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Photonics of styrylquinoline dyads

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Abstract: Three types of bichromophoric styrylquinoline (SQ) dyads are discussed in the review: bis-styrylquinoline dyads, styrylquinoline-merocyanine dyads, and styrylquinoline-naphthol dyads, in comparison with the corresponding model monochromophoric compounds. A variety of photochemical and photophysical processes is observed in the dyads: photoluminescence, reversible and kinetic-driven one-way photoisomerization, \([2+2]\) photocycloaddition with formation of a single \(rctt\)-isomer of the cyclobutane derivative, Forster resonance energy transfer (FRET) where the SQ chromophore can act as an energy donor or acceptor. Operation of the dyads as photoswitches and molecular logic gates is also considered.

Keywords: bichromophoric dyad; 2-styrylquinoline; electronic energy transfer (FRET); photoisomerization; molecular switches and logic gates.

1 Introduction

Supramolecular bichromophoric molecular systems attract an attention from the viewpoint of investigating different photophysical and photochemical properties such as exciplex and excimer formation \([1, 2]\), electron and energy transfer \([3–10]\), with possible applications, for example, in light harvesting and artificial photosynthesis \([11–13]\). Dyads with photoactive chromophores – photochromes – can be reversibly switched between different states upon light excitation and used as models of molecular devices \([14–16]\), switches \([17, 18]\), and logic gates \([19–24]\).

In this review we discuss the properties of the bichromophoric dyads based on 2-styrylquinoline (SQ), which has been chosen as a chromophore since the SQ molecule contains two functional groups, a central (ethyleneic) double bond and an endocyclic (quinoline) nitrogen atom and comprises several useful properties:

1) photoisomerization of the ethylenic group allows switching between two isomeric states, \(trans\) (E) and \(cis\) (Z),
2) no side photochemical reactions,
3) both isomeric states are thermally stable,
4) protonation of the nitrogen atom allows shifting the absorption spectrum, thus changing the spectral region of photosensitivity,
5) both photoisomerization and protonation are reversible,
6) \(pK_a\) increases on going from \(S_0\) to \(S_1\) state.

In order to build bichromophoric dyad, SQ fragment should be connected to another chromophore (photoactive fragment), for this the SQ molecule should contain additional functional group. As a general building block we have chosen 2-(4-hydroxystyryl)quinoline, which by functionalization at the hydroxy group can be connected with chromophore X by bridge B (linking group), Scheme 1. Bridge B can be polymethylene chain or \(\omega\)-xylylene group. Chromophore X can be another SQ fragment, as in the case of bis-styrylquinoline dyads S3S and SoS, merocyanine fragment, as in the case of styrylquinoline-merocyanine dyads SQnMC, or naphthol fragment, as in the case of styrylquinoline-naphthol dyads SQnNp. For all bichromophoric dyads, 2-(4-methoxystyryl)quinoline MeSQ is a model compound (or one of the models, see below).

Every dyad has its own peculiarities. In bis-styrylquinoline dyads S3S and SoS, the photoisomerization of the SQ fragments takes place similar to the model MeSQ but reaction kinetics of bichromophoric dyads differs from that of monochromophoric model. Additionally, the dyad SoS undergoes stereospecific head-to-head \([2+2]\) photocycloaddition between two \(E\)-SQ fragments with formation of a single \(rctt\)-isomer of the cyclobutane derivative.

In styrylquinoline-merocyanine dyads SQnMC (n = 3, 11), the Forster resonance energy transfer (FRET) from the SQ fragment to the merocyanine (MC) one results in quenching of the former and sensitization of the latter. This appears in decrease (for SQ) or increase (for MC) in photoluminescence and photoisomerization quantum yields of fragments. Additionally, two chro-
mophores in the dyads have similar but differently charged \( \pi \)-systems, because they are relatives: merocyanine is really an N-alkylated derivative of styrylquinoline. Due to this, by protonation of the SQ fragment, non-symmetric "semi-charged" (one-charged) styrylquinoline-merocyanine dyad can be transformed to quasi-symmetric double-charged "bis-merocyanine" dyad where both fragments are photoactive. This possibility can be used to launch a cycle of kinetic-driven one-way photoisomerization of the SQ fragment.

In the third type of the dyads studied, the styrylquinoline-naphthol dyads SQnNp \((n = 2 - 5)\), the FRET from naphthol (Np) moiety to styrylquinoline one is observed. Additionally, in the dyads SQnNp, the SQ fragment is a photobase whereas the Np fragment is a photoacid that can be used for the excited-state intramolecular proton transfer (ESIPT). The SQ-fragment photoisomerization quantum yield of the SQnNp proved to be independent on the methylene group number \(n\), whereas the Np-fragment fluorescence decreases with the \(n\) decreasing being minimal for the dyad with three-methylene chain.

Due to photochemical activity of the constituting fragments, the styrylquinoline dyads can operate as photonic molecular switches and logic gates.

Before discussing properties of the SQ-based dyads, it is worthwhile to consider briefly the properties of the SQ photochrome itself.

\[ \text{Scheme 1: General structure of the styrylquinoline dyads and the model 2-(4-methoxystyryl)quinoline MeSQ (s-trans conformers are shown).} \]

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### 2 Photonics of 2-styrylquinoline

2-Styrylquinoline has a long-wavelength absorption band (LWAB) with maximum \( (\lambda_{\text{max}}) \) at 338 – 340 nm (in ethanol) and a molar absorption coefficient \( (\epsilon_{\text{max}}) \sim 2.7 – 2.9 \times 10^4 \text{ M}^{-1}\text{cm}^{-1} \) [25, 26]. In acidic media, upon protonation of the nitrogen atom, the LWAB is red-shifted to 380 – 381 nm with \( \epsilon_{\text{max}} \) increasing to 3.8 – 4.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}.

In the neutral form, SQ emits at 377 nm with the fluorescence quantum yield \( (\phi_f) \) 0.04; in acidic media, the emission band is red-shifted to 435 nm without the \( \phi_f \) changing [25]. The \( pK_a \) value of 2-styrylquinoline increases from \( pK_a = 4.8 \) to \( pK_a^* = 12.0 \) in the excited S\(_1\) state, therefore, this compound is a photobase [25].

2-Styrylquinoline is a photochrome, the quantum yield of trans-cis photoisomerization \( (\phi_{tc}) \) is 0.2 – 0.27 and that of cis-trans photoisomerization \( (\phi_{ct}) \) is 0.27 – 0.38 [25, 26]. In protonated form, according to different data, the \( \phi_{tc} \) value increases to 0.62 – 0.83, the \( \phi_{ct} \) value varies in the range of 0.36 – 0.67 [25, 26].

Thus, full cycle of the reversible transformations of 2-styrylquinoline is depicted by Scheme 2.
clization reaction of 2-styrylquinoline (in $S_0$ state) [30, 31]. The closed-ring compounds (DHPs), if formed in the excited state, due to thermal instability decompose rapidly with ring opening in the ground state that prevents their observation in steady-state photolysis.

Figure 1 shows the calculated potential energy surface (PES) profile (cross section) along the coordinate of the isomerization reaction (change in the dihedral angle $\beta$ between two aromatic nuclei during rotation around the ethylenic bond) in the ground ($S_0$) and excited ($S_1$) states for the $s$-cis conformer of 2-styrylquinoline [32]. In the $S_0$ state, the $E$ and $Z$ isomers are separated by high potential barrier peaked in the region of the perpendicular conformer ($perp$-conformer, $\beta = 90^\circ$). On the PES of the $S_1$ state, the $perp$-conformer corresponds to the global minimum. The shallow minimum of the excited $E$-isomer is separated from the global minimum by a small barrier. The barrier arises due to the avoided crossing between the “aromatic” excited state in the region of the Franck–Condon transition of the $trans$-isomer and “ethylenic” excited state in the region of the $perp$-conformer. On moving along the isomerization reaction coordinate from the $trans$-isomer to the $perp$-conformer, the characteristic changes in the nature and localization of the frontier molecular orbitals take place [32].

In general, this picture corresponds to the photoisomerization diabatic mechanism. After the $S_1 \rightarrow S_0$ transition, the $perp$-conformer with equal probability can form both $trans$-isomer and $cis$-isomer, partitioning factor is considered to be 0.5. Therefore, for diabatic reaction, the limiting value of the photoisomerization quantum yield cannot exceed 0.5.

3 Photonics of bis-styrylquinoline dyads. Photoisomerization and photocycloaddition

Bis-styrylquinoline dyad S3S with tri-methylene bridge

The simplest bis-styrylquinoline dyad S3S ($EE$-1,3-bis(4-(2-quinoline-2-vinyl)phenoxy)propane), where two SQ fragments are linked by tri-methylene chain, was synthesized by condensation of quinaldine with bis(4-formylphenoxy)propane in the presence of zinc chloride with microwave irradiation of the reaction mixture, Scheme 4 [33].

Figure 2 demonstrates absorption spectra of the $EE$ isomer of the S3S dyad (spectrum 1) and the $trans$-isomer of the model styrylquinoline MeSQ. A comparison of two spectra (Fig. 2, spectra 1 and 2) shows that the absorption spectrum of the bichromophoric dyad is actually a doubled spectrum of monochromophoric styrylquinoline, a fact that indicates the lack of significant interaction be-
tween the π-systems of two covalently bound SQ fragments in the ground state (S₀) of the dyad.

Figure 2: Absorption spectra in ethanol of (1) the EE isomer of bis(styrylquinoline) dyad S₃S and (2) the trans-isomer of the styrylquinoline MeSQ; (3) luminescence (excitation at 360 nm) and (4) luminescence excitation (observation at 440 nm) spectra of the S₃S dyad.

Figure 2 also presents the luminescence (3) and luminescence excitation (4) spectra of the EE isomer of the S₃S. The emission band of the S₃S is bathochromically (red) shifted by 8 nm as compared to the model MeSQ and has a maximum at 432 nm; the fluorescence quantum yield for both compounds is 0.02. Slight shifts of the emission bands are observed for both compounds (S₃S and MeSQ) upon excitation at the short- and long-wavelength edges of the absorption bands, which are associated with the presence of conformers (rotamers). This conclusion is also confirmed by certain differences in shape of the luminescence excitation spectrum (Fig. 2, spectrum 4) in comparison with the absorption spectrum (Fig. 2, spectrum 1) and by slight changes in the excitation spectrum with varying the detection wavelength. The phenomenon of conformational isomerism due to rotation of aromatic substituents about the quasi-single bonds in the ethylene group is well known for diarylethylenes including styrylquinolines [34].

Generally, dyad with two photoisomerizable groups can exist in four isomeric forms, as EE, EZ, ZE, and ZZ isomers, Scheme 5. In this particular case, due to the symmetry of the dyad S₃S, two of these forms, namely, EZ and ZE isomers coincide and are spectrally indistinguishable.

Spectral changes on irradiation of the EE-S₃S with UV light are similar to those for the model E-MeSQ and characteristic for the trans-cis photoisomerization reaction, Fig. 3. Spectral changes finish in a photostationary state PS₁ (PS₃₆₅ on Fig. 3, spectrum 9), whose composition depends on the irradiation wavelength λ. Using different PSs, the spectrum of the dyad ZZ-isomer (Fig. 3, spectrum 10) is calculated by the Fischer method [35]; this spectrum is a doubled that of Z-MeSQ.

The isosbestic point at 259 nm (Fig. 3) indicates the involvement of only two chromophores in the reaction; these chromophores correspond to two isomeric forms, trans- and cis-, of the SQ moieties of the dyad. The principal component analysis (PCA) of the spectral changes confirms this conclusion, Fig. 4.

Each point on Fig. 4 corresponds to the particular spectrum of the dyad S₃S or model MeSQ photolysis reaction mixture. PCA reveals slight differences between the dyad and the model spectra. The limiting points corresponding to pure isomers of the dyad and model are located close to each other but do not coincide. However, single directed spectral changes are observed for both cases, and the linearity of graphs (Fig. 4) during the entire irradiation time indicates that only one reaction - photoiso-
merization of the styrylquinoline nucleus - proceeds in solutions, and absorption of the dyad is determined by two chromophores only, the trans-form and the cis-form of the SQ fragment.

Nevertheless, two SQ chromophores are distributed between different dyad isomers, EE, EZ(ZE) and ZZ, and this appears in reaction kinetics.

![Figure 4: Principal component analysis of the spectral changes during the photolysis of the dyad 53S (1) and model styrylquinoline MeSQ (2); the experimental spectra are presented in the basis of two first singular vectors p1 and p2. Marked are the data points that correspond to the initial spectra of EE and trans-isomers, to the photostationary states PS365, and to the spectra of ZZ and cis-isomers.](image)

### Photoisomerization kinetics

Figure 5 shows the kinetics of the photoisomerization reaction of the model MeSQ and the dyad 53S. The initial portion of the curves have the same slope, but then they vary and curve 2 characterizing the reactivity of the dyad flattens out to a higher PS plateau.

The kinetics of change in absorbance (A) of the solution during the photolysis of MeSQ (2 isomers, 2 reactions) is described by the system of three equations:

\[
A = A_t + A_c = \varepsilon_t \cdot c_t \cdot l + \varepsilon_c \cdot c_c \cdot l
\]

\[
dc_t/dt = (-\phi_{tc} \cdot A_t + \phi_{ct} \cdot A_c) \cdot I_0 (1 - 10^{-A})/(A \cdot l)
\]

\[
dc_c/dt = (\phi_{tc} \cdot A_t - \phi_{ct} \cdot A_c) \cdot I_0 (1 - 10^{-A})/(A \cdot l),
\]

where \( A_t \) and \( c_t \) are an absorbance and molar absorption coefficient (L mol\(^{-1}\) cm\(^{-1}\)) of the \( t \)-th isomer at the irradiation wavelength, and \( c_t \) is its concentration. \( \phi_{tc} \) and \( \phi_{ct} \) are the quantum yields of trans-cis and cis–trans photoisomerization, \( I_0 \) is an intensity of acting light, and \( l \) is an optical path length. This system is reduced to differential equation 1.

\[
dA/dt = -(\varepsilon_t - \varepsilon_c) \cdot (\phi_{tc} \cdot A_t - \phi_{ct} \cdot A_c) \cdot I_0 \cdot (1 - 10^{-A})/A
\]  

(1)

The complete kinetic scheme describing photochemical processes during the photolysis of the bichromophoric dyad (in general case) includes four isomers and eight reactions and is described by the system of five equations [33]. The system can be significantly simplified provided the following conditions are satisfied:

1) the MACs of the dyad are the sums of the MACs of the corresponding isomers of MeSQ, \( \varepsilon_{EE} \), \( \varepsilon_{EZ} = \varepsilon_{EZ} = \varepsilon_{EZ} = \varepsilon_{E} + \varepsilon_{Z} \) and \( \varepsilon_{ZZ} = \varepsilon_{Z} \), (where \( \varepsilon_{E} \) and \( \varepsilon_{Z} \) (this corresponds to the experimental fact that the absorption spectrum of the dyad is a sum of the spectra of two SQ fragments);

2) all SQ fragments have equal quantum yields of trans-cis photoisomerization \( \phi_{EZ} \) and cis–trans photoisomerization \( \phi_{EE} \) no matter in which dyad isomer the fragment is (this corresponds to the experimental data that only two chromophore units are present in the solution during the entire time of the dyad photolysis).

As a result, the system of five equations is reduced to differential equation 2.

\[
dA/dt = -2(\varepsilon_t - \varepsilon_c) \cdot (\phi_{EE} \cdot (A_{EE} + A_{ZE}) + \phi_{EE} \cdot (A_{ZE} + A_{ZZ})) \cdot I_0 \cdot (1 - 10^{-A})/A.
\]  

(2)

For the initial portion of the kinetic curve (at \( t \rightarrow 0 \)) equation 1 is reduced to equation 3, and equation 2 transforms
into equation 4.
\[ dA/dt = (\epsilon_t - \epsilon_c) \cdot \phi_{tc} \cdot I_0 \cdot (1 - 10^{-A}) \] (3)
\[ dA/dt = 2(\epsilon_E - \epsilon_Z) \cdot \phi_{EZ} \cdot I_0 \cdot (1 - 10^{-A}) \] (4)

It is seen that the slope of the kinetic curve in the initial part is determined by the difference in MACs of two isomers and the quantum yield of trans-cis photoisomerization and does not depend on the quantum yield of the reverse reaction of cis–trans photoisomerization. Since the slopes of the initial portions of the photolysis rate curves of the dyad S3S and the model MeSQ coincide, hence, comparing equations 3 and 4, we find \( \phi_{EZ} = 0.5 \phi_{tc} \). Upon light absorption by the bichromophoric dyad, excitation is distributed with equal probability between two chromophores, therefore, the photoisomerization quantum yield per SQ fragment (\( \phi_{EZ} \)) is half that of monochromophoric styrylquinoline (\( \phi_{tc} \)).

Another limiting case, \( t \to \infty \), corresponds to a photostationary state PS\( _1 \), when \( dA/dt = 0 \). Thus, \( (\phi_{tc} \cdot A_t)_{PS} = (\phi_{ct} \cdot A_c)_{PS} \) and equation 1 transforms to equation 5
\[ (\phi_{tc} \cdot \epsilon_t \cdot (c_t)_{PS})_{PS} = (\phi_{ct} \cdot \epsilon_c \cdot (c_c)_{PS})_{PS} \] (5)

Under the same condition \( (t \to \infty) \), equation 2 gives \( \phi_{EZ} \cdot (A_{EE} + A_{ZE}) = \phi_{ZE} \cdot (A_{ZE} + A_{ZZ}) \). The total concentration of the SQ fragments of the dyad in the trans-form is \( c'_t = (2c_{EE} + c_{ZE} + c_{EZ}) \), and that in the cis-form is \( c'_c = (2c_{ZZ} + c_{ZE} + c_{EZ}) \), with \( c_{ZE} = c_{EZ} \). After rearrangements, we obtain the equation 6 for the PS of the bichromophoric dyad.
\[ \phi_{EZ} \cdot \epsilon_E \cdot \left( c'_c - (1 - \epsilon_E/\epsilon_Z) \cdot c_{ZE} \right)_{PS} = = \phi_{ZE} \cdot \epsilon_Z \cdot \left( c'_t + (\epsilon_E/\epsilon_Z - 1) \cdot c_{ZE} \right)_{PS}. \] (6)

From equations 5 and 6 the equation 7 can be obtained for the concentration ratio of isomers in the PSSs of the bichromophoric dyad and monochromophoric styrylquinoline.
\[ \left( \left( c'_c - (1 - \epsilon_E/\epsilon_t) \cdot c_{ZE} \right) / c_{PS} \right)_{PS} = = \left( \left( c'_t + (\epsilon_E/\epsilon_c - 1) \cdot c_{ZE} \right) / c_{PS} \right) \] (7)

Equations 1 and 2 are solved numerically. Curve 1 in Fig. 5 shows the optimal approximation of the experimental kinetic curve for the model methoxystyrylquinoline MeSQ using equation 1; the photoisomerization quantum yields obtained are \( \phi_{tc} = 0.56 \) and \( \phi_{ct} = 0.43 \).

Curve 2 in Fig. 5 represents the optimal approximation of the experimental kinetic curve for the dyad S3S using equation 2; the photoisomerization quantum yields obtained in this case are \( \phi_{EZ} = 0.34 \) and \( \phi_{ZE} = 0.23 \). These values are almost half the respective photoisomerization quantum yields of MeSQ, which is in agreement with equation 4.

Figure 5 also presents versions of experimental data approximation for the dyad using equation 1 under the assumption of two unbound chromophores. Theoretical curve 3 in Fig. 5 calculated formally using the quantum yields equal to those for model styrylquinoline MeSQ (\( \phi_{tc} = 0.56 \) and \( \phi_{ct} = 0.43 \)) describes well the initial portion, but its gives underestimated absorbance values for the photostationary state, which has the composition determined by equation 5 rather than equation 6 in this case.

Curve 4 in Fig. 5 represents the optimized approximation curve according to equation 1 under condition of independent light absorption by each SQ fragment. The photoisomerization quantum yields are \( \phi_{tc} = 0.55 \) and \( \phi_{ct} = 0.78 \) with the root-mean-square error of absorbance \( (\Delta A) \) being significantly higher than for the approximation according to equation 2, 0.013 and 0.0018, respectively. A comparison with the data for MeSQ shows that the trans–cis photoisomerization quantum yields (\( \phi_{tc} \)) coincide for the dyad and for the model in agreement with the equal initial slopes of the rate curves. However, the optimized quantum yield of the cis–trans photoisomerization reaction (\( \phi_{ct} \)) for the dyad (0.78) is almost two times that for the model (0.43), a difference that is due to the necessity to increase the fraction of the trans-isomer by increasing its formation quantum yield in order to make the calculated PS composition of the dyad consistent with the higher absorbance.

As mentioned above, the SQ fragments in the trans- and cis-forms are distributed in the dyad S3S between different isomers. Figure 6 shows the kinetics of changes in relative concentrations of the dyad isomers and SQ fragments in the trans- and cis-forms. The fraction of the trans-form monotonically decreases during the dyad photolysis, and that of the cis-form symbatically increases as in the case of MeSQ photolysis. At the same time, the concentration curve of the nonsymmetrical E\( Z \) (ZE) isomers of the dyad passes through a maximum, and the ZZ isomer accumulation curve is an S-shaped in character with an induction period.
A comparison of Figures 5 and 6 leads to the conclusion that the change of the photolysis kinetics in the case of integration of the SQ groups into the covalently-bound dyad is due to the formation of the nonsymmetrical EZ (ZE) isomers of the dyad. Indeed, the data in Fig. 5 show that the most significant differences between curves 4 and 2 calculated according to two different models are observed in the time range of 35–120 s. As is evident from Fig. 6, it is at this time range that the concentration of EZ (ZE) isomers of the dyad reaches a peak value and the reaction kinetics in general is determined to a significant extent by the reactivity of the unsymmetrical isomers. Unlike the case of symmetrical EE and ZZ isomers, absorbed light is distributed unevenly between the two SQ fragments in the unsymmetrical isomers, thereby altering the photolysis kinetics of the dyad as compared with the photolysis of the mixture of two unbound MeSQ isomers.

Thus, integration of two styrylquinoline fragments into the covalently bound dyad actually does not affect the spectral properties and initial kinetics of photolysis, but it changes the slope of the kinetic curve at medium photolysis times and results in enrichment of the photostationary state in the isomer with the higher MAC at the wavelength of irradiation (trans-isomer at the wavelength of 365 nm).

As mentioned in introduction, bichromophoric dyads are convenient models for the study of energy transfer. However, observation of energy migration between identical chromophores (donor–donor transfer) requires fluorescence anisotropy to be measured [36]. In dyads with different chromophores, energy transfer is experimentally manifested in the fact of emergence of bands corresponding to energy donor absorption in the fluorescence excitation spectrum of the energy acceptor, see below.

The fluorescence spectrum of the styrylquinoline cis-isomer is unknown; this compound has a very low quantum yield of luminescence if at all. With allowance for the hypsochromic shift of the absorption spectrum of the styrylquinoline cis-isomer relative to the trans-isomer, the suggested emission spectrum of the former should overlap with the absorption spectrum of the latter.

Figure 7 depicts the absorption spectrum of the photostationary mixture PS\textsubscript{365} obtained by irradiation of the dyad S3S with 365 nm light (spectrum 1), the luminescence spectrum of this mixture (spectrum 2), and a luminescence excitation spectrum (spectrum 3). The amounts of the symmetrical isomers in PS\textsubscript{365} are 6 % for the EE-isomer and 66 % for the ZZ-isomer, and the total amount of the nonsymmetrical isomers ZE (EZ) is 28 %. It is in these dyad isomers that energy transfer from the SQ fragment in the cis-form to the SQ fragment in the trans-form is possible.

Comparing Figures 7 and 2, we see that the PS luminescence spectrum (Fig. 7, spectrum 2) is equal to the emission spectrum of the SQ trans-isomer (Fig. 2, spectrum 3). The luminescence excitation spectrum (Fig. 7, spectrum 3) does not correlate with the PS\textsubscript{365} absorption spectrum (Fig. 7, spectrum 1), but it coincides with the absorption and luminescence excitation spectra of the EE-isomer (Fig. 2, spectrum 4). This indicates the nonoccurrence of energy transfer from the excited SQ fragment in the cis-form to the SQ fragment in the trans-from in the ZE (EZ) isomer of the dyad.

The efficiency of energy transfer is determined by the ratio of rate constants of energy transfer \(k_{ET}\) and spontaneous donor deactivation \(k_d\). In this case, the \(k_d\) value is
determined to a significant extent by the rate of the cis–
trans isomerization reaction, which proceeds on the pi-
second timescale for the cis-isomers of diarylethlenes. For example, the measured lifetime of excited cis-stilbene is approximately $\sim 1$ ps; hence, the deactivation rate constant $k_d$ is approximately $\sim 10^{12}$ c$^{-1}$ [37]. The rate constant of energy transfer $k_{ET}$ in the styrylquinoline-naphthol dyad is approximately $\sim 10^{10}$ c$^{-1}$ (see below). Using these values as the first approximation, we can estimate the rate constant ratio as $k_d \gg k_{ET}$ for the dyad S3S, which explains the lack of energy transfer in the ZE (EZ) isomer of the dyad.

As it is clear from the above discussion, due to the flexibility of the trimethylene bridge, the SQ fragments in the dyad S3S does not practically interact with each other. To promote more essential intramolecular interaction between chromophores, two SQ fragments have been connected by ortho-xylylene bridge.

**Bis-styrylquinoline dyad SoS with ortho-xylylene bridge**

The bis-styrylquinoline dyad SoS (1,2-bis-(E)-(4-[2-quinolin-2-yl-vinyl]-phenoxymethyl)benzene), where two SQ fragments are linked by ortho-xylylene group, was synthesized by alkylation of (E)-2-(4-hydroxy styryl)quinoline with 1,2-bis(bromomethyl)benzene, Scheme 6 [38, 39]

![Scheme 6: Synthesis of bis-styrylquinoline dyad SoS.](image)

Similar to the dyad S3S, the absorption spectrum of the dyad SoS is doubled that of the model MeSQ (with little addition of the o-xylylene absorption at $\sim 260$ nm). Also similar to the dyad S3S, irradiation of a solution of the EE-SoS with light of 365 nm results in a fast reaction with the spectral changes which correspond to those observed under irradiation of the model MeSQ and are attributed to trans-cis photoisomerization, Fig. 8, spectra 1 – 5. However, in contrast to MeSQ and S3S, spectrum 5 proves to belong not to a real but quasi-photostationary state; subsequent prolonged irradiation results in a gradual decrease and, finally, the disappearance of the LWAB and appearance of a structured blue-shifted absorption band with maxima at 306 and 319 nm (spectrum II). Comparison with the spectrum of quinaldine (Fig. 8, spectrum I2) testifies that spectrum II is characteristic of the separate (without $\pi$-conjugation) quinoline rather than styrylquinoline nucleus.

![Figure 8: Spectral variations during irradiation of an air-saturated solution of EE-SoS (2.9×10$^{-5}$ mol dm$^{-3}$) in ethanol with light of 365 nm, intensity 4.8×10$^{-9}$ Einstein cm$^{-2}$ s$^{-1}$, irradiation time: 0 (1), 5 (2), 15 (3), 30 (4), 60 (5), 780 (6), 1560 (7), 2460 (8), 4260 (9), 7860 (10), 19260 s (11); (12) is a spectrum of quinaldine.](image)

The principal component analysis of the spectral changes reveals definitely two photochemical reactions in the dyad SoS, Fig. 9. The first five points on Fig. 9 from the EE to PS$^{365}$ correspond to the spectra I – 5 in Fig. 8 and are situated at the straight line 1 connecting the EE and ZZ isomers. The straightness of the graph means that only one reaction involving only two chromophores takes place in the solution (or, if a greater number of chromophores, their ratio is maintained throughout the reaction time). In this case, the line 1 characterizes reversible photoisomerization between trans- and cis-isomers of the SQ-fragments.

The final points on Fig. 9 from PS$^{365}$ to photoproduct X are situated at the other straight line 2. Therefore, after (fast) achieving photostationary state, only (slow) reaction of the X formation contributes to the spectral changes, whereas the ratio of the trans- and cis-isomers concentrations maintains constant thus ensuring straightness of graph 2 on Fig. 9. However, Figure 9 does not allow determining which of the isomers is involved in the second reaction.

According to ESI mass-spectrum, the photoproduct X has the same m/z value as the starting dyad SoS (597, MH$^+\)$. The IR spectrum has a broad intense peak at
1055 cm\(^{-1}\) in the range, characteristic for ring deformations of substituted cyclobutanes [40]. Theoretically, photocycloaddition of the dyad SoS can result in several possible cyclobutane regioisomers. However, analysis of the \(^1\)H NMR spectrum, two-dimensional (2D) NOESY \(^1\)H NMR, and \(^13\)C NMR spectra of an evaporated reaction mixture shows that residue consists of a single compound, \(r\)-\(c\)-\(t\)-\(t\) cyclobutane isomer, which is formed in result of head-to-head photocycloaddition between two \(E\)-\(S\)-\(Q\) fragments of the dyad SoS, Scheme 7. Upon irradiation with light of 365 nm, the dyad SoS can be completely converted to the cyclobutane derivative, since the latter does not absorb at this wavelength (see Fig. 8). The photocycloaddition is reversible upon irradiation with the shorter wavelength light (313 nm).

**Scheme 7:** Reaction of [2+2] photocycloaddition between \(s\)-\(t\) conformers of the \(S\)-\(Q\)-fragments of the \(E\)-\(E\)-SoS.

In contrast to other photochemical reactions of diarylethylenes – photoisomerization and intramolecular photocyclization, in dilute solutions (< 10\(^{-5}\) M), the (intermolecular) photocycloaddition can take place only in (pre)organized supramolecular systems. Pre-organization (or pre-orientation) can be achieved by connecting two components using non-covalent interactions or with covalent bonding [41]. In the last case, the properties of supramolecular system depend on the structure of a covalent bridge.

We can compare the pre-organizing action of different molecular bridges (or spacers) – trimethylene, ortho-, meta- and para-xylylene – on the [2+2] photocycloaddition. The trimethylene bridge is the most flexible one and does not promote photocycloaddition. The bis-styrylquinoline dyad S3S with this bridge undergoes only photoisomerization, as well as crown containing bis-styrylbenzothiazole dyad [42]. Nevertheless, the latter can form isomeric cyclobutanes upon irradiation of sandwich complexes with Ca\(^{2+}\) and Ba\(^{2+}\) cations (so called “molecular pincers”). The photochemistry of the dyad with crown-containing styryl dyes connected by a para-xylylene bridge is limited to photoisomerization because intramolecular photocycloaddition is impossible for steric reasons, whereas analogous dyad with a meta-xylylene bridge undergoes photoisomerization in free form but photocycloaddition in a pseudocyclic complex with the 1,3-diammoniumpropane dication [43]. Only in the dyad SoS with ortho-xylylene bridge photocycloaddition takes place without addition of special reagents that pulls together the two photoactive fragments forming a pseudocyclic structure.

Figure 10 shows the kinetics of the photochemical reactions of the model MeSQ and the dyad SoS. Similar to the S3S, the SoS dyad kinetic curve achieves a higher PS plateau as compared to MeSQ, but in contrast to the S3S (and MeSQ), for the SoS dyad it is a quasi-photostationary state.

As indicated above, assuming that all SQ fragments have equal quantum yields in all the dyad isomers, the dyad photoisomerization kinetics can be treated using equation 1. However, in the case of the dyad SoS, equation 8 should be added in order to take into account consumption of the dyad in the photocycloaddition reaction with quantum yield \(\Phi_{\text{pca}}\).

\[
\frac{dA}{dt} = -\varepsilon_1 \cdot \Phi_{\text{pca}} \cdot A_1 \cdot I_0 \cdot (1 - 10^{-A})/A
\]  

Simultaneous numerical solution of equations 1 and 4 gives an approximating curve shown in Fig. 10, with quantum yields \(\Phi_{\text{ic}} = 0.47\), \(\Phi_{\text{ct}} = 0.71\), and \(\Phi_{\text{pca}} = 7 \times 10^{-3}\).

Comparison with the data for MeSQ indicates that the SQ fragments in the dyad SoS maintain high activity in photoisomerization, similar to the dyad S3S. And similar to the dyad S3S, use of simplified equation 1 instead of 2 results in overestimation of the quantum yield of the cis-trans photoisomerization \(\Phi_{\text{ct}}\).
Figure 10: Kinetics of absorbance at 365 nm during the photolysis of the model MeSQ, where the symbols (○) and the curve refer to the experimental data points and optimal approximation by equation (1), and the dyad SoS, where the symbols (●) and the curve refer to the experimental data points and optimal approximation by equations 1 and 4. Insert: the initial parts of the kinetic curves.

Efficiency of the photocycloaddition of the dyad SoS is much lower than photoisomerization. From the investigations in the crystalline state, it is known that for the photocycloaddition to occur, the distance between the reactive double bonds must be less than 4.2 Å [44]. According to quantum-chemical calculations (B3LYP/6-31G*), in the most stable dyad conformer (Fig. 11, A), the distance between the centers of the ethylenic groups is 8.5 Å. The conformer with this distance fixed to 4.2 Å (Fig. 11, B) is 5 kcal/mol higher in energy. Using the Maxwell-Boltzmann distribution function, we can calculate that at room temperature the abundance of the dyad conformers, where PCA can occur, does not exceed 0.02 %.

Figure 11: Conformers of the dyad EE-SoS (B3LYP/6-31G* data).

Thus, in the dyad SoS, ortho-xylene bridge disposes two SQ fragments in such a manner that the [2+2] photocycloaddition becomes possible albeit with rather low quantum yield as compared with photoisomerization. The photocycloaddition takes place with high stereo- and regioselectivity and gives rise to the only rctt-cyclobutane isomer, which is formed in result of head-to-head interaction between two E-SQ fragments of the dyad SoS.

4 Photonics of styrylquinoline-merocyanine dyads. Styrylquinoline as an energy donor

The drawbacks of the symmetric bis-styrylquinoline dyads are impossibility of selective excitation of a particular chromophore, and impossibility to distinguish spectrally some dyad isomers. To correct these drawbacks, non-symmetric styrylquinoline-merocyanine dyads SQnMC, n = 3, 11, where two chromophores have different absorption spectra, are synthesized and investigated [45–47].

The dyads are prepared according to the general procedure by alkylation of (E)-2-(4-hydroxystyryl)quinoline with α,ω-dibromoalkane, subsequent reaction with 4-hydroxybenzaldehyde, and condensation with N-ethylquinoidalium iodide followed by an ion exchange (Scheme 8).

Scheme 8: Synthesis of the dyads SQnMC. Structure of the model MeMC, 1-ethyl-2-(4-methoxystyryl)quinolinium perchlorate, is also shown.

The photophysical and photochemical properties of the dyads are studied in comparison with those of the individual model components, MeSQ and 1-ethyl-2-(4-methoxystyryl)quinolinium perchlorate; the latter can be regarded as an O-methylated merocyanine MeMC, see Scheme 8.

Absorption spectrum of the EE isomer of the SQnMC dyad, Fig. 12, is a superposition of the spectra of the model compounds, E-MeSQ and E-MeMC. This implies an absence of considerable interaction between two chromophoric groups of SQnMC in the ground state.

From comparison with the model spectra it follows also that the LWAB of the dyads in the region of 410 –
490 nm belongs to MC fragment only, SQ fragment does not absorb in this region. Both chromophoric systems absorb at wavelengths shorter than 400 nm, however, second intense band of the dyads at ~360 nm, in the region of MeSQ LWAB (Figure 12), principally characterizes absorption of the SQ moiety: the ratio of MACs for the two models (MeSQ/MeMC) is 4.5 at 361 nm and achieves 7.8 at 343 nm, in the region of MeMC absorption minimum.

Figure 12: Absorption spectra of dyads EE-SQ3MC and EE-SQ11MC, models E-MeSQ, Z-MeSQ, E-MeMC and Z-MeMC (ethanol).

Both model compounds possess weak luminescence, emission band maxima and fluorescence quantum yields are 423 nm and \(1.5 \times 10^{-2}\) for MeSQ, and 512 nm and \(2.7 \times 10^{-3}\) for MeMC. Figure 13 shows luminescence and excitation spectra of the dyads SQnMC. Excitation of SQ3MC within LWAB, as could be expected, results in absorption and subsequent emission of the MC fragment only (Figure 13, spectrum 1) with fluorescence quantum yield which within error of measurement is equal to that of the model MeMC. Provided excitation at 310 nm, where both fragments absorb light, emission bands of both fragments are observed in the luminescence spectra of the dyads, Figure 13, spectra 2 and 3. However, emission of the SQ fragment relative to the MC fragment is markedly reduced, especially in the SQ3MC spectrum 2.

Considerable reduction of the SQ fragment emission in the dyad testifies about the singlet-singlet Forster resonance energy transfer (FRET) from the SQ to the MC moiety. The existence of the FRET is corroborated by the fluorescence excitation spectra, Figure 13, spectra 4 and 5. Despite monitoring at 515 nm, where only the MC fragment emits, in excitation spectra we observe maxima belonging to both fragments of the dyad: SQ at ~360 nm and MC at ~420 nm. Therefore, after excitation of the SQ fragment, the intramolecular FRET occurs to the MC fragment with subsequent emission of the latter.

As one can see from comparison of Figures 12 and 13, the MC absorption band at ~420 nm (Fig. 12) overlaps SQ emission band at ~410 nm (short-wavelength bands in the spectra 2 and 3, Fig. 13). The overlap of two bands can be seen also in Fig. 13, where short-wavelength bands in spectra 2 and 3 (these bands characterize emission of the SQ fragment) are exactly below long-wavelength bands in spectra 4 and 5 (these bands characterize excitation of the MC fragment).

Figure 13: Normalized luminescence spectra in ethanol: (1) dyad EE-SQ3MC (excited at 424 nm), (2) dyad EE-SQ3MC (excited at 310 nm), (3) dyad EE-SQ11MC (excited at 310 nm); luminescence excitation spectra provided monitoring at 515 nm: (4) dyad EE-SQ3MC, (5) dyad EE-SQ11MC.

The overlap of absorption band of an energy acceptor and emission band of an energy donor is necessary condition for the FRET [48]. The FRET results in quenching of the SQ-fragment fluorescence in the dyads.

The Forster resonance energy transfer

According to the Forster’s theory [48], the rate constant for the singlet-singlet energy transfer (ET) \(k_{ET}\) via the mechanism of dipole-dipole inductive resonance is given by equation 9,

\[
k_{ET} = k_D (R_0/R)^6 = (1/\tau_D) \cdot (R_0/R)^6, \tag{9}
\]

where \(\tau_D\) is the lifetime of the excited donor in the absence of acceptor, \(R\) is the distance between donor and acceptor molecules, and \(R_0\) is the critical quenching radius or Forster radius, a distance at which the donor is quenched.
by half, i.e., $k_{ET} = k_D$, where $k_D (= 1/\tau_D)$ is the rate constant of spontaneous deactivation of the excited donor in the absence of acceptor. The Förster radius is defined by equation 10:

$$R_0^6 = 9000(ln10)\phi_D k^2/f/128\pi^3 N_A n_r^6,$$  \hspace{1cm} (10)

where $\phi_D$ is the fluorescence quantum yield of the donor in the absence of acceptor, $k$ is an orientation factor; $N_A$ is the Avogadro’s number, $n_r$ is the refractive index of the medium in the ET region, and $f$ is the spectral overlap integral, which is calculated according to equation 11.

$$J = \int I_D(\lambda)\varepsilon_A(\lambda)\lambda^2 d\lambda; \int I_D(\lambda)d\lambda = 1$$  \hspace{1cm} (11)

In equation 11, $I_D(\lambda)$ is the donor fluorescence intensity depending on the wavelength, with the full emission spectrum of the donor being normalized to unit area, and $\varepsilon_A(\lambda)$ is the molar absorption coefficient of the acceptor (M$^{-1}$ cm$^{-1}$). For the MeSQ-MeMC pair, $J = 8.42 \times 10^{-14}$ M$^{-1}$ cm$^{-1}$ nm$^4$.

In the dyads SQnMC, two chromophoric groups are linked by flexible polymethylene chains, so it is reasonable to assume that they are randomly oriented. Therefore, the dynamic average value of $k^2 = 2/3$ can be accepted as a first approximation, wherefrom the Förster radius is calculated to be $R_0 = 2.45$ nm for the MeSQ-MeMC pair.

Quantitatively, the ET efficiency ($\phi_{ET}$) is defined by equation 12:

$$\phi_{ET} = 1 - \phi'_D/\phi_D,$$  \hspace{1cm} (12)

where $\phi_D$ and $\phi'_D$ are donor (SQ) fluorescence quantum yields in the absence of quencher in free MeSQ and in the presence of quencher (which is MC) in the dyads SQnMC. For the system under study, $\phi_D = 1.5 \times 10^{-2}$, $\phi'_D$ is equal to $6 \times 10^{-4}$ for SQ3MC and $1.9 \times 10^{-3}$ for SQ11MC, therefore $\phi_{ET} = 0.96$ for SQ3MC and $\phi_{ET} = 0.87$ for SQ11MC.

The ET efficiency and the Förster radius are connected by equation 13.

$$\phi_{ET} = R_0^6/(R_0^6 + R^6)$$  \hspace{1cm} (13)

Based on experimental $\phi_{ET}$ values, and using equation 13, formal “average” distances between donor and acceptor ($R$) are calculated to be 1.44 nm in SQ3MC and 1.78 nm in SQ11MC.

According to quantum chemical calculations for the S3S dyad, which coincides in size with the SQ3MC dyad, but instead of MC-fragment contains the second SQ-fragment, van der Waals size of the unfolded conformation (fully transoid in methylene chain) along the long axis is 3.49 nm [33]. The distance between the centers of two chromophores can be estimated as ~1.9 nm. In all other conformations of the dyad, the distance between the chromophores should be less than is consistent with the calculated average value of $R = 1.44$ nm.

In dyad SQ11MC, the polymethylene chain length is increased by 8 units, so the distance between the two chromophores in the unfolded conformation can be estimated as ~2.9 nm. This is substantially greater than the calculated average distance ($R = 1.78$ nm). Obviously, the ethanol, being a hydrophilic polar solvent, stimulates twisting of the hydrophobic methylene chain in the dyad SQ11MC, which leads to the convergence of the dyad fragments.

Photoisomerization

Similar to bis-styrylquinoline dyads, styrylquinolineremoxyanine dyads contain two photochromes and can exist in four isomeric forms, EE, EZ, ZE and ZZ; however, in this case EZ and ZE isomers are different, Scheme 9.

The FRET appears in the photochemical properties of the SQnMC dyads. Especially, this can be seen in comparative experiment. As an example, Figure 14 shows the spectral changes upon irradiation of equimolar mixture of the model compounds MeSQ+MeMC and the SQ3MC dyad of the same concentration. At this concentration, the distance between the molecules of the free donor and acceptor is 29.6 nm that is more than an order of magnitude greater than the calculated Förster radius for this donor-acceptor pair (2.45 nm). Consequently, we can neglect the intermolecular ET and assume that both chromophores in the model mixture react independently.

Comparison shows that upon irradiation at 365 nm, where both chromophores (SQ and MC) absorb light, both model compounds undergo photoisomerization, absorption bands of the both compounds reduce in intensity, Figure 14a. In the dyad, only the LWAB belonging to the MC fragment changes testifying about this fragment photoiso...
merization, whereas second absorption band at 360 nm, belonging mainly to the SQ fragment, remains practically unchanged, Figure 14b. For the SQ11MC, the similar picture is observed, but the depth of the spectral changes in the region of 360 nm was greater than for the SQ3MC.

Figure 15 shows the principal component analysis of the observed spectral changes. The experimental spectra are represented in the basis of the first two singular vectors of the decomposition matrix of the model spectra of four isomers, EE, EZ, ZE and ZZ. Vertices of the quadrangle in Fig. 15 correspond to the spectra of the pure isomers of the dyad, which are calculated as the sum of the spectra of the related isomers of the model compounds MeSQ and MeMC. Endpoints in the graphs correspond to the spectra of the photostationary states for each reaction series.

Quadrangle in Fig. 15 correlates with the cycle of photochemical reactions shown in Scheme 9. Movement along the EE-ZE side (and EZ-ZZ side) describes the SQ fragment isomerization, and that along the EE-EZ side (and ZE-ZZ side) describes the MC fragment isomerization. Curve 1 in Fig. 15 is inside the quadrangle and passes close to the main diagonal EE-ZZ, i.e. during photolysis of the model mixture, both chromophores photoisomerize in parallel.

The initial portions of the curves 2 and 3 are beyond the quadrangle in Fig. 15. This deviation characterizes the differences in the spectra of the dyads and model compounds associated with the inductive effect of the alkyl substituent at the oxygen atom of the styryl fragment. Curve 2 in Fig. 15 lies along the EE-EZ side of the quadrangle showing clearly that upon photolysis of the dyad SQ3MC, mainly the MC fragment photosomerizes and only after reaching this photostationary state curve deviates slightly towards the SQ fragment photosomerization.

There are two distinct parts on the curve 3 (Fig. 15) describing the dyad SQ11MC photolysis. Initially, curve, similar to the dyad SQ3MC, goes also along the EE-EZ side, i.e. the MC fragment photoisomerization proceeds. Then this reaction achieves photostationary state, and further spectral changes are associated only with the SQ fragment isomerization, curve runs parallel to the EE-ZE and EZ-ZZ sides, describing the transformation of this fragment only.

Before discussing the reaction kinetics, the following should be noted. Upon irradiation of the dyads (or the model mixture) with visible light at 436 nm, within LWAB belonging to the MC fragment, only this fragment undergoes photoisomerization. During this photolysis, there are isosbestic points, where trans- and cis- isomers of the MC fragment have equal absorbance. Absorbance changes at these points characterize transformation of the SQ fragment only, as well as those at LWAB maxima characterize transformation of the MC fragment only. Therefore, we can observe only the MC fragment kinetics by monitoring spectral changes at the LWAB maximum (422 nm for MeMC, 424 nm for SQ3MC, 427 nm for SQ11MC), and only the SQ fragment kinetics by monitoring spectral changes at isosbestic point (347.2 for the model mixture, 352.1 nm for SQ3MC, 348.2 nm for SQ11MC). Using different wavelengths, we can monitor selectively photoisomerization of one or another fragment.

The kinetic curves measured at the above isosbestic points are shown in Fig. 16a, and those measured at the LWAB wavelengths – in Fig. 16b. Curve 1 in Fig. 16a describes the kinetics of the SQ chromophore photolysis in the model mixture, curve 2 - in the dyad SQ3MC, and curve...
3 • in the dyad SQ11MC. It can be seen that the SQ fragment in the dyads reacts slower than MeSQ in the model mixture, and the effect increases with decreasing methylene chain length on the transition from the dyad SQ11MC to SQ3MC.

Curve 1 in Fig. 16b describes the kinetics of the MC chromophore photolysis in the mixture, curve 2 • in the dyad SQ3MC, and curve 3 • in the dyad SQ11MC. Here, on the contrary, in the initial part, photolysis of the MC fragment in the dyads is faster than photolysis of MeMC in the model mixture, but then the curve 1 describing the mixture goes to the low PS plateau, as compared to the curves 2 and 3.

![Figure 16: Kinetics of absorbance change during irradiation of air-saturated solutions in ethanol with light of 365 nm: (1) model mixture of E-MeSQ and E-MeMC, (2) E-E-SQ3MC, (3) E-E-SQ11MC; a) at isosbestic points (see text), b) at the LWAB maxima.](image)

As stated above, kinetics of the monochromic model photoisomerization is described by equation 1 and that of the bichromophoric dyad photoisomerization – by equation 2. In this case, both model mixture and dyads contain two different photochromes. To simplify kinetic scheme, for the purpose of comparison, we have assumed that all transformations of every photoactive fragment can be characterized by set of two averaged quantum yields, \( \phi_{tc} \) and \( \phi_{ct} \). With this assumption, simultaneous numerical solution of two equations 1 describing kinetics of the absorbance change of the SQ and MC fragments (provided that \( A \) is the total optical density of all four isomers) gives a set of the quantum yields, which are listed in the Table 1. It is worth mentioning that these values are calculated taking into account light absorbed by definite fragment.

One can see that trans-cis photoisomerization quantum yields of the SQ fragments in the dyads decrease whereas those of the MC fragments increase as compared to the model compounds. Obviously, this is a result of the FRET which gives rise to quenching of the SQ photoisomerization and sensitization of the MC photoisomerization in the dyads.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SQ-fragment</th>
<th>MC-fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \phi_{tc} )</td>
<td>( \phi_{ct} )</td>
</tr>
<tr>
<td>MeSQ+MeMC</td>
<td>0.56</td>
<td>0.43</td>
</tr>
<tr>
<td>SQ3MC</td>
<td>0.01</td>
<td>0.46</td>
</tr>
<tr>
<td>SQ11MC</td>
<td>0.067</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Let us consider at first data for the SQ, which is an energy donor. Since both processes in E-SQ – emission (fluorescence) and photoisomerization – take place from the same (lowest singlet) excited state, we should expect the same effect of the FRET on these processes. Really, calculation of the ET efficiency from the photoisomerization quenching by equation 12, taking \( \phi_{tc} \) data for the SQ in MeSQ instead of \( \phi_{D} \) and \( \phi_{ct} \) data for the SQ in the dyads instead of \( \phi_{D}^* \), gives \( \phi_{ET} = 0.98 \) for the dyad SQ3MC and \( \phi_{ET} = 0.88 \) for the dyad SQ11MC, which are close to the values calculated above from the fluorescence quenching.

As can be seen from Table 1, the reverse cis-trans photoisomerization of the SQ fragments in the dyads proceeds with the same efficiency as in the model MeSQ, the observed \( \phi_{ct} \) values are the same. The SQ cis-isomer is a poor energy donor and is not quenched in contrast to the trans-one. This difference can be explained taking into account properties of trans- and cis-isomers of diarylethlenes. The fluorescence quantum yield of cis-isomer is generally much less than that of trans-isomer, for example, for stilbene they differ by 500 times [37]. Lifetime of trans-stilbene is two orders of magnitude longer than that of cis-stilbene [49]. Both these facts are consequences of the potential energy surface (PES) structure. On the PES of the excited state, trans-stilbene is separated from perpendicular (perp) conformer by potential barrier whereas cis-stilbene transforms to perp-conformer in barrierless process. Due to the high rate of chemical reactions in the excited cis-isomer; any other radiative and non-radiative processes can not compete with these reactions.

One should expect the same lifetime ratio for the SQ isomers. Therefore, energy transfer to MC moiety competes effectively with isomerization in relatively long-lived excited trans-SQ (resulting in its quenching) and does not compete in short-lived cis-SQ, which undergoes effective isomerization.

As compared to the SQ, observed quantum yields of the MC photoisomerization in the dyads are more than unity that is a result of an additional sensitized reaction of the MC as an energy acceptor. According to Fig. 15, photo-
toisomerization of the MC in the dyad proceeds mainly in two isomers, EE and EZ, where the SQ fragment is in trans-form.

From the ratio of MACs for the models MeSQ and MeMC at 365 nm, we can calculate that, upon irradiation of the EE isomer of the dyad, the SQ fragment absorbs 77% of incident light, but the MC fragment only 23%. For the EZ isomer, where the MC fragment is in cis-form, the ratio is already 82% and 18%, respectively. Taking into account the ET efficiency, the percentage of the MC fragments excited by ET (sensitization) is 3 – 4 times higher than that of the MC fragments directly excited as a result of light absorption. This leads to a substantial increase in the observed quantum yield of the MC photoisomerization. We can conclude that upon irradiation with light of 365 nm, the MC fragment photoisomerization in the dyads occurs primarily as a result of the sensitized reaction after the ET from the SQ fragment.

Sensitization of the MC fragment appears also in its enhanced fluorescence, an increase in the $\phi_f$ value being proportional to the MAC ratio. On example of the dyad SQ3MC, Fig. 17 shows the dependence on wavelength of the MAC ratio $\epsilon_{SQ}/\epsilon_{MC}$ (which is proportional to the fraction of light absorbed by the SQ fragment), curve 1, and the observed quantum yield $\phi_f$ of the MC fragment fluorescence, curve 2. One can see that curve 2 reproduces the curve 1, and the effect of sensitization reaches a maximum at the maximum of MAC ratio. Provided excitation in UV region of 300 – 370 nm, where absorption of the SQ fragment prevails over that of the MC fragment, both fluorescence and photoisomerization of the latter in the EE isomers of the dyads are mainly sensitized processes. At a wavelength of 427 nm (the right point on the curve 2, Fig. 17), the MC fragment absorbs all the light, and the $\phi_f$ value coincides with that in the absence of sensitization (in MeMC).

Figure 18 shows an energy level diagram for the styrylquinoline-merocyanine dyads (the EE isomers). The terms are assigned to particular fragments by comparing with the spectra of the model compounds.

If the irradiation results in selective excitation of the MC fragment (right part of the diagram), we observe its fluorescence and photoisomerization with quantum yields corresponding to those for the model merocyanine MeMC. Upon excitation of the SQ fragment (left part of the diagram), the main process is ET to the MC fragment, giving rise to quenching of the first fragment and sensitization of the second one. As a result of ET, the observed quantum yields of fluorescence and trans-cis photoisomerization for the SQ fragment are significantly reduced compared with the values for the model MeSQ. For the MC fragment these parameters may increase in proportion to the light absorbed by the SQ fragment relative to the MC one.

Proton-driven one-way photoisomerization

One of the consequences of ET in the case of the dyad SQ3MC is a practical impossibility of obtaining ZE and ZZ...
isomers (with the SQ fragments in cis-form) under direct photolysis of the dyad due to quenching of the SQ fragment. However, this limitation can be circumvented, taking into account that two chromophores in the dyad are relatives: MC fragment is really an N-alkylated SQ one. Both chromophores have similar π-systems, but the SQ moiety is neutral whereas the MC moiety is positively charged. The SQ fragment can be charged also by protonation of the nitrogen atom, this reaction being reversible. After protonation of the SQ fragment, bis-merocyanine dyad is formed, Scheme 10. In Scheme 10, to underline the different charges of the dyad fragments in non-symmetric EE-SQ3MC, this semi-charged (one-charged) isomer is denoted as \( E^0E^- \); double-charged symmetric \( E^+E^- \) isomer has two similar charged chromophoric π-systems (more precisely, dyad \( E^+E^- \) is quasysymmetric, because chemically two fragments in \( E^+E^- \) isomer differ slightly: one fragment is N-protonated SQ derivative whereas other fragment is N-ethylated SQ derivative). In quasysymmetric dicationic dyad both photochromic fragments undergo photosomerization. After photolysis and neutralization, we obtain a set of isomers of the initial SQ3MC dyad which is unattainable under direct photolysis.

Scheme 10: Protolytic transformations of SQ3MC (anions are omitted).

Figure 19 shows spectral variations taking place during different impacts on solution of the dyad SQ3MC. Spectrum 1 corresponds to the starting \( E^0E^- \) isomer. Addition of HCl resulted in twofold increase in intensity of LWAB and disappearance of the second band at 360 nm, spectrum 2. Spectrum 2 in Figure 19 coincides practically with that of \( E^-E^- \) (Fig. 12, spectrum 5). Obviously, this is an evidence of formation of symmetric bis-merocyanine \( E^+E^- \) isomer. Irradiation of \( E^+E^- \) isomer with 470 nm light induced \( trans \rightarrow cis \) photosomerization of both photoactive chromophores, spectrum 3 (Fig. 19) corresponds to the final \( PS_{470} \). Photostationary mixture contains all four possible dyad isomers, \( E^+E^- Z^+Z^- \), \( E^+Z^+ E^- Z^- \) and \( E^-Z^- E^+ Z^+ \), cis-isomers of two fragments being distributed between the last three isomers. Neutralization of this solution with ammonia resulted in reduction of band at 420 nm belonging to MC chromophore and re-appearance of band at 360 nm, belonging to the neutral SQ fragment, spectrum 4 in Fig. 19. Obviously, this is the same mixture of the four dyad isomers but already with non-charged \( trans \)- and \( cis \)- isomers of the SQ fragment, \( E^0E^+ Z^0E^+ Z^0Z^- \) and \( Z^0Z^+ \). One should underline that \( Z^0E^+ \) and \( Z^0Z^+ \) isomers, containing \( cis \)-isomer of the neutral SQ fragment, cannot be obtained under direct photolysis of the \( E^0E^- \) isomer of the dyad SQ3MC.

Further transformations of the reaction mixture are shown in Fig. 20. Irradiation of the neutralized solution of \( PS_{470} \) with light of 313 nm (spectra 1 – 9) gives rise to increase in intensity of both main dyad absorption bands in the region of 360 nm and 420 nm testifying about \( cis \) \( \rightarrow \) \( trans \) isomerization of both SQ and MC fragments. The final spectrum 9, Fig. 20, corresponds to photostationary state \( PS_{313} \) and coincides with the spectrum of this state obtained under direct photolysis with 313 nm light. As limiting boundaries of possible spectral changes, Figure 20 shows also spectra of the dyad \( EE \) isomer (10) and \( ZZ \) isomer (11).

Scheme 11 summarizes photochemical and protolytic transformations of the dyad SQ3MC. In the starting semi-charged \( E^0E^+ \) isomer only \( trans \rightarrow cis \) photosomerization of the MC fragment takes place; analogous photosomerization of the SQ fragment is quenched due to energy transfer to MC one. Thus, direct photolysis of the \( E^0E^+ \) isomer results in interconversion between \( E^0E^+ \) and \( E^0Z^- \) isomers which are the main components of the reaction mixture, see left reaction cycle in Scheme 11.

In acidic media, the SQ fragment of the \( E^0E^+ \) isomer is protonated that results in formation of double charged (quasi)symmetric bis-merocyanine \( E^+E^- \) isomer. Irradia-
Photonics of styrylquinoline dyads

Figure 20: Spectral variations during irradiation of an air-saturated neutralized solution of photostationary state PS470 of the dyad SQ3MC (see Fig. [19]) in ethanol with light of 313 nm, intensity \(2.4 \times 10^{-10}\) Einstein cm\(^{-2}\) s\(^{-1}\), irradiation time, s, (1) – (9): 0, 30, 70, 150, 300, 500, 700, 1000, 6000. Spectrum 1 corresponds to spectrum 4 in Fig. 19. Spectrum 10 corresponds to the EE-SQ3MC, spectrum 11 – to the model ZZ-SQ3MC.

Scheme 11: Reversible and one-way processes in the dyad SQ3MC.

The reason why photoisomerization of the neutral SQ fragment in the dyad SQ3MC occurs in \(cis \rightarrow trans\) direction and does not practically occur in \(trans \rightarrow cis\) direction (compare Figures 14b and 20), i.e. why \(cis\)-isomer of the SQ fragment in dyad is not quenched in contrast to the \(trans\)-isomer, is discussed above.

Obviously, we cannot say that we switch off energy transfer in bis-merocyanine dyad. Really, in this (quasi)symmetric dyad one should expect forward and backward energy transfer, i.e. excitation hopping between two identical chromophores [50, 51]. This can results in fluorescence anisotropy decay but does not affect photochemical activity of the chromophores (see previous section). Therefore, we can say that we switch off quenching action of energy transfer in (quasi)symmetric dyad. Due to this fact, in bis-merocyanine dyad all cycle of possible transformations between four isomers is observed (right reaction cycle in Scheme 11).

It should be noted that one-way \(cis \rightarrow trans\) photoisomerization is a famous property of diarylethynes with large aryl substituents [52]. In such diarylethynes excitation is localized on large aromatic nucleus, term of the excited \(trans\)-isomer on the PES goes down lower than terms of the \(perp\)-conformer and \(cis\)-isomer. As a result, the system "glides" on the descending excited-state PES from \(cis\)-isomer to \(trans\)-isomer, photoisomerization mechanism changes from diabatic to adiabatic one, and photoisomerization does not go in \(trans \rightarrow cis\) direction [53]. In this case \(cis\)-isomer cannot be obtained from \(trans\)-isomer photochemically but only by special synthetic procedures (majority of synthetic methods of double bond formation produce diarylethynes in \(trans\)-configuration).

One can say that in large diarylethynes, effect of one-way reactivity is thermodynamic in nature and based on the difference in energies of the excited-state isomers. In dyad SQ3MC, this effect is kinetic in nature and based on the difference in rates of competing processes in the excited state. Two-way reactivity is switched on in protonated quasisymmetric dyad where positively charged SQ fragment obtains the same chromophoric \(\pi\)-system as in MC chromophore. Energy transfer from protonated SQ to MC is compensated by back energy transfer from MC to protonated SQ (excitation hopping). In the dyad SQ3MC, \(cis\)-isomer of the SQ fragment can be obtained photochemically but only by special synthetic procedures (majority of synthetic methods of double bond formation produce diarylethynes in \(trans\)-configuration).

After deprotonation, photoisomerization of the SQ fragment in \(trans \rightarrow cis\) direction is again switched off but goes in \(cis \rightarrow trans\) direction. This is a case of proton-switchable one-way photoisomerization. The cycle: protonation \(\rightarrow trans\rightarrow cis\) photoisomerization (reversible) \(\rightarrow\) deprotonation \(\rightarrow cis\rightarrow trans\) photoisomerization (one-way) – can be repeated and used for design of controlled molecular photoswitches.
5 Photonics of styrylquinoline-naphthol dyads. Styrylquinoline as an energy acceptor

In styrylquinoline-naphthol dyads SQ\(n\)Np \((n = 2-5)\), the SQ fragment is linked by dioxypolymethylene bridge -O-(CH\(_2\))\(_n\)-O- with fragment of 2-naphthole (Np) [54–58]. Two fragments in the dyads SQ\(n\)Np possess opposite acid-base properties. As mentioned above, 2-styrylquinoline is a photobase, its pK\(_a\) value increases from pK\(_a\) = 4.8 to pK\(_a^*\) = 12.0 in the excited S\(_1\) state. On the contrary, 2-naphthol is a photoacid, its pK\(_a\) value decreases from pK\(_a\) = 9.5 to pK\(_a^*\) = 2.8 on going from the S\(_0\) to S\(_1\) state [59].

The dyads SQ\(n\)Np are prepared according to the general procedure by alkylation of \((E)\)-2-(4-hydroxystyryl)quinoline with \(\alpha\),\(\omega\)-dibromoalkane and subsequent reaction with 2,3-dihydroxynaphthaline, Scheme 12 [55]. The photophysical and photochemical properties of the dyads are studied in comparison with those of the individual model components, MeSQ and 3-methoxynaphthol-2 MeNp, Scheme 12.

Similar to the above-studied dyads, in the styrylquinoline-naphthol dyads, the dyad absorption spectrum does not depend on the bridge length and is a sum of the spectra of the constituting SQ and Np fragments, Table 2 [58]. As a representative of the series, the absorption spectrum of the dyad SQ3Np is depicted in Fig. 21 in comparison with the spectra of model compounds, MeSQ and MeNp. Sum of the spectra of the model compounds is almost identical to the absorption spectrum of the dyad. Therefore, we can conclude that there is no significant interaction between two chromophoric subsystems of the dyads in the ground state.

From comparison with the model spectra it follows also that the LWAB in the range of 340–390 nm with a maximum at 356 nm belongs entirely to the SQ fragment, the naphthol (Np) fragment does not absorb in this region. Both chromophoric systems absorb at wavelengths shorter than 330 nm. Intense 230 nm band principally characterizes absorption of the Np moiety, its absorption coefficient exceeds that of styrylquinoline by a factor of ~3. The sharp peak with maximum at 325 nm also characterizes absorption of the naphthalene nucleus; however, already the SQ fragment predominantly absorbs at this wavelength, the absorption coefficient ratio of the SQ to the Np moiety is ~7.

In contrast with absorption spectrum, the dyad luminescence spectrum depends on the bridge length, as can be seen in Fig. 22: the relative intensity of the short-wavelength band increases with the \(n\) number. Based on comparison with emission spectra of the model compounds, the structured short-wavelength band in the region of 330-370 nm with maximum at 344 nm should be attributed to the Np fragment, whereas wide long-wavelength band at 380-520 nm with maximum at 430 nm belongs to the SQ fragment. Both these bands are observed in dyad emission spectrum provided excitation in the wavelength range of \(\lambda < 330\) nm where both chromophoric groups absorb light. Upon excitation within LWAB (340–390 nm), where only the SQ fragment absorbs light, only emission band of this fragment is observed.

Fluorescence quantum yield of the SQ fragment in dyads within error of measurement is equal to that of the model MeSQ (0.02), Table 2. At the same time, the Np-fragment fluorescence is quenched in the dyads. The \(\phi_f\) (Np) value is equal to 0.43 for the model MeNp, decreases by more than order of magnitude for SQ5Np, and drops further with methylene group number decreasing,
Table 2: Spectral properties of the styrylquinoline-naphthol dyads (trans-isomers) and model compounds: absorption band maximum ($\lambda_{\text{max}}$) and molar absorption coefficient ($\varepsilon_{\text{max}}$), emission band maximum ($\lambda_{\text{em}}$) and fluorescence quantum yield ($\phi_f$) of the naphthol (Np) and styrylquinoline (SQ) fragments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>$\varepsilon_{\text{max}}$, M$^{-1}$·cm$^{-1}$</th>
<th>$\lambda_{\text{em}}$(Np)</th>
<th>$\lambda_{\text{em}}$(SQ)</th>
<th>$\phi_f$(Np)</th>
<th>$\phi_f$(SQ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ2Np</td>
<td>355</td>
<td>32000</td>
<td>344</td>
<td>428</td>
<td>0.0021</td>
<td>0.018</td>
</tr>
<tr>
<td>SQ3Np</td>
<td>356</td>
<td>29900</td>
<td>344</td>
<td>429</td>
<td>0.0012</td>
<td>0.021</td>
</tr>
<tr>
<td>SQ4Np</td>
<td>356</td>
<td>30200</td>
<td>344</td>
<td>430</td>
<td>0.013</td>
<td>0.023</td>
</tr>
<tr>
<td>SQ5Np</td>
<td>356</td>
<td>31600</td>
<td>344</td>
<td>430</td>
<td>0.031</td>
<td>0.019</td>
</tr>
<tr>
<td>MeNp</td>
<td>323</td>
<td>3130</td>
<td>343</td>
<td>-</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>MeSQ</td>
<td>356</td>
<td>30000</td>
<td>-</td>
<td>430</td>
<td>-</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Figure 22: Normalized fluorescence spectra of the dyads SQ-nNp in ethanol, excitation at 280 nm.

Table 2. Fluorescence of the Np fragment is practically completely quenched in the dyads SQ2Np and SQ3Np.

These facts, dependence of the emission spectrum on the bridge length and quenching of the Np-fragment fluorescence, testify about the FRET from the Np to the SQ moiety. The existence of the FRET is corroborated by dependence of the fluorescence excitation spectrum on the observation wavelength, as shown in Fig. 23 on the example of the dyad SQ5Np.

Provided observation at the Np-fragment emission band (344 nm), the excitation spectrum corresponds to the absorption spectrum of the naphthol chromophore only, as follows from comparison of the spectrum 1 in Fig. 23 with the spectrum 3 in Fig. 21. However, upon observation at the SQ-fragment emission band (430 nm), the excitation spectrum (spectrum 2 in Fig. 23) qualitatively corresponds to the absorption spectrum of the dyad as a whole, as follows from comparison with the spectrum 1 in Fig. 21. The important feature of the excitation spectrum in this case is a presence of maxima which correspond to the absorption of the Np fragment. Therefore, after excitation of the Np fragment, the intramolecular singlet-singlet ET occurs to the SQ fragment with subsequent emission of the latter. The overlap of the Np fluorescence spectrum (band at 344 nm, Fig. 22) with the absorption spectrum of the SQ moiety (band at 356 nm, Fig. 21), promotes the ET.

For the MeNp-MeSQ donor-acceptor pair, the energy donor, naphthol, can exist in neutral or anionic form depending on the medium acidity. The energy acceptor, styrylquinoline, can exist in neutral or cationic form, and additionally, it can isomerize from trans-isomer to cis-isomer. Using the absorption and luminescence spectra of the model compounds in different conditions and equation 11, the spectral overlap integrals for the pair of MeSQ and MeNp can be calculated in dependence on the donor and acceptor ionic and isomeric forms, Table 3.

Protonation of trans-MeSQ results in bathochromic shift of the absorption band, whereas isomerization to cis-
MeSQ results in hypsochromic shift of the band. Both these impacts decrease the spectral overlap integral from 3.81 to 1.70 and 1.38 ($\times 10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^{-4}$), respectively (Table 3). This results in decrease in the FRET efficiency, and is accompanied by increase in relative intensity of the Np-fragment fluorescence in the dyad that is observed experimentally.

Table 3: Spectral overlap integrals ($J/10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^{-4}$) for the pair of energy donor (MeNp) and acceptor (MeSQ) in different states (forms).

<table>
<thead>
<tr>
<th>Donor MeNp</th>
<th>Acceptor MeSQ</th>
<th>neutral</th>
<th>cation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>trans</td>
<td>cis</td>
<td>trans</td>
</tr>
<tr>
<td>neutral</td>
<td>3.81</td>
<td>1.38</td>
<td>1.70</td>
</tr>
<tr>
<td>anion</td>
<td>0.51</td>
<td>0.12</td>
<td>9.13</td>
</tr>
</tbody>
</table>

From Table 3 one can see that the overlap integral achieves extreme values when the Np fragment is in anionic form. In anionic form, the emission spectrum of the Np fragment is shifted from 344 to 408 nm. Minimal value of the overlap integral is calculated for the case when the SQ fragment is in the cis-neutral form. Transformation of the SQ fragment to the trans-cationic form gives rise to the integral increasing by near two orders of magnitude, and $J$ achieves maximal value of 9.13 in corresponding units, Table 3. The dyad state with cationic SQ fragment and anionic Np fragment may be formally regarded as arising in result of proton transfer from the naphthol OH group to the quinoline nitrogen atom. There are examples of the long-range solvent-mediated excited state intramolecular proton transfer [60–62]. This process is thermodynamically possible provided that corresponding ratio between the acidity constants of the fragments is achieved in the ground and excited states (see below), and should be facilitated in the folded dyad conformers.

Using equation 10, the Forster radius is calculated to be $R_0 = 3.8$ nm for the MeNp–MeSQ pair in neutral form. Due to flexibility of the polymethylene bridges, the dyads SQNnP can exist in many conformations with different distances between the chromophores. Calculation of the distance distribution is a separate task [63–65], however, we can assess the upper limit of the dyads sizes. According to calculations by PM3 method (program MOPAC2009 [66]), the length of the most elongated dyad conformer with trans-configuration of all single C-C and C-O bonds is 2.67, 2.75, 2.92, and 3.00 nm along long axis for the dyad SQNnP with $n = 2, 3, 4, 5$, respectively.

Therefore, for all the possible conformers of the dyads, the distance between donor and acceptor is less than the Forster radius (3.8 nm), $R < R_0$, wherefrom $k_{ET} > k_D$, that qualitatively correlates with the observed efficient naphthol fluorescence quenching due to ET to the SQ-fragment.

The ET efficiency ($\phi_{ET}$) values, calculated by equation 12, are given in Table 4.

Table 4: Energy transfer efficiency ($\phi_{ET}$), trans-cis ($\phi_{tc}$) and cis-trans ($\phi_{ct}$) photoisomerization quantum yields (error $\pm 20\%$) for the styrylquinoline-naphthol dyads (in acetonitrile).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{ET}$</th>
<th>$\phi_{tc}$</th>
<th>$\phi_{ct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ2Np</td>
<td>0.995</td>
<td>0.47</td>
<td>0.51</td>
</tr>
<tr>
<td>SQ3Np</td>
<td>0.997</td>
<td>0.55</td>
<td>0.49</td>
</tr>
<tr>
<td>SQ4Np</td>
<td>0.97</td>
<td>0.56</td>
<td>0.55</td>
</tr>
<tr>
<td>SQ5Np</td>
<td>0.93</td>
<td>0.50</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The most efficient ET is observed for the dyad SQ3Np. This can be compared with "Hirayama rule" that diaryl alkane (covalently linked dyad) with three-methylene carbon chain has the highest ability to form intramolecular excimer [1, 67]. There are other examples when three-methylene bridge between two fragments creates the most favorable conditions for the interfragment interaction in bichromophoric dyads [68, 69]. It should be noted that optimal bridge length for the strongest interaction between chromophores depends on the chromophore nature and may differ from three-methylene chain [70].

Based on experimental $\phi_{ET}$ values (Table 4), and using equation 13, formal "average" distances between donor and acceptor ($R$) are calculated to be 1.57, 1.44, 2.13, and 2.47 Å for the dyad SQNnP with $n = 2, 3, 4, 5$, respectively. These values correlate qualitatively with the PM3-calculated sizes of the dyads. The value for SQ3Np falls out of the series because in this case the assumption about randomly oriented donor and acceptor is broken.

We can compare the ET parameters for two dyads, SQ3Np and SQ3MC, which have identical trimethylene bridges but different donor-acceptor pairs.

For the dyad SQ3Np, where MeNp is a donor ($\tau_D = 9$ ns [56]), and MeSQ is an acceptor: $J = 3.81 \times 10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^{-4}$, $R_0 = 3.8$ nm, $R = 1.44$ nm, $\phi_{ET} = 0.997$, $k_{ET} = 3.6 \times 10^{10}$ s$^{-1}$.

For the dyad SQ3MC, where MeSQ is a donor ($\tau_D < 0.2$ ns [56]), and MeMC is an acceptor: $J = 8.42 \times 10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^{-4}$, $R_0 = 2.45$ nm, $R = 1.44$ nm, $\phi_{ET} = 0.96$, $k_{ET} > 1.2 \times 10^{11}$ s$^{-1}$.

These dyads have identical calculated average distances between two chromophores, $R = 1.44$ nm, that
is not surprising, taking into account identical trimethylene bridges. However, the MeNp-MeSQ pair has the lesser overlap integral as compared to the MeSQ-MeMC pair, but higher Forster radius $R_0$, due to the high value of the donor (MeNp) fluorescence quantum yield ($\phi_D = 0.43$). This results in the higher ET efficiency in the dyad SQ3Np (under the same $R$). However, the short lifetime of the MeNp excited state results in the lesser ET rate constant in the dyad SQ3Np (see equation 9).

Figure 24 shows the spectral changes upon irradiation of the styrylquinoline-naphthol dyads with UV light on the example of SQ2Np. During irradiation, the Np absorption band remains unchanged, whereas the LWAB, which characterizes the SQ fragment absorption, reduced in intensity and shifted hypsochromically. These spectral changes are characteristic for the photoisomerization reaction, the same changes were observed upon irradiation of the model MeSQ. The observation of isosbestic point at 263 nm indicated the absence of secondary reactions.

Figure 24: Spectral variations during irradiation of an air-saturated solution of $E$-SQ2Np ($2.58 \times 10^{-5}$ M) in acetonitrile with light of 365 nm, intensity $1.11 \times 10^{-9}$ Einstein cm$^{-2}$ s$^{-1}$, irradiation time, s: 0 (1), 15 (2), 30 (3), 60 (4), 100 (5), 600 (6), the last spectrum corresponds to photostationary state PS$_{365}$; (7) spectrum of cis-SQ2Np (calculated by Fischer’s method [35]).

In the dyads $SQnNp$ only one photochrome undergoes photoisomerization, so the quantum yields are calculated by equation 1. As one can see from Table 4, the photoisomerization quantum yields, within error of measurement, do not depend on the length of the linking bridge between two fragments, and coincide with the data for the model MeSQ, $\phi_{ic} = 0.48$ and $\phi_{et} = 0.50$ (in acetonitrile). Thus, in dyads $SQnNp$, the styrylquinoline chromophoric group maintains high photochemical activity with photoisomerization quantum yield near limit (0.5), which characterizes diabatic reaction (provided partitioning factor is equal to 0.5) [26]. Chemical reaction is the main deactivation channel of the singlet excited styrylquinoline chromophore that results in low fluorescence quantum yield.

Figure 25 compares in graphical form the effect of methylene group number $n$ on the photophysical and photochemical parameters of the dyads $SQnNp$: the quantum yield of the Np-fragment fluorescence and the SQ-fragment photoisomerization.

![Figure 25: The dependence of the Np-fragment fluorescence ($\phi_{fl}$) and the SQ-fragment photoisomerization ($\phi_{ic}$, $\phi_{ct}$) quantum yields of the dyads $SQnNp$ on the methylene group number $n$. Data for the model compounds MeNp and MeSQ (“free” SQ and Np fragments) are shown as right-sided limits.](image)

As stated above, dependence of the $\phi_{fl}(Np)$ on the bridge length manifests the ET between two fragments. Energies of the lowest excited singlet states (the 0-0 transitions) localized on the Np ($S_1(Np)$) and the SQ ($S_1(SQ)$) chromophores are 3.79 and 3.21 eV, correspondingly, as calculated from the crossing points between the absorption and the fluorescence spectra. The ratio $S_1(Np) < S_1(SQ)$ implies the ET in one direction, Np $\rightarrow$ SQ, and explains absence of the Np influence on the singlet excited SQ.

In addition to ET, the photoinduced electron transfer can also take place in dyads. It can occur upon excitation of both electron donor and electron acceptor. The electron transfer rate constant can be estimated theoretically from the redox potentials and excitation energies of the chromophores. However, based on experimental data, we can exclude electron transfer from consideration. The result of
electron transfer is formation of a radical ion pair. Isomerization of diarylethenes in radical or radical ion forms is known to occur in the cis-to-trans direction only [71]. Therefore, if the SQ radical anion was an intermediate, we could not observe cis-isomer as a reaction product.

**Acid-base properties**

The acid-base properties of the dyads are discussed on the example of SQ4Np. In acidic media, a significant bathochromic shift of the LWAB from 357 nm to 413 nm is observed, and a new band at 260 nm appears due to the protonation of the SQ nucleus, with the Np band at 231 nm and 326 remained unchanged, Fig. 26, spectrum 2. Conversely, in basic media, due to deprotonation of the Np-fragment, the short-wavelength band is shifted to 246 nm and the band at 326 nm disappears. The LWAB characterizing the SQ-fragment remains in place, and overlaps with the Np anion band, leading to hypsochromic shift of the maximum to 347 nm, Fig. 26, spectrum 3. Corresponding acid-base equilibria of the SQ4Np dyad are shown on Scheme 13.

**Figure 26:** Absorption spectra of the dyad E-SQ4Np in ethanol in different forms: (1) neutral, (2) protonated, (3) deprotonated.

**Scheme 13:** Acid-base equilibria of the dyad E-SQ4Np (s-trans conformer).

The ground state pK_a values for the dyad SQ4Np are 5.0 (quinoline ring) and 10.6 (hydroxyl group), as determined by spectrophotometric titration. These values coincide with the same data for the model compounds MeSQ (4.9) and MeNp (10.5).

As mentioned above, the acidity of two chromophores in the dyads SQnNp changes in opposite directions upon excitation. The acidity in the excited state (pK_a*) is calculated by Forster cycle method according to following formula [72]:

\[
pK_a^* = pK_a + \frac{(E_1 - E_2)}{2.3RT},
\]

where \(E_1\) and \(E_2\) are the energies of the absorption bands of the basic and acidic forms of the compound, respectively. Calculated pK_a* values are 11.6 (quinoline ring) and 6.5 (hydroxyl group). The ratio pK_a*(SQ) > pK_a(Np) creates thermodynamical prerequisite for the proton transfer from the Np fragment to the excited SQ fragment, whereas ratio pK_a(SQ) < pK_a*(Np) is insufficient for the proton transfer from the excited Np fragment to the SQ fragment. Compared to unsubstituted 2-naphthol, acidity of the hydroxyl group in the excited Np fragment decreased, pK_a* changed from 2.8 to 6.6.

Obviously, this is an effect of oxygen atom in the neighboring alkoxy group. According to B3LYP/6-31G* calculation for the model MeNp, there is an intramolecular hydrogen bond between hydroxyl and alkoxy group. The conformer with hydroxyl hydrogen turned to the neighboring oxygen is 4.3 kcal/mol more stable than the conformer with opposite disposition of hydroxyl hydrogen. In the former conformer the calculated distance between hydroxyl hydrogen and alkoxy oxygen is 2.05 Å that is less than the sum of van der Waals radii (1.2 Å for H and 1.52 Å for O) [73]. The hydrogen bond hinders the dissociation of the naphthol hydroxyl group, especially in the excited state.

Table 5 shows the quantum yields of the SQ fragment photoisomerization in different forms of the dyad SQ4Np: neutral, protonated and deprotonated. In neutral and protonated forms of the dyad, where the SQ fragment undergoes photoisomerization with high quantum yield, the Np fragment is in neutral form. Therefore, the neutral Np fragment has no effect on photoisomerization of the SQ-fragment, no matter in what form is the last - in protonated or neutral.

In alkaline medium, the photoisomerization quantum yields decrease, especially in the *trans-cis* direction, Table 5. The anionic Np-fragment hinders photoisomerization of the SQ-fragment (the latter is in the neutral form). One can explain the inhibitory effect of the Np anion as follows. The Np fragment possesses weak electron donor properties which significantly enhance upon formation
Table 5: Photoisomerization quantum yields for the SQ4Np dyad in different forms (see Scheme 13), ethanol, error ± 20%.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{le}$</th>
<th>$\phi_{ct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ4Np</td>
<td>0.58</td>
<td>0.52</td>
</tr>
<tr>
<td>SQ4Np$^-$</td>
<td>0.66</td>
<td>0.75</td>
</tr>
<tr>
<td>SQ4Np$^+$</td>
<td>0.36</td>
<td>0.43</td>
</tr>
</tbody>
</table>

of the Np anion. This can result in the formation of an intramolecular charge transfer complex in the ground state or an exciplex in the excited state, at least in those conformers of the dyad, where the Np and SQ fragments are in sufficient proximity of each other. Numerous studies of aromatic complexes indicate that they may have different geometric structure, but in any case involve contact between the molecules, which limits the mobility of the components of the complex [74]. Naturally, in such structure, the isomerization of the central (ethylenic) double bond is hindered, which leads to a decrease in the quantum yield values.

Figure 27 shows an energy level diagram for the dyad SQ4Np in different forms, calculated on the basis of the experimental absorption and luminescence spectra. On the example of the neutral form, the diagram shows the processes occurring upon excitation of the dyad. The terms are assigned to particular fragments by comparing with the spectra of the model compounds. The terms of the lowest singlet excited states localized on the Np ($S_{1,Np}$) and SQ ($S_{1,SQ}$) fragments show the positions of the 0-0 transitions, calculated from the intersection of absorption and luminescence spectra. The terms of the higher excited states ($S_n$) give vertical (Franck-Condon) transitions, calculated from the positions of the maxima of the absorption bands.

Upon irradiation in the region of $\lambda < 330$ nm, where both fragments absorb light, any of the fragments can be excited. It should be noted that under used intensities (the light of a mercury lamp), only one of the fragments absorbs a photon and is excited. Figure 27 shows processes in two dyad fragments, but these processes do not occur in parallel in both fragments, but only in that fragment, which absorbs a photon. To excite "simultaneously" both fragments, dyad must absorb second photon during the lifetime of the excited state that is possible only provided using high-power lasers.

Depending on the photon energy, one of the highest excited states ($S_n$) is populated and then relaxes to one of the lowest locally excited states, $S_{1,Np}$ or $S_{1,SQ}$. These states emit (fluorescence) at 350 nm (the Np-fragment), and at 430 nm (the SQ-fragment). In both fragments, there are processes competing with fluorescence: in Np-fragment - the ET to the SQ-fragment, in the SQ-fragment - photoisomerization. The photoisomerization quantum yields of the SQ fragment in the dyad coincide with the corresponding values for the model MeSQ, i.e. in the neutral form; the Np-fragment has no effect on photoisomerization of the SQ-fragment.

In acidic medium, the SQ fragment is protonated with formation of the cation that leads to dramatic decrease in the $S_{1,Np}$ term (Fig. 27, left). This manifests in bathochromic shift of the LWAB by 56 nm and bathofloric (red) shift of the emission band by 95 nm. At the same time, the photoisomerization quantum yields maintain high.

In basic medium, the Np fragment is deprotonated with formation of the anion that lowers the $S_{1,Np}$ level (Fig. 27, right). As a result, the locally excited state of the naphthol anion (0-0 transition, 3.40 eV) is lower than the vertically excited state of the SQ fragment (3.46 eV) that creates prerequisites for the ET from the SQ to Np fragment. This process, as well as a possible formation of an intramolecular complex (exciplex) between naphthol anion and the SQ fragment, can result in a decrease in the photoisomerization quantum yield of the SQ-fragment in alkaline medium.

The third effect that may contribute to the decrease in the photoisomerization quantum yield of the dyad in the anionic form is an effect of "inner shield" (or "internal shutter"). As noted above, the absorption band of the anionic Np fragment shifts bathochromically and overlaps with the SQ-fragment absorption band. Therefore, a part of the incident light is absorbed by the Np anion, which operates in this case as an "inner shield" that reduces the quantity of photons absorbed by the SQ fragment. This leads to
a decrease in the observed photoisomerization quantum yield.

6 Molecular photoswitches and logic gates

Due to variety of photoprocesses observed in the dyads, they possess high potential as controllable molecular photo-switches. Undoubted advantage of the dyads as photonic molecular switches is that they require neither wires nor addition of chemicals, since switching from one state to another is performed by irradiation with light.

Because of reversibility of photoisomerization, it is impossible to convert trans-isomer completely to cis-isomer, however, upon irradiation a photostationary state is achieved, which is enriched by one or another isomer. Since different isomers have different spectral-luminescent properties, different photostationary states can be used as different states of a photo-switch.

In the styrylquinoline-merocyanine dyads, both photochromes undergo photoisomerization and possesses luminescence, but they emit only in trans-forms. The E-SQ fragment emits at 414 nm, and the E-MC fragment emits at 516 nm. Changing abundance of the E-SQ and E-MC fragments, we can switch between preferential emission at 414 nm or 516 nm wavelength. As an example, Figure 28a shows the fluorescence spectra of the dyad SQ11MC in different states. Spectrum 1 characterizes emission of the EE dyad isomer where both fragments are in trans-forms and emission of the MC fragment prevails with ratio $I_{414}/I_{516} = 3.4$. During irradiation with light of 470 nm, the photostationary state $PS_{470}$ is achieved (spectrum 2), where two bands at 414 nm and 516 nm have reverse ratio $I_{414}/I_{516} = 2.4$. Thus, relative intensity of the SQ fragment increases by near 8 times; that corresponds to the switching between two emission channels of the dyad SQ11MC.

In the styrylquinoline-naphthol dyads, both fragments emit but only the SQ fragment undergoes photoisomerization. Nevertheless, we can obtain the same effect of photo-switching between two emission channels. As follows from Table 3, transformation of the SQ fragment from the trans isomeric form to the cis one results in decrease in the spectral overlap integral that should reduce the FRET efficiency and affect the relative intensity of the two bands in emission spectrum. Figure 28b shows the fluorescence spectra of the dyad SQ4Np in different states. Spectrum 1 characterizes emission of the dyad with the SQ fragment in the trans isomeric form, the ratio of the fluorescence intensity at 344 nm (the Np fragment) to that at 425 nm (the SQ fragment) $I_{344}/I_{425}$ being equal to 0.26. Upon irradiation at 365 nm, the band of the Np fragment at 344 nm increases while that of the SQ fragment at 425 nm decreases; spectrum 2 characterizes emission of the dyad in photostationary state $PS_{365}$, the ratio $I_{344}/I_{425}$ being equal to 1.24. Thus, relative intensity of the Np fragment increases by near 5 times.

The photoswitching between two emission channels in the dyad SQ4Np is a result of two effects: (i) reduction of the SQ fragment emission due to conversion of the trans-isomer to the non-emissive cis-isomer, and (ii) enhancement of the Np fragment emission due to reduction of the spectral overlap integral.

The bichromophoric styrylquinoline dyads can function as molecular logic gates (MLGs). A logic gate is a switch, in which the input and output signals can take only values of "0" and "1". The dependence of the output signal on the input signals is defined by the truth table of the logic gate [75]. The truth tables for some of the most important logic functions are given in Table 6.

<table>
<thead>
<tr>
<th>Input</th>
<th>State</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>in1</td>
<td>in2</td>
<td>AND</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>(0,0)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>(1,0)</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>(0,1)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>(1,1)</td>
</tr>
</tbody>
</table>

We have shown that 2-styrylquinoline simulates the operation of two-address MLGs, for which the input signals are light exposure and protonation [76, 77]. The disadvantage of these MLGs is the need to add extra chemicals:
acids (which play the role of the input signal) or base (to return the MLG to its original state).

Photonic devices are completely devoid of this disadvantage; to switch them from one state to another only light exposure is necessary [20]. Let’s consider an algorithm of the photonic double-address MLG design using the dyad S3S [78].

As an example, take the ZZ isomer as an initial state of the MLG (0,0). In the symmetric dyad S3S, both SQ-fragments are indistinguishable, so during irradiation, the left fragment can isomerize (forming an EZ isomer) with the same probability as the right fragment (forming a ZE isomer). However, for definiteness, we assume that the signal applied to input 1 (in1) acts on the left SQ-fragment; i.e., it transforms the ZZ isomer to the EZ isomer, which in this case corresponds to the MLG state (1,0). The signal applied to input 2 (in2) affects the right SQ fragment and turns the ZZ isomer to the ZE isomer, which corresponds to the MLG state (0,1). The impact on both inputs of MLG leads to the isomerization of both SQ-fragments; herewith the EE isomer is formed which corresponds to the final state of the MLG (1,1). Under this correspondence between the input signals and isomerized fragments, the structural transformations occurring under the action on the dyad can be represented by Scheme 14.

![Scheme 14: The ZZ isomer of the S3S dyad as the initial state of the MLG (0,0).](image)

We considered the ZZ isomer as the initial state of the MLG (0,0). Since transformations between four isomeric forms of the dyad are completely reversible, any of these forms can be selected as the initial state of the MLG. Carrying out a comparison between the input signals and the isomerized fragments in each case similarly to the above, we obtain a table of correspondence between the state of MLG and the isomeric form of the dyad S3S, depending on the choice of the initial form of the dyad as the (0,0) state of the MLG (Table 7).

Table 7: Correspondence between the state of the MLG and the S3S isomer depending on the chosen initial isomer.

<table>
<thead>
<tr>
<th>Input in1</th>
<th>in2</th>
<th>MLG state</th>
<th>Isomer of the dyad</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0,0</td>
<td>EE EZ ZE ZZ</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1,0</td>
<td>ZE ZZ EE EZ</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0,1</td>
<td>EZ EE ZZ ZE</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1,1</td>
<td>ZZ ZE EZ EE</td>
</tr>
</tbody>
</table>

The EZ isomer and the ZE isomer are spectrally indistinguishable that restricts the range of logic operations that can be performed using an MLG based on the bis-styrylquinolone dyad. The states of the logic gates corresponding to these two isomers can have only the same signals at the output ("0" or "1"). As can be seen from Table 7, if the initial state of the MLG is the EZ isomer (or ZE isomer), the final state will be the ZE isomer (or EZ isomer), and therefore, the MLG states (0,0) and (1,1) corresponding to these isomers must have the same output signals. If the initial state of the MLG is the EE isomer (or ZZ isomer) and the final state is a ZZ isomer (or EE isomer), then the ZE and EZ isomer are intermediate states, so the same output signals must have (1,0) and (0,1) MLG states.

Another limitation on the type of logic operations that can be performed using the bis-styrylquinoine dyad is due to the fact that the spectral properties of the EE isomer and ZZ isomer, by contrast, are different, so the states of the MLG state corresponding to these isomers should have different output signals (0 and 1). Two pairs of isomers, EE and ZZ, as well as EZ and ZE, occupy opposite corners of the reaction square in Scheme 14; therefore, they may be pairwise either initial (0,0) and final (0,1) MLG states or intermediate (1,0) and (0,1) states. If the initial and final MLG states are the same (by output signal), two intermediate states should differ, and vice versa, if output signals of the intermediate states of MLG are the same, the initial and final states should differ. Taking into account this limitation, the S3S dyad, for example, cannot model a function of logic gates XOR and XNOR. However, there are six logic operations that can be done. In each case it is necessary to select the isomer of the dyad for the initial MLG state, the wavelength of acting light for the input signal, and the threshold value of the output signal to convert the analog signal (the magnitude of the optical density or intensity of luminescence) to digital (0 or 1).

As noted above, in reality it is impossible to obtain "clean" states of an MLG corresponding to the specific compounds listed in the Table 7 since, due to the reversibility of the photoisomerization reaction upon irradiation.
with light, a cis-isomer cannot be fully converted into a trans-isomer and vice versa. In real conditions, the photostationary state PS\(_3\) is reached consisting of a mixture of cis- and trans-isomers (see equation 5), the relative content of which depends on the wavelength of acting light \(\lambda\). The PS\(_3\) composition can be expressed by the content of the cis-isomer \(\eta_3\):

\[
\eta_3 = (c_c)_{ps}/((c_t)_{ps} + (c_c)_{ps})
\]

where \((c_j)_{ps}\) is a concentration of the \(i\) isomer in the mixture. If the initial reactant is a trans-isomer, then \(\eta\) is a degree of conversion during the irradiation of the system.

For the dyad S3S, in photostationary states PS\(_{313}\) and PS\(_{365}\) (formed by irradiation with light of 313 and 365 nm), \(\eta_{313} = 54\%\) and \(\eta_{365} = 80\%\). From these data it is clear that the PS\(_{365}\) is enriched by the cis-isomer; it can be roughly compared with the ZZ isomer of the dyad. The input signal for MLG in this case will be an exposure with light of 313 nm; moreover, both input signals are identical; i.e., \(in_1 = in_2\). In the PS\(_{313}\), the proportion of the trans-isomer is increased; it can be roughly compared with the EE isomer of the dyad. The input signal in this case will be an exposure with light of 365 nm, and both input signals are also the same \((in_1 = in_2)\). The state which is intermediate between PS\(_{313}\) and PS\(_{365}\) can be associated with an asymmetric ZE isomer (or EZ isomer), which under the influence of input signals must be converted to the EE or ZZ isomer. To obtain the EE isomer, irradiation with a light of 313 nm is necessary; a light of 365 nm is needed to obtain the ZZ isomer. Therefore, in this case the input signals are different: one of them is irradiation with a light of 313 nm; the other is with a light of 365 nm.

We now consider a simulation of MLG operation using the PS\(_{365}\) as the initial state \((0,0)\) of a logic gate. This state is associated with the ZZ isomer of the dyad, and structural transformations occurring under the influence of the dyad are shown in Scheme 14. Input signals \((in_1 = in_2)\) are irradiation with light of 313 nm.

The response of the MLG to input signals \((in_1\text{ and/or } in_2)\) - irradiation with a light of 313 nm - and the function of reset - irradiation with a light of 365 nm - is shown in Fig. 29.

The output signal of luminescence is read at a wavelength of the maximum emission of the EE isomer (440 nm). A similar form (with a different scale of ordinates) has a graph of the optical density change, the reading of which was performed at an absorption maximum wavelength of 360 nm for the EE isomer.

Upon irradiation with light of 313 nm, there is an increase in optical density and luminescence intensity due to reaction of the cis-trans photoisomerization resulting in increase in the EE isomer concentration. The single impact to one of the inputs \((in_1\text{ or } in_2)\) transforms MLG into the \((1,0)\) or \((0,1)\) state; the two-fold impact at both inputs \((in_1\text{ and } in_2)\) transforms MLG into the \((1,1)\) state. From any of these three states, \((1,0), (0,1),\) or \((1,1)\), the system returns to the \((0,0)\) state under irradiation with light of 365 nm. Therefore, in this case, irradiation with light of 365 nm corresponds to the function “reset.”

The last stage of the modeling of MLG operation is a conversion of the received analog signal - the optical density or the intensity of luminescence - into digital signal. For this it is necessary to establish a threshold value below which the output signal is assumed to be “0” and above which it is “1.” In Fig. 29 two threshold values of luminescence intensity, 70 and 88, are shown by horizontal dashed lines.

It is clear from Fig. 29 that at the threshold value of 70, the intensity of luminescence \(I_{440} < 70\) only in the initial state of the dyad. Consequently, only in the MLG state \((0,0)\) the output signal is “0.” After any impact on the MLG (to one of the inputs or both), the luminescence increases to \(I_{440} > 70\); i.e., the output signal is set to “1.” As can be seen from Table 6, such a ratio between the input and output signals corresponds to the logic gate “OR.”

At the threshold value of 88, the luminescence intensity \(I_{440} > 88\) only after exposure to both inputs of the logic gate (Fig. 29). Consequently, only in the MLG state \((1,1)\) the output signal is set to “1”; in all other states \(I_{440} < 88\); i.e., the output signal has a value “0.” As can be seen from Ta-
ble 6, such a ratio between the input and output signals corresponds to the logic gate “AND.”

Note that the function “OR” and “AND” are operations of logic (Boolean) addition and multiplication, respectively. On the basis of these functions, complemented by a function of the negation “NOT,” one can construct any other logic function.

Another option for the simulation of MLG operation may be obtained by using the photostationary state of the dyad PS$_{313}$ as the initial state (0,0) of the logic gate. This state was matched with the $EE$ isomer of the dyad; therefore, structural transformations occurring under the influence on the dyad can be represented by Scheme 15.

Input signals ($\text{in1} = \text{in2}$) in this case are the irradiation with light of 365 nm, and the reset function is performed by irradiation with light of 313 nm. Upon irradiation with light of 365 nm, there is a decrease in optical density and luminescence intensity due to reaction of the trans-cis photoisomerization resulting in decrease in the $EE$ isomer concentration. The response of the MLG to input signals and the function of the reset are shown in Fig. 30. It can be seen that, at the threshold luminescence intensity of 70, the S3S dyad simulates the operation of logic gate “NOT-AND” (“NAND”), while, increasing the threshold value to 100, it simulates the action of logic gate “NOT-OR” (“NOR”).

As shown above, one can choose an intermediate state of the dyad between the PS$_{313}$ and PS$_{365}$, which is comparable with the asymmetric $EZ$ isomer, as an additional version of the initial state of MLG (0,0). Conventionally, this state can be defined as 0.5(PS$_{313} + $PS$_{365}$), and structural transformations occurring under the influence to the dyad are shown in Scheme 16.

In this case, two input signals differ in irradiation wavelengths: $\text{in1}$ corresponds to irradiation with light of 365 nm (whereas reset corresponds to irradiation with light of 313 nm), and $\text{in2}$ corresponds to irradiation with light of 313 nm (whereas reset corresponds to irradiation with light of 365 nm). Note that, with the sequential operation on both inputs of the MLG, one input signal, in fact, annihilates the effect of the other one, so the final state of the dyad coincides with the initial state ($EZ$ and $ZE$ isomers are indistinguishable); i.e., the logic gate without the reset is ready for the next cycle of the operation.

Figure 31 shows the response of the MLG to input signals and the function of the reset. It is seen that at the threshold luminescence intensity of 70, the dyad S3S simulates the operation of the logic gate “IMPLICATION” (“IMP”). When the threshold value of the luminescence inten-
tensity is 83, the dyad S3S simulates the operation of logic gate “INHIBIT” (“INH”), Table 6.

![Figure 31](image)

**Figure 31:** The change in the luminescence intensity of the S3S dyad at a wavelength of 440 nm as a response to external stimuli: the initial state is 0.5(PS\textsubscript{313} + PS\textsubscript{365}), input signal in1 is exposure with light of 365 nm (reset is exposure with light of 313 nm), and in2 is exposure with light of 313 nm (reset is exposure with light of 365 nm). The horizontal dashed lines indicate the threshold values of the luminescence intensity for logic gates “IMP” and “INH.”

Thus, a variety of logic operations (“AND,” “OR,” “NAND,” “NOR,” “IMP,” and “INH”) can be performed on the basis of the bis-styrylquinoline dyad S3S. The input signal for the MLG is an exposure with light of 313 and/or 365 nm. The output signal is an optical density or luminescence. The type of operation performed by the MLG depends on the choice of isomer (form) of the dyad S3S as an initial state of the logic gate (0,0), as well as on the threshold value of the optical density or the intensity of luminescence below and above which the output is assumed to be “0” or “1,” respectively.

7 Conclusion

In conclusion, we can compare properties of the considered three types of dyads, proceeding from their possible application as photoswitches and molecular logic gates (MLGs).

The styrylquinoline-naphthol (SQnNp) dyads, due to a photochromism of the SQ fragment, can be switched between preferential emission of one or another fragment. The SQ fragment emission is changed as a result of transformation between the emissive trans-isomer and non-emissive cis-isomer; the Np fragment emission is changed as a result of a dependence of the FRET efficiency (and quenching effect) on isomeric form of the SQ fragment. Additionally, one can use photo-basic and photo-acidic properties of the SQnNp dyads. Selective excitation of the SQ fragment (in the long-wavelength region of the spectrum) should result in the local pH increasing, whereas preferential excitation of the Np fragment (in the short-wavelength region of the spectrum) – in the local pH decreasing in the vicinity of the dyad. Thus, the pH gradient can be generated for directional proton transfer (“proton photopump”).

The same effect of photo-switching between two emission channels can be achieved in styrylquinoline-merocyanine dyads SQnMC, but in this case both chromophoric fragments can undergo photoisomerization. So, every fragment (SQ or MC) can be switched independently. The FRET from the SQ to the MC fragment results in quenching of the former and sensitization of the latter; the FRET efficiency being dependent on the number of methylene groups n. Due to specific relationship between π-systems of the two fragments, protonation of the SQ fragment transforms non-symmetric one-charged styrylquinoline-merocyanine dyad to a quasi-symmetric double-charged "bis-merocyanine" dyad where both fragments are photoactive, and thus launches a cycle of kinetic-driven one-way photoisomerization of the SQ fragment.

As compared to the SQnMC dyads, the symmetric bis-styrylquinoline S3S dyad has a drawback. Due to symmetry, it is impossible to excite selectively one or another fragment, and it is impossible to distinguish some dyad isomers. Nevertheless, this dyad can act as a two-addressable MLG with two identical input signals. The S3S dyad as a logic gate demonstrates a unique property that is typical specifically for molecular systems: the compatibility of multiple logic devices in one or the tunability of logic devices on a different type of work. This property is essentially inaccessible in semiconductor elements that are currently in use, where for each logic operation a separate device is required.

Additionally, the molecular logic gates based on the S3S dyad allow one to read the output signal using luminescence. In this case, both inputs and outputs are photons; i.e., homogeneity of input and output signals is observed. Due to compliance with the condition of homogeneity for input and output signals, this is a prerequisite for the construction of more complex circuits based on molecular logic gates where the output signal of one element of the circuit can be directed to the input of another element. The creation of such chains is, perhaps, a
next step in the replacement of modern semiconductor elements with molecular analogues.

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