Dyes and Pigments 93 (2012) 1544–1548

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

Short communication

Supramolecular cyclodextrin-dye complex exhibiting selective and efficient quenching by lead ions

Sooyeon Jeong[a], Won Young Kang[a], Chung Kun Song[b], Jong S. Park[a,c,*]

[a] *Laboratory of Polymer and Electronic Materials, Department of Textile Industry, Dong-A University, Busan 604-714, South Korea*
[b] *Media Device Center, Department of Electronic Engineering, Dong-A University, Busan 604-714, South Korea*
[c] *Department of Nano Engineering, Dong-A University, Busan 604-714, South Korea*

ARTICLE INFO

Article history:
Received 15 June 2011
Received in revised form
15 August 2011
Accepted 18 August 2011
Available online 31 August 2011

Keywords:
Cyclodextrin
Supramolecular complex
Inclusion complex
Metal sensing
Stern–Volmer equation
Fluorescence quenching

ABSTRACT

In this article, we describe a supramolecular complex made of cyclodextrin and a chromophoric dye, in which anistropy occurred by the formation of the hexagonal packing of cylindrical cyclodextrin channels. The obtained complex exhibited effective fluorescence quenching in the presence of lead ions based on supramolecular wire assembly and dissociation. Selective and effective fluorescence quenching of the complex is attributed to the break-ups of the supramolecular wire and the unthreading of included dye molecules by lead ions. Though we are not yet sure about the origin of such a high selectivity, a topic that will be elaborated in subsequent investigations, these CD-templated supramolecular properties will be useful in analytical applications as a novel platform for metal ion sensing.

1. Introduction

Supramolecular assemblies have drawn increasing attention due to their unusual, intrinsic properties that are useful in various fields, including drug delivery, chemo- and bio-sensors, and electronic devices [1–3]. Self-assembly is considered to be the most practical method for the formation of these assemblies, and there have been numerous reports on accomplishing well-defined nanostructures and the precise control of the supramolecular response at the molecular level. In particular, rod-like assemblies are of great interest because of their biomimetic characteristics and liquid crystalline behavior [4,5]. Self-assembly of such synthetic building blocks by non-covalent interactions is attractive especially for sensing applications if these supramolecular structures can be assembled or dissembled depending on the presence of a specific analyte.

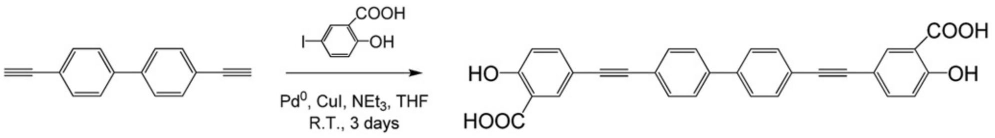
Cyclodextrins (CDs) are cyclic oligosaccharides, most commonly consisting of 6-, 7- or 8-glucose units, which are called α-, β- or γ-CDs, respectively. CDs are well-known host materials, and many organic molecules have been reported to form inclusion complexes with them by non-covalent interactions [6–8]. Among them, γ-cyclodextrin (γ-CD) has a large cavity with a diameter of up to 9 Å. The large cavity size allows the inclusion of more than one molecule and the proximity of included molecules facilitates electronic interaction. Some interesting examples include 2,5-diphenyl-1,3,4-oxadiazole (PPD) and 1,6-diphenyl-1,3,5-hexatriene (DPH), which self-assemble to form extended aggregates that are supported together when included inside CD channels [9,10]. These studies have successfully demonstrated the formation of chromophore-anchored supramolecular aggregates and the role of CDs for nanotubular channels under appropriate conditions.

Numerous CD-based inclusion complexes have been made which exhibit stimuli-responsive properties to external sources, such as heat, light, pH, and chemicals [11–13]. As far as we are aware, however, few studies have dealt with a system that is specific to the presence of lead ions. Lead is a well-known heavy metal that plays a critical role in environmental politics due to its high neurotoxicity, and its long-term harmful effects on humans and the environmental system are significant, even upon exposure to a trace amount [14,15]. Selective detection and determination of this metal ion, therefore, is an important task, and in spite of impressive results to date, there is still increasing pressure to develop promising novel systems.

---

* Corresponding author. Laboratory of Polymer and Electronic Materials, Department of Textile Industry, Dong-A University, Busan 604-714, South Korea. Tel.: +82 51 200 7330; fax: +82 51 200 7540.
E-mail address: jongpark@dau.ac.kr (J.S. Park).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.08.011



Scheme 1. Synthesis of the acetylene dye.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich (Sigma–Aldrich Korea, Korea) and used without further purification. γ-CD was obtained from Tokyo Chemical Industry (TCI Korea, Korea), and recrystallized twice from water.

2.2. Experimental methods

X-ray measurements were performed on a multi-purpose X-ray diffractometer (X'pert Pro MPD, PANalytical, Korea Basic Science Institute) with Cu Ka radiation ($\lambda = 1.54$ Å, 3 kW) at 25 °C. The UV absorbance spectra were collected using a Lambda 7 spectrometer (Perkin Elmer) in a 1 cm cuvette. The steady-state fluorescent spectra were collected using a Perkin Elmer LS-45 spectrofluorophotometer using a cuvette of (path-length: 1 cm). The 2D-ROESY spectrum was measured on a Bruker Avance II 900 (900 MHz, Korea Basic Science Institute), with a relaxation delay of 2 s and a ROESY spinlock time of 250 ms.

2.3. Synthesis

The acetylene dye, 5,5′-(biphenyl-4,4′-diylbis(ethyne-2,1-diyl)) bis(2-hydroxybenzoic acid), was prepared by the Pd-catalyzed Heck-Cassar-Sonogashira-Hagihara reaction following the previous report (Scheme 1) [16]. The detailed synthetic precedure is as follows: 4,4′-diethynylbiphenyl (270 mg, 1.3 mmol) and 2-hydroxy-5-iodobenzoic acid (739 mg, 2.8 mmol) were dissolved in THF (4 mL) in the presence of piperidine (2 mL), $(Ph_3P)_2PdCl_2$ (49 mg, 0.01 mmol), and CuI (9.5 mg, 0.05 mmol). The mixture was reacted overnight under nitrogen at room temperature. After the reaction, the mixture was diluted with aqueous KOH solution (1 M, 30 mL), filtered, and then acidified to below pH 1 with dilute HCl. The precipitate was collected by filtration, washed profusely with water, and dried in air overnight at room temperature. The product was isolated by column chromatography on silica using methylethylketone/ammonium hydroxide/1-propanol (0.5/1.0/1.0 vol%) as an eluent, followed by drying under vacuo (0.352 g, yield 57%). ^{1}H NMR (600 MHz, DMSO-d$_6$): 7.8 (d, 2H), 7.7 (d, 4H), 7.5 (d, 4H), 7.4 (q, 2H), 6.6 (d, 2H); ^{13}C NMR (600 MHz, DMSO-d$_6$): 172.0, 159.5, 139.0, 136.3, 135.1, 131.6, 127.0, 121.1, 119.0, 116.4, 115.0, 90.6, 89.2; *m*/*z* (negative MALDI-TOF) 473.1 (M$^-$).

3. Results and discussion

The chromophoric moiety of the acetylene dye used in the current work is identical to the monomer unit of poly(*p*-phenyleneethynylene)s (PPEs) in its chemical structure. Thus, it shows high fluorescence emission in most polar solvents [17–19], but due to its inherent rigid and linear structure, it inevitably exhibits limited solubility at a high molar concentration, which leads to a considerable decrease in emission intensity. However, in a mixture with γ-CD, its fluorescence emission is much enhanced mainly due to a remarkable increase in the dye's solubility. As the concentration of the complex increases, an anisotropic architecture is easily observed with the naked eye. At an elevated temperature, this anisotropic phase disappears, leading to a clear isotropic solution, but the

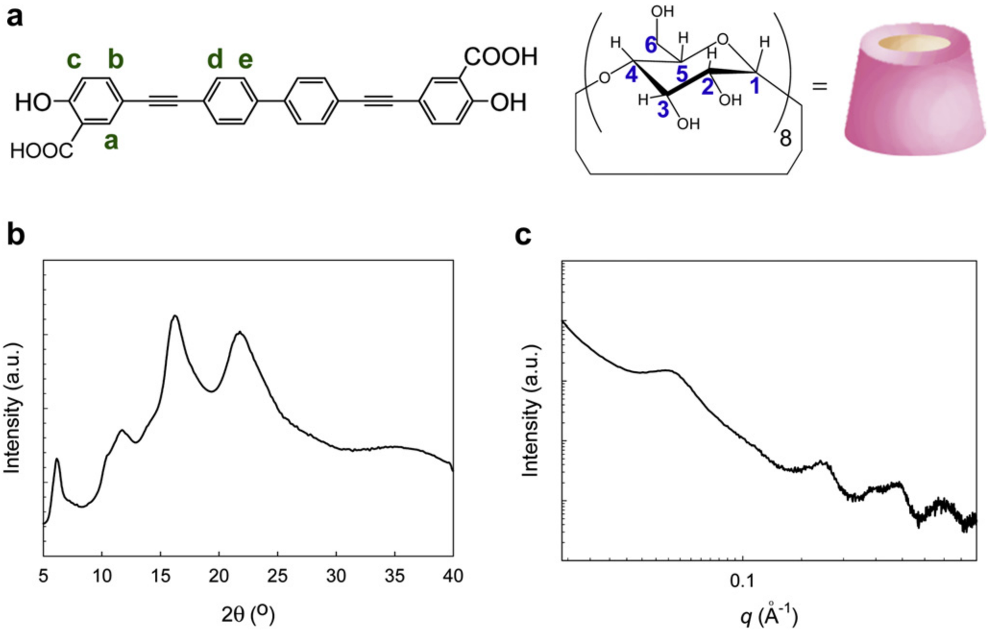


Fig. 1. (a) Chemical structures of γ-CD and acetylene dye, (b) X-ray powder diffraction patterns (WAXD) of the vacuum-dried complex, and (c) small-angle X-ray scattering (SAXS) data of the complex in regard to the *q* vector. The complex consists of dye (1.0×10^{-2} mol L^{-1}) and γ-CD (2.0×10^{-2} mol L^{-1}).

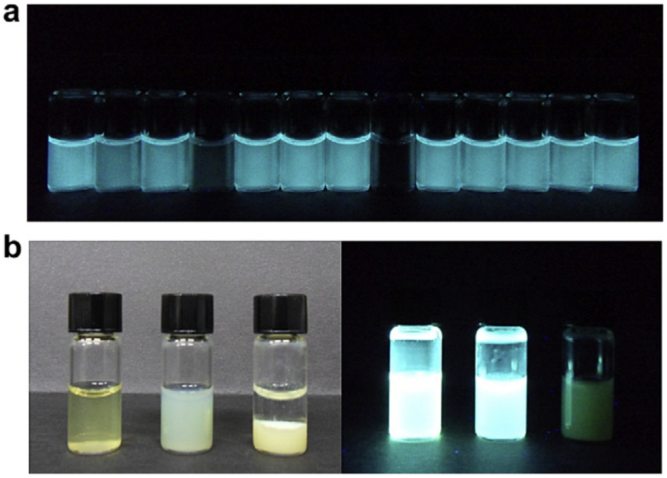


Fig. 2. (a) Photographic images of the complex taken under UV light ($\lambda_{excitation} = 365$ nm) after it was standing for 24 h with the addition of metal ions. The complex is prepared with dye (1.0×10^{-4} mol L^{-1}) and γ-CD (2.0×10^{-4} mol L^{-1}) for an increased visual clarification. The order of the added metal ions was as follows: none, Al^{3+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Li^{+}, Mg^{2+}, Pb^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} (left-right). All solutions were prepared in a HEPES buffer solution (pH 7.5). Cu^{2+} shows a similar effect to that of Pb^{2+}, but it is rather weak and slow. (b) Photographic images of the complex under normal light (left) and under UV light (right). The complex was prepared at increased concentrations of dye (1.0×10^{-2} mol L^{-1}) and γ-CD (2.0×10^{-2} mol L^{-1}). The order of the added metal ions was as follows: none, Cr^{3+}, and Pb^{2+} (left-right).

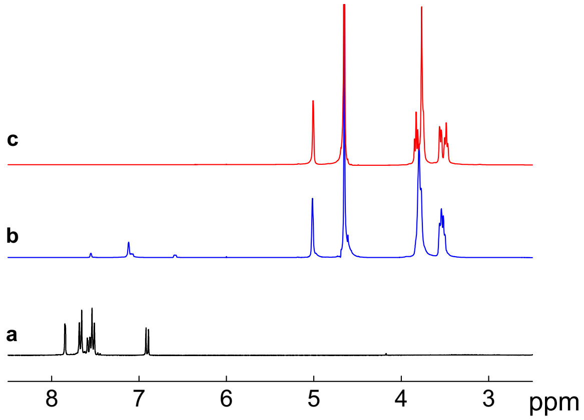


Fig. 4. ^{1}H NMR spectra of (a) a dye only, (b) a mixture made of dye and γ-CD, and (c) the mixture with equimolar Pb^{2+}. In all cases, the concentrations of dye (1.0×10^{-2} mol L^{-1}) and γ-CD (2.0×10^{-2} mol L^{-1}) are fixed. All measurements were made using D_2O as a solvent at 25 °C.

anisotropy reappears when cooled down. X-ray scattering measurements ($\lambda = 1.54$ Å) reveal a strong peak at $2\theta = 5.9°$ (Fig. 1a). This peak is attributable to the characteristic reflection at the (200) plane of the hexagonal CD packing [20]. While scanning at a scattering vector q, we observed several peaks at 0.062, 0.172, and 0.282 $Å^{-1}$ (Fig. 1b), which indicate the existence of a sublayer with a regular spacing of 10.2 nm. This corresponds to a stacking value of 21.8 γ-CD (0.79 nm × 12.9 = 10.2 nm). Hexagonal packing allows γ-CD units to stack on top of each other to form cylindrical CD channels, which are reinforced by hydrogen bonding between the included chromophore molecules and neighboring γ-CD molecules. Consequently, the tightly-packed CD crystal constructs anisotropic textures with the aid of included chromophoric threads inside CDs, which strengthens the extended hexagonal channels.

After obtaining the above results, we turned our attention to the influence of metal ions on the current supramolecular complex. The objective here was to investigate the response of the complex to metals featuring a guest chromophore containing salicylic acid. In our preliminary experiment, Pb^{2+} was distinguished from all other metals: the fluorescence of the supramolecular complex was completely quenched in its presence (Fig. 2a). No other tested metal ions exhibited such an effective quenching. The response to Pb^{2+} occurred exclusively in the CD-dye complex, but not in the chromorphore itself, and such behavior occurred only in the presence of γ-CD, not in either α-CD or β-CD. At higher concentrations, the anisotropic texture disappeared because of the metal ion, followed by precipitation of the chromophore from the solution after it was left standing for a day (Fig. 2b). As a comparison, the addition of Cr^{3+} caused the complex to become turbid with slight changes in both absorption and emission of the complex.

The Stern–Volmer equation is a useful tool for quantitatively measuring fluorescence quenching: $[Q]$ is the quencher concentration, K_{SV} is the Stern–Volmer constant, F_0 is the fluorescence intensity measured without an additional quencher, and $F[Q]$ is the fluorescence intensity with the quencher at a given $[Q]$ [21,22]. The slope of the graph ($F_0/F[Q]$) versus $[Q]$ yields K_{SV} according to the equation $F_0/F[Q] = 1 + K_{SV}[Q]$. The more sensitive a system is to a specific quencher, the steeper the Stern–Volmer plot, which results in a higher K_{SV} value. We observed linear Stern–Volmer plots with a large K_{SV} value for lead ion as a quencher. The complex exhibited significant fluorescence quenching for lead salts as quenchers, with $K_{SV} = 1.3 \times 10^5$ (Fig. 3a). An anisotropic

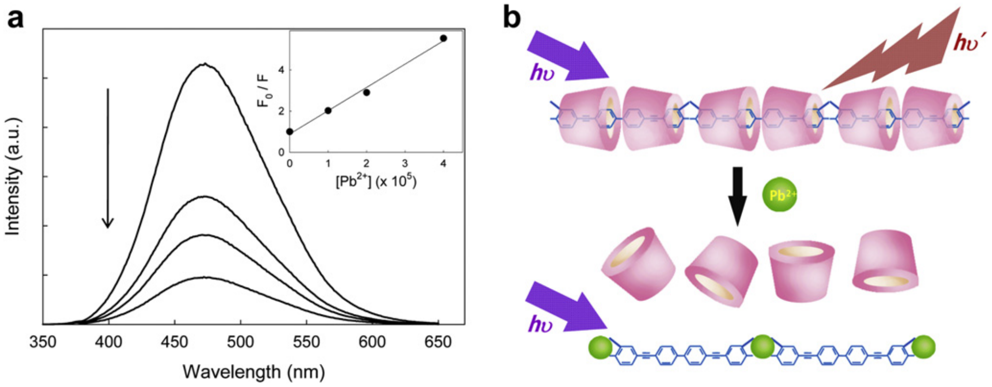


Fig. 3. (a) Fluorescence emission spectra of the complex with the addition of Pb^{2+}. The arrow indicates an increasing amount of Pb^{2+}, and the inset represents relative intensities with the concentration of Pb^{2+}. The complex consists of dye (1.0×10^{-5} mol L^{-1}) and γ-CD (2.0×10^{-5} mol L^{-1}). (b) Schematic representation of the complex break-up induced by lead ion, which provides apparent advantages over small molecules for sensing applications.

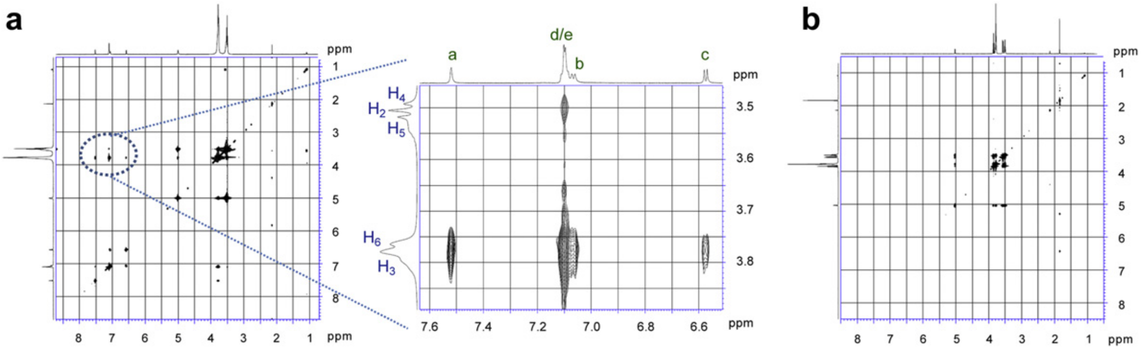


Fig. 5. ROESY spectrum of the complex (a) before and (b) after adding equimolar Pb^{2+}. Magnified inset in (a) shows strong NOE interactions between the dye and γ-CD. The concentrations of the dye and γ-CD are 1.0×10^{-2} mol L^{-1} and 2.0×10^{-2} mol L^{-1}, respectively. Measurements were made using D_2O as a solvent at 25 °C.

supramolecule, as mentioned earlier, is constructed by multiple hydrogen bonding between adjacent CD stacks. Consequently, it is more susceptible to the attack of lead metal ions, which is considered responsible for the quenching enhancements. Such behavior is similar to the molecular wire effect of conjugated polymers associated with electronic communication along the polymer backbone [23,24]. From the above results, a possible quenching mechanism may be proposed, in which the break-up of the supramolecular chain is induced by lead ions, which provides apparent advantages over small molecules in sensing applications (Fig. 3b). Meanwhile, with Cr^{3+}, the complex was modestly quenched with a K_{SV} value of $\sim 10^3$; hence the complex still exhibited fluorescence even in its presence.

To estimate the interactive behavior of the complex with metal ions, ^1H NMR spectra of the complex in the absence and presence of equimolar Pb^{2+} in D_2O were measured (Fig. 4). In the CD complex, as expected, the resonance signals of aromatic protons significantly decreased and CD proton signals were shifted and merged, which indicates that the chromophores were wrapped inside the γ-CD cavity and that their flexibility was affected by non-covalent associations [25,26]. The dye within the CD cavity obviously experienced a shielding effect. By adding Pb^{2+}, on the other hand, the proton signals of the CD resolved into those of the pristine CD; thereby the addition of Pb^{2+} excluded the chromophore from the CD cavity, ultimately leading to precipitated dye and uncomplexed CD molecules. From these results, therefore, we conclude that Pb^{2+} complexed more with the chromophore than with the CD, and this behavior was found to be more effective in destroying the CD-dye inclusion complex.

The 2D-ROESY NMR spectrum confirmed the rotational NOE interactions between the inner protons of γ-CD and the phenyl protons of the included dye (Fig. 5). However, after the addition of Pb^{2+}, these NOE cross-peaks almost disappeared and, in addition, the aromatic signals of the dye are no longer observed. This clearly indicates that the chromophore molecule, tightly included in the hydrophobic cavity, was expelled from the γ-CD cavity by forming precipitates of dye–metal complexes, which ultimately led to selective and efficient fluorescence quenching of the supramolecular complex.

In summary, we have described a supramolecular CD-chromophoric dye complex, in which anistropy occurred via the formation of a hexagonal packing of cylindrical CD channels. The obtained complex exhibited effective fluorescence quenching in the presence of Pb^{2+} based on supramolecular assembly and dissociation. Selective and effective fluorescence quenching of the complex is attributed to the break-ups of supramolecular wire and the unthreading of included dye molecules by lead ion. Though we are not yet sure what causes such a high selectivity of the supramolecular complex, a topic that will be elaborated in subsequent investigations, these CD-templated supramolecular properties may be useful in analytical applications as a novel platform for metal ion sensing.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (Grant No. 2010-0007145).

References

[1] Whitesides GM, Grzybowski B. Self-assembly at all scales. Science 2002;295:2418–21.
[2] Palermo V, Samori P. Molecular self-assembly across multiple length scales. Angew Chem Int Edit 2007;46:4428–32.
[3] Zhao X, Zhou SX, Chen M, Wu LM. Supramolecular architecture, spectroscopic properties and stability of CI Basic Violet 10 (Rhodamine B) at high concentration. Dyes Pigm 2009;80:212–8.
[4] Shimura H, Yoshio M, Hoshino K, Mukai T, Ohno H, Kato T. Noncovalent approach to one-dimensional ion conductors: enhancement of ionic conductivities in nanostructured columnar liquid crystals. J Am Chem Soc 2008;130:1759–65.
[5] Kerr RL, Miller SA, Shoemaker RK, Elliott BJ, Gin DL. New type of Li ion conductor with 3D interconnected nanopores via polymerization of a liquid organic electrolyte-filled lyotropic liquid-crystal assembly. J Am Chem Soc 2008;131:15972–3.
[6] Harada A. Cyclodextrin-based molecular machines. Acc Chem Res 2001;34:456–64.
[7] Cacialli F, Wilson JS, Michels JJ, Daniel C, Silva C, Friend RH, et al. Cyclodextrin-threaded conjugated polyrotaxanes as insulated molecular wires with reduced interstrand interactions. Nat Mater 2002;1:160–4.
[8] Wenz G, Han BH, Muller A. Cyclodextrin rotaxanes and polyrotaxanes. Chem Rev 2006;106:782–817.
[9] Agbaria RA, Gill D. Extended 2,5-diphenyloxazole-gamma-cyclodextrin aggregates emitting 2,5-diphenyloxazole excimer fluorescence. J Phys Chem 1988;92:1052–5.
[10] Das R, Mallick A, Sarkar D, Chattopadhyay N. Probe-induced self-aggregation of gamma-cyclodextrin: formation of extended nanotubular suprastructure. J Phys Chem C 2008;112:9600–3.
[11] Harada A, Hashidzume A, Yamaguchi H, Takashima Y. Polymeric rotaxanes. Chem Rev 2009;109:5974–6023.
[12] Park JS, Jeong S, Chang DW, Kim JP, Kim K, Park E, et al. Lithium-induced supramolecular hydrogel. Chem Commun 2011;47:4736–8.
[13] Wei HL, Yu HQ, Zhang AY, Sun LG, Hou DD, Feng ZG. Synthesis and characterization of thermosensitive and supramolecular structured hydrogels. Macromolecules 2005;38:8833–9.
[14] Toscano CD, Guilarte TR. Lead neurotoxicity: from exposure to molecular effects. Brain Res Rev 2005;49:529–54.
[15] Papanikolaou NC, Hatzidaki EG, Belivanis S, Tzanakakis GN, Tsatsakis AM. Lead toxicity update. A brief review. Med Sci Monitor 2005;11:RA329–36.
[16] Park JS, Wilson JN, Hardcastle KI, Bunz UHF, Srinivasarao M. Reduced fluorescence quenching of cyclodextrin-acetylene dye rotaxanes. J Am Chem Soc 2006;128:7714–5.
[17] Kim J, Swager TM. Control of conformational and interpolymer effects in conjugated polymers. Nature 2001;411:1030–4.

[18] Bunz UHF. Poly(aryleneethynylene)s: synthesis, properties, structures, and applications. Chem Rev 2000;100:1605–44.

[19] Bunz UHF. Poly(aryleneethynylene)s. Macromol Rapid Comm 2009;30:772–805.

[20] Higashi K, Ideura S, Waraya H, Moribe K, Yamamoto K. Incorporation of salicylic acid molecules into the intermolecular spaces of gamma-cyclodextrin-polypseudorotaxane. Cryst Growth Des 2009;9:4243–6.

[21] Wang J, Wang DL, Miller EK, Moses D, Bazan GC, Heeger AJ. Photoluminescence of water-soluble conjugated polymers: origin of enhanced quenching by charge transfer. Macromolecules 2000;33:5153–8.

[22] Barbero N, Barni E, Barolo C, Quagliotto P, Viscardi G, Napione L, et al. A study of the interaction between fluorescein sodium salt and bovine serum albumin by steady-state fluorescence. Dyes Pigm 2009;80:307–13.

[23] Zhou Q, Swager TM. Fluorescent chemosensors based on energy migration in conjugated polymers: the molecular wire approach to increased sensitivity. J Am Chem Soc 1995;117:12593–602.

[24] Mammen M, Choi SK, Whitesides GM. Polyvalent interactions in biological systems: implications for design and use of multivalent ligands and inhibitors. Angew Chem Int Edit 1998;37:2754–94.

[25] Eliadou K, Yannakopoulou K, Rontoyianni A, Mavridis IM. NMR detection of simultaneous formation of [2]- and [3] pseudorotaxanes in aqueous solution between alpha-cyclodextrin and linear aliphatic alpha, omega-amino acids, an alpha, omega-diamine and an alpha, omega-diacid of similar length, and comparison with the solid-state structures. J Org Chem 1999;64:6217–26.

[26] Steed JW, Foster JA. Exploiting cavities in supramolecular gels. Angew Chem Int Edit 2010;49:6718–24.