Dyes and Pigments 92 (2012) 1126–1131

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis, absorption and fluorescence properties of *N*-triazinyl derivatives of 2-aminoanthracene

M. El-Sedik[a], N. Almonasy[a,*], M. Nepraš[a], F. Bureš[a], M. Dvořák[b], M. Michl[b], J. Čermák[c], R. Hrdina[a]

[a] Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic
[b] Department of Physical Electronics, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, v Holešovičkách 2, CZ-180 00 Prague, Czech Republic
[c] Research Institute for Organic Syntheses, Rybitví 296, CZ-533 54 Pardubice 20, Czech Republic

ARTICLE INFO

Article history:
Received 17 May 2011
Received in revised form
25 August 2011
Accepted 27 August 2011
Available online 12 September 2011

Keywords:
2-aminoanthracene
Synthesis
N-derivatives
UV/Vis spectra
Fluorescence quantum yield
Fluorescence quenching

ABSTRACT

N-(4,6-dichloro-1,3,5-triazin-2-yl)-2-aminoanthracene was synthesized by substitution of one chlorine atom of 2,4,6-trichloro-1,3,5-triazine with 2-aminoanthracene. A new series of *N*-triazinyl-2-aminoanthracenes was prepared by nucleophilic substitution of one or both chlorine atoms on *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-2-aminoanthracene with electron-donating methoxy or phenylamino groups. The UV/Vis absorption, fluorescence and excitation spectra as well as the fluorescence quantum yields of the prepared compounds were measured in 1,4-dioxane, ethyl acetate, dibutyl ether and acetonitrile; nanosecond kinetics of the fluorescence decay was measured in different solvents. The influence of the character of the substituent on triazinyl ring and of the solvent polarity upon the absorption and fluorescence spectra and fluorescence quantum yields are discussed.

1. Introduction

The ideal bichromophoric compound consists from two chromophores separated and at the same time electronically decoupled by a molecular unit (spacer). Thus, the absorption spectrum of the bichromophoric system should consist from the absorption spectra of individual chromophores. In molecular systems with different chromophores, the excitation energy localized (at least temporarily) on one chromophore may be transferred to another chromophore. This process is known as the excitation (or electronic) energy transfer (EET) and was first described by Foerster [1]. The manifestation of EET is a more or less complete quenching of fluorescence of the donor chromophore and the appearance of fluorescence of the acceptor chromophore. The influence of molecular structure of chromophores and spacers on EET has been an area of recent great interest, inspired by biology and optoelectronics, e.g. [2]. We have investigated the synthesis, UV/Vis absorption and fluorescence spectra and photo-physical properties of bi- and trichromophoric systems consisting from 1-aminopyrene, and 3-aminobenzanthrone as the chromophores and s-triazinyl ring as the spacer [3]. A better understanding of interesting features of EET in these systems needed study of the potential role of photo-physical characteristics of corresponding molecular subsystems, i.e. of the *N*-triazinyl derivatives of the aminochromophores.

During the past several years, we have investigated the synthesis, UV/Vis absorption and fluorescence spectra and photo-physical properties of *N*-triazinyl derivatives of 1- and 2-aminopyrenes [4], and 3-aminoperylene [5]. We have found that the number of chlorine atoms on the triazinyl ring and the solvent polarity are the most significant factors affecting the fluorescence quantum yield (q_F) of the studied compounds. The gradual replacement of chlorine atoms with electron-donating groups (methoxy or phenylamino groups) leads to increasing of q_F. This effect was observed for all studied compounds. Recently, we have explained this phenomenon by semi-empirical quantum chemical calculations of *N*-triazinyl derivatives of L-aminopyrene [6]. As the chlorine atoms increase the withdrawing character of the triazinyl ring and by its electronegativity, new strong polar excited states (CT states) accompanied with a transfer of π-electrons from the aminopyrene moiety to the triazinyl ring were revealed. Owing to a solvent relaxation, the energy of these CT states could decrease close or even below an emitting S_1 state and thus open a new nonradiative deactivation channel.

* Corresponding author. Tel.: +420 466 038 500; fax: +420 466 038 004.
E-mail address: numan.almonasy@upce.cz (N. Almonasy).

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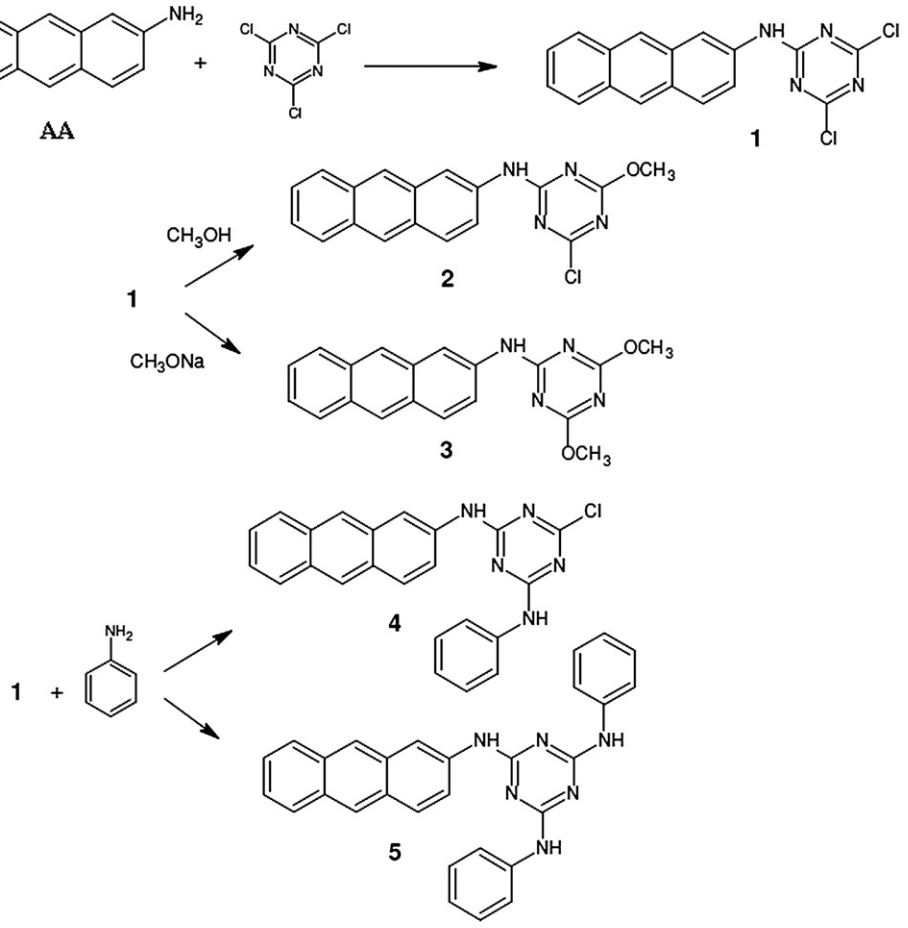
doi:10.1016/j.dyepig.2011.08.018



Scheme 1.

Herein, to confirm the common validity of this model, we present the synthesis of new 2-aminoanthracene-derived *N*-triazines. The influence of the chromophore structure and the solvent effects on the absorption and fluorescence spectra, the fluorescence lifetime and the fluorescence quantum yield were studied. The obtained results will be important for the study of EET in bi- and trichromophoric systems with 2-aminoanthracene chromophore, the synthesis of that is now in progress in our laboratory.

2. Experimental

2.1. General

Cyanuric chloride, 2-aminoanthracene (AA), aniline, methanol and other solvents were used as received without further purification. Sodium methanolate was prepared according to the literature procedure [7]. The course of the reactions and purity of the substances were checked by TLC, HPLC, and by comparison of fluorescence excitation spectra with absorption spectra of the final products. The melting points of the synthesized compounds were determined on a Buchi 510 melting point apparatus.

The samples for absorption spectra and fluorescence measurements were prepared by preparative TLC on Silufol UV 254 plates. All the solvents used were of spectroscopic grade and were checked for their own fluorescence.

The absorption spectra were measured on a UV/Vis Perkin–Elmer Lambda 35 spectrophotometer at room temperature. The steady-state fluorescence spectra were measured on a Hitachi Perkin–Elmer LS 55 spectrophotometer. The instrument provides corrected excitation spectra directly; the fluorescence spectra were corrected for the characteristics of the emission monochromator and for the detection photomultiplier response. For fluorescence measurements, very weakly absorbing solutions (optical density ~ 0.05 at the exciting wavelength in 1-cm cell) were used. The fluorescence quantum yields (q_F) were measured using quinine

Table 1
Absorption (λ_A) and fluorescence (λ_F) maxima (nm) and fluorescence quantum yields (q_F).

NO	Dibutylether			Dioxan			Ethylacetate			Acetonitril		
	λ_A[a]	λ_F	q_F	λ_A[a]	λ_F	q_F	λ_A[a]	λ_F	q_F	λ_A[a]	λ_F	q_F
1	395	–	–	396	–	–	394	–	–	398	–	–
2	396	405, 429	0.25	394	411, 432	0.25	398	409, 430	0.12	397	410, 431	0.03
3	398	411, 435	0.39	394	415, 435	0.45	395	414, 432	0.26	395	414, 431	0.37
4	398	412, 430	0.35	398	415, 436	0.42	396	413, 433	0.23	397	418, 432	0.18
5	402	420, 441	0.41	402	424, 442	0.62	402	424, 440	0.30	401	425, 441	0.43

[a] λ_A corresponds to the maximum of the first long-wavelength vibronic band.

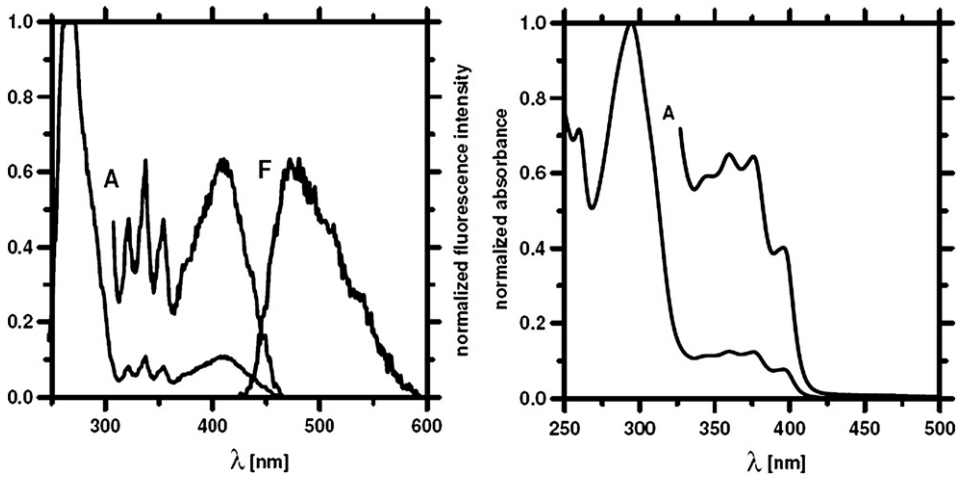


Fig. 1. Absorption (A) and fluorescence (F) spectra of AA (left) and absorption spectrum of **1** (right) in 1,4-dioxane.

sulphate (q_F = 0.54 in 0.5 mol/L H_2SO_4) [8] as the standard. Deaeration of the samples by bubbling with N_2 did not change the spectra and q_F; therefore, the data presented here correspond to aerated solutions.

The fluorescence kinetics was performed on an Edinburgh Analytical Instruments FS/FL spectrophotometer that employs time-correlated single photon counting (TCSPC) detection. Pulse diode IBH Nanoled-03 (370 nm ns LED) was used as the excitation source to excite the set of studied compounds near the centre of the absorption band. Instrument response function FWHM was <1.5 ns. The fluorescence signal was recorded at 450 nm at the maximum of the fluorescence band. The fluorescence lifetimes were obtained by multiexponential reconvolution fitting process.

The chemical structures were confirmed by MS, ^{1}H and ^{13}C NMR spectra and elemental analysis.

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively, with a Bruker AVANCE 400 instrument at 25 °C. Chemical shifts are reported in ppm relative to the signal of Me_4Si. The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference (DMSO-d_6 – 2.55 and 39.51 ppm). Apparent resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet) and m (multiplet).

Mass spectra were acquired on a LC/MS system LC-MSD TRAP XCT Plus (Agilent Technologies, USA) using direct infusion measurement. Negative and positive-ion APCI mass spectra were recorded in mass range 50–1500 Da. The ion trap analyzer was tuned to obtain an optimal response in the range of expected m/z values. Other APCI ion source parameters were as follows: a drying gas flow of 7 l min^{-1}, a nebulizer gas pressure of 60 psi and drying gas temperature 350 °C. The samples were dissolved in acetonitrile for HPLC (Sigma–Aldrich) at appropriate concentrations for MS identification.

The synthesis of target compounds **1**–**5** is shown in Scheme 1.

*2.1.1. N-(4,6-dichloro-1,3,5-triazin-2-yl)-2-aminoanthracene (**1**)*

Cyanuric chloride (1.8 g, 9.8 mmol) and $NaHCO_3$ (0.5 g) were dissolved in acetone (100 mL). The solution was cooled to 0–5 °C in an ice bath. Subsequently 2-aminoanthracene (2 g, 10.03 mmol) in 10 ml of acetone was added dropwise. The reaction mixture was stirred at 0–10 °C and the reaction course was monitored by TLC until the 2-aminoanthracene spot had completely disappeared. After 3 h, the product was isolated by filtration, washed with water and dried to obtain 1 g of **1** in 29% yield; m.p 219–221 °C. MS: (APCI$^+$): m/z 341 $[M + H]^+$ (M.W. 340 g/mol). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.52–7.58 (m, 2H,), 7.74 (d, 1H, J = 9.2 Hz), 8.10–8.17 (m, 3H), 8.41 (s, 1H), 8.57 (d, 2H, J = 10.0 Hz), 11.46 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 117.26, 121.77, 125.41, 125.59, 125.84, 126.03, 127.84, 128.08, 128.84, 129.00, 130.89, 130.99, 131.75, 134.05, 163.96, 168. Anal. calcd. for $C_{17}H_{10}Cl_2N_4$: C (59.84%) H (2.95%) Cl (20.78%) N (16.42%); found: C (59.79%) H (2.81%) Cl (20.74%) N (16.36%).

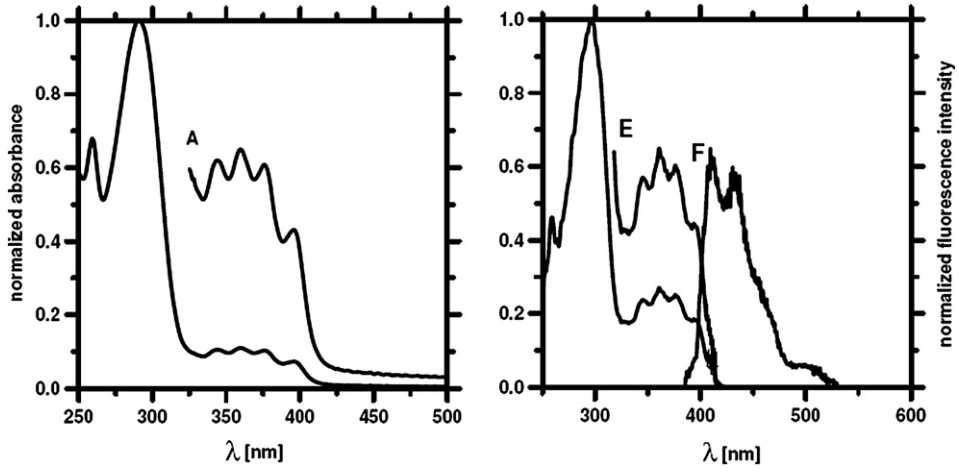


Fig. 2. Absorption (A), excitation (E) and fluorescence (F) spectra of **2** in 1,4-dioxane.

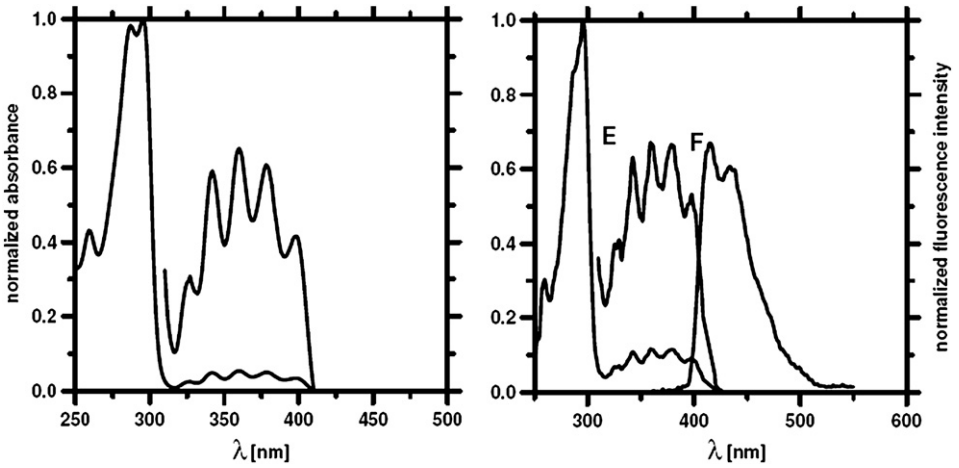


Fig. 3. Absorption (A), excitation (E) and fluorescence (F) spectra of **3** in 1,4-dioxane.

*2.1.2. N-(4-chloro-6-methoxy-1,3,5-triazin-2-yl)-2-aminoanthrace-ne (**2**)*

Compound **1** (0.5 g, 1.5 mmol) was dissolved in a mixture of methyl alcohol (5 mL) and DMF (10 mL) whereupon $NaHCO_3$ (0.5 g) was added. The reaction mixture was stirred at room temperature for 1 h, was diluted with water (30 ml) and the product was filtered off to obtain 0.2 g (59% yield) of **2**, m. p 222–225 °C. MS: ($APCI^-$): *m/z* 335 $[M - H]^-$ (M.W. 336 g/mol). ^1H NMR (DMSO-d_6, 400 MHz): $\delta = 4.09$ (s, 3H), 7.49–7.55 (m, 2H), 7.75 (d, 1H, $J = 8.8$ Hz), 8.08–8.11 (m, 3H), 8.48–8.59 (m, 3H), 10.98 (br s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 55.56$, 115.98, 121.68, 125.14, 125.34, 125.71, 125.89, 127.74, 128.07, 128.58, 128.75, 130.67, 131.33, 131.74, 135.01, 164.88, 169.47, 171.08. Anal. calcd. for $C_{18}H_{13}Cl\ N_4O$: C (64.19%) H (3.89%) Cl (10.53%) N (16.64%) O (4.75%); found: C (64.14%) H (3.84%) Cl (10.48%) N (16.58%) O (4.69%).

*2.1.3. N-(4,6-dimethoxy-1,3,5-triazin-2-yl)-2-aminoanthracene (**3**)*

A mixture of methyl alcohol (5 mL) and sodium methanolate (10 mL) were added to compound **1** (0.5 g, 1.5 mmol). The reaction mixture was refluxed for 2 h, was diluted with water (50 mL) and the product was filtered off to obtain 0.35 g of **3** in 70% yield. m. p 206–208 °C. MS: ($APCI^-$): *m/z* 331 $[M - H]^-$ (M.W. 332 g/mol). ^1H NMR (DMSO-d_6, 400 MHz): $\delta = 4.02$ (s, 6H), 7.47–7.54 (m, 2H), 7.79 (d, 1H, $J = 8.8$ Hz), 8.07 (d, 3H, $J = 8.8$ Hz), 8.50 (d, 2H, $J = 13.2$ Hz), 8.65 (s, 1H), 10.44 (br s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 54.64$, 115.11, 122.03, 124.93, 125.03, 125.62, 125.81, 127.71, 128.09, 128.40, 128.53, 130.46, 131.64, 131.75, 136.04, 166.20, 172.14. Anal. calcd. for $C_{19}H_{16}\ N_4O_2$: C (68.66%) H (4.85%) N (16.86%) O (9.63%); found: C (68.63%) H (4.98%) N (16.90%) O (9.67%).

*2.1.4. N-(4-chloro-6-anilino-1,3,5-triazin-2-yl)-2-aminoanthracene (**4**)*

Aniline (1.6 mL, 17.2 mmol) was added dropwise with stirring to a mixture of **1** (0.7 g, 2.1 mmol), acetone (50 mL) and $NaHCO_3$ (0.5 g). The reaction mixture was stirred at 60 °C for 2 h, diluted with water (50 mL) and the product was filtered off to obtain 0.5 g of **4** in 61% yield; m. $p > 300$ °C. MS: ($APCI^+$): *m/z* 398 $[M + H]^+$ (M.W. 397 g/mol). ^1H NMR (DMSO-d_6, 400 MHz): $\delta = 7.19$–7.30 (m, 1H,), 7.39–7.58 (m, 4H), 7.62–7.80 (m, 3H), 8.10 (d, 3H, $J = 8.4$ Hz), 8.29 (br s, 1H), 8.55 (s, 2H), 10.43 (br s, 1H), 10.62 (br s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta = 115.77$, 121.97, 122.14, 124.17, 124.92, 125.09, 125.82, 125.94, 127.71, 128.15, 128.53, 128.62, 128.80, 130.54, 131.55, 131.69, 135.42, 138.30, 164.06, 164.22, 168.16. Anal. calcd. for $C_{23}H_{16}Cl\ N_5$: C (69.43%) H (4.05%) Cl (8.91%) N (17.60%); found: C (69.39%) H (4.08%) Cl (8.97%) N (17.66%).

*2.1.5. N-(4,6-dianilino-1,3,5-triazin-2-yl)-2-aminoanthracene (**5**)*

A mixture of acetone (50 mL), compound **1** (0.7 g, 2.1 mmol), aniline (3.2 mL, 34.4 mmol) and $NaHCO_3$ (0.5 g) was placed in

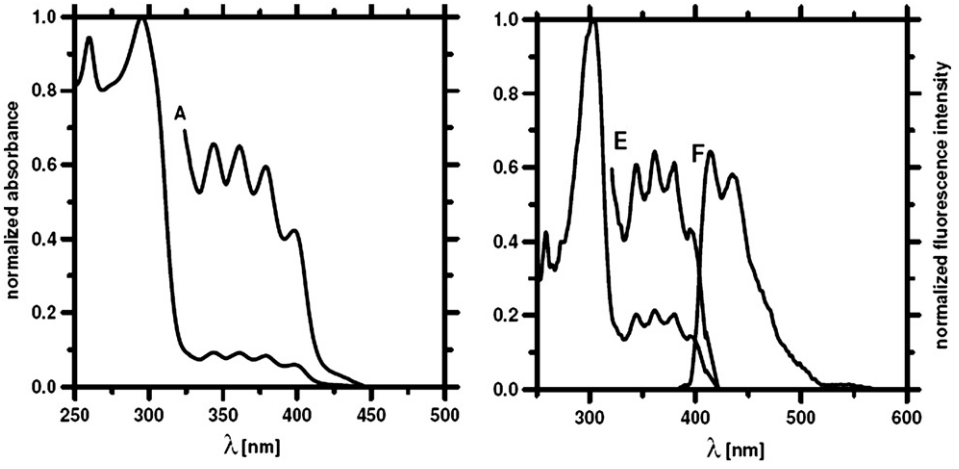


Fig. 4. Absorption (A), excitation (E) and fluorescence (F) spectra of **4** in 1,4-dioxane.

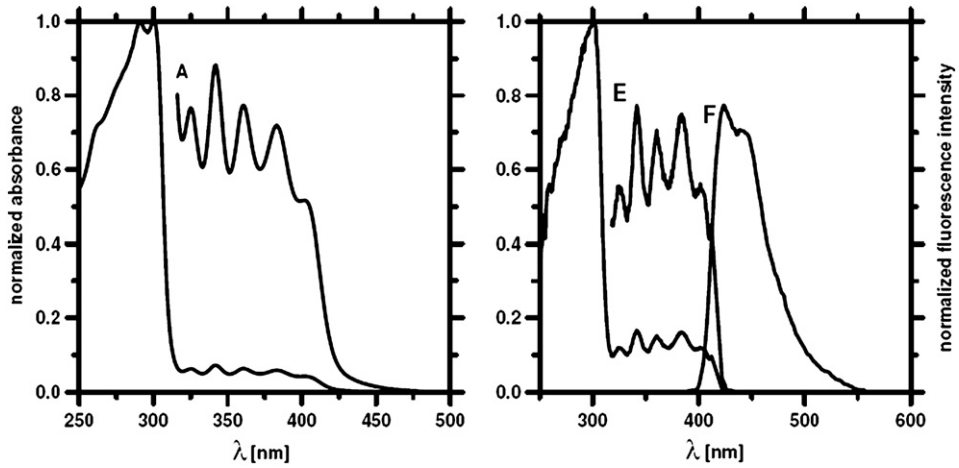


Fig. 5. Absorption (A), excitation (E) and fluorescence (F) spectra of **5** in 1,4-dioxane.

a 100 mL Parr autoclave under autogenous pressure. The vessel was sealed and heated to 140 °C in an oil bath for 5 h. The reaction mixture was cooled to room temperature, diluted with water (30 mL) and the product was filtered off to obtain 0.6 g in 65% yield; m. p 235–237 °C. MS: (APCI$^+$): m/z 455 $[M + H]^+$ (M.W. 454 g/mol). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.03–7.12 (m, 2H,), 7.39 (t, 4H, J = 7.8 Hz), 7.47–7.56 (m, 2H), 7.85–7.93 (m, 5H), 8.08 (t, 3H, J = 7.4 Hz), 8.42 (br s, 1H), 8.52 (s, 1H), 8.82 (br s, 1H), 9.42 (br s, 2H), 9.63 (br s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 114.21, 120.61, 122.25, 122.53, 124.53, 124.66, 125.62, 125.75, 127.56, 128.22, 128.24, 128.49, 128.83, 130.18, 131.64, 132.12, 137.03, 139.94, 164.21, 164.29. Anal. calcd. for $C_{29}H_{22}N_6$: C (76.63%) H (4.88%) N (18.49%); found: C (76.59%) H (4.91%) N (18.44%).

3. Results and discussion

3.1. Synthesis

As shown in the above reaction scheme, the preparation of target compounds is based on the same principle as the previous syntheses of *N*-triazinyl derivatives of the other aromatic amines [4,5]. For instance, compound **1** was prepared by the substitution of the cyanuric chloride with 2-aminoanthracene at 0–5 °C. When the temperature exceeds +5 °C, substitution of the second chlorine atom also occurred. Hence, 2,4-di(2-anthracenylamino)-6-chloro-1,3,5-triazine was identified as the by-product. The spectral and photo-physical properties of this compound will be investigated in connection with the study of bi- and trichromophoric compounds with s-triazinyl spacer.

Because of a high reactivity, the nucleophilic substitution of the second chlorine atom on triazinyl ring by methoxy group could be performed only by methanol at room temperature. Since the solubility of compound **1** in methanol is very low, we used a mixture of methanol-dimethylformamide as the solvent system. Beside the target product **2**, a trace of compound **3** was detected by MS analysis. This compound fluoresces very intensely and could be detected by TLC as well. The crude product was simply precipitated from the reaction mixture by dilution with water, filtration and rinsing with a small amount of hot acetone.

The reaction of **1** with 2 equiv of sodium methanolate leads to substitution of both chlorine atoms of triazinyl ring yielding compound **3**. The product was isolated almost quantitatively and with a very high purity.

Treatment of **1** with a 1 mol equiv of aniline in boiling acetone for 2 h afforded compound **4**. The product was isolated and purified in similar way as described above.

The substitution of both chlorine atoms in **1** by amino phenyl group was carried out in acetone as the solvent. Under the described conditions, the reaction proceeded with a high reaction selectivity by compared to compound **3**.

3.2. Absorption and fluorescence spectra

The absorption spectrum of anthracene has been in literature many times well described and interpreted: the first absorption band (La) corresponding to HOMO → LUMO transition is formed by several vibronic bands in the region 310–380 nm. The second absorption band (Lb) corresponding to the mixture of HOMO → LUMO + 1 and HOMO − 1 → LUMO configurations is strictly forbidden and is completely overlapped by L_a band. By the substitution with amino group in position 2, an extension of π-conjugation occurs and, in the same time, the system losses the

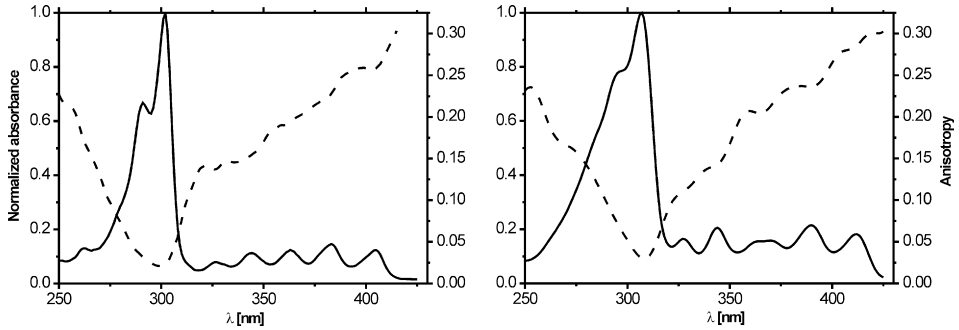


Fig. 6. Absorption (solid line) and fluorescence anisotropy (dotted line) of **3** (left) and **5** (right) in 2-MTHF at 140 K.

Table 2
Fluorescence lifetimes of the compounds in dioxan and ethyl acetate.

NO	Dioxan	Ethyl acetate
3	12.2 ns	8.2 ns
4	10.3 ns	6.6 ns
5	13.3 ns	9.0 ns

symmetry. Consequently, two absorption bands with practically the same middle intensity appear: the broad band in the region 360–440 nm (λ_{max} = 400 nm), the second band with clear-cut vibronic structure in the region 320–350 nm e.g. [9].

The substitution of hydrogen atom on amino group of 2-aminoanthracene by electron-withdrawing triazinyl group causes a decrease in conjugation of the amino $2p_\pi$ electrons with the anthracene π-system; consequently, a hypsochromic shift of the first absorption band was observed. Simultaneously, a well defined vibronic structure of the spectra of *N*-triazinyl derivatives was recorded. Neither solvent polarity nor a substituent on triazinyl ring influenced the position of the absorption maxima of *N*-triazinyl derivatives (Table 1, Figs. 1–5).

From the shape of the absorption spectra and from the character of fluorescence anisotropy for **3** and **5** in 2-methyltetrahydrofuran (2-MTHF) at 140 K in the spectral range 320–410 nm (Fig. 6), two well separated bands exhibiting a very similar clear-cut vibronic structure are evident. According to our CNDO/S calculations (WinMOPAC 2.0 Package, unpublished results) of presented compounds, both bands correspond to electronic transitions to the excited states mixed from L_b and L_a states localized on aminoantracenyl moiety; the second shorter wavelength transition shows somewhat higher character of L_a state (a higher CI coefficient of HOMO-LUMO configuration). The oscillator strength of the first transitions are 0.08 (**3**) and 0.122 (**5**), of the second ones are 0.190 (**3**) and 0.205 (**5**). A similar vibronic structure of both bands proves a significant participation of anthracene L_a state in both transitions. According to our theoretical results, the difference of transition moment directions between the first and the second transition is large (45° for **3** and 65° for **5**) and is small between the second transition and the transition corresponding to B_b, λ_{max} = 300–310 nm (15° for **3** and 4° for **5**). These results are in agreement with the decrease of anisotropy degree in the range 320–410 nm.

The fluorescence spectra of studied compounds show a vibronic structure and approximate mirror symmetry with the first absorption band. With decreasing electronegativity of triazinyl ring and with increasing the solvent polarity, the fluorescence maxima are shifted slightly bathochromically. The Stokes shifts are small ($1–2 \times 10^3$ cm^{-1}). The excitation fluorescence and absorption spectra are almost identical.

3.2.1. *Fluorescence quantum yields*

Similar to *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-1-aminopyrene [4] and *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-3-aminoperylene [5], the substitution of hydrogen atom of the amino group of 2-aminoanthracene by cyanuric chloride causes almost total fluorescence quenching of **1** in all used solvents. The substitution of one chlorine atom of compound **1** by electron-donating methoxy or phenylamino group causes a significant raising of q_F of the corresponding derivative in non polar (1,4-dioxane, DBE) and low polar (ethyl acetate) solvents; but a small increasing of q_F was found in highly polar acetonitrile for **2**. Dimethoxy and dianilino derivatives exhibit relatively high q_F in all used solvents. These dependences may result from an interplay of electronegativity of triazinyl ring (number of chlorine atoms, methoxy or phenylamino substituent) and solvent polarity and the efficiency of nonradiative subnanosecond deactivation processes (internal conversion, intersystem crossing).

Similar to *N*-triazinyl-1-aminopyrenes [6], our unpublished semi-empirical computations revealed strongly polar excited states connected with electron transition from anthracenyl moiety to triazinyl ring. Their energy decreases dramatically with the number of chlorine atoms on triazinyl ring and with increasing the solvent polarity. As a result, these CT states could influence the deactivation mechanism of the emitting excited state and consequently the fluorescence quantum yield of studied compounds.

In the same way as the fluorescence quantum yields, the fluorescence lifetimes (Table 2) decrease with increasing electron-withdrawing nature of triazinyl ring and with increasing of the solvent polarity.

To confirm a common validity of the theoretical results presented for *N*-triazinyl-1-aminopyrenes [6], i.e. the dominant role of CT states for fluorescence quenching, the detailed theoretical study of *N*-triazinyl derivatives of a series of polynuclear aromatic amines is now in progress in our laboratory.

4. Conclusion

Five new *N*-triazinyl derivatives of 2-aminoanthracene were prepared; their structure was confirmed by elemental analysis, MS and NMR spectra. The UV/Vis absorption and fluorescence spectra, fluorescence quantum yields and lifetimes were measured in four solvents. It was found that a character of a substituent on triazinyl ring and the solvent polarity do not influence the shape and the position of the absorption and fluorescence spectra. On the other hand, the character of appended *N*-substituent and the solvent polarity affect the q_F of studied compounds significantly. In the same way as for *N*-triazinyl 1-aminopyrene and 3-aminoperylene, the dichloro derivative of *N*-triazinyl 2-aminoanthracene does not fluoresce at all. The gradual substitution of chlorine atoms by electron-donating groups causes a strong increasing of q_F. We suppose that a dramatic fluorescence quenching of dichloro derivative is caused by a participation of CT states in deactivation cascade, as has been recently theoretically explained for *N*-triazinyl derivatives of 1-aminopyrene.

Acknowledgements

The financial support provided by the Czech Ministry of Education Youth and Sports (grant VZ MSMT No 0021627501).

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