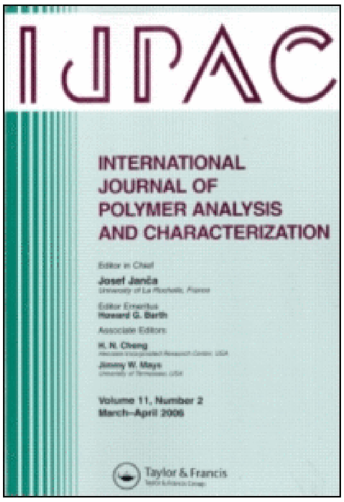

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Fluorescence Property of Poly (MMA-co-ACNF) and Its Ability to Detect Fe^{3+} Ion

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Abstract: The photophysical properties of the copolymer of methyl methacrylate and a new acryloyl derivative of norfloxacin (poly (MMA-co-ACNF)) have been studied in N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and water solutions. The ability of the poly (MMA-co-ACNF) to detect different metal cations (Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) has been evaluated in DMF solution. The results have shown clearly that only Fe^{3+} could be efficiently detected and the plot of log [Fe^{3+}] against the relative fluorescence intensity was linear for Fe^{3+} concentration in the range of 6.67×10^{-6} to 2.67×10^{-4} M.

Keywords: Fluorescence properties; Fe^{3+}; Norfloxacin; Quenching

INTRODUCTION

In recent years, environmental pollution has been a major concern in industrial societies.[1,2] The development of different sensors able to detect metal cations in soil and water sources has become a very important scientific goal. Since iron plays an important role in metabolic processes, biological materials and different dyes have been used for spectral iron detection in either immobilized or free form. The advantages of fluorescence-based sensors are well known. They are the most highly

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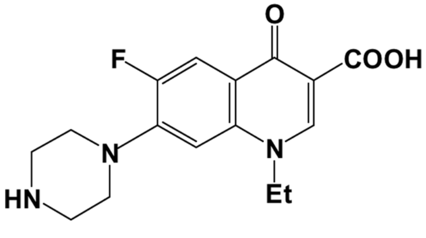
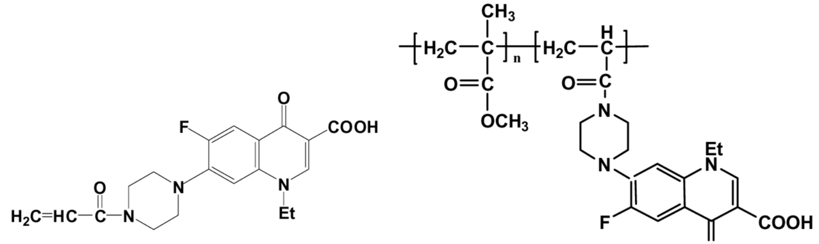
developed because of their high sensitivity, versatility, and fairly good selectivity compared to absorption sensors. Oter et al.[3] embedded a fluorescent benzofuran derivative and a synthesized Schiff base into a PVC matrix using a selective fiber optics sensor for Fe^{3+}. Capitan-Vallvey et al.[4] developed an optical sensor for determination of iron, which was based on the formation of the Fe^{3+}-eferrozine complex. An organic supra-molecular compound synthesized from pyrochatechol units was previously used as a stable chelating agent for Fe^{3+} in solution.[5] The azlactone derivative dye embedded in plasticized PVC matrix has been used in monitoring Fe^{3+} by Ozturk et al.[6] Grabchev et al.[7] evaluated the ability of the naphthalimide derivative called polyamidoamine dendrimer to detect metal cations in acetonitrile by monitoring the quenching of the fluorescence intensity. However, a limited number of studies reported the use of optical polymer sensors designed by grafting dyes on the polymer chain to avoid the pervasion out of the small molecule in use. We report here for the first time usage of poly (methyl methacrylate) grafted by 4′-N-acrylated norfloxacin for spectrofluorimetric determination of Fe^{3+}.

Fluoroquinolones (FQs) are a group of synthetic antimicrobial agents that exhibit excellent potencies and a broad spectrum of activity against a variety of gram-positive and gram-negative bacteria as well as mycoplasma. Norfloxacin (NF) [1-ethyl-6-fluoro-1,4-dihydro-4-oxoquinoline-7-(1-piperazinyl)-3-carboxylic acid] is a member of the fluoroquinolone antibiotics, which show very good antimicrobial activity against various types of bacteria. Many researchers have made use of the excellent fluorescence of FQs. They investigated the chemiluminescence system of FQs and applied the complex of NF with metal ions such as zirconium, molybdenum, vanadium, and tungsten[8] and rare earths such as Tb^{3+} and Y^{3+}[9–11] into the technology of trace determination, which could be applied in biomedical and environmental tests. The chemical structure of NF is shown in Scheme 1.

We prepared an acryloyl derivative of NF called 7-[1-(4′-N-acryloyl)-piperazinyl]-1-ethyl-6-fluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic acid



Scheme 1. Structure of NF.



ACNF

Poly (ACNF-co-MMA)

Scheme 2. Structure of ACNF and poly (MMA-co-ACNF).

(ACNF) and its copolymer with methyl methacrylate (MMA), (poly (MMA-co-ACNF)). The chemical structures of ACNF and poly (MMA-co-ACNF) are shown in Scheme 2.

The photophysical behavior of poly (MMA-co-ACNF) was measured in three different solvents, and the influence of metal ions on the fluorescence of poly (MMA-co-ACNF) was investigated in detail in view of their potential implementation as indicators of environmental pollutants.

EXPERIMENTAL SECTION

Norfloxacin (NF) of analytical grade was purchased from Shenda Industry & Trade Company (Guangxi, China). The monomer MMA was distilled from copper powder under reduced pressure before being used. Acrylic acid and benzoyl chloride, which were used to prepare acryloyl chloride, were of analytical grade. Triethylamine was refluxed with acetic anhydride and then distilled, refluxed with KOH, and again distilled. Azo-bis-isobutylonitrile (AIBN) was recrystallized from ethanol. Reagents such as N, N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were of guaranteed reagent grade and used without further purification. Water used in this work was double distilled.

ACNF was synthesized by the reaction of NF with acryloyl chloride in the presence of triethylamine. A mixture of NF (0.80 g, 0.0025 mol), triethylamine (0.70 mL, 0.0050 mol), and 20 mL chloroform was put into a 50 mL three-necked round-bottom flask equipped with a thermometer, a condenser, a dropping funnel, and a magnetic stirring bar. The flask was then maintained at 0°–5°C, while 0.41 mL of (0.0050 M) acryloyl chloride dissolved in 10 mL of chloroform was dropped into the round-bottom flask over 30 min. The reaction mixture was stirred at 5°C for 2 h and then kept at room temperature overnight. The chloroform solution was removed by vacuum roto-evaporation. The resulting solid was filtered and washed three times with methanol, then purified by silica gel column chromatography. Sequential elution of the compound with chloroform: methanol = 3:1 was used to separate the product. Yield = 45%. Mp 256°–258°C.

Characterization: UV (dissolved in DMF) $\lambda_{max} = 283\,nm$ (ε, 40740 L $mol^{-1}\ cm^{-1}$), 325 nm (ε, 12400 L $mol^{-1} cm^{-1}$); ^1H NMR (CCl_3D, 200 MHz, ppm) δ: 1.59 (3H, $-CH_3$), 3.33–3.86 (8H, piperazine N-CH_2), 4.3 (2H, N_1-CH_2), 5.82 (1H,=CH–), 6.41–6.55 (2H,=CH_2), 6.87 (1H, ArH), 8.10 (1H, ArH), 8.70 (1H, ArH). FT-IR (KBr, $\tilde{v}/cm^{-1}$): 3051 (ν=CH_2), 1604 (νC=C), 919 (δ=CH_2), 1724 (νC=O), 1635 (νO=CN–), 1619 (νCOO^-). MS, m/z calculated for molecule = 373.13; 373.13; found (M+H): 374.14, error = 0.8 ppm. Elemental analysis, calculated for $C_{19}H_{21}FN_3O_4$: 61.16% C, 5.67% H, 17.15% O; found: 61.21% C, 5.60% H, 17.25% O.

The poly (MMA-co-ACNF) was prepared by the copolymerization of ACNF and MMA with AIBN as a thermal initiator. A solution of 0.075 g (2.0×10^{-4} mol) ACNF, 1.0 g (1.0×10^{-2} mol) MMA, and 0.016 g (1×10^{-4} mol) AIBN in 5 mL DMF was introduced into a dry polymerization tube. The solution was deoxygenated by purging with N_2 gas for 5 min. The tube was sealed and placed in a regulated thermostat bath at 70°C for 24 h. The solution was allowed to precipitate in excessive methanol. After the product was redissolved in DMF, it was filtered and reprecipitated into methanol. Acetone, CCl_3, DMF, and DMSO were the good solvents of the resulting solid. The molar concentration of the dye molecule in the copolymer was 1.21% as determined by ultraviolet spectrophotometry. FT-IR (KBr, $\tilde{v}/cm^{-1}$): 2997 (νCH_3), 2952 (νCH_2), 2844, 1731 (νC=O), 1677 (νO=CN–), 1626 (νCOO^-), 1482 (δ CH_2), 1450 (δ_{as} CH_3), 1387 (δ_s CH_3). ^1H NMR (CCl_3D, 200 MHz, $\geq$4.5 ppm) δ: 6.80 (1H, ArH), 8.00 (1H, ArH), 8.63 (1H, ArH).

IR spectra were recorded on a Nicolet Neus 670 Fourier transform-infrared (FT-IR) spectrophotometer. ^1H nuclear magnetic resonance (NMR) experiments were performed on an Avance DRX 200 MHz (Bruker Daltonics, USA) for the monomer and macromolecule ligand in $CDCl_3$. Mass spectroscopy (MS) and elemental analysis were performed on an APEXIIFT-MS (Bruker Daltonics, USA). Fluorescent excitation and emission spectra were measured with an LS 55 Luminescence Spectrometer (Perkin Elmer). UV-visible spectra were measured by a Lambda 35 UV/Vis Spectrometer (Perkin Elmer). All of the absorption spectra have the absorption of the solvents eliminated.

The stock polymer solution was directly dissolved with DMF and stored at 0°–5°C away from light. The working solutions were freshly prepared by diluting 0.5 mL of the stock solution with DMF, DMSO, and water to 10.00 mL.

The effect of the metal cations on the fluorescence intensity was examined by adding a few microliters of stock solution of the metal cations to a known volume of the polymer solution (3.0 mL). The addition was limited to 0.1 mL, so that the dilution of the polymer solution remained insignificant.[7,12] $CuCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, and $CoCl_2{\cdot}6H_2O$ were used as sources of metal cations.

RESULTS AND DISCUSSION

UV-Vis Absorption and Fluorescence Emission Spectroscopy Studies

In order to perform the spectral characterization of poly (MMA-co-ACNF), absorption, excitation, and emission spectra were recorded in the solvents DMF, DMSO, and water. Well-defined absorption maxima were at the wavelengths of 283, 281, and 283 nm with the molar extinction coefficients of 480, 480, and 510 $L\,mol^{-1}\,cm^{-1}$ in the solvents

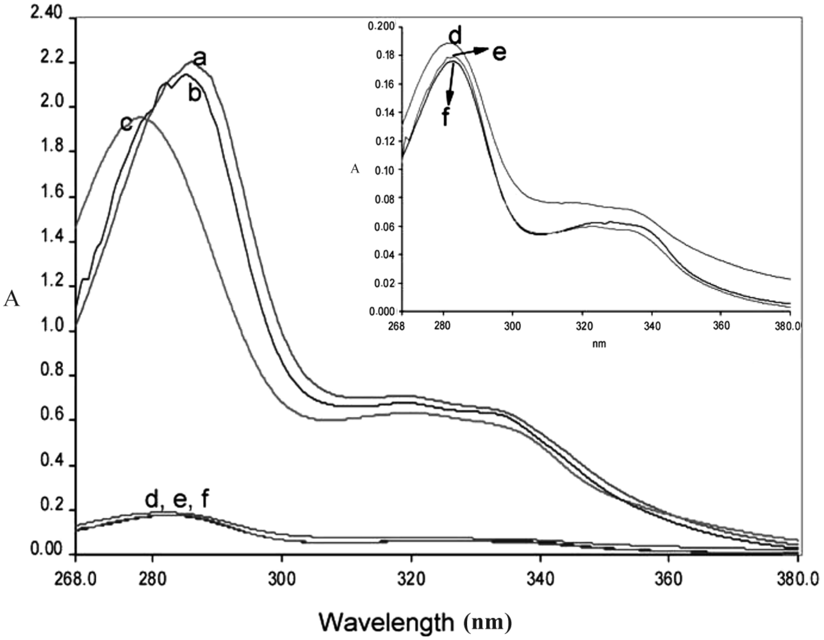


Figure 1. UV-Vis absorption spectra of 5.4×10^{-5} mol/L ACNF in DMF (b), DMSO (a), and water (c) solutions and UV-Vis absorption spectra of 3.65×10^{-4} mol/L poly (MMA-co-ACNF) in DMF (e), DMSO (f), and water (d) solutions.

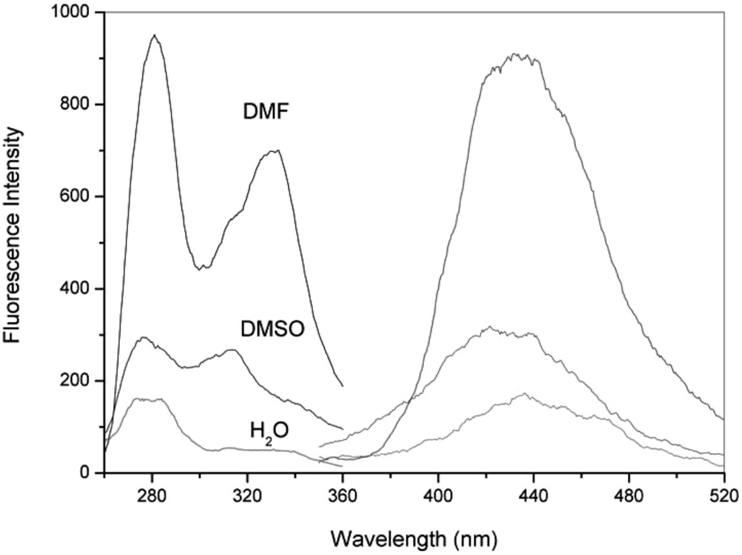


Figure 2. Excitation (left) and emission (right) spectra of poly (MMA-co-ACNF) in DMF, DMSO, and water solutions ($\lambda ex = 280\,nm$).

DMF, DMSO, and water, respectively. The absorption maxima of the shoulders that appeared in longer wavelengths were not obvious in the solvents. As shown in Figure 1, the absorption positions of ACNF and poly (MMA-co-ACNF) were similar. It indicated that the polymer chain of PMMA had no influence on the absorption of the dye molecule in the polymer chain but acted just as a thinner and carrier.

Figure 2 represents the excitation and emission spectra of poly (MMA-co-ACNF) in DMF, DMSO, and water solutions. Poly (MMA-co-ACNF) was characterized by an intense excited band with a maximum in the 260–290 nm regions and a weaker band centered at 300–350 nm. The fluorescence emission was recorded at $\lambda ex \approx 280\,nm$. In DMF, the emission spectra of poly (MMA-co-ACNF) were strong, broad structureless bands with a large Stokes shift. The emission intensity in water solution decreased and the maximal wavelength exhibited a bathochromic shift.

Response to Metal Ions

Relative fluorescence intensity (I/I_0) has been used as a quantitative measure of the effect of metal cations on fluorescence intensity. I_0 is the fluorescence intensity of the solution free of metal cations and I is

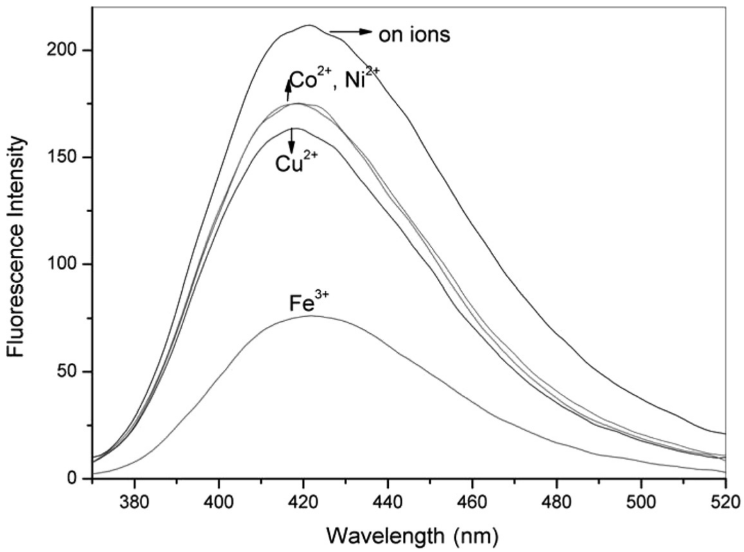


Figure 3. Emission spectra of poly (MMA-co-ACNF) in DMF with different ions. The mass concentration of ions was 1.33×10^{-4} mol/L.

the fluorescence intensity of the solution after metal cation addition. The I/I_0 values observed in the presence of Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} cations at the same concentration of $1.33 \times 10^{-4} \mathrm{mol\,L^{-1}}$ were 0.36, 0.83, 0.83, and 0.77, respectively (as shown in Figure 3). Fe^{3+} ions exhibited remarkable fluorescence intensity quenching to poly (MMA-co-ACNF), while the effects of Cu^{2+}, Co^{2+}, and Ni^{2+} were less pronounced. The selective and strong response of dye to Fe^{3+} can be attributed to the strong quencher characteristic of Fe^{3+}. This quenching effect of poly (MMA-co-ACNF) may be related to an energy transfer from the dye molecule part to the metal complex part by the formation of a complex between the macromolecular ligand and added Fe^{3+} cations.[12]

Figure 4 shows comparative response of poly (MMA-co-ACNF) to Fe^{3+} in DMF solutions. The dependence of the relative fluorescence intensity (I/I_0) versus the logarithm of concentration of Fe^{3+} (log [Fe^{3+}]) in the concentration range of 6.67×10^{-6} to 2.67×10^{-4} mol/L exhibits quite good linear correlation described by a function $I/I_0 = -1.31 - 0.43 \log [Fe^{3+}]$ with the correlation coefficient $R^2 = 0.99$.

The highly selective quenching effect and a good linear correlation produced by Fe^{3+} cations may therefore be utilized for the detection of

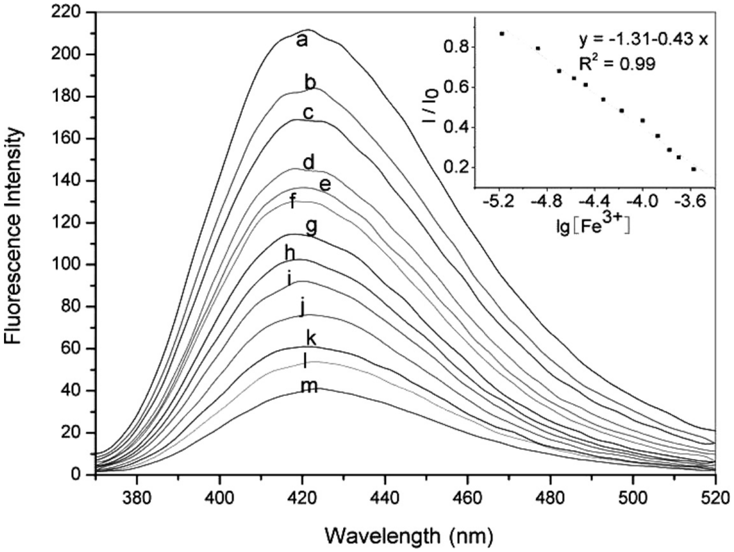


Figure 4. Fluorescence spectra of poly (MMA-co-ACNF) in DMF solution ($\lambda ex = 280\,nm$) at various concentrations of Fe^{3+} cations. The concentrations of Fe^{3+} are in the order of decreasing intensity (a) 0, (b) 6.67×10^{-6}, (c) 1.33×10^{-5}, (d) 2.0×10^{-5}, (e) 2.67×10^{-5}, (f) 3.33×10^{-5}, (g) 4.67×10^{-5}, (h) 6.67×10^{-5}, (i) 1.00×10^{-4}, (j) 1.33×10^{-4}, (k) 1.67×10^{-4}, (l) 2×10^{-4}, and (m) $2.67 \times 10^{-4}\,mol\ L^{-1}$. The poly (MMA-co-ACNF) concentration is $5.0 \times 10^{-3}\,mol\,L^{-1}$. The insert shows the plot of the relative fluorescence intensity (I/I_0) vs. the logarithm of concentration of Fe^{3+} (log [Fe^{3+}]).

this cation in the environment. The applied polymer is expected to serve as a new polymer-based metal ion sensor to iron (III) ion.

CONCLUSION

The photophysical characteristics of synthesized poly (MMA-co-ACNF) have been studied in DMF, DMSO, and water solutions. Different ions (Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) have been used to determine the sensitiveness of poly (MMA-co-ACNF) to metal ions. In the presence of these metal cations the fluorescence intensity of poly (MMA-co-ACNF) is quenched, and the quenching depends strongly on the nature of metal cations. The results revealed that the new poly (MMA-co-ACNF) has a high selectivity and sensitivity to Fe^{3+} cations and could be a reliable sensor of Fe^{3+} pollution.

REFERENCES

[1] De Silva, A. P., N. Q. N. Gunatatne, T. Gunnlauggson, A. J. M. Huxley, C. P. McCoy, J. T. Radmancher, and T. E. Rice. (1997). Signaling recognition events with fluorescent sensors and switches. *Chem. Rev.* **97**, 1515.

[2] Rurack, K. (2001). Flipping the light switch 'ON' – The design of sensor molecules that show cation-induced fluorescence enhancement with heavy and transition metal ions. *Spectrochim. Acta Part A* **57**, 2161.

[3] (a) Oter, O., K. Ertekin, C. Kirilmis, M. Koca, and M. Ahmedzadeb. (2007). Characterization of a newly synthesized fluorescent benzofuran derivative and usage as a selective fiber optic sensor for Fe(III). *Sens. Actuators B* **122**, 450–456; (b) Oter, O., K. Ertekin, R. Kılıncarslan, M. Ulusoy, and B. Cetinkaya. (2007). Photocharacterization of a novel fluorescent Schiff Base and investigation of its utility as an optical Fe3t sensor in PVC matrix. *Dyes Pigm.* **74**, 730–735.

[4] Capitan-Vallvey, L. F., E. Arroyo, C. Berenguer, M. D. Fernandez-Ramos, and R. Avidad. (2001). Single-use optical sensor for the determination of iron in water and white wines. *Fresenius' J. Anal. Chem.* **369**, 139–144.

[5] Mlika, R., H. B. Quada, R. Kalfat, G. Gamoudi, F. Mhenni, and N. Jaffrezic-Renault. (1997). Thin sensitive organic membranes on selective iron-ion sensors. *Synth. Met.* **90**, 239–243.

[6] Ozturk, G., S. Alp, and K. Ertekin. (2007). Fluorescence emission studies of 4-(2-furylmethylene)-2-phenyl-5-oxazolone embedded in polymer thin film and detection of Fe^{3+} ion. *Dyes Pigm.* **72**, 150–156.

[7] Grabchev, I., J. M. Chovelon, and C. Petkov. (2007). An iron(III) selective dendrite chelator based on polyamidoamine dendrimer modified with 4-bromo-1,8-naphthalimide. *Spectrochim. Acta Part A.*

[8] El-Kommos, M. E., G. A. Saleh, S. M. El-Gizawi, and M. A. Abou-Elwafa. (2003). Spectrofluorometric determination of certain quinolone antibacterials using metal chelation. *Talanta* **60**, 1033–1050.

[9] You Fangtian, Jin Linpei, and Zhao Huichun (1999). Study on fluorescence of the Tb(III)-enoxacin system and the determination of enoxacin. *Anal. Commun.* **36**, 231–233.

[10] Miao, Y., J. Liu, F. Hou, and C. Jiang. (2006). Determination of adenosine disodium triphosphate (ATP) using norfloxacin-Tb^{3+} as a fluorescence probe by spectrofluorimetry. *J. Lumin.* **116**, 67–72.

[11] Han, Y., X. Wu, J. Yang, and S. Sun. (2005). The fluorescence characteristic of the yttrium-norfloxacin system and its analytical application. *J. Pharm. Biomed. Anal.* **38**, 528.

[12] Grabchev, I. and S. Guittonneau. (2006). Sensors for detecting metal ions and protons based on new green fluorescent poly (amidoamine) dendrimers peripherally modified with 1,8-naphthalimides. *J. Photochem. Photobiol. A Chem.* **179**, 28–34.