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A new polymerizable fluorescent PET chemosensor of fluoride (F^-) based on naphthalimide–thiourea dye

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ABSTRACT

A novel N-allyl-4-amino-substituted 1,8-naphthalimide dye, containing thiourea functional group with intense yellow-green fluorescence was successfully synthesized. Copolymerization was done with styrene. The photophysical characteristics of dye and its copolymer in solution and solid film were investigated in the presence of halide ions. The results reveal that the fluorescence emissions of the monomer dye and also its polymer were 'switched off' in the presence of fluoride ions. The dye showed spectral shifts and intensity changes in the presence of more fluoride ions which lead to detect certain fluoride concentrations of 10–150 mM at visible wavelengths. By adding the fluoride ions, green-yellow to purple color changes occurs and the green fluorescence emission quenches, all of which easily observed by naked eyes. These phenomena are essential for producing a dual responsive chemosensor for fluoride ions. The polymeric sensor, in the film state exhibited a fast response to the fluoride ions.

1. Introduction

To date, many hundreds of naphthalimide derivatives have been synthesized and found wide applications as fluorescent sensors. Because of the easily modified N-head group and the 4-substituent and their well-studied emission properties, 1,8-naphthalimides have found applications in many different areas of physical and biomedical studies [1]. In recent years, more attention has been paid to the design, synthesis and applications of novel fluorescent polymer materials [2,3]. It has been shown that photoinduced electron transfer (PET) proceeding in the 1,8-naphthalimide also takes place in the solid polymer films of its copolymer with some conventional commercial monomers [4,5]. Hence, these functionalized copolymers can also act as sensors for transition metal ions or protons [6–9]. Considerable efforts have been made to design chemosensors for anions. The reason for this huge interest is the importance of detection and quantification of anions in disciplines such as biology and environmental science. Among the interests in biologically functional anions, fluoride is of particular importance owing to its established role in dental care and treatment of osteoporosis. As the smallest and the most electronegative atom, fluoride has unique chemical properties and can form the strongest hydrogen-bond interaction with hydrogen-bond donors. The majority of the reported fluoride sensors are based on colorimetric changes or fluorescent quenching [10].

The most important advantage of functionalized copolymer as a sensor is firmly bonded to the main chain which eliminates any migrations of chromoionophors from the matrix. Copolymers of 1,8-naphthalimide with vinyl monomers have been obtained using free radical mass polymerization [11], cation solution polymerization [12] and condensation polymerization [13]. To the best of our knowledge no report is available on polymerizable base sensor for F^- ions. The chemosensors employ the photoinduced electron transfer process that is quenched upon cation complexation or anion bonding and the fluorescence is switched on, i.e. this is an 'off–on' sensor type. If the complexation with the receptor unit is somehow perturbed, the interaction can take place at another chelating site and may result in fluorescence quenching, i.e. the sensor is of an 'on–off' type [14].

In this paper, the design and synthesis of new polymerizable 1,8-naphthalimide dye containing phenyl thiourea functional group was reported. The ability of dye to copolymerize with vinyl monomers of styrene was examined by free radical copolymerization. The obtained dye and copolymer were characterized by FTIR, ^{1}H NMR, ^{13}C NMR, elemental analysis, DSC, GPC, UV–visible and fluorescence spectroscopic techniques. The photophysical characteristics of synthesized dye in various solvents and a transparent copolymer in solid film were recorded. The absorption and fluorescent spectra of DMF solution of the dye and the transparent

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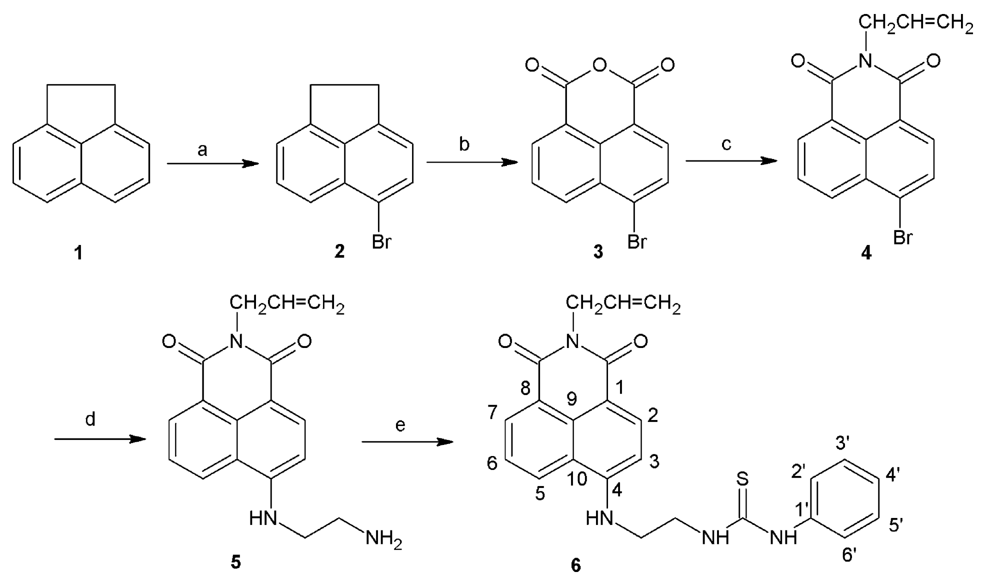


Scheme 1. Synthesis of dye: (a) NBS, DMF, room temperature, 75%; (b) $Na_2Cr_2O_7$, AcOH, reflux 5 h, 80%; (c) allylamine, EtOH, reflux 4 h, 92%; (d) ethylenediamine, DMF, reflux 5 h, 60.2%; (e) isothiocyanate, $CHCl_3$, 75%.

copolymer in solid film were investigated in the presence of halide ions.

2. Experimental

2.1. Materials

All solvents were of analytical grade. Acenaphthene, allyamine, ethylenediamine, phenyl isothiocyanate were purchased from Merck Chemical Co. and used as received. After purifying by distillation under vacuum the resulting styrene (St) was used. Dibenzoyl peroxide (DBP) was also used as the initiator for free radical copolymerization.

2.2. Analysis

UV–visible spectrophotometric measurements of the dye and styrene copolymer (St-co-dye) in DMF solution were performed on a CECIL CE9200 spectrophotometer. The fluorescence spectral of the dye, the copolymer in DMF solution and as a thin film, was measured on an Osean optic usb2000flg spectrophotometer. Fluorescence quantum yield was determined based on the absorption and fluorescence spectra, using fluorescein as reference ($\Phi_{st} = 0.95$) [14]. For all the absorption and fluorescent measurements, the dye concentration in DMF was 5×10^{-5} mol l^{-1}. The concentration of polymer in solution for all measurements was 5 g L^{-1}. A thin polymeric film, used for the fluorescent investigations, was obtained from depositing a 10% solution of copolymer in chloroform on a glass surface. The thickness of the copolymer film was 35 μm. FTIR spectra were recorded on a SPECTRUM ONE spectrometer using KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded with Brucker DRX AVANCE NMR spectrophotometer at 500 MHz and 125 MHz in DMSO, respectively. Molecular weights and polydispersity index of synthesized polymer were determined by Gel Permeation Chromatography (GPC) with a Atilent 1100 RI (reflectometer index) PLGell 10 μm, 300 mm (500 A, l0^3 A, 10 A in a series) relative to polystyrene standards in chloroform solution. Differential scanning calorimetric (DSC) and glass transition temperatures (T_g) of the copolymer was performed using Perkin-Elmer-pyris 6 DSC under the nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

2.3. Dye synthesis

2.3.1. The intermediate synthesis

Synthesis of the aforementioned polymerizable dye **6** is shown in Scheme 1. The intermediate, compound **3**, was synthesized from acenaphthene, according to the literature [15,16]. Compound **4** was prepared at 92% yield by the reaction of **3** with allylamine and it was subsequently converted into compound **5** by refluxing the solution of ethylenediamine and **4** in DMF [5].

2.3.2. Synthesis of 1-(2-{[1,3-dioxo-2-(prop-2-en-1-yl)-2, 3-dihydro-1H-benzo [de]isoquinolin-6yl] amino} ethyl)-3-phenylurea (6)

This dye was synthesized by treating **5** (0.27 mmol) with phenyl isothiocyanate (0.27 mmol) in chloroform and stirring the reaction mixture at room temperature for 5 days under nitrogen. The precipitate was collected by vacuum filtration and washed off with chloroform to obtain the desired product as a yellow-orange solid (65%) after recrystalization in ethanol [17,18]. mp. 224.22 °C. ^1H NMR (500 MHz, DMSO-d_6): 9.69 (1H, s, PhNH), 8.69 (1H, d, $J = 8.3$ Hz, naphthalimide, H-5), 8.43 (1H, d, $J = 7.1$ Hz, naphthalimide, H-7), 8.25 (1H, d, $J = 8.5$ Hz, naphthalimide, H-2), 7.94 (1H, b s, NHCS), 7.90 (1H, b s, NH.), 7.70 (1H, t, $J = 7.5$ Hz, naphthalimide, H-6), 7.12–7.30 (5H, C_6H_5), 6.96 (1H, d, $J = 8.5$ Hz, naphthalimide, H-3), 5.9 (1H, m, CH=), 5.07 (2H, =CH_2), 4.61 (2H, d, $J = 3.9$ Hz, N—CH_2), 3.85 (2H, CH_2), 3.61 (2H, CH_2). ^{13}C NMR (125 MHz, DMSO-d_6): 181.4 (C=S), 163.4 (C=O), 163.0 (C=O), 152.0 (naphthalimide, C-4), 135.1 (benzene, C-1), 134.1 (naphthalimide, C-2,7), 131.6 (CH=), 129.6 (benzene, C-3′,5′), 129.5 (benzene, C-4′), 125.4 (benzene, C-2′), 125.2 (benzene, C-6′), 124.4 (naphthalimide, C-9), 122.6 (naphthalimide, C-8), 121.1 (naphthalimide, C-10), 116.8 (=CH2), 104.9 (naphthalimide, C-3), 43.0, 42.1 (CH2 aliphatic); FTIR (KBr): ν 3357, 3234.2 cm^{-1} (N—H str. three secondary amine), 3179 cm^{-1} (C—H str. aromatic), 2928 cm^{-1} (C—H str. aliphatic), 1684 cm^{-1} (C=C str. allyl), 1669, 1643 cm^{-1} (C=O str. carbonyl), 1586 cm^{-1} (C=C str. aromatic), 1242 cm^{-1} (C=S str.). Anal. Calcd (%) for $C_{24}H_{22}N_4O_2S$

(MW 430.52): C, 66.95; H, 5.15; N, 13.01; found: C, 67.02; H, 5.5; N, 12.5.

2.4. Copolymerization

Free radical copolymerization of styrene with the produced dye was carried out in bulk [19–23]. The polymerization in styrene was carried out in an ampoule flushed with pure dry nitrogen, in the presence of 0.1 wt.% of dye in styrene and 0.5 wt.% of DBP within the monomer mixture. The ampoule was sealed and heated at 80 °C for 24 h. The obtained transparent colored polymers were dissolved in chloroform and precipitated in ethanol four times until the filtrate became colorless. In the last step the polymer was purified and desiccated under vacuum at 40 °C to reach a constant weight.

Poly(St-co-dye); yield: 55%, T_g: 83.29 °C, FTIR (KBr): ν 3451 cm^{-1} (N—H str. secondary amine), 3067, 3034 cm^{-1} (C—H str. aromatic), 2921 cm^{-1} (C—H str. aliphatic), 1614, 1634 cm^{-1} (C═O str. carbonyl), 1604, 1483 cm^{-1} (C═C str. aromatic), 1018 cm^{-1} (C—N str. amine).

3. Results and discussion

3.1. Synthesis and characterization of dye

The synthesis of the desired dye is shown in Scheme 1. The dye made from readily available acenaphthene as a starting material. The precursor was **6**, made in four steps at 60% yield form 4-bromo-1,8-naphthalic anhydride **3**; then reacted with allylamine in ethanol and nucleophilic displacement was done using an excess of ethylenediamine (neat), followed by recrystallization in ethanol. Consequently phenyl isothiocyanate reacted with 4-(2-aminoethylamino)-1,8-naphthalimide **5** at room temperature in dry $CHCl_3$ to give the dye at 65% yield.

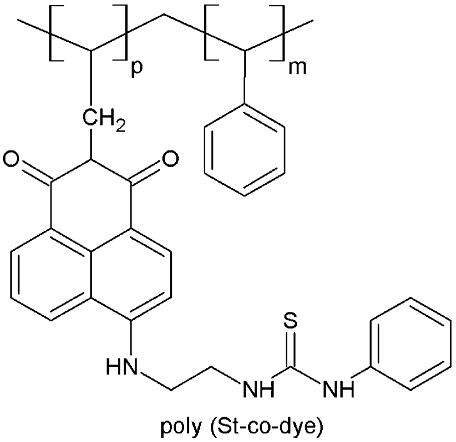
The dye was characterized by FTIR, ^{1}H NMR, ^{13}C NMR, elemental analysis and UV–visible spectroscopy. The results recorded by FTIR spectra of the dye shows the strong imid-groups vibration about 1600 cm^{-1}; the vibration of allyl-group and amino-groups appeared at around 1680–1690 cm^{-1} and 3100–3300 cm^{-1},respectively. The ^{1}H NMR spectra in DMSO-d6 of the dye display the existence of hydrogen around naphthalimide and phenyl rings, allyl group and amino-hydrogen, as a result of nucleophilic displacement. The dye showed the presence of two thiourea protons at 9.69 ppm, whereas the amino proton appeared as a broad singlet peak at 7.94 ppm.

3.2. Polymerization investigations

Polystyrene is a widely used polymer that attributes to many applications. Experiments for the copolymerization of styrene with dye was carried out in bulk with 0.1 wt.% of dye and 0.5 wt.% DBP, according to a procedure described elsewhere [19–23]. After the copolymerization of styrene with dye, a solid and transparent yellow polymer with an intense yellow-green fluorescence was obtained. The polymer was purified after successive and selective dissolving and precipitating with properly chosen solvents of chloroform and ethanol. The colored copolymer was isolated from ethanol .It is a good solvent for the monomer dye but not for its polymer. The copolymer's retained color and fluorescence, indicates that the compound was chemically bonded to the polymer chain (Scheme 2).

3.2.1. Molecular weight estimation

The molecular weight characteristics of the poly(St-co-dye) have been determined using GPC, listed in Table 1. The molecular weights (M_w and M_n) and the molecular weight distribution, M_w/M_n, confirm the formation of a high molecular weight polymer.



Scheme 2. Schematic presentation of poly(St-co-dye).

Table 1
Results of polymerization and characterization.

Polymer	$M_n \times 10^{-5}$ (g/mol)	$M_w \times 10^{-5}$ (g/mol)	M_w/M_n
poly(St-co-dye)	0.97684	3.3461	3.42

M_n, number average molecular weight; M_w, weight average molecular weight.

3.2.2. Characterization of the polymer produced

The difference between dye and its copolymer was determined by FTIR spectroscopy. FT-IR spectra of poly(St-co-dye), monomer dye and pure styrene are shown in Fig. 1. Because of the low percentage of dye in the polymer (0.1 wt.%), complete overlapping of the spectral bands was observed. Comparison between the spectra (a) and (b) shows a considerable difference in the spectral range of 720–790 cm^{-1}, 1600–1700 cm^{-1} and 3300–3500 cm^{-1}. The C—H out-of-plane bending vibrations of the dye are observed in spectrum (c) at 772 and 730 cm^{-1}. In spectrum (a) the rocking vibrations $(CH_2)_n$ of pure styrene appear as doublet peaks in the solid state at 697 and 766 cm^{-1}. Spectrum (b) indicates the overlapping of these two types of vibration in the range studied. The stretching vibration of C═C of the dye is seen at 1684 cm^{-1}. Stretching vibration of C═C bond of pure styrene is observed at 1683 cm^{-1}.

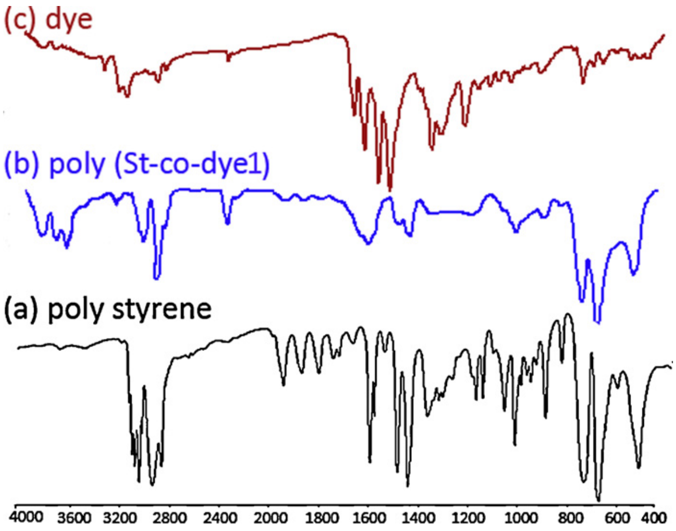


Fig. 1. FT-IR spectra of (a) pure styrene, (b) poly(St-co-dye) and (c) dye.

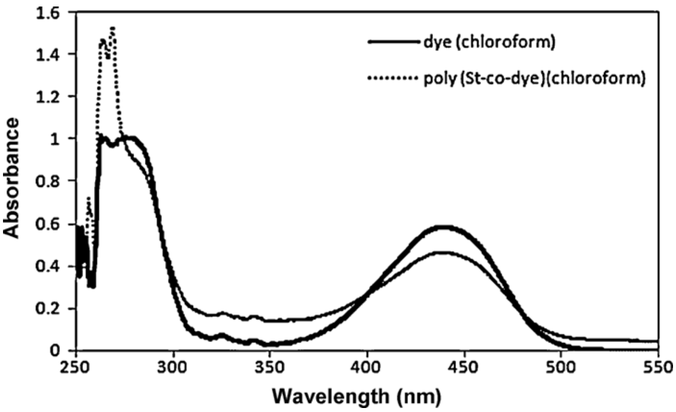


Fig. 2. UV–vis spectra of dye and colored poly(St-co-dye) in chloroform solution.

Spectrum (b) indicates that these two types of vibrations disappear in the studied range. Also the bands at 3357 cm^{-1} and 3451 cm^{-1} are related to the stretching vibration of N—H in the dye and the poly(St-co-dye). Compared with pure styrene, characteristic peaks at 3357 cm^{-1} and 3451 cm^{-1} of N—H in pure styrene disappeared.

3.2.3. Providing an evidence for a chemical bond between copolymer and dye

The presence of a covalent bond between the monomer dye units and the main polymer chain has been proved by UV–visible, fluorescence spectroscopy and by Gel Permeation Chromatography (GPC) [24]. The amount of dye incorporated into the polymer molecules determined using UV–visible spectroscopy. UV–Visible absorption spectra of the precipitated polymer in chloroform solution were compared to its monomer dye. Likewise, dye (1 g) and colored polymer (1 g) were dissolved in chloroform (25 mL). UV–vis spectra were taken and depending on the relation of the absorption of the colored polymer to that of its dye, the percent content of the covalently bound was calculated. Fig. 2 demonstrates the UV–visible spectra of dye and colored poly(St-co-dye). In these spectra, no change in λ_{max} was registered. This was an indication that there were no changes in the basic chromophore dye either during the polymerization or as a result of its bonding to the polymer chain. For this reason the free chromophore and the copolymer with styrene possesses identical λ_{max}. This makes it possible to determine the percent content of the covalently bound chromophore [24]. The experimental data concerning quantity of the dye, chemically bound to the polymer, is 75%. It can be clearly seen over 75% of the initial dye that to the polymer chain are attached which means that they are fully consumed and incorporated into the styrene chain during the polymerization process.

3.3. Spectroscopic properties

The basic spectral characteristics of 1,8-naphthalimides depend on the polarization of naphthalimide molecules, due to the electron donor–acceptor interaction occurring between the substituent at position C-4 and the carbonyl groups from the imide moiety of the chromophoric system [25]. This interaction strongly depends on the medium, especially, on the polarity of organic solvents. Organic solvents with different dielectric constants were used to investigate this effect on the photophysical properties of the dye.

The absorption spectra of the dye demonstrated a structured naphthalimide band with two peaks at 281 nm and a broad one at 440 nm. Table 2 presents the spectral characteristics of the monomeric 1,8-naphthalimide dye and its polymer in DMF solution and as a thin film; the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient ($\log \varepsilon$), Stokes shift (υ_A–υ_B), oscillator strength (f), quantum yield of fluorescence (Φ_F) and energy yield of fluorescence (E_F). Fig. 3 shows the excitation and fluorescence spectra of the dye in DMF solutions at 10^{-5} M and solid poly(St-co-dye) in DMF and as a thin film. The dye exhibits a yellow-green color with absorption maxima at $\lambda_A = 440$ nm. The long wavelength band for the dye has an extinction coefficient of 18,458 $l\,mol^{-1}\,cm^{-1}$. The dyes' molar absorption (ε) in the longest wavelength band of the absorption spectra is higher than 10,000 $l\,mol^{-1}\,cm^{-1}$ (Table 2), indicating that this is a charge transfer (CT) band, due to ($\pi \to \pi^*$) character of the $S_0 \to S_1$ transition [26]. In DMF solution, the compound under study displayed yellow-green fluorescence due to the charge transfer in the 1,8-naphthalimide moieties from the electron donating group at C-4 position to the carbonyl groups. The dye emission was observed in the visible region with well-pronounced maxima (λ_F) at 525 nm.

Viewing the application of the poly(St-co-dye) as a heterogeneous sensor, its spectral characteristics have been studied in DMF solution and the solid state in the form of a thin polymeric film (35 μm) (Fig. 3). The poly(St-co-dye) has an absorption maximum at 438 and 376 nm and emits fluorescence at 523 and 505 nm (Table 2). The absorption spectra have broad bands in the visible region. The copolymer is yellow and shows intense green fluorescence in DMF and solid state. The maxima in thin polymeric film are hypsochromically shifted in comparison to that of the dye taken in DMF solution. The shift is probably caused by the firmly fixed chromophore naphthalimide system in the solid state. Thus, there is a minimal possibility for conformation changes [27].

As seen in Fig. 3, fluorescence curve is approximately a specular image of the absorption one in DMF solution. This indicates preservation of the fluorophore molecular structure in the exited state. The overlap between the absorption and the fluorescence bands is small and an aggregation effect at the concentration of 10^{-5} $mol\,l^{-1}$ has not been observed [24].

An important characteristic of dyes is the oscillator strength (f) which can be calculated using Eq. (1), where $\Delta\upsilon_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2\,\varepsilon_{max}$ [28].

$$f = 4.32 \times 10^{-9}\, \Delta\nu_{1/2}\varepsilon_{max} \qquad (1)$$

The values obtained for the dye and its polymer 0.304 and 0.341 in DMF and the poly(St-co-dye), in thin film, is 0.166.

The Stokes shift values are 3663 and 4283 cm^{-1} for the dye and its polymer in DMF, and is 6793 cm^{-1} for the poly(St-co-dye) in solid thin film. The value of Stokes shift for poly(St-co-dye) is higher than its monomer. This means that the conformation change in the polymer macromolecules is more pronounced, owing to the presence of styrene units and their influence on the chromophoric 1,8-naphthalimide structure [25,29].

The fluorescence quantum yield (Φ_F) was determined on the basis of the absorption and fluorescence spectra of the dye using

Table 2
Photophysical charactristic of dye in DMF solution at 10^{-5} M and poly(St-co-dye) in DMF and as a thin film.

Compounds	λ_A (nm)	λ_F (nm)	$\log \varepsilon$ ($l\,mol^{-1}\,cm^{-1}$)	υ_A–υ_B (cm^{-1})	$\Delta\upsilon_{1/2}$ (cm^{-1})	f	Φ_F	E_F[a]
Dye	440	525	4.26	3663	3813	0.304	0.365	0.306
Poly(St-co-dye) in DMF	438	523	–	3711	4283	0.341	–	–
Poly(St-co-dye) in thin film	376	505	–	6793	2090	0.166	–	–

[a] E_F, energy yield of fluorescence [32].

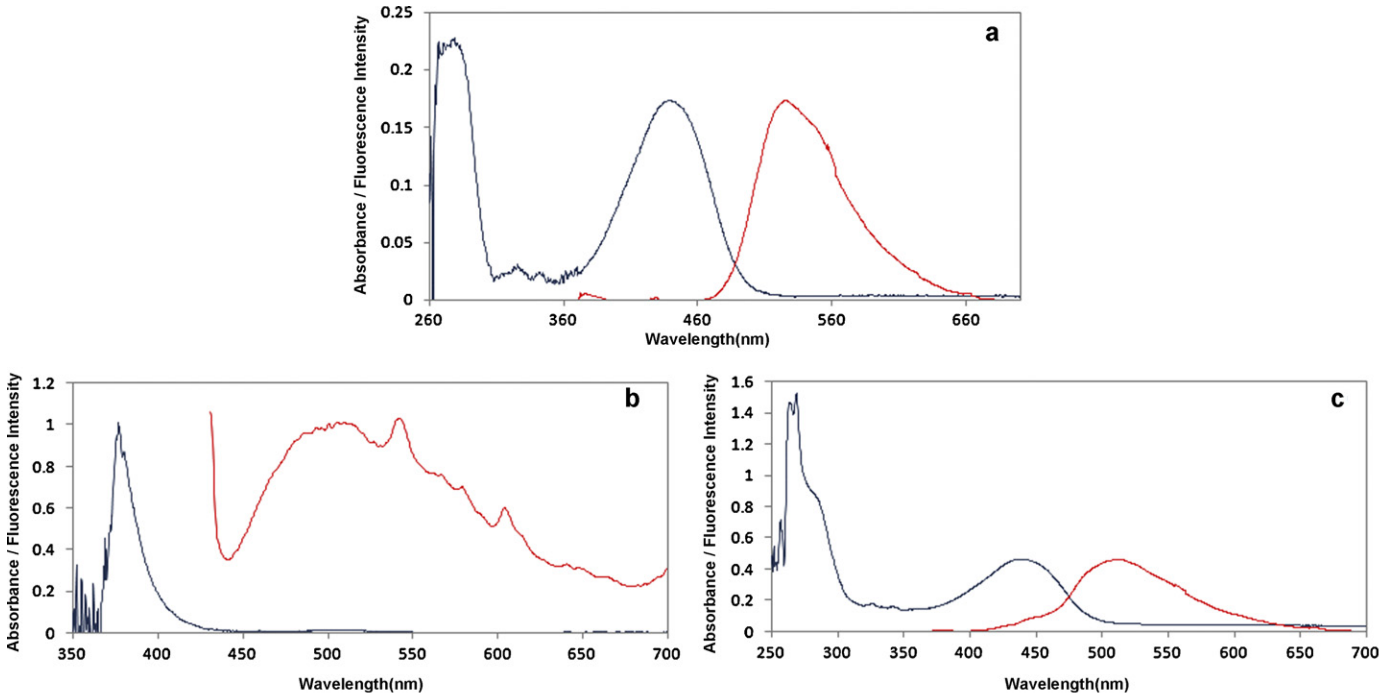


Fig. 3. Excitation (absorbance) and fluorescence emission spectra of (a): the dye in DMF solution; (b) poly(St-co-dye) as a thin film and (c) poly(St-co-dye) in DMF solution.

fluorescein as a reference $\Phi_F = 0.95$ [14,29–31]. The fluorescence quantum yield is determined on the basis of the absorption and fluorescence spectra of the dyes taken in DMF. As it can be seen from the data in Table 2, the 1,8-naphthalimide dye has quantum yield values of $\Phi_{st} = 0.365$ in DMF.

As seen from the data collected in Table 3 and the plot in Fig. 4 the solvent dielectric constant (ε) does not significantly influence the position of the absorption maxima, while in more polar solvents the fluorescence maxima are bathochromically shifted. As the dipole moment of the molecule is enhanced upon excitation due to electron density redistribution, the excited molecule is better stabilized in polar solvents because of the stronger interactions with the solvent dipoles. This effect causes the red shift in the fluorescence maxima [27]. For the calculated Stokes shift values one observes that in the less polar medium, the value of Stokes shift was lower than that obtained in the more polar medium (Table 3).

As seen from the data in Table 3, the monomer dye has quantum yield values between $\Phi_{st} = 0.532$ in carbon tetrachloride solution and $\Phi_{st} = 0.156$ in methanol solution. The results obtained could be explained by the formation of hydrogen bonding effect, photo-induced electron transfer (PET) processes in more polar solvents [33].

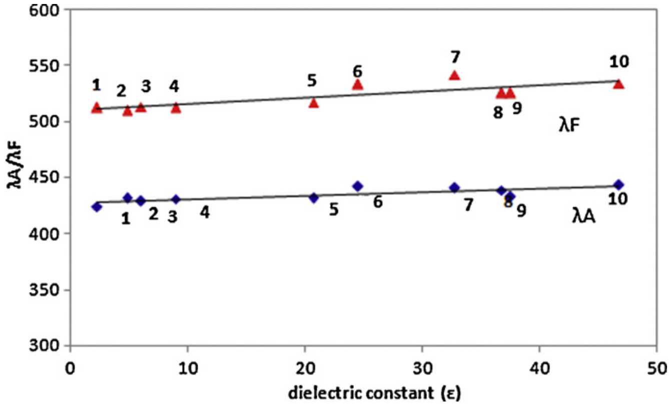


Fig. 4. Absorption and fluorescence maxima of the monomeric 1,8-naphthalimide dye as a function of the solvent polarity parameter ET (30): (1) carbon tetrachloride, (2) chloroform, (3) ethyl acetate, (4) dichloromethane, (5) acetone, (6) ethanol, (7) methanol, (8) DMF, (9) acetonitrile and (10) DMSO.

Also in all organic solvents under study, the monomeric 1,8-naphthalimide displayed yellow-green color and intense fluorescence. The dye has yellow-green color with absorption maxima at 423–443 nm and fluorescence emission maxima at 509–541 nm in all the organic solvents at room temperature.

3.4. *Photophysical characteristics of the dye in the presence of different halide ions*

The photophysical properties of the dye as a receptor in the presence of different halide ions (F^-, Cl^-, Br^- and I^-) were investigated in DMF solution in respect of its potential sensor application. Prior to the assessment, the sensor ability of the monomer bonded to a polystyrene chain was determined.

3.4.1. *Colorimetric investigations*

The interactions of the dye with various halide ions were first investigated by UV–visible titration spectra. Observable color changes took place in DMF solution. Upon addition of 15 equiv. of fluoride ions, the yellow-green solutions of the dye became yellow-orange in DMF. No color changes of the receptors in DMF were observed in the presence of chloride, bromide and iodide anions.

First the interactions of the dye with various halide ions were investigated by UV–vis titration spectra. The halide ions (F^-, Cl^-, Br^- and I^-) were added as tetrabutylammonium salts to 5×10^{-5} M solutions of the dye. Fig. 5 demonstrated the absorption spectral changes of the dye after addition of increasing amount of F^-.

The absorption spectrum of the dye shows four transitions in DMF. It has a strong absorption band centered at 438 nm ($\log \varepsilon = 4.261\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$) due to its ICT character and a second band at 280 nm ($n \to \pi^*$). Upon the addition of halide ions, only F^- gave rise to changes in these absorption bands but no detectable spectral changes were observed even in the presence of larger excess of hundred equivalents of the corresponding anions such as

Table 3
Photophysical properties of dye in organic solvents of different polarity.

Solvents	Dielectric constant (ε)	λ_A (nm)	λ_F (nm)	$\upsilon_A-\upsilon_F$ (cm^{-1})	Φ_F
Carbon tetrachloride	2.24	423.8	512.3	4076.2	0.532
Chloroform	4.81	431.6	509.4	3538.6	0.420
Ethyl acetate	6.02	428.9	513.0	3833.9	0.272
Dichloromethane	8.93	430.7	511.9	3682.9	0.479
Acetone	20.7	431.3	516.6	3828.4	0.391
Ethanol	24.5	441.5	533.5	3905.9	0.235
Methanol	32.7	440.3	541.5	4244.5	0.156
DMF	36.7	438.2	525.3	3783.9	0.363
Acetonitrile	37.5	432.2	524.9	4086.2	0.433
DMSO	46.7	443.3	533.9	3828.0	0.331

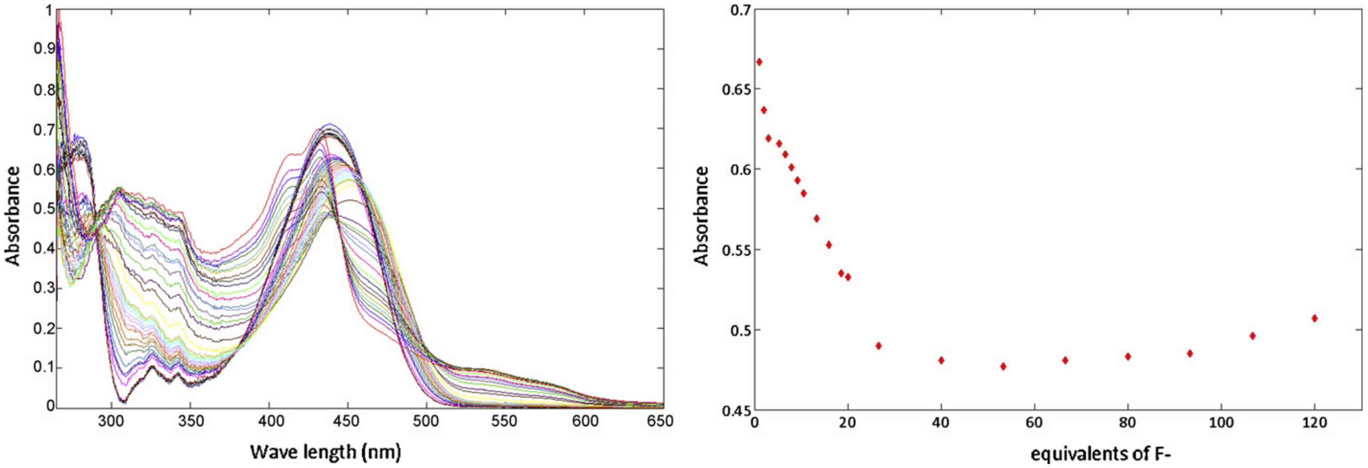


Fig. 5. The UV–vis titration spectra of dye (5×10^{-5} M in DMF) after addition of increasing amount of F$^-$. The right is the nonlinear curve fitting of absorbance at 438 nm as a function of equivalent of F$^-$.

Cl$^-$, Br$^-$ and I$^-$, which made it clear that the dye could sense F$^-$ over other halide ions. This observation could be attributed to the small size and higher electronegativity of the F$^-$ compared to the other halide ions. Upon titration of the dye with F$^-$, the absorptions at 438 and 280 nm were substantially reduced with the formation of new bands at 537 and 342 nm and concomitant formation of three isosbestic points at ca. 501, 380 and 288 nm. Although these isosbestic points were very clear at lower concentrations, at higher concentrations some broadenings was observed (possibly due to aggregation) [34]. The changes in the absorption spectra of the dye upon titrating with F$^-$, shown in Fig. 5, clearly demonstrate that by formation of a clear isobestic point at 501 nm, the ground state is somewhat affected upon recognition of the anion where the absorption was shifted to longer wavelengths. Furthermore, some changes were observed at shorter wavelengths. The concurrent changes of these absorption peaks implied that 4-amino NH of naphthalimide and thiourea N—H were synchronously involved in F$^-$ binding and the deprotonation of the amino moiety by F$^-$ rather than hydrogen bonds [35]. This causes a significant increase in the charge density on the amino nitrogen with associated enhancement in the push–pull character of the ICT transition, bathochromically shifting the absorption. As demonstrated above, the absorption at 438 nm was almost ‘switched off’ upon gradual addition of F$^-$ and the 537 nm absorption was ‘switched on’ [36].

Addition of some protic solvent (such as methanol) to the titrated solution could restore the color of the solution to greenish yellow, indicating that the protic solvent destroyed the complexation between dye and F$^-$. Confirming that the interaction between dye and F$^-$ was hydrogen bond in essence. Excess of F$^-$ often caused the deprotonation of 4-amino NH of naphthalimide fragment, leading to drastic color alteration and great spectral changes. When 80 equiv. of F$^-$ was added to the dye, an orange red solution was seen along with the appearance of new absorption peaks at 342 nm and 537 nm, as shown in Figs. 5 and 6.

The recognition behavior of the dye toward halide (F$^-$, Cl$^-$, Br$^-$ and I$^-$) ions was also investigated by fluorescence spectrophotometric methods in DMF solution. In contrast to the changes in the ground state (UV–visible spectra), the fluorescence of the dye was dramatically affected upon titration of F$^-$. The halide ions (F$^-$, Cl$^-$, Br$^-$ and I$^-$) were added as tetrabutylammonium salts to 5×10^{-5} M solution of the dye. A dramatic quenching of fluorescence intensity in the presence of the guest halide ions was only observed in the case of F$^-$. The influence of the halide ions on fluorescence quenching is presented in Fig. 7. Upon addition of F$^-$, the emission of the

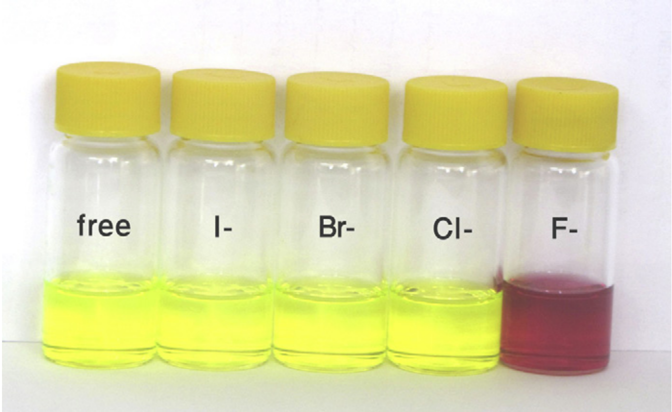


Fig. 6. The color change of dye 1 (5.0×10^{-5} M in DMF) after addition of 80 equiv. of halide ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

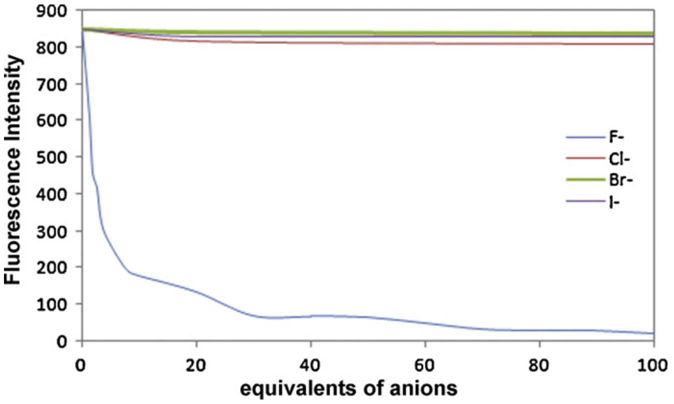


Fig. 7. Changes in the fluorescence emission of dye in the presence of different halide ions.

dye was almost fully quenched, with no noticeable changes in λ_{max} for the additions of 0–40 equiv. of the F$^-$, as shown in Fig. 8.

The mechanism for this quenching is via PET, which takes place from the thiourea receptor to the excited state of the naphthalimide fluorophore upon anion recognition. Unlike many PET sensors for cations, the fluorescence of the dye is 'switched off' rather than 'switched on' upon ion recognition. We propose that this quenching process is due to the following; prior to the recognition process, the excited state of the fluorophore is not, or is only to a minor extent, quenched by electron transfer from the receptor to the fluorophore. However, after adding the F$^-$ the formation of the anion-receptor hydrogen bonding complex occurred and the reduction potential of the receptor is increased, making the electron transfer more feasible. This subsequently gives rise to enhanced fluorescence quenching. This is clearly demonstrated in Fig. 8, showing the additions of F$^-$ to the dye in DMF. Here the fluorescence emission of the dye is effectively quenched or completely 'switched off' after the addition of 40 equivalents of F$^-$. The addition of methanol or water to this solution 're-switched on' the emission, demonstrating that the process was fully reversible, i.e. the hydrogen bonding interactions were broken [35].

3.5. *Photophysical characteristics of poly(St-co-dye) in the presence of different halide ions*

To obtain a heterogeneous fluorescent sensor, the effects of different halide ions on the fluorescent intensity of a poly(St-co-dye), its thin film (35 μm thick), was investigated. The solid polymer was placed in an aqueous solution comprising tetrabutylammonium salts of halides at different concentrations. The effect of the halide ions on the fluorescence of poly(St-co-dye) is signaled by the fluorescence intensity. The rigid polymer structure of the poly(St-co-dye) film perturbs the diffusion of halide ions and their contact with the fluorophore receptors. Therefore poly(St-co-dye) film needs a longer time to exhibit its sensor abilities than homogeneous sensors do. Its fluorescence emission in the presence of halide ions has been investigated for a period of 7 min. As seen from Fig. 9, the poly(St-co-dye) film reacts only to the presence of F$^-$. The

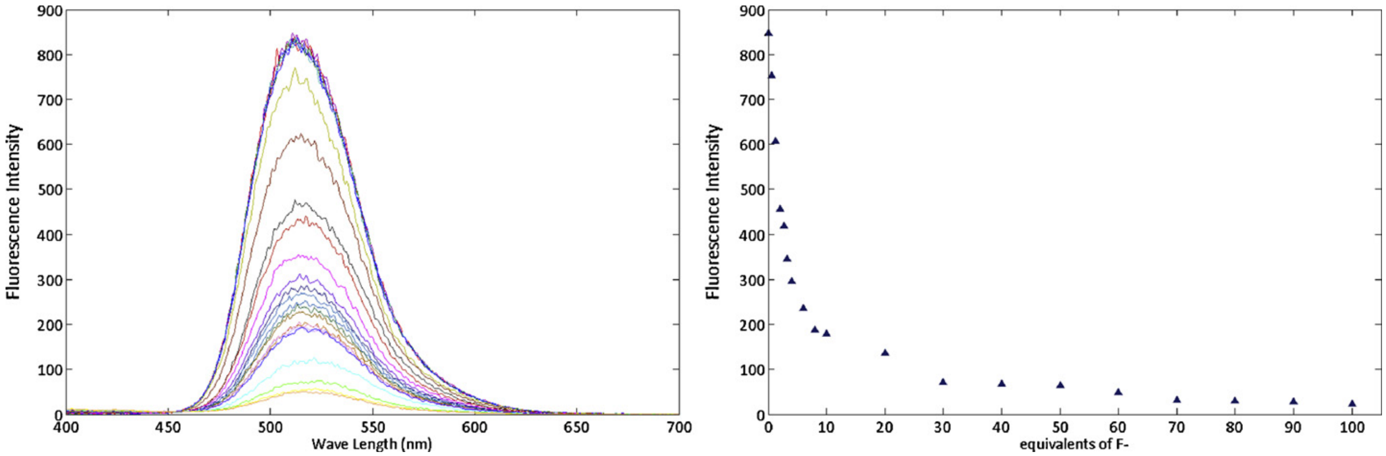


Fig. 8. Changes in the fluorescence emission spectrum of dye upon titration with F$^-$. The right panel shows the change in the fluorescence intensity as a function of the equivalents of F$^-$ ions added.

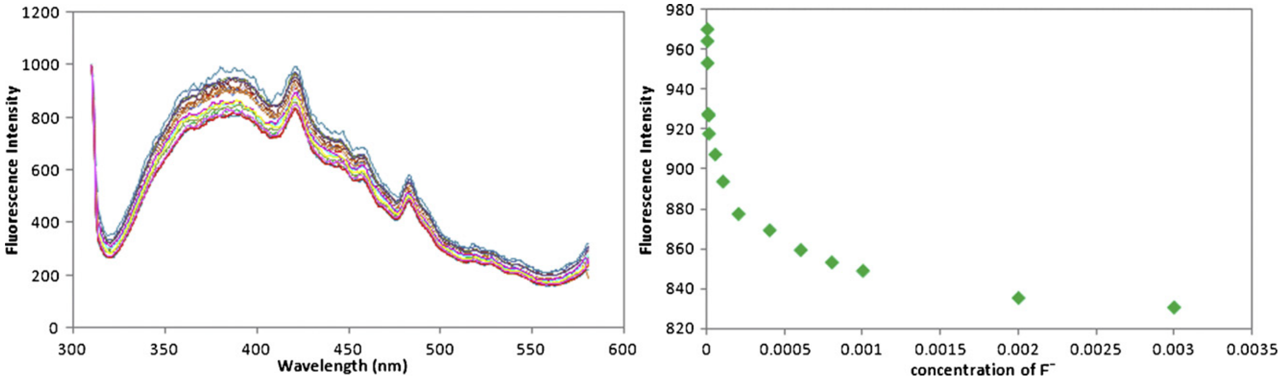


Fig. 9. Fluorescence spectra of poly(St-co-dye) taken in aqueous solution at different concentration of F$^-$. The right panel is the nonlinear curve fitting of fluorescence at 505 nm as a function of equivalent of F$^-$.

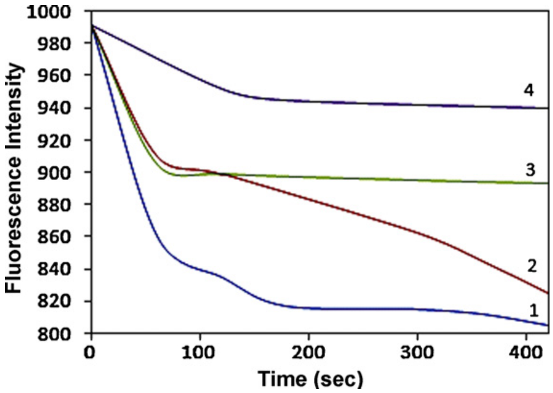


Fig. 10. Changes in the fluorescence emission of poly(St-co-dye) at different concentrations of F^- ions: 1 (1×10^{-3} mol l^{-1}); 2 (1×10^{-4} mol l^{-1}); 3 (1×10^{-5} mol l^{-1}) and 4 (1×10^{-6} mol l^{-1}).

addition of F^- leads to a decline in the fluorescence intensity. In the case of Cl^-, Br^- and I^- ions the effect on the fluorescence intensity is negligible while at the same concentration F^- ions quench ca. 25% of the fluorescence intensity.

Fig. 10 shows the changes in the fluorescence intensity of the poly(St-co-dye) for four different concentrations of F^-; the fluorescence quenching was 5% at 1×10^{-6} mol l^{-1}, 10% at 1×10^{-5} mol l^{-1}, 17% at 1×10^{-4} mol l^{-1} and 25% at 1×10^{-3} mol l^{-1}. These findings reveal the potential of the poly(St-co-dye) as an effective and selective heterogeneous sensor for detecting F^- in aqueous solutions.

The fact that F^- ions in aqueous solutions fail to produce a significant fluorescence quenching effect of the dye reveals that the poly(St-co-dye) film is a highly useful F^- selective sensor in aqueous solutions. On the other hand, the good functional properties, namely the mechanical stability of the poly(St-co-dye), the eliminated migration of the fluorophore from the polymer matrix give prospects for multiple and long usages for detecting F^- ions in water sources. The films should simply be cleansed from the trapped ions [33]. In contrast to the reversibly process of the dye in methanol or water, in the solid state the rigidity of the 1,8-naphthalimide fluorophore, after its bonding to the main polymer chain, the formation of the anion-receptor hydrogen bonding complex was strong and was not broken.

4. Conclusion

In this work, we described the synthesis and characterization of a new polymerizable fluorescent monomer based on N-allyl-1,8-naphthalimide containing thiourea functional group at a good yield. The photophysical characteristics of a polymerizable 1,8-naphthalimide dye in DMF solution and transparent copolymer in DMF and solid film were investigated. The absorption and fluorescent spectra of the DMF solution of the dye and the transparent copolymer in solid film were investigated in the presence of halide ions. The measurements of sensing behavior to various halide ions, that is F^-, Cl^-, Br^-, and I^-, reveal that the monomer and the polymer were fluorescent chemosensors for fluoride ion. The fluorescence emission of these sensors was 'switched off', with significant changes in the UV–visible spectra. According to the present investigations it can be assumed that the monomer 1,8-naphthalimide dye is suitable for obtaining fluorescent polymer sensors for F^-. Investigations on their sensor characteristics are the object of our future work.

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