

# Highly Fluorescent Fluoride-Responsive Hydrogels Embedded with CdTe Quantum Dots

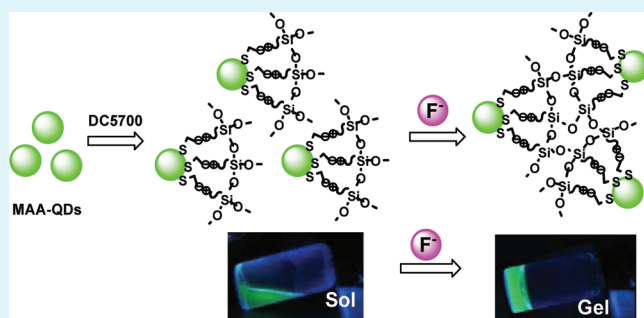
Juan Zhou and Haibing Li\*

Key Laboratory of Pesticide and Chemical Biology (CCNU), Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P.R. China

## S Supporting Information

**ABSTRACT:** Functionalized CdTe quantum dots (QDs) synthesized via ion exchange demonstrated a selective response toward fluoride in aqueous solutions based on a rapid sol–gel transition that was visible to the naked eye. The fluoride-induced hydrogel exhibited excellent fluorescent performance because of the incorporation of QDs. As a result, this highly fluorescent fluoride-induced hydrogel may pave a new way to sense fluoride using a visible sol–gel transition.

**KEYWORDS:** fluoride, quantum dots, responsive hydrogel, sol–gel transition



## 1. INTRODUCTION

As known “smart” materials, responsive hydrogels have sparked active research because of potential applications in tissue engineering, drug delivery, and biomedicine.<sup>1</sup> Responsive hydrogels based on different stimuli, such as temperature,<sup>2</sup> light,<sup>3</sup> magnetic fields,<sup>4</sup> chemical entities,<sup>5</sup> and even multi-response<sup>6</sup> have been widely investigated. Among these stimuli, anion response has attracted extensive attention<sup>7</sup> because it is related to vital processes in biology, chemistry, and the environment.<sup>8</sup> However, highly selective anion-responsive hydrogels based on the gel–sol transition have seldom been realized.<sup>9</sup> In recent years, responsive hydrogels incorporating semiconductor quantum dots (QDs) have received increasing interest to expand the applications of hydrogels and achieve novel functions. QDs have been used in optical sensors, optoelectronics, and biological labels<sup>10</sup> because of their unique optical properties. Hydrogels containing QDs can exhibit intense fluorescence and may be developed as biological, medicinal, or multiresponsive materials. Nevertheless, most of the previous investigations of fluorescent hydrogels measure their response to temperature or pH.<sup>11</sup> Studies concerning the anion response of highly fluorescent hydrogels have not been published to date.

Among anions, fluoride is of great significance because of its important roles in environmental monitoring<sup>12</sup> (such as water analysis) and biomedicine, which is closely associated with organism health including dental, skeleton, gastric, and kidneys.<sup>13</sup> Though fluoride-responsive gels have been proposed, most of the previous investigations operate in organic solvents,<sup>14</sup> which severely limit their application. In addition, it is known that achieving anion response in an aqueous system is rather difficult owing to their strong anion solvation. Therefore,

to construct a hydrogel with a fluorescent sol–gel transition that has a selective response to fluoride is potentially of great use. Such a strategy may not only overcome the drawbacks of anion response that are encountered in conventional colorimetric and fluorimetric techniques but also induce unique functions due to their sol–gel transition and optical properties, making it especially promising for sensing applications.

In this paper, we develop a highly fluorescent, selectively fluoride-responsive hydrogel embedded with CdTe QDs. An electropositive siloxane coupling agent  $[(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-]$  (DC5700, Scheme 1a) was selected for two reasons. First, it can encapsulate the fluorescent QDs into this system through ion exchange (electrostatic interactions); and second, the siloxane group is sensitive to fluoride ion.<sup>15</sup> As shown in Scheme 1b, DC5700-QDs were prepared via electrostatic interactions between carboxylate anions and ammonium cations. The as-synthesized DC5700-QDs were characterized by FT-IR spectroscopy and steady-state emission (see Figure S1 in the Supporting Information). A rapid sol–gel transition can be observed by the naked eye a few minutes after treating an aqueous solution of DC5700-QDs with fluoride to form a highly fluorescent hydrogel (Scheme 1c).

## 2. EXPERIMENTAL SECTION

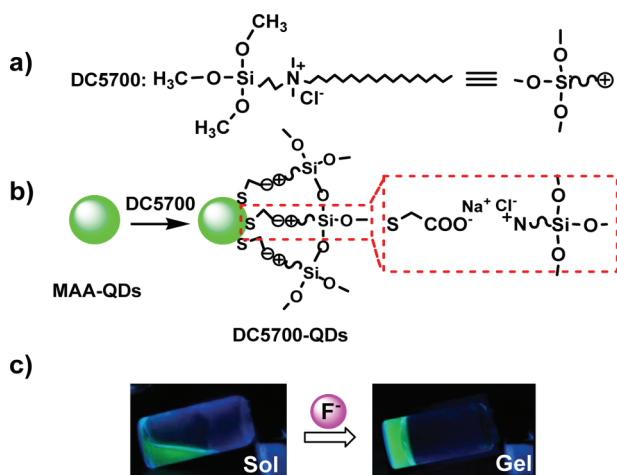
**2.1. Chemicals and Materials.** All chemicals used were of analytical grade or the highest purity available. Tellurium (powder, 99.999%, about 200 mesh), mercaptoacetic acid (MAA, 99%),

Received: October 1, 2011

Accepted: January 4, 2012

Published: January 4, 2012

**Scheme 1.** (a) Chemical Structure of DC5700, (b) Preparation of DC5700-QDs via Ion Exchange, and (c) Sol–Gel Phase Transition of DC5700-QDs Solutions Treated with  $F^-$  (fluoride sodium) under Ultraviolet Lamp (excitation wavelength = 365 nm)<sup>a</sup>



<sup>a</sup>The concentration of  $F^-$  is  $10^{-3}$  M.

$CdCl_2 \cdot 2.5H_2O$  (99%),  $NaBH_4$  (96%), and DC5700 (40% Gelest) were purchased from Aldrich (Milwaukee, WI). All of the anion solutions were prepared with double-distilled, deionized water.

**2.2. Preparation of Water-Soluble CdTe QDs.** MAA-capped CdTe QDs (MAA-QDs) were prepared according to the literature with minor alterations.<sup>16</sup> In a typical procedure,  $CdCl_2 \cdot 2.5H_2O$  (95 mg) and MAA (70  $\mu$ L) were mixed in a three-necked flask in double-distilled water (3 mL). The pH of the solution was adjusted to 11 using NaOH (1 M). The mixture was stirred for about 30 min under the protection of nitrogen gas. A Te source was prepared by reacting Te power (33 mg) with  $NaBH_4$  (148 mg) in double-distilled water (2 mL). The formed colorless aqueous NaHTe was then quickly injected into the three-necked flask. After heating under reflux in an oil bath at 90 °C for 2 h, the product was purified by repeated centrifugation to give highly fluorescent MAA-QDs. Finally, the as-prepared QDs were diluted with double-distilled water and adjusted to a pH of 7–8 for the following modification.

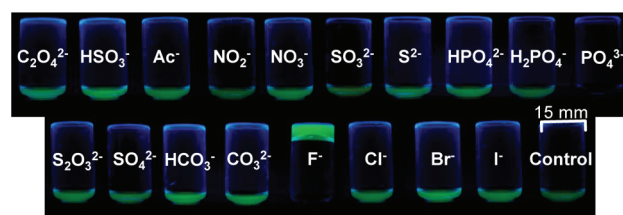
**2.3. Formation of Fluoride-Induced Hydrogels Embedded with QDs.** DC5700-QDs were formed by adding DC5700 (40% Gelest, 100  $\mu$ L) to an aqueous solution of MAA-QDs (0.5 mL) and then stirring for 0.5 h. A variety of anion solutions ( $10^{-3}$  M, 125  $\mu$ L) containing the sodium salts of  $C_2O_4^{2-}$ ,  $HSO_3^-$ ,  $CH_3COO^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $S^{2-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ ,  $PO_4^{3-}$ ,  $S_2O_3^{2-}$ ,  $SO_4^{2-}$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  were added to the DC5700-QDs system, respectively. A gel formed in a few minutes in response to addition to  $F^-$ , resulting in appreciable phase transition from sol to gel compared with the other anions tested.

**2.4. Characterization.** Fluorescence spectra were acquired on a right-angle fluorometer (Cary Eclipse Fluorescent Spectrometer, FL1008M018), with an excitation wavelength of 450 nm and a slit width of 5 nm. The corresponding UV–visible (UV–vis) absorption spectra were obtained at room temperature on a spectrophotometer (UV-2501, Shimadzu, Japan) with a variable wavelength between 200 and 800 nm. The modulus  $G'$  and  $G''$  of the control and the gel, respectively, were recorded by a strain-controlled rheometer (Rheometrics Fluids Spectrometer, ARES-RFS) as the temperature was increased from 20 to 80 °C. IR spectra were collected on an IR spectrometer (Thermo Nicolet NEXUS) in the wavenumber range of 400–4000  $cm^{-1}$  using KBr pellets. The morphology of the materials was examined using a scanning electron microscope (SEM, Hitachi S-4700 electron microscope), and transmission electron microscope (TEM) images were obtained on a TEM (JEOL-JEM 2010) operating at 200 kV. The static contact angle was measured with a contact angle

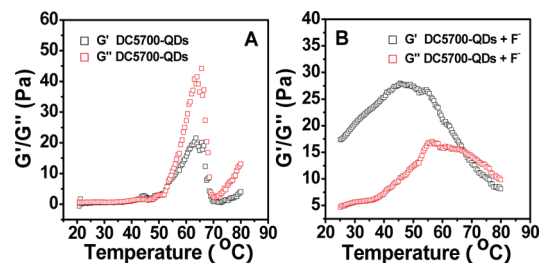
system (OCA 20, Dataphysics), and all of the photographs were shot by a digital camera.

### 3. RESULTS AND DISCUSSION

The high selectivity of fluoride to form a gel with the DC5700-QD system was demonstrated by turning all of the sample bottles upside down, as shown in Figure 1. All of the samples quickly flowed downward indicating their solution state except for the sample treated with  $F^-$  ions, which exhibits a distinct state transformation from aqueous solution to a gel. Moreover, embedding with QDs endows the as-formed gel with excellent optical performance, which was confirmed from the fluorescent and UV–vis spectra (see Figure S2 in the Supporting Information). The fluoride-induced hydrogel possesses stable fluorescent properties without obvious changes in positions and intensities compared with that of DC5700-QDs solutions, illustrating that the fluoride ions do not affect the QDs but impact the outer siloxane layer.

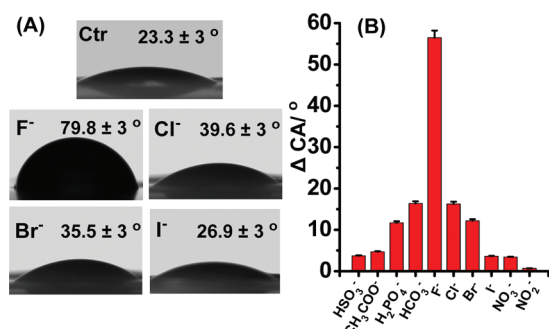


**Figure 1.** Photographic images of DC5700-QDs solutions added with various anions of  $10^{-3}$  M concentration under ultraviolet lamp (excitation wavelength = 365 nm). The highly fluorescent hydrogel was merely observed with the presence of  $F^-$ , indicating evident selectivity of fluoride in forming a gel.



**Figure 2.** Modulus–temperature traces of (A) DC5700-QDs and (B) DC5700-QDs after adding  $F^-$ . By comparison, a critical temperature at 68 °C can be observed for the gel. When the temperature is below 68 °C, the material shows a gel state; however, the control DC5700-QDs do not show an obvious gel state during the whole testing.

Additionally, the as-formed hydrogel was further characterized to investigate its sol–gel transition performance in depth. The modulus–temperature traces presented in Figure 2 provide valuable information about the dependence of the gel–sol of the system on temperature. The fluoride-induced hydrogel converted from gel to sol with increasing temperature, compared with the DC5700-QDs control (Figure 2A), which displays a sol state over the whole temperature range because most of the temperature spectrum exports as  $G'' > G'$ .<sup>17</sup> However, as Figure 2B shows, both  $G'$  and  $G''$  increased at the beginning, and an obvious  $G' > G''$  can be observed during this stage, which indicates further gelation with increasing temperature from 25–50 °C. However, a gradual gel–sol transition occurs as the temperature continues rising, until the sample forms a sol ( $G'' > G'$ ). A critical temperature  $T_c$  of 68 °C can be



**Figure 3.** (A) Water drop profile changes of DC5700-QDs treated with analogous anions (control, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>, the concentration of anions is 10<sup>-3</sup> M) measuring on glass slides. (B) The histogram directly shows the changes of CA ( $\Delta CA = CA_{\text{anions}} - CA_{\text{control}}$ ) with adding different anions, indicating a high selectivity of fluoride-responsive wettability.

observed in the temperature spectrum. Thus, the material presents a gel state below 68 °C, while at temperatures higher than 68 °C, it acts as a sol. This is consistent with the results from heating experiments (See Figure S3 in the Supporting Information). A reversible sol–gel transition can be observed with alternate heating and cooling for a short period of time. All of the samples became permanent gels overnight because of Si–O–Si covalent cross-linking; however, both the gel and the sol exhibit excellent fluorescent performance. Adding Fe<sup>3+</sup> to the gel is another effective way to trigger phase transformation of the hydrogel (see Figure S4 in the Supporting Information), which is caused by the strong complexation between Fe<sup>3+</sup> and F<sup>-</sup>. However, in this case, the fluorescence of the QDs is quenched.

Furthermore, the morphology of the xerogel was studied by SEM (see Figure S5 in the Supporting Information). For DC5700-QDs, although slightly aggregated blocks can be observed because of slow cross-linking between DC5700 molecules, most of the small micelles are well-dispersed. In contrast, the gel formed by adding F<sup>-</sup> was a single piece of film, implying that the fluoride ions induced strong cross-linking of DC5700-QDs particles. To further characterize the structure of the QDs in the system, TEM images were obtained (see Figure S6 in the Supporting Information). These indicated that the size of the QDs did not change during gelation, and as a result, the as-obtained hydrogel maintains the fluorescence of the original sol.

The high selectivity for fluoride and its crucial role in gelation are also supported by contact angle (CA) measurements. The CA of DC5700-QDs is 23.3°, showing its hydrophilic nature. However, a remarkable increase of CA to 79.8° is observed after treatment with fluoride compared with that induced by other analogous anions (Figure 3A). Figure 3B shows the change in CA before and after adding different anions to DC5700-QDs, revealing a remarkable selectivity for fluoride based on CA. The possible mechanism of fluoride-responsive wettability was considered. As described in Figure S7 (Supporting Information), the hydrophilic nature of DC5700-QDs is attributed to the hydroxyl groups formed during the hydrolytic process. However, the change of the system to a weak hydrophilic nature after adding fluoride may be caused by intermolecular hydrogen bonding between fluoride ions and hydroxyl groups.

Finally, the probable mechanism of gelation induced by fluoride in the whole system is considered. Gelation may be caused by the following two aspects: (i) F<sup>-</sup> is known to possess a small radius, which is beneficial to attack silicon through nucleophilic substitution.<sup>15</sup> (ii) Together with the strong hydrogen bonding between F<sup>-</sup> and water molecules in aqueous solution, more water molecules were present around DC5700-QDs following addition of F<sup>-</sup>. As a result, more –OH groups are rapidly substituted for –OCH<sub>3</sub> groups in DC5700, which promoted cross-linking in the outer layer of DC5700-QDs via Si–O–Si covalent bonding, as shown in Scheme 2. As a result, large blocks were formed, and finally a hydrogel can be observed after just a few minutes.

#### 4. CONCLUSIONS

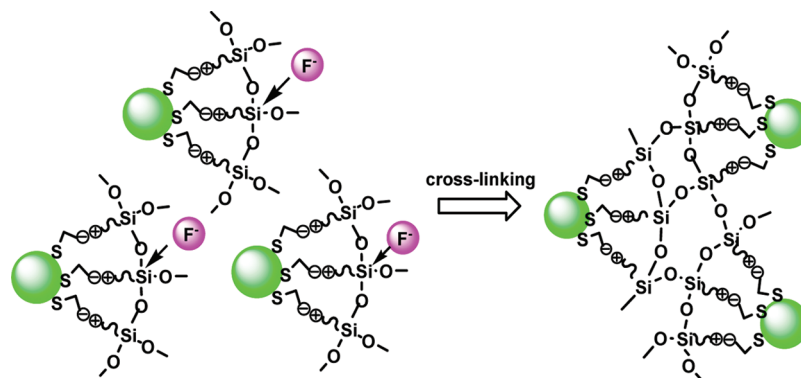
In conclusion, a fluoride-induced prominent sol–gel transition was used to produce a highly fluorescent hydrogel for the first time. An evident selectivity for fluoride ions based on surface wettability was established. Such a technique may pave a new way to sense fluoride ions using the sol–gel transition.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

FT-IR and fluorescent spectra of DC5700-QDs; fluorescent spectra and UV–vis absorption spectra of DC5700-QDs and the as-formed hydrogel; gel–sol transition triggered by temperature and Fe<sup>3+</sup>; SEM and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### Scheme 2. Schematic Process of Gelation upon Adding Fluoride into the DC5700-QDs System



## ■ AUTHOR INFORMATION

## Corresponding Author

\*Tel.: + 86-27-67866423. E-mail: lhbing@mail.ccnu.edu.cn.

## ■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (21072072, 21102051), PCSIRT (No. IRTO953), and Program for New Century Excellent Talent in University (NCET-10-0428).

## ■ REFERENCES

(1) (a) Ozay, O.; Ekici, S.; Baran, Y.; Aktas, N.; Sahiner, N. *Water Res.* **2009**, *43*, 4403. (b) Jang, J. H.; Jhaveri, S. J.; Rasin, B.; Koh, C.; Ober, C. K.; Thomas, E. L. *Nano Lett.* **2008**, *8*, 1456. (c) Thornton, P. D.; Mart, R. J.; Ulijn, R. V. *Adv. Mater.* **2007**, *19*, 1252.

(2) (a) Gong, Y. J.; Gao, M. Y.; Wang, D. Y.; Möhwald, H. *Chem. Mater.* **2005**, *17*, 2648. (b) Li, J.; Hong, X.; Liu, Y.; Li, D.; Wang, Y. W.; Li, J. H.; Bai, Y. B.; Li, T. J. *Adv. Mater.* **2005**, *17*, 163.

(3) (a) Liao, X. J.; Chen, G. S.; Liu, X. X.; Chen, W. X.; Chen, F.; Jiang, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4409. (b) Muraoka, T.; Kinbara, K.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 11600. (c) Peng, K.; Tomatsu, I.; Kros, A. *Chem. Commun.* **2010**, *46*, 4094. (d) Kloxin, A. M.; Kasko, A. M.; Salinas, C. N.; Anseth, K. S. *Science* **2009**, *324*, 59. (e) Gu, Z.; Tang, Y. *Lab Chip* **2010**, *10*, 1946.

(4) Ghosh, S.; Cai, T. *J. Phys. D: Appl. Phys.* **2010**, *43*, 415504.

(5) (a) Thornton, P. D.; Mart, R. J.; Ulijn, R. V. *Adv. Mater.* **2007**, *19*, 1252. (b) Rodríguez-Llansola, F.; Miravet, J. F.; Escuder, B. *Chem. Commun.* **2011**, *47*, 4706. (c) Gu, Z.; Zhao, M. X.; Sheng, Y. W.; Bentolila, L. A.; Tang, Y. *Anal. Chem.* **2011**, *83*, 2324. (d) Dave, N.; Chan, M. Y.; Huang, P. J.; Smith, B. D.; Liu, J. W. *J. Am. Chem. Soc.* **2010**, *132*, 12668. (e) He, C.; Kim, S. W.; Lee, D. S. *J. Controlled Release* **2008**, *127*, 189. (f) Qiu, Y.; Park, K. *Adv. Drug Delivery Rev.* **2001**, *53*, 321. (g) Ge, Z. S.; Hu, J. M.; Huang, F. H.; Liu, S. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 1798.

(6) (a) Liu, J. H.; Chen, G. S.; Guo, M. Y.; Jiang, M. *Macromolecules* **2010**, *43*, 8086. (b) Chang, C. Y.; He, M.; Zhou, J. P.; Zhang, L. *Macromolecules* **2011**, *44*, 1642.

(7) Becker, T.; Goh, C. Y.; Jones, F.; McIlldowie, M. J.; Mocerino, M.; Ogden, M. I. *Chem. Commun.* **2008**, *33*, 3900.

(8) (a) Gale, P. A.; Garcia-Garrido, S. E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151. (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (c) Martínez-Mañez, R.; Sancenón, R. *Chem. Rev.* **2003**, *103*, 4419.

(9) Shen, J. S.; Li, D. H.; Cai, Q. G.; Jiang, Y. B. *J. Mater. Chem.* **2009**, *19*, 6219.

(10) (a) Alivisatos, A. P. *Science* **1996**, *217*, 933. (b) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59. (c) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.

(11) (a) Li, J.; Hong, X.; Liu, Y.; Li, D.; Wang, Y. W.; Li, J. H.; Y. Bai, Y. B.; Li, T. J. *Adv. Mater.* **2005**, *17*, 163. (b) Bappaditya, R.; Abhijit, S.; Aluri, E.; Arun, K. N. *Soft Matter* **2010**, *6*, 3337.

(12) Qu, Y.; Hua, J. L.; Tian, H. *Org. Lett.* **2010**, *12*, 3320.

(13) (a) Horowitz, H. S. *J. Public Health Dent.* **2003**, *63*, 3. (b) Singh, P. P.; Barjatiya, M. K.; Dhing, S.; Bhatnagar, R.; Kothari, S.; Dhar, V. *Urol. Res.* **2001**, *29*, 238.

(14) (a) Kim, T. H.; Choi, M. S.; Sohn, B. H.; Park, S. Y.; Lyoo, W. S.; Lee, T. S. *Chem. Commun.* **2008**, *20*, 2364. (b) Džolić, Z.; Cametti, M.; Cort, A. D.; Mandolini, L.; Žinić, M. *Chem. Commun.* **2007**, *34*, 3535. (c) Yang, H.; Yi, T.; Zhou, Z. G.; Wu, J. C.; Xu, M.; Li, F. Y.; Huang, C. H. *Langmuir* **2007**, *23*, 8224.

(15) (a) Kim, S. Y.; Park, J.; Koh, M.; Park, S. B. *Chem. Commun.* **2009**, *31*, 4735. (b) Yang, X. F.; Qi, H.; Wang, L.; Su, Z.; Wang, G. *Talanta* **2009**, *80*, 92. (c) Kim, S. Y.; Hong, J. I. *Org. Lett.* **2007**, *9*, 3109. (d) Pope, E. J. A.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1986**, *87*, 185. (e) Nassau, N.; Raghavachari, K. *J. Non-Cryst. Solids* **1988**, *104*,

181. (f) Zhang, J. F.; Lim, C. S.; Bhuniya, S.; Cho, B. R.; Kim, J. S. *Org. Lett.* **2011**, *13*, 1190.

(16) (a) Gao, M. Y.; Kirstein, S.; Mohwald, H.; Rogach, A. L.; Kornowski, A.; Eychmüller, A.; Weller, H. *J. Phys. Chem. B* **1998**, *102*, 8360. (b) Talapin, D. V.; Haubold, S.; Rogach, A. L.; Komowski, A.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2001**, *105*, 2260. (c) Rogach, A. L. *Mater. Sci. Eng., B* **2000**, *69–70*, 435.

(17) Xu, P. X. *Polymer Rheology and Their Application*; Chemical Industry Press: Beijing, 2003; Vol. 1, pp 3–13.