

Aggregation-Induced Emission of Hyperbranched Polyester Polyols

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Abstract

Aromatic compounds, because of their well-defined benzene ring, rigid planar structure, and conjugated P electrons, show a higher probability of returning to the ground state through fluorescence emission after being excited. However, the problem of fluorescence quenching, which is caused by aggregation, limits their further application: the discovery of the aggregation-induced emission phenomenon has been important to overcome this problem. Compared with traditional linear macromolecules, hyperbranched structures have a more compact molecular conformation: their branch points often comprise electron-rich heteroatoms, making it easier to form clusters and to cause electron cloud overlap to produce photoluminescence. Hyperbranched polyester polyols contain more hydroxyl groups and are often used in resin synthesis and modification; however, their photoluminescence properties have been seldom studied. Here, an incremental method is presented aimed at preparing hyperbranched polyester polyols of different generations. To summarize, the effects of the orbital transition types and their concentrations of hyperbranched polyester polyols on the fluorescence emission intensity were investigated, thus broadening the research on unconventional luminescent polymers. Moreover, it is also found that Fe^{3+} exert a significant quenching effect on fluorescence intensity of the hyperbranched polyester polyol-ethanol solutions; thus, they can be applied in the preparation of fluorescent probes.

Keywords: Polyester Polyols, Aromatic compounds, Polymers

Introduction

Traditional light-emitting organics are usually constituted by a well-defined aromatic ring in which both conjugated P electrons and a rigid planar structure reduce the energy loss caused by non-radiation pathways. However, because of the aggregation-caused quenching (ACQ) problem, their application in the aggregated state is limited [1-3]. This problem has been solved by Tang et al since 2001 through several researches on the aggregation-induced emission (AIE) phenomenon; [4-6] moreover, it has been extensively studied in the fields of organic light-emitting materials, explosive and ion detection, and stimuli-responsive polymers [7-13]. According to further researches [14-17], some unconventional light-emitting polymers, which not contain benzene rings, have attracted attention because of their good biocompatibility, environmental friendliness, and certain water solubility. Furthermore, their molecular chains often contain N, O, P, S, and other heteroatoms with unbounded electrons [14-20]. Such heteroatoms are influenced by both molecular chain entanglement and intermolecular interaction forces: unbounded electrons are closer to each other allowing electron cloud overlap, which is known as clustering-triggered emission (CTE) effect, to occur, producing photoluminescence phenomenon [21-25]. Furthermore, these heteroatoms have broad application prospects in fluorescent probes [20,26], biological imaging [27,28], anti-counterfeiting [29,30], and lighting and displays [31-33].

Recently, non-traditional light-emitting polymers with hyperbranched structures such as poly (amino esters) [18,26], phosphate [16,34], polyether [20] and polysiloxane [29,35], have been extensively studied. In summary, their photoluminescence performance depends on the accumulation of electron-rich heteroatoms in the dendritic branches [15,36]. Compared with traditional linear polymers, hyperbranched polymers have a 3D spherical structure and more end groups, which induce a compact molecular conformation.³⁷ However, the ending groups of hyperbranched polyester polyols (HBP) are constituted by a large number of hydroxyl groups, which often lead to strong intra- or inter-molecular hydrogen bonding and further reduce the distance between electron-rich heteroatoms, leading to photoluminescence. Due to the above cited abundance of terminal hydroxyl groups, HBPs is often used in material modification and coating synthesis [38-41]. However,

studies of HBP in non-traditional light-emitting polymers is rarely reported, and thus an evaluation of the photoluminescence properties of HBP is of paramount importance both in academic and application matters.

Materials and Methods

Materials

Pentaerythritol (PE) and 2,2-Bis(hydroxymethyl)propionic acid (DMPA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.; p-toluenesulfonic acid (P-TSA) was purchased from Tianjin Damao Chemical Reagent Factory; ethanol was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. Acetone and n-hexane were purchased from Tianjin Damao Chemical Reagent Factory. While PE and DMPA are dried in an oven at 80 °C for 24 h before use; Ethanol, P-TSA, acetone and n-hexane are used without any further purification.

Measurements

Fourier transform infrared spectroscopy (FT-IR) spectra were tested with Nicolet iS50 from Thermo Fisher Scientific, USA; nuclear magnetic resonance (NMR) with AVANCE III 400 MHz and 600 MHz respectively, from Bruker, Germany. The selected reagent was deuterated dimethyl sulfoxide (DMSO). Fluorescence excitation and emission spectra were measured using RF-5301pc from Shimadzu Corporation; the slit width was 5 nm. Furthermore, the UV absorption spectrum was measured by the TU-1810 UV-Vis spectrophotometer of Beijing Puxi General Instrument Co., Ltd.

Synthesis of HBP

Hyperbranched polyester polyols are synthesized by melt polycondensation. Pentaerythritol (PE) as a core, dimethylolpropionic acid (DMPA) is the AB₂ type monomer. A total of 1.36 g of PE (0.01 mol) was added in a three-necked flask and stirred at 140 °C in a nitrogen atmosphere. As a next step, a mixture composed by 5.36 g of DMPA (0.04 mol) and 0.052 g of P-TSA (0.0003 mol) was gradually added to the reactor. After 6 hours, the reaction was carried out under vacuum for 1 h under reduced pressure to obtain HBP10, the first generation of HBP. The second (HBP20) and the third generation (HBP30) were gradually added with DMPA (firstly 10.72 g, 0.08 mol, then 32.19 g, 0.24 mol) starting from HBP10: the reaction time was extended to 8 h and 12 h respectively. The crude product was dissolved

in acetone, precipitated with n-hexane, and purified by vacuum drying.

Results and Discussion

In the present research, we describe an innovative incremental method for preparing HBP of different generations (HBP10, HBP20, HBP30) through the esterification reaction between dimethylolpropionic acid (DMPA) and pentaerythritol

(PE). The HBP structure features, which have been determined by means of infrared, ^1H NMR and ^{13}C NMR spectroscopy, is shown in Figure 1. Furthermore, here we analyze the orbital transition type of HBP by means of ultraviolet-visible spectrophotometry (UV-Vis); the effect of HBP concentration on fluorescence emission intensity is discussed, as well as the effect of different metal ions on the fluorescence intensity of hyperbranched polyester polyol-ethanol solutions.

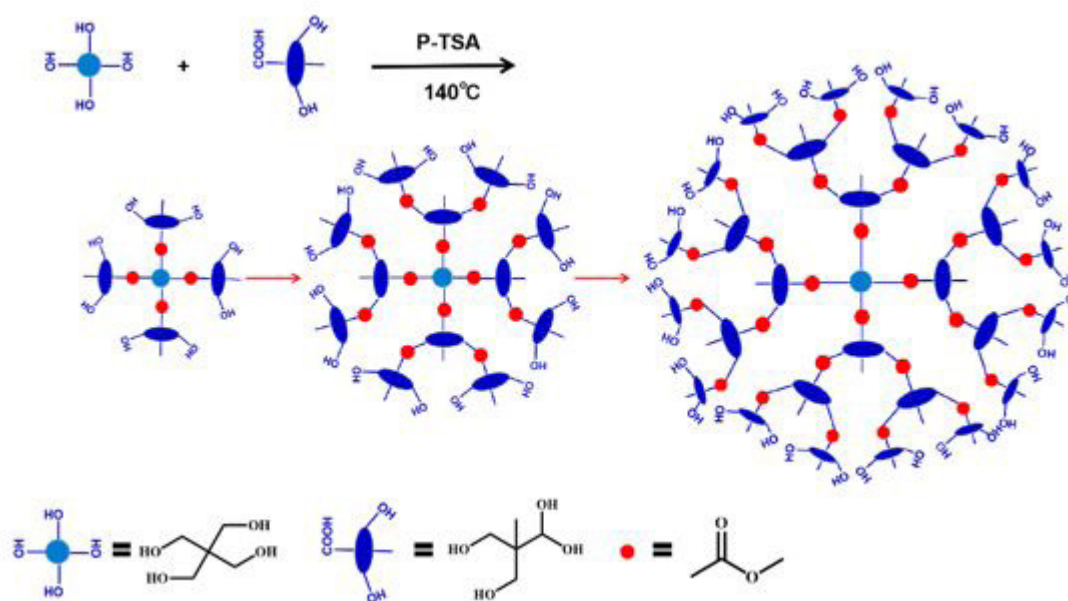


Figure 1 Structure features of HBP

FT-IR spectra

Figure 2(a) shows the FT-IR spectra of HBP10, HBP20, and HBP30: the characteristic absorption peak of $-\text{OH}$ is located at 3365 cm^{-1} , which gradually increases as HBP generation increases. To summarize, the absorption peak at 1730 cm^{-1} corresponds to the stretching vibration of $-\text{C}=\text{O}$; the absorption peaks at 1045 and 1130 cm^{-1} to the asymmetric and stretching vibration of $-\text{C}-\text{O}$, respectively; and 1730 , 1130 and 1045 cm^{-1} are the characteristic peaks of ester groups [42].

Furthermore, the stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$ are located at 2890 and 2950 cm^{-1} , respectively, whereas the 1465 cm^{-1} peak corresponds to the asymmetric bending vibration of $-\text{CH}_3$.

^1H NMR spectra

The product structural information was confirmed using ^1H NMR spectroscopy. Results show that the chemical shift at $1.0\text{--}1.3\text{ ppm}$ is the absorption vibration peak of $-\text{CH}_3$ (Figure 2b), while the chemical shifts at 1.08 , 1.14 , and 1.20 ppm represent the $-\text{CH}_3$ absorption in the branch (D), linear (L), and terminal unit (T), respectively (Figure 2c), thus indicating that the final product has a branched structure. Moreover, the chemical shift at $3.3\text{--}3.7\text{ ppm}$ is the absorption vibration peak of $-\text{CH}_2\text{OH}$; the shift at $4.0\text{--}4.3\text{ ppm}$ is of $-\text{CH}_2\text{OCO}$; the shift at $4.5\text{--}5.1\text{ ppm}$ is of the T and the L unit $-\text{OH}$ [42].

^{13}C NMR spectra

As per the results shown in Figure 2d, the chemical shift at 17.1–17.9 ppm is the absorption vibration peak of $-\text{CH}_3$, and the shift at 46.0–51.0 ppm is of Quaternary carbon atoms. Fur-

thermore, the chemical shifts at 50.4, 48.4, and 46.4 ppm represent the absorption vibration peaks of Quaternary carbon atoms in the T, L and D unit, respectively (Figure 2e), thus showing that the final product has a branched structure.

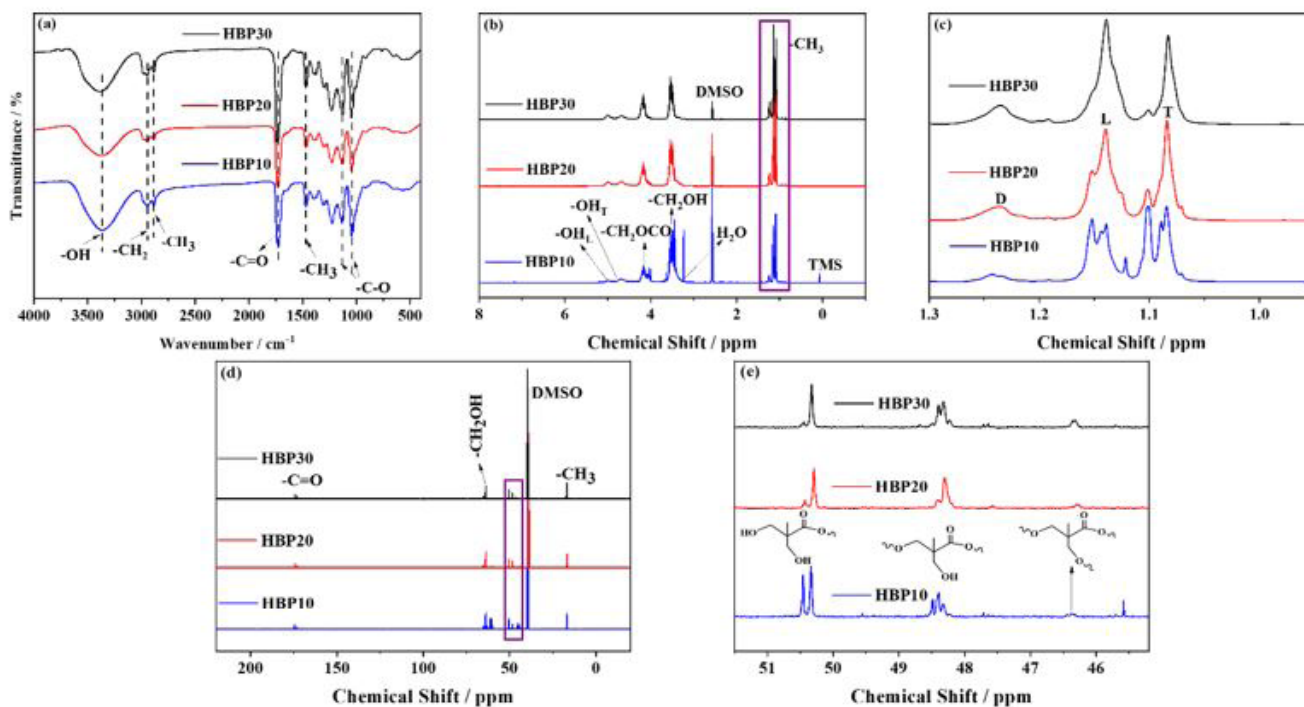


Figure 2: Structural characterization of HBP. (a) FT-IR spectra of HBP with different generations. (b) ^1H NMR spectra of HBP. (c) Partially enlarged view of ^1H NMR spectra. (d) ^{13}C NMR spectra of HBP. (e) Partially enlarged view of ^{13}C NMR spectra

The degree of branching (DB) of hyperbranched molecules is calculated by the Frechet equation:⁴³

$$\text{DB} = (N_D + N_T) / (N_D + N_T + N_L)$$

where N_D , N_T , and N_L are branched, linear and terminal unit, respectively. DB can be calculated by integrat-

ing the corresponding peak areas in ^1H NMR and ^{13}C NMR spectra. Results are shown in Table 1, The degree of branching of the product decreases gradually with the increase of generation. Combining IR absorption spectroscopy, ^1H NMR and ^{13}C NMR spectra, we can notice that three HBP of different generations have been successfully synthesized.

Table 1: Branching degree (DB) of different generations HBP calculated from ^1H NMR and ^{13}C NMR data

	HBP10	HBP20	HBP30
^1H NMR	0.55	0.50	0.46
^{13}C NMR	0.58	0.48	0.46

Photophysical property

As a next step, we examined the photophysical properties of HBP10: the difference in solvent polarity would shift the UV absorption peak of the substance, thus helping to determine the group transition type. As shown in Figure 3(a), in THF with a concentration of 3×10^{-3} mol/L, as the volume of ethanol increases, the polarity of the solvent increases, the UV absorption peak of HBP10 shifts to the shortwave direction (blue-shifted). Thus, the ultraviolet absorption of HBP10 near 230 nm is caused by a $n-\pi^*$ transition, whereas shoulder peaks found at 260 nm are attributed to a $n-\pi$ transition. Subsequently, we used UV-

Vis to explore the relation between HBP10 concentration and UV absorption peak. As shown in Figure 3(b), as the former increases, the intra- and intermolecular interactions of HBP are enhanced, clusters are larger and the number of electron-rich atoms increases, resulting in an enhanced through-space conjugation (TSC) [15,24]. Furthermore, the energy gap of the $n-\pi^*$ transition is reduced: this causes the UV absorption peak close to 230 nm to have a red shift. Moreover, the intensity of the shoulder peak near 260 nm gradually increases as HBP10 concentration increases. Therefore, regarding HBP, two transitions, known as $n-\pi^*$ and $n-\pi$, might occur after being excited by ultraviolet light. To summarize, as the concentration of HBP in the ethanol solution increases, the probability of $n-\pi$ transitions increases.

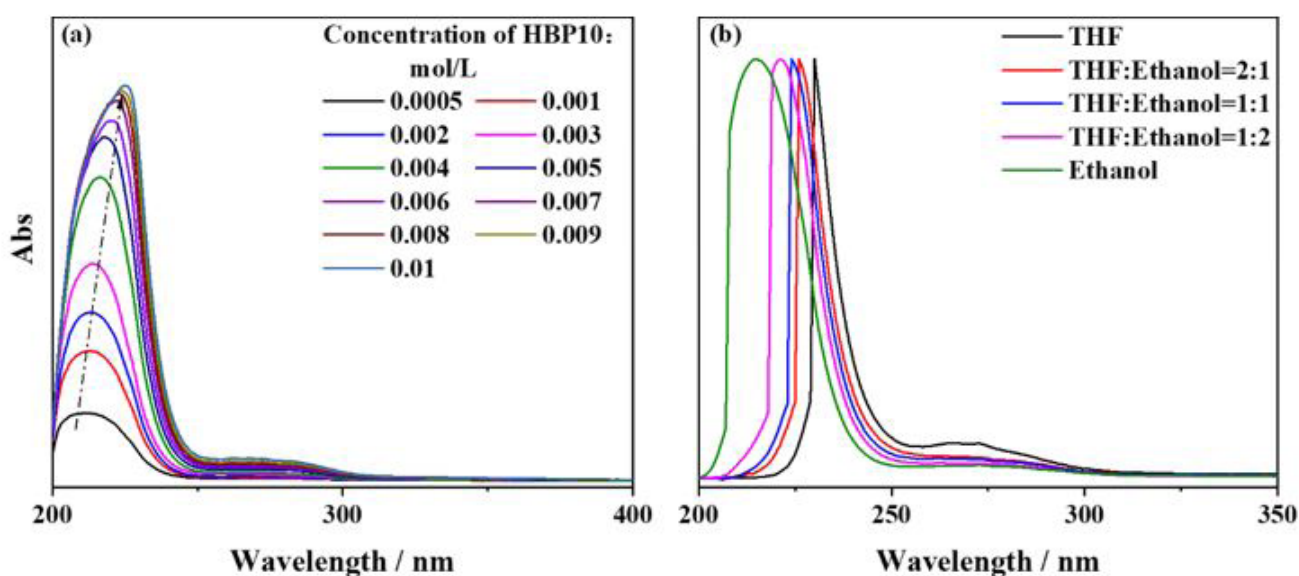


Figure 3: Ultraviolet absorption spectra of HBP10 (a) with different polar solvent ratios (b) and different solvent concentrations of ethanol

Subsequently, we determined the excitation and emission wavelengths of HBP10-anhydrous ethanol solution (5 mg/mL) by fluorescence spectroscopy, as shown in Figure 4(a), and found that its maximum emission wavelength was 285 ± 5 nm; The excitation wavelength was 260 ± 5 nm. Therefore, we used 260 nm ultraviolet light as the excitation wavelength to further test the relationship between the fluorescence intensity and the concentration of hyperbranched polyester polyols, as shown in Figure 4 (b,d). With the increase of HBP10 concentration in ethanol solution, the corresponding emission peak intensity increased and the fluorescence intensity increased. This shows that

for compounds that do not contain aromatic rings but have more electron-rich atoms, the atoms in the molecule are easily aggregated under the forces such as hydrogen bonds, and the electron-rich atoms are sterically conjugated and cause photoluminescence. It can be seen from Figure 4 (c) that with the increase of excitation wavelength, the emission peak of the solution exhibits a red shift, which is due to the formation of clusters of oxygen atoms in the hyperbranched polymer molecules. In addition, due to the non-uniform molecular weight distribution of hyperbranched polymers, the clusters formed vary in size, resulting in the existence of multiple fluorescence emission peaks.

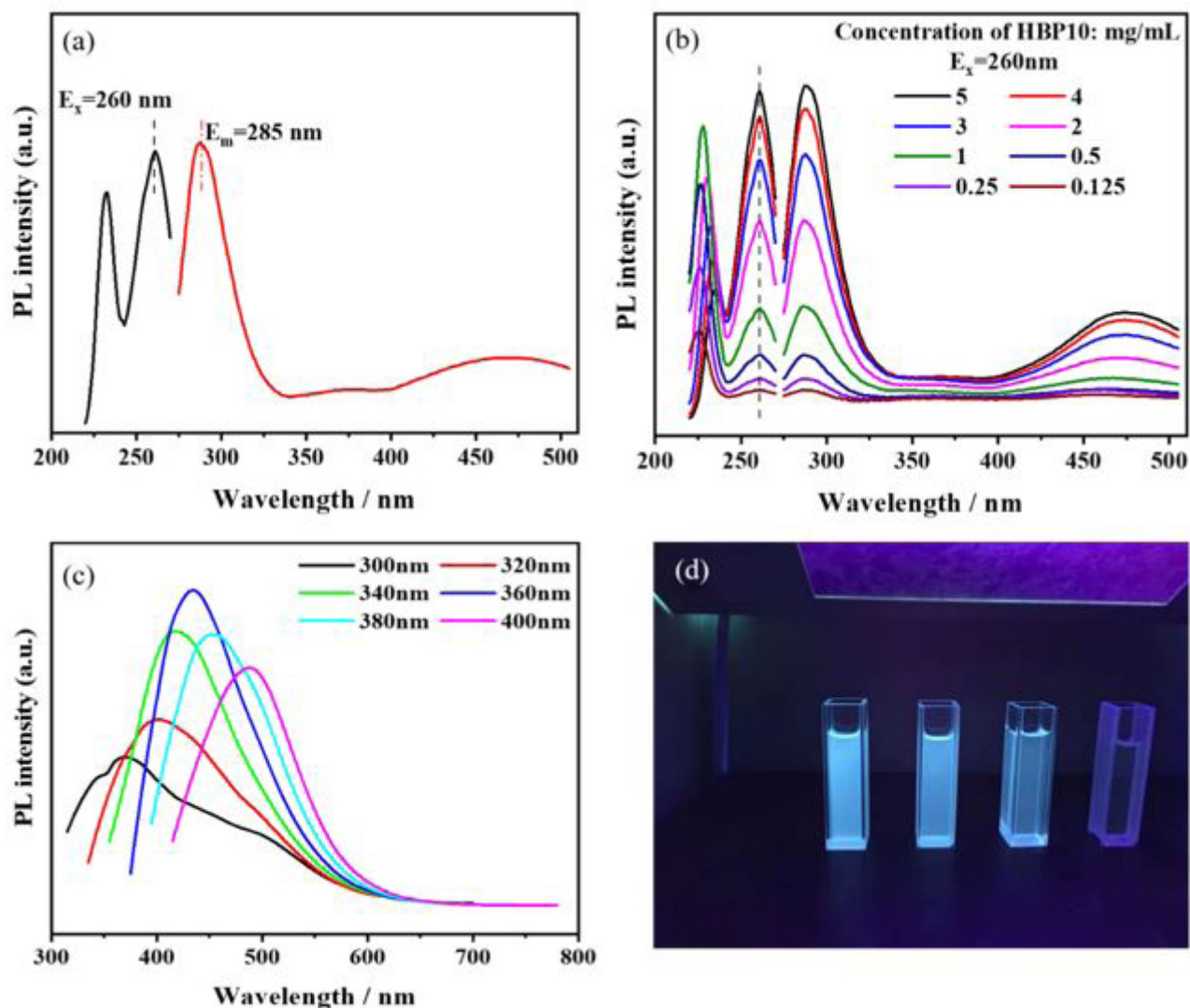


Figure 4: Fluorescence spectra of hyperbranched polyester polyols (a) excitation and emission spectra (b) fluorescence emission spectra at different concentrations (c) fluorescence emission spectra at different excitation wavelengths (d) fluorescence intensity changes with HBP10 concentration under 365 nm

Fluorescence lifetime is an inherent property of aggregation-induced emission materials and depends on the nature and environment of the fluorescent spot. Therefore, we tested the fluorescence lifetime of HBP10-ethanol solution (5 mg/mL) at 320 nm, as shown in Figure 5, its fluorescence lifetime was 2.06 ns. Subsequently, the fluorescence quantum yield (QY) of the solution was determined by integrating sphere, and it was

55.84%. This may be because the hyperbranched polyester polyols have more terminal hydroxyl groups, which are easy to form hydrogen bonds and cause the aggregation of oxygen atoms, which increases the probability of energy dissipation through radiation transitions after being irradiated by ultraviolet light. Meanwhile, according to the CIE chromaticity diagram, the coordinates of 5 mg/mL hyperbranched polyester polyol-ethanol solution are ($x = 0.15593$, $y = 0.02599$).

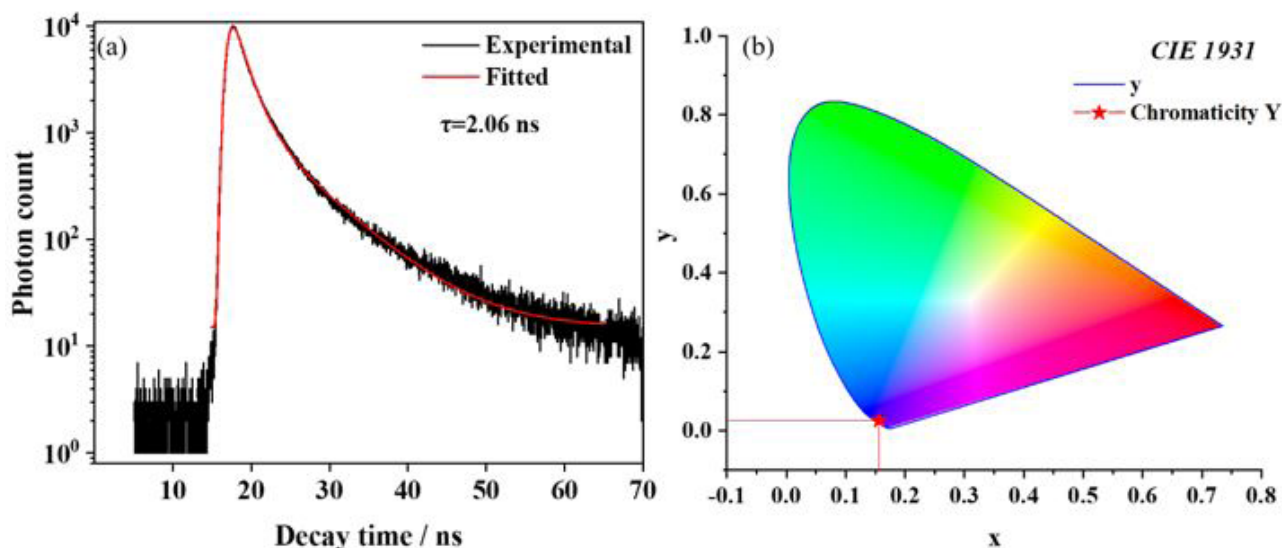


Figure 5 (a) The fluorescence lifetime of HBP (b) CIE chromaticity diagram

The terminal hydroxyl groups in the hyperbranched polyester polyol molecule increase with the increase of its generation, which may lead to the increase of fluorescence intensity. Therefore, we compared the fluorescence intensities of different generations of hyperbranched polyester polyols; as shown in Figure 6, the excitation wavelengths and emission wavelengths of the three generations of hyperbranched polyester polyols are

basically the same, indicating that their structures are similar. In the third-generation hyperbranched polyester polyols, the fluorescence intensity of the first generation was weaker, while the fluorescence intensity of the second and third generations increased slightly, but the difference was not significant. This may be due to the higher degree of aggregation of oxygen atoms as the number of terminal hydroxyl groups increases.

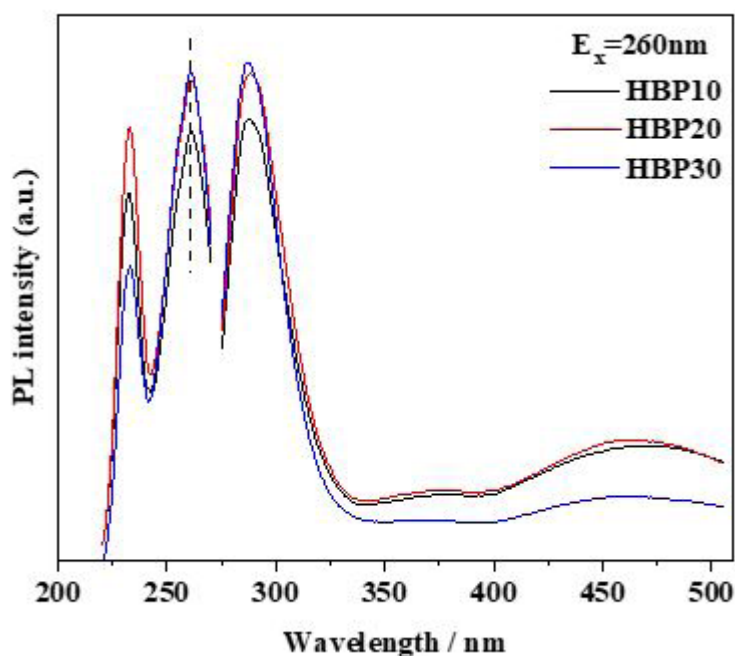


Figure 6: Effects of different HBP on luminescence intensity

The phenomenon of cluster luminescence is based on the proximity and aggregation of electron-rich atoms in molecules; metal ions often lack of electrons, so ligands might be formed with electron-rich molecules, leading to energy transfer and to reducing energy dissipation via radiation transitions. Some past researches reported that Fe^{3+} will quench the fluorescence of polymers; [16,25] thus, we examined the influence of commonly used metal ions on the fluorescence of HBP30 and

observed its role as an ion probe. As shown in Figure 7(a), Fe^{3+} have the greatest impact on HBP30 when adding nine different metal ions with a concentration of 5×10^{-4} mol/L, considering a 2.5 mg/mL HBP30-ethanol solution. We tested the influence of different concentrations of Fe^{3+} on HBP30 fluorescence intensity. As shown in Figure 7(b), when Fe^{3+} with a concentration of 10^{-3} mol/L are added to 2.5 mg/mL HBP30-ethanol solution, their fluorescence is almost completely quenched.

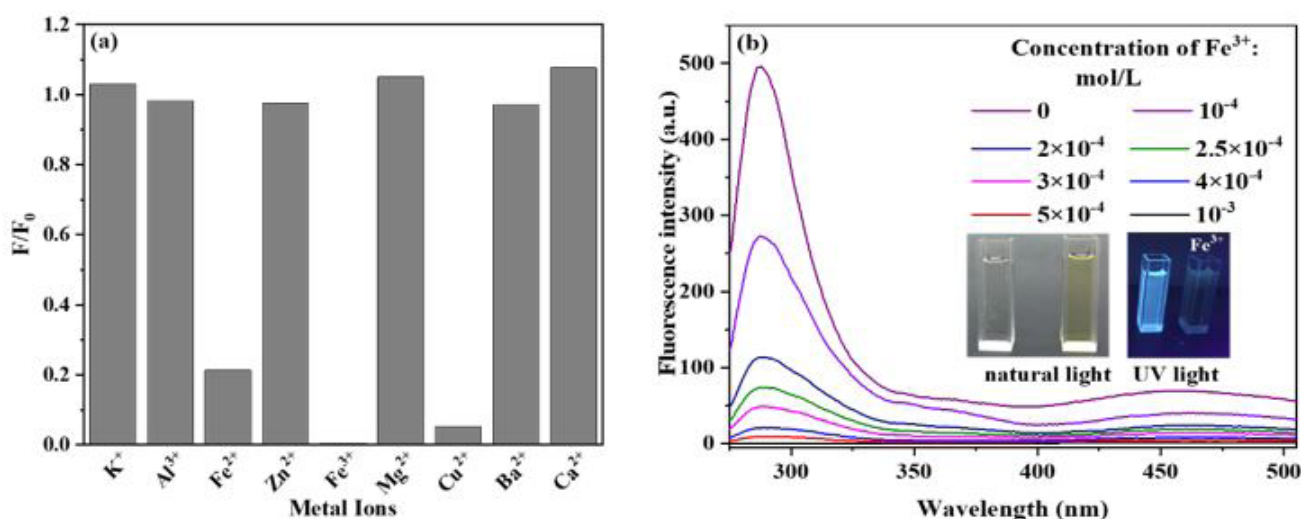


Figure 7(a): Influence of different metal ions on HBP30 (ion concentration: 5×10^{-5} mol/L; HBP30 concentration: 2.5 mg/mL, ethanol used as a solvent). **b)** Influence of different concentrations of Fe^{3+} on HBP30 fluorescence intensity. Inset shows the fluorescence of a 2.5 mg/mL HBP30-ethanol solution with 10^{-3} mol/L of Fe^{3+} under natural light and a 365 nm ultraviolet light

Conclusions

In this study, hyperbranched polyester polyols of different generations were successfully synthesized using an incremental method by dimethylolpropionic acid and pentaerythritol. The photophysical properties of hyperbranched polyester polyols were investigated by UV-Vis and fluorescence spectroscopy, demonstrating that hyperbranched polyester polyols have two transition types: $n-\pi^*$ and $n-\pi$. When an electron is excited, these transitions dissipate the absorbed energy through the emission of a 285 nm fluorescence. For hyperbranched polyester polyols that do not contain aromatic rings but contain more oxygen atoms, the oxygen atoms are easily aggregated under the action of hydrogen bonds and other forces, resulting in steric conjugation, resulting in photoluminescence. In addition, due to the non-uniform molecular weight distribution of hyperbranched polymers, the clusters formed vary in size,

resulting in the existence of multiple fluorescence emission peaks. Furthermore, among the common metal ions, Fe^{3+} have a greater impact on fluorescence intensity of hyperbranched polyester polyols. Therefore, the latter may serve as a potential Fe^{3+} probe.

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