Novel heterogeneous PET fluorescent sensors selective for transition metal ions or protons: polymers regularly labelled with naphthalimide

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4-(N,N-Dimethylaminoethylene)amino-N-allyl-1,8-naphthalimide has been synthesized as a new polymerizable dye in monomeric form, and can increase its fluorescence intensity in the presence of protons or metal cations. Two intensely yellow–green fluorescent co-polymers of the dye with methyl methacrylate (MMA) and styrene (ST) have been obtained. These polymeric fluorophores, which could be used as heterogeneous photoinduced electron transfer (PET) fluorescent sensors, show different fluorescence behaviour in the presence of protons and Cu^{2+} ions, depending on the structures of their main polymer chains. The fluorescence of poly(MMA–co-dye) is not sensitive towards H^+ ions, but it is to Cu^{2+} ions. That of poly(ST–co-dye) is sensitive to the presence of both H^+ and Cu^{2+} ions, the signal increasing and decreasing, respectively.

Introduction

Photoinduced electron transfer (PET) fluorescent sensors are of great interest and promise because of their various applications.[1] For most applications they are usually mixed with the target (*e.g.* metal ions or protons) in homogeneous liquid systems. In 1998, de Silva *et al.* designated the first heterogeneous fluorescent sensors with mixed fluorophores in polyvinylchloride matrix, they reported on the pH dependence of the fluorescence intensity of the heterogeneous sensors, in which plasticizers and additives were used to prevent the fluorescent dye from crystallizing inside the polymer.[2]

If the fluorophores are bonded *regularly* to the polymer molecules by *covalent* bonds, which generally do not crystallize in the polymer matrix, we speculate that the fluorophore will show stronger PET activity and produce strong changes in fluorescence upon binding with protons or transition metal ions. Moreover, it is known that the fluorophores covalently bound to the polymer molecules ensure that the fluorescence effect is resistant to physical influences.[3] In this case, the fluorophores do not sublime. They are resistant to wet treatment and solvents,[4] and can be used for the determination of ions in solution without contaminating the solution. The latter fact allows repeated usage of the co-polymers as sensors.

Fluorescent 1,8-naphthalimide derivatives find application in a variety of different areas,[5] and naphthalimide derivatives with high photostability are being investigated as polymerisable fluorophores.[3,6–9] In protonated water–ethanol solution, some 1,8-naphthalimide derivatives exhibit good fluorescence PET off–on switching and can be used as fluorescent sensors.[10,11] The fluorescence intensities of some naphthalimides are also sensitive to the presence of metal ions.[12–14]

In this paper, we report on the design and synthesis of new polymerizable 1,8-naphthalimide dye and its co-polymers with methyl methacrylate and styrene, as well as on its functional properties, with the prospect that it might act as a PET fluoroionophore.

Experimental

Materials

4-Nitro-N-allyl-1,8-naphthalic anhydride was synthesized according to the method described recently.[15] Commercial styrene (ST) and methyl methacrylate (MMA) were used after purification by distillation under reduced pressure. Dibenzoyl peroxide (DBP) (Fluka), recrystallized from chloroform and methanol, was used as the initiator for free radical co-polymerization. $Cu(NO_3)_2 \cdot 3H_2O$ was used for ionic experiments.

Synthesis of 4-(N,N-dimethylaminoethylene)amino-N-allyl-1,8-naphthalimide

4-Nitro-N-allyl-1,8-naphthalic anhydride was reacted in an equimolar ratio with N,N-dimethylethylenediamine (DMEA) in 60 ml N,N-dimethylformamide (DMF) for 24 h at room temperature. After that, 600 ml of water were added to the solution. The precipitate was filtered off, washed with water and then dried under vacuum at 40 °C. Monomeric 1,8-naphthalimide was obtained in 94% yield. M.p. 93–95 °C. FT-IR (KBr) v/cm^{-1}: 3456, 2940, 1700, 1662, 1567, 1457, 1373, 1342, 1236, 1000, 931, 779. ^{1}H-NMR (CDCl$_3$, 400 MHz, ppm): 2.49 (s, 6H, CH$_3$); 2.93 [s, 2H, CH_2N(CH$_3$)$_2$]; 3.51 (d, 2H, $J = 5.2$ Hz, NHCH_2CH$_2$); 4.79 (d, 2H, $J = 5.2$ Hz, NCH_2CH=); 5.27 (dd, 2H, $J = 9.6$, 16.0 Hz, =CH$_2$); 5.99 (m, 1H, –CH=); 6.65 (d, 1H, $J = 8.4$ Hz, ArH-2); 7.65 (t, 1H, $J = 8.4$ Hz, ArH-4); 8.36 (d, 1H, $J = 8.4$ Hz, ArH-1); 8.56 (d, 1H, $J = 8.4$ Hz, ArH-3); 8.59 (d, 1H, $J = 7.2$ Hz, ArH-5). ^{13}C-NMR (CDCl$_3$, 75 MHz, ppm): 40.1, 42.3, 45.0, 57.1, 96.3, 104.5, 110.4, 117.2, 120.7, 123.1, 124.9,

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129.0, 139.1, 131.5, 132.9, 134.8, 136.2, 139.4, 149.8, 150.5, 159.4, 164.1, 164.6. EI-MS m/z: 324 (M^+).

Copolymerization

Free radical co-polymerization of styrene and methyl methacrylate monomers with 4-(N,N-dimethylaminoethylene)-amino-N-allyl-1,8-naphthalimide was carried out in bulk:[16]

(a) Styrene monomer. 1 g Purified styrene, 0.01 g of the monomeric dye and 0.01 g DBP were mixed in an ampoule flushed with pure dry nitrogen. The ampoule was sealed and heated at 80 °C in a thermostat for 8 h.

(b) Methyl methacrylate monomer. 1 g Purified methyl methacrylate, 0.01 g of the monomeric dye and 0.01 g DBP were mixed in an ampoule flushed with pure dry nitrogen. The ampoule was sealed and heated at 70 °C in a thermostat for 10 h.

The transparent side-group co-polymers, which have an intense yellow–green fluorescence, were dissolved in dichloromethane and precipitated several times with methanol in order to remove unreacted monomer. The precipitated co-polymers were dried under vacuum at 40 °C to a constant weight.

Thin polymeric films (30 μm thickness) for all spectral investigations were obtained from 10% solutions of the respective co-polymers in dichloromethane.

Analysis

UV-vis spectrophotometric investigations of monomeric 4-(N,N-dimethylaminoethylene)amino-N-allyl-1,8-naphthalimide in dichloromethane and ethanol, and of the respective co-polymers in dichloromethane solution or as thin films were performed on a Hewlett-Packard 845X spectrophotometer. The fluorescence of the monomeric 1,8-naphthalimide dye (in dichloromethane and ethanol), and that of the co-polymers in dichloromethane solution and as thin films were measured on a PTI 700 spectrophotometer. For all absorption measurements, the dye concentration in the solutions was 10^{-5} mol L^{-1}. The fluorescent measurements were carried out with dye concentrations of 10^{-6} mol L^{-1}. The concentration of polymer in solution for all measurement was 5 g L^{-1}. The films of the new co-polymers were subjected to repeat experiments. The reproducibility of the results was 98%.

The percentage of covalently bound dye was determined by fluorescence spectroscopy from the difference in the fluorescence intensity of non-precipitated and precipitated co-polymers in dichloromethane solution.[16]

IR spectra were recorded on a Bruker IFS-113v spectrometer from KBr pellets (or discs) for the monomeric dye and directly from the thin polymeric films at a 2 cm^{-1} resolution.

The ^{1}H and ^{13}C-NMR spectra of the monomeric 1,8-naphthalimide were recorded on a Varian Zuova 400 spectrometer at 400 and 75 MHz, respectively. Deuteriochlorform and tetramethylsilane were used as the solvent and internal standard, respectively.

Thin layer chromatographic (TLC) analysis of the monomeric dye was followed on silica gel (Fluka F_{60} 254 20 × 20; 0.2 mm) using the solvent system n-heptane–acetone (1:1, v/v) as eluent.

The molecular weights of the co-polymers were determined on a GPC Water 244 apparatus equipped with combination of 100 and 1000 A, linear Ultrastyragel columns; the solvent was THF at a flow rate of 1.0 ml min^{-1} at 45 °C. Both differential refractive index and UV-vis absorption detectors ($\lambda_A = 420$ nm) were used. Polystyrene calibration was used for all molecular weight calculations.

Results and discussion

Synthesis of monomeric and polymeric fluorescent sensors

4-(N,N-Dimethylaminoethylene)amino-N-allyl-1,8-naphthalimide was obtained in good yield by nucleophilic substitution of 4-nitro-N-allyl-1,8-naphthalimide with N,N-dimethylethylenediamine in DMF (Scheme 1). In this case, the electron-accepting carbonyl group of the naphthalimide molecule favours the nucleophilic substitution reactions of the nitro group with aliphatic amines.[17]

The co-polymerization of methylmethacrilate or styrene with the monomeric 4-(N,N-dimethylaminoethylene)amino-N-allyl-1,8-naphthalimide was carried out in bulk. Transparent fluorescent co-polymers having an intense green fluorescence were obtained. The co-polymers are soluble in solvents commonly used for the dissolution of homopolymers. After precipitation three or four times in order to remove the unreacted monomer, the co-polymers retain their colour, which is an indication that the dye has been chemically bonded to the polymer chain.[3,6,9]

The molecular characteristics obtained by GPC of the co-polymers are listed in Table 1. The molecular weight and molecular weight distribution M_w/M_n confirm the formation of high molecular weight polymers: $M_w = 1.21 \times 10^5$ and $M_n = 0.64 \times 10^5$ for poly(ST–co-dye) and $M_w = 0.98 \times 10^5$ and $M_n = 0.57 \times 10^5$ for poly(MMA–co-dye). The double detection shows close values for the elution time in the both chromatograms, indicating the presence of co-polymers, which absorb at about 420 nm.

The amount of dye incorporated into the macromolecules was determined using fluorescence spectrophotometry as a more precise analytical method than the absorption method. The results show that 0.94 and 0.86 wt% for poly(MMA–co-
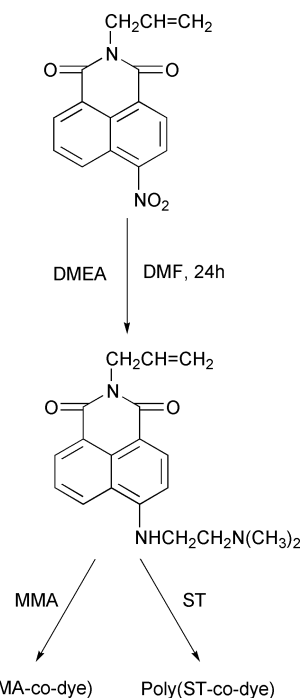
Scheme 1 Synthesis of monomeric and polymeric fluorescent sensors.

Table 1 Molecular characteristics of the co-polymers

	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n
Poly(MMA–co-dye)	0.98	0.57	1.72
Poly(ST–co-dye)	1.21	0.64	1.89

dye) and poly(ST–co-dye), respectively, of the dye is bonded to the polymer chain.

Functional properties of the monomeric and polymeric fluorophores

The basic spectral characteristics of 1,8-naphthalimides depend on the polarization of naphthalimide molecule, due to the electron donor–acceptor interaction occurring between the substituents at position C-4 and the carbonyl groups from the imide moiety of the chromophoric system. Table 2 presents the spectral characteristics of the monomeric 1,8-naphthalimide dye in dichloromethane and ethanol solutions: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (log ε), Stokes shift ($v_A - v_F$), and quantum yield of fluorescence (Φ_F).

The dye exhibits a yellow–green colour with absorption maxima at $\lambda_A = 429$ nm in dichloromethane and $\lambda_A = 436$ nm in ethanol solutions. The fluorescence maxima are $\lambda_F = 502$ nm in dichloromethane and $\lambda_F = 521$ nm in ethanol, respectively. The absorption and fluorescence maxima in dichloromethane are hypsochromically shifted ($\Delta\lambda_A = 7$ nm and $\Delta\lambda_F = 19$ nm) by comparison with those in protic ethanol. This might be related to the different polarity of the solvents as well as to the specific dye–solvent interactions causing a change in the dye polarization.

An important characteristic of dyes is the oscillator strength (f), it reveals the effective number of electrons whose transition from the ground S_0 to the excited S_1 state gives the absorption area in the spectrum. Values for the oscillator strength can be calculated using eqn. (1):[18]

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

where $\Delta v_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2\varepsilon_{max}$.

The values obtained for f are 0.210 in dichloromethane and 0.299 in ethanol solution. The higher values in ethanol correlate well with the hypsochromic effect of the dye in this solvent.

The Stokes shift is a parameter which indicates the difference in the properties and structure of the dyes between the ground state S_0 and the first exited state S_1. The Stokes shift values are 3290 cm^{-1} for dichloromethane and 3742 cm^{-1} for ethanol solution. The fluorescence quantum yield Φ_F is determined on the basis of the absorption and fluorescence spectra of the dye taken in dichloromethane and ethanol. As can be seen from the data in Table 2, the 1,8-naphthalimide dye has quantum yield values of $\Phi_F = 0.73$ (dichloromethane) and 0.008

(ethanol). This great difference in quantum yields can be explained by the photo-induced electron transfer processes, which are accelerated in polar solvents.[19] The results in ethanol solution are very different from those in our previous studies on similar 1,8-naphthalimide polymerizable dyes, which have various alkyl secondary amino groups in position C-4 and showed a strong increase in Φ_F values ($\Phi_F = 0.70$–0.99), wherein PET does not occur.[20,21]

This study also covers the spectral characteristics of structurally modified co-polymers as well (Table 3). The absorption spectra have broad bands in the visible region. Both in the solid state and in solution the co-polymers are yellow in colour and show intense green fluorescence.

Fig. 1 and 2 show the excitation and fluorescence spectra of poly(MMA–co-dye) in dichloromethane solution and a poly(ST–co-dye) thin film as an example. Table 3 present the data obtained from the absorption and fluorescence spectra of poly(MMA–co-dye) and poly(ST–co-dye) in dichloromethane solution and as thin polymer films. In dichloromethane solution, the absorption maxima λ_A occur at 396
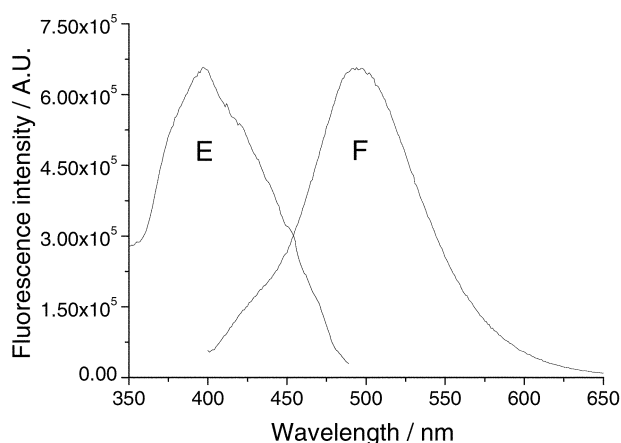

Fig. 1 Excitation (E) and fluorescence (F) spectra of poly(MMA–co-dye) in dichloromethane solution.
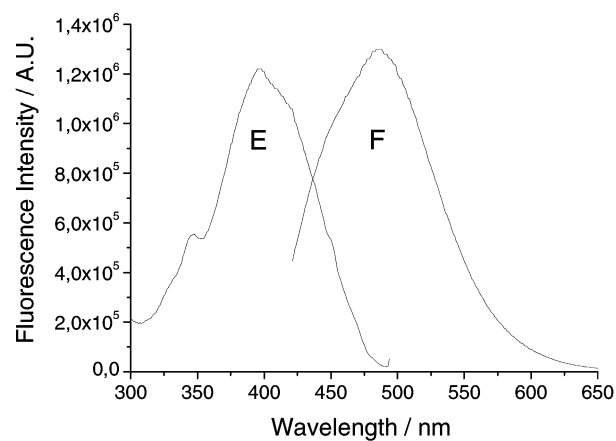

Fig. 2 Excitation (E) and fluorescence (F) spectra of poly(ST–co-dye) as a thin film.

Table 2 Spectral characteristics of 4-(N,N-dimethylaminoethylene)-amino-N-allyl-1,8-naphthalimide in dichloromethane and ethanol solutions

	Dichloromethane	Ethanol
λ_A/nm	429	436
ε/L M^{-1} cm^{-1}	11 890	16 100
λ_F/nm	502	521
$(v_A - v_F)$/cm^{-1}	3290	3742
f	0.210	0.299
Φ_F	0.73	0.008

Table 3 Absorption (λ_A) and fluorescence (λ_F) maxima of co-polymers in dichloromethane solution and as thin films

Polymers	Dichloromethane			Thin film		
	λ_A/nm	λ_F/nm	$(v_A - v_F)$/cm^{-1}	λ_A/nm	λ_F/nm	$(v_A - v_F)$/cm^{-1}
Poly(MMA–co-dye)	396	485	4634	401	503	5057
Poly(ST–co-dye)	385	483	5270	397	497	5068

and 385 nm, and their fluorescence spectra show maxima at $\lambda_F = 485$ and 483 nm, respectively. In the solid state, the absorption maxima of the co-polymers appear at 401 and 397 nm, and the fluorescence maxima are seen at 503 and 497 nm, respectively. As can be seen, the differences in the absorption and fluorescence maxima of the co-polymers between the solid state and solution are small. Obviously, the results do not show any structural changes in the chromophoric system, owing to the polymer matrix. This means that the chromophoric system of the monomeric dye is preserved during the co-polymerization.

Photoinduced electron transfer of the monomeric and polymeric fluorophores

Fig. 3 presents the pH dependence of fluorescence intensity of monomeric dye. It is seen that the fluorescence intensity depends strongly on pH values. The results reveal that the protonation of the terminal dialkylamino group of the naphthalimide molecule increases the florescence intensity. A small hypsochromic shift of the fluorescence maxima ($\Delta\lambda = 4$ nm) is observed. The fluorescence enhancement (FE) in this case is 18 (Table 4), which indicates an inhibition of PET.

PET can be expected to cause relatively minor changes in the fluorescence of the co-polymers, since it is not very strong in solid state if compared with that in polar solution. Fig. 4 and 5 show the changes in fluorescence intensity of poly(-MMA–co-dye) and poly(ST–co-dye) at different pH values. To our surprise, in the case of poly(MMA–co-dye), the pH dependence of the fluorescence is minimal. The small amount of proton-induced fluorescence enhancement (FE 20%) in this case might be due to the possible formation of an weak intermolecular interaction amongst the protonated amine receptor of the naphthalimide and the poly(methyl methacrylate) carbonyl groups, which weakens the inhibition of PET from receptor to fluorophore. Of course, the presence of possible intermolecular hydrogen bonds between the hydrogen atom on amino group at the C-4 position of the naphthalimide mole-
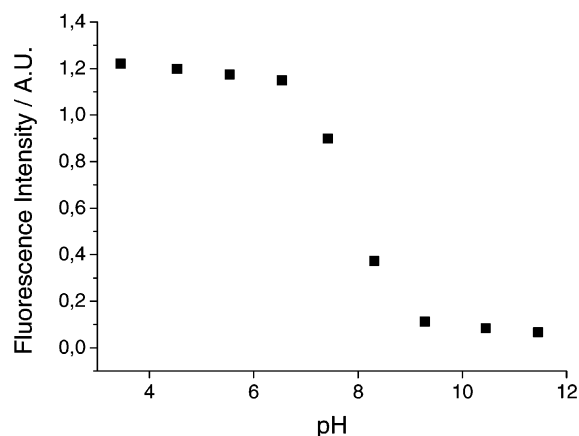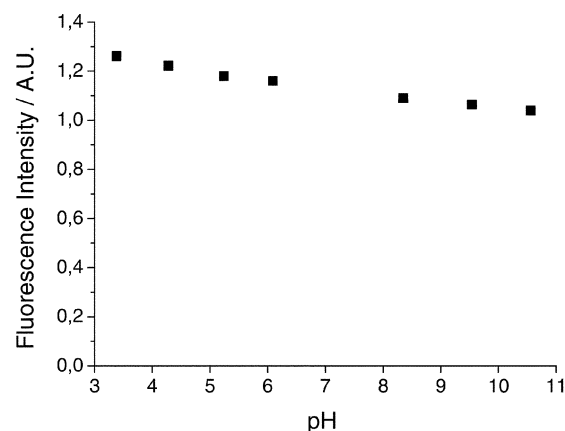

Fig. 4 pH dependence of fluorescence intensity of poly(MMA–co-dye) in aqueous solution. The pH values, in order of decreasing intensity, are 3.38, 4.28, 5.24, 7.22, 8.35, 9.54 and 10.56. The excitation wavelength is 400 nm.
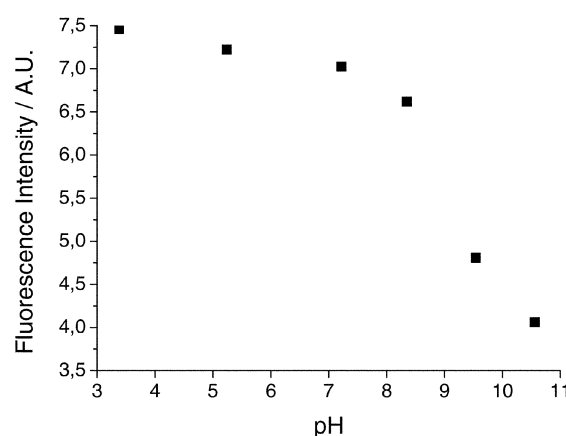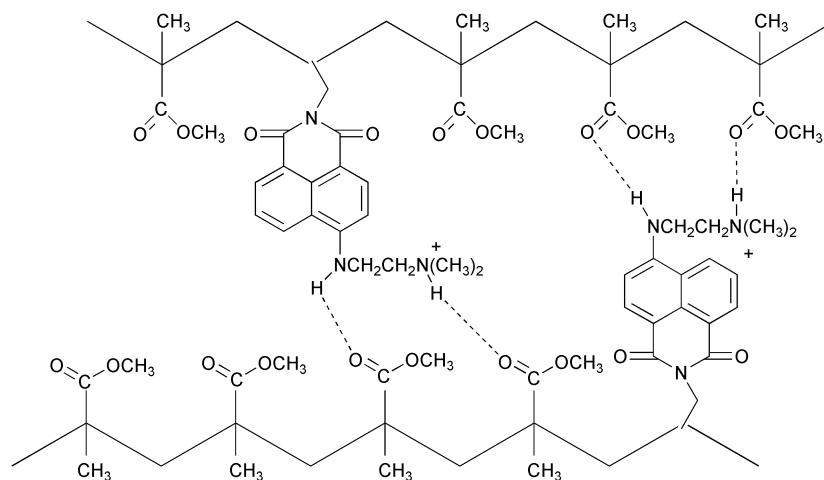

Fig. 5 pH dependence of fluorescence intensity of poly(ST–co-dye) in aqueous solution. The pH values, in order of decreasing intensity, are 3.38, 5.24, 7.22, 8.35, 9.54 and 10.56. The excitation wavelength is 416 nm.

cules and carbonyl groups from the main polymer chain (Scheme 2) also influence on the fluorescence.

In the case of poly(ST–co-dye), a pronounced pH dependence of the fluorescence intensity was observed. The proton-induced fluorescence enhancement is 90% in the pH range 3.4–10.6.[2] The fluorescence maxima are bathochromically shifted from acidic to basic pH values. The better results obtained for poly(ST–co-dye), compared with poly(MMA–co-dye), can be explained by the different nature of the main polymer structure; a weak interaction between the fluorophore and polymer molecules is impossible in the former.

Fig. 6 shows the effect of Cu^{2+} ions upon the fluorescence spectrum of monomeric 1,8-naphthalimide dye in acetonitrile solution. After the addition of the Cu^{2+} ions into the dye solution up to concentration of 1.25×10^{-5} M, the fluorescence emission increases, corresponding to the formation of intramolecular bidentate chelation with the Cu^{2+} ions.[22] Above this concentration, the fluorescence intensity decreases, owing to the increasing quenching interaction between the transition metal cations and the fluorophore. The Cu^{2+} ions induce a hypsochromic shift of the absorption ($\Delta\lambda_A = 13$ nm) and fluorescence maxima ($\Delta\lambda_F = 15$ nm; see Table 5), which demonstrates the interaction between the dye molecules and metal ions in the exited state.

Fig. 7 and 8 plot the influence of different concentrations of Cu^{2+} ions on the fluorescence intensity of poly(MMA–co-dye)

Fig. 3 pH dependence of fluorescence intensity of monomeric 1,8-naphthalimide dye in MeOH–H$_2$O (1:4, v/v). The pH values, in order of decreasing intensity, are 3,45, 4.53, 6.54, 7.42, 8.31, 9.29, 10.45 and 11.45. The excitation wavelength is 438 nm.

Table 4 pH dependence of fluorescence in aqueous solution

Property	Monomeric dye	Poly(MMA–co-dye)	Poly(ST–co-dye)
λ_F (acid)/nm	527	498	486
λ_F (base)/nm	531	501	488
FE	18	0.2	0.9

Scheme 2 Schematic representation of possible intramolecular hydrogen bonds in an acidic aqueous solution of poly(MMA–co-dye)
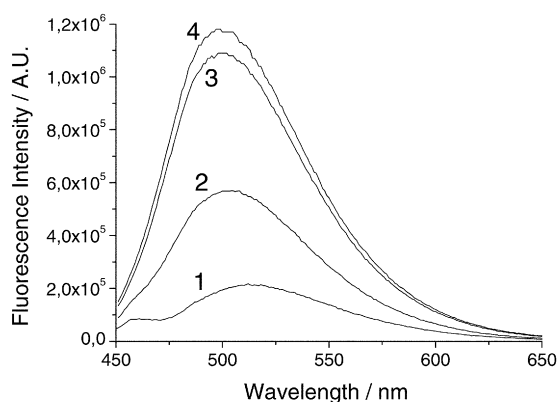

Fig. 6 Fluorescence spectra of monomeric 1,8-naphthalimide dye in acetonitrile for various concentrations of Cu^{2+} ions. The concentrations of Cu^{2+} ions are (1) 0, (2) 5×10^{-6}, (3) 1×10^{-5} and (4) 1.25×10^{-5} M.

Fig. 7 Fluorescence spectra of poly(MMA–co-dye) in aqueous solutions containing various concentrations of Cu^{2+} ions. (1) 0, (2) 5×10^{-5}, (3) 9.6×10^{-5}, (4) 5×10^{-4} M.

Table 5 Fluorescence maxima before addition of, λ_F (B), and in the presence of Cu^{2+}, λ_F (P), and fluorescence enhancement (FE) of the fluorophores

Property	Monomeric dye[a]	Poly(MMA–co-dye)[b]	Poly(ST–co-dye)[b]
λ_F (B)/nm	512	499	497
λ_F (P)/nm	497	502	488
$\Delta\lambda_F$/nm	15	−3	9
FE	4.4	2.2	−0.62

[a] In acetonitrile solution. [b] In aqueous solution.

and poly(ST–co-dye) co-polymers in aqueous solution. In the case of the poly(MMA–co-dye), the presence of Cu^{2+} ions increases the fluorescence intensity and an FE of 2.2 has been determined. The higher fluorescence intensity correlates well with the strong interaction of Cu^{2+} ions with the terminal nitrogen atom. For the poly(ST–co-dye), a decrease in the fluorescence intensity in the presence of Cu^{2+} ions in aqueous solution (FE = −0.62) was observed. This might be due to the poly(ST–co-dye) co-polymer having a different micro-structure; the rigidity and density of the macromolecules is higher, compared with poly(MMA–co-dye), and Cu^{2+} ions are unable to form an intramolecular bidentate chelation with the nitrogen atoms of the amino receptor and the amino group at the C-4 position of the 1,8-naphthalimide. Thus, the Cu^{2+} ions probably attack the carbonyl groups or naphthalene ring of
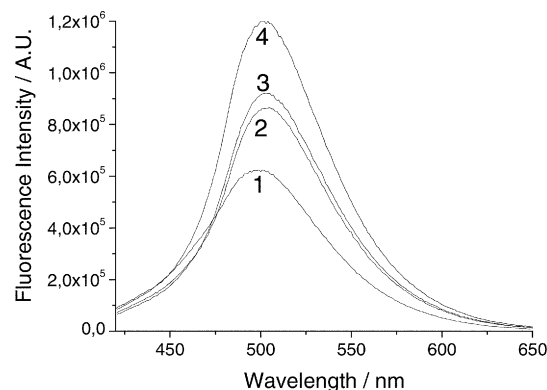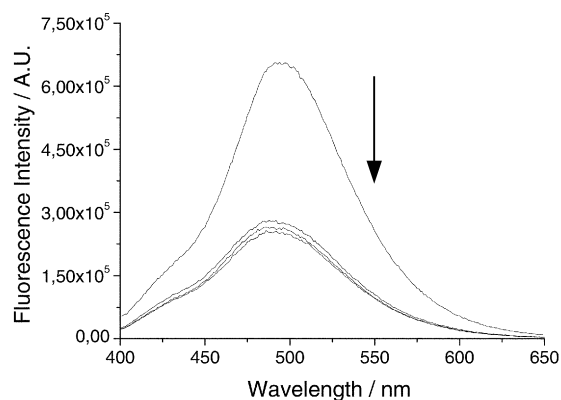

Fig. 8 Fluorescence spectra of poly(ST–co-dye) in aqueous solutions containing various concentrations of Cu^{2+} ions. (1) 0, (2) 5×10^{-5}, (3) 9.6×10^{-5}, (4) 5×10^{-4} M.

dye, which leads to a decrease in the intensity of the fluorescence.

These results show the selective influence of Cu^{2+} ions on the fluorescence intensities of poly(MMA–co-dye) and poly(ST–co-dye) co-polymers.

The different behaviour of the co-polymers in the presence of H^+ and Cu^{2+} ions is noteworthy. Poly(MMA–co-dye) is not active towards H^+ ions, while it is towards Cu^{2+} ions. This means that this co-polymer can be used as a PET sensor only

for Cu^{2+} ions. Poly(ST–co-dye) is sensitive to the presence of H^+ and Cu^{2+} ions, with a different activity in each case. The hydrogen ions enhance the fluorescence intensity, but in the presence of Cu^{2+} ions, the fluorescence emission decreases.

In addition, the good functional properties, namely the mechanical stability of the co-polymers, the fact that the fluorophore cannot migrate from the polymer matrix and the photo-stability of the fluorescence of previously studied similar co-polymers suggest that multiple uses of the same film and extended usage times are a possibility. The films can simply be cleansed of the trapped ions and re-used, with no loss of performance.

Conclusion

A new polymerizable 1,8-naphthalmide dye for use as fluorescent sensor has been synthesized in high yield and purity. It has been shown that the monomeric 1,8-naphthalimide dye is suitable for the structural modification of poly(methyl methacrylate) and polystyrene polymers. The co-polymers obtained are transparent, coloured and show intense green fluorescence in the solid state and in dichloromethane solution, and as such could be used as heterogeneous PET sensors. The poly(MMA–co-dye) co-polymer can be used as a PET sensor only for Cu^{2+} ions, while the fluorescence intensity of the poly(ST–co-dye) co-polymer is only enhanced in acidic media, hence it can find application as a PET sensor for protons.

Acknowledgements

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