Synthesis of benzanthron derivatives for selective detection by fluorescence of copper ions

Stephane Dumas [a,*], Ivo Grabchev [b], Polia Stoikova [b], Jerome Chauvin [c], Jean-Marc Chovelon [a]

[a] Institut de Recherche sur la catalyse et l'Environnement de Lyon, IRCELYON, UMR-CNRS 5256, Université Lyon 1, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France
[b] Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[c] Université Joseph Fourier Grenoble 1/CNRS, Département de Chimie Moléculaire, UMR-5250, Institut de Chimie Moléculaire de Grenoble FR-CNRS-2607, BP-53, 38041 Grenoble cedex 9, France

ARTICLE INFO

ABSTRACT

The paper reports on the synthesis of two new benzanthron derivatives with intense yellow-orange fluorescence and their copolymers with styrene. The photophysical characteristics of the new low and high molecular weight fluorescent compounds have been studied in organic solvents of different polarity. The effect of the chemical nature of the C-3 substituent on the photophysical properties of the new dyes is discussed. The complexes formed between the benzanthron fluorophores and metal cations in solution have been studied with regard to potential applications as fluorescent sensors for metal ion contamination. The results show that the C-3 substituent determines a selective response to the presence of Cu^{2+} cations. In the case of copolymers the effect of the metal cations on the fluorescence intensity is negligible.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Derivatives of benzo[de]anthracen-7-one (benzanthron) exhibit bright yellow-green or orange-red fluorescence depending on their chemical structure both in solution and in the solid state [1]. Their excellent bright colours characteristics conditioned by the emitted fluorescence and high photo stability make them preferable for dying polymer materials [2]. They can also be used as daylight fluorescent pigments [3], disperse dyes for synthetic fibres [4], as laser dyes [5]. The introduction of polymerizable groups into the benzanthron molecule allows the combination of two processes dying and formation of a polymer. During the polymerization process the benzanthron dyes bind covalently to the polymer chain, ensuring a dying and fluorescent effect resistant to the chemical and mechanical influences [2]. It has also been shown that some 3-oxy- and 3-aminosubstituted benzanthron derivatives are suitable luminophores for application in nematic liquid crystals for electro-optical displays [6].

In the last few years the fluorescent sensors arise growing interest. They are one of the fluorescent systems capable of changing their photophysical properties under certain conditions. Presently many fluorescent chemosensors of different structure are being used for the detection of metal cations and protons in the environment [7]. Recently Staneva et al. described for the first time the utilization of benzanthron luminophores as fluorescent sensors for protons based whose response is based on internal charge transfer [8]. The design of the fluorescent sensitive polymers has become an important trend in applied polymer chemistry. For the purpose the fluorescent probes are covalently bonded to the polymer chain or inserted into the different polymer matrixes thus producing an effect very similar to that of monomeric sensors [9].

In this paper the results from the investigations on the synthesis of two new polymerizable benzanthron derivatives and their copolymers with styrene are presented. Their photophysical characteristics in organic solvents have been studied. The influence of metal cations on the fluorescence intensity of both fluorophores as homogeneous fluorescent sensors is discussed. To our knowledge these are the first benzanthron derivatives used as fluorescent sensors for metal cations.

* Corresponding author. Tel.: +33 4 72432783.
E-mail address: stephane.dumas@ircelyon.univ-lyon1.fr (S. Dumas).

2. Experimental

2.1. Materials

The synthesis of 2-allyloxy-4-dimethylamino-6-chloro-1,3,5-triazine and 2-allyloxy-4-morpholyno-6-chloro-1,3,5-triazine [10] and 3-aminobenzanthron [11] have been described recently. Commercial styrene (St) was used after purification by distillation under reduced pressure. Dibenzoyl peroxide (DBP) (Fluka), recrystallized from chloroform and methanol, was used as initiator for free radical copolymerization. $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2$ and $Zn(NO_3)_2 \cdot 4H_2O$, were investigated as sources for metal cations and used as obtained from Aldrich.

### 2.2. General method for the synthesis of monomeric benzanthron dyes B1 and B2

0.6 g (0.001 mol) 3-aminobenzanthron was reacted with 0.001 mol 2-allyloxy-4-dimethylamino-6-chloro-1,3,5-triazine (B1) or 2-allyloxy-4-morpholyno-6-chloro-1,3,5-triazine (B2) in 10 ml dioxan for 8 h, at 80 °C. The reaction was followed by TLC. The product was precipitated by pouring the reaction mixture into 100 ml of water, the precipitate was then filtered off, washed with water and dried under vacuum at 40 °C (Scheme 1).

2.3. Characteristic data of benzanthron derivative B1

Yield: 88% m.p. 98–100 °C; FTIR (KBr), cm^{-1}: 3072, 2931, 1644, 1607, 1541, 1407, 1310, 1100, 806, 772; ^{1}H NMR (CDCl$_3$, δ, ppm): 8.76 (d, J = 7.2 Hz, 1H), 8.46 (d, J = 8.5 Hz, 2H), 8.36 (d, J = 8.7 Hz, 2H), 8.23 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 7.4 Hz, 1H), 6.10–5.96 (m, CH=, 1H), 5.40 (dd, J = 30.1, 36.0 Hz, CH$_2$=), 4.83 (d, J = 5.2 Hz, OCH$_2$, 2H), 3.18 (d, J = 10.2 Hz, CH$_3$, 6H); ^{13}C NMR (CDCl$_3$, δ, ppm): 183.6, 170.7, 148.7, 135.6, 133.8, 131.1, 130.4, 129.9, 128.7, 128.3, 128.0, 127.1, 126.7, 124.6, 122.9, 119.3, 118.7.
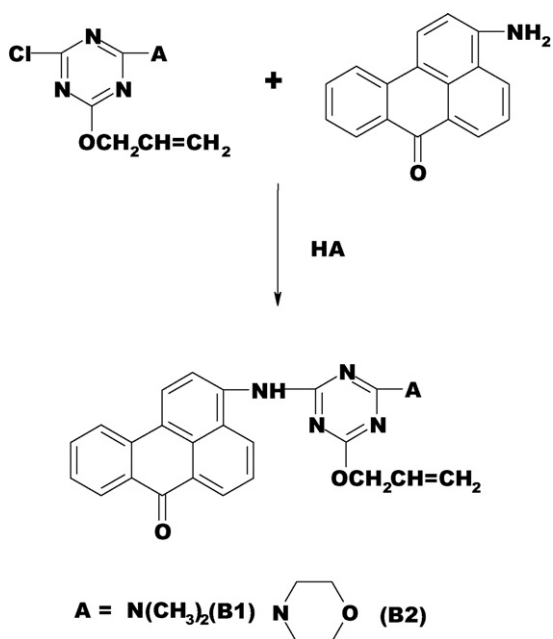
Scheme 1. Synthesis of benzanthron dyes B1 and B2.
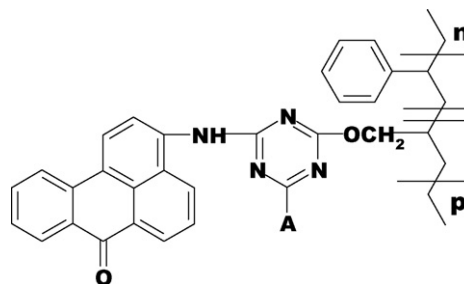
Scheme 2. Chemical structure of poly(St-co-B).

2.4. Characteristic data of benzanthron derivative B2

Yield: 84% m.p. 169–171 °C; FTIR (KBr), cm^{-1}: 3067, 2959, 2854, 1648, 1572, 1495, 1405, 1307, 1114, 809, 776; ^{1}H NMR (CDCl$_3$, δ, ppm): 8.69 (d, J = 7.2 Hz, 1H), 8.42 (d, J = 8.2 Hz, 2H), 8.32 (d, J = 8.4 Hz, 2H), 8.18 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H), 6.05–5.94 (m, CH=, 1H), 5.30 (dd, J = 33.1, 27.7 Hz, CH$_2$=), 4.79 (d, J = 8.3 Hz, OCH$_2$, 2H), 3.77 (d, J = 2.9 Hz, N(CH$_2$)$_2$, 4H), (d, J = 3.9 Hz, O(CH$_2$)$_2$, 4H); ^{13}C NMR (CDCl$_3$, δ, ppm): 183.8, 170.5, 165.9, 136.0, 133.3, 132.5, 130.2, 129.7, 128,7, 128,2, 128,1, 127,9, 127.7, 126.5, 126.1, 124.4, 122.3, 120,2, 118.2, 67.6, 66.6, 43.6.

2.5. Synthesis and characterization of fluorescent poly(St-co-B)

The radical copolymerization of benzanthron dyes B1 or B2 with styrene was carried out in ampoules previously purged with pure dry N$_2$ (Scheme 2). The process of copolymerization was conducted under conditions used for other alike fluorescent monomers: in the presence of 1.0 wt% dyes and 1.0 wt% dibenzoyl peroxide under N$_2$ at 80 °C for 8 h. The side-chain copolymers thus obtained were several times reprecipitated with ethanol from the toluene. The precipitated copolymers were repeatedly washed with ethanol, recovered by filtration and dried in vacuum to constant weight. Transparent fluorescent copolymers of intensive yellow-orange emission were obtained. All spectrophotometric measurements were carried out with precipitated coloured polymers.

2.6. Methods

UV–vis spectrophotometric investigations were performed on a Kontron 630 spectrophotometer at concentrations of 10^{-5} mol l^{-1}. The steady-state emission spectra were recorded on a JASCO FP-6500 spectrofluorimeter at the same concentrations to afford any re-absorption phenomena. Fluorescence quantum yield Φ_L was determined with a fluorescein aqueous solution ($\Phi_L^{Ref} = 0.85$) as a standard, according to Eq. (1)

$$\Phi_L^S = \frac{I_L^S}{I_L^{Ref}} \frac{(1 - 10^{-OD^{Ref}})}{(1 - 10^{-OD^S})} \frac{n_S^2}{n_{Ref}^2} \Phi_L^{Ref} \tag{1}$$

where I_L, the emission intensity, was calculated from the spectrum area $\int I(\lambda) d\lambda$, OD represents the optical density at the excitation wavelength and n the optical density of each solvent. The superscripts "S" and "Ref" refer to the sample and to the standard, respectively.

The luminescence lifetime of the complexes were performed after irradiation at $\lambda = 400$ nm obtained by the second harmonic of Titanium: Sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB). The Fluotime 200 from AMS technologies is used for decay acquisition. It consist of a GaAs microchannel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single photon counting system from picoquant

(PicoHarp300). The ultimated time resolution of the system was close to 30 ps. These measurements were recorded using the technical support from the chemistry platform "NanoBio campus" in Grenoble (France).

The effect of the metal cations upon the fluorescence intensity was examined by adding a few μl of stock solution of the metal cations to a known volume of the polymer solution (3 ml). The addition was limited to 0.08 ml so that the dilution remains insignificant [12].

The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^{1}H and ^{13}C, respectively using a dual 5 mm probe head. The measurements were carried out in CDCl$_3$ solution at ambient temperature. The chemical shift was referenced to tetramethylsilane (TMS), standard experiments with 30° pulses, 1 s relaxation delays, 16k time domain points, zero-filled to 64k for protons and 32k for carbons were performed. The distortionless enhancement by polarisation transfer (DEPT) spectra were recorded under the same conditions as the ^{13}C NMR spectra and $\tau = (2 \ ^1J_{CH})^{-1} = 3.45 \ \mu s$ was used. The 2D ^{1}H/^{1}H correlated spectra (COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, size 1k × 1k. The 2D ^{1}H/^{13}C heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for ^{1}H and 9000 Hz for ^{13}C, relaxation delay 1.5 s, FT size 1k × 256 W.

The molecular weights were determined on a GPC Waters 244 apparatus equipped with a combination of 100A, 1000A, 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.

3. Results and discussion

3.1. Polymer characteristics

The presence of a covalent bond between the units of the monomeric dyes B1 and B2 and the polymer chain has been proved by UV–vis spectroscopy methods and by GPC techniques.

The molecular characteristics of the copolymers obtained by GPC are listed in Table 1. The molecular weight and molecular weight distribution confirm the formation of high molecular weight polymers. The molecular weights are at $M_w = 9.60 \times 10^4$ and 8.94×10^4 and $M_n = 4.95 \times 10^4$ and 4.73×10^4 for Poly(St-co-BD1) and Poly(St-co-BD2), respectively. The double detection shows close values for the elution time in both chromatograms indicating the presence of copolymers which absorb at about 426 nm. The polydispersity M_w/M_n is in the region 1.89 and 1.94. It is seen that the chemical structure of benzanthron dyes does not influence the molecular weight polymer characteristics.

The UV–vis absorption spectra of the precipitated polymers have absorption maxima similar to those of the monomeric dyes, showing that the basic chromophore of the dye does not change, neither during the polymerization, nor as a result of its bonding to the polymer chain (Fig. 1). This fact allows to use the standard curve method when determining the percentage of the dye bonded chemically to the polymer chain. It has been found that 0.80% of dye B1 and 0.84% of dye B2 are chemically bonded to the main polymer chain. Considering that the values are obtained for repeatedly precipitated
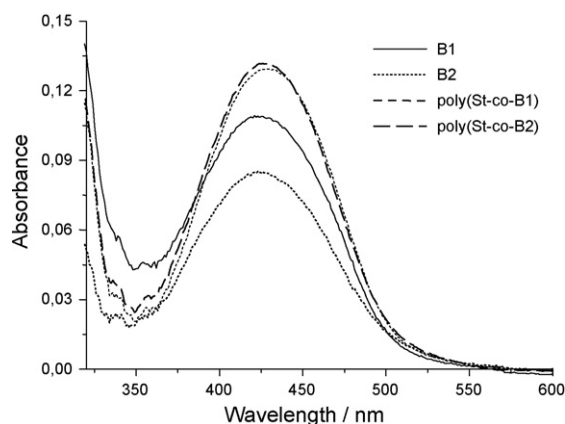

Fig. 1. Absorption spectra of benzanthron derivatives B1 and B2 and poly(St-co-B) in CH$_3$CN.

Table 2
Photophysical characteristics of B1 in organic solvents.

Solvents	λ_A (nm)	ε	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_L
DMF	438	10,600	541	4346	0.75
Acetonitrile	426	10,100	541	4990	0.75
Acetone	432	12,300	534	4422	0.81
Methanol	432	8,200	577	5817	0.27
THF	433	11,100	526	4083	0.98
Chloroform	438	10,900	537	4209	0.83
Toluene	437	10,700	517	3593	0.99
Propanol-2	433	10,900	559	5206	0.39
Diethyl ether	426	13,800	513	3981	0.95

polymers where low molecular fractions have been removed during precipitation, the results are rather satisfactory and imply that the dyes are suitable for the production of coloured fluorescent copolymers.

3.2. Photophysical characteristics of the dilute solution of compounds in organic solvents

The electron donor acceptor interaction of the chromophoric systems of 3-substituted benzanthron derivatives occurs between the electron donating groups at C-3 position and the electron accepting carbonyl group [12]. In the absorption spectra of this compounds the long wave band in the visible region has a charge transfer character due to a $\pi \rightarrow \pi^*$ electron transfer.

The photophysical characteristics of B1 and B2 dyes in organic solvent with different polarity have been investigated. The absorption (λ_A) and fluorescence (λ_F) maxima, the molecular extinction coefficient (ε), the Stockes shift ($\nu_A - \nu_F$), and the quantum fluorescence yield (Φ_L) are presented in Tables 2 and 3.

The main chromophoric system of B1 and B2 is 3-aminobenzanthron. The absorption of 3-aminobenzanthron in the visible region is very sensitive to solvent polarity and the $S_0 \rightarrow S_1$ transition presents a charge transfer character due to an electron donor–acceptor interaction between its electron accepting carbonyl group and the electron donating groups in the C-3 position of the chromophoric system [6a,8]. Compared to the band assigned to the initial 3-aminobenzantron the visible absorption one is hypsochromically shifted. The absorption band depends

Table 1
Molecular and spectral characteristics of the poly(St-co-B).

	M_w (×10^{-4})	M_n (×10^{-4})	M_w/M_n	λ_A (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_L
Poly(St-co-B1)	9.60	4.95	1.94	428	545	5015	0.52
Poly(St-co-B2)	8.94	4.73	1.89	426	542	5023	0.50

Table 3
Photophysical characteristics of B2 in organic solvents.

Solvents	λ_A (nm)	ε	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_L
DMF	435	6600	539	4435	0.69
Acetonitrile	432	8500	541	4990	0.78
Acetone	435	9300	532	4192	0.66
Methanol	432	5000	573	5696	0.31
THF	436	7300	526	3924	0.98
Chloroform	435	6100	537	4366	0.98
Toluene	435	6200	513	3495	0.99
Propanol-2	436	4900	557	4982	0.53
Diethyl ether	427	6500	512	3888	0.95

slightly on the substituent at the C-3 position. Aminobenzanthron has a strong electron donating primary group, replacement of the amino group by other subsituent decreases the electron donating ability of the nitrogen atom. Attachment of an electron accepting triazine moiety leads to the competition between this subsituent and the electron accepting carbonyl group. These changes result into a decrease of the charge transfer ability, to a decrease of the dipole transition moment of the molecule and to a hypsochromic shift of the absorption maximum.

Contrary to 3-amino benzanthron [12] the absorption maxima of B1 and B2 are not dependant on solvent polarity as can be seen from Fig. 2.

The low sensitivity of the longest wavelength absorption band of the benzanthron derivatives to solvent polarity could be explained, by a decrease of the charge transfer character of the $S_0 \rightarrow S_1$ transition. Fluorescent emission behaviour is different. The principal wavelength emission band is slightly shifted to longer wavelength with increasing solvent polarity. The effect of solvent polarity on the location of the longest wavelength emission band of benzanthron derivatives indicates that the molecular dipole moment changes on excitation. These results confirm a conformational change in the singlet excited state S_1 upon excitation of S_0. A similar result has been achieved with different benzanthron derivatives [13,14].

The ability of the dye molecule to emit the absorbed light energy is quantitatively characterized by the fluorescence quantum yield (Φ_L), which has been estimated from the absorption and fluorescence spectra. As seen from the data in Tables 2 and 3, the quantum yields of the monomeric benzanthron dyes B1 and B2 depend on the polarity of organic solvents. The quantum yields for B1 are between $\Phi_L = 0.27$ and $\Phi_L = 0.99$. The respective values for B2 are in the range $\Phi_L = 0.39$–0.98. The quantum yield is considerably higher in non-polar solvents. In protic solvents the dyes exhibit weaker emission. This variation arises from the solvent dependence of the nonradiative rate constant [14] or by the possibility for the formation of hydrogen bonds. The hydrogen bonds between the hydroxyl groups
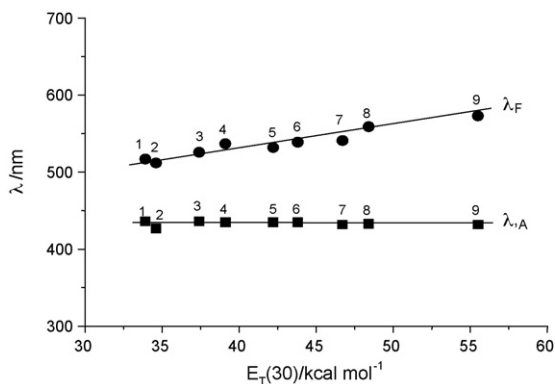

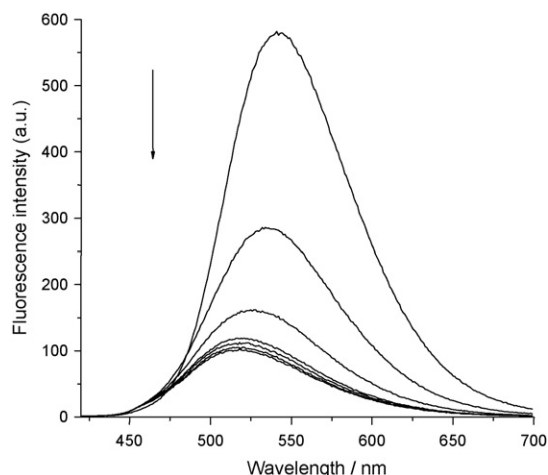**Fig. 2.** Absorption (■) and fluorescence (●) maxima of B1 dye as a function of the solvent polarity parameter E_T (30).

Fig. 3. Fluorescence spectra of B1 before and after addition of equivalents of Cu^{2+} in CH$_3$CN.

from the alcohols and carboxylic oxygen atom (C=O) from the benzantron system occur in the hydroxylated alcohol solutions. These H-bonds favour radiationless transition, causing a decrease of the fluorescence quantum yield of B1 and B2 The fluorescence spectra of both monomeric and high molecular weight benzanthrons are a mirror image of their absorption spectra in the visible region. The Stokes shift is a parameter that indicates the difference in the properties and structure of the ground state (S_0) and the first excited singlet state (S_1) of the chromophore systems. The Stokes shift has a relatively high value, probably, due to conformational changes or to a redistribution of electron density upon excitation. The values obtained are in agreement with those for similar compounds in the literature [6a,13]. The larger Stokes shift indicates a conformational change in the singlet excited state S_1.

Concerning the copolymers, the visible absorption spectrum is similar to the one observed for the monomeric benzanthron dyes B1 and B2 (Table 1). Their intense bands are centred to 428 nm for poly(St-co-B1) and 426 nm for poly(St-co-B2). The emission spectra of the two copolymers are similar to that obtained for B1 and B2 molecules, whereas the quantum yields are lower. These results show that there are other ways to deactivate the singlet excited state in a polymer. Radiationless deactivations are favoured in polymer structure.

3.3. Influence of metal cations on the photophysical properties

In order to estimate the potential of B1 and B2 as luminescent chemosensors, we performed titration experiments with different transition metal ions (Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Cu^{2+}). The absorption and emission spectra were recorded upon addition of these transition metal ions to the benzanthron dyes B1 and B2 in acetonitrile solution.

The addition of Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, does not affect the fluorescence of both B1 and B2 benzanthron derivatives. Such behaviour could be explained in two ways: either by the fact that these species do not complex benzanthron derivatives or assuming that the benzanthron derivative does not modify the spectral properties of dyes upon their complexation. On the contrary, the addition of Cu^{2+} causes strong decrease of the fluorescence intensity and a gradual blue shift of the fluorescence maximum as shown in Fig. 3.

The quenching of luminescence is not complete even if a large excess of Cu^{2+} is added. A residual fluorescence at 525 nm can be observed after the addition of 15 equivalents. The ability of Cu^{2+} to quench the fluorescence of the benzanthron derivative

can be explained on the basis of electron or energy transfer processes involving the benzanthron excited state and the metal ion (Scheme 2).

To clarify this behaviour we performed competition experiments. The addition of the metal ions (Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+}) to a solution of B1 and Cu^{2+} (or B2 and Cu^{2+}) did not lead to any recovery of the fluorescence, showing that they did not interfere in any way with the copper complex formation. The selectivity of B1 and B2 derivatives towards Cu^{2+} did not depend on the size of the metal ion but can be related to its redox potential. Compared to other metal ions the copper one is easily reducible, favouring an electron donor–acceptor interaction.

The metal complex with Cu^{2+} ions is accompanied by a quenching of the fluorescent excited state of the benzanthron unit and a gradual blue shift $\Delta\lambda_F = 23$ nm. Such behaviour could be interpreted in three different ways: (i) a fraction of benzanthron remain free and the residual fluorescence is due to the free benzanthron derivative (B1 or B2), (ii) a fraction of benzanthron remain free and the residual fluorescence is the sum of the fluorescence of the complexe ([B1Cu^{2+}] or [B2Cu^{2+}]) and of the free benzanthron derivative (B1 or B2) and (iii) if all the benzanthron derivatives are involved in a complex formation, the fluorescence is due to benzanthron in the complex ([B1Cu^{2+}] or [B2Cu^{2+}]) (the fluorescence is only partly quenched).

In order to interpret the results of steady-state emission, the fluorescence lifetime of the compound B1 and B2 have been measured in the absence and in the presence of metal ions (Fig. 4).

In the absence of a metal ion, the fluorescence decay of B1 can be fitted with a single exponential ($\tau_1 = 8.9$ ns). The addition of a metal ion leads to a change in the fluorescence decay. In this case, the fluorescence decay is fitted with a double exponential model yielding two lifetimes, ($\tau_1 = 8.9$ ns and $\tau_2 = 2.9$ ns). These two lifetimes remain unvaried during titration while their relative weight changes in favour of the shorter one (Table 4). Similar results have been obtained for B2 with $\tau_1 = 8.7$ ns and $\tau_2 = 2.6$ ns.

Such lifetimes are coherent with two limit situations: in the first one, the benzanthron derivative is free while in the second the benzanthron derivative is interacting strongly with metal ions. The pre-exponential terms obtained by fitting the decay curve are in agreement with that obtained for steady-state emission experiments, indicating that a quenching process occurs.

It comes out that the fluorescence lifetime of B1 is $\tau_1 = 8.9$ ns and the fluorescence of B1 in the complex is $\tau_2 = 2.9$ ns and
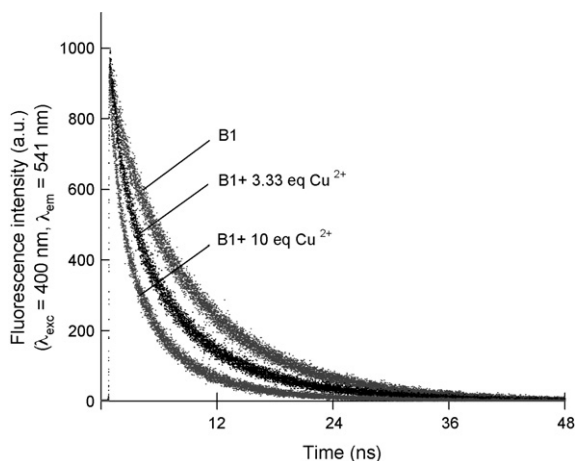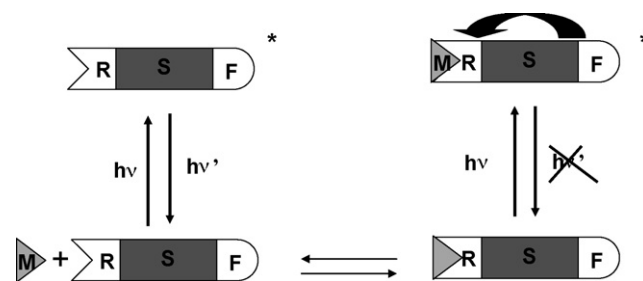
Table 4
Relative weight of pre-exponential terms determined to the curve fitting equation: $I(t) = \alpha e_1^{-kt} + \beta e_2^{-kt}$ with $k_1 = 1/\tau_1$ and $k_2 = 1/\tau_2$.

| Equivalent of Cu^{2+}	α (%)	β (%)
0	100	0
3.33	49	51
6.66	28	72
10	20	80
13.33	20	80
16.66	20	80

Scheme 3. Schematic process of fluorescence quenching.

that a fraction of benzanthron derivative remains free even after the addition of an excess of metal ions. The residual steady-state fluorescence is the sum of the free benzanthron derivative (B1, $\tau_1 = 8.9$ ns) and of the fluorescence of benzanthron in the complexe ([B1Cu^{2+}], $\tau_2 = 2.9$ ns). The spectroscopic properties of [B1Cu^{2+}] have been determined using the deconvolution of the fluorescence spectra and the excitation spectra (Scheme 4).

Scheme 3 presents the fluorescent spectroscopic properties of the dyes in the presence and absence of metal ions. The partial positive charge generated by the cation leads to a cation-induced blue shift of the absorption and fluorescence spectra as described by Prasanna de Silva et al. [7a]. It is worth noting that the addition of an excess of the metal ions (Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}) to a solution of B1 does not lead any change in fluorescence lifetime, the fluorescence decay remains monoexponential with a fluorescence lifetime of $\tau_1 = 8.9$ ns. Taking into account the pre-exponential terms the complexation constant of Cu^{2+} with B1 can be estimated about $4 \times 10^4 \pm 10\%$.

The effect of metal cation on the fluorescent intensity for the polymer was also investigated. In polymer, fluorescence is not quenched by the addition of metal ion. The fluorescence poly(St-co-B1) and poly(St-co-B2) lifetime have been measured in the absence and in the presence of metal ions. The fluorescence decay is monoexponential. As expected, the fluorescence lifetime (respectively 8.1 and 7.9 ns for poly(St-co-B1) and poly(St-co-B2)) and the pre-exponential term remain unchanged even after addition of copper. This result confirms the noncomplexation of Cu^{2+} by poly(St-co-B1) or poly(St-co-B2) which is probably not accessible in the polymer matrix. Probably, in this case the rigidity and the density of the macromolecules are higher, and metal cations are unable to form an

Fig. 4. Emission decay of B1 before and after addition of 0.33 and 10 equivalents of Cu^{2+} in CH_3CN.
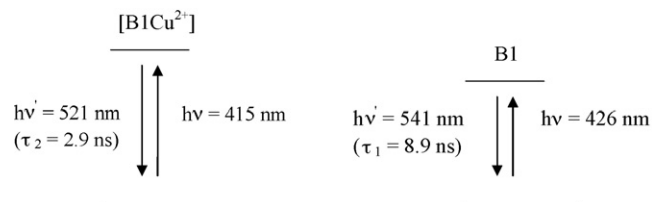
Scheme 4. Schematic presentation of the fluorescent spectroscopic properties of B1.

intramolecular chelation with the nitrogen atoms from the amino group of B1 or B2.

4. Conclusions

In this work the synthesis of two new polymerizable benzanthron derivatives and their photophysical characteristics in different media have been described. The effect of various metal cations (Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Cu^{2+}) upon the fluorescent intensity has been studied in acetonitrile solution. A specific interaction appears with Cu^{2+} compared to the other metallic ions probably due to the more oxidative potential value of Cu^{2+}. This interaction leads to a decrease of the fluorescence intensity for both benzanthron derivatives (B1 and B2). These properties allow their use as monomeric fluorescent sensor in the synthesis of high molecular weight sensors. The new polymeric sensors based on the new compounds emit yellow-orange fluorescence as the monomeric benzanthron derivatives. The metal cations do not produce the expected effect upon the fluorescence response of the newly synthesized copolymers.

Acknowledgement

References

[1] I. Grabchev, I. Moneva, E. Wolarz, D. Bauman, S. Stoyanov, Z. Naturforsch. 56a (3) (2001) 289–395.
[2] T. Konstantinova, P. Meallier, H. Konstantinov, D. Staneva, Polym. Degrad. Stabil. 48 (1995) 161.
[3] F.M. Carlini, C. Paffoni, G. Boffa, Dyes Pigments 3 (1982) 59–69.
[4] (a) N. Ayangar, R. Lahoti, R. Wagle, Indian J. Chem. 16B (1973) 106–108;
    (b) I. Grabchev, I. Moneva, R. Betcheva, G. Elyashevich, Mater. Res. Innovations 6 (2002) 34.
[5] O. Hrolova, N. Kunavin, I. Komlev, M. Tavrizova, S. Trofimova, V. Madii, J. Appl. Spectrosc. 41 (1984) 53–57.
[6] (a) I. Grabchev, I. Moneva, Dyes Pigments 38 (1998) 155–164;
    (b) I. Grabchev, V. Bojnov, I. Moneva, Dyes Pigments 48 (2001) 143.
[7] (a) A. Prasanna de Silva, H.Q. Nimal Gunaratne, T. Gunnlaugson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515;
    (b) K. Rurack, Spectrochem. Acta Part A 57 (2001) 2161;
    (c) A.P. de Silva, B. McCaughan, B.O.F. McKiney, M. Querol, Dalton Trans. (2003) 1902.
[8] (a) D. Staneva, R. Betcheva, J.-M. Chovelon, J. Photochem. Photobiol. A: Chem. 183 (2006) 159–164;
    (b) D. Staneva, R. Betcheva, Dyes Pigments 74 (2007) 148;
    (c) D. Staneva, R. Betcheva, J.-M. Chovelon, J. Appl. Polym. Sci. (2007).
[9] B. Adhikari, S. Majumdar, Prog. Polym. Sci. 29 (2004) 699.
[10] T. Konstantinova, I. Grabchev, Bulg. Chem. Commun. 28 (1995) 74–79.
[11] I. Grabchev, V. Bojinov, I. Moneva, J. Mol. Struct. 471 (1998) 19–25.
[12] B. Ramachamdram, G. Saroja, N.B. Sankaran, A. Samanta, J. Phys. Chem. B 104 (2000) 11824.
[13] M. Nepras, O. Machalicky, M. Seps, R. Hrdina, P. Kapusta, V. Filder, Dyes Pigments 35 (1997) 31.
[14] P. Kapusta, O. Machalicky, R. Hrdina, M. Nepras, M.B. Zimmt, V. Filder, J. Phys. Chem. 107 (2003) 9740.