

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

# Multiplicate sensitization of novel near-infrared luminescent linear copolymers based on Er, Nd and Yb-complexes

Jianxin Luo,<sup>\*a,b</sup> Chunyan Zhang,<sup>a,b</sup> Changhong Li,<sup>a</sup> Hanxiang Hu<sup>a</sup> and Bonian Hu<sup>a</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

**Abstract:** A series of novel near-infrared (NIR) luminescent linear copolymers, PCzLnQL<sub>2</sub> (Cz=carbazole; Ln=Er, Nd, and Yb; Q=8-hydroxyquinoline; L=8-hydroxyquinoline, 5-[(carbazole-9-yl)methyl]-8-hydroxyquinoline and 2-thenoyltrifluoroacetone) covalently linked with Ln-complexes were synthesized and characterized. The obtained copolymers exhibit appropriate molecular weight, good solubility-processability and thermal stability for PLEDs application. The photophysical properties of the copolymers were studied by UV-vis absorption, steady state and transient fluorescence spectra. Monitoring the characteristic emission of the corresponding Ln<sup>3+</sup>, the copolymers show broad excitation band extended from UV light to the region of visible light. Upon excitation with UV-vis light, the copolymers display high efficient near-infrared (NIR) luminescence of the corresponding Ln<sup>3+</sup>. Effects of N-vinylcarbazole segments and ligands on the NIR-luminescence of Ln<sup>3+</sup> were investigated carefully. The results indicate that the NVK segments are not only used as light-harvesting group, but also as barrier to form a special microenvironment for the Ln-complex moieties. The three ligands can sensitize the three lanthanide ions, but the sensitized efficiency is not identical. Based on the observed luminescence phenomenons and the reported energy transfer theories, energy transfer mechanism for the NIR-luminescence of the copolymers was also investigated, which will provide rule for designing perfect NIR-luminescence materials.

## 1. Introduction

In recent years, near-infrared (NIR) luminescent lanthanide ions such as erbium (Er), neodymium (Nd) and ytterbium (Yb), have attracted much attention as emissive materials in photonic devices,<sup>1</sup> such as light emitting diodes (LEDs),<sup>2-4</sup> active optical waveguides,<sup>5-9</sup> laser<sup>7-9</sup> and bio-imaging probes.<sup>9-11</sup> However, they have an intrinsically low molar absorption coefficient due to their forbidden characteristic of intra-4f transitions, which is difficult to generate efficient NIR-luminescence by direct excitation of these lanthanide ions.<sup>7</sup> Generally, one solution to enhance NIR-luminescence of these lanthanide ions is to indirectly excite the lanthanide ions through an effective energy transfer from the triplet state of organic chromophores to the luminescent excited state of the lanthanide ions. The organic chromophores may be a ligand direct coordinated with lanthanide ions; or a sensitizer covalently attached on a simple ligand that coordinated with lanthanide ions. Recently, NIR-luminescence originating from sensitizer-functionalized ligand-based lanthanide complexes have been reported widely.<sup>12-19</sup> Nevertheless, the inappropriate single sensitizer may lead to low absorption efficiency and energy transfer efficiency, and following lead to low NIR-luminescent efficiency. The co-excitation of multiplicate sensitizers may improve the NIR-luminescent efficiency of lanthanide ions.

As is well known, polymers possess a number of advantages

because of their low-cost, flexibility, good solution-processability and convenient control of various optical parameters such as refractive index, birefringence, and optical transparency bandwidth.<sup>20</sup> Particularly, all kinds of functional groups can be covalently attached on the polymers linkages. As a consequent, plenty of functional polymers applied as luminescent materials have been designed and synthesized.<sup>20-26</sup> For example, several red-luminescent copolymers containing [Eu( $\beta$ -diketonate)] moieties and N-vinylcarbazole segments were synthesized by copolymerization of Eu-complexes monomers and N-vinylcarbazole.<sup>21-23</sup> Intramolecular energy transfer from the carbazole groups to the europium complex moieties were confirmed in the photoluminescence process of the copolymers solution and film. Moreover, the copolymers were used as luminescent materials to prepare single layer high luminance polymeric light-emitting diodes (PLEDs). In addition, a series of bipolar Alq<sub>3</sub>-based copolymers containing Alq<sub>3</sub> moieties and carbazole segments were obtained in our previously work, which showing high efficient energy transfer from the carbazole segments to Alq<sub>3</sub> moieties.<sup>25</sup> We also reported a NIR-luminescent linear copolymer based on tris(8-hydroxyquinoline)erbium, which has good solution-processability, thermal stability, and NIR-luminescent properties.<sup>27</sup>

In this work, a series of NIR-luminescent linear copolymers containing Ln-complex (Ln= Er, Nd, and Yb) moieties and N-vinylcarbazole segments were designed and synthesized. A

polymerizable 8-hydroxyquinoline derivate with methacrylate, 5-(2-methacryloyl-2-hydroxyethyl)-8-quinolinol (HEMA-CH<sub>2</sub>-Q), was copolymerized with N-vinylcarbazole (NVK) to obtain a polymeric ligand P0 firstly. Meanwhile, three different ligands (8-hydroxyquinoline, 5-[(carbazole-9-yl)methyl]-8-hydroxyquinoline and 2-thenoyltrifluoroacetone) were coordinated with three lanthanide ions to obtain nine Ln-complex precursors respectively. The nine Ln-complex precursors following coordinated with the polymeric ligand P0 to prepare nine linear copolymers containing Ln-complex (Ln= Er, Nd, and Yb) moieties and N-vinylcarbazole segments. The effects of the ligands and NVK segments on the NIR-luminescence of the Ln ions were investigated in detail. Moreover, the energy transfer mechanism in the NIR-luminescence of the copolymers were studied and proposed.

## 2. Experimental

### 2.1. Materials

8-Hydroxyquinoline (Q), triethylamine (NEt<sub>3</sub>), and all solvents were obtained commercially and used as received. 2-Thenoyltrifluoroacetone (TTA) was purchased from Aldrich Chemical Company. Ln<sub>2</sub>O<sub>3</sub> (Ln=Er, Nd and Yb; 99.99%) was purchased from a Chinese company. N-vinylcarbazole (NVK) and azobisisobutyronitrile (AIBN) were purified and dried before use. 5-(2-Methacryloyl-2-hydroxyethyl)-8-quinolinol (HEMA-CH<sub>2</sub>-Q) and 5-[(carbazol-9-yl)methyl]-8-hydroxyquinoline (CzHQ) and Tris(8-hydroxyquinoline) neodymium (NdQ<sub>3</sub>) was prepared according to the reported procedure.<sup>25,26</sup> LnCl<sub>3</sub> ethanol solution was obtained as described in reference.<sup>15</sup> The rare earth oxide (Ln<sub>2</sub>O<sub>3</sub>) was dissolved in concentrated hydrochloric acid (HCl), and the surplus HCl was removed by evaporation. The residue was dissolved with anhydrous ethanol. The concentration of the rare earth ion was measured by titration with a standard ethylenediaminetetraacetic acid (EDTA) aqueous solution.

### 2.2. Synthesis of the copolymers

The synthesis route of the copolymers is shown in Scheme 1. Firstly, Polymeric ligand (P0) was prepared according to the previous report.<sup>27</sup> The mole ratio of HEMA-CH<sub>2</sub>-Q/NVK in feed is 1/50. Thereafter, nine Ln-complex precursors (LnL<sub>2</sub>Cl·2H<sub>2</sub>O) were obtained according to the reference with slightly modification.<sup>16</sup> About 10 mL ethanol solution of LnCl<sub>3</sub> (concentration: about 1 mol/L) was added to 20 mL methanol solution of ligands (concentration: 1 mol/L) under stirring with the molar ratio of Ln<sup>3+</sup>/L being 1:2. Additionally, about 10 mL water was added. After stirring at 65 °C for 10 h, about 30 mL water was added to the mixture and more precipitates were obtained. The yellow precipitates were collected by filtration, washed with water and cold methanol for three times.

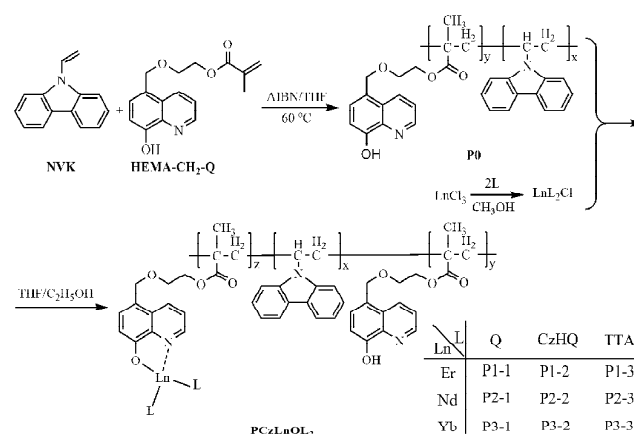
Then, 5 mmol LnL<sub>2</sub>Cl·2H<sub>2</sub>O and a proper amount of P0 (the mole ratio of LnL<sub>2</sub>Cl·2H<sub>2</sub>O to the HQ in P0 is 5/1) were dissolved in 30 mL THF, and heated under reflux for one day. Meanwhile, appropriate NEt<sub>3</sub> was added to adjust pH ≈ 7. Thereafter, the reaction mixture was cooled to room temperature and purified by several solution-precipitation cycles. The resulting solid was further purified by Soxhlet extraction with boiling methanol for two days and finally dried in a vacuum oven at 70 °C for 24 h.

### 2.3. Synthesis of the reference copolymers

Firstly, a polymeric ligand containing HEMA-CH<sub>2</sub>-Q and MMA (mole ratio in feed: HEMA-CH<sub>2</sub>-Q/MMA=1/50) was prepared according to the reported procedure.<sup>26</sup> Then, the polymeric ligand was coordinated with the Nd-complex precursor LnL<sub>2</sub>Cl·2H<sub>2</sub>O to obtain a copolymer (PMMA-NdQ<sub>3</sub>) containing NdQ<sub>3</sub> moieties and MMA segments, as shown in Figure 1S, which was expected as a reference copolymer to investigate the effect of NVK segments on the NIR-luminescence of the titled copolymers.

### 2.4. Characterization

The FT-IR spectra were carried out using a RFX-65A (Analects) Fourier Transform Infrared Spectrometer. Elemental analyses (C, H, and N) were performed with a Vario EL elemental analyzer, and lanthanide ion was analyzed by complexometric titration with EDTA. The molecular weight of the copolymer was determined by Waters 1515-2414 GPC gel permeation chromatography, using THF as an eluent and polystyrene as the standard. Differential scanning calorimetry (DSC) made on Pyris 7 Diamond TA LAB system at a heating rate of 20°C/min under nitrogen. Thermogravimetric analysis (TGA) was performed with Pyris 1 TGA instrument at a heating rate of 10°C/min under nitrogen atmosphere. UV-vis absorption spectra of the polymer solutions (concentration: 0.01g/L, solvent: THF) were determined on a Shimadzu spectrophotometer. The polymer films were prepared under identical conditions by KW-4A Spin Coater. The thickness of polymer films was measured by an Alpha-step 500 surface profiler and is found to be about 100 nm. The excitation and emission spectra and the time-resolved measurements of the polymer films were recorded by an Edinburgh FLS 920 fluorescence spectrometer. The NIR luminescence lifetime of these polymers were measured at room temperature by using an excitation wavelength of 390 nm and monitored around the most intense emission line. The luminescent decay curve was fitted by double exponential functions. The emission lifetime of carbazole in these polymers were measured at room temperature by using an excitation wavelength of 305 nm and monitored around the most intense emission.



Scheme 1 Synthesis of the copolymers

## 3. Results and Discussion

### 3.1. Synthesis and characterization

These linear copolymers, involving N-vinylcarbazole (NVK),

isolated 8-hydroxyquinoline (Q), ligands (Q, CzHQ and TTA) and lanthanide ions, were synthesized through the ligand exchange reaction according to the reported procedure,<sup>16</sup> as shown in **Scheme 1**. All of the obtained copolymers exhibit good solubility in a wide range of organic solvents, such as toluene, THF, chloroform, DMF and DMSO. GPC measurements reveal that the weight average molecular weight ( $M_w$ ) of the copolymers, as shown in **Table 1**, is around 16,000 g/mol, which is higher than that of the polymeric ligand P0. Due to the dissolubility and appropriate molecular weight, the copolymers can be easily cast into uniform thin films with good mechanical flexibility.

According to the contents of these elements (C, H, N, and Ln), the mole ratio of NVK/Q/LnQL<sub>2</sub> (x/y/z) in the copolymers was calculated roughly and presented in **Table 1**. The results indicate that the titled copolymers have been synthesized successfully. Due to steric effect of the bulky and rigid LnL<sub>2</sub>Cl·2H<sub>2</sub>O, covalently linked 8-hydroxyquinoline in the polymer ligand P0

can not be coordinated with lanthanide ion completely, consequently, there are always some isolated 8-hydroxyquinoline groups in the copolymers. Moreover, one can found that large bulk CzHQ (P1-2, P2-2 and P3-2) leads to higher content of non-coordinating 8-hydroxyquinoline groups in the corresponding copolymers compared with other copolymers.

The FT-IR absorption spectra of the copolymers have been measured and exhibit similar absorption peaks, as shown in **Figure 2S**. Compared with the polymeric ligand, the copolymers have four new absorption peaks at 1264 cm<sup>-1</sup>, 802 cm<sup>-1</sup>, 525 cm<sup>-1</sup> and 423 cm<sup>-1</sup>, assigned to the asymmetric stretching vibration of aryl ether, ring deformation, the stretching of O–Ln and N–Ln, respectively.<sup>28</sup> Moreover, the intensity of stretching vibration of O–H (3430 cm<sup>-1</sup>) and C–O (1097 cm<sup>-1</sup> and 1022 cm<sup>-1</sup>) increases in comparison with those of the polymeric ligand. All of the results suggest that the titled copolymers have been synthesized successfully.

**Table 1** Composition, GPC and thermal analysis data of the copolymer

Copolymer	Contents (wt.%)				Mole ratio of x/y/z	$M_w$ (10 <sup>4</sup> g/mol)	<i>PDI</i>	$T_g$ (°C)	$T_d^a$ (°C)	$R_w^b$ (%)
	C	H	N	Ln						
P0	86.48	5.71	7.19	0	51/1/0	1.57	2.09	181	342	0
P1-1 <sup>c</sup>	84.94	5.60	7.15	1.47	51/0.07/0.93	1.64	2.32	200	368	2.13
P1-2	85.08	5.57	7.17	1.34	51/0.13/0.87	1.62	2.29	212	371	1.95
P1-3	83.68	5.51	7.06	1.53	51/0.02/0.98	1.60	2.17	202	366	2.06
P2-1	85.08	5.58	7.16	1.30	51/0.05/0.95	1.66	2.25	201	367	1.89
P2-2	85.19	5.57	7.18	1.20	51/0.10/0.90	1.65	2.34	214	370	1.78
P2-3	83.86	5.52	7.08	1.32	51/0.02/0.98	1.59	2.19	201	368	1.84
P3-1	84.85	5.57	7.14	1.54	51/0.06/0.94	1.70	2.13	201	372	2.11
P3-2	84.97	5.56	7.16	1.45	51/0.09/0.91	1.67	2.28	211	374	2.07
P3-3	83.64	5.50	7.06	1.57	51/0.03/0.97	1.62	2.31	201	369	2.04

<sup>a</sup> The temperature at which 5% weight loss of the copolymer was reached from TGA under nitrogen atmosphere. <sup>b</sup> The weight percentage of the residual determined from TGA at 800 °C. <sup>c</sup> The data of P1-1 were obtained from our previous report.<sup>27</sup>

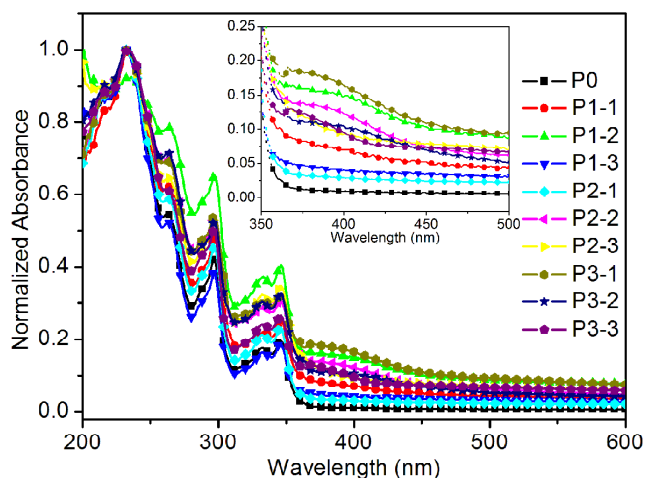
### 3.2. Thermal properties

The thermal stabilities of the copolymers were studied in comparison with that of the polymeric ligand P0 and evaluated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under nitrogen atmosphere. The obtained thermal properties data are listed in **Table 1**. The glass transition temperature ( $T_g$ ) and the temperature of 5% weight loss ( $T_d$ ) for the copolymers are above 200 °C and 365 °C respectively, which increased about 20 °C in comparison with those of the polymer ligand. These results indicate that the copolymers have excellent thermal stability PLEDs application. The polymeric ligand has been decomposed completely at 800 °C, but about 2.00% of residual percentage weight at 800 °C assigned to Ln<sub>2</sub>O<sub>3</sub> was observed for the copolymers.

### 3.3. UV-vis absorption properties

Normalized UV-vis absorption (Abs) spectra of the polymeric ligand and these copolymers in solution are shown in **Figure 1**. All of the absorption spectra have five main absorption peaks of carbazole in the wavelength region of 200 nm to 350 nm: three strong absorption peaks around 238, 261 and 295 nm are attributable to the <sup>1</sup>A → <sup>1</sup>C<sub>a</sub>, <sup>1</sup>A → <sup>1</sup>L<sub>a</sub> and <sup>1</sup>A → <sup>1</sup>B<sub>a</sub> transition of carbazole groups, respectively; two weaker peaks (330 and 345 nm) correspond to the <sup>1</sup>A → <sup>1</sup>L<sub>b</sub> transition of carbazole groups.<sup>22</sup> These results indicate that NVK segments are the main

composition in both the polymeric ligand and the copolymers. Since the content of the LnQL<sub>2</sub> moieties in these copolymers is rather low, the characteristic absorption band of the LnQL<sub>2</sub> is rather weak. However, a new absorption band around 390 nm arisen from metalloquinolate can be observed in the insert of **Figure 1**, which further suggests that Ln-complex precursors are coordinated with polymeric ligand successfully.

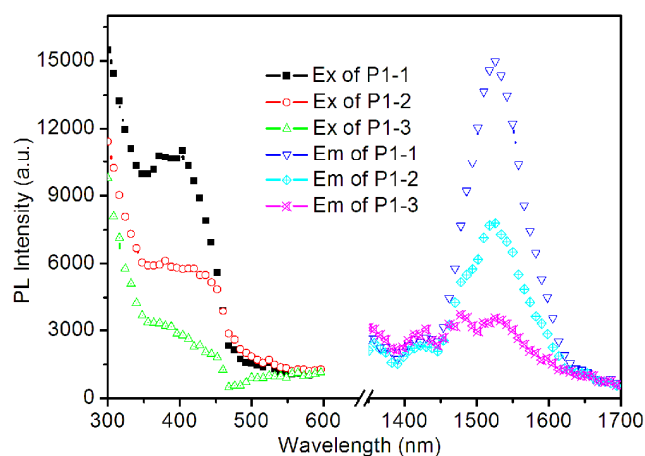


**Figure 1** UV-vis absorption spectra of the copolymers in solution

### 3.4. Photoluminescence (PL) properties



The photoluminescence spectra of the P1-series copolymers containing Er-complexes are shown in **Figure 2**. In the excitation spectra of these copolymers, the broad bands extending to 500 nm are assigned to the absorption of metalloquinolate. Except for the LnQL<sub>2</sub> moieties, the main components of these copolymers are identical (NVK segments). Therefore, the excitation spectra of these copolymers are similar. Upon excitation of metalloquinolate at 390 nm, the emission spectra of these P1-series copolymers were obtained. The emission bands cover large spectrum ranges, extended from 1450 to 1650 nm, which attributes to the transition from the first excited state to the ground state ( $^4I_{13/2} \rightarrow ^4I_{15/2}$ ) of the Er<sup>3+</sup>. The full width at half-maximum (FWHM) of the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition for P1-1 and P1-2 are 95 and 111 nm, respectively. In comparison with other Er-complex materials, the FWHM of the copolymers are quite broad, which is necessary for getting a wide gain bandwidth for optical amplification.<sup>8</sup>

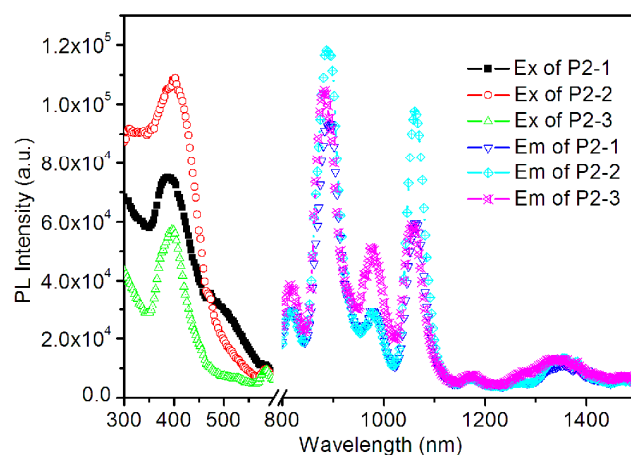


**Figure 2** PL excitation (Ex) and emission (Em) spectra of the P1-series copolymers containing Er-complexes in film ( $\lambda_{em}=1525$  nm,  $\lambda_{ex}=390$  nm)

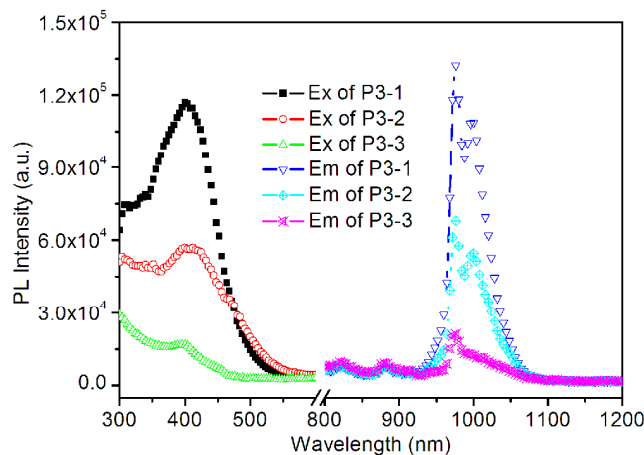
**Figure 3** displays the PL excitation and emission spectra of the P2-series copolymers containing Nd-complexes. The excitation spectra were obtained by monitoring the main emission of Nd<sup>3+</sup> at 1060 nm. A broad excitation band from UV light to visible light can be observed, which is assigned to the absorption of metalloquinolate, superimposed with excitation band (at 581 nm) originating from the characteristic absorption transition  $^4I_{9/2} \rightarrow ^2G_{7/2}$  of the Nd<sup>3+</sup>. It should be noted that the absorption transition at 581 nm of the Nd<sup>3+</sup> is much weaker than that of the ligands, which indicate that the PL sensitization via exciting the ligands is much more efficient than directly exciting the absorption energy level of the Nd<sup>3+</sup>. The PL emission spectra of these P2-series copolymers were obtained upon excitation of metalloquinolate ( $\lambda_{ex}=390$  nm), as shown in **Figure 3**. The emission spectra of these copolymers consist of three main bands around 886 nm, 1060 nm, and 1340 nm, corresponding to the f-f transitions of  $^4F_{3/2} \rightarrow ^4I_{9/2}$ ,  $^4F_{3/2} \rightarrow ^4I_{11/2}$ , and  $^4F_{3/2} \rightarrow ^4I_{13/2}$ , respectively. In addition, there are two apparent emission peaks around 817 nm and 980 nm, which may be assigned to the f-f transitions of  $^4F_{5/2} \rightarrow ^4I_{9/2}$ , and  $^4F_{5/2} \rightarrow ^4I_{11/2}$  respectively. Moreover, the strongest emission was observed around 886 nm, which is different with the previous reported.<sup>7,8</sup> These phenomena may be attributing to the function of the NVK segments.

The excitation spectra of the P3-series copolymers containing

Yb-complexes in film (**Figure 4**) were obtained by monitoring the characteristic emission of the Yb<sup>3+</sup> at 980 nm. The excitation spectra are dominated by a broad band ranging from 300 to 550 nm, which should be assigned to the absorption of metalloquinolate. The emission spectra of the P3-series copolymers (**Figure 4**) were obtained by direct excitation of metalloquinolate ( $\lambda_{ex}=390$  nm). Except for the difference of emission intensity, the emission spectra of these copolymers are similar. In all of the curves, the prominent 980 nm emission band can be observed, which is assigned to the  $^2F_{5/2} \rightarrow ^2F_{7/2}$  transition of Yb<sup>3+</sup>. It should be noted that the emission band of Yb<sup>3+</sup> is not a single sharp transition but an envelope of bands arising at lower energies. Similar splitting has been reported previously,<sup>7,8,15,16</sup> which result from the crystal field splitting.<sup>29</sup>



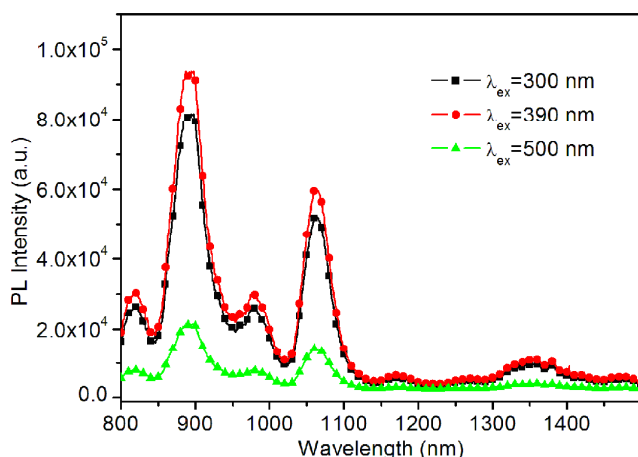
**Figure 3** PL excitation (Ex) and emission (Em) spectra of the P2-series copolymers containing Nd-complexes in film ( $\lambda_{em}=1060$  nm,  $\lambda_{ex}=390$  nm)



**Figure 4** PL excitation (Ex) and emission (Em) spectra of the P3-series copolymers containing Yb-complexes in film ( $\lambda_{em}=980$  nm,  $\lambda_{ex}=390$  nm)

Monitoring the characteristic emission of the corresponding Ln<sup>3+</sup>, all of the copolymers show broad excitation band extended to the region of visible light. Excited with different wavelength (300~500 nm) of UV-vis light, the copolymer P2-1 displays similar emission peaks except for the difference of emission intensity, as shown in **Figure 5**. Excited by 390 nm or 300 nm light, the copolymer P2-1 generates more intense NIR emission than that excited by 500 nm. The results indicate that the copolymers have broadband sensitized NIR-luminescence

property, which provides an access to multicomposite in optical application, such as in medical diagnostic probe, laser, and optical amplifications.<sup>8</sup>



5 **Figure 5** PL emission spectra of the copolymer P2-1 exciting with different excitation wavelength

**Table 2** Photoluminescent data of the copolymers in solid state

Copolymer	$\tau_1/\alpha_1$ ( $\mu\text{s}$ ) / (%)	$\tau_2/\alpha_2$ ( $\mu\text{s}$ ) / (%)	$\langle \tau \rangle$ ( $\mu\text{s}$ )	$\phi$ (%)	$k_{\text{DA}}$ ( $10^5 \text{ s}^{-1}$ )	$\tau_q$ (ns)	$\tau_u$ (ns)	$k_{\text{EnT}}$ ( $10^7 \text{ s}^{-1}$ )
P1-1	12.57/35.2	2.23/64.8	5.87	0.042	1.70	7.6	13.4	5.70
P1-2	14.90/13.7	1.97/86.3	3.74	0.027	2.67	7.3	13.4	6.24
P1-3	1.54/84.9	12.06/15.1	3.11	0.022	3.22	7.1	13.4	6.62
P2-1	-----	-----	1.46	0.584	6.85	5.9	13.4	9.49
P2-2	1.16/87.5	15.05/12.5	2.90	1.160	3.45	4.2	13.4	16.35
P2-3	1.13/83.0	12.5/17.0	3.06	1.224	3.27	3.8	13.4	18.85
P3-1	15.69/48.1	6.53/51.9	10.94	0.547	0.91	4.7	13.4	13.81
P3-2	3.19/77.8	11.09/22.2	4.94	0.247	2.02	5.9	13.4	9.49
P3-3	1.34/86.1	13.58/13.9	3.04	0.152	3.29	6.4	13.4	8.16

25 However, these lifetimes are much shorter than the intrinsic radiative lifetime of lanthanide ions excited state ( $\tau_{\text{RAD}}$ ), which is due to the non-radiative (NR) deactivation of NIR transition of lanthanide ions. Furthermore, the intrinsic radiative lifetime ( $\tau_{\text{RAD}}$ ) is far more than the non-radiative lifetime ( $\tau_{\text{NR}}$ ). Therefore,

30  $\frac{1}{\langle \tau \rangle} = \frac{1}{\tau_{\text{RAD}}} + \frac{1}{\tau_{\text{NR}}} \approx \frac{1}{\tau_{\text{NR}}}$ . According to reference,<sup>30</sup> the rate constants of non-radiative deactivation,  $k_{\text{DA}} = \frac{1}{\tau_{\text{NR}} \langle \tau \rangle}$ , were

determined and listed in **Table 2**. By considering that the PL efficiency ( $\phi$ ) is determined by equation  $\phi = \frac{\langle \tau \rangle}{\tau_0}$  ( $\tau_0$  is the

35 intrinsic radiative lifetime of the lanthanide ions excited state, the values of  $\tau_0$  for  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  are 14 ms, 0.25 ms and 2 ms). The PL efficiencies (NIR emission efficiency) of all the copolymers, listed in **Table 2**, are also higher than that of the corresponding Ln-complexes.<sup>32,33</sup> According to the PL emission lifetime of carbazole in both polymeric ligand ( $\tau_u$ ) and copolymers ( $\tau_q$ ), as shown in **Table 2**, the energy transfer rate can be determined accord to equation  $k_{\text{EnT}} = \tau_q^{-1} - \tau_u^{-1}$ . The energy transfer rates are also listed in **Table 2**. The results indicate that the energy transfer rate determines the NIR emission efficiency to some extent and most of the energy transferred may lead to NIR 40 emissions.

### 3.5. Effects of NVK segments on the NIR-luminescence of $\text{Ln}^{3+}$

The lifetime measurement of the copolymers was investigated by using an excitation wavelength of 390 nm and monitored around the main emission of their corresponding emission 10 spectra. The decay curve for P2-1 is single exponential, while the decay curves of other copolymers can be fitted by the double-exponential function. The values of the lifetime ( $\tau_1$  and  $\tau_2$ ) and the corresponding fractions ( $\alpha_1$  and  $\alpha_2$ ) are listed in **Table 2**.

According to the values of the lifetime and the corresponding 15 fractions, the average PL lifetimes of the copolymers were calculated according to equation:

$$\langle \tau \rangle = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i}$$

lifetimes of the P1-series copolymers lay in the region of 3.11 to 5.87  $\mu\text{s}$ , which is one order of magnitude higher than that of 20 hybrid materials covalently linked with tris(8-hydroxyquinolate)-erbium.<sup>8</sup> In addition, the average PL lifetimes of the P2-series and P3-series copolymers are also higher than that of the corresponding Ln-complexes materials.<sup>8,15</sup>

As discussed above, the average PL lifetimes and PL efficiencies of the copolymers are higher than that of the corresponding Ln-complexes reported previously. The results can be explained by the function of the NVK segments in the PL of the copolymers. In order to study the function of the NVK segments in the PL of the copolymers, both P0 and the copolymer P2-1 are excited with excitation wavelength of 305 nm, and the emission spectra of the 50 copolymers in film are presented in **Figure 6**. As can be seen, the characteristic emission of carbazole groups in P2-1 was quenched largely in comparison of that of P0. Moreover, the near-infrared luminescence intensity of P2-1 is higher than that of  $\text{NdQ}_3$  and the reference copolymer (PMMA- $\text{NdQ}_3$ ), as shown in **Figure 7**. 60 All of the results suggest that the excitation energy of the carbazole in P2-1 can transfer to  $\text{LnQL}_2$  moieties effectively, and following enhanced the near-infrared luminescence of  $\text{LnQL}_2$  moieties.

As mentioned above, the copolymers involve NVK segments, 65 three different ligands and Ln ions. The Ln ions are used as luminescence center, which coordinated with ligands to form  $\text{LnQL}_2$  moieties. The mole ratios of NVK segments and  $\text{LnQL}_2$  moieties in the copolymers are about 51/1. It is mean that each  $\text{LnQL}_2$  moiety is surrounded with about 51 NVK segments. NVK 70 segments encircle the  $\text{LnQL}_2$  moieties to form a special microenvironment. Due to the bulky and hydrophobic of the carbazole groups, water and solvent are prevented outside of the special microenvironment of the  $\text{LnQL}_2$  moieties to some extent. As a consequent, the nonradiative decay associated with the

vibration of O-H or C-H bonds is restrained partly, and also following enhanced the NIR- luminescence of LnQL<sub>2</sub> moieties.

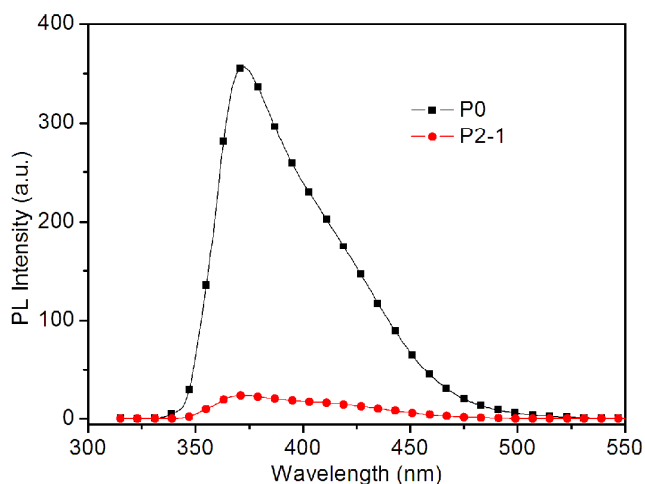


Figure 6 PL emission spectra of P0 and P2-1 in film ( $\lambda_{\text{ex}}=305$  nm)

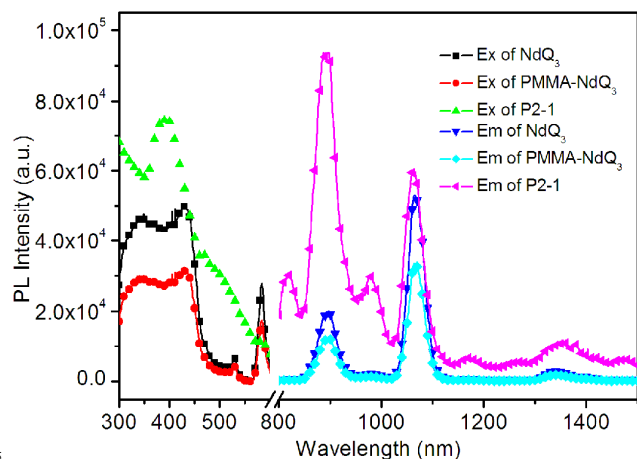


Figure 7 PL emission and excitation spectra of NdQ<sub>3</sub>, PMMA-NdQ<sub>3</sub> and P2-1 ( $\lambda_{\text{ex}}=305$  nm)

Based on the two reasons discussed above, the average PL lifetimes and PL efficiencies of the copolymers are improved compared to the corresponding Ln-complexes. Therefore, we can come to the farther conclusion that the NVK segments are used as both light-harvesting group and barrier for enhancing the near-infrared luminescence of LnQL<sub>2</sub> moieties.

### 3.6. Effects of ligands on the NIR-luminescence of the Ln<sup>3+</sup>

To study the effects of ligands on the NIR-luminescence of the Ln<sup>3+</sup>, the PL excitation and emission spectra of these copolymers containing different ligands were compared and presented in Figure 2, Figure 3 and Figure 4 respectively. Comparing the PL spectra of the P1-series copolymers containing Er-complex (Figure 2), the intensity order is P1-1 > P1-2 > P1-3. Moreover, the PL efficiencies of the P1-series copolymers listed in Table 2 also show the same sequence. These results reveal that the sensitized efficiency of the ligands for Er<sup>3+</sup> is: Q > CzHQ > TTA. In other words, 8-hydroxyquinoline is the most appropriate ligand for Er<sup>3+</sup>. For Nd<sup>3+</sup>, the PL intensity order is P2-2 > P2-3 > P2-1, as shown in Figure 3, indicating CzHQ is the most appropriate ligand for Nd<sup>3+</sup>. Also, the PL spectra of P3-series copolymers

containing Yb-complex were compared and depicted in Figure 4. Both PL intensity and efficiency orders of the P3-series copolymers are P3-1 > P3-2 > P3-3, which also indicate that the sensitized efficiency of the ligands for Yb<sup>3+</sup> is: Q > CzHQ > TTA.

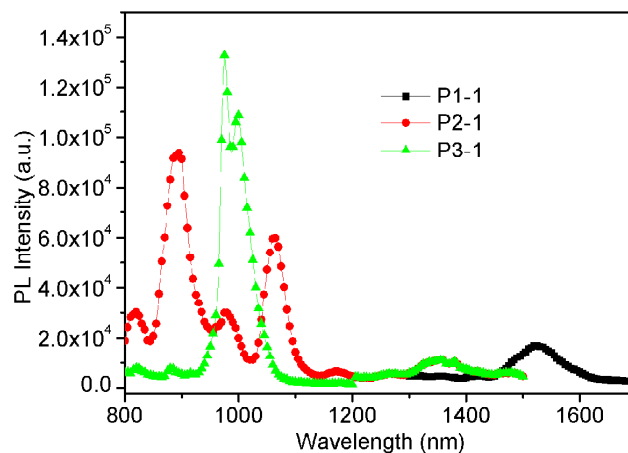


Figure 8 PL emission (Em) spectra of the copolymers based on 8-hydroxyquinoline ligand in film ( $\lambda_{\text{ex}}=390$  nm)

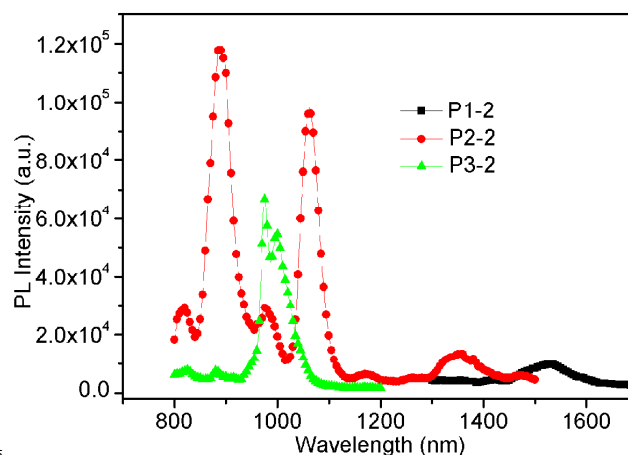


Figure 9 PL emission (Em) spectra of the copolymers based on CzHQ ligand in film ( $\lambda_{\text{ex}}=390$  nm)

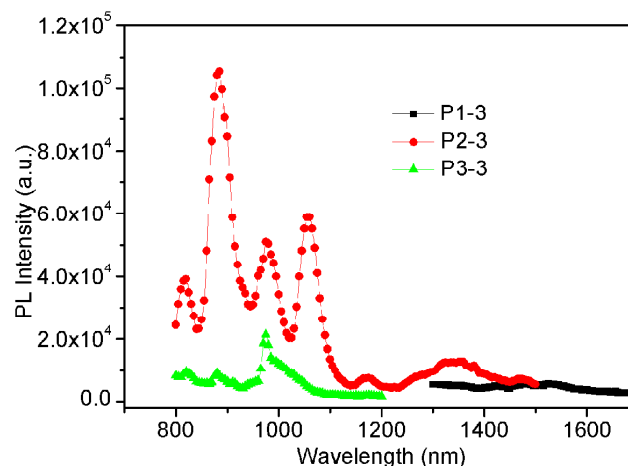


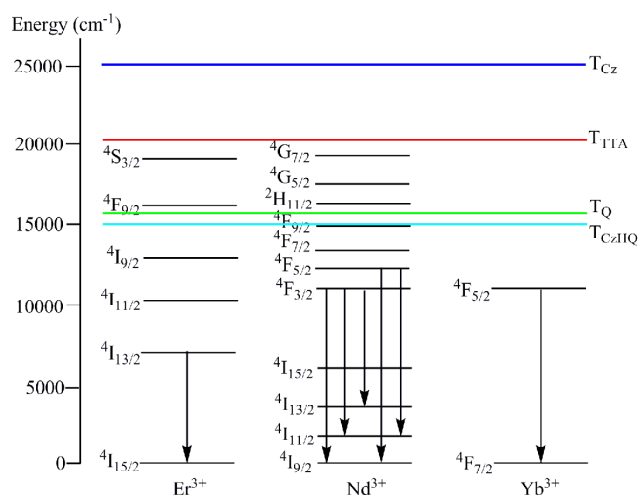
Figure 10 PL emission (Em) spectra of the copolymers based on TTA ligand in film ( $\lambda_{\text{ex}}=390$  nm)

According to the discussion above, we know the sensitized order of different ligands for a special lanthanide ion. Thereinafter, the sensitized order of different lanthanide ions with a special ligand was also investigated according to **Figure 8**, **Figure 9** and **Figure 10**. As can be seen from **Figure 8**, we can find that the emission intensity order of the copolymers with 8-hydroxyquinoline ligand is P3-1 > P2-1 > P1-1. The result indicates that the sensitization of 8-hydroxyquinoline ligand for Yb<sup>3+</sup> is the most effective, and for Er<sup>3+</sup> is the worst. As for Czhq, the emission intensity order of the Ln<sup>3+</sup> is Nd (P2-2) > Yb (P3-2) > Er (P1-2), as shown in **Figure 9**. This order reveal that the sensitized order of Czhq for different lanthanide ions is Nd > Yb > Er. Similarly, the sensitized order of TTA for different lanthanide ions is also Nd > Yb > Er, as indicated in **Figure 10**.

### 3.7. Energy transfer mechanism

As is well known, energy transfer is based on the energy level difference between the excited triplet state of the ligand and the resonance energy level of the central rare earth ion. Too large or too small energy level differences decrease the efficiency of energy transfer.<sup>34</sup> The suitable energy level difference for an efficient ligand-to-Ln<sup>3+</sup> intramolecular energy transfer lies in the range of 500–2500 cm<sup>-1</sup>.<sup>34</sup> There are four chromophores in the copolymers: carbazole (Cz), 8-hydroxyquinoline (Q), ligands (Q, Czhq and TTA) and Ln<sup>3+</sup>. In order to further investigate the energy transfer mechanism, the excitation state energy levels of the chromophores (Cz, Q, TTA and Ln<sup>3+</sup>) were obtained from the previous reported reference<sup>27,28,34,35</sup>, and depicted in **Scheme 2**. Additionally, the excitation state energy levels of Czhq were calculated by Gauss soft, and also depicted in **Scheme 2**.

According to the energy level diagram, the energy level difference between the excited triplet state of the three ligands (Q, Czhq and TTA) and the excited state of the Ln<sup>3+</sup> is appropriated for energy transfer. It is mean that the energy can transfer from the excited triplet state of the three ligands to the high excited state of Ln<sup>3+</sup>, and following to the emission state of the Ln<sup>3+</sup>, which leads to NIR emission of Ln<sup>3+</sup>. However, part of energy has been consumed in the process of energy transfer from high excited state to the emission state of the Ln<sup>3+</sup>. Due to relative higher excited triplet state energy level, the energy transfer from the excited triplet state of TTA to the emission state of Ln<sup>3+</sup> should go through more excited state than that of the other ligands. Therefore, the sensitized efficiency of TTA for Ln<sup>3+</sup> is low than that of the other two ligands. In addition, one can find that the excited triplet state energy level of carbazole (~25000 cm<sup>-1</sup>) is too high and the energy level difference with the emission state energy level of Ln<sup>3+</sup> (Er<sup>3+</sup>: ~7000 cm<sup>-1</sup>, Nd<sup>3+</sup>: ~12000 cm<sup>-1</sup>, Yb<sup>3+</sup>: 11000 cm<sup>-1</sup>) is too large ( $\Delta E > 13000$  cm<sup>-1</sup>). The energy level difference between the excited triplet state energy level of carbazole and the highest excited state energy level of Ln<sup>3+</sup> is also above 6000 cm<sup>-1</sup>. Moreover, the distance between the carbazole and Ln<sup>3+</sup> is long in the copolymers. Thus, energy transfer from carbazole to Ln<sup>3+</sup> directly is not very efficient. However, the excited state energy of carbazole can transfer to the ligands and following to the Ln<sup>3+</sup> as discussed in our previous report.<sup>27</sup> Thus, no apparent characteristic emission of carbazole was observed in the PL spectra of the copolymer under different excitation wavelength.



**Scheme 2** Energy levels of Ln<sup>3+</sup> excited states and the triplet state of the ligands

## Conclusions

A series of novel near-infrared (NIR) luminescent linear copolymers, involving N-vinylcarbazole (NVK), isolated 8-hydroxyquinoline (Q), ligands (Q, Czhq and TTA) and lanthanide ions, have been prepared and characterized. The copolymers exhibit appropriate molecular weight as well as good solubility-processability. The glass transition temperature ( $T_g$ ) and the temperature of 5% weight loss ( $T_d$ ) for the copolymers are above 200 °C and 365 °C respectively, which will be advantageous for fabrication of optoelectronic device. The UV-vis absorption and photoluminescence properties of the copolymers were studied. The results indicate that the obtained copolymers show broadband sensitized and highly efficient near-infrared luminescence, which provide an access to multicomposite in optoelectronic applications, such as in optical amplifications, medical diagnostic, laser, and optics, etc. Effects of N-vinylcarbazole segments and ligands on the NIR-luminescence of Ln<sup>3+</sup> were investigated. The NVK segments are not only used as light-harvesting group, but also as barrier to form a special microenvironment for the LnQL<sub>2</sub> moieties. The three ligands can sensitize the three lanthanide ions, but the sensitized efficiency is different. Based on the observed luminescence phenomena and the reported energy transfer theories, energy transfer mechanism for the NIR-luminescence of the copolymers was proposed, which will provide rule for designing perfect NIR-luminescence materials.

## Acknowledgements

This project was supported by the National Natural Science Foundation of China (Grant No.: 21176061), Hunan Provincial Natural Science Foundation of China (Grant No.: 13JJ4109), Scientific Research Fund of Hunan Provincial Education Department (Grant No.:13C203) and the Construct Program of the Key Discipline in Hunan province.

## Notes and references



- <sup>a</sup> Key Laboratory of green functional building materials, Department of Materials and Chemical Engineering, Hunan Institute of Technology, Hengyang, Hunan 421002, PR China.  
E-mail: luojianxin392@163.com; Tel: +86-0150-96045469
- <sup>b</sup> Institute of Organic Polymer Materials, Hunan Institute of Technology, Hengyang, Hunan 421002, PR China.
- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
- 1 J.-C.G. Bünzli, S. V. Eliseeva, *J. Rare Earths*, **2010**, 28, 824.
  - 2 L.H. Sloof, A. Polman, F. Cacialli, R.H. Friend, G.A. Hebbink, F.C.J.M. Veggel van, D.N. Reinhoudt, *Appl. Phys. Lett.*, **2001**, 78, 2122.
  - 3 Z.Q. Chen, F. Ding, Z.Q. Bian, C.H. Huang, *Org. Electron.*, **2010**, 11, 369.
  - 4 Z. Li, J. Yu, L. Zhou, H.J. Zhang, R.P. Deng, Z.Y. Guo, *Org. Electron.*, **2008**, 9, 487.
  - 5 P.C. Beeker, N.A. Olsson, J.R. Simpson, Erbiurn-doped fiber amplifiers: fundamentals and technology. New York: AeademiePress, 1999.
  - 6 J.-C.G. Bünzli, C. Piguet, *Chem. Soc. Rev.*, **2005**, 34, 1048.
  - 7 X.M. Guo, H.D. Guo, L.S. Fu, L.D. Carlos, R.A.S. Ferreira, L.N. Sun, R.P. Deng, H.J. Zhang, *J. Phys. Chem. C*, **2009**, 113, 12538.
  - 8 L.N. Sun, S. Dang, J.B. Yu, J. Feng, L.Y. Shi, H.J. Zhang, *J. Phys. Chem. B*, **2010**, 114, 16393.
  - 9 K. Kuriki, Y. Koike, Y. Okamoto, *Chem. Rev.*, **2002**, 102, 2347.
  - 10 S. Faulker, S.J.A. Pope, B.P. Burton, *Appl. Spectrosc. Rev.*, **2005**, 40, 1.
  - 11 J.-C.G. Bünzli, *Chem. Lett.*, **2009**, 38, 104.
  - 12 F. Pointillart, A. Bourdolle, T. Cauchy, O. Maury, Y.L. Gal, S. Golhen, O. Cadour, L. Ouahab, *Inorg. Chem.*, **2012**, 51, 978.
  - 13 H.B. Xu, J. Li, L.X. Shi, Z.N. Chen, *Dalton Trans.*, **2011**, 40, 5549.
  - 14 H.S. He, L.P. Si, Y.H. Zhong, M. Dubey, *Chem. Commun.*, **2012**, 48, 1886.
  - 15 S. Dang, J.B. Yu, X.F. Wang, Z.Y. Guo, L.N. Sun, R.P. Deng, J. Feng, W.Q. Fan, H.J. Zhang, *J. Photochem. Photobiol. A*, **2010**, 214, 152.
  - 16 L.N. Sun, H.J. Zhang, J.B. Yu, S.Y. Yu, C.Y. Peng, S. Dang, X.M. Guo, J. Feng, *Langmuir*, **2008**, 24, 5500.
  - 17 X.J. Zhu, W.K. Wong, W.Y. Wong, X.P. Yang, *Eur. J. Inorg. Chem.*, **2011**, 4651.
  - 18 M.E. Gallina, C. Giansante, P. Ceroni, M. Venturi, J. Sakamoto, A.D. Schlüter, *Eur. J. Inorg. Chem.*, **2011**, 1479.
  - 19 P.F. Yan, S. Chen, P. Chen, J.W. Zhang, G.M. Li, *CrystEngComm*, **2011**, 13, 36.
  - 20 D. Liu, Z.G. Wang, *Polymer*, **2008**, 49, 4960.
  - 21 Q.D. Ling, Y. Song, J. Ding, C. Zhu, D.S.H. Chan, D.L. Kwong, E.T. Kang, K.G. Neoh, *Adv. Mater.*, **2005**, 17, 455.
  - 22 Q.D. Ling, Q.J. Cai, E.T. Kang, K.G. Neoh, R.R. Zhu, W. Huang, *J. Mater. Chem.*, **2004**, 14, 2741.
  - 23 Z.G. Zhang, J.B. Yuan, H.J. Tang, H. Tang, L.N. Wang, K.L. Zhang, *J. Polym. Sci.: Part A: Polym. Chem.*, **2009**, 47, 210.
  - 24 H. Xu, R. Zhu, P. Zhao, L.H. Xie, W. Huang, *Polymer*, **2011**, 52, 804.
  - 25 J.X. Luo, C.L. Yang, J. Zheng, J.Y. Ma, L.Y. Liang, M.G. Lu, *Eur. Polym. J.*, **2011**, 47, 385.
  - 26 Q.B. Mei, N.Y. Du, M.G. Lu, *Eur. Polym. J.*, **2007**, 43, 2380.
  - 27 J.X. Luo, C.Y. Zhang, C.L. Yang, M.G. Lu, *Synth. Met.*, **2012**, 162, 431.
  - 28 J. Thompson, R.I.R. Blyth, G. Gigli, R. Cingolani, *Adv. Funct. Mater.*, **2004**, 14, 979.
  - 29 W.G. Perkins, G.A. Crosby, *J. Chem. Phys.*, **1965**, 42, 407.
  - 30 A. Monguzzi, R. Tubino, F. Meinardi, A.O. Biroli, M. Pizzotti, F. Demartin, F. Quochi, F. Cordella, M.A. Loi, *Chem. Mater.*, **2009**, 21, 128.
  - 31 A. Monguzzi, A. Milani, L. Lodi, M.I. Trioni, R. Tubino, C. Castiglioni, *New J. Chem.*, **2009**, 33, 1542.
  - 32 A. Nonat, D. Imbert, J. Pécaut, M. Giraud, M. Mazzanti, *Inorg. Chem.*, **2009**, 48, 4207.
  - 33 N.M. Shavaleev, R. Scopelliti, F. Gumy, J.C.G. Bünzli, *Inorg. Chem.*, **2008**, 47, 9055.
  - 34 X.M. Guo, H.D. Guo, L.S. Fu, H.J. Zhang, L.D. Carlos, R.P. Deng, J.B. Yu, *J. Photochem. Photobiol. A*, **2008**, 200, 318.
  - 35 M.D. Ward, *Coord. Chem. Rev.*, **2007**, 251, 1663.