV-HEG)-Eu³⁺ complex in both heating and cooling cycles are shown in figure 4 [see figure SF15 and figure SF16 for other complexes]. In figure 4a, upon heating the solution from 20 to 100° C, the characteristic emission peak intensities of the Eu³⁺ ion (major peak at 615 nm) gradually decreased and the

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complexes became completely non-luminescent above 70 °C. In the subsequent cooling cycles, from 100 °C to 20 °C, the luminescent peak at 615 nm re-emerged below 70 °C and stayed up to the room temperature. The reversibility of the temperature sensing behaviours is checked for atleast 10 cooling and heating cycles and they are perfectly reproducible. This clearly supported the fact that the photosensitizing ability of the polymer-Eu³⁺ ion complexes was highly sensitive to the temperature of the medium.



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Figure 3. Photographs of polymer (a) and polymer- Eu^{3+} complex (b) in chlorobenzene at different temperatures. The sample vials were excited with hand held UV-lamp (excitation $\lambda = 360$ nm).

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Figure 4. Temperature dependent emission spectra of Poly(OPV-HEG) in chlorobenzene (a) and thin film (b) in heating and cooling cycles (excitation excitation $\lambda = 360$ nm). Plots of PL intensity versus temperature (c) and their break points (d) of polymer complexes.

The temperature dependent emission characteristics of the polymer-Eu ion complexes was further checked in other protic and hydrocarbon solvents such as: N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), 1,4-xylene and 1,2-dichlorobenzene (ODCB) . The variable temperature emission spectra of the polymer-Eu³⁺ complex in these solvents are given in the supporting information (figure SF17). Along with the temperature dependent luminescent behaviors, partial self-emission from the OPV chromophores were also observed in THF, DMSO and DMF solvents. On the other hand, ODCB, chlorobenzene and xylene did not show any chromophore self-emission and only the temperature dependent emission behaviors were observed from the metal center. Hence, the protic solvents like DMF and DMSO were not good solvents for thermo-sensing studies. Further, the effect of concentrations of the polymer chromophores on the thermosensing ability was also investigated for 10⁻⁶ M to 10⁻⁵ M OPVs in chlorobenzene (see supporting information, figure SF18). It was found that the thermo-response behaviors of the

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polymer-Eu³⁺ complex were retained even at very low concentration (10⁻⁶ M) and suggesting that they polymer-lanthanide ion system is very potential for temperature sensing applications.



Figure 5. Temperature dependent luminescent decay profiles of Poly(OPV-HEG) in chlorobenzene in the heating (a) and cooling (b) cycles (excitation $\lambda = 360$ nm). Plots of τ_1 versus temperature (c) and decay rate constants verses 1/T (d) of the polymer complexes.

In order to check the thermo-sensitive luminescent characteristics in the solid state, thin films were cast on quartz plate and subjected to photoluminescence studies. In figure 4b, both the emission spectra and the photographs clearly support the thermo-reversibility of luminescence properties of these π -conjugated polymer- Eu³⁺ complexes in the solid state. This is for the first time, thermo-sensitive lanthanide complexes were found to show complete thermo-reversible luminescent behavior in solution as well as in solid state. It is very important to mentioned that the solid state samples in fact showed small amount of emission at 100 °C which was completely absent in the solution (figure SF19). This observation was attributed to the closer packing of the polymer chains in film whereas they remained apart in solution at high temperature. All other polymer complexes were also found

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to be thermo-reversible in their luminescent behaviors (the details are provided in the figure SF15 and SF16). In order to compare the thermo-reversibility across the various segmented polymers, the optical density (O.D.) of the OPV chromophores were maintained as O.D. = 0.1 in chlorobenzene and their emission spectra were recorded at various temperatures (see figure SF15 and SF16). The PL-intensity of these spectra at 615 nm (with respect to Eu³⁺ ion) were plotted against the temperature and shown in figure 4c. From the plots, it is clearly evident that all the polymer complexes showed perfect temperature dependent luminescent properties. However, the temperature at which the turn-on/turn-off and vice versa occurred was varied with polymer structures. The temperature break points are nothing but the region in which the luminescent probe became active in the temperature window of 20 to 100 °C. These break points were determined by linear fits and the values are plotted for different polymers and shown in figure 4d. These values suggested that with the increase in the PEG chain length in the segmented polymer, the break points were increased from 55° to 72 °C (for TEG, HEG and PEG-450 segmented units). The sensitivity of the thermo-probe was determined as reported by Brites et al. based on the emission intensity and the values are summarized in table ST4).^{7a,7j} These molecular probes were found to have sensitivity of 1.5 to 1.6 K⁻¹ which matched with the literature reports.^[7a] This suggested that the temperature range at which the turn-on or turn-off probes worked as highly dependent on the structure of the polymer backbone. Based on the appropriate chain backbone, one could selectively choose a particular polymer (see scheme-1) for sensing sharp temperature change within $\pm 10^{\circ}$ difference. Thus, the segmented polymer structural design (like OPV chromophores) in the backbone is a very crucial parameter for making successful thermo-reversible π -conjugated polymer-Eu³⁺ complex systems.

Further, temperature dependent luminescence decay profiles of the complexes were recorded to trace their radiative pathways. The luminescent decay profiles for Poly(OPV-HEG)-Eu³⁺ are given in figure 5a [see figure SF20 for other complexes]. The luminescent decays became predominant at higher temperatures (from 20 to 100° C) and the decay profiles were found to be completely reversibility in the subsequent cooling cycles (see figure 5b). The same trend was observed for other polymer-Eu³⁺ complexes in the heating and cooling cycles (see figure SF20). The decay profiles were fitted with exponential decay fits and their lifetime values are given in table ST3 in the supporting information. Up to 70 °C, the decay profiles followed single exponential fit whereas at higher temperatures (above 70 °C) they were best fitted with bi-exponential fits. The plots of fast decay lifetime (τ_1) versus

temperature are showed in figure 5c. The thermo-sensing trends of the plots in the lifetime were almost identical to that of observed based on PL-intensity of the polymer complexes (see figure 4c). Therefore, the reproducibility of the thermo-sensitive characteristics of the polymer-Eu³⁺ ion complexes were confiremd by two independent photophysical techniques: (i) vataion in the PL-intesity (see figure 4c) and (ii) PL excited state lite times (figure 5c). Hence, the turn-On and turn-off luminescent behaviors are molecular properties of the π -conjugated polymer-Eu³⁺ ion complexes and mainly controlled by the segmented polymer chain structure in solution and in solid state.

Arrhenius equation directly correlates the radiative decay rate constant of the luminescent properties with respect to the change in the temperatures as:¹⁷

$$k = Ae^{(-Ea/RT)}$$
(1)

where E_a is energy gap between the emitting levels (equivalent to activation energy), A is Arhenius pre-exponential factor, R the gas constant and T is absolute temperature. For decay rate constants at various temperatures (Δ T), the above expression is modified as:^{7a}

$$\ln (k - k_0) = \ln A - (E_a/RT)$$
 (2)

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where k is decay rate constant at temperature at T and k_0 is the decay rate constant in which the molecule is less influenced by thermal disturbance (k at 20° C). The rate constant (k) is determined from the equation $k = 1/\tau_1$, where τ_1 is the fast decay life time of the excited species.^{7f,7b} From the plots ln(k- k_0) vs 1/T (see figure 5d), the activation energy (E_a) and the frequency factor 'A' is directly obtained from the slope and intercept, respectively (see table ST4 for values). The activation energy (E_a) of all the polymer complexes was found in the range of 3.14 - 3.62×10² KJ mol⁻¹ which are in accordance with earlier reports.^[7f,8] This confirmed that the nature of the decay of the excited species from ⁵D₀ emitting level of Eu³⁺ ion followed typical Arrhenius linear trend with temperature irrespective of the variation in segmented polymer structure backbone. Therefore, the variation in the temperature break points (see figure 4d) with respect to the segmented polymer structures were not due to the difference in the ⁵D₀ emitting level of Eu³⁺ ion in their complexes.

In general, the emission of Eu^{3+} ion complexes were influenced at higher temperatures in two ways: (i), the deactivation of Eu^{3+} ion 5D_0 excited state and non-radiative decay of the excitation energy and (ii) less excitation energy transfer from the ligand to the europium excited states (5D_0 and 5D_1). These two processes are schematically shown in figure 6a. Upon photoexcitation (excitation $\lambda = 360$ nm), OPV chromophores in the polymer chains excited to their higher energy states. The excited polymeric ligand species could lose its

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excitation energy in two possible ways: (i) self-emission of conjugated chromophore in the blue region (emission at $\lambda = 360$ nm) (route-1) or (ii) transfer the excitation energy from π conjugated chromophore to metal ions and subsequently produced sharp emission in the range of 570-720 nm from the Eu³⁺ metal center (route-2). The photographs of the vials in figure 3b and their respective emission spectra in figure 4 confirmed that the excitation energy was completely transferred from the polymer to the metal center (through route-2) at 20 °C for red-emission (the polymer self-emission was completely absent in both solution and solid state, see figure 4b and 4c). Therefore, the vanishing of red-emission at 100 °C is occured either by the deactivation of the excited states Eu³⁺ ion (⁵D₀ excited state) or may be due to the structural changes in the polymer chains at high temperatures.



Figure 6. Mechanism of energy transfer processes in the polymer- Eu^{3+} ion complexes (a). The intercation of OPV chromophores in short chain (b) or long chain segmented polymers (c) in the heating and cooling cycles.

Recently, Paris et al. and Shiraki et al. independently reported the change in the polymer topology as one of the main reasons for the temperature sensing of the BODIPY attached PMMA and curdlan complexed with polythiophene.^{3e,18} In the case of BODIPY, the emission intensity increased reversibly while assembling the chrmophores towards the lower critical solution temperature (LCST). In curdlan, the exposure to the methanol vapour was used as stimuli to partially disassociate its complexation with polythiophene to attain vaporchromism. On the other hand, in the present investigation, the polymer backbone itself acting as chromophores compared to these examples. Therefore, the change in the topology of the polymer chains was investigated by variable temperature absorption and emission studies. For this study, two PEG-based segmented polymers [Poly(OPV-TEG) and **Poly(OPV-HEG)**] and polymethylene segmented **Poly(OPV-DD)** were chosen for variable tempetaure studies in chlorobenzene (see figure SF21 and SF22). The variable temperature absorbance spectra of the polymers (alone) did not show any aggregated peaks in the heating and cooling cycles (see figure SF21). Hence, the occurrence of large change in the topology of the polymer chains as the cause for the temperature dependent luminescent behavior of metal ions was rule out. The straight line in the K-values (in figure 5d) for the complexes over the temperature confirmed that all the polymer complexes followed almost similar decay pathway for ${}^{5}D_{0} \rightarrow {}^{7}F_{i}$ transitions. Therefore, the energy deactivation process was attributed to the thermo-sensitivity and their turn-On and turn-Off' processes. The deactivation mechanism was further confirmed by carefully analyzing the emission spectra of the polymer- Eu³⁺ ion complexes in the region which corresponded to the polymer self-emission (see figure SF23). With increase in the temperature, the self-emission of polymer did not show any major changes in the complex (very faint blue self-emission and not to the extent of the strong blue-emission of polymer alone, compare figure 3a and 3b at 100 °C). Therefore, neither the route-1 process (see figure 6a) or change in the polymer topology significantly influenced the decay of Eu³⁺ ion emission at high temperatures. Hence, the deactivation of Eu^{3+} ion excited state (⁵D₀) primarily accounted for the thermal decay of red-luminescence at

high temperatures.

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Nevertheless, it is not possible to ignore the role of the polymer structure completely. If one assumes that the variation in the polymer structures do not have a role to play on the luminescent properties, then all the polymer complexes could be expected to show identical temperature break points. However, the temperature region at which the turn-On/Off probe works (temperature break points) was mainly decided by the structure of the segmental

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polymers (see figure 4c, 4d and 5c). To explain this point, two polymer structures Poly(OPV-HEG) and Poly(OPV-TEG) were chosen and their possible chain orientations with respect to temperature changes in solution are schematically shown in figure 6b and 6c. These two polymer streutures were varied only by the number of -CH₂CH₂O- units which tied the OPV chromophores in the backbone by either triethylene or hexaethylene glycol segments. Though both polymers have identical OPV chromophores for photosensitization, the flexible HEG-segmented polymer complex showed break points at 72 °C which was almost 18 °C much higher than that of the TEG-polymer complex (at 57 °C). As shown in the figure-6, the conjugated chromophore-Eu³⁺ ion species in the Poly(OPV-TEG)-Eu³⁺ complex were expected to be kept closely whereas they were apart in the more flexible Poly(OPV-HEG)- Eu^{3+} complex. While increasing the temperature, the closely placed species were more susceptible to thermal changes; as a result the excited state deactivation process became active at much lower temperatures. As a result, the thermo-sensitive turn-On/Off process occured at much lower temperature in Poly(OPV-TEG)-Eu³⁺ complex (at 57 °C). When the OPV chromophores weer kept apart in the chains, they tend to undergo only partial separation from metal-ion center at low temperature and need more thermal energy to for complete disassociation. As a result, the turn On/Off process became active only at higher temperature (at 72 °C). Hence, in the present investigation, the luminescence probe active temperature region as directly dictated by the length of the segmented polymer chain. Interestingly, all the polymer- Eu^{3+} complexes were very stable and showed complete reversibility in the temperature dependent luminescence process in solution as well as in solid state. The molecular thermo-probes demonstrated here could be very useful for tracing the temperature changes in the biological systems or studying the molecular assemblies in material science below 100 °C. We are currently exploring these possibilities which will be addressed in the future work. Thus, appropriate design of the optical chromophores and their arrangements in the polymer main chains are two crucial parameters for photosensitizing as well as thermo-sensing ability of π -conjugated polymers-lanthanide metal ions complexes.

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Conclusions

In summary, new class of segmented π -conjugated oligo-phenylenevinylene polymers with carboxylic acid functionality were synthesized through tailor made approaches and successfully utilized as photosensitizer for Eu³⁺ ion. Upon photoexcitation, the excitation energy transfer from the blue luminescent polymeric ligand to metal center produced strong and sharp metal centerd red-emission. These polymer complexes were found to show complete reversible temperature-sensitive luminescence properties in solution as well as in the solid state (in thin films). Detailed photophysical studies and the luminescent decay dynamics revealed that the thermal deactivation of the Eu³⁺ ion accounted for the decay of the red luminescence at the high temperature. The temperature break points at which the 'Turn-On and Turn-Off' luminescence switch (red to colorless) occurred was found to be highly dependent on the structure of the segmented chain backbone. Based on the detailed photophysical analysis, the change in the topology of the polymer at the high temperature was ruled out. Segmented polymer chains with shorter spacer length showed the break point at much lower temperatures compared to that of their long flexible counterparts. Hence, it could be concluded that the arrangements of optical chromophores in the segmented polymer chain backbone directly control the temperature break points. Further, structurally similar oligomer-complex was found to be less efficient as photosensitizer and also did not show any thermo-sensitive behavior. Thus, the design of the segmented π -conjugated polymer is a very crucial factor for making reversible thermo-sensitive luminescent molecular probes. In the present investigation, this concept was demonstrated by designing appropriate π -conjugated segmented polymers with photoactive OPV chromophores and their complexes with Eu³⁺ ion. Though the approach demonstrated here pertains to π -conjugated polymers having OPV chromophores and Eu³⁺ ion, however, it is not restricted to any particular type of π conjugated polymeric systems or lanthanide ions. This finding opens up new concept in macromolecular ligand design for lanthanide ions and their potential for many applications in temperature sensitive molecular probes.

Experimental Section

The experimental section containing syntheses and characterization of compounds, GPC, Thermal analysis (TGA and DSC), Photophysical studies of polymers and their Eu³⁺complexes, Temperature dependent absorption and emission spectra of polymers,

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polymer-Eu³⁺ complexes in solution and solid state and luminescent decay profiles Eu³⁺ complexes are provided. ¹H NMR, ¹³C-NMR, MALDI spectra, XPS spectra are also provided in the supporting information.

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Figure and Scheme Captions:

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Figure 1. Approach for thermo-sensitive π -conjugated polymer-Eu³⁺ ion complexes and their turn-on and turn-off switching pathways

Figure 2. Excitation spectra (a) of the polymer and oligomer complex in chlorobenzene (emission $\lambda = 615$ nm). Emission spectra of polymer and oligomer complex in chlorobenzene solution (b) and in solid state (film)(c) (excitation $\lambda = 360$ nm). Luminescent decay profiles of polymer and oligomer complex in chlorobenzene (d) (excitation source $\lambda = 360$ nm).

Figure 3. Photographs of polymer (a) and polymer- Eu^{3+} complex (b) in chlorobenzene at different temperatures. The sample vials were excited with hand held UV-lamp (excitation $\lambda = 360$ nm).

Figure 4. Temperature dependent emission spectra of Poly(OPV-HEG) in chlorobenzene (a) and thin film (b) in heating and cooling cycles (excitation excitation $\lambda = 360$ nm). Plots of PL intensity versus temperature (c) and their break points (d) of polymer complexes.

Figure 5. Temperature dependent luminescent decay profiles of Poly(OPV-HEG) in chlorobenzene in the heating (a) and cooling (b) cycles (excitation $\lambda = 360$ nm). Plots of τ_1 versus temperature (c) and decay rate constants verses 1/T (d) of the polymer complexes.

Figure 6. Mechanism of energy transfer processes in the polymer- Eu^{3+} ion complexes (a). The intercation of OPV chromophores in short chain (b) or long chain segmented polymers (c) in the heating and cooling cycles.

Scheme-1. Synthesis of Segmented π -conjugated polymer having OPV units