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Spectral-luminescent and solvatochromic properties of 2-(3′-coumarinyl)-5-(2′-(R-amino)-phenyl)-1,3,4-oxadiazoles

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ABSTRACT

Spectral-luminescent properties of the newly synthesized 2-(3′-coumarinyl)-5-(2′-(R-amino)-phenyl)-1,3,4-oxadiazoles has been investigated in solvents of various polarity and hydrogen-bonding ability. It has been found that for all the studied compounds no excited state intramolecular proton transfer occurs despite the presence of coumarinyl fragment – electron acceptor effect of the coumarinyl fragment is not sufficient to increase the excited state acidity of the amino group. It has been found that the absorption spectra of the studied compounds shift to higher energy with increase in solvent polarity, whereas corresponding fluorescence spectra shift to lower energy with solvent polarity increase. It has been suggested that long-wavelength shifts of the fluorescence spectra of the studied compounds with increase in solvent polarity is caused by the solvent relaxation. The observed solvent relaxation effect allow us to propose some of the studied compounds as potential probes to monitor changes in solvent relaxation in low-polar media and as potential probes for rigidochromic effect.

1. Introduction

Heterocyclic compounds containing coumarinyl or oxadiazolyl fragments are known for their biological activity [1,2]. In order to search for new compounds with biological/pharmacological activities, we synthesized 2-(3′-coumarinyl)-5-(2′-(R-amino)-phenyl)-1,3,4-oxadiazoles (**1**–**3**) (Scheme 1).

In our previous articles [3,4] we reported the study of the correlation between the molecular structure and the rates of the excited state intramolecular proton transfer (ESIPT) reaction and of radiationless deactivation of the phototautomer form for ortho-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole [3] and ortho-hydroxy derivatives of 2-(coumarinyl-3)-5-diphenyl-1,3,4-oxadiazole [3,4]. Compounds **1**–**3** are also interesting as model compounds to investigate the possibility of excited state intramolecular proton transfer (ESIPT) from amino group to nitrogen atom of oxadiazole cycle.

Oxadiazole-containing molecules are known to exhibit photoinduced charge transfer and fluorochromism [4,5] – the most recent examples of the fluorochromism have been reported for arylamine–oxadiazole based systems [6,7].

The molecules **1**–**3** containing electron donor amino group and electron acceptor oxadiazole and coumarinyl fragments could undergo photoinduced charge transfer, thus, such molecules should be sensitive to the changes of solvent polarity [8–12], i.e. compounds **1**–**3** should exhibit solvato- and fluorochromism.

In this work we report the absorption and fluorescence emission properties of newly synthesized 2-(3′-coumarinyl)-5-(2′-(R-amino)-phenyl)-1,3,4-oxadiazoles (**1**–**3**) in different solvents.

2. Experimental details

2.1. Materials

Derivatives of coumarinylphenyl-l,3,4-oxadiazoles were synthesized by a previously described method [13]. 2-Iminocoumarin-3-carboxamides and hydrazides of N-substituted antranilic acids were used as starting materials.

Melting points were determined on Buchi B-520 apparatus. ^{1}H NMR spectra of the compounds in DMSO-d_6 solutions were recorded at 200 MHz with a Varian Mercury VX-200 NMR spectrometer. Chemical shifts (δ) were determined in ppm from TMS signal (internal standard). For the compounds synthesized signals for the aromatic protons were observed at 6.7–8.0 ppm, a singlet for the proton at position 4 of the coumarin ring was observed at 9.0 ppm, and the signal for the NH proton was observed at 6.8 ppm – for compound **1**, at 7.4 ppm – for compound **2**, at 9.1 ppm – for compound **3**. Mass spectra were recorded at 70 eV with Varian 1200L mass spectrometer. IR spectra of the compounds

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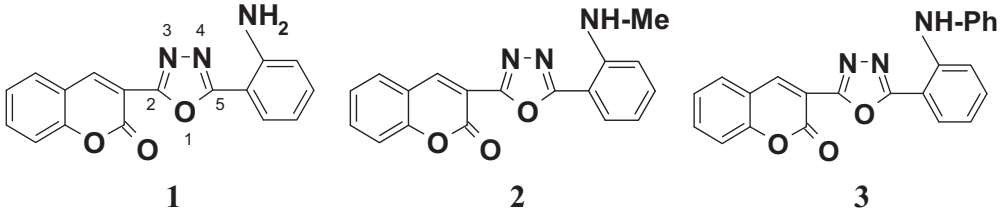

Scheme 1. Formulas of 2-(3′-coumarinyl)-5-(2′-(R-amino)-phenyl)-1,3,4-oxadiazoles (**1**–**3**): 2-(3′-coumarinyl)-5-(2′-(amino)-phenyl)-1,3,4-oxadiazole (**1**), 2-(3′-coumarinyl)-5-(2′-(methylamino)-phenyl)-1,3,4-oxadiazole (**2**), 2-(3′-coumarinyl)-5-(2′-(phenylamino)-phenyl)-1,3,4-oxadiazole (**3**).

synthesized as 1% suspensions in KBr pellets were recorded with a Brucker Tensor 27 spectrometer. A strong band of the C=O group of a lactone ring was observed at 1744–1752 cm^{-1}, vibrations of the C=C bonds of the aromatic and heterocyclic rings were observed at 1606–1609 cm^{-1}, valent vibrations of the N–H bond were observed in the 3284–3437 cm^{-1} region.

2.1.1. 2-(3′-Coumarinyl)-5-(2′-(amino)-phenyl)-1,3,4-oxadiazole (*1*)

Yield: 79%; m.p. = 256–7 °C (from DMF–ethanol); ^{1}H NMR, δ (ppm): 6.71 (t, 1H, J = 7.3 Hz, H-5′), 6.79 (s, 2H, NH_2), 6.91 (d, 1H, J = 8.1 Hz, H-3′), 7.29 (t, 1H, J = 7.7 Hz, H-8), 7.44 (t, 1H, J = 7.3 Hz, H-4′), 7.50 (d, 1H, J = 7.7 Hz, H-6), 7.75 (t, 1H, J = 7.7 Hz, H-7), 7.81 (d, 1H, J = 7.3 Hz, H-6′), 7.95 (d, 1H, J = 7.3 Hz, H-5), 9.02 (s, 1H, H-4); mass-spectra m/z ($I_{relative}$) [M^+]: 305 (15.3), 304 (83.5), 274 (1.6), 246 (6.6), 218 (10.8), 191 (2.4), 169 (16.1), 162 (2.1), 146 (4.3), 130 (6.7), 118 (44.3), 117 (74.7), 116 (99.9), 112 (7.6), 97 (14.1), 90 (53.2), 89 (86.1), 88 (28.5), 73 (30.8), 70 (16.6), 47 (12.3), 46 (33.8); IR (KBr) (cm^{-1}): 3432, 3324, 3060, 1752, 1705, 1625, 1609, 1578, 1538, 1496, 1445, 1322, 1241, 1161, 1028, 959, 863, 821, 765, 748, 670.

2.1.2. 2-(3′-Coumarinyl)-5-(2′-(methylamino)-phenyl)-1,3,4-oxadiazole (*2*)

Yield: 72%; m.p. = 199–200 °C (from DMF-ethanol); ^{1}H NMR, δ (ppm): 2.97 (d, 3H, J = 4.8 Hz, CH_3), 6.78 (t, 1H, J = 7.3 Hz, H-5′), 6.85 (d, 1H, J = 8.4 Hz, H-3′), 7.36–7.53 (m, 4H, H-6,8,4′,NH), 7.76 (t, 1H, J = 7.3 Hz, H-7), 7.90 (d, 1H, J = 7.7 Hz, H-6′), 7.97 (d, 1H, J = 7.7 Hz, H-5), 9.03 (s, 1H, H-4); mass-spectra m/z ($I_{relative}$) [M^+]: 319 (2.9), 318 (14.1), 317 (47.0), 232 (1.8), 202 (2.2), 187 (4.7), 170 (99.9), 142 (88.0), 127 (15.4), 119 (2.7), 115 (63.7), 112 (17.4), 102 (32.5), 98 (3.4), 88 (53.6), 75 (115), 74 (25.5), 72 (39.2), 57 (13.9), 47 (31.4), 41 (8.0); IR (KBr) (cm^{-1}): 3437, 3332, 3045, 2994, 2929, 2895, 2821, 1744, 1701, 1606, 1584, 1523, 1462, 1446, 1422, 1327, 1302, 1277, 1240, 1173, 1119, 1028, 1014, 979, 940, 820, 760, 748, 597.

2.1.3. 2-(3′-Coumarinyl)-5-(2′-(phenylamino)-phenyl)-1,3,4-oxadiazole (*3*)

Yield: 66%; m.p. = 204–5 °C (from DMF-ethanol); ^{1}H NMR, δ (ppm): 7.00 (t, 1H, J = 7.7 Hz, H-5′), 7.11 (t, 1H, J = 7.3 Hz, H-4″), 7.29–7.53 (m, 8H, H-6, 8, 3′, 4′, 2″, 3″, 5″, 6″), 7.77 (t, 1H, J = 8.4 Hz, H-7), 7.97 (d, 1H, J = 8.4 Hz, H-6′), 8.02 (d, 1H, J = 8.4 Hz, H-5), 9.05 (s, 1H, H-4), 9.15 (s, 1H, NH); mass-spectra m/z ($I_{relative}$) [M^+]: 381 (8.1), 380 (48.1), 323 (2.2), 207 (11.3), 206 (25.5), 194 (66.0), 193 (99.9), 178 (29.4), 171 (74.8), 170 (95.1), 166 (9.7), 165 (48.3), 164 (84.6), 149 (10.2), 139 (23.1), 117 (7.3), 97 (14.9), 79 (39.9), 74 (26.3), 65 (13.5), 47 (40.0), 40 (20.4); IR (KBr) (cm^{-1}): 3436, 3284, 3107, 3038, 1749, 1694, 1609, 1598, 1581, 1524, 1477, 1450, 1324, 1304, 1279, 1244, 1160, 1122, 983, 939, 820, 758, 739, 692, 597.

The organic solvents used were all of spectroscopic grade and were used as supplied from Fluka. Quinine sulfate used as fluorescence standard for quantum yield determination was purchased from Fluka.

2.2. Spectroscopic measurements

The electronic absorption spectra were measured using Jasco V-530 UV/Vis Spectrophotometer. Fluorescence emission and excitation spectra were recorded on PTI-QM1 fluorescence spectrophotometer. Fluorescence quantum yields were calculated with reference to the absorption and fluorescence spectra of Quinine sulfate in 0.5 M H_2SO_4 solution (φ_f = 0.546) [14]. The calculated relative fluorescence quantum yields were the values corrected for refraction index differences between the measured and standard solutions [15]. All fluorescence measurements were conducted for dilute solutions in absorbance range of 0.1–0.15 at the excitation wavelength (concentrations 10^{-5}–10^{-6} mol dm^{-3}).

2.3. Theoretical calculations

Semi-empirical calculations were performed using the original AM1 [16] parametrisation (included in MOPAC version 6.0 [17]). Restricted Hartree-Fock (RHF) formalism was used.

The calculations were carried out with full ground state geometry optimization without any assumption of symmetry: Polak-Ribiere (conjugate gradient) geometry optimization algorithm was used with convergence cut-off criterion 0.1 kcal/mol.

Excited state calculations were conducted by means of single point calculations (closed shell, singles) of the structures with already optimized ground state geometry: CI matrix with 3 HOMO's and 3 LUMO's has been used.

In order to check the validity of 3 × 3 CI matrix for excited state calculations, a few calculations with CI matrix 5 × 5 were made, but no considerable difference in results of both calculations was noticed. For this reason, the majority of the excited state calculations was performed with the usage of 3 × 3 CI matrix.

The degree of redistribution of electronic density between different fragments of the studied molecules on transition from the ground to the excited state (Δq) was determined as the difference of total charges on atoms which compose these fragments in the S_0 and S_1 states:

$$\Delta q = \Sigma q_i^{(S_1 \text{ state})} - \Sigma q_i^{(S_0 \text{ state})} \quad (1)$$

where q_i are the charges on atoms that are included in the particular fragment [3,18–21].

The DFT calculations of the ground-state structure and electron density were carried out using the density functional theory (DFT) method. The GAMESS-US program, version R3, was used for the DFT calculations [22].

3. Results and discussion

The spectral properties of the substituted ortho-amino derivatives of 2-(coumarinyl-3)-5-phenyl-l,3,4-oxadiazole (**1**–**3**) are presented in Tables 1 and 2. The most typical absorption spectra of

Table 1
UV–vis spectral properties[a] of comp. **1**–**3** in the solvents used.

Solvent	ε	λ_{abs}		
		Comp. **1**	Comp. **2**	Comp. **3**
Tetrachloromethane	2.24	377	400	402
Benzene	2.28	376	398	396
Toluene	2.38	376	398	396
Chloroform	4.70	375	396	395
Ethylacetate	6.02	374	392	392
THF	7.6	374	392	392
Dichloromethane	8.90	372	391	391
Iso-propanol	18.3	375	391	390
Methanol	32.6	375	390	388
Acetonitrile	36.2	369	386	383
DMF	36.7	375	386	383

[a] Here ε is the dielectric permittivity of the solvent; λ_{abs} is the position of the long-wavelength absorption band maximum (nm), THF-tetrahydrofuran, DMF-dimethylformamide.

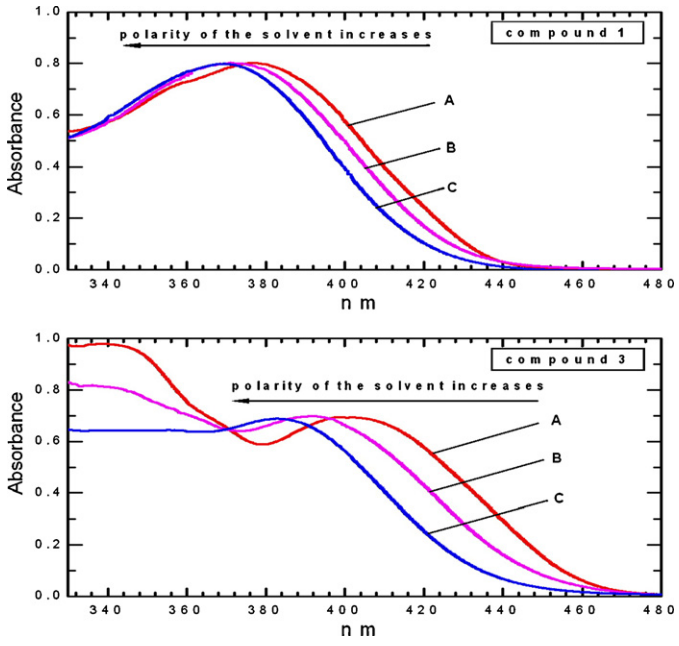

Fig. 1. Absorption spectra of compounds **1** and **3**: A – in tetrachloromethane, B – in dichloromethane, C – in acetonitrile.

1 and **3** in various solvents are presented in Fig. 1. The fluorescence spectra of **1** and **2** in low-polar solvents are presented in Fig. 2.

3.1. UV-vis absorption spectra

The long-wavelength absorption bands of compounds **1**–**3** are associated with π–π^* transitions.

The long-wavelength absorption band of **1** is shifted bathochromically (~375 nm) in comparison with the

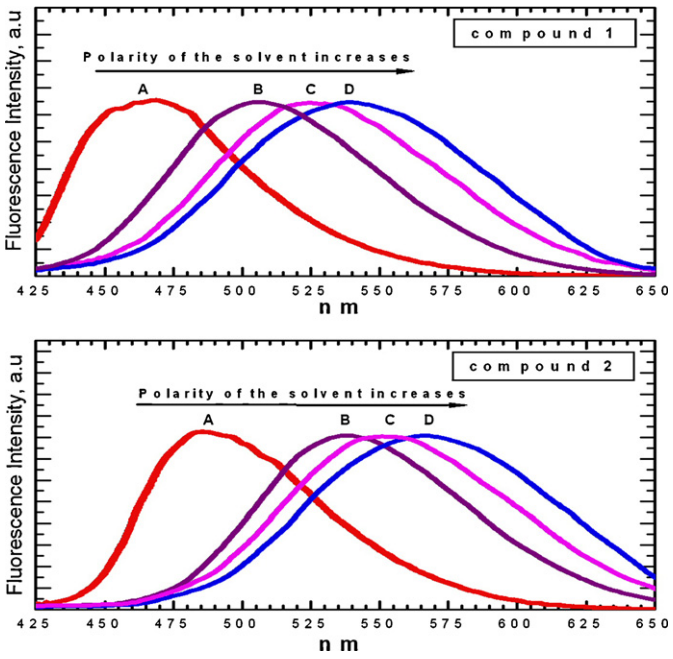

Fig. 2. Fluorescence spectra of compound **1** and **2**: A – in tetrachloromethane, B – in toluene, C – in chloroform, D – in dichloromethane.

corresponding bond of ortho-methoxy 2-(coumarinyl-3)-5-(2-phenyl)-1,3,4-oxadiazole (~340 nm), due to the greater electron-donor effect of ortho-amino group in comparison with the corresponding ortho-methoxy group [4]. The absorption spectra of **2** and **3**, in their turn, are shifted to the long-wavelength region (~400 nm) in comparison with the absorption spectra of **1** (~375 nm), because of electron-donor effect of methyl group (in case of compound **2**) and because of extension of π-system (in case of compound **3**).

The long-wavelength absorption maxima of **1**–**3** are shifted to short-wavelength region with the increase in the solvent polarity (e.g. on going from carbon tetrachloride to acetonitrile, see Table 1 and Fig. 1). This fact points out that the dipole moments of **1**–**3** in excited state are lower than the corresponding dipole moments in ground state [8,9].

3.2. Fluorescence spectra

The fluorescence emission spectra of **1**–**3** consist of only one wide fluorescent band in all the solvents used (see Table 2 and Fig. 2). The fluorescence spectra are independent on the excitation wavelength and have no vibronic structure even in non-polar solvents (Fig. 2).

The Stokes' shifts of the fluorescence of compounds **1**–**3** are quite large even in low-polar solvents. As could be seen from the Table 2, there is no significant influence of the substituents in the aminogroup on the Stokes' shift values.

Table 2
Spectral-luminescent characteristics[a] of compounds 1–3 in solvents with different polarities.

Solvent	Comp. **1**			Comp. **2**			Comp. **3**		
	λ_f	$\Delta\lambda_{ST}$	φ_f	λ_f	$\Delta\lambda_{ST}$	φ	λ_{fl}	$\Delta\lambda_{ST}$	φ_f
Tetrachloromethane	468	91	0.022	485	85	0.007	490	88	0.002
Benzene	506	130	0.019	532	134	0.005	535	139	0.001
Toluene	507	131	0.015	539	141	0.005	–	–	–
Chloroform	527	152	0.004	553	157	0.002	–	–	–
Dichloromethane	540	168	0.003	567	176	0.001	–	–	–

[a] Here λ_f and $\Delta\lambda_{ST}$ are the positions of the maxima in the fluorescence spectra (nm), and the Stokes shift of the fluorescence (nm), respectively; φ_f is the quantum yield of fluorescence.

Table 3
Changes of charges (Δq)[a] on the fragments in **1–3** on excitation.

Comp.	Fragment			
	Coumarin	Oxadiazole	Anilinophenyl	Phenyl
1	−0.174	+0.023	+0.151	–
2	−0.186	+0.024	+0.162	–
3	−0.179	0.000	+0.139	+0.04

[a] The negative values of Δq correspond to increase and positive values Δq correspond to decrease of electronic density [18–21].

The large Stokes' shifts (i.e. red-shifted fluorescence) may be caused by photophysical processes (solvent relaxation) or by photochemical processes leading to an emissive product state [23–25].

According to the structure of **1–3**, the expected photochemical mechanisms leading to large Stokes' shifts could be: (a) twisted intramolecular charge transfer (TICT) – the formation of highly polar TICT state [25–29], which involves mutual twisting of two chromophores directly connected by a single bond and simultaneous charge transfer from the donor to the acceptor chromophore; (b) excited-state intramolecular proton transfer (ESIPT) [30,31], which involves tautomerization, i.e., transfer of a proton from one to another basic site in the same molecule.

The formation of highly polar TICT structure is not consistent with the decrease in the dipole moments for **1–3** on excitation, suggested by the blue shift in the absorption spectra of **1–3** with the increase in the solvent polarity (Table 1 and Fig. 1).

It is commonly understood that main driving force of ESIPT reaction is the coordinated increase of the acidity of the proton donor group and increase of the excited state basicity of the proton acceptor group. Such changes in protolytic properties are regulated by the excited state redistribution of electron density in the molecules capable of the proton phototransfer reaction [30,31].

As we reported previously [3,4], for ortho-hydroxy 2,5-diphenyl-1,3,4-oxadiazole [3] and for ortho-hydroxy 2-(coumarinyl-3)-5-diphenyl-1,3,4-oxadiazole [4], OH-group excited state acidity is affected by the substituents introduced into the proton accepting part of the molecule to a greater extent than the corresponding excited state basicity of the nitrogen atoms of oxadiazole heterocycle. For instance, on introduction of electron excessive $N(CH_3)_2$ group in the proton accepting part of the coumarinyl-oxadiazole molecule – no ESIPT is observed: excited state acidity of proton donor centre (OH-group) is decreased dramatically.

While ortho-amino 2,5-diphenyl-1,3,4-oxadiazole exhibits no ESIPT [3], the ESIPT is observed for ortho-benzoylamino 2,5-diphenyl-1,3,4-oxadiazole [3], when electron accepting benzoyl group increases the acidity of proton donor centre (N–H) and makes possible the proton phototransfer reaction.

It is interesting to know whether introduction of electron acceptor coumarinyl fragment into the proton accepting part of the molecule could increase excited state acidity of the amino group in order to observe the ESIPT.

According to the quantum chemical calculations (see Tables 3 and 4), the main direction of charge redistribution in the excited molecules **1–3** is from the ortho-amino-substituted benzene ring towards the coumarinyl fragment (see Table 3). The amino group and oxadiazole nitrogen atoms are electron donors on excitation, while carbonyl group of coumarin ring and oxadiazole oxygen atom are charge acceptors on excitation (see Table 4). Thus, RAM1 quantum-chemical calculations predicted increase of proton donor group (amino group) acidity on excitation with simultaneous decrease of proton acceptor group (oxadiazole nitrogen N_4) basicity.

We also conducted DFT calculation of the HOMO and LUMO distribution for compounds **1–3**. The results are schematically shown in Fig. 3. It was found that the HOMOs are mainly localized on the anilinophenyl and oxadiazole fragments of the molecules, whereas the LUMOs are delocalized over of the whole molecules. These findings indicate, that following the electronic excitation from the HOMO to the LUMO, the electronic density redistribution occurs from aryloxadiazole towards the coumarinyl fragment, which appears to be the main electron acceptor unit.

Despite the presence of coumarinyl fragment, no evidence of the excited state proton transfer reaction was observed for **1–3**: (i) positions of the fluorescence bands for compound **1** and for previously studied 2-(coumarinyl-3)-5-(2′-methoxyphenyl)-1,3,4-oxadiazole [4] in tetrachloromethane, are rather close: 467 nm and 453 nm, respectively; (ii) the long-wavelength emission of the product of the excited state proton transfer reaction (i.e. of phototautomer form) is absent for all three compounds **1–3**.

Thus, electron acceptor effect of coumarinyl fragment is not sufficient to increase excited state acidity of aminogroup in order to observe the ESIPT.

Noticeable long-wavelength solvatofluorochromic shift is observed for compounds **1–3** with increase in solvent polarity (e.g. on going from tetrachloromethane to dichloromethane, Table 2).

It should be noted that spectral-luminescent characteristics of **1–3** are presented only for low-polar solvents with very low hydrogen-bonding ability (see Table 2), because in polar solvents and in solvents with high hydrogen-bonding ability compounds **1–3** are non-fluorescent. For this reason, the number of solvents, which could be used for solvatofluorochromic studies of **1–3** is limited: we used five solvents for solvatofluorochromic study of **1** and **2**, and, only two solvents have been used for solvatofluorochromic study of **3**.

Interestingly, the emission bands of compounds **1–3** are shifted to the lower energies with the increase in solvent polarity, while the absorption bands are clearly shifted to shorter wavelength by the same solvent effect (see Tables 1 and 2; Figs. 1 and 2).

This is possible when the orientation of the ground-state dipole moment is not parallel with that of the first excited-state dipole moment. In this case the respective solvent cages will not match to the solute excited state dipole moment orientation. Different dipole moment orientations will induce a dielectric solvent relaxation, and thus will produce an extra shift of the solute fluorescence to the red [10,11].

To analyse solvatofluorochromic data we selected P_y polarity scale as based on fluorescence [32] and well justified both theoretically and experimentally.

As could be seen from Fig. 4, P_y scale was found to give rather good description of the solvatofluorochromic behaviour of **1–3**.

Table 4
Changes of charges (Δq)[a] on the heteroatoms in **1–3** on excitation.

Comp.	Heteroatom				
	N aminogroup	N_3 oxadiazole	N_4 oxadiazole	O_1 oxadiazole	$O_{c=o}$ coumarin
1	+0.037	+0.091	+0.026	−0.016	−0.015
2	+0.038	+0.091	+0.028	−0.016	−0.017
3	+0.062	+0.081	+0.033	−0.012	−0.013

[a] The negative values of Δq correspond to increase and positive values Δq corresponds to decrease of electronic density [18–21].

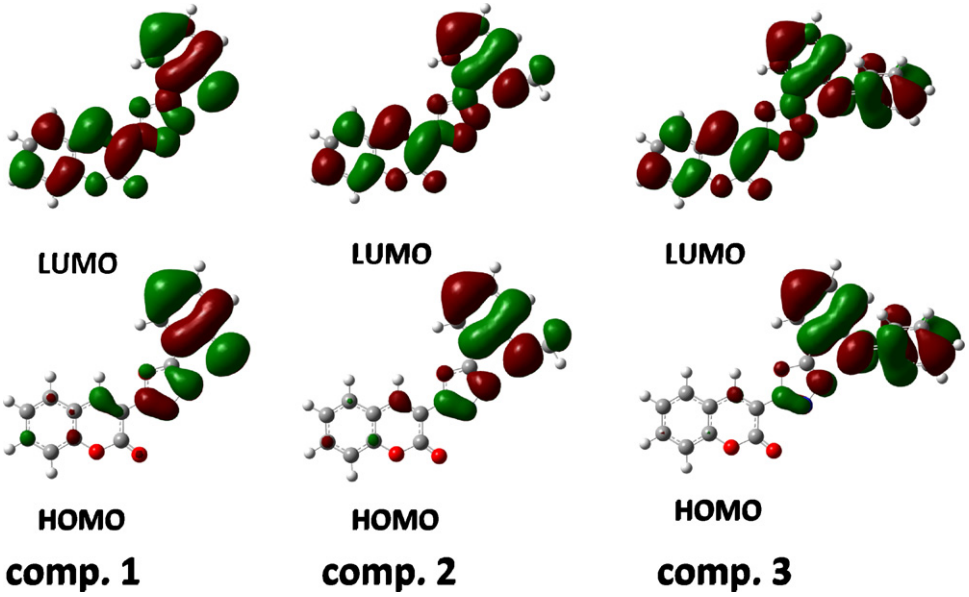

Fig. 3. The distribution of the HOMO and the LUMO over the molecules of **1**–**3** calculated with DFT (B3LYP/cc-pVDZ). Red and green circles represent the difference in the signs of the coefficients when the MOs are represented as linear combinations of atomic orbitals. According to the figure, the electron density transfer from the aryloxadiazole unit to the coumarinyl fragment occurs following the electronic excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Although approximate and best performing in the case of co-linear dipoles, which seems not to hold for the synthesized compounds, the Lippert-Mataga's plot (Fig. 5) affords some estimate on the difference in dipole moments for ground and excited states of **1** and **2**. The difference between ground and excited state dipole moments ($\Delta\mu$) was estimated to be quite large: i.e. 16.1 Debye – for compound **1** and 15.9 Debye – for compound **2**.

The observed solvent relaxation effect precludes the use of the studied compounds as polarity probes, however, allow us to propose compounds **1** and **2** as potential probes for rigidochromic effect [35–39]. Rigidochromism is defined as a blue shift in the energy of an emission band with increasing rigidity of the local environment [35–39]. The origin of the effect is the reorientation of solvent molecule dipole moments. If reorientation occurs before the luminescence (in nonrigid media), there is a red shift of the band maximum. In rigid media, reorientation is suppressed, leading to a higher energy emission [35–39].

The fluorescence quantum yields within the studied series of substituted ortho-amino derivatives of 2-(coumarinyl-3)

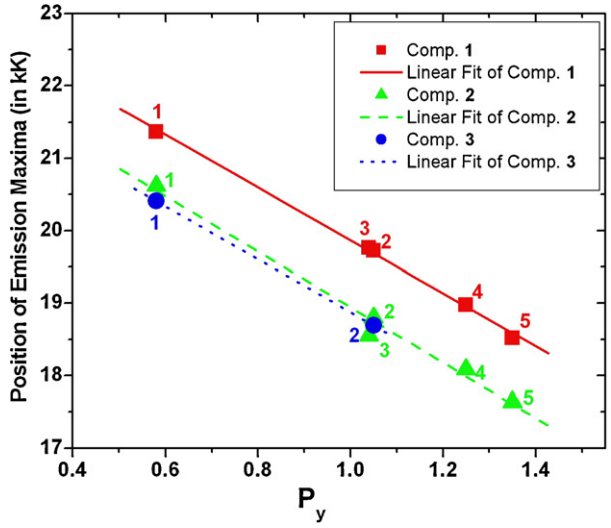

Fig. 4. Fluorescence emission maxima of **1**–**3** (in kK, 1 kK = 1000 cm^{-1}) vs. corresponding P_y values of the solvents used: 1 – tetrachloromethane, 2 – benzene, 3 – toluene, 4 – chloroform, 5 – dichloromethane. The results of linear fit: for compound **1**, $\nu^{EM} = (23.52 \pm 0.12) - (3.66 \pm 0.11)\ P_y$, $R = -0.999$, SD = 0.064 kK; for compound **2**, $\nu^{EM} = (22.78 \pm 0.25) - (3.84 \pm 0.23) \cdot P_y$, $R = -0.995$, SD = 0.135 kK; for compound **3**, $\nu^{EM} = 22.53 - 3.65\ P_y$. By analogy with cyclohexane, P_y value for tetrachloromethane was assumed to be 0.58.

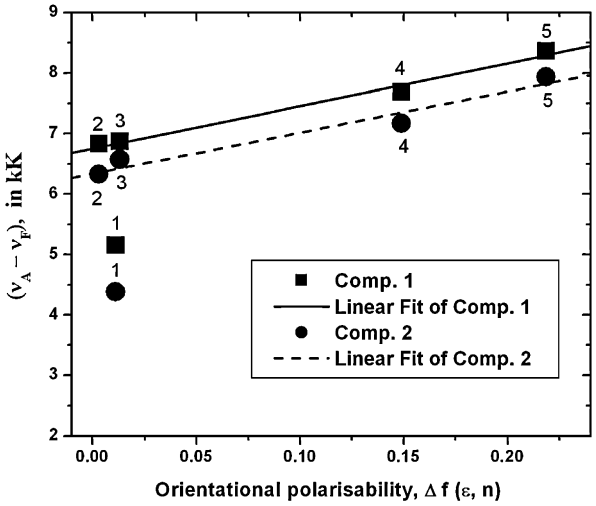

Fig. 5. Lippert-Mataga's plot for **1** and **2** (i.e. plot of Stokes' shift (in kK, 1 kK = 1000 cm^{-1}) vs. the orientation polarizability, defined as $\Delta f = ((\varepsilon - 1)/(2\varepsilon + 1)) - ((2n^2 - 1)/(2n^2 + 1))$, where ε – dielectric permittivity of the solvent, n – refractive index of the solvent). The solvents used: 1 – tetrachloromethane, 2 – benzene, 3 – toluene, 4 – chloroform, 5 – dichloromethane. The results of linear fit: for compound **1**, $\nu_A - \nu_F = (6.75 \pm 0.07) - (7.06 \pm 0.53) \cdot \Delta f$, $R = 0.994$, SD = 0.095 kK; for compound **2**, $\nu_A - \nu_F = (6.34 \pm 0.14) - (6.78 \pm 1.08) \cdot \Delta f$, $R = 0.976$, SD = 0.193 kK. The differences beetween ground and excited state dipole moments ($\Delta\mu$) for **1** and for **2** were estimated by Lippert-Mataga's equation [33,34]: $\Delta\mu$ values for **1** and **2** were estimated to be 16.1 and 15.9 Debye, correspondingly. Onsager's cavity radii used for $\Delta\mu$ estimations were determined from AM1 optimized geometries of **1** and **2**: the values of Onsager's cavity radius were 7.18 and 7.2 Å for **1** and **2**, correspondingly.

-5-phenyl-l,3,4-oxadiazole (**1**–**3**) are rather low: in apolar aprotic solvents they do not exceed 0.02.

Quantum yields of compound **3** in apolar aprotic solvents are sufficiently lower than the corresponding quantum yields of compounds **1** and **2**. Such enhancement of the non-radiative decay rate in case of **3** could be due to the intramolecular librations with great amplitude of the phenyl in anilinophenyl fragment.

The increase of solvent polarity could affect the fluorescence intensity of **1**–**3** in two ways. On the one hand, if the non-radiative deactivation **1**–**3** is linked with the participation of low-lying triplet $n\pi^*$ excited states of carbonyl group, the increase of solvent polarity would change the arrangement of the $n\pi^*$ and $\pi\pi^*$ levels, energy gap between S_1 ($\pi\pi^*$) and T ($n\pi^*$) levels would increase, hence, the probability of intersystem conversion could be decreased and, in result, fluorescence intensity could increase [9–11,40].

On the other hand, the increase of the solvent polarity could decrease the fluorescence intensity of **1**–**3**. This quenching with the increase in the solvent polarity should be linked to the energy gap law, which controls the rates of non-radiative deactivations. As the energy of the excited state (e.g. S_1) is lowered by solvation in polar solvents, so the radiationless transitions $S_1 \rightarrow S_0$ generally become faster, and at the same time the corresponding radiative transitions which depend on the frequency as ν^3 will be slower.

Our experimental results show that the quenching action of solvent polarity is much more pronounced – drastic decrease of the quantum yield values φ of **1**–**3** with the increase of solvent polarity is observed (see Table 2).

4. Conclusion

Spectral-luminescent properties of the newly synthesized 2-(3′-coumarinyl)-5-(2′-(R-amino)-phenyl)-1,3,4-oxadiazoles have been investigated in solvents of various polarity and hydrogen-bonding ability.

It has been found that for all the studied compounds no excited state intramolecular proton transfer occurs despite the presence of coumarinyl fragment – electron acceptor effect of the coumarinyl fragment is not sufficient to increase the excited state acidity of the amino group.

It has been found that the absorption spectra of the studied compounds shift to higher energy with increase in solvent polarity, whereas corresponding fluorescence spectra shift to lower energy with solvent polarity increase. It has been suggested that considerable long-wavelength shifts of the fluorescence spectra of the studied compounds with increase in solvent polarity is caused by the solvent relaxation. The observed solvent relaxation effect allow us to propose the compounds **1**–**3** as potential probes to monitor changes in solvent relaxation in low-polar media and as potential probes for rigidochromic effect (i.e. probes with hypsochromic shift of their luminescence bands when their solution environment becomes more rigid).

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