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“Off-On-Off” fluorescent proton switch synthesized by RAFT polymerization

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ABSTRACT

A polymeric chemosensor (PNa) containing naphthalimide signal moiety and piperazinyl ring recognition moiety for the detection of proton was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization, which can guarantee narrow molecular weight distribution, high purity and precise polymeric structure. PNa and its corresponding monomer (Na) showed both fluorescence enhancement in low proton concentration and fluorescence suppression in high proton concentration, which can be observed by both naked eyes and optical responses. Quarternization of the alkylated amine of Na (NaI) can better support the “Off-On-Off” mechanism shown by PNa and Na. In addition, PNa displayed better sensitivity than Na. The effect of proton on thin PNa film was also investigated, and the addition of proton led to a decrease of the fluorescence intensity.

1. Introduction

Recently, considerable attention has been focused on the synthesis and property investigations of proton chemosensors due to the importance of proton in environmental protection, biological health [1] and other potential applications [2]. Quite a few fluorescent chemosensors, both monomeric and polymeric sensors, have been successfully developed and studied these years [3]. However, most proton sensors are limited to the narrow pH-response, ranging mainly 3–12 [4]. Sensors with high proton concentrations are rarely studied, which restrict the further application in some special fields, such as water pollution evaluation, sewage treatment and so on. Besides, most of the previous proton polymer sensors were synthesized by ordinary radical polymerization [5], which was difficult to purify and control the molecular weight, polydispersity and molecular topology and consequently, negatively affected the sensing capacity.

Monomer Na and polymer PNa (Scheme 1) were prepared to avoid or reduce the above-mentioned shortcomings. Though their structures were not innovative [6], they were studied under wide pH-response range and were synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT), which was one of the most promising controlled/living radical polymerization methods that can control the polymer molecular weight and its distribution with the usage of chain transfer agent, such as esters disulfide compounds [7]. This appeared to be a very attractive method for the synthesis of fluorescent polymers. Fluorescent polymers with desirable polymerization degrees and low polydispersity can be synthesized due to the controllability and it was first used in fluoride sensing in our recent research [8]. To the best of our knowledge, the application of RAFT method to proton signaling was also an initiative.

The signaling of Na and PNa were based on photo-induced electron transfer (PET) mechanism, which was deeply studied in many references [9]. In the case of Na, the PET process occurred from the alkylated amine donor to the 4-amino-1,8-naphthalimide fluorophore through the piperazinyl ring, thus the fluorescence was quenched. The PET path can be switched off by the protonation or quarternization of the alkylated amine, which can result in the fluorescent recovery [10]. If the electron-donating aromatic amine linked directly to the 4-position of the naphthalimide ring was replaced by an electron-withdrawing substituent, such as a nitro group, the fluorescence of the naphthalimide fluorophore of this naphthalimide derivatives drastically decreased [11]. When the aromatic amine in this naphthalimide derivative was protonated at much lower pH values, an electron-withdrawing effect, leading to fluorescence quenching, can also be induced chemically. So Na can display opposite (fluorescent enhancement or decrease) under solutions with different proton concentrations, that was, at low proton concentrations, mainly from pH 12 to 3.5, the fluorescence enhanced with the addition of proton. On the contrary, at high proton concentrations, mainly from pH 3 to −0.6, the fluorescent intensity decreased. Thus the Na and PNa can serve as “Off-On-Off” switches. To confirm the proposed mechanism above, NaI was prepared (Scheme 1) to take control experiments. In addition, the thin film of PNa was also investigated on addition of proton. Detailed discuss was processed in the following text.

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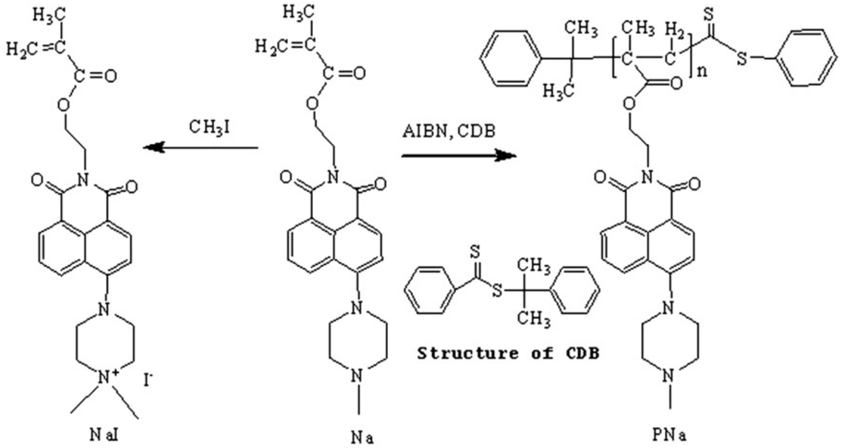

Scheme 1. Chemical structures of Na, NaI, PNa and CDB.

2. Experimental section

2.1. Materials

The different pH solutions were modulated by hydrochloride or sodium hydroxide solutions, which were all analytical purity and used without further treatment. 1-Methyl-2-pyrrolidinone (NMP) was used immediately after it was distilled under vacuum. Azobisisobutyronitrile (AIBN, 97%) was recrystallized from ethanol twice, dried at room temperature under vacuum, and stored at −10 °C in the fridge. Na and cumyl dithiobenzoate (CDB) was synthesized according to the method described previously (See Figure S1 and Figure S2 for ^{1}H, ^{13}C and MS-ESI spectra of Na) [12]. All other reagents were of analytical purity and used without further treatment.

2.2. Characterization

^{1}H NMR and ^{13}C NMR measurements were recorded on a Bruker AV-500 spectrometer with deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent and tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) measurements were carried out on ESI mass spectroscopy. The number-average molecular weight (M_n) and polydispersity indices (PDIs) of the polymers were determined with a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector and calibrated with polystyrene (PSt) standard samples. Dimethylformamide (DMF) was used as the eluent at a flow rate of 1.0 mL/min at 30 °C. The pH values were measured by a pHS-25 pH meter. UV-Vis absorption spectra were performed on a Varian Cray 500 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer; both spectrophotometers were standardized. The melting points were measured with an X4 Micro-melting point apparatus.

2.3. Preparation of NaI

Methyl iodide (0.9 mL, 13.5 mmol) was added to the THF solution (150 mL) of Na (1.5 g, 3.7 mmol) in ice bath. After stirring for 24 h under room temperature, some yellow suspension appeared. Yellow solid was obtained by removing the THF solvent under vacuum. The crude product was recrystallized from ethanol to afford golden yellow solid 1.4 g. Yield: 68%. ^{1}H NMR (500 MHz, DMSO, ppm) $\delta = 1.89$ (s, 3H, CH_3, $C{=}CH_2$), 3.32 (s, 6H, CH_3–piperazin), 3.60 (t, 4H, CH_2–N), 3.76 (t, 4H, CH_2–N^+), 4.43 (t,2H, CH_2–O, $J = 4.99$ Hz), 4.45 (t, 2H, CH_2–Naph, $J = 5.01$ Hz), 5.52 (s, 1H, $CH_2{=}$), 6.08 (s, 1H, $CH_2{=}$), 7.50 (d,1H, H–Naph, $J = 8.09$ Hz), 7.88 (t, 1H, H–Naph, $J = 8.07$ Hz), 8.46 (d, 1H, H–Naph, $J = 8.02$ Hz), 8.51 (t, 2H, H–Naph, $J = 7.21$ Hz, $J = 7.01$ Hz). ^{13}C NMR (500 MHz, DMSO, ppm) $\delta = 17.8$, 35.8, 46.0, 60.8, 61.5, 116.3, 116.7, 112.5, 125.4, 125.7, 126.5, 129.0, 130.4, 130.8, 131.9, 135.6, 153.7, 163.1, 163.5, 166.4. (See Figure S3 for ^{1}H and ^{13}C NMR spectra) MS-ESI: 422[M-I]. (See Figure S4 for MS-ESI spectra) Melting Point: >250 °C.

2.4. Preparation of PNa

A Schlenk tube was filled with Na (198.6 mg, 0.448 mmol), AIBN (0.3 mg, 0.0025 mmol), CDB (1.36 mg 0.005 mmol) and NMP (2.0 mL) as solvent. The Schlenk was sealed and immerged in liquid nitrogen for five minutes to make the solvents frozen, then eliminate the small amount of residual oxygen and lastly charged with argon, repeat this procedure three times to remove the oxygen thoroughly. Then, the Schlenk tube was placed in a constant-temperature oil bath of 70–75 °C to polymerize. After 36 h, the tube was cooled in liquid nitrogen and then opened. The polymer (PNa) were purified by precipitating twice from THF to diethyl ester, and once from NMP to a mixture of diethyl ether/methanol (1:1, v/v:), lastly the grey polymer was obtained after filtration and were put in a vacuum oven overnight at 50 °C to dry. It was measured to be 110 mg.

3. Results and discussion

3.1. RAFT polymerization

The polymer PNa was prepared via RAFT polymerization using cumyl dithiobenzoate (CDB) (Scheme 1) as chain transfer agent

Table 1
Absorption spectra data of Na, NaI and PNa for different proton concentrations in mixed solvent of DMSO/H_2O (v/v = 1:1). The proton concentrations were modulated by $HCl_{(aq)}$ and $NaOH_{(aq)}$.

	Na	NaI	PNa
λ_{ab}^{max}/nm (pH = 11.2)	413.8	396.6	413.9
λ_{ab}^{max}/nm (pH = 7.6)	405.8	396.4	411.2
λ_{ab}^{max}/nm (pH = 3.4)	390.1	395.2	394.0
λ_{ab}^{max}/nm (pH = −0.6)	390.2	395.0	388.8

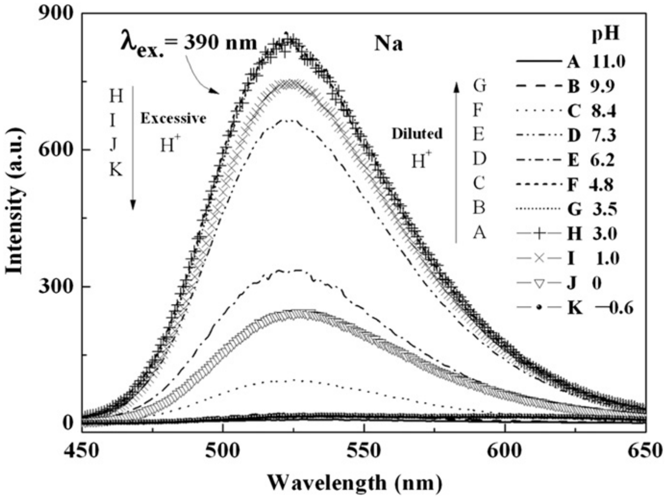

Fig. 1. Fluorescent spectra of Na on addition of various concentrations of proton in the mixed solvent.

(CTA), azobisisobutyronitrile (AIBN) as initiator and 1-methyl-2-pyrrolidinone (NMP) as solvent at 70 °C. The main advantage of RAFT polymerization was the desirable controllability of molecular weight and low polydispersity index [13]. The average molecular weights determined to be 39100 g/mol, with a polydispersity of 1.15 by GPC, which were consistent with the theoretical values, and the polydispersities were all distributed within desirable range, which can prove the advantages of calculable molecular weight and narrow polydispersity of RAFT polymerization.

3.2. Colorimetric properties

The absorption properties of Na, NaI and PNa under different proton concentrations were investigated in mixed solvent of DMSO/H_2O (v/v = 1:1). The concentration of Na and NaI were 10^{-5} M and the naphthalimide segment in PNa was equivalent to 1×10^{-5} M, too. Upon addition of protons from pH 12 to −0.7 (equivalent to 5 M), the absorption bands of both Na and PNa were blue-shifted about 23 nm and 25 nm respectively, contrarily, the maximum wavelength of NaI was nearly unchanged, as listed in Table 1 (See Figure S5, Figure S6 and Figure S7 for the absorption spectra of Na, NaI and PNa). The only difference between Na and NaI was the quarterization of the alkylated amine, thus the blue-shift should be ascribed to the protonation of alkylated amino of Na and PNa, and further protonation of the aromatic amines do not result in any further blue-shift.

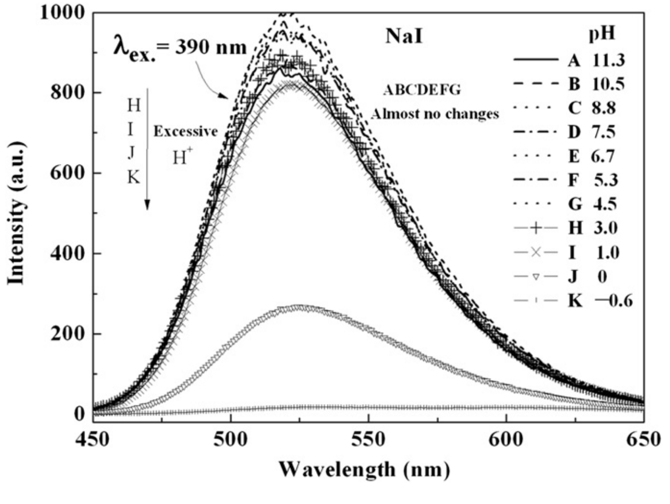

Fig. 2. Fluorescent spectra of NaI on addition of various concentrations of proton in the mixed solvent.

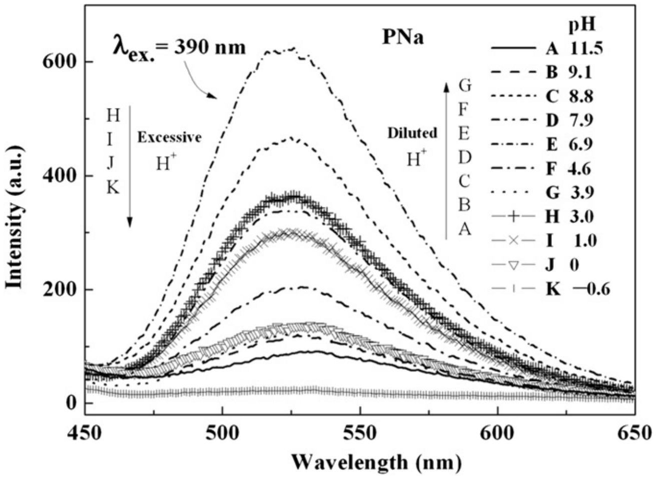

Fig. 3. Fluorescent spectra of PNa on addition of various concentrations of proton in the mixed solvent.

3.3. Fluorescent properties

The fluorescent properties of Na, NaI and PNa were also studied in the same mixed solvent at the same concentrations with those in the colorimetric study. As shown in Fig. 1, because of the PET effect of the alkylated amine, the fluorescent intensity of Na was very weak. When pH values changed from 11 to 3.5 (A–G), the fluorescence of Na increased, which was due to the inhibition of the PET process from the alkylated amine to the naphthalimide after the protonation of the alkylated amine. This can be substantiated by the spectra of NaI, as shown Fig. 2. Because of the methylation of the alkylated amine, no obvious changes were observed when pH values changed through the same range, from 11.3 to 3.0 (A–H). Thus in this pH range (11–3.5), Na acted as fluorescence enhancement chemosensor, switch status changing from "Off" to "On". While further proton addition brought opposite fluorescent

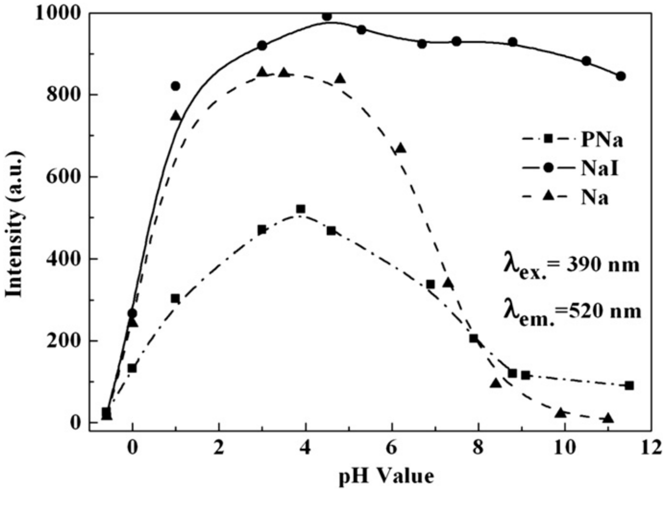

Fig. 4. Fluorescent intensity versus pH for Na, NaI and PNa.

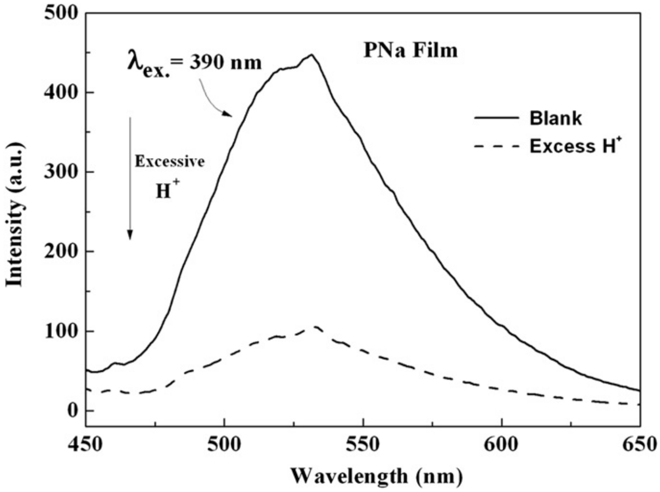

Fig. 5. Fluorescent spectra of PNa processed on thin polymer film.

property, as can be seen from H to K in Fig. 1, the fluorescent intensity of Na decreased steeply to about 1/50 of its original level at pH 3.5 on addition of high concentration proton, this fluorescent changes were probably caused by the protonation of the aromatic amine at much lower pH value, and the electronic dense was substantially changed [14]. Thus in this pH range (from 3 to −0.6), Na acted as fluorescence-decrease chemosensor, switch status changing from “On” to “Off”. This diprotonation of both aromatic and alkylated amine was better supported by the fluorescent spectra of NaI, which present similar behavior when high concentrated proton was added, because only the aromatic amine could be protonated for NaI. In fact, the spectra of Na in high proton concentrations should be the sum of that of diprotonated and monoprotonated species [6]. The fluorescent changes were not only optical, but also naked eyes recognizable under ultraviolet lamp at 365 nm, as presented in the graphic abstract.

The main changing trend of PNa (Fig. 3) was consistent with those of Na. However, though the fluorescent intensity of PNa was not as strong as Na’s, the “Off-On-Off” changes, upon addition of various concentrations of proton, were much obvious than Na. the changing point of PNa was exactly at pH 3.5, while for Na, it ranged from pH 2.6–4.6, as shown in Fig. 4. In the polymer solution, there were several chromophores on each flexible chain of the polymers, therefore, compared to the monomer detecting system, the polymer solution would be much easier to recognize proton in the solution [8,15] and thus displayed more sensitive fluorescent changes.

The effect of proton on fluorescence in thin polymer films of about 10 μm was also investigated. The polymer films were immersed in proton solution (pH = 3.5), and after drying for 20 min the absorbance spectra were monitored, the band at 530 nm dramatically decreased, as can be seen in Fig. 5, with quenching effect of 76.6%. The quenching effect could also be observed under ultraviolet lamp at 365 nm, as shown in the graphic abstract. On the basis of the present investigation, it can be assumed that the polymer sensors can be made and applied as convenient detecting apparatus for environmental researchers for detection of proton.

4. Conclusion

A new polymeric chemosensor (PNa) for the selective detection of proton was synthesized by RAFT polymerization. The polymer and the monomer showed both fluorescence enhancement in low proton concentration solution and fluorescence suppression in high proton concentration solution. The better sensitivity of PNa than Na was also observed. NaI was synthesized to successfully investigate the “Off-On-Off” mechanism. Thin PNa film also showed fluorescent changes upon addition of proton.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.10.003.

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