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A recyclable, fluorescent, and colorimetric sensor for fluoride anion in water using a crosslinked polymer functionalized with hydroxyl quinolinium

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This study aimed to develop a recyclable, fluorescent, and colorimetric sensor for fluoride anion (F^-) in aqueous media with fast response, good selectivity, and high sensitivity. A crosslinked polymer CpA1T5 was designed and synthesized as a sensor using (E)-1-allyl-4-(4-hydroxylphenyl) vinyl) quinolinium bromide as functional monomer, trimethylopropane trimethacraylate as crosslinker, and azobisisobutyronitrile as initiator. When F^- was introduced to CpA1T5 suspension in deionized water, a change in color from gray to yellow and fluorescence enhancement accompanied with a redshift from 531 nm to 540 nm of fluorescence emission were immediately observed. This F^- sensor can be recycled many times, making it cost efficient and beneficial to the environment. Analytical application of CpA1T5 to measure F^- concentration in two commercial mouthwash samples was explored with good accuracy.

Introduction

The recognition and sensing of anions are attracting significant research interest because of their widespread use in biological, chemical, and environmental processes.[1] Among all anions, F^- is the most biologically active and acts as a frequent constituent of most drug molecules. F^- is also used in hypnotics, anesthetics, psychiatric drugs, and cockroach poisons.[2,3] However, excessive ingestion of fluoride may cause nephrotoxic changes in both humans and animals and lead to urolithiasis. Therefore, determination of F^- is significant. Compared with widely used F^- detecting techniques such as electrochemical methods[4] and ^{19}F NMR analysis,[5] colorimetric and fluorescent sensing[6] has attracted widespread research attention because of its high sensitivity, detection convenience, fast response, and capability for use in intracellular F^- monitoring.

Numerous monomeric-based colorimetric and/or fluorescent chemosensors for F^- have focused on systems containing imidazole,[7–10] urea,[11,12] thiourea,[13] naphthalimide,[14–17] coumarin,[18] spiropyran,[19] triarylborane,[20] phenanthroline,[21] quinoline,[22,23] arylaldoxime,[24] Rhodamine-Furan,[25] Si-O,[26] indole,[27] metal-organic frameworks,[28] diketopyrrolopyrrole,[29] or calix[4]pyrrole[30,31] moieties. In recent years, polymeric colorimetric and/or fluorescent sensors for F^- have attracted significant research interest because of advantages such as presence of multiple recognition sites, possibility of signal application, and ease of incorporation into devices. The recognition units are incorporated as pendant group moieties[32–48] or within the polymer main chain.[49–53] They are also included in the monomeric complex in a polymer matrix.[54,55] The signal fluorophores are typically attached to high-specificity recognition units, and the interaction of anion with the polymeric sensor causes colorimetric and fluorescent change. Most of these polymers are in a linear structure, and can form a solution in a suitable organic solvent, thereby achieving anion recognition in an organic solution or organic-water mixture. Few studies have been conducted on colorimetric and fluorescent polymer-based F^- probes in aqueous medium even though anion recognition and quantitative detection in water is desirable from a practical application standpoint.[34] Therefore, design and fabrication of F^- polymeric sensors with the properties of detection convenience, fast response, reliability, and high selectivity in protic solvents or aqueous environments, are necessary.

The primary objective of this study is to design and synthesize a crosslinked polymer-based recyclable, colorimetric, and fluorescent probe functionalized with hydroxyl quinolinium for F^- in water. Compared with the solution formation in organic or organic-water solvent for the linear polymer, suspension is

formed for a crosslinked polymer; therefore, the polymeric sensor can be recycled after detection. To achieve this objective, an allyl group was introduced on a quinolinium ring to form the functional monomer, (E)-1-allyl-4-(4-hydroxy phenyl) vinyl) quinolinium bromide (AHPEQB),[56] which was further copolymerized with a crosslinker (trimethylopropane trimethacraylate, TRIM) to form a crosslinked polymer. This crosslinked polymer displayed both colorimetric and fluorescent response to F^- in water with fast response, good selectivity, high sensitivity, and recyclability.

Results and discussion

Synthesis of polymer

Adoption of radical polymerization techniques has allowed the synthesis of crosslinked polymer (Fig. 1). Main factors (such as

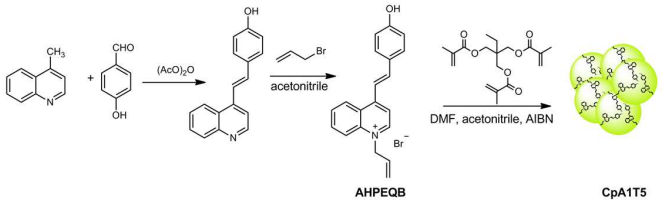

Fig. 1 Schematic of polymer preparation

type and percentage of porogenic solvent, molar ratio of monomer/crosslinker, amount of initiator, reaction temperature, and reaction time) that affect the polymer structure and the recognition properties of anions have been optimized. The optimum conditions are as follows: a mixture of acetonitrile and DMSO (5:1, v/v) as the porogenic solvent, a monomer/crosslinker with a molar ratio of 1:5, 0.1 g of AIBN as the initiator, reaction temperature of 65 °C, and reaction time of 24 h. Among the four crosslinked polymers, CpA1T5 performs best (ESI, S. Fig. 1). Thus, the following discussion focuses mainly on CpA1T5.

Characterization of CpA1T5

The polymer CpA1T5 was verified using FTIR. Fig. 2 presents the FTIR spectra of the monomer AHPEQB and the polymer CpA1T5. The broad absorption observed at approximately

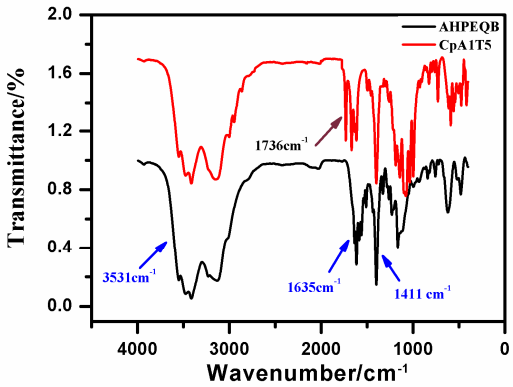

Fig. 2 FTIR spectra of AHPEQB and CpA1T5

3531–3100 cm^{-1} in both AHPEQB and CpA1T5 indicates the existence of phenolic hydroxyl in the two compounds. The appearance of adsorptions at 1736 cm^{-1} (C=O stretching in TRIM) and 1411 cm^{-1} (C=C stretching in the quinoline rings and benzene ring) supports the successful copolymerization of AHPEQB and TRIM.

CpA1T5 was also characterized via SEM, DLS, TGA, and N_2 adsorption-desorption analysis. The morphology of the crosslinked polymer (CpA1T5) is amorphous (ESI, S. Fig. 2). DLS illustrates that the particle size of CpA1T5 is around 200 nm (Fig. 3). TGA demonstrates that CpA1T5 is thermally stable below 300 °C (ESI, S. Fig. 3). The pore analysis demonstrates that CpA1T5 has a microporous and mesoporous structure, which mainly ranges between 1.0–4.5 nm and 4.5–10 nm (S. Fig. 4).

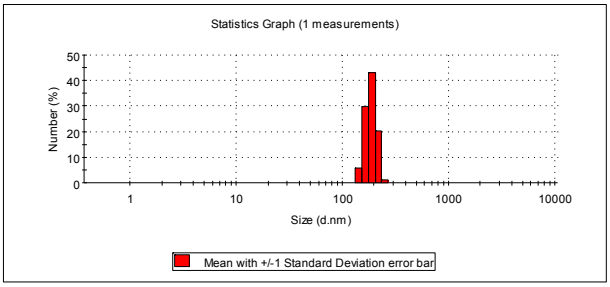

Fig. 3 Size distribution of CpA1T5 in DI water as obtained from DLS measurement.

Selectivity of CpA1T5

In ethanol, AHPEQB displayed colorimetric response toward CN^-.[56] However, in deionized (DI) water, AHPEQB displayed colorimetric and fluorescent response toward F^- over other competing anions (Cl^-, Br^-, I^-, AcO^-, CN^-, $H_2PO_4^-$, and HSO_4^-) (ESI, S. Fig. 5). These results demonstrated that the solvent significantly influenced anion sensing. The behavior of crosslinked CpA1T5 functionalized with hydroxyl quinolinium toward a variety of anions (F^-, Cl^-, Br^-, I^-, AcO^-, CN^-, $H_2PO_4^-$, and HSO_4^-) was exploited using UV-Vis and fluorescence spectroscopy. CpA1T5 displayed two weak absorption peaks at 430 and 600 nm in DI water (S. Fig. 6), and upon the introduction of F^-, the intensity decreased at 600 nm but increased at 430 nm. Simultaneously, a noticeable color change from gray to yellow was observed by the naked eye (Fig. 4b). However, other anions produced slight changes in color and UV-Vis spectra. However, the baselines of UV-Vis spectra were not very stable, which was probably due to the insolubility of CpA1T5 in DI water. The fluorescent spectrum of CpA1T5 was very good; thus, the following discussion mainly focused on fluorescence study. CpA1T5 displayed good selectivity toward F^- over other interfering anions in DI water, as observed through fluorescence spectral analysis and rapid color changes (Fig. 4).

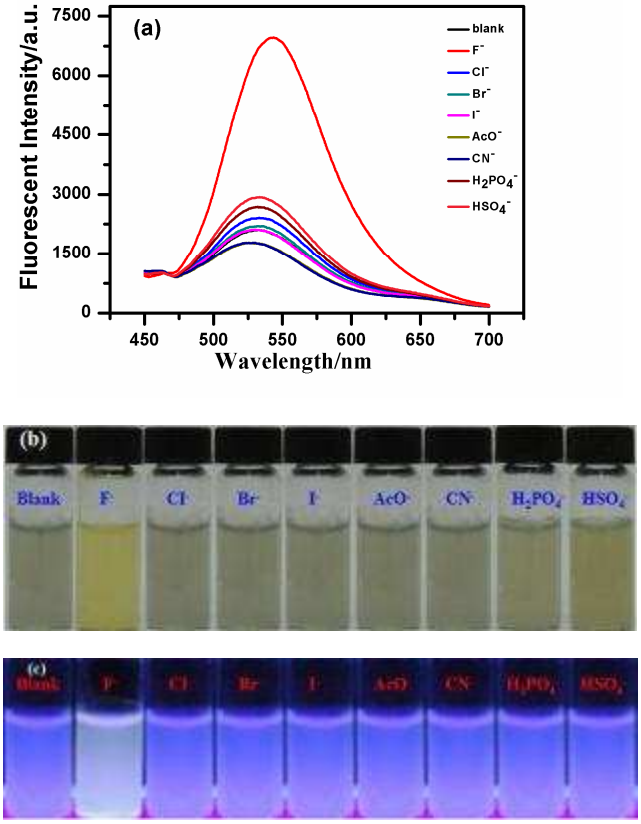

Fig. 4 Fluorescent emission spectra (λ_{ex} = 420 nm) of CpA1T5 aqueous suspension (0.6 mg/mL) upon addition of various anions (1.0 × 10^{-4} mol/L) (a). The color changes (b) and emission images by UV 365 nm excitation (c) of CpA1T5 in DI water (0.6 mg/mL) upon the addition of various anions (1.0 × 10^{-4} mol/L). Left to right: blank, F^-, Cl^-, Br^-, I^-, AcO^-, CN^-, $H_2PO_4^-$, and HSO_4^-.

CpA1T5 exhibited a fluorescence emission at 531 nm (Fig. 2a). The original fluorescent emission of CpA1T5 at 531 nm underwent a redshift to 540 nm accompanied by a significant increase in the fluorescence intensity upon the addition of F^-, which may be ascribed to strong hydrogen bonding interaction between hydroxyl groups of CpA1T5 and F^-.[56] However, no significant changes were observed in the emission spectra of CpA1T5 suspensions containing other interfering anions. A fluorescent color change from weak to strong was also visually observed by the naked eye in F^--containing suspension, whereas almost no change was observed in the presence of other competing anions (Fig. 2c). This interesting feature demonstrates that CpA1T5 could be used as a selective fluorescent chemosensor for F^- in water, and has potential application for analyzing F^- in biological media. Similar results were observed in 2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulfonic acid (HEPES) buffer at pH 7.0 (S. Fig. 7).
The anti-jamming ability of CpA1T5 was evaluated by adding F^- (1.0 × 10^{-4} mol/L) to the CpA1T5 suspension in the presence of commonly employed interfering anions (1.0 × 10^{-4} mol/L), and results showed that coexistence with competing anions could not induce significant interference in F^- recognition (S. Fig. 9).

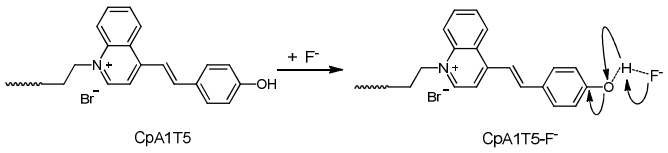

Fig. 5 Possible sensing mechanism of CpA1T5 for F^-.

These results indicate that CpA1T5 is an excellent colorimetric and fluorescent receptor for F^- in DI water, as indicated by its fast response and good selectivity over other interfering anions. The sensing mechanism of CpA1T5 for F^- was probably due to the interaction of F^- with the hydroxyl group of CpA1T5 through hydrogen bonding, resulting in charge transfer to quinolinium ring and subsequent fluorescent enhancement (Fig. 5).

Fluorescence titration studies

Fig. 6a displays the evolution of emission spectra of CpA1T5 with F^- in different concentrations. Upon gradual increase of the F^- concentration, the fluorescence emission peak of CpA1T5 in DI water at 531 nm gradually increased (from 1719 to 5974) and accompanied a redshift to 540 nm. The emission intensity at 540 nm reached a saturation level when the concentration of F^- was up to 1.0 × 10^{-5} mol/L. Fluorescence enhancement of CpA1T5 was demonstrated by a fluorescence intensity increase of approximately 3.48 times.

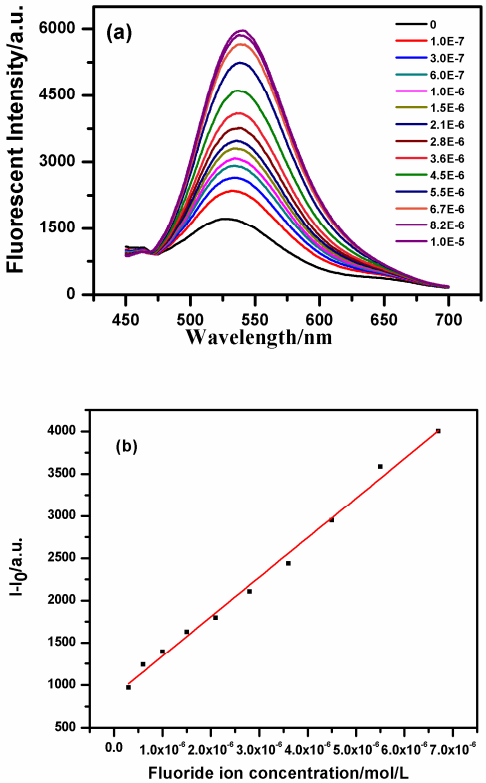

Fig. 6 Fluorescent emission spectra (λ_{ex} = 420 nm) of CpA1T5 suspension (0.6 mg/mL in DI water) in the presence of different concentrations (0–1.0 × 10^{-5} mol/L) of F^- (a). Change in fluorescence intensity (F_{540}–F_{531}) of CpA1T5 suspension (0.6 mg/mL in DI water) versus F^- concentration.

The limit of detection (LOD) of CpA1T5 as a fluorescent probe for F^- was evaluated from the plot of the change in fluorescence intensity at 540 nm of CpA1T5 suspension as a function of F^- concentration. Based on the plot of the linear region, the LOD of CpA1T5 for F^- was found to be 1.0×10^{-7} mol /L (Fig. 6b). Benesi–Hildebrand plots yielded an association constant of 8.99×10^4 M^{-1}, which was greater than that obtained in previous studies.[6,28]

Recyclability of CpA1T5

Most importantly, the crosslinked polymer-based colorimetric and fluorescent chemosensor for F^- could be recycled after detection of anions because of the formation of suspension instead of solution. Reuse of sensor is cost-efficient and beneficial to the environment. For example, in CpA1T5 for F^- via fluorescence spectroscopy (Fig. 7), the fluorescence spectrum of CpA1T5 suspension in DI water displays weak emission intensity (~1687) at 531 nm. The emission intensity at 540 nm significantly increases (~6153) upon addition of F^- to this suspension. Then, CpA1T5 was collected by centrifuging the suspension and was subsequently washed with 10 wt.% Na_2CO_3 aqueous solution under ultrasonic stirring to remove F^-. The resultant suspension was neutralized by HCl (0.01 mol/L) and centrifuged, and the supernatant was discarded. The solid was washed several times with HCl-ethanol mixed solution at pH 5–6, and finally dried under vacuum for 24 h. The recycled CpA1T5 was used for a second time. The fluorescent intensity at 540 nm for the recycled CpA1T5 suspension in distilled water and upon the addition of F^- were 1657 and 6500, respectively, which were close to the values obtained in the first cycle. A similar procedure was conducted to recycle the CpA1T5. As shown in Fig. 7, no obvious decrease in the fluorescence intensity at the characteristic emission peak (540 nm) was observed, denoting that the crosslinked polymer, CpA1T5, could be used several times without an apparent reduction in sensing properties.

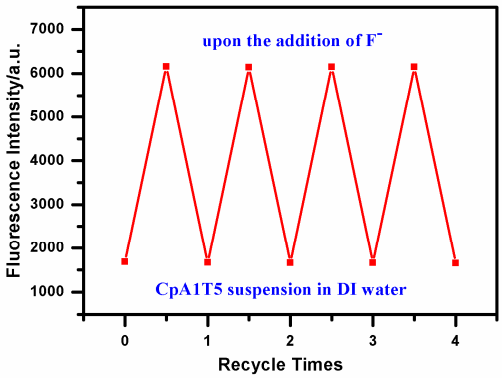

Fig. 7 Fluorescence emission intensity of CpA1T5 suspension in DI water at 531 nm and upon addition of F^- at 540 nm in recovery test.

Analytical application

As described in the previous section, the polymer CpA1T5 is a colorimetric and fluorescent receptor for F^- in DI water with good selectivity, fast response, high sensitivity, recyclability, and convenient detection. Therefore, CpA1T5 should have broad applications in fields containing F^-. In the present study, the application of CpA1T5 for the ultrasensitive determination of F^- in two mouthwash samples was studied using Fig. 4b as the calibration curve. The mouthwash samples were commercially available from a local supermarket and were diluted 100 times for analysis. Approximately 1.8 mg of CpA1T5 and 30 μL of diluted mouthwash solution were placed in a 3.0 mL cuvette, and DI water was subsequently added to adjust the total volume to 3.0 mL. Approximately 1.8 mg of CpA1T5 in 3.0 mL DI water was used as the blank. Characterization was conducted via fluorescence spectroscopy (S. Fig. 10). The average concentration of F^- in the two mouthwash samples was deduced from the calibration curve after deduction of the blank. The experiment was repeated 6 times. Determination results are presented in Table 1. The results indicate that the crosslinked polymer-based colorimetric and fluorescent chemosensor CpA1T5 developed in this study could be used for the ultrasensitive detection of F^- in real samples with good accuracy.

Table 1 Determination of F^- in two commercial mouthwash samples

Mouthwash samples	Detected concentration (mol/L)	Labeled concentration (mol/L)
1#	0.0050±0.0006	0.0048
2#	0.0068±0.0008	0.0072

Experimental

Reagent and apparatus

4-Methylquinoline (98%), 4-hydroxybenzaldehyde (98%), acetic anhydride (98%), azobisisobutyronitrile (AIBN, AR, 99%), trimethylolpropane trimethacrylate (TRIM, AR, 98%), and allyl bromide (98%) were purchased from Aladdin Co., Shanghai, China. All anions in the form of tetrabutylammonium salts were also purchased from Aladdin Co. All chemical reagents and solvents used were purchased from commercial suppliers and used without further purification.

Fluorescence spectra were recorded on an F380 system (Tianjing Gangdong Technology Co. Ltd., Tianjin, China). Fourier transform infrared spectra (FTIR) were recorded on a Perkin-Elmer Model GX spectrometer using KBr pellet method. The surface morphology of the polymer was studied via scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan). DLS was performed on an Autosizer 4700 dynamic/static light scattering (DLS) instrument (England). TGA was conducted on an SDT Q600 thermal analyzer (USA) at a heating rate of 10 °C/min up to 800 °C under flowing N_2 (100 mL/min). N_2 adsorption-desorption analysis was conducted at 77 K on an Autosorb-1 apparatus (Quantachrome, USA). Specific surface areas and pore diameters were calculated by the BET and BJH models, respectively.

Synthesis of crosslinked polymer

AHPEQB was synthesized in accordance with a previously reported procedure.[56] Polymeric materials were prepared from AHPEQB by precipitation polymerization using TRIM as the crosslinker and in the presence of AIBN as the radical initiator. A series of crosslinked polymers with AHPEQB/TRIM molar ratios of 1:1, 1:3, 1:5, and 1:7 was prepared. These polymers were labeled as CpA1T1, CpA1T3, CpA1T5, and CpA1T7. A typical procedure for preparing CpA1T5 (a copolymer with AHPEQB:TRIM molar ratio of 1:5) is described as follows.

AHPEQB (0.22 g, 0.60 mmol), TRIM (1.00 g, 3.00 mmol), and acetonitrile-DMSO (15 mL, 5:1, v/v) were placed in a 100 mL conical flask to form an orange solution. The mixture was placed in the dark at room temperature for 12 h after ultrasonic stirring for 15 min. Then, AIBN (0.10 g) was added and the resultant mixture was degassed with N_2 for at least 20 min before being sealed under N_2 by a rubber cap. The mixture was then placed in an oil bath at 65 °C for 24 h. After cooling to room temperature, the mixture was filtered; the precipitate was copiously washed with DI water and ethanol, resulting in a green powder. The powder was further washed using Soxhlet extraction with 200 mL of a methanol-acetic acid (9:1, v/v) for 24 h followed by 200 mL of methanol for 24 h in the dark. The process was monitored by UV-Vis until no change was observed in the solution. Finally, CpA1T5 was obtained as a green powder after the precipitate was dried at 40 °C for 24 h under vacuum.

Anion response studies

A stock suspension of polymer (8.0 mg/mL) was prepared by dissolving 400.0 mg of polymer in 50.0 mL of DI water. Solutions of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, CN^-, $H_2PO_4^-$, and HSO_4^-; 1.0×10^{-3} mol/L) were prepared by dissolving the corresponding tetrabutylammonium salts in DI water.

Approximately 225 μL of polymer suspension and 300 μL of anion solution were placed in a 3.0 mL cuvette. Subsequently, DI water was added to this mixture to a total volume of 3.0 mL. Characterization was conducted by fluorescence spectroscopy.

Fluorescence Titration of F^-

Titration experiments were conducted at 25 °C. Approximately 225 μL of polymer suspension and varying volumes of F^- solution were placed in a 3.0 mL cuvette. Then, DI water was added to adjust the total volume to 3.0 mL. Fluorescence spectra were recorded after 3 min equilibration at 25 °C.

Conclusions

A crosslinked polymer containing hydroxyl quinoline, CpA1T5, was developed as a fluorescent and colorimetric chemosensor for F^- in water. Such a crosslinked polymer exhibited poor solubility; thus, suspension instead of solution was formed in the solvent. The suspension of CpA1T5 in DI water immediately displayed fluorescence enhancement accompanied by a redshift in emission spectrum and an obvious change in color from gray to yellow upon the introduction of F^-, which provided a rapid detection method for F^- in aqueous media. Furthermore, the chemosensor could be recycled many times without an obvious decrease in sensing property. This chemosensor was used for the ultrasensitive determination of F^- in real samples with good accuracy. Our findings imply that the sensor has broad applications in fields that require F^- determination.

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Notes and references

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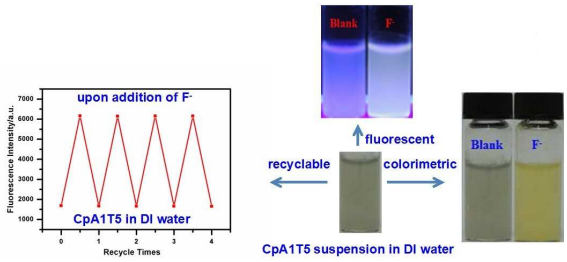
Electronic Supplementary Information (ESI) available: [Synthetic scheme for polymer; optimization of AHPEQB/TRIM; SEM, TGA, and N_2 adsorption-desorption results; anion response of AHPEQB; UV-Vis spectra of CpA1T5 upon addition of various anions; anion response of CpA1T5 in HEPES buffer at pH 7.0; anion response of CpA1T5 at lower concentration; determination of fluoride anion concentration in mouthwash samples]. See DOI: 10.1039/b000000x/

1 P. A. Gale, *Chem. Soc. Rev.,* 2010, **39**, 3746.
2 H. Aboubakr, H. Brisset, O. Siri and J. M. Raimundo, *Anal. Chem*., 2013, **85**, 9968.
3 M. Jo, J. Lim and O. S. Miljani, *Org. Lett*., 2013, **15**, 3518.
4 K. Itai and H. Tsunoda, *Clin. Chim. Acta*, 2001, **308**, 163.
5 P. Konieczka, B. Zygmunt and J. Namiesnik, *Bull. Environ. Contam. Toxicol.*, 2000, **64**, 794.
6 Y. Zhou, J. F. Zhang and J. Yoon, *Chem. Rev*., 2014, **114**, 5511.
7 C. Y. Wang, G. Li and Q. C. Zhang, *Tetrahedron Lett*., 2013, **54**, 2633.
8 J. Liu, Y. Q. Xie, Q. Lin, B. B. Shi, P. Zhang, Y. M. Zhang and T. B. Wei, *Sensor. Actuat. B*, 2013, **186**, 657.
9 S. Madhu and M. Ravikanth, *Inorg. Chem*., 2014, **53**, 1646.
10 C. L. Yang, J. Xu, J. Y. Li, M. G. Lu, Y. B. Li and X. L. Wang, *Sensor. Actuat. B*, 2014, **196**, 133.
11 T. D. Thangadurai, G. Chung, O. Kwon, D. R. Jin and Y. I. Lee, *Tetrahedron Lett*., 2011, **52**, 6465.
12 H. Y. Liu, X. J. Wan, T. Q. Liu, Y. Q. Li and Y. W. Yao, *Sensor. Actuat. B*, 2014, **200**, 191.
13 S. Areti, J. K. Khedkar, R. Chilukula and C. P. Rao, *Tetrahedron Lett*., 2013, **54**, 5629.
14 L. Y. Zhao, G. K. Wang, J. H. Chen, L. M. Zhang, B. Liu, J. F. Zhang, Q. H. Zhao and Y. Zhou, *J. Fluorine Chem*., 2014, **158**, 53.
15 A. Bamesberger, C. Schwartz, Q. Song, W. W. Han, Z. Wang and H. S. Cao, *New J. Chem*., 2014, **38**, 884.
16 Y. M. Kai, Y. H. Hu, K. Wang, W. B. Zhi, M. M. Liang and W. G. Yang, *Spectrochim. Acta A*, 2014, **118**, 239.
17 X. J. Zheng, W. C. Zhu, D. Liu, H. Ai, Y. Huang and Z. Y. Lu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7996.
18 A. K. Mahapatra, K. Maiti, P. Sahoo and P. K. Nandi, *J. Luminescence*, 2013, **143**, 349.
19 Y. H. Li, Y. Duan, J. Zheng, J. S. Li, W. J. Zhao, S. Yang and R. H. Yang, *Anal. Chem*., 2013, **85**, 11456.
20 P. C. A. Swamy, S. Mukherjee and P. Thilagar, *Anal. Chem*., 2014, **86**, 3616.
21 C. L. Yang, J. Xu, W. Chen, M. G. Lu, Y. B. Li and X. L. Wang, *J. Mater. Sci*., 2014, **49**, 7040.
22 C. Kar, S. Samanta, S. Mukherjee, B. K. Datta, A. Ramesh and G. Das, *New J. Chem*., 2014, **38**, 2660.

23 U. N. Yadav, P. Pant, D. Sharma, S. K. Sahoo and G. S. Shankarling, *Sensor Actuat. B*, 2014, **197**, 73.
24 C. B. Rosen, D. J. Hansen and K. V. Gothel, *Org. Biomol. Chem*., 2013, **11**, 7916.
25 Y. S. Mi, Z. Cao, Y. T. Chen, S. Long, Q. F. Xie, D. M. Liang, W. P. Zhu and J. N. Xiang, *Sensor. Actuat. B*, 2014, **192**, 164.
26 B. C. Zhu, H. Kan, J. K. Liu, H. Q. Liu, Q. Wei and B. Du, *Biosensor. Bioelectro*., 2014, **52**, 298.
27 X. M. Liu, Q. Zhao, Y. Li, W. C. Song, Y. P. Li, Z. Chang and X. H. Bu, *Chin. Chem. Lett*., 2013, **24**, 962.
28 F. M. Hinterholzinger, B. Rühle, S. Wuttke, K. Karaghiosoff and T. Bein, *Scientific Reports*, 2013, **3**, 2562.
29 M. Kaur, M. J. Cho and D. H. Choi, *Dyes Pigments*, 2014, **103**, 154.
30 B. Taner, O. Alici and P. Deveci, *Supramol. Chem*., 2014, **26**, 119.
31 B. Taner, A. N. Kursunlu and E. Güler, *Spectrochim. Acta A*, 2014, **118**, 903.
32 F. Cheng, E. M. Bonder and F. Jäkle, *J. Am. Chem. Soc*., 2013, **135**, 17286.
33 W. Lu, D. Chen, H. Jiang, L. M. Jiang and Z. Q. Shen, *J. Polym. Sci. Pol. Chem*., 2012, **50**, 590.
34 H. Mori, E. Takahashi, A. Ishizuki and K. Nakabayashi, *Macromolecules*, 2013, **46**, 6451.
35 R. Sakai, S. Okade, E. B. Barasa, R. Kakuchi, M. Ziabka, S. Umeda, K. Tsuda, T. Satoh and T. Kakuchi, *Macromolecules*, 2010, **43**, 7406.
36 L. Wang and M. E. Meyerhoff, *Anal. Chim. Acta*, 2008, **611**, 97.
37 T. H. Kim and T. M. Swager, *Angew. Chem. Int. Ed*., 2003, **42**, 4803.
38 K. Parab, K. Venkatasubbaiah and F. Jäkle, *J. Am. Chem. Soc*., 2006, **128**, 12879.
39 M. H. Park, T. Kim, J. O. Huh, Y. Do and M. H. Lee, *Polymer*, 2011, **52**, 1510.
40 C. L. Yang, J. Xu, J. Y. Ma, D. Y. Zhu, Y. F. Zhang, L. Y. Liang and M. G. Lu, *Polym. Chem*., 2012, **3**, 2640.
41 C. Y. Wu, M. S. Chen, C. A. Lin, S. C. Lin and S. S. Sun, *Chem. Eur. J*., 2006, **12**, 2263.
42 G. Saikia, A. K. Dwivedi and P. K. Iyer, *Anal. Methods*, 2012, **4**, 3180.
43 N. Singh, N. Kaur, J. Dunn, R. Behan, R. C. Mulrooney and J. F. Callan, *Eur. Polym. J*., 2009, **45**, 272.
44 P. Alaei, S. Rouhani, K. Gharanjiga and J. Ghasemi, *Spectrochim. Acta A*, 2012, **90**, 85.
45 P. Zhao, J. B. Jiang, B. Leng and H. Tian, *Macromol. Rapid Commun*., 2009, **30**, 1715.
46 J. M. Hu, C. H. Li, Y. Cui and S. Y. Liu, *Macromol. Rapid Commun*., 2011, **32**, 610.
47 Y. Qu, J. L. Hua, Y. H. Jiang and H. Tian, *J. Polym. Sci. Pol. Chem*., 2009, **47**, 1544.
48 J. B. Jiang, X. Xiao, P. Zhao and H. Tian, *J. Polym. Sci. Pol. Chem*., 2010, **48**, 1551.
49 Q. H. Chu, D. A. Medvetz and Y. Pang, *Chem. Mater*., 2007, **19**, 6421.
50 G. Kwak, M. Fujiki and T. Masuda, *Macromolecules*, 2004, **37**, 2422.
51 J. F. Ding and M. Day, *Macromolecules*, 2006, **39**, 6054.
52 R. J. Gilliard Jr., S. T. Iacono, S. M. Budy, J. D. Moody, D. W. Smith Jr. and R. C. Smith, *Sensor. Actuat. B*, 2009, **143**, 1.
53 H. J. Kim, J. H. Lee, T. H. Kim, W. S. Lyoo, D. W. Kim, C. J. Lee and T. S. Lee, *J. Polym. Sci. Pol. Chem*., 2007, **45**, 1546.
54 I. H. A. Badr and M. E. Meyerhoff, *Anal. Chim. Acta*, 2005, **553**, 169.
55 Y. Kang, J. W. Kampf and M. E. Meyerhoff, *Anal. Chim. Acta*, 2007, **598**, 295.
56 H. M. Nie, C. B. Gong, Q. Tang, X. B. Ma and C. F. Chow, *Dyes Pigments*, 2014, **106**, 74.

Table of Content



A crosslinked polymer-based recyclable, fluorescent, and colorimetric sensor for F^- in water