Ag Nanoparticles-enhanced Fluorescence of Terbium-Deferasirox Complexes for the Highly Sensitive Determination of Deferasirox

Jafar ABOLHASANI,[†] Roza NADERALI, and Javad HASSANZADEH

Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

We describe the effect of different sized gold and silver nanoparticles on the terbium sensitized fluorescence of deferasirox. It is indicated that silver nanostructures, especially 18 nm Ag nanoparticles (AgNPs), have a remarkable amplifying effect compared to Au nanoparticles. Based on this observation, a highly sensitive and selective method was developed for the determination of deferasirox. Effects of various parameters like AgNPs and Tb³⁺ concentration and pH of media were investigated. Under the optimal conditions, a calibration curve was plotted as the fluorescence intensities *versus* the concentration of deferasirox in the range of 0.1 to 200 nmol L⁻¹, and detection limit of 0.03 nmol L⁻¹ was obtained. The method has good linearity, recovery, reproducibility and sensitivity, and was satisfactorily applied for the determination of deferasirox in urine and pharmaceutical samples.

Keywords Terbium-sensitized fluorescence, deferasirox, Ag nanoparticles, urine

(Received September 7, 2015; Accepted October 13, 2015; Published April 10, 2016)

Introduction

Iron overload is usually caused by repeated blood transfusions in patients with sickle cell disease and/or chronic anemia.¹ Also, people with hereditary hemochromatosis and thalassemia major develop secondary iron overload resulting from regular red blood cell transfusions. Excess iron can accumulate as hemosiderin in body organs such as the liver, spleen, and several endocrine organs. Myocardium can result from gradually impaired function of such organs and ultimately lead to death.² Iron chelation therapy with new oral chelator (deferasirox) has shown desired results for avoiding long-term problems.³

Deferasirox, 4-[(3Z,5E)-3,5-bis(6-oxocyclohexa-2,4-dien-1-ylidene)-1,2,4-triazolidin-1-yl] benzoic acid (Def), as an orally absorbed chelator of Fe³⁺ is currently used as first-line therapy for thalassemia and transfusional iron overload.⁴⁻⁶ Its long half-life (11–19 h depending on dose) provides once-daily dosing which can be present in plasma for 24 h. Single oral administration of 40 mg kg⁻¹ of the drug leads to peak plasma concentration levels of 44.4 µg mL⁻¹, approximately 1.5 h after dosing.^{7,8} Understanding whether Def plasma levels are related to specific characteristics of patients could help physicians to devise a drug regimen better tailored to the individual patient.

Few analytical methods have been reported for the determination of Def in dosage forms or biological fluids, and most of these methods are based on chromatography techniques.^{1,9,10} The electrocatalytic oxidation of Def using cyclic voltammetry, chronoamperometry and electrochemical impedance techniques has also been reported.¹¹ Manzoori has recently developed a terbium-sensitized fluorescence method for the determination of Def in biological fluids and tablets.¹²

Trivalent lanthanide ion complexes with appropriate ligands have been recently applied in useful probes and sensors in chemical and biomedical analyses, due to their specific properties and electronic structure.^{13,14} In these complexes, after excitation of the ligand by irradiation of light at its excitation wavelength, absorbed energy is transferred from the ligand to the central lanthanide ion, and emission will be obtained at its characteristic emission wavelengths.¹⁴ The upper emitting levels of the lanthanides are more effectively excited by efficient intramolecular energy transfer than the direct form, producing an enhanced fluorescence of the lanthanide by several orders of magnitude.

Lanthanide produce a narrow and long-lived (in the high microsecond or the low millisecond range) luminescence with extremely large Stokes' shift (~200 nm) and high quantum efficiency. These unique properties of lanthanide's luminescence allow for highly sensitive and selective detection methods.

Lanthanide, especially terbium-sensitized systems, are selective and are widely employed in many different fields of bimolecular and medical research, based on the fluorescence quenching or the enhancement of these chelates.¹²⁻²⁹ However, a further improvement of sensitivity of these methods would allow the detection of even lower analyte concentrations. Therefore, the combination of amplification strategies with lanthanide luminescence is a highly promising approach.

In recent years, nanoparticles have been introduced in lanthanide luminescence measurements as surface enhancers and could amplify and sensitize them.^{22-25,27-29} Yu *et al.* has reported determination of norfloxacin using Ag nanoparticles (AgNPs) enhanced chemiluminescence sensing of Tb³⁺-NFLX-Ce(IV)-Na₂SO₃ system.²³ Kamruzzaman *et al.* applied Ag nanoparticles enhanced fluorescence sensing of terbium complex for sensitive determination of fluoroquinolones.²⁴

In this work, we study metal nanoparticles-enhanced fluorescence sensing of terbium ion complexed with Def.

[†] To whom correspondence should be addressed.
E-mail: Abolhasani@iaut.ac.ir

Ag and AuNPs of different sizes were applied and it is observed that 18 nm AgNPs have remarkably strong enhancement effect on native luminescence of the terbium ions. Furthermore, increases in the fluorescence intensity were proportional to the amount of Def. Based on this effect, a simple, sensitive, efficient, and economical spectrofluorometric method was developed for the determination of Def in urine and pharmaceutical preparations.

Experimental

Materials and apparatus

Most of the applied materials were obtained from Merck (Darmstadt, Germany). Terbium(III) chloride hexahydrate ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$) was obtained from Acros Organics (Geel, Belgium) and Chloroauric acid (HAuCl_4) was purchased from Alfa Aesar (Karlsruhe, Germany). Doubly distilled deionized water (obtained from Kasra Co., Tabriz, Iran) was used throughout. A stock standard solution of 100 mg L^{-1} deferasirox (from Osveh Pharmaceutical Company, Tehran, Iran) was prepared in water and ethanol and stored at 4°C in a sealed volumetric flask, and for experiments freshly diluted in water, in order to have less than 2% ethanol.

Fluorescence spectra and intensity measurements were conducted on a Shimadzu RF-5301 spectrofluorophotometer (Japan) equipped with a quartz cell ($1 \times 1 \text{ cm}$). UV/Vis absorption spectra were obtained with a UV-1800 spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) images of the NPs were obtained using a Leo 906 transmission electron microscope (Germany).

Preparation of Au and Ag nanoparticles of different sizes

Colloidal AuNPs of approximately 8, 22, 32 nm in diameter were prepared by the reported procedures.^{30,31} The prepared NPs were stored at 4°C and characterized by transmission electron microscopy (TEM). TEM images indicated that average diameters of synthesized gold NPs were about 8 ± 1.9 , 22 ± 2.1 and $32 \pm 2.6 \text{ nm}$.

AgNPs of 18 and 38 nm in diameter were prepared according to references,^{32,33} respectively. Ag seed NPs with diameter size of about 6 nm were prepared following the literature procedure.³⁴ The resulting NPs were characterized by TEM and statistical analysis revealed that the average diameter of particles was 6 ± 1.2 , 18 ± 1.4 and $38 \pm 1 \text{ nm}$, respectively. The concentration of synthesized AgNPs (18 nm) was calculated to be $4.32 \times 10^{-7} \text{ mol L}^{-1}$.³⁵

Sample preparation

Pharmaceutical tablets containing 125 mg deferasirox were prepared from one local drug store in Tabriz. Ten tablets were ground to a fine powder and a 0.34-g aliquot of homogenized powder (about equal to one tablet) was dissolved in ethanol and then filtered through a filter paper and diluted to 250 mL to obtain a solution containing about 500 mg L^{-1} , according to the label on the tablets. This solution was diluted 100 times with double-distilled water and convenient aliquots from the diluted solution were taken for the determination of Def using the proposed procedure.

Human urine samples containing the drug concerned was obtained by adding a suitable amount of standard Def solution to the drug-free urine. An amount of 1 mL of this sample was gently mixed with 1 mL of $0.1 \text{ mol L}^{-1} \text{ Ba(OH)}_2$ and $0.1 \text{ mol L}^{-1} \text{ ZnSO}_4$ solution was put aside at room temperature for 5 min, and then centrifuged (2700g for 10 min). In this condition, any

Fig. 1 Proposed chemical structure for the Tb-deferasirox complex.

protein and reducing substances were precipitated to prevent any probable interfering effect. The clear supernatant was diluted to the appropriate concentration.³⁶

General procedure

Fluorescence determination of Def was performed as follows. Briefly, 0.75 mL Tris (Tris(hydroxymethyl)amino methane) buffer solution (0.1 mol L^{-1} , pH 7), 0.5 mL Tb^{3+} solution (0.01 mol L^{-1}) and 120 μL prepared 18 nm AgNPs solution ($\sim 4.32 \times 10^{-7} \text{ mol L}^{-1}$) were added to 5 mL calibrated flasks containing a certain amount of deferasirox standard or sample solution. The solutions were diluted to 5 mL with double-distilled water and then corresponding fluorescence intensity (at 545 nm) were recorded with excitation at 328 nm.

Results and Discussion

Terbium(III) interaction with deferasirox in the presence of AgNPs

Terbium(III) fluorescence systems are attracting more attention due to their unique emission properties and high quantum yield. Tb^{3+} solution generates a very weak fluorescence emission because of its weak absorption. In contrast, some ligands can enhance this fluorescence *via* the energy transfer process. Tb^{3+} is a good energy acceptor from the lowest triplet state of organic ligand with strong absorption in UV region. The transfer of intermolecular energy from ligands to Tb^{3+} is a well-known phenomenon.¹³⁻¹⁵

Tb^{3+} complex with deferasirox has been previously studied by Manzoori *et al.*¹² They reported that intense fluorescence can be generated from the Tb-Def complex. Here, we investigate Tb-Def complex formation and its fluorescence characteristics in the presence of Au and AgNPs. The maximum emission wavelength occurred at 490 and 545 nm for Tb^{3+} in the presence of Def, with the maximum excitation wavelength at 328 nm. These emission peaks are according respectively to $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ion, which were observed after excitation of Def and energy transfer to Tb^{3+} $^5\text{D}_4$ state.¹⁴ This is the result of 1:1 complex between Tb and Def (Fig. 1).¹² Figure 2a shows the fluorescence of the Tb-Def complex in the presence of different sizes of Au and AgNPs. It is clear that AuNPs have a decreasing effect on the fluorescence of Tb, probably due to their absorption and inner filter effect. The absorption of AuNPs completely overlap the Tb fluorescence (in 545 nm). In contrast, AgNPs can sensibly increase the fluorescence emission intensity of the Tb-Def complex. Moreover, AgNPs with 18 nm size diameter (TEM image is shown in Fig. 2b) had the most increasing effect. This increasing can lead to high sensitivity in the determination of Def.

On the other hand, the complex formation and its interaction with AgNPs were investigated with UV-Vis absorption studies

(Fig. 3). The absorption spectra of Def in ~ 300 nm shifted to high wavelengths (325 nm) in the presence of Tb. This indicates complex formation between Tb and Def. Also, the surface plasmon resonance peak of AgNPs in ~ 400 nm decreased in the presence of Def and Tb-Def complex. Investigations on low concentrations of AgNPs showed that Def and its complex with Tb can even alter the absorption peak of NPs and lead to a sensible red shift (Fig. S1, Supporting Information). This change indicates interaction between the Tb-Def complex and AgNPs. Thus, nanoparticles can modify absorption properties

of fluorophores by changing their free space absorption condition. By exciting the Tb(III)-Def-AgNPs assembly with an external light source, the energy transfers or couples between the electronically excited state and the surface plasmon in metallic nanostructures occurs leading to fluorescence improvement.

With respect to this, we can suggest that the Tb(III)-Def complex may interact with the surface plasmon electrons of AgNPs. Fluorophores are in close vicinity to AgNPs, and the increased electric field nearby NPs enhance the absorption of light by the Tb-Def-AgNPs system.^{22,23} Increasing of local excitation fields around the edges of particles also may be the reason for the observed enhancement effect of AgNPs on the luminescence of the Tb-Def complex.²²

Thus, as indicated in Scheme 1, when Tb-Def complexes on the surface of AgNPs are excited by an external light source, the energy of the electronically excited state was transferred or coupled to the surface plasmon of AgNPs. Then, luminescence was emitted by the AgNPs-Tb-Def system with the same spectral characteristics of Tb emission.

Optimization of experimental conditions

The effect of pH on the fluorescence intensity of Tb-Def-AgNPs was investigated (Fig. 4a). The maximum fluorescence intensity was obtained at pH 7, which is optimum pH value for Tb-Def complex formation. Above this pH, the hydroxylation of Tb^{3+} ions would occur. In contrast, lower pHs would probably protonated the hydroxyl groups of Def that destroy its complex

Fig. 2 a) Fluorescence spectra of Tb(III)-Def complex in the absence (4) and presence of (1) 32 nm AuNPs, (2) 22 nm AuNPs, (3) 8 nm AuNPs, (5) 38 nm AgNPs, (6) 6 nm AgNPs, and (7) 18 nm AgNPs [in optimized condition, Def: 50 nmol L^{-1}]; b) TEM image of synthesized 18 nm AgNPs.

Scheme 1 Schematic diagram of AgNPs enhanced luminescence of Tb^{3+} -Def complex.

Fig. 3 a) UV-vis absorption spectra of deferisirox, Tb^{3+} and their complexes; b) UV-vis absorption spectra of AgNPs in the absence and presence of Tb^{3+} and deferisirox [in Tris buffer (pH 7), Def: $10^{-5} \text{ mol L}^{-1}$, Tb^{3+} : $2 \times 10^{-5} \text{ mol L}^{-1}$].

Fig. 4 Effect of a) pH [Tb^{3+} : $0.0025 \text{ mol L}^{-1}$, deferasirox: $10^{-5} \text{ mol L}^{-1}$, Tris-HCl: 0.025 mol L^{-1} and AgNPs: $100 \mu\text{L}$]; b) buffer concentration [Tb^{3+} : $0.0025 \text{ mol L}^{-1}$, deferasirox: $10^{-5} \text{ mol L}^{-1}$, pH 7 and AgNPs: $100 \mu\text{L}$]; c) Tb^{3+} concentration [deferasirox: $10^{-5} \text{ mol L}^{-1}$, Tris-HCl: 0.015 mol L^{-1} , pH 7 and AgNPs: $100 \mu\text{L}$] and d) AgNPs concentration [Tb^{3+} : 0.001 mol L^{-1} , deferasirox: $10^{-5} \text{ mol L}^{-1}$, Tris-HCl: 0.001 mol L^{-1} and pH 7] on the fluorescence intensity of Tb^{3+} -Def-AgNPs system.

with Tb. In order to adjust pH to 7, several buffers (phosphate, carbonate, acetate, and Tris) were tested. In the presence of phosphate buffer, fluorescence was remarkably decreased, probably due to the complex formation between Tb^{3+} and phosphate ions. Other buffers can enhance Tb fluorescence by joining to the Tb-Def complex and replacing H_2O molecules. H_2O can decrease Tb fluorescence by non-radiative energy absorption through O-H vibrations. Tris buffer caused the highest fluorescence of all the studied buffers, due to greater tendency of Tris molecules to Tb.

Next, the effect of the concentration of Tris buffer on the fluorescence signal was investigated. It can be seen in Fig. 4b that the fluorescence of Tb-Def-AgNPs improves when increasing the Tris concentration up to 0.015 mol L^{-1} and then decreases gradually. Tris molecules in lower concentrations do not completely bind to terbium ions, leading to a decrease in fluorescence.

The effect of concentration of fluorescent reagent (Tb^{3+}) was studied in the range of $3 \times 10^{-3} - 35 \times 10^{-3} \text{ mol L}^{-1}$ (Fig. 4c). The maximum sensitivity was obtained in $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Tb}^{3+}$. Below this concentration, there is not a sufficient amount of Tb^{3+} for complex formation with Def.

Finally, effect of the amount of AgNPs on the fluorescence intensities was studied (Fig. 4d). The fluorescence intensity of the Tb^{3+} -DFX system reached a maximum when $120 \mu\text{L}$ of synthesized AgNPs solution was added.

Under the obtained optimum conditions, the fluorescence intensity was stable for about 100 min after addition of all

Table 1 Interference of different ions on the determination of deferasirox in optimum conditions with $1 \mu\text{mol L}^{-1}$ Def

Coexisting substance	Tolerance limit	$\Delta F\%$ variation
Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Cl^- , NO_3^-	6000	< 2.6%
Mg^{2+} , Al^{3+} , PO_4^{3-} , Mn^{2+} , SO_4^{2-} , CO_3^{2-} , HCO_3^- , CH_3COO^-	2500	< 3.1%
Fe^{2+} , Fe^{3+} , Zn^{2+} , Cr^{3+}	500	< 1.9%
Vitamins B ₁ , B ₂ , alanine, lactose, sucrose, L-leucine, fructose, glycine	1500	< 2.3%
Glucose, ascorbic acid, oxalate, uric acid	500	< 4.0%
Citrate, Hg^{2+}	200	< 3.9%
Glutathione, cysteine, Ni^{2+} , I^- , Pb^{2+} , Cd^{2+}	100	< 4.3%

reagents because of rapid complex formation reaction between Tb^{3+} and Def. A time of 5 min was selected as the fixed time for all fluorescence intensity measurements.

The experiments show that temperature and also addition order of reagents did not have a significant effect on the fluorescence intensity. Therefore, all experiments were carried out at room temperature (25°C).

Study of interferences

In order to test the interference effect of some potentially interfering substances on the fluorescence intensity of Tb-Def-

Fig. 5 a) Fluorescence spectra of Tb^{3+} -Def-AgNPs system with various concentrations of Def and b) corresponding calibration graph [optimized condition, 1 – 12: 0.1, 0.2, 0.6, 1, 2, 6, 10, 20, 60, 100, 150, 200 nmol L^{-1} Def, respectively].

AgNPs, increasing amounts of these species were added into a solution of 50 nmol L^{-1} Def and determination was performed under the optimal conditions. The tolerable concentration ratios for interferences in relative error of $<5\%$ are shown in Table 1. As can be seen, the amounts of most of the potentially interfering species in real samples are below their tolerable levels, so there would be no interferences from these species in Def determination. On the other hand, diluting urine samples eliminated the slight interference of uric acid.

Analytical figures of merit

The fluorescence intensity of the proposed system is proportional to the Def concentration and based on this phenomenon a sensitive method was developed for the determination of Def. In optimum conditions, the fluorescence intensity (F) was plotted versus the concentration of Def in $\mu\text{mol L}^{-1}$ (C). The calibration graph and corresponding fluorescence spectra are shown in Fig. 5. The linear dynamic range was 0.1 – 200 nmol L^{-1} , with a detection limit (3σ) of 0.03 nmol L^{-1} . The regression equation was: $F = 82.42C + 99.5$ with a correlation coefficient of 0.9999. The relative standard deviations (RSD%) for five replicate determinations of 1, 30 and 150 nmol L^{-1} Def were 3.22, 1.86 and 1.34%, respectively. These results indicate that this terbium-AgNPs system has good linearity, relatively high sensitivity and adequate precision.

Analysis of real samples

The procedure was easily applied to the determination of Def in pharmaceutical and human urine samples (Tables S1 and S2, Supporting Information). In order to validate the method, known quantities of Def were added into the samples before the pretreatment step, and then the samples were prepared and analyzed according to the general procedure (Tables S1 and S2, Supporting Information). Statistical analysis of these results using Student t-test showed that there are no significant differences between the added and found values.

Conclusions

The effect of Au and AgNPs of different size was studied on the fluorescence emission of the deferasirox-Tb(III) complex. AgNPs with diameter size of 18 nm indicated the best positive effect. Based on this effect, a sensitive method for the simple determination of deferasirox has been developed. The method was applied for the determination of deferasirox in pharmaceutical and spiked human urine samples without complex pretreatment.

Supporting Information

Supporting Information includes results for the determination of Def in the real samples (Tables S1 and S2). This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. H. Pligoropoulou, A. Vonaparti, and I. Panderi, *J. Chromatogr. B*, **2012**, 893–894, 114.
2. N. F. Olivieri, *N. Engl. J. Med.*, **1999**, 341, 99.
3. J. J. Meerpohl, G. Antes, G. Rücker, N. Fleeman, E. Motschall, C. M. Niemeyer, and D. Bassler, *Cochrane Database Syst Rev*, 2012;2:CD007476. doi:10.1002/14651858.CD007476.pub2.
4. M. Otto-Duessel, M. Aguilar, N. Hanspeter, R. Moats, and J. C. Wood, *Exp. Hematol.*, **2007**, 35, 1069.
5. E. Wimazal, T. Nosslinger, C. Baumgartner, W. R. Sperr, M. Pfeilstocker, and P. Valent, *Eur. J. Clin. Invest.*, **2009**, 39, 406.
6. G. Metzgeroth, D. Dinter, B. Schultheis, A. Dorn-Beineke, K. Lutz, O. Leismann, R. Hehlmann, and J. Hastka, *Ann. Haematol.*, **2009**, 88, 301.
7. A. S. Ibrahim, T. Gebermarian, Y. Fu, L. Lin, M. I. Hussein, S. W. French, J. Schwartz, C. D. Skory, J. E. Edwards, and B. J. Spellberg, *J. Clin. Invest.*, **2007**, 117, 2649.
8. F. Mattioli, M. Puntoni, V. Marini, C. Fucile, G. Milano, L. Robbiano, S. Perrotta, V. Pinto, A. Martelli, and G. L. Forni, *Eur. J. Haematol.*, **2015**, 94, 310.
9. G. J. M. Bruin, T. Faller, H. Wiegand, A. Schweitzer, H. Nick, J. Schneider, K. O. Boernsen, and F. Waldmeier, *Drug Metab. Dispos.*, **2008**, 36, 2523.
10. M. C. Rouan, C. Buffet, L. Masson, F. Marfil, H. Humbert, and G. Maurer, *J. Chromatogr. B*, **2001**, 754, 45.
11. M. Hajjizadeh, A. Jabbari, H. Heli, A. A. Moosavi-Movahedi, A. Shafiee, and K. Karimian, *Anal. Biochem.*, **2008**, 373, 337.
12. J. L. Manzoori, A. Jouyban, M. Amjadi, V. Panahi-Azar,

- E. Tamizi, and J. Vaez-Gharamaleki, *Luminescence*, **2011**, 26, 244.
13. J. P. Leonard and T. Gunnlaugsson, *J. Fluoresc.*, **2005**, 15, 585.
14. A. Dossing, *Eur. J. Inorg. Chem.*, **2005**, 8, 1425.
15. A. Gomez-Hens and M. P. Aguilar-caballos, *TrAC, Trends Anal. Chem.*, **2002**, 21, 131.
16. A. S. Ndao, A. Buzady, J. Erostyak, and I. Hornyak, *J. Fluoresc.*, **2008**, 18, 649.
17. A. V. Yegorova, Y. V. Scripinets, A. Duerkop, A. A. Karsyov, V. P. Antonovich, and O. S. Wolfbeis, *Anal. Chim. Acta*, **2007**, 584, 260.
18. A. Jouyban, M. Shaghghi, J. L. Manzoori, J. Soleymani, and J. Vaez-Gharamaleki, *Iranian J. Pharm. Res.*, **2011**, 10, 695.
19. F. Yu, L. Li, and F. Chen, *Anal. Chim. Acta*, **2007**, 610, 257.
20. A. Ruiz-Medina, E. J. Llorent-Martinez, P. Ortega-Barrales, and M. L. F. D. Cordova, *Appl. Spectrosc. Rev.*, **2011**, 46, 561.
21. S. M. Z. Al-Kindy, Z. Al-Harasi, F. E. O. Suliman, A. Al-Hamadi and A. Pillay, *J. Fluoresc.*, **2009**, 19, 249.
22. A.-M. Alam, M. Kamruzzaman, S. H. Lee, Y. H. Kim, S. Y. Kim, G. M. Kim, H. J. Jo, and S. H. Kim, *Microchim. Acta*, **2012**, 176, 153.
23. X. Yu, Z. Jiang, Q. Wang, and Y. Guo, *Microchim. Acta*, **2010**, 171, 17.
24. M. Kamruzzaman, A. M. Alam, S. H. Lee, Y. H. Suh, Y. H. Kim, G. Y. Kim, and S. H. Kim, *Microchim. Acta*, **2011**, 174, 353.
25. M. N. Khan, J. Shah, M. Rasul Jan, and S. H. Lee, *J. Fluoresc.*, **2013**, 23, 161.
26. E. J. Lorent-Martinez, J. Jimenez-Lopez, I. Delgado-Blanca, P. Ortega-Barrales, and A. Ruiz-Medina, *Anal. Lett.*, **2013**, 46, 1816.
27. S. H. Lee, S. M. Wabaidur, Z. A. Alothman, and S. M. Alam, *Luminescence*, **2011**, 26, 768.
28. H. C. Zhao, F. Ding, X. Wang, H. Ju, A. Li, and L. P. Jin, *Spectrochim. Acta, Part A*, **2008**, 70, 332.
29. M. Kamruzzaman, A. M. Alam, K. M. Kim, S. H. Lee, Y. S. Suh, Y. H. Kim, S. H. Kim, and S. H. Oh, *J. Nanosci. Nanotechnol.*, **2012**, 12, 6125.
30. E. G. Zisimopoulos, G. Z. Tsogas, D. L. Giokas, N. I. Kapakoglou, and A. G. Vlessidis, *Talanta*, **2009**, 79, 893.
31. G. Frens, *Nat. Phys. Sci.*, **1973**, 241, 20.
32. J. Z. Guo, H. Cui, W. Zhou, and W. Wang, *J. Photochem. Photobiol., A*, **2008**, 193, 89.
33. H. Chen, F. Gao, R. He, and D. X. Cui, *J. Colloid Interface Sci.*, **2007**, 315, 158.
34. D. Aherne, D. M. Ledwith, and M. Gara, *Adv. Funct. Mater.*, **2008**, 18, 2005.
35. J. R. Navarro and M. H. Werts, *Analyst*, **2013**, 138, 583.
36. J. Abolhasani and J. Hassanzadeh, *Luminescence*, **2014**, 29, 1053.
-