

Time-Resolved Emission Spectroscopy of Pyrene Derivatives

by J. Dobkowski*, V.A. Galievsky**, J. Jasny and I.V. Sazanovich**

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
E-mail: dobkowski@ichf.edu.pl*

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An improved model of the picosecond time-resolved spectrofluorimeter equipped with an optical Kerr shutter was designed and constructed. The instrument was applied for measurements of time-resolved fluorescence (TRF) spectra of 4'-(pyrenyl-1-yl)acetophenone (Py-BK) and 4'-(pyrenyl-1-yl)benzonitrile (Py-BN). The experimental results indicate that both molecules relax after excitation by mutual twisting of two subunits towards a more planar geometry. In the case of Py-BK the kinetics of creation of excited state hydrogen-bonded complexes was discussed in detail.

Key words: time-resolved spectroscopy, TICT model

Excited state photoinduced charge transfer phenomena, occurring in molecules with donor and acceptor groups linked by a single bond, have been the subject of intensive studies during the last three decades. It was well-established, that cyano [1–3] and carbonyl [4,5] derivatives of N,N-dimethylaniline in polar solvents emit dual fluorescence. These observations have been explained by Grabowski and coworkers. They postulated, that the short-wavelength fluorescence is emitted from the primarily excited state (b^* , Lippert notation [1]), characterized by the planar geometry; the long-wavelength fluorescence originates from the secondary state (a^*). This state is characterized by the donor (D) and acceptor (A) moieties twisted by 90° with the respect to each other; one-electron transfer occurs from the donor to the acceptor [6]. The a^* state, also named Twisted Intramolecular Charge transfer (TICT) state, can be approximated by the structure of a bonded radical pair [7]. For the “small” donors group ($-NR_2$) the TICT model explains observed experimental facts very well [8]. In the case of molecules with more extended π -electron systems of the donor or acceptor groups, the interpretation of the experimental results in terms of the TICT hypothesis produces some difficulties [9–12]. The typical representatives of this class of molecules are pyrene and antracene derivatives. Due to the sterical hindrance, resulting in a strongly twisted ground state conformation, these molecules

* Author for correspondence.

** Permanent address: Institute of Molecular and Atomic Physics, Academy of Sciences of Belarus,
F. Skaryna Avenue 70, 220072 Minsk, Belarus.

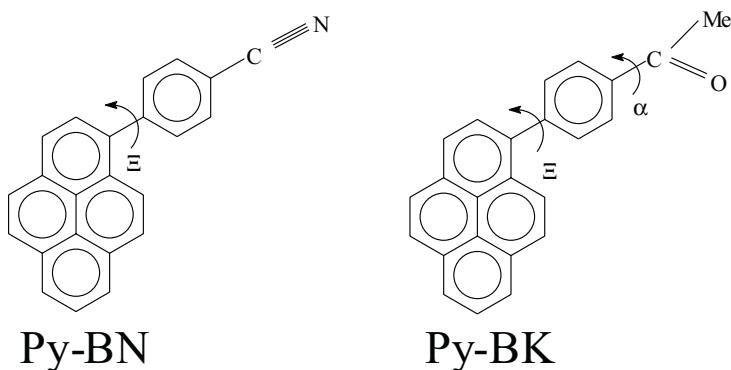
cannot be completely planar in the lowest excited state. There are two possibilities: (i) relaxation towards planarity or (ii) towards a TICT state (perpendicular geometry).

The quantum chemical calculations performed earlier favour the case (i) [11–13]. The results of the transient absorption experiments [11,12] and careful analysis of stationary emission in the terms of Marcus theory [14] also support the hypothesis of flattening after excitation.

The time-resolved fluorescence (TRF) was selected as a good method for monitoring the excited state relaxation processes leading to structural changes. This was the reason, why we have decided to build a picosecond spectrofluorimeter. The inspiration was borrowed initially from the apparatus constructed in Bordeaux by Rullière and his students [15], then modified and completed in many respects.

In this paper we compare two electron-donor-acceptor systems: 4'-(1-pyrenyl) benzonitrile (Py-BN) and 4'-(1-pyrenyl) acetophenone (Py-BK) (Scheme 1). These molecules have identical donors but different acceptors. The goal of this work is to understand the processes occurring, after excitation, along the relaxation path: $S_0 \rightarrow S_1$ (ground state geometry) $\rightarrow S_1$ (excited state geometry) and recognize the role of the specific interaction with the alcohol.

Scheme 1



EXPERIMENTAL

Py-BK and Py-BN were synthesized as described previously [11,12]. Butanol (Merck, spectral grade) was used without further purification. Fluorescence decay curves were recorded with a time resolved single-photon-counting apparatus (FS900, Edinburgh Instruments) with resolution equal to 0.3 ns (applying the deconvolution procedure). TRF spectra were recorded by means of a home-made picosecond spectrofluorimeter (Fig. 1). The spectrofluorimeter is based on a passively mode-locked Nd:YAG laser system (EKSPLA, Lithuania) as the light source (Fig. 1).

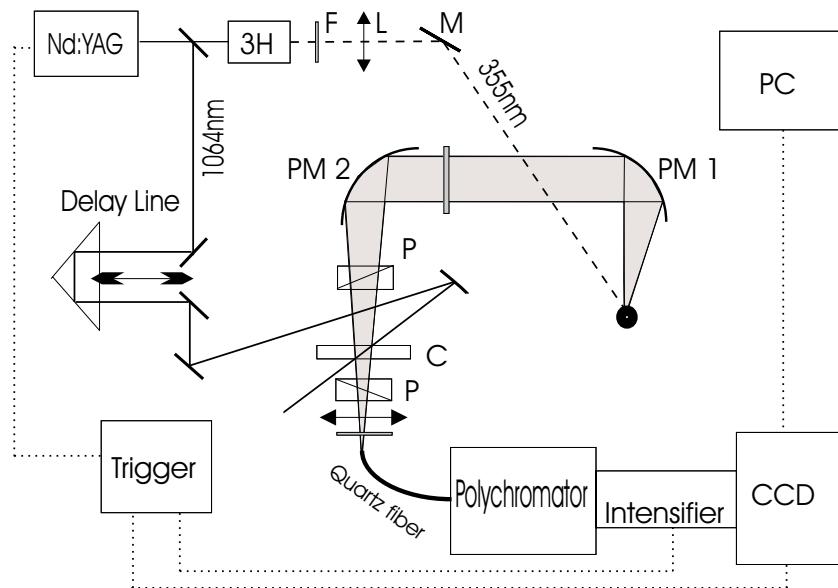


Figure 1. Optical scheme of the picosecond spectrofluorimeter. 3H – third harmonic generator, F – filter, L – lens, M – mirror, PM – off axis parabolic mirror, P – Glan polarizers, C – cell with CS_2 or chlorobenzene.

The negative feedback control system stabilizes the mean pulse energy. A single pulse ($\Delta t = 30$ ps fwhm, $\lambda = 1064$ nm, repetition rate 3 Hz) is selected by an opto-electronic pulse selector, amplified and split in two channels (pulse energy about 20 mJ each). The first beam is directed into the KDP crystals to generate the third harmonic ($\lambda = 355$ nm) used as the excitation beam. The second beam is passed through the optical Kerr shutter, (Fig. 1), consisting of a cell with CS_2 or chlorobenzene placed between two crossed Glan polarizers. Fluorescence emitted by the sample is collected and transferred by two spherical off axis parabolic mirrors (Janos Technology Inc.). The laser pulse (1064 nm) opens the Kerr shutter, so the fluorescence can be transmitted by the shutter only during the time window of 30 ps. The opening pulse is delayed with respect to the excitation pulse by an optical delay line (maximum delay 3000 ps, 0.1 ps/step). Next, fluorescence is transmitted by a quartz fiber to the detection system. The detection system consists of the: polychromator (Acton), an image intensifier, and a CDD detector (products of the Princeton Instruments Inc. (Fig. 1)). The signal from the negative feedback unit of the Nd:YAG laser is used for intensifier triggering. The spectra were accumulated 60 times, and the background has been subtracted. The linear correlation between the energy of the opening pulse and the intensity of the time resolved fluorescence was checked using rhodamine 6G in methanol (see Fig. 2).

Temporal resolution (Δt) of the spectrofluorimeter was measured by delaying the opening pulse (1064 nm) with respect to the second harmonic (CS_2) or to the third harmonic (chlorobenzene), see Fig. 3. In the case of CS_2 Δt was equal to 30 ps, in the case of chlorobenzene $\Delta t = 60$ ps. This significant difference of the Δt value is connected with the optical response of the Kerr medium. For chlorobenzene relaxation time(s) are not available but for benzene [16] the “slow” response due to the reorientational dynamics was reported.

TRF spectra were not corrected for the apparatus spectral response. To obtain the kinetic curves of the emission rise and decay, the time resolved emission bands recorded for various delay times were integrated within the selected spectral range. Time "0 ps" corresponds to the maximum of the excitation pulse, see Fig. 3. The decay times were evaluated applying the deconvolution procedure.

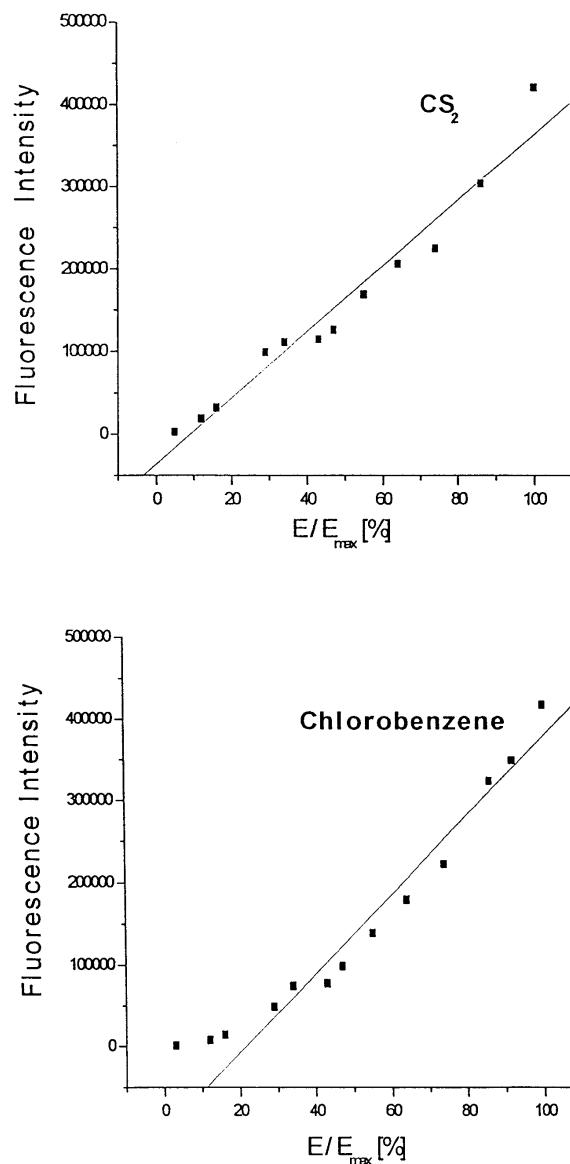


Figure 2. The TRF intensity of rhodamine 6G in methanol recorded as a function of the relative energy of the opening pulse in the case of CS_2 and chlorobenzene as the Kerr medium. Lines – the result of the fitting applying the linear function (for chlorobenzene two initial points were neglected). Typical limits of E/E_{max} 60%–80% ($E_{\text{max}} = 20$ mJ).

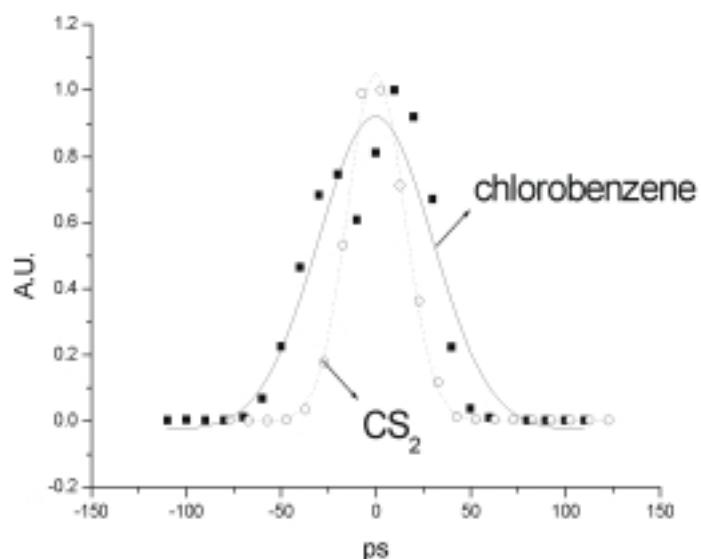


Figure 3. The relative intensity of the second harmonic (532 nm) and the third harmonic (355 nm) recorded as a function of the delay time from the opening pulse (1064 nm) for CS_2 and chlorobenzene used as Kerr media. Experimental points were fitted to a Gauss function.

RESULTS AND DISCUSSION

TRF spectra of Py-BK and Py-BN were recorded in butanol at room temperature for a number of delay times (Fig. 4). Py-BK reveals a much more complex TRF pattern than Py-BN. In the case of Py-BK the shape and the maximum of the TRF bands strongly depend on the delay time, whereas in the case of Py-BN no significant time-dependent solvatochromic shift of the emission was observed (see Fig. 5).

Solvent relaxation around a polar molecule is accompanied by time-dependent fluorescence spectral shift which is monitored and analyzed using empirical solvation function $c(t)$ defined by: $c(t) = \{\tilde{\nu}(t) - \tilde{\nu}(\infty)\} / \{\tilde{\nu}(0) - \tilde{\nu}(\infty)\}$; where: $\tilde{\nu}(0)$, $\tilde{\nu}(t)$, $\tilde{\nu}(\infty)$ are the fluorescence maxima immediately after excitation, at some time after excitation, and at the time sufficiently long to reach equilibrium, respectively. In the case of Py-BK the $c(t)$ plot was determined using the fluorescence maximum as well as the center of mass of the TRF spectra (see Fig. 6). In both cases the experimental points were well-fitted by a monoexponential function.

Kinetic curves of the rise and decay of the TRF band evaluated for Py-BK and Py-BN are shown in Figures 7A and 8 respectively. For Py-BK kinetic the curves were also obtained by integrating the short and long parts of the TRF spectra (Figs. 7B,C).

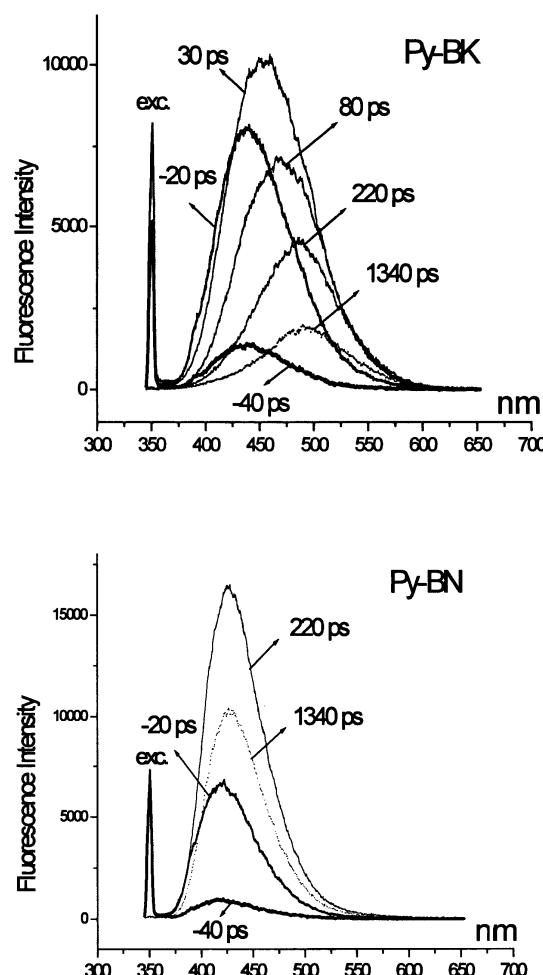


Figure 4. TRF spectra of Py-BK and Py-BN in butanol at 293 K recorded for various delay times.

In the case of Py-BK the experimental data were well-fitted by two exponential decays, whereas for Py-BN, a monoexponential decay was observed.

Because the long component in the biexponential decays of Py-BK fluorescence was recorded with limited number of points (Fig. 7), the fluorescence decays were also recorded using single photon counting technique (Fig. 9). And again for two different observation wavelengths: 450 nm and 500 nm, the experimental points could be well fitted by two-exponential decays. The resolution of the single photon counting apparatus was 0.3 ns, so we can only conclude that a short component exists, but the obtained value of 0.1 ns is rather accidental.

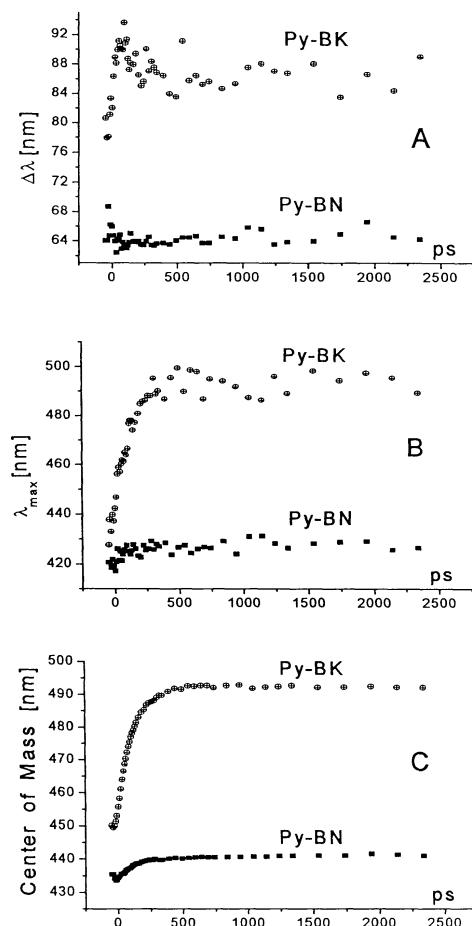


Figure 5. Py-BK and Py-BN in butanol at 293 K: halfwidth (A), position of the maximum (B), and the center of mass (C) of the TRF spectra recorded as a function of the delay time.

The decay times evaluated from the decay curves recorded for PyBK with the picosecond spectrophotometer and the single photon counting (SPC) apparatus are summarized below.

Observation [nm]	ps spectrophotometer		SPC
	τ_1 (ps)	τ_2 (ps)	τ (ns)
<380–620>	70	1770	
<380–430>	39	2020	
450±10			3.30
500±10			3.15
<520–620>	40(r)	1950	

Error = $\pm 10\%$, r – risetime.

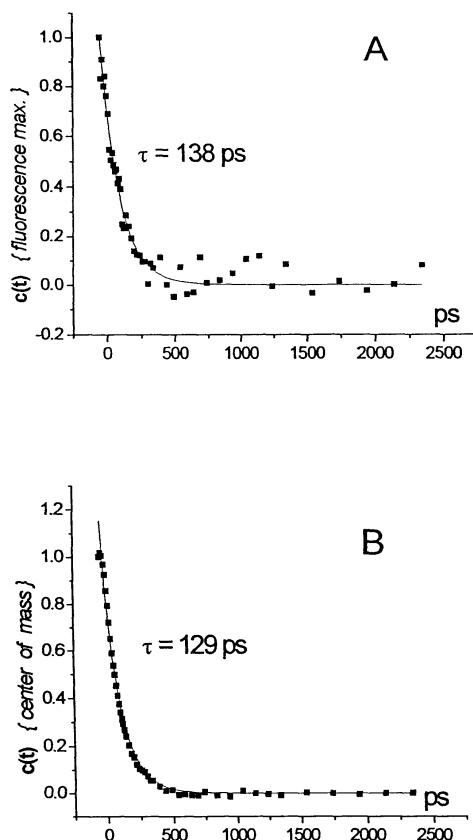


Figure 6. The $c(t)$ plot determined using the fluorescence maxima (A) and the center of mass (B) for Py-BK in butanol at 293 K. Solid line – monoexponential fit to the experimental points (τ – decay time).

Due to the better statistic and accessible time scale, the long component of the fluorescence decay was recorded more correctly with the single photon counting apparatus.

Molecular mechanics and INDO/S calculations performed earlier for Py-BN indicate, that the most stable ground state conformation is obtained for $\Theta = 69^\circ$, whereas the minimum energy of the lowest excited singlet state corresponds to $\Theta = 40^\circ$, where Θ is the angle between the planes of benzonitrile and pyrene moieties (Scheme 1) [12]. The TRF maxima recorded for delay times of -40 and 1340 ps are 24050 cm^{-1} (416 nm) and 23500 cm^{-1} (426 nm), respectively. The time-dependent Stokes shift is equal to 650 cm^{-1} . The calculated ground state energy destabilization $S_0(40^\circ) - S_0(69^\circ)$ is equal to 500 cm^{-1} , so the excited state energy stabilization generated by flattening of the molecule is about 150 cm^{-1} .

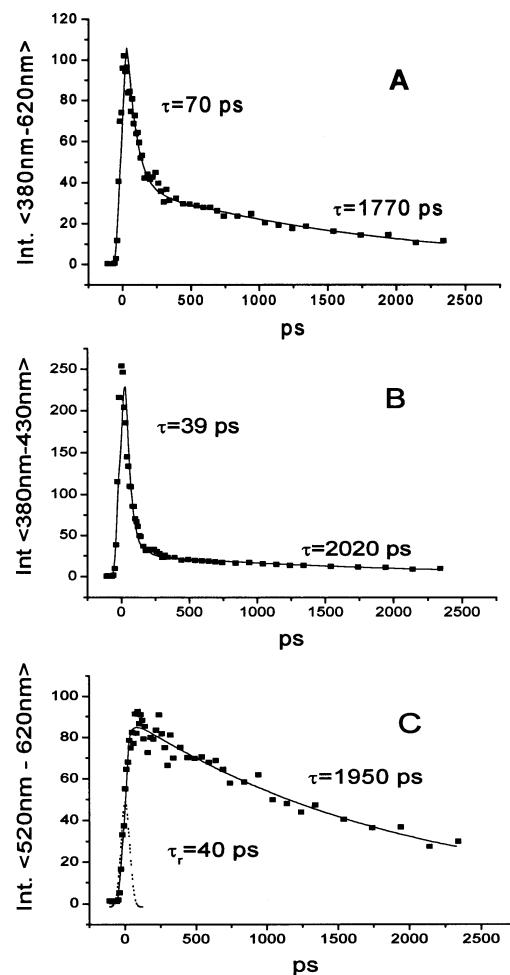


Figure 7. Kinetics of the TRF for Py-BK in butanol at 293K: experimental points and biexponential fit (τ – decay time, τ_r – rise time, the deconvolution procedure was applied). Integration limits: **A** – $\langle 380\text{--}620\text{ nm} \rangle$, **B** – $\langle 380\text{--}430\text{ nm} \rangle$ (blue part of the TRF spectra), **C** – $\langle 520\text{--}620\text{ nm} \rangle$ (red part of the TRF spectra). Laser pulse (Gauss fit) – dotted line.

Possible conformers of Py-BK can be described by two angles: Θ , the angle between the acetophenone and pyrene moieties and α , the twist angle of the COCH_3 group. Molecular mechanics and INDO/S calculations performed for Py-BK show that the most stable ground state conformation is obtained when the acetophenone subgroup is twisted with respect to the pyrene moiety by $\Theta = 60^\circ$ (62° from the X-ray experiment) [11]. The experimentally obtained value of α is 9° (Scheme 1) [11]. The results of INDO/S calculations show that the excited state minimum is located at $\Theta = 30^\circ\text{--}40^\circ$ and is not sensitive to the variation of angle α [11]. The maxima of the TRF spectra recorded for the delay times –40 and 1340 ps are 22840 cm^{-1} (438 nm)

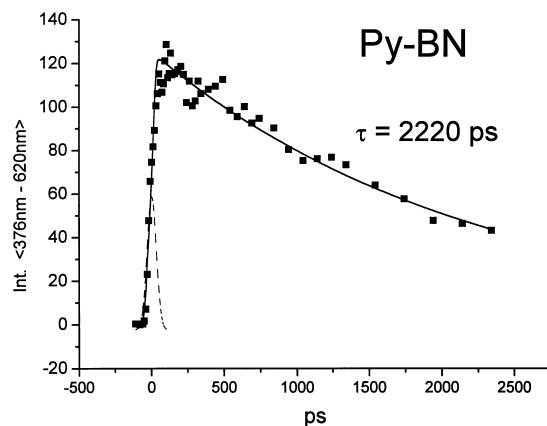


Figure 8. Kinetics of the TRF for Py-BN in butanol at 293K: experimental points and a monoexponential fit (τ – decay time, deconvolution procedure was applied). Integration limits: $\langle 376\text{--}620\text{nm} \rangle$. Laser pulse (Gauss fit) – dashed line.

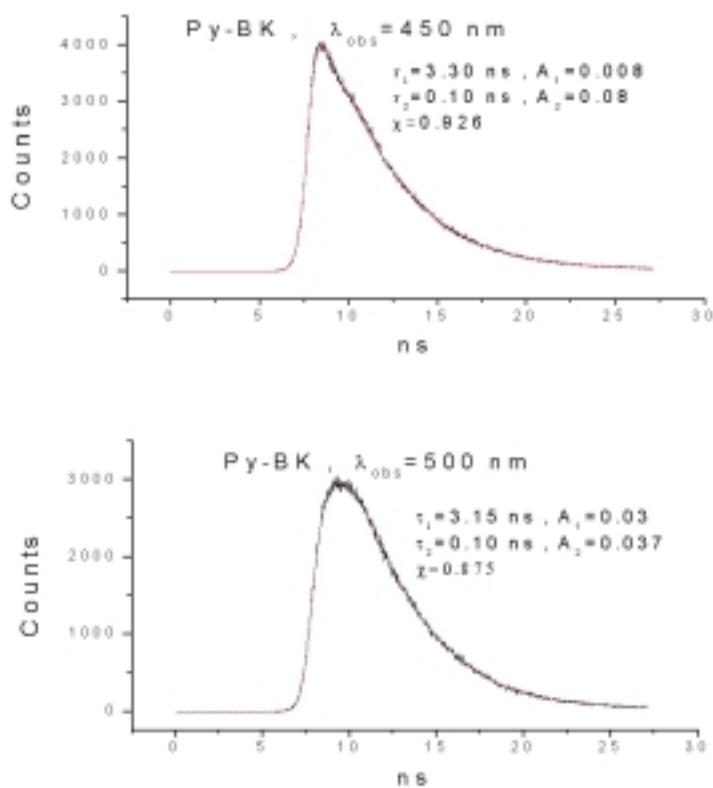


Figure 9. Experimental single-photon-counting decays for $\lambda_{\text{obs.}} = 450\text{ nm}$ and $\lambda_{\text{obs.}} = 500\text{ nm}$ for Py-BK in butanol at 293 K. The deconvolution procedure was applied, τ – decay times, A – amplitudes, χ – statistical factor.

and 20320 cm^{-1} (492 nm), respectively. The calculated ground state energy destabilization $S_0(35^\circ) - S_0(60^\circ)$ is about 900 cm^{-1} , so the excited state energy stabilization is equal to 1620 cm^{-1} .

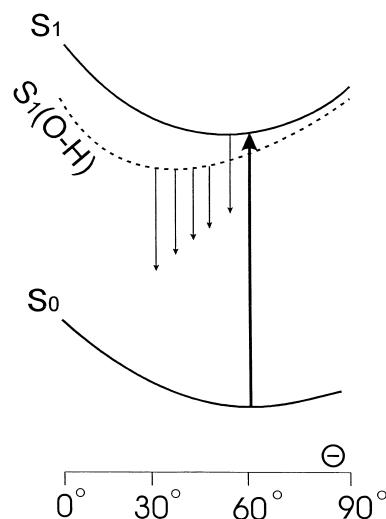


Figure 10. Potential energy cross section along the θ coordinate.

Contrary to Py-BN, the Py-BK molecule interacts specifically with alcohols. The stationary absorption spectra of Py-BK are solvent-independent, which suggests that ground state interaction between Py-BK and alcohols is negligible [11]. Our experimental data indicate that strong hydrogen-bonding interaction is generated in the excited state. The temporal evolution of the solvent cage in the case of butanol is described by four relaxation times: $\tau_1 = 0.243\text{ ps}$, $\tau_2 = 5.03\text{ ps}$, $\tau_3 = 42.6\text{ ps}$, and $\tau_4 = 133\text{ ps}$ [16]. Two short relaxation times describe the inertial and diffusive components of the monomer response. Two long relaxation times describe reorganization of aggregates. The fast component of the fluorescence decay of Py-BK was equal to 40 ps – 70 ps (Fig. 7), the relaxation time calculated from the experimentally obtained $c(t)$ function was equal to 129 ps – 138 ps (Fig. 6). These facts indicate that after excitation the generation of Py-BK hydrogen-bonded complexes is connected with some reorganization of the butanol aggregates. The decay time (39 ps) evaluated from the fast component of the kinetics obtained for integration limits $<380\text{--}430\text{ nm}>$, blue part of the TRF spectra, (Fig. 7B) corresponds well to the rise time (40 ps) evaluated from the kinetics obtained for integration limits $<520\text{--}620\text{ nm}>$ (Fig. 7C). This experimental fact indicates directly that kinetic interaction between species emitting fluorescence in the short and long-wavelength region of the TRF spectrum takes place. We can suspect that the short-wavelength fluorescence originates from Py-BK itself, whereas the long-wavelength emission, from the {Py-BK:butanol} complex. The decay time

(70 ps) evaluated from the fast component of the kinetics obtained for the total band integration (Fig. 7A) is much longer than decay time of the short-wavelength edge of the TRF spectra. This result indicates that the rate constant of the excited state reaction Py-BK \rightarrow {Py-BK:butanol} is the function of the time. In other words, the time necessary for the excited state complex creation depends on the local ground state arrangement of the butanol molecules around Py-BK.

We can conclude, that after excitation two processes take place: the excited state flattening (Py-BN and Py-BK) which is faster than the resolution of the equipment, and in the case of Py-BK, the alcohol complex formation (Fig. 10).

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