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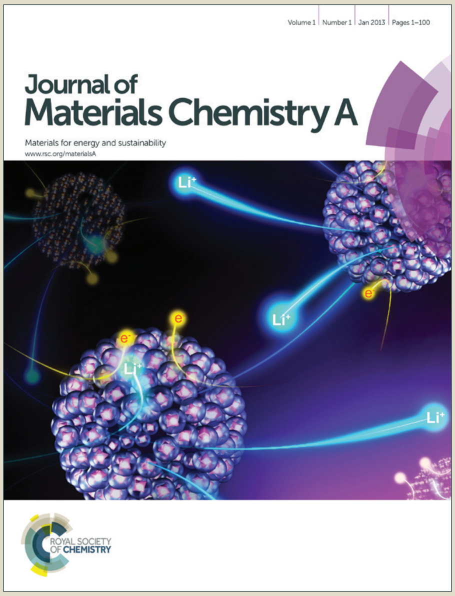

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ARTICLE TYPE

Facile Functionalization of Tetrahedron-like PEG Macromonomer-based Fluorescent Hydrogel with High Strength and Its Heavy Metal Ions Detection

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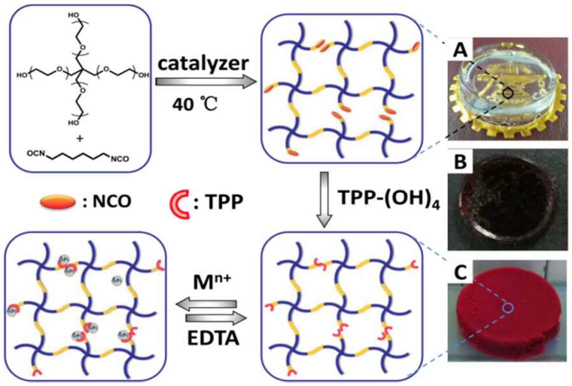
Tetrahedron-like PEG macromonomer-based fluorescent hydrogel was fabricated by a facile method. The functional hydrogel shows comparable high strength, up to megapascals and sensitivity to heavy metal ions, such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+} and Ni^{+}, which allows potentially rapid visual response, trace analysis and one-step recyclable sensor for metal ion detection.

Introduction

Hydrogels have been considered as promising material in myriad applications[1-4]. For decades, a great deal of effort has been done to improve hydrogels mechanical properties and endow them with functionalities respectively. To obtain excellent mechanical properties, hydrogels with different types of structure consisting of double-network gel[5], macromolecular microsphere composite gel[6], nanocomposite gel[7], slide-ring gel[8] and tetrahedron-like macromonomer gel[9] have been established. In the mean time, various stimuli-sensitive hydrogels have been developed, which can respond to stimulus of temperature[10], light[11, 12], pH[10], chemicals[13, 14] and so on. For various practical applications, hydrogels should not only hold good mechanical strength, but also possess functionalities. Xia et al. have reported a smart hydrogel which shows highly elastic properties and rapidly responsive to temperature, by constructing a nano-structured architecture with activated nanogels as nano-crosslinkers[1]. Besides, Rodrigo París et al. have reported a thermo-responsive polyurethane hydrogel by combining poly(ε-caprolactone) diols and four-arm hydroxyl terminated poly(ethylene glycol) with hexamethylene diisocyanate[15]. Further, detection of heavy metal ions in water has attracted a lot of attention due to their environmental and biological relevance. Therefore, development of materials and methods for detection metal ions has increased constantly. For example, a boronate hydrogel film containing organized two-component dyes as a multicolour fluorescence sensor for heavy metal ions in water was invented[16]. Besides, thermoresponsive PNIPAM microgels was investigated to detect Cu^{2+} ions[17].

Herein we take tetrahedron–like 4-arm poly(ethylene glycol) as macromonomer and hexamethylene diisocyanate (HDI) to prepare a hydrogel with outstanding mechanical strength and specific metal ions sensitivity using a simple method. 4-Arm PEG has been used to form the skeleton of hydrogel with highly mechanical strength because of its homogeneous network[9]. HDI plays dual roles of cross-linker and reactive site to introduce functional groups. Due to their high reactivity and efficiency[18], the reaction between isocyanate (-NCO) and hydroxyl (-OH) groups can make cross-linking reaction and functionalization of the hydrogel quite easy[19]. Moreover, porphyrins and their derivatives have been proven sensitive to certain metal ions, such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+} and Ni^{+} and reported to act as both ion receptors and signaling fluorophores[20,21]. On this basis, 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (TPP-$(OH)_4$)[22] is chosen as functional compound in this work. Through tuning the mole ratio of -NCO/-OH of HDI and 4-arm PEG, excess -NCO terminal groups are remained to react with TPP-$(OH)_4$. The obtained PEG-HDI$_X$-TPP (X refers to the feed ratio of -NCO groups on HDI to -OH groups on PEG) hydrogel has outstanding compressive strength, 4.5 MPa, and rapid detection to low concentration of metal ions (μM level). Noteworthily, the hydrogel can be recycled easily by rinsed in EDTA-2Na aqueous solution.

Scheme 1. Preparation procedure of PEG-HDI$_X$-TPP hydrogel. (A-C). Photograph of PEG-HDI$_X$, PEG-HDI$_{1.2}$-TPP under visible light and PEG-HDI$_{1.2}$-TPP under 365 nm irradiation.



Result and Discussion

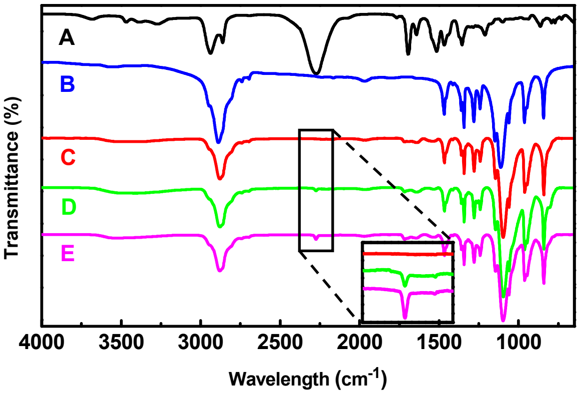


Fig. 1 FTIR spectra of (A) HDI, (B) PEG, (C-E) dried PEG-HDIX (X =1.0, 1.2 and 1.4) gels: 3298 cm-1 (N-H stretch), 1716 cm-1 (C=O stretch), 1642 cm-1 (N-H bend) and 2276 cm-1 (-NCO stretch).

The procedure of preparing PEG-HDI$_X$-TPP (X refers to the feed mole ratio of -NCO/-OH) hydrogel is shown in scheme 1, and the details are described in experimental section**.** PEG-HDI$_X$-TPP hydrogel is constructed by 4-arm PEG, HDI and TPP-(OH)$_4$. Through tuning mole ratio of -NCO/-OH of 4-arm PEG and HDI, excess -NCO groups are remained to react with -OH groups on TPP-(OH)$_4$. From FTIR spectra of PEG-HDI$_{1.0}$ hydrogel (Fig.1C), the appearance of absorption band at 3298 cm-1 (N-H stretch), 1716 cm^{-1} (C=O stretch), and 1642 cm^{-1} (N-H bend), as well as the disappearance of absorption band at 2276 cm^{-1} (-NCO stretch), confirms the reaction between -OH and -NCO group to produce –NHCOO-[23]. Furthermore, with the excess addition of HDI **(**Fig. 1C-E), the absorption band of -NCO appears again and increases with increasing mole ratio of -NCO/-OH, demonstrating that the -NCO terminal groups of PEG-HDI$_X$ hydrogel could be tuned by the feed ratio of 4-arm PEG and HDI. Therefore, it's possible to control the amount of functional groups introduced into the PEG-HDI$_X$-TPP hydrogel. The more -NCO groups terminate the branches of PEG, the more prophyrin can be introduced.

The influence of mole ratio of -NCO/-OH of HDI and 4-arm PEG on the compressive strength and network of relevant hydrogels were studied. Fig. 2A shows the stress-strain curves for the PEG-HDI$_X$-TPP hydrogel and PEG-HDI$_X$ hydrogels (X = 1.0, 1.2, 1.4). It's interesting to find that with the decrease of X values, the compressive strength of PEG-HDI$_X$ hydrogels increased. As X = 1, it reaches the maximum of 6.8 MPa, and the hydrogel shows distinct uniform lays with interconnected, porous network structure distributing in between (Fig. 2B). When X value raises, the compressive strength of the hydrogels reduces, with texture of their network becomes less regular. This phenomenon can be explained from the molecular structure of respective hydrogels (On the top right of the SEM images). As X = 1, the structure trends to be perfect tetrahedron-like. However, with the increase of X value, the entangling chains ended with -NCO become more and more, destroying the tetrahedron-like structure. As a result, the mechanical strength of the hydrogels, as well as the regularity of corresponding texture, decreases. As a whole, compression strength of these PEG-HDI$_X$ hydrogels all remains in MPa level, which can be explained from the homogeneity of hydrogel network and has been discussed in other literature[24]. In order to obtain PEG-HDI$_X$-TPP hydrogel with considerable compressive strength and moderate amount of TPP, PEG-HDI$_{1.2}$ hydrogel was chosen to further fabricate the targeting hydrogel, and the resulting hydrogels, denoted as PEG-HDI$_{1.2}$-TPP, as expected, show excellent compressive strength, 4.5 MPa.

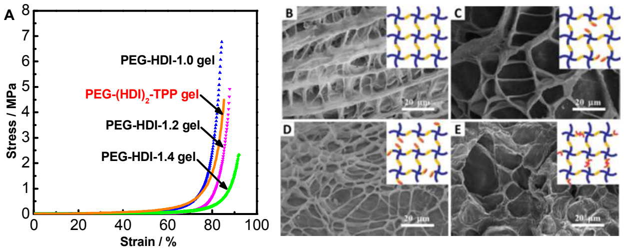


Fig. 2 (A) Stress-strain curves for PEG-HDI$_{1.2}$-TPP hydrogel and PEG-HDI$_X$ (X = 1.0, 1.2, 1.4) hydrogels. (B-D) SEM images of PEG-HDI$_X$ gels with X values of 1.0, 1.2 and 1.4, respectively, and (E) PEG-HDI$_{1.2}$-TPP gel.

Since it's well known that pH values of the environment have an impact on porphyrin's responsibility to metal ions through protonation of porphyrin and hydrolysis of the metal ions[21], the effect of pH values from 2.0 to 8.0 on the fluorescence intensity of PEG-HDI$_{1.2}$-TPP hydrogels was investigated. As Fig. 3 shows, when the pH values were in the lower section (from 2.0 to 4.0), fluorescence emission of the hydrogels was obviously influenced by proton in solution. With the decrease of pH values, fluorescence intensity of the hydrogels becomes weaker, which is attributed to the protonation of porphyrin on the hydrogels. However, when the pH values range from 4.0 to 8.0, fluorescence intensity nearly remains unchanged, indicating that sensitivity to metal ions of the hydrogels was hardly effected by protonation in this range.

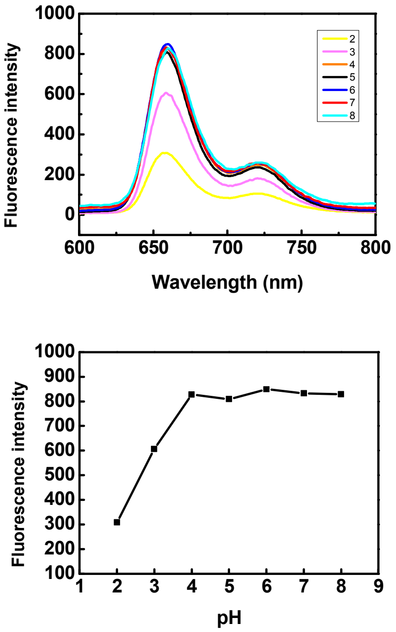


Fig. 3 A) Fluorescence spectra of PEG-HDI1.2-TPP hydrogels in metal ions-free solutions with different pH values; B) Effect of pH on the fluorescence intensity of PEG-HDI-TPP hydrogels at 660 nm without the presence of heavy metal ions.

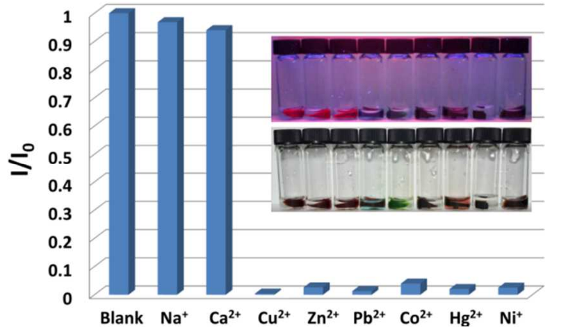


Fig. 4 Fluorescent intensity of PEG-HDI$_{1.2}$-TPP hydrogels in different metal ions aqueous solution (0.25 M) at 420 nm. Insert: respective photographs of PEG-HDI$_{1.2}$-TPP hydrogels at 365 nm irradiation and visible light. (from left to right: blank, Na$^+$, Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+}, Ni$^+$).

Thereupon, eight kinds of metal ions (Na$^+$, Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+} and Ni$^+$) were chosen to study the metal ions selectivity of PEG-HDI$_{1.2}$-TPP hydrogel. Before this, the pH values of these sample solutions with different metal ions were measured (Na$^+$: 5.9, Ca^{2+}: 5.7, Cu^{2+}: 4.71, Zn^{2+}: 5.66, Pb2$^+$: 4.2, Co2$^+$: 4.21, Hg^{2+}: 4.32, Ni$^+$: 6.2), which mainly distribute from 4.0 to 7.0. Consequently, there is no need to strictly control the pH value of samples. Fig. 4 illustrates the fluorescence intensity of PEG-HDI$_{1.2}$-TPP hydrogels after immersed in different metal ions aqueous solutions including Na$^+$, Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+}, Ni$^+$ and solution without metal ions (blank) at 420 nm excitation. Obviously, in comparison with Na$^+$, Ca^{2+} and blank, the heavy metal ions selected were able to quench the fluorescence emission of TPP on PEG-HDI$_{1.2}$-TPP at 659 nm, demonstrating the heavy metal ions sensing of PEG-HDI$_{1.2}$-TPP hydrogel. The reason of PEG-HDI$_{1.2}$-TPP's sensitivity to metal ions is ascribed to the functional groups, porphyrin, incorporated. And mechanism of TPP's sensitivity to metal ions has been verified in other literatures before. It's the coordination between Hg^{2+} and the four nitrogen atoms on the endocycli porphyrin that results in the electronic states change of porphyrin moiety. And there is a red-shift in the UV-vis absorption spectra of TPP after combined with metal ions. According to these analyse, the most reasonable explanation of the sensitivity to metal ions is the effect of reverse photoinduced electron transfer (PET) caused by Hg^{2+} and porphyrin. As for the rapid responsibility, on the one hand, it's contributed to the porphyrin's property, on the other hand, it's the high swelling of PEG-HDI$_{1.2}$-TPP that make metal ions penetrate into the interior of the hydrogel swiftly.

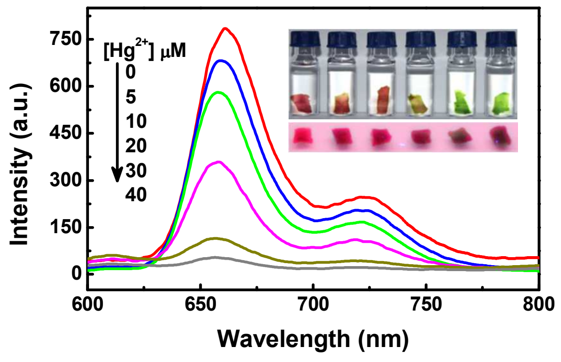


Fig. 5 Fluorescence emission spectra of PEG-HDI$_{1.2}$-TPP hydrogels in the presence of different concentrations of Hg^{2+} ions at 420 nm excitation. Insert: respective photographs of PEG-HDI$_{1.2}$-TPP hydrogels at 365 nm irradiation and visible light. (From left to right: 0, 5, 10, 20, 30, 40 μM)

For further study the sensitivity of metal ion detection property of PEG-HDI$_{1.2}$-TPP hydrogel, Hg^{2+} was taken as an example, since Hg^{2+} is considered as one of the most toxic cations for the environment because of its wide distribution in air, water and soil[25]. Fluorescence emission spectra of PEG-HDI$_{1.2}$-TPP hydrogel, in the presence of different concentrations of Hg^{2+} ions are shown in Fig. 5. The addition of a little Hg^{2+} ions leads to significant quenching of fluorescence emission from PEG-HDI$_{1.2}$-TPP hydrogels. For 40 μM Hg^{2+} solution, a 93% decline in intensity at 660 nm is observed, demonstrating the hydrogel's trace detection property of the hydrogel. In addition, upon exposure to metal ions, the color of PEG-HDI$_{1.2}$-TPP hydrogel films changed from red to green homogeneous in visible light, which not only demonstrates the even introduction of porphyrin, also implies the convenient visualized judgment of sensitivity to heavy metal ions.

Absorption kinetics of PEG-HDI$_{1.2}$-TPP hydrogel was investigated in 20 μM and 40 μM Hg^{2+} aqueous solutions. As Fig. 6 shows, PEG-HDI$_{1.2}$-TPP hydrogel, immersed in 20 μM Hg^{2+} aqueous solution, reached absorption equilibrium when it came to 5 h, and nearly 1h in 40 μM solution. Encouragingly, when the concentration of Hg^{2+} solution was increased to mM level (20 mM and 40 mM), the responsiveness of the hydrogel was so rapid that it cost less than 30 s to reach the equilibrium (Fig. 7). These phenomena reflect the hydrogel's fast-responsibility to specific heavy metal ion.

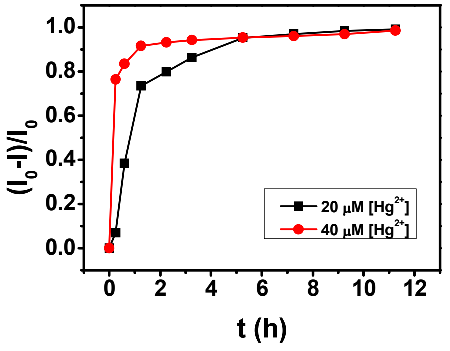
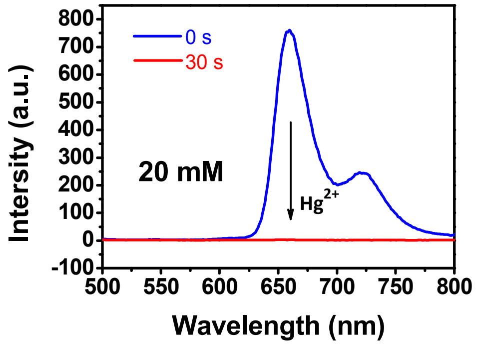


Fig. 6 Fluorescence intensity of PEG-HDI$_{1.2}$-TPP hydrogels, which immersed in Hg^{2+} aqueous solution (20 μM and 40 μM) at 660 nm versus the time. The excitation wavelength was 420 nm.



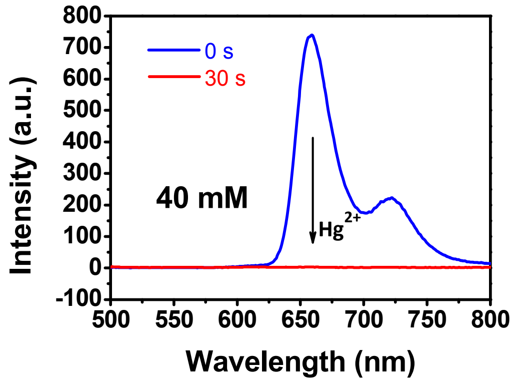


Fig. 7 Fluorescence emission spectra of PEG-HDI$_{1.2}$-TPP hydrogels, before and after immersed in Hg^{2+} aqueous solution (20 mM and 40 mM) for 30 s.

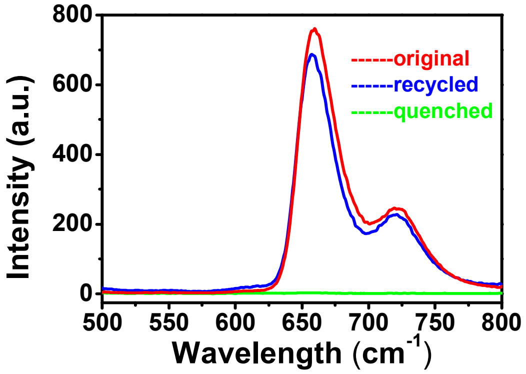


Fig. 8 Fluorescence emission spectra of PEG-HDI$_{1.2}$-TPP hydrogels: original (red), quenched by Hg^{2+} (green) and immersed in the saturated DETA-2Na aqueous solution for 24 h after quenched (blue). The excitation wavelength is 420 nm.

Further research revealed that PEG-HDI$_{1.2}$-TPP hydrogel could be easily recycled. Due to the stronger combination between metal ions and EDTA-2Na than metal ions and prophyrin, EDTA-2Na has the ability to capture the metal ions that prophyrin coordinated. Consequently, EDTA-2Na was used to recycle the fluorescence quenched PEG-HDI$_{1.2}$-TPP hydrogel. After it was immersed in the saturated EDTA-2Na aqueous solution for 24 h, intensity of fluorescence emission was almost recovered by 90% (Fig. 8), which indicates the simple recycling property of the hydrogel. Attributing to these intriguing properties, such as trace analysing, quick response to specific metal ions and recycling possibility, PEG-HDI$_{1.2}$-TPP hydrogel has the potential to become a promising sensor material for heavy metal ions.

Conclusion

In conclusion, we have designed and fabricated PEG-HDI$_X$-TPP hydrogel with functional heavy metal ions receptors. The hydrogel not only possesses favourable compressive strength, up to megapascals, but also exhibits rapid, significant and visual sensitivity to low concentration of specific heavy metal ions. Besides, it can be recycled conveniently. The hydrogel could serve as ideal candidate for many applications, such as environment pollution treatment and heavy metal ions detection. And it may lead to development of a new type of facile functionalized hydrogel system. As long as the functional compounds own reactive hydrogen groups, such as -NH$_2$, -OH and -SH, they would possibly be incorporated into the hydrogel by one-step reaction.

Experimental

1. Materials

4-arm polyethylene glycol (4-arm PEG, Mn = 20000, hydroxyl value = 11.2 mg KOH/g) was obtained from Xiamen Sinopeg Biotech Co. Ltd, Xiamen, China, and dried at 85℃ in vacuum for 2 hours. Hexamethylene diisocyanate (HDI) and catalyst, stannous octanoate, were purchased from Adamas Reagent, Ltd. Tris was obtained from Aladdin Reagent, Ltd. Dichloromethane (CH_2Cl_2), ethyl alcohol absolute, perchloric acid and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were purchased from Shanghai Chemical Reagent Corporation. CH_2Cl_2 was distilled from CaH_2 under dry N_2 purge. 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (TPP-(OCH$_3$)$_4$,95%), Boron tribromide (BBr_3), triethylamine (TEA), $NaClO_4$, $Ca(ClO_4)_2$, $Ni(ClO_4)_2$, $Co(ClO_4)_2$ • $6H_2O$, $Pb(ClO_4)_2$, $Zn(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $Hg(ClO_4)_2$ were purchased from J&K.

2. Synthesis of TPP-(OH)$_4$

TPP-(OH)$_4$ was synthesized according to a literature procedure1. TPP-(OCH$_3$)$_4$ (0.5 g, 0.65 mmol) was dissolved in CH_2Cl_2 (15 mL) under vigorous stirring at room temperature. The solution of BBr_3 (6.26g, 25 mmol) in CH_2Cl_2 (25 mL) was added at 0 ℃ dropwise. Then resulting solution was stirred for 24 h at room temperature. When the color of solution changed into dark red, methanol (5 mL) was used to quench the solution, and TEA (15 mL) to neutralize it. The resulting products were purified with chromatography (silica gel, acetone/light petroleum = 1:1) to give TPP-(OH)$_4$ (299 mg, 67.78% yeild).

3. Gel Preparation

PEG-HDI$_X$ hydrogels were prepared as follows: 4-arm PEG (0.2 g, 0.01 mmol) was completely dissolved in CH_2Cl_2 (2.2 mL) at room temperature. HDI in CH_2Cl_2 solution and stannous octanoate in CH_2Cl_2 solution (0.05 g/mL, 40 uL) were added at room temperature, different compositions of PEG-HDI$_X$ hydrogels were obtained by varying the molar ratios of NCO/OH. The reaction mixture was stirred in an ultrasonic bath (50 W, 40 kHz) at room temperature for 30 min, and then kept it at 50℃ for 12 h. Resultant gels were immersed in ethyl alcohol absolute, refreshed daily, for 3 d and then immersed in deionized water, which also refreshed daily, for 1 week to remove the reagent residues completely. The obtained hydrogels were denoted as PEG-HDI$_X$, where X represented the feed molar ratios of NCO/OH.

The PEG-HDI$_{1.2}$-TPP hydrogel was prepared as follows: 4-arm PEG (0.2 g, 0.01 mmol) and TPP-(OH)$_4$ (0.0068 g, 0.01 mmol) were completely dissolved in CH_2Cl_2 (2.2 mL) at room temperature, together. HDI in CH_2Cl_2 solution (0.298 M, 80 uL) and stannous octanoate in CH_2Cl_2 solution (0.05 g/mL, 40 uL) were added at room temperature. Resulting solution was stirred in an ultrasonic bath (50 W, 40 kHz) at room temperature for 30 min, and then kept it at 50℃ for 12 h to get PEG-HDI$_{1.2}$-TPP gel. Successively, PEG-HDI$_{1.2}$-TPP gel was immersed in CH_2Cl_2, ethyl alcohol absolute and deionized water, which all refreshed daily, for 3 d to wash away the residual chemicals.

4. Gel Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of dry PEG-HDI$_{1.2}$-TPP and PEG-HDI$_X$ gels were recorded on a Paragon 1000 (Perkin Elmer) spectrometer to confirm the successful preparation of hydrogels. Dry gels were obtained by drying in vacuum until weight was constant. Scanning electron microscope (SEM) images were obtained using a Philips Sirion 200 instrument. Photographs were taken with a digital camera (IXUS 800IS, Canon, Japan). Fluorescence spectra were performed on a Perkin Elmer LS 50B fluorescence spectrometer. Equilibrium water contents (EWCs) of the hydrogels were measured when they were fully equilibrated in distilled water for 3 days at room temperature. The EWC was calculated by eqn:

$$EWC = (m_{wet} - m_{dry}) / m_{wet} \times 100\%$$

where m_{wet} and m_{dry} were referred to the weight of wet and dry hydrogels. Each sample was measured three times to get the average values. The EWC of PEG-HDI$_{1.2}$-TPP is 97.2%.

5. Compression Testing

A compressive tester was used to measure the mechanical performance of PEG-HDI$_{1.2}$-TPP and PEG-HDI$_X$ hydrogels. The cylindrical samples were about 10 mm in diameter and 6 mm in thickness and compressed by two parallel metal platens at a crosshead speed of 2 mm/min^{-1}.

6. Metal Ions Sensing Testing

6.1 Effect of pH value to the fluorescence intensity of PEG-HDI$_{1.2}$-TPP hydrogels

A series of buffered solution (Tris-$HClO_4$) with pH values from 2.0 to 8.0 were prepared, and then PEG-HDI$_{1.2}$-TPP hydrogel films with the same weight (0.1g) and similar shape were dip in respectively for 24 hours. Finally, fluorescence intensity of each hydrogel films were tested under the excited wavelength 420nm.

6.2 Sensitivity to Different Metal Ions and Recycle

PEG-HDI$_{1.2}$-TPP hydrogel with the same weight and shape were immersed in metal ions (Na^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+} and Ni^+) and without metal ions (blank) solutions for 24 h, respectively, and then their fluorescent photographs were recorded under a UV lamp at 365 nm. The fluorescence spectra of the PEG-HDI$_{1.2}$-TPP hydrogel immersed in different metal ion solutions were measured when the exciting wavelength was 420 nm. The fluorescence spectra of recycled PEG-HDI$_{1.2}$-TPP hydrogel were obtained after the quenched PEG-HDI$_{1.2}$-TPP hydrogel was immersed in the saturated EDTA-2Na aqueous solution for 24 h.

6.3 Detection to Low Concentration

PEG-HDI$_{1.2}$-TPP hydrogels with the same weight (0.1g) and similar shape were immersed in Hg^{2+} aqueous solutions with different concentration, from 0 to 50 μM, for 24 h. Then their fluorescent spectra and photographs were recorded as the above mentioned.

6.4 Absorption Kinetics

PEG-HDI$_{1.2}$-TPP hydrogels were immersed in 3 mL Hg^{2+} aqueous solutions with different concentration (20 μM, 40 μM, 20 mM, 40 mM), and then their fluorescent spectra were recorded, periodically.

6.5 Recycle

The fluorescence quenched PEG-HDI$_{1.2}$-TPP hydrogels were immersed in saturated EDTA-2Na aqueous solution for 24 hours. Thus, measure the fluorescence intensity of original hydrogels, quenched hydrogels and the recycled hydrogels.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Materials and methods, characterization of gels, compression testing, metal ions detection experiments. See DOI: 10.1039/b000000x/

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