

A Chiral Polymer-Based Turn-On Fluorescent Sensor for Specific Recognition of Hydrogen Sulfate

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Received 26 March 2012; accepted 7 June 2012; published online 16 July 2012

DOI: 10.1002/pola.26230

ABSTRACT: A new kind of polymeric chemosensor containing chiral naphthaldimine moiety in the side chain was synthesized by the reversible addition-fragmentation chain transfer polymerization of *N*-{[2-(4-vinylbenzyloxy)-1-naphthyl]-methylene}-(*S*)-2-phenylglycinol (VNP). The resulting polymers (PVNP) showed high selectivity for hydrogen sulfate relative to other anions including F^- , Cl^- , Br^- , $H_2PO_4^-$, $CH_3CO_2^-$, and NO_3^- in tetrahydrofuran (THF) solution as judged from UV–vis, fluorescence, and circular dichroism spectrophotometric titrations. Compared with its monomer, the polymer has proven to be more attractive for detection of HSO_4^- in terms of sensitivity

and reproducibility. Upon addition of the anion it gives remarkable spectral responses concomitant with detectable color change from colorless to pale yellow. Furthermore, the HSO_4^- -induced CD or fluorescence signal can be totally reversed with addition of base and eventually recovered the initial state, leading to a reproducible molecular switch with two distinguished “on” and “off” states. © 2012 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 4191–4197, 2012

KEYWORDS: anion recognition; chiral polymer; fluorescent sensor; hydrogen sulfate; RAFT polymerization

INTRODUCTION Fluorescent chemosensors for the anion recognition have attracted increasing attention due to the simplicity and high sensitivity of fluorescence detection methods.¹ In this field, the development of fluorescence “turn-on” sensors for detection of anionic species of biological importance still remains a challenging task due to the fact that general anions can act as fluorescence quenchers.² Another difficult problem involves the preparation of receptors having high sulfate/nitrate selectivity, which is associated with an appreciation of the role they could play in radioactive waste remediation.³

Among the various anions, HSO_4^- and SO_4^{2-} ions are of particular interest because of their significance in biological and environmental sciences. For example, amphiphilic hydrogen sulfate tends to dissociate at high pH to yield toxic sulfate ions, causing irritation of skin and eyes and even respiratory paralysis.⁴ Therefore, it is especially important for developing an improved method for the selective discrimination of hydrogen sulfate and related anions in the chemosensor research field. However, only a few examples of HSO_4^- -receptors have been reported till now and most of them are based on small molecules.⁵

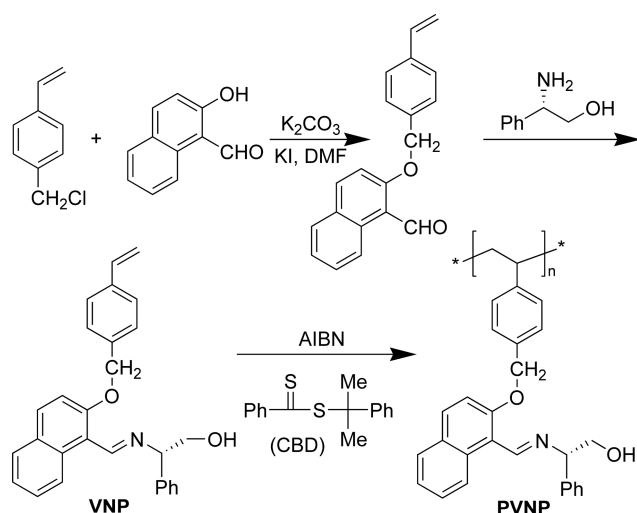
In comparison to small molecular receptors, the polymeric fluorescent counterparts offer several potential advantages,

such as fluorescence efficiency enhancement and possible cooperative effects of multiple recognition sites.⁶ Besides, as a unique feature, such polymeric sensory materials allow facile fabrication of detecting devices and development of the multifunctional sensors.⁷ Recently, Nishide and coworkers described a film fluorescent device for oxygen detection based on a terpolymer.^{7(d)} Tian et al. developed novel polymer sensors for recognition of anions such as F^- and $P_2O_7^{4-}$, exhibiting high selectivity in both solution and/or thin film states.⁸

Our recent work demonstrated that *N*-naphthaldimine derivatives of chiral α -phenylethylamine exhibited dramatic and reversible variations in the absorption, emission, and circular dichroism (CD) spectra upon acid/base stimulus, which mainly attributed to the conformational transition induced by the directed rotation of C–C single bond.⁹ This fact prompted us to design a non-conjugated polymer bearing optically active naphthaldimine chromophores in the side chain [poly(*N*-{[2-(4-vinylbenzyloxy)-1-naphthyl]-methylene}-(*S*)-2-phenylglycinol), PVNP, Scheme 1) to explore its potential as a new class of chemosensors with chiroptical channel. It is expected that such a chiral polymer should display evident CD signals, because the chiroptical property is very sensitive to dissymmetric spatial arrangement of interacting chromophores, with the latter strongly influenced by the

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SCHEME 1 Synthesis of monomer VNP and its polymerization.

host-guest interactions. Herein, we present the synthesis of the chiral polymer PVNP via reversible addition-fragmentation chain transfer (RAFT) method and its sensing capacity toward the envisaged anions. The results showed that this sensory system binds hydrogen sulfate anion with specific selectivity relative to other anions including F^- , Cl^- , Br^- , $H_2PO_4^-$, $CH_3CO_2^-$, and NO_3^- . Interestingly, it exhibited pronounced absorbance, fluorescence, and CD responses upon HSO_4^- complexation in “turn-on” fashion. To the best of our knowledge, there are very few currently reported applications of polymers in anion detection; especially, chiral polymer-based receptors for selective HSO_4^- recognition have scarcely been described so far.¹⁰

EXPERIMENTAL

Materials

All anions, in the form of tetra-*n*-butylammonium (TBA) salts of analytical grade, were purchased from J&K Chemicals and used as received. 2-Hydroxy-1-naphthaldehyde (Aladdin), 4-vinylbenzyl chloride (J&K), and other chemicals were used as received. All solvents were analytical reagents. THF for the spectroscopy was high performance liquid chromatography (HPLC) grade. Azobis(isobutyronitrile) (AIBN, 97%) was recrystallized from ethanol twice and dried at room temperature under vacuum. RAFT reagent cumyl dithiobenzoate (CDB) was synthesized according to the literature procedure.¹¹

Measurements

1H - and ^{13}C NMR spectra were recorded on a Bruker Avance AMX-400 and AMX-500 spectrometer in $CDCl_3$, 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. Gel permeation chromatography (GPC) was performed at ambient temperature using a PL-GPC 220 apparatus equipped with a set of PLgel columns (MIXED-B 300 \times 7.5 mm) and a differential refractometer detector in THF at the flow rate of 1.0 mL/min. The number-average

molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. UV-vis and CD spectra were measured at 25 °C in a 1-cm path length quartz cell using 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, λ_{ex} = 320 nm).

Synthesis of Monomer VNP

To a solution of 2-hydroxy-1-naphthaldehyde (3.5 g, 20.3 mmol) and 4-vinylbenzyl chloride (4 g, 26.2 mmol) in distilled dimethyl formamide (DMF) (50 mL) were added potassium carbonate (10 g) and potassium iodide (1 g). After stirring at room temperature for 72 h under dry N_2 atmosphere, the reaction mixture was poured into deionized water (~1 L) to precipitate the crude product as yellowish solid (6.7 g, 90%). The unpurified intermediate (1.488 g) and (*S*)-(+)-phenylglycinol (0.71 g, 5.2 mmol) were dissolved in absolute ethanol (70 mL) and the resulting solution was allowed to reflux for 12 h. After removing the solvent under reduced pressure, the obtained product was recrystallized twice from ethyl acetate/*n*-hexane (1:5, vol/vol) to give the desired product *N*-[2-(4-(vinylbenzyloxy)-1-naphthyl)methylene]-(*S*)-2-phenylglycinol (VNP) as white needle-shaped crystals (1.5 g, 68.2% yield). $[\alpha]_D^{20}$ = +9.0 (*c* 0.5, THF); m.p. = 109.5–111.0 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 9.39 (d, *J* = 8.7 Hz, 1H), 9.14 (s, 1H), 8.01 (d, *J* = 9.1 Hz, 1H), 7.87 (d, *J* = 7.92 Hz, 1H), 7.63–7.19 (m, 12H), 6.73 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.83 (d, *J* = 17.5 Hz, 1H), 5.35 (s, 2H), 5.27 (d, *J* = 11.1 Hz, 1H), 4.94 (t, *J* = 5.6, 5.6 Hz, 1H), 4.41 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.84–3.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8, 157.6, 137.7, 136.6, 136.3, 132.9, 141.1, 132.3, 129.6, 128.8, 128.4, 128.3, 127.8, 127.7, 127.6, 126.7, 125.8, 124.5, 118.2, 114.6, 114.5, 78.4, 71.6, 68.2. FTIR (KBr, cm^{-1}): 3317, 2870, 1633, 1508, 1230, 1002, 701. MS (EI, *m/z*): 408.3 [*M*+1]. Anal. calcd for $C_{28}H_{25}NO_2$: C 82.55, H 6.14, N 3.44; found: C 82.37, H 6.19, N 3.46.

RAFT Polymerization

All the polymerization reactions were performed under dry N_2 using Schlenk techniques. A typical experimental procedure is described below. VNP (0.55 g), AIBN (0.3 mg), CDB (1.36 mg), and distilled DMF (1 mL) were placed in a Schlenk tube. The mixture was degassed with four freeze-pump-thaw cycles, and sealed under vacuum. Then, the vial was placed in a constant-temperature oil bath of 75 °C for 48 h. The polymerization mixture was precipitated from petroleum ether. The polymers were recovered by drying the crude product, taking the soluble material up in THF and precipitate the dissolved polymer into methanol. Repeating this process twice, the desired PVNP samples were then dried in a vacuum at 60 °C for 24 h.

General Procedure for Anion Recognition

About 0.1 mol/L stock solutions of TBA salts were prepared in dimethyl sulfoxide (DMSO) and then diluted to prepare working solutions. The polymer solution was prepared in

TABLE 1 Results on Polymerizations of VNP Using CDB as the RAFT Agent and AIBN as Initiator in DMF at 75 °C (48 h)

No.	VNP/CDB/AIBN (mole ratio)	Polymer (PVNP)				
		Yield (%)	M_n^a	M_w^a	PDI ^a	$[\alpha]_D^{20b}$
1	34/1/0.2	23	2,300	2,500	1.10	+33.0
2	74/1/0.2	26	5,600	6,400	1.13	+33.0
3	100/1/0.2	20	6,700	8,000	1.19	+32.0
4	110/1/0.2	25	9,100	9,800	1.08	+35.7
5	123/1/0.2	30	10,000	13,300	1.23	+35.7
6	205/1/0.2	28	14,400	19,500	1.35	+37.5

^a Taken from GPC and calibrated against standard polystyrenes.^b $c = 0.5$ g/dL in THF solution.

THF and its concentration was calculated on the basis of the monomeric unit (1.5×10^{-4} mol/L). Before the measurements, the mixed solution containing the polymer and anion with different molar ratios was allowed to stand at room temperature for 1–2 h with the view of insuring complete host–guest complexation.

Computations

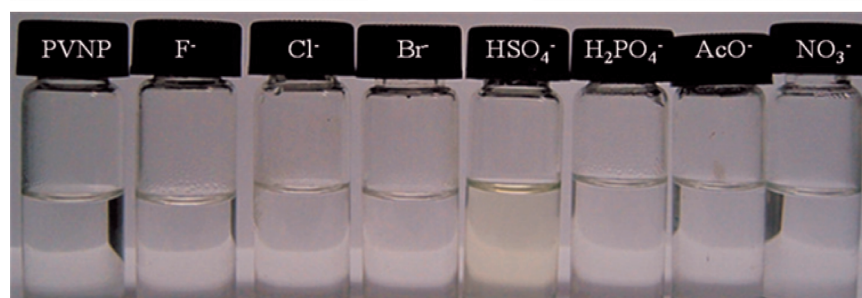
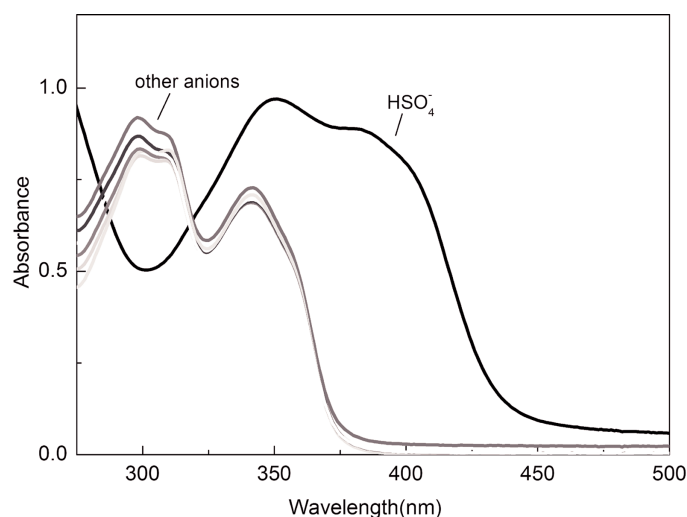
Geometry optimizations and zero-point energies of the compounds were performed by the density functional theory (DFT) calculations at the B3LYP level¹² with a 6-31G(d) basis set using “Gaussian program”.¹³ Vibration frequencies were

used to confirm intermediates (number of imaginary frequencies = 0).

RESULTS AND DISCUSSION

Synthesis of VNP and Polymerization

As shown in Scheme 1, the optically active monomer VNP was easily prepared by two-step reactions in decent yield, including the nucleophilic substitution of 4-vinylbenzyl chloride with 2-hydroxy-1-naphthaldehyde and subsequent Schiff-base formation reaction. Various spectral

**FIGURE 1** UV–vis spectra (upper) and color change (lower) of PVNP-3 (see: No.3 in Table 1) in dry THF (1.5×10^{-4} mol L⁻¹) upon addition of F⁻, Cl⁻, Br⁻, HSO₄⁻, H₂PO₄⁻, CH₃CO₂⁻, NO₃⁻ (5 equiv).

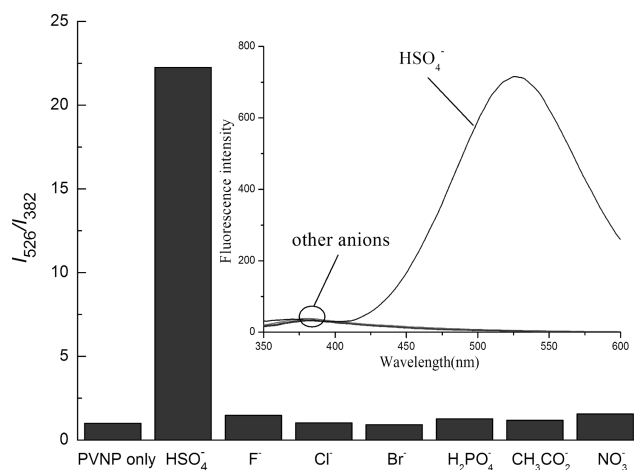


FIGURE 2 Relative fluorescence intensity (I_{526}/I_{382}) of PVNP-3 (1.5×10^{-4} mol L $^{-1}$) in THF upon addition of various anions (5 equivalents). Inset: corresponding fluorescence spectra ($\lambda_{\text{ex}} = 320$ nm).

characterizations verified its well-defined chemical structure (see Experimental Section and Supporting Information).

Table 1 summarizes the RAFT polymerization results of VNP. As evidenced by the nearly linear relationship between the VNP/CDB ratio and number-average molecular masses (M_n), a good control of polymerization was achieved with this system. The average molecular weights determined by GPC analysis were consistent with the theoretical values for these polymers. This control of the polymerization was also supported by the relatively low polydispersity, with M_w/M_n values ranging from 1.08 to 1.35. All of polymer samples are completely soluble in common organic solvents such as THF, chloroform, DMSO, and DMF at ambient temperature, but they are insoluble in methanol and aqueous media. The specific rotations of polymers are larger than that of the corresponding monomer ($[\alpha]_D^{20} = +9^\circ$ for VNP) with the same sign of optical activity. However, there seemed to be no evident correlation between the $[\alpha]_D^{20}$ values and the molecular weights. ^1H NMR and IR spectra of the PVNPs are provided in the Supporting Information.

Anion-Sensing Property of Chiral Polymer PVNP

The binding and recognition of PVNP toward various anions in dry THF were investigated through UV-vis, fluorescence, and CD spectroscopy. The polymer showed characteristic absorption bands at 300 and 340 nm, which is attributed to the $\pi-\pi^*$ transition of pendent naphthalene moiety (see Supporting Information Fig. S1). As shown in Figure 1, upon addition of HSO_4^- (30 equiv.), the absorption band at 300 nm disappeared; the band at 340 nm was remarkably increased with red shift and a shoulder peak around 380 nm concomitantly appeared. Meanwhile, an apparent color change from colorless to pale yellow was readily visible with the naked eye. No other anions (F^- , Cl^- , Br^- , H_2PO_4^- , CH_3CO_2^- , NO_3^-) produced any noticeable change in absorption spectra.

The fluorescence emission spectra of PVNP recorded with excitation at 320 nm also displayed distinct changes when

HSO_4^- was added to the solution (Fig. 2). The combination of PVNP with the anion promoted a new strong emission band at 526 nm while the original emission at 382 nm almost remained. The relative emission intensity, I_{526}/I_{382} , reached 22-fold with 5 equivalents of HSO_4^- . Under the same conditions, the monomer VNP showed a fluorescence increment at 456 nm upon addition of HSO_4^- , but the magnitude was much less than that of PVNP (Supporting Information Fig. S3), indicating the polymer is a more effective receptor for HSO_4^- ion. In contrast, neither PVNP nor VNP receptors gave detectable fluorescence responses toward other tested anions.

Corresponding to the UV-vis absorption peaks, PVNP exhibited the first and second Cotton effects at 340 nm and 300 nm in its CD spectra (Supporting Information Fig. S2). The CD responses of PVNP with various anions in THF are shown in Figure 3. It can be clearly seen that only HSO_4^- addition produced an intensive negative Cotton effect around 387 nm in the CD spectra. The other anions have no meaningful effect on the CD spectral pattern. Given that the chiroptical properties depend greatly on the dissymmetric spatial arrangement of interacting chromophores,¹⁴ the emergence of Cotton effect at 387 nm may be ascribed to the exciton-coupling of the side-chain neighboring groups arranged in a mutual chiral orientation as a result of the hydrogen-bonding interaction. Nevertheless, the monomer VNP did not show any noticeable CD change related to the UV-vis absorptions in the presence of HSO_4^- , indicating the absence of the chiral assembly in solution. Thus, the distinctive CD response of chiral PVNP offers a new signaling channel to recognize HSO_4^- ion.

To gain a preliminary insight into the interaction between PVNP and HSO_4^- , spectrophotometric titration was carried out by stepwise addition of $\text{TBA}^+\text{HSO}_4^-$ to a THF solution of PVNP. Figure 4(a) shows that with increasing concentration of HSO_4^- , the absorption band at 300 nm decreased and the band at 340 nm enhanced evidently with a red-shift of 10

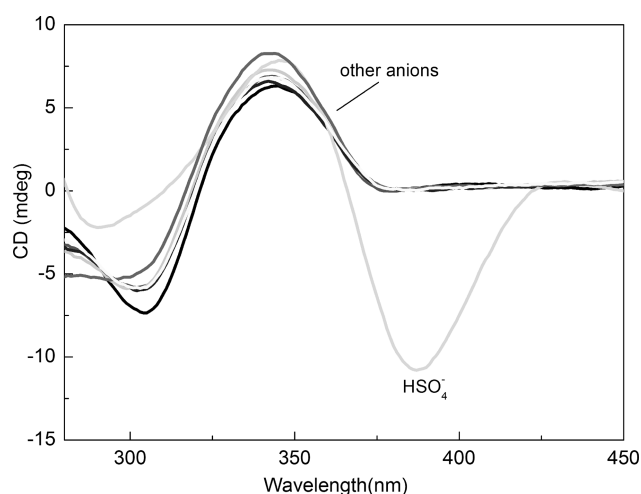


FIGURE 3 CD spectra of PVNP-3 (1.5×10^{-4} mol L $^{-1}$) in dry THF upon addition of F^- , Cl^- , Br^- , HSO_4^- , H_2PO_4^- , CH_3CO_2^- , NO_3^- (30 equiv).

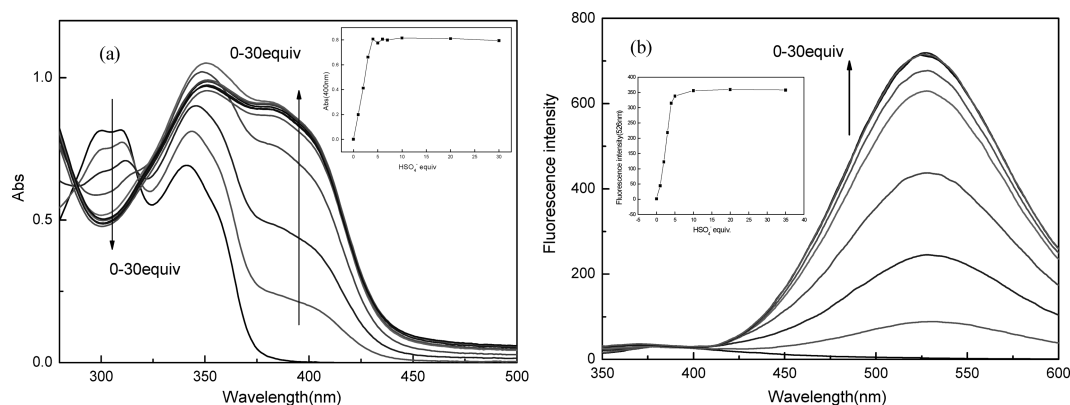


FIGURE 4 Changes in UV-vis spectra (a) and fluorescence spectra (b) of PVNP-3 (1.5×10^{-4} mol L⁻¹) in dry THF upon successive addition of TBA⁺HSO₄⁻. $\lambda_{\text{ex}} = 320$ nm; insert: normalized absorption/fluorescence changes versus equiv. of TBA⁺HSO₄⁻.

nm. The presence of two sharp isosbestic points at 288 nm and 316 nm indicate the formation of a stable host-guest complex throughout the titration process. In the corresponding fluorescence titration spectra [Fig. 4(b)], it can be seen that the new emission peak at 526 nm increased linearly in proportion to the HSO₄⁻ concentration when its amount is less than 5 equivalents. However, higher HSO₄⁻ concentration did not lead to further absorption/emission enhancement (inset, Fig. 4).

For the sake of elucidating the binding mode of PVNP with HSO₄⁻, we conducted ¹H NMR titration experiments using VNP as a model molecule. Figure 5 shows that the peak intensity of hydroxyl proton (Ha) decreased with a slight downfield shift over the course of the titration and finally disappeared on addition of 2 equivalent of HSO₄⁻. Meanwhile, the added HSO₄⁻ ions also disturbed the adjacent proton signals of -CH₂CH₂OH group to some extent. The Job's plot of VNP with HSO₄⁻ indicated the formation of ratio of 1:2 complex VNP:(HSO₄⁻)₂ (Supporting Information Fig. S5), which is con-

firmed by the geometry optimized structure according to the DFT. As depicted in Supporting Information Figure S6, the complex exists three intermolecular hydrogen bonds involving two hydrogen sulfate anions, one between the oxygen of the HSO₄⁻ and the hydrogen (-OH) of VNP, another between the hydrogen of the HSO₄⁻ and the nitrogen of imine moiety in VNP, and a third between the hydrogen of another HSO₄⁻ and the oxygen of VNP. In this way, VNP bonds hydrogen sulfate strongly but does not display detectable affinity for other anions lacking of sufficient hydrogen-bonding ability.

On the basis of the above observations, we assume that the "turn-on" fluorescence mechanism of PVNP or VNP sensors may be related to the intramolecular charge transfer (ICT).¹⁵ The modulation in the electron-donating ability of the imine groups directly influences the ICT effect. In the host-guest recognition, the hydrogen bond formation between imine moieties and HSO₄⁻ results in a significant decrease in the charge density on the nitrogen, with associated enhancing in the push-pull effect of the ICT transition.

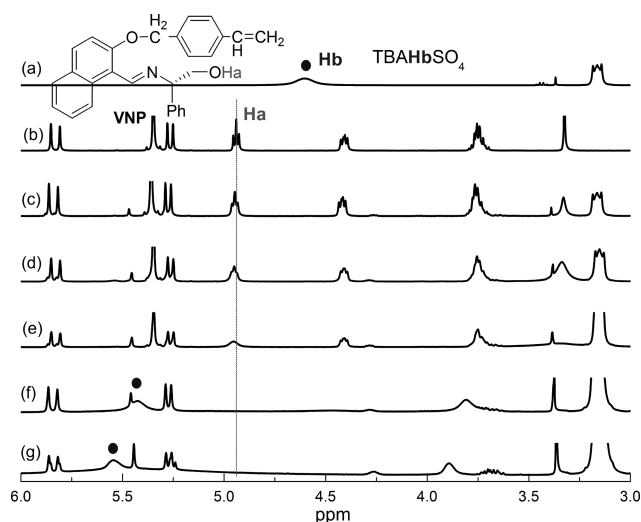


FIGURE 5 ¹H NMR of TBA⁺HSO₄⁻ (a), ¹H NMR of VNP in DMSO-d₆ in the absence (b) and presence of 0.25 (c) 0.5 (d) 1.0 (e) 2.0 (f) 5.0 equivalent (g) of TBA⁺HSO₄⁻.

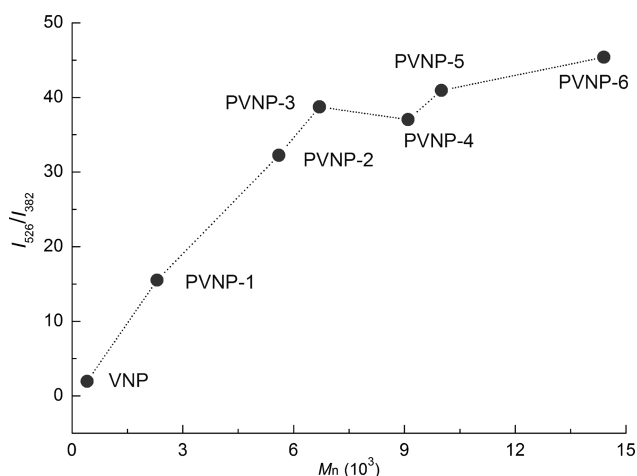


FIGURE 6 Plot of I_{526}/I_{382} of PVNPs (1.5×10^{-4} mol L⁻¹) as a function of M_n upon addition of 5 equiv. of HSO₄⁻ in THF solution.

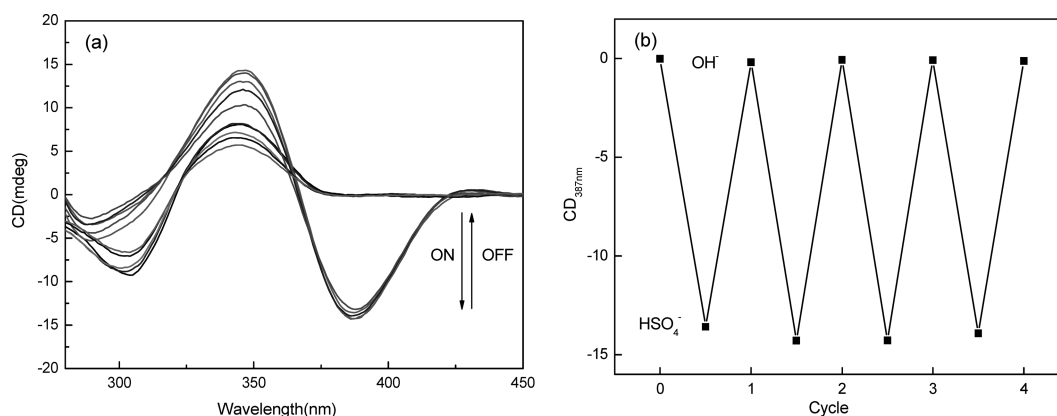


FIGURE 7 (a) CD spectra changes of PVNP-3 in THF solution (1.5×10^{-4} mol L $^{-1}$) upon alternate addition of HSO $_4^-$ (5 equiv.) and OH $^-$ (0.3 equiv.); (b) the corresponding reversible and reproducible chiroptical switch with “on” and “off” states at 387 nm.

Influence of Molecular Weight of PVNP on its Anion-Sensing Ability

Reportedly, the sensing ability of polymer-based receptors is frequently dependent on their molecular weights.^{15(d)} However, for a polymeric sensory system it is difficult to obtain the binding constant to describe its recognition ability like the small molecule receptors.¹⁶ With this in mind, we employed the relative emission intensity (I_{526}/I_{382}) to evaluate the sensing capacity of the present polymers with different molecular weights. The relationship between the I_{526}/I_{382} and number-average molecular masses (M_n) of PVNPs is plotted in Figure 6. As expected, PVNPs having larger molecular weight exhibited a stronger sensing capacity, which may be attributed to the cooperative effect of chromophores connected to the polymer main chain.^{6,17} Nevertheless, the enhancing trend slows down for the polymers having larger molecular weight than that of PVNP-3.

Circular Dichroism and Fluorescence Switching of PVNP Sensor

As shown in Figure 7, the HSO $_4^-$ -induced CD signal at 387 nm can be totally reversed with addition of base and eventually recovered the initial state, leading to a polymer-based chiroptical switch with two distinguished “on” and “off” states. Upon alternate addition of HSO $_4^-$ and base, the chiroptical signal reversibly changes and this cycle can be repeated five times without a distinct decay in the intensity. CD signals remained consistent after many acid–base reaction cycles, proving that robust reversibility was established. As a chemosensor, this reproducibility is significant in terms of practical applications.^{16(a)} Similarly, a reversible fluorescence switching process can also be created based on the modulation of fluorescence intensity of PVNP at 526 nm via control of ICT. However, in this case the signal intensity gradually became weaker with increasing the cycle times (Supporting Information Fig. S7).

CONCLUSIONS

A novel chiral polymer-based fluorescent receptor has been synthesized. It demonstrated the high selectivity to HSO $_4^-$ over other anions including F $^-$, Cl $^-$, Br $^-$, H $_2$ PO $_4^-$, CH $_3$ CO $_2^-$,

and NO $_3^-$ in absorption, fluorescence, and CD response in THF solution. One distinguishing feature of the present multi-channel sensing system is the specific discrimination of HSO $_4^-$ in “turn-on” fashion, making it very useful in several applications, such as HSO $_4^-$ detection in physiological treatment. Such polymeric materials might also be expected to find potential use in nuclear waste remediation applications requiring the selective removal of hydrogen sulfate from nitrate-rich waste mixture. Moreover, highly reversible and drastic changes in CD can be achieved by cyclical additions of acid and base, which enables the polymers to function as ON/OFF chiroptical molecular switches. The main drawback of this polymer sensor is that it was applicable only for organic systems. However, we have found that the incorporation of VNP in the polymer of 2-hydroxyethyl methacrylate matrices is one of very effective methods, which providing an improved sensory material being capable of detecting HSO $_4^-$ ion in aqueous media. The related study is currently being carried out and will be reported in due course.

ACKNOWLEDGMENTS

The authors are indebted the financial support by the National Natural Science Foundation of China (Grant No. 21074107).

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