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To what extent are the photophysical properties of quinoxaline- and quinoxalinone-based chromophores predictable?

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Abstract

A series of chromophores containing quinoxaline or quinoxalinone electron-acceptor (A) and dialkylaminostyryl electron-donor (D) units linked by π electronic bridge has been synthesized. Electronic emission and absorption spectra of the novel D-π-A, D-π-A-π-D or D-π-A-π-A-π-D systems cover a broad range from ultraviolet to near infrared. Positions and relative intensities of their absorption bands are shown to depend strongly on structural modifications of the molecules, while emission in solution strongly depends on both the structure of the solute and the solvent polarity. Quantum chemical modeling provided a reliable description of the observed absorption spectra and reproduced the positions of the emission bands. Quantum yields of emission are shown to be qualitatively predictable on the basis of empirical rules connecting the luminescence intensity with the chemical structures of both quinoxaline- and quinoxalinone-based luminopohores and the polarity of the solvents used. Theoretical assessment of the character of the main electronic transitions suggests that simultaneous presence of D and A units conjugated via π -bridges ensures intramolecular charge-transfer effects probably underlying the observed similar the solvatochromism for all the studied systems irrespective of their polarity.

Introduction

Organic molecules composed of electron-donor (D) and electron-acceptor (A) fragments linked by π electronic bridge (D- π -A) are widely used in various applications such as non-linear optical (NLO) materials,¹⁻⁴ organic light-emitting diodes (OLEDs), ⁵⁻¹³, pH/polarity sensors¹⁴⁻²¹ and light-harvesting components of organic solar cells.²²⁻²⁶ D- π -A systems often demonstrate a remarkable sensitivity to structural modifications or environmental effects (solvatochromic shifts, protonation/deprotonation color changes, thermochromism, galochromism, etc.). The introduction and/or replacement of chemical substituents at different positions of the chromophore core allow regulation of properties and functions of novel compounds. The further fine-tuning of these properties can be achieved through the variation of the π -bridges between the D and A units. Various aromatic heterocycles, such as thiophene,²⁷⁻³⁰ thiazole,³¹⁻³⁴ pyrrole,^{35, 36} phenothiazine,³⁷ and various diazines,³⁸ have been considered to date as π -linkers. In our recent works quinoxalinone (*Qon*) and quinoxaline (*Q*) derivatives extended this list,^{2, 39-45} and were tested as π -bridging fragments for NLO-phores. Besides, *Q* derivatives were used in emissive layers of the OLEDs.⁴⁶⁻⁵²

Due to their π -deficient character Qs and Qons could act as electron-withdrawing units in π conjugated push-pull structures. Similarly to other chromophores of this type,^{15-21, 53, 54,55-57}
emission of Q derivatives is highly sensitive to media effects.⁴⁵ In addition, intramolecular charge
transfer (ICT), inherent for such systems, can induce tunable luminescence as well.

Typically the development of D- π -A systems is mainly based on trial and error approach because of the absence of general schemes allowing the predictions of optical properties on grounds of the chemical structures only. Quite recently⁴⁴ we have tried to make a small step towards the development of such a scheme for *Qon*-based D- π -A systems. Their absorption and emission turned out to depend dramatically on simple variation of the position of the electron-donor *N*,*N*-dimethylaminostyryl (DMAS) group relative to electron-acceptor *Qon* core.

In the present contribution we take the next step in the attempt to connect the chemical structures of D- π -A systems in general, and diazines in particular, with their photophysical properties. We provide a comprehensive study of a series of novel *Q*-based structural analogs of the previously reported *Qons*⁴⁴, possessing luminescent properties. Both families show quite similar dependencies of their optical behavior on the observed structural variations, and in particular, on the position of the DMAS moiety. This suggests that the spectra-structure correlations revealed earlier⁴⁴ are not random in character, but are representative of inherent features of such chromophores. To further check their generality we have also studied some other *Q*- and *Qon*-based systems of different architecture, e.g. A- π -A, D- π -A- π -D or D- π -A- π -A- π -D.

In this respect, molecular model and simulation strategies could significantly help in guiding the synthesis of fluorophores with targeted properties, and providing rationales for their interpretation. On the basis of density functional theory (DFT) and time dependent DFT (TD-DFT) quantum chemical calculations the experimental findings were reliably interpreted also in terms of the nature of the excited states and of the electronic density reorganization. The accuracy and reliability of the electron transition energies computed at both the ground (S_0) and the first singlet excited state (S_1) equilibrium geometries with the use of hybrid PBE0 and long-range (LR) corrected CAM-B3LYP functionals have also been assessed.

2. Results and discussion

2.1 Synthesis of dyes

Scheme 1 shows the synthesis of quinoxaline and quinoxalinone dyes **1-10** (Chart 1) with two, three or four cyclic moieties. Knoevenagel condensation of 6- and 7-bromo-2-phenyl-3-methylquinoxalines (**11,12**), 3,7-dimethyl-2-phenylquinoxalines (**13**), and 7-bromo-3-methyl-1-propylquinoxalin-2-one (**14**) with *p*-*N*,*N*-dimethylaminobenzaldehyde leads to 3-styrylquinoxalines **1**, **2**, **5** and **16**, respectively. The Heck reaction between compounds **11**, **12**, **14** and *N*,*N*-dialkyl-4-vinylaniline produces 6(7)-aminostyrylquinoxaline derivatives **3**, **4**, **18** while the reaction of **1**, **2**, **16** with *N*,*N*-dialkyl-4-vinylaniline results in **6**, **8**, **9** containing two aminostyryl moieties. The oxidation of quinoxalines **15** and **18** by selenium dioxide results in aldehydes **17** and **19** as major products and dyes **7** and **10** as by-products, respectively. Furthermore bisquinoxalinones **7** and **10** have also been

synthesized in moderate yields by condensation of methylquinoxalinones **15** and **18** with quinoxalinonylcarbaldehydes **17** and **19**, respectively. Coupling constants of the order of 16 Hz for vinyl protons of compounds **5-10** in their ¹H NMR spectra indicate that only *trans*-isomer is formed in each case. The symmetrical structure of dyes **7** and **10** is confirmed by the presence of a single singlet with double intensity in the ¹H NMR spectra corresponding to the proton of the central vinyl moiety, half the number of carbon signals in the ¹³C NMR spectra and also by $[M+H]^+$ values in their MALDI mass-spectra. It should be noted that dibutylamino moieties have been introduced to increase the solubility in the organic solvents used.



XY=-N=C(Ph)- (1,2,5,6,8,11-13); Z = 6-Br (1); Z = 7-Br (2); Z = 6-HC=CH-C₆H₄NMe₂ (3); Z = 7-HC=CH-C₆H₄NMe₂ (4); Z = 7-Me (5); Z = 6-HC=CH-C₆H₄NBu₂ (6); Z = 7-HC=CH-C₆H₄NBu₂ (8); Z = 6-Br, W=Me (11); Z = 7-Br, W=Me (12); Z = 7-Me, W=Me (13); X = NPr, Y = CO (9,14-16); Z = 7-HC=CH-C₆H₄NBu₂ (9); Z=7-Br, W=Me (14); Z=7-Me, W=Me (15); Z = 7-Br (16)
Scheme 1. Synthesis of the chromophores. Reagents and Conditions: (*i*) *p*-Me₂NC₆H₄CHO, Ac₂O, Py 1.5 h, 220 °C or NaOH, H₂O, Aliquat 336, 15-24 h, 100 °C; (*ii*) *p*-Me₂NC₆H₄CH=CH₂ or *p*-Bu₂NC₆H₄CH=CH₂, Pd(OAc)₂, (*o*-Tol)₃P, Et₃N, DMF, 100-120 °C, 4-24 h; (*iii*) SeO₂, 60-70 min, 85-100 °C, argon, dioxane; (*iv*) Ac₂O, 140 °C, 40 min. * - for the compound 16 an alternative name
2-Qon has been used for more convenience upon comparison with quionxaline-based analogue 2 (see the text).

2.2. Optical properties

Steady-state electronic absorption and fluorescence spectra of **1-10** (Chart 1) have been registered in solvents of different polarity (Figure 1). A rather moderate influence of solvent polarity on the absorption spectral characteristics of **1-9** is clearly visible from Figure 1, while the emission spectra reveal a notable positive solvatochromic behavior. Emission of D- π -A systems **1-5** covers a wide spectral range of ca. 450-850 nm, while the longest-wave electronic absorptions maxima (λ_{max}) are generally identified as the most intensive bands falling in a much narrower range of ca. 400-450 nm. The experimental data on λ_{max} and emission maxima wavelengths (λ_{emi}) are collected in Table 1.

The absorption spectra of Qs 1-5 display three main bands, which differ mainly in their relative intensities. The absorption spectra of isomers 1 and 2 almost superpose (Figure 1), being simultaneously rather close to the spectrum of 2Qon - Qon-based structural analog of 2 (Figure S1). The position of the DMAS group strongly influences the relative intensity of the second absorption band (~360-362 nm) in the spectra of isomers 3, 4 and 5, but has only a minor impact on λ_{max} values and extinction coefficients (ε) of the lowest-energy absorption (Table 1). This is in contrast to the case of analogous *Qon*-based systems, where the lowest-energy band dominates the spectra of isomers 2*Qon*, 4*Qon* and 5*Qon*, but weak in the case of 3*Qon* (analog of 3) and thus is hidden under the much brighter second lowest-energy band.⁴⁴











Figure 1. Experimental electronic absorption and emission spectra of solutions of **1-10** in three solvents of different polarity (1,4-dioxane – diox, dichloromethane – DCM and acetonitrile –ACN). Presented relative absorption/emission intensities were normalized to unity for the most intensive bands.

Emission spectra of Qs 1-5 in 1,4-dioxane solutions are quite close to the corresponding spectra of their *Qon*-based structural analogs 2*Qon*-5*Qon* (Figure S1): λ_{emi} for both series almost coincide, except for the case of 4 (526 nm vs. 497 nm for 4Qon⁴⁴), while the quantum yields (φ) of Qs 1-5 differ only moderately from the corresponding values reported⁴⁴ for 2Qon-5Qon (Table S1). In particular, similarly to the case of **4***Qon* the maximal φ value is found for isomer **4**. The rather substantial solvatochromic shifts ($\Delta \lambda_{emi}$) of 1-5 are also similar to the ones reported for 2Qon-5Qon, being maximal for acetonitrile solutions. The maximal similarity of $\Delta \lambda_{emi}$ is exhibited by the structural analogs 4 / 4Qon: 0.26 / 0.27 and 0.43 / 0.45 eV for dichloromethane and acetonitrile, respectively, and relative to 1,4-dioxane (the corresponding shifts in nm equal to 64 / 61 and 115 / 112 nm). The quantum yields of 4 / 4Qon also exhibit very similar dependencies on the solvent polarity: 0.52 / 0.81, 0.21 / 0.62 and 0.01 / 0.03 for 1,4-dioxane, dichloromethane and acetonitrile solutions, respectively. The same trend for these solutions is found also for 3 / 3Qon pair: 0.29 / 0.13, 0.09 / 0.03 and 0.01 / <0.01. Almost the same φ values are found for solutions of isomers 5 / 5Qon and their brominated derivatives 2 / 2Qon in 1,4-dioxane and dichloromethane. In contrast, the fluorescence of 5 and 2 is almost quenched in acetonitrile, while only negligible differences in φ values are found for dichloromethane and acetonitrile solutions of their structural analogs 2Qon and 5Qon (Table S1).

Table 1. Collected experimental photophysical data on the positions of the most long-wave electronic absorption maxima (λ_{max}), fluorescence maxima (λ_{emi}), Stokes shifts, extinction coefficients (ϵ), and quantum yields (φ) measured for solutions of **1-10** in 1,4-dioxane, dichloromethane (CH₂Cl₂) and acetonitrile (CH₃CN).

compound 1,4-dioxane	CH ₂ Cl ₂	CH ₃ CN
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		λ _{max}	λ_{emi}	Stokes shift	λ _{max}	λ _{emi}	Stokes shift	λ_{max}	λ _{emi}	Stokes shift
	nm	445	555	110	453	601	148	448	643	195
1	eV	2.79	2.23	0.55	2.74	2.06	0.67	2.77	1.93	0.84
	ε/φ	26500	0.14		27900	0.17		27700	0.01	
	nm	445	555	110	453	602	149	448	648	200
2	eV	2.79	2.23	0.55	2.74	2.06	0.68	2.77	1.91	0.85
	ϵ / φ	24800	0.19		27500	0.17		27500	0.01	
	nm	415	526	111	407	596	189	407	646	239
3	eV	2.99	2.36	0.63	3.05	2.08	0.97	3.05	1.92	1.13
	ε/φ	30200	0.29		28700	0.09		25800	0.01	
	nm	403	526	123	408	590	182	400	641	241
4	eV	3.08	2.36	0.72	3.04	2.10	0.94	3.10	1.93	1.17
	ε/φ	24700	0.52		23800	0.21		25500	0.01	
	nm	430	528	98	436	571	135	433	614	181
5	eV	2.88	2.35	0.54	2.84	2.17	0.67	2.86	2.02	0.84
	ε/φ	29100	0.13		28800	0.18	2	28500	0.04	
	nm	458	540	82	468	627	159	462	650	188
6	eV	2.71	2.30	0.41	2.65	1.98	0.67	2.68	1.91	0.78
	ϵ / φ	44700	0.17		48500	< 0.01		45600	< 0.01	
	nm	434	484	50	434	490	56	431	502	71
7	eV	2.86	2.56	0.30	2.86	2.53	0.33	2.88	2.47	0.41
	ε/φ	33300	0.20		20000	0.21		33100	0.15	
	nm	475	549	74	482	615	133	487	661	174
8	eV	2.61	2.26	0.35	2.57	2.02	0.56	2.55	1.88	0.67
	ε/φ	52700	0.44	$\langle \rangle'$	53800	0.24		54000	0.02	
	nm	481	559	78	494	611	117	488	651	163
9	eV	2.58	2.22	0.36	2.51	2.03	0.48	2.54	1.90	0.64
	ε/φ	54200	0.26		63300	0.20		64100	0.04	
	nm	528	630	102	549	736	187	_	_	-
10	eV	2.35	1.97	0.38	2.26	1.68	0.58	_	_	_
	ε/φ	82800	0.18		74300	0.01		-	-	

Close similarity of luminescence of Q- and Qon-based fluorophores seems to be typical not only for D- π -A, but also for D- π -A- π -D systems: λ_{emi} for the newly synthesized Q and Qonderivatives 8 and 9, respectively, almost coincide for all the solvents, and φ values differ only moderately, hence 8 and 9 demonstrate very similar solvatochromic behavior. Moreover, the solvatochromic effects found for these D- π -A- π -D systems are practically the same as the ones for D- π -A systems 1-5 discussed above. Interestingly, all the quantitative characteristics of luminescence for compounds 8 and 4 (Table 1) differ rather negligibly. Thus, the inclusion of dibutylaminostyryl (DBAS) substituent to Q core in 8 instead of methyl group in 4 has only a minor impact on the emission of the Q derivatives. Strikingly similar dependencies of the optical properties of D- π -A and D- π -A- π -D systems on the position of the D unit relative to Q core are also observed when comparing D- π -A isomers **3** and **4** and their D- π -A- π -D analogs **6** and **8**. The positions of DBAS moiety in **6** and **8** are the same as the positions of DMAS group in **3** and **4**, respectively, resulting in similar quantum yields φ : in 1,4-dioxane solutions φ (**6**) and φ (**3**) amount to 0.17 and 0.29, respectively, while for isomers **8** and **4** φ values increase up to 0.44 and 0.52, respectively. The same close parallelism of the φ values for these pairs of isomers is also evident for dichloromethane and acetonitrile (Table 1).

The expansion of the conjugated π -system in **6**, **8** and **9** as compared to the structurally related D- π -A species **3**, **4** and **5** results in the red shifts of absorption maxima (λ_{max}) by ca. 0.3-0.5 eV (30-78 nm) and an almost two-fold increase of the extinction coefficients (ε) (Table 1). To assess the possible impact of a further elongation of the conjugation on the photophysical behavior the D- π -A- π -A- π -D chromophore **10** have been synthesized. The bathochromic shift found for this compound relative to **9** amounts to 0.23-0.25 eV (47-55 nm), while ε increases by ca. 20-50% (Table 1, Figure 1). In contrast, the absorption of A- π -A system **7**, i.e. an analog of **10** for whom the bridge's conjugation pattern has been shortened, is blue-shifted relative to **9** by ca. 0.3 eV (46 nm) while ε decreases by ca. 60%, clearly demonstrating that origin of the aforementioned strong bathochromic effects is not connected to the presence of A- π -A core in **10**. The emission of **10** also differs dramatically from the fluorescence spectrum of **7**: λ_{emi} and φ of the former strongly depend on solvent polarity, while the photophysical characteristics of the latter remain almost constant for all solutions.

To better understand the observed photophysical behavior of **1-10** quantum chemical calculations have been performed. Electronic absorption spectra simulated with the use of hybrid PBE0 functional (Figure 2, Table 2) satisfactorily reproduce the experimental results. The energies of the first vertical electronic transitions, $S_0 \rightarrow S_1$, are predicted by PBE0 gas-phase calculations almost quantitatively, though being slightly underestimated in some cases. Globally, the deviations from the corresponding experimental values found for 1,4-dioxane solutions do not exceed 0.17 eV. However, if the PBE0 simulations well reproduce the positions of the absorption bands the accuracy of the predictions of their relative intensities is less remarkable (Figure 2).







Figure 2. Absorption spectra of the compounds under study. Experimental spectra (black) are registered for solutions in 1,4-dioxane. Gas-phase spectra simulated with the use of PBE0/def2-TZVP (**a**) and CAM-B3LYP/def2-TZVP (**b**) methods (red lines) are obtained by broadening of the vertical straight lines by Gaussian functions with a full-width at half maximum of 0.4 eV. All the electronic transitions calculated with CAM-B3LYP/def2-TZVP have been red-shifted (0.4-0.5 eV) to better match the experimental spectra. The heights of the vertical straight lines correspond to the calculated oscillator strengths of the corresponding vertical transitions.

Since the electronic excited states of systems with D- π -A architecture are often characterized by, at least partial, ICT character, we have considered the use of the LR-corrected CAM-B3LYP functional, to assess one of the common source of errors experienced by conventional hybrid functionals. It should be mentioned that an alternative reason of the computational errors could be related to the absence of vibronic transitions consideration (for details see⁵⁸). As already reported⁵⁹ LR functionals and CAM -B3LYP systematically overestimate the electron transition energies by ca. 0.3-0.5 eV (Table 2), as a consequence and to facilitate the comparison of the simulated spectra with their experimental counterparts, the calculated absorption bands in Figure 2.b are shifted so that the positions of the lowest-energy absorptions in the theoretical and experimental spectra coincide for each molecule under study. After such correction the CAM -B3LYP simulations reproduce even the minor spectral features appearing as shoulders in the 300-400 nm spectral region. Indeed, such an accurate description of the spectral bands shape is important for predictions of chemical colours ⁶⁰, ⁶¹. Nevertheless, the intensities of all the bands relative to the lowest-energy absorption band (λ_{max}) are systematically underestimated by CAM-B3LYP calculations. It should be noted that according to both functionals (Figure 2 a and b) and for all the compounds, the minimum energy band should be ascribed to only one isolated vertical transition (i.e. $S_0 \rightarrow S_1$) displaying the largest (the second largest in the only case of 4) oscillator strength (f). Such pattern is also typical for closely related Qons, 2Qon, 4Qon and 5Qon, though excited states of a qualitatively different character was found for **30on**⁴⁴ (vide supra). Noteworthy, both functionals also preview qualitatively similar trends for the dependence of the $S_0 \rightarrow S_1$ oscillator strengths on the chromophore structure (Table 2), this trends being in general agreement with the experiment (see ε values in Table 1)

Table 2. Characteristics of vertical electronic transitions calculated at optimized geometries of ground (S_0) and first singlet excited (S_1) states in comparison to experimental values

Com- pound	Expe di ad	eriment ir oxane ^a ar cetonitril	n 1,4- nd e ^b		Calculations				
	λ _{max,} nm/ eV	$\lambda_{emi,}$ nm/ eV	Stokes shift, eV		$S_0 \rightarrow S_1$	$S_1 \rightarrow S_0$	μ_{S0}^{d} , D	Stokes shift, eV	ΔE_{abs} / ΔE_{emi}
2	445/	555/	0.56 ^a		gas PBE0				
2	2.79 ^a	2.23 ^a		f^{e}	0.638	0.347	7.40	0.35	-0.01/

a

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				E, nm	447	511			0.19
	448/	648/	0.85 ^b	E, eV	2.77	2.43			
	2.77°	1.91				PCM A	Acetonitrile	e PBE0	
				f^{e}	0.796	1.062			0.24/
				E, nm	491	580	10.27	0.38	-0.24/
				E, eV	2.52	2.14			0.25
						gas	CAM-B3I	LYP	
				f^{e}	1.019	1.055			0.51/
				E, nm	376	436	6.68	0.46	0.51/
				E, eV	3.30	2.84			0.01
							gas PBE0		
				f^{e}	0.906	0.903			0.17/
				E, nm	440	486	4.40	0.27	-0.1 //
				E, eV	2.82	2.55			0.20
	415/	526/	0.63 ^a			PCM A	Acetonitrile	e PBE0	
2	2.99	2.36		f^{e}	0.984	1.448			0.46/
3	407/	646/	1	E, nm	479	579	5.82	0.45	-0.40/ 0.22 ^g
	3.05 ^b	1.92^{b}	1.13	E, eV	2.59	2.14			0.22
						gas	CAM-B3I	LYP	
				f ^e	1.306	1.436			0.44/
				E, nm	362	434	3.39	0.57	0.44/
				E, eV	3.43	2.86			0.50
					Y		gas PBE0		
				f^{e}	0.503	0.244			0.12/
				E, nm	420	487	4.13	0.41	-0.12/
	402/	50.61		E, eV	2.95	2.55			0.17
	403/	526/	0.72 ^a			PCM A	Acetonitrile	e PBE0	
4	5.08	2.30		f^{e}	0.643	0.919			0.37/
-	400/	641/	, , , , , h	E, nm	455	545	5.49	0.45	-0.377 0.34 ^g
	3.10 ^b	1.93 ^b	1.17°	E, eV	2.73	2.28			0.01
			\bigcirc			gas	CAM-B3I	LYP	
			7	f ^e	1.341	1.533			0.55/
				E, nm	342	399	3.36	0.52	0.75
)		E, eV	3.62	3.11			
							gas PBE0		
				f^{e}	0.624	0.375			0.01/
	430/	528/	0.54 ^a	E, nm	429	491	4.25	0.36	0.18
	2.88^{a}	2.35 ^a	0.54	E, eV	2.89	2.53			
5	400 /	C1 4 1				PCM A	Acetonitrile	e PBE0	
	433/	614/	0.84 ^b	f ^e	0.777	1.106			-0.23/
	2.80	2.02		E, nm	471	558	6.32	0.41	0.20^{g}
1				.	0 (1	2 2 2			
				E, eV	2.64	2.22			

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				f^{e}	0.980	1.029			0.50/	
				E, nm	367	428	3.81	0.48	0.50/	
				E, eV	3.38	2.90			0.55	
							gas PBE0			
				f ^e	0.883	0.761			0.061	
				E, nm	469	515	5.13	0.24	-0.06/	
				E, eV	2.64	2.41			0.11	
	458/	540/	0			PCM A	Acetonitril	e PBE0		
	2.71ª	2.30ª	0.41ª	f ^e	1.011	1.346			0.00/	
0	162/	650/	0.78 ^b	E, nm	520	602	7.59	0.33	-0.30/	
	402/ 2.68 ^b	1 91 ^b	0.78	E, eV	2.39	2.06			0.15	
	2.00	1.71				gas	CAM-B3I	YP		
				f ^e	1.392	1.435		7	0.70/	
				E, nm	384	436	4.43	0.39	0.52/	
				E, eV	3.23	2.84			0.55	
							gas PBE0	1		
				f ^e	1.079	1.188	D		0.00/	
				E, nm	447	515	0.31	0.36	-0.09/	
				E, eV	2.77	2.41			-0.15	
	434/ 484/	0.30^{a}		PCM Acetonitrile PBE0						
_	2.86ª	2.56ª		f ^e	1.216	1.572			0.04/	
7	431/ 502/ 2 88 ^b 2 47 ^b	502/		E, nm	469	620	0.24	0.64	-0.24/	
		$2 \sqrt{7^{b}}$	0.41 ^b	E, eV	2.64	2.00			-0.47	
	2.00	2.47			gas CAM-B3LYP					
				f ^e	1.185	1.264			0.00/	
				E, nm	390	485	0.28	0.62	0.32/	
				E, eV	3.18	2.56			-0.01	
							gas PBE0			
				f ^e	1.560	1.637			0.01/	
		/		E, nm	476.0	525.6	1.54	0.25	0.01/	
			()	E, eV	2.60	2.36			0.10	
	475/	549/	0.35 ^a			PCM A	Acetonitril	e PBE0		
0	2.61"	2.26"		f ^e	1.717	2.327			0.01/	
ð	187/	661/		E, nm	530	647	1.92	0.42	-0.21/	
	2.55 ^b	1.88 ^b	0.67 ^b	E, eV	2.34	1.92			0.04	
	2.55	1.00				gas	CAM-B3I	LYP		
	Y			f ^e	1.976	2.069			0.52/	
				E, nm	395	466	1.11	0.47	0.53/	
				E, eV	3.14	2.66			0.40	
	481/	559/	0.258				gas PBE0			
0	2.58^{a}	2.22 ^a	0.36"	f^{e}	2.096	2.205			0.05/	
9			0.64 ^b	E, nm	490	547	2.75	0.26	-0.05/	
	488/	651/	0.04	E, eV	2.53	2.27			0.05	

	2.54 ^b	1.90 ^b			PCM Acetonitrile PBE0						
				f ^e	2.197	2.620			0.27/		
				E, nm	545	695	4.08	0.49	-0.27/ 0.12 ^g		
				E, eV	2.28	1.78			-0.12		
						gas	CAM-B3I	LYP			
				f ^e	2.184	2.176			0.41/		
				E, nm	415	501	2.89	0.51	0.41/		
				E, eV	2.99	2.48			0.20		
					gas PBE0						
				f^{e}	2.647	2.949	0.94	0.25	-0.20/		
				E, nm	578	655					
				E, eV	2.14	1.89			-0.08		
					PCM Acetonitrile PBE0						
10	528/	630/	0.38 ^a	f^{e}	2.635	3.356					
10	10 2.35 ^a 1	1.97 ^a	0.38	E, nm	676	887	1.34	0.43	-		
				E, eV	1.83	1.40	~				
					gas CAM-B3LYP						
				f ^e	2.936	2.952			0.20/		
				E, nm	453	568	0.97	0.56	0.39/		
						E, eV	2.74	2.18			0.21

a - 1,4-dioxane was chosen as the least polar solvent for a better comparison with gas-phase calculations; b - acetonitrile was used for comparison with PCM calculations;

c – errors for absorption/emission ($\Delta E_{abs}/\Delta E_{emi}$) represent the energy difference in eV between experimental $\lambda_{max}/\lambda_{emi}$ and respective calculated $E_{S0\rightarrow S1}/E_{S1\rightarrow S0}$ values: $\Delta E_{abs} = \lambda_{max}(eV) - E_{S0\rightarrow S1}$ and $\Delta E_{emi} = \lambda_{emi}(eV) - E_{S1\rightarrow S0}$. $\lambda_{max}/\lambda_{emi}$ for comparison with gas-phase computations are taken from the corresponding experiments for 1,4-dioxane solutions, while PCM computations are compared with the experiments for acetonitrile solutions of all compounds except 10, which is insoluble in acetonitrile.

d – dipole moment calculated at the ground state (S₀) geometry.

e - oscillator strength.

The energies of the vertical $S_1 \rightarrow S_0$ transitions $(E_{S1\rightarrow S0})$ computed at the first singlet excited state (S_1) in vacuo optimized geometries with the use of PBE0 functional are slightly overestimated by ca. 0.2 eV relative to the experimental emission energies for all the D- π -A compounds (2-5) in the least polar 1,4-dioxane. Smaller, but less systematic deviations of -0.15-0.11 eV from the experiment are found for compounds 6-10. It should be noted that similar reasonably good accuracy was demonstrated by analogous PBE0 computations for a broad variety of phospholes ⁶².

As mentioned above, the deviations of transition energies obtained with the use of CAM-B3LYP functional from the corresponding experimental values are more pronounced and systematical. Mean values of ΔE_{abs} and ΔE_{emi} (Table 2) amount to 0.46 and 0.42 eV, respectively. If the corresponding systematic shifts are subtracted from the overestimated computed transition energies, standard deviations (SD) of the corrected CAM-B3LYP energies from absorption and emission experiment for 1,4-dioxane solutions amount to 0.08 and 0.23 eV for $E_{S0\rightarrow S1}$ and $E_{S1\rightarrow S0}$, respectively.

In order to computationally assess the experimentally observed solvatochromism, the polarizable continuum model (PCM) with standard parameters for acetonitrile has been applied. According to Figure S2 (ESI) such an implicit treatment of solvent effects has only a moderate impact on the shape of the simulated absorption bands producing only parallel and systematically overestimated red shifts of their positions (Table 2). At the same time, the PCM results for emission are in reasonable accordance with the experimental data reported on solvatochromism. Linear response PCM fails only in the case of the almost non-polar molecule 7 (cf. dipole moments in Table 2): indeed PCM computations strongly overestimate the red shift for λ_{emi} of 7 in acetonitrile solutions (Table 2). Formally only state-specific solvation models can provide a physically sound description of the polarization response of the environment during photon emission, but these models come at a significantly increased computational cost. In the present case, the LR approximation seems sufficient for our purposes, with the exception of 7, providing significant improvement in the description of the emission spectral properties for acetonitrile solutions. Deviations of ca. 0.2-0.3 eV found for the computed $E_{S1\rightarrow S0}$ values from the corresponding experimental emission energies are comparable to those found for the gas-phase computations relative to the measured for 1,4-dioxane solutions (vide supra).

To analyze in more details the nature of the first low-lying excited states the natural transition orbitals (NTOs) have been considered (Figure 3 and Figure S3 in ESI). The NTOs for the first electronic excitation are presented in Figure 3. Additionally the ICT has been semi-quantitatively assessed using the recently introduced quantum mechanical descriptor ϕ_s^{63-65} based on the topological analysis of detachment/attachment transition density matrices (for more details see the computational section). Here we only remind that ϕ_s close to unity corresponds to pure local transition, while a value of zero represents a pure and long-range charge transfer state.







Figure 3. NTOs for the first electronic excitation $S_0 \rightarrow S_1$. NTOs have been plotted with threshold value equal to 0.03.

The visual analysis of the NTOs clearly demonstrates the participation of delocalized π -orbitals spread on all the fragments of the molecule simultaneously, hence the transitions can be safely classified as $\pi \rightarrow \pi^*$. For all the compounds, except the A- π -A system 7, the electronic density is transferred from the entire π -conjugated system delocalized over the whole backbone of the molecule (occupied NTO) to the more electron-withdrawing Q or Qon moieties (virtual NTO), hence giving a partial ICT state. An almost negligible participation of the π orbitals of the Ph moieties at Q cores is also seen in Figure 3. These qualitative observations are confirmed by the analysis of ϕ_s indexes varying within 0.56-0.79 for 2-6, 8-10, which points to partial ICT character of the transition. The maximal value of $\phi_s = 0.83$ calculated for 7 is indicative of a more local character of the S₀ \rightarrow S₁ transition. The less preeminence of ICT for the S₁ state of this molecule probably explains its peculiarly weak solvatochromism also registered for emission spectrum. It should be noted that for 6 and 8 - 10 all the electronic transitions include a transfer from all D fragments simultaneously to Q or Qon acceptor units (Figure 3). That is, in spite of architecture different from strongly polar D- π -A systems 1-5, even low-polar molecules 8-10 demonstrate a

partial charge transfer in the S₁ state relative to S₀ state, this probably being a basis of similarity of the solvatochromic effects found for **1-5** and **6**, **8** - **10**. Note also that the relatively large values of ϕ_s point to only partial charge-transfer character and in particular justify the relative good behavior of hybrid functionals as compared to long-range corrected ones.

Conclusions

We have introduced a series of novel quinoxaline- and quinoxalinone-based chromophores absorbing and emitting radiation in a broad range spanning from the UV to the NIR. The positions and relative intensities of their absorption bands are shown to depend strongly on the structural modifications of the molecules. Quantum chemical calculations within the framework of TD-DFT approach provided reliable theoretical description of the observed spectral features. In particular, the energies of the $S_0 \rightarrow S_1$ excitations were predicted with accuracy to ca. ± 0.1 eV.

The positions and intensities of emission bands in the spectra in solution strongly depend on both the structure of the solute and the polarity of the solvent. As expected, the precision of the computational determination of the excitation energies for the $S_1 \rightarrow S_0$ transitions in this case is lowered to ca. ± 0.2 eV. The reliable theoretical prediction of quantum yields (φ) of emission is all the more difficult, and we have to rely on empirical rules connecting the chemical structures of luminophores and their luminescence. Present study suggests that φ values of various *Q*- and *Qon*based systems of D- π -A, D- π -A- π -D or D- π -A- π -A- π -D architecture depend on the positions of the electron-donor *N*,*N*-dialkylaminostyryl groups relative to electron-acceptor *Q* or *Qon* moieties in a rather similar way. Moreover, solvatochromic effects found for similar isomeric forms of a rather broad variety of structures turned out to be qualitatively the same. The theoretical assessment of the character of the main electronic transitions suggests that the simultaneous presence of electrondonor and -acceptor units conjugated via π -bridges favors a partial ICT effect probably underlying the similarity of solvatochromism for all the studied systems irrespective of the concrete type of D-A architecture.

The capability of the chosen quantum chemical methods and empirical spectra-structure correlations to reproduce the relation between the structure and the photophysical properties of a rather broad variation of Q- and Qon-based chromophores suggests the possible use of combination of the both approaches as a predictive tool in the rational design of the related chromophores presenting improved optical and photophysical features.

3. Experimental and computational details

3.1. Materials and instrumentation

The IR, NMR, UV–vis, MALDI spectra were registered on the equipment of Assigned Spectral-Analytical Center of FRC. Infrared (IR) spectra were recorded on the Bruker Vector-22 FT-IR spectrometer. All NMR experiments were performed with Bruker AVANCE-600 and AVANCE-400 (600 and 400 MHz for ¹H NMR, 150 and 100 MHz for ¹³C NMR) spectrometers. Chemical shifts (δ , in ppm) are referenced to the solvent (CDCl₃ or acetone- d_6). The mass spectra were obtained on Bruker UltraFlex III MALDI TOF/TOF instrument with *p*-nitroaniline as a matrix. The melting points of compounds **5-10** were determined on a Boetius hot-stage apparatus. Compounds **1-4, 11, 12, 14, 16, 18** and **19** were obtained according to literature [^{41, 43}]. Electronic absorption (UV-Vis) and steady state fluorescence spectra were recorded at room temperature on a Perkin-Elmer Lambda 35 spectrometer and a Cary Eclipse Fluorescence Spectrophotometer (Varian), respectively, using 10 mm quartz cells. Absorption spectra were registered with a scan speed of 480 nm/min, using a spectral width of 1 nm. All samples were prepared as solutions in three solvents: 1,4-dioxane (Dioxane), dichloromethane (CH₂Cl₂/DCM), acetonitrile (CH₃CN) with the concentrations ranging from ~10⁻⁵ to ~10⁻⁴ mol·L⁻¹. The absorbance at excitation wavelength was less than 0.1 to avoid the "inner filter effect". Fluorescence quantum yields were measured using aqueous solution of quinine sulfate ($\lambda_{ex} = 350$ nm, $\varphi = 0.57$ in 0.1 M H₂SO₄) and Rhodamine 6G ($\lambda_{ex} = 530$ nm, $\varphi = 0.92$ in H₂O) as the standards. Appropriate corrections were made for the optical density of the solutions and the refractive index of the medium ⁶⁶

3.2 Synthesis of (E)-3-(4-(dimethylamino)styryl))-7-methyl-2-phenylquinoxalin (5)

of 3,7-dimethyl-2-phenylquinoxaline (13) (100 mg, mixture 0.43 mmol), N,N-Α dimethylaminobenzaldehyde (65 mg, 0.43 mmol), Aliquat 336 (14 mg, 0.42 mmol) and aqueous sodium hydroxide (5M, 2 mL) was refluxed for 24 h. The reaction mixture was cooled, and extracted with CH₂Cl₂. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent petroleum ether – EtOAc, 100:1) to give compound 5 (70 mg). Yield 45%, red-orange powder. R = 0.32 (hexane : ethyl acetate=10:1); mp 119–120 °C. ¹H NMR (600 MHz, acetone-d₆): δ 7.99 (d, J=15.4 Hz, 1H, H ethene), 7.90 (d, J=8.2 Hz, 1H, H-5 quinoxaline), 7.84 (s, 1H, H-8 quinoxaline), 7.76 (d, J=7.8 Hz, 2H, o-Ph), 7.62-7.54 (m, 4H, m,p-Ph, H-6 quinoxaline),7.40 (d, J=8.6 Hz, 2H, 3,5-H aniline), 7.18 (d, J=15.6 Hz, 1H, H ethene), 6.73 (d, J=8.6 Hz, 2H, 2,6-H aniline), 3.0 (s, 6H, Me), 2.60 (s, 3H, Me). 13 C NMR (150 MHz, acetone- d_6): δ 154.1, 152.2, 150.2, 142.6, 141.1, 140.2, 140.0, 137.5, 131.8, 130.6, 129.7, 129.6, 129.1, 128.3, 125.4, 120.1, 113.0, 40.2, 21.8. IR (v_{max}, cm⁻¹, KBr): 3024 (C-H), 2917 (C-H), 2854 (C-H), 2804(C-H), 1601 (C=N, C=C), 1522 (C=C), Elemental Analysis for C₂₅H₂₃N₃: found C, 82.06; H, 6.29; N, 11.56%, requires C, 82.16; H, 6.34; N, 11.50%.

3.3 Synthesis of dyes 6, 8 and 9

A mixture of bromoquinoxalines **1**, **2**, **16** (0.12 mmol), *N*,*N*-dibutyl-4-vinylaniline (27 mg, 0.12 mmol), tri(*o*-tolyl)phosphine (4.0 mg, 0.012 mmol), Pd(OAc)₂ (1.3 mg, 0.006 mmol), Et₃N (0.30 g, 0.30 mmol), and anhydrous DMF (1 mL) was stirred for 4 h at 120 °C. The reaction mixture was cooled, poured into water, and extracted with CH₂Cl₂. The organic layer was separated, washed with water, dried over anhydrous MgSO₄ and filtered. The solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent petroleum ether – EtOAc, 100:1 \rightarrow 15:1) to give compounds **6**, **8**, **9**, respectively.

3.3.1 6-((E)-4-(Dibutylamino)styryl)-3-((E)-4-(dimethylamino)styryl)-2-phenylquinoxaline (6)

Yield 33% (23 mg), red-orange powder. R_{f} =0.52 (hexane : ethyl acetate=10:3); mp 179–180 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.04 (s, 1H, H-5 quinoxaline), 7.99 (d, *J*=15.5 Hz, 1H, H ethene), 7.98 (d, *J*=8.7 Hz, 1H, H-7 quinoxaline), 7.87 (d, *J*=8.7 Hz, 1H, H-8 quinoxaline), 7.75 (d, *J*=7.5 Hz, 2H, *o*-Ph), 7.54 (dd, *J*=7.5, 7.3 Hz, 2H, *m*-Ph), 7.50 (dd, *J*=7.3, 7.3 Hz, 1H, *p*-Ph), 7.46 (d, *J*=8.7 Hz, 2H, 3,5-H aniline), 7.27 (d, *J*=16.2 Hz, 1H, H ethene), 7.18 (d, *J*=15.5 Hz, 1H, H ethene), 7.08 (d, *J*=16.2 Hz, 1H, H ethene), 6.69 (d, *J*=8.7 Hz, 2H, 2,6-H aniline), 6.67 (d, *J*=8.7 Hz, 2H, 2,6-H aniline), 3.32 (t, *J*=7.6 Hz, 4H, NCH₂), 3.00 (s, 6H, Me), 1.64–1.59 (m, 4H, NCH₂CH₂), 1.42–1.35 (m, 4H, N(CH₂)₂CH₂), 0.98 (t, *J*=7.5 Hz, 6H, CH₃). ¹³C NMR (150 MHz, CDCl₃): δ 153.0, 150.9, 149.9, 148.3, 142.4, 140.4, 140.1, 139.0, 136.7, 131.4, 129.7, 129.03, 129.00, 128.8, 128.5, 128.2, 127.1, 125.0, 124.8, 124.1, 122.7, 120.0, 112.1, 111.7, 50.8, 40.3, 29.5, 20.4, 14.0. IR (v_{max}, cm⁻¹, KBr): 2956 (C-H), 2927 (C-H), 2871 (C-H), 1501 (C=N, C=O), 1517 (C=C). MALDI-TOF: 581 [M+H]⁺, Elemental Analysis for C₄₀H₄₄N₄: found C, 82.81; H, 7.58; N, 9.71%, requires C, 82.72; H, 7.64; N, 9.65%.

3.3.2 7-((E)-4-(Dibutylamino)styryl)-3-((E)-4-(dimethylamino)styryl)-2-phenylquinoxaline (8)

Yield 41% (29 mg), red-orange powder. R_f =0.52 (hexane : ethyl acetate=10:3); mp 115–116 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.03 (s, 1H, H-8 quinoxaline), 8.02 (d, *J*=8.7 Hz, 1H, H-6 quinoxaline), 7.98 (d, *J*=15.6 Hz, 1H, H ethene), 7.94 (d, *J*=8.7 Hz, 1H, H-5 quinoxaline), 7.76 (d, *J*=7.3 Hz, 2H, *o*-Ph), 7.55 (dd, *J*=7.3, 7.3 Hz, 2H, *m*-Ph), 7.52 (dd, *J*=7.3, 7.3 Hz, 1H, *p*-Ph), 7.45 (d, *J*=8.8 Hz, 2H, 3,5-H aniline), 7.43 (d, *J*=8.8 Hz, 2H, 3,5-H aniline), 7.25 (d, *J*=16.2 Hz, 1H, H ethene), 7.18 (d, *J*=15.6 Hz, 1H, H ethene), 7.06 (d, *J*=16.2 Hz, 1H, H ethene), 6.68 (d, *J*=8.7 Hz, 2H, 2,6-H aniline), 6.66 (d, *J*=8.7 Hz, 2H, 2,6-H aniline), 3.32 (t, *J*=7.3 Hz, 4H, NCH₂), 3.00 (s, 6H, Me), 1.64–1.57 (m, 4H, NCH₂<u>CH₂</u>), 1.42–1.35 (m, 4H, N(CH₂)₂<u>CH₂</u>), 0.98 (t, *J*=7.3 Hz, 6H, CH₃). ¹³C NMR (150 MHz, CDCl₃): δ 154.3, 150.8, 148.6, 148.2, 141.5, 141.3, 139.1, 139.0, 136.3, 131.1, 129.7, 128.9, 128.8, 128.6, 128.4, 128.2, 127.9, 125.3, 125.0, 124.1, 122.7, 120.0, 112.1, 111.7, 50.8, 40.2, 29.5, 20.3, 14.0. IR (v_{max}, cm⁻¹, KBr): 2953 (C-H), 2924 (C-H), 2857 (C-H), 1597 (C=N, C=O), 1519 (C=C). MALDI-TOF: 581 [M+H]⁺, Elemental Analysis for C₄₀H₄₄N₄: found C, 82.79; H, 7.70; N, 9.69%, requires C, 82.72; H, 7.64; N, 9.65%.

3.3.3 7-((E)-4-(Dibutylamino)styryl)-3-((E)-4-(dimethylamino)styryl)-1-propylquinoxalin-2(1H)-one (9).

Yield 28% (19 mg), dark-red powder. R_f =0.40 (hexane : ethyl acetate=10:3); mp 113–115 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J*=16.0 Hz, 1H, H ethene), 7.75 (d, *J*=8.4 Hz, 1H, H-5 quinoxaline), 7.59 (d, *J*=8.8 Hz, 2H, 3,5-H aniline), 7.56 (d, *J*=16.0 Hz, 1H, H ethene), 7.50 (dd, *J*=8.4, 1.4 Hz, 1H, H-6 quinoxaline), 7.42 (d, *J*=8.7 Hz, 2H, 3,5-H aniline), 7.21 (d, *J*=1.4 Hz, 1H, H-8 quinoxaline), 7.13 (d, *J*=16.2 Hz, 1H, H ethene), 6.95 (d, *J*=16.2 Hz, 1H, H ethene), 6.71 (d, *J*=8.8 Hz, 2H, 2,6-H aniline), 4.29 (t, *J*=7.8 Hz, 2H, NCH₂), 3.31 (t, *J*=7.6 Hz, 4H, NCH₂), 3.02 (s, 6H, Me), 1.92–1.82 (m, 2H, NCH₂CH₂), 1.64–1.54 (m, 4H, NCH₂CH₂), 1.42–1.33 (m, 4H, N(CH₂)₂CH₂), 1.11 (t, *J*=7.4 Hz, 3H, CH₃), 0.97 (t, *J*=7.3 Hz, 6H,

CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 155.2, 151.5, 151.1, 148.3, 139.3, 138.0, 133.1, 132.3, 131.0, 129.7, 129.4, 128.2, 125.1, 123.9, 122.7, 121.0, 117.7, 112.1, 111.7, 110.9, 50.8, 43.7, 40.2, 29.5, 20.7, 20.3, 14.0, 11.5. IR (v_{max}, cm⁻¹, KBr): 2956 (C-H), 2928 (C-H), 2871 (C-H), 1648 (C=O), 1595 (C=N, C=C), 1521 (C=C). MALDI-TOF: 563 [M+H]⁺, Elemental Analysis for C₃₇H₄₆N₄O: found C, 78.82; H, 8.30; N, 9.91%, requires C, 78.96; H, 8.24; N, 9.96%.

3.4 Synthesis of dyes 7 and 10

Method I. A mixture of 3-methylquinoxalin-2-one **15** or **18** (1.50 mmol), selenium dioxide (196 mg, 1.76 mmol) and dioxane (6 mL) was stirred at 100 °C for 1 h under argon and then cooled to room temperature. After removal of the solvent by rotary-evaporation, the residue was purified by silicagel column chromatography (eluent petroleum ether – EtOAc, $30:1\rightarrow2:1$) to give aldehyde **17** or **19** as major product and bis-quinoxalinones **7** or **10** as by-product, respectively.

Method II. A mixture of 3-methylquinoxalin-2-one **15** or **18** (0.11 mmol), aldehyde **17** or **19** (0.13 mmol), respectively, and acetic anhydride (1 mL) was stirred at 140 °C for 40 min and then cooled to room temperature. After removal of the solvent by rotary-evaporation, the residue was purified by silica-gel column chromatography (eluent petroleum ether – EtOAc, $30:1\rightarrow3:1$).

3.4.1 (E)-1,2-Bis(7-methyl-1-propylquinoxalin-2(1H)-on-3-yl)ethene (7)

Yield 4% (13 mg, method I), 24% (11 mg, method II); yellow powder. R_f =0.23 (hexane : ethyl acetate=10:3); mp 268–279 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.57 (s, 2H, H ethene), 7.78 (d, *J*=8.1 Hz, 2H, H-5 quinoxaline), 7.15 (d, *J*=8.1 Hz, 2H, H-6 quinoxaline), 7.07 (s, 2H, H-8 quinoxaline), 4.25 (t, *J*=7.7 Hz, 4H, NCH₂), 2.52 (s, 6H, Me), 1.86–1.79 (m, 4H, NCH₂<u>CH₂</u>), 1.07 (t, *J*=7.3 Hz, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 154.9, 151.0, 141.2, 132.6, 132.1, 130.6, 130.4, 125.1, 113.6, 43.7, 22.3, 20.6, 11.4. IR (vmax, cm–1, KBr): 3089 (CH), 2959 (CH), 2874 (CH), 1650 (C=O), 1609 (C=N, C=C), 1572 (C=C). MALDI-TOF: 429 [M+H]⁺, 451 [M+Na]⁺, 467 [M+K]⁺, Elemental Analysis for C₂₆H₂₈N₄O₂: found C, 72.91; H, 6.62; N, 13.10% requires C, 72.87; H, 6.59; N, 13.07%.

3.4.2 (E)-1,2-Bis(7-((E)-4-(dibutylamino)styryl)-1-propylquinoxalin-2(1H)-on-3-yl)ethene (10)

Yield 5% (32 mg, method I), 33% (31 mg, method II); violet powder. R_{f} =0.26 (hexane : ethyl acetate=10:3); mp 245–246 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.53 (s, 2H, H ethene), 7.78 (d, *J*=8.4 Hz, 2H, H-5 quinoxaline), 7.50 (dd, *J*=8.4, 1.2 Hz, 2H, H-6 quinoxaline), 7.40 (d, *J*=8.8 Hz, 4H, 3,5H aniline), 7.17 (d, *J*=1.2 Hz, 2H, H-8 quinoxaline), 7.14 (d, *J*=16.2 Hz, 2H, H ethene), 6.93 (d, *J*=16.2 Hz, 2H, H ethene), 6.63 (d, *J*=8.8 Hz, 4H, 2,6-H aniline), 4.28 (t, *J*=7.6 Hz, 4H, NCH₂), 3.31 (t, *J*=7.7 Hz, 8H, NCH₂), 1.91–1.81 (m, 4H, NCH₂<u>CH₂</u>), 1.64–1.56 (m, 8H, NCH₂<u>CH₂</u>), 1.42–1.33 (m, 8H, N(CH₂)<u>2CH₂</u>), 1.11 (t, *J*=7.4 Hz, 6H, CH₃), 0.98 (t, *J*=7.4 Hz, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 155.0, 150.3, 148.4, 140.8, 133.2, 133.0, 131.8, 130.9, 130.2, 128.3, 123.7, 122.5, 121.1, 111.6, 110.8, 50.8, 43.7, 29.5, 20.6, 20.3, 14.0, 11.5. IR (v_{max}, cm⁻¹, KBr): 2955 (C-H), 2925 (C-H), 2856 (C-H), 1657 (C=O), 1590 (C=N, C=C), 1519 (C=C). MALDI-TOF: 859 [M+H]⁺, 881 [M+Na]⁺, Elemental Analysis for C₅₆H₇₀N₆O₂: Found C, 78.39; H, 8.17; N, 9.72% requires C, 78.28; H, 8.21; N, 9.78%.

3.4.3 7-Methyl-1-propylquinoxalin-2(1H)-one-3-carbaldehyde (17)

Yield 73%(239 mg), yellow powder. $R_f = 0.09$ (hexane : ethyl acetate=10:3); mp 138–140 °C. ¹H NMR(400 MHz, CDCl₃): 10.45 (s, 1H, CHO), 7.94 (d, *J*=8.3 Hz, 1H, H-5), 7.24 (dd, *J*=8.3 Hz, 1.1 Hz, 1H, H-6), 7.14 (s, 1H, H-8), 4.25 (t, *J*=7.8 Hz, 2H, NCH₂), 2.56 (s, 3H, CH₃), 1.77-1.87 (m, 2H, CH₂CH₃), 1.08 (t, *J*=7.4 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 189.5, 154.5, 145.8, 145.6, 134.2, 132.6, 131.4, 126.0, 113.9, 43.5, 22.6, 20.6, 11.3. IR (vmax, cm–1, KBr): 3073 (CH), 3045 (CH), 2963 (CH), 2933 (CH), 2874 (CH), 1704 (C=O), 1652 (C=O), 1606 (C=N, C=C), Elemental Analysis for C₁₃H₁₄N₂O₂: Found C, 67.74; H, 6.09; N, 12.11%, requires C, 67.81; H, 6.13; N, 12.17%.

3.4.4 (E)-7-(4-(Dibutylamino)styryl)-1-propylquinoxalin-2(1H)-one-3-carbaldehyde (19). Yield: 68% (455 mg) [⁴¹].

3.5 Synthesis of 3,7-Dimethyl-1-propylquinoxalin-2-one (15)

In three-neck round bottom flask ethanol (1L) was added, then a solution of 4-methyl-1,2diaminobenzene (27.40 g, 224 mmol) in ethanol (0.5 L) and a solution of ethyl pyruvate (26.10 g, 224 mmol) in ethanol (0.5 L) were added dropwise for 3 h at room temperature under stirring. The reaction mixture was stirred for 6 h and left overnight in a refrigerator at temperature of 10°C. Precipitated crystals were filtered, washed with ethanol. Isomeric mixture (17.0 g) of 3,7-, and 3.6dimethylquinoxalin-2(1*H*)-ones of 5:1 ratio (according to ¹H NMR spectrum) was obtained. Ethanol was evaporated from the filtrate under reduced pressure, the precipitate was washed with ethanol. Isomeric mixture (17.5 g) of 3,7 -, and 3.6-dimethylquinoxalin-2(1H)-ones of 1:1 was obtained. Total yield 88%. A suspension of isomeric mixture of 3,7- and 3,6-dimethylquinoxalin-2(1H)-ones (12.0 g, 69 mmol), KOH (7.75 g, 138 mmol), and dioxane (40 ml) was stirred for 2 minutes at 100 °C and then cooled. The solution of PrI (14.05 g, 83 mmol) in dioxane (20 ml) was added. The reaction mixture was stirred for 4 h at 100 °C, then cooled, poured into water and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The isomers mixture (14.2 g, yield 95%) was obtained. 3,7-dimethyl derivative 12 was isolated by the fourfold recrystallization from hexane. Yield 29% (4.12 g), white powder. Rf = 0.40(ethylacetate: hexane = 1:3); mp 66-67 °C (hexane). ¹H NMR (acetone-d6): 7.59 (d, J=8.1 Hz 1H, H5), 7.33 (s, 1H, H8), 7.13 (dd, J=8.1, 1.0 Hz, 1H, H6), 4.20 (t, J=7.7 Hz, 2H, NCH₂), 2.48 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 1.70-1.79 (m, 2H, <u>CH₂CH₃</u>), 1.09 (t, *J*=7.4 Hz 3H, CH₃). ¹³C NMR (100 MHz, acetone-d6): δ 156.6, 154.6, 139.9, 132.6, 131.0, 129.1, 124.1, 114.0, 43.0, 21.0, 20.5, 20.4, 10.6. IR (Nujol mull), v, cm⁻¹:1649 (C=O), 1613 (C=N, C=C), 1566 (C=C). Elemental Analysis for C₁₃H₁₆N₂O: found C, 72.00; H, 7.39; N, 13.05%, requires C, 72.19; H, 7.46; N, 12.95; O, 7.40%.

3.7. Computational details

All density functional theory (DFT) calculations were performed with the Gaussian 09 program package.⁶⁷ In general the spherical def2-TZVP atomic orbital (AO) basis set was used ^{68, 69}

All the structures were optimized with the use of hybrid PBE0 functional^{70, 71} and long-range corrected CAM-B3LYP⁷² functional. The nature of $S_0 \rightarrow S_n$ transitions (n = 1, 2, 3) has been

characterized by the analysis of the NTOs supported by the quantitative topological analysis based on the detachment/attachment density matrices^{63-65, 73}. We remind that the NTO representation allows to consider any TD-DFT electronic excited state as a transition from the first (occupied) NTO to the second (virtual) orbital, as a consequence the occupied NTO should be considered as representative of the hole density, while the virtual NTO will describe the particle density. Excited states topology was analyzed by a post processing of the Gaussian output performed using the NANCY EX 2.0 software suite,⁷⁴ in order to obtain natural transition orbitals (NTOs) and ϕ_s index. Stationary points were characterized as minima by frequency analyses. Solvent effects on the photophysical properties have been taken into accounts using the polarizable continuum model (PCM)⁷⁵⁻⁷⁹ within linear-response (LR) implemented in Gaussian 09 software. Time-dependent density functional response theory (TD-DFT)⁸⁰⁻⁸² has been employed to compute the vertical excitation energies (i.e., absorption and emission wavelengths) and oscillator strengths on the ground state (GS/S_0) and first singlet excited state (S_1) equilibrium geometries, each optimized in the gas phase as well as with the use of PCM model with standard parameters for acetonitrile as a solvent. No energy shift has been applied for PBE0 while for CAM-B3LYP calculations all the excitations energies have been red-shifted by an error factor computed as the difference between $E_{S0\to S1}$ and corresponding experimental λ_{max} in order to better match experimental spectral curves. Simulated electronic absorption spectra, calculated as 20 vertical excitations at the optimized ground state (GS) geometries were empirically broaden by single Gaussian type functions with full-width at half maximum (FWHM) equals to 0.4 eV. The dipole length representation is used to calculate oscillator strengths discussed in the present paper.

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Highlights

- a series of novel quinoxaline- and quinoxalinone-based chromophores is synthesized
- absorption/emission of the chromophores span from the UV to the NIR
- the absorption spectra are reliably simulated quantum chemically
- the positions of the emission bands are also reproduced by the computations
- quantum yields of emission are qualitatively predictable by empirical rules

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