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Luminescence of the nitronyl nitroxide radical group in a spin-labelled pyrazolylquinoline



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ABSTRACT

The synthesis, structure and photoluminescence of a group of substituted 2-pyrazolylquinolines, including a spin-labelled derivative, are described. A comparative study of photoluminescence from the synthesized compounds demonstrates that introduction of a nitronyl nitroxide radical group results not only in the expected reduction in photoluminescence from the pyrazolylquinoline moiety, but also gives rise to a new red photoluminescence band (maximum at 692 nm in acetonitrile) from the radical fragment.

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1. Introduction

An important trend in modern chemistry is the synthesis of polyfunctional luminescing organic compounds containing heterocyclic nitrogen nuclei and luminescing metal complexes from such ligands [1–7] due to potential applications of these compounds in luminescing devices and sensors [8–11]. Luminescing nitrogen heterocycles include quinoline derivatives [12–15], e.g., recently photoluminescence (PL) was reported from 2-(3,5-dimethylpyrazol-1-yl)-4-methylquinoline [16] and a chiral pyrazolylquinoline, a derivative of natural terpene (+)-3-carene [17].

Apart from a broad interest in the luminescence of diamagnetic heterocyclic species, the luminescence properties and photophysical processes in series of aromatic compounds spin-labelled with an imino and/or nitronyl nitroxide are being actively studied today [18–25]. It was found that the nitronyl nitroxide moiety *per se* as a fluorophore shows a weak PL in the solid phase at low temperature in the range of 650–900 nm [26–29]. However, the level of accumulated knowledge is still far from being sufficient to predict

the PL properties of a nitronyl nitroxide moiety linked with a given heterocycle.

In the present work, we report the first luminescence spectroscopy studies of an organic paramagnetic **1** compound combining a good fluorophore moiety, pyrazolylquinoline, and a nitronyl nitroxide radical group in the same molecule. We found that the addition of a nitronyl nitroxide group to the pyrazolylquinoline system (Scheme 1) results not only in the expected reduction in PL from the pyrazolylquinoline moiety, but also gives rise to a near-infrared luminescence centered on the radical ligand.

2. Experimental section

2.1. Spectroscopic instrumentation

Excitation and PL spectra of compounds **1**, **3** and **4** in the solid phase and in acetonitrile were taken at room temperature with a FLS920 spectrofluorimeter (Edinburg Instruments). The PL spectra and kinetics of the solids were taken in a thin layer of powder produced by grinding crystals between two quartz glasses that were then set at an angle of 45° to the excitation beam. To measure the spectra in acetonitrile, a standard 1 cm quartz cuvette was used. Solutions were prepared by means of spectrally pure acetonitrile.

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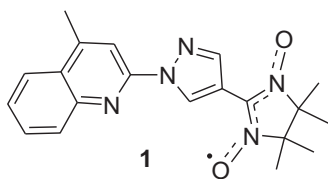
When necessary, oxygen was removed by blowing argon through the solution for 30 min. As excitation sources a Xe900 xenon lamp and EPLED laser diodes (280, 300, 320 nm, pulse length 600 ps) or an EPL-375 diode laser (375 nm, pulse length 60 ps) were used. Electronic absorption spectra were taken with an HP 8453 spectrometer (Agilent Technologies).

2.2. 4,4,5,5-Tetramethyl-2-(1-(4-methylquinolin-2-yl)-1H-pyrazol-4-yl)-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (**1**)

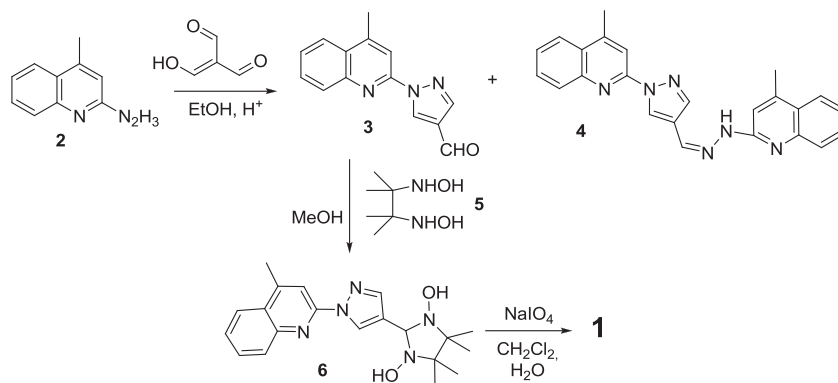
To a stirred solution of **6** (0.25 g, 0.68 mmol), CH₂Cl₂ (20 mL) and water (10 mL) were added along with NaIO₄ (0.218 g, 1.019 mmol). The reaction was stirred at room temperature for 40 min. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (15 mL). The combined organic solutions were dried with Na₂SO₄ and concentrated. The product was purified using column chromatography followed by multiple recrystallizations from a CH₂Cl₂–heptane mixture (v/v=1:2). Yield 0.178 g (72%), blue crystals, m.p. 142–145 °C. $\mu_{\text{eff}}=1.73 \mu_{\text{B}}$ (in temperature range 50–300 K). ESR: $g_{\text{iso}}=2.0065$, $a_{\text{N}(\text{N}-\text{O})}(2 \text{ N})=0.749 \text{ mT}$, $a_{\text{H}(\text{Me})}(12 \text{ H})=0.022 \text{ mT}$, $a_{\text{H}}(1 \text{ H})=0.065 \text{ mT}$, $a_{\text{H}}(1 \text{ H})=0.029 \text{ mT}$. IR, ν/cm^{-1} : 3425, 3171, 3064, 2987, 1597, 1513, 1494, 1471, 1455, 1429, 1408, 1361, 1330, 1295, 1218, 1180, 1125, 1062, 1011, 968, 893, 848, 754. Found (%): C, 65.8; H, 5.9; N, 18.9. C₂₀H₂₂N₅O₂. Calculated (%): C, 65.9; H, 6.1; N, 19.2.

2.3. X-ray diffraction study

Reflection arrays were collected on a SMART APEX II CCD diffractometer (Bruker AXS) (Mo K α , $\lambda=0.71073 \text{ \AA}$; absorption was taken into account using Bruker SADABS software, ver. 2.10). The structures were solved by direct methods and refined using full-matrix LS techniques in anisotropic approximation for all non-hydrogen atoms. The H atoms were calculated geometrically and included as riding groups in the refinement. All calculations for structure solving and refining were performed using the Bruker Shelxtl software suite, ver. 6.14. It should be noted that crystals of **3** and **4** had the form of thin plates (about 0.01–0.02 mm thick), while the crystals of **6** were fine needles (0.02 × 0.02 × 0.28 mm³), so they reflected very poorly. Our numerous attempts to crystallize



Scheme 1. Structure of radical **1** combining pyrazolylquinoline and nitronyl nitroxide radical group.



Scheme 2. The scheme for synthesis of the radical **1** through the successive synthesis of **2**, **3**, **6** compounds.

compounds from different solvents in order to obtain crystals in another form were unsuccessful.

2.4. Computational details

DFT calculations were performed for isomers A and B of **1** with the GAUSSIAN03 program [34] using the B3LYP functional in conjunction with the 6–31+G(d,p) basis set. The ground state and the first excited state geometries were optimized using the DFT and TD-DFT methods, respectively. In all calculations (geometry optimizations and single point TD-DFT calculations), solvent effects were included within the SCRF method (solvent=acetonitrile).

3. Results and discussion

To obtain **1**, a substituted hydrazine **2** was condensed with trimethylmethane (TFM) in EtOH in the presence of HCl to give formylpyrazolylquinoline **3**. To avoid the formation of substantial amounts of hydrazone **4** as a byproduct, a hot solution of **2** in ethanol was added to an ethanol solution of a double excess of TFM at 70 °C. In this synthetic scenario the yields of aldehyde **3** reached 59% (Scheme 2). On the other hand, gradual reaction of **2** with TFM (0.5 h) and performance of the process at room temperature resulted in the formation of hydrazone **4** as the main product (57%). Condensation of the obtained aldehyde **3** with dihydroxyamine **5** produced imidazole **6**, which was subsequently oxidized with NaIO₄ in a biphasic CH₂Cl₂–H₂O system into the target nitronyl nitroxide **1**.

3.1. Structure of synthesized compounds

The molecular and crystal structures of all obtained compounds were established using X-ray diffraction analysis (XRD). The purity of the products was confirmed by spectral methods and elemental analysis, further supported in the case of the nitroxyl radical **1** with the results from magnetochemical measurements and ESR spectroscopy (Supplementary material).

The structure of the nitroxyl radical **1** is formed by two crystallographically independent molecules A and B (Fig. 1) that differ mainly in the angle between the planes of the quinoline and nitronyl nitroxide (CN₂O₂) fragments, which is equal to 10.3° in molecule A and 28.7° in molecule B. Each molecule forms its own centrosymmetric dimer (Fig. 2 A and B): in {A...A} pyrazolylquinoline the fragments overlap with minimal interplane distances of ~3.6 Å, while in {B...B} dimers the only overlapping is by quinoline fragments with interplane distances of ~3.3 Å.

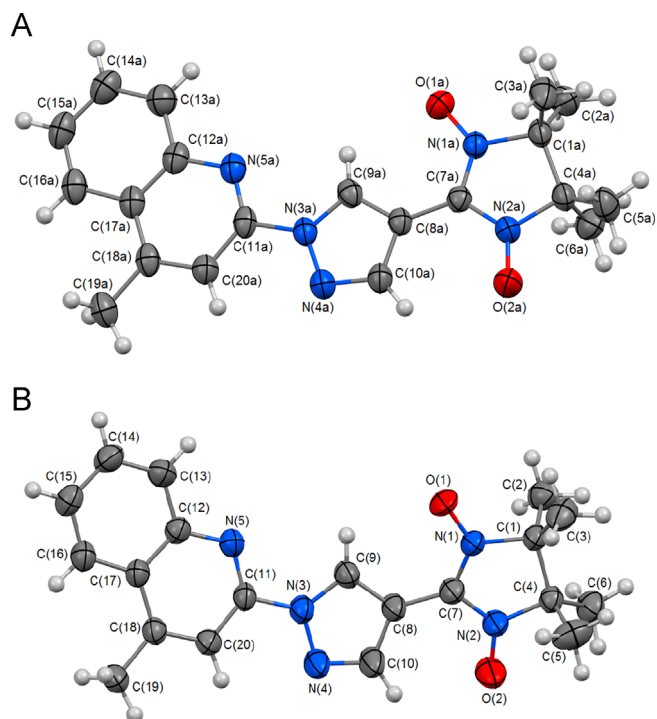


Fig. 1. Molecular structure of radical **1**. Thermal ellipsoids are shown for 50% probability.

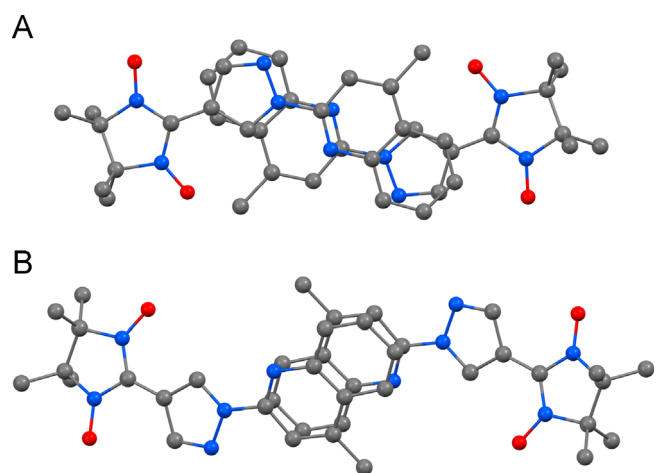


Fig. 2. Dimers [A...A] (A) and [B...B] (B) in the structure of solid radical **1**.

3.2. Absorption spectra. Luminescence in the solid state

Fig. 3 shows optical absorption spectra of compounds **1**, **3** and **4** in acetonitrile. Formylpyrazolylquinoline **3** was characterized by the vibrational structure of the longer wavelength band, with maxima at 302, 315, and 330 nm, arising due to the presence of the quinoline moiety. The electronic absorption spectrum of hydrazone **4** showed higher intensity bands due to the presence of two quinoline moieties. Radical **1** demonstrated additional relatively weak absorption bands in the red region, typical of aryl-substituted nitronyl nitroxides, with maxima at 512, 556, 600 ($\epsilon=955 \text{ M}^{-1} \text{ cm}^{-1}$), and 655 nm [30–32].

The spectra and kinetics of photoluminescence of compounds **1**, **3** and **4** were determined for powder samples and acetonitrile solutions. All these compounds in the solid state had broad PL bands in the 350–850 nm region (Fig. 4, Table 1). Compound **3** had a luminescence band with a maximum at 375 nm and a long tail

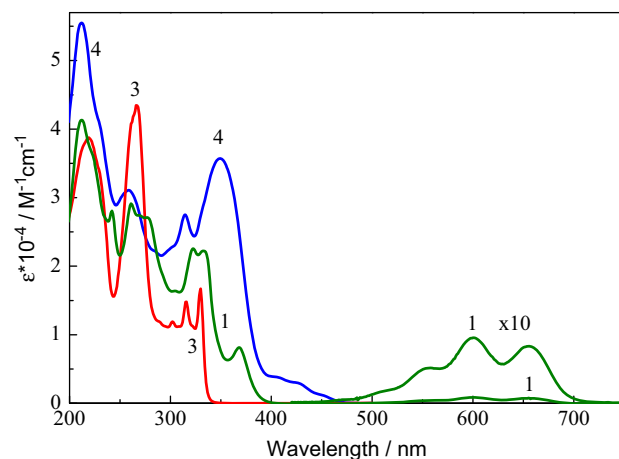


Fig. 3. Optical absorption spectra of compounds **1**, **3** and **4** in acetonitrile.

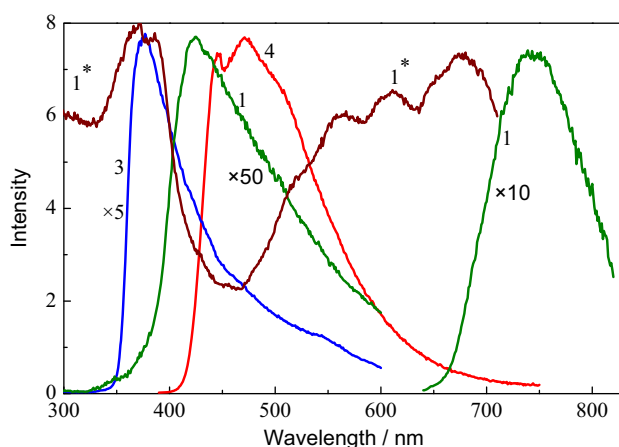


Fig. 4. The PL spectra of compounds **1**, **3** and **4** in solid state (spectra **1**, **3** are multiplied); 1^* – excitation spectrum of radical **1** with registration at 745 nm.

Table 1

Positions of bands maxima (excitation at 280 nm) and photoluminescence lifetimes for compounds **1**, **3** and **4** in solid state. Kinetic traces were evaluated in mono- or biexponential approximations.

Compound	λ_{max} (nm)	τ_1 (ns)	$A_1 \tau_1$ (% emitted quanta)	τ_2 (ns)	$A_2 \tau_2$ (% emitted quanta)
1	425	0.055	95	1.12	5
	745	1.76	100		
3	375	0.04	94	1.04	6
4	445,	0.40	90	4.2	10
	470				

extending beyond 600 nm. For hydrazone **4**, with two quinoline fragments, the PL band is five times more intense and has maxima at 445 and 470 nm with a shoulder around 510 nm. A comparison of PL band intensities for compounds **3** and **4** with the band intensity for naphthalene powder provides an estimate of the quantum yields of these compounds of $\varphi_3 \leq 0.01$ and $\varphi_4 \leq 0.05$, respectively.

The presence of the pyrazolylquinoline moiety in the nitronyl radical **1** gives rise to a broad PL band with a maximum at 425 nm in the solid state, which is 50-fold less intense compared to the band of hydrazone **4** due to the presence of the radical center. The presence of the nitronyl nitroxide moiety, with absorption bands in the red region (Fig. 3), gives rise to another PL band with a maximum at 745 nm (Fig. 4). The intensity of this band is about 5-fold greater than the intensity of the band of radical **1** at 425 nm. The excitation spectrum of the red photoluminescence

(spectrum **1***, Fig. 4) reproduces the absorption spectrum of radical **1** (Fig. 3). The appearance of a PL band at 745 nm upon excitation in the 500–700 nm range, where only the radical center is absorbing, indicates that the “red” band belongs to this center.

It should be noted that red luminescence (650–900 nm) for compounds containing a nitronyl nitroxide moiety has previously been found in the solid state [26–29]; however, only at low temperature (5 K). Apparently, due to the low intensity of this luminescence, the kinetics and excitation spectra were not recorded. In the case of radical **1** we were able to detect the excitation spectra and kinetics both in the solid state and in solution.

The PL kinetics in the 375–510 nm range (excitation at 280 nm) for all three compounds in the solid state is determined by their short lifetimes in the 40–400 ps range. For nitroxyl radical **1** the band with a maximum at 425 nm emits with a lifetime of 55 ± 10 ps, while the red luminescence in the band at 745 nm has a longer lifetime and decays exponentially with a characteristic time of 1.76 ± 0.10 ns (Fig. 5, Table 1). The low quantum yield of the pyrazolquinoline nucleus luminescence in radical **1** can be determined by the energy transfer to the radical moiety, giving rise to a PL band with a maximum at 745 nm.

3.3. Luminescence of compounds in acetonitrile solutions

In acetonitrile solutions formylpyrazolylquinoline **3** displayed luminescence bands with maxima at 324, 336 and 346 nm (Fig. 6) and a complex kinetics that can be described only in three exponential approximations with times of 0.1, 3.75 and 58 ns (Table 2). This wide dispersion of times most likely is a result of the collection of different conformational states of this molecule. The quantum yield of luminescence is an order of magnitude smaller than unity (Table 2).

The wide luminescence band of hydrazone **4** in acetonitrile is shifted to 485 nm (Fig. 6). The kinetics in this case is also complex, with three times (Table 2); however, the main exponent has a short time of about 0.36 ns (85% of emitted quanta). The excitation spectra for compounds **3** and **4** in acetonitrile are coincident with the absorption spectra.

As in the solid state, radical **1** in acetonitrile has weak dual luminescence with bands at 390 nm and 692, 750 sh nm (Fig. 6, Table 2). In the first case (390 nm), the luminescence kinetics is exponential with a time of 2.79 ns. The main component (98% of emitted quanta) of the red luminescence (692 nm) of **1** has a time of 0.91 ns (Table 2). The excitation spectra in the UV and the red luminescence of radical **1** in CH₃CN are shown in Fig. 7. The red

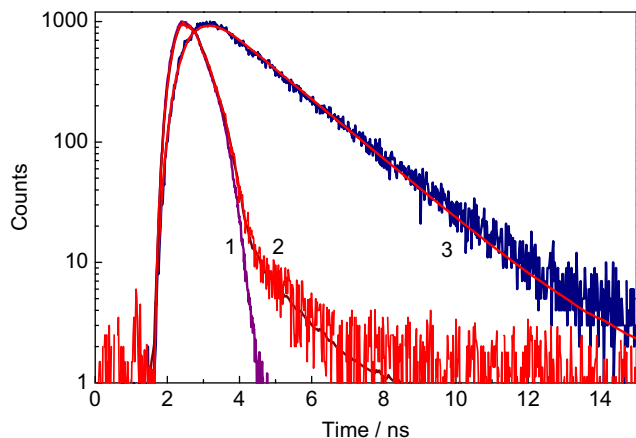


Fig. 5. Kinetic traces of photoluminescence of nitroxyl radical **1** in solid state. (1) – response function, (2, 3) – kinetics at 425 and 745 nm, respectively. Solid lines – mono- (line 3) and bi- (line 2) exponential approximation (results of approximation are given in Table 1).

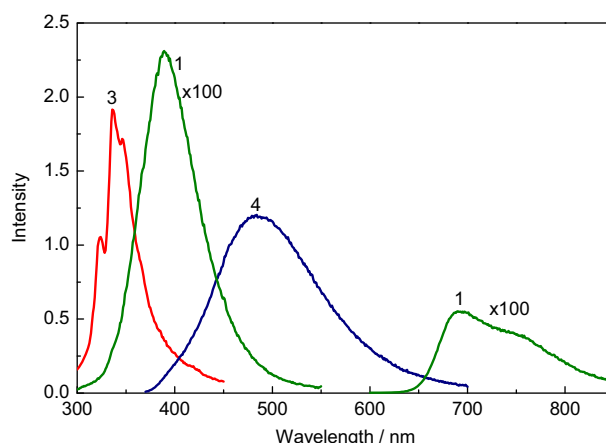


Fig. 6. Luminescence spectra of compounds **1**, **3**, and **4** in acetonitrile (excitation at 280 nm). The bands of radical **1** are multiplied by 100.

Table 2

PL quantum yields, bands maxima and lifetimes for compounds **1**, **3** and **4** in acetonitrile. Kinetic traces were evaluated in mono- or three-exponential approximations.

Compound	λ_{\max} (nm)	ϕ	τ_1 (ns)	$A_1\tau_1$ (%)	τ_2 (ns)	$A_2\tau_2$ (%)	τ_3 (ns)	$A_3\tau_3$ (%)
1	390	0.0012	2.79	100				
	692, 750 sh	0.0004	0.14	2	0.91	98		
3	324, 336,	0.12	0.10	15	3.75	46	58	39
	346							
4	485	0.22	0.36	85	3.63	12	11.7	3

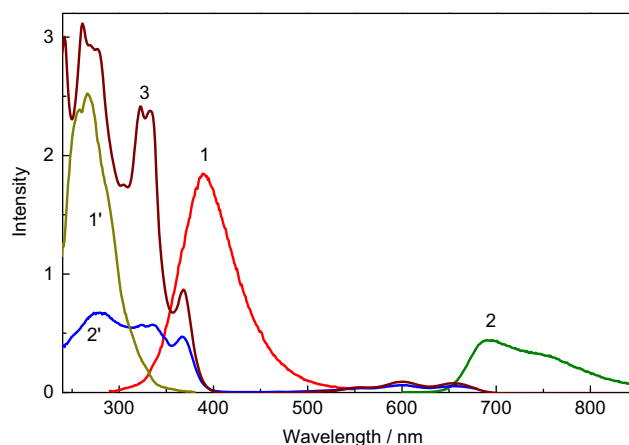


Fig. 7. Luminescence (1, 2) and excitation (1', 2') spectra of radical **1** in acetonitrile. The first UV luminescence band at 390 nm (1) and second red band at 692 nm (2). (3) – absorption spectrum of **1** in acetonitrile.

luminescence can be excited by the irradiation both in UV absorption bands at 322, 332, 368, and in visible absorption bands at 556, 600 and 656 nm. The UV luminescence band (390 nm) corresponds to the absorption band at 268 nm. So, the near UV and VIS absorption bands (320–700 nm) are determined by the transitions in the nitronyl nitroxide system. The appearance of the red luminescence upon excitation at 268 nm (Fig. 7, spectrum 2') (the excitation of the pyrazolylquinoline moiety) is due to the energy transfer from the pyrazolylquinoline fragment of radical **1** to the nitronyl nitroxide system.

It should be noted that the luminescence spectrum is not a mirror image of the lowest-energy absorption band of radical **1**. The expansion of absorption spectrum in acetonitrile (Fig. 3) for the Gaussian components gives at least five peaks with widths at

half height in a range of 1000–1775 cm^{-1} . The energy intervals between components (1408–1330 cm^{-1}) indicate that the absorption spectra corresponds to a vibronic progression. The luminescence spectrum of radical **1** in acetonitrile solution (Fig. 6) also can be decomposed to the Gaussian components. The first two peaks at 14,500 and 13,395 cm^{-1} have widths at half height 1060 and 2120 cm^{-1} with energy intervals of 1105 cm^{-1} . The further peaks, if they exist, have a small intensity to become apparent in the luminescence spectrum. So, the intensity distributions of vibronic progression in the luminescence and absorption spectra differ from each other. A similar mismatch of intensity distribution was detected in the luminescence and absorption spectra of some crystalline nitronyl nitroxide radicals at low temperature (5 K) [27]. The authors explained this effect by the structural changes between the ground and emitting states.

3.4. TD-DFT calculations

To understand the nature of the excited state that determines the formation of the new red PL band of radical **1** at 745 nm in the solid state and 692 nm in acetonitrile solutions, TD-DFT calculations accounting for the solvent effects were performed. It should be noted that the transition energy calculations performed for the optimized geometries of both isomers A and B (Fig. 1) lead to identical results. Fig. 8 shows the experimental absorption spectrum of **1** in acetonitrile and the positions of the calculated transitions. The bar height corresponds to the calculated oscillator strength of a transition (Supplementary material). The calculated absorption spectrum reproduces the main features of the experimental one. The first excited state corresponds to the HOMO→LUMO electron transition; the two orbitals are mainly (HOMO) and fully (LUMO) localized on the nitronyl nitroxide group (Fig. 8 and Supplementary material). The calculated long-wave absorption and red emission energies associated with the ground and first excited states (Supplementary material) are well consistent with those experimentally observed (Fig. 8).

3.5. Interaction of the pyrazolylquinoline system and a nitronyl nitroxide group

The presence of the pyrazolylquinoline system and a nitronyl nitroxide group twisted relative to each other in radical **1** allows one to think that the interaction between them is weak and they can be regarded as independent subsystems. It is important to pay attention to the very low luminescence quantum yield of

the pyrazolylquinoline system (Table 2, the band at 390 nm) in radical **1** versus the quantum yields of compounds **3** and **4**. One of the reasons for the low quantum yield could be the rapid energy transfer from the pyrazolylquinoline system to the nitronyl nitroxide group. This effect may be responsible for quenching the luminescence of organic molecules of this type by free or chemically bounded nitroxyl radicals [25,33]. In this case it can be assumed that the lifetime of the pyrazolylquinoline system in radical **1** is determined mainly by the energy transfer.

Under this assumption, the excitation of radical **1** in the bands of the pyrazolylquinoline moiety should lead to population of the S_1 excited state in this system and to relaxation due to energy transfer to the doublet D_1 excited state of the nitronyl nitroxide radical group. Fig. 9 shows the kinetics of blue (390 nm) and red (692 nm) luminescence in acetonitrile. The kinetics at 390 nm is monoexponential with a time of 2.79 ns, which, in accord with the above assumption gives the rate constant of energy transfer to be determined ($k_{ET} \approx 3.6 \times 10^8 \text{ s}^{-1}$). The value of the quantum yield (Table 2) allows the determination of the radiative rate constant in this case ($k_r \approx 4.3 \times 10^5 \text{ s}^{-1}$).

The kinetics at 692 nm is biexponential with times of 0.91 and 2.8 ns. The simplified model of the photophysical processes can be described by the differential equations

$$\frac{d[S_1]}{dt} = -k_{ET}[S_1]; \quad \frac{d[D_1]}{dt} = k_{ET}[S_1] - k_1[D_1] \quad (1)$$

where k_1 is the rate constant of the radical center D_1 state decay. The solid lines in Fig. 9 show the solution of this differential equations with $k_{ET} \approx 3.6 \times 10^8 \text{ s}^{-1}$ and $k_1 \approx 1.1 \times 10^9 \text{ s}^{-1}$. Except for the rate constants, the varied parameter is the ratio of the initial concentrations of the D_1 and S_1 states after a light pulse. The rise time in kinetics of red luminescence (692 nm) due to the energy transfer $S_1 \rightarrow D_1$ cannot be observed if both the pyrazolylquinoline and nitronyl nitroxide group are excited simultaneously at an excitation wavelength. The solution of the differential equations (1) shows that the equal concentrations of the S_1 and D_1 states after a light pulse are already sufficient for the disappearance of the rise time in the kinetics of red luminescence (692 nm).

The low quantum yield of red luminescence (692 nm) is determined by the high rate constant of radiationless transition ($k_{nr} \approx k_1 \approx 1.1 \times 10^9 \text{ s}^{-1}$) for the nitronyl nitroxide radical group. This low quantum yield of the red luminescence may be a reason why the luminescence of nitroxyl radicals was not observed for many nitroxide-fluorophore adducts [33].

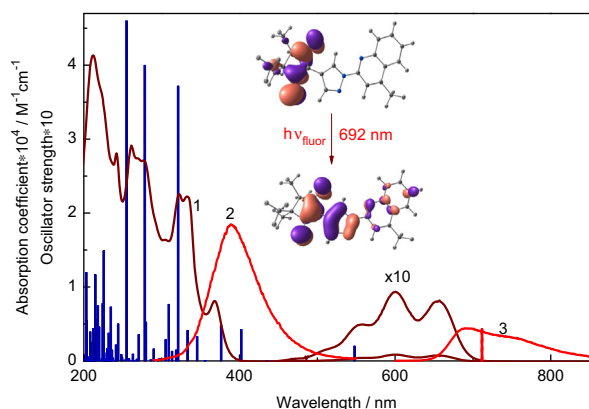


Fig. 8. The positions of calculated transitions in absorption spectrum of radical **1**. The height of a vertical bar corresponds to the calculated oscillator strength. (1) – absorption spectrum of **1** in acetonitrile, (2) – the first UV band of dual luminescence of **1** in acetonitrile, and (3) – the second red band of dual luminescence. At top, the shapes of orbitals involved in the transition with the lowest energy and with formation of red luminescence are presented.

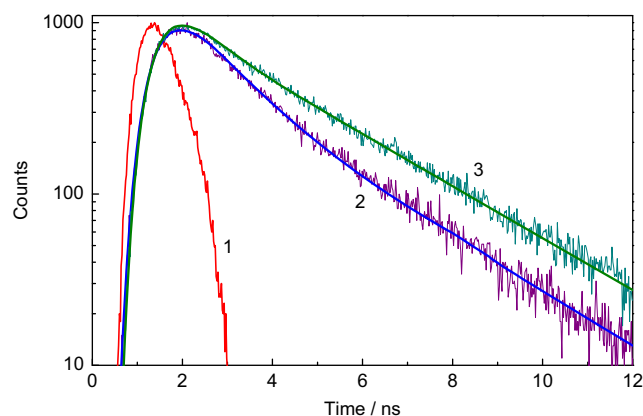


Fig. 9. Kinetic traces of photoluminescence of nitroxyl radical **1** in acetonitrile with the excitation at 320 nm. (1) – response function, (2, 3) – kinetics at 692 and 390 nm, respectively. Solid lines – the solution of the differential equations (3) with $k_{ET} \approx 3.6 \times 10^8 \text{ s}^{-1}$ and $k_1 \approx 1.1 \times 10^9 \text{ s}^{-1}$. The ratio of initial concentrations of D_1 and S_1 states after light pulse is 1.2.

4. Conclusion

Thus, in this work we developed the synthesis and studied the structure of a group of substituted 2-pyrazolylquinolines including a spin-labelled derivative. The study of photoluminescence demonstrated that introduction of a nitronyl nitroxide group results not only in the expected reduction in photoluminescence from the pyrazolylquinoline moiety, but also gives rise to a new PL band in the 650–850 nm region. Certainly, this new band can be excited by irradiation in the absorption bands of a nitronyl nitroxide group in the visible range (450–700 nm). The considerable drop in pyrazolylquinoline luminescence in the presence of the nitronyl nitroxide group can be understood by intramolecular energy transfer from the photoexcited pyrazolylquinoline backbone to the π -system of the radical fragment. This should be taken into account in further studies of photoluminescence properties of complexes of lanthanides with the obtained nitronyl nitroxide.

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Appendix A. Supplementary material

General synthetic details and syntheses of compounds 3, 4, and 6; discussion of the crystal structures, the ORTEP diagrams, X-ray crystallographic data; ESR investigation and static magnetic susceptibility measurements for 1.

CCDCs 935319–935322 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlum.2013.11.017>.

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