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# Application of Heterocyclic Polymers in the Ratiometric Spectrophotometric Determination of Fluoride

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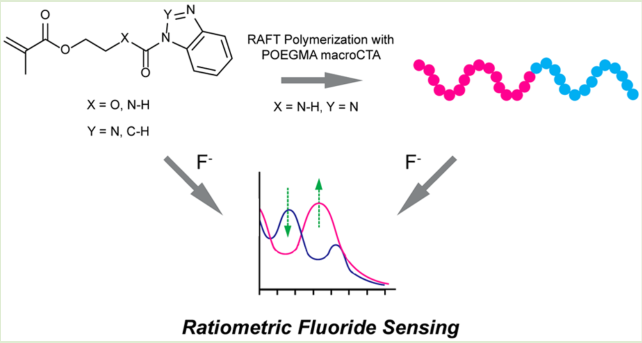
S *Supporting Information*



**ABSTRACT:** Herein we report the use of heterocyclic functional polymers in the ratiometric spectrophotometric determination of fluoride ($F^-$). Polymers incorporating benzo[d][1,2,3]triazole moieties linked to the polymer backbone via urea links are demonstrated to have utility for the ratiometric detection of the $F^-$ ion, with a detection limit in the order of ~2 $\mu$M. The hydrogen-bonding recognition between the benzo[d][1,2,3]triazole moiety and $F^-$ ion was investigated using UV−vis spectrophotometry and NMR analysis. The importance of the urea linkage was elucidated by investigating a second benzo[d][1,2,3]triazole functional monomer wherein the heterocyclic group is attached to the polymerizable group via a carbamate linkage. The replacement of the urea link with a carbamate group led to significantly reduced $F^-$ sensitivity. Moreover, by examining an analogous benzo[d]imidazole monomer it was demonstrated that having a nitrogen atom in the 2-position of the heterocycle was important for maximizing the sensitivity of the assay. Taken together, these results demonstrated that the urea-substituted benzo[d][1,2,3]triazole motif greatly enhances $F^-$ ion detection. Importantly, the $F^-$ ion sensing capability of the monomer is retained after incorporating into a diblock copolymer using reversible addition−fragmentation chain transfer (RAFT) polymerization.

Sensing and quantitative detection of anions is of significance in a variety of biological and environmental settings.[1−9] In particular, there has been considerable interest in developing novel approaches for the sensing of the fluoride ($F^-$) ion. While $F^-$ is of considerable benefit for dental health, overexposure to $F^-$ may lead to chronic conditions such as skeletal fluorosis or acute gastric and renal damage.[10] Although the $F^-$ ion is often added to water sources because of the clear dental benefits, some water sources have naturally high $F^-$ content which may necessitate further processing for the removal of the ion. Moreover, industrial contamination of water supplies may cause elevated levels that require monitoring due to the potential health and environmental impacts. It is therefore of interest to develop highly efficient and reliable strategies to monitor $F^-$ ion concentration.

A variety of different strategies have been employed for the design of $F^-$ ion probes. Specifically, some monitoring approaches have exploited chemical reactions involving the $F^-$ ion,[11−15] while others have made use of fluoride's Lewis base properties in Lewis acid−base recognition.[16−22] Other studies have utilized the significant electronegativity of fluorine to construct assays which rely on hydrogen bonding interactions.[23−25] Overall, hydrogen bonding recognition has been the most widely studied interaction, with a number of small-molecule-based hydrogen donors having been synthesized to detect $F^-$ ion concentration. These include (thiol)-ureas,[26−30] amides,[31−33] Schiff bases,[34,35] and pyrroles.[36−38]

Significantly, in comparison to the wide array of small molecule $F^-$ ion sensors, polymeric $F^-$ ion probes have received less attention. Considering that polymeric probes may hold additional advantages, such as tunable detection sensitivity, versatile processability, and multifunctionality,[39−41] a number of polymeric $F^-$ ion probes have been reported. For example, Swager and co-workers[42] developed a ratiometric $F^-$ sensor based on conjugated polymers wherein the $F^-$ ion mediates Si−O bond cleavage. Liu et al.[43] extended this concept and devised a $F^-$ ion probe which could be operated in purely aqueous media by copolymerization of the $F^-$ ion-sensitive fluorophore into a double hydrophilic block copolymer. Further, a $F^-$ ion probe based on Lewis acid−base interaction has been reported recently by Jäkle et al.[44] These authors devised a dual-responsive $F^-$ sensor based on a triarylborane-containing block copolymer which utilized the electron deficiency of the borane monomer. Hydrogen-bonding recognition has also been used

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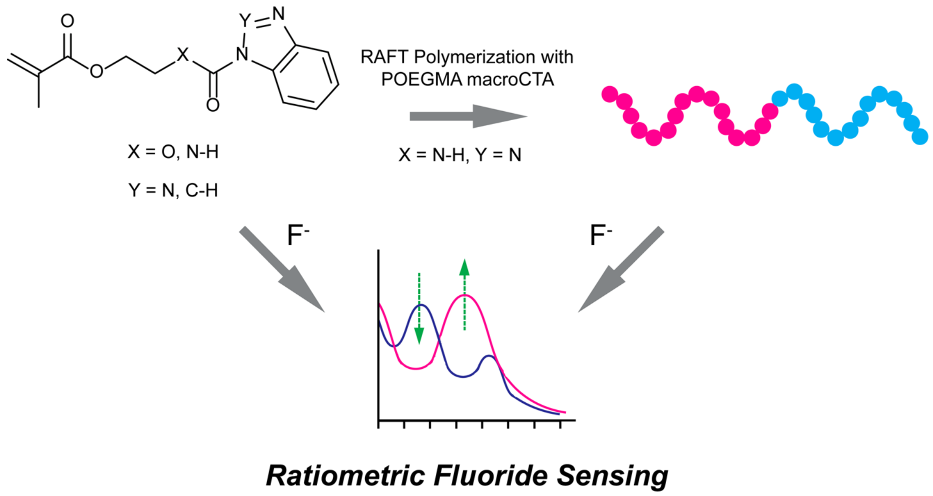
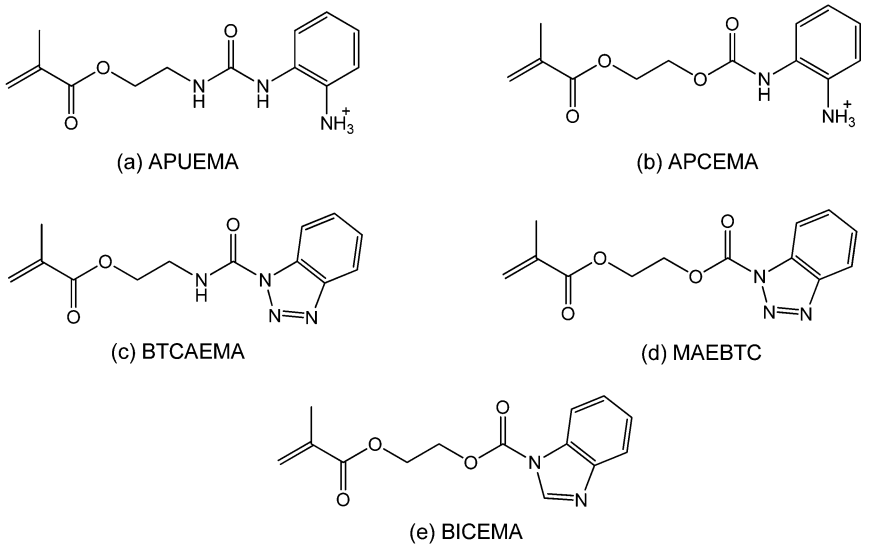
Scheme 1. Schematic Illustration of Ratiometric F$^-$ Ion Sensing by Heterocyclic Monomers and Polymers



Scheme 2. Monomers Screened for F$^-$ Ion Sensing Performance: (a) 2-(3-(2-Aminophenyl)ureido)ethyl Methacrylate (APUEMA), (b) 2-(((2-Aminophenyl)carbamoyl)oxy)ethyl methacrylate hydrochloride (APCEMA), (c) 2-(1*H*-Benzo[d][1,2,3]triazole-1-carboxamido)ethyl Methacrylate (BTCAEMA), (d) 2-(Methacryloyloxy)ethyl 1*H*-Benzo[d][1,2,3]triazole-1-carboxylate (MAEBTC), and (e) 2-(1*H*-Benzo[d]imidazole-1-carboxamido)ethyl Methacrylate (BICEMA)


(a) APUEMA
(b) APCEMA
(c) BTCAEMA
(d) MAEBTC
(e) BICEMA

to design a diverse range of F$^-$ ion probes. For example, Tian and co-workers[45] demonstrated that naphthalimide moieties containing an amide group were able to probe F$^-$ ion concentration by virtue of hydrogen bonding recognition between the F$^-$ ion and amide bonds. In other work, Liu et al.[46,47] demonstrated a colorimetric and fluorometric F$^-$ ion probe which exploited the supramolecular association between 7-nitro-2,1,3-benzoxadiazole (NBD) and the F$^-$ ion and developed a ratiometric F$^-$ ion sensor by introduction of a fluorescence donor (polyfluorene).

Recently, we have developed polymers which are responsive to the presence of nitric oxide (NO), a ubiquitous messenger molecule in animals and plants. These polymers were rendered responsive by the introduction of a NO-reactive *o*-phenylenediamine moiety, which effectively captures NO thereby yielding polymers with a benzo[d][1,2,3]triazole moiety.[48] We hypothesized that, depending on the specific attachment of the benzotriazole to the polymer backbone, these polymers may be able to function as effective F$^-$ sensors given the close proximity of hydrogen bonding acceptor and donor atoms. Herein, we report on a novel highly selective and sensitive ratiometric F$^-$ ion probe based on benzo[d][1,2,3]triazole moieties, wherein the moiety is attached to the polymer backbone via a urea linkage.[48] The resultant urea-linked benzo[d][1,2,3]triazole motif can efficiently recognize F$^-$ ions with a remarkable ratiometric ultraviolet absorbance change (Scheme 1), with the detection limit determined to be ~2 $\mu$M. Moreover, by comparison with molecules having unreacted *o*-phenylenediamine moieties, benzo[d]imidazole groups, or benzo[d][1,2,3]triazole groups attached via a carbamate, we elucidate that the nitrogen atom in the 2-position and N−H in the urea linkage are important for ensuring that the sensor is operable with maximum sensitivity. These results demonstrate the considerable scope for the design of efficient anion sensors using heterocyclic pendants on polymer chains.

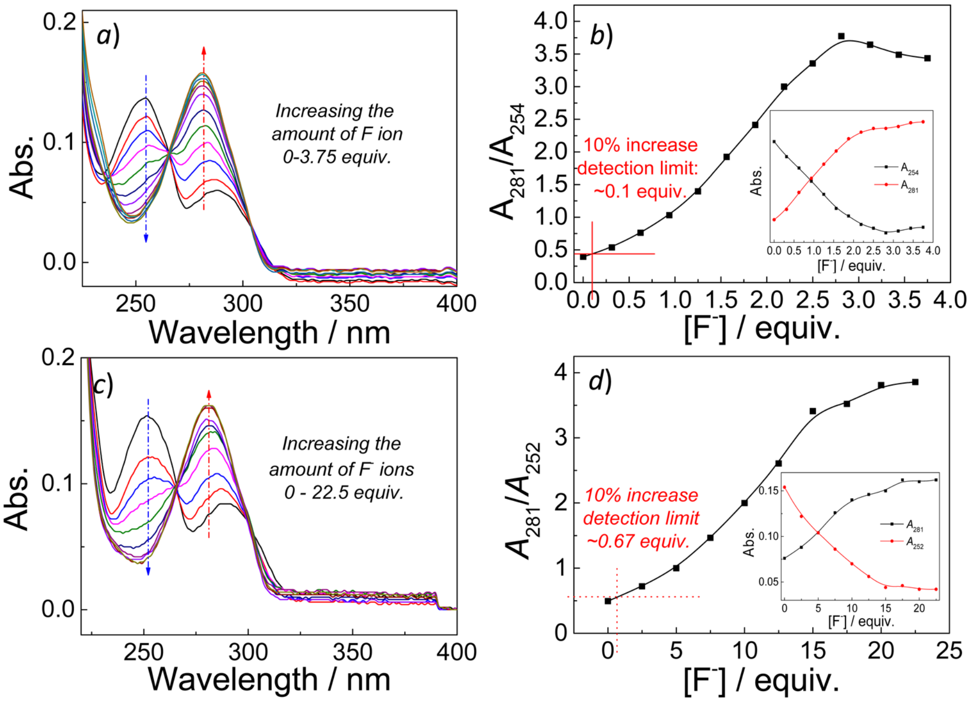


**Figure 1.** (a and c) Absorbance spectra and (b and d) absorbance intensity changes recorded in MeCN solution (20 $\mu$M) for (a and b) BTCAEMA and (b and d) MAEBTC monomers upon addition of varying amounts of $F^-$ ion.

Chemical sensors for NO often operate by the reaction of an *o*-phenylenediamine motif with NO, thereby forming a benzo[d][1,2,3]triazole moiety. We have recently reported a monomer incorporating an *o*-phenylenediamine group, 2-(3-(2-aminophenyl)ureido)ethyl methacrylate (APUEMA), which reacts with NO to form 2-(1*H*-benzo[d][1,2,3]triazole-1-carboxamido)ethyl methacrylate (BTCAEMA), a monomer that includes a urea-linked benzo[d][1,2,3]triazole motif and has long-term stability in aqueous solution (Scheme 2).[48] Given the urea link includes the nitrogen in the 2-position of the benzotriazole, both the precursor and the resulting monomer effectively include an asymmetrical urea moiety. As such, we hypothesized that BTCAEMA and APUEMA may have some utility for $F^-$ sensing.[26−30] Although the molecular recognition between urea moieties and the $F^-$ ion has been previously studied, the interaction of $F^-$ with asymmetrical urea moieties having a single N−H bond and a lone pair on the second nitrogen has received less attention. In addition, to further investigate the structure−property relations for $F^-$ ion sensing performance, a second *o*-phenylenediamine monomer was synthesized wherein the urea linkage was replaced with a carbamate linkage. Specifically, 2-(((2-aminophenyl)-carbamoyl)oxy) ethyl methacrylate hydrochloride (APCEMA) was synthesized as an analogue to APUEMA (Scheme S1, Supporting Information). Upon reaction with NO, APCEMA yields 2-(methacryloyloxy)ethyl 1*H*-benzo[d][1,2,3]triazole-1-carboxylate (MAEBTC). The only difference between the chemical structures of APUEMA and APCEMA is that the urea linkage in the APUEMA monomer is replaced by a carbamate linkage in the APCEMA monomer. Likewise, the only variation between the BTCAEMA and MAEBTC is replacement of the urea link with a carbamate. By titrating this palette of monomers with $F^-$ we sought to develop an understanding of how monomer structure influences the spectrophotometric response.

The APUEMA monomer was synthesized via the reaction of *o*-phenylenediamine with 2-isocyanatoethyl methacrylate, as has previously been reported.[48] The APCEMA monomer was prepared via the coupling of *o*-phenylenediamine with 1,1′-carbonyldiimidazole-activated 2-hydroxyl methacrylate (HEMA) in the presence of 4-dimethylaminopyridine (DMAP) catalyst, followed by protonation of the free amine groups in the presence of hydrogen chloride (Scheme S1, Supporting Information). The chemical structures of the intermediate compounds as well as the target APCEMA monomer were confirmed by $^1$H and $^{13}$C NMR analysis (Figures S1 and S2, Supporting Information).

Subsequently, the MAEBTC monomer was synthesized by sparging the APCEMA monomer with NO gas. The conversion was examined using UV−vis spectrophotometry to follow the formation of the benzo[d][1,2,3]triazole moiety. While the APCEMA monomer has an absorbance peak centered at ~285 nm, upon gradual NO addition the emergence of two new peaks (~259 and 296 nm) is observed (Figure S3, Supporting Information). The absorption intensity reached a plateau after exposure to ~1.25 equiv of NO, indicating a high reactivity of the APCEMA monomer toward NO and the relative ease of the synthetic methodology. The MAEBTC was subsequently isolated and analyzed by NMR spectroscopy (Figure S4, Supporting Information), which indicated formation of the desired carbamate-functionalized benzotriazole derivative. BTCAEMA was synthesized by exposing APUEMA to NO, as detailed in our previous publication.[48]

Following successful synthesis of the benzo[d][1,2,3]triazole functional polymers, a series of experiments was conducted to examine the utility of this palette of monomers for spectrophotometric $F^-$ ion sensing. First, molecular recognition between the APUEMA and APCEMA monomers and $F^-$ ion was investigated. The APUEMA monomer exhibited an absorbance peak at ~294 nm in acetonitrile. Upon addition

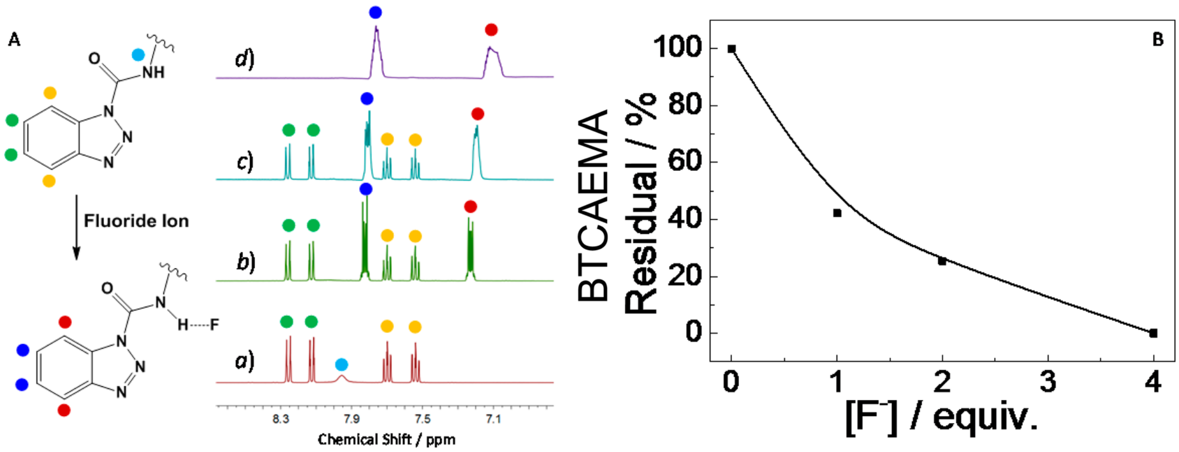


**Figure 2.** (A) Partial $^1$H NMR spectra recorded in $CD_3CN$ for the BTCAEMA monomer (50 mM) upon addition of varying amounts of $F^-$ ion: (a) 0 equiv; (b) 1 equiv; (c) 2 equiv; and (d) 4 equiv, respectively. (B) BTCAEMA monomer residual upon varying amounts of $F^-$ ion addition was determined by $^1$H NMR analysis.

of the $F^-$ ion, the absorbance peak underwent a slight increase over the $F^-$ concentration range of 0–500 $\mu$M (0–25 equiv relative to the APUEMA monomer) (see Figure S5a and b, Supporting Information). Similar absorbance changes were observed for the APCEMA monomer in the same $F^-$ ion concentration range. Importantly, these increases were accompanied by a commensurate rise in the baseline, which likely indicates increased turbidity. Further, the nonprotonated counterparts of both APUEMA and APCEMA undergo very little change to the UV spectra with addition of the $F^-$ ion (Figure S5c and d, Supporting Information). Taken together, these results suggest that while there may be ionic interactions between the protonated forms of APUEMA and APCEMA and the $F^-$ ion these interactions lead to only minor spectral changes.

Further studies were conducted to examine the $F^-$ ion sensing capability of BTCAEMA and MAEBTC, which include urea- and carbamate-linked benzotriazole groups, respectively. A ratiometric UV–vis absorbance change was observed for the BTCAEMA monomer upon titration with the $F^-$ ion. More specifically, upon gradual $F^-$ ion addition, the absorbance of BTCAEMA centered at ~254 nm decreased markedly, accompanied by a concomitant increase in the absorbance at 294 nm and a gradual blue-shift of the absorbance peak from ~294 to ~281 nm. The absorbance ratio changes of BTCAEMA ultimately plateaued after addition of ~3.0 equiv of the $F^-$ ion (Figure 1a). The detection limit (the $F^-$ ion concentration at which a 10% absorbance ratio change could be measured) was determined to be ~2 $\mu$M (Figure 1b). Although similar UV–vis absorbance ratio changes were observed for the MAEBTC monomer, the $F^-$ ion concentration required to induce those changes was much higher than for the BTCAEMA monomer (Figures 1c and 1d). This significant difference in $F^-$ ion sensing concentration range was likely attributed to the unique chemical structure of the BTCAEMA monomer, which includes an asymmetrical urea-derived benzo[d][1,2,3]triazole motif (Scheme 1). The MAEBTC monomer, which includes a carbamate linkage and therefore lacks a hydrogen bonding donor, gives significantly diminished response to $F^-$ titration, thereby demonstrating the important role played by the N–H group in the $F^-$ sensing chemistry. In order to rule out the possibility of the benzo[d][1,2,3]triazole moiety becoming protonated and binding fluoride ions via an ionic interaction, the BTCAEMA monomer was titrated with varying amounts of trifluoroacetic acid (TFA). Both the ultraviolet and $^1$H NMR spectra suggested a negligible change in the BTCAEMA monomer with addition of TFA (Figures S6 and S7, Supporting Information). As such, the recognition of the $F^-$ ion by the BTCAEMA monomer can be confidently attributed to hydrogen bonding with the benzotriazole-substituted asymmetric urea groups.

To further elucidate the structural features of the of the urea-linked benzo[d][1,2,3]triazole which contribute to the efficient $F^-$ ion sensing capability, a similar monomer bearing a urea-linked benzo[d]imidazole, 2-(1*H*-benzo[d]imidazole-1-carboxamido)ethyl methacrylate (BICEMA) was synthesized (Figure S8, Supporting Information). The primary structural difference between BICEMA and BTCAEMA is that the nitrogen atom in the 2 position of the heterocyclic benzo[d]-[1,2,3]triazole is replaced with the C–H group of an imidazole. Although BICEMA has different absorption peaks in comparison with the BTCAEMA monomer, a qualitatively similar spectral variation was observed when titrated over approximately the same concentration range of $F^-$ ions (Figure S9, Supporting Information). However, the variations in the absorbance ratio are nowhere near as marked as they are for BTCAEMA. These results indicate that, in addition to the crucial role played by the N–H, the nitrogen in the 2 position of the benzo[d][1,2,3]triazole also has a significant impact on the hydrogen bonding interaction between the $F^-$ ion and the monomer.

To further investigate the interactions between the BTCAEMA monomer and $F^-$ ion, $^1$H NMR spectra were recorded in the presence of varying equivalents of the $F^-$ ion (Figure 2). Before $F^-$ ion addition, the characteristic signal expected from the urea N–H was visible (~7.95 ppm, Figure 2a). This signal disappeared in the presence of 1.0 equiv of the $F^-$ ion (Figure 2b), clearly demonstrating the strong hydrogen bonding interaction between the N–H and $F^-$ ion. Moreover, as more $F^-$ ion was added the signals arising from the benzo[d][1,2,3]triazole protons gradually shifted to higher field, with the peaks becoming increasingly broad. In the presence of 4.0 equiv of $F^-$ ion, all the peaks associated with BTCAEMA monomer had disappeared (Figure 2A-d). These results were consistent with the absorbance ratio changes observed for the same $F^-$ ion concentration (Figure 1a). Taken

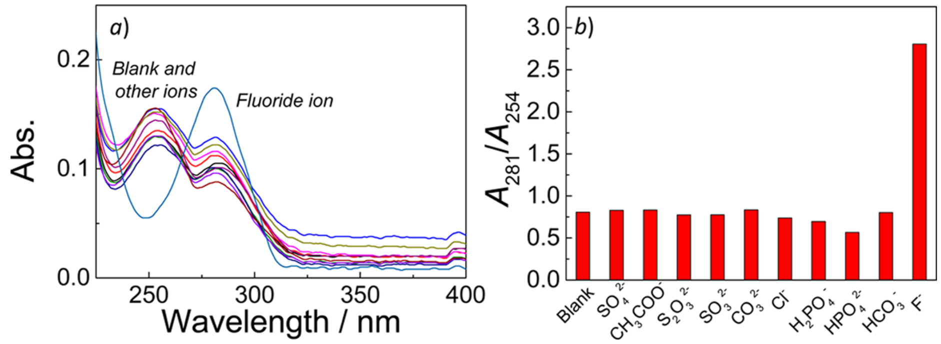


**Figure 3.** (a) Absorption spectra and (b) absorption ratio changes ($A_{281}/A_{254}$) recorded in MeCN for BTCAEMA monomer in the presence of various anions (0.25 mM) and $F^-$ ion (75 $\mu$M), respectively.

together, these results further confirm the strong hydrogen bonding interaction between the BTCAEMA monomer and $F^-$ ion. These hydrogen bonding interactions result in the observed ratiometric absorbance changes to the UV−vis spectra and therefore the possibility of highly sensitive $F^-$ ion sensing.

For the currently described $F^-$ sensor to be useful there must be some degree of ionic specificity for the observed ratiometric changes. As such, the selectivity of the BTCAEMA monomer toward the $F^-$ ion was examined. As shown in Figure 3, a number of different anions ($SO_4^{2-}$, $CH_3COO^-$, $S_2O_3^{2-}$, $SO_3^{2-}$, $CO_3^{2-}$, $Cl^-$, $H_2PO_4^-$, $HPO_4^{2-}$, $HCO_3^-$, and $F^-$) were tested to determine the specificity of the absorbance changes. Only the $F^-$ ion simultaneously induced the absorbance decrease at 254 nm and absorbance increase at 281 nm (Figure 3a). As such, the BTCAEMA monomer could be employed as a highly sensitive and selective $F^-$ ion probe through the molecular recognition between the urea-functionalized benzo[d][1,2,3]-triazole motif and $F^-$ ion. Nevertheless, further studies will be required to optimize the anionic selectivity toward the $F^-$ ion, especially for distinguishing $F^-$ in a complex mixed solution.

As noted above, polymeric sensors may confer considerable advantages in sensing applications, such as detection performance, long-term structural stability, and processability. As such, we examined the $F^-$ ion sensing capability of polymers incorporating BTCAEMA. Poly(oligoethylene glycol monomethyl ether methacrylate) (POEGMA)-*b*-PAPUEMA copolymer was synthesized using reversible addition−fragmentation chain transfer (RAFT) polymerization (Scheme S2, Supporting Information). The copolymer was subsequently exposed to NO in order to convert the APUEMA repeat units to BTCAEMA units, thereby yielding POEGMA-*b*-PBTCAEMA. Successful synthesis of the benzo[d][1,2,3]triazole functional polymer was confirmed by NMR analysis and GPC traces (Figures S10 and S11, Supporting Information). The $F^-$ ion sensing performance of the POEGMA-*b*-PBTCAEMA was then examined. Similarly to the BTCAEMA monomer, gradual addition of the $F^-$ ion led to a steady decrease in the absorbance at 254 nm and a gradual increase in the absorbance at 281 nm for the copolymer (Figure 4a). Moreover, the absorbance ratio ($A_{281}/A_{254}$) exhibited a ~5.84-fold rise over the $F^-$ ion concentration range examined (0−0.25 mM) (Figure 4b). These results demonstrate that incorporation of the benzo[d][1,2,3]triazole groups into a polymeric matrix does not compromise the $F^-$ ion sensing capability. Moreover, this suggests that urea-linked benzo[d]-[1,2,3]triazole groups may indeed be useful in the preparation of a novel polymeric $F^-$ ion probe.

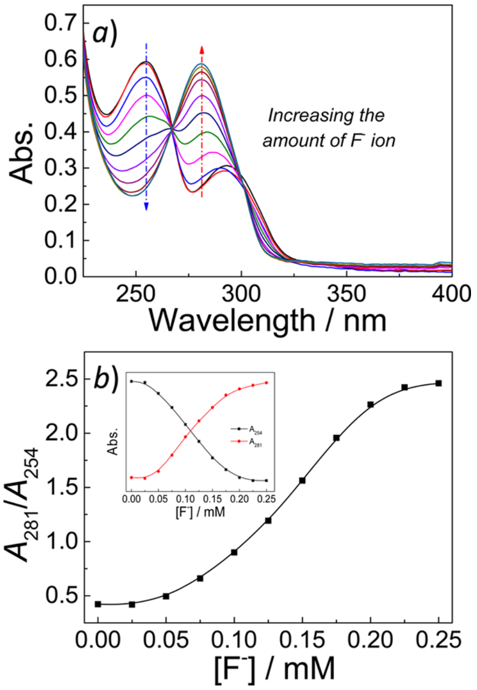


**Figure 4.** (a) Absorption spectra and (b) absorption ratio changes ($A_{281}/A_{254}$) recorded in MeCN for the POEGMA-*b*-PBTCAEMA block copolymer (0.05 g/L, [BTCAEMA] ~ 0.1 mM) in the presence of varying amounts of $F^-$ ion (0−0.25 mM), respectively.

In summary, a suite of *o*-phenylenediamine and benzo[d]-[1,2,3]triazole functional monomers were successfully prepared and examined for their potential as highly sensitive and selective $F^-$ ion probes. Monomers incorporating an *o*-phenylenediamine group such as APUEMA and APCEMA exhibited negligible $F^-$ ion sensing capability, which was likely due to their positively charged nature. However, benzo[d]-[1,2,3]triazole functional polymers showed some promise as ratiometric $F^-$ ion probes, with urea-linked benzo[d][1,2,3]-triazole monomer BTCAEMA showing the best performance of the examined monomers. The presence of an N−H group in the linker and the incorporation of a nitrogen atom in the 2-position of the heterocycle were shown to be especially important to the sensing capability of the monomer. Additionally, we demonstrated that benzo[d][1,2,3]triazole moieties could be integrated into polymeric matrix by chain extending POEGMA with APUEMA via RAFT polymerization and then treating the copolymer with NO to yield POEGMA-*b*-PBTCAEMA, a polymer having demonstrated $F^-$ ion detection capability. This work introduces a novel family of polymeric $F^-$ probes which operate through specific recognition between a monofunctional urea-functionalized benzotriazole motif and $F^-$ ion. These materials may find ultimate application in environmental and biological sensing of $F^-$ ions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures, NMR, and UV−Vis. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Jakle, F. *Chem. Rev.* **2010**, *110*, 3985−4022.
(2) Duke, R. M.; Veale, E. B.; Pfeffer, F. M.; Kruger, P. E.; Gunnlaugsson, T. *Chem. Soc. Rev.* **2010**, *39*, 3936−3953.
(3) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486−516.
(4) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609−1646.
(5) Kubik, S. *Chem. Soc. Rev.* **2009**, *38*, 585−605.
(6) Amendola, V.; Fabbrizzi, L. *Chem. Commun.* **2009**, 513−531.
(7) Gale, P. A.; Garcia-Garrido, S. E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151−190.
(8) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094−3117.
(9) Gale, P. A. *Coord. Chem. Rev.* **2006**, *250*, 2917−2917.
(10) Zhou, Y.; zhang, J. F.; Yoon, J. *Chem. Rev.* **2014**, *114*, 5511−5571.
(11) Hu, R.; Feng, J. A.; Hu, D. H.; Wang, S. Q.; Li, S. Y.; Li, Y.; Yang, G. Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 4915−4918.
(12) Zhang, J. F.; Lim, C. S.; Bhuniya, S.; Cho, B. R.; Kim, J. S. *Org. Lett.* **2011**, *13*, 1190−1193.
(13) Roy, A.; Kand, D.; Saha, T.; Talukdar, P. *Chem. Commun.* **2014**, *50*, 5510−5513.
(14) Ke, B. W.; Chen, W. X.; Ni, N. T.; Cheng, Y. F.; Dai, C. F.; Dinh, H.; Wang, B. H. *Chem. Commun.* **2013**, *49*, 2494−2496.
(15) Zheng, F. Y.; Zeng, F.; Yu, C. M.; Hou, X. F.; Wu, S. Z. *Chem.—Eur. J.* **2013**, *19*, 936−942.
(16) Sole, S.; Gabbai, F. P. *Chem. Commun.* **2004**, 1284−1285.
(17) Xu, S.; Chen, K. C.; Tian, H. *J. Mater. Chem.* **2005**, *15*, 2676−2680.
(18) Melaimi, M.; Gabbai, F. P. *J. Am. Chem. Soc.* **2005**, *127*, 9680−9681.
(19) Liu, X. Y.; Bai, D. R.; Wang, S. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 5475−5478.
(20) Saxena, A.; Fujiki, M.; Rai, R.; Kim, S. Y.; Kwak, G. *Macromol. Rapid Commun.* **2004**, *25*, 1771−1775.
(21) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6793−6794.
(22) Hudson, Z. M.; Wang, S. N. *Acc. Chem. Res.* **2009**, *42*, 1584−1596.
(23) Zhao, Y. P.; Zhao, C. C.; Wu, L. Z.; Zhang, L. P.; Tung, C. H.; Pan, Y. J. *J. Org. Chem.* **2006**, *71*, 2143−2146.
(24) Ashokkumar, P.; Weisshoff, H.; Kraus, W.; Rurack, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 2225−2229.
(25) Zheng, X.; Zhu, W. C.; Liu, D.; Ai, H.; Huang, Y.; Lu, Z. Y. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7996−8000.
(26) Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. *J. Am. Chem. Soc.* **2003**, *125*, 12376−12377.
(27) He, X. M.; Herranz, F.; Cheng, E. C. C.; Vilar, R.; Yam, V. W. W. *Chem.—Eur. J.* **2010**, *16*, 9123−9131.
(28) Boiocchi, M.; Del Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507−16514.
(29) Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717−5720.
(30) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445−3448.
(31) Sun, X. H.; Li, W. Y.; Xia, P. F.; Luo, H. B.; Wei, Y. L.; Wong, M. S.; Cheng, Y. K.; Shuang, S. M. *J. Org. Chem.* **2007**, *72*, 2419−2426.
(32) Qu, Y.; Hua, J. L.; Jiang, Y. H.; Tian, H. *J. Polym. Sci., Polym. Chem.* **2009**, *47*, 1544−1552.
(33) Liu, B.; Tian, H. *J. Mater. Chem.* **2005**, *15*, 2681−2686.
(34) Lin, Z. H.; Zhao, Y. G.; Duan, C. Y.; Zhang, B. G.; Bai, Z. P. *Dalton Trans.* **2006**, 3678−3684.
(35) Chawla, H. M.; Shrivastava, R.; Sahu, S. N. *New J. Chem.* **2008**, *32*, 1999−2005.
(36) Qu, Y.; Hue, J. L.; Tian, H. *Org. Lett.* **2010**, *12*, 3320−3323.
(37) Palacios, M. A.; Nishiyabu, R.; Marquez, M.; Anzenbacher, P. *J. Am. Chem. Soc.* **2007**, *129*, 7538−7544.
(38) Gale, P. A.; Sessler, J. L.; Kral, V.; Lynch, V. *J. Am. Chem. Soc.* **1996**, *118*, 5140−5141.
(39) Hu, J. M.; Liu, S. Y. *Macromolecules* **2010**, *43*, 8315−8330.
(40) Adhikari, B.; Majumdar, S. *Prog. Polym. Sci.* **2004**, *29*, 699−766.
(41) Kim, H. N.; Guo, Z. Q.; Zhu, W. H.; Yoon, J.; Tian, H. *Chem. Soc. Rev.* **2011**, *40*, 79−93.
(42) Kim, T. H.; Swager, T. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4803−4806.
(43) Jiang, Y. Y.; Hu, X. L.; Hu, J. M.; Liu, H.; Zhong, H.; Liu, S. Y. *Macromolecules* **2011**, *44*, 8780−8790.
(44) Cheng, F.; Bonder, E. M.; Jakle, F. *J. Am. Chem. Soc.* **2013**, *135*, 17286−17289.
(45) Zhao, P.; Jiang, J. B.; Leng, B.; Tian, H. *Macromol. Rapid Commun.* **2009**, *30*, 1715−1718.
(46) Hu, J. M.; Zhang, G. Y.; Geng, Y. H.; Liu, S. Y. *Macromolecules* **2011**, *44*, 8207−8214.
(47) Hu, J. M.; Li, C. H.; Cui, Y.; Liu, S. Y. *Macromol. Rapid Commun.* **2011**, *32*, 610−615.
(48) Hu, J. M.; Whittaker, M. R.; Duong, H.; Li, Y.; Boyer, C.; Davis, T. P. *Angew. Chem., Int. Ed.* **2014**, *53*, 7779−7784.