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Highly luminescent hydrogels synthesized by covalent grafting of lanthanide complexes onto PNIPAM *via* one-pot free radical polymerization

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Highly luminescent PNIPAM-Ln(DPA)$_3$ hydrogels have been synthesized by one-pot free radical polymerization in aqueous system at room temperature. We firstly synthesized a bifunctional chelating ligand named as 4-vinylpyridine-2,6-dicarboxylic acid (4-VDPA), which contains two different moieties: (1) a pyridine-2,6-dicarboxylic acid (DPA) moiety that can sensitize the luminescence of Tb^{3+} and Eu^{3+}, (2) a reaction functional group that can be polymerized by free radical initiation. Therefore, the luminescent lanthanide complexes can be grafted onto the hydrogel matrix *via* one-pot free radical polymerization of [Ln(4-VDPA)$_3$]$^{3-}$, N-isopropylacrylamide (NIPAM) and N, N'-Methylenebis(2-propenamide) (MBA). The results indicated that the final hydrogels possess bright luminescence, long luminescent lifetimes and high quantum efficiency. Moreover, the emission colors of the hydrogels can be tuned from red, reddish orange, orange-yellow, yellow, and green by varying the molar ratio of added Eu^{3+} to Tb^{3+}. These hydrogels are promising in the use of optical systems, controlled drug release, ion detection, bio-imaging and so on.

Introduction

Hydrogels have gained considerable momentum due to their unique three-dimensional polymeric networks structure, multiple-stimulus responsive properties and applications in controlled drug/protein release, sensing, adsorption, *etc*.[1-5] Recently, great efforts have been made toward modifying hydrogels with certain functional groups to expand their potential applications. Therefore, numerous multifunctional hydrogels have been obtained by self-assembly technique or chemical synthesis methods.[6-8] Among them, luminescent hydrogels are widely investigated due to their extra optical application in luminescent probes, optical imaging, optoelectronic devices, and so on. A variety of luminophores such as organic luminescent dyes, up-conversion luminescent particles and carbon dots were incorporated into the hydrogel matrixes by physical or chemical methods to prepare the luminescent hydrogels.[9-12] For instance, Wang *et al*. prepared an intelligent luminescent hydrogels by physically incorporating a propeller-shaped dye molecule, and these luminescent hydrogels possess organic solvents/thermal dual-responsive properties.[13] Jr and co-works synthesized supramolecular lanthanide luminescent hydrogels by self-assembled hydrothermal reactions of β-amino acid and lanthanide ions.[14] Lin *et al* developed a new pH-induced thermally responsive luminescent hydrogel by grafting of up-

conversion luminescent microspheres of NaYF$_4$:Yb^{3+}/Er^{3+} onto the smart hydrogel poly[(N-isopropylacrylamide)-*co*-(methacrylic acid)],[15] and the as-prepared hybrid hydrogel can be used as a luminescent probe for controlled drug release and cell imaging.

Poly(N-isopropylacrylamide) (PNIPAM) is a temperature-responsive polymer, which shows a unique reversible phase transition at the lower critical solution temperature (LCST) around 32 °C. Thus, luminescent PNIPAM hydrogels may simultaneously exhibit luminous and temperature-sensitive characteristics. Actually, there are some reports on the synthesis of luminescent PNIPAM hydrogels, and the luminophores were successfully grafted onto the polymer matrix by covalently attaching organic fluorescent dyes like pyrene or 3-hydroxyflavones to PNIPAM chains.[16,17] However, the broadband emission and aggregation-caused quenching characteristics of dye molecules make them difficult to obtain a luminescent PNIPAM hydrogel with high luminescent efficiency and color purity.

Among all the luminophores, lanthanide complexes are considered as one of the most promising optical materials due to their outstanding emission properties, including high luminous efficiency and color purity, long luminescent lifetime, wide range of emission wavelengths from ultraviolet (UV) to near-infrared (NIR) regions.[18-21] In these lanthanide complexes, pyridine-2, 6-dicarboxylic acid (DPA) and its derivatives are a well known chelate group for sensitizing the luminescence of Tb^{3+} or Eu^{3+} ions.[22-25] The lowest energy level of the triplet state of DPA (26600 cm^{-1}) is higher than the resonant energy level of Tb^{3+} (^{5}D$_4$, 20430 cm^{-1}) and Eu^{3+} (^{5}D$_0$, 17250 cm^{-1}), indicating that the energy transfer can be proceeded between the DPA ligand and the centers of Tb^{3+} or Eu^{3+} ions.[26] Moreover, lanthanide ions are able to coordinated with three nitrogen atoms and six carboxylate oxygen atoms from three

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different DPA moieties, and water molecule is excluded from the coordination sphere of Ln^{3+}.[22,23] Hence, it is reasonable to envisage the combination of DPA complexes with PNIPAM hydrogels to obtain new luminescent materials. Herein, we report the synthesis of luminescent PNIPAM-Ln(DPA)$_3$ hydrogels based on lanthanide complexes by one-pot free radical polymerization. Firstly, we synthesized a bifunctional chelating ligand named as 4-vinylpyridine-2, 6-dicarboxylic acid (4-VDPA), which contains two functional groups: (1) chelating group for lanthanide ions; (2) electron deficient double bond that can be polymerized by free radical initiation. And then the corresponding luminescent lanthanide complexes were introduced into temperature-sensitive PNIPAM hydrogel by chemical copolymerization of [Ln(4-VDPA)$_3$]$^{3-}$ with N-isopropylacrylamide (NIPAM) and N, N'-Methylenebis(2-propenamide) (MBA). Considering their unique luminescence properties, we hope that this work could provide a new strategy for fabricating lanthanide luminescent PNIPAM hydrogels through one-pot free radical polymerization.

Results and discussion

The synthesis procedure of 4-VDPA and luminescent hydrogels PNIPAM-Ln(DPA)$_3$ is illustrated in Scheme 1. The bifunctional organic ligand (4-VDPA) was synthesized starting from chelidamic acid. Luminescent PNIPAM-Ln(DPA)$_3$ hydrogels were prepared by free radical polymerization of N-isopropyl acrylamide (NIPAM) and N, N'-Methylenebis(2-propenamide) (MBA) with [Ln(4-VDPA)$_3$]$^{3-}$. The obtained PNIPAM, PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ hydrogels show the transparent characteristic under daylight, while PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ exhibit strong visible green and red luminescence under irradiation with a UV lamp (Fig. 1). The microstructures of PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ are very similar to that of PNIPAM (Fig. S1).
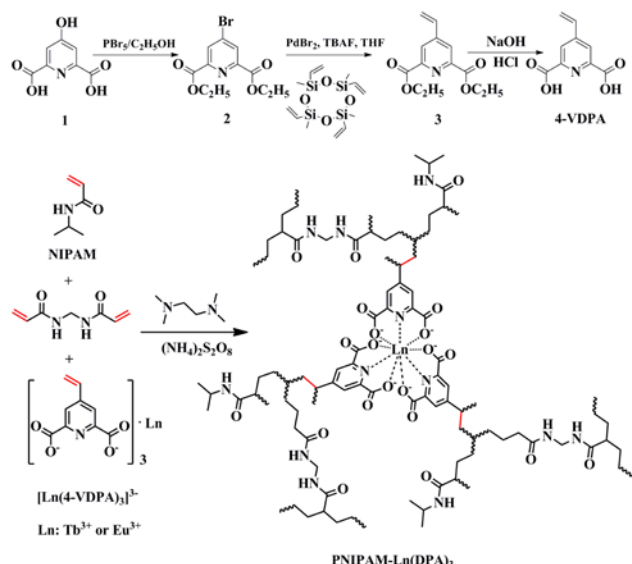

Scheme 1 Synthesis procedures of 4-vinylpyridine-2, 6-dicarboxylic acid (4-VDPA) and the luminescent hydrogels PNIPAM-Ln(DPA)$_3$. The wavy lines represent the polymeric portion of the hydrogels (P(NIPAM-co-MBA-co-[Ln(4-VDPA)$_3$]$^{3-}$))

Fig. 1 Digital photos of the hydrogels: PNIPAM (a), PNIPAM-Tb(DPA)$_3$ (b) and PNIPAM-Eu(DPA)$_3$ (c) under daylight, and PNIPAM-Tb(DPA)$_3$ (d) and PNIPAM-Eu(DPA)$_3$ (e) under UV light (254 nm, 6 W)

NMR analysis

The coordination modes of 4-VDPA to lanthanide ions were investigated by monitoring changes in the ^{1}H-NMR spectra of 4-VDPA upon titration with paramagnetic lanthanide ions (Fig. 2).[27,28] In order to facilitate the analysis by NMR, we select moderately paramagnetic Yb^{3+} ion as the tested lanthanide ion. When small amount of Yb^{3+} ions was added into 4-VDPA solution, the peak intensity of 4-VDPA signals decreased and some new signals corresponding to coordination of 4-VDPA and Yb^{3+} with 3:1 ratio ([Yb(4-VDPA)$_3$]$^{3-}$) generated (peaks labelled with star in Fig. 2b), showing slow exchange between 4-VDPA and Yb^{3+} in NMR timescale. When the ratio of Yb^{3+} and 4-VDPA is larger than 1:3, the peak intensity of [Yb(4-VDPA)$_3$]$^{3-}$ signals decreased and some new signals corresponding to coordination of 4-VDPA and Yb^{3+} with 2:1 ratio ([Yb(4-VDPA)$_2$]$^{-}$) generated (peaks labeled with star in Fig. 2c). When the ratio of Yb^{3+} and 4-VDPA is larger than 1:2, the peak intensity of [Yb(4-VDPA)$_2$]$^{1-}$ signals decreased and some new signals corresponding to coordination of 4-VDPA and Yb^{3+} with 1:1 ratio ([Yb(4-VDPA)]$^{+}$) generated (peaks labelled with star in Fig. 2d). The titration experiments showed that there are three manners for Yb^{3+} coordinated with 4-VDPA, and the unique complex of [Yb(4-VDPA)$_3$]$^{3-}$ could be obtained by tuning the ratio of 4-VDPA and Yb^{3+} larger than 3:1. Because the similar chemical characteristic of lanthanides, the coordination modes of 4-VDPA to Tb^{3+} or Eu^{3+} should be identical to that of 4-VDPA to Yb^{3+}.
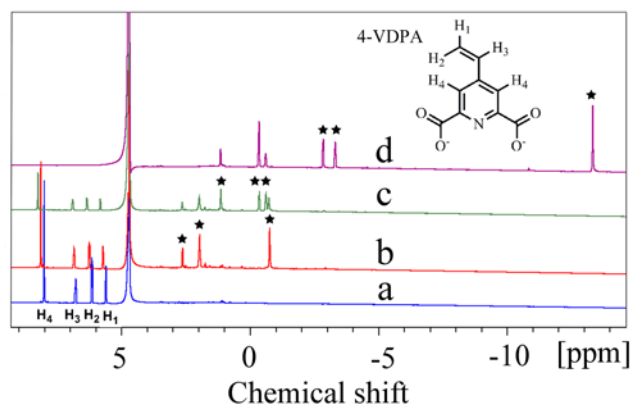
Fig. 2 NMR spectra of 0.5mL, 1mM 4-VDPA (a), upon titration with 10mM Yb^{3+}, 13μL (b), 22μL (c), 58μL (d)

FT-IR spectra

The FT-IR spectra of $Na_3[Tb(4\text{-}VDPA)_3]$, PNIPAM, PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ are displayed in Fig. 3. The peaks at 3431cm^{-1} are attributed to the stretching vibration bands of N-H,[29,30] whereas the peaks at 2972, 2926 and 2874 cm^{-1} can be attributed to asymmetric and symmetric stretching vibration modes of saturated C-H, respectively (Fig. 3b to d),[30] and the characteristic peaks at 1637 and 1536 cm^{-1} are attributed to the C=O stretching vibration of secondary amide.[29] Meanwhile, three bands appeared at 1608, 1425 and 1395 cm^{-1} correspond to the skeleton vibration of pyridine ring (Fig. 3a, c and d),[19] proving the successful incorporation of DPA complexes onto PNIPAM.
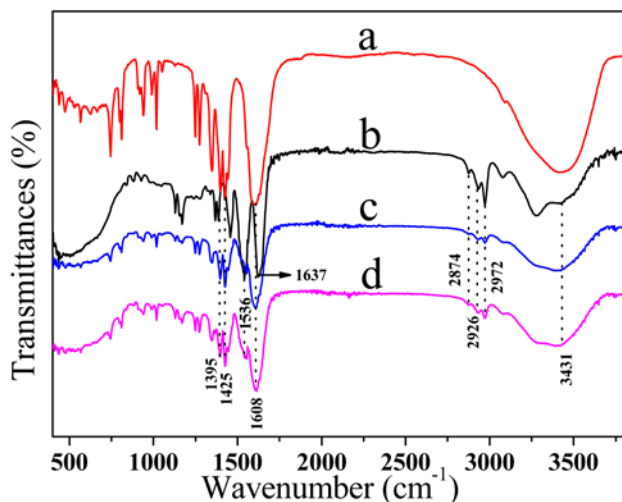
Fig. 3 FT-IR spectra of $Na_3[Tb(4\text{-}VDPA)_3]$ (a), PNIPAM (b), PNIPAM-Tb(DPA)$_3$ (c) and PNIPAM-Eu(DPA)$_3$ (d)

Thermal analysis
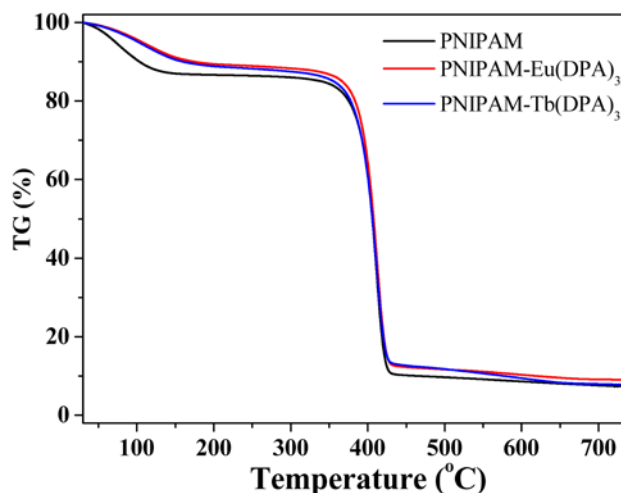
Fig. 4 Thermogravimetry (TG) curves of PNIPAM, PNIPAM-Eu(DPA)$_3$ and PNIPAM-Tb(DPA)$_3$

The thermal stabilities of PNIPAM, PNIPAM-Eu(DPA)$_3$ and PNIPAM-Tb(DPA)$_3$ were evaluated by thermogravimetric analysis (TGA). The TGA curve of PNIPAM-Eu(DPA)$_3$ and PNIPAM-Tb(DPA)$_3$ is quite similar to that of PNIPAM (Fig. 4). From the TGA curve of PNIPAM, PNIPAM-Eu(DPA)$_3$ and PNIPAM-Tb(DPA)$_3$, three main steps of weight loss can be observed. The initial weight loss below 350 °C, is ascribed to the loss of physically adsorbed water and other small molecules. While the large weight loss occurs from 350°C to 430 °C, which is ascribed to the thermal decomposition of organic moieties. Then it is followed by a slight weight loss in the temperature of 430-900 °C. In addition, it is difficult to find the weight loss of lanthanide complexes in the hydrogels from the TGA curves because the lanthanide complexes are only accounted for about 1% (wt) of the entire dry hydrogel. The weight fraction (ω) of lanthanide complex in the dry lydrogel was calculated by the equation as follow:
ω = Weight of added lanthanide complex/Weight of dry hydrogel

Optical properties

The photoluminescence (PL) properties of PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ were investigated as shown in Fig. 5. Both the PL excitation spectra of PNIPAM-Tb(DPA)$_3$ (Fig. 5a) and PNIPAM-Eu(DPA)$_3$ (Fig. 5c) exhibit a similar broad band with a maximum value at 282 nm, which can be related to the $\pi \rightarrow \pi^*$ electronic transition of the lanthanide complexes. This result shows that both of the hydrogels can be excited by the UV light with the same wavelength. As expected, upon excitation at 282 nm, the emission spectrum of PNIPAM-Tb(DPA)$_3$ shows the characteristic emission of Tb^{3+} peaked at 491, 542, 582, 621 nm, ascribed to the $^5D_4 \rightarrow {}^7F_J$ (J=6, 5, 4, 3) transitions of Tb^{3+} ions, [31-36] respectively (Fig. 5b), while PNIPAM-Eu(DPA)$_3$ gives the four prominent peaks at 591, 615, 649 and 696 nm, assigned to the $^5D_0 \rightarrow {}^7F_J$ (J= 1, 2, 3, 4) transitions of Eu^{3+} ions,[37-43] respectively (Fig. 5d). It is noteworthy that the emission peaks of PNIPAM-Tb(DPA)$_3$ appear obvious splitting at 542 and 582 nm (Fig. 5b, inside the red dashed box), proving that the mole ratio of metal (Tb^{3+}) to ligand (DPA) is 1:3 in PNIPAM-Tb(DPA)$_3$.[44] This finding is consistent with the result of NMR titration (Fig. 2).
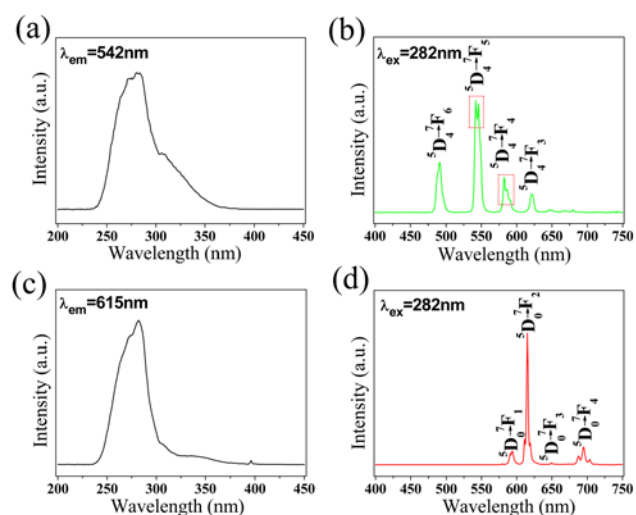
Fig. 5 Excitation and emission spectra of PNIPAM-Tb(DPA)$_3$ (a, b) and PNIPAM-Eu(DPA)$_3$ (c, d)

As observed by digital photos, PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ show bright green and red emission under UV light excitation (Fig. 1). The Commission Internationale de I'Eclairage (CIE) chromaticity coordinates also indicates that the emission of PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ lie in green (x = 0.32, y = 0.58) and red (x = 0.66, y = 0.33) region, respectively (Fig. S2). Moreover, the CIE chromaticity coordinate of the PNIPAM-Eu(DPA)$_3$ is close to the National Television Standard Committee (NTSC) standard values for red (x = 0.67, y = 0.33), which indicates that PNIPAM-Eu(DPA)$_3$ exhibits a high color purity.

The lifetime value of Tb^{3+} or Eu^{3+} in the hydrogel is determined by the corresponding decay curve that can be well fitted into a single exponential function (Fig. 6), which implies that the average coordination environment of Tb^{3+} or Eu^{3+} is uniform in PNIPAM-Ln(DPA)$_3$ (Ln = Tb or Eu) hydrogels. According to the fitting results, the lifetime values of Tb^{3+} and Eu^{3+} are determined to be 1.43 and 1.86 ms, respectively. The obtained PNIPAM-Ln(DPA)$_3$ (Ln = Tb or Eu) hydrogels have excellent luminescent properties and the quantum efficiency of the PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ are about 63.8% and 71.5%, respectively. The optical data like excitation wavelength (λ_{ex}), emission wavelength (λ_{em}), lifetimes (τ) and quantum efficiency (η) of our samples and other analogous luminescent material are listed in Table 1. It appears that the lifetimes of PNIPAM-Ln(DPA)$_3$ are longer than those of other hybrid materials containing DPA complexes (Ln-dpa-Si-MSNs).[45] The quantum efficiency of [Tb(DPA)$_3$]$^{3-}$ or [Eu(DPA)$_3$]$^{3-}$ in the aqueous solution was lower than that of PNIPAM-Tb(DPA)$_3$ or PNIPAM-Tb(DPA)$_3$, respectively (dry hydrogel) (Table 1). The reason is probably that the luminescence of lanthanide complexes is easily quenched in aqueous solution by non-radiative processes through O-H vibrations of water molecular.
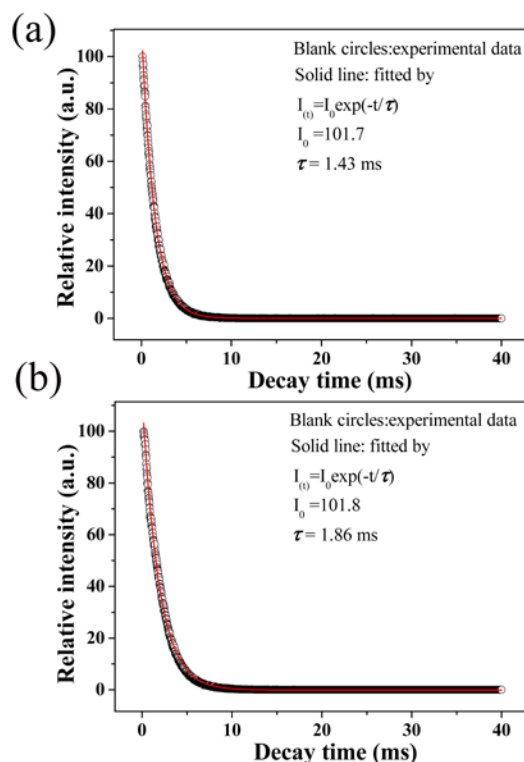
Fig. 6 Luminescence decay curve of PNIPAM-Tb(DPA)$_3$ (a) and PNIPAM-Eu(DPA)$_3$ (b)

Table 1 The PL data, including excitation wavelength (λ_{ex}), emission wavelength (λ_{em}), lifetimes (τ) and quantum efficiency (η) of [Ln(4-VDPA)$_3$]$^{3-}$, [Ln(DPA)$_3$]$^{3-}$, PNIPAN-Ln(DPA)$_3$ and other analogous luminescent material Ln-dpa-Si-MSNs, Ln = Tb or Eu), ^{a} 0.1 mmol/L aqueous solution.

Sample	λ_{ex} (nm)	λ_{em} (nm)	τ (ms)	η (%)
[Tb(4-VDPA)$_3$]$^{3-\,a}$	−	−	−	−
[Eu(4-VDPA)$_3$]$^{3-\,a}$	315	594, 615, 649, 696	0.86	1.8
[Tb(DPA)$_3$]$^{3-\,a}$	286	492, 543, 582, 622	2.01	39.9
[Eu(DPA)$_3$]$^{3-\,a}$	286	592, 615, 649, 695	1.58	34.6
Tb-dpa-Si-MSNs [ref45]	281	490, 546, 582, 622	0.86	−
Eu-dpa-Si-MSNs [ref45]	281	592, 614, 650, 694	0.62	−
PNIPAM-Tb(DPA)$_3$	282	491, 542, 581, 621	1.43	63.8
PNIPAM-Eu(DPA)$_3$	282	591, 615, 649, 696	1.86	71.5

However, the hydrogels (PNIPAM-Tb(DPA)$_3$ or PNIPAM-Eu(DPA)$_3$) have no obvious Tb^{3+} or Eu^{3+} emission under the irradiation with a UV lamp at the beginning of the polymerization, and the luminescent intensities of PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ were gradually enhanced as the polymerization reaction was occured. Hence we measured the luminescent properties of [Tb(4-VDPA)$_3$]$^{3-}$ and [Eu(4-VDPA)$_3$]$^{3-}$. As expected, [Tb(4-VDPA)$_3$]$^{3-}$ has no characteristic emission of Tb^{3+} under the irradiation of UV light (Fig. S3), and [Eu(4-VDPA)$_3$]$^{3-}$ shows very weak emission of Eu^{3+} compared with that of [Eu(DPA)$_3$]$^{3-}$ (Fig. S4), the luminescent

intensity and quantum efficiency of $[Ln(4-VDPA)_3]^{3-}$ are also much lower and lifetimes are shorter (Fig S5) than those of $[Ln(DPA)_3]^{3-}$ (Ln = Tb or Eu) (Table 1). These results show that 4-VDPA is not an efficient ligand for sensitizing the luminescence of Tb^{3+} and Eu^{3+} ions. However, when the polymerization reaction is completed, the vinyl group ($H_2C=CH-$) of 4-VDPA (Fig. 7a) was converted to a saturated C-C bond ($-CH_2-CH_2-$) and then a $[Ln(DPA)_3]^{3-}$ complex moiety was generated (Fig. 7b). Therefore, the PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ show bright green and red emission, respectively. Besides, this characteristics of $[Ln(4-VDPA)]^{3-}$ also make it suitable for application in the luminescent detection of free radicals. Moreover, the excitation spectra of PNIPAM-Tb(DPA)$_3$ or PNIPAM-Eu(DPA)$_3$ (Fig. 5a or c) are very similar to those of Na$_3$[Tb(DPA)$_3$] or Na$_3$[Eu(DPA)$_3$] (Fig. S6), respectively, which also indicates that the lanthanide complexes are successfully grafted onto the hydrogels *via* one-pot free radical polymerization.
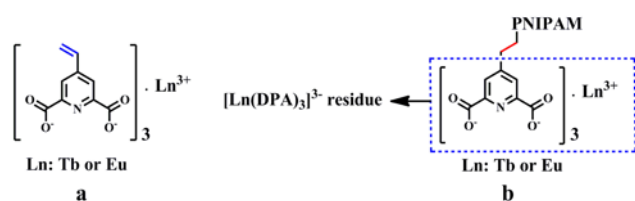
Fig. 7 Structure diagram of $[Ln(4-VDPA)_3]^{3-}$ complexes and PNIPAM-Ln(DPA)$_3$ (Ln = Tb or Eu)

As mentioned above, PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ have prominent luminescent properties and multiple color emission under the excitation of UV light with the same wavelength, hence the luminescent color of hydrogels should be tuned by changing the relative content of Tb^{3+} and Eu^{3+}.[44] As shown in Fig. 8, the emission spectra of PNIPAM-Eu$_x$Tb$_y$(DPA)$_3$ show characteristic emission peaks of Eu^{3+} ions at 591, 615, 649 and 696 nm and Tb^{3+} ions at 491, 542, 582 and 622 nm, respectively. Moreover, the intensity ratio of the red to green emission decreases drastically upon increasing the Tb^{3+} concentration. Therefore, the luminescent colors of PNIPAM-Eu$_x$Tb$_y$(DPA)$_3$ varied from red, reddish orange, orange-yellow, yellow to green correspondingly (Fig. S7). However, the luminescent lifetime values of the excited state $^5D_4$ (Tb^{3+}) in PNIPAM-Eu$_x$Tb$_y$(DPA)$_3$ are almost unchanged, which indicated that the energy transfer from Tb^{3+} to Eu^{3+} is not obvious in these hydrogels (Fig. S8). [47, 48] Taking into account the transparent, long luminescent lifetimes, high quantum efficiency, multi-color emission and temperature-responsive characteristics of PNIPAM-Ln(DPA)$_3$, these hydrogels are promising in the application of optical systems, controlled drug release, ion detection, bio-imaging and so on.
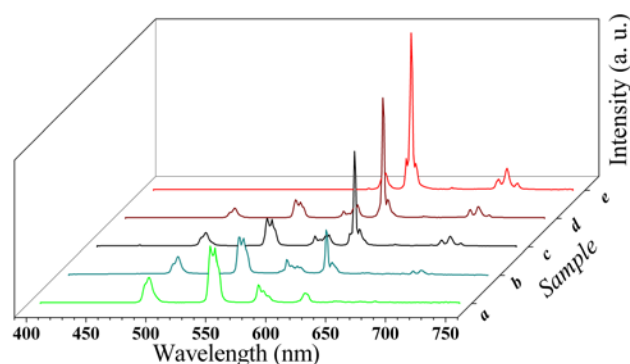
Fig. 8 The emission spectra of the luminescent hydrogel upon excitation at 282 nm: (a) PNIPAM-Tb(DPA)$_3$; (b) PNIPAM-Eu$_1$Tb$_3$(DPA)$_3$; (c) PNIPAM-Eu$_1$Tb$_1$(DPA)$_3$; (d) PNIPAM- Eu$_2$Tb$_1$(DPA)$_3$; (e) PNIPAM-Eu(DPA)$_3$

Conclusions

In summary, we developed a novel strategy for preparing luminescent hydrogels through one-pot free radical polymerization. Lanthanide DPA complexes were successfully grafted onto the PNIPAM hydrogel through constructing the proper bifunctional organic ligand. It is worthy to point out that the luminescent intensities of the hydrogels were gradually enhanced as the polymerization is conducted, implying that luminescent lanthanide complexes were successfully grafted onto the hydrogel matrix. Upon an excitation with UV light, the obtained PNIPAM-Tb(DPA)$_3$ and PNIPAM-Eu(DPA)$_3$ hydrogels exhibit the characteristic emission of Tb^{3+} (green) and Eu^{3+} (red), long luminescent lifetimes and high quantum efficiency. Moreover, the emission colors of the hydrogels can be tuned by modulating the molar ratio of added Eu^{3+} to Tb^{3+}.

Experimental section

Diethyl 4-bromopyridine-2, 6-dicarboxylate (Compound 2)[49]

Diethyl 4-bromopyridine-2, 6-dicarboxylate was synthesized from chelidamic acid, as previously reported. ^{1}H-NMR (400MHz, CDCl$_3$) δ ppm: 8.45 (2H, s), 4.52 (4H, q, J=7.14Hz), 1.48 (6H, t, J=7.14Hz). ^{13}C-NMR (100MHz, CDCl$_3$) δ ppm: 163.5, 149.5, 134.9, 131.1, 62.7, 14.1.

Diethyl 4-vinylpyridine-2, 6-dicarboxylate (Compound 3) [50]

Diethyl 4-bromopyridine-2, 6-dicarboxylate (1.2g, 4 mmol), PdBr$_2$ (53 mg, 0.2 mmol), 2-(di-tert-butylphosphino)biphenyl (120 mg, 0.4 mmol), tetrabutylammonium fluoride (TBAF; 8 mL, 8 mmol) in tetrahydrofuran stock, and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (1.4 g, 4 mmol) were added to tetrahydrofuran (20 mL). The resulting solution was stirred at 60 °C for about 3 h under an atmosphere of argon, and then cooled down to room temperature. Solvent was removed by distillation using a rotary evaporator, and then ethyl acetate (20 mL) was added to the residue. The organic phase was washed with brine, dried with anhydrous Na$_2$SO$_4$. After filtration and distillation, the resulting yellowish oil was purified by column chromatography on silica gel using ethyl acetate:petroleum ether (1:3 by volume) as eluent to

yield a pale yellow oil (0.75g, 76%). ^{1}H-NMR (400MHz, CDCl$_3$) δ ppm: 8.25 (2H, s), 6.80 (1H, dd, J=17.58, 10.81), 6.18 (1H, d, J=17.58), 5.67 (1H, d, J=10.81), 4.50 (4H, q, J=7.14), 1.47 (6H, t, J=7.14). ^{13}C-NMR (100MHz, CDCl$_3$) δ ppm: 164.5, 148.9, 147.3, 133.3, 124.5, 121.0, 62.1, 14.0.

4-vinylpyridine-2, 6-dicarboxylic acid (4-VDPA)

Diethyl 4-vinylpyridine-2, 6-dicarboxylate (0.7 g) was added to 8 mL of water and alcohol mixed solution (1:1 by volume), and then NaOH solution (2 mol/L, 3.5 mL) was added. This solution was stirred at room temperature for about 5 h, and the pH of the above mixture was adjusted to about 2 by hydrochloric acid. The resulting white suspension was filtered, washed with deionized water and dried under vacuum. ^{1}H-NMR (400MHz, D$_2$O, pD $\geq$ 12) δ ppm: 7.91 (2H, s), 6.77 (1H, dd), 6.08 (1H, d), 5.52 (1H, d). ^{13}C-NMR (100MHz, D$_2$O, pD $\geq$ 12) δ ppm: 172.8, 153.3, 147.4, 134.2, 122.0, 120.0. MS: 192.0296 (M-1)$^-$.

Preparation of lanthanide complexes [Ln(4-VDPA)$_3$]$^{3-}$

4-VDPA (29 mg, 0.15 mmol) and LnCl$_3$·6H$_2$O (Ln = Tb or Eu, 0.05 mmol) were dissolved in distilled water, and then the pH of the mixture was adjusted to 7.0 (total volume 5.0 mL).

Synthesis of luminescent hydrogels PNIPAM-Eu$_x$Tb$_y$(DPA)$_3$

N-isopropylacrylamide (NIPAM, 0.6 g), N, N,-Methylenebis(2-propenamide) (MBA, 10 mg), [Ln(4-VDPA)$_3$]$^{3-}$ (Ln^{3+} = Tb^{3+}, Eu^{3+} or Tb^{3+} and Eu^{3+} in different molar ratio, 1 mL) were dissolved in 4 mL H$_2$O, the mixture was degassed by bubbling with N$_2$ gas for about 0.5 h in an ice-water bath. And then N,N,N',N'-tetramethyl ethylene diamine (20 μL), ammonium persulfate (4 mg) were added to this solution. After standing for three days, the obtained hydrogels, denoted as PNIPAM-Eu(DPA)$_3$, PNIPAM-Eu$_2$Tb$_1$(DPA)$_3$, PNIPAM-Eu$_1$Tb$_1$(DPA)$_3$, PNIPAM-Eu$_1$Tb$_3$(DPA)$_3$, PNIPAM-Tb(DPA)$_3$, were immersed into deionized water to remove the residual monomers. PNIPAM was prepared by this method without using [Ln(4-VDPA)$_3$]$^{3-}$. The corresponding dry hydrogels were obtained after drying under vacuum at 60 °C for 24h.

Characterization

FT-IR spectra were collected on a Thermo Nicolet 5700 spectrophotometer within the wavenumber range 4000-400 cm^{-1} (KBr pellet). Thermogravimetric curves were measured on a Perkin-Elmer STA 6000 thermal analyzer at a heating rate of 10 °C min^{-1} under N$_2$ atmosphere. The luminescence spectra and lifetime measurements were measured on an Edinburgh FLS920P spectrofluorimeter. Quantum efficiency was measured using an integrating sphere whose inner face was coated with Benflect, and more details on the measurement of quantum efficiency are described in Ref. 23. ^{1}H-NMR and ^{13}C-NMR spectra were acquired on a Bruker AV400 or AV600 NMR spectrometer. Mass spectrometry was obtained on an Agilent 6520 Q-TOF mass spectrometer.

Notes and references

1 F. Wu, M. X. Sun, W. C. Jiang, K. Zhang, A. Xie, Y. Wang and M. Y. Wang, *J. Mater. Chem. C,* 2016, **4**, 82-88.
2 W. F. Lai, and H. C. Shum, *Nanoscale*, 2016, **8**, 517-528.
3 F. B. Zeynabad, R. Salehi, E. Alizadeh, H. S. Kafil, A. M. Hassanzadeh and M. Mahkam, *RSC Adv.*, 2015, **5**, 105678-105691.
4 A. Gulzar, S. L. Gai, P. P. Yang, C. X. Li, M. B. Ansari and J. Lin, *J. Mater. Chem. B*, 2015, **3**, 8599-8622.
5 D. Buenger, F. Topuz and J. Groll, *Prog. Polym. Sci.*, 2012, **37**, 1678-1719.
6 W. Ha, J. Yu, X. Y. Song, Z. J. Zhang, Y. Q. Liu and Y. P. Shi, *J. Mater. Chem. B*, 2013, **1**, 5532-5538.
7 R. Kennedy, W. U. Hassan, A. Tochwin, T. Y. Zhao, Y. X. Dong, Q. Wang, H. Y. Tai and W. X. Wang, *Polym. Chem.*, 2014, **5**, 1838-1842.
8 Y. Wang, P. Zhang, C. F. Liu and C. Z. Huang, *RSC Adv.*, 2013, **3**, 9240-9246.
9 P. K. Sukul, D. Asthana, P. Mukhopadhyay, D. Summa, L. Muccioli, C. Zannoni, D. Beljonne, A. E. Rowan and S. Malik, *Chem. Commun.*, 2011, **47**, 11858-11860.
10 R. C. Lv, P. P. Yang, F. He, S. L. Gai, G. X. Yang, Y. L. Dai, Z. Y. Hou and J. Lin, *Biomaterials*, 2015, **63**, 115-127.
11 Y. Y. Zhang, X. W. He and W. Y. Li, *RSC Adv.*, 2015, **5**, 71030-71034.
12 A. Cayuela, S. R. Kennedy, M. L. Soriano, C. D. Jones, M. Valcárcel and J. W. Steed, *Chem. Sci.*, 2015, **6**, 6139-6146.
13 H. Y. Zheng, C. Y. Li, C. C. He, Y. Q. Dong, Q. S. Liu, P. F. Qin, C. Zeng and H. L. Wang, *J. Mater. Chem. C*, 2014, **2**, 5829-5835.
14 F. F. da Silva, F. L. de Menezes, L. L. da Luz and S. A. Jr, *New J. Chem.*, 2014, **38**, 893-896.
15 Y. L. Dai, P. A. Ma, Z. Y. Cheng, X. J. Kang, X. Zhang, Z. Y. Hou, C. X. Li, D. M. Yang, X. F. Zhai and J. Lin, *ACS Nano.*, 2012, **6**, 3327-3338.
16 C. Y. Chen and C. T. Chen, *Chem. Commun.*, 2011, **47**, 994-996.
17 S, W. Hong, D. Y. Kim, J. U. Lee and W. H. Jo, *Macromolecules*, 2009, **42**, 2756-2761.
18 J. Feng and H. J. Zhang, *Chem. Soc. Rev.*, 2013, **42**, 387-410.
19 B. Yan, *RSC Adv.*, 2012, **2**, 9304-9324.
20 K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283-4373.
21 L. D. Carlos, R. A. S. Ferreira, V. de Z. Bermudez and S. J. L. Ribeiro, *Adv. Mater.*, 2009, **21**, 509-534.
22 J. G. Kim, S. K. Yoon, Y. Sohn and J. G. Kang, *J. Alloys. Compd.*, 1998, **274**, 1-9.
23 Q. F. Li, D. Yue, G. W. Ge, X. D. Du, Y. C. Gong, Z. L. Wang and J. H. Hao, *Dalton Trans.*, 2015, **44**, 16810-16817.
24 J. B. Lamture, Z. H. Zhou, A. S. Kumar and T. G. Wensel, *Inorg. Chem.*, 1995, **34**, 864-869.

25 A. L. Gassner, C. Duhot, J. C. G. Bünzli and A. S. Chauvin, *Inorg. Chem*., 2008, **47**, 7802-7812.

26 P. K. Sharma, A. R. van, Doorn and A. G. J. Staring, *J. Lumin*., 1994, **62**, 219-225.

27 I. Bertini, I. Gelis, N. Katsaros, C. Luchinat and A. Provenzani, *Biochemistry*, 2003, **42**, 8011-8021.

28 I. Bertini, A. Coutsolelos, A. Dikiy, C. Luchinat, G. A. Spyroulias and A. Troganis, *Inorg. Chem*., 1996, **35**, 6308-6315.

29 P. Chakraborty, P. Bairi, B. Roy and A. K. Nandi, *RSC Adv*., 2014, **4**, 54684-54693.

30 X. X. Ma, D. W. Yu, N. Tang and J. C. Wu, *Dalton Trans*., 2014, **42**, 9856-9859.

31 L. N. Sun, Y. Liu, S. Dang, Z. Y. Wang, J. L. Liu, J. F. Fu and L. Y. Shi, *New J. Chem*., 2016, **40**, 209-216.

32 S. Biju, D. B. A. Raj, M. L. P. Reddy, C. K. Jayasankar, A. H. Cowley and M. Findlater, *J. Mater. Chem*., 2009, **19**, 1425-1432.

33 T. W. Duan and B. Yan, *J. Mater. Chem. C*, 2015, **3**, 2823-2830.

34 T. T. Wen, H. R. Li, Y. G. Wang, L. Y. Wang, W. J. Zhang and L. Zhang, *J. Mater. Chem. C*, 2013, **1**, 1607-1612.

35 J. R. Diniz, J. R. Correa, D. D. A. Moreira, R. S. Fontenele, A. L. D. Oliveira, P. V. Abdelnur, J. D. L. Dutra, R. O. Freire, M. O. Rodrigues and B. A. D. Neto, *Inorg. Chem*., 2013, **52**, 10199-10205.

36 C. L. Tan and Q. M. Wang, *Inorg. Chem*., 2011, **50**, 2953-2956.

37 Z. Q. Li, P. Li, Q. Q. Xu and H. R. Li, *Chem. Commun*., 2015, **51**, 10644-10647.

38 V. Nuñez, S. Upadhyayula, B. Millare, J. M. Larsen, A. Hadian, S. Shin, P. Vandrangi, S. Gupta, H. Xu, A. P. Lin, G. Y. Georgiev and V. I. Vullve, *Anal. Chem*., 2013, **85**, 4567-4577.

39 A. Picot, A. DAléo, P. L. Baldeck, A. Grichine, A. Duperray, C. Andraud and O, Maury, *J. Am. Chem. Soc*., 2008, **130**, 1532-1533.

40 S. M. Wang, B. Zhang, Y. H. Hou, C. X. Du and Y. J. Wu, *J. Mater. Chem. C*, 2013, **1**, 406-409.

41 S. S. Nobre, C. D. S. Brites, R. A. S. Ferreira, V. de Z. Bermudez, C. Carcel, J. J. E. Moreau, J. Rocha, M. W. C. Man and L. D. Carlos, *J. Mater. Chem*., 2008, **18**, 4172-4182.

42 L. N. Sun, X. Q. Ge, J. L. Liu, Y. N. Qiu, Z. W. Wei, B. Tian and L. Y. Shi, *Nanoscale*, 2014, **6**, 13242-13252.

43 Y. Liu, L. N. Sun, J. L. Liu, Y. X. Peng, X. Q. Ge, L. Y. Shi and W. Huang, *Dalton Trans*., 2015, **44**, 237-246.

44 G. Jones II and V. I. Vullev, *Photochem. Photobiol. Sci.,* 2002, **1**, 925-933.

45 D. J. Zhang, D. H. Tang, X. M. Wang, Z. A. Qiao, Y. T. Li, Y. L. Liu and Q. S. Huo, *Dalton Trans*., 2011, **40**, 9313-9319.

46 T, R. Wang, P. Li and H. R. Li, *ACS Appl. Mater. Interfaces* 2014, **6**, 12915-12921.

47 C. Gao, A. M. Kirillov, W. Dou, X. L. Tang, L. L. Liu, X. H. Yan, Y. J. Xie, P. X. Zhang, W. S. Liu and Y. Tang, *Inorg. Chem*., 2014, **53**, 935-942.

48 A. R. Ramya, D. Sharma, S. Natarajan and M. L. P. Reddy, *Inorg. Chem*., 2012, **51**, 8818-8826.

49 A. M. Raitsimring, C. Gunanathan, A. Potapov, I. Efremenko, J. M. L. Martin, D. Milstein and D. Goldfarb, *J. Am. Chem. Soc*., 2007, **129**, 14138-14139.

50 S. E. Denmark and C. R. Butler, *Org. Lett*., 2006, **8**, 63-66.