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Research Article

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Improved fluorescence and solubility properties of N-substituted carboxyl poly(1,8-diaminonaphthalene) in the presence of europium cations

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ABSTRACT

A simple and effective synthesis method for the dissolved poly(1,8-diaminonaphthalene)(P18DAN) with multifunctionality is a main challenge. Herein, a strategy is reported for the facile synthesis of N-substituted carboxyl group poly(1,8-diaminonaphthalene) by an oxidative polymerization of the N-substituted carboxyl 1,8-diaminonaphthalene monomer, prepared by a nucleophilic substitution reaction using chloroacetic acid and 1,8-diaminonaphthalene as reactants in N,N-dimethylformamde (DMF) solution. The europium doped carboxyl modified poly(1,8-diaminonaphthalenen) was fabricated in acidic solution containing europium ions. Their structures were characterized by the spectra of FT-IR, NMR, UV-vis, XRD, XPS. Structural analysis indicates that only one amino group can participate in nucleophilic substitution reaction, and the interaction of N-substituted carboxyl Poly(1,8-diaminonaphthalene) (PNDAN) with rare earth cations occurs at the nitrogen atom of imine and carboxyl groups on polymeric chain backbones. The isolated five-membered ring and the conjugated six-membered structure are formed among Eu^{3+} *ions and nitrogen atom and carboxyl group at P18NDAN chain. The emission wave will shift from 405 to 462nm comparison with P18DAN polymer, whereas the fluorescent intensity only causes slightly change.*

Key words: Poly(1,8-diaminonaphthalene); rare earth ions; N-substituted carboxyl group; fluorescence.

INTRODUCTION

Polydiaminonaphthalene (PDAN), prepared by chemically/or electrochemically oxidative polymerization in acidic medium, is similar to polyaniline (PANI) with single and double bond alternating in a π-orbital system. The electrical properties of polymer can also be reversibly modulated by doping and undoping processes. In contrast to PANI polymer, the polydiaminonaphthalene prepared by using chemically oxidative polymerization in acidic media have shown to have a large number of amino and imine groups in polymer chains. It has been demonstrated that poly(1,8-diaminonaphthalene) (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 [1-3]. Polydiaminonaphthalene, as a functionality polymer, mainly including poly(1,8-diaminonathphalene) and poly(1,5-diaminonaphthalenene), has been applied in electrocatalysts, absorbents, as well as using for chemical and biological sensors [4-6]. These properties of polydiaminonaphalene, such as the collection of heavy metal ions [2, 7-11] and coupling biomolecules with an extra free amine group [12,13], have been widely investigated. Additionally, due to the performance of fluorescent emission, and capable of exhibiting excimer fluorescence at longer wavelength region [14,15], naphthalene and its derivative are extensively applied in light-emitting materials. The excited electronic states of substituted naphthalene molecules may give rise to a charge transfer and large dipole moment when the hydrogens on the naphthalene ring are substituted by the electron donating groups (e.g. $-NH_2$,-OH) and/or an electron withdrawing group (e.g. -CN,$-NO_2$) [16]. Thus, the ploydiaminonaphthalene with a large number of amino and imine groups in polymer chains sever as excimer, and are also excellent affinity host. These model compounds should be helpful in revealing the nature of naphthalene-based fluorescence probes, due to the

N-terminal amine is stringently required for metal ions high-affinity binding. The deduction had been verified in our recent work [17]. The fluorescence property of poly(1,5-diaminonaphthalenene) (P15DAN) nanoparticles depends on the polarity of solvent due to π-π* interactions between the polymer and the solvent molecules. It is also found that the fluorescence of P15DAN nanoparticles regularly quenches as the concentration of Cu^{2+} and Zn^{2+} ions rise. This quenching phenomenon is attributed to metal-ion π-cation interaction with the nanoparticles. These results imply that the unfold polymer chain and large conjugated π electron system are advantageous in fluorescence emission. However, fabricating a long conjugated chain and excellent solubility of polydiaminonaphthalene is a challenge. To improve the conjugation of conductive polymer, in our previous work, we has demonstrated that another kind of metal ions, for example, rare earth ions, can heighten the fluorescence of PANI through improving the conjugated structure of polymeric chains, whereas the fluorescent emission of rare earth ions disappears in polyaniline environment[18]. The interaction of the organic compound with π-orbital system combining with rare earth ions results in enhanced fluorescence due to energy transfer from the triplet excited state of organic to the adjacent rare earth ions via non-radiative way. Therefore, in this paper, we will report a novel P18DAN composite with improved conjugated structure and excellent solubility. Firstly, a novel N-substituted carboxyl 1,8-diaminonaphthalene (1,8-NDAN) monomer was synthesized by a nucleophilic substitution reaction using chloroacetic acid and 1,8-diaminonaphthalene as reactants in DMF solution. Then, the doped N-substituted carboxyl poly(1,8-diaminonaphthalenen) was fabricated in acidic solution containing rare earth cations. The introduction of carboxyl groups can substantially enhance the solubility of poly(1,8-diaminonaphthalene) to increase the compatibility of the composite, and what's more, the synergy effect of the carbonyl groups and/or hydroxyl group in the carboxyl group can effectively stabilize the combination of polymer and rare earth ions to improve the intensity of fluorescence and emission wavelengths of polymer.

EXPERIMENTAL SECTION

2.1Materials

1,8-diaminonaphthalene of analytical grade was purchased from Aldrich. Europium oxide and chloroacetic acid of analytical grade was purchased from Aladdin Reagent Company. Other reagents were used without further purification**.**

2.2 Measurements

Fourier transform infrared (FTIR) spectra of all samples were recorded on a PerkinElmer FTIR spectrometer in KBr pellets. The UV/vis absorption spectrum of all samples dissolved in N-methylpyrrolidone was recorded on a PerkinElmer Lambda 35 spectrophotometer. Emission and excitation spectra of all samples dissolved in NMP at room temperature were collected by means of a Cary Eclipse spectropotofluorometer using the corresponding excitation wavelength with 2.5nm slits. X-ray diffraction (XRD) was carried out using a D/max 2550 model X-ray diffractometer (Bruker) with CuKa radiation at a scanning rate of $10^{o}\,min^{-1}$ in the reflection mode over a 2θ range from 5 to 70^{o}. ^{1}H-NMR spectrum was obtained on Bruker-400 made in Germany. The polymer solubility was evaluated as follows: polymer powder (2 mg) was added to 1 mL solvent and dispersed drastically after shaking intermittently for 2 h at ambient temperature.

2.3 Synthesis of N-substituted carboxyl 1,8-diaminonaphthalene monomer

The N-substituted carboxyl 1,8-diaminonaphthalene monomer was synthesized by a nucleophilic substitution reaction using chloroacetic acid and 1,8-diaminonaphthalene as reactants in N,N-dimethylformamide (DMF) solution. A typical preparation procedure is as follows: 3.16g (0.02mol) 1,8-diaminonaphthalene (18DAN) and 4.725g (0.05mol) chloroacetic acid are added to 15mL DMF with ultrasound for 5min, and adequately dissolve. The mixture solution is poured into a three-necked round bottom flask, and then triethylamine of 15mL is added to the mixture solution under N_2 atmosphere with stirring. The reaction is carried out at 90 °C for 12h, at the same time, opportunely supplement triethylamine in reaction process. The crude product is obtained in ice water, and the precipitate is filtered and washed with absolute alcohol and deionized water for several times, finally the obtained product is dried under vacuum at 60°C. For purification, the obtained product was dissolved in THF. The resulting products are collected by column chromatography using ethyl acetate: chloroform: cyclohexane (5:3:3) mixture as eluent, which presents a reddish brown powder. The structure characterization of the resulting product is as follows: ^{1}HNMR (400 MHZ, DMSO-d_6), δ: 10.04 (s, 1H); 7.42-7.44 (d, 1H); 7.16-7.42 (m, 3H); 6.96-6.98 (d, 1H); 6.75-6.96 (d, 1H); 6.73-6.75 (d, 1H); 6.36 (s, 1H); 3.73 (s, 2H). ^{13}CNMR (125 MHZ, DMSO-d_6), δ: 170.4, 145.2, 136.1, 133.6, 125.0, 124.7, 123.1, 119.3, 116.5, 114.2, 110.0, 51.1。IR (KBr), *ν*, cm^{-1}: 3455, 3324, 2976, 1686, 1587, 1430, 1385, 1248, 1063, 821, 743. In order to confirm the effect of the ratio of the reactions, various samples were synthesized by changing the ratio of 1,8-diaminonaphthalene to chloroacetic acid for 1:1, 1:2, 1:2.5, respectively. ^{1}HNMR analysis found that only one amino group was able to interact with chloroacetic acid in the nucleophilic reaction, it is possibly caused by the steric effect of naphthalene ring, and has nothing to do with the ratio of the reactions.

2.4 Chemical synthesis of the N-substituted carboxyl poly (1,8-diaminonaphthalene)

The N-substituted carboxyl poly (1,8-diaminonaphthalene) were prepared by chemical oxidative polymerization using $(NH_4)_2S_2O_8$ as oxidant in acetonitrile. A typical preparation procedure is as follows: 3.24g (0.015mol) of N-substituted carboxyl 1,8-diaminonaphthalene was dissolved in 50 mL acetonitrile, ammonium persulfate 3.42g (0.015mol) was dissolved in 20 mL of 6 mol·L^{-1} hydrochloric acid solution. The oxidant solution was slowly dropped into the monomer solution with magnetic stirring. The resulting product presents a black powder after reacting for 20h at room temperature, and then the precipitate is filtered and washed with 95% ethanol for several times, finally the obtained product is dried at 60°C for 12h. The synthesis of dedoped product adopts a conventional method by deprotonated with excess 0.1M NH_4OH solution.

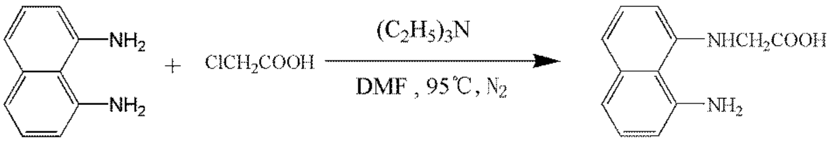
2.5 Synthesis of the Eu^{3+}-doped N-substituted carboxyl poly (1,8-diaminonaphthalene)

In order to exclude the influence of different counter-ions, the rare-earth oxide was first dissolved in the hot concentrated HCl. An anhydrous rare earth chloride salt is obtained by using vacuum dry to remove water from solution. The doped N-substituted carboxyl poly (1,8-diaminonaphthalene) with rare earth ions have been carried out in acetonitrile solution containing different amount of rare earth ions according to the certain mass ratio of europium ions to P18NDAN at room temperature. The suspension of P1,8NDAN powder is maintained 12h under constant stirring, and then the precipitate is filtered and washed with 95% ethanol for several times, finally the obtained product is dried at 60°C for 24h.

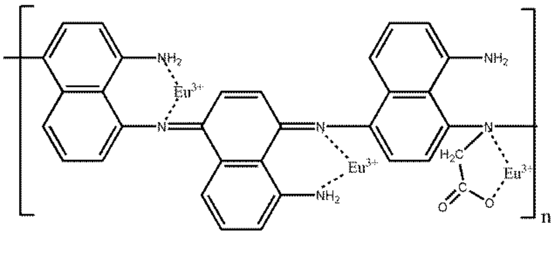
RESULTS AND DISCUSSION

3.1 FTIR spectra

Figure 1 shows the FTIR spectra of the dedoped P18DAN (a), the dedoped P18NDAN (b), Eu^{3+}-P18DAN (c), and Eu^{3+}-P18NDAN (d). Main absorption peaks and their corresponding stretching mode were listed in Table1.The broad peak at 3100~3600cm^{-1} is ascribed to the stretching vibration of N-H bonds, especially in Figure 1d, which exhibits a broad and intense peak. It is possible associated with O-H stretching vibration of the carboxyl group and that of N-H bonds, and the peaks at 3436cm^{-1} shifts to 3410 cm^{-1} compared with the corresponding peak for P18NDAN(b). The absorption peaks at 1400~1650 cm^{-1} mainly correspond with C-N=C, C=C characteristic absorption of the aromatic ring or quinone ring [19,20]. However, the unchanged absorption peaks is found at 1674 cm^{-1} assigned to C=O stretching vibration absorption comparing Figure 1d with Figure1b, indicating that carbonyl groups do not participate in complex reaction process. As shown in Figure 1a, the peak around 1269 cm^{-1} can be attributed to C-N stretching vibration absorption. Comparing to EB-P18DAN, some shifted-bands in the spectra of the polymer doped with Eu^{3+} ions are able to be observed, as shown in Table1. the typical absorption bands assigned to N=Q=N stretching vibration at 1541cm^{-1} and N-B-N stretching vibration at 1382cm^{-1} sifted to higher frequency after the P18DAN doped with Eu^{3+} ions, while only a slight shift is found for the corresponding to absorption bands in Eu-P18NDAN. Similarly, as the incorporation of Eu^{3+} ions into the EB-P18DAN, the absorption peaks at 1111 and 1034cm^{-1} attributed to B-NH^+-B and Q=NH^+-B bending vibration shift to1127 and 1069 cm^{-1}, respectively, whereas the absorption peaks corresponding to Stretching mode shift from 1130 and 1056 cm^{-1} to 1132 and 1076 cm^{-1}, respectively. The results suggest that the shift of the IR absorption peaks is referred to be the degree of charge delocalization of polymerization increase with the doping of the rare earth ions, and the rare earth ions were introduced into polymer backbone by the process that was considered to be complexation or *pseudo*-protonation process of the imine nitrogen [21].



Scheme 1 The synthetic routes of N-substituted carboxyl 1,8-diaminonaphthalene



Scheme 2 The complex structure of P18NDAN and Eu^{3+} ions

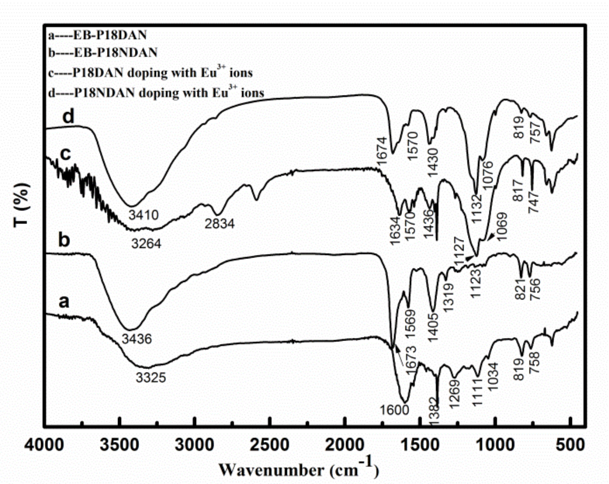


Figure 1 IR spectrum of EB-P18DAN (a), EB-P18NDAN (b), P18DAN (c) and P18NDAN (d) doping with Eu^{3+} ions

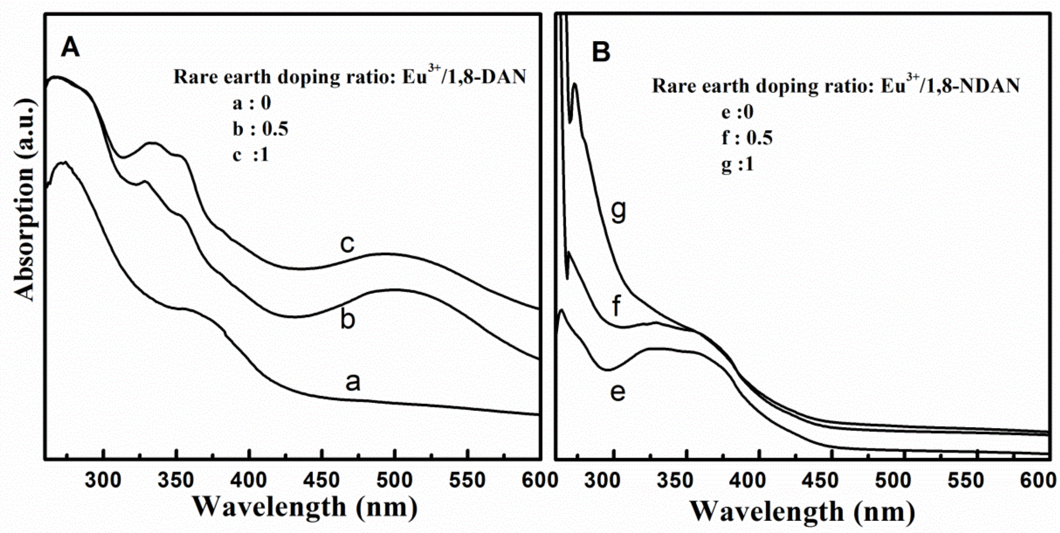


Figure 2 UV-visible absorption spectra of P18DAN and P18NDAN doping with different content of Eu^{3+} ions: Eu^{3+}/18DAN= a: 0, b: 0.5, c: 1; Eu^{3+}/18NDAN=e: 0, f: 0.5, g: 1

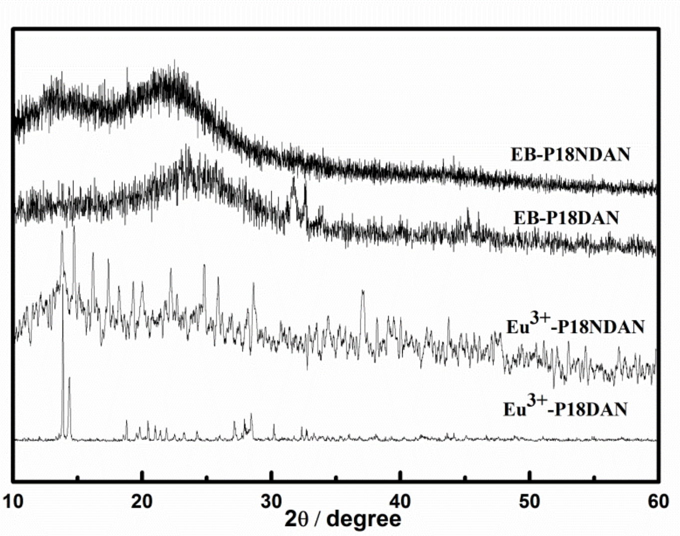


Figure 3 Wide-angle X-ray diffraction patterns of the different polymers

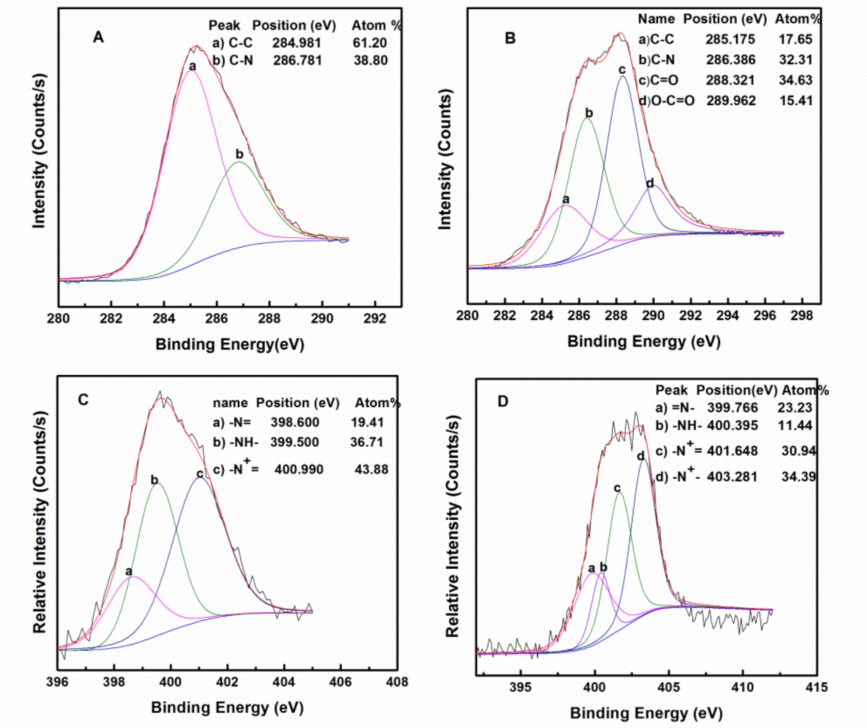


Figure 4 C1s and N1s core level spectrum of of P18DAN and P18NDAN doped with different content of Eu(Ⅲ) ions

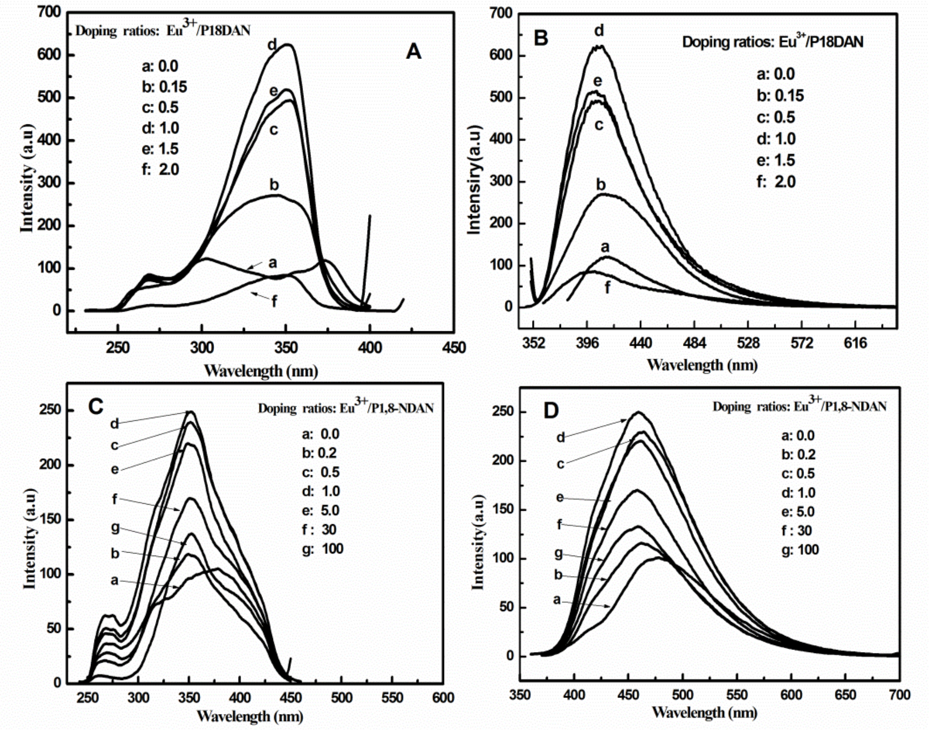


Figure 5 Fluorescent excitation and emission spectra of P18DAN and P18NDAN doped with different content of Eu(Ⅲ) ions

Comparing with IR spectra of both polymer, it is found that shift of the N-H and C-N stretching vibration absorption peaks for poly1,8-diaminonaphthalene is larger than those of N-substituted carboxyl poly (1,8-diaminonaphthalene), and a significant impact on conjugated structure of the benzene ring is able to be observed, indicating that an increase degree of charge delocalization on the Eu-P18DAN polymer backbone since the shift frequency of the IR absorption peaks depends on the conversion of the quinoid rings to the benzenoid rings due to the formation of six-membered ring structure between Eu^{3+}ions and two adjacent amino groups in P18DAN. In the case of Eu-P18NDAN polymer, a red shift of 26 cm^{-1} is also found for the absorption bands around 3436 cm^{-1}. This implies

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that the hydroxyl group in carboxyl interacts with Eu^{3+} ions, as well as the amino and/or imine group participate the formation of complex.

3.2 The UV-vis spectra

Figure2 presents UV-Vis spectra for P18DAN(A) and P18NDAN(B) doped with various amounts of Eu^{3+} ions solution in NMP. As shown in Figure2A, the absorption spectra of Eu-P18DAN solution shows two distinct absorption bands located at 278 and 360 nm, The former corresponds to the π~π* transition, the band at 360 nm is attributed to the n-π* transition of C=N in quinoid structure[22,19], It is noted that they occur blue shift after treatment with Eu^{3+} ions in NMP. The peak assigned to the n-π* transition will shift to 300 nm, and a new the absorption band at 502 nm appears, which is associated with the presence of quinoid segments [23-25]. This result may be caused by a better delocalization of electrons in the matrix of P18DAN due to the combination of rare earth ions with amino and/or imine group on P18DAN backbone. However, in the case of N-substituted carboxyl poly(1,8-diaminonaphthalene), a blue shift of 14nm for the absorption peak assigned to the π~π* transition is found by comparing with P18DAN polymer in Figure2B, moreover, the absorption peak, which is attributed to the n-π* transition of C=N in quinoid structure, become a broader band at range of 320～380nm, which intensity decreases as the content of europium increase. However, the band relating to the polaron transition is not observed as the introduction of europium ions, indicating that the interaction between hydroxyl group and europium ions reduces the degree of charge delocalization of polymer. A possible reason for disappearance of the polaron transition peak is that the large steric configuration of complex between hydroxyl group and europium ions may result in the distortion of the conjugated chains of polymer. The complex structure of P18NDAN and Eu^{3+} ions is showed in Scheme 2 in according to UV-vis spectra characters.

3.3 XRD

The X-ray diffraction patterns of EB-P18DAN, EB-P18NDAN, Eu^{3+}-P18DAN and Eu^{3+}-P18NDAN are shown in Figure 3. A polymer chain in a matrix generally includes both amorphous and crystalline domains. As shown in Figure 3, only a broad peaks centered at $2\theta=24.3^o$ is observed in the EB-P18DAN, whereas two broad peaks located in $2\theta=13.9^o$ and 22.2^o are exhibited in the diffraction pattern of N-substituted carboxyl 1,8-diaminonaphthalene. Two polymers mainly display amorphous structure due to van der Waals forces and hydrogen bond intensive interaction between polymer chains, but the crystallinity of N-substituted carboxyl poly(1,8-diaminonaphthalene) distinctly increase by contrast with P18DAN probable due to the side carboxyl group increasing interval space of molecule chain, leading to an ordered arrays through free adjustment of polymer chain structure. Such a diffraction pattern proves the partly crystalline nature of poly(diaminonaphthalene) polymer and/or its derivative [13]. More sharp diffractive peaks are exhibited in Figure 3 for two polymers as the introduction of Eu^{3+} ions. This indicates that the incorporation of Eu^{3+} ions into two polymers results in dramatic changes in the polymer structure, and trends to highly ordered arrays. Contrasting to both diffraction patterns, it is found that the X-ray diffraction pattern of Eu^{3+}-P18DAN complexes present an intense peak at $2\theta=14^o$, and no reflections assigned to the P18DAN structure can be distinguished (Figure 3). Such diffraction patterns consisting of a single “crystalline” peak are similar to the diffraction patterns of nematic liquid crystals, the molecules of which are parallel in the crystalline randomly distributed domains [26]. In the case of Eu-P18NDAN complexes, the P18NDAN structure can be markedly displayed in Figure 3. The result suggests a parallel and perpendicular periodic chains structure.

3.4 XPS spectra

The XPS C1s spectrum of Eu^{3+}-P18DAN exhibit two dominant peaks at 284.98 and 286.78eV (Figure 4a), which are assigned to C-C and C-N groups, respectively. However, two peaks at 288.32, 289.96eV(Figure 4b), corresponding to C=O and O=C-O, respectively, have added for the N-substituted carboxyl poly(1,8-diaminonaphthalene) as well C-C and C-N groups. The result showed that carboxyl group has been introduced into poly(1,8-diaminonaphthalene). The same conclusion can also be confirmed by the XPS N1s spectrum of polymer in Figure4(c-d). For the Eu^{3+}-P18DAN sample(Figure4c), N1s could be fitted into three species with varied fractions, namely nitride (–N=), amine (–NH–) and imine ($–N^{\bullet+}=$) at binding energies of about 398.6, 399.5 and 400.99 eV, respectively. The atom ratio of $N^{\bullet+}$/N%=43.88%, indicating that the doping level of the Eu^{3+}-P18DAN sample is very high, corresponding to HCl doping P18DAN main chain and Eu^{3+} ions doping backbone to form a six-membered ring. By comparison, the N1s core level of the Eu^{3+}-P18NDAN sample exhibits four peaks at 399.766, 400.395, 401.648 and 403.281 eV corresponding to nitride(–N=), amine (–NH–) and imine ($–N^{\bullet+}=$), nitrogen ions($–N^{+}–$), respectively. It is worth noting that the peak at 403.281eV for nitrogen ions($–N^{+}–$) is assigned to a five-membered ring, which can be formed by the interaction of Eu^{3+} ions and nitrogen atom of P18NDAN main chain and carboxyl group. The XPS result of the Eu^{3+}-P18NDAN composites is consistent with the conclusion, which is deduced by the UV-vis spectra.

3.5 Solubility and solvatochromism of NPAN

The solubility of P18NDAN in various solvents with different polarity indexes is listed in Table 2. The de-doped

P18NDAN polymer is soluble in all polar solvents, including NMP, DMSO, DMF, and is highly soluble in acetonitrile and THF, whereas the H^+-doped P18NDAN exhibits low solubility in the most polar solvents, except NMP, DMF and DMSO. However, the de-doped P18DAN is mainly soluble in polar solvents such as NMP, DMF and DMSO and is only slightly soluble in most other polar solvents. These results suggest that the solubility is primarily controlled by the molecular structure. The carboxyl group is likely responsible for the significant variation in the solubility because the introduction of a carboxyl group on the nitrogen atom increases the distance between molecular chains. In addition, the range of solvents in which P18NDAN is soluble is increased; it is even soluble in water. This improved solubility is due to the presence of a carboxylate group, which can form during the de-doping process.

The color of P18NDAN in a solution is listed in Table 2. As shown Table 2, compared with P18DAN, the colors of P18NDAN solutions exhibit brown and yellow in NMP and DMF, respectively. The UV-visible maximum absorption wavelength of the polymer solutions gradually decrease when the solvent is changed from NMP or DMSO to THF. This result implies that the polymers exhibit solvatochromic properties because the polymer chains may have different conformations, and therefore different conjugation lengths, in different solvents [27].

3.6 Fluorescence spectra

The fluorescence behavior of Eu-P18DAN and Eu-P18NDAN in NMP is shown in Figure 5. To confirm the effect of the rare earth ions on polymer chains, it is useful to investigate the doping consent of Eu^{3+} ions on polymer chains, all samples are carried out by changing the metal cations concentration at a constant mass of polymer. The doping content of the cations in the sample is determined by conductively coupled plasma atomic emission spectrometer. Figure 5A is the excitation spectra of different mass ratio of Eu^{3+} ions to P18DAN. The P18DAN displays two weak peaks at 301 and 372nm, which are attributed to the π~π^* transition and the n-π^* transition of C=N in quinoid structure respectively. However, a distinctly blue shift can be observed in all doped samples, one becomes broad and strength peak at range of 345~352 nm, and the peak intensity of excitation of polymer is obviously increased after doping with the rare earth ions, another is weak peak at 268nm. Under 347nm excitation, all emission spectra for the P18DAN doped with the rare earth ions with various mass ratios of Eu^{3+} ions to polymer are shown in Figure 5B. Only an emission peak was observed in Figure5B, which is possibly attributed to the overlap of naphthal units and the typical of the rare earth ions emission. However, these emission peaks present a blue-shifted from 412 to 397nm with the mass ratios of Eu^{3+} ions to polymer increase, and the emission strength depend on the mass ratios. Gradually, the characteristic peaks of the rare earth ions solutions are observed around 500~600nm, but the interaction of P18DAN with the rare earth ions improved the fluorescent feature characteristic, because the fluorescent emission of the rare earth ions solutions depends on polarization of the ion in the field of a ligand or solvate envelop, and it is normally suppressed in a symmetric environment [26], a charge transition easily achieves from the central europium ion to ligand. Eventually, disappearance of characteristic emission peaks of rare earth ions in the red region and appearance of a broad band centered at 410 nm can be observed in Figure 5B, which intensity will increase as the mass feed ratio of rare earth ions to P18DAN at range from 0 to 1, then, the fluorescent quenching and a slight blue-sifted can be found as the increase of the contents of Eu^{3+} ions in Figure5B. A significant factor for fluorescence enhancement is possible attributed to the amino groups on polymer chains restrict the photo-induced electrons transfer from the excited naphthalene unit under the low Eu^{3+} ions. However, the fluorescent quenching may originate from the interaction of the π electron of naphthalene ring in P18DAN chains with Eu^{3+} ions because the electrons easily transfer from the electron rich naphthalene ring to the lacked electron europium in a conjugated system. Figure 5C shows excitation spectra of Eu^{3+}-P18NDAN. As shown in Figure 5C, the fluorescent excitation intensity will increase with the contents of Eu^{3+} ions increase before molar ratio of Eu^{3+} ions to monomer for 1:1, then, the fluorescent excitation intensity displays a decrease. The change tendency is a typical consequence of the concentration quenching effect [28,29]. Excitation wavelength occurred an obvious blue sifted comparing with pure P18NDAN polymer from 376nm to 351nm. It is probably due to the interaction of P18NDAN with Eu^{3+} ions forming a nonconjugated five-membered ring, which leads to the electron delocalization of conjugated polymer decrease. Emission spectra of P18NDAN are shown in Figure 5D. Emission spectrum under excitation at 351 nm presents a broad emission band centered at 475 nm. An increasing tendency for the fluorescent intensity can be observed before the mass feed ratio of the rare earth ions to P18DAN at range from 0 to 1, then, only a slight decrease for the fluorescent intensity are exhibited in spite of the mass ratio of europium increase to 100. The result indicates that a non-conjugated system is formed between the polymer chains and rare earth ions possible due to formation of N, O-Multi-coordinate rare earth ion complexes leading to the insensitivity of the fluorescence emission to rare earth ions. Additionally, a red-shifted can be found from 405 to 462nm comparing with the complexion of poly 1,8-diaminonaphthalene and rare earth ions in Figure5B. This implies that the incorporation of Eu^{3+} ions into poly1,8-diaminonaphthalene mainly form a conjugated system to transfer π electrons from the electron rich naphthalene ring to the lacked electron europium, while the N-substituted carboxyl-modified poly1,8-diaminonaphthalene derivative constitutes independent five-membered ring due to the easy combination of the carboxyl group and Eu^{3+} ions.

Table 1 Main IR vibrational frequencies(cm^{-1}) of EB-P18DAN, Eu^{3+}-P18DAN, EB-P18NDAN and Eu^{3+}-P18NDAN.

EB-P18DAN	**Eu^{3+}-P18DAN**	**EB-P18NDAN**	**Eu^{3+}-P18NDAN**	**Stretching mode**
3325	3264	3436	3410	N-H or O-H stretching
—	—	1673	1674	C=O stretching
1600	1634	1569	1570	N=Q=N stretching
1541	1570			
1455	1436	1405	1430	N-B-N stretching
1269	1261	1319	1325	N-H bending
1168	1214	1237	1214	C-N stretching
1111	1127	1178	1121	B-NH^{+}-B or ^{a}Q=NH^{+}-B
1034	1069	1123	1076	
819	817	821	819	Out -of-plane C-H bending
758	747	756	757	

Table2 solubility of different polymers in common solvent

Sample	Solubility[a] and solution color[b]						
	NMP (6.7)[c]	DMF (6.4)[c]	DMSO (6.5)[c]	CH_3CN (5.8)[c]	THF (4.2)[c]	$CHCl_3$ (4.1)[c]	H_2O (10)[c]
P18DAN[d]	MS, db	MS, db	MS, db	SS, sb	SS, sb	IS, sb	IS
P18NDAN[d]	S, b	S, y	S, y	MS, ly	MS, ly	PS, t	PS, t
P18NDAN[e]	S, b	S, y	S, y	PS, ly	PS, ly	SS, t	SS, t

[a] IS: insoluble; MS: mainly soluble; PS: partially soluble; S: soluble; SS: slightly soluble. [b] db: dark brown; y: yellow; b: brown; ly: light yellow; t: taupe. [c] Polarity index of the solvents. [d] The de-doped polymers. [e] H-doped polymers

CONCLUSION

The N-substituted carboxyl 1,8-diaminonaphthalene monomer has been synthesized by a nucleophilic substitution reaction using chloroacetic acid and 1,8-diaminonaphthalene as reactants in DMF solution. Then, The doped N-substituted carboxyl poly(1,8-diaminonaphthalene) was prepared in acidic solution containing rare earth cations. Structural analysis indicated that an N-substituted carboxyl 18-diaminonaphthalene monomer can be formed by the amino group substituting the chlorine atom of trichloroacetic acid, and the interaction of PNDAN with rare earth cations occurs at the nitrogen atom of imine and carboxyl groups on polymeric chain backbones. The incorporation of Eu^{3+} ions into poly1,8-diaminonaphthalene mainly form a conjugated system to transfer π electrons from the electron rich naphthalene ring to the lacked electron europium, while the N-substituted carboxyl group poly(1,8-diaminonaphthalene) derivative constitutes independent five-membered ring between the carboxyl group and Eu^{3+} ions. Rare earth ions can sensitize the fluorescence of polymer by improving the structure of polymeric chains, whereas the fluorescent emission of rare earth ions disappears in polymer environment.

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