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Bright NIR-luminescent Nd³⁺ complexes with pyrazole-substituted 1,3-diketones demonstrated an unusual spectral lines branching ratios

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ABSTRACT

A series of novel highly NIR-emitting Nd³⁺ complexes with specially designed 1,3-diketones bearing a pyrazole moiety and a linear $C_x F_{2x+1}$ group (x = 1,3,6) was obtained and exhaustively investigated. It was demonstrated that for the complexes with an increased number of fluorine atoms, the triplet level energy of the ligands is decreased and phonon relaxation processes are suppressed. This provides a remarkable increase in the photoluminescence quantum yield up to 1.1%, which is close to the highest values reported for Nd^{3+} complexes with 1,3-diketones. The photoluminescence spectra of the complexes exhibited the Stark splitting indicative of non-cubic symmetry. Low symmetry of coordination environment was confirmed by the X-ray structural data and analysis of calculated Judd-Ofelt intensity parameters. Besides, it was revealed that the most intense band in the PL spectrum is attributed to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition (at 880 nm) which is commonly rather weak for simple diketonate complexes. The calculations showed that the unexpectedly high branching ratio of the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition raises with elongation of the fluorinated chain and reaches 59% for the complex with x = 6. The studies were conducted for solutions of the complexes as well as for solid samples, and the corresponding changes in their optical behavior were discussed. Uncommon properties of the synthesized Nd³⁺ complexes make them promising materials for various state-of-the-art luminescent applications, e.g., luminescent markers with an unusual spectral intensity distribution. Based on the electroluminescence studies, we also estimated the potential of the complexes for purely NIR-emitting OLEDs fabrication.

1. Introduction

To date, lanthanide coordination compounds are extensively used in advanced photonics, optoelectronics, and spectroscopy [1–6]. Special interest in Nd³⁺, Er³⁺, and Yb³⁺ is due to their IR emission in the range of 880–1600 nm; in particular, Nd³⁺ emission bands at 880, 1060, and 1330 nm fall within the telecommunication range and the transparency region of biological tissues [7–9]. Fabrication of lanthanide-based electroluminescent devices is also justified by the much narrow spectral bands of IR luminescence, in comparison with devices based on the ions of the platinum group, such as Os²⁺ or Ir³⁺ [10,11], that have similar values of the IR luminescence quantum yield [12,13]. However, there

is a fairly limited number of articles demonstrating efficient NIR-OLEDs based on neodymium complexes [14–17].

First, the emission efficiency depends heavily on the difference between the triplet energy level of the ligand environment and the resonant acceptor level of the rare earth ion [18]. In the case of Nd³⁺, the corresponding energy gap is usually large. Since the resonant level ${}^{4}F_{3/2}$ of the IR-emitting Nd³⁺ is located at 11700 cm⁻¹, it is necessary to develop the ligands having the triplet level within 12000–15000 cm⁻¹ to achieve efficient ligand-to-ion energy transfer. Second, for lanthanide complexes, the emission efficiency is highly sensitive to the

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Received 17 March 2020; Received in revised form 27 April 2020; Accepted 15 May 2020 Available online 23 May 2020 0143-7208/© 2020 Elsevier Ltd. All rights reserved. presence of CH and OH groups in the ion coordination sphere causing multiphonon relaxation [19,20]. Quenching can be substantially reduced by replacing these high-frequency-oscillating groups with the low-frequency-oscillating ones, e.g., fluor-containing groups [21]. The elongation of fluorinated chains in the ligands can additionally increase the efficiency of lanthanide-centered luminescence [20].

The 1,3-diketonate ligands allow the design of highly luminescent lanthanide complexes [22]. However, the NIR-luminescent Ln^{3+} ions are dramatically sensitive to the phonon interactions with ligands. The reported values of luminescence quantum yields for Nd³⁺ complexes with this type of ligands are typically in the range of 0.1–0.6% [23–25] and hardly ever achieve 1.5% [26].

In this paper, we investigate a series of Nd³⁺ complexes with 1,3diketones containing linear $C_x F_{2x+1}$ groups (x = 1, 3, 6) and a pyrazole moiety, and a 1,10-phenanthroline ancillary ligand aimed at removing the solvent molecules from the inner coordination sphere of the ion [27]. Previously, we have reported on the synthesis of Nd^{3+} complexes with symmetrical pyrazolic 1,3-diketones [28]. The replacement of one of the pyrazole fragments with perfluorinated groups in the ligand leads to a dramatic enhancement of the photoluminescence quantum yield (PLQY) for the corresponding neodymium complexes. Essentially, the measured quantum yield values of our compounds are close to the highest ones reported for other Nd³⁺ complexes with 1,3diketonate ligands and achieve 1.08%. The employment of modern spectroscopic techniques combined with the Judd-Ofelt calculations provided a means to elucidate the effect of fluorinated chain length in the ligand environment on the luminescent properties of the corresponding Nd³⁺ complexes. Also, important are the changes in the luminescence behavior revealed for the complexes in two different types of environment, namely in the DMSO solvent and KBr pellets. The potential for successful application of the proposed type of synthesized complexes for fabrication of organic light-emitting diodes (OLEDs) has been demonstrated.

2. Experimental section

2.1. Materials and methods

The main ligands were synthesized by the previously described method [29]. All other reagents were purchased from Aldrich and used without further purification. Elemental analysis was performed on an Elementar CHNO(S) analyzer. FTIR spectra were obtained on a Bruker Vector 22 instrument in KBr pellets. Neodymium content was determined by complexometric titration with standard Trilon B solution in the presence of Xylenol Orange as an indicator. Complexes were decomposed by heating with 70% HNO₃ before the analysis.

X-ray diffraction data were collected with the use of a Bruker SmartAPEX II CCD diffractometer (graphite monochromator) with K_{α} molybdenum radiation (0.71072 Å) and ω -scans at 120 K. The frames were integrated by a Bruker SAINT v7.23A (2005) software package by means of a narrow-frame algorithm, and a semiempirical absorption correction was applied with the SADABS program using intensity data of the equivalent reflections.

For X-ray powder diffraction data acquisition, the samples were placed between two polyimide films and mounted into a Bruker AXS D8 Advance Vario X-ray powder diffractometer equipped with a primary Ge(111) monochromator (Cu-K_{a1}, $\lambda = 1.54056$ Å) and a LynxEye PSD. The data were collected in the transmission mode at ambient temperature for 2θ range of 2–90° with a step of 0.01°. The diffraction patterns were processed with Bruker TOPAS 5 software [30].

¹H, ¹⁹F{¹H} NMR spectra were recorded from CD_2Cl_2 solutions with a Bruker Avance 300 FT-NMR spectrometer (¹H frequency of 300.13 MHz). The measurements were done using the residual signals of this deuterated solvent (¹H 5.32 ppm). The ¹⁹F NMR chemical shifts were referenced to external CFCl₃. UV absorption spectra of Nd³⁺ complexes and neat ligands dissolved in acetonitrile (HPLC SuperGradient, Panreac, Spain) were recorded by a Specord M40 spectrophotometer operating within 220–380 nm. Concentrations of the solutions were 5×10^{-5} M and 5×10^{-3} M. Absorption spectra of Nd³⁺ complexes in KBr pellets and DMSO (dimethylsulfoxide, HPLC SuperGradient, Panreac, Spain) solutions with concentrations of 3×10^{-3} M were recorded by the same instrument operating within 500– 850 nm. For solutions, the measurements were performed using quartz cells with a 1 cm pathlength.

IR absorption spectra of Nd³⁺ complexes in KBr pellets were recorded with an Infraspec FSM2201 Fourier-transform infrared (FTIR) spectrometer.

NIR photoluminescence and excitation spectra of the complexes were measured at room temperature by a Horiba Jobin-Yvon Fluorolog FL3-22 spectrofluorimeter using a 450 W xenon arc lamp. The experiments were carried out for DMSO solutions of the complexes poured into quartz cells.

Time-resolved experiments in the NIR region were done with the use of a LeCroy WR62xi digital oscilloscope coupled to a Hamamatsu H10330B-75 InP/InGaAsP-photocathode photomultiplier operating in the photon counting mode. A pulsed Nd:YAG laser emitting at 355 nm with a 5 ns pulse duration and diode laser emitting at 808 nm with a 100 ns pulse duration were used for luminescence excitation.

Photoluminescence quantum yields were measured for solid samples by a custom-made setup based on a MgO-covered integrating sphere with a diameter of 180 mm and an FD-10G photodiode detector; a 365 nm emitting LED was used as the excitation source.

For all optical measurements, the corresponding instrument response functions were taken into account. The experiments were performed in air at atmospheric pressure. Degradation of the optical properties was not observed during the experiments.

Oscillator strengths of f–f electric dipole transitions, luminescence branching ratios, and excited-state radiative lifetimes were calculated using the Judd–Ofelt (JO) theory [31,32].

The OLED test structure was developed with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) hole injection material, Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) host material, and 2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) electron transport material, as well as LiF and Al cathode materials. All of them were purchased from Luminescence Technology Corp. and used without further purification. ITO-coated glass substrates were washed in an alcohol solution of KOH followed by ultrasonic treatment in bidistilled water for 20 min. The substrates were dried in a nitrogen flow. A 50 nm layer of PEDOT:PSS was spin-coated onto the ITO surface and baked at 130 °C for 15 min. Then, a composite film based on TCTA:(complex with x = 3) (5:1 wt) was spin-coated and baked at 100 °C for 20 minutes. This composition was employed to avoid the film crystallization during annealing [33]. Next, a 15 nm TPBi electron transport layer, followed by 1 nm of LiF cathode and 100 nm of Al contact was deposited by thermal evaporation at 10^{-3} Pa in a Leybold-Heraeus Univex 300 vacuum deposition chamber. Currentvoltage measurements were done using an automated setup consisting of a Keithley 6485 picoammeter, Agilent 34401A voltmeter, and a Motech 2019 power supply. OLED optical power was measured by a Coherent FieldMaxII Laser Power Meter equipped with a High-Sensitivity Optical Power Sensor OP-2 VIS with a set point at 1060 nm. Electroluminescence (EL) spectra were obtained with an Ocean Optics Maya 2000 Pro CCD spectrometer.

2.2. Synthesis

Syntheses of tris(1-(1,3-dimethyl-1H-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dionato)(1,10-phenanthroline) neodymium (III) (complex *a*), tris(1-(1-methy-1H-pyrazol-4-yl)-4,4,5,5,6,6,6-heptafluorohexane-1, 3-dionato)(1,10-phenanthroline) neodymium (III) (complex *b*) and tris (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-1-(1-methyl-1H-pyrazol-4-yl) nonane-1,3-dionato)(1,10-phenanthroline) neodymium (III) (complex *c*) were as follows (Fig. 1).



Fig. 1. Synthesis of Nd³⁺ complexes.

2.2.1. Complex a

Neodymium oxide Nd_2O_3 (99.99%, 2.102 g, 6.25 mmol) was dissolved in a minimum amount of concentrated HCl (high purity grade), and the solution was evaporated to dryness on a water bath and transferred to a volumetric flask. The volume was brought to 25 mL with deionized water to obtain a 0.5 M stock solution of NdCl₃.

Ligands 1-(1,3-dimethyl-1H-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3dione (HL₁) (0.351 g, 1.5 mmol) and 1,10-phenanthroline (0.09 g, 0.5 mmol) were dissolved in warm ethanol (8 mL); 0.5 M solution of NdCl₃ (1 mL) followed by 1 M NaOH (1.5 mL) were added dropwise with stirring. The greenish-blue solution that formed was filtered, stored at 55 °C for 2 h, and left to stand for 24 h at room temperature. Then, the solvent was evaporated to dryness at reduced pressure, and the residue was extracted with 30 mL of warm acetone. The solution was filtered and left in an open beaker at room temperature. After evaporation of the solvent, the glassy residue was re-dissolved in a minimum amount of warm MeCN. Crystallization was induced by careful addition of an equal volume of Et_2O with rubbing the walls by a glass rod. The pale greenish powder was separated, washed with hexane and dried at reduced pressure (50 ° C and 0.1 Torr) to constant weight. The yield was 0.347 g (67%).

For C₃₉H₃₂F₉N₈NdO₆ (FW 1023.95)

Calcd., %: C, 45.75; H, 3.15; N, 10.94; Nd, 14.09.

Found, %: C, 45.91; H, 3.23; N, 11.09; Nd, 14.24.

IR v(cm⁻¹): 1657, 1540, 1465, 1345.

NMR assignment: ¹H NMR (CD₂Cl₂), δ (ppm): -0.6 (br. s, 9H, C-CH₃), 1.26 (br. s, 2H, 2H-phen), 3.92 (br. s, 9H, N-CH₃), 5.89 (br. s, 2H, 3H/4H-phen), 6.15 (br. s, 2H, 3H/4-phen), 6.52 (br. s, 2H, 6H-phen), 9.46 (br. s, 3H, 5H-pyr), 10.88 (br. s, 3H, CH-acac). ¹⁹F{¹H} NMR (CD₂Cl₂), δ (ppm): -75.68 (s, CF₃).

2.2.2. Complex b

This complex was prepared similar to complex *a* with 1-(1-methyl-1H-pyrazol-4-yl)-4,4,5,5,6,6,6-heptafluorohexane-1,3-dione (HL_2) (0.384 g, 1.2 mmol), 1,10-phenanthroline (0.072 g, 0.4 mmol), 0.8 mL

of a NdCl₃ stock solution, and 1.2 mL of 1 M NaOH. A precipitate was formed upon standing. It was separated, extracted by 30 mL of warm acetone, and the pure solution was evaporated in an open beaker at room temperature. The crystalline powder was collected, washed with water, 30% aqueous EtOH, and hexane, and dried at reduced pressure (50 °C and 0.1 Torr) to constant weight. The yield of the pale greenish-blue powder was 0.397 g (77%).

For C₄₄H₂₆F₂₁N₈NdO₆ (FW 1281.91)

Calcd., %: C, 39.35; H, 2.04; N, 8.74; Nd, 11.25.

Found, %: C, 39.48; H, 2.15; N, 8.91; Nd, 11.39.

IR v(cm⁻¹): 1657, 1540, 1465, 1345.

NMR assignment: ¹H NMR (CD₂Cl₂), δ (ppm): 1.26 (br. s, 2H, 2H-phen), 3.77 (br. s, 9H, N-CH₃), 6.02 (br. s, 2H, 3H/4H–phen), 6.12 (d, ³*J*_{H-H} = 7.7 Hz, 2H, 3H/4H-phen), 6.62 (d, ³*J*_{H-H} = 7.7 Hz, 2H, 6H-phen), 7.87 (br. s, 3H, 3H-pyr), 8.33 (br. s, 3H, 5H-pyr), 11.14 (br. s, 3H, CH-acac). ¹⁹F{¹H} NMR (CD₂Cl₂), δ (ppm): -126.32 (br. s, 2F, 1-CF₂), -116.00 (q, ³*J*_{H-H} = 7.1 Hz, 2F, 2-CF₂), -81.05 (t, ³*J*_{H-H} = 7.1 Hz, 3F, CF₃).

2.2.3. Complex c

This complex was prepared similar to complex *a* with 4,4,5,5,6,6,7, 7,8,8,9,9,9-tridecafluoro-1-(1-methyl-1H-pyrazol-4-yl)nonane-1,3-dione (HL₃) (0.423 g, 0.9 mmol), 1,10-phenanthroline (0.054 g, 0.3 mmol), 0.6 mL of a NdCl₃ stock solution and 0.9 mL of 1 M NaOH. A gel was formed upon standing. The reaction mixture was diluted with 50 mL of CH₂Cl₂, filtered, and the precipitate was washed with 30 mL of hot EtOH. The solvent was evaporated to dryness under diminished pressure. The solid residue was extracted by 15 mL of acetone, filtered through a 0.45 μ m Teflon syringe filter and left in an open beaker at room temperature. The crystalline powder was collected, washed with water, 30% aqueous EtOH, and hexane, and dried at reduced pressure (50 °C and 0.1 Torr) to constant weight. The yield of the pale greenish-blue powder was 0.355 g (68%).

 $\begin{array}{l} \mbox{For } C_{51} H_{26} F_{39} N_8 N dO_6 \mbox{ (FW 1731.98)} \\ \mbox{Calcd., } \%: \mbox{C, } 35.37; \mbox{H, } 1.51; \mbox{N, } 6.47; \mbox{Nd, } 8.33. \\ \mbox{Found, } \%: \mbox{C, } 35.59; \mbox{H, } 1.63; \mbox{N, } 6.47; \mbox{Nd, } 8.60. \\ \end{array}$

IR v(cm⁻¹): 1657, 1540, 1465, 1345.

NMR assignment: ¹H NMR (CD₂Cl₂), δ (ppm): 1.25 (br. s, 2H, 2Hphen), 3.74 (br. s, 9H, N-CH₃), 5.99 (br. s, 2H, 3H/4H-phen), 6.07 (br. s, 2H, 3H/4H-phen), 6.60 (br. s, 2H, 6H-phen), 7.77 (br. s, 3H, 3H-pyr), 8.52 (br. s, 3H, 5H-pyr), 11.14 (br. s, 3H, CH-acac). ¹⁹F{¹H} NMR (CD₂Cl₂), δ (ppm): -126.64 (br. s, 2F, 1-CF₂), -123.24 (br. s, 2F, 2-CF₂), -121.84 (br. s, 4F, 3,4-CF₂), -115.04 (br. s, 2F, 5-CF₂), -81.35 (br. s, 3F, CF₃).

3. Results and discussion

3.1. X-ray structural analysis

Crystals of complex *a* suitable for X-ray diffraction experiments were obtained by slow diffusion of Et_2O vapors into a saturated solution of the complex in MeCN. Since an air-dried complex was used, a small amount of hexane was apparently presented in solution.

Crystals of complex *a* (C₃₉H₃₂F₉N₈NdO₆, FW 1067.05) are orthor hombic with space group Pbca; at 120(2) K, crystal structure parameters are a=18.7354(18) Å, b=20.782(2) Å, c=24.188(2) Å, V=9417. 9(16) Å³, Z(Z')=8(1), d_{calc}=1.505 g · cm⁻³. Intensities of 110599 reflections were measured with a Bruker APEX-II CCD (λ (Mo_{Ka})) = 0.71072 Å, $2\theta < 58^{\circ}$), and 12519 (R_{int} =0.0214) independent reflections were used in further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F² in the anisotropic–isotropic approximation. The contribution of strongly disordered hexane solvate molecules to the intensities of the reflections was excluded by means of the SQUEEZE procedure. The disordered CF₃ group and one of the pyrazole rings were refined with restraints on the anisotropic displacement (EADP) and positional parameters



Fig. 2. General view of complex *a* with atoms presented by thermal ellipsoids (p = 50%). Hydrogen atoms and disordered atoms are omitted for clarity.

(DFIX). The refinement converged to wR₂=0.1083 and GOF=1.026 for all independent reflections (R_1 =0.0407 was calculated against F for 10235 observed reflections with I > 2 σ (I)). All calculations were performed using the SHELX software [34]. Crystallographic data for complex *a* were deposited at the Cambridge Crystallographic Data Centre as supplementary no. CCDC 1905085.

The crystal structure of complex *a* with the numbering scheme is displayed in Fig. 2. Nd^{3+} is coordinated by six oxygen atoms from three HL_1 ligands and by two nitrogen atoms from the 1,10-phenanthroline ligand. The coordination polyhedron of Nd^{3+} is a tetragonal antiprism. The Nd–O bonds vary in the range of 2.367(2)–2.423(2) Å, while the Nd–N ones are 2.635(3) and 2.648(3) Å. It should be noted that the observed variation of Nd–O bond lengths cannot be associated with the substituent effect in the ligand or with the degree of coplanarity of the metal–ligand cycle, and may be due to steric repulsion. The analysis of crystal packing revealed the stacking interaction between two pyrazole cycles (interplane distance ≈ 3.3 Å, Fig. 3) as well as the presence of rather short F..F contacts: F(4)..F(8) 2.774(2) Å, C-F(4)..F(8) angles of 158°, C-F(8)..F(4)angles of 108.5°.

3.2. X-ray powder analysis

The powder sample of complex *a* is single-phased, and its structure is identical to that determined by the single-crystal analysis. Cell parameters at ambient temperature determined by the Pawley fit are a=18.833(3)Å, b=21.008(4) Å, c=24.594(6) Å, V=9730(3) Å³, d_{calc}=1.457 gcm⁻³.

Broadening of diffraction peaks observed for complex b and complex c indicates an increase in the amorphization degree as compared to complex a.

3.3. NMR assignment

The signature of NMR spectra for many paramagnetic lanthanide complexes is large paramagnetic chemical shifts (up to several hundred ppm). Nevertheless, Nd^{3+} complexes usually show low magnetic anisotropy with respect to other lanthanide ions [35], resulting in low pseudocontact shifts. Signals in ¹H and ¹⁹F{¹H} NMR spectra of the synthesized Nd^{3+} complexes expectedly lie near the diamagnetic

range (see Figures 14–16 of Supplementary materials). The only proton with a non-characteristic aromatic chemical shift is α -H of the 1,10-phenanthroline fragment (1.25–1.26 ppm), that is the proton nearest to the paramagnetic metal ion. This causes a significant contact shift. The number of signals in the ¹H and ¹⁹F{¹H} NMR spectra of the synthesized Nd³⁺ complexes and the ratios of their integral intensities confirm their composition in the solution as well. The NMR characteristics for all three Nd³⁺ complexes are quite similar, which implies that the perfluorine fragment length has little effect on the electronic structure of the complexes.

3.4. UV-Vis absorption spectra

UV absorption spectra for the complexes and corresponding neat ligands are shown in Fig. 4. Intensive absorption bands with maxima at 228 and 270 nm are characteristic of the 1,10-phenanthroline ligand, whereas the band peaked at 320 nm corresponds to the absorption of the 1,3-diketonate ligands with $C_x F_{2x+1}$ groups. The small maximum within 290–300 nm is supposed to be also connected with the mentioned 1,3-diketonate ligands perturbed by Nd³⁺ ion. Weak absorption observed in the 500–850 nm region is associated with the resonant absorption of Nd³⁺ (see Fig. 5). For the most intense band observed at 583 nm, molar absorption coefficients for Nd³⁺ do not exceed 40 mol⁻¹ · cm⁻¹.

Based on the measured absorption spectra, we can conclude that bonding the considered pyrazolic 1,3-diketonate and 1,10-phenanthroline ligands to Nd^{3+} provides the complexes with intensive absorption, with the extinction coefficient reaching $10^5 \text{ mol}^{-1} \cdot \text{cm}^{-1}$ compared to the resonant absorption of Nd^{3+} .

The FTIR spectra for the investigated complexes were recorded within 600–3700 cm⁻¹, see Figure 17 of Supplementary materials. The positions of absorption bands are almost the same for all investigated complexes. Intensive absorption of the complexes within 1400–1700 cm⁻¹ is associated with the carbonyl groups of 1,3-diketonate ligands. Additional weak overtone at 2950 cm⁻¹ is observed. Another weak peak at 2360 cm⁻¹ corresponds to the C–H bond stretching. The absorption bands with maxima at about 1184 cm⁻¹, 1240 cm⁻¹, and 1345 cm⁻¹ are related to the C–F vibrational transitions. Several bands within 720–900 cm⁻¹ are most likely associated with the C–H stretching in 1,10-phenanthroline. A low-intensity broad band in the 3200–3600 cm⁻¹ region indicates the presence of water traces in KBr. Significant overlapping of the absorption bands observed within 1100–1700 cm⁻¹ indicate that the investigated complexes have low symmetry.

3.5. Photoluminescence, optical excitation, and impact of symmetry

Photoluminescence spectra for the investigated Nd³⁺ complexes under 365 nm CW optical excitation are presented in Figure 6. The spectra of the Nd³⁺ complexes have pronounced peaks associated with the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ (880 nm), ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ (1060 nm), and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ (1334 nm) transitions in Nd³⁺. The most intensive emission band is observed at 1060 nm.

The excitation spectra for the complexes were recorded within the emission band corresponding to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ transition in Nd³⁺, see Figure 6. We observe intensive luminescence of Nd³⁺ at excitation wavelengths longer than 400 nm. An artifact at 530 nm is connected with the second diffracted order detected by the CCD. The obtained spectra qualitatively resemble the recorded absorption spectra. Based on the absorption and luminescence excitation data for the investigated complexes, we conclude that ligand-to-metal energy transfer occurs (Figure 7).

We classified the symmetry types of coordination polyhedra for complexes *a*, *b*, and *c* on the basis of the Stark splitting of the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ emission band since the crystals suitable for X-ray structural analysis could not be grown for complexes *b*, and *c*. The positions



Fig. 3. Crystal packing of complex a.

of the bands were determined from the centers of Gaussian fittings of the low-temperature photoluminescence spectra (see Figure 18 of Supplementary materials).

In fact, the ligand environment has little effect on the positions of the spectral bands associated with transitions in the ion. However, incorporation of the ion into the crystalline structure cancels the spherical symmetry of the electromagnetic field characteristic of a free ion. This effect leads to Stark splitting of the energy levels. Here the degree of degeneracy depends on the point symmetry of the rare earth environment. For a Nd³⁺ ion with an odd number of electrons occupying the 4f orbital, the degeneracy of the ${}^{4}F_{3/2}$, ${}^{4}I_{11/2}$, and ${}^{4}I_{13/2}$ levels is 1, 4, and 5 in the case of cubic symmetry. Otherwise, the degeneracy is J + 1/2 [36].

For the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ radiative transition, we observe due to Stark splitting eight equidistant peaks separated by ~70 cm⁻¹. This fact indicates non-cubic symmetry of the coordination polyhedron of Nd³⁺ in the complexes.

3.6. Energy transfer

A simplified energy diagram of the levels involved in the energy transfer and radiative relaxation processes is presented in Figure 7. After absorption of a photon, an electron transition from the ground singlet state ${}^{1}S_{0}$ to the excited vibrational state ${}^{1}S_{1}^{*}$ occurs in the organic environment with subsequent relaxation to the lowest excited vibrational state ${}^{1}S_{1}$. The energy of the ${}^{1}S_{1}$ level for each complex was obtained from the intersection point of the emission and fluorescence spectra (see Table 1 and also Figure 12 of Supplementary materials).

Then, there are two possible ways of the ${}^{1}S_{1} \rightarrow {}^{1}S_{0}$ relaxation, i.e., by fluorescence with a transition rate of about 10^8 s^{-1} [37] or by a nonradiative process. Direct energy transfer from the singlet level of the ligand environment to the ion levels is also possible. Additionally, intersystem crossing (ISC) can give rise to transitions from the ¹S₁ singlet level to the T triplet level. Generally, the relaxation from T to ${}^{1}S_{0}$ is forbidden by the selection rules since it requires a spin flip. However, in lanthanide complexes, these selection rules are partially lifted due to the spin-orbit interaction. Therefore, nonradiative and radiative $T \rightarrow {}^{1}S_{0}$ relaxation can take place in the ligand environment; the latter occurs at a rate lower than 10^3 s^{-1} [38]. However, there is an alternative process, i.e., energy transfer (ET) from the triplet level of the ligand environment to the matching non-emitting level of Nd³⁺. The energy of this level must be close to that of the triplet level. In our case, this condition is satisfied by the Nd³⁺ levels between ${}^{2}K_{15/2}$ and ${}^{4}G_{5/2}$.

Table 1

Singlet and triplet level energies of the main ligand for the corresponding Nd^{3+} complexes. Data on the energy gap ΔE between the triplet level and the ${}^{4}F_{3/2}$ level of Nd^{3+} are also provided.

Sample	Singlet level, cm ⁻¹	Triplet level, cm ⁻¹	ΔE , cm ⁻¹
Complex a	27854	22055	10355
Complex b	28234	21000	9300
Complex c	28016	20476	8776

For the 1,10-phenanthroline ancillary ligand, the energy of the triplet level is about 22100 cm⁻¹ [39]. The positions of the triplet energy levels for the HL₁, HL₂, and HL₃ ligands were determined from the low-temperature phosphorescence spectra of the corresponding Gd³⁺ complexes. The results of experiments at 77 K are presented in Figure 13 of Supplementary materials. According to Lewis and Kasha [40], the position of the triplet level was taken as the maximum of the zero-phonon line. This line corresponds to the highest-energy component in the Gaussian fitting of the spectrum. The obtained data presented in Table 1 indicate a substantial decrease in the energy gap ΔE (from 10355 to 8776 cm⁻¹) between the triplet level and the ⁴F_{3/2} level of Nd³⁺ with elongation of fluorinated chains in the ligand environment.

Luminescence of Nd³⁺ is associated with the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{J}$ transitions (J = 9/2, 11/2, or 13/2), see Figure 7. Although the triplet level energy is decreased with extension of the fluorinated chains in the ligands, direct T $\rightarrow {}^{4}F_{3/2}$ energy transfer is improbable since the corresponding energy gap is quite large (8776–10355 cm⁻¹). This gap by far exceeds the energy difference required to achieve efficient luminescence. For example, according to an empirical Latva rule [18], this difference is to be 2000–2500 cm⁻¹ for Eu³⁺ and 2000–4000 cm⁻¹ for Tb³⁺. Here a contradiction arises since, despite such a large energy gap, we do observe Nd³⁺ luminescence. Consequently, ligand-to-metal energy transfer is followed by a series of cascade transitions through the ion levels having higher energies than that of ${}^{4}F_{3/2}$. The cascade relaxation leads to very low sensitization efficiency as energy is partially lost due to nonradiative processes. This fact should manifest itself in a decrease in the luminescence lifetimes.

3.7. Photoluminescence decays

The photoluminescence decays for DMSO solutions and solid samples of the Nd³⁺ complexes were recorded within the emission bands corresponding to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ (874–876 nm), $^4F_{3/2} \rightarrow ^4I_{11/2}$ (1058–1066 nm), and $^4F_{3/2} \rightarrow ^4I_{13/2}$ (1329–1337 nm) transitions.



Fig. 4. Absorption spectra for acetonitrile solutions of complexes a, b and c, 1,10-phenanthroline ligand (phen), and pyrazolic 1,3-diketonate ligands with $C_x F_{2x+1}$ groups. Concentrations were $5 \cdot 10^{-5}$ M and $5 \cdot 10^{-3}$ M.

Table 2

Luminescence decay times τ_{exp} for solid samples of the investigated Nd³⁺ complexes *a*, *b*, and *c* obtained for different spectral bands.

Sample	λ , nm	$\tau_{\mathrm{exp}},\ \mu\mathrm{s}$
Complex a	876	0.989 ± 0.005
	1058	0.993 ± 0.005
	1332	0.970 ± 0.006
Complex b	874	0.936 ± 0.002
	1066	0.941 ± 0.002
	1337	0.952 ± 0.005
Complex c	875	0.923 ± 0.001
	1066	0.957 ± 0.004
	1337	0.922 ± 0.005

These decays can be presented as

$$I_{exp}(t) = \int_0^\infty I_{irf}(t') I_{exp}(t-t') dt.$$
 (1)

Here $I_{\rm irf}(t)$ is the instrument response function (IRF). The decay lifetimes for the investigated Nd^{3+} complexes were deduced from the

experimental data by means of the Levenberg–Marquardt deconvolution technique. The measured IRF appears as a single exponent with the corresponding decay time of 1-1.5 ns.

The data obtained by the deconvolution procedure can be fitted by single-exponential relaxation models, for both solid samples (see Figure 8) and solutions (Figure 9). We present the results for the band corresponding to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ (1058–1066 nm) transition only since the decays for the other bands look essentially the same. The decay times derived for solid samples and solutions under optical excitation at 355 nm are given in Tables 2 and 3, respectively. The decay times $\tau_{\rm res}$ measured for the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition with excitation at 808 nm for solid samples are evaluated to be $1.032 \pm 0.003 \ \mu$ s, $0.994 \pm 0.004 \ \mu$ s, and $0.986 \pm 0.010 \ \mu$ s for complexes *a*, *b* and *c*, respectively. Though the resonant excitation of Nd³⁺ in the complexes allows to reduce the nonradiative processes such as ISC and ligand-to-metal energy transfer, the obtained decay times are similar to the values reported for other Nd³⁺ complexes with organic ligands [41–43], and, most probably, this is due to the energy transfer processes within the ion.

It should be noted that the decay times obtained for the solutions are 1.5 times longer than those for solid samples. One of the possible



Fig. 5. Absorption spectra within 500–850 nm for complexes a, b and c in DMSO solutions and KBr pellets with concentrations of $3 \cdot 10^{-3}$ M.

explanations of such result for solid samples, according to Riseberg's monograph [44], is the energy migration between two neighboring rare earth ions of closely packed complexes in the crystalline lattice. Moreover, there is a direct correlation between the elongation of fluorinated chains in the ligand environment and the increase in the decay times for the complexes in solutions. However, these times are reduced for solid samples with longer chains. An increase in the volume density of oscillators with elongation of fluorinated chains can also lead to an increased probability for interactions between phonons and the rare earth ion.

3.8. Electroluminescence

To check the potential of Nd^{3+} complexes with pyrazolic 1,3diketones for OLED applications, we fabricated an electroluminescent test structure with an emission layer based on one of the complexes, complex *b*, which appeared to be more stable during the device fabrication.

In the electroluminescence spectrum (Figure 10), we observe two bands characteristic of $\rm Nd^{3+}$ emission at about 808 and 880 nm, connected with the ${}^4F_{5/2} + {}^2H_{9/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions. An

Table 3

Luminescence decay times $\tau_{\rm exp}$ for DMSO solutions of complexes $a, \, b,$ and c obtained for different spectral bands.

Sample	λ , nm	$\tau_{\mathrm{exp}},\ \mathrm{\mu s}$
Complex a	875	1.456 ± 0.021
	1058	1.459 ± 0.016
	1329	1.455 ± 0.067
Complex b	877	1.494 ± 0.026
	1058	1.565 ± 0.019
	1327	1.561 ± 0.108
Complex c	875	1.514 ± 0.025
	1058	1.585 ± 0.013
	1331	1.561 ± 0.056

additional broad band with maxima at about 560 nm most probably arises due to formation of exciplexes [45,46] since there are no peaks characteristic of the neat HL_2 ligand (maximum at ~470 nm [47]) or 1,10-phenanthroline ancillary ligand (maximum at ~360 nm) [48], and there is a peak at (~405 nm [49]) corresponding to TPBi electroluminescence due to the incomplete energy transfer.

The maximum power efficiency of the fabricated OLED structure was 0.4 μ W/W, and the maximum obtained light power density corresponding to the integrated electroluminescence intensity of the infrared band was 0.2 μ W/cm² at 8 V. The external quantum efficiency was obtained to be 0.008% with the current density of 76 mA/cm².

Thus, we have demonstrated successful implementation pyrazolesubstituted 1,3-diketone complexes of Nd^{3+} having unique optical properties in an OLED structure. However, further optimization of the architecture and composition of the OLED would improve its performance. Therefore, targeted search for proper transport and host materials to adjust the charge carrier balance is essential, which will be subject to future research.

3.9. Judd–Ofelt analysis

We have applied the standard Judd–Ofelt theory [31,32] to determine the oscillator strengths, branching ratios, radiative lifetimes, and quantum yields for both DMSO solutions of the investigated complexes and solid samples.

The absorption spectra (see Fig. 5) measured for complexes *a*, *b*, and *c* within 500–850 nm exhibit four pronounced features corresponding to the transitions from the ground ${}^{4}I_{9/2}$ level to the upper ${}^{4}F_{5/2} + {}^{2}H_{9/2}$, ${}^{4}F_{7/2} + {}^{4}S_{3/2}$, ${}^{4}G_{5/2} + {}^{2}G_{7/2}$, and ${}^{4}G_{7/2} + {}^{4}G_{9/2} + {}^{2}K_{13/2}$ levels. Here the "+" sign means that the considered levels have close energies.

The oscillator strengths of the transitions were determined from the absorption spectra in Fig. 5 by the following relation:

$$f^{\exp} = 4.319 \times 10^{-9} \frac{\text{mol} \cdot \text{cm}^2}{\text{l}} \int \epsilon(\bar{\nu}) d\bar{\nu}, \qquad (2)$$

where $\epsilon(\bar{v})$ is the molar extinction coefficient depending on wavenumber \bar{v} specified in cm⁻¹ [50]. The values of f^{exp} obtained by numerical integration of the absorption spectra within particular bands are given in Supplementary materials, Tables 5, and 7. According to the Judd– Ofelt theory, the oscillator strength for electric dipole transition from the initial state $|\Psi J\rangle$ to the excited state $|\Psi' J'\rangle$ is expressed as

$$f^{calc} = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{t=2,4,6} \Omega_t |\langle \Psi J \| U^t \| \Psi' J' \rangle|^2,$$
(3)

where *m* is the electron mass, *c* is the speed of light in vacuum, *h* is the Planck's constant, $\overline{\lambda}$ is the peak wavelength of a particular absorption band, *J* is the total angular momentum of the initial state $|\Psi J\rangle$, *n* is the refractive index of the sample, Ω_t (t = 2, 4, 6) are the Judd–Ofelt intensity parameters, and $|\langle \Psi J || U^t || \Psi' J' \rangle|^2$ are the squared reduced matrix elements which are generally considered to be independent of the host material. The matrix elements were taken from [51]. Magnetic-dipole oscillator strengths f^{MD} were not taken into account as they are much smaller than the electric-dipole oscillator strengths f^{ED} [52]. The refractive index for KBr pellets was calculated according to [53] and references therein. For liquid samples, we used n = 1.47 for the DMSO solvent at wavelengths longer than 500 nm [54,55].

We arrive at an overdetermined system of linear equations by setting the calculated oscillator strengths (3) to be equal to the respective oscillator strengths derived from the experimental data (2). The system is solved by least-squared fitting with respect to the Ω_r parameters. The accuracy of the fitting procedure is given by the relative root-mean-square (RMS) deviation

$$\delta_{\rm rms}^{\rm rel} = \sqrt{\frac{1}{N-3} \sum_{i=1}^{N} \left(\frac{f_i^{exp} - f_i^{calc}}{f_i^{exp}} \right)^2} \tag{4}$$

between the oscillator strengths derived from the theory and experimental data. Here *N* is the number of the experimental oscillator strengths and corresponding equations. For all complexes, this parameter was set as N = 4. The intensity parameters Ω_t and calculated oscillator strengths f^{calc} obtained for the investigated complexes are presented in Supplementary materials, Tables 5, and 7. The amplitude of the oscillator strength for the ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2} + {}^{2}G_{7/2}$ field-hypersensitive transition is proportional to the reduced matrix element $|\langle \Psi J || U^2 || \Psi' J' \rangle|^2$ and intensity parameter Ω_2 . The Ω_2 value depends on the degree of symmetry of the ligand environment surrounding the lanthanide ion as well as on the type of bonding between the lanthanide ion and coordinated atoms (N or O). For large Ω_2 , the bonding type is mostly covalent and the degree of symmetry is low [56]. For small Ω_2 , the bonding type is ionic and the complex is of high symmetry. Inorganic systems, such as glasses and crystals, containing Nd³⁺ ions usually have $\Omega_2 ~(4-12)\times 10^{-20}$ cm² [57,58]. For organic complexes, Ω_2 usually falls within the (24–34)×10⁻²⁰ cm² range [59,60]. Previously, we have obtained $\Omega_2 = 22.6 \times 10^{-20}$ cm² and $\Omega_2 = 28.8 \times 10^{-20}$ cm² for Nd³⁺ complexes with a similar ligand environment [28].

The high Ω_2 values obtained for the investigated complexes are within $(14.5-21.6)\times 10^{-20}$ cm², which indicates that the degree of symmetry of coordination polyhedra in our compounds is higher compared with similar organic complexes. But again, the X-ray diffraction analysis revealed that the coordination polyhedron of complex *a* is a tetragonal antiprism, which corresponds to a relatively low degree of symmetry. The observed Stark splitting confirms this fact. For the solid-state samples, Ω_2 values decrease in the following order: a > b > c, indicating the highest degree of symmetry for complex c. For complexes in DMSO solutions, the trend is different though: Ω_2 values decrease as b>c>a. The fact that the Ω_2 values exhibit different trends for the investigated complexes in solutions and in the solid phase, indicates structural changes resulting in the differences in the symmetry of the coordination polyhedra. Thus, the correlation between Ω_2 values and the symmetry of the coordination polyhedra should be determined for complexes in similar media.

Once the intensity parameters Ω_t are obtained, the probability $A_{rad}^{ED}(\Psi J, \Psi' J')$ (s⁻¹) of the radiative transition between the initial manifold $|\Psi J\rangle$ and terminal manifold $|\Psi' J'\rangle$ can be calculated by the following expression:

$$A_{rad}^{ED}(\Psi J, \Psi' J') = \frac{64\pi^4 e^2}{3h(2J+1)\overline{\lambda}^3} \frac{n(n^2+2)^2}{9} S^{\text{ed}},$$
(5)

where S^{ed} is the electric dipole line strength described in terms of the Ω_t parameters and squared reduced matrix elements:

$$S^{\text{ed}} = \sum_{t=2,4,6} \Omega_t |\langle \Psi J \| U^t \| \Psi' J' \rangle|^2.$$
(6)

The obtained radiative transition probabilities provide a means to calculate the emission cross-section at the peak wavelength λ by the relationship:

$$\sigma_{em}(\Psi J, \Psi' J') = \frac{\lambda^4 A_{rad}^{ED}(\Psi J, \Psi' J')}{8\pi n^2 c \Delta \lambda},$$
(7)

where $\Delta\lambda$ is the full-width at half-maximum of a fluorescence line. The emission cross-sections obtained for the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions are presented in Supplementary materials, Table 9.

The calculated radiative lifetimes $\tau_{\rm rad}^{\rm calc}$ and branching ratios $\beta_{\rm calc}$ for the ${}^{4}\text{F}_{3/2} \rightarrow {}^{4}\text{I}_{J'}$ electric dipole transitions (J' = 9/2, 11/2, or 13/2) were evaluated by the following relations:

$$\tau_{\rm rad}^{\rm calc} = \frac{1}{\sum_{\Psi'J'} A_{rad}^{ED}(\Psi J, \Psi'J')},\tag{8}$$

$$\beta_{\text{calc}}(\Psi J, \Psi' J') = \frac{A_{rad}^{ED}(\Psi J, \Psi' J')}{\sum_{\Psi' J'} A_{rad}^{ED}(\Psi J, \Psi' J')}.$$
(9)

The calculated quantities as well as the branching ratios β_{exp} derived from the relations between the intensities of the observed Nd³⁺ emission bands are presented in Supplementary materials, Tables 6 and 8. The values obtained for β_{exp} agree with β_{calc} within the accuracy of the calculations.

Table 4

Quantum yields Φ calculated for DMSO solutions and solid samples of complexes a, b, and c.

	Complex a	Complex b	Complex c
	DMSO solution		
Φ,%	0.52	0.57	0.66
Relative error, %	12.7	17.1	21.5
	Solid phase		
Φ,%	0.44	0.42	0.52
Relative error, %	5.6	30.2	8.3

It should be mentioned that the DMSO solvent was chosen for measuring the absorption spectra of the complexes in solutions due to its low saturation capacity. However, some solvents can significantly change the spectroscopic properties of organic compounds [61,62]. Therefore, we have checked the solvent effect on our complexes by comparing the absorption spectra of complex a in three different solvents: acetonitrile, DMSO, and dichloromethane. The concentrations were of the same order in all cases. From Figure 22 of Supplementary materials, we have found no evidence of solvatochromism for complexes of the considered type. Moreover, the absorption spectra obtained for solutions of the complexes in DMSO and dichloromethane, which is incapable of coordinating the lanthanide in 1,3-diketonate compounds, were found to be essentially the same, with slight differences in extinction coefficients. So, we have calculated the radiative lifetime for complex a, based on the absorption data for dichloromethane and acetonitrile solutions. The value of 251 µs obtained for the dichloromethane solution is comparable to that obtained for DMSO, whereas for acetonitrile, the radiative lifetime is as low as 208 µs. Such difference in $\tau_{\rm rad}^{\rm calc}$ may result from the symmetry changes in different solvents and the presence of a larger number of pronounced vibrational absorption bands in the 3200–2000 cm^{-1} and 1700–1300 cm^{-1} regions in the case of acetonitrile as compared to DMSO and dichloromethane [63-65].

For each investigated complex, the branching ratio and emission cross-section of the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition are higher than those for the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ transition. It is quite uncommon since, in the literature, only the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ transition is generally considered suitable for lasing. Our calculations of the stimulated emission cross-section of the ${}^4\mathrm{F}_{3/2} \rightarrow {}^4\mathrm{I}_{11/2}$ transition give $\sigma_{em} = 4.92 \times 10^{-20} \mathrm{~cm^2}$ for complex b dissolved in DMSO, and for the solution of complex c, σ_{em} reaches $5.65 \times 10^{-20} \ {\rm cm}^2.$ These values exceed σ_{em} obtained in the literature for the Nd³⁺ complexes with similar 1,3-diketonate ligands. Indeed, Wang et al. [59] report $\sigma_{em} = 3.02 \times 10^{-20}$ cm² for the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition for Nd³⁺ complexes dissolved in poly(methyl methacrylate). Authors, however, do not provide any information on the stimulated emission cross-section for the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. According to Krupke et al. [66], where this transition has been considered in neodymiumdoped gadolinium scandium gallium garnet, σ_{em} is $3.0\times10^{-20}~{\rm cm}^2.$ In our calculations, the maximum values of σ_{em} for the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition were obtained for complex c. For the solid sample, we have $\sigma_{em} = 1.72 \times 10^{-19} \text{ cm}^2$, which is twice as large as the result obtained for the solution: $\sigma_{em} = 8.21 \times 10^{-20} \text{ cm}^2$.

For DMSO solutions of complexes *a*, *b*, and *c*, radiative lifetimes τ_{rad}^{calc} calculated in the framework of the Judd–Ofelt theory are 279 µs, 268 µs, and 240 µs, respectively. The corresponding times for the complexes in KBr pellets are shorter, and their estimates are 221 µs, 221 µs, and 167 µs. Quantitative estimations of the quantum yields of lanthanide-centered luminescence with excitation via ligand environment can be obtained as $\Phi = \tau_{exp}/\tau_{rad}^{calc}$. The results are presented in Table 4. The calculated values are more than twice as large as those for the Nd³⁺ 1,3-diketonate complexes with pyrazole-substituted ligands containing no CF groups [28].

The quantum yield of complex *a* was measured as 0.93%, for complex *b* we obtained 0.75%, and the corresponding value for complex *c* was 1.08%; relative measurement error was 20%. The measured

and calculated quantum yields Φ_{ext} agree within the corresponding errors. The measured quantum yields considerably exceed the typical values (0.1–0.6%) reported for neodymium complexes with other 1,3-diketonate ligands [23–25].

From the data on the measured decay times τ_{exp} and the radiative lifetimes τ_{rad}^{calc} calculated in the framework of the Judd–Ofelt theory, we obtain the nonradiative relaxation rates for the investigated complexes in solutions. The results are presented in Supplementary materials, Tables 6 and 8. It follows from these data that the nonradiative rate for complex *c* decreases by 8% with respect to that for complex *a*. Therefore, we conclude that the increase in the fluorinated chain length in pyrazolic 1,3-diketonate ligands suppresses the nonradiative processes. Nevertheless, we observe an opposite effect for solid samples, which can be due to the interaction with phonons.

4. Conclusion

Herein, we synthesized a series of novel intensive NIR-emitting Nd³⁺ complexes with pyrazolic 1,3-diketone main ligands bearing $C_x F_{2x+1}$ groups, and a 1,10-phenanthroline ancillary ligand. Based on the spectroscopic studies, we demonstrate that, with increasing the number of fluorine atoms in the diketone, a gradual decrease in the energy gap between the triplet level of the ligand environment and the ${}^{4}F_{3/2}$ resonant level of Nd3+ occurs, enhancing the measured PLQY up to 1.1% that significantly exceed the typical values for neodymium complexes with 1,3-diketonate ligands. The latter effect is also governed by the suppression of nonradiative relaxation processes, as shown by the Judd-Ofelt analysis. Thus, for the DMSO solution of the complex with x = 6, the nonradiative relaxation rate decreases by 8% with respect to that of the complex with x = 1. The most intensive luminescence of the complexes is observed for the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ transition commonly used for lasing in inorganic matrices (qlass, garnet crystals, etc.). However, in the complexes under investigation, the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition unexpectedly makes the major integral contribution to the luminescence of the compounds. Moreover, performed calculations revealed that the high branching ratio of the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition corresponding to the 880 nm emission substantially increases with elongation of fluorinated chains, which makes the synthesized Nd³⁺ complexes promising candidates for luminescent materials with an uncommon branching ratio distribution. These complexes are suitable for OLED applications as purely NIR-emissive layers.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108558.

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