Dyes and Pigments 87 (2010) 49-54

Contents lists available at ScienceDirect

Dyes and Pigments

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

# Colorimetric sensing of Cu<sup>2+</sup> using a cyclodextrin–dye rotaxane

Jong S. Park<sup>a,b,\*</sup>, Sooyeon Jeong<sup>a</sup>, Seongkook Dho<sup>b</sup>, Myungwon Lee<sup>c,d</sup>, Chungkun Song<sup>c,d</sup>

<sup>a</sup> Laboratory of Polymer and Electronic Materials, Dong-A University, Busan 604-714, Republic of Korea

<sup>b</sup> Department of Textile Industry, Dong-A University, Busan 604-714, Republic of Korea

<sup>c</sup> Media Device Laboratory, Dong-A University, Busan 604-714, Republic of Korea

<sup>d</sup> Department of Electronic Engineering, Dong-A University, Busan 604-714, Republic of Korea

#### ARTICLE INFO

Article history: Received 19 January 2010 Accepted 19 February 2010 Available online 1 March 2010

Keywords: Azo dye Cyclodextrin Rotaxane Cu<sup>2+</sup> Metal sensing Sensor

## 1. Introduction

Many heavy metals are hazardous to both humans and the environment, of which, copper is highly toxic to various organisms and is harmful to humans at high concentration [1,2]; in recent years, copper has been linked to organ damage in infants. For this reason, the concentration of copper in drinking water is strictly regulated; drinking water containing  $>3 \text{ mg L}^{-1}$  is harmful to human health [3]. Moreover, copper ions are associated with a number of serious diseases, such as Alzheimer's and prion diseases [4,5]. Hence, the accurate and facile detection of copper ions is important. Classic detection methods include atomic absorption spectrometry, inductively coupled plasma mass spectroscopy, X-ray fluorescence spectrometry and electrochromic techniques, all of which are based on instrumental analysis [6-9]. Although several papers describe fluorescent chemosensors which offer the advantages of rapid, sensitive and nondestructive detection methods [10,11], these sensors possess limitations related to low signal intensity and quenching by other compounds; moreover, they require a fluorescence measuring device.

A rotaxane comprises a supramolecular assembly in which a macrocycle is located around a dumb-bell shaped molecular axis

E-mail address: jongpark@dau.ac.kr (J.S. Park).

# ABSTRACT

A dye rotaxane having 8-hydroxyquinoline as coupling component was prepared in the presence of  $\alpha$ -cyclodextrin and its structure identified using NMR. The dye rotaxane displayed high color strength regardless of the solvent used and responded to changes in pH based on tautomeric equilibrium, without any interference by the cyclodextrin macrocycle. Compared to the non-rotaxanated forms, the dye rotaxane displayed a characteristic spectral response to the presence of Cu<sup>2+</sup> which was attributed to the formation of a polymeric, metal–dye rotaxane complex which was of high solubility because of the presence of cyclodextrin. Thus, this approach can clearly be used as a facile and efficient sensor for copper ions.

© 2010 Elsevier Ltd. All rights reserved.

[12,13]. Cyclodextrins (CDs) are conically shaped, cyclic oligosaccharides in which the primary hydroxyl groups are situated on the narrow side of torus glucose residues and the secondary hydroxyl groups are located on the wider side. Several rotaxane dyes have been synthesized using the hydrophobic effect of CDs to direct rotaxane formation, in which the CDs were claimed to reduce fluorescent quenching, enhance fluorescence and photostability and, in addition, to increase resistance to bleaching [14–16].

The present work concerns a dye rotaxane that exhibits high selectivity and sensitivity towards Cu<sup>2+</sup>, this being achieved by using 8-hydroxyquinoline (8-HQ) as the blocking group. 8-HQ is a well-known ligand with high reactivity toward metal ions [17,18]; its complexes have been used as an important component of organic light-emitting devices. Although azo dyes in conjunction with 8-HQs, which are collectively termed azoxines, have been reported, none was rotaxanated [19], by means of which, the dyes are able to display colorimetric response to copper ions. This color change can be identified easily by the naked eye, which mitigates the need for instrumental assessment.

## 2. Experimental

## 2.1. Materials

The chemicals used in the synthesis and purification of the rotaxane dye were 4,4'-diaminostilbene dihydrochloride, 8-hydrox-yquinoline, sulfanilic acid,  $\alpha$ -cyclodextrin ( $\alpha$ -CD), HCl (37%), NaNO<sub>2</sub>,





<sup>\*</sup> Corresponding author. Laboratory of Polymer and Electronic Materials, Dong-A University, Busan 604-714, Republic of Korea. Tel.: +82 51 200 7330; fax: +82 51 200 7540.

<sup>0143-7208/\$ –</sup> see front matter  $\odot$  2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2010.02.003



Scheme 1. Synthesis of dye rotaxane 1.

sodium acetate, methanol, ethanol, silica, methylethylketone, ammonium hydroxide, 1-propanol, and DMSO- $d_6$ . All chemicals used in the syntheses were of laboratory reagent grade.

## 2.2. Dye synthesis

The rotaxane dye **1** and its non-rotaxanated counterpart **2** were prepared using the following known methods [14,15] (Scheme 1).

### 2.2.1. Dye rotaxane 1

4,4'-Diaminostilbene dihydrochloride (1 g, 3.53 mmol) was dissolved in water (20 mL) containing HCl (37%, 1.47 mL), to which was added,  $\alpha$ -CD (9.7 g, 9.96 mmol) in water (20 mL) and the ensuing mixture was stirred for 12 h at room temperature. The temperature was lowered to 0–5 °C, and a 5% aq. NaNO<sub>2</sub> solution (7.06 mmol, 10 mL) was added dropwise. The resulting solution was stirred for 60 min at 0–5 °C to complete diazotization. 8-Hydrox-yquinoline (1.025 g, 7.06 mmol) in 0.5 N NaOH (16 mL) was then added dropwise over 60 min and stirring continued at room temperature overnight, after which time, the pH was adjusted to 7.5–8.0 using dilute aq. sodium acetate solution and the precipitated dye was collected by filtration and dried under vacuum. The dye was dissolved in aq. KOH (pH 12) and the insoluble component was removed by filtration. The pH of the filtrate was adjusted to neutral and the resulting precipitate was collected,

washed with water and dried in a vacuum oven. The crude product was refluxed in methanol and ethanol for 12 h, respectively, followed by hot filtration and washing with hot ethanol. The product was isolated using column chromatography on silica using methylethylketone/ammonium hydroxide/1-propanol (1/1/1 vol%) as an eluent and was subsequently dried in a vacuum oven (yield 8%). 1H (500 MHz, DMSO- $d_6$ ): 9.4 (d, 1H), 9.3 (d, 1H), 8.6 (m, 2H), 8.5 (d, 1H), 8.0 (q, 2H), 7.8 (d, 1H), 7.7 (d, 2H), 7.6 (d, 2H), 7.4 (d, 1H), 7.3 (d, 1H), 7.1 (d, 2H), 7.0 (d, 2H), 6.2 (q, 2H), 5.3 (s, 12H), 4.7 (s, 6H), 4.3 (s, 6H), 3.8–3.2 (m, 36H).

#### 2.2.2. Bisazo dye **2**

The synthesis method was the same as that described above but without the addition of  $\alpha$ -CD (yield 30%). 1H NMR (500 MHz, DMSO- $d_6$  with NaOH): 9.1 (d, 2H), 8.5 (m, 2H), 8.0 (d, 4H), 7.6 (q, 4H), 7.4 (m, 4H), 7.2 (m, 2H), 6.4 (m, 2H).

# 2.2.3. Monoazo dye 3

Sulfanilic acid (1.221 g, 7.06 mmol) was dissolved in water (20 mL) containing HCl (37%, 1.47 mL), the temperature of the solution was lowered to 0-5 °C, and 5% aq. NaNO<sub>2</sub> solution (7.06 mmol, 10 mL) was added dropwise. The ensuing solution was stirred for 60 min at 0-5 °C to complete diazotization and 8-Hydroxyquinoline (1.025 g, 7.06 mmol) in 0.5 M aq. NaOH solution (16 mL) was added dropwise over 60 min and stirring continued at



Fig. 1. <sup>1</sup>H NMR spectra of dyes 1, 2, and 3.



Scheme 2. Tautomeric equilibrium of azo dye rotaxane 1 having 8-HQs as coupling components: Azo tautomer A, hydrazone tautomer B, and resonance structures C at a higher pH.

room temperature overnight. After this time, the pH was adjusted to 7.5–8.0 using dilute aq. sodium acetate solution. The precipitated dye was collected by filtration. The crude product was recrystallized twice in water (50 mL) and then dried in a vacuum oven (yield 35%). 1H NMR (500 MHz, DMSO-*d*<sub>6</sub>): 9.3 (d, 1H), 9.0 (m, 1H), 9 (d, 2H), 7.8 (d, 2H), 7.7 (q, 2H), 7.2 (d, 1H).

#### 2.3. Absorbance measurement

The UV absorbance spectra were collected using a Lambda 7 spectrometer (Perkin Elmer) in a 1 cm cuvette. For the pH adjustment, HEPES and phosphate buffer solutions with 5 mmol buffer strength were prepared for pH 7.5 and pH 11, respectively. For metal ion screening, the concentrations of both the dye and the metal ions were fixed at  $4.0 \times 10^{-6}$  mol L<sup>-1</sup>. For concentration titration, a dye solution of  $4.0 \times 10^{-6}$  mol L<sup>-1</sup> was prepared and the corresponding

amount of  $Cu^{2+}$  was added using micro-pipette. For complete mixing, 5 min of standing was allowed before measurement of the spectra.

# 3. Results and discussion

The structures of the rotaxane dye 1 and its non-rotaxanated counterpart **2** were confirmed by NMR (Fig. 1). Due to the presence of both inter- and intra-molecular hydrogen bonding with 8-HOs. it was difficult to find a suitable NMR solvent for 2: a small amount of KOH aided solubility. Peak assignment in the aromatic region was quite straightforward. 2 has a symmetrical structure around the stilbene group, which is clearly apparent in the aromatic region. Owing to the deprotonation of the OH groups in 8-HQs by the addition of KOH, all peaks were slightly shift to the upfield region. In comparison, 1 readily dissolved in organic solvents, including DMSO- $d_6$ , which can be ascribed to the presence of hydroxyl groups in the CDs. The NMR spectrum shows a nonequivalent environment at both ends of the dye molecule due to the additional split and complex peaks, which can be attributed to the conical shape of CD, from which the threading of the azo chromophore within the cavity of the CD could be confirmed.

**1** exhibited higher color strength (27,140 at 440 nm) compared to its unrotaxanated analogue **2** (19,040 at 410 nm, DMF: water = 80:20, pH 7.5). The same result was observed in water-rich conditions (22,500 at 470 nm for dye **1** vs. 20,500 at 410 nm for dye **2**, DMF:water = 20:80, pH 7.5). Under both conditions, **2** exhibited a red shift due to the presence of  $\alpha$ -CD macrocycle, as previously reported, which hinders aggregation of the dye and promotes the monomeric state [20,21]. **2** was also very sensitive to pH changes, existing in two possible tautomeric forms namely the azo **A** and the hydrazone **B**; at higher pH, deprotonation leads to its anionic form



**Fig. 2.** Colors of dye rotaxane **1** after an addition of equivalent metal ions under different pHs (DMF:water = 80:20, wt%): (a) pH 7.5, (b) pH 11. The concentrations of both the dye and metal ions were fixed at  $4.0 \times 10^{-6}$  mol L<sup>-1</sup>. The order of the metal cations added was as follows: none,  $Al^{2+}$ ,  $Cr^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Li^+$ ,  $Mg^{2+}$ ,  $Pb^{2+}$ ,  $Ca^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  (left ~ right).



**Fig. 3.** Absorbance spectra of dye rotaxane **1** upon an addition of different concentrations of  $Cu^{2+}$  under different pHs: (a) pH 7.5, (b) pH 11. Mixed solvents (DMF:water = 80:20, wt%) were used. The concentrations of all dyes were fixed at  $4.0 \times 10^{-6}$  mol L<sup>-1</sup>. Insets indicate the absorption changes upon the addition of  $Cu^{2+}$ . Note that the absorbance at 520 nm increases regardless of pHs by adding  $Cu^{2+}$ .



**Fig. 4.** Colors after an addition of equivalent metal ions in a mixed solvent of water and DMF (80:20, wt%); (a) dye rotaxane **1** (pH 7.5), (b) dye rotaxane **1** (pH 11), (c) bisazo dye **2** (pH 7.5), (d) bisazo dye **2** (pH 11). The concentrations of both the dye and the metal ions were fixed at  $4.0 \times 10^{-6}$  mol L<sup>-1</sup>. The order of the metal cations added was as follows: none, Al<sup>2+</sup>, Cr<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Li<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> (left ~ right).

**C** in resonance (Scheme 2) [22]. As a result, the absorption maximum shifts to longer wavelength, this color change being completely reversible. This indicates that the CD macrocycle does not interfere with the tautomeric equilibrium of the threaded chromophore.

The influence of metal ions is easily recognized from inspection of the dye solutions. Eleven different metal ions were prepared and for simplicity, 1:1 solutions of dye **1** and various metals were prepared. The rotaxane dye exhibited a color change upon the addition of metal ions (Fig. 2) of which, its response towards  $Cu^{2+}$  is characteristic, showing that the color shift depended upon pH namely, a red shift, from orange to red (pH 7.5) as well as a blue shift from blue to red (pH 11). Other metal ions, such as Ni<sup>2+</sup> and Zn<sup>2+</sup>, imparted similar, but comparatively weak, red shifts at pH 7.5; however, none of these metals imparted a blue shift at pH 11. Under acidic conditions (pH 5), an identical spectral response to that of pH 7.5 was observed. Hence, the azo tautomer is the likely dominant species at neutral to acidic pH, leading to identical response to the different metal ions.

Fig. 3 shows the absorbance spectra of **1** in the presence of various concentrations of Cu<sup>2+</sup>. Upon the addition of Cu<sup>2+</sup>, at pH 7.5–80 nm red shift was observed, from  $\lambda_{max}$  440–520 nm. Until 1 equivalent  $Cu^{2+}$  was added to the dye solution, the absorbance at 440 nm decreased gradually with the appearance of a new absorption peak at the longer wavelength (520 nm); adding more than 1 equivalent lead to a slight decrease in absorbance at 520 nm. It is known that the N, O trans geometry that results from quinoline N together with carbonyl O, effectively binds metal ions. In such a case, the  $D-\pi-D'$  structure of 8-HO-containing the azo dve transforms to the Di $-\pi$ -A structure [23,24], which increases the absorbance at 520 nm, this being responsible for the observed red shift. Meanwhile, dye **1** underwent a ~ 40 nm blue shift at pH 11, from  $\lambda_{max}$  560–520 nm in the presence of Cu<sup>2+</sup>. The binding of Cu<sup>2+</sup> prevents resonance stabilization of the anion C, resulting in the observed spectral shift. In addition, at high pH, metal uptake will increase significantly. The absorbance of **1** at 520 nm continuously increases with increasing  $[Cu^{2+}]$  until 2 equivalents of  $Cu^{2+}$  are added, which is related to the formation of metal hydroxides [25]. At higher pH, the electron pair of the nitrogen of 8-HQs is more likely to interact with metal ions and the aromatic -OH group also presents greater metal ion attraction, by means of which, dye-metal complexes are formed. Hence, more  $Cu^{2+}$  is consumed under alkaline conditions than at neutral pH.

In order to understand the role of the CDs, azo dyes without CD were examined. **2** responded to the presence of  $Cu^{2+}$ , but it was

responsive only in DMF-rich conditions (Fig. 4). In water-rich conditions, the dye did not show spectral changes but rather, its absorbance decreased gradually with the addition of metal ions due to its limited aqueous solubility. The structure of **2** resembles that of a disperse dye whereas, in contrast, the rotaxane **1** exhibits an identical colorimetric shift that is independent of the solvent. Even under water-rich conditions, **1** remains stable because of the hydroxyl groups in CD, despite the fact that there is no solubilizing group in its molecular structure. It appears that the OH groups in CD provide a sufficiently hydrophilic environment for the thread chromophore. As a result, a strong spectral shift with Cu<sup>2+</sup> was observed, even under water-rich conditions.

The sensitivity of **1** to Cu<sup>2+</sup> was very high; indeed, color was generated upon the addition of <1 µmol of Cu<sup>2+</sup>, this being equivalent to 0.17 µg mL<sup>-1</sup>, which is 10 times more sensitive than EPA regulations regarding the copper content of drinking water. The large  $\pi$ -conjugated structure and presence of two 8-HQs in **1** are responsible for its ability to chelate metal ions and form the corresponding, polymeric metal complexes. This extended conjugation reportedly decreases the loss of energy by thermal vibrational decay while exhibiting a red shift [23,24]. Moreover, CDs provide



**Fig. 5.** Absorbance spectra of monoazo dye **3** upon the addition of different concentrations of  $Cu^{2+}$  (pH 7.5, DMF:water = 8:2). The concentration of the dye was  $2.0 \times 10^{-5}$  mol  $L^{-1}$ . The concentration of  $Cu^{2+}$  was increased from 0 to 20 µmol, as indicated.



Fig. 6. <sup>1</sup>H NMR spectra of α-CD in (a) dye rotaxane 1, and (b) upon the addition of an equivalent amount of Cu<sup>2+</sup>. Subscript number indicates the position of carbon atom in glucose unit.

Table 1
Elemental analysis of dye ${f 1}$ and its complex with ${f Cu}^{2+}$ and comparison with possible
empirical formulas.

Empirical formula	Measured (calculated) (%)		
	С	Н	N
Dye <b>1</b>	48.48	5.96	6.82
	(48.29)	(5.89)	(6.83)
Complex of dye ${\bf 1}$ and ${\rm Cu}^{2+}$	46.65	5.62	6.58
	(46.62)	(5.69)	(6.58)

increased solubility of the polymeric forms. Thus, high sensitivity toward copper ions is exhibited regardless of the solvent used.

The sensitivity of **1** was compared to that of **3**, which possessd one 8-HQ and thus cannot form a polymeric structure. **3** showed lower response levels towards  $Cu^{2+}$  and its absorbance decreased markedly upon the addition of the metal ion (Fig. 5).

The <sup>1</sup>H NMR spectra of the CD components of **1** both before and after the addition of  $Cu^{2+}$  were compared (Fig. 6). The peaks of the CDs broadened when complexed with  $Cu^{2+}$ . It was assumed that, upon metal coordination, the conformational flexibility of the CDs would be reduced due to the formation of a polymeric structure [26]. From this, the formation of an extended structure was also recognized. Elemental analysis of dye **1** and its copper complex is given in Table 1, from which the proposed formula of the complex is obtained. These data agree well to an empirical formula of  $[dye1-Cu^{2+}\cdot 6H_2O]$ ; one dye molecule coordinates with one metal ion at one end. The stoichiometry of the metal complex is, therefore, estimated to be 1:1 (dye1:Cu). Water molecules,  $6H_2O$ , are considered to be a hydrated form of  $\alpha$ -CD, and still exist both in dye rotaxane and in its  $Cu^{2+}$  complex.

# 4. Conclusions

In summary, an azo dye rotaxane **1** was prepared using 8-HQ as a coupling component. Compared to unrotaxanated forms, it shows a characteristic spectral shift in the presence of  $Cu^{2+}$  with a high sensitivity. This is attributed to formation of a polymeric structure of metal–dye rotaxane with increased solubility provided by CD macrocycles. This approach can clearly be used as a facile and efficient sensor for metal ions.

# Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (Grant No. 2009-0070801).

# References

- [1] Frausto da Silva JJR, Williams RJP. The biological chemistry of elements: the inorganic chemistry of life. Oxford: Clrendon Press; 1993.
- [2] Harris HH, Pickering IJ, George GN. The chemical form of mercury in fish response. Science 2004;303(5659):764–6.
- [3] Board on Environmental Studies and Toxicology. Copper in drinking water. Washington DC: The National Academies Press; 2000.
- [4] Jackson GS, Murray I, Hosszu LLP, Gibbs N, Waltho JP, Clarke AR, et al. Location and properties of metal-binding sites on the human prion protein. Proceedings of the National Academy of Sciences of the United States of America 2001;98(15):8531–5.
- [5] Gaggelli E, Kozlowski H, Valensin D, Valensin G. Copper homeostasis and neurodegenerative disorders (Alzheimer's, Prion, and Parkinson's diseases and amyotrophic lateral sclerosis). Chemical Reviews 2006;106(6):1995–2004.
- [6] Wang ZK, Fu Z, Ye CL. Journal of Hazardous Materials 2009;170(2-3):705-10.
- [7] Kolokassidou K, Szymczak W, Wolf M, Obermeier C, Buckau G, Pashalidis I. Hydrophilic olive cake extracts: characterization by physicochemical properties and Cu(II) complexation. Journal of Hazardous Materials 2009;164 (2–3):442–7.
- [8] Pancras JP, Ondov JM, Zeisler R. Multi-element electrothermal AAS determination of 11 marker elements in fine ambient aerosol slurry samples collected with SEAS-II. Analytica Chimica Acta 2005;538(1-2):303-12.
- [9] Gao GG, Xu L, Wang WJ, An WJ, Qiu YF, Wang ZQ, et al. Electrochromic multilayer films of tunable color by combination of copper or iron complex and monolacunary Dawson-type polyoxometalate. Journal of Physical Chemistry B 2005;109(18):8948–53.
- [10] Jiang W, Wang W. A selective and sensitive "turn-on" fluorescent chemodosimeter for Hg<sup>2+</sup> in aqueous media via Hg<sup>2+</sup> promoted facile desulfurization-lactonization reaction. Chemical Communications 2009; 26:3913–5.
- [11] Zhang H, Han LF, Zachariasse KA, Jiang YB. 8-Hydroxyquinoline benzoates as highly sensitive fluorescent chemosensors for transition metal ions. Organic Letters 2005;7(19):4217–20.
- [12] Nepogodiev SA, Stoddart JF. Cyclodextrin-based catenanes and rotaxanes. Chemical Reviews 1998;98(5):1959–76.
- [13] Harada A. Cyclodextrin-based molecular machines. Accounts of Chemical Research 2001;34(6):456–64.
- [14] Craig MR, Hutchings MG, Claridge TDW, Anderson HL. Angewandte Chemie International Edition 2001;40(6):1071–4.
- [15] Craig MR, Claridge TDW, Hutchings MG, Anderson HL. Synthesis of a cyclodextrin azo dye [3]rotaxane as a single isomer. Chemical Communications 1999;16:1537–8.
- [16] Park JS, Wilson JN, Hardcastle KI, Bunz UHF, Srinivasarao M. Reduced fluorescence quenching of cyclodextrin-acetylene dye rotaxanes. Journal of the American Chemical Society 2006;128(24):7714–5.

- [17] Wang SN. Luminescence and electroluminescence of Al(III), B(III), Be(II) and Zn (II) complexes with nitrogen donors. Coordination Chemistry Reviews 2001; 215:79–98.
- [18] Chen CH, Shi JM. Metal chelates as emitting materials for organic electroluminescence. Coordination Chemistry Reviews 1998;171:161–74.
- [19] Hollingshead RGW. Oxine and its derivatives. London: Butterworths; 1954.
- [20] Karakstis KK, Perelman LA, Wong WK. Spectroscopic characterization of azo dye aggregation on dendrimer surfaces. Langmuir 2002;18(26):10363-71.
- [21] Park JS, Koh J. The synthesis and spectral properties of an encapsulated aminoacobenzene dye. Dyes and Pigments 2009;82(3):347–52.
- [22] Gordon PF, Gregory P. Organic chemistry in colour. Berlin Herdleberg: Spinger-Verlag; 1987.
- [23] Cheng YF, Zhang M, Yang H, Li FY, Yi T, Huang CH. Azo dyes based on 8-hydroxyquinoline benzoates: synthesis and application as colorimetric Hg2+-selective chemosensors. Dyes and Pigments 2008;76(3):775–83.
- [24] Huang H, Zhong C, Zhou Y. Synthesis and luminescent properties of polymeric metal complexes containing bis(8-hydroxyquinoline) group. European Polymer Journal 2008;44(9):2944–50.
- [25] Sankar R, Vijayalakshmi S, Subramanian S, Rajagopan S, Kliyappan T. Synthesis and chelation properties of new polymeric ligand derived from 8-hydroxy-5-azoquinoline hydroxy benzene. European Polymer Journal 2007;43(11):4639–46.
- [26] Zhao T, Beckham HW. Direct synthesis of cyclodextrin-rotaxanated poly (ethylene glycol)s and their self-diffusion behavior in dilute solution. Macromolecules 2003;36(26):9859–65.