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MARY spectroscopy in the presence of coordination compound $Zn(hfac)_2(PPO)_2$

N.V. Sergey [a,*], A.B. Burdukov [b], N.V. Pervukhina [b], L.V. Kuibida [a,c], I.P. Pozdnyakov [a,c], D.V. Stass [a,c]

[a] *Institute of Chemical Kinetics and Combustion SB RAS, 3, Institutskaya Str., 630090 Novosibirsk, Russia*
[b] *Nikolaev Institute of Inorganic Chemistry, 3, Acad. Lavrentiev Ave., 630090 Novosibirsk, Russia*
[c] *Novosibirsk State University, 2, Pirogova Str., 630090 Novosibirsk, Russia*

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ABSTRACT

MARY spectroscopy is finding increasing use in the studies of transient organic radical ions and their reactions. Extending this technique to organometallic species will broaden the class of potential target compounds and can help answer important mechanistic questions in organometallic and spin chemistry. We probed this approach using a tailored $Zn(hfac)_2(PPO)_2$ complex. The synthesized complex has quantum yield and fluorescence lifetime (*n*-decane solution) $\varphi \sim 0.8$ and $\tau \sim 1.3$ ns, respectively. For this type of complex it is the first observation of MARY spectra different from those of free ligand, thus implying participation of the complex in the development of the observed signal.

1. Introduction

A clear trend in chemistry today is targeted synthesis of new compounds, which requires an advanced level of understanding and control over reaction mechanisms. However, often the critical stage of a chemical transformation involves a known or postulated short-lived intermediate that actually determines the chemistry, but cannot be readily isolated and conveniently studied. Important clues on the mechanism can then be deduced from indirect physicochemical experiments that probe the intermediate 'on the fly' imprinting its properties on some observable data such as polarization pattern in an NMR spectrum, or the magnetic field dependence of fluorescence intensity [1]. Probing short-lived paramagnetic intermediates, such as radical and radical ion pairs, with static and oscillating magnetic fields has provided a wealth of important data on the reaction mechanisms for organic chemistry [2]. Short-lived transient species in inorganic chemistry is a less commonly discussed subject, although they undoubtedly play roles similar to their organic counterparts, and redox and bond cleavage processes can also proceed via radical – or radical-ion – type species derived from inorganic complexes or clusters. As these transient species are very reactive and thus have rather short lifetimes, they cannot be isolated and studied by conventional methods, such as XRD, suitable for stable compounds. New methods are needed to study short-lived intermediates in inorganic processes and reaction mechanisms that they mediate. Furthermore, the sensitivity of such a method to certain specific property of the assumed intermediate, such as the presence of spin and/or charge, can be a particular advantage over the more general techniques like optical absorption spectroscopy.

In this work we explore the possibility of adapting one of the recently developed spin-sensitive techniques, MARY (level-crossing) spectroscopy of radical ion pairs in non-polar solutions, to the study of transient organometallic species. The method was formulated for organic radical ions, and has proved useful in detecting several important classes of hitherto unseen radical ions with lifetimes of just several nanoseconds, such as primary solvent radical cations (holes) in irradiated alkanes [3] and radical ions of several fluorinated [4] and methylated [5] benzenes. The method is also useful for studies of reactions involving short-lived radical ions, such as the reactions of ion-molecular charge transfer [6,7], dimerization and higher aggregation [8], and monomolecular chemical decay [9]. Being useful for short-lived organic radical ions, the method looks promising for the study of short-lived transient states of metal-centered complexes, provided these can play the role of radical ions of the original radical ion pairs. In case of success, a new highly specialized but also highly sensitive method would become available to study the mechanisms and intermediates, e.g., unusual transient valent states, for inorganic chemistry. On the other hand, a whole new class of systems will be also opened for magnetic field effect studies, including but not limited to MARY spectroscopy. Radical-ionic states of complexes based on central metal ions are very interesting in this respect since the metal ion can have nuclear spin other than ½ or 1, to which nuclei in organic radicals are usually limited, and rather high hyperfine couplings to these heavy nuclei. Furthermore, complex compounds can be very useful for magnetic and spin effect studies as the central ion can be readily changed without changing the ligand environment, and thus a series of similar systems can be generated that can have widely varying magnetic properties. In the next

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* Corresponding author. Fax: +7 383 3331561.
E-mail address: arabadzhi@kinetics.nsc.ru (N.V. Sergey).

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sections we briefly summarize the method of MARY spectroscopy to outline its requirements, discuss the choice of a suitable candidate complex, and then describe our results for the first successfully created system of this type.

1.1. MARY spectroscopy and the choice of complex

The implementation of MARY spectroscopy that is used in this work is a steady-state method based on the continuous cycle of generating spin-correlated radical ion pairs by X-irradiation of non-polar solution of suitable charge acceptors, spin evolution of these pairs in applied static magnetic field, and singlet state recombination of the pairs producing electronically excited molecules that are observed by fluorescence, provided one of the chosen acceptors is also a luminophore [5]. Sweeping of the applied magnetic field in the region of weak fields produces MARY spectra – the dependencies of fluorescence intensity on magnetic field, with characteristic features reflecting the magnetic constitution of the partners of the recombining radical ion pair.

Here we aim to check whether organometallic complexes can substitute for the charge acceptors/luminophores in the described setting, and whether the transient radical-ionic states of such complexes can thus be detected. To this end a suitable model system is needed that has to meet a number of requirements. A non-polar solvent is a critical requirement for the method, and to avoid background processes an alkane solvent, such as *n*-decane, is normally chosen, so the complex has to be soluble in alkanes. This limits us to non-ionic complexes, with the ligands compensating the charge of the central metal ion. We chose acetylacetonate-type bidentate charge-compensating ligands, using hexafluoroacetylacetonate (hfac) for improved solubility in alkanes provided by fluorine substitution. As the detectable signal in the experiment is fluorescence, we further need a luminophore in the radical ionic system, which is preferably the same complex as the charge acceptor, so a known luminophore 2,5-diphenyloxazole (PPO) was chosen as the additional ligand in the complex.

Regarding the central ion, for the first model system we wanted the magnetically simplest possible case of diamagnetic initial complex with the central ion having zero nuclear spin, and chose zinc as the central ion in the complex (natural abundance of ^{67}Zn with spin 5/2 is only 4%). Two hfac ligands compensate the charge of Zn^{2+} and use four of the six available coordination sites of the Zn^{2+} ion, with the remaining two being occupied by the nitrogen atoms of the two PPO ligands to produce the complex $Zn(hfac)_2(PPO)_2$. To take part in the cycle of processes leading to formation of the observed signal, the candidate complex should be able to donate or accept an electron (thus generating the 'radical ion'). The ionization potential (IP) of $Zn(hfac)_2$ is 10.0–10.1 eV [10], IP for the $Zn(hfac)_2(PPO)_2$ complex is not known, but should be lower due to the presence of two PPO ligands, and *n*-decane used as the solvent has IP 9.5–9.7 eV [10], so positive charge transfer yielding 'radical cation' of the complex may be possible. The specific data on the electron affinity of $Zn(hfac)_2$ and $Zn(hfac)_2(PPO)_2$ are not available, but it is known that metals have large electron affinity, so we can expect that our complex will act as electron acceptor.

2. Experimental

2.1. Synthesis of $Zn(hfac)_2(PPO)_2$

$Zn(hfac)_2$ H_2O was prepared as described in [11]. 2,5-Diphenyloxazole (46 mg, 0.2 mmol) was dissolved in methylene chloride (1 mL). $Zn(hfac)_2{\cdot}2H_2O$ (50 mg, 0.1 mmol) was dissolved in methylene chloride (10 mL) in a separate flask, the solution was filtered and added to the solution of 2,5-diphenyloxazole. The mixture was filtered again, hexane (10 mL) was added, and the mixture was left at room temperature in a semi-closed flask for slow crystallization. In four days large clear tabular crystals precipitated, which were collected on a glass filter, washed with hexane and dried in air, affording the title complex in 33% yield. The compound was characterized with X-ray structural analysis, unit cell parameters are: $a = 9.5873(4)$ Å, $b = 10.2574(5)$ Å, $c = 11.0795(4)$ Å, $\alpha = 86.93(0)°$, $\beta = 65.48(0)°$, $\gamma = 72.22(0)$, $V = 940.56(58)$ Å^3, $Z = 1$, space group P(−1). Elemental analysis: calculated for $C_{40}H_{32}F_{12}N_2O_6Zn$: C 52.1; H 2.0; F 24.8; N 3.0, found: C 52.4; H 2.7; F 24.9; N 3.1.

X-ray quality single crystals were obtained from the synthesis. Data collection was carried out on a Bruker X8 Apex CCD diffractometer at 150 K using graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) [12]. Reflection intensities were integrated using SAINT software and corrected for absorption by semi-empirical method with SADABS [13]. The structure was solved by the direct method and refined by full-matrix least squares against F^2 in anisotropic approximation for non-hydrogen atoms using SHELX program package [14]. Hydrogen atoms were set in geometrical positions. Final agreement factors were $R_1 = 0.0431$, $wR_2 = 0.1121$ for 5829 reflections ($I > 4\sigma_I$), GOF = 1.058. The structure has been deposited to the Cambridge Structural Database (CCDC 798462) and is available free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

Solution IR spectra of $Zn(hfac)_2(PPO)_2$ and PPO in n-decane were taken on a Bruker Vector 22 FT-IR spectrometer in a 0.15 mm NaCl cuvette at concentrations 10^{-4}–10^{-3} M.

Optical absorption spectra were taken on a Shimadzu UV-2401 spectrophotometer. Fluorescence spectra and kinetics of fluorescence were obtained using an FLS920P system (Edinburgh Instruments). Fluorescence measurements were taken for solutions of $Zn(hfac)_2(PPO)_2$ and PPO in *n*-decane with excitation at 300 nm with a Xe900 xenon lamp (450 W), optical density of solutions 0.1, slit width 1 nm for both excitation and detection beams (Czerny-Terner monochromators, 1.8 nm/mm, F/4.2, 1800 lines grating). Fluorescence kinetics were registered at 357 nm, with pump pulse (pulse diode, 100 ps) at 320 nm.

The experimental setup for MARY spectroscopy was described in [5]. The samples containing about 1 ml of solution in a quartz cuvette are degassed by repeated freeze–pump–thaw cycles and placed in the magnetic field of a Bruker ER-200D CW ESR spectrometer equipped with an X-ray tube for sample irradiation (Mo, 40 kV × 20 mA), a pair of coils with a separate current source to provide the constant 'negative' shift of the field required to sweep through the zero of the field, and a PMT (FEU-130) for fluorescence detection. The scanned magnetic field was modulated at a frequency of 12.5 kHz with an amplitude up to 1 mT. A Stanford SR-810 Lock-In Amplifier and computer averaging over 20 scans of 512 points and 200 s sweep time each were used to obtain the shown spectra, obtained as the first derivatives of the actual field dependencies. No microwave pumping was applied to the samples. All experiments were carried out at room temperature. The purified solvent – *n*-decane – was treated with sulphuric acid, potassium permanganate, dried over calcium chloride and passed through a column with a mixture of activated MgO and Al_2O_3 (courtesy of Mrs. N. Ivanova).

3. Results and discussions

A novel complex of Zn(II) hexafluoroacetylacetonate with two molecules of 2,5-diphenyloxazole (PPO), $Zn(hfac)_2(PPO)_2$, was synthesized and characterized. The solubility of the complex in alkanes is about 1 mmol/L and is sufficient for MARY experiments. The PPO component in the complex acts as the luminescent fragment and was introduced in a $Zn(hfac)_2{\cdot}2H_2O$ complex via

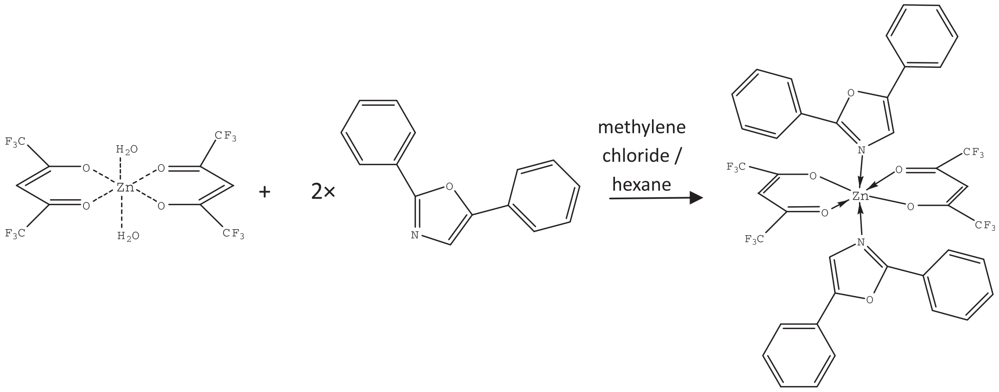

Figure 1. Synthesis of $Zn(hfac)_2(PPO)_2$ from zinc(II) hexafluoroacetylacetonate and 2,5-diphenyloxazole.

exchange reaction between H_2O and PPO as shown in the scheme of synthesis in Figure 1. The molecular structure of the complex was determined by X-ray crystallography. The structural features of the $Zn(hfac)_2$ and PPO moieties are well known and their discussion is beyond the scope of this study. Details of syntheses and characterization can be found in the Section 2.

To check in which form the complex $Zn(hfac)_2(PPO)_2$ is present in alkane solutions, IR spectra of $Zn(hfac)_2(PPO)_2$ and PPO solutions in *n*-decane were taken, with magnified most important region shown in Figure 2. The spectra were compared, all lines of PPO vibrations were found in the spectra for $Zn(hfac)_2(PPO)_2$ (marked with asterisk in Figure 2), and the known lines of $Zn(hfac)_2$ vibrations [15] were also found in the spectra of $Zn(hfac)_2(PPO)_2$ (marked with '+' in Figure 2). The two yet unidentified bands are marked with ellipses in Figure 2.

To understand the origin of the new lines for the complex we compared IR spectra of PPO and $Zn(hfac)_2(PPO)_2$ in KBr pellets (not shown here) and in *n*-decane solution. The solid state spectra for both the free ligand and the complex show the split lines around 950 cm^{-1} and 770 cm^{-1}, for the free ligand in solution the split lines merge into single lines, but for the complex the lines are again split as shown in ellipses in Figure 2 – two resolved lines are present in the region of 950 cm^{-1} and a broadened poorly resolved line is found at 770 cm^{-1}. The complex in solution thus shows characteristic features found for its ligand in a pellet, which is explained by coordination of the ligand to the central Zn ion in $Zn(hfac)_2(PPO)_2$, leading to collective vibrations similar to those found in the solid state. The conclusion is that in alkane solution of $Zn(hfac)_2(PPO)_2$ at least a substantial fraction of PPO has local environment similar to its environment in the solid pellet, i.e., PPO is indeed part of the complex and is not lost into the bulk. We thus have a complex that is soluble in alkane and has a fluorescing ligand in it.

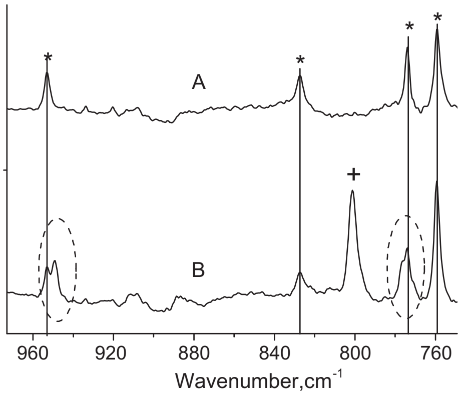

Figure 2. FT-IR spectra for solutions of 10^{-3} M PPO (A) and Zn(hfac)2(PPO)2 (B) in *n*-decane. Asterisk marks vibrations found both in PPO and in $Zn(hfac)_2(PPO)_2$, the plus sign marks $Zn(hfac)_2$.

Figure 3a shows optical absorption and fluorescence spectra of the complex and the free ligand in alkane solution. The absorption spectra of $Zn(hfac)_2(PPO)_2$ and PPO are similar, but the spectrum of $Zn(hfac)_2(PPO)_2$ has a more pronounced band at 300 nm, and the extinction coefficient of $Zn(hfac)_2(PPO)_2$ at the absorption maximum ($6.9 \times 10^4\ M^{-1}cm^{-1}$) is noticeably higher then the doubled extinction coefficient of the free ligand PPO ($2.6 \times 10^4\ M^{-1}cm^{-1}$). Fluorescence spectra of $Zn(hfac)_2(PPO)_2$ and PPO are similar for both compounds. As the quantum yield of PPO is known to be one (in cyclohexane) [16], we used it as internal reference to estimate the quantum yield of $Zn(hfac)_2(PPO)_2$. The quantum yield of fluorescence with excitation at 300 nm for $Zn(hfac)_2(PPO)_2$ is about 0.8 in *n*-decane relative to PPO with equal amounts of absorbed excitation photons.

To determine the fluorescence lifetime of the complex, kinetics of fluorescence were measured with the pump pulse at 320 nm and detection at 357 nm. The fluorescence kinetics of the complex is shown in Figure 3b and is practically monoexponential, the fluorescence parameters of PPO are known and were taken from [16]. Fluorescence lifetimes for $Zn(hfac)_2(PPO)_2$ and PPO were found to be identical within experimental accuracy and equal to 1.3 ns. Although MARY spectroscopy is a steady-state technique and thus is not critical to fluorescence lifetimes, this time is short enough to allow more sophisticated time-resolved magnetic field experiments with this system.Finally, MARY spectra were obtained for different concentrations of $Zn(hfac)_2(PPO)_2$ solution in *n*-decane and were compared with the spectra for the free ligand PPO substituting for the complex. A selection of MARY spectra is shown in Figure 4, where to aid in comparing similar looking curves the spectra are grouped into separate panels in pairs having either equal concentrations of the complex and the ligand (three left panels), or concentrations of free ligand equal to twice the concentration of the complex, i.e., for equal concentrations per PPO molecule (three right panels). The spectra are taken and shown as first derivatives with respect to magnetic field, and their characteristic features are the inflection point B_σ (the maximum of the derivative), which is determined by effective hyperfine couplings in the partners of the recombining radical ion pair $A_{1,2} = \sqrt{1/3\sum a_i^2 I_i(I_i+1)}$ as $B_\sigma = 2\frac{A_1^2+A_2^2}{A_1+A_2}$ [8,17,18], and the narrow inversion in zero field [19].

To understand the expected changes in MARY spectra let us first discuss what radical ion pairs may form in this system and what contribution they will give to the observed spectrum. X-irradiation of alkanes initially produces solvent radical cations ($Alk^{+\bullet}$) and

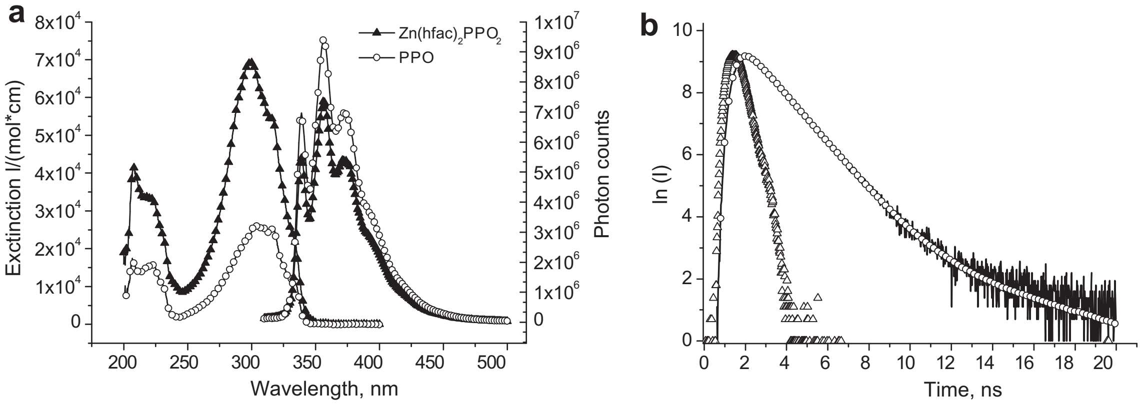

Figure 3. (a) Optical absorption (shorter wavelengths, left axis) and fluorescence (longer wavelengths, right axis, excitation at 300 nm) spectra for solutions of $Zn(hfac)_2(PPO)_2$ and PPO in *n*-decane. (b) Kinetics of fluorescence (excitation at 320 nm, detection at 357 nm) for solution of $Zn(hfac)_2(PPO)_2$ in *n*-decane. Open triangles show the instrument function, solid line shows the measured fluorescence response, and open circles show approximation of the experimental kinetics with a standard fitting function $F = A + B_1.\exp(-t/T_1) + B_2.\exp(-t/T_2)$, approximation parameters are $T_1 = 1.3 \times 10^{-9}$ s, $B_1 = 3.4 \times 10^{-2}$, 99%, $T_2 = 4.8 \times 10^{-9}$ s, $B_2 = 1.1 \times 10^{-4}$, 1%.

excess electrons. If a compound with sufficient electron affinity, in this case $Zn(hfac)_2(PPO)_2$ or PPO, is present in solution, it captures the electrons forming the radical anion $L^{-\bullet}$, where L stands for both free ligand and complex. Due to lower ionization potentials as compared to alkane both the complex and the free PPO can also capture the positive charge from $Alk^{+\bullet}$ and thus form the radical cations $L^{+\bullet}$. MARY spectroscopy is sensitive to recombining radical ion pairs containing at least one luminophore, and in this case two types of pairs, $(Alk^{+\bullet}/L^{-\bullet})$ and $(L^{+\bullet}/L^{-\bullet})$, can contribute to the observed signal. To a first approximation their contributions to the spectrum will be additive and will differ in the widths of the magnetic field effect B_σ, as the effective hyperfine coupling *A* in the alkane radical cation $Alk^{+\bullet}$ is substantially higher than the couplings for aromatic radical ions of L (both for the complex and for the free ligand). Therefore, magnetic field effect for the pair $(Alk^{+\bullet}/L^{-\bullet})$ is wider than for the pair $(L^{+\bullet}/L^{-\bullet})$. The relative amounts of the pairs depend on the concentration of L. The radical anions $L^{-\bullet}$ form rapidly due to high mobility of excess electrons and are always present, even at concentrations of L below 10^{-4} M. On the other hand, the radical cations $L^{+\bullet}$ form much slower due to lower mobility of solvent holes, and build up appreciable concentrations only at higher concentrations of L of about 10^{-3} M needed to compete with recombination. Thus at low concentrations of L only the broad signal from the pair $(Alk^{+\bullet}/L^{-\bullet})$ is present in the observed spectrum, but as the concentration of L is increased a narrower contribution from the pair $(L^{+\bullet}/L^{-\bullet})$ progressively appears. This produces apparent narrowing of the experimental spectra with increasing concentration of L.

Figure 5 demonstrates this more clearly. Fig 5a shows three curves: the spectrum for the maximum possible ligand concentration containing contributions of broad and narrow signals from both types of pairs; the smoothed spectrum for the minimum reasonable concentration of L with the broad magnetic field effect from the pairs $(Alk^{+\bullet}/L^{-\bullet})$, and their difference approximating the spectrum with the narrow magnetic field effect from the pairs $(L^{+\bullet}/L^{-\bullet})$. Thus the spectrum for high concentration of L has been decomposed into two components. Every experimental spectrum can now be represented as a weighed sum of these two components. As an example, Figure 5b shows a reconstruction of the upper left panel from Figure 4.

Returning now to experiment shown in Figure 4, at low concentrations of acceptors MARY spectra for equal concentrations of $Zn(hfac)_2(PPO)_2$ and PPO in *n*-decane are different, the spectrum for the complex has significantly lower B_σ field (approximately 1.5 vs 2.5 mT), and, unexpectedly, much better signal to noise ratio than the spectrum of free PPO. In the spectra for $Zn(hfac)_2(PPO)_2$ at low concentrations of the complex the contribution of the narrow signal is higher as compared to the spectrum of free ligand, both for equal concentrations of the acceptor (left panels) and for equal concentrations of the luminophore molecules in the system (right panels). For solutions of PPO the acceptor is clearly PPO itself, while for solutions of the complex this can be, in principle, either the complex itself or some its derivative, including PPO^- expelled upon electron capture, and this point requires further clarification. What is positive, the complex is not completely dissociated in solution prior to electron capture, and the right curves in Figure 4 support this conclusion. However, at the highest equal concentrations of 6.6×10^{-4} M (bottom left in Figure 4) the MARY spectra for the complex and for the free ligand completely coincide, while upon comparison of the 2:1 spectra (bottom right in Figure 4, spectra of 6.6×10^{-4} M PPO and of 3.3×10^{-4} M $Zn(hfac)_2(PPO)_2$) they already differ in the tails beyond the equal B_σ fields. This is due to the increase in the positive charge acceptor concentration, and is observed both for the complex and for PPO simply upon doubling their concentrations.

All concentration-dependent transformations of MARY spectra can be ascribed to more efficient (rapid) charge capture to the complex as compared to free PPO, which can be explained by the following simple model. The processes of charge capture from $Alk^{+\bullet}$ to L in the systems under study are diffusion-limited, proceeding with the diffusion rate constant $k_D = 4\pi R_{eff} D_{eff}$, where R_{eff} is the effective reaction radius, often taken as the sum of geometrical radii of the molecules, D_{eff} is the effective diffusion coefficient, the sum of diffusion coefficients of the reaction participants. The geometrical size of the complex is about three times larger than the size of the free ligand, but this per se does not lead to more efficient reaction, as according to the Stokes–Einstein relation $D = k_B T/6\pi\eta R$ the diffusion coefficient for the complex should be three times smaller than for the ligand, and the product DR remains the same. However, the gain in the diffusion constant for a pair of reagents can be provided by the domination of diffusion coefficient for the second reaction partner, i.e., the positive charge carrier should have high mobility. Indeed in some cases alkane radical cations are known to have high mobility, with most of the data concerning cycloalkanes, e.g., cyclohexane [20]. There also was some evidence of high hole mobility at short times for non-cyclic radical cations, and highly mobile squalane hole was reported [21,22]. Although for other alkanes the mobile holes have not been unequivocally identified, they are periodically implied upon in picosecond and faster radiolysis studies [23]. Then in the reaction of positive charge transfer from the solvent hole to charge acceptor, i.e., the complex or the free ligand, the effective diffusion coefficient is

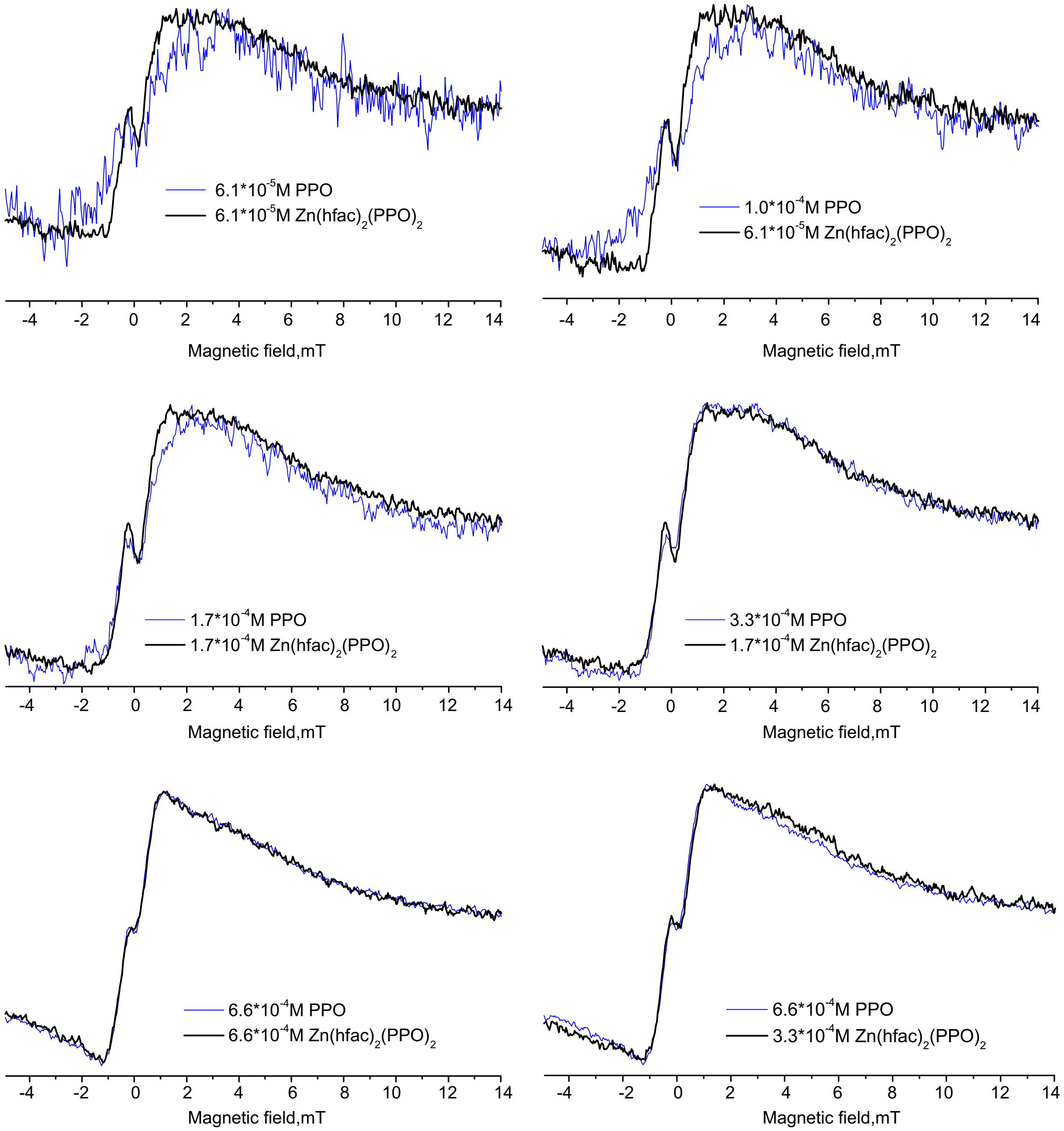

Figure 4. Pairwise comparison of MARY spectra of Zn(hfac)$_2$(PPO)$_2$ (bold lines) and PPO (lighter lines) at indicated concentrations in *n*-decane.

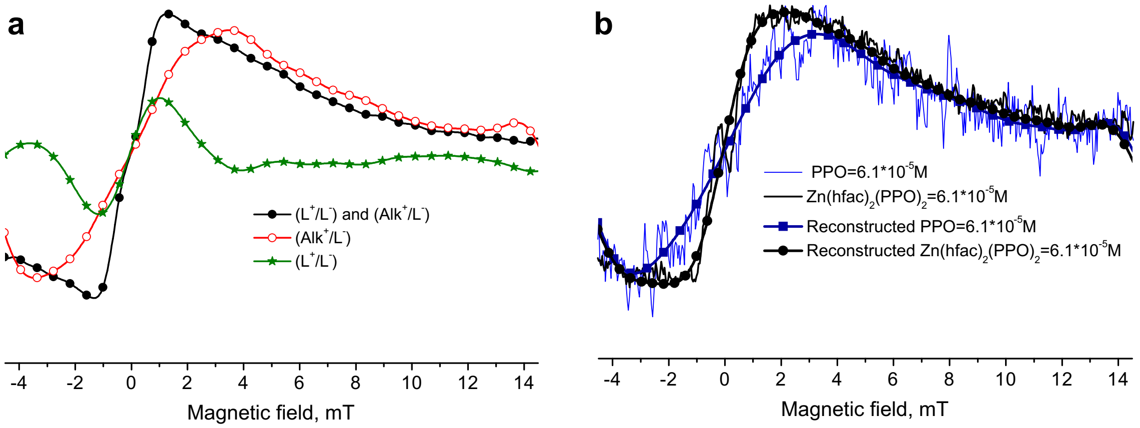

Figure 5. (a) Decomposition of experimental spectrum for 6.6×10^{-3} M PPO (filled circles) into two components, the wide (6.1×10^{-5} M PPO, smoothed, open circles) and narrow (derived, stars) magnetic field effects. (b) Reconstruction of the upper left panel from Figure 4 as a weighed sum of the two components: the ratio of broad:narrow is 1:0 for the apparently broader spectrum (squares) and 1:0.75 for the apparently narrower spectrum (circles).

determined mostly by the solvent hole, while the larger complex contributes mostly to the reaction radius. The experiments are then interpreted as follows: $Zn(hfac)_2(PPO)_2$, showing more efficient hole capture, forms the signal with the smaller B_σ from the pairs ($L^{+\bullet}/L^{-\bullet}$) at lower concentrations than free PPO, but with increasing concentration of acceptor this effect is gradually saturated, the spectra for the complex and the free ligand coincide and then behave similarly with further increase in concentration.

4. Conclusions

In this work we implemented MARY spectroscopy in the presence of a tailored complex $Zn(hfac)_2(PPO)_2$ to extend this technique to organometallic species. The synthesized complex is moderately soluble in alkanes and does not loose its ligands into the bulk. In *n*-decane solution the complex can capture both negative and positive charges forming 'radical ionic' states, and has quantum yield and lifetime of fluorescence $\varphi \sim 0.8$ and $\tau \sim 1.3$ ns, respectively, and thus can be used in spin chemical studies under X-irradiation with fluorescence detection. The first MARY spectra with the participation of the complex ('radical ions' of $Zn(hfac)_2(PPO)_2$) were obtained bearing characteristic features that can be attributed to the radical cation and radical anion of the complex. The concentration-dependent transformations of the spectra can be explained by a larger positive charge capture radius of the complex as compared to the free ligand.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.01.056.

References

[1] K.M. Salikhov, R.Z. Sagdeev, A.L. Buchachenko, Yu.N. Molin, Spin Polarization and Magnetic Field Effects in Radical Reactions, Elsevier, Amsterdam, 1984.
[2] U.E. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.
[3] F.B. Sviridenko, D.V. Stass, Yu.N. Molin, Chem. Phys. Lett. 297 (1998) 343.
[4] E.V. Kalneus, D.V. Stass, K.L. Ivanov, Yu.N. Molin, Mol. Phys. 104 (2006) 1751.
[5] E.V. Kalneus, D.V. Stass, Yu.N. Molin, Appl. Magn. Reson. 28 (2005) 213.
[6] D.V. Stass, N.N. Lukzen, B.M. Tadjikov, V.M. Grigoryantz, Yu.N. Molin, Chem. Phys. Lett. 243 (1995) 533.
[7] G. Grampp, P.J. Hore, M. Justinek, S. Landgraf, N.N. Lukzen, Res. Chem. Intermed. 31 (2005) 567.
[8] V.N. Verkhovlyuk, D.V. Stass, N.N. Lukzen, Yu.N. Molin, Chem. Phys. Lett. 413 (2005) 71.
[9] F.B. Sviridenko, D.V. Stass, Yu.N. Molin, Mol. Phys. 101 (2003) 1839.
[10] NIST electronic database, http://webbook.nist.gov.
[11] F.A. Cotton, R.H. Holm, J. Am. Chem. Soc. 82 (1960) 2979.
[12] Bruker AXS Inc., APEX2 (Version 1.08), Bruker Advanced X-ray Solutions, Madison, Wisconsin, USA, 2004.
[13] G.M. Sheldrick, SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998.
[14] G.M. Sheldrick, SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998.
[15] M.L. Morris, R.W. Moshier, R.E. Sievers, Inorg. Chem. 2 (1963) 411.
[16] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic press, New York, 1971.
[17] H. Staerk, R. Treichel, A. Weller, Chem. Phys. Lett. 96 (1983) 28.
[18] M. Justinek, G. Grampp, S. Landgraf, P.J. Hore, N.N. Lukzen, J. Am. Chem. Soc. 126 (2004) 5635.
[19] C.R. Timmel, U. Till, B. Brocklehurst, K.A. McLauchlan, P.J. Hore, Mol. Phys. 95 (1998) 71.
[20] J.M. Warman, in: J.H. Baxendale, F. Busi (Eds.), The Study of Fast Processes and Transient Species by Pulse Radiolysis, Reidel, Boston, 1981, p. 433.
[21] I.A. Shkrob, M.C. Sauer Jr., A.D. Trifunac, J. Phys. Chem. 100 (1996) 5993.
[22] O.M. Usov, D.V. Stass, B.M. Tadjikov, Yu.N. Molin, J. Phys. Chem. A 101 (1997) 7711.
[23] A. Saeki, S. Tagawa, Pure Appl. Chem. 81 (2009) 45.