Synthesis and Properties of Poly(1,8-Diaminonaphthalene) using Tetravalent Cerium as Oxidant

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The poly(1,8-diaminonaphthalene) (P18DAN) was readily synthesized by chemical oxidative polymerization. The structure of Ce^{3+}-P18DAN was characterized by the spectra of FT-IR, Raman, UV-VIS and WXRD. Red-shifted change for the quinoid and benzenoid structure stretching vibration are observed in IR and Raman spectra after doping Ce^{3+} ions and a new UV absorption peak presents at 610 nm. The results show that the interaction had occurred between Ce^{3+} ions and amino or imine groups on P18DAN backbone. A more keen-edged diffractive peak is exhibited at $2\theta = 24.3º$ for Ce^{3+}-P18DAN in WXRD, while the peak at 16.9º ascribed to the periodicity parallel chains disappears. Comparing to H^+-P18DAN, the excitation and emission peaks centered at 388 nm and 512 nm, respectively, have a red-shifted for 51 nm and 107 nm. Additionally, the conductivities of P18DAN are increased from 2.37×10^{-6} to 5.70×10^{-4} S cm^{-1} after doping Ce^{3+} ions, suggesting that the degree of electrons delocalization are improved by complexing with Ce^{3+} ions.

Key Words: Poly(1,8-diaminonaphthalene), Complex, Fluorescence, Conductivity.

INTRODUCTION

In recent years, polydiaminonaphthalene (PDAN) synthesized by electrochemically or chemically oxidative polymerization[1-4] have sparked intense interest because of possessing chelating properties and/or reduction properties owing to the electron donating groups (amine and secondary amino groups) on the polymer chains. As a new functionality, it have been applied in electrocatalysts[5], absorbents[6-8], chemical and biological sensors[9-10].

The conductivity of conducting polymer can be improved by the method of doping at present. For instance, polyaniline (PANI) has many intrinsically inherent oxidation states, it can change from the reduced *leucoemeralaine* to oxidized *pernigraniline* after doping H^+ ions, as a result of doping its conductivity can reach 10 s/cm[11]. This conducting form of polyaniline was called protonation process. Protonation preferentially occurs at imine nitrogen atoms followed by an internal redox reaction and resulting the formation of semi-quinone segments[12]. In contrast to polyaniline polymer, the polydiaminonaphthalene prepared by using chemically oxidative polymerization in acidic media have proved that it has a large number of amino and imine groups in polymer chains. It has been demonstrated that poly(1,8-diamino-naphthalene) (P18DAN) is sensitive to heavy metal ions and able to extract some heavy metal ions including Ag^+, Cu^{2+}, Hg^{2+}, Pb^{2+}, VO^{2+}, Cr^{3+} from their dilute solutions *via* complexation with amine groups on the polymer[6-8]. However, the electroconductivity of the protonation polydiaminonaphthalene was lower than that of the polyaniline. According to doping mechanism, the possible reason is that P18DAN have formed a shorter semiquinone segment at polymerization process. Although protonation is the most useful way to achieve high conductivity, this can also attained by using another species to interact with nitrogen atoms of PDAN polymeric chains. There are some researches had indicated that the polymer can obtain a higher conductivity[13-16] when metal ions or transition metal ions are introduced into polymer. Therefore, it will be a promising method to improve the conductivity of polymer by doping metal ions or transition metal ions.

Among the rare-earth materials, cerium compounds attract researcher's attention owing to their applications as ion conductors, catalysts, magnetic and fluorescence materials. The existence of alterable oxidation states for the cerium ion will result in compounds with a new structural frameworks and interesting properties[17,18]. These characteristics make it suitable for increase the conductivity of P18DAN through doping cerium ions in polymeric chains. Poly(1,8-diamino-naphthalene) is a kind of high-absorbing chelating reagent because of the existence of amino and imine group[7,8]. Metal ions are able to coordinate with amino and imine nitrogen atoms in the P18DAN. In this case, the conductivity of P18DAN can promise to be improved by the interaction of amino and imine nitrogen atoms with the metal cations.

The conductivity of the P18DAN can not only be improved after cerium ions introduced into polymeric chains, but the efficient of energy transfer and fluorescence were also be enhanced, because the energy level of π-π^* transition from the conjugated polymer can match with the excitation level of Ce^{3+} ions. In this paper, we present a simple synthetic approach to construct a series of highly efficient luminescent Ce-containing polymers. P18DAN is readily synthesized by chemical oxidative polymerization using ceric ammonium nitrate as an oxidant in acidic media. The fluorescent properties of the Ce^{3+}-doping P18DAN were investigated in detail in solution. The energy transfer processes and the influence of polymer conformation will be discussed.

EXPERIMENTAL

1,8-Diamanonaphthalene (Aldrich) and acetonitrile was distilled under reduced pressure. Other reagents were used without further purification. Ceric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$, ethanol, *N*-methylpyrrolidone (NMP) were commercially obtained as chemical pure reagents and used without further purification.

Synthesis of poly(1,8-diaminonaphthalene)(P18DAN): The Ce^{3+}-doping P18DAN was synthesized through the chemically oxidative polymerization at acetonitrile solution and ceric ammonium nitrate as an oxidant in acidic medium. A typical procedure for preparation of the monomer and oxidant solution for a poly(1,8-diamanonaphthalene) doped by Ce^{3+} ion was as follows: 0.316 g (2 mmol) of 1,8-diamino-naphthalene was dissolved in 20 mL of acetonitrile at room temperature. Then, ceric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6$; 1.096 g, 2 mmol] (used as the oxidant) was added to 10 mL of 1 mol L^{-1} $HClO_4$ solution with shaking. Then the oxidant solution was added dropwise to the monomer solution at a rate of one drop every 3 s at 25 ºC over a period of 0.5 h. The reaction mixture was stirred continuously by using a magnetic stirrer for 24 h in a water bath at 25 ºC. The virgin Ce^{3+} doping P18DAN were isolated from the reaction mixture by filtration and washed with acetonitrile and ethanol, respectively, to remove the oxidant and oligomers. A black powder was left in 60 ºC to dry for one week.

Characterization: IR spectra were recorded on Perkin-Elmer spectrometer within the 4000-400 cm^{-1} wavenumber range on KBr pellet. UV-VIS spectra of polymers in *N*-methyl-pyrrolidone solution were obtained on Perkin Elmer Lambda 35 UV-visible spectrometer within the 200-800 nm range at a scanning rate of 480 nm min^{-1}. Wide-angle X-ray diffraction of the microparticles was performed with a Bruker Axs D_8 advance X-ray diffractometer made in Germany with CuK_α radiation (40 kV and 40 mA) at a step width of 0.020. The content of Eu^{3+} ion was obtained by Varian 720 ES inductive coupled plasma emission spectrometer (ICP) made in America. Raman spectroscopy at 632.8 nm excitation wavelength (He-Ne laser) was recorded in a Bruker laser confocal Raman spectrometer (Lab RAM HR, Jobin Yvon) made in Germany. The electric conductivity was obtained by four-point probe tester (RTS-8) made in china. The fluorescence spectra were obtained by Varian cary eclipse fluorescence spectrometer at a scanning rate of 600 nm min^{-1} and the excitation and emission slit were 5 nm.

RESULTS AND DISCUSSION

IR spectra of P18DAN: The IR spectra of P18DAN prepared by chemically oxidative polymerization using $(NH_4)_2S_2O_8$ and $(NH_4)_2Ce(NO_3)_6$ as oxidant were showed in Fig. 1, respectively. Some differences can be found between the IR spectra of monomer and polymer. The peaks at 3600-3100 cm^{-1} may be assigned to N-H stretching vibration, in this range, monomer has a narrow sharp peaks at 3380 and 3300 cm^{-1} respectively, which are attributed to symmetric and asymmetric -NH_2 stretching vibration. However, it presents a broad absorption band in the polymeric IR spectra, suggesting some amino group structure has gradually transferred into the imine after polymerization, thus the number of amino is reduced in the chains of polymer. The peak centered at 1247-1100 cm^{-1} is derived from the C-N stretching vibration. Absorption peaks appeared at 1650-1600 cm^{-1} and 1460-1420 cm^{-1} are attributed to C-N=C and C=C stretching vibration of aromatic or quinone ring[19,20]. The peak at 700-900 cm^{-1} is belonged to γ(C-H) absorption peak and this absorption peak is very useful for discerning the information about the substituted structure of aromatic ring. Comparing the IR spectra of polymer prepared by using $(NH_4)_2S_2O_8$ and $(NH_4)_2Ce(NO_3)_6$ as oxidant, some subtle distinctions can also be found. The most typical distinction is that the absorption peaks of Ce-P18AND attributed to C-N=C and C=C stretching vibration at 1602 cm^{-1} and 1426 cm^{-1}, respectively, blue-shifted to 1630 cm^{-1} and 1455 cm^{-1}. It is attributed the interaction between aromatic amino and Ce^{3+} ions, thereby increasing the degree of electron delocalization in the polymer chains and some quinone structure had transformed into semiquinone segment. Surprisingly, the peak attributed to C-N vibration absorption has emerged red-shifted at 1269 cm^{-1}. This may be that a pseudo-protonation process had occurred between the Ce^{3+} ions and the amino/imino in the polymer chains. Additionally, the pseudo-protonation process will also increase the degree of electron delocalization in the polymer chains[21]. The structure of polymer and the interactions between Ce^{3+} ions and P18DAN are presented in the **Scheme-I**. The intensity of absorption peak attributed to C-N stretching is significantly larger after doping Ce^{3+} ions, indicating that the number of C-N structure increased after doping Ce^{3+} ions in the polymer chains, it also confirms the foregoing analysis that the quinone segment had transformed into semiquinone segment.

Raman spectroscopy of P18DAN: The Raman spectra of polymer are presented in the Fig. 2. Their doped mechanism of polymers oxidized by $(NH_4)_2S_2O_8$ and $(NH_4)_2Ce(NO_3)_6$ are different, the former can be interpreted as an acid doped form and the latter is an acid and Ce^{3+} co-doped form. Raman spectrum of Ce-P18DAN emerges several new Raman scattering peaks. The two strong broad Raman peaks at 1580 cm^{-1} and 1383 cm^{-1} in the Fig. 2b, attributed to ν(C=C) characteristic Raman scatter and the C-N$^+$. Semiquinone structure resonance Raman peaks respectively. The existence of C-N$^+$. Semiquinone segment in the polymer chains confirms the fact that the delocalized degree of conjugate electronic was increased with doping Ce^{3+} or H^+ ions, it can also be verified by the change of polymeric conductivity listed in the Table-1. The peak of ν(C=N) at 1470 cm^{-1} is absent, it may be due to the number of

C=C are larger than the C=N in the molecular chains, thus its resonance Raman scattering peak is masked. Similarly, the Raman peaks attribute to the γ(C-N) and β(C-H) at 1186 cm^{-1} and 1136 cm^{-1} are masked as well. When Ce^{3+} ions were doped into the polymer chains, owing to the interaction between Ce^{3+} ions and the amino and imino group, the resonance Raman peaks attributed to ν(C=C) of the naphthalene/quinone ring and the C-N$^{+·}$ Semiquinone structure shift to 1551 cm^{-1} and 1339 cm^{-1} in Fig. 2a, respectively. Additionally, the molecular polarizability and electron configuration were changed in the molecule chains due to the strong inductive effect of Ce^{3+} ions. Consequently, the Raman activity was aroused and the resonance Raman peaks emerged at 1186 cm^{-1} and 1136 cm^{-1}, attributed to γ(C-N) and β(C-H) Raman scattering, respectively. This result is consistent with the analysis of the IR spectra.
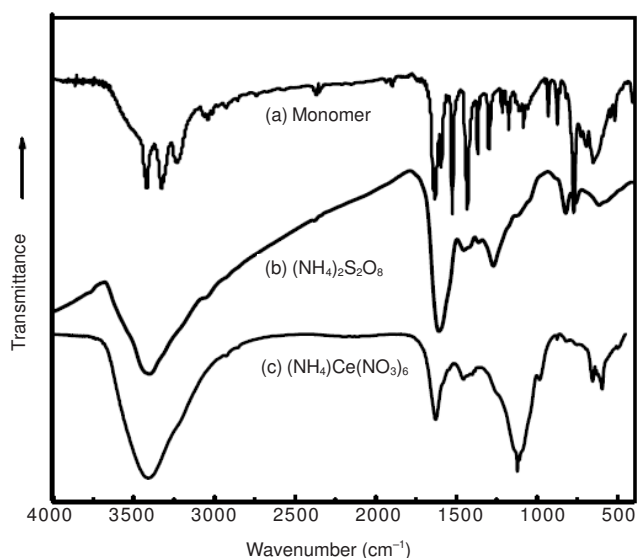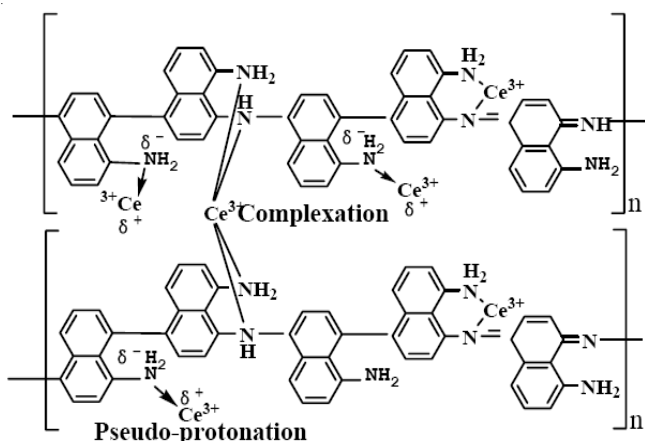
ponding to oxidant/monomer are listed in Table-1. As the Table shows, we can find when the oxidant/monomer at the ratio of 1.25:1 in the reaction system, the polymeric conductivity is largest (5.70 × 10^{-4} s/cm) and the doped quantities of Ce^{3+} ions reach to 5.53 %. Although the doped quantities of Ce^{3+} ions do not have strict relationship with the variation tendency of oxidant/monomer, it is increasing accompany with the ratio of oxidant/monomer enlarging from 0.75:1 to 1.5:1. When the ratio of oxidant/monomer is outside this scope, because of insufficient or excessive of oxidant, the molecular weight of polymer will be very lower and the number of amino and imino will increase naturally. Additionally, when these amino and imino will chelate with more Ce^{3+} ions, resulting the doped quantities of Ce^{3+} ions will be larger than the others. On the contrary, the shorter conjugated chains will result in little conductivity.
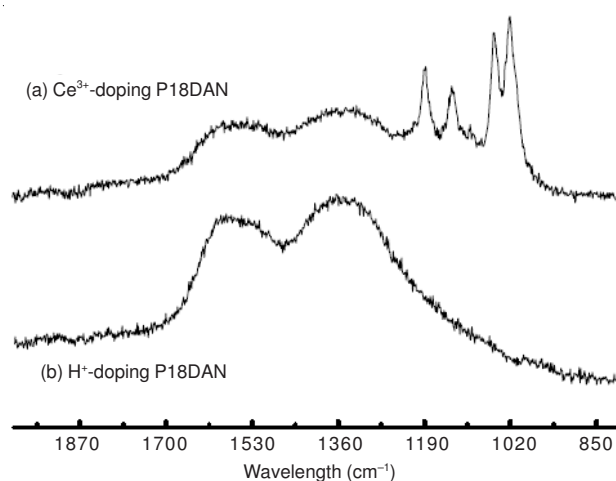

Fig. 1.   FTIR absorption spectra of the monomer (a) and P18DAN prepared by using $(NH_4)_2S_2O_8$ (b) and $(NH_4)_2Ce(NO_3)_6$ (c), respectively, as oxidant

Fig. 2.   Raman spectra of the P18DAN with different doping states, (a) H^{+}-doping state; (b) Ce^{3+}-doping state

TABLE-1
INFLUENCE OF THE PROPERTIES OF P18DAN AT THE DIFFERENT MOLAR RATIO OF [O]/[M]

Polymer		Doping content (%)	Fluorescent peak (nm)	Conductivity (S/cm)
[O]/[M]	Yield (%)			
0.5	45	6.34	517	2.30 × 10^{-7}
0.75	71	3.73	514	3.20×10^{-5}
1.0	84	4.21	515	1.53×10^{-4}
1.25	75	5.53	512	5.70×10^{-4}
1.5	65	5.08	513	1.20×10^{-5}
2.0	45	6.23	515	2.34×10^{-6}

Scheme-I: Polymer structure and the forms of interaction between Ce^{3+} ions and P18DAN

In order to further confirm the Ce^{3+} ions have doped into P18DAN molecule chains, we use inductively coupled plasma emission spectrometry (ICP) to characterize the content of Ce^{3+} ions in the polymer. The doped quantities of Ce^{3+} ions corres-

UV spectra of polymers: The polymers oxidized by different oxidant are dissolved in N-methyl pyrrolidone and their UV spectra are shown in Fig. 3. Two absorption peaks can be found from the spectra: the first one located at 270-285 nm is attributed to the π-π* transition of the aromatic structure and quinone segment in the polymer chains. the second weak broad peak near 350-430 nm is assigned to n-π* characteristic transition absorption of C=N structure in the quinone segment and it reflected the transformation from the naphthalene ring segment to the quinone segment of molecular structure after doping H^{+} or Ce^{3+} ions. Comparing the UV absorption spectra of two polymers, the peak belonged to π-π* electron transition occurs red-shifted from 273 nm to 285 nm, this phenomenon due to the degree of conjugated electrons delocalization are

increased with doping Ce³⁺ ions. In addition, the absorption peak corresponded with quinone segment exhibits a red-shifted from 358 nm to 424 nm, indicating that the electronic delocalization is increased in the conjugate ring of polymer after doping with Ce³⁺ ions, this is because of the strong interaction between the Ce³⁺ ions and amino/imino group. Additionally, a new UV absorption peak attributed to the electron polaron transition[22] can be found at 610 nm from the Fig. 3b, which is a typical behaviour of bipolaron for a conducting polymer[19], thus it can be the direct evidence that Ce³⁺ ions had doped into the polymer chains.
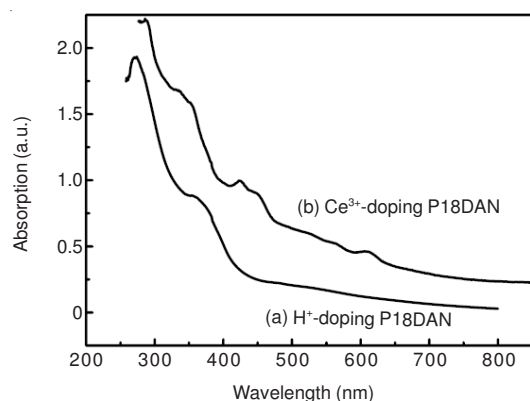

Fig. 3. UV-VIS absorption spectra of the P18DAN with different doping states, (a) H⁺-doping state; (b) Ce³⁺-doping state

Characteristic of wide-angle X-ray diffraction: Fig. 4 is the X-ray diffraction pattern of H⁺-P18DAN and Ce³⁺-P18DAN. There are two broad peaks concentrated in $2\theta = 16.9°$ and $24.3°$ in the diffraction pattern of H⁺-P18DAN, which are attributed to the parallel and perpendicular periodic chains[23], respectively. However, it can only find one sharp diffraction peak at $2\theta = 24.3°$ in the polymeric diffraction patterns of Ce³⁺-P18DAN and the diffraction peaks at 16.9° have disappeared, this indicates that the polymer have produced more perpendicular chains after doping Ce³⁺ ions. The regularity of molecular chains improved that may be owing to Ce³⁺ ions are not only have interaction with one molecular chains, but also complex with the amino and imino around the others polymeric chains. All conclusions of these structural analysis reveal that the interaction had occurred between Ce³⁺ ions and amino or imine groups on P18DAN backbone and some of the quinone structure had transformed into semiquinone segment. Finally, the degree of electron delocalization is increased in the polymer chains after doping Ce³⁺ ions, simultaneously, the conductivity has a change to go along with its variation.

As a conductive polymer material, poly(1,8-diaminonaphthalene) oxidized by $(NH_4)_2S_2O_8$ have a very lower conductivity for 2.37×10^{-6} S cm⁻¹, comparing with polyaniline. It is due to the shorter chains of conjugated structure. However, the conductivity of two orders of magnitude is observed in P18DAN by using $(NH_4)_2Ce(NO_3)_6$ as oxidant, with value of 5.70×10^{-4} S cm⁻¹. This indicates that the molecular chains of polymer have transformed into the configuration that it is good for the electrons delocalizing on the chains after doping Ce³⁺ ions. This may be because of the inductive effect of Ce³⁺ ions and forming a bigger six-ring conjugated plane structure with

the amino or imino groups. Additionally, the conductivity of P18DAN depends on the mole ratio of oxidant/monomer. Although the doping content is larger at the mole ratio of 0.5, the lower conductivity is exhibited in Table-1, indicating that the high conductivity depend on the conjugated structure and the doping content of Ce³⁺ ions. Therefore, the highest conductivity of P18DAN is the mole ratio of oxidant/monomer for 1.25:1.
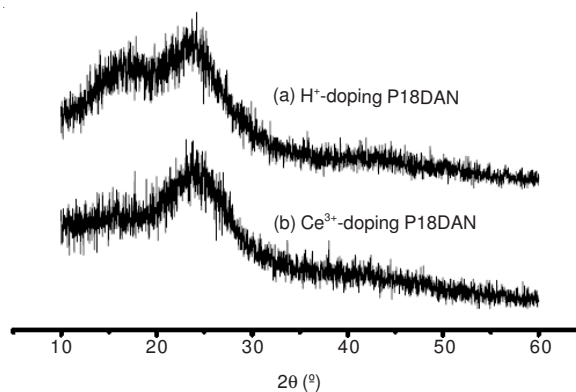

Fig. 4. Wide-angle X-ray diffraction patterns of the P18DAN with different doping states, (a) H⁺-doping state; (b) Ce³⁺-doping state

Fluorescent spectra of P1,8DAN: The fluorescence spectra of polymers dissolved in *N*-methyl pyrrolidone are shown in Fig. 5. The excitation peak present a red-shifteded from 337 nm to 388 nm and the fluorescent emission peak also shift from 405 nm to 512 nm comparing to both polymer. This may be due to the interaction of the amino and imino of polymers chains with Ce³⁺ ions, a larger conjugated plane can be constituted by forming a six-ring structure and the polymeric chains will become more rigid. All of changes will lead to the energy of fluorescent excitation to diminish, so that the polymeric excitation and emission wavelengths have a red-shifted naturally. Stokes shifts of excitation and emission corresponding to both H⁺-P18DAN and Ce³⁺-P18DAN are 68 nm and 124 nm, respectively, indicating that they have a very good light conversion function. Especially in the Ce³⁺-P18DAN, they can absorb the ultraviolet light and emit a green light. The emission spectrum of the P18DAN and the absorption spectrum of the Ce³⁺-P18DAN have an overlap in the fluorescence spectrum, this reflect that the energy level of P18DAN and Ce³⁺ ions are matching mutually. Thus, an energy transfer process may be exist from P18DAN to the Ce³⁺ ions by dipole coupling (Förster transfer)[24] and resulting the emission peak of Ce³⁺-P18DAN occur a red-shifted from 405 nm to 512 nm, simultaneously, the colour of emission light show a transition from purple to green after doping Ce³⁺ ions. In conclusion, the Ce³⁺ ions not only alter the structure of P18DAN chains, but also the conductivity and the luminous properties are influenced after doping them.

Conclusion

The poly(1,8-diaminonaphthalene) can be prepared by chemical oxidation polymerization using Ce⁴⁺ ions of rare earth as oxidant. The advantage of Ce⁴⁺ ions is that it can be reduced to Ce³⁺ ions and the Ce³⁺ ions can interact with the amino and imino by complex or pseudo-protonation on molecular
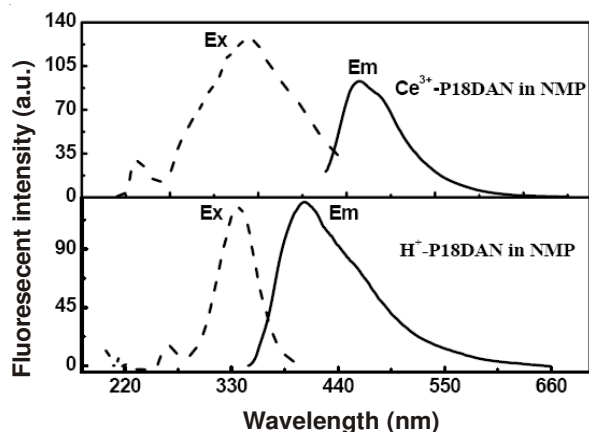
Fig. 5. Fluorescent excitation and emission spectra of the P18DAN doped by Ce^{3+} and H^+ ions, respectively

chains. Ultimately, the fluorescent emission wavelengths of Ce^{3+}-P18DAN have a large red-shifted after the interaction of polymer with Ce^{3+} ions. The fluorescence indicated an energy transfer from the polymer to the Ce^{3+} ions and its down-conversion luminescence process showed the colour of emitting light change from purple to green. Comparing to the P18DAN using ammonium persulfate (APS) as oxidant, the conductivity of 2 orders of magnitude is observed in Ce^{3+}-P18DAN samples, with values of 5.70×10^{-4} S cm^{-1}. The conductivity of polymers depends on the doping quantities of Ce^{3+} ions, the molecular conjugated structure and the ratio of oxidant/monomer. Finally, these studies provide a theoretical basis for the conductive material of P18DAN. Basing on the catalytic properties of rare earth, it will also provide a more effective method for the electrocatalysis.

ACKNOWLEDGEMENTS

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