

# Synthesis and Properties of a New Green Water-Soluble Polymer for Proton and Metal-Cation Sensing

Yulin Hu, Baoyan Wang, Zhixing Su

*Institute of Polymer and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China*

Received 16 March 2008; accepted 9 August 2008

DOI 10.1002/app.29215

Published online 6 November 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A novel water-soluble colored polymer, based on 1,8-naphthalimide, was synthesized through a series of easy reactions with high yields. It emitted green fluorescence both in an aqueous solution and in a solid state. Fluorescence characteristics of the polymer as a function of pH were investigated in aqueous solutions. The polymer solution showed weaker fluorescence in a more acidic medium. When the pH of the solution was higher than 5, stronger fluorescence could be seen with a  $pK_a$  value of 3.5. The presence of metal cations ( $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,

$Cu^{2+}$ , and  $Zn^{2+}$ ) could quench the fluorescence intensity of an aqueous solution of this polymer to different levels. It was highly sensitive to  $Cu^{2+}$  and  $Fe^{3+}$  present in the studied system. The results suggest that this newly synthesized compound could work as a polymeric sensor responding to water polluted by  $Cu^{2+}$ ,  $Fe^{3+}$ , and protons. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1931–1935, 2009

**Key words:** fluorescence; metal-polymer complexes; photophysics; sensors

## INTRODUCTION

Since a fluorescent polymeric material was first proposed by Wolf and Pressley in 1963,<sup>1</sup> syntheses and studies of new fluorescent polymers have continued for decades. Stomphorst et al.<sup>2</sup> indicated that polymer matrices can prevent dye molecules from aggregating in water and organic solvents. Fluorescent polymers include polymers with pendant chromophores and polymers with chromophores in their backbone. Thus, the development of a new functional fluorescent compound is important for expanding the utilization of fluorescent polymers.

1,8-Naphthalimide derivatives are remarkable for their high stability and quantum yield, which make them well known among solvatochromic fluorophores. The design of new 1,8-naphthalimide derivatives and their use as proton and ion probes based on the mechanism of photoinduced electron transfer (PET) have been reported in several articles recently.<sup>3–6</sup> In the PET model, the quenching of the excited state of the fluorophore can be observed because of the intermolecular electron transfer from the receptor to the excited 1,8-naphthalimide. Upon recognition of species such as metal cations, the electron availability of the receptor is reduced, and so PET is inhibited and the fluorescence intensity is enhanced.

With its intrinsic fluorescence, norfloxacin (NF) has been widely studied for its photophysical and photochemical properties because of intramolecular electron transfer from the nitrogen on the piperazinyl ring to the aromatic fluoroquinolone system.<sup>7–10</sup>

A novel water-soluble colored polymer, based on 1,8-naphthalimide, was synthesized through a series of easy reactions with a high yield. This colored polymer emitted green fluorescence in both aqueous solutions and in a solid state. The effects of protons and six metal cations ( $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ ) on the fluorescence of this colored polymer were investigated; protons and metal cations quenched the fluorescence of the polymer solution. The mechanism of the fluorescence quenching that we propose here is rather different from the previous proposal and is discussed in detail.

## EXPERIMENTAL

### Materials

4-Bromo-1,8-naphthalic anhydride (BNa) was purchased from Anshan Hifi Chemicals Co., Ltd. (Liaoning, China). NF (analytical-grade) was purchased from Shenda Industry and Trade Co. (Guangxi, China). Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The acrylamide (AM) monomer was analytical-grade and was used directly. Acrylic acid and benzoyl chloride, which were used to prepare acryloyl chloride, were analytical-grade. Triethylamine (Tianjin Chemistry Reagent Co.) was refluxed with acetic anhydride, then distilled, refluxed with KOH, and again distilled. All

Correspondence to: Z. Su (suzx@lzu.edu.cn).

other chemicals such as *N,N*-dimethylformamide (DMF), ethanol, and other reagents were analytical-grade, and the water used in this work was doubly distilled.

### Instrumentation

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 670 FTIR spectrophotometer (Nicolet, USA).  $^1\text{H-NMR}$  experiments were performed on a Bruker 400-MHz BB spectrometer (Bruker Daltonics, USA) for compound **3** in  $\text{CCl}_3\text{D}$  and for compound **1** in  $\text{D}_2\text{O}$ . Mass spectroscopy for compound **3** was performed on a HP 5988 A (Hewlett Packard, USA) instrument. Elemental analysis was carried out on an Elementar Analysensysteme GmbH VarioEL V3.00 elemental analyzer. Fluorescent excitation and emission spectra were recorded with an LS 55 luminescence spectrometer (PerkinElmer, USA). The pH of the solutions was adjusted with a pHs-25 digital meter (Shenqci Co., Shanghai, China).

### Synthesis of the colored water-soluble polymer (see Scheme 1)

#### Synthesis of compound **4**

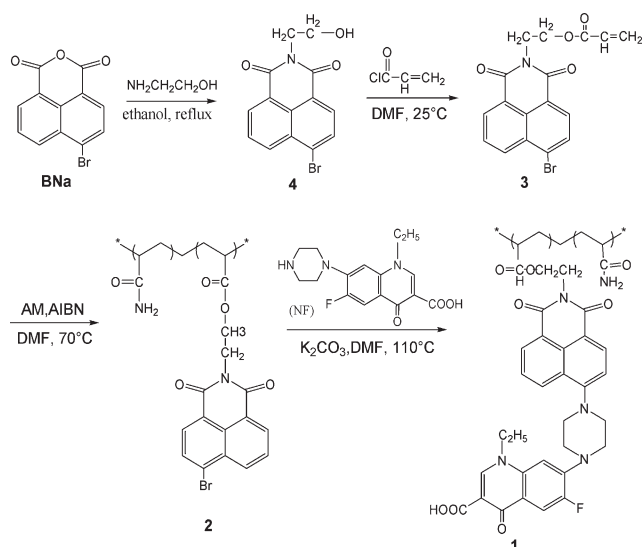
According to the literature,<sup>5</sup> compound **4** was synthesized by the refluxing of BNa (4.0 g) and ethanolamine (1.0 g) in ethanol as a solvent, and the pale product of compound **4** was obtained with a yield of 82%.

FTIR (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3392 ( $\nu\text{OH}$ ), 3089 ( $\nu=\text{CH}_2$ ), 2969, 2889 ( $\nu\text{CH}_2$ ), 1697 ( $\nu\text{asN}-\text{C}=\text{O}$ ), 1664 ( $\nu\text{sN}-\text{C}=\text{O}$ ), 566 ( $\nu\text{C}-\text{Br}$ ). ANAL. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{O}_3\text{NBr}$ : C, 52.66%; H, 3.13%; N, 4.39%. Found: C, 51.15%; H, 3.18%; N, 4.27%.

#### Synthesis of compound **3**

Compound **4** (3.20 g) was mixed with 2.20 mL of triethylamine in anhydrous DMF (40 mL) and was reacted with 1.50 mL of acrylic chloride for 5 h at room temperature. The reaction mixture was cooled, poured into water (120 mL), and filtered. A pale yellow solid (2.78 g) was obtained with a yield of 74.5%.

FTIR (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3066 ( $\nu=\text{CH}_2$ ), 2958 ( $\nu\text{CH}_2$ ), 1725 ( $\nu\text{COO}$ ), 1703 ( $\nu\text{asN}-\text{C}=\text{O}$ ), 1662 ( $\nu\text{sN}-\text{C}=\text{O}$ ); 1615 ( $\nu\text{C}=\text{C}$ ); 1588, 1569 ( $\nu\text{C}=\text{C}$  benzene ring), 563 ( $\nu\text{C}-\text{Br}$ ).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 4.00 (2H, t,  $J = 13$  Hz,  $\text{CH}_2-\text{O}$ ), 4.49 (2H, t,  $J = 13$  Hz,  $\text{N}-\text{CH}_2$ ), 5.80 (1H, d,  $J = 26$  Hz,  $=\text{CH}_2$ ), 6.05 (1H, q,  $J = 18.26$  Hz,  $=\text{CH}$ ), 6.35 (1H, d,  $J = 44$  Hz,  $=\text{CH}_2$ ), 7.83 (1H, m,  $J = 8, 12$  Hz, naphthalimide, H-3), 8.05 (1H, t,  $J = 7.13$  Hz, naphthalimide, H-6), 8.40 (1H, t,  $J = 7, 11$  Hz, naphthalimide, H-2), 8.55 (1H, t,  $J = 18$  Hz, naphthalimide, H-7), 8.64 (1H, t,  $J = 7, 11$  Hz, naphthalimide, H-5). Mass spectroscopy ( $m/z$ ),  $\text{M}^+$ : 373.



Scheme 1 Synthesis process.

#### Synthesis of compound **1**

Compound **2** was synthesized by the copolymerization of monomer **3** and AM in DMF with AIBN as an initiator at 70°C for 24 h. The molar ratio of the dye to the AM monomer was 1 : 100. The precipitate was filtered and dried at room temperature to a constant weight. Then, compound **2** (1.0 g), NF molecules (0.2 g), and anhydrous potassium carbonate (0.1 g) were added to 10 mL of DMF. The suspension was heated rapidly to 110°C and refluxed for 5 h. Then, the solid product was filtered and extracted with DMF for 24 h in a Soxhlet extractor to remove the unreacted molecules. The orange copolymer of compound **1** was obtained.

FTIR (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3369 ( $\nu=\text{CH}_2$ ), 3196 ( $\nu\text{NH}_2$ ) 2934 ( $\nu\text{CH}_2$ ), 2777 ( $\nu\text{CH}$ ), 1662 ( $\nu\text{NH}_2$ ), 1612 ( $\nu\text{C}=\text{O}$ ).

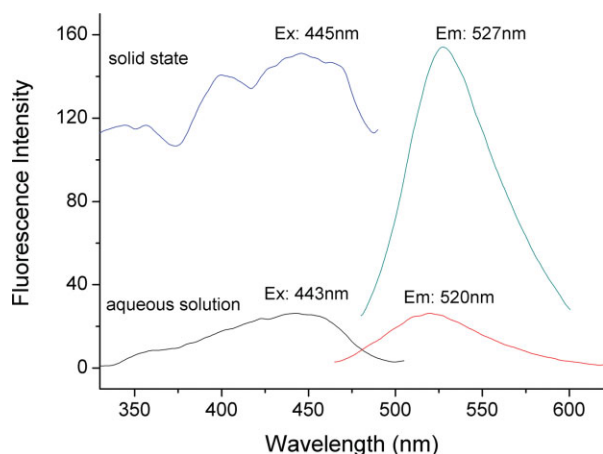
New peaks (compared to the IR spectra of polyacrylamide) appearing at 1490, 1255, 1015, 929, 896, 825, and 737  $\text{cm}^{-1}$  could be due to the dye molecules appending on the polymer chain.

$^1\text{H-NMR}$  (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ ): 1.20 (20H, q,  $\text{CH}_3$ ), 1.24 (437H, d,  $\text{CH}_2$ ), 2.02 (211H, d,  $\text{CH}$ ), 2.98–3.06 (68H, d,  $\text{N}-\text{CH}_2$  on piperaziny ring), 6.73–8.19 (48H, aromatic protons).

From the numbers of the protons, the molar ratio of the dye units to the AM units was calculated to be 1 : 44.

#### Fluorescence methods

For fluorescence emission measurements, a  $10 \times 10$  mm<sup>2</sup> quartz cell was used for detection. Fluorescence intensities against pH were obtained by the recording of the emissions in solutions with different pHs at a fixed wavelength of 443 nm. During the measurement, concentrated HCl and NaOH were used to adjust the pHs to the desired values, and



**Figure 1** Excitation and emission spectra of compound **1** in an aqueous solution and in the solid state. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the samples were used at room temperature. The pHs of the samples were changed from 0 to 11 with a digital pH controller. The effect of the metal ions on the fluorescence intensity was examined by the addition of a few microliters of a stock solution of the metal cations to a known volume of the colored polymer solution (3 mL). The addition was limited to 0.10 mL so that the dilution of the polymer solution remained insignificant.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$  were used as sources of metal cations.

## RESULTS AND DISCUSSION

### Spectral characteristics of colored compound **1** in an aqueous solution and in a solid state

The colored copolymer, compound **1**, emitted green fluorescence both in solution and in a solid state. As shown in Figure 1, compound **1** in an aqueous solution excited at about 443 nm and emitted at about 520 nm; its excitation and emission wavelengths in a solid state were 445 and 527 nm, respectively. In solution, the luminescence spectrum exhibited the characteristic of an individual chromophore because of the low concentration and separation of chromophore moieties. In the solid state, the dye molecules interacted with one another because of the high concentration. Therefore, the long wavelength band in the luminescence spectrum might have resulted from the formation of an excimer.<sup>11</sup>

### Influence of protons on the fluorescence intensity of colored copolymer **1**

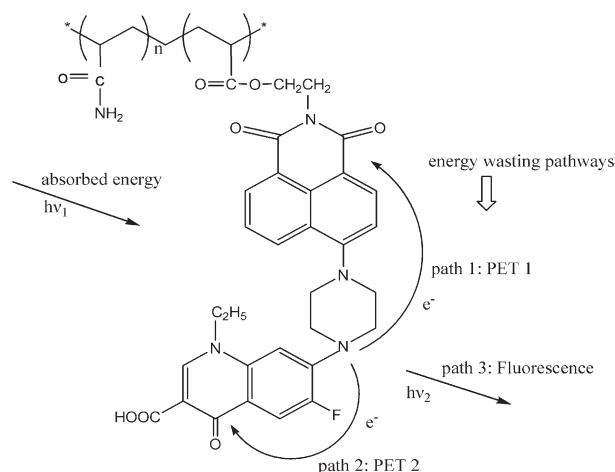
Three pathways for energy absorption by the dye appending on the polymer chain are shown in

Scheme 2. One is the PET process between photoexcited 1,8-naphthalimide and the nitrogen on the piperazinyl ring (PET 1). The second is the PET process from the nitrogen of the piperazinyl ring to the fluoroquinolone system (PET 2). These two PET processes are efficient energy-wasting pathways. In the third way, energy is emitted as fluorescence.

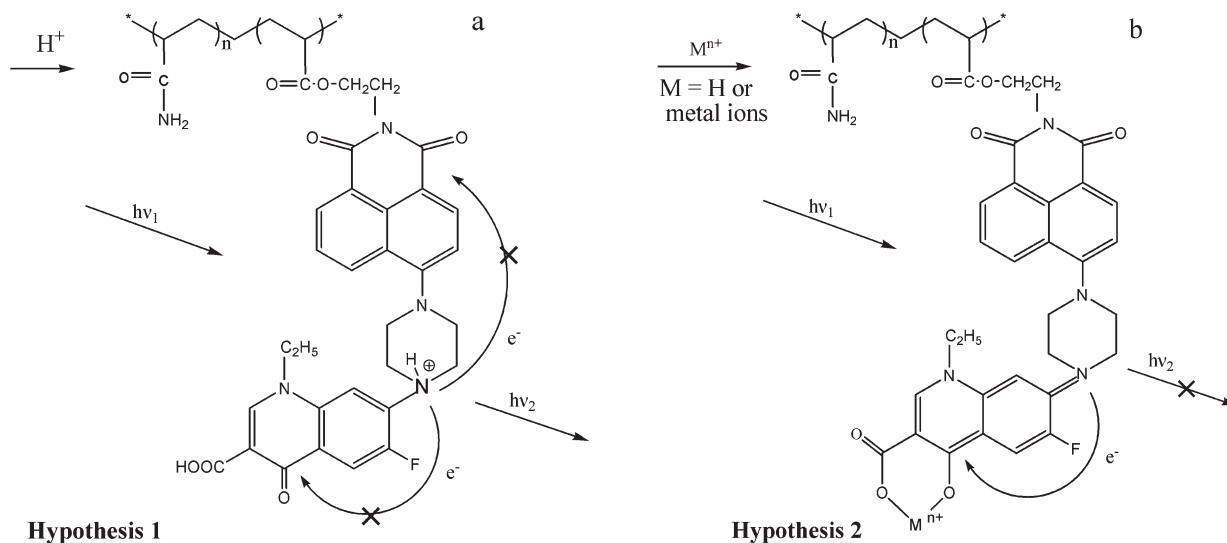
Two hypotheses for the effect of protons on dyes appending on the polymer chain are illustrated in Scheme 3. In hypothesis 1, which is shown in Scheme 3(a), the lone nitrogen pair is blocked as a result of protonation in an acidic medium. This protonation may cause the free lone nitrogen pairs to be devolved in conjugation with the aromatic fluoroquinolone system and also reduce the possibility of the PET 1 process. Neither energy-wasting pathway 1 nor energy-wasting pathway 2 will happen efficiently. Thus, the energy will be emitted as fluorescence. This will consequently lead to an enhancement of fluorescence in an acidic medium in comparison with the fluorescence intensity in a basic environment.<sup>5,6(b),6(c)</sup>

In hypothesis 2, which is shown in Scheme 3(b), the hydrogen bond between protons and oxygens of carbonyl and carboxylic acid redistributes the electrons of the aromatic fluoroquinolone system and increases the transferability of the lone nitrogen pair to the fluoroquinolone system, which accelerates the PET 2 process. This will induce fluorescence quenching in a lower pH medium because of the occurrence of efficient energy wasting in pathway 2.

The influence of protons on the photophysical properties of compound **1** in an aqueous solution was investigated in the pH range of 0.5–11. The fluorescence intensity of compound **1** against the pH is plotted in Figure 2. It shows clearly that the copolymer had a weaker fluorescence intensity in a more acidic medium. The fluorescence of compound **1** at



**Scheme 2** Three energy-wasting pathways for the absorbed energy of the colored polymer.



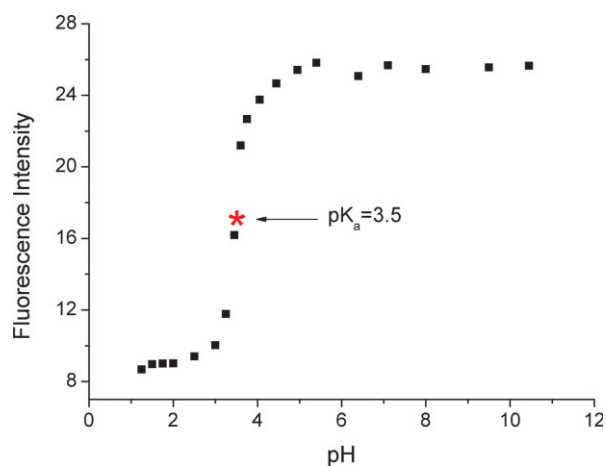
**Scheme 3** Two hypotheses for the response mechanism.

520 nm remained unaffected between pHs 11 and 5.50 and then gradually decreased from pH 5.50 to 3.00; below pH 3.00, no change in fluorescence was observed, and this led to a sigmoidal curve. The experimental results were in accordance with the mechanism of hypothesis 2. The following experiments about the response to metal cations further justify the correctness of hypothesis 2.

According to the nonlinear Gauss–Newton–Marquardt equation, the  $pK_a$  value of the immobilized indicator was 3.5:

$$pK_a = \text{pH} + \log \frac{I_x - I_b}{I_a - I_x}$$

where  $I_a$  and  $I_b$  are the intensities of the acidic and basic forms, respectively, and  $I_x$  is the intensity at a pH close to the  $pK_a$ .



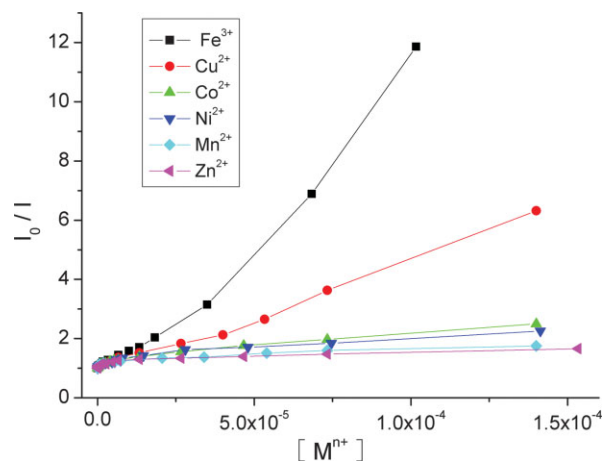
**Figure 2** pH dependence of the fluorescence intensity of the polymer solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Influence of metal cations on the fluorescence intensity of colored copolymer 1

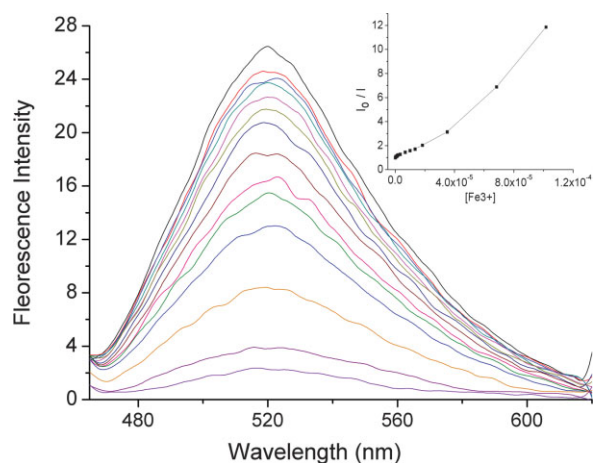
The response of compound 1 to some transition-metal cations was tested by the addition of increasing concentrations of metal cation ( $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ ) solutions to aqueous solutions of compound 1. The concentrations varied from  $1.33 \times 10^{-7}$  to  $1.5 \times 10^{-4}$  M. As shown in Figure 3, the fluorescence intensity of compound 1 decreased with the ion concentrations, and this agreed with the Stern–Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$

$Q$  is the concentration of the quencher, where  $I_0$  and  $I$  are the fluorescence intensities in the absence and presence of metal cations, respectively, and  $K_{SV}$  is the Stern–Volmer constant.



**Figure 3** Fluorescence intensity response of compound 1 in an aqueous solution to different metal cations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** Fluorescence spectra of the colored polymer in an aqueous solution in the presence of different concentrations of  $\text{Fe}^{3+}$  cations (from top to bottom, the concentrations of  $\text{Fe}^{3+}$  were 0,  $3.33 \times 10^{-7}$ ,  $6.67 \times 10^{-7}$ ,  $1.0 \times 10^{-6}$ ,  $1.33 \times 10^{-6}$ ,  $1.67 \times 10^{-6}$ ,  $3.33 \times 10^{-6}$ ,  $6.67 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$ ,  $1.33 \times 10^{-5}$ ,  $1.83 \times 10^{-5}$ ,  $3.50 \times 10^{-5}$ ,  $6.83 \times 10^{-5}$ , and  $1.02 \times 10^{-4}$  mol/L). The inset shows the dependence of the relative fluorescence intensity ( $I_0/I$ ) on the concentration of the  $\text{Fe}^{3+}$  cations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The results showed that the quenching degree of the fluorescence emission depended on the nature of the metal cations. The higher quenching effects were observed for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  cations with  $K_{\text{SV}}$  values of  $5.77 \times 10^4$  and  $3.63 \times 10^4$  L/mol, respectively. In cases with  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$  cations, the values of  $K_{\text{SV}}$  were  $1.04 \times 10^4$ ,  $8.56 \times 10^3$ ,  $5.18 \times 10^3$ , and  $3.84 \times 10^3$  L/mol, respectively. The mechanism of the fluorescence quenching caused by metal cations could also be explained by hypothesis 2, as described in Scheme 3(b). The metal cations, which have many free orbits, could be electron receptors. The formation of the complex between the metal cations and the dye molecule accelerated the PET 2 process, which induced fluorescence quenching.

The fluorescence emission spectra of aqueous solutions of compound 1 in the presence of different  $\text{Fe}^{3+}$  concentrations are presented in Figure 4 as typical examples. The range of  $\text{Fe}^{3+}$  concentrations was  $1.33 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  M.

Valeur<sup>12</sup> reported that when a cation receptor is linked to an intramolecular charge-transfer fluorophore so that the bound cation can interact with either the donor group or the acceptor group; the electron transfer process is perturbed. The resultant changes in the photophysical properties of the fluorophore can be used for sensing cations. The results from the photophysical properties of the colored copolymer in the presence of different metal cations revealed that this newly synthesized material is highly sensitive to  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ . This makes it

useful as a new polymeric sensor to detect  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  cation pollutants.

## CONCLUSIONS

A novel water-soluble colored polymer was synthesized on the basis of 1,8-naphthalimide through a series of easy reactions with high yields. It emitted green fluorescence both in aqueous solutions and in a solid state. The effects of protons and several transition-metal cations ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) on the photophysical properties of the polymer were investigated. The results showed that the fluorescence of compound 1 at 520 nm remained unaffected between pHs 10.50 and 5.50 and then gradually decreased from pH 5.50 to 3.00; below pH 3.00, no change in fluorescence was observed, and this led to a sigmoidal curve. Its  $\text{p}K_a$  value was calculated to be 3.5. In addition, the fluorescence intensity was quenched by the addition of metal cations, and this agreed with Stern–Volmer kinetics; this effect was much stronger in the presence of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ . The fluorescence quenching caused by both protons and metal cations could be due to the interaction between the cations and the dye activating the electron transfer from the nitrogen on the piperazinyl ring to the aromatic fluoroquinolone system. All these results proved that this synthesized green water-soluble luminescence polymer can be used as a novel and multifunctional fluorescent material in the future in applications such as fluorescence pH indicators and sensors for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  pollutants.

## References

- Wolf, N. E.; Pressley, R. J. *Appl Phys Lett* 1963, 2, 152.
- Stomphorst, R. G.; van der Zwan, G. *J Phys Chem A* 2001, 105, 4235.
- Li, Z.; Niu, C.; Zeng, G.; Liu, Y.; Gao, P.; Huang, G.; Mao, Y. *Sens Actuators B* 2006, 114, 308.
- Mu, H.; Gong, R.; Ma, Q.; Sun, Y.; Fu, E. *Tetrahedron Lett* 2007, 48, 5525.
- Bojinov, V. B.; Georgiev, N. I.; Nikolov, P. S. *J Photochem Photobiol A* 2008, 193, 129.
- (a) Grabchev, I.; Bojinov, V.; Betcheva, R. *J Appl Polym Sci* 2001, 81, 2463; (b) Grabchev, I.; Chovelon, J. M. *Dyes Pigments* 2008, 77, 1; (c) Grabchev, I.; Sali, S.; Betcheva, R.; Gregoriou, V. *Eur Polym J* 2007, 43, 4297; (d) Grabchev, I.; Guittonneau, S. *J Photochem Photobiol A* 2006, 179, 28.
- Navaratnam, S.; Claridge, J. *Photochem Photobiol* 2000, 72, 283.
- (a) Park, H. R.; Lee, H. C.; Kim, T. H.; Lee, J. K.; Yang, K.; Bark, K. M. *Photochem Photobiol* 2000, 71, 281; (b) Park, H. R.; Oh, C. H.; Lee, H. C.; Lee, J. K.; Yang, K.; Bark, K. M. *Photochem Photobiol* 2002, 75, 237.
- Albini, A.; Monti, S. *Chem Soc Rev* 2003, 32, 238.
- Cuquerella, M. C.; Miranda, M. A.; Bosca, F. *J Phys Chem A* 2006, 110, 2607.
- Guan, X.; Liu, X.; Su, Z.; Liu, P. *React Funct Polym* 2006, 66, 1227.
- Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley: Weinheim, 2001; Chapter 3, p 62.