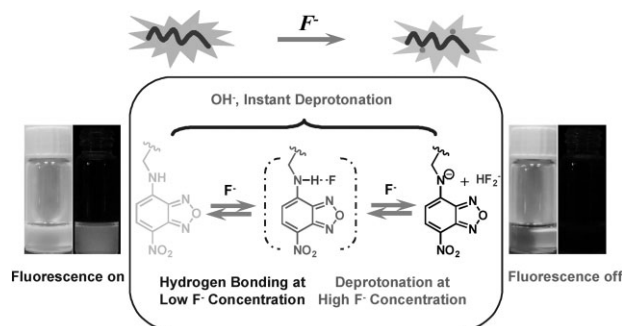


# Highly Selective Colorimetric and Fluorometric Probes for Fluoride Ions Based on Nitrobenzofurazan-containing Polymers<sup>a</sup>

Jinming Hu, Changhua Li, Yue Cui, Shiyong Liu\*

We report on a novel colorimetric and fluorometric chemosensor for fluoride ions based on 4-(2-acryloyloxyethylamino)-7-nitro-2,1,3-benzoxadiazole (NBDAE)-labeled polymers. Upon gradual addition of fluoride ions ( $F^-$ ), the green fluorescence emission of NBDAE moieties can be dramatically quenched, accompanied with the distinct colorimetric transition from green to yellow. NBDAE moieties are capable of selectively recognizing  $F^-$  ions via hydrogen-bonding ( $H$ -bonds) interactions at low  $F^-$  concentration and subjected to further deprotonation process at high  $F^-$  concentration. NBDAE-labeled polymers in organic solvents possess high selectivity and fluorescence “turn-off” characteristics toward the sensing of  $F^-$  ions with the detection limit down to  $\approx 0.8 \mu\text{M}$ .



## Introduction

Extensive research has focused on the recognition and sensing of anions in the past decade due to their vital roles in biological, environmental, and industrial processes. In particular, the sensing of fluoride ions ( $F^-$ ) is highly relevant to health care, drinking water analysis, and the detection of chemical warfare agents.<sup>[1]</sup> The design strategies employed for  $F^-$  probes can be divided into three types, mainly based on supramolecular recognition (e.g., hydrogen bonding interactions,  $H$ -bonds),<sup>[2]</sup> Lewis acid–base interactions,<sup>[3]</sup>

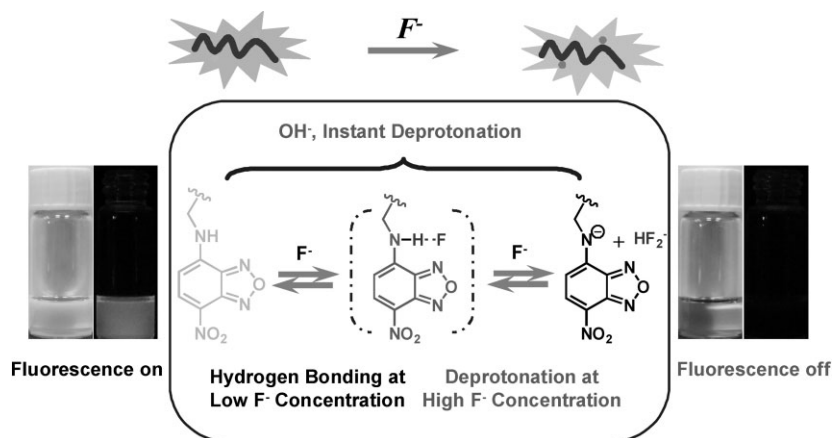
and fluoride ion-induced chemical reactions.<sup>[4]</sup> It should be noted that  $H$ -bonds based recognition is the most common strategy employed for  $F^-$  sensing, and a variety of  $H$ -bonds recognition moieties such as amides,<sup>[5]</sup> pyrroles,<sup>[6]</sup> ureas,<sup>[7]</sup> thioureas,<sup>[8]</sup> and hydrazone,<sup>[2a]</sup> which recognize and bind with anionic ions via  $N-H-X$   $H$ -bonds, have been employed to construct colorimetric and fluorometric  $F^-$  probes.<sup>[9]</sup> At low concentrations,  $F^-$  ions can form  $H$ -bonds with the above mentioned species, whereas at relatively high concentrations they can act as a strong base to promote the deprotonation process via Brønsted acid–base interactions. This unique property has been ascribed to their small size and high electronegativity.<sup>[10]</sup>

Recently, during the synthesis of dye-labeled fluorescent polymers via the copolymerization of 4-(2-acryloyloxyethylamino)-7-nitro-2,1,3-benzoxadiazole (NBDAE) with alkylsilyl-protected monomers, we happened to discover that  $F^-$  ions, acting as an alkylsilyl deprotection agent, can dramatically quench the fluorescence emission of NBDAE moieties. We then synthesized a series of NBDAE-containing polymers and investigated in detail the underlying mechanism. We found that both NBDAE and NBDAE-

S. Liu, J. Hu, C. Li, Y. Cui

CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China  
Fax: (+86) 551 3607 348; E-mail: sliu@ustc.edu.cn

<sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.



**Scheme 1.** Schematic illustration of the construction of selective and highly efficient fluoride ion probes based on 4-(2-acryloyloxyethyl-amino)-7-nitro-2,1,3-benzoxadiazole (NBDAE) and NBDAE-containing polymers. Also shown are photographs taken under visible light and UV light, respectively, for NBDAE-containing polystyrene, P(St-co-NBDAE), in THF in the absence and presence of tetra-*n*-butylammonium fluoride.

containing polymers can serve as highly selective and sensitive probes for F<sup>-</sup> ions, accompanied with dramatic fluorescence quenching and colorimetric changes (Scheme 1). Moreover, the polymer matrix can exhibit considerable effects on the detection sensitivity. We believe that this work represent a novel type of small molecule and polymeric F<sup>-</sup> probes based on secondary amine moieties (–NH–) in nitrobenzofurazan derivatives.

## Experimental Part

### Materials

*N*-Isopropylacrylamide (NIPAM) (97%, Tokyo Kasei Kagyo Co.) was purified by recrystallization twice from a benzene/*n*-hexane (*v/v* = 1:3) mixture. Styrene (St, 99.5%, Sinopharm Chemical Reagent Co. Ltd.) was successively washed with aqueous NaOH (5.0 wt.-%) and saturated NaCl solution, then distilled over CaH<sub>2</sub> at reduced pressure. Methyl methacrylate (MMA, Sinopharm Chemical Reagent Co.) was distilled over CaH<sub>2</sub> at reduced pressure. 4-Chloro-7-nitrobenzofurazan (NBD-Cl, 99%) was purchased from Alfa and used as received. 2,2-Azoisobutyronitrile (AIBN) was recrystallized from 95% ethanol. Tetra-*n*-butylammonium fluoride (TBAF, 98%, Aldrich) and tetra-*n*-butylammonium hydroxide (TBAOH, 10% aqueous solution, Aldrich) were used as received. Tetrahydrofuran (THF) was dried over sodium prior to use. NBDAE<sup>[11]</sup> and S-1-propyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid)trithio-carbonate (PDMAT)<sup>[12]</sup> were synthesized according to literature procedures.

### Sample Synthesis

Synthetic routes employed for the preparation of NBDAE containing copolymers are shown in Scheme S1.

Materials  
Views

www.MaterialsViews.com

**Synthesis of P(St-co-NBDAE) (Scheme S1):** Typical procedures employed for the synthesis of NBDAE-labeled PS, P(St-co-NBDAE)<sub>18</sub>, are as follows. A reaction tube was charged with St (1.04 g, 10.0 mmol), NBDAE (5.6 mg, 0.02 mmol), PDMAT (23.8 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), and 1,4-dioxane (1.2 g). The mixture was carefully degassed by three freeze-pump-thaw cycles and then sealed under vacuum. The polymerization was conducted at 80 °C for 12 h. The viscous mixture was diluted with THF and then precipitated into an excess of methanol for three times. The yellow solids were collected and dried in a vacuum oven overnight at 25 °C. P(St-co-NBDAE)<sub>18</sub> was thus obtained as a powder (0.18 g, yield: 17%;  $\overline{M}_{n,GPC}$  = 2.2 kDa,  $\overline{M}_w/\overline{M}_n$  = 1.04; see Supporting Information Figure S1).

**Synthesis of P(MMA-co-NBDAE) (Scheme S1):** Typical procedures employed for the synthesis of NBDAE labeled PMMA, P(MMA-co-NBDAE)<sub>82</sub>, are as follows. A reaction tube was charged with MMA (1.0 g, 10.0 mmol), NBDAE (5.6 mg, 0.02 mmol), PDMAT (23.8 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), and 1,4-dioxane (1.2 g). The mixture was carefully degassed by three freeze-pump-thaw cycles and then sealed under vacuum. The polymerization was conducted at 60 °C for 3 h. The viscous mixture was diluted with THF and then precipitated into an excess of methanol for three times. The solids were collected and dried in a vacuum oven overnight at 25 °C. P(MMA-co-NBDAE)<sub>82</sub> was obtained as a yellowish powder (0.83 g, yield: 80%;  $\overline{M}_{n,GPC}$  = 8.5 kDa,  $\overline{M}_w/\overline{M}_n$  = 1.11; see Supporting Information Figure S1).

**Synthesis of P(NIPAM-co-NBDAE) (Scheme S1):** Typical procedures employed for the synthesis of NBDAE labeled PNIPAM, P(NIPAM-co-NBDAE)<sub>76</sub>, are as follows. A reaction tube was charged with NIPAM (1.13 g, 10 mmol), NBDAE (5.6 mg, 0.02 mmol), PDMAT (23.8 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), and 1,4-dioxane (1.2 g). The mixture was carefully degassed by three freeze-pump-thaw cycles and then sealed under vacuum. The polymerization was conducted at 60 °C for 3 h. The viscous mixture was diluted with THF and then precipitated into an excess of diethyl ether for three times. The solids were collected and dried in a vacuum oven overnight at 25 °C. P(NIPAM-co-NBDAE)<sub>76</sub> was obtained as a yellowish powder (0.85 g, yield: 73%;  $\overline{M}_{n,GPC}$  = 8.9 kDa,  $\overline{M}_w/\overline{M}_n$  = 1.14; see Supporting Information Figure S1).

### Characterization

All <sup>1</sup>H NMR spectra were performed at 25 °C on a Bruker AV400 NMR spectrometer (resonance frequency of 400 MHz for <sup>1</sup>H) operating in the Fourier transform mode. CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as the solvents.

### Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C). It used a series of two linear Styragel columns (HT2

and HT4) at an oven temperature of 45 °C. The eluent was THF at a flow rate of 1.0 mL·min<sup>-1</sup>. A series of low polydispersity polystyrene standards were employed for the GPC calibration.

### Fluorescence Measurements

Fluorescence spectra were recorded using a F-4600 (Hitachi) spectrofluorometer. The slit widths were both set at 5 nm for excitation and emission, the excitation wavelength was fixed at 470 nm.

### UV-Vis Spectroscopy

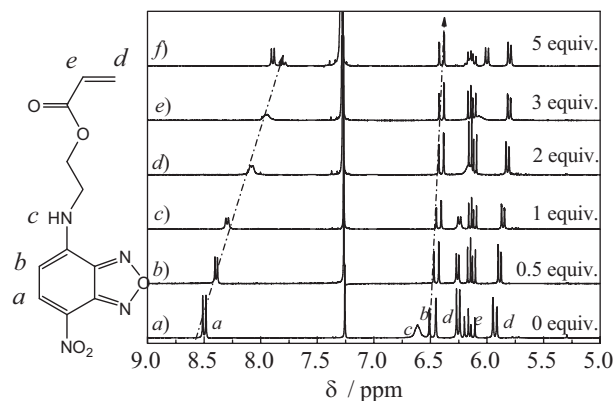
All UV-Vis spectra were acquired on a RF-5301/PC (Shimadzu) spectrofluorometer.

## Results and Discussion

The polymerizable NBDAE monomer was synthesized from commercially available non-fluorescent 4-chloro-7-nitrobenzofurazan (NBD-Cl) via the substitution reaction with ethanolamine followed by esterification.<sup>[11]</sup> Well-defined NBDAE-labeled polymers, P(St-co-NBDAE), P(MMA-co-NBDAE), and P(NIPAM-co-NBDAE), were synthesized via the reversible addition-fragmentation chain transfer (RAFT) copolymerization of NBDAE (0.2 mol-% feed molar content) with St, MMA, and NIPAM, respectively (Scheme S1). The molecular weights and molecular weight distributions of NBDAE-labeled polymers were characterized by GPC (Supporting Information Figure S1) and the results are listed in Table S1, together with the dye labeling contents as determined by UV-Vis spectroscopy from a standard curve calibrated against NBDAE.

For small molecule NBDAE dye in THF, it exhibits strong fluorescence emission with a maximum at ≈515 nm. Upon the addition of 0–20 equiv. TBAF into the THF solution of NBDAE (3.6 μM), significant fluorescence quenching can be discerned (see Supporting Information Figure S2). The presence of ≈10.0 equiv. fluoride ions leads to almost complete fluorescence quenching, with the quenching efficiency,  $(I_0 - I)/I_0$ , being >95%. This implies that NBDAE dye can serve as a sensitive fluorometric sensor for F<sup>-</sup> ions.

<sup>1</sup>H NMR characterization was further employed to investigate the underlying mechanism of NBDAE fluorescence emission quenching by F<sup>-</sup> (Figure 1). In the absence of TBAF, resonance signals characteristic of nitrobenzofurazan protons and the secondary amine proton appear at 8.5, 6.5, and 6.6 ppm (peaks *a*, *b*, and *c*), respectively. Upon gradual addition of TBAF (0–5.0 equiv.), peaks *a* and *b* exhibit an apparent upfield shift, accompanied with the broadening and weakening of resonance signals. In the presence of 1.0 equiv. (relative to the NBDAE moieties) of TBAF, peaks *a* and *b* shifted to 8.3 and 6.4 ppm, respectively. In the presence of 5.0 equiv. F<sup>-</sup> ions, peaks *a* and *b* shifted to 7.9 and 6.3 ppm, respectively. It is worthy of noting that the



**Figure 1.** The chemical structure of NBDAE monomer and partial <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> for NBDAE monomer upon addition of varying amounts of TBAF: (a) 0 equiv., (b) 0.5 equiv., (c) 1.0 equiv., (d) 2.0 equiv., (e) 3.0 equiv., and (f) 5.0 equiv.

shift of peak *b* turns to be less sensitive to the presence of >2.0 equiv. F<sup>-</sup> ions. Previously, Chawla et al.<sup>[2a]</sup> reported that calix[4]arene derivatives containing hydrazone moieties can recognize F<sup>-</sup> ions and exhibit colorimetric transitions from yellow to dark purple. They found that two main processes, namely *H*-bond interaction and deprotonation, can dominate at low and high F<sup>-</sup> concentrations, respectively. The NMR results (Figure 1) obtained in the current case suggested that the initial addition of F<sup>-</sup> ions mainly led to *H*-bonds interaction between F<sup>-</sup> and the secondary amine (-NH-) of NBDAE moieties, whereas the addition of excess amount of F<sup>-</sup> ions resulted in the deprotonation of -NH- within NBDAE. A closer examination of Figure 1 revealed that even in the presence of 0.5 equiv. TBAF, the resonance signals of the secondary amine (-NH-) proton (peak *c*) completely disappeared. This implies that the presence of less stoichiometric amount of TBAF might also be able to induce the deprotonation process, and the quick and dynamic exchange of protons between protonated and unprotonated -NH- residues leads to the complete disappearance of NMR resonance signals (Scheme 1).

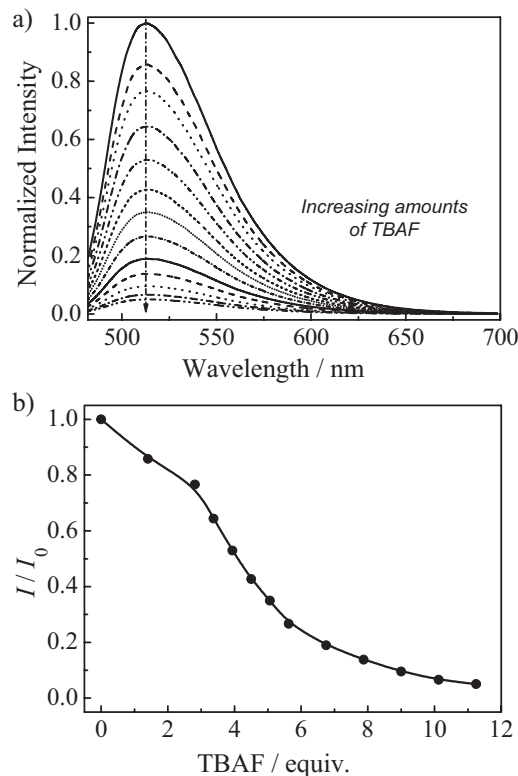
To further confirm the deprotonation process upon addition of F<sup>-</sup> ions, UV-Vis, fluorescence measurements, and <sup>1</sup>H NMR titration experiments were performed upon addition of varying amount of TBAOH. The UV-Vis spectra (see Supporting Information Figure S3) revealed that the characteristic absorption peak of NBDAE moieties red shift from 450 to 460 nm, accompanied with the appearance of two new absorption peaks at 395 and 408 nm, respectively. The further addition of >1.5 equiv. TBAOH only led to negligible changes in the UV-Vis spectrum. The fluorescence measurements were performed in the THF solution of NBDAE (3.6 μM) upon addition of varying amounts of TBAOH (see Supporting Information Figure S4). We can

observe the almost complete quenching of fluorescence emission at  $>1.5$  equiv. TBAOH, which agrees with the UV-Vis titration results as shown in Figure S3 of Supporting Information. This suggested that TBAOH, as a strong base, can more easily acquire the proton of secondary amine within NBDAE moieties as compared to that by  $F^-$  ions (see Supporting Information Figure S2).<sup>[9]</sup> The  $^1H$  NMR titration experiments further confirmed the deprotonation process (see Supporting Information Figure S5). The upfield shift of peaks *a* and *b* upon addition of TBAOH can be observed, which is quite similar to those in the presence of fluoride ions (Figure 1). All of these results revealed that the addition of  $F^-$  ions into the THF solution of NBDAE can induce the deprotonation of  $-NH-$  moiety within NBDAE residues. We propose that strongly basic TBAOH can lead to the instant deprotonation of  $-NH-$  moiety in NBDAE, whereas at low  $F^-$  concentration,  $H$ -bonds ( $N-H-F$ ) dominate and the further addition of  $F^-$  ions (especially at  $>2.0$  equiv.) can induce the prominent deprotonation via the efficient formation of  $HF_2^-$  species (Scheme 1).<sup>[9-10]</sup>

Recently, polymeric sensors combining the advantageous properties of polymers, especially responsive polymers, and small molecule detection moieties have aroused considerable interests due to the improved processability and capability of facile incorporation into devices.<sup>[13]</sup> The  $F^-$  sensing capability of NBDAE-labeled polymers was then examined. Upon addition of varying amounts of TBAF into the THF solution of P(St-co-NBDAE) ( $0.05\text{ g}\cdot\text{L}^{-1}$ ,  $[NBDAE] = 0.85\text{ }\mu\text{M}$ ), significant fluorescence quenching was observed (Figure 2 and Scheme 1). Similar to that of small molecule NBDAE, the presence of  $\approx 10.0$  equiv.  $F^-$  ions (relative to NBDAE residues) also leads to almost complete emission quenching. Thus, the incorporation of NBDAE moieties into polymer chains does not affect its sensing capability for fluoride ions. If we define the detection limit of  $F^-$  as the concentration at which a 10% fluorescence quenching can be achieved by employing  $0.05\text{ g}\cdot\text{L}^{-1}$  THF solution of P(St-co-NBDAE), the detection limit was determined to be  $0.8\text{ }\mu\text{M}$ . An apparent colorimetric transition from green to yellowish can also be visually discerned upon addition of TBAF (Scheme 1).

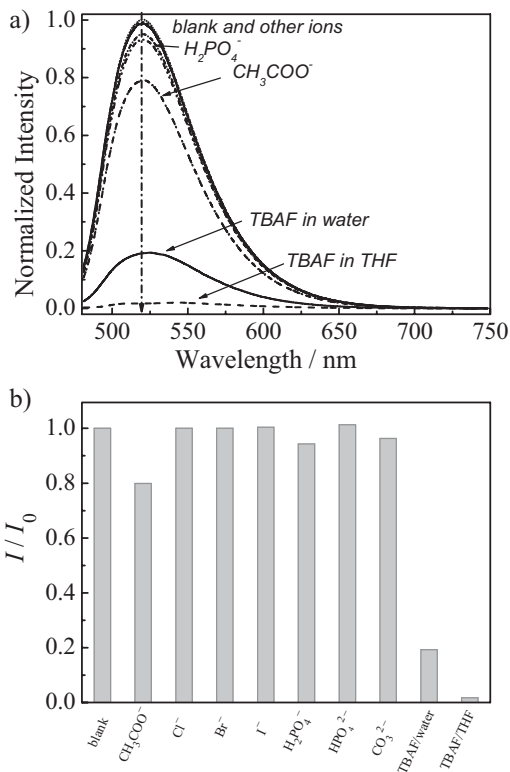
The UV-Vis absorption spectra of P(St-co-NBDAE) in THF revealed an intense characteristic band at  $\approx 450\text{ nm}$  (see Supporting Information Figure S6). Upon addition of TBAF, the absorption peak at  $450\text{ nm}$  gradually red shifted to  $\approx 460\text{ nm}$  and stabilized out at  $\approx 10$  equiv. TBAF. Additionally, two new absorption bands at  $395$  and  $409\text{ nm}$  appeared, with the intensities of which increased with TBAF concentrations. Thus, P(St-co-NBDAE) can also serve as a colorimetric  $F^-$  probe with high sensitivity (Scheme 1). It seems that the incorporation of NBDAE into the polymer matrix does not affect its  $F^-$  sensing capability.

To assess the sensing selectivity of NBDAE-labeled copolymers toward  $F^-$  over other common anions, further



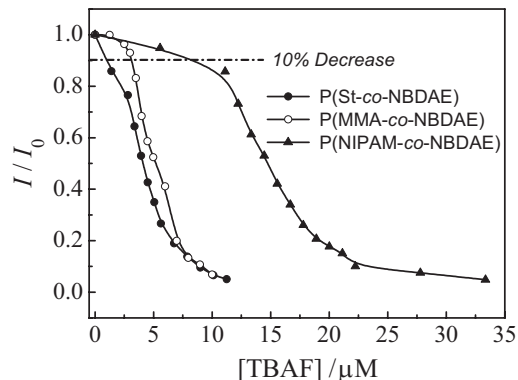
**Figure 2.** (a) Normalized fluorescence spectra and (b) changes in relative fluorescence intensities recorded for  $0.05\text{ g}\cdot\text{L}^{-1}$  P(St-co-NBDAE) copolymer in THF ( $[NBDAE] = 0.85\text{ }\mu\text{M}$ ) upon addition of varying amounts of TBAF ( $\lambda_{\text{ex}} = 470\text{ nm}$ , Ex.  $5\text{ nm}$ , Em.  $5\text{ nm}$ ).

competition experiments were conducted (Figure 3). Aqueous solutions (10 equiv.,  $20\text{ }\mu\text{L}$ ) of  $\text{CH}_3\text{COOK}$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{K}_2\text{CO}_3$ , TBAF, and THF solution of TBAF (10 equiv.,  $20\text{ }\mu\text{L}$ ) were added into  $2.0\text{ mL}$  THF solution of P(St-co-NBDAE) ( $0.05\text{ g}\cdot\text{L}^{-1}$ ,  $[NBDAE] = 0.85\text{ }\mu\text{M}$ ). Among them, only the addition of TBAF in THF resulted in  $\approx 95\%$  fluorescence quenching (Figure 3), whereas the addition of  $20\text{ }\mu\text{L}$  aqueous TBAF led to  $\approx 81\%$  fluorescence quenching. It seems that the presence of as low as  $\approx 1\%$  (v/v) of water can greatly weaken the hydrogen bonding interaction between NBDAE and fluoride ions. Further experiments revealed that the increase of water content to  $\approx 10\%$  (v/v) can almost completely recover the NBDAE fluorescence emission (data not shown). This suggests that the recognition and interaction of  $F^-$  ions by NBDAE is quite reversible in nature. This is reasonable considering the strong tendency of hydration of  $F^-$  ions by water molecules.  $\text{CH}_3\text{COO}^-$  ions often serve as a competitive ion during the sensing of  $F^-$  ions,<sup>[5-8]</sup> however, in the current system, the presence of 10.0 equiv.  $\text{CH}_3\text{COO}^-$  only leads to  $\approx 21\%$  emission quenching. All the above results suggest the high selectivity of NBDAE-labeled polymers toward the sensing of  $F^-$  ions in organic media.



**Figure 3.** (a) Normalized fluorescence spectra and (b) changes in relative fluorescence intensities ( $\lambda_{ex} = 470$  nm, Ex. 5 nm, Em. 5 nm) recorded for  $0.05$  g·L $^{-1}$  P(St-co-NBDAE) in THF ([NBDAE] =  $0.85$   $\mu$ M; 2 mL) upon addition of 10.0 equiv. (relative to NBDAE moieties) aqueous solution (20  $\mu$ L) of KCl, KBr, KI,  $KH_2PO_4$ ,  $K_2HPO_4$ ,  $K_2CO_3$ ,  $CH_3COOK$ , and TBAF, and THF solution of TBAF (20  $\mu$ L), respectively.

To evaluate effects of the chemical structure and polarity of polymeric matrix on the  $F^-$  sensing capabilities of NBDAE-labeled polymers, we further employed P(MMA-co-NBDAE) and P(NIPAM-co-NBDAE) to check their sensing performance (see Supporting Information Figure S7 and S8). Upon addition of varying amounts of TBAF, the fluorescence emission intensities were both significantly quenched. In the presence of 10 equiv. TBAF, the residual emission intensities of P(St-co-NBDAE) and P(MMA-co-NBDAE) reach  $\approx 5$  and 6% of their original values, respectively. On the other hand, P(NIPAM-co-NBDAE) seems to be a bit more inert to  $F^-$  ions. Approximately 92 and <20% fluorescence quenching were achieved in the presence of  $\approx 32.5$  and 10.0 equiv. of TBAF, respectively. The  $F^-$  sensing capability of these three types of NBDAE-containing copolymers were summarized in Figure 4. Among them, P(St-co-NBDAE) and P(MMA-co-NBDAE) exhibit the best performance toward the sensing of  $F^-$  ions. Whereas P(NIPAM-co-NBDAE), which contains amide residues and is more polar as compared to the former two types of copolymers, apparently shows hysteretic response in terms



**Figure 4.** Changes in relative fluorescence intensities ( $\lambda_{ex} = 470$  nm, Ex. 5 nm, Em. 5 nm) recorded for  $0.05$  g·L $^{-1}$  P(MMA-co-NBDAE) ([NBDAE] =  $0.96$   $\mu$ M), P(St-co-NBDAE) ([NBDAE] =  $0.85$   $\mu$ M), and P(NIPAM-co-NBDAE) ([NBDAE] =  $0.85$   $\mu$ M) in THF upon addition varying amounts of TBAF.

of fluorescence quenching by fluoride ions. The amide residues in P(NIPAM-co-NBDAE) seems to be able to weaken the interactions between NBDAE and TBAF and slow down the deprotonation process of NBDAE by fluoride ions, possibly via the competitive hydrogen bonding interaction between amide residues and  $F^-$  ions.<sup>[5]</sup> This leads to the observed decreased  $F^-$  detection efficiency.

## Conclusion

In summary, well-defined NBDAE-containing copolymers were prepared via RAFT polymerization. Both NBDAE monomer and NBDAE-labeled copolymers can serve as highly selective colorimetric and fluorometric probes for fluoride ions. In the presence of 10 equiv. TBAF, P(St-co-NBDAE), and P(MMA-co-NBDAE) in THF exhibit  $\approx 95\%$  quenching of fluorescence emission, accompanied with the colorimetric transition from green to yellowish, and the latter can be discerned by the naked eye. The fluorometric detection limit of  $F^-$  ions can be down to  $\approx 0.8$   $\mu$ M at a polymer concentration of  $0.05$  g·L $^{-1}$ . Moreover, the presence of amide moieties in the copolymer matrix can considerably weaken the  $F^-$  sensing performance due to the competitive hydrogen bonding interactions between amide residues and fluoride ions. To the best of our knowledge, the current detection system represents a novel type of small molecule and polymeric  $F^-$  probes based on secondary amine moieties in nitrobenzofurazan derivatives.

**Acknowledgements:** The financial support from National Natural Scientific Foundation of China (NNSFC) Project (20874092, 91027026, and 51033005), Fundamental Research Funds for the

Central Universities, and Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP) is gratefully acknowledged.

Received: January 11, 2011; Published online: March 7, 2011; DOI: 10.1002/marc.201100024

Keywords: colorimetric probes; copolymerization; detection limit; fluorescence; nitrobenzofurazan

- [1] [1a] P. D. Beer, P. A. Gale, *Angew. Chem., Int. Ed.* **2001**, *40*, 486; [1b] F. P. Schmidtchen, M. Berger, *Chem. Rev.* **1997**, *97*, 1609; [1c] S. Kubik, *Chem. Soc. Rev.* **2009**, *38*, 585; [1d] V. Amendola, L. Fabbrizzi, *Chem. Commun.* **2009**, 513.
- [2] [2a] H. M. Chawla, R. Shrivastava, S. N. Sahu, *New J. Chem.* **2008**, *32*, 1999; [2b] Y. P. Zhao, C. C. Zhao, L. Z. Wu, L. P. Zhang, C. H. Tung, Y. J. Pan, *J. Org. Chem.* **2006**, *71*, 2143; [2c] T. H. Kim, M. S. Choi, B. H. Sohn, S. Y. Park, W. S. Lyoo, T. S. Lee, *Chem. Commun.* **2008**, 2364; [2d] E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon, K. C. Nam, *J. Am. Chem. Soc.* **2003**, *125*, 12376.
- [3] [3a] Z. M. Hudson, S. N. Wang, *Acc. Chem. Res.* **2009**, *42*, 1584; [3b] M. Melaimi, F. P. Gabbai, *J. Am. Chem. Soc.* **2005**, *127*, 9680; [3c] X. Y. Liu, D. R. Bai, S. N. Wang, *Angew. Chem., Int. Ed.* **2006**, *45*, 5475; [3d] S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, *124*, 8816; [3e] S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2000**, *122*, 6793; [3f] A. Saxena, M. Fujiki, R. Rai, S. Y. Kim, G. Kwak, *Macromol. Rapid Commun.* **2004**, *25*, 1771; [3g] S. Arimori, M. G. Davidson, T. M. Fyles, T. G. Hibbert, T. D. James, G. I. Kociok-Kohn, *Chem. Commun.* **2004**, 1640; [3h] S. Xu, K. C. Chen, H. Tian, *J. Mater. Chem.* **2005**, *15*, 2676.
- [4] [4a] X. F. Yang, S. J. Ye, Q. Bai, X. Q. Wang, *J. Fluoresc.* **2007**, *17*, 81; [4b] R. Hu, J. A. Feng, D. H. Hu, S. Q. Wang, S. Y. Li, Y. Li, G. Q. Yang, *Angew. Chem., Int. Ed.* **2010**, *49*, 4915; [4c] T. H. Kim, T. M. Swager, *Angew. Chem., Int. Ed.* **2003**, *42*, 4803; [4d] S. Y. Kim, J. I. Hong, *Org. Lett.* **2007**, *9*, 3109.
- [5] [5a] S. O. Kang, R. A. Begum, K. Bowman-James, *Angew. Chem., Int. Ed.* **2006**, *45*, 7882; [5b] P. Zhao, J. B. Jiang, B. Leng, H. Tian, *Macromol. Rapid Commun.* **2009**, *30*, 1715; [5c] S. V. Bhosale, S. V. Bhosale, M. B. Kalyankar, S. J. Langford, *Org. Lett.* **2009**, *11*, 5418; [5d] B. Liu, H. Tian, *J. Mater. Chem.* **2005**, *15*, 2681; [5e] Y. Qu, J. L. Hua, Y. H. Jiang, H. Tian, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1544.
- [6] [6a] P. A. Gale, J. L. Sessler, V. Kral, V. Lynch, *J. Am. Chem. Soc.* **1996**, *118*, 5140; [6b] M. A. Palacios, R. Nishiyabu, M. Marquez, P. Anzenbacher, *J. Am. Chem. Soc.* **2007**, *129*, 7538; [6c] F. P. Schmidtchen, *Org. Lett.* **2002**, *4*, 431.
- [7] [7a] G. X. Xu, M. A. Tarr, *Chem. Commun.* **2004**, 1340; [7b] X. M. He, F. Herranz, E. C. C. Cheng, R. Vilar, V. W. W. Yam, *Chem. Eur. J.* **2010**, *16*, 9123; [7c] M. Boiocchi, L. Del Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, *J. Am. Chem. Soc.* **2004**, *126*, 16507; [7d] E. Kim, H. J. Kim, D. R. Bae, S. J. Lee, E. J. Cho, M. R. Seo, J. S. Kim, J. H. Jung, *New J. Chem.* **2008**, *32*, 1003.
- [8] [8a] D. A. Jose, D. K. Kumar, B. Ganguly, A. Das, *Org. Lett.* **2004**, *6*, 3445; [8b] A. F. Li, J. H. Wang, F. Wang, Y. B. Jiang, *Chem. Soc. Rev.* **2010**, *39*, 3729.
- [9] [9a] P. A. Gale, S. E. Garcia-Garrido, J. Garric, *Chem. Soc. Rev.* **2008**, *37*, 151; [9b] T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger, F. M. Pfeffer, *Coord. Chem. Rev.* **2006**, *250*, 3094; [9c] E. J. O'Neil, B. D. Smith, *Coord. Chem. Rev.* **2006**, *250*, 3068; [9d] P. A. Gale, R. Quesada, *Coord. Chem. Rev.* **2006**, *250*, 3219; [9e] J. W. Steed, *Chem. Soc. Rev.* **2009**, *38*, 506.
- [10] [10a] T. Ghosh, B. G. Maiya, M. W. Wong, *J. Phys. Chem. A* **2004**, *108*, 11249; [10b] T. Gunnlaugsson, P. E. Kruger, T. C. Lee, R. Parkesh, F. M. Pfeffer, G. M. Hussey, *Tetrahedron Lett.* **2003**, *44*, 6575; [10c] X. J. Peng, Y. K. Wu, J. L. Fan, M. Z. Tian, K. L. Han, *J. Org. Chem.* **2005**, *70*, 10524; [10d] D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, *J. Org. Chem.* **2005**, *70*, 5717; [10e] T. Gunnlaugsson, P. E. Kruger, P. Jensen, J. Tierney, H. D. P. Ali, G. M. Hussey, *J. Org. Chem.* **2005**, *70*, 10875; [10f] T. Gunnlaugsson, P. E. Kruger, P. Jensen, F. M. Pfeffer, G. M. Hussey, *Tetrahedron Lett.* **2003**, *44*, 8909; [10g] V. Amendola, M. Boiocchi, B. Colasson, L. Fabbrizzi, *Inorg. Chem.* **2006**, *45*, 6138.
- [11] [11a] T. Wu, G. Zou, J. M. Hu, S. Y. Liu, *Chem. Mater.* **2009**, *21*, 3788; [11b] C. H. Li, Y. X. Zhang, J. M. Hu, J. J. Cheng, S. Y. Liu, *Angew. Chem., Int. Ed.* **2010**, *49*, 5120; [11c] S. Uchiyama, Y. Matsumura, A. P. de Silva, K. Iwai, *Anal. Chem.* **2003**, *75*, 5926.
- [12] J. T. Lai, D. Filla, R. Shea, *Macromolecules* **2002**, *35*, 6754.
- [13] [13a] H. N. Kim, Z. Q. Guo, W. H. Zhu, J. Y. Yoon, H. Tian, *Chem. Soc. Rev.* **2011**, *40*, 79; [13b] J. M. Hu, S. Y. Liu, *Macromolecules* **2010**, *43*, 8315.