

Polymer-Based Fluoride-Selective Chemosensor: Synthesis, Sensing Property, and Its Use for the Design of Molecular-Scale Logic Devices

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ABSTRACT: A new styryl-type monomer, 2-(4-vinylbenzyloxy)-1-naphthaldehyde thiosemicarbazone (VNT), was synthesized and then copolymerized with methyl methacrylate (MMA) by reversible addition fragmentation chain transfer polymerization affording a series of poly(MMA-co-VNT)s with different functional unit content, predetermined molecular weight, and narrow molecular-weight distribution. The desired copolymers were structurally confirmed by various spectroscopic characterizations. Colorimetric and fluorescent titration spectra revealed that the copolymers are highly selective toward fluoride anions over other competitive species including Cl^- , Br^- , I^- , H_2PO_4^- , AcO^- , and HSO_4^- . On addition of F^- , a remarkable colorless-to-yellow color change is easily observed by naked eyes. The influence of the copolymer composition and molecular weight on its sensing capacity was then carefully investigated. The results showed that higher VNT-incorporation amount within

the copolymer chains leads to higher sensitivity toward F^- ions. Interestingly, the chromogenic process of the polymeric sensor can be switched back and forth by successively adding F^- and HSO_4^- anions into the dimethyl sulfoxide solution of the polymer, which may be represented by a complementary "IMPLICATION/INHIBIT" logic gate at molecular level using both the ions as the chemical inputs. Based on such a reversible and reproducible sensing system, we designed a molecular-scale sequential information processing circuit displaying "writing–reading–erasing–reading" behavior and "multiwrite" function in the form of binary logic. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 590–598, 2012

KEYWORDS: fluorescence; molecular logic gates; molecular recognition; reversible addition fragmentation chain transfer (RAFT); sensor

INTRODUCTION Real-time monitoring and accurate detection of fluoride anions have been of particular interest owing to its extremely important role in medical and environmental sciences. Numerous investigations have been conducted to develop both monomeric and polymeric chemosensors for fluoride, in which much effort is focused on the systems containing urea,¹ thiourea,² sulfonamide,³ amide,⁴ or amine units.⁵ Usually, these neutral receptors containing the N–H fragment are able to behave as hydrogen-bond donors for the fluoride. On interaction with the anion, the deprotonation of the sensors produces detectable spectral response, and mostly concomitant with a visible color change.

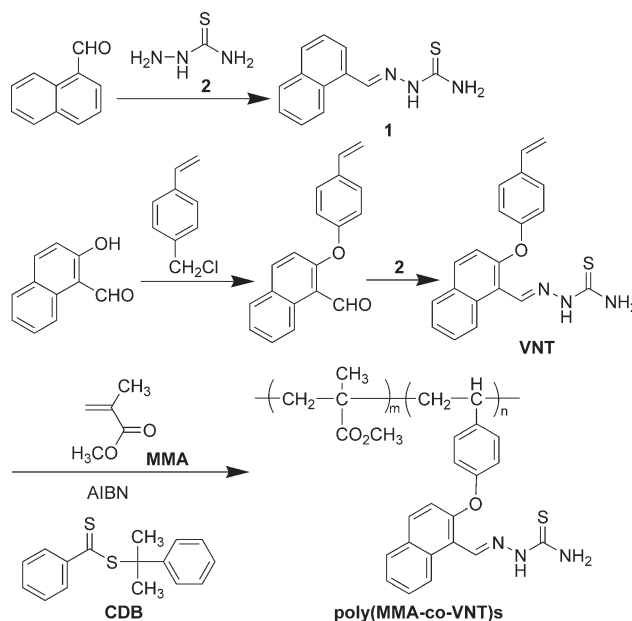
In the design of small molecule-based receptors, the calixarene scaffold or steroidal backbone with preorganized structures are often used to bound two or more the recognition units to improve the affinity toward the envisaged analyte.^{6,7} Nevertheless, this strategy needs sophisticated and laborious synthetic work. In contrast, it is relatively easy to incorporate various sensing units into the polymeric matrix through a

polymerization process. Moreover, the as-prepared polymers have the advantage of facile fabrication of detecting devices and development of the multifunctional sensors.^{8–10} For example, Nishide and coworkers recently reported a film fluorescent device for oxygen detection based on a terpolymer.⁹ As one effective controlled/living radical polymerization technique, reversible addition fragmentation chain transfer (RAFT) polymerization may provide a feasible way to synthesize polymer-based sensory materials, because this method can not only control both the polymer molecular weight and its distribution but also allow the incorporation of polar recognition units within the polymer main chain or as pendant groups.

On the other hand, as the demand for miniaturization of information technology increases, the molecular-scale logic devices (like logic gates,^{11–15} molecular keypad locks,¹⁶ or information storage devices¹⁷) have been drawing much attention during the last decade. Such a logic instrument is believed to transfer the molecular-level information to the observable optical signals.¹⁴ Since the pioneering work by de

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SCHEME 1 Synthesis of monomer VNT and poly(MMA-co-VNT)s.

Silva et al.¹¹ in 1993, diverse digital functionalities (AND,¹¹ OR,¹² XOR,¹³ INHIBIT,¹⁴ etc.) have been realized by various logic gates based on small organic molecules. However, there is quite a few reports on the combinatorial molecular logic gates displaying complementary IMPLICATION/INHIBIT (IMP/INH) logic functions.¹⁸ As a basic unit, IMP/INH logic gate is crucial for the construction of many complex logic systems, such as half-adders and subtractors,¹⁹ multiplexers,²⁰ encoders,²¹ and molecular keypad locks.^{16,22}

The output of these combinatorial systems, like the aforementioned logic gates or adders–subtractors, is exclusively a Boolean function of the current inputs. In contrast, in sequential logic circuits such as molecular keypad locks, the output is determined by the current state of the system, which is usually a function of the previous input and the present input.^{17(c)} In this case, the molecular-based system that can remember and store information about the previous inputs is required. Thus, the construction of sequential logic circuits with memory function has become another research hotspot in the field of molecular information technology. However, the sequential information memory or storage systems, especially those based on the artificial receptor molecules capable of performing multiple logic operations are rarely reported.¹⁷

In a previous paper, we described a simple and efficient fluoride-receptor (**1**) based on thiosemicarbazide derivative of 1-naphthaldehyde (Scheme 1).²³ Distinguishing from the early reported F^- -sensing systems, the ratiometric fluorescent sensor is not only highly selective to fluoride ions but also the F^- -induced chromogenic process could be totally reversed with the addition of HSO_4^- . In this work, we synthesized a styryl-type monomer containing the same receptor fragment as **1**, 2-(4-vinylbenzyloxy)-1-naphthaldehyde thiosemicarbazone (VNT), and then copolymerized with MMA by RAFT polymerization technique to

develop new polymer-based sensory materials. As expected, the resulting copolymer exhibited highly selective response toward F^- and HSO_4^- , like its small molecule counterpart. Based on such a molecular switching between both chemical inputs (F^- , HSO_4^-), we designed a sequential information processing circuit displaying writing–reading–erasing–reading behavior and multiwrite function in the form of binary logic. To our knowledge, although quite a number of small molecule-based logic instruments have been developed, the reports on exploring the polymer-based logic systems with integrated functions are still limited up to now.²⁴

EXPERIMENTAL

Characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AMX-400 and AMX-500 NMR instrument, respectively. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112 analyzer. A Bruker Vector 22 Fourier Transform Infrared spectrometer was applied for recording spectra in KBr pellets. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PL-GPC 220 apparatus equipped with a set of PLgel columns (MIXED-B 300×7.5 mm) and a differential refractometer detector (eluent, tetrahydrofuran; a flow rate of 1.0 mL/min). The GPC chromatogram was calibrated against standard polystyrenes. UV-vis spectra were obtained in dimethyl sulfoxide (DMSO) at 25 °C using a quartz cell of 1 cm on a BioLogic MOS-450 spectrometer (France). Steady-state fluorescence spectra were recorded on a PerkinElmer LS-55 fluorescence spectrometer in the right-angle geometry (90° collecting optics).

Materials

α,α' -Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent) was purified by recrystallization from methanol. *N,N*-

Dimethyl formamide (DMF) and DMSO were distilled in the presence of CaH_2 under reduced pressure before use. 2-Hydroxy-1-naphthaldehyde, thiosemicarbazide, and all tetra-butylammonium salts were purchased from Aladdin Shanghai Reagent. 1-(Chloromethyl)-4-vinylbenzene was purchased from Aldrich. RAFT reagent cumyl dithiobenzoate (CDB) was synthesized according to the reported method.²⁵

Monomer Synthesis

Into a solution of 2-hydroxy-1-naphthaldehyde (3.50 g, 20 mmol) in DMF (50 mL) were added 1-(chloromethyl)-4-vinylbenzene (4.00 g, 20 mmol), K_2CO_3 (8.00 g), and KI (1.00 g). After stirring at room temperature for 5 days, the reaction mixture was poured into a large amount of deionized water to precipitate the desired product (2-(4-vinylbenzyloxy)-1-naphthaldehyde, yield 90%, 6.70 g). The intermediate was directly used in the next step reaction.

Thiosemicarbazide (2.00 g, 22 mmol) was added into a solution of 2-(4-vinylbenzyloxy)-1-naphthaldehyde (6.00 g, 21 mmol) in CH_3OH (50 mL). After heating the mixture at 70 °C for 12 h, the solvent was removed under reduced pressure. The resulting solid matter was recrystallized from ethyl acetate to give the target product, VNT, in 82% yield (6.20 g, yellow).

^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 5.20 (d, 1H; $\text{CH}=\text{}$), 5.35 (s, 2H; $\text{CH}_2\text{—Ar}$), 5.85 (d, 1H; $\text{CH}=\text{}$), 6.75 (m, 1H; $\text{CH}=\text{}$), 7.40 (m, 1H; ArH), 7.61 (m, 6H; ArH), 7.88 (m, 1H; ArH), 8.00 (m, 1H; ArH), 8.25 (s, 1H; ArH), 8.92 (s, 1H; CH), 8.95 (d, 2H; NH_2), 11.60 (s, 1H; NH). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 178.1, 157.3, 141.9, 137.3, 136.9, 136.8, 132.8, 131.2, 129.3, 128.9, 128.8, 128.5, 126.7, 126.0, 124.7, 115.5, 115.3, 115.0, 70.9. Anal. calcd. for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{OS}$: C 69.31, H 5.26, N 11.63. Found: C 69.17, H 5.48, N 11.55.

RAFT Copolymerization

A typical experimental procedure for poly(MMA-co-VNT)s is described below. In a flask with side arm, the monomer VNT (0.5 g), MMA (0.5 g), CDB (10.5 mg), and AIBN (1.64 mg) were dissolved in 1 mL of DMF. The mixture was degassed with four freeze-pump-thaw cycles, and sealed under vacuum. The vial was then immersed in a preheated oil bath at 70 °C for 48 h. The reaction mixture precipitated from methanol or hexane (200 mL). To completely remove the unreacted monomers and PMMA from the crude product, a Soxhlet extraction by toluene was conducted for 48 h and then was dissolved in 10 mL of DMF. Filtering out an extremely small amount of undissolved matter (the homopolymer of VNT), the solution was poured into methanol to precipitate the desired copolymers. The purified samples were dried in a vacuum at 60 °C for 24 h.

RESULTS AND DISCUSSION

Monomer Synthesis and RAFT Polymerization

In our previous work, 1-naphthaldehyde thiosemicarbazone (**1**) has proven to be useful as highly sensitive fluorescent sensor for the recognition of fluoride anions in dry DMSO solution.²³ Nevertheless, the chemosensor does not work in a protic solvent (e.g., the mixture of $\text{DMSO}/\text{H}_2\text{O}$), like the existing analogous receptors containing the N—H fragment. To

address the drawback, its copolymers are taken into consideration and MMA was thought as a proper copolymerization monomer. We chose MMA as the comonomer with the expectation that the desired copolymers would gain good solubility in common organic solvents and high affinity for target analytes resulting from the flexibility of main chains.²⁶ Also, such polymeric sensory materials should have the potential to be used for the construction of solid detecting devices.

As shown in Scheme 1, the functional monomer (VNT) was synthesized by two-step reactions in a total yield of 72%. Its well-defined chemical structure has been verified by spectroscopic measurements (see: Supporting Information for details). The copolymerization of VNT with MMA was carried out in DMF at 70 °C using CDB as the chain transfer agent and AIBN as the initiator. The results summarized in Table 1 indicate that the RAFT polymerization exhibited a decent controllability of molecular weight and low polydispersity index, which provided a series of suitable samples for the structure–property investigation. The obtained copolymers were completely soluble in common organic solvents such as THF, chloroform, DMSO, and DMF at ambient temperature, but they are nearly insoluble in toluene, especially for the samples with high content of VNT. Compared with the copolymers, the homopolymer of VNT showed poor solubility in these solvents. The VNT content incorporated into the polymer chains was determined to be in range of 1.4–30.3 mol % according to the reported method.²⁷ Average molecular weights of the polymers from GPC analysis were consistent with the theoretical values. All of samples show a narrower molecular weight distribution (polydispersity index ≤ 1.37); however, a small enlargement for PDI was observed with the increasing content of VNT within the polymer chains.

The structure of poly(MMA-co-VNT)s was characterized by ^1H NMR and IR spectra (Fig. S1, in Supporting Information). In the ^1H NMR, the resonance peaks at 7–8 ppm are ascribed to the aromatic protons in VNT. Besides, the characteristic IR absorption band from N—H stretching motions was present at 3500 cm^{-1} . These observations combining

TABLE 1 Results on Copolymerization of VNT with MMA^a

Sample Code	VNT/MMA Feed Ratio ^b	Yield (%)	$M_n(\text{GPC})$	$M_w(\text{GPC})$	PDI	VNT Content (mol %) ^c
P1	99/1	65	14,000	16,600	1.18	1.4
P2	96/4	60	12,800	15,000	1.17	3.2
P3	92/8	56	13,700	16,200	1.18	7.3
P4	90/10	61	14,000	17,200	1.23	8.9
P5	80/20	66	11,200	15,400	1.37	17.0
P6	70/30	58	11,800	14,500	1.23	18.0
P7	60/40	61	13,200	17,200	1.30	20.0
P8	50/50	59	12,000	15,300	1.28	30.3

^a CDB as the chain transfer agent, AIBN as the initiator, DMF, 70 °C, 48 h.

^b The molar ratio.

^c Measured by UV–vis absorption analysis.²⁷



FIGURE 1 Color change of the DMSO solution of P3 (0.115 mg/mL) in the presence of various TBA salts (15 equiv.). Added anions from left to right: none, F^- , $H_2PO_4^-$, AcO^- , Cl^- , Br^- , I^- , and HSO_4^- .

with the narrow and symmetric GPC curves (Fig. S2, in Supporting Information) clearly verified the presence of VNT components in the copolymer chains.

Anion-Sensing Property of Poly(MMA-co-VNT)s

The interaction of poly(MMA-co-VNT)s with various anions was investigated in dry DMSO. In a typical experiment, $n\text{-Bu}_4N^+$ (TBA) salts were slowly added to a standard DMSO solution of the copolymer. As shown in Figure 1, on fluoride addition, the colorless solution immediately turned yellow, whereas none of any other anions (Cl^- , Br^- , I^- , $H_2PO_4^-$, AcO^- , and HSO_4^-) produced any color change. Accompanying with the colorless-to-yellow color change, the absorption maximum in the UV-vis spectrum was red-shifted from 365 to 425 nm; meanwhile, the original fluorescence emission was quenched sharply on the addition of F^- (Fig. 2). However, other anions did not bring noticeable changes in both absorption and emission spectra. These results indicated that the copolymer is an excellent F^- -selective sensor. Note also that the polymeric sensor has a distinct advantage over its small molecule-based counterpart **1**, that is, it is applicable for detecting fluoride anions in aqueous organic media like DMSO/ H_2O (95/5, v/v) with fairly high selectivity and sensitivity (see: Supporting Information Fig. S6). From the practical point of view, this property is significant, because fluoride ions are dissolved in aqueous solution in most analytes.

As generally accepted, the signaling mechanism for the polymeric sensor is related to the deprotonation process of thiosemicarbazone lateral groups, which is supported by 1H NMR titration experiments. Considering the low resolution of the polymer spectra, we used the functional monomer VNT as a model compound for measuring 1H NMR titration spectra toward TBAF in DMSO- d_6 . It can be seen from Figure 3 that on stepwise addition of fluoride, the $N-H_a$ signal at 11.60 ppm significantly decreases and eventually totally disappears when 2 equiv. of fluoride was added. In the meantime, the peak due to $N-H_b$ gradually shifts downfield from δ 8.95 to 9.25 without obvious intensity drop. Apparently, the above-observed absorption and fluorescence responses may be attributed to the F^- -induced deprotonation effect of $N-H_a$ segments, leading to an expansion of the π -electron

delocalization. A yellow color formation is visible evidence for this.

Similar to that seen in the case of **1**, the fluoride-induced chromogenic process of poly(MMA-co-VNT)s can be totally

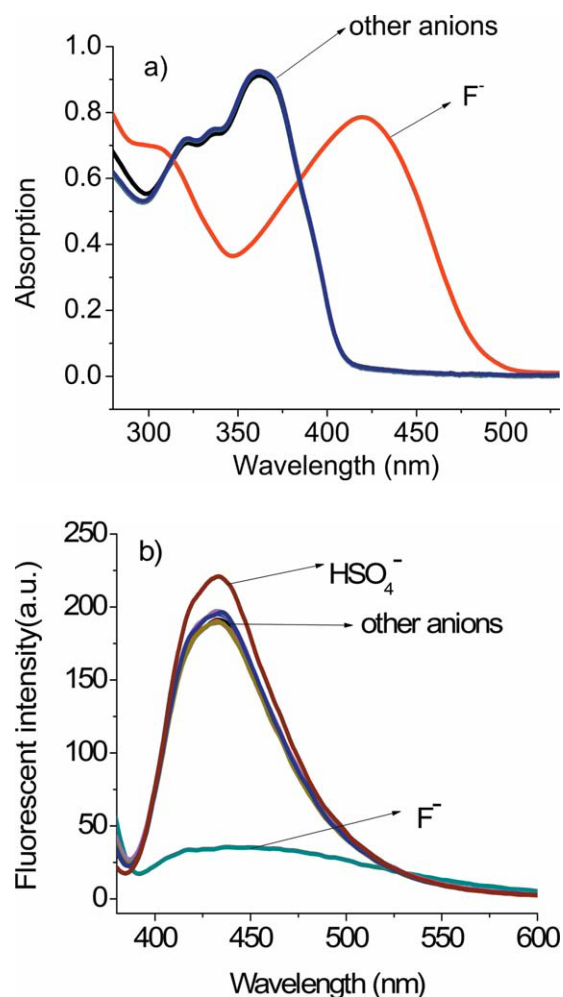


FIGURE 2 (a) UV-vis spectra and (b) fluorescence spectra of P3 in DMSO (0.115 mg/mL) on addition of F^- , $H_2PO_4^-$, AcO^- , Cl^- , Br^- , I^- , and HSO_4^- (15 equiv.).

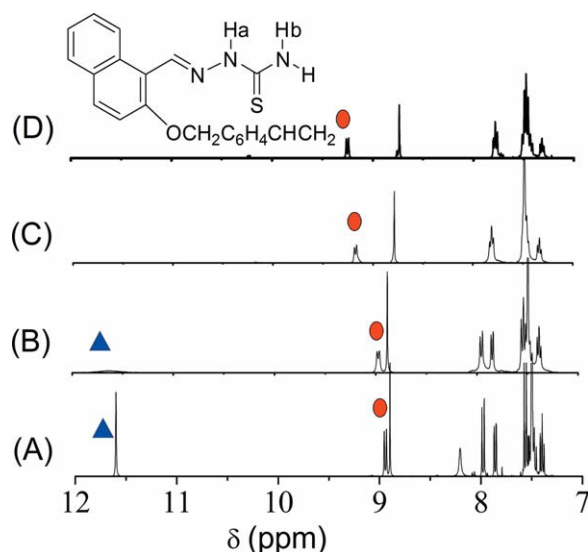


FIGURE 3 ^1H NMR spectra of VNT in the absence (A) and presence of (B) 1 equiv., (C) 2 equiv., and (D) 5 equiv. of TBAF in $\text{DMSO}-d_6$. $\blacktriangle$ and $\bullet$ represent H_a and H_b , respectively.

reversed by adding 1 equiv. of proton (aqueous hydrochloric acid solution) or adding HSO_4^- anions (*vide infra*), suggesting that the significant variations in the absorption and fluorescence profiles do not arise from the chemical changes of polymer chain structure. As evidenced by GPC and ^1H NMR observations (Supporting Information Figs. S2 and S3), the addition of fluoride does not result in the cross-linking or chain-cleavage of polymer backbones.

It is well known that the basicity difference is an important factor for anion recognition.²⁸ Accordingly, it is understandable that poly(MMA-co-VNT)s have no response to the anions of low basicity such as Cl^- , Br^- , I^- , H_2PO_4^- , and HSO_4^- . However, the observation that the polymer sensor exhibited high selectivity of F^- over AcO^- seems to be surprising, as acetate is slightly more basic than fluoride.²⁹ This result may be explained by the idea that fluoride ion has much larger charge density than AcO^- , and hence strongly interacts with N—H fragments leading to the deprotonation. Also, the configuration of acetate anion most likely does not match with the acidic site of the sensor, which is probably another reason.

To understand the interaction between poly(MMA-co-VNT) and F^- , UV-vis and fluorescence titration experiments were conducted. From Figure 4(a), it can be seen that with increasing amount of F^- the absorption peak centered at 365 nm gradually decreases, concomitant with the emergence and enhancement of a new peak at 425 nm. The corresponding fluorescence titration spectra showed that the copolymer emits intense fluorescence centered at 435 nm in DMSO when excited at 365 nm [Fig. 4(b)]. On complexation with fluoride, the emission at 435 nm decreased dramatically and was finally quenched by 15 equiv. of F^- ions. These data

provide further support to the deprotonation mechanism. The presence of two well-defined isosbestic points at 313 and 384 nm indicated the formation of a stable complex poly(MMA-co-VNT)-F during the course of titration (Scheme 2).

For the sake of removing the possibility of the photochemical reactions involved with naphthalene moieties causing the fluorescence quenching (FQ), a control experiment was carried out where the emission intensity of the polymer solution was monitored in a continuous irradiation in the absence of fluoride anion.³⁰ The results showed that no distinct change was observable in the fluorescence spectra. Consequently, the spectral responses of poly(MMA-co-VNT)s toward F^- should be attributed to the enhanced internal charge transfer effect resulting from the fluoride-induced deprotonation.³¹

Influence of Copolymer Composition and Molecular Weight on the Sensing Capacity

For a polymeric sensory system, it is difficult to obtain the corresponding binding constant to represent its recognition

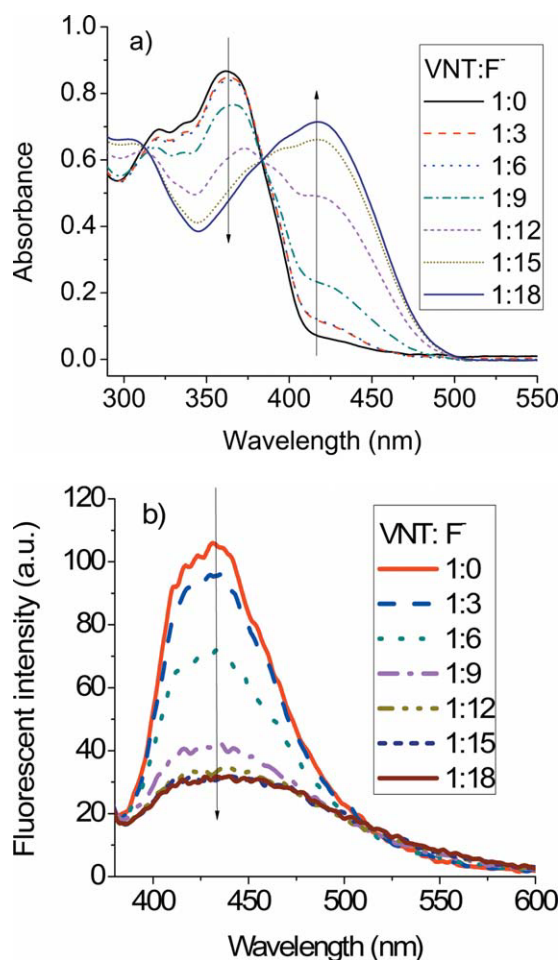
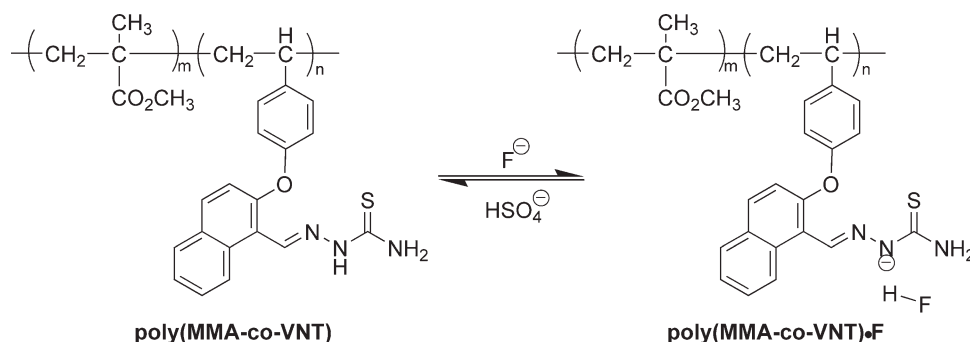


FIGURE 4 (a) UV-vis titration spectra and (b) fluorescence titration spectra of P3 in dry DMSO (0.115 mg/mL) on addition of TBAF. VNT: F^- represents the molar ratio of functional units within the copolymer to fluoride.



SCHEME 2 F^- -induced deprotonation process of poly(MMA-co-VNT)s.

ability like the case of small molecule receptors.³² In view of this, we applied the FQ ratio ($\text{FQ} = I_0/I_F$) to evaluate the sensing property of the present polymer sensor toward fluoride anions.³³ A larger FQ value means a stronger recognition capacity and sensitivity at a certain analyte concentration.

It was found that the sensing capacity of poly(MMA-co-VNT)s toward fluoride is dependent on both the content of functional units and the analyte concentration (Supporting Information Fig. S4). In the presence of 12 equiv. of F^- , as the amount of VNT in the polymer chain increases, the FQ value initially rises, reaches a maximum (5.5) at about 7.3 mol % VNT incorporation and then falls to a platform (~ 5.35) as more VNT is incorporated into the polymer. Compared with the monomeric receptor, the higher sensitivity for the copolymer may be ascribed to the cooperative hydrogen bonding of the pendent thiosemicarbazone groups to enhance its affinity toward F^- . Besides, increasing fluoride concentration is beneficial for improving the detection sensitivity of both polymeric and monomeric sensors.

It is noteworthy that the sensing capacity of poly(MMA-co-VNT)s with close VNT contents is almost irrelevant to their molecular weight. As shown in Supporting Information Figure S5 and Table S1, the FQ values are nearly same at a certain fluoride concentration for the polymers with different molecular weights. It is conceivable that in a good solvent, the flexible polymer chains would preferentially adopt a random coil conformation, which allows the cooperative interaction of lateral groups to bind fluoride without serious interference from the molecular size.

A Reversible and Reproducible Colorimetric Switch Based on the Complementary “INH/IMP” Logic Gate

As discussed above, on addition of fluoride, the absorption maximum of the DMSO solution of poly(MMA-co-VNT)s was red-shifted near 60 nm accompanying with a color change from colorless to yellow. Moreover, the F^- -induced chromogenic process could be totally reversed with HSO_4^- anions as shown in Figure 5. This eye-detected change was clearly reflected in the UV-vis spectra, in which the addition of 5 equiv. of HSO_4^- results in vanishing of the band at 425 nm and reappearance of the absorption at 365 nm.

More interestingly, the colorless-yellow-colorless cycle could be repeated for several times by the alternate addition of 15 equiv. of F^- and 5 equiv. of HSO_4^- ions to the DMSO solution of the copolymer. However, to achieve this reversible chromogenic switching, the sequence of the feeding of anions must be to feed F^- first and then add HSO_4^- ; the reverse feeding order does not cause any noticeable change in both the color and spectra for the polymer solution. The results demonstrated that the presence of HSO_4^- anions should inhibit the interaction of F^- with the polymer, as HSO_4^- is more acidic than the receptor. As shown in Scheme 2 the interaction of HSO_4^- with the complex poly(MMA-co-VNT)·F releases the receptor, meanwhile F^- ions would be converted into other species, such as HF and HF_2^- .³⁴ This also explains why the colorimetric switch can work in a reproducible manner, despite the fact that the added F^- and HSO_4^- anions are not of equal molar amount in one single cycle.

As depicted in Figure 6, the reversible and reproducible chemical switching may be represented via a molecular “INHIBIT” logic gate, using F^- (InF) and HSO_4^- (InH) as the inputs and the absorbance at 425 nm as the output. When the absorbance at 365 nm is used as another output, an “IMPLICATION” logic gate can be fabricated. In this way, the complementary IMP/INH logic functions are realized using the polymer-based sensing system.

Thus, the color change (optical output) of poly(MMA-co-VNT)s in DMSO can be controlled by the inputs of two anions: F^- “switches” ON the optical output, whereas HSO_4^- switches OFF it. By alternately adding F^- (15 equiv.) and HSO_4^- (5 equiv.) into the receptor solution, a reversible colorimetric switch could be created in a reproducible manner (Fig. 7). This kind of reversible and reproducible switch is very significant for information processing at molecular level. In the field of information technology, the switching process must be based on a reversible chemical process to perform any useful calculation.³⁵ However, most of newly reported logic systems are actually based on irreversible chemical processes. Although these logic devices have already found some applications in medicine as novel approaches toward anticancer therapy,³⁶ they are not suitable for computational operations. Therefore, the present logic device has a great advantage over early reported relative systems at least in terms of the reversible and reproducible characteristics.

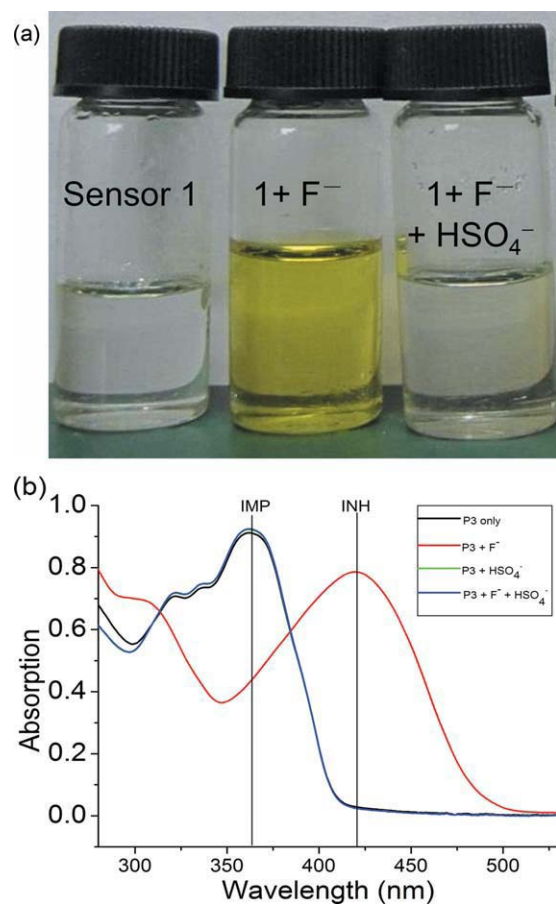


FIGURE 5 (a) Color change and (b) UV-vis spectra of the DMSO solution of P3 with various combinations of F⁻ (15 equiv.) and HSO₄⁻ (5 equiv.), as well as the corresponding molecular logic function IMP (365 nm) and INH (425 nm).

The Memory Unit with Multiwrite Function Based on the Reversible and Reproducible Colorimetric Switch

Figure 8 shows a sequential logic circuit based on the reversible and reproducible colorimetric switch, which displays writing-reading-erasing-reading behavior in the form of binary logic for molecular-level information processing. In this concrete system, the ON state (Output 2 = 1) is defined as the high absorption at 425 nm, whereas the OFF state (Output 2 = 0) corresponds to the significantly low absorption at this

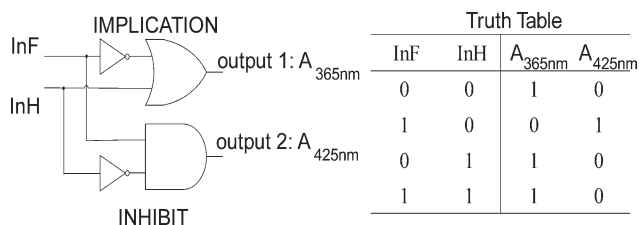


FIGURE 6 The complementary IMP/INH logic gate and its truth table. InF and InH represent Input F⁻ and Input HSO₄⁻, respectively.

wavelength. The inputs are constituted by F⁻ (InF) and HSO₄⁻ (InH) for the set (S) and reset (R), respectively. The operation of this memory unit is as follows: whenever the set input is high (S = 1), the system writes and memorizes the binary state 1; on the other hand, when the reset input is high (R = 1), the 1 state is erased and the 0 state is written and memorized. As shown in Figure 8(a), the reversible and reconfigurable sequences of set/reset logic operations in a feedback loop demonstrate the memory feature with writing-reading-erasing-reading functions with the absorbance at 425 nm as the output. Also, Figure 8(b) defines the bistability behavior, “ON-OFF” state, of the polymer and reveals the non-volatile nature of the memory effect. More importantly, the ON-OFF states could be repeated for many times, suggesting that writing-reading-erasing-reading cycles could be conducted. In other words, this system exhibits multiwrite ability without obvious degradation in its optical output (the absorbance at 425 nm). As a result, this kind of sequential logic circuits possessing the same behavior as the traditional logic devices constructed by semiconducting materials would promote the development of molecular microprocessors for memory elements of integrated logic circuits in the future.³⁷

CONCLUSIONS

In summary, a new kind of polymeric sensors containing naphthalene signal moieties and thiourea recognition units to bind fluoride has been synthesized by RAFT polymerization of MMA with VNT. The resulting poly(MMA-co-VNT)s have proved to be highly selective for fluoride and show a remarkable color change and FQ on fluoride binding in DMSO solution, which enable us to discriminate F⁻ ion from other anions including Cl⁻, Br⁻, I⁻, H₂PO₄⁻, AcO⁻, and HSO₄⁻ by naked eye only. Moreover, the polymeric sensor is applicable for detecting fluoride anions in aqueous organic media like DMSO/H₂O (95/5, v/v) with fairly high selectivity

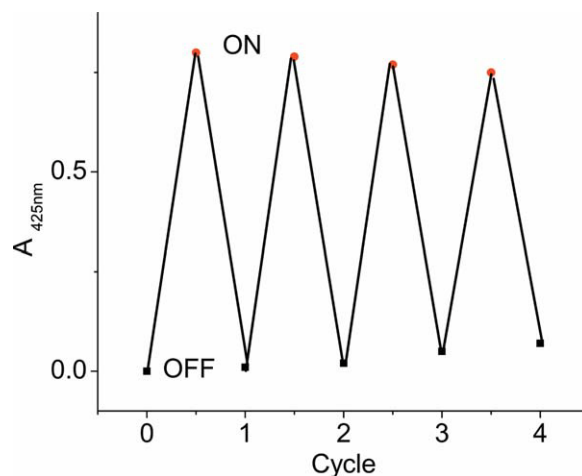


FIGURE 7 The reversible and reproducible colorimetric switch controlled by alternately adding F⁻ (15 equiv.) and HSO₄⁻ (5 equiv.) into the DMSO solution of P3 (5 × 10⁻⁵ mol/L).

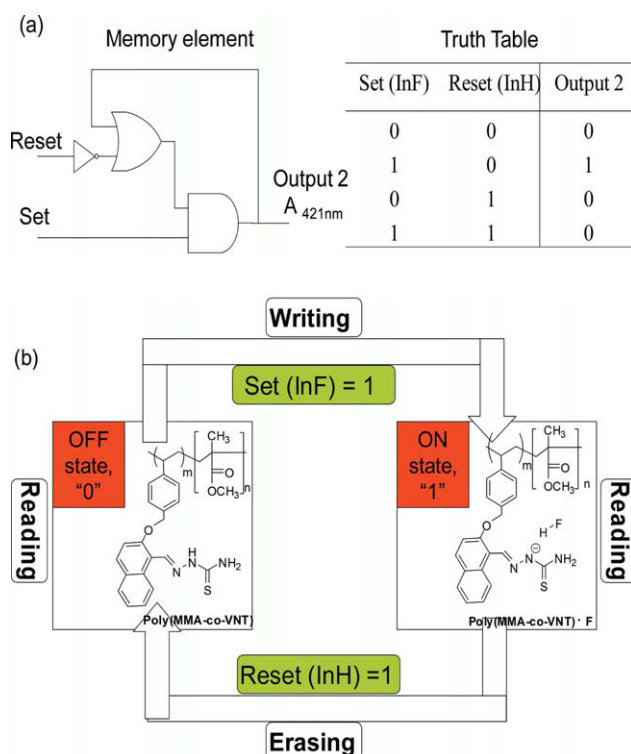


FIGURE 8 (a) Sequential logic circuit that displays the memory machine and its truth table and (b) feedback loop exhibiting reversible logic operations for memory element with writing–reading–erasing–reading behavior and multiwrite functions.

and sensitivity. The sensing capacity of the copolymers toward fluoride was found to be mainly dependent on both the content of VNT units and the analyte concentration. Higher VNT incorporation within the polymer chain and/or higher fluoride concentration is beneficial for improving the polymer's detection sensitivity. Interestingly, the F^- -induced chromogenic process could be totally reversed by the addition of HSO_4^- , which may be represented by the molecular-level complementary IMPLICATION/INHIBIT logic gate using F^- and HSO_4^- as the inputs. Based on the reversible and reproducible colorimetric switch, we have designed a molecular-scale sequential information processing circuit displaying writing–reading–erasing–reading behavior and multiwrite function in the form of binary logic.

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