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# Time-Resolved Fluorescence Study of Exciplex Formation in Diastereomeric Naproxen–Pyrrolidine Dyads

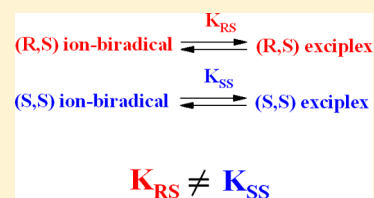
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**ABSTRACT:** The influence of chirality on the elementary processes triggered by excitation of the (S,S)- and (R,S)- diastereoisomers of naproxen-pyrrolidine (NPX–Pyr) dyads has been studied by time-resolved fluorescence in acetonitrile–benzene mixtures. In these systems, the quenching of the <sup>1</sup>NPX\*–Pyr singlet excited state occurs through electron transfer and exciplex formation. Fluorescence lifetimes and quantum yields revealed a significant difference (around 20%) between the (S,S)- and (R,S)-diastereoisomers. In addition, the quantum yields of exciplexes differed by a factor of 2 regardless of solvent polarity. This allows us to suggest a similar influence of the chiral centers on the local charge transfer resulting in exciplex and full charge separation that leads to ion-biradicals. A simplified scheme is proposed to estimate a set of rate constant values ( $k_1$ – $k_5$ ) for the elementary stages in each solvent system.



## INTRODUCTION

Most biologically active molecules, either natural or synthetic, are optically active agents. This has attracted very intensive investigation in the field, yet many questions still remain unanswered. Specifically, stereoisomers may display significantly different photochemical properties;<sup>1</sup> however, the literature data devoted to the influence of chirality on the photochemical reactivity are insufficient to provide a fully satisfactory understanding of this complex phenomenon.<sup>1–9</sup> Thus, it is difficult to identify the stage where chirality can exert an important influence. In this context, the recent reports<sup>9–11</sup> about the configuration-dependent rate of photoinduced single electron transfer (PET) in naproxen–pyrrolidine dyads (R,S)-NPX–Pyr and (S,S)-NPX–Pyr (Chart 1) are intriguing. Indeed, PET is one of the key elementary reactions in chemistry, including the processes going on in living systems.

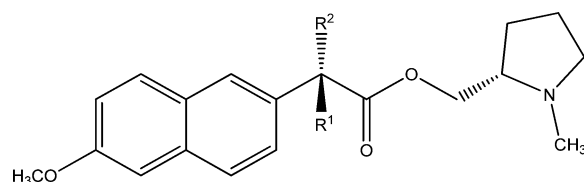
Quenching of the excited NPX chromophore of chiral dyads in solution has been investigated by means of photochemistry and spin chemistry methods.<sup>9–13</sup> It has been shown that the

quenching process involves not only PET, which leads to ion-biradical formation, but also singlet exciplex, in a fast equilibrium with PET. It has also been suggested that exciplex is the stage where stereodifferentiation is created.<sup>12,13</sup>

The exciplex displays a broad range of charge transfer and is characterized by a wide degree of mixing between ionic and locally excited states. When the former is much lower in energy, mixing is nearly negligible, and the exciplex is equivalent to a contact radical ion pair (CRIP). In polar solvents, solvation is favored, and CRIP are in equilibrium with solvent separated radical ion pairs (SSRIP).<sup>14,15</sup>

Short-lived, highly reactive exciplexes have attracted considerable interest because of their potential participation in many photochemical and photophysical processes (photosynthesis, light-harvesting, isomerizations).<sup>14–16</sup> Special attention to processes occurring in exciplexes is connected with the influence of external magnetic field (magnetic field effects, MFE) on exciplex fluorescence.<sup>14,15,17</sup> The manifestation of MFE is only possible when CRIP, as a form of exciplex in polar media, is in fast equilibrium with SSRIP. Such mechanism is typical for so-called linked systems, in which donor and acceptor groups are connected by rigid or flexible bridges consisting of covalently bonded atoms. Linked systems have been widely studied for the last two decades with different physical methods, including laser photolysis, time-resolved fluorescence and spin chemistry. The interest in them is due to the fact that they are regarded as models of photosynthetic and enzymatic processes.<sup>18</sup>

Chart 1. Structure of Naproxen–Pyrrolidine Dyads



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One of the main problems in spin chemistry of linked systems is related to the influence of solvent polarity on the equilibrium between exciplexes and ion-biradicals.<sup>10–12,14,16</sup> Such equilibrium cannot be determined by diffusion of free radical ions into the volume, as in bimolecular systems, and the key factors involved have not been fully established yet.<sup>15,17</sup> It is assumed that the difference between linked and bimolecular systems is determined by the peculiarities of molecular dynamics in the former.

It has been previously shown by means of chemical polarization (CIDNP) analysis that the dependence of PET efficiency on solvent polarity for (*R,S*)- and (*S,S*)-NPX–Pyr dyads, similar to several other linked systems, does not exhibit monotone profiles.<sup>12,13</sup> This has been related with the shift of equilibrium between SSRIP and CRIP.

In this context, it seems interesting to study the role of exciplex in the photoinduced processes of the (*R,S*)- and (*S,S*)-stereoisomers of NPX–Pyr dyad in solvents with different polarity, using time-resolved fluorescence measurements, and trace the influence of chirality on intramolecular fluorescence quenching.

## EXPERIMENTAL SECTION

**Materials.** Synthesis of (*S,S*)- and (*R,S*)-NPX–Pyr dyads (Chart 1) has been achieved by esterification of (*S*)- or (*R*)-naproxen (NPX) with (*S*)-*N*-methyl-2-pyrrolidinemethanol according to the procedure that was described earlier.<sup>9,10</sup> Stock solutions were prepared with concentration  $1.0 \times 10^{-4}$  M in two solvents: acetonitrile (Cryochrom,  $\epsilon = 36.8$ <sup>19</sup>) and benzene (Soyuzchemprom,  $\epsilon = 2.28$ <sup>20</sup>). The values of dielectric constants are shown for 20 °C.

**Spectroscopic Measurements.** Absorption spectra were measured with a HP 8453 diode array spectrophotometer (Agilent Technologies). The excitation and fluorescence spectra were recorded with a FLS920 spectrofluorometer (Edinburg Instruments). Lifetime measurements are based on single-photon-counting using an EPLED-320 laser diode ( $\lambda = 320$  nm, pulse duration  $\sim 600$  ps) as the excitation source. The kinetic traces were fitted by biexponential decay functions using a reconvolution procedure to separate the fluorescence of the sample from the laser pulse profile (with the application of FLS920 program or the FAST program provided by Edinburg Instruments). Naphthalene and anthracene were used as standards for quantum yield determinations.

All measurements were performed at room temperature (23 °C). Solutions were deaerated by argon bubbling for 30 min. Cuvettes with 1 cm optical path length were used, and the absorbance at excitation wavelength was kept ca. 0.1 to avoid nonlinear effects like self-absorption or inhomogeneous transient distribution.

The dielectric constants of acetonitrile–benzene mixtures were taken from the literature.<sup>21</sup>

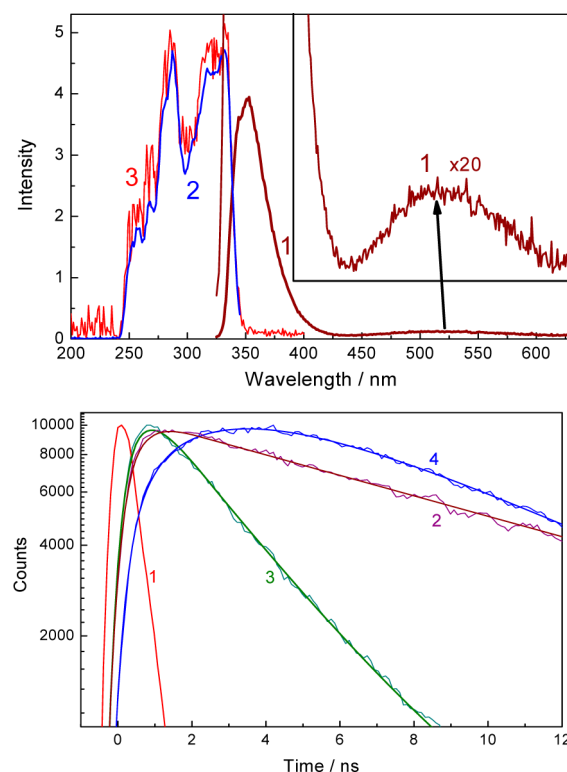
In numeric kinetic simulations the differential equations were solved using proprietary software (SPARK) based on the fourth-order Runge–Kutta method. The program allows calculations and fitting to experimental kinetic curves simultaneously at many wavelengths.

## RESULTS AND DISCUSSION

**Photophysical Properties of NPX–Pyr Dyads in Acetonitrile.** The absorption spectra of both stereoisomers, namely (*S,S*)-NPX–Pyr and (*R,S*)-NPX–Pyr were presented in

previous work.<sup>9–11</sup> These absorptions are ascribed to  $\pi$ – $\pi^*$ -type transitions. Besides, a chiral configuration does not influence the spectral distribution and the oscillator strength of the  $\pi$ – $\pi^*$ -transitions.

The fluorescence spectra of the NPX–Pyr in CH<sub>3</sub>CN displayed two emission bands: with a maximum at 351 nm (Figure 1 top), a weak band with a maximum at 520 nm, which



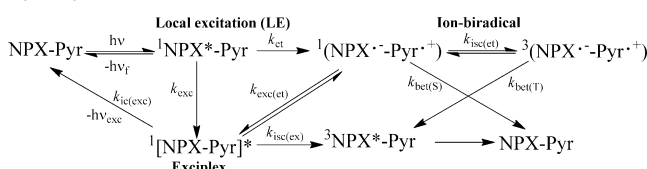
**Figure 1.** Top: fluorescence (1), excitation with registration at 351 nm (2), and excitation with registration at 520 nm (3) spectra of the (*R,S*)-NPX–Pyr dyad in acetonitrile. The inset shows a magnified emission spectrum in the long-wavelength range ( $>400$  nm). Bottom: Emission decay kinetics of NPX and the (*R,S*)-NPX–Pyr dyad in acetonitrile: (1) response function; (2) NPX at 351 nm; (3) NPX–Pyr at 351 nm; (4) NPX–Pyr at 520 nm. Solid lines are the two exponential fittings of experimental curves.

according to work<sup>9–11</sup> refers to the exciplex (inset of Figure 1 top). The excitation spectra for the 351 and 520 nm bands were identical (Figure 1 top, spectra 2 and 3). Figure 1 bottom presents the kinetics of NPX and (*R,S*)-NPX–Pyr luminescence in CH<sub>3</sub>CN. For example, the fluorescence lifetime of (*R,S*)-NPX–Pyr excited singlet state at 351 nm was almost 5 times shorter (2.7 ns) than that of NPX itself (12.8 ns). Moreover, the exciplex at 520 nm showed a rise time of fluorescence (2.35 ns), which is close to the decay time of the 351 nm band of the NPX–Pyr, and a decay time of 8.2 ns.

Because the NPX moiety in the dyad excited singlet state has an emission spectrum similar to that of free NPX, it can be assumed that the rate constants of radiationless, radiative, and  $S_1 \rightarrow T_1$  transitions retain their values in the dyad. Hence, it is reasonable to ascribe the decrease of the luminescence lifetime of the band at 351 nm in the dyads to the appearance of a new  $S_1$  excited state relaxation channel.

The proposed mechanism of photoinduced processes for the NPX–Pyr dyads (Scheme 1) was based on the results obtained by spin chemistry methods (CIDNP and MFE).<sup>12,13</sup> According

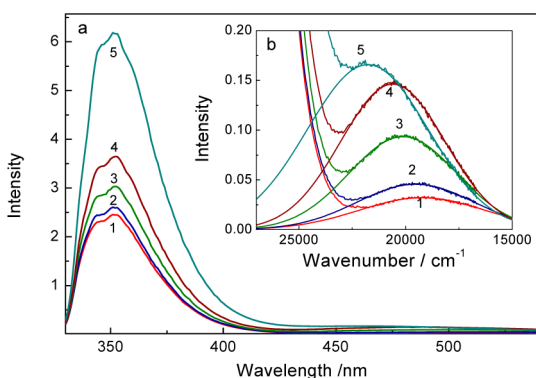
### Scheme 1. Quenching of Excited Singlet State of the NPX–Pyr Dyads in Solution<sup>12,13</sup>



to this mechanism the quenching of singlet excited state ( $S_1$ ) of the NPX–Pyr dyad involves electron transfer ( $k_{et}$ ) that results in the formation of ion-biradical. These species are in fast dynamic equilibrium with exciplex ( $k_{exc(et)}$ ). In solvents with weak polarity, the exciplex can be formed from the  $S_1$  state too ( $k_{exc}$ ). The exciplex decays through emission ( $-h\nu_{exc}$ ), internal conversion to the ground state ( $k_{ic(ex)}$ ), and intersystem crossing ( $k_{isc(ex)}$ ). The rate constants of back electron transfer from  $\text{NPX}^{\bullet-}$  to  $\text{Pyr}^{\bullet+}$  in the singlet and triplet spin states of ion-biradical are designated as  $k_{bet(S)}$  and  $k_{bet(T)}$ , respectively. Formation of the ground state of dyad can also occur from the local excited state (LE).

**Photophysical Properties of NPX–Pyr Dyads in Acetonitrile–Benzene Mixtures.** Calculations using the Rehm–Weller equation<sup>12</sup> show that the exciplex is favored in nonpolar and weakly polar solvents, whereas PET has to dominate in polar media (beyond  $\epsilon = 13$ ).<sup>9–13</sup>

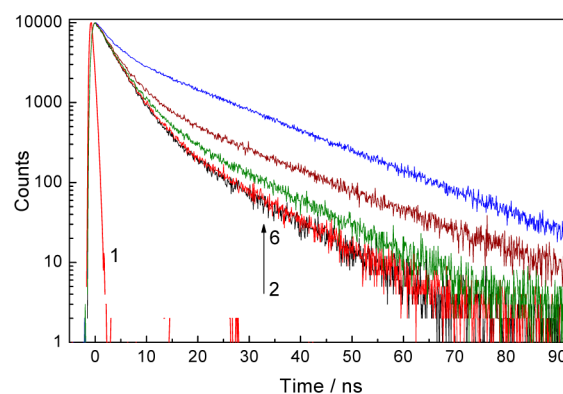
Hence, the fluorescence spectra and kinetics of the singlet excited states of (R,S)- and (S,S)-NPX–Pyr dyads were examined in solvents with different polarity (mixtures of acetonitrile and benzene). Figures 2 and 3 present the spectra obtained for the (S,S)-NPX–Pyr dyad, which contain bands belonging to the fluorescence of dyad itself and the exciplex.



**Figure 2.** (a) Emission spectra of the (S,S)-NPX–Pyr dyad in acetonitrile and benzene mixtures ( $\lambda_{exc} = 320$  nm): (1) 100%  $\text{CH}_3\text{CN}$  ( $\epsilon = 36.8$ ); (2) 80%  $\text{CH}_3\text{CN}$  ( $\epsilon = 29.6$ ); (3) 60%  $\text{CH}_3\text{CN}$  ( $\epsilon = 21.6$ ); (4) 40%  $\text{CH}_3\text{CN}$  ( $\epsilon = 14.5$ ); (5) 20%  $\text{CH}_3\text{CN}$  ( $\epsilon = 8.1$ ). (b) Fitting of exciplex bands by Gaussian functions.

The decrease of polarity led to the increase of the intensity and quantum yield of both the NPX local excited state and the exciplex (Figure 2). The emission maximum of NPX remained in place (351 nm), whereas the maximum of exciplex band shifted to the blue (Figure 2 inset). The decay of the NPX fragment fluorescence at 351 nm (Figure 3) was completely described in the framework of two exponential approximation.

The influence of polarity on emission quantum yields for the (R,S)-NPX–Pyr and (S,S)-NPX–Pyr dyads is shown in Table 1. As the solvent polarity decreased, the lifetime corresponding



**Figure 3.** Emission decay traces at 351 nm of the (S,S)-NPX–Pyr dyad in acetonitrile benzene mixtures ( $\lambda_{exc} = 320$  nm): (1) response function; (2) 100%  $\text{CH}_3\text{CN}$  ( $\epsilon = 36.8$ ); (3) 80%  $\text{CH}_3\text{CN}$  ( $\epsilon = 29.6$ ); (4) 60%  $\text{CH}_3\text{CN}$  ( $\epsilon = 21.6$ ); (5) 40%  $\text{CH}_3\text{CN}$  ( $\epsilon = 14.5$ ); (6) 20%  $\text{CH}_3\text{CN}$  ( $\epsilon = 8.1$ ).

to the first term ( $\tau_1$ ) remained without change; however, its contribution ( $A_1$ ) to the total intensity of the band with a maximum at 351 nm was reduced from  $\sim 80\%$  ( $\epsilon = 36.8$ , acetonitrile) to  $\sim 20\%$  ( $\epsilon = 8.1$ , 20% acetonitrile + 80% benzene). On the other hand, the preexponential factor for the second term ( $A_2$ ) and its corresponding lifetime ( $\tau_2$ ) showed an increase with decreasing solvent polarity. Therefore, the enhancement of the quantum yield of the fluorescence for the band at 351 nm is associated with the higher contribution of the second term ( $A_2$ ). The rise time of exciplex ( $\tau_{rise}$ ) was found to be independent of the solvent polarity and close to  $\tau_1$ , whereas the exciplex decay time ( $\tau_{decay}$ ) was much longer (Table 1 and Figure 4).

To understand the source of the two exponential kinetics of dyad luminescence and to describe the kinetics curves of the local excited state of the dyad and exciplex in the solutions with different polarities, we attempted to analyze the simplified version of Scheme 1 (Scheme 2). The main distinguishing feature of this scheme is the absence of the stage of the back-transition of the ion-biradical to the exciplex. We have changed the equilibrium between them by the variation of  $k_s$  values only. Moreover, we have added to the scheme the transfer between exciplex and local excited state of NPX–Pyr. The reason for taking into account the formation of  $^1\text{NPX}^*-\text{Pyr}$  (LE) from the exciplex was the above-mentioned proximity of the two times: the time of exciplex decay and the lifetime corresponding to the second term ( $A_2$ ) of the biexponential kinetics of  $^1\text{NPX}^*$  emission (Table 1).

The solution of the differential equations shows that in the frame of Scheme 2 the kinetics of  $^1\text{NPX}^*-\text{Pyr}$  ( $N_1(t)$ ) and exciplex ( $N_2(t)$ ) luminescence is determined by the following expressions:<sup>22</sup>

$$N_1(t) = A_1 e^{-k_{obs}^{fast} t} + A_2 e^{-k_{obs}^{slow} t} \quad (1)$$

$$N_2(t) = A_3 (e^{-k_{obs}^{fast} t} - e^{-k_{obs}^{slow} t}) \quad (2)$$

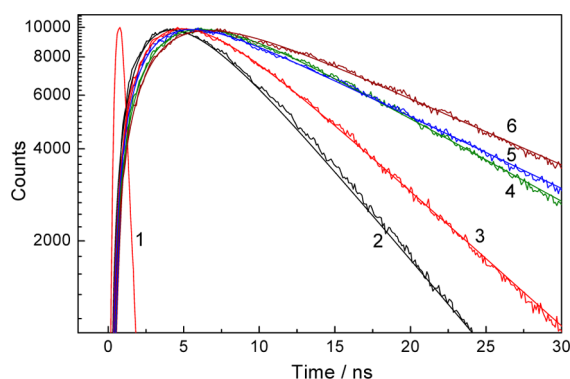
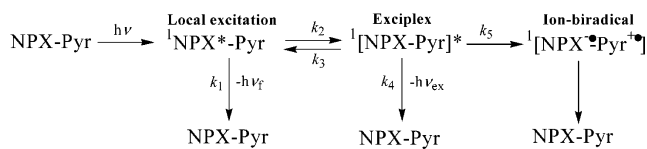
where

$$k_{obs}^{fast} = \frac{1}{2} [(k_1 + k_2 + k_3 + k_4 + k_5) + \sqrt{(k_1 + k_2 - k_3 - k_4 - k_5)^2 + 4k_2k_3}]$$



**Table 1.** Emission Quantum Yields and Lifetimes of the Local Excited State of the Dyads (LE) ( $\lambda_{\text{max}} = 351$  nm) and Exciplex ( $\lambda_{\text{max}} = 520\text{--}460$  nm) in the Process of Photoirradiation of Dyad Isomers in Solvents with Different Dielectric Constants

(R,S)-NPX-Pyr								
LE (351 nm)						exciplex		
$\epsilon$	$\varphi_f$	$\tau_1/\text{ns}$	$A_1/\%$	$\tau_2/\text{ns}$	$A_2/\%$	$\varphi_{\text{exciplex}} (\lambda_{\text{max}}/\text{nm})$	$\tau_{\text{rise}}/\text{ns}$	$\tau_{\text{decay}}/\text{ns}$
36.8	0.110	2.71	82.2	11.2	17.8	0.0156 (520)	2.35	8.20
29.6	0.146	2.70	80.8	11.2	19.2	0.0206 (512)	2.44	9.28
21.6	0.142	2.76	73.0	13.5	27.0	0.0389 (497)	2.56	15.9
14.5	0.183	2.81	58.3	17.9	41.7	0.0589 (486)	2.58	20.0
8.1	0.276	2.39	17.3	17.7	82.7	0.0774 (459)	2.14	18.4
(S,S)-NPX-Pyr								
LE (351 nm)						exciplex		
$\epsilon$	$\varphi_f$	$\tau_1/\text{ns}$	$A_1/\%$	$\tau_2/\text{ns}$	$A_2/\%$	$\varphi_{\text{exciplex}} (\lambda_{\text{max}}/\text{nm})$	$\tau_{\text{rise}}/\text{ns}$	$\tau_{\text{decay}}/\text{ns}$
36.8	0.138	3.36	77.5	11.4	22.5	0.0086 (522)	2.88	7.30
29.6	0.148	3.40	76.0	11.4	24.0	0.0110 (515)	3.06	9.50
21.6	0.179	3.43	69.5	13.0	30.5	0.0200 (500)	3.28	15.2
14.5	0.222	3.51	58.8	16.7	41.2	0.0297 (488)	3.31	19.0
8.1	0.364	2.94	21.0	17.0	79.0	0.0367 (460)	2.65	17.7

**Figure 4.** Exciplex decay kinetics of the (S,S)-NPX-Pyr in acetonitrile/benzene mixtures ( $\lambda_{\text{exc}} = 320$  nm): (1) response function; (2) 520 nm, 100%  $\text{CH}_3\text{CN}$  ( $\epsilon = 36.8$ ); (3) 510 nm, 80%  $\text{CH}_3\text{CN}$  ( $\epsilon = 29.6$ ); (4) 500 nm, 60%  $\text{CH}_3\text{CN}$  ( $\epsilon = 21.6$ ); (5) 490 nm, 40%  $\text{CH}_3\text{CN}$  ( $\epsilon = 14.5$ ); (6) 470 nm, 20%  $\text{CH}_3\text{CN}$  ( $\epsilon = 8.1$ ). Solid lines are the two exponential fittings of experimental curves.**Scheme 2**

$$k_{\text{obs}}^{\text{slow}} = \frac{1}{2}[(k_1 + k_2 + k_3 + k_4 + k_5) - \sqrt{(k_1 + k_2 - k_3 - k_4 - k_5)^2 + 4k_2k_3}]$$

On the other side, the numerical solution of differential equations in the framework of Scheme 2 allows us to calculate the kinetics of the local excited state of dyads (351 nm) and exciplex luminescence (520–460 nm) and compare them with the experimental curves (solid lines in Figure 4). The decay of LE fluorescence and exciplex formation are mainly determined by  $k_1$ ,  $k_2$ , and  $k_3$  rate constants. The kinetics of the exciplex decay is formed by the sum  $k_4 + k_5$ . To identify  $k_4$  and  $k_5$  rate constants, the quantum yields of the dyads LE ( $\varphi_f$ ) and exciplex ( $\varphi_{\text{ex}}$ ) luminescence (Table 1), which are determined by the following expressions, can be used:

$$\varphi_f = \varphi_f^0 \frac{k_1}{k_1 + k_2 - \frac{k_2 \times k_3}{k_3 + k_4 + k_5}} \quad (3)$$

$$\varphi_{\text{ex}} = \varphi_f \frac{k_r^{\text{Ex}}}{k_r^f} \times \frac{k_2}{k_3 + k_4 + k_5} \quad (4)$$

where the quantum yield of free NPX fluorescence  $\varphi_f^0 = 0.47^{10}$  and  $k_r^f$  and  $k_r^{\text{Ex}}$  are the rate constants of radiative processes for the dyad's local excited state and exciplex. For free NPX the rate constant of radiative process is  $k_r = 0.37 \times 10^8 \text{ s}^{-1}$  and it can be calculated using the quantum yield and lifetime (12.8 ns) of the NPX fluorescence and the quantum yield of the triplet state ( $\varphi_T = 0.28$ ).<sup>10</sup>

The set of  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4 + k_5$  rate constants calculated from the dyad's LE and exciplex luminescence kinetics and the values of quantum yields  $\varphi_f$  and  $\varphi_{\text{ex}}$  allow us to determine the ratio  $k_r^{\text{Ex}}/k_r^f$ . As  $k_r^f = 0.37 \times 10^8 \text{ s}^{-1}$  is determined from the luminescence of NPX, it is easy to calculate  $k_r^{\text{Ex}}$ . For the (S,S)-NPX-Pyr dyad in solutions with 100–40% content of acetonitrile  $k_r^{\text{Ex}}/k_r^f = 0.066 \pm 0.013$  and therefore  $k_r^{\text{Ex}} = (2.4 \pm 0.5) \times 10^6 \text{ s}^{-1}$ . The corresponding values for the (R,S)-NPX-Pyr dyad are  $k_r^{\text{Ex}}/k_r^f = 0.085 \pm 0.012$  and  $k_r^{\text{Ex}} = (3.3 \pm 0.5) \times 10^6 \text{ s}^{-1}$ . It is interesting that for solutions with 20% content of acetonitrile, the ratio  $k_r^{\text{Ex}}/k_r^f$  considerably increases to  $k_r^{\text{Ex}}/k_r^f = 0.12 \pm 0.02$  for (S,S)-isomers and  $k_r^{\text{Ex}}/k_r^f = 0.28 \pm 0.03$  for (R,S)-isomers. It is worth noting the increase of the  $k_3$  rate constant for 20% solution. Assuming that the radiationless process for the exciplex is absent, we can equate  $k_4$  and  $k_r^{\text{Ex}}$ . Tables 2 and 3 contain the set of  $k_1$ – $k_5$  rate constants, which were calculated under this assumption.

The analysis of experimental variation in the quantum yields of the dyad's and exciplex's fluorescence (Table 1) demonstrates the regular dependence on solvent polarity and indicates that the PET stage plays a role in the quenching singlet excited states of NPX-Pyr dyads in the whole range of the investigated polarity. This conclusion is in full accordance with the results of the CIDNP investigation of the systems under study.<sup>12,13</sup> The CIDNP effects detected during the UV irradiation of NPX-Pyr dyads in solvents with low polarity shows that even under these conditions the fast (nanosecond range) exchange between the exciplex and ion-biradical exist. The dependence of exciplex

**Table 2. Rate Constants ( $10^{-8}k$ ,  $s^{-1}$ ) of Separate Stages of (R,S)-NPX–Pyr Dyad Luminescence Quenching Calculated in Accordance with Scheme 2 in Solvents with Different Dielectric Constants**

$\epsilon$	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
8.1	0.78	2.0	1.60	0.103	0.233
14.5	0.78	2.5	0.31	0.033	0.443
21.6	0.78	2.6	0.20	0.033	0.593
29.6	0.78	2.6	0.16	0.033	1.093
36.8	0.78	2.6	0.17	0.033	1.293

**Table 3. Rate Constants ( $10^{-8}k$ ,  $s^{-1}$ ) of Separate Stages of (S,S)-NPX–Pyr Dyad Luminescence Quenching Calculated in Accordance with Scheme 2 in Solvents with Different Dielectric Constants**

$\epsilon$	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
8.1	0.78	1.2	1.03	0.043	0.337
14.5	0.78	1.8	0.30	0.024	0.486
21.6	0.78	1.8	0.28	0.024	1.076
29.6	0.78	1.8	0.23	0.024	1.153
36.8	0.78	2.0	0.26	0.024	1.622

fluorescence decay time on solvent polarity also takes place, but this effect is expressed weakly. Really, the decrease in exciplex decay time with increasing solvent polarity in donor–acceptor systems is usually attributed to the existence of the equilibrium between exciplex and radical-ion pair.<sup>15,16</sup>

It was noted above that the rise time of exciplex fluorescence ( $\tau_{\text{rise}}$ ) is sufficiently close to the lifetime of the short component of dyad fluorescence ( $\tau_1$ ) (Table 1). Therefore, the very short rise time of the band, which refers to the exciplex, along with the weak dependence of this time on solvent polarity is consistent with the exciplex being formed both from the ion-biradical and from the local excited  $S_1$  state of NPX–Pyr dyad.

**Stereodifferentiation between the Photoinduced Processes of (R,S)- and (S,S)-NPX–Pyr Dyads.** The analysis of data from Table 1 demonstrates that there is a significant difference between the fluorescence lifetimes and quantum yields for the (R,S)- and (S,S)- diastereomeric dyads. Thus, the time of dyads LE fluorescence decay ( $\tau_1$ ) and exciplex fluorescence rise time ( $\tau_{\text{rise}}$ ) differ by 20–30% for (S,S)- and (R,S)-NPX–Pyr. Specifically, the locally excited singlet state of the (S,S)-form lives longer and accordingly the (S,S)-exciplex is accumulated more slowly.

However, the comparison of fluorescence quantum yields of exciplexes of (R,S)- and (S,S)-diastereoisomers of NPX–PYR dyads, measured in solvents with strong and weak polarities, demonstrates a marked stereodifferentiation which reaches 2-fold. The difference of fluorescence quantum yields of the singlet excited state of dyads is within the range 20%. It is important that these differences are practically not dependent on solvent polarity.

Note that according to eqs 3 and 4 there are several elementary processes, which impact the quantum yields; so it is difficult to estimate the influence of chiral centers on the separate stages. But there is a further point to be made here.

The observable difference in the scale of the influence of absolute configuration of the chiral centers on fluorescence quantum yields of dyads themselves (20–30%) and exciplexes (2-fold) is connected with the difference between absolute values of these yields only. Likewise, the appearance of the

stereodifferentiation average in all solvent mixtures points to the similar influence of the stereochemistry on the process of partial charge transfer (exciplex, CRIP) and full charge transfer (ion-biradical, SSRIP).

## CONCLUSION

Thus, the investigation of time-resolved fluorescence of (R,S)- and (S,S)-NPX–Pyr dyads has demonstrated the participation of PET and exciplex in the quenching of the excited NPX chromophore. It has also been shown that chiral centers can influence the fluorescence quantum yields and rates of the fluorescence quenching of dyads themselves and exciplexes. It seems reasonable that steric hindrance, which is the source of stereodifferentiation, has a similar influence on local and full charge transfer. These results constitute a clear example of the influence of chirality on the rate of elementary photochemical processes.

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### Notes

The authors declare no competing financial interest.

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