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The synthesis of bi- and trichromophoric dyes bearing an *s*-triazinyl ring spacer

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ABSTRACT

An alternative procedure has been described for the syntheses of several bi- and trichromophoric compounds consisting of 1-aminopyrene and 3-aminobenzanthrone chromophoric subsystems connected by an *s*-triazinyl ring spacer. The synthetic method used, which utilises an autoclave under autogenous pressure, is suitable for the nucleophilic substitution of both chlorine atoms within the triazinyl ring by weakly basic aromatic amines. The structures of the synthesized compounds were confirmed using elemental analysis, ^{1}H NMR, and mass spectra. UV/vis absorption and fluorescence spectra and fluorescence quantum yields were measured. The dependence of fluorescence intensity and fluorescence quantum yields on solvent polarity was investigated.

1. Introduction

The ideal bichromophoric compound consists of two distinct chromophores separated by a molecular unit (spacer) that separates both chromophores in a well defined way and at the same time is electronically decoupled from both of them. Thus, the absorption spectrum of the bichromophoric system should be the superposition of the corresponding spectra of the two chromophores. However, upon electronic excitation intramolecular coupling should become non-negligible and different important photophysical processes should be induced. The structure of the system will determine which of these processes will play a key role.

In molecular systems with different chromophores, the excitation may be localized (at least temporarily) and then transferred to another chromophore. This process is known as the electronic [or excitation] energy transfer (EET) and was first described by Foerster [1]. The manifestation of EET is a strong or complete quenching of the donor fluorescence, accompanied by the corresponding appearance of the acceptor emission. At present, EET is a widely studied photophysical process that plays an important role in many light-induced processes in nature (e.g. primary steps in photosynthesis, dynamics of photochemical reactions, etc.) and technical applications (e.g. designing new non-linear optical materials for optoelectronics).

Fidler et al. [2] reported on the photo-physics of a semi-rigidly linked bichromophoric compound consisting of 1-aminopyrene and 3-aminobenzanthrone chromophoric sub-units connected by a chlorotriazinyl spacer.

The intramolecular electronic excitation energy flow was investigated in these systems. An unambiguous piece of evidence was first directly observed for an ultrafast energy transfer in a stiff bichromophore; it may be significant for further development of relevant theory.

Kapusta et al. [3] and Šoustek et al. [4] have reported on the synthesis and photo-physics of *N*-substituted 3-aminobenzanthrones and *N*-substituted 1-aminopyrenes respectively, i.e. of relevant component model compounds. These systems closely mimic the spectral and photophysical properties of acceptor and donor sub-units in this bichromophore.

Now, we present the synthesis of bi- and trichromophoric compounds consisting of 1-aminopyrene and 3-aminobenzanthrone chromophoric subsystems connected by a triazinyl ring spacer.

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2. Experimental

2.1. General

Thin-layer chromatography (TLC) was performed by a Kieselgel 60 F254 (Merck, Darmstadt, Germany). The melting points of the synthesized compounds were determined on a Büchi 510 melting point apparatus and are uncorrected. The elemental analysis was established using an EA 1108 FISONS instrument. The ^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.13 MHz in DMSO-d_6 solutions with TMS as an internal standard (δ (^{1}H) = 0.00). Mass spectra were acquired on an LC/MS system LC-MSD Trap XCT Plus (Agilent Technologies) using direct infusion measurement. Negative and positive-ion APCI mass spectra were recorded in the mass range of 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, a nebulizer gas pressure of 60 psi, and a drying gas temperature of 350 °C. The samples were dissolved in acetonitrile for HPLC (Sigma–Aldrich) in appropriate concentrations for MS detection. The absorption spectra were measured on a Perkin–Elmer Lambda 35 UV/vis spectrophotometer. The steady-state fluorescence spectra were measured using a Hitachi Perkin–Elmer LS 5 spectrophotometer. The pure compounds for spectral measurements and elemental analysis were isolated by TLC chromatography on Silufol UV 254 plates. The fluorescence spectra were recorded by excitation at absorption maxima, the excitation spectra were recorded at

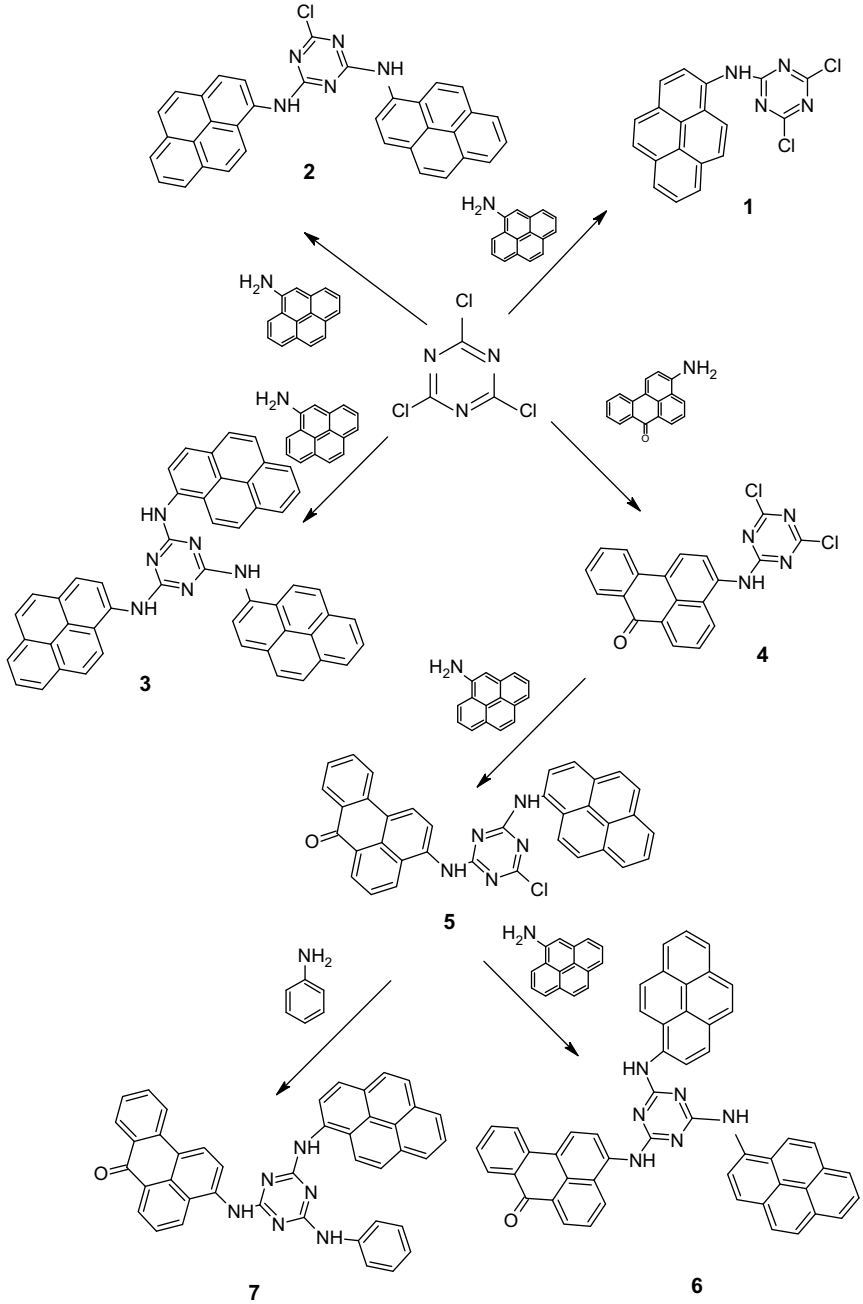

Fig. 1. Reaction scheme for the prepared compounds.

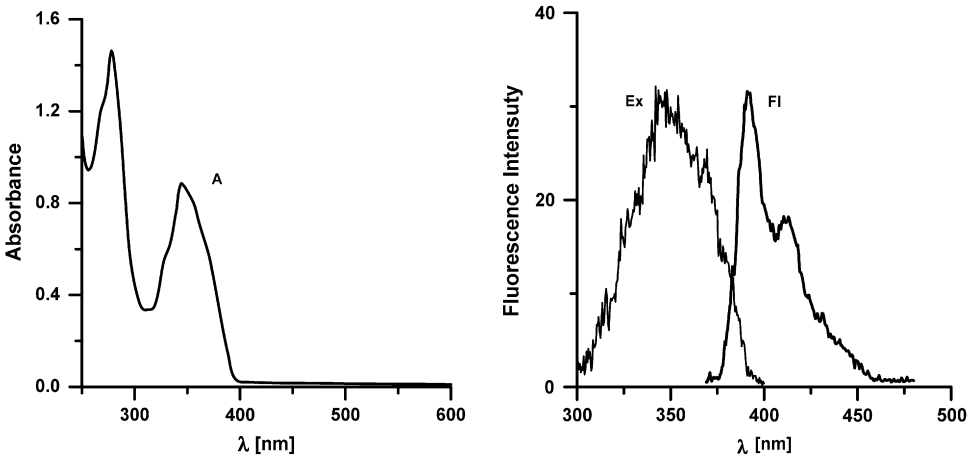

Fig. 2. Absorption (A), Excitation (Ex) and Fluorescence (Fl) spectra of **2** in 1,4-dioxane.

fluorescence maxima. The fluorescence quantum yields (q_{Fl}) were measured using a quinine sulphate ($q_{Fl} = 0.54$ in 0.5 mol/L H_2SO_4) [5] standard. The used solvents dibutylether (DBE), 1,4-dioxane (DO), ethylacetate (EtAc) and acetonitrile (MeCN) were of spectral grade and were checked for their own fluorescence under relevant conditions.

2.2. Synthesis

Synthesis of 1-nitropyrene, 1-aminopyrene, *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-1-aminopyrene (**1**) and *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-3-aminobenzanthrone (**4**) was performed according to literature procedures [3,4].

The synthesis of compounds **3**, **5**, **6**, and **7** were performed in a Parr autoclave (100 mL) with stirring under autogenous pressure. The autoclave was heated on oil bath and the reaction mixture was stirred for the desired time. The synthesis pathway of the title compounds is shown in Fig. 1.

2.2.1. 2,4-Di(1-pyrenylamino)-6-chloro-1,3,5-triazine (*2*)

Cyanuric chloride (0.4 g, 2.2 mmol), 1-aminopyrene (1 g, 4.6 mmol) and $NaHCO_3$ (0.4 g, 4.8 mmol) were added to acetone (100 mL). The reaction mixture was stirred at room temperature for 32 h. The precipitate was filtered and washed with acetic acid to obtain the first portion of **2**. The solid that precipitated upon dilution of the mother liquor was filtered to get the second portion of product, and yielded 0.9 g (75%) as a greenish solid; m.p 275–281 °C. ^{1}H NMR (500.13 MHz, DMSO-d_6): δ (^{1}H) = 10.54 (br s, 2H, 2 × NH), 7.93–8.39 (m, 18H, H (arom)). MS (APCI$^-$): *m*/*z* 544 [M − H]$^-$ (M.W. 545 g/mol). Anal. calcd. for $C_{35}H_{20}ClN_5$: C 76.99%, H 3.69%, Cl 6.49%, N 12.83%; found: C 77.02%, H 3.72%, 6.55 Cl %, N 12.98%.

2.2.2. 2,4,6-Tri(1-pyrenylamino)-1,3,5-triazine (*3*)

The reactions were carried out in a100 mL Parr autoclave under autogenous pressure. The reactor was charged with acetone (50 mL), cyanuric chloride (0.17 g, 0.92 mmol), 1-aminopyrene (1 g, 4.6 mmol) and $NaHCO_3$ (0.3 g, 3.6 mmol). The reaction mixture was heated in an oil bath and kept at 100 °C for 8 h. After cooling to room temperature, the greenish precipitate was collected by filtration and washed with acetic acid. The yield was 0.5 g (74%); greenish powder of **3**, m.p. >300 °C. ^{1}H NMR (500.13 MHz, DMSO-d_6): δ (^{1}H) = 9.85 (br s, 3H, 3 × NH), 7.95–8.37 (m, 27H, H (arom)). MS (APCI$^-$): *m*/*z* 725 [M − H]$^-$ (M.W. 726 g/mol). Anal. calcd. for $C_{51}H_{30}N_6$: C 84.28%, H 4.16%, N 11.56%; found: C 84.53%, H 4.51%, N 11.68%.

2.2.3. 2-[(3-Benzanthronylamino)-4-(1-pyrenylamino)]-6-chloro-1,3,5-triazine (*5*)

The reactions were carried out in a 100 mL Parr autoclave under autogenous pressure. The reactor was charged with acetone (50 mL), **1** (1 g, 2.74 mmol), 3-aminobenzanthrone (0.7 g, 2.74 mmol) and $NaHCO_3$ (0.5 g, 6 mmol). The reaction mixture was

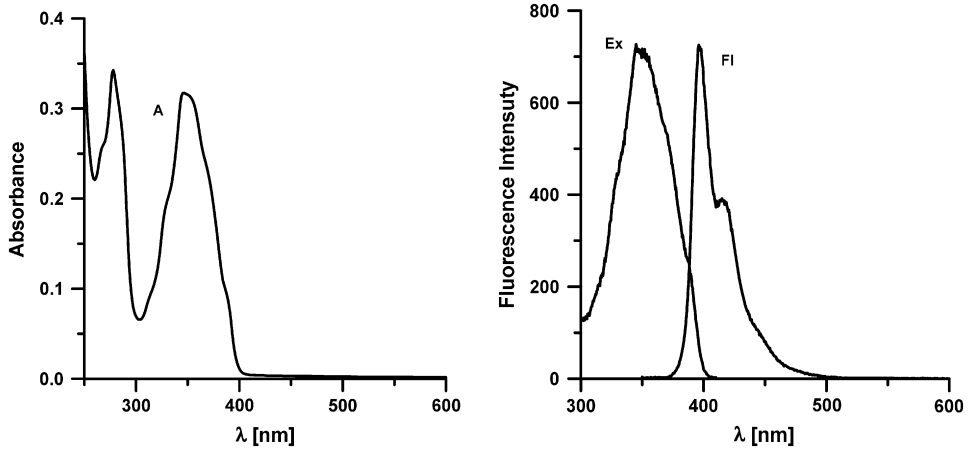

Fig. 3. Absorption (A), Excitation (Ex) and Fluorescence (Fl) spectra of **3** in 1,4-dioxane.

Table 1
Absorption (A_{max}, nm) and fluorescence (F_{max}, nm) maxima of the prepared compounds in different solvents.

Solvent		2	3	5	6	7
DBE	A_{max}	343	344	343	343	343
				423	440	430
	F_{max}	391	395	515	528	530
DO	A_{max}	344	346	343	345	343
				421	433	422
	F_{max}	391	396	525	539	540
EtAc	A_{max}	343	355	345	345	345
				422	439	437
	F_{max}	390	397	524	539	543
MeCN	A_{max}	343	351	345	344	345
				419	436	434
	F_{max}	–	397	–	–	–

heated in an oil bath and kept at 100 °C for 6 h. After cooling to room temperature, the precipitate was filtered to give **5** (tan powder, 0.8 g) in a 51% yield, m.p. >300 °C, lit. >340 °C [2]. ^{1}H NMR (500.13 MHz, DMSO-d_6): δ (^{1}H) = 10.45 (br s, 1H, NH), 10.32 (br s, 1H, NH), 7.45–8.72 (m, 18H, H (arom)). MS (APCI$^-$): *m/z* 572 [M − H]$^-$ (M.W. 573 g/mol). Anal. calcd. for $C_{36}H_{20}ClN_5O$: C 75.32%, H 3.51%, Cl 6.18%, 12.20N %; found: C 75.43%, H 3.59%, Cl 6.25%, N 12.33%.

2.2.4. 2-[(3-Benzanthronylamino)-4-(4,6-di(1-pyrenylamino))]-1,3,5-triazine (*6*)

A mixture of acetone (50 mL), **4** (1 g, 2.5 mmol), 1-aminopyrene (1.1 g, 5 mmol) and $NaHCO_3$ (0.4 g, 4.76 mmol) were placed in a Parr autoclave under autogenous pressure (100 mL), and then the vessel was sealed and heated to 180 °C in an oil bath for 3 h. The reaction mixture was cooled to room temperature, the formed precipitate was filtered off to obtain 0.8 g of colourless crystals of **6** in a 42% yield; m.p. 260–265 °C. ^{1}H NMR (500.13 MHz, DMSO-d_6): 9.72 (br s, 2H, 2 × NH), 9.59 (br s, 1H, NH), 7.60–8.57 (m, 27H, H (arom)). MS (APCI$^-$): *m/z* 753 [M − H]$^-$ (M.W. 754 g/mol). Anal. calcd. for $C_{52}H_{30}N_6O$: C 82.64%, H 4.01%, N 11.13%; found: C 82.75%, H 4.11%, N 11.26%.

2.2.5. 2-[(3-Benzanthronylamino)-4-(phenylamino)-6-(1-pyrenylamino)]-1,3,5-triazine (*7*)

Compound **5** (1 g, 1.74 mmol) and aniline (0.2 g, 2.15 mmol) were added to acetone (50 mL) in a100 mL Parr autoclave under autogenous pressure. The reaction mixture was heated in an oil bath and kept at 170 °C for 4 h. After cooling to room temperature, the precipitate was filtered. The filter cake was dried to give the first portion of **7** (0.04 g), the mother liquor was diluted with water to obtain a second portion of product (0.6 g), with a yield of 54%; m.p. 253–255 °C, ^{1}H NMR (500.13 MHz, DMSO-d_6): 9.79 (br s, 2H, 2 × NH), 9.26 (br s, 1H, NH), 7.60–8.26 (m, 23H, H (arom)). MS (APCI$^-$): *m/z* 629 [M − H]$^-$ (M.W. 630 g/mol). Anal. calcd. for $C_{42}H_{26}N_6O$: C 79.98%, H 4.16%, N 13.33%; found: C 79.88%, H 4.27%, N 13.45%.

Table 2
Molar absorptivity (ε) of the studied systems at the absorption maxima of *N*-triazinyl aminopyrene and aminobenzanthrone derivatives in 1,4-dioxane.

Compound	ε_A (APyT-) × 10^{-3}	ε_A (ABAT-) × 10^{-3}
1	21.0	–
2	25.4	–
3	41.6	–
4	–	1.8
5	16.3	7.1
6	48.8	11.7
7	12.8	5.1

Table 3
Fluorescence quantum yields of the studied compounds in different solvents.

Compound	DBE	DO	EtAc
2	0.28	0.05	<0.01
3	0.98	0.88	0.50
5	0.16[a]	0.12[a]	0.04[a]
	0.18[b]	0.15[b]	0.05[b]
6	0.28[a]	0.22 [a]	0.04[a]
	0.36[b]	0.24[b]	0.05[b]
7	0.25[a]	0.27[a]	0.04[a]
	0.31[b]	0.32[b]	0.05[b]

[a] Excitation at the absorption maximum of the aminopyrene subsystem.
[b] Excitation at the absorption maximum of aminobenzanthrone subsystem.

3. Results and discussion

3.1. Synthesis

Compounds **1** and **4** were readily prepared using the procedures [3,4] described above, i.e. by reacting one of the equivalents of the corresponding amines with cyanuric chloride.

Compound **2** was prepared by reacting cyanuric chloride with 2 equiv. of 1-aminopyrene in acetone. The product was isolated in a pure form; MS shows only one peak, corresponding to the named compound. The absorption and fluorescence spectra show characteristics typical for pyrene derivatives of this type.

Compound **3** was obtained by the reaction of 3 equiv. of 1-aminopyrene with one equivalent of cyanuric chloride in an autoclave at 110 °C; however, beside the main product, small amounts of compound **2** were identified by MS analysis. The formation of this by product was depressed by increasing the amount of 1-aminopyrene; consequently the highest yield of the target compound was obtained by the reaction of 1-aminopyrene with cyanuric chloride with a ratio of 5:1. The excess 1-aminopyrene was removed by washing the crude product with acetic acid to create a high purity product. Compound **6** was prepared by reacting **4** with 1-aminopyrene under the same conditions described for the synthesis of **3**. The crude product was isolated in a relatively pure form; it contained only a small amount of the starting compound **4**.

The synthesis of compounds **5** and **7** was already described by Fidler et al. [2]. In the same way as described for **2** and **6**, we modified this procedure by using an autoclave. The target product **5** was contaminated with a small amount of **6**. Compound **7** was isolated in a very pure form.

3.2. Absorption and fluorescence spectra

Absorption spectra of **1** [3], **2** and **3** show practically the same character: the first broad band at 345 nm corresponds to overlapped L_b and L_a pyrene type transitions and the second stronger absorption band at 280 nm corresponds to the pyrene B_b transition (Figs. 2 and 3). The influence of the solvent on the position and the shape of the bands is very small [Table 1]. The absorption coefficients of the maxima of the first absorption bands are on the order of 10^4 and they increase in the ratio 1:1.2:2.0 with the number of aminopyrene chromophores [Table 2]. Fluorescence spectra of **2** and **3** show a vibronic structure and in this way are practically identical to a series of *N*-triazinyl aminopyrenes with phenylamino or methoxy groups on the triazinyl ring [4].

While compound **1** does not fluoresce at all in any solvent [4], compound **2** exhibits fluorescence only in DBE (dielectric constant 3.08) (Table 3, Fig. 2); the fluorescence of this compound is reduced in DO (dielectric constant 2.22) this solvent behaves like a more polar solvent even though its dielectric constant is small [3,6]. The

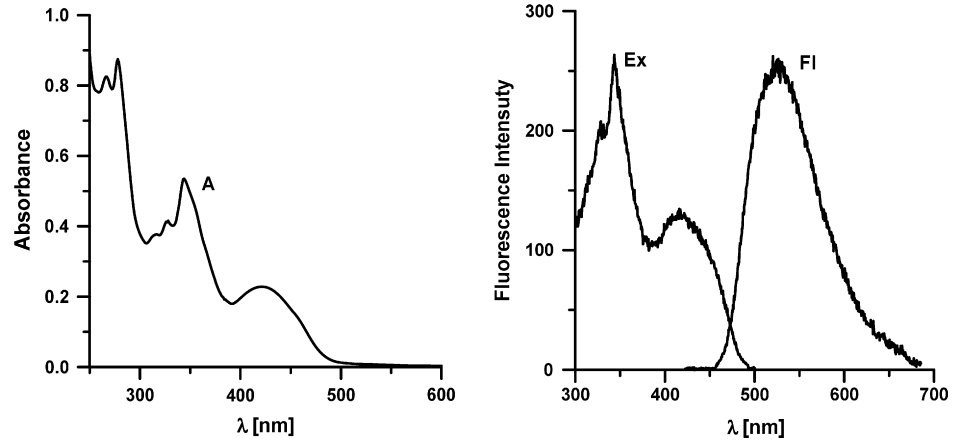

Fig. 4. Absorption (A), Excitation (Ex) and Fluorescence (Fl) spectra of **5** in 1,4-dioxane.

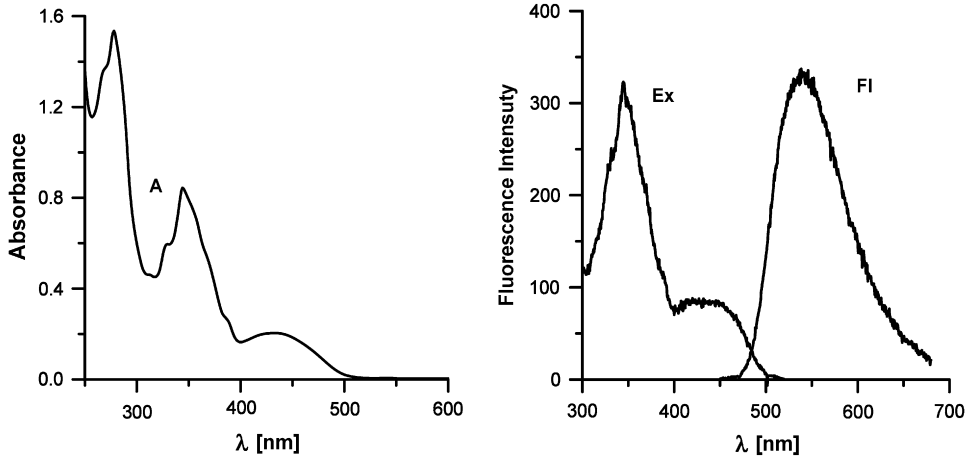

Fig. 5. Absorption (A), Excitation (Ex) and Fluorescence (Fl) spectra of **6** in 1,4-dioxane.

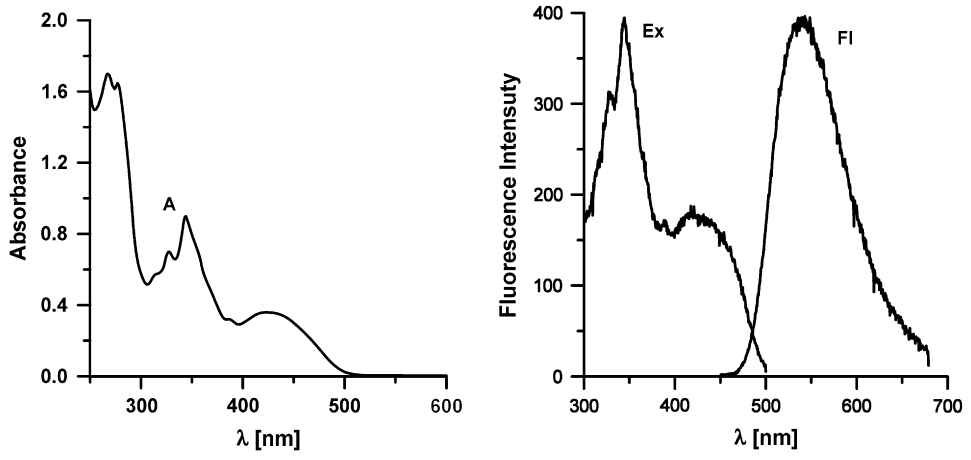

Fig. 6. Absorption (A), Excitation (Ex) and Fluorescence (Fl) spectra of **7** in 1,4-dioxane.

fluorescence is reduced in EtAc (dielectric constant 6.02) and fully quenched in MeCN (dielectric constant 35.94). Compound **3** exhibits a very strong fluorescence in DBE and in DO (Fig. 3), the q_F is roughly halved in the more polar EtAc (Table 3) and a very weak fluorescence was found in MeCN ($q_F = 0.05$).

The absorption spectra of the bi- and trichromophoric compounds with 1-aminopyrene and 3-aminobenzanthrone chromophores connected by a triazinyl ring spacer show the features typical for non-conjugatively bonded chromophores (Figs. 4–6): the band at 345 nm belongs to the *N*-triazinyl

Table 4
Ratio of absorption band intensities of *N*-triazinyl aminopyrene and aminobenzanthrone chromophores within bi- and trichromophoric compounds.

Compound	DBE	DO	EtAc	MeCN
5	2.57	2.38	2.31	2.38
6	4.29	4.18	3.91	4.10
7	2.63	2.52	2.33	2.37

aminopyrene subsystem (APyT-) and the band at 420–440 nm belongs to the *N*-triazinyl aminobenzanthrone subsystem (ABAT-) [3]. The influence of the solvent on the position of the absorption bands is small. While the ratio of intensities of the absorption bands in model systems, i.e. **1** (345 nm) and **4** (408 nm) is 11.7 in DO (Table 2), this ratio is only 2.3–2.6 for **5** and **7** and 3.9–4.3 for **6** in all solvents used (Table 4). The absorption coefficient (ε_A) of the band at 345 nm for **6** is about 3 times greater than that for **5**, 2.3 times greater than that for **1** and about 4 times greater than that for **7**. The ε_A at 420 nm for **6** is 1.6 times greater than that for **5**, 2.3 times greater than that for **7** and 6.5 times greater than that for **4** (Table 2). These results prove a coupling of the chromophores through the triazinyl ring.

Fluorescence spectra of the bi- and trichromophoric compounds represent the only fluorescence corresponding to those of ABAT-subsystem that can be detected for any excitation wavelength from 300 to 470 nm. The fluorescence bands are broad and structureless (Figs. 4–6). No blue fluorescence corresponding to the APyT-subunit was detected. Excitation spectra are almost identical to the absorption spectra. In comparison with **5**, the F_{max} of **6** and **7** (i.e. the compounds without a chlorine atom on triazinyl ring) in all used solvents is shifted bathochromically by 13–19 nm. In comparison with the F_{max} in DBE, the F_{max} of **5**, **6** and **7** is bathochromically shifted by about 10 nm in more polar DO and EtAc (Table 1).

In contrast to the absorption and fluorescence spectra, the q_F of compounds **5**, **6** and **7** is much more significantly influenced by both the structure and the solvent polarity (Table 3):

- in nonpolar DBE and low polar DO only small differences of q_F were found; the fluorescence is reduced in more polar EtAc; the q_F is completely quenched in highly polar MeCN;
- the q_F of compound **5** in DBE and in DO is approximately half of the q_F of **6** and **7**, i.e. of the compounds without a chlorine atom;
- whereas compound **4** and its chloromethoxy-triazinyl (**4a**) and dimethoxy-triazinyl (**4b**) derivatives exhibit a strong increase of q_F as solvent polarity increases (Table 5), the changes in q_F for **5**, **6** and **7** show an opposite dependence;
- in contrast to **4** and **4a**, a chlorine atom does not cause any significant fluorescence quenching for **5** in nonpolar DBE;
- the excitation wavelength dependence of the q_F of compounds **5**, **6** and **7** provides a piece of evidence for the presence of two different excitation/relaxation pathways in these compounds; the decrease of q_F under excitation at the absorption maximum of the aminopyrene subsystem indicates, besides fast EET, the existence of additional non-radiative losses.

Table 5
Absorption (A_{max}, nm) and fluorescence (F_{max}, nm) maxima and fluorescence quantum yields (q_F) of *N*-triazinyl derivatives of 3-aminobenzanthrone in different solvents [3].

Compound	Solvent								
	DBE			EtAc			MeCN		
	A_{max}	F_{max}	q_F	A_{max}	F_{max}	q_F	A_{max}	F_{max}	q_F
4	401	496	0.02	403	512	0.14	403	527	0.43
4a	404	507	0.05	411	520	0.34	407	538	0.52
4b	422	516	0.22	419	523	0.58	414	554	0.59

Recently, we reported on the quenching influence of chlorine atoms and solvent polarity on the q_F of the methoxy and aniline derivatives of *N*-triazinyl aminopyrene [4]. We could exclude a photochemical reaction and an S–T transition as efficient non-radiative deactivation processes leading to fluorescence quenching of *N*-chlorotriazinyl derivatives in polar solvents. We have now found that the same effect is caused by successive substitution of chlorine atoms on the triazinyl ring by the aminopyrene chromophores. As the chlorine atoms enhance the electron withdrawing character of the triazinyl ring, a strong polar excited state connected with π-electron transfer from the aminopyrene moiety to the triazinyl ring and simultaneous changing of geometry of the molecule could operate. Due to a solvent relaxation, the energy of such a polar state could decrease below a fluorescent state and open a new efficient deactivation channel. Such a state could also be involved in the deactivation cascade of compounds **5**, **6** and **7**, even though, probably due to a bathochromic shift of the emitting state localized on the aminobenzanthronyl chromophore, it is only effective in polar solvents.

A rigorous explanation of the fluorescence features of the presented series of compounds also requires a detailed theoretical investigation of the character and energy of their electronic excited states. Quantum chemical calculations on a semi-empirical level are now in progress.

4. Conclusions

A new synthetic method was developed for the synthesis of bi- and trichromophoric compounds with a triazinyl ring spacer. The *N*-triazinyl bi- and trichromophoric systems with 1-aminopyrene and 3-aminobenzanthrone chromophores were prepared. The structure of the compounds was confirmed by MS and NMR spectra and by elemental analysis. The UV/vis absorption and fluorescence spectra and fluorescence quantum yields in various solvents were measured. Some relationships between the structure and spectral characteristics of the prepared compounds and the influence of solvent polarity were revealed.

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