Spectrochimica Acta Part A 83 (2011) 149–154

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A novel fluorescent sensor for Cr^{3+} based on rhodamine-cored poly (amidoamine) dendrimer

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ARTICLE INFO

Article history:
Received 24 March 2011
Received in revised form 15 July 2011
Accepted 7 August 2011

Keywords:
Poly (amidoamine) dendrimer
Rhodamine B
1-Phenyl-3-methyl-5-pyrazolone
Ring opening
Photoinduced electron transfer

ABSTRACT

A novel poly (amidoamine) (PAMAM) dendrimer, comprising rhodamine B unit in the core and 1-phenyl-3-methyl-5-pyrazolone unit at the periphery, has been synthesized and characterized. The dendrimer shows dramatic increase in its fluorescence intensity in the presence of proton and metal cations, especially in the presence of Cr^{3+}. The complex formed by dendrimer and Cr^{3+} in ethanol solution has also been studied, considering the potential application for Cr^{3+} fluorescent sensor. The influence of the unique chemical structure and resulted photoinduced electron transfer, as well as spirolactam ring-opening on the photophysical properties of the product has been investigated.

1. Introduction

Trivalent chromium ion plays an important role as a necessary trace element in human nutrition. Chromium deficiency can increase the risk of getting diabetes and cardiovascular diseases. In addition, chromium is a well-known environmental pollutant which accumulates due to agricultural and industrial activities. Due to the vital importance of chromium in biological system and industry, a narrow window of concentration between essentiality and toxicity warrants the determination of chromium. Although sophisticated analytical techniques, such as ICP-AES, X-ray fluorescence, HPLC and DPP, have been employed for trace level determination, they are of high cost and inconvenient for routine analysis. Therefore, it is important to develop a more convenient, faster, and lower cost method for trace Cr^{3+} determination, for instance, analyzing by ion-selective sensors [1–6].

A review of literature revealed that poly (amidoamine) (PAMAM) dendrimer can act as effective photoinduced electron transfer (PET) fluorosensors for metal cations and proton [7–11]. Furthermore, it was reported that PAMAM functionalized dendrimers possessing 1,8-naphthalimides at the periphery might enhance their selectivity towards some specific metal cations [12–16], such as Li^+ and Cu^{2+}. However, better design of such kind of sensors is still needed due to their bad anti-jamming ability to foreign ions and low fluorescence quantum yield. As few fluorescent PAMAM derivatives for Cr^{3+} ions were reported, the design of PAMAM-based fluorescent sensors for Cr^{3+} ion is still an attractive prospect.

Rhodamine based chemodosimetric sensors are popular for their excellent photophysical properties, such as low excitation energy, high fluorescence quantum yield, large extinction coefficient and their spirolactam ring-opening reaction, which can provide a strong fluorescence emission and a distinct color upon selective opening of rhodamine spirolactam ring in the presence of specific metal cations [17–22]. Several successful attempts have been made to develop selective sensors for Cr^{3+} ion based on rhodamine [6]. Thus, in our work, rhodamine B was chosen as the fluorophore component in the dendrimer core in view of its peculiar merit of high fluorescence efficiency [23] and its ring-opening process in PAMAM-based PET sensors [24].

Of particular interest, the PET fluorescent sensors are designed so that the electron transfer occurs between the fluorophore (signaling unit) and the receptor ("switch" of the fluorescence intensity) [25–27]. The receptor unit with shorter wavelength absorption has been connected chemically to fluorophore, where the PET between them is occurred effectively [28–30]. Therefore, an electron-donating compound, which can absorb short wavelength light and chelate with metal ions effectively, was chosen as the receptor unit. As a strong UV absorption chromophore, 1-phenyl-3-methyl-5-pyrazolone can transfer electron easily and chelate to Cr^{3+} ion effectively [31]. It is a good candidate for the receptor unit. Keeping this in mind, we have designed a chemosensor by

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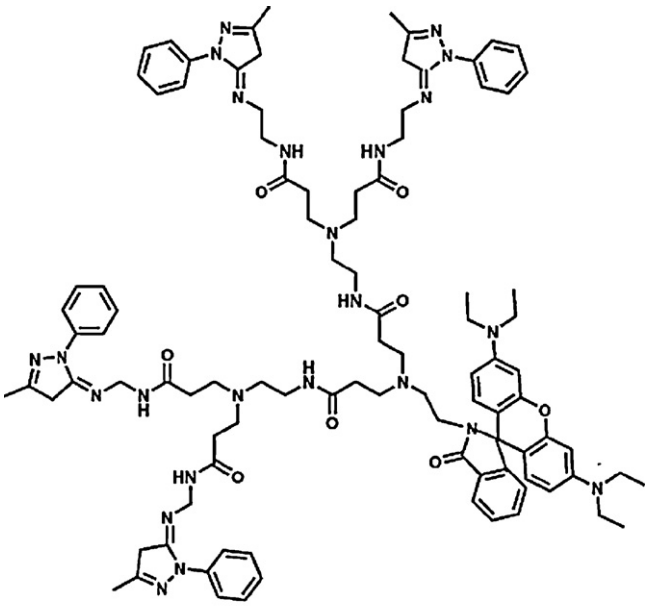
doi:10.1016/j.saa.2011.08.006



dendrimer G3

Scheme 1. Chemical structures of dendrimer G3.

linking 1-phenyl-3-methyl-5-pyrazolone as an appended group to the PAMAM periphery, and expect it could give the dendrimer desired fluorescent properties and transmit the recognition signal.

In the present work, we designed and synthesized a novel PAMAM dendritic polymer (dendrimer G3, as shown in Scheme 1). Rhodamine B unit in the core of PAMAM and 1-phenyl-3-methyl-5-pyrazolone fluorescent unit performed as fluorophore reporter and receptor, respectively. By introducing typical photoactive units both in and outside of PAMAM, unique properties, such as interesting PET process and ring opening process of rhodamine were expected. Furthermore, according to the simultaneous effect of PET and ring-opening mechanism, we first designed a Cr^{3+} sensor containing photoactive PAMAM structure, which simultaneously contained rhodamine and pyrazolone units. In this work, the photophysical properties of the obtained dendrimers have been investigated in detail, and their relationship with the PET and ring-opening effect was also discussed.

2. Experimental

2.1. Materials

1-Phenyl-3-methyl-5-pyrazolone, rhodamine B, ethylene diamine, thionyl chloride, and methylacrylate were purchased form Shanghai Chemical Reagents (Shanghai). All organic solvents (including methanol, ethanol) used in this study were of analytical reagent grade. $Cr(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3$, $Ba(NO_3)_2$, $SrCl_2{\cdot}2H_2O$, $Al(NO_3)_3$, $Hg(NO_3)_2$, $Ni(NO_3)_2$, $CaCO_3$, KCl were the metal cation sources and were obtained from Chengdu Chemical Reagent Factory (Chengdu).

2.2. Methods

UV–vis spectrophotometric investigations were performed on a UV-3150 spectrophotometer with the solution concentration of 1×10^{-5} mol L^{-1}. The fluorescence spectra were recorded by a PE LS55 spectrofluorimeter. The NMR spectra were obtained by a Bruker AV II spectrometer, operating at 400 MHz for ^1H using $CDCl_3$ as solvent. The chemical shifts were referenced to tetramethylsilane (TMS). The IR spectra were measured on a Spectrum One (Version BM) FTIR spectrometer with 2 cm^{-1} resolution using KBr pellet method.

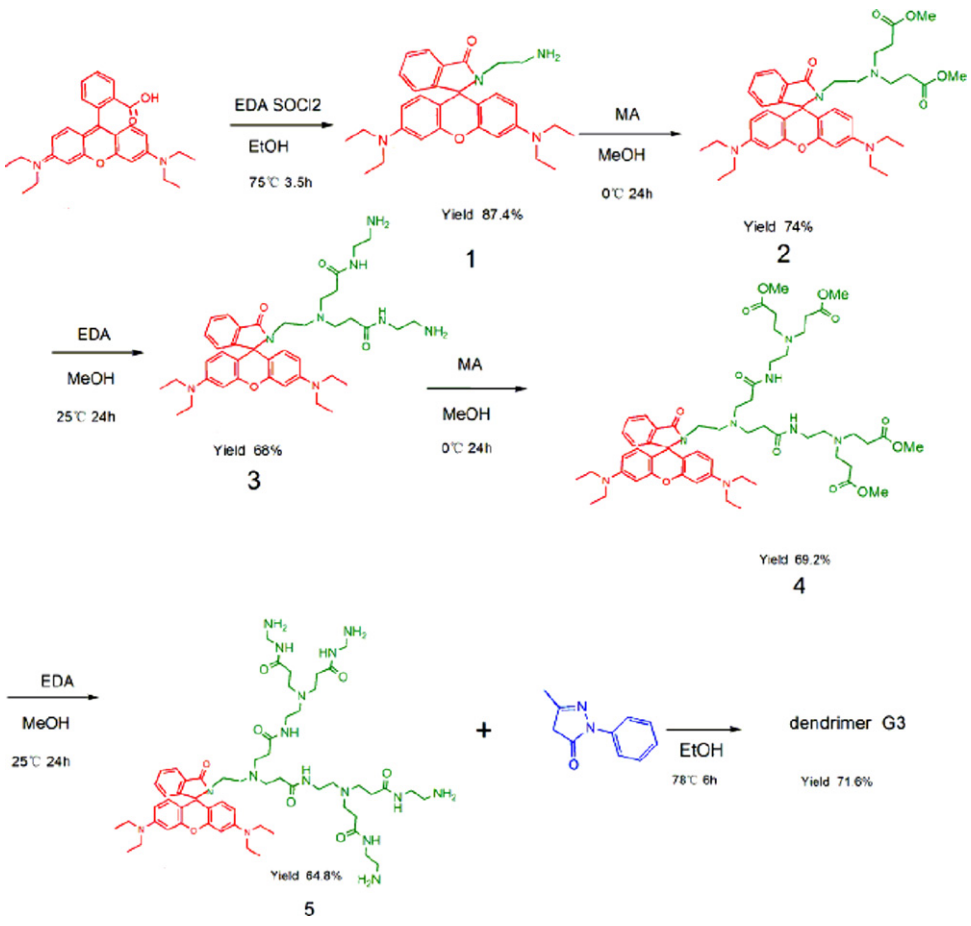
The effect of the metal cations and proton on the fluorescence intensity was examined by adding a few μL of stock solution of metal cations to a fixed volume of dendrimer solution (3 mL). The addition amount of the cations solution was limited to 0.08 mL to make sure the dilution effect was insignificant. The pH was adjusted by addition of HCl or NaOH into 3 mL of solvent. All spectral measurements in this study were performed at room temperature.

2.3. Synthesis of new dendrimer G3

Dendrimer G3 was readily prepared according to Scheme 2. Step one: diamine (0.03 mol) was dissolved in 50 mL of ethanol, and then rhodamine B (0.01 mol) and thionyl chloride (0.5 mL) were added dropwise under vigorous stirring at room temperature within 30 min. The mixture solution was heated at 75 °C for 5 h under vigorous stirring. The solvent was removed by distillation under the vacuum of 0.093 MPa at 75 °C. The obtained product was named with "compound 1" which had a yield of 87.4%. It was purified by double re-crystallization with ethanol and dried in vacuum at room temperature.

Step two: compound 1 (0.005 mol), methylacrylate (0.02 mol) and methanol (50 mL) were mixed and stirred at 0 °C under a nitrogen atmosphere for 24 h. Then, the mixture was distilled under the vacuum of 0.093 MPa at 0 °C, and the residue was washed by methanol. The obtained product was named with "compound 2" which had a yield of 74%. Subsequently, 0.002 mol compound 2 was reacted with 0.02 mol of ethylene diamine in 50 mL of methanol under nitrogen atmosphere for 24 h at room temperature. The solvent was removed by vacuum distillation of 0.093 MPa at 75 °C, and the residue was dried in vacuum at 25 °C. The obtained product was named with "compound 3" which had a yield of 68%.

The same procedure was conducted for the synthesis of compound 5. It was produced from compound 3 using the above mentioned "step two". Finally, 0.001 mol of compound 5, 0.004 mol of 1-phenyl-3-methyl-5-pyrazolone and 30 mL of ethanol were heated and refluxed for 6 h. Then, the solvent was removed under vacuum condition. With these efforts, the final product dendrimer G3 was obtained after solvent removal, and purified by column chromatography using silica gel as stationary phase and dichloromethane methanol (12:1) mixture as mobile phase. The yield of dendrimer G3 was of 71.6%, and the corresponding FT-IR and ^1H NMR data were listed as follows. FT-IR (KBr), cm^{-1}: 3428, 3063.8, 2961.9, 2925, 2797, 1948, 1713.7, 1657.7, 1621.6, 1596.4, 1499.1, 1457.4, 1436.8, 1403, 1361.4, 1320.2, 1262.1, 1099.4, 1028.5, 905.7, 800.1, 756.9, 692.1, 662.1, 505.0; ^1H NMR ($CDCl_3$, 400 MHz, ppm): 1.14 (t, 12H, CH_3CH_2N), 1.246 (s, 12H, CH_3CNN), 1.408 (m, 8H, $NCCH_2C$), 2.006 (m, 4H, $OCCH_2CH_2N$), 2.093 (m, 8H, $OCCH_2CH_2N$), 2.207 (m, 4H, $OCCH_2CH_2N$), 2.240 (m, 8H, $OCCH_2CH_2N$), 2.335 (m, 2H, NCH_2CH_2NH), 2.376 (m, 4H, $CONHCH_2CH_2N$), 2.605 (m, 8H, $CONHCH_2CH_2N$), 2.855 (m, 2H, $ArCONHCH_2CH_2N$), 2.937 (m, 4H, $(CH_3)_2NCH_2CH_2NH$), 3.187 (m, 8H, $CNCH_2CH_2N$), 3.420 (q, 8H, CH_3CH_2N), 7.174 (m, 2H, C_6H_3), 7.193 (m, 2H, C_6H_3), 7.215 (m, 2H, C_6H_3), 7.255 (br s, 4H, $CONHCH_2CH_2N$), 7.313 (s, 4H, C_6H_5), 7.332 (s, 4H, C_6H_5), 7.352 (d, 4H, C_6H_5), 7.403 (d, 1H, C_6H_5), 7.421 (d, 1H, C_6H_5), 7.625 (s, 1H, C_6H_4), 7.644(br s, 2H, $CONHCH_2CH_2N$), 7.831 (m, 1H, C_6H_4), 7.914 (m, 1H, C_6H_4), 7.966 (br s, 1H, $ArCONHCH_2CH_2N$), 8.235 (m, 1H, C_6H_4). Analysis: $C_{100}H_{129}ClN_{24}O_8$, Calcd: C 65.30, H 7.51; N 18.27, Found: C, 65.61; H, 7.10; N, 18.36.



Scheme 2. Synthesis route of dendrimer G3.

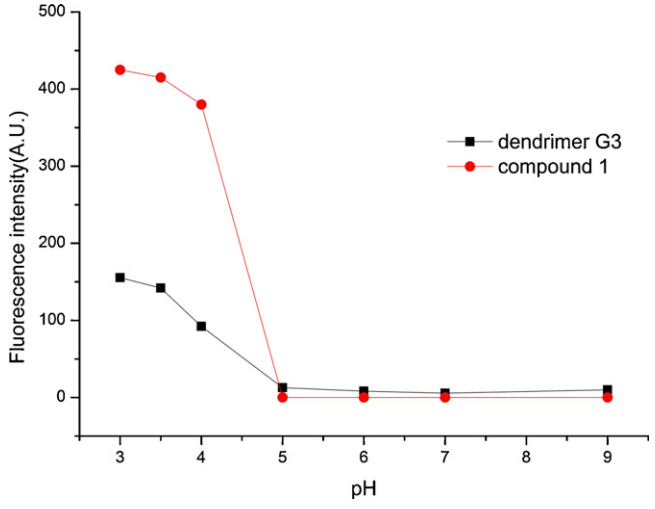


Fig. 1. pH vs. fluorescence intensity of the dendrimer G3 in ethanol at concentration of 10^{-5} mol L^{-1}.

3. Results and discussion

3.1. Influence of proton on the fluorescence properties of dendrimer G3

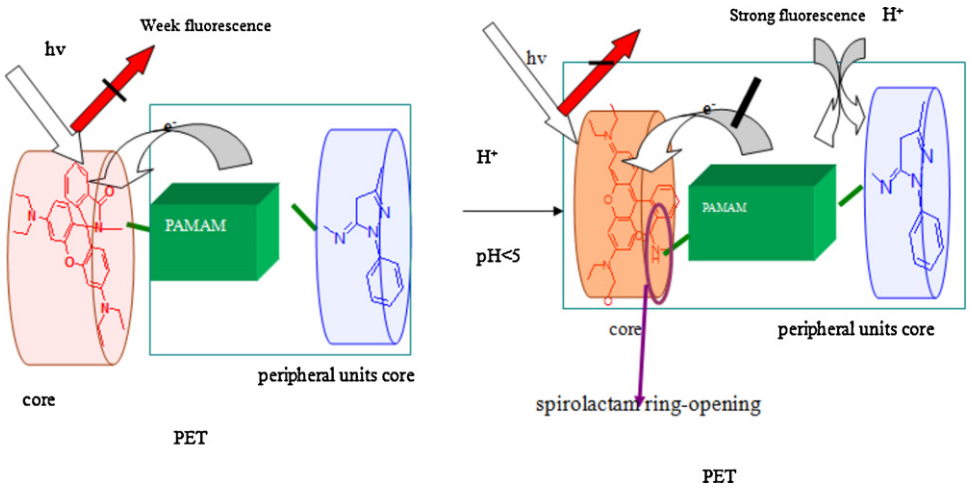
Fig. 1 presents the fluorescence response of the dendrimer G3 and compound 1 in ethanol solution with various pH values. The experiments were carried out in a pH range of 3–9. The result showed that it was quite different of the two compounds' fluorescence behavior. The pH titration control experiments revealed that the compound 1 did not show any obvious fluorescence emission when the pH value was between 5 and 9. However, it had a strong fluorescence response in acid media (pH 3–4). These changes are similar to most rhodamine-based spirolactam chemosensors, which attribute to the ring opening of spirolactam in acid media (pH 3–4) and the formation of a highly delocalized conjugated structure.

However, the dendrimer G3 shows weak fluorescence when the pH value was between 5 and 9. In this pH range, the spirolactam ring of dendrimer G3 was closed like compound 1. But for the effect of steric hindrance, the molecular distortion of dendrimer G3 was less than that of compound 1, and the delocalized conjugated degree of dendrimer G3 was larger. Thus, a weak fluorescence emission was observed.

Compared to compound 1, a stronger fluorescence response of dendrimer G3 was also observed in acid media (pH 3–4), which could be explained by the ring-opening mechanism (Scheme 3). Moreover, in acid media (pH 3–4), the fluorescence response of dendrimer G3 was much weaker than that of compound 1 at the same pH. This fluorescence response may be caused by electronic transfer from the nitrogen of PAMAM part and terminal pyrazolone moieties of dendrimer G3 to the rhodamine core, which leads to a decreased fluorescence intensity of rhodamine core.

3.2. Influence of metal cations on the fluorescence properties of dendrimer G3

The supramolecular fluorescence properties of dendrimer G3 in the presence of different metal cations (Cr^{3+}, Ba^{2+}, Ca^{2+}, Sr^{2+},



Scheme 3. The reaction scheme of dendrimer with H^+.

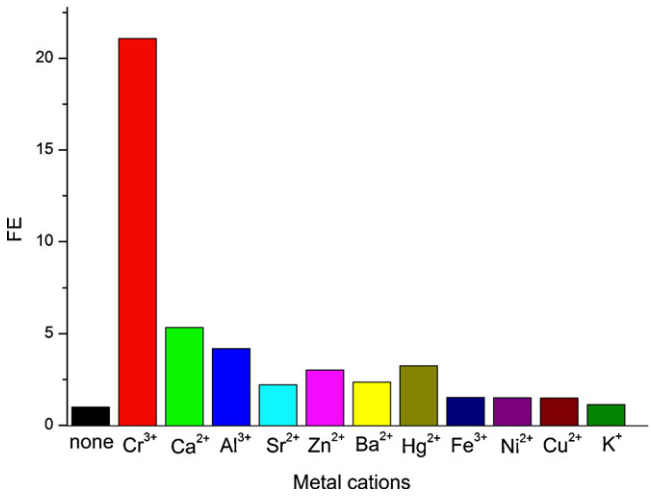


Fig. 2. Fluorescence enhancement of G3 in the presence of different metal cations ($C = 1 \times 10^{-5}$ mol L^{-1}) in ethanol. The dendrimer G3 concentration in the solution is $C = 1 \times 10^{-5}$ mol L^{-1}.

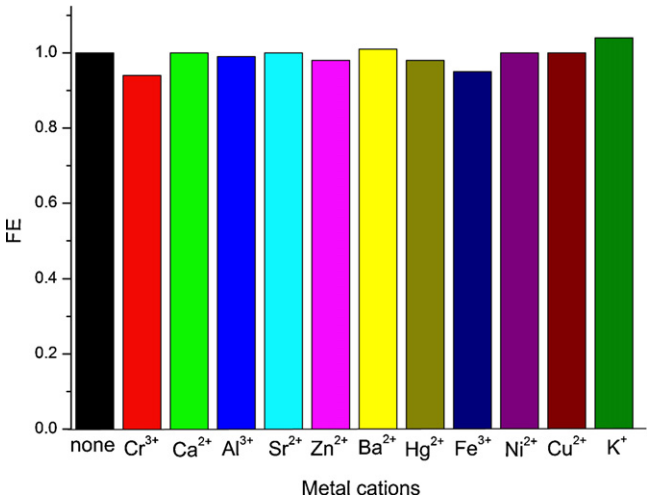


Fig. 3. Fluorescence enhancement of rhodamine B in the presence of different metal cations ($C = 1 \times 10^{-5}$ mol L^{-1}) in ethanol. The rhodamine B concentration in the solution is $C = 1 \times 10^{-5}$ mol L^{-1}.

Fe^{3+}, Al^{3+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+} and K^+) have been studied with regard to their application as sensors for these cations. The ability of dendrimer G3 to detect metal cations has been tested in ethanol solution by monitoring the changes of fluorescence spectrum in the presence of these cations.

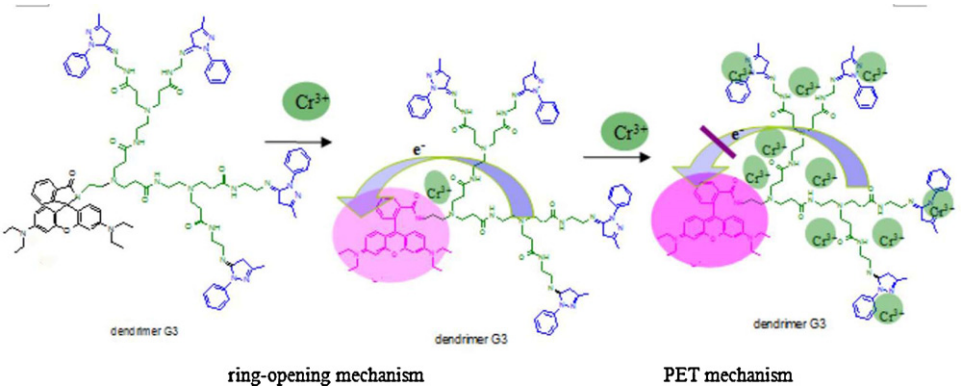
The fluorescence response of the guest metal cations in the G3 solution is signaled quantitatively by fluorescence enhancement factor (FE, $FE = I/I_0$). Herein, "I" represents the fluorescence intensity after addition of guest metal ions, and "I_0" is the fluorescence intensity without metal ions. Fig. 2 presents the dependence of fluorescence enhancements of dendrimer G3 in ethanol solution on the above mentioned metal cations. The result showed that the highest FE value of dendrimer G3 could be observed in the presence of Cr^{3+} ion. The FE value for Cr^{3+} ions used in this study was very good, since at least a 20-fold increase in fluorescence intensity is found. The FE value for Cr^{3+} ion was 21.08, which was 4 times larger than that for Ca^{2+}. While other metal cations, such as Ba^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+} and K^+, provided weaker spectral response than Cr^{3+} ion did in parallel condition. The unique selectivity for Cr^{3+} ion is probably a result of simultaneous effect of some factors, such as suitable coordination geometry conformation of the receptor, radius of the Cr^{3+} ion and the amide deprotonation ability of the Cr^{3+} ion. These results indicated that the presented dendrimer G3 could be used as an efficient sensor for Cr^{3+} ion.

Fig. 3 shows the FE data of rhodamine B. Almost no change of the fluorescence enhancement could be observed even in the presence of the same cations. This phenomenon can be reasonably explained by the ring-opening of spirolactam of rhodamine B. Thus, the interaction between rhodamine B and these metal cations cannot affect the delocalized conjugated degree of rhodamine B molecular. The comparative experiment indicated that the Cr^{3+} ion selectivity of dendrimer G3 is better than that of rhodamine B.

To confirm the Cr^{3+} recognition ability of dendrimer G3, further investigation was carried out by mixing Cr^{3+} ion with other background metal cations. As shown in Fig. 4, the Cr^{3+} fluorescence response of dendrimer G3 was barely affected by the background metal cations. The results indicated that dendrimer G3 had remarkable selectivity for Cr^{3+} ion and could be used as a high sensitive sensor for Cr^{3+} ion.

3.3. Study on the complexation behavior between Cr^{3+} and dendrimer G3

The complexation behavior between dendrimer and different concentrations of Cr^{3+} ion has been tested in ethanol solution by



Scheme 4. The reaction scheme of dendrimer G3 with Cr^{3+}.

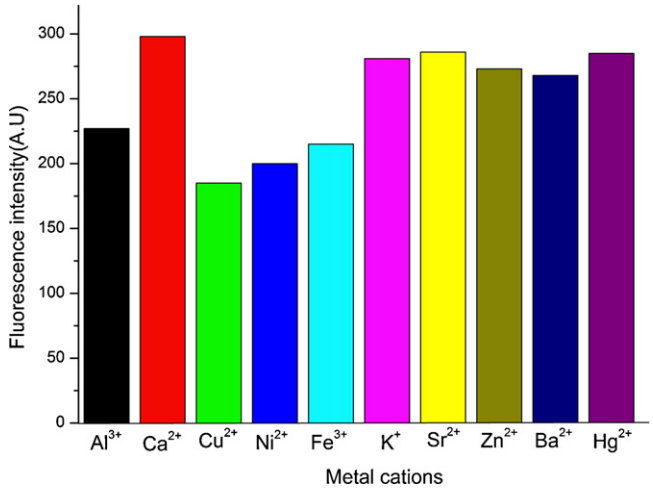


Fig. 4. The fluorescence responses of dendrimer G3 to 10^{-5} mol L^{-1} Cr^{3+} in the presence of other selected metal cations ($C = 1 \times 10^{-5}$ mol L^{-1}) in ethanol. The dendrimer G3 concentration in the solution is $C = 1 \times 10^{-5}$ mol L^{-1}.

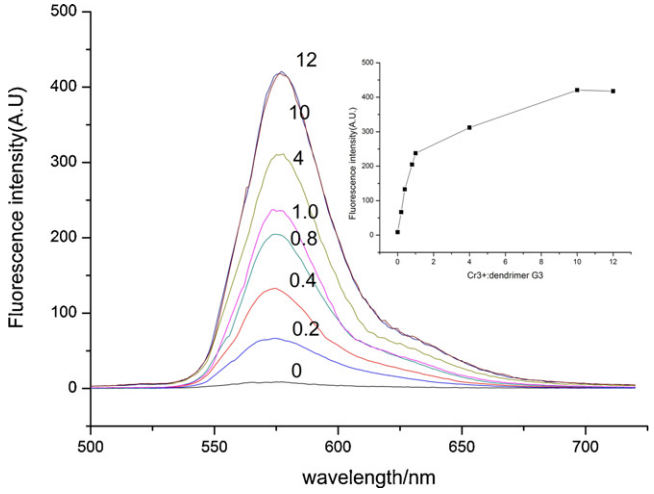


Fig. 5. Fluorescence spectra of dendrimer G3 in ethanol at different concentrations of Cr^{3+} cations (0–1.2×10^{-4} mol L^{-1}). The dendrimer G3 concentration in the solution is $C = 1 \times 10^{-5}$ mol L^{-1}.

monitoring the fluorescence spectral changes. In ethanol solution the dendrimer was colorless with the fluorescence maximum at $\lambda_F = 571$ nm which is caused by π–π^* transition of the limited extent of delocalization in the xanthene moiety of core group-rhodamine B.

Fig. 5 shows the fluorescence spectrum of dendrimer G3 with various Cr^{3+} concentrations (i.e. 0–1.2×10^{-4} mol L^{-1}). The effect of Cr^{3+} ion on the fluorescence intensity of dendrimer G3 was also plotted in the figure. It clearly showed that the fluorescence intensity at 571 nm dramatically increased with the increase of Cr^{3+} which was exited at 548 nm. We noticed that, when the concentration of Cr^{3+} reached to a certain limit (i.e. 1.0×10^{-5} mol L^{-1}), the dendrimer G3 solution turned to red, and the fluorescence intensity increased slowly with the increase of Cr^{3+}. Finally, the fluorescence intensity remained constant and the curve turned to a plateau when the concentration of Cr^{3+} was above 1.0×10^{-4} mol L^{-1}. These results indicated that 10 equiv. of Cr^{3+} and 1 equiv. of dendrimer G3 could quickly react and reach the equilibrium with the formation of a dendrimer G3/Cr^{3+} complex stoichiometrically.

3.4. Binding model of the complexes

The photophysical properties revealed that 1:10 complex was formed between dendrimer G3 and Cr^{3+} ion. But the sensor gave different fluorescence responses in different Cr^{3+} concentration ranges ($C = 0$–1.0×10^{-5} mol L^{-1} and $C = 1.0 \times 10^{-5}$–1.0×10^{-4} mol L^{-1}). The possible mechanism for these fluorescence responses is shown in Scheme 4. According to some reported rhodamine-based chemosensors similar to our compound in literatures [19,32], the nitrogen and amide oxygen atoms of spirolactam will combine with nearby nitrogen and amide oxygen atoms to form a nice binding pocket for the complexation of metal ion. Thus, we supposed that the recognition of Cr^{3+} in our case has the similar mechanism, i.e. one nitrogen atom and two amide oxygens provide a nice binding pocket for the complexation of Cr^{3+}, which will induce ring-opening of spirolactam and lead to the fluorescence enhancement of dendrimer G3 as shown in Scheme 4. When the concentration of Cr^{3+} is more than 1.0×10^{-5} mol L^{-1}, the fluorescence enhancement most likely attributes to the complexation of Cr^{3+} with some other part of dendrimer G3. This complexation will block the PET process and increase the fluorescence intensity. The ring-opening process was supported by the fact that the fluorescence intensity of dendrimer G3 (1 equiv.) induced by Cr^{3+} ion (1 equiv.) cannot be further suppressed by adding excess chelator (e.g. EDTA). It suggests an irreversible sensing process of dendrimer G3 to Cr^{3+} ion. Besides, the PET process was further confirmed by the fact that the fluorescence intensity of dendrimer G3 (1 equiv.) induced by Cr^{3+} ion (10 equiv.) can change into the one induced by 1 equiv. of Cr^{3+} ion by adding excess chelator (e.g. EDTA). This suggests a reversible sensing process of dendrimer G3 to Cr^{3+} ion.

4. Conclusion

The third generation of poly (amidoamine) dendrimer with 1-phenyl-3-methyl-5-pyrazolone fluorescent unit as periphery and rhodamine B unit as core has been synthesized and characterized for the first time. The obtained dendrimer G3 showed a considerable fluorescence intensity increase in acidic solution and in presence of metal cations. Among the tested metal cations, Cr^{3+} ion provided the strongest enhancement of the fluorescence intensity. The formation of a dendrimer G3/Cr^{3+} complex with stoichiometric proportion of 1:10 was proved. The particular interesting photophysical properties of the dendrimer significantly depended on the spirolactam ring-opening process and photoinduced electron transfer effect. Moreover, the novel synthesized dendrimer is proved to be a much better sensor for Cr^{3+} ion than rhodamine B only. On the basis of this present investigation, the produced dendrimer G3 shows a potential to be applied in fluorescent sensor of Cr^{3+} ion in the environmental and biological system.

Acknowledgement

This work was supported by a grant from the National High Technology Research and Development Program of China (863 Program) (No. 2009AA035002).

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