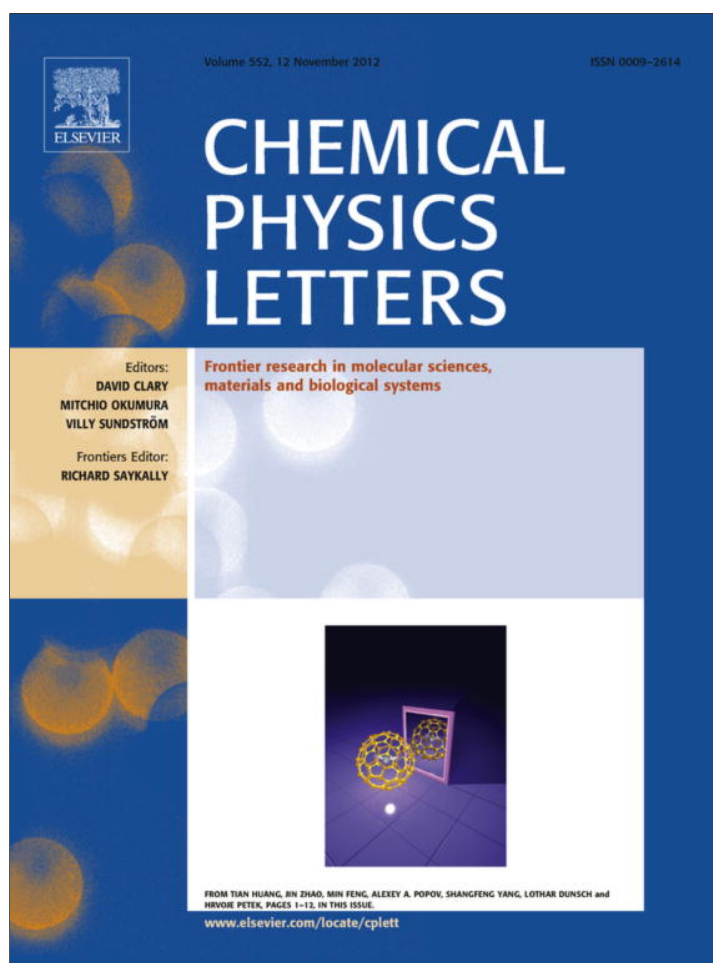


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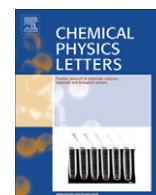
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Registration of radical anions of Al, Ga, In tris-8-oxyquinolinates by magnetosensitive and spectrally resolved recombination luminescence in benzene solutions

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ABSTRACT

Formation and recombination of transient radical anions of Al, Ga, and In tris-8-oxyquinolinates (Alq₃, Gaq₃, and Inq₃), the key species in certain organic electroluminescing devices, was studied in X-irradiated benzene solution. The spectra of recombination luminescence were obtained and effective yields of recombination luminescence referred to Alq₃ were estimated as 0.3 (Gaq₃) and 0.15 (Inq₃). Magnetic field effects in recombination luminescence involving the radical anions of the three oxyquinolinates were obtained, from which hyperfine coupling constants at the central ions were estimated as 0.45 ($I_{Al} = 5/2$), 0.8 ($I_{Ga} = 3/2$), and 0.6 ($I_{In} = 9/2$) mT for radical anions of Alq₃, Gaq₃, and Inq₃, respectively.

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1. Introduction

Aluminum oxyquinolinates (Alq₃) are representative electroluminescing and charge transport agents for organic electro-optical systems [1]. The luminescent properties of Alq₃ and the possible ways of their tuning by external factors therefore draw much attention in view of improving the efficiency of electro-optical conversion and creation of multifunctional devices, including magneto-controlled organic light-emitting diodes (OLEDs) [2] and OLED-based magnetometers [3]. However, despite the recent boost of studies in this area [4], the mechanism of magnetic field effects in electroluminescing organic systems is still far from being completely understood. One of the hindering factors is the complexity of such devices, commonly multilayer heterogeneous systems with several functionally distinct layers made of different pure or highly doped materials [5]. The experimentally observed characteristics for such structures, e.g., the yield of electroluminescence as a function of applied bias voltage, are ultimately determined by the properties of this system as a whole, including the interfaces, which complicates the link between the observed experimental curves and the microscopic properties of individual charge carriers or luminophores present in the system.

The understanding of the underlying mechanisms of magnetic field modulation in organic electroluminescing systems can be enhanced by studying the properties of the isolated radical ions and excited states forming upon recombination of these radical ions in model systems. In this Letter we generated radical anions of Al, Ga, In oxyquinolinates as constituents of a spin-correlated radical ion pair by X-ray irradiation of benzene solution, obtained the spectra of their recombination luminescence that closely mimics electroluminescence in OLEDs, and studied their magnetic properties with MARY (Magnetically Affected Reaction Yield) spectroscopy using magnetic field modulation of the intensity of recombination luminescence.

2. Experimental

2.1. Preparation of Al, Ga, In tris-8-oxyquinolinates

Al(III) Tris-8-oxyquinolate (Alq₃) was prepared by mixing ethanol solution of 8-hydroxyquinoline (151.2 mg, 1.0 mmol) and water-ethanol solution of aluminum sulfate (49.2 mg, 0.18 mmol) under moderate heating and continuous stirring, pH was adjusted to pH ~ 6 with aqueous NH₃. Concentration of the reaction mixture gave Alq₃ as a yellow residue that was collected and dried in air. Calculated for Alq₃: N 9.2 C 70.6 H 3.92, Found: N 8.9 C 69.5 H 4.3. Powder X-ray diffraction demonstrated that the crystalline phase consisted of the fac-Alq₃ isomer [For this and other compounds the experimental diffraction patterns were compared to

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theoretical ones generated from the single crystal data (Cambridge Structural Database ver. 5.32), www.ccdc.cam.ac.uk].

To obtain Ga(III) tris-8-oxyquinolate (GaQ_3), Ga(III) chloride was prepared by dissolving metallic gallium (254.25 mg) in hydrochloric acid under moderate heating. The acid was evaporated and distilled water was added to obtain the working GaCl_3 solution. One milliliter of the prepared Ga(III) chloride solution (0.365 mmol) was mixed with ethanol solution of 8-hydroxyquinoline (153.0 mg, 1.06 mmol), and pH was adjusted to $\text{pH} \sim 8$ with aqueous NH_3 . The precipitated yellow solid was collected by filtration, washed several times with hot water and alcohol, and air-dried. Calculated for $\text{GaQ}_3 \cdot \text{EtOH}$: N 7.7, C 63.5, H 4.4. Found: N 7.6 C 61.1 H 4.4. Powder X-ray diffraction demonstrated that the crystalline phase consisted of a solvate of mer- $\text{GaQ}_3 \cdot \text{EtOH}$ isomer. To remove crystallization alcohol, the compound was heated at 210°C for 4 h, as TGA demonstrated that this leads to desolvation without causing decomposition of Ga tris-8-oxyquinolate itself. X-ray diffraction confirmed that fac- GaQ_3 isomer without the solvated ethanol was thus obtained.

To obtain In(III) tris-8-oxyquinolate (InQ_3) a solution of In(III) nitrate was prepared by dissolving metallic indium (95.55 mg) in nitric acid upon heating (the reaction does not proceed without heating). The acid was removed by an air stream to avoid decomposition of the nitrate, and distilled water was added to obtain the working solution. The prepared In(III) nitrate solution (0.83 mmol) was mixed with ethanol solution of 8-hydroxyquinoline (362.3 mg, 2.5 mmol), and pH was adjusted to ~ 9 with aqueous NH_3 . The precipitated yellow solid was collected by filtration, washed several times with hot water and alcohol, and air-dried. Calculated for $\text{InQ}_3 \cdot \text{EtOH}$: N 7.1, C 58.7, H 4.0. Found: N 7.1, C 57.5, H 4.0. Powder X-ray diffraction demonstrated that the crystalline phase consisted of the mer- $\text{InQ}_3 \cdot \text{EtOH}$ isomer. To remove crystallization alcohol, the compound was heated at 210°C for 4 h, as TGA demonstrated that this leads to desolvation without causing decomposition of In tris-8-oxyquinolate itself. Powder X-ray diffraction confirmed that fac- InQ_3 isomer without the solvated ethanol was obtained.

Experiments on radiation and photoinduced luminescence were performed on a home-built setup comprising an X-ray tube (BSV-27, Mo, $40\text{ kV} \times 20\text{ mA}$) for steady-state generation of radical ion pairs and a PMT (FEU-100) with a system of lenses and a grating monochromator (MDR-206, objective focus length 180 mm, grating 1200 lines/mm, inverse linear dispersion 4.3 nm/mm) for registration of luminescence spectra. To compare the spectra of luminescence under X-ray and photo generation from the same sample the X-ray tube was substituted with a high pressure mercury lamp DRSh-500 with double monochromator DMR-4 to select spectral line for excitation. All presented spectra were recorded in cylindrical ampoules made of molybdenum glass with outer diameter 5 mm and inner diameter 3 mm placed in a tight lead jacket with outer diameter 9 mm having two 2 mm wide vertical collimating slits at 90° to each other for the incident radiation and the detected luminescence, which suppresses the residual intrinsic X-ray generated luminescence of the glass. Regular Suprasil or other quartz ampoules produce much stronger intrinsic luminescence under X-irradiation, contaminating the luminescence spectrum, and had to be avoided for taking luminescence spectra under X-rays. The registration optical system collects light from the entire illuminated spot and was calibrated by black body radiation using a reference incandescent lamp with known temperature of the filament illuminating a sputtered MgO diffuser. For all presented spectra the input and output slits of the registration monochromator were set at 2.2 and 2.2 mm, the spectra were obtained by averaging over six wavelength scans each with total time for six scans about 2 h. All shown spectra of luminescence were

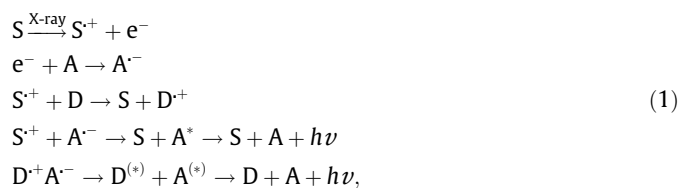
recorded in identical conditions in the same ampoule and were corrected for the spectral sensitivity curve of the registration system, all photoinduced spectra were reduced to the same fraction of absorbed light, the spectra of radiation-induced luminescence were not additionally processed. For comparison, standard photoinduced luminescence spectra were also recorded on a factory calibrated FLS-920P spectrofluorimeter (Edinburgh Instruments), which turned out to be practically identical to spectra taken on the described home-built setup with excitation at the 366 nm line of the mercury lamp. Optical absorption spectra were recorded on a Shimadzu UV-2401 spectrophotometer in a 2 mm cuvette.

Experiments on MARY spectroscopy were performed on a home-built setup described elsewhere [6] based on a modified CW-ESR spectrometer. The typical look of the MARY spectrum and its interpretation can also be found in the cited work. The presented MARY spectra are steady-state magnetic field effects on the intensity of recombination luminescence generated by X-ray irradiation. A sample in a quartz ampoule was placed in the magnetic field of a Bruker ED-200D ESR spectrometer equipped with an X-ray tube (BSV-27, Mo, $40\text{ kV} \times 20\text{ mA}$) for steady-state generation of radical ion pairs and a PMT (FEU-130) with quartz lightguide for registration of fluorescence, no spectral selection was employed. An additional shift coil with a dedicated power supply is placed on one of the poles of the ESR magnet to create a constant field opposing the scanned field of the magnet. In the presented spectra this shifted field is shown as 'negative'. As in conventional ESR spectrometer, field modulation and lock-in detection are used for producing first-derivative spectra. The PMT signal was fed to a Stanford Research Systems SR-810 Lock-In Amplifier synchronized with the modulation unit of the spectrometer. The scanned field was modulated at 12.5 kHz with amplitude 0.2–1 mT. The output of the lock-in amplifier was fed to PC for averaging and storage. The field was scanned at a rate of 200 sec/scan with time constant of the lock-in amplifier 1 s and 512 points per scan, a total of 20–100 scans per spectrum were accumulated.

Prior to experiment all samples were degassed down to $\sim 10^{-3}$ mmHg (0.1 Pa) with several 'freeze-pump-thaw' cycles to remove paramagnetic oxygen from solution. All experiments were performed at room temperature in benzene solutions. The solvent, benzene (Aldrich 99.8%), and the compounds were used without additional purification. In all experiments the initial Ga and In solvates and the dried compounds behaved identically, the spectra for the solvates are presented below. The type of the isomer taken for sample preparation is also not important, as in solution fac-isomer rapidly converts into mer-isomer [7], and when working with solution we always have the mer-isomers. The required sample volume to register luminescence spectra and MARY spectra was 0.3 and 0.6 mL, respectively.

3. Results and discussion

Solvent holes and free electrons forming upon ionization of solvent by X-irradiation can be captured by electron donor and acceptor molecules, respectively. In benzene solution tris-8-oxyquinolates of Al, Ga, and In can be expected to act both as electron donor and acceptor, as they have relatively low ionization potentials and high electron affinity. Gas phase ionization potential for benzene is 9.24 eV [8], theoretically estimated ionization potential and electron affinity for AlQ_3 amount to about 6 and 1 eV, respectively [9]. However, these values have been reported only for the aluminum complex and were optimized for compact solid phase, so the question of radical ion formation in benzene solution is still open. The following standard scheme of radiation-chemical processes in the systems under study is adopted [10]:



where S is solvent (benzene), D is electron donor (oxyquinolate or another donor deliberately added to the system, *vide infra*), and A is electron acceptor (oxyquinolate).

First, the spectra of radiation-induced luminescence for benzene solutions of Al, Ga, and In tris-8-oxyquinolates were obtained (Figure 1) and compared with the spectra of luminescence induced by optical irradiation at 366 nm, which is within the absorption band of all three oxyquinolates (Figure 2). The emission spectra are a single broad unresolved line with maximum at about 525 nm for Alq₃, slightly shifting to longer wavelength with increasing the mass of the central ion. Radiation-induced luminescence spectra are similar to photoinduced spectra, both obtained here and reported in the literature [11]. The free ligand itself, 8-hydroxyquinoline, in these conditions does not produce luminescence (spectra not shown), and furthermore it is not expected to appear here. When the spectrum of photoinduced luminescence for Alq₃ was scaled so that the maxima of photoinduced and radiation-induced spectra of Alq₃ coincided (see Figure 1), the area under the radiation-generated spectrum coincided with the area under the photoinduced spectrum within 5%. All this leads to the conclusion that upon X-ray irradiation of the benzene solution of the quinolates, despite a different mechanism for generation of the excited state as compared to direct optical excitation, it is the corresponding oxyquinolate that produces the observed luminescence. The differences between the three complexes are only in the area under the spectra of luminescence, and thus in different quantum yields of photoinduced luminescence and different effective yields of radiation-induced luminescence for the compounds under study.

All yields were estimated relative to Alq₃. The absolute quantum yields of fluorescence for Alq₃ in ethanol and chloroform are 0.116 and 0.223, respectively [12], we failed to find a reference for the absolute quantum yield in benzene. The relative quantum yields of photoinduced luminescence for Gaq₃ and Inq₃ in benzene solution calculated from the ratio of areas under the spectra were found to be 0.43 and 0.85 for Gaq₃ and Inq₃, respectively, this ordering of the quantum yields of the three quinolates agrees

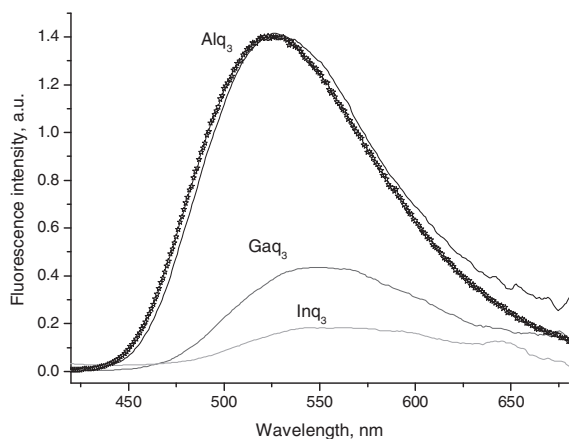


Figure 1. Spectra of luminescence for 10⁻³ M solutions of Al, Ga, In tris-8-oxyquinolates in benzene (solid lines, top to bottom) under X-ray irradiation of the sample. For comparison stars show photoinduced luminescence spectrum of Alq₃ in benzene solution taken on a FLS-920P spectrofluorimeter.

with literature [13]. The relative yields of radiation-induced luminescence were also estimated from the ratio of areas under the corresponding spectra (Figure 1). Taking the spectrum of radiation-induced luminescence of Alq₃ under X-ray irradiation as the reference, the relative yields of the radiation-induced luminescence for the two other oxyquinolates were estimated as 0.3 and 0.15 for Gaq₃ and Inq₃, respectively.

The relative quantum yields of photoinduced luminescence differ from the effective yields of the radiation-induced luminescence for the three compounds both numerically and by the ordering of the three complexes. It can be inferred that the effective yield of radiation-induced luminescence upon generation of the luminescing excited state via radiation-induced radical ion pairs is determined not only by the intrinsic luminescence quantum yield of the excited state, but also by the preceding processes of its generation similar to electroluminescent devices [13]. As demonstrated the magnetic field experiments described below, in the discussed radiation-induced generation of the luminescing excited state of Mq₃ several consecutive processes are involved. First Mq₃ radical ions are generated as constituents of a singlet spin-correlated radical ion pair, then singlet-triplet spin evolution of the pair takes place, and its spin-selective recombination leads to a singlet or triplet-state product, with probability of forming the ground S₀ or excited S₁ singlet state upon pair recombination depending on the relative position of the energy levels of the radical ion pair and the product.

Many of the mentioned processes are also called upon to explain the operation of electroluminescing devices [1–5]. Basically, in a forward-biased OLED holes and electrons are injected from two electrodes into the hole and electron transport layers, respectively, and migrate in the applied electric field toward the inter-layer interface. Here the polaron pairs recombine to produce singlet or triplet excitons, depending on the multiplicity of the pair. Since the pairs were initially not correlated, the fractions of the singlet and triplet excitons are governed by spin statistics and are 1/4 and 3/4, respectively. The singlet-state excitons emit the desired quantum of electroluminescence, but the 3/4 of the pairs that happened to be in triplet spin state produce dormant triplet excitons – the efficiency with which those can be converted into quanta determine the ultimate optical efficiency of the device. One option is to introduce a suitable secondary emitter with high yield of phosphorescence into the material. However, the long-lived triplet excitons can also undergo fission into a triplet-correlated polaron pair partially followed by back recombination, which can produce singlet excitons if spin conversion can proceed in the separated pair. Furthermore, at high charge injection densities the concentration of the triplet excitons can be high enough to open the second-order channel of triplet-triplet recombination, also partially leading to singlet exciton formation. Another complication of the higher polaron densities in an operated OLED is the possibility of bipolaron formation and spin-dependent polaron scattering – the processes that are impossible in dilute X-irradiated solutions. Further studies of the effective yield of radiation-induced luminescence in the suggested simpler systems can help optimize the properties of electro-optical devices.

In the MARY spectroscopy [14–21] experiments we first checked that blank solvent produces no magnetosensitive luminescence, i.e., recombination of solvent radical cations and electrons in X-irradiated benzene does not produce observed MARY signal, and the latter appears only after introducing the complex into solution [22]. Benzene has non-zero quantum yield of luminescence [23] and, as the measurement shows, fluoresces under X-rays in the conditions of the described experiment (its band is found to the left of the Mq₃ band and was cut off in luminescence spectra given in Figure 1). Furthermore, trace amounts of impurities present in the solvent could have acted as charge acceptors

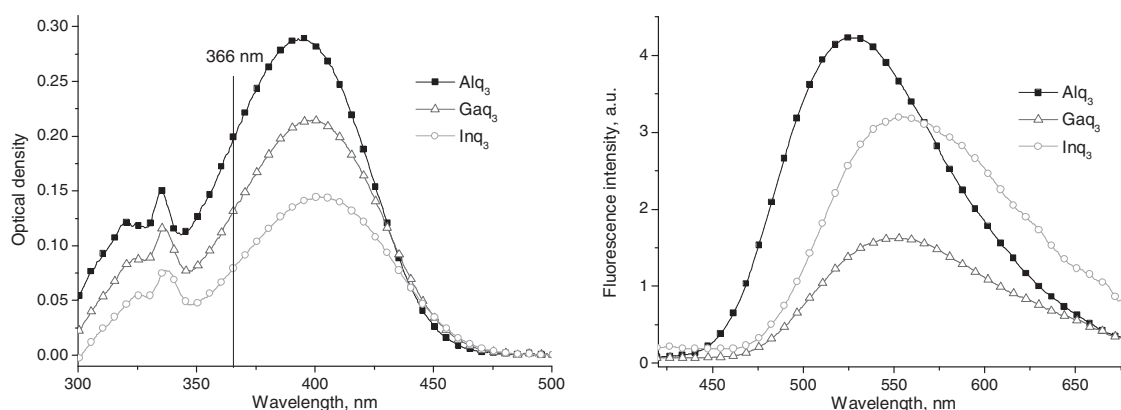


Figure 2. Optical absorption spectra of 1.8×10^{-4} M Al, Ga, In tris-8-oxyquinolinates in 2 mm cuvette corrected for solvent absorption and baseline (left); spectra of luminescence for 3×10^{-4} M solutions of Al, Ga, In tris-8-oxyquinolinates in benzene under optical excitation at 366 nm (right).

to produce radical ion pairs. However, it was verified that emission from neat benzene used as the solvent in these experiments was not magnetosensitive. Addition of 1,2,4,5-tetramethylbenzene (durene), a well-known electron donor and luminophore, to benzene also did not produce magnetosensitive signal due to fast recombination of the pair $\text{durene}^{\cdot+}/\text{e}^-$ comprising free electron with very high mobility.

Adding any of the three oxyquinolinates into benzene gives rise to magnetosensitive luminescence, with typical MARY spectra shown in Figure 3, consistent with earlier reported magnetic field effects reported for electroluminescing devices comprising Alq_3 [24–27]. The phase of the effect (increase of emission yield with increasing magnetic field) is consistent with initial singlet spin state of the X-ray generated radical ion pairs and the observed

singlet excited product of recombination. The range of magnetic fields over which the effect develops indicates a hyperfine-induced mechanism of magnetic field effect, which is also invoked for discussing magnetic and spin effects in OLEDs. However, as thoroughly discussed in [27], the observed magnetic field effects in Alq_3 -based OLEDs may vary with actual device construction and material used for electrodes and hole transport layer and the applied bias voltage. Furthermore, the mechanism of polaron mobility, i.e., hopping over the matrix, is different from diffusion in solution and leads to averaging out the hyperfine interactions. Finally, the critical contribution of spin-selective processes involving triplet excitons has been implied for OLEDs. The presented spectra are much simpler and straightforward to interpret, they look like normal solution spectra from pairs built of organic radical ions [6], and will be further analyzed as such.

This appearance of the MARY spectra together with the X-ray generated luminescence spectra indicate that irradiation of benzene solutions of the oxyquinolinates produces their radical anions ($\text{Mq}_3^{\cdot-}$), and the observed luminescence is generated via recombination of these radical anions with the counter-ions (exchange-narrowed radical cation of benzene) and generation of electronically excited state of the corresponding oxyquinolinolate. As Figure 3 shows, the three complexes produce different MARY spectra: the width of the magnetic field effect (the distance from the zero of the field to the maximum of the derivative curve) determined by the overall hyperfine interactions in the recombining pair [28], and the width of the low-field line (an inflection in the vicinity of zero field, referred to as MARY line or LFE) due to coherent locking of spin evolution in the pair in the points of energy level crossing [29–35], both increase in the series from Al to In, and MARY line becomes more pronounced. Such a behavior of MARY spectra in a series of systems with similar structures is typical for increasing second moment of the ESR spectrum of the pair partner with dominant hyperfine couplings (HFC) [6], in this case – oxyquinolinolate radical anions. Since all three complexes have an equal number of identical ligands, the difference in magnetic field effect comes from the central ion, which thus must participate in formation of signal from the radical anion of the corresponding complex.

Next the magnetic parameters of the radical anion were estimated from modeling of the experimental MARY spectra. The latter are mostly determined by the overall magnetic interactions in the radical ions of the pair (the second moments of their ESR spectra) [36–38], and the experimental spectra can be reproduced in different models. The spectra were modeled using a Maple 10 program developed together with Prof. J.B. Pedersen in [39] that is scalable for arbitrary numbers and spins of the considered nuclei and can

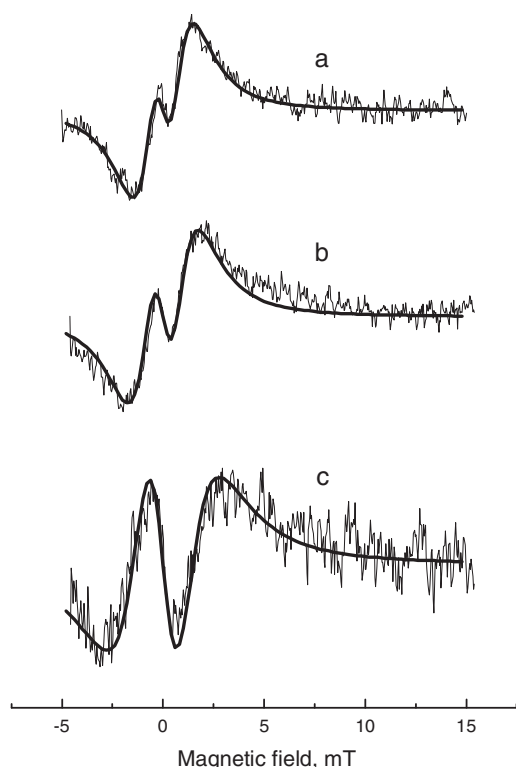


Figure 3. Normalized by maximum MARY spectra for solutions of 10^{-3} M Al (a), Ga (b), In (c) tris-8-oxyquinolinates in benzene and their modeling with the following parameters: (a) $a(I=5/2) = 0.45$ mT, $\tau = 4.5$ ns; (b) $a(I=3/2) = 0.8$ mT, $\tau = 4.5$ ns, (c) $a(I=9/2) = 0.6$ mT, $\tau = 4$ ns (see text for details).

use any recombination kinetics. The calculated spectra shown in Figure 3 were obtained within the following model: radical anion has one nucleus with spin corresponding to the central metal ion ($I(\text{Al}) = 5/2$, $I(\text{Ga}) = 3/2$, $I(\text{In}) = 9/2$), inhomogeneous width of the ESR spectrum of the radical cation was set to zero, the spectra were calculated using exponential distribution of pair spin evolution time. The varied parameters were the HFC constant at the metal center and the spin evolution time τ . On one hand, the chosen model is very simple, and on the other hand it adequately reproduces the actual state of affairs. The modeling turned out to be not sensitive to substituting a power law kinetics [40,41] for the exponential one and to introducing additional spin $1/2$ nuclei in the radical anion, but did require no appreciable HFC in the radical cation. Inhomogeneous width of the ESR spectrum of the radical cation tends to zero due to fast degenerate electron exchange reaction of the radical cation in the matrix of its parent molecules, and for the benzene radical cation it is estimated to be below 0.01 mT. Almost identical experimental spectra were also obtained for solutions of Al tris-8-oxyquinolate in deuterated benzene and in toluene, confirming the participation of the exchange-narrowed solvent radical cation as the radical cation partner of the observed pair. The homogeneous spectrum width for the recombining pair partners is determined by time τ .

This modeling produced a reasonable agreement with experiment and yielded the following HFC constants at metal centers: 0.45, 0.8, and 0.6 mT for Al, Ga, and In, respectively. A literature search demonstrated that the HFC constants at the metal center in similar matrix-stabilized radicals studied by ESR are indeed not large and comparable with those estimated here [42]. The low HFC constant values are probably due to the fact that in such octahedral complexes the unpaired electron in the radical anion delocalizes onto a practically pure d-orbital (of the d_{xy} , d_{xz} , d_{yz} subset) of the metal ion, while substantial s-character is observed mostly for hybrid {spd} orbitals forming the octahedrally directed bonds, which lack the unpaired electron. Furthermore, according to reference data [42], minor HFC couplings can also be present for certain magnetic nuclei (N, H) of the ligands. However, the calculations show that accounting for such constants in modeling MARY spectra for the Mq_3 complexes practically does not change the result. The insensitivity of the modeling to additional nuclei is rationalized as follows. The second moment of the ESR spectrum of the radical anion is mostly determined by HFC with the high-spin metal nucleus, as in this case the ESR spectrum has a characteristic box-like shape with a large contribution from the outermost lines, and addition of magnetic nuclei in organic ligands with comparable HFC constants only weakly changes the second moment. Thus the values of HFC constants obtained within such a simple model are a quite reasonable estimate.

A well-established direct measure of effective hyperfine couplings that can be obtained from experimental spectra without modeling is the field $B_{1/2}$ where the magnetic field effect curve reaches half its saturation value. This metric was first suggested and verified in [28] for non-modulated measurements and was later adapted for more convenient modulated MARY spectra as used in this Letter in [37]. Combining the needed results from these two papers, the position of the maximum at the derivative MARY spectrum B_p can be written as:

$$B_p = 2 \frac{\sigma_1^2 + \sigma_2^2}{\sigma_1 + \sigma_2}, \quad \sigma_i^2 = \sqrt{\frac{1}{3} \sum_{ix} I_{ix}(I_{ix} + 1) a_{ix}^2}, \quad (2)$$

where $\sigma_{1,2}^2$ is the conventional second moment of the ESR spectrum for each of the pair partners, with the assumption that the zero field MARY line is not too prominent and can be neglected, and also ignoring additional broadening due to the processes of degenerate electron exchange. When one of the partners has negligible

hyperfine couplings, as is the case for the solvent radical cation here, this reduces to:

$$B_p = 2\sigma. \quad (3)$$

The measured B_p values and the calculated σ values for the three spectra in Figure 3 were found to be 1.5 (0.77), 1.8 (0.89), and 2.8 (1.72) for Alq_3 , Gaq_3 , and Inq_3 , respectively. It can be seen that relation (3) indeed holds very well for Alq_3 and Gaq_3 , and the apparent discrepancy for Inq_3 comes from the well-developed MARY line in the spectrum, so that the expression (2) is no longer valid. We also note that there is no noticeable exchange broadening from the Mq_3 radical anion in the spectrum, and indeed for the used concentrations (10^{-3} M) and solvent viscosity (0.65 cP for benzene at room temperature) its contribution should be well below 0.1 mT.

To directly verify that the observed MARY signal is generated in the pairs 'radical anion of the complex/solvent radical cation' the following experiment was performed. An electron donor producing a radical cation with well-known magnetic parameters, 1,2,4,5-tetramethylbenzene (durene), was added to benzene solutions of the complexes in concentration 10^{-2} M, which is an order of magnitude higher than complex concentration and ensures efficient capture of radical cations. Durene radical cation has 12 equivalent protons with HFC constants $a = 1.15$ mT [43]. Figure 4 shows a typical MARY spectrum of Alq_3 with durene in benzene solution, similar spectra were produced by the other two complexes. For all three complexes the width of the magnetic field effect increases and the low-field MARY line (LFE) practically disappears, as could be expected for a radical ion pair with both partners having comparable and substantial hyperfine couplings [44]. The spectra were modeled by taking the radical anion from the previous model, and taking the known parameters of durene radical cation for the second partner. Such a modeling, an example of which for Alq_3 is also shown in Figure 4, reproduces the observed spectra rather well. Thus, all the observed MARY spectra are indeed generated via recombination of pairs comprising the oxyquinolate radical anion and either solvent hole or durene radical cation as the counter-ion.

As mentioned earlier, the studied complexes in the conditions of the described experiment could produce radical cations as well, since their known or estimated ionization potentials (about 6 eV) [9] are much lower than for benzene used as solvent. However, no traces of their presence were found in MARY spectra. In line with the durene experiment described above, in which the radical cation of the pair was substituted for a known one, experiments were performed with standard electron acceptors, hexafluorobenzene and 1,4-difluorobenzene, that form radical anions with known hyperfine parameters and produce themselves excellent MARY spectra

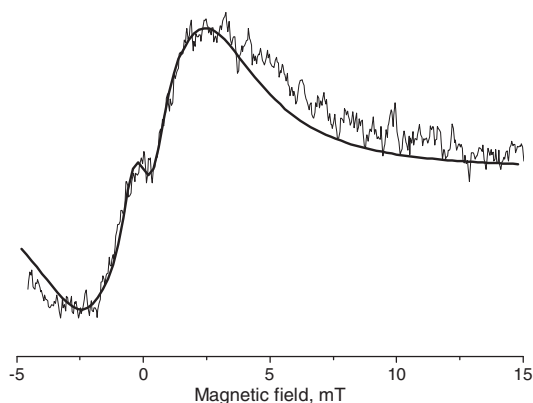


Figure 4. MARY spectrum for 10^{-3} M solution of Al tris-8-oxyquinolate and 10^{-2} M durene in benzene and its modeling with the following parameters: radical anion ($I = 5/2$, $a = 0.45$ mT), radical cation ($12 \times I = 1/2$, $a = 1.15$ mT), $\tau = 6$ ns.

in benzene from the pairs of the type ($S^+/\text{C}_6\text{F}_6^-$). However, in these cases the spectra turned out to be a pure superposition of spectra from the pairs ($S^+/\text{C}_6\text{F}_6^-$) and (S^+/Alq_3^-), no signs of signals from the cross pair ($\text{Alq}_3^+/\text{C}_6\text{F}_6^-$) were found. These experiments indicate that the pairs comprising the radical cation of the complex either do not form in the described conditions, or, more likely, are not observable in the discussed experiment. This can be if the energy releasing upon pair recombination is not sufficient to produce an excited singlet state capable of fluorescing. A known example of such 'dark' recombination is the pair of hexafluorobenzene radical anion and tetramethylphenylenediamine (TMPD) radical cation in alkane solution, in which the high electron affinity of C_6F_6 (0.7 eV [8]) and low ionization potential of TMPD (6.2 eV [45]) together render the recombination into singlet excited state of the product energetically impossible [46,47]. The estimated ionization potential and electron affinity of tris-8-oxyquinolinates are quite similar to the corresponding values for the TMPD/ C_6F_6 pair.

4. Conclusions

In this Letter we demonstrated that radical anions of Al, Ga, and In tris-8-oxyquinolinates are formed in benzene solution under X-irradiation. The radical anions produce recombination luminescence with emission spectrum identical to photoinduced luminescence of the complexes themselves. The relative yields of radiation-induced luminescence (arbitrary taking the yield for Alq_3 as one) were estimated as 0.3 and 0.15 for Gaq_3 and Inq_3 , respectively, with the ordering of the complexes by the efficiency of recombination luminescence differing from their ordering by the quantum yield of photoinduced luminescence, which was previously mentioned for electroluminescing devices as well. For radical ion pairs 'solvent radical cation/complex radical anion' MARY spectra were obtained that confirm participation of the central ions in formation of the signal of magnetosensitive luminescence. Hyperfine coupling constants for the central ions in the radical anions of tris-8-oxyquinolinates were estimated as 0.45 ($I_{\text{Al}} = 5/2$), 0.8 ($I_{\text{Ga}} = 3/2$), and 0.6 ($I_{\text{In}} = 5/2$) mT for Al, Ga, and In, respectively.

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