Observation of a photoexcited state of a paramagnetic transition metal complex by time-resolved electron paramagnetic resonance spectroscopy

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The first observation of a spin polarized excited state of a paramagnetic metal-complex using time-resolved electron paramagnetic resonance (TREPR) spectroscopy is reported for octaethylporphinatooxovanadium(IV). The TREPR spectra show well resolved orientation dependent hyperfine splitting to the $I = 7/2$ vanadium nucleus. The reduction of the hyperfine splitting by a factor of 3 compared to the ground state and the observation of a multiplet pattern of spin polarization allow the TREPR spectra to be assigned to the excited quartet state of the complex. The spin polarization patterns evolve with time and it is postulated that this is a result of the equilibration between the lowest excited quartet and doublet states.

Introduction

When a paramagnetic species is generated by a photophysical/photochemical process, its spin sublevels are often selectively populated. This non-equilibrium population distribution, known as spin-polarization, depends on how the species was generated and can be measured by transient electron paramagnetic resonance (TREPR) spectroscopy. Since the first observations of light-induced spin polarization,[1,2] TREPR has found widespread use for the determination of reaction intermediates and the elucidation of the mechanisms by which they are formed. This technique has also become an important complement to X-ray crystallography by providing structural information about the functional states of photoactive proteins.[3–6]

Despite these successes, a long-standing challenge has been the detection of the spin polarization expected in the excited states of paramagnetic metal-complexes. Recently there has been renewed interest in this problem because of the need for more detailed information about the excited state dynamics in supramolecular complexes designed as light-activated redox agents or switchable molecular magnets. TREPR should be an ideal method for such studies because it allows the spin-multiplicities of the states to be established unambiguously and is sensitive to their dynamics. Despite these advantages, there

are no TREPR measurements of the excited states of paramagnetic metal complexes in the literature apart from a brief report of a broad featureless signal from a Co(II) porphyrin.[7] A number of recent results suggest that nonetheless such measurements may be possible. Several TREPR studies of organic complexes consisting of a chromophore with one or more attached stable free radicals[8–30] have shown that the excited doublet,[17,24,25] quartet[14,15,18,25–27] and quintet[19,22,26,27,30] states are observable. Light-induced spin polarization has also been observed in the ground state of some paramagnetic metal complexes[31,32] and in the excited states of a chromophore that is weakly coupled to a metal.[33–36] In these systems the spin–orbit coupling contribution to the zero field splitting and the anisotropy of the g- and hyperfine tensors are both comparatively small. Hence, for paramagnetic metal complexes for which this is also the case, the excited states might be also be observable. Since the anisotropy in the magnetic tensors tends to be smaller in complexes of light transition metals such as vanadium, we have investigated the possibility of observing light-induced spin polarization in oxovanadium complexes. Here, we report the first observation of spin polarization in the excited states of a paramagnetic metal-complex using octaethylporphinatooxovanadium(IV) (OEPVO).

The vanadium in OEPVO has a single unpaired electron in its d_{xy} orbital and the $(\pi, \pi*)$ triplet manifolds of the porphyrin are split into doublet and quartet states due to the exchange interaction between the unpaired d-electron and the porphyrin π-electrons.[37,38] Because this splitting is relatively small, the electronic states of the molecule are usually referred to as "sing-doublet"(^{2}S), "trip-doublet"(^{2}T) and "trip-quartet"(^{4}T) to indicate the states of the porphyrin ring that they are derived from and the overall spin multiplicity. As shown in Fig. 1, excitation to the lowest sing-doublet (^{2}S$_1$) state leads to prompt intersystem crossing[39,40] to the lowest trip-doublet state (^{2}T$_1$) which then equilibrates with the lowest trip-quartet state (^{4}T$_1$) and both states decay to the ground state. The energy gap between the ^{2}T$_1$ and ^{4}T$_1$ states is $\sim$40 cm^{-1} as estimated from the
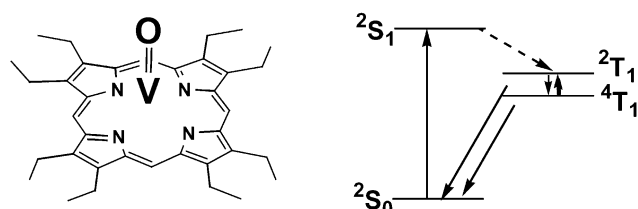
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Fig. 1 OEPVO and its energy diagram for the low-lying excited states.

temperature dependence of the emission lifetimes of vanadyl etioporphyrin, in PMMA film.[38] Which of these two states can be observed by TREPR depends on whether they become spin polarized. A recent theoretical treatment of such systems[41,42] suggests that the trip-quartet can acquire both net and multiplet polarization but that the trip-doublet remains unpolarized.
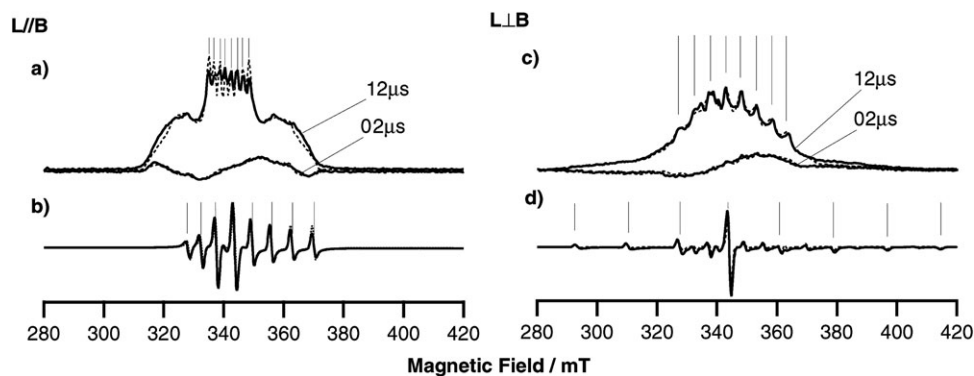
Experimental

A sample of OEPVO in the liquid crystal (LC) E7 (Merck Ltd.) was prepared and partially ordered by freezing it in the presence of a strong magnetic field.[43] The sample was then placed with the LC director either parallel or perpendicular to the field. For each orientation the steady state continuous wave EPR (CWEPR) spectrum of the ground state and the light-induced TREPR time/field dataset were recorded. Spin-polarized TREPR spectra were then extracted from the dataset. Details of the EPR setup and methods used to extract the spectra from the raw data are presented elsewhere.[35,36]
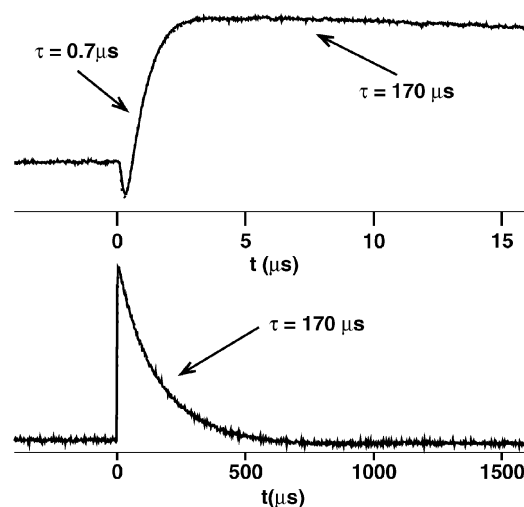
Results and discussion

Fig. 2 Shows the EPR spectra of OEPVO in E7 for the two orientations of the director. Spectra a and b (left) were taken with the director parallel to the field (L ∥ B) while for spectra c and d (right), the director is perpendicular to the field (L ⊥ B). The top spectra (a and c) are light-induced spin polarized TREPR spectra extracted from the full dataset at delay times of 0.2 μs and 12 μs after the laser flash. The bottom spectra (b and d) are corresponding CWEPR spectra measured without laser irradiation. Note that the TREPR spectra have been obtained using the direct detection method and that positive and negative signals correspond to microwave absorption and emission, respectively. The CWEPR spectra, on the other hand, are taken using the standard field modulation technique and are the first derivative of the absorptive EPR transitions.

From Fig. 2 it is clear that although OEPVO is a paramagnetic metal complex it shows strong, highly structured spin polarized TREPR spectra (a and c). The most prominent feature of these spectra is the orientation dependent pattern of eight sharp hyperfine (hf) components due to the $I = 7/2$ vanadium nucleus. The vertical lines in Fig. 2 indicate the

Fig. 3 TREPR time traces of OEPVO in E7 taken on two different timescales at a magnetic field of ∼330 mT. The top trace was measured with the director parallel to the field, the bottom trace was taken for an unoriented sample. The emissive (negative) feature seen at early time in the upper trace is not resolved in the lower trace.

positions of the hf components in each spectrum and comparison of these lines shows that the hf splitting in the TREPR spectra (a and c) is ∼1/3 of that in the corresponding CWEPR spectra (b and d). Hence, the TREPR spectra are not due to spin polarization of the ground state. In addition, the polarization changes with time from a multiplet pattern (equally intense absorptive and emissive components) at early time to a net absorptive pattern at later time but the width of the spectra remains constant.

Fig. 3 shows transients measured near the centre of the dataset (∼330 mT), where the early spectrum is emissive. The upper trace is taken on a short timescale and a fit of the transient shows that the early multiplet pattern evolves to the net polarization pattern with a time constant of 0.7 μs. The decay of the net absorptive polarization with a lifetime of 170 μs is shown in the lower trace which is measured on a longer timescale. This decay time is the same as that of the optical emission measured at the same temperature (data not shown).

Fig. 2 TREPR (a and c) and CWEPR (b and d) spectra of OEPVO in the LC E7 at 50 K. The vertical lines indicate the positions of the eight vanadium hyperfine lines that should be preferentially observed in each spectrum. The solid black spectra are the experimental data and the red or dashed spectra are corresponding simulations.

Table 1 Parameters obtained from the simulation of the EPR spectra of the ground state and excited trip-quartet state of OEPVO in the liquid crystal E7

g-Tensors[a]	g_{xx}	g_{yy}	g_{zz}
Ground state	1.980	1.980	1.960
Trip-quartet	1.995	1.995	1.988
Vanadium hyperfine-tensor/mT[b]	A_{xx}	A_{yy}	A_{zz}
Ground state	5.80	5.80	17.05
Trip-quartet	1.84	1.84	5.40
Zero field splitting/mT[c]	D		E
Trip-quartet	17.5		1.5
Order matrix	S_{xx}	S_{yy}	S_{zz}
	0.2	0.2	−0.4

[a] Error in g-values ±0.001. [b] Error in hfs ±0.01 mT. [c] Error in ZFS ± 1 mT.

These features of the polarization patterns can be used to make an initial assignment of the spectra. Under the conditions that apply here (*i.e.* low temperature and strong spin–spin interactions) multiplet polarization is expected only for the states with $S > 1/2$. Hence, the spectrum observed at 0.2 μs most likely arises from the excited trip-quartet state. This state is also predicted to have a hyperfine splitting that is a factor of three smaller than that of the ground state[44] suggesting that the TREPR spectra at 12 μs also arises from the $^4T_1$ state. Consistent with this initial assignment the net polarization decays with the excited state lifetime observed optically. The assignment of the polarization to the trip-quartet state is confirmed by the fact that the CWEPR and TREPR spectra in Fig. 2 can be simulated very well using a single set of parameters for all of them. The simulated spectra are shown as dashed curves in Fig. 2 and the parameters are given in Table 1. In the simulations, both the net and multiplet polarization patterns are calculated as the trip-quartet state while the CWEPR spectra are from the ground state. The values of D and E are comparable to those of the triplet state of ZnOEP and ZnTTP.[45] It is important to note that the TREPR spectrum expected for the trip-doublet state is much narrower than the observed spectra because it does not contain a contribution from zero-field splitting. The initial population of the trip-quartet is assumed to follow the internal symmetry of the molecule and both the net and multiplet contributions to the polarization are taken to be time dependent.

Such a scheme is consistent with initial population of the trip-quartet state by spin–orbit coupling mediated intersystem crossing from the trip-doublet state. We postulate that the change of the polarization from the initial multiplet pattern to the predominantly net polarization pattern is the result of the subsequent equilibration between the trip-quartet and trip-doublet states. Calculations of the effect of this process on the spin polarization are in progress and will be presented elsewhere along with an in-depth discussion of the excited state dynamics of OEPVO.

Preliminary results of several other paramagnetic metal complexes suggest that OEPVO is not an isolated case but that for transition-metal complexes in which the spin–orbit contribution to the zero-field splitting is not large, time dependent light-induced spin polarization is often observable. This is a significant finding since it provides a new avenue for studying the excited state dynamics of this important class of compounds at a level of detail previously unavailable.

Acknowledgements

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