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A copolymer of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide with methylmethacrylate as a selective fluorescent chemosensor in homogeneous systems for metal cations

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Abstract

The basic photophysical characteristics of two fluorophores: monomeric *N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide and methylmethacrylate based copolymer including *N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide are described both in the absence and presence of Fe^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+} cations. It is shown that both the fluorophores can be used as homogeneous photo-induced electron transfer fluorescent sensors exhibiting fluorescence enhancement induced by metal ions. The copolymer is more responsive to the Fe^{2+} cations than to other cations under study.

Keywords: 1,8-Naphthalimides; Poly(methylmethacrylate); Fluorescent sensors; Photo-induced electron transfer

1. Introduction

In the last few years a growing interest on the investigation of fluorescent systems capable to change its photophysical properties under certain conditions occurred. Photo-induced electron transfer (PET) fluorescent sensors are one of these systems. They have been of great interest due to their various prospective applications [1,2]. PET systems are generally multi-component systems containing a fluorophore as the signaling moiety, a receptor (substituted amine with an unbound electron pair) as the guest binding site, and a spacer to connect the fluorophore and the receptor. The PET interaction between fluorophore and receptor quenches "switches off" the fluorescence. The "switches on" state of fluorescence takes place in the presence of a "guest", e.g. protons, because the electron pair of the nitrogen atom is tied up to the guest, which turns off the PET between fluorophore and receptor. Another guests are different alkaline, alkaline-earth metals ions [1,2]. Much less attention has been paid on the transition or heavy metal ions [3,4].

Usually PET fluorescent sensors are applied as a mixture with a target (e.g. metal cations or protons) in a homogeneous liquid system. There are many fluorescent sensors of this type with different molecular structures for detection of metal ions [1–5]. Another important structural manner are the fluorescent sensory polymers. In this case, the fluorescent probes have been covalently bonded to the polymer chain, thus showing very similar effect as monomeric fluorophore [2,6].

Because of its strong fluorescence and good photostability, the 1,8-naphthalimide derivatives were used in different scientific areas [7]. The copolymers of 1,8-naphthalimide with some traditional monomers have intensive blue and green fluorescence [8].

Recently, a new polymerizable 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide as a sensor for protons or metal cations has been synthesized [9]. It has been demonstrated that the copolymers of this material with methylmethacrylate or styrene can be used as heterogeneous PET fluorescent sensors for Cu^{2+} cations and protons depending on their structures of main polymer chain.

In this paper, we present the results of investigations on the functional properties of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide alone or as copolymer with methylmethacrylate in organic solvents with different polarity. The influence of metal cations on the fluorescence intensity of both low- and high-molecular weight sensors are discussed.

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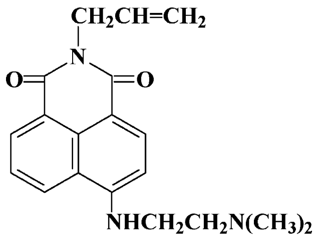


Scheme 1. Molecular structure of monomeric 1,8-naphthalimide dyes.

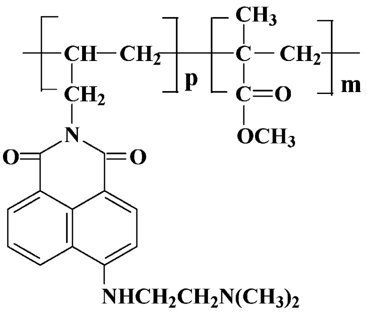
2. Experimental part

Both the monomeric and polymeric fluorescent compounds were prepared recently [9]. 4-*N*,*N*-Dimethylaminoethylene-*N*-allyl-1,8-naphthalimide used as monomeric moiety had the structure presented in Scheme 1.

The methylmethacrylate copolymer associated with the fluorescent moiety had the structure presented in Scheme 2. The amount of the monomeric dye in the polymer macromolecule is 0.94 wt.%.

UV-Vis spectrophotometric investigations were performed on a UVIKON 930 spectrophotometer (KONTRON instruments). The fluorescence spectra were taken on a SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yield of the monomeric dye have been determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as reference ($\Phi_0 = 0.88$). For all absorption measurements, the dye concentration in the solutions were 10^{-5} mol l^{-1}. The fluorescent measurements were in 10^{-6} mol l^{-1}. The polymer concentration in solution for all measurement were 5 g l^{-1}. For all fluorescent measurements, solutions were exited at its absorption maxima. All the organic solvents used were spectrophotometric grade.

A solar simulator (Suntest CPS+, HERAEUS), equipped with a 1.5 kW xenon arc lamp, protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm, was used and the experiments were carried out in ordinary atmosphere at 20 °C.



Scheme 2. Molecular structure of poly(MMA-co-dye).

3. Results and discussion

3.1. Spectral characteristics of 4-N,N-dimethylaminoethylene-N-allyl-1,8-naphthalimide and poly(MMA-co-dye)

The basic spectral characteristics of 1,8-naphthalimide derivatives depend mainly on the polarization of 1,8-naphthalimide molecule due to the electron donor–acceptor interaction occurring between the substituents at C-4 position and the carbonyl groups from the imide structure of the chromophoric system, and on the other hand may be influenced by the environmental effect of the media upon the interaction [10,11]. Clearly the bands of the absorption and emission of the 1,8-naphthalimide derivatives largely depend on the electron donating power of the substituents at position C-4.

The organic solvents play a significant role on the photophysical properties of 1,8-naphthalimide derivatives [3b,3c,10,11]. The effect of solvent polarity on the photophysical properties was investigated using organic solvents with different polarity (ε: dielectric constants). Table 1 summarizes the spectral characteristics of the 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide in these organic solvents: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient ($\log \varepsilon$), Stokes shift ($\nu_A - \nu_F$), quantum yield of fluorescence (Φ_F) and the energy fluorescent yield E_F.

In all organic solvents under study, the monomeric 1,8-naphthalimide dye displayed yellow-green color and intense fluorescence. Fig. 1 shows an example of the absorption and fluorescence spectra of monomer dye in chloroform solution. The long-wavelength band of the absorption spectra in the visible region was a band of charge transfer (CT) due to $\pi \to \pi$ electron transfer on $S_0 \to S_1$ transition [12]. In this case, the absorption maxima, λ_A, were in the visible region, at 407–438 nm and respective fluorescence maxima are in 454–520 nm. The dependence of dye absorption and fluorescence maxima from the solvent polarity is shown in

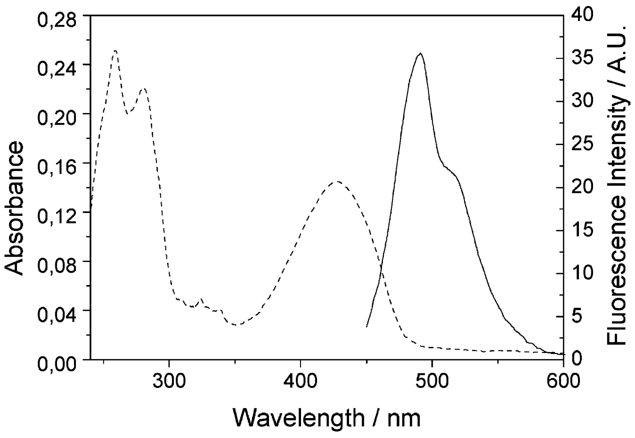


Fig. 1. Absorption and fluorescent spectra of monomeric dye in chloroform solution.

Table 1
Photophysical properties of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide in organic solvents with different polarity

Solvent	Dielectric constant	λ_A nm	ε ($M\,l^{-1}\,cm^{-1}$)	λ_F nm	$\nu_A - \nu_F$ (cm^{-1})	Φ_F	E_F
n-Hexane	1.88	407	18300	454	2543	0.96	0.86
Diethylether	4.34	416	18900	480	3205	0.90	0.78
Chloroform	4.81	427	14560	492	3094	0.86	0.75
Ethylacetate	6.02	426	19650	492	2984	0.88	0.76
Trichloroethylene	7.43	430	10200	500	3258	0.14	0.12
Tetrahydrofurane	7.58	431	9850	492	2876	0.20	0.17
Dichloromethane	8.93	429	11900	502	3290	0.73	0.62
2-Methyl-2-propanol	12.5	435	10300	520	3758	0.02	0.016
Ethanol	24.6	436	16100	521	3742	0.0080	0.0067
Methanol	32.7	433	13100	519	3827	0.0079	0.0066
DMF	36.7	438	11900	520	3600	0.04	0.03

See text.

Fig. 2. As seen from the figure, the nature of the solvents influences significantly the spectral properties of the dye. Changes in the position of the CT band of the dye in the solvents are brought about by the solvatochromic effect of the solvent. In comparison with the polar solvents, the absorption and fluorescent maxima in apolar solvents are hypsochromically shifted ($\Delta\lambda_A = 31$ nm and $\Delta\lambda_F = 76$ nm), as the polarization of the dye molecules depend strongly on the solvent's polarity as well as to the specific interactions of dye–solvent causing a change in the polarization of the dye chromophoric system. As it can be seen, the dye under study has a positive solvatochromism.

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 between 2542 and 3827 cm^{-1}. From Fig. 2, it is also seen then the Stokes shift that depend on the organic solvents and it is bigger in the case of the more polar solvents.

It was very interesting to investigate the dependence of quantum efficiency of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide from different environments. The ability of the dye molecule to emit absorbed light energy was characterized quantitatively by the quantum yield of fluorescence Φ_F. The quantum fluorescence yield have been determined on the basis of the absorption and fluorescence spectra of the dye. As seen from the data in Table 1, the monomeric1,8-nahphalimide dye has quantum yield with values between $\Phi_F = 0.96$ (*n*-hexane) and $\Phi_F = 0.0079$ (methanol). In Fig. 3 has been plotted the dependence of the quantum fluorescence yield from the solvent polarity. As can be seen, the quantum yield is considerably higher in a polar media. In polar organic solvents, the dye exhibit much weaker emission. The great difference in the quantum yields can be explained by the photo-induced electron transfer (PET) processes, which are accelerated in polar solvents. This behavior has also been noted recently by Brawn and co-workers, investigating a similar 1,8-naphthalimide dye in different organic solvents [3b].

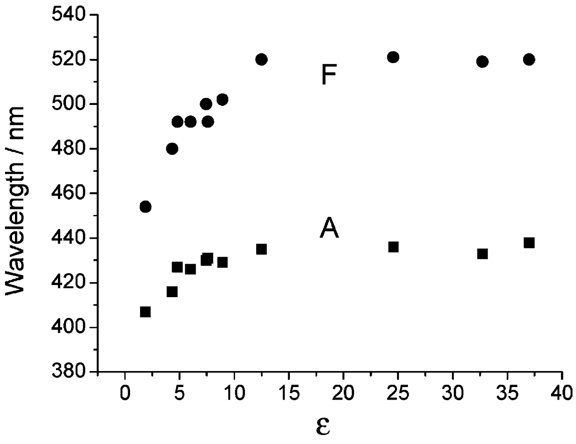


Fig. 2. Absorption (A) and fluorescence (F) maxima of monomeric dye as a function of the solvent polarity parameter ε.

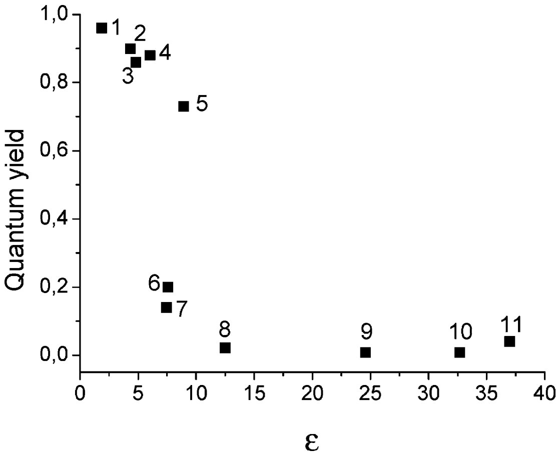


Fig. 3. Quantum yields of monomeric dye as a function of solvent polarity (ε): (1) *n*-hexane, (2) diethylether, (3) chloroform, (4) ethylacetate, (5) dichloromethane, (6) tetrahydrofurane, (7) trichloroethylene, (8) 2-methyl-2-propanol, (9) ethanol, (10) methanol, (11) *N*,*N*-dimethylformamide.

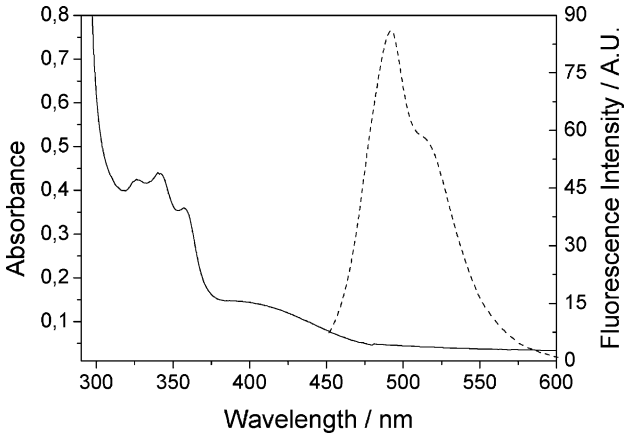


Fig. 4. Absorption and fluorescence spectra of poly(MMA-co-dye) in chloroform solution.

Besides Φ_F, the energy yield of fluorescence E_F can also be used [13]:

$$E_F = \frac{\Phi_F \lambda_A}{\lambda_F}$$

The respective results E_F were from 0.0066 to 0.86. The dependence of E_F from dielectric constant of the solvents is the same as the one presented in Fig. 3.

The study covered the spectral characteristics of structurally modified polymethylmethacrylate as well. In order to evaluate this copolymer poly(MMA-co-dye) for homogeneous fluorescent chemosensor for metal ions, it is useful to study the functional properties of the material in solution. In solid state [9] and in solution, the copolymer is colored yellow-green with intensive green fluorescence. In chloroform solution, the absorption spectrum of the copolymer has broad band in the visible region as can be see in Fig. 4 with an absorption maximum near to 400 nm. The fluorescence spectrum shows a well defined maximum at 491 nm. Fig. 5 presents the fluorescence spectra of monomeric dye and poly(MMA-co-dye) in solid state and in chloroform solution. It is seen then the fluorescence spectra of monomeric dye and copolymers in chloroform are identical. The fluorescence maxima of thin solid film differ significantly from those in solution being hypsochromically shifted, because of the rigidity of the structure. Obviously the results do not provide evidence about any structural changes in the dye chromophoric system, but showed the polymeric matrix and/or to the co-polymerization process could alter their spectral properties.

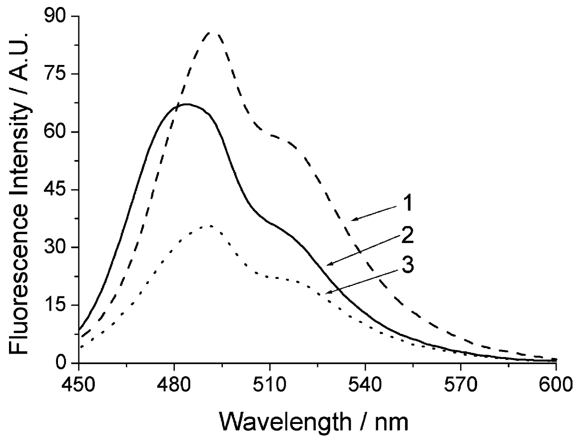


Fig. 5. Fluorescence spectra of poly(MMA-co-dye) in: (1) chloroform, (2) solid thin film and (3) monomeric dye in chloroform.

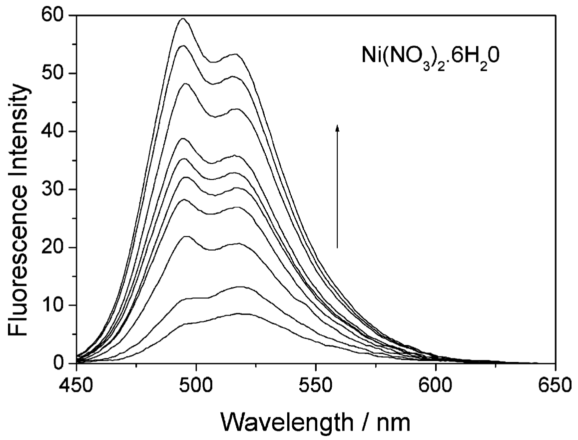


Fig. 6. Fluorescence spectra of monomeric dye in *N*,*N*-dimethylformamide at various concentrations of Ni^{2+} cations. The concentrations of Ni^{2+} cations are in order of increasing intensity from 0 to 6×10^{-3} M. The dye concentration is 1×10^{-6} M.

3.2. PET of the monomer fluorophore

The influence of some metal cations on the dye fluorescence intensity have been investigated and the respective fluorescence responses are presented in Figs. 6–9. In the absence of metal ions, the dye has a very weak fluorescence emission in DMF ($\Phi_F = 0.04$), as expected for a good PET

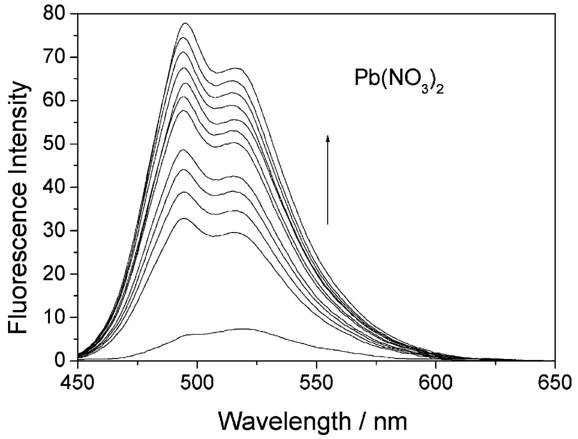


Fig. 7. Fluorescence spectra of monomeric dye in *N*,*N*-dimethylformamide at various concentrations of Pb^{2+} cations. The concentrations of Pb^{2+} cations are in order of increasing intensity from 0 to 8×10^{-3} M. The dye concentration is 1×10^{-6} M.

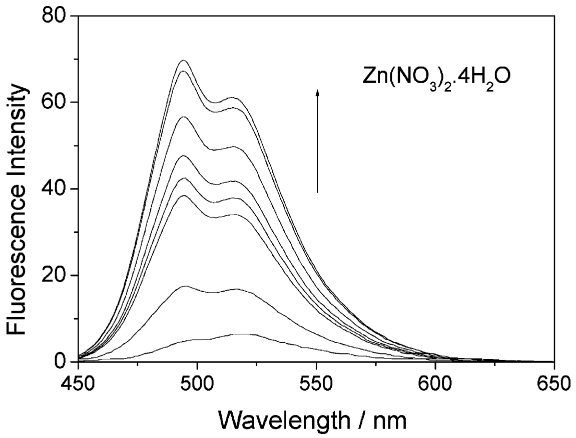


Fig. 8. Fluorescence spectra of monomeric dye in *N*,*N*-dimethylformamide at various concentrations of Zn^{2+} cations. The concentrations of Zn^{2+} cations are in order of increasing intensity from 0 to 8×10^{-3} M. The dye concentration is 1×10^{-6} M.

fluorescence switch. As it can be seen, the addition of metal cations leads to an increase of the fluorescence intensity of the dye system different for each metal ions. The fluorescence emission increases after the addition of metal ions into the dye solution up to one concentration different for the different metal cations. Above this concentration the fluorescence intensity decreases due to the increasing of quenching from high concentration of the metal cations. The metal ions induce a weak hypsochromic shift $\Delta\lambda_F = 3$–5 nm of the fluorescence maxima ($\lambda_F = 515$–517 nm). On the other hand, all metal ions under study induce a stronger second maximum ($\lambda_F = 494$–495 nm) hypsochromically shifted $\Delta\lambda_F = 25$–26 nm, indicating also that an interaction between the dye molecules and metal ions in the exited state occurred. The hypsochromic shift can be explained by the binding of receptor dimethylamine with metal ion, while the second fluorescent maximum, in this case can be explained by the formation of co-ordination interaction between nitrogen aromatic atom at C-4 position of the naphthalene ring and the nitrogen atom from the receptor dimethylamino group and the metal cations (Me^{2+}) as it can be seen in Scheme 3.

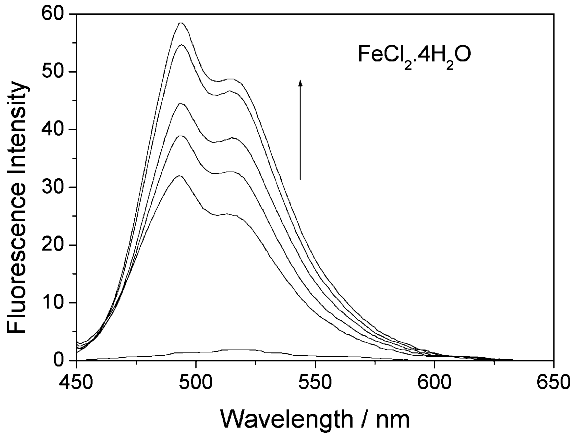
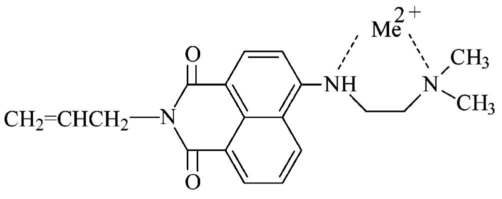


Fig. 9. Fluorescence spectra of monomeric dye in *N*,*N*-dimethylformamide at various concentrations of Fe^{2+} cations. The concentrations of Fe^{2+} cations are in order of increasing intensity from 0 to 1×10^{-4} M. The dye concentration is 1×10^{-6} M.



Scheme 3.

The presence of the guest metal cations into dye solution is signaled by fluorescence enhancement (FE). The FE was determined from the ratio of maximum fluorescence intensity (after metal ions addition) and minimum fluorescence intensity (metal cations free). The highest FE value was observed in the presence of Fe^{2+} cations FE = 32.46 (Table 2). For the other metal cations a good FE have also been observed being, respectively, 8.91 (Ni^{2+}), 11.25 (Zn^{2+}), and 12.26 (Pb^{2+}). The blue shift in the fluorescence spectra in the presence of either of these cations indicated that the switch might bind metal cations via a bidental chelation with both nitrogen atoms of the receptor and aromatic amine (Scheme 3). This chelation had two different effects. On one hand, the photo-induced electron transfer from the receptor amine to the fluorophore was inhibited, which resulted in fluorescence enhancement. On the other hand, the aromatic amine's in position C-4 electron-donating effect for then push–pull fluorophore was weakened, and so, the spectra shifted to shorter wavelength [14].

In Table 2 are presented also the photophysical characteristics of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide in *N*,*N*-dimethylformamide (DMF) in the presence of metal cations. In all cases, the metal cations increase the quantum yield of fluorescence of the dye ($\Phi_F = 0.41$–0.72) as higher values were observed compared to the solution free of ions. The higher effect have been observed in the presence of Fe^{2+} cations ($\Phi_F = 0.72$) and a rank can be given as the following:

$$Fe^{2+} > Pb^{2+} \geq Zn^{2+} > Ni^{2+}.$$

Table 2
Photophysical characteristics of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide in *N*,*N*-dimethylformamide in the presence of metal cations

Metal ions	λ_A (nm)	λ_F (nm)	FE	Stokes shift (cm^{-1})	Φ_F	E_F
Ni^{2+}	428	495, 515	8.91	3231	0.48	0.41
Pb^{2+}	428	494, 516	12.26	3272	0.58	0.50
Zn^{2+}	429	495, 517	11.25	3164	0.57	0.49
Fe^{2+}	428	495, 515	32.46	3121	0.83	0.72

See text.

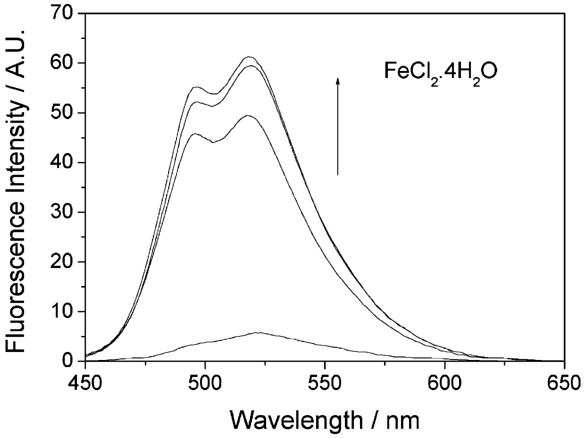


Fig. 10. Fluorescence spectra of poly(MMA-co-dye) in *N*,*N*-dimethylformamide at various concentrations of Fe^{2+} cations. The concentrations of Fe^{2+} cations are in order of increasing intensity from 0 to 1×10^{-4} M. The polymer concentration in solution is $5\,g\,l^{-1}$.

The dye complex with metal ions have a smaller Stokes shift, in comparison to dye free solution, indicating of the stabilization of the planarity of the dye structure. In this case, the emissionless deactivation during the transition from S_1 to the ground state S_0 is smaller, thus increasing the quantum and energy yields of fluorescence.

3.3. PET of copolymer associated with the fluorophore

With regard for the application of the homogeneous polymeric fluorescent sensors for metal ions it is worth studying the influences of metal cations on the fluorescence ability of the polymer. In Figs. 10 and 11 are plotted the fluorescence spectra of poly(MMA-co-dye) in DMF solution without and with different amount of Fe^{2+} and Zn^{2+} cations. It is seen that the metal cations provoke the enhancement of fluorescence intensity increasing with the concentration of the cations. But, when the concentration is risen above 5×10^{-5} M (corresponding to the formation of intra-molecular bisdental chelation with metal cations [14a] the fluorescence intensity decreases owing to the increasing of quenching between transition metal cations and fluorophore. In Fig. 12 are presented the dependence of FE versus the nature of metal ions. The highest FE value was observed in the presence of Fe^{2+} cations. It has been observed the similar influence from the nature of metal ions on the fluorescence intensity as in the case of monomer in the same solution (Table 2).

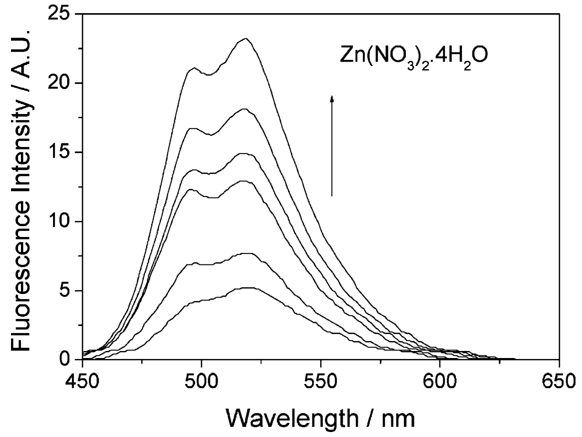


Fig. 11. Fluorescence spectra of poly(MMA-co-dye) in *N*,*N*-dimethylformamide at various concentrations of Zn^{2+} cations. The concentrations of Zn^{2+} cations are in order of increasing intensity from 0 to 5×10^{-4} M. The polymer concentration in solution is $5\,g\,l^{-1}$.

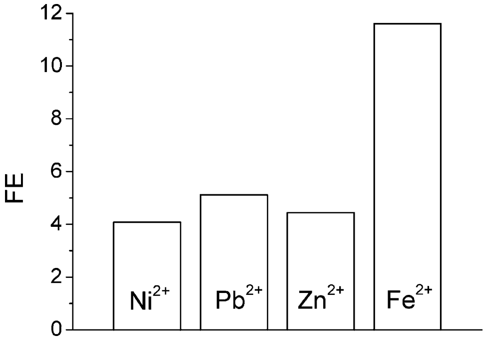


Fig. 12. Fluorescence enhancement (FE) of poly(MMA-co-dye) in the presence of different metal ions in *N*,*N*-dimethylformamide solution.

An important property of fluorescence sensors is their respond to the presence of metal cations. From Fig. 10, it is seen that the addition of Fe^{2+} concentration of 10^{-6} M causes a significant increases of fluorescence intensity (FE = 8.86) until in the case of other metal ions under study, the FE is in range between 1.5 and 1.9. This fact indicates a very good response of the polymer sensor to the Fe^{2+} cations. The monomer sensor has a weaker response to the Fe^{2+} cations compared to the polymer sensor.

Thus, our plan for designing the homogeneous polymeric fluorescent sensors for metal cations was justified. The good performance of the polymeric sensors can be ascribed to the monomeric polymerizable dye (sensor) in which the substituent in position C-4 played an important role for the sensibility of the polymer to the metal cations.

4. Conclusion

In this paper, we have presented results of PET and photophysical investigation of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide in organic solvents with different polarity for use as co-monomer in fluorescence polymer sensor based of polymethylmethacrylate. It was shown that the fluorescence intensity depend strongly on the polarity of the solvents. We have also shown that in the presence of metal cations (Fe^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+}) the fluorescence intensity of the monomer is higher than that in the solution free of metal cations due to formation of metal complexes with the 4-distal nitrogen atom of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide.

The relative affinities of the monomeric 1,8-naphthalimide dyes to form metal complexes between the cations studied and 4-distal nitrogen of 4-*N*,*N*-dimethylaminoethylene-*N*-allyl-1,8-naphthalimide increase in the range: $Fe^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+}$, as increase in the quantum fluorescence yield in the presence of the respective metal cations. By binding the monomer fluorophore to the polymethylmethacrylate macromolecules we obtained a linear polymer sensor that have pendant 4-*N*,*N*-dimethylaminoethylene-1,8-naphthalimide. This copolymer have a PET, which is quenched in the presence of metal ions. By using a copolymer with side-chain fluorescence sensor units bonded to the main polymer chain we can amplify the response of monomeric sensor. It was shown that the copolymer is more responsive to the Fe^{2+} cations. To our knowledge, this is the first example of homogeneous polymeric sensor, containing a 1,8-naphthalimide as co-monomer, for metal cations. On the basis of the present investigation, it can assumed that the new monomeric and polymeric fluorescent compounds are suitable for the homogeneous low- and high-molecular weight sensors. The sensors can be utilized for metal ions test based on the quenching of PET processes in the 1,8-naphthalimide fluorophore.

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