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## $\pi$ -Conjugated polymer-Eu<sup>3+</sup> complexes: versatile luminescent molecular probes for temperature sensing†

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We report  $\pi$ -conjugated polymer-Eu<sup>3+</sup> ion complexes as new potential luminescent thermo-sensitive molecular probes. Carboxylic acid functionalized segmented  $\pi$ -conjugated polymers having oligophenylenevinylene (OPV) chromophores in the poly(ethyleneoxide) or polymethylene backbones were custom designed, synthesized and utilized as efficient photosensitizers for Eu<sup>3+</sup> ions. These  $\pi$ -conjugated polymer-Eu<sup>3+</sup> 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 Eu<sup>3+</sup> ion excited state was highly sensitive to temperature which drove the functioning of optical switches. The decay rate constants followed a typical Arrhenius trend over a 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 determine the temperature range of the luminescent on-off process. The emission characteristics of the oligomer-Eu<sup>3+</sup> ion complex were found to be non-thermosensitive which emphasized the need for the segmented  $\pi$ -conjugated polymer ligand structure for the probes based on Eu<sup>3+</sup> ion complexes. The present strategy opens up new concept and molecular design principles for  $\pi$ -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 materials science and in biological processes.<sup>1</sup> These classes of materials are typically made by blending or anchoring thermo-sensitive dye molecules such as benzofuran, BODIPY, benzoxazole and pyridinyl on the polyacrylic or the polystyrene backbone and the temperature dependent structural changes in the dyes are read as sensing output signals.<sup>2</sup> Poly(*N*-isopropylacrylamide) is another example for temperature-sensitive polymers based on lower critical solution temperature (LCST) as a probe by the selective precipitation of polymer chains in the heating-cooling cycles.<sup>3</sup>  $\pi$ -Conjugated polymers (or oligomers) based on diacetylene linkages were also reported as thermo-responsive probes due to their ability to change optical properties from blue to red depending upon the temperature, pH and mechanical stress and so on.<sup>4</sup> 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  $\pi$ -conjugated polymer chains were found to be some of the inherent limitations in these materials for the sharp detection of temperature changes.<sup>4b,i</sup> 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.<sup>5</sup> Typically, small organic or macro-molecular ligands are coordinated with lanthanide ions and the photoemissions occur *via* excitation energy transfer from the ligand to the metal core.<sup>6</sup> The photophysical characteristics and energy transfer pathways are completely different in lanthanide metal complexes compared to other dye based systems like BODIPY (or poly(*N*-isopropylacrylamide)). Recent studies revealed that the excited state energy levels of Ln<sup>3+</sup> ions were highly sensitive to the temperature and this property was exploited for temperature sensing applications in Tb<sup>3+</sup> and Eu<sup>3+</sup> complexes.<sup>7</sup> However, the disassociation of the metal-ligand interaction of small molecular ligand-Ln<sup>3+</sup> complexes at high temperatures restricted their thermal reversibility.<sup>8</sup> We have recently reported functionalized  $\pi$ -conjugated polymers such as poly(phenylenevinylene) and poly(*m*-phenylene) as photosensitizers for Tb<sup>3+</sup> and Eu<sup>3+</sup> ions to produce white light generation, selective red light emission and so on.<sup>9</sup> The utilization of a  $\pi$ -conjugated polymer backbone as a 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

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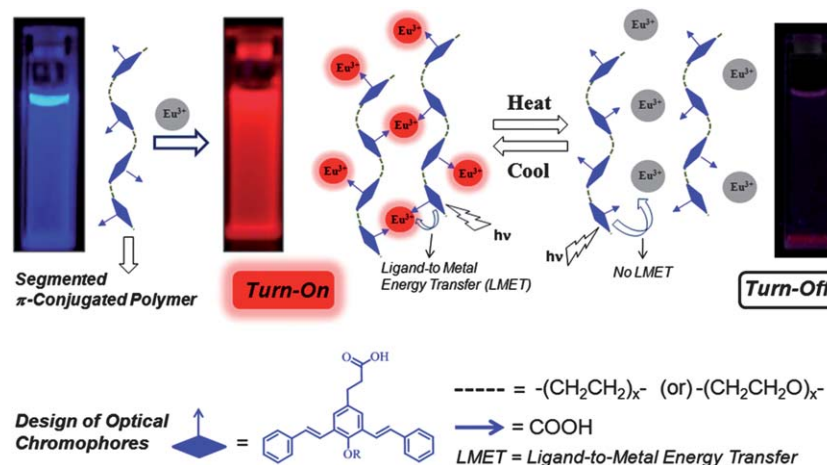
ligand based approaches.<sup>10</sup> Hybrid blends of non-luminescent polymer-lanthanide complexes were also reported and here the polymers were typically employed to enhance the processability of the lanthanides.<sup>11</sup> Rybaltovskii *et al.* reported the doping of  $\text{Eu}(\text{fod})_3$  molecules ( $\text{fod} = 6,6,7,7,8,8,8\text{-heptafluoro-2,2-dimethyl-3,5-octadione}$ ) with polymers such as polypropylene and oligo(urethane methacrylate) by soaking in a supercritical  $\text{CO}_2$  solution.<sup>11i</sup> These blends were tested for temperature sensors, however, the polymer chains did not participate in the energy transfer mechanism and they were just used as a mechanical support. To the best of our knowledge, there has been no report known until now for utilizing the  $\pi$ -conjugated polymer-lanthanide ion complexes as temperature-sensitive sources in the literature. This is partially associated with the non-availability of suitable  $\pi$ -conjugated polymers 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  $\pi$ -conjugated polymer-lanthanide ion complexes is one of the very important research activities for both fundamental understanding as well as developing new materials for innovative temperature sensing applications in the polymer-inorganic chemistry interface.

Herein, we report a unique carboxylic acid functionalized  $\pi$ -conjugated polymer- $\text{Eu}^{3+}$  ion complexes as thermo-sensitive luminescent molecular probes both in solution and in solid state (see Fig. 1). A blue light emitting oligophenylenevinylene (OPV) unit was chosen as an optical chromophore and a 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 regular intervals. The newly designed segmented OPV polymers were found to be efficient photosensitizers for  $\text{Eu}^{3+}$  ions to produce strong red emission from the metal center. The polymer- $\text{Eu}^{3+}$  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

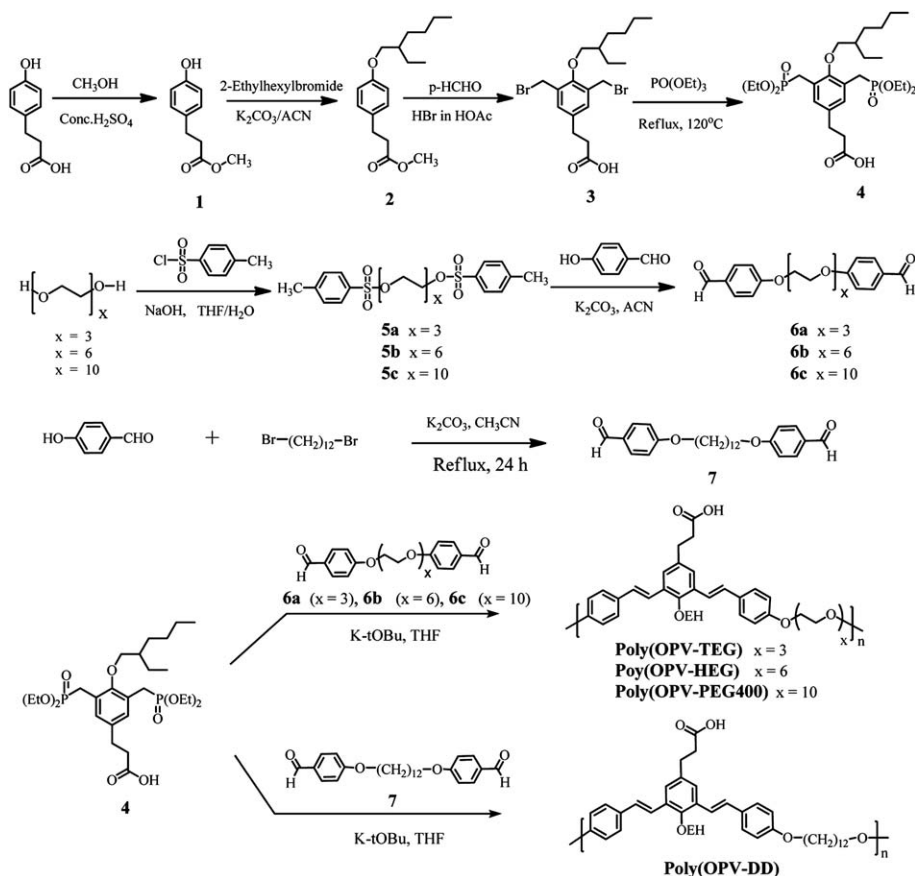
segmented polymer backbone, their temperature sensing ability 'turn-on' or 'turn-off'<sup>9c</sup> varied from 20 to 100 °C (see Fig. 1). Photophysical experiments based on absorbance, emission, and luminescent decay time measurements were carried out to trace the mechanistic aspects of the luminescent pathways. The decay process was further investigated using the Arrhenius equation which suggested that the kinetic rate constants of the polymer complexes followed a typical linear relationship over a wide range of temperature in which the probes were active. The nature as well as the length of the segmented chain (hydrophilic or hydrophobic) were found to be very crucial factors in determining their temperature sensing ability. Thus, the present approach opens up a new molecular design for  $\pi$ -conjugated polymer- $\text{Eu}^{3+}$  ion complexes for temperature sensor applications based on luminescent molecular probes.

## Results and discussion

The carboxylic acid functionalized  $\pi$ -conjugated segmented polymers were synthesized by the A-A + B-B polycondensation approach *via* the Wittig-Horner route as shown in Scheme 1. 4-Hydroxyphenylpropionic acid was converted into its methyl ester by acid catalysed esterification to obtain methyl 3-(4-hydroxyphenyl)propanoate (1). Compound 1 was substituted with 2-ethylhexylbromide in the presence of  $\text{K}_2\text{CO}_3$  to give methyl 3-(4-((2-ethylhexyl)oxy)phenyl)propanoate (2). It was treated with  $\text{HBr}$ /acetic acid in the presence of *p*-formaldehyde to yield 3-(3,5-bis(bromomethyl)-4-(2-ethylhexyloxy)phenyl)propanoic acid (3). Compound 3 was converted into its corresponding bis-phosphate 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 presence of sodium hydroxide to obtain their corresponding tosylates (5a-c) and (ii) they were further reacted with 4-hydroxybenzaldehyde in acetonitrile in the presence of  $\text{K}_2\text{CO}_3$  to yield 4,4'-(((ethane-1,2-diylbis(oxy)))bis(ethane-2,1-diyl))bis(oxy)) dibenzaldehyde (6a-c). The reaction of 1,12-dibromododecane



**Fig. 1** Approach for thermo-sensitive  $\pi$ -conjugated polymer- $\text{Eu}^{3+}$  ion complexes and their turn-on and turn-off switching pathways.



**Scheme 1** Synthesis of segmented  $\pi$ -conjugated polymers having OPV units.

with 4-hydroxybenzaldehyde produced the alkylated bis-benzaldehyde derivative (7). The segmented polymers were synthesised by reacting equimolar amounts of dialdehydes (6 and 7) with bisphosphonate ester (4) in the presence of potassium tertiarybutoxide as a base in dry-THF. The polymerization reaction produced two kinds of carboxylic acid functionalized oligophenylenevinylene (OPV) containing segmented polymers with either polyethyleneoxy chain or polymethylene chain segmented backbones. These polymers were referred to as Poly(OPV-X): **Poly(OPV-TEG)**, **Poly(OPV-HEG)**, **Poly(OPV-PEG400)** and **Poly(OPV-DD)**, where X represents 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 of a benzaldehyde derivative (8) having triethyleneglycol monomethyl as terminal units (see Scheme S1†).

The structures of the monomers, oligomers and polymers were characterized by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR, and MALDI-TOF analysis (see ESI†). The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran using polystyrene as a standard (GPC chromatograms are provided in Fig. SF1†). The molecular weights  $M_w$ ,  $M_n$ , and polydispersity are given in Table ST1 in the ESI.† The molecular weights of the polymers were obtained in the range of  $M_w = 18\,000$ – $37\,000$  with a polydispersity of 1.9–3.0.<sup>13</sup>

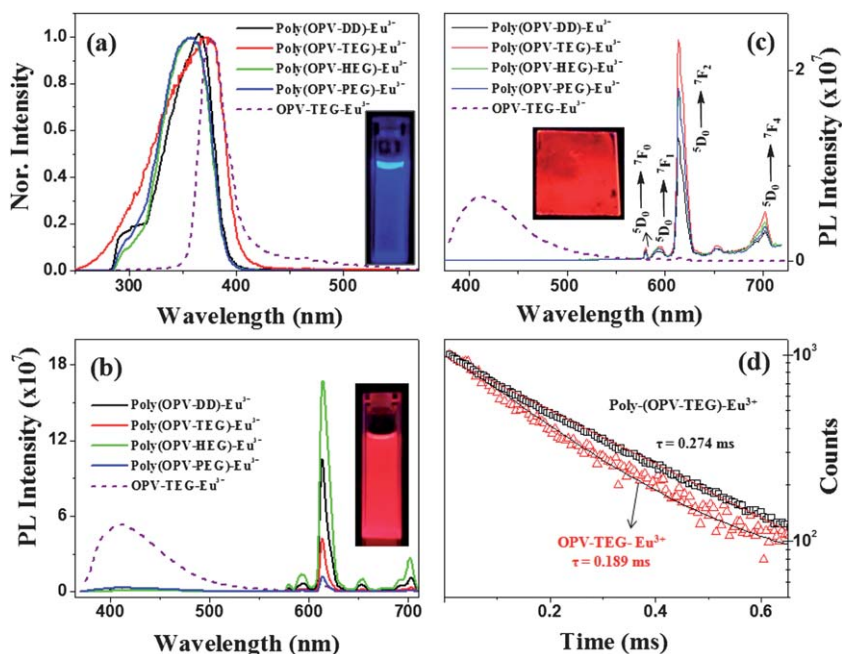
Thermogravimetric analysis showed that the polymers were thermally stable up to  $250^\circ\text{C}$  (see Table ST1† for values, TGA plots are shown in Fig. SF2†). DSC analysis of the polymers did not show any melting or crystallization peaks in the heating-cooling cycles indicating that they were highly amorphous in nature (see Fig. SF3 and ST1†). With increase in the PEG chain length, the glass transition temperature ( $T_g$ ) of the segmented polymers decreased from  $70^\circ\text{C}$  to  $8^\circ\text{C}$ . This confirmed that rigidity of the polymeric backbone decreased with increase in the PEG chain length. The  $T_g$  of the rigid hydrophobic segmented polymer **Poly(OPV-DD)** was  $84^\circ\text{C}$ , which was much higher compared to PEG-segmented polymers. The photo-physical properties of the polymers and oligomers were studied in solutions and drop cast films (see Fig. 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) were slightly red shifted (10–50 nm) with respect to the difference in their polymer structures. The absorption and emission maxima of **OPV-TEG** were found to be identical to those of its polymer. The quantum yields of the polymers (also oligomers) were determined using quinine sulfate ( $\phi_r = 0.53$ , in 0.1 N conc.  $\text{H}_2\text{SO}_4$ ) as a standard (see Table ST1†).<sup>12</sup> The quantum yields of polymers (also oligomers) were obtained in the range

of 0.13–0.27 in chlorobenzene (Table S1†) which is in accordance with earlier reports.<sup>12c</sup>

Newly synthesized carboxylic acid functionalized polymers were complexed with  $\text{Eu}^{3+}$  ions using theonyl acetylacetone (TTA) as a co-ligand in the polymer–Eu complex. FT-IR spectra of these complexes showed peaks corresponding to the carbonyl stretching frequency at  $1615\text{ cm}^{-1}$  with respect to the  $\text{C}=\text{O}\cdots\text{Eu}^{3+}$  complex and confirmed the formation of the expected complex (see Fig. S5†).<sup>14</sup> In order to prove the binding of TTA and OPV carboxylic acid functionalities in the  $\text{Eu}^{3+}$  ion complex, MALDI-TOF-MS analysis of the OPV–Eu complex was carried out (see ESI, S6†). MALDI-TOF-MS spectra of the complex showed a mass peak at 1434.21 amu with respect to  $(\text{OPVTEG})(\text{TTA})_2\text{Eu}^{3+}(\text{H}_2\text{O})_2$ . The  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  ion complex formation. A similar MALDI-TOF-MS analysis for the polymer complex was found to be not successful due to the large polydispersity of the samples. In order to confirm the formation of the polymer–(TTA)– $\text{Eu}^{3+}$  ion complex (TTA was used as a co-ligand), the X-ray photoelectron spectroscopy (XPS) technique was employed. The XPS measurements were carried out for the **Poly(TEG-OPV)–(TTA)– $\text{Eu}^{3+}$**  complex and the details are provided in the ESI, Fig. S7.† 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  $\text{Eu}^{3+}$  ions coordinated with oxygen

atoms.<sup>15a</sup> The binding energies of C1s photoelectrons appeared as a broad peak in the range of 283–292 eV which was further fitted with a multiple-Gaussian programme as reported by others.<sup>15b</sup> The first major peak 287.2 eV was assigned to C1s electrons 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 the  $\text{Eu}^{3+}$  ion. The actual binding energies of the present complex were almost similar to the polyacrylic systems which was attributed to the aliphatic COOH group in the conjugated OPV chromophore.<sup>15c,d</sup> Similarly O1s electron binding energies of the  $\text{Eu}^{3+}$  complex matched with the expected values (see ESI†).<sup>15e</sup> These results clearly confirmed that the  $\text{Eu}^{3+}$  metal ion was coordinated by the carboxylate unit of the OPV chromophore in the polymeric chain.

Absorption, emission and excitation spectra of the polymer– $\text{Eu}^{3+}$  complexes were recorded in solution (chlorobenzene) and in film (solid state). In Fig. 2a, the solution excitation spectra of all  $\text{Eu}^{3+}$  complexes showed broad absorption from 260 to 430 nm with peak maxima at 350 nm corresponding to  $\pi\text{--}\pi^*$  transition of the aromatic OPV chromophore (see also Fig. S8 and S9†). The emission spectra of the polymer– $\text{Eu}^{3+}$  complexes in solution (Fig. 2b) and film (Fig. 2c) showed characteristic  $\text{Eu}^{3+}$  strong metal centered sharp emission peaks at 580, 593, 614, 650 and 702 nm corresponding to the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_3$  (weak emission), and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transitions, respectively.<sup>5</sup> In both solution as well as in the solid state, the emission spectra of the polymeric  $\text{Eu}^{3+}$  complexes did not show polymer self-emission (at 410 nm) from the  $\pi$ -conjugated backbone. This confirmed that the excitation energy of the



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



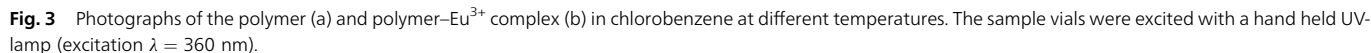
$\pi$ -conjugated OPV chromophore in the polymer backbone was completely transferred to the  $\text{Eu}^{3+}$  ion during the photoexcitation process. The photographs of polymer- $\text{Eu}^{3+}$  complexes showed homogeneous red emission in solution and in film (see Fig. 2). Interestingly, the photosensitizing ability of the polymer- $\text{Eu}^{3+}$  ion complexes was found to be almost the 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 acid functionalized OPV segmented polymers were efficient photosensitizers for  $\text{Eu}^{3+}$  ion in solution and in solid state. The absorption spectrum of OPV-TEG- $\text{Eu}^{3+}$  and polymer- $\text{Eu}^{3+}$  complexes was almost the same in solution (see Fig. SF8†). However, the solid state excitation spectra of polymer- $\text{Eu}^{3+}$  complexes were blue-shifted compared to their oligomer complex (see Fig. 2a). The reason for the blue-shift in the polymer was attributed to the close packing of OPV chromophores in the polymer chains which was completely lacking in the oligomer species. The photoexcitation spectra of the structurally identical oligomer OPV-TEG- $\text{Eu}^{3+}$  complex are shown along with the polymers in Fig. 2b and 2c. Both in solution (chlorobenzene) and in solid state, this oligomer complex showed only weak emission from the  $\text{Eu}^{3+}$  ion (at 615 nm). Additionally, a strong self-emission 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)- $\text{Eu}^{3+}$  and OPV-TEG- $\text{Eu}^{3+}$  complexes indicated that for a given identical chromophore structure, the polymeric ligand was an efficient photosensitizer for complete excitation energy transfer from the ligand to the metal center compared to that of small molecular systems.

To further understand the energy transfer mechanism and trace the role of the 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 oligomers are shown in the ESI (see Fig. SF10 and SF11†). According to Latva's empirical rule, energy transfer from a ligand to an excited state of an  $\text{Eu}^{3+}$  metal ion was more effective when  $\Delta E$  ( $^3\pi\pi^* \rightarrow ^5\text{D}_0$ ) was equal to 2500–4000  $\text{cm}^{-1}$ .<sup>16a</sup> As shown in Fig. SF11,† the energy gap  $\Delta E$  ( $^3\pi\pi^* \rightarrow ^5\text{D}_0$ ) between the triplet excited state of the polymer (or oligomer) ligand and the excited state of  $\text{Eu}^{3+}$  ion is obtained as 5755–5880  $\text{cm}^{-1}$ . Therefore, according to Latva's rule, the direct energy transfer from the polymer ligand to  $\text{Eu}^{3+}$  ion is not possible. The triplet state energy level of TTA was much lower than that of the triplet state of polymers (or oligomers) and at the same time the difference in the energy levels between TTA and the excited state of the  $\text{Eu}^{3+}$  ion was only 2910  $\text{cm}^{-1}$ . Hence, it may be postulated that during the photoexcitation process, the energy was initially transferred from the triplet state of polymers (or oligomers) to the triplet state of TTA and subsequently it was transferred to the  $\text{Eu}^{3+}$  ion metal centre for the luminescence.<sup>16b</sup> In order to confirm this hypothesis, controlled experiments were carried out by varying the amounts of TTA in the Poly(TEG-OPV)-(TTA)- $\text{Eu}^{3+}$  ion complex. The Poly(TEG-OPV) polymer was complexed with  $\text{Eu}^{3+}$  ion using various equivalents of TTA (zero, one, two and three mole equivalents) and further these complexes were

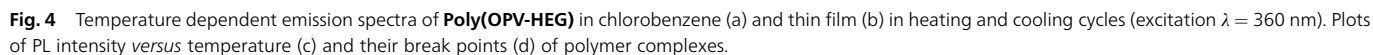
subjected to excitation and emission studies (see ESI for detailed characterization, Fig. SF12 and SF13†). In the absence of TTA, the emission spectrum of the  $\text{Eu}^{3+}$  complexes showed a large amount of self-emission from the OPV polymer backbone indicating the incomplete photoexcitation energy 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 Fig. 2d. The lifetime decay profiles of the  $\text{Eu}^{3+}$  complexes were fitted with first order decay (see Fig. SF14† for other polymer complexes, see Table ST2†). The  $^5\text{D}_0$  excited state lifetime of the polymer- $\text{Eu}^{3+}$  complexes was obtained to be 270  $\mu\text{s}$  whereas the lifetime of the OPV-TEG- $\text{Eu}^{3+}$  complex was found to be much lower (180  $\mu\text{s}$ ) 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  $\text{Eu}^{3+}$  ion complexes in chlorobenzene and the photographs are shown in Fig. 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 Fig. SF15 and SF16†). Interestingly, the polymer- $\text{Eu}^{3+}$  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 the Poly(OPV-HEG)- $\text{Eu}^{3+}$  complex in both heating and cooling cycles are shown in Fig. 4 [see Fig. SF15 and SF16† for other complexes]. In Fig. 4a, upon heating the solution from 20 to 100 °C, the characteristic emission peak intensities of the  $\text{Eu}^{3+}$  ion (major peak at 615 nm) gradually decreased and the 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 remained up to the room temperature. The reversibility of the temperature sensing behaviours is checked for at least 10 cooling and heating cycles and they are perfectly reproducible. This clearly supported the fact that the photosensitizing ability of the polymer- $\text{Eu}^{3+}$  ion complexes was highly sensitive to the temperature of the medium.

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- $\text{Eu}^{3+}$  complex in these solvents are given in the ESI (Fig. SF17†). Along with the temperature dependent luminescent behaviors, partial self-emission from the OPV chromophores was also observed in THF, DMSO and DMF solvents. On the other hand, ODCB,



thermo-sensing studies. Further, the effect of concentrations of the polymer chromophores on the thermo-sensing ability was also investigated for  $10^{-6}$  M to  $10^{-5}$  M OPVs in chlorobenzene (see ESI, Fig. SF18†). It was found that the thermo-response

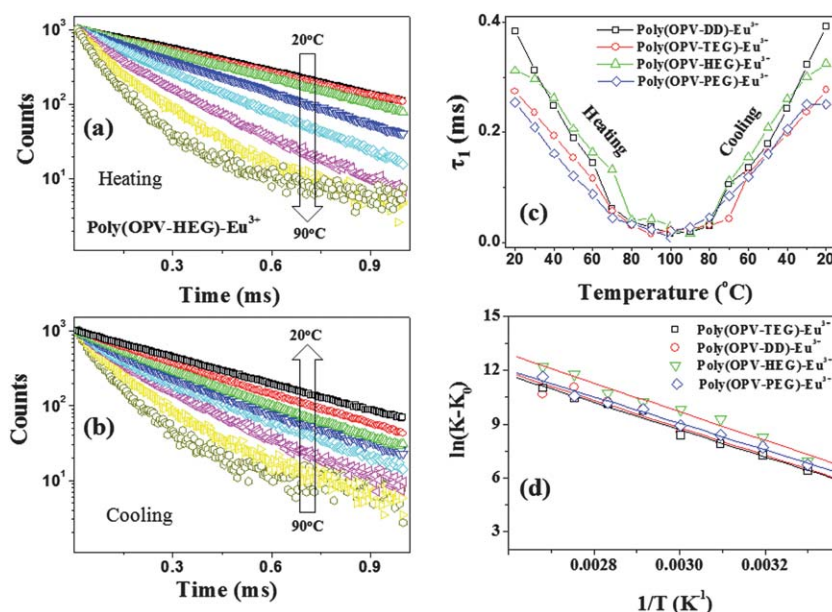


behaviors of the polymer-Eu<sup>3+</sup> complex were retained even at a very low concentration (10<sup>-6</sup> M), suggesting that the polymer-lanthanide ion system is a potential candidate for temperature sensing applications.

In order to check the thermo-sensitive luminescent characteristics in the solid state, thin films were cast on a quartz plate and subjected to photoluminescence studies. In Fig. 4b, both the emission spectra and the photographs clearly support the thermo-reversibility of luminescence properties of these  $\pi$ -conjugated polymer-Eu<sup>3+</sup> complexes in the solid state. This is the first time that 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 mention that the solid state samples in fact showed a small amount of emission at 100 °C which was completely absent in the solution (Fig. SF19†). This observation was attributed to the closer packing of the polymer chains in the film whereas they remained apart in solution at high temperature. All other polymer complexes were also found to be thermo-reversible in their luminescent behaviors (the details are provided in Fig. SF15 and SF16†). In order to compare the thermo-reversibility across the various segmented polymers, the optical densities (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 Fig. SF15 and SF16†). The PL intensities of these spectra at 615 nm (with respect to the Eu<sup>3+</sup> ion) were plotted against the temperature and are shown in Fig. 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 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 Fig. 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†. These molecular probes were found to have a sensitivity of 1.5 to 1.6 K<sup>-1</sup> which matched with the literature reports.<sup>7a,i</sup> This suggested that the temperature range at which the turn-on or turn-off probes worked was 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 a 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  $\pi$ -conjugated polymer-Eu<sup>3+</sup> 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)-Eu<sup>3+</sup> are given in Fig. 5a [see Fig. 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 reversible in the subsequent cooling cycles (see Fig. 5b). The same trend was observed for other polymer-Eu<sup>3+</sup> complexes in the heating and cooling cycles (see Fig. SF20†). The decay profiles were fitted with exponential decay fits and their lifetime values are given in Table ST3 in the ESI.† 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 ( $\tau_1$ ) versus



**Fig. 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  $\tau_1$  versus temperature (c) and decay rate constants versus  $1/T$  (d) of the polymer complexes.



temperature are shown in Fig. 5c. The thermo-sensing trends of the plots in the lifetime were almost identical to that observed based on the PL intensity of the polymer complexes (see Fig. 4c). Therefore, the reproducibility of the thermo-sensitive characteristics of the polymer-Eu<sup>3+</sup> ion complexes was confirmed by two independent photophysical techniques: (i) variation in the PL intensity (see Fig. 4c) and (ii) PL excited state life times (Fig. 5c). Hence, the turn-on and turn-off luminescent behaviors are molecular properties of the  $\pi$ -conjugated polymer-Eu<sup>3+</sup> ion complexes and mainly controlled by the segmented polymer chain structure in solution and in solid state.

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

$$k = Ae^{(-E_a/RT)} \quad (1)$$

where  $E_a$  is the energy gap between the emitting levels (equivalent to activation energy),  $A$  is the Arrhenius pre-exponential factor,  $R$  is the gas constant and  $T$  is the absolute temperature. For decay rate constants at various temperatures ( $\Delta T$ ), the above expression is modified as:<sup>7a</sup>

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

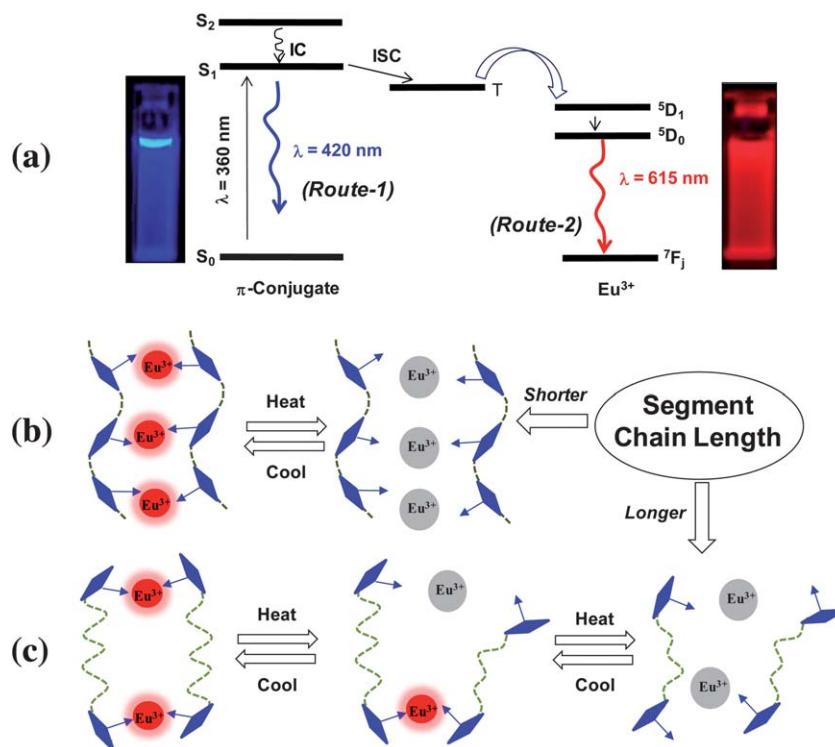
where  $k$  is the decay rate constant at temperature  $T$  and  $k_0$  is the decay rate constant in which the molecule is less influenced by thermal disturbance ( $k$  at 20 °C). The rate constant ( $k$ ) is determined from the equation  $k = 1/\tau_1$ , where  $\tau_1$  is the fast decay life time of the excited species.<sup>7bf</sup> From the plots  $\ln(k - k_0)$  vs.  $1/T$  (see Fig. 5d), the activation energy ( $E_a$ ) and the frequency factor 'A' are directly obtained from the slope and intercept, respectively (see Table S4† for values). The activation energies ( $E_a$ ) of all the polymer complexes were found to be in the range of 3.14 to  $3.62 \times 10^2$  kJ mol<sup>-1</sup> which is in accordance with earlier reports.<sup>7f8</sup> This confirmed that the nature of the decay of the excited species from the <sup>5</sup>D<sub>0</sub> emitting level of the Eu<sup>3+</sup> ion followed a typical Arrhenius linear trend with temperature irrespective of the variation in the segmented polymer structure backbone. Therefore, the variation in the temperature break points (see Fig. 4d) with respect to the segmented polymer structures was not due to the difference in the <sup>5</sup>D<sub>0</sub> emitting level of the Eu<sup>3+</sup> ion in their complexes.

In general, the emission of Eu<sup>3+</sup> ion complexes was influenced at higher temperatures in two ways: (i) the deactivation of the Eu<sup>3+</sup> ion <sup>5</sup>D<sub>0</sub> excited state and non-radiative decay of the excitation energy and (ii) less excitation energy transfer from the ligand to the europium excited states (<sup>5</sup>D<sub>0</sub> and <sup>5</sup>D<sub>1</sub>). These two processes are schematically shown in Fig. 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 excitation energy in two possible ways: (i) self-emission of the conjugated chromophore in the blue region (emission at  $\lambda = 360$  nm) (route-1) or (ii) transfer the excitation energy from the  $\pi$ -conjugated chromophore to metal ions and subsequently produced sharp emission in the range of 570–720 nm from the Eu<sup>3+</sup> metal center (route-2). The photographs of the vials in Fig. 3b and their respective

emission spectra in Fig. 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 Fig. 4b and c). Therefore, the vanishing of red-emission at 100 °C occurred either by the deactivation of the excited states Eu<sup>3+</sup> ion (<sup>5</sup>D<sub>0</sub> excited state) or may be due to the structural changes in the polymer chains at high temperatures.

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.<sup>2e,18</sup> In the case of BODIPY, the emission intensity increased reversibly while assembling the chromophores towards the lower critical solution temperature (LCST). In curdlan, the exposure to the methanol vapour was used as a stimulus to partially disassociate its complexation with polythiophene to attain vaporochromism. On the other hand, in the present investigation, the polymer backbone itself acts 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 temperature studies in chlorobenzene (see Fig. 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 Fig. SF21†). Hence, the occurrence of a large change in the topology of the polymer chains as the cause for the temperature dependent luminescent behavior of metal ions was ruled out. The straight line in the  $K$ -values (in Fig. 5d) for the complexes over the temperature confirmed that all the polymer complexes followed almost similar decay pathways for <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> 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-Eu<sup>3+</sup> ion complexes in the region which corresponded to the polymer self-emission (see Fig. SF23†). With increase in the temperature, the self-emission of the 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 the polymer alone, compare Fig. 3a and b at 100 °C). Therefore, neither the route-1 process (see Fig. 6a) or change in the polymer topology significantly influenced the decay of Eu<sup>3+</sup> ion emission at high temperatures. Hence, the deactivation of the Eu<sup>3+</sup> ion excited state (<sup>5</sup>D<sub>0</sub>) primarily accounted for the thermal decay of red-luminescence at high temperatures.

Nevertheless, it is not possible to ignore the role of the polymer structure completely. If one assumes that the variation in the polymer structures does 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 polymers (see Fig. 4c and d and 5c). To explain this point, two polymer structures Poly(OPV-HEG)



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

and **Poly(OPV-TEG)** were chosen and their possible chain orientations with respect to temperature changes in solution are schematically shown in Fig. 6b and c. These two polymer structures were varied only by the number of  $-\text{CH}_2\text{CH}_2\text{O}-$  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  $72^\circ\text{C}$  which was almost  $18^\circ\text{C}$  higher than that of the TEG-polymer complex (at  $57^\circ\text{C}$ ). As shown in Fig. 6, the conjugated chromophore- $\text{Eu}^{3+}$  ion species in the **Poly(OPV-TEG)- $\text{Eu}^{3+}$**  complex were expected to be kept closely whereas they were apart in the more flexible **Poly(OPV-HEG)- $\text{Eu}^{3+}$**  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 occurred at much lower temperatures in the **Poly(OPV-TEG)- $\text{Eu}^{3+}$**  complex (at  $57^\circ\text{C}$ ). When the OPV chromophores were kept apart in the chains, they tended to undergo only partial separation from the metal-ion center at low temperature and need more thermal energy for complete disassociation. As a result, the turn on/off process became active only at a higher temperature (at  $72^\circ\text{C}$ ). Hence, in the present investigation, the luminescence probes active temperature region was directly dictated by the length of the segmented polymer chain. Interestingly, all the polymer- $\text{Eu}^{3+}$  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 materials science below  $100^\circ\text{C}$ . 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  $\pi$ -conjugated polymer-lanthanide metal ion complexes.

## Conclusions

In summary, a new class of segmented  $\pi$ -conjugated oligophenylenevinylene polymers with carboxylic acid functionality were synthesized through tailor made approaches and successfully utilized as photosensitizers for  $\text{Eu}^{3+}$  ions. Upon photoexcitation, the excitation energy transfer from the blue luminescent polymeric ligand to metal center produced strong and sharp metal centered 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  $\text{Eu}^{3+}$  ion accounted for the decay of the red luminescence at high temperatures. The temperature break points at which the 'turn-on and turn-off' luminescence switch (red to colorless) occurred were 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 a 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, a structurally similar oligomer-complex was found to be less efficient as a photosensitizer and also did not show any thermo-sensitive behavior. Thus, the design of the segmented  $\pi$ -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  $\pi$ -conjugated segmented polymers with photoactive OPV chromophores and their complexes with  $\text{Eu}^{3+}$  ion. Though the approach demonstrated here pertains to  $\pi$ -conjugated polymers having OPV chromophores and  $\text{Eu}^{3+}$  ion, it is not restricted to any particular type of  $\pi$ -conjugated polymeric systems or lanthanide ions. This finding opens up a 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  $\text{Eu}^{3+}$  complexes, temperature dependent absorption and emission spectra of polymers, polymer- $\text{Eu}^{3+}$  complexes in solution and solid state and luminescent decay profiles of  $\text{Eu}^{3+}$  complexes is provided.  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, MALDI spectra, and XPS spectra are also provided in the ESI.†

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