

# Fluorescence Anisotropy of Branched Molecules Containing 1-Aminopyrene Chromophores

Miroslav Dvořák · Martin Michl · Numan Almonasy ·  
Miloš Nepraš · Nemiah Ladd · Vlastimil Fidler

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**Abstract** Fluorescence anisotropy measurements were performed on a set of multichromophoric compounds, which contain a different number of aminopyrenyl moieties linked to a triazine ring, in order to reveal the nature of both the electronic excited states and relaxation pathways of the compounds. Our experimental results complement quantum chemical calculations. We propose that the lowest excited state from which fluorescence proceeds is localized on a single individual aminopyrene moiety. In contrast, excitation to a higher excited state is likely followed by a migration of energy to another nearby aminopyrene chromophore before the internal conversion to the emitting state takes place. We suggest that this migration is responsible for the experimentally measured decrease of fluorescence anisotropy of the studied compounds.

**Keywords** Fluorescence anisotropy · Energy migration · Aminopyrene · Multichromophores

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M. Dvořák (✉) · M. Michl  
Department of Physical Electronics, Faculty of Nuclear Sciences  
and Physical Engineering, Czech Technical University in Prague,  
V Holešovičkách 2,  
180 00 Praha 8, Czech Republic  
e-mail: dvorakm@fjfi.cvut.cz

N. Almonasy · M. Nepraš  
Institute of Organic Chemistry and Technology,  
Faculty of Chemical Technology, University of Pardubice,  
Studentská 95,  
532 10 Pardubice, Czech Republic

N. Ladd · V. Fidler  
Department of Natural Sciences, Faculty of Biomedical  
Engineering, Czech Technical University in Prague,  
Sítňá sq. 3105,  
272 01 Kladno 2, Czech Republic

## Introduction

Developing an understanding of the relaxation pathways and the character of the electronic excited states in multichromophoric compounds is essential in order to exploit such compounds for molecular electronics [1, 2]. Moreover, the collective optical properties of multichromophoric arrays have been recognized as a possible way to carry out quantum computing [3, 4]. For both these reasons, a considerable amount of both theoretical and experimental studies dealing with such arrays has recently appeared [5–8].

There have been a number of investigations of pyrene and its derivatives that deal with the nature and dynamics of its excited states [9–11]. It is generally assumed that the first absorption band of pyrene corresponds predominantly to the excitation  $n$  of the molecule to its second electronic excited state (S2) because the transition to the lowest excited state (S1) has a vanishing oscillator strength. The photoexcited molecule then undergoes a fast S2→S1 internal conversion and the forbiddenness of the fluorescence transition from S1 to the ground state results in the long pyrene's fluorescence lifetime. However, it is not fully understood how this photophysical picture changes in single- and multichromophoric pyrenyl derivatives.

In this contribution, we present the results of fluorescence anisotropy measurements of a set of multichromophores that consist of different numbers (1–3) of aminopyrene moieties linked to a triazine ring. Our experimental results are supported by quantum chemical calculations. This combination of experimental results and theoretical calculations brings new insight into the character of the excited states and reveals details of the relaxation processes that occur in such multi-chromophoric compounds.

## Compounds and methods

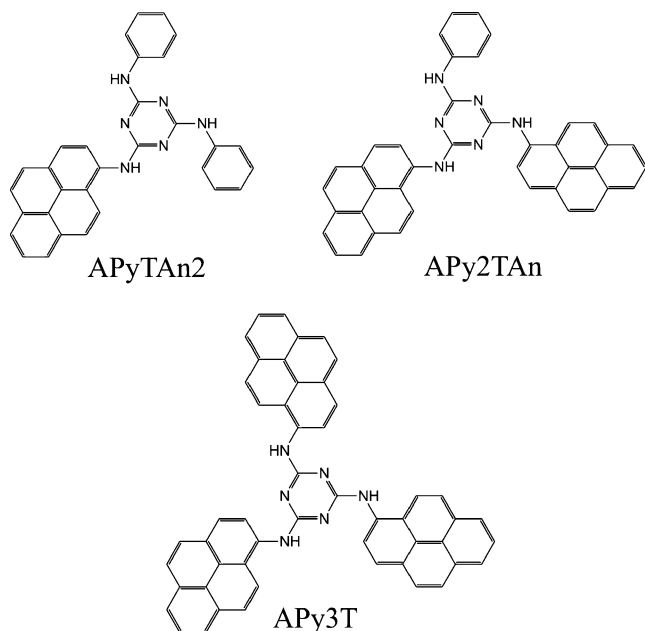
Chart 1 depicts the structures of the compounds that were studied in this work. The synthesis and spectral characteristics of APyTAN2 and APy3T are described in [12] and [13], respectively. APy2TAN was prepared by reaction of 2,4-di(1-pyrenylamino)-6-chloro-1,3,5-triazine with aniline according to the standard method [13].

Stabilized 2-methyltetrahydrofuran (2-MTHF) was obtained from Merck Chemicals. For the spectroscopic measurements, appropriate amount of 2-MTHF was purified in order to remove the stabilizing agent and moisture, and used immediately. The purification procedure consisted in 2 h refluxing with potassium hydroxide and consequent addition of fresh potassium hydroxide and distillation.

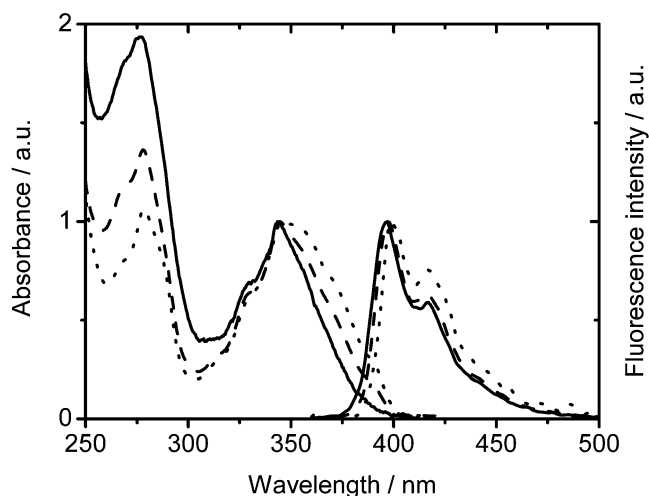
The absorption spectra were measured using a Shimadzu UV 1601 spectrophotometer at room temperature.

The fluorescence anisotropy measurements were performed with Edinburgh Instruments—EAI FS/FL900 spectrofluorimeter. This system is equipped with electronically driven Glen-Thompson polarizers, which control the orientation of the polarization of the excitation and emission light. Very low concentration (optical density less than 0.05) solutions frozen to 146 K by an Oxford Instruments OptistatDN cryostat head were used.

Two fluorescence excitation spectra  $I_{VH}(\lambda)$  and  $I_{VV}(\lambda)$  were recorded with an emission polarizer in horizontal and vertical positions, respectively, while the excitation polarizer stayed in the vertical position for both measurements. The fluorescence anisotropy  $r$  was then calculated using



**Chart 1** Chemical structures



**Fig. 1** Absorption and fluorescence emission spectra (excitation at 350 nm) of APyTAN2 (*solid*), APy2TAN (*dashed*) and APy3T (*dotted*) in 2-MTHF at room temperature. The absorption spectra were normalized to the maxima of absorption bands at 350 nm. The fluorescence spectra were normalized to their maxima at around 400 nm

these two fluorescence signals and an appropriate G-factor [14] as

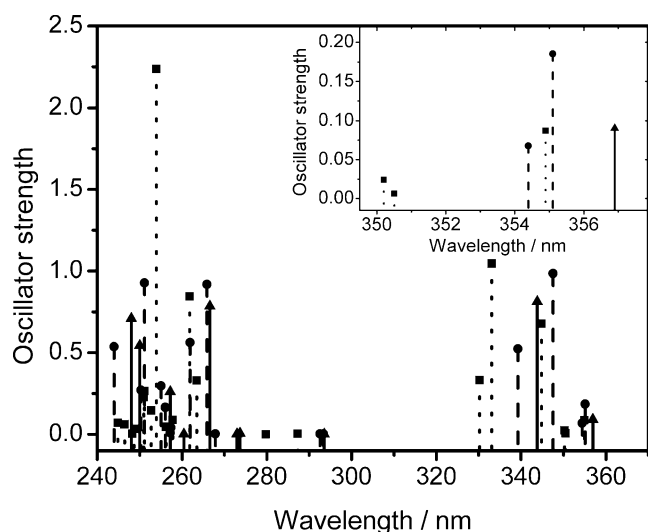
$$r(\lambda) = \frac{I_{VV}(\lambda) - GI_{VH}(\lambda)}{I_{VV} + 2GI_{VH}(\lambda)}$$

Quantum chemical calculations of the electronic excited states were performed on the molecules, using the assumption that the ground state molecular geometry was the way it was optimized for the molecule in a vacuum. These geometries were optimized using Gaussian 03 [15] on the B3LYP/6-31G (d,p) level. The properties of the excited states and the electron density redistributions were calculated using ArgusLab 4.0 [16] by the ZINDO/CI method.

## Results and discussion

The three compounds under study have absorption spectra characterized by two distinguished absorption bands centered at 280 and 350 nm. The position and shape of the absorption bands are not affected by the number of aminopyrene moieties attached to the triazine ring (see Fig. 1). The only characteristic that varies significantly is the extinction coefficient, which rises as the number of aminopyrene moieties increases (we observed extinction coefficients with values of  $3 \times 10^4$ ,  $4.5 \times 10^4$  and  $6 \times 10^4$  in dioxane for APyTAN2, APy2TAN and APy3T, respectively).

The absorption band at 280 nm has a complicated origin. Quantum chemical calculations indicate that there is a mixture of higher excited states (see Fig. 2) localized on aminopyrene or aniline, along with excited states with a



**Fig. 2** Calculated energies and oscillator strengths of transitions of APyTan2 (solid, triangle), APy2TAN (dashed, circle) and APy3T (dotted, square). The upper right inset represents a more detailed view on the region of the lowest (S1-like) excited states

strong CT character. The fluorescence anisotropy value under excitation through this band is close to zero for all three compounds (see Fig. 3), even for APyTan2, which bears only one aminopyrene chromophore. This fact suggests that a number of excited states, with different directions of their transition moments, are populated, which causes the resulting fluorescence to be completely depolarized.

The situation is more interesting in the case of the absorption band at 350 nm. According to the generally accepted conception, there are only two transitions that contribute to the absorption of pyrene near this region. The first  $S_0 \rightarrow S_1$  transition has a vanishing oscillator strength due to symmetrical forbiddenness and the transition dipole moment is directed along the shorter axis of the molecule. The second  $S_0 \rightarrow S_2$  transition, on the other hand, is allowed and its transition dipole moment is collinear with the molecule's main axis, i.e. it is perpendicular to that of the lowest transition [17, 18]. Traditionally, the bands corresponding to these transitions are referred to as  $L_b$  and  $L_a$ , respectively [19].

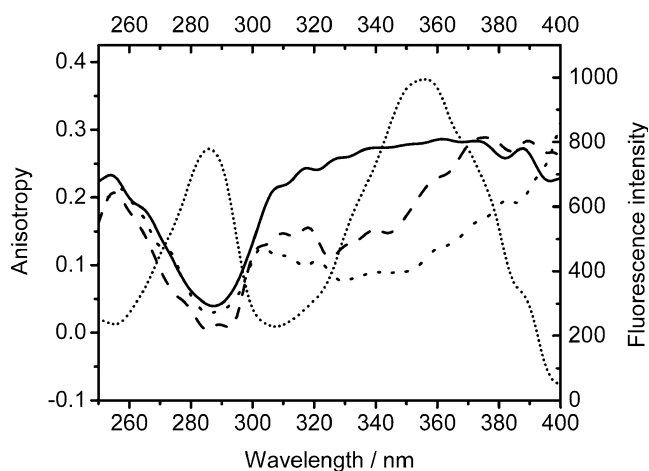
The amino substituent at the 1-position of pyrene causes a red shift of these transitions in the 1-aminopyrenyl derivatives, due to the conjugation of the lone electron pair on nitrogen with the  $\pi$ -electrons of pyrene. This effect is, however, constrained to a certain extent in the case of the compounds studied here because of the electron-withdrawing nature of the triazine ring [12]. A more substantial change from the pyrene-like situation is represented here by the perturbation of the molecular symmetry, which causes the originally perpendicular transition dipole moments of S1 and S2 to adopt a more closed angle and their forbiddenness to be less strict.

The calculations performed for APyTan2 show that there is a transition at 357 nm to the lowest excited state

with an oscillator strength of 0.09 and a transition at 344 nm to the second excited state with an oscillator strength of 0.81. The angle between their transition dipole moments is  $20^\circ$ . Similar excited states localized on each individual aminopyrene chromophore are predicted in the case of APy2TAN and APy3T (see Fig. 2). The lowest two pairs in APy2TAN and the three pairs of excited states in APy3T possess the same character, in terms of energy, oscillator strength and electron density redistribution, as the S1, S2 pair in APyTan2.

The fact that the longest wavelength absorption band of the examined compounds maintains its features and is not disturbed in presence of additional aminopyrenes indicates that the individual chromophores attached to the triazine ring interact rather weakly and that they can still be viewed as individual independent moieties. This weak interaction, along with the nature of the transitions described above, further signifies that the absorption band centered at 350 nm corresponds only to the overlapping bands caused by the transitions to the S1- and S2-like states localized on the individual aminopyrene moieties in all three of the studied molecules.

The important feature in which the studied compounds differ substantially is the excitation wavelength dependence of their fluorescence anisotropy in the 300 to 400 nm spectral region. While the fluorescence anisotropy of APyTan2 is almost constant, rising only mildly with the excitation wavelength and approaching a value of 0.3, the fluorescence anisotropy of APy3T is about 0.1 for excitation at 310 nm excitation and steadily rises to a value of 0.3 at an excitation of about 380 nm, which represents the red edge of the absorption band located at 350 nm. The anisotropy values of APy2TAN are between the values of APyTan2 and APy3T and reach the same value of 0.3 when excited at the red edge of the absorption band.



**Fig. 3** Excitation anisotropy spectra of APyTan2 (solid), APy2TAN (dashed) and APy3T (dotted) in 2-MTHF at 146 K. The fluorescence signal was detected at 420 nm. Fluorescence excitation spectrum of APy3T (short dash), recorded at 420 nm, is added for comparison

In other words, the fluorescence anisotropy approaches the value of 0.3 under excitation at the red edge of the longest wavelength absorption band for all three compounds, while it drops down to 0.1, on the blue edge of this band, when more than one chromophore is present in the molecule. We propose the following explanation: 1) the fluorescence proceeds from the S1-like states, 2) the emitting states are dominantly populated by fast S2→S1 internal conversion but they can also be directly populated by excitation in the 380–400 nm range, 3) in contrast to S1-like states, the electronic excitation energy of molecules in S2-like states can migrate among neighbouring aminopyrenes before the internal conversion takes place; this explanation can be justified by the difference in the corresponding transition of the dipole moment magnitudes.

In the case of APy2TAn and APy3T, the possible energy migration explains the low values of the fluorescence anisotropy, as the information about the identity of the absorbing aminopyrene chromophore is lost due to the migration. As the excitation wavelength increases, the anisotropy rises due to the increasing probability of direct absorption into the emitting S1-like states.

In the single chromophoric APyTAn2 compound, no such depolarizing energy migration can occur, so the fluorescence anisotropy is determined dominantly by the angle between the S0→S2 and S1→S0 transition dipole moments. This angle amounts to 26° for the anisotropy value of 0.28 at 350 nm which is in reasonable agreement with the calculated value of 20°.

The fluorescence depolarization mechanism described above would take place on comparable or faster timescale than the S2→S1 internal conversion. As far as we know, there is no such data for 1-aminopyrenes. However, it is claimed that the S2→S1 transition occurs within less than 100 fs for pyrene and 1-arylpyrenes in acetonitrile [20]. Further study of the compounds described here is in progress.

## Conclusion

We measured the wavelength dependence of fluorescence anisotropy of a set of multichromophoric compounds that bear different numbers of aminopyrene moieties connected to an s-triazine ring, and observed a decrease of fluorescence anisotropy at the short-wavelength side of the lowest excitation band of the compounds that bear two or three aminopyrenes, compared to that bearing only one. This decrease is interpreted as a sign of the migration of the excitation energy between the S2 states of neighbouring chromophores. We assume that the lowest excited state S1, which is the emitting state, is localized on a single individual chromophore and is not involved in the energy migration process.

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