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(*E*)-2-(hydroxystyryl)-3-phenylquinazolin-4(3*H*)-ones: synthesis, photochemical and luminescent properties

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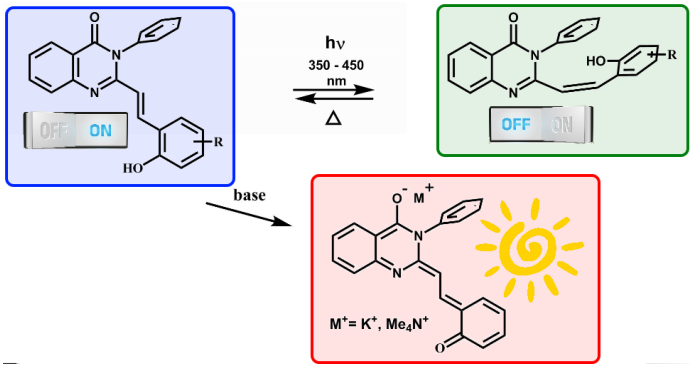
Abstract

The new (*E*)-2-(hydroxyarilethenyl)-3-phenylquinazolin-4(3*H*)-ones with various substituents in phenyl fragment were synthesized. The effect of electron donor and acceptor substituents (±*M*) in quinazolinones on luminescence intensity and dual emission in 550-650-nm wavelength range was shown. The fact of the reversible photo/thermal *E-Z* isomerization for several substances was established. The (*E*)-2-(5-chloro-2-hydroxystyryl)-3-phenylquinazolin-4(3*H*)-one had shown the best combination of photochemical (*E-Z* isomerization) and photophysical properties. The (*E*)-2-(2-hydroxy-5-morpholinostyryl)-3-phenylquinazolin-4(3*H*)-one had revealed the best ESIPT-luminescence (Φ_{rel} = 5.3 %).



Keywords: (*E*)-2-(Hydroxystyryl)quinazolinones, ESIPT-luminescence, photoacids, reversible photo/thermal isomerization, photoswitching

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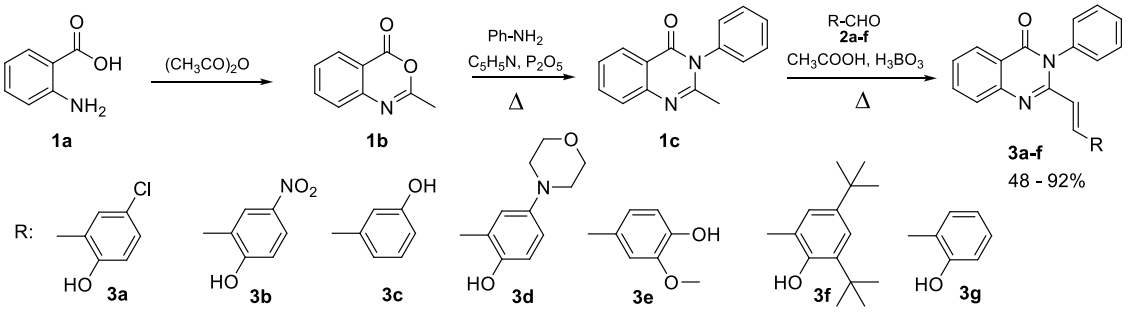
Introduction

Diarylethenes and its heterocyclic analogues form the basis of modern electroluminescent and photochromic materials, widely used in nonlinear optics, lasers with tunable frequency, optoelectronic devices for recording and storage of information, and molecular photoswitches[1,2]. Unsymmetrical derivatives are of great interest among hetarylstylbenes[3]. The presence of acceptor azine (azinone) core in combination with donor (aryl) fragment in stilbene molecules might considerable influence the photochemical and photophysical properties of luminophores because of the n,π* state contribution[4]. However, the amount of publications devoted to the study of unsymmetrical (het)arylethens is not as numerous as for symmetric ones[3]. There are several publications concerning the synthesis of (*E*)-2-styrilquinozaline-4(3*H*)-ones and studying of their photophysical properties[3,5-9]. It should be noted that compounds of this push-pull type possessing a specific emission ability and a profound tendency to a photoinduced *E*-*Z*-isomerization[8,9] are quite promising for the development of base- and acid-sensitive photochromic materials. Our researches have shown that the incorporation of the hydroxyl group in the *ortho* position of the arylethenyl fragment of quinazolinones **3** (Scheme 1)[10,11], generates photocontrolled processes like ESIPT luminescence[12] with a typical broadband spectrum in visible 400-600-nm wavelength range and reversible *E*-*Z* isomerization of the vinylene moiety. Appropriate mechanisms of proton transfer in excited state (ESIPT) to the diazinone fragment and back in the course of tautomeric transitions in the conjugated chromophore system were proposed. In this communication we wish to report about influence of donor and acceptor substituents in phenol fragment of (*E*)-2-(hydroxyarylethenyl)-3-phenylquinazolin-4(3*H*)-ones on ESIPT and geometric isomerization of chromophore system. Such system may be useful for white-light emitting materials.

Results and Discussion

The C=C bond formation techniques in the series of (het)arylstilbenes have often a specific nature, while condensation of 2-methylazines[4] with aromatic aldehydes in the presence of zinc chloride or sodium acetate does not provide high yields of the target compounds. We have established that using boric acid as the catalyst in the proposed method (Scheme 1)[11,12] afford to synthesize 2-(arylethenyl)-3-phenylquinazolin-4(3*H*)-ones with various acceptor and donor functional groups, including hydroxyl ones, with yields from moderate to excellent. Synthesized substances are the *E*-isomers. The *trans*-isomerization of **3a-f** is confirmed by the presence of doublets of vicinal protons of C=C bonds in range of δ 7.79—8.25 and 6.14—6.75 ppm with the spin-spin coupling constant of ~15.5 Hz in their ^{1}H NMR spectra.



Scheme 1. Synthesis of (*E*)-2-(hydroxyarylethenyl)-3-phenylquinazolin-4(3*H*)-ones.

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Photophysical properties of luminophores 3

The photophysical properties of phenols have been studied by UV-Vis in neutral, basic (Me_4NOH and *t*-BuOK) and acidic (CH_3COOH) solutions in DMF. In neutral DMF solutions the compounds **3a-f** exhibited similar spectral characteristics with absorption maxima in the range 340-400 nm. Compared to the 355-nm absorption maximum of model *ortho*-hydroxystyryl substituted **3g**[10], the absorption bands in UV spectra of the compounds **3a-f** demonstrate the following differences. The electron-donor groups (+*M*) in compounds **3a**, **3f** and **3e** compounds provide bathochromic shift of this absorption maximum up to 3-10 nm. The presence of morpholine fragment in quinazolinone 3d structure leads to a splitting of the absorption band with the emergence of a long-wave shoulder at 365-480 nm. On the contrary, the electron withdrawing nitro group in **3b** and OH group in the *meta* position of **3c** provide hypsochromic shift up to ~ 12 nm.

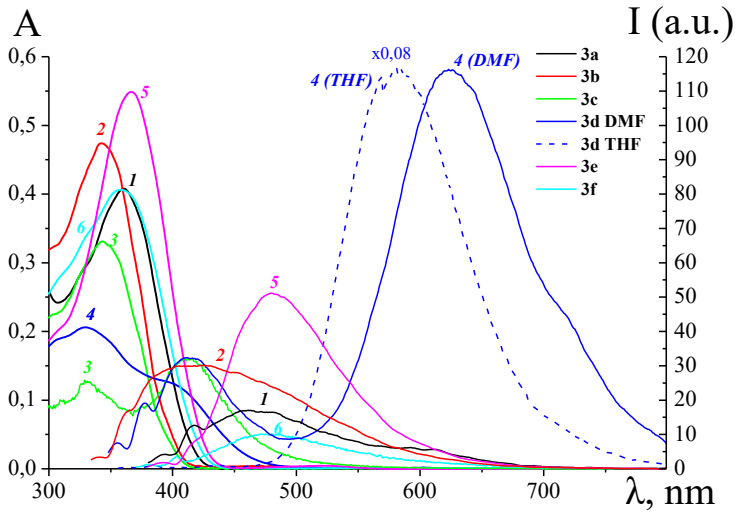

Figure 1. The electron absorption spectra and fluorescence emission spectra (λ_{ex} in the table 1) of solutions of compounds *E*-**3** ($2 \cdot 10^{-5}$ mol L^{-1}, in DMF), *E*-**3a** (*1*), *E*-**3b** (*2*), *E*-**3c** (*3*), *E*-**3d** (*4*), *E*-**3e** (*5*), *E*-**3f** (*6*).

Fluorescence spectra of the neutral solutions *E*-**3** demonstrate the following features. The OH group in the *ortho* and *para* positions of the phenolic moiety, which is included in the common conjugation chain, leads to a significant broadening of the emission band in the 400-700-nm region compared with that for the *meta* substituted *E*-**3c** (~ 400-530 nm). At the same time, a bathofluoric shift of the emission band maximum from 420 nm to 485 nm is observed upon the transition from the electron withdrawing nitro derivative *E*-**3b** to the *E*-**3a**, *E*-**3f** and *E*-**3e** with electron donor substituents (+*M*). It was previously shown that *E*-**3g** and its alkoxy derivatives have dual emission in neutral media[10,11] associated with proton transfer in molecules in the excited state (ESIPT). This process is characterized by the emergence in the spectra of long-wavelength emission bands in the 500 - 700 nm region with large Stokes shift values (≥ 6000 cm^{-1})[12] due to the free phenolate-anion and quinonoid-anion forms that are present in solutions along with an excited undissociated phenol form. The quinazolinones *E*-**3a** and *E*-**3d** in neutral media demonstrate the similar behavior. In the emission spectrum of *E*-**3a**, like of *E*-**3g**, an excited undissociated phenol form **A** (normal Franck-Condon excited state) and quinonoid-anion form **B** (**C**), which are in protolytic equilibrium in photostationary state solutions (PSS), are characterized by maxima at 445 and 600 nm, respectively (Figure 1, Scheme 2). In irradiated solutions of *E*-**3d** the equilibrium is totally shifted to the free phenolate-anion and quinonoid-anion forms (Figure 1, Scheme 2) with emission band maximum at 625 nm in DMF or at 583 nm in THF, like for the *ortho*-hydroxystyryl

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substituted *E*-**3g** in Et_3N solutions[11]. Apparently, the formation of quinonoid-anion form **G** is directly related to the transfer of the proton to the morpholine nitrogen atom in the excited planar conjugated chromophore *E*-**3d** to form the morpholinium zwitterion **D** (Scheme 2). These arguments are confirmed by quantum-chemical calculations according to which the amino group is involved in the electron density of the chromophore HOMO localized on the phenol fragment (S-Table 3). It is worth noting a certain hypsochromic shift of the emission maximum by 42 nm in irradiated solutions of *E*-**3d** in THF, compared with that in DMF, and an increase by two orders of emission intensity with quantum yield of 5.3 % ($\underline{<}$ 0.1% for the other substances). These differences observed in the spectra can be explained by the predominance of the free phenolate-anion form **G** in equilibrium medium (Scheme 2).

Table 1. Photophysical and photochemical characteristics of quinazolinones *E*-**3** in DMF

Compound	λ_{ex}/nm	λ_{fl}/nm	Stokes shift/cm^{-1}	$\lambda_{max(abs)}$[a]/nm (ε)		$t_{E\text{-}Z}$[b]/s	$t_{Z\text{-}E}$[c]/m
				Starting *E*-isomer	Reaction mixture		
E-**3a**	358	455 600	5955 11267	360 (20380)	359 (17855)	20	40
E-**3b**	342	420	5430	348 (21950)	309 (17715)	180	40
E-**3c**	343	411	4823	343 (16565)	343 (14720)	18	–
E-**3d**	338	625 583 (THF)	9000 7847	329 (10295) 400 (6040)	–	–	–
E-**3e**	365	485	6191	356 (21730)	348 (10835)	12	80
E-**3f**	356	475	6925	358 (20345)	316 (10760)	16	30
E-**3g**	358	455 600	5955 11266	358 (20100)	358 (9950)	16	40

[a]The absorption maxima and the corresponding extinction coefficients [14] (L mol^{-1} cm^{-1}) of 3 ($2 \cdot 10^{-5}$ mol L^{-1}).
[b]Duration of photochemical *E*-*Z* isomerization of solutions upon exposure to irradiation.
[c]Duration of thermal *Z*-*E* isomerization of solutions thermostated at 75 °C

The validity of the assignment of 600-nm long-wavelength luminescence to the quinonoid-anion form is confirmed by the spectral data of titration of *E*-**3** solutions with *t*-BuOK and Me_4NOH bases. Similarly to *E*-**3g**[11], significant changes associated with redistribution and appearance of a new absorption band in the 400-500 nm visible wavelength range are observed in spectra of *E*-**3** basic solutions with the exception of *E*-**3c** and *E*-**3d**. The luminescence spectra demonstrate high intensity 600-nm emission band. These changes are related to the tautomeric transformation of conjugated system *E*-**3** into the quinonoid form *E*-**4** (Scheme 2, Table 2, Fig. 2) and the formation of charge transfer complexes. Earlier obtained results of 2D homo- and heteronuclear NMR experiments in the case with steady-state basic solutions of *E*-**3g** had unequivocally confirmed the formation of the quinonoid form *E*-**4g** with the transfer of a negative charge from the phenolate anion to the oxygen atom of the keto-group[10] (Scheme 2). Similar changes of proton signal positions occur in ^{1}H NMR spectra, e.g. *E*-**3a** (Experimental Section, S-Fig. 1). Consequently, a significant luminescence at 600 nm has been the result of the direct excitation of the quinonoid-anion form *E*-**4** (similarly *E*-**3g**[10]) and exhibited a normal Stokes' shift (Δν 1665 – 5327) and high quantum yield (Table 2). The quantum yield of chlorine substituted *E*-**3a** reaches the highest values (23.4%) and its decrease by two orders for *E*-**3b** is caused by luminescence quenching because of nitro group.

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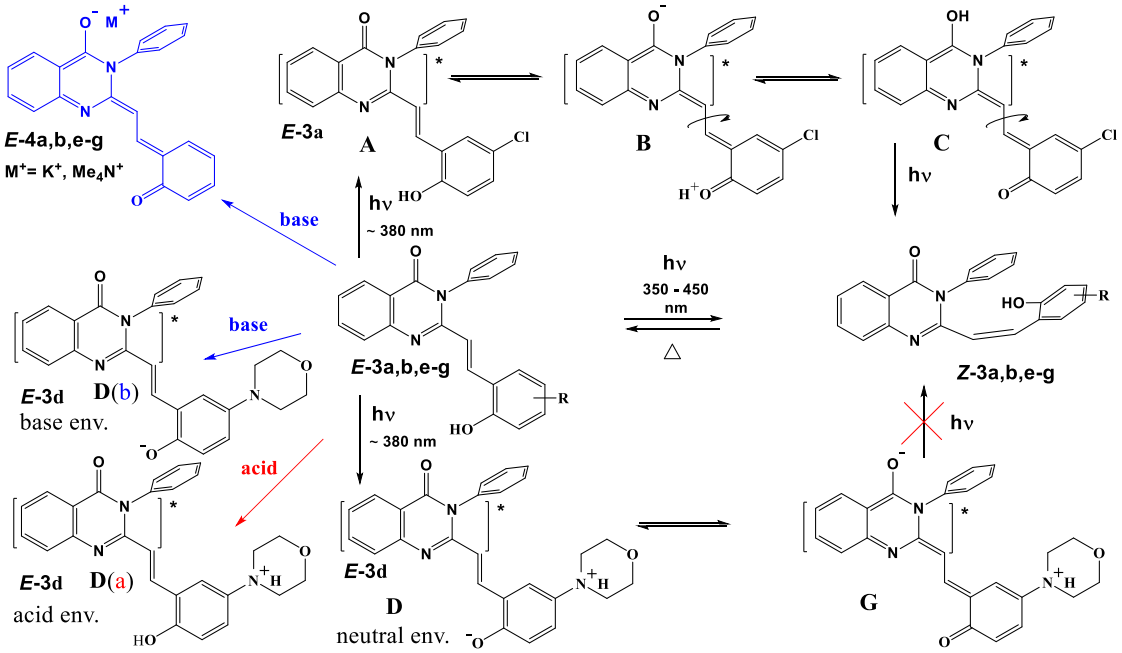

Scheme 2. Photophysical and photochemical processes in (*E*)-2-(hydroxyarylethenyl)-3-phenylquinazolin-4(3*H*)-ones.

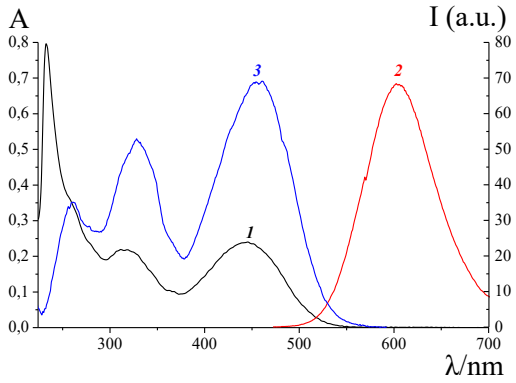

Figure 2. The electron absorption (*1*), fluorescence emission (*2*) and excitation (*3*) spectra of the quinonoid form of *E*-**3a** ($2 \cdot 10^{-5}$ mol L^{-1}) in DMF after the addition of Me_4NOH in the molar ratio of 1:20 (excitation and emission wavelength, λ/nm: 457 and 605, respectively).

Table 2. Selected photophysical characteristics of the quinonoid form *E*-**4** of *E*-**3** ($2 \cdot 10^{-5}$ mol L^{-1}) in basic media (DMF and Me_4NOH or *t*-BuOK), $C_{E\text{-}3}$:C_{base} as 1:20.

Compound ($2 \cdot 10^{-5}$ mol L^{-1})	λ_{abs}/nm	λ_{ex}/nm	λ_{em}/nm	Stokes' shift / cm^{-1}	Φ_{rel} (%)
4a	443	457	604	5327	23,4
4b	490	505	555	2390	0,2
3c	337	276	385	3699	-
3d	329 (400 *shoulder*)	338	625	9000	0.8
4e	513	518	567	1856	0.3
4f	548	580	642	1665	12,2
4g	520	520	607	2757	12,5

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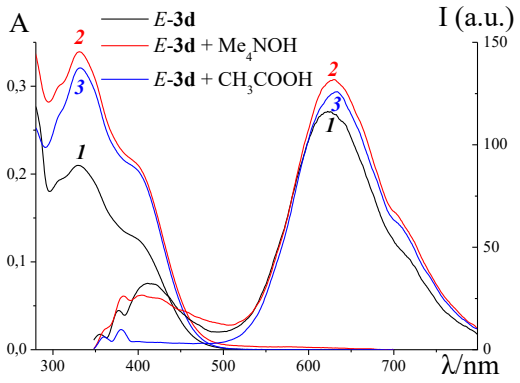

Figure 3. The electron absorption and fluorescence emission spectra (λ_{ex}~338 nm) of *E*-**3d** ($2\cdot10^{-5}$ mol L^{-1}) in DMF (*1*) and after the addition of Me_4NOH in the molar ratio of 1:20 (*2*) and CH_3COOH (0.1 N in DMF) (*3*).

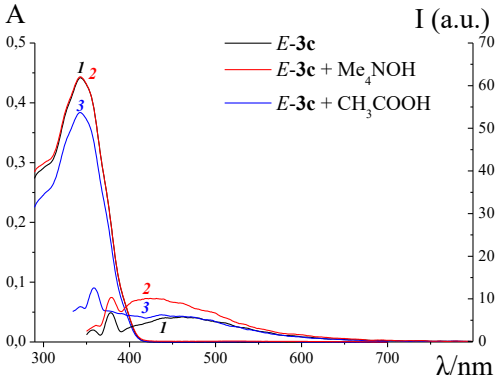

Figure 4. The electron absorption and fluorescence emission spectra (λ_{ex}~343 nm) of *E*-**3c** ($2\cdot10^{-5}$ mol L^{-1}) in DMF (*1*) and after the addition of Me_4NOH in the molar ratio of 1:20 (*2*) and CH_3COOH (0.1 N in DMF) (*3*).

Another confirmation of ESIPT-luminescence of *E*-**3a** is its quenching in the process of the spectrophotometric titration of solutions with acetic acid (0.1 N CH_3COOH), accompanied by the disappearance of the maximum in λ_{max} at 600 nm in their emission spectra (S-Fig. 3). Similar changes were observed earlier for *E*-**3g** and its alkoxy derivatives[11]. The well known cause of ESIPT-luminescence quenching in such photoacids as aromatic alcohols is rapid reprotonation of any excited alcoholate ion under acidic conditions[13].

The absence of any changes in absorption and emission band positions in optical spectra of *ortho* and *para* hydroxy derivative *E*-**3b**, *E*-**3e** and *E*-**3f** indicates the presence of the excited undissociated phenol forms having a normal emission with maximum at 420 – 485 nm in steady-state neutral and acid solutions. At the same time, their basic solutions demonstrate a tendency to tautomeric transformations under more stringent conditions.

The positions of the absorption and emission bands in the optical spectra of *E*-**3c** and *E*-**3d** in steady-state neutral, basic and acidic solutions remain unchanged as well, but the causes of these observed phenomena are different. The lack of conjugation between the hydroxy group and the chromophoric system of the heterocycle *E*-**3c** proved to be the main reason for the existence of only excited undissociated phenol form in irradiated solutions at various acidity and basicity values (Fig. 4). On the contrary, electro-negative amino group included in the common conjugated system of (*E*)-2-(hydroxyarylethenyl)-3-phenylquinazolin-4(3*H*)-ones *E*-**3d** successfully competes for the binding of a proton (cation) with diazinone cycle during the formation of the zwitterionic, morpholinium cationic (a) and phenolate-anion (b) forms in neutral, acidic and basic media (Scheme 2, Table 2, Fig. 3). This is obviously the main reason for inhibiting the formation of quinonoid form *E*-**4d** in basic media in the ground state.

Photochemical properties of chromophores 3

The tendency of *E*-**3** ligands to photoinduced *E-Z* isomerization has been investigated by ultraviolet light irradiating (365-nm wavelength band, mercury lamp) of their DMF solutions and estimated by absorption and fluorescence spectroscopy. The *E*-isomers **3a,b,e,f** have been found to demonstrate reverse *E-Z-E*

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photo/thermal isomerization in a neutral medium, identical to *E*-**3g**[10,11]. The *E*-*Z* isomerization process has been accompanied by a decrease in the intensity of the absorption band to a photostationary state (PSS) with characteristic isobestic points on the absorption titration curves in their UV-Vis spectra. The formation of the *Z*-isomer has been confirmed by the appearance of doublets of the vicinal protons of the C=C bond in the range of δ 5.9-6.6 ppm with a spin-spin interaction constant of 12.5 Hz in ^{1}H-NMR spectra, for example, of irradiated solutions of **3a** in DMSO-d_6 (experimental Section, S-Fig. 4).

According to spectroscopic studies, the nature of the introduced substituents in the *para*/*ortho* position to the OH group of phenols *E*-**3** has a substantial effect on the time required to achieve a PSS. So the electron donor substituents of *E*-**3a**, *E*-**3e** and *E*-**3f** provide a commensurate with *E*-**3g** rate of *E*-*Z* isomerization in DMF about 16 – 20 s (Table 2), whereas the presence of an electron-withdrawing nitro group in *E*-**3b** leads to a significant deceleration of isomerization from 16 to 180 s. The reversible thermal *Z*-*E* isomerization has passed by solution thermostating at 75° C similarly *E*-**3g** (S-Fig. 4). In general, the time of the dark *Z*-*E* isomerization (30-40 m) of diazinones **3a,b** and **3f** comparable to that for previously studied derivative *E*-**3g**[10,11], while the reaction time of the *para*-hydroxy substituted **3e** is doubled (Table 1).

The *meta* position of the OH group in the chromophore *E*-**3c** hasn't practically an effect on the rate of photoinduced *E*-*Z* isomerization but completely inhibits the reversible thermal *Z*-*E* isomerization process, i.e. the photoisomerization reaction in this compound becomes irreversible.

According to the spectral data, the morpholino-substituted *E*-**3d** in the irradiated solutions has not isomerized. Apparently, the action of the amino group associated with the formation of morpholinium zwitterion **D** is aimed at stabilization of the *trans* geometry of excited molecules and, accordingly, a complete PSS equilibrium shift from the photochemical toward the competitive photophysical processes in chromophore solutions. Moreover, the competitive proton transfer to the amino group of the phenolic fragment, rather than the C=O and C=N heterocycle groups[10], can also be a determining factor in the slowing or inhibition of photo/thermal isomerization processes (Table 1). A possible competitive photoinduced transfer of a proton to nitro group as a result of the electron density shift in the phenolic fragment with the formation of 4-oxocyclohexa-2,5-dienylideneazinic acid residue is a probable cause of a significant slowdown in the photoisomerization reaction of *E*-**3b**. In favor of the probable proton transfer to the amino or nitro group of the phenolic fragment, quantum-chemical calculations of HOMO and LUMO of *E*-**3b,d** show the localization of the electron density on the phenolic fragment involving the above substituents (S-Table 3) and the smallest values of the band gap energy.

The hindered transfer of the proton to the heterocycle due to the large spatial distance between the hydroxy group and the diazinonic fragment can be an explanation of deceleration in thermal *Z*-*E* isomerization of **3e**. The lack of conjugation and the similar remoteness of the OH group is, apparently, the main reason for the inhibition of thermal isomerization in *E*-**3c** molecules.

Conclusions

In summary, the spectroscopic studies of the synthesized *E*-isomers of 2-(arylethenyl)-3-phenylquinazoline-4(3*H*)-ones **3a**-**f** with various acceptor and donor functional groups (+*M*) into the *ortho*, *para* and *meta* position of the phenolic fragment allowed to establish the correlation between structural features of molecules and their photophysical and photochemical properties. It is shown that the *ortho* and *para* positions of the OH group included in the conjugated chromophoric system lead to a significant broadening of the emission band in the 400-700 nm range. Moreover, the *ortho* position of the OH group is an important factor

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in the successful operation of the photoswitches **3a** and **3f**, i.e. reversible photo/thermal *E-Z-E* isomerization. In this case, the most optimal conditions for the transfer of a proton to the spatially-close electronegative diazinone cycle and back in the isomerization process are formed in the conjugate system. The *ortho* position of the OH group is also the crucial factor in the photophysical transformations associated with ESIPT-luminescence. The transfer of a proton from the OH group to a heterocycle in the chloro-substituted *E*-**3a** apparently provides the coherence of the action of photochemical (*E-Z* isomerization) and photophysical (ESIPT-luminescence) transformations. On the contrary, the competitive binding of a proton by an electronegative amino group in morpholino-substituted *E*-**3d** results in a shift in the equilibrium toward photophysical transformations (ESIPT luminescence) and inhibition of photochemical isomerization. As a whole, the data obtained allow us to consider these compounds as potential components for supramolecular ionic devices and white light-emitting organic materials[17] in the field of molecular ionics.[18]

Experimental Section

General. IR spectra were registered on IR-Fourier spectrometer PerkinElmer Spectrum One using diffuse reflectance sampling accessory (DRA). Electron absorption spectra were recorded on a UV-2600 PC double-beam spectrophotometer (Shimadzu, Japan) in the range of 190–700 nm with the wavelength setting accuracy of ±0.3 nm using a Shimadzu scan standard program UVProbe. Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer with mutually perpendicular beams, the wavelength setting accuracy of 0.5 nm. Quartz cuvette SUPRASIL 111-QS 10 ("Hellma", Germany) were used for recording in the range 190-800 nm, the bandwidth around the stationary point of excitation and emission was 10 nm. The excitation point wavelength was set based on the maximum in absorption and emission spectra, the emission point wavelength, based on the maximum in excitation spectra. In spectra luminescence of solvents was taken into account. The relative quantum yields of solutions of compounds 3 were measured at 22 ± 1°C by the method available on www.jyhoriba.co.uk (Jobin Yvon Ltd. 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ UK). Samples of comparison were fluorescein (Φ_{abs} = 0,85[1]) in 0.1 N aqueous solution of KOH and quinine bisulfate (Φ_{abs} = 0,546[14]) in 0.1 N aqueous H_2SO_4 solution. NMR spectra the ^1H and ^{13}C were recorded in DMSO-d_6 solution on devices "Bruker DRX-400" (400 and 100 MHz) and "Bruker AVANCE-500" (500 and 126 MHz) using TMS and DMSO-d_6 (δC 39.5 pps) as an internal standard. Full assignment of signals in ^1H and ^{13}C NMR spectra performed using two-dimensional experiments ^1H-^1H COSY, ^1H-^1H NOESY, ^1H-^{13}C HSQC and HMBC. Melting point was determined on the microheating table "Boetius". TLC was performed on plates Silufol UV-254. The spot was shown the light of a low pressure mercury lamps (6 watts) or iodine vapor. The 2-methyl-3,1-benzoxazin-4-one was prepared by boiling anthranilic acid in freshly distilled acetic anhydride[15].

2-Methyl-3-phenylquinazolin-4(3*H*)-one (1c) The synthesis was carried out by the method described in.[10] Analytical characteristics of the compound were consistent with literature data.

Aniline (0.7 g, 7.5 mmol) and P_2O_5 (1 g) were added to 2-methyl-3,1-benzoxazin-4-one (1.2 g, 7.5 mmol) in pyridine (15—20 mL). The reaction mixture was heated for 26 h at 90—95 °C. After the reaction reached completion, the solvent was evaporated; water (50 mL) was added to the residue. The product was filtered off and purified on a chromatographic column (SiO_2), eluent ethyl acetate—hexane, 3:2. The yield was 1.5 g (89%). Analytical characteristics of this compound agreed with those given in the literature.[10]

(*E*)-2-Styrilquinazolin-4(3*H*)-ones (3). 1.7 mmol of the corresponding aldehyde **2a-f** and equimolar amount of H_3BO_3 (1.3 mmol) were added to 0.3 g (1.3 mmol) of compound **1** in acetic acid (30 ml). The reaction mixture

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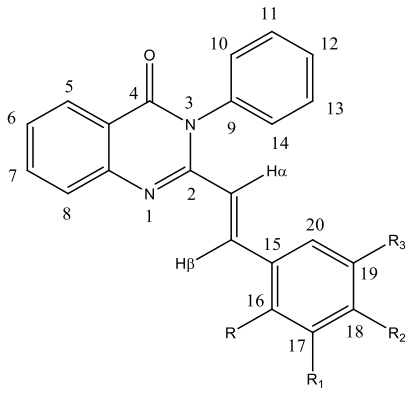
was boiled for 6-8 hours. After completion of the reaction, the solvent was distilled off. The product has been purified by column chromatography from various impurities and *Z*-isomer formed in small quantities in the synthesis process (2-7 %). Chromatographic separation was carried out on a column (SiO_2), making eluent with a mixture of ethyl acetate and hexane, gradient changing the ratio of the concentrations of solvents from 1:4 to 4:1, respectively. Target product was crystallized from EtOH or CH_3CN (**3a-f**).



(*E*)-2-(5-Chloro-2-hydroxystyryl)-3-phenylquinazolin-4(3*H*)-one (3a). Pale yellow, yield 330 mg (72%), mp 309 - 311° C (CH_3CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 10.44 (s, 1H, OH), 8.13 (d.d, *J* 8.0, 1.3 Hz, 1H, H-5), 7.95 (d, *J* 15.6 Hz, 1H, Hβ), 7.87 (d.d.d, *J* 8.1, 7.0, 1.3 Hz, 1H, H-7), 7.77 (d, *J* 8,0 Hz, 1H, H-8), 7.55 – 7.63 (m, 3H, H-11, H-13, H-12), 7.53 (d.d.d, *J* 8.0, 7.0, 1.0 Hz, 1H, H-6), 7.45 (m, 2H, H-10, H-14), 7.19 (d, *J* 2,5 Hz, 1H, H-20), 7.18 (d.d, *J* 8.5, 2.5 Hz, 1H, H-18), 6.84 (d, *J* 8.5 Hz, 1H, H-17), 6.63 (d, *J* 15.6 Hz, 1H, Hα); ^{13}C NMR (126 MHz, DMSO-d_6) δ/ppm 161.77, 155.94, 152.37, 147.89, 137.59, 135.17, 134.51, 130.54, 130.05 (2), 129.52, 129.41 (2), 128.77, 127.63, 126.92, 126.87, 123.88, 123.25, 122.10, 120.99, 118.21. IR(DRA): 695, 721, 762, 812, 849, 898, 976, 1015, 1113, 1169, 1246, 1282, 1306, 1337, 1352, 1425, 1470, 1492, 1550, 1572, 1633, 1666, 3047, 3310 cm^{-1}; Anal. Calcd for $C_{22}H_{15}ClN_2O_2$: C, 70.50; H, 4.03; N, 7.47, Cl, 9.46. Found: C, 70.58; H, 3.84; N, 7.13.

(Z)-2-(5-chloro-2-hydroxystyryl)-3-phenylquinazolin-4(3H)-one (Z-3a). ^{1}H NMR (DMSO-d_6) *δ*/ppm: 10.04 (s, 1H, OH), 8.15 (d.d, *J* 8.3, 1.2 Hz, 1H, H-5), 7.81 (d.d.d, *J* 8.4, 6.9, 1.5 Hz, 1H, H-7), 7.49 – 7.55 (m, 3H, H-11, H-13, H-12 H-8, H-6), 7.47 (d, *J* 2,6 Hz, 1H, H-20), 7.40 (m, 2H, H-10, H-14), 7.13 (d.d, *J* 8.7, 2.6 Hz, 1H, H-18), 6.76 (d, *J* 8.7 Hz, 1H, H-17), 6.62 (d, *J* 12.5 Hz, 1H, Hβ) 5.92 (d, *J* 12.5 Hz, 1H, Hα).

The quinonoid form E-4a (a solution of *E*-**3a** in a 20-fold excess of the base ($Me_4NOH{\cdot}5H_2O$)): ^{1}H NMR (DMSO-d_6, 500 MHz) *δ*/ppm: 8.76 (br.d, *J* 8.2 Hz, 1H, H-8), 7.92 (br.d.d, , *J* 7.7, *J* 1.6 Hz,1 H, H-5), 7.44 (d, *J* 16.0 Hz, 1H, Hβ), 7.19 (m, 2 H, H-11, H-13), 7.11 (d.d.d, *J* = 8.5, 6.8, 1.5 Hz, 1 H, H-7), 6.87 (t.t, *J* = 7.3, 1.1 Hz, 1 H, H-12), 6.72 — 6.79 (m, 4 H, H-6, H-10, H-14, Hα), 6.65 (d, *J* = 3.0 Hz, 1 H, H-20,), 6.59 (d.d, *J* = 8.9, 3.0 Hz, 1 H, H-18), 6.01 (d, *J* 8.9 Hz, 1H, H-17).

(*E*)-2-(2-Hydroxy-5-nitrostyryl)-3-phenylquinazolin-4(3*H*)-one (3b). Yellow, yield 440 mg (92%), mp 351 - 353° C (DMF); ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 11.78 (s, 1 H, OH), 8.12 (d.d, *J* 8.0, 1.0 Hz, 1H, H-5), 8.10 (d, *J* 2.8 Hz, 1H, H-20), 8.06 (d.d, *J* 9.0, 2.8 Hz, 1H, H-18), 8.02 (d, *J* 15.6 Hz, 1H, Hβ), 7.89 (d.d.d, *J* 8.1, 7.0, 1.5 Hz, 1H, H-7), 7.80 (d, *J* 8.1 Hz, 1H, H-8), 7.59 – 7.65 (m, 3H, H-11, H-12, H-13), 7.54 (d.d.d, *J* 8.0, 7.0, 1.0 Hz, 1H, H-6), 7.47 (m, 2H, H-10, H-14), 6.98 (d, *J* 9.0 Hz, 1H, H-17), 6.75 (d, *J* 15.6 Hz, 1H, Hα); ^{13}C NMR (126 MHz, DMSO-d_6) δ/ppm 162.32, 161.21, 151.55, 147.30, 139.69, 137.04, 134.68, 133.32, 129.57 (2), 129.07, 128.92 (2), 127.19, 126.56, 126.37, 125.99, 125.13, 122.87, 122.19, 120.57, 116.49. IR(DRA): 699, 721, 736, 750, 771, 832, 855, 900, 911, 977, 1015, 1085, 1120, 1170, 1239, 1251, 1288, 1340, 1365, 1439, 1469, 1494, 1518, 1553, 1586, 1637, 1660, 3011, 3082, 3234 cm^{-1}; Anal. Calcd for $C_{22}H_{15}N_3O_4$: C, 68.57; H, 3.92; N, 10.90. Found: C, 68.24; H, 3.63; N, 10.81.

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(*E*)-2-(3-Hydroxystyryl)-3-phenylquinazolin-4(3*H*)-one (3c). White, yield 240 mg (67%), mp 272 - 274° C (CH_3CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.57 (s, 1 H, OH), 8,13 (d.d, *J* 8.0, 1,0 Hz, 1H, H-5), 7.87 (d.d.d, *J* 8.0, 7.0, 1.5 Hz, 1H, H-7), 7.79 (d, *J* 15.5 Hz, 1H, Hβ), 7.78 (d, *J* 7.9 Hz, 1H, H-8), 7.57 – 7.64 (m, 3H, H-11, H-12, H-13), 7.53 (d.d.d, *J* 8.0, 7.0, 1.0 Hz, 1H, H-6), 7.47 (m, 2 H, H-10, H-14), 7.15 (t, *J* 7.8 Hz, 1H, H-19), 6.79 (d, *J* 7.7 Hz, 1H, H-20), 6.74 (d.d, *J* 8.0, 1.7 Hz, 1H, H-18), 6.68 (br.s, 1H, H-16), 6.24 (d, *J* 15.5 Hz, 1H, Hα); ^{13}C NMR (126 MHz, DMSO-d_6) δ/ppm 161.25, 157.66, 151.32, 147.38, 138.96, 137.02, 136.05, 134.74, 130.05, 129.66 (2), 129.20, 128.93 (2), 127.17, 126.56, 126.41, 120.57, 119.67, 118.98, 117.13, 113.11. IR(DRA): 691, 762, 779, 845, 952, 980, 1017, 1121, 1177, 1243, 1281, 1337, 1382, 1431, 1452, 1472, 1547, 1571, 1594, 1651, 3031, 3166 cm^{-1}; Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.67; H, 4.60; N, 8.24.

(*E*)-2-(2-Hydroxy-5-morpholinostyryl)-3-phenylquinazolin-4(3*H*)-one (3d). White, yield 230 mg (52%), mp 255 - 257° C (CH_3CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.59 (s, 1 H, OH), 8.11 (d.d, *J* 7.9, 1.2 Hz, 1H, H-5), 7.96 (d, *J* 15.5 Hz, 1H, Hβ), 7.86 (d.d.d, *J* 8.1, 7.0, *J* 1.5 Hz, 1H, H-7), 7.76 (d, *J* 8.0 Hz, 1H, H-8), 7.55 – 7.63 (m, 3H, H-11, H-12, H-13), 7.51 (d.d.d, *J* 7.9, 7.0, *J* 0.9 Hz, 1H, H-6), 7.44 (m, 2H, H-10, H-14), 6.84 (d.d, *J* 8.8, 2.8 Hz, 1H, H-18), 6.73 (d, *J* 8.8 Hz, 1H, H-17), 6.67 (d, *J* 2.8 Hz, 1H, H-20), 6.60 (d, *J* 15.5 Hz, 1H, Hα), 3.69 and 2.87 (both t, *J* 4.5 Hz, 8H, $NC_4\underline{H}_8O$); ^{13}C NMR (126 MHz, DMSO-d_6) δ/ppm 161.34, 152.36, 150.72, 147.60, 144.18, 137.33, 136.29, 134.68, 129.54 (2), 128.95 (2), 128.88, 127.05, 126.40, 126.20, 121.57, 120.46, 120.44, 119.81, 116.70, 116.31, 66.11 (2), 49.77 (2). IR(DRA): 694, 727, 767, 831, 888, 925, 987, 1016, 1121, 1182, 1219, 1252, 1272, 1302, 1359, 1433, 1474, 1532, 1574, 1625, 1687, 2854, 2956, 3066, 3226 cm^{-1}; Anal. Calcd for $C_{26}H_{23}N_3O_3$: C, 73.39; H, 5.45; N, 9.88. Found: C, 72.99; H, 5.48; N, 9.73.

(*E*)-2-(4-Hydroxy-3-methoxystyryl)-3-phenylquinazolin-4(3*H*)-one (3e). White, yield 220 mg (56%), mp 281 - 283° C (CH_3CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.53 (s, 1H, O$\underline{H}$), 8.12 (d.d, *J* 8.1, 1.2 Hz, 1H, H-5), 7.86 (d.d.d, *J* 8.1, 7.0, 1.6 Hz, 1H, H-7), 7.81 (d, *J* 15.4 Hz, 1H, Hβ), 7.73 (d, *J* 8.0 Hz, 1H, H-8), 7.58 – 7.63 (m, 3H, H-11, H-12, H-13), 7.51 (d.d.d, *J* 8.0, 7.0, 0.8 Hz, 1H, H-6), 7.46 (m, 2H, H-10, H-14), 6.91 (d, *J* 1.7 Hz, 1H, H-16), 6.79 (d.d, *J* 8.1, 1.7 Hz, 1H, H-20), 6.74 (d, *J* 8.1 Hz, 1H, H-19), 6.08 (d, *J* 15.4 Hz, 1H, Hα), 3.71 (s, 3H, OC$\underline{H}_3$); ^{13}C NMR (126 MHz, DMSO-d_6) δ/ppm 161.25, 151.84, 151.77, 147.71, 147.55, 139.35, 137.14, 134.65, 129.56 (2), 128.99, 128.92 (2), 126.92, 126.39, 126.37, 126.13, 120.67, 120.36, 116.57, 115.91, 111.88, 55.45. IR(DRA): 689, 759, 772, 807, 835, 908, 975, 1016, 1037, 1119, 1132, 1165, 1213, 1261, 1286, 1340, 1361, 1400, 1469, 1516, 1542, 1598, 1657, 2839, 2956, 3013, 3065, 3319 cm^{-1}; Anal. Calcd for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56. Found: C, 74.49; H, 4.69; N, 7.51.

(*E*)-2-(3,5-Di-*tert*-butyl-2-hydroxystyryl)-3-phenylquinazolin-4(3*H*)-one (3f). White, yield 230 mg (48%), mp 214 - 216° C (CH_3CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 8.90 (s, 1H, O$\underline{H}$), 8.25 (d, *J* 15.4 Hz, 1Hβ), 8.15 (d.d, *J* 8.1, 1.1 Hz, 1H-5), 7.88 (d.d.d, *J* 8.1, 7.0, 1.5 Hz, 1H, H-7), 7.77 (d, *J* 8.1 Hz, 1H, H-8), 7.58 – 7.65 (m, 3H, H-11, H-12, H-13), 7.53 (d.d.d, *J* 8.0, 7.0, 0.9 Hz, 1H, H-6), 7.46 (m, 2H, H-10, H-14), 7.19 (d, *J* 2.2 Hz, 1H, H-18), 6.79 (d, *J* 2.2 Hz, 1H, H-20), 6.14 (d, *J* 15.4, Hz, 1H, Hα), 1.34 (s, 9H, 3C$\underline{H}_3$), 1.12 (s, 9H, 3C$\underline{H}_3$); ^{13}C NMR (126 MHz, DMSO-d_6) δ/ppm 161.21, 152.17, 151.76, 147.52, 141.74, 138.89, 137.29, 135.40, 134.74, 129.52 (2), 128.99, 128.88 (2), 127.02, 126.43, 126.28, 125.20, 124.62, 120.48, 119.96, 119.26, 34.72, 33.77, 31.00 (3), 29.66 (3). IR(DRA): 699, 724, 781, 879, 957, 970, 1018, 1025, 1128, 1175, 1209, 1232, 1280, 1302, 1359, 1431, 1441, 1469, 1490, 1542, 1574, 1624, 1680, 2872, 2962, 2999, 3030, 3062, 3251 cm^{-1}; Anal. Calcd for $C_{30}H_{32}N_2O_2$: C, 79.61; H, 7.13; N, 6.19. Found: C, 79.48; H, 7.19; N, 6.27.

Investigation of photophysical and photochemical properties of 3a-f. Solvents were distilled and dried according to standard procedures. The irradiation was carried out with a 250 W mercury ball gas discharge lamp DRSh-250 with a concave mirror and a quartz lens for focusing radiation at the cuvette. To irradiate and obtain absorption and luminescence spectra, Hellma QS-111 quartz cuvettes with a rubbed lid were used, the optical path length was 1 cm. The cuvettes were placed in the focus of the photoreactor. Air is used for cooling

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cells and reactor. The desired range of light was allocated by means of filters SZS-7 (thermal filter) and UFS-6 (UV filter). The total power of the light flux after the filters was 150 mW, determined using a meter of average power and energy of laser radiation IMO-2N[16]. The luminous flux was directed to the meter by means of quartz optical fibers.

Kinetic studies using absorption spectroscopy

1. The control of photochemical transformations of *E*-**3a-c,e-f** ($2\cdot10^{-5}$ M) in *n*-butanol, acetonitrile and DMF and *E*-**3d** in THF was carried out by recording the uv spectra of irradiated solutions every 2 seconds (up to photostationary state (PSS) of solutions).

2. The control of the thermal transformation of the photostationary solutions *Z*-**3** ($2\cdot10^{-5}$ M) thermostated at 75 °C was carried out by registration of UV spectra every 10 minutes. The choice of temperature is determined by [10].

3. Spectrophotometric titration of solutions *E*-**3a,b,e,f** ($2\cdot10^{-5}$ M) by strong bases Me_4NOH or *t*-BuOK was carried out until unchanged state using a series of solutions with a concentration ratio of $C_{E\text{-}3}$: C_{base} from 1:1 to 1:25.

Kinetic studies using NMR. The 1 ml of DMSO-d_6 solution of 0.06 mmol *E*-**3** was prepared. Monitoring of photochemical transformations of *E*-**3** was carried out by recording the ^{1}H NMR spectra of irradiated solutions.

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Supplementary Materials

^{1}H NMR spectra of **3a** and **3d**, luminescence data of compound **3a**, energies and structures of HOMO and LUMO of **3a-f** are given in the Supplementary Material file associated with this article.

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