

ELECTRONIC SUPPLEMENTARY INFORMATION

Light-induced spin state switching in heterospin complexes of Cu(hfac)₂ with pyridine-based nitroxides

Konstantin V. Zaitsev,^{1,2} Svyatoslav E. Tolstikov,¹ Artem S. Bogomyakov,¹ Sergey L. Veber,^{1,2}
Renad Z. Sagdeev,¹ Matvey V. Fedin^{1,2*}

¹*International Tomography Center SB RAS, Novosibirsk, 630090, Russia*

²*Novosibirsk State University, Novosibirsk, 630090, Russia*

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I. Simulation of CW EPR spectra in SS and WS states

All simulations in this work were performed using EasySpin toolbox for Matlab [S1].

Figure S1 shows magnified simulations of CW EPR spectra measured for powdered $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ compounds at 300 K. The spectra were approximated by Lorentzian line with variable FWHM (full width at half magnitude) with the center corresponding to g_{eff} value. The obtained g_{eff} and FWHM values are given in Table 1 of the main text.

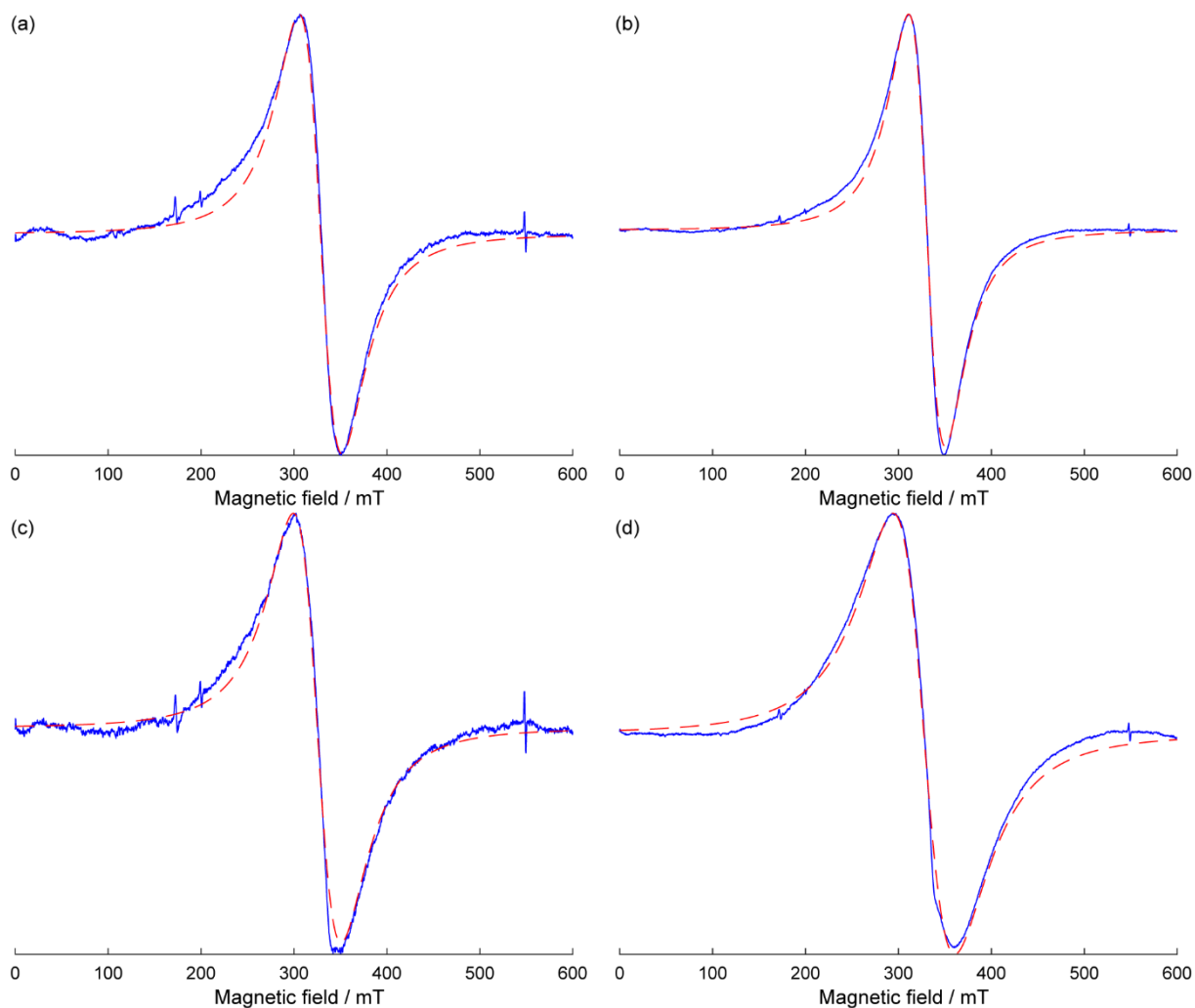


Figure S1. Experimental and simulated CW EPR spectra of powdered $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ complexes in WS state with R = Et (a), i-Pr (b), n-Bu (c) and CP (d).

Figure S2 shows magnified data for simulation of CW EPR spectra of powdered $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ samples at 80 K (SS states). In this case the spectra of compounds with R = i-Pr, n-Bu and CP were modeled by $S=1/2$ spin with anisotropic g - and A -tensors (typical for Cu(II) ions), whose values were adjusted. In case of R = Et complex, we used two $S=1/2$ spins (equally weighted) in modeling to obtain better agreement, as is justified on the basis of previous structural data [S2]. The obtained components of g - and A -tensors are listed in Table 1 of the main text.

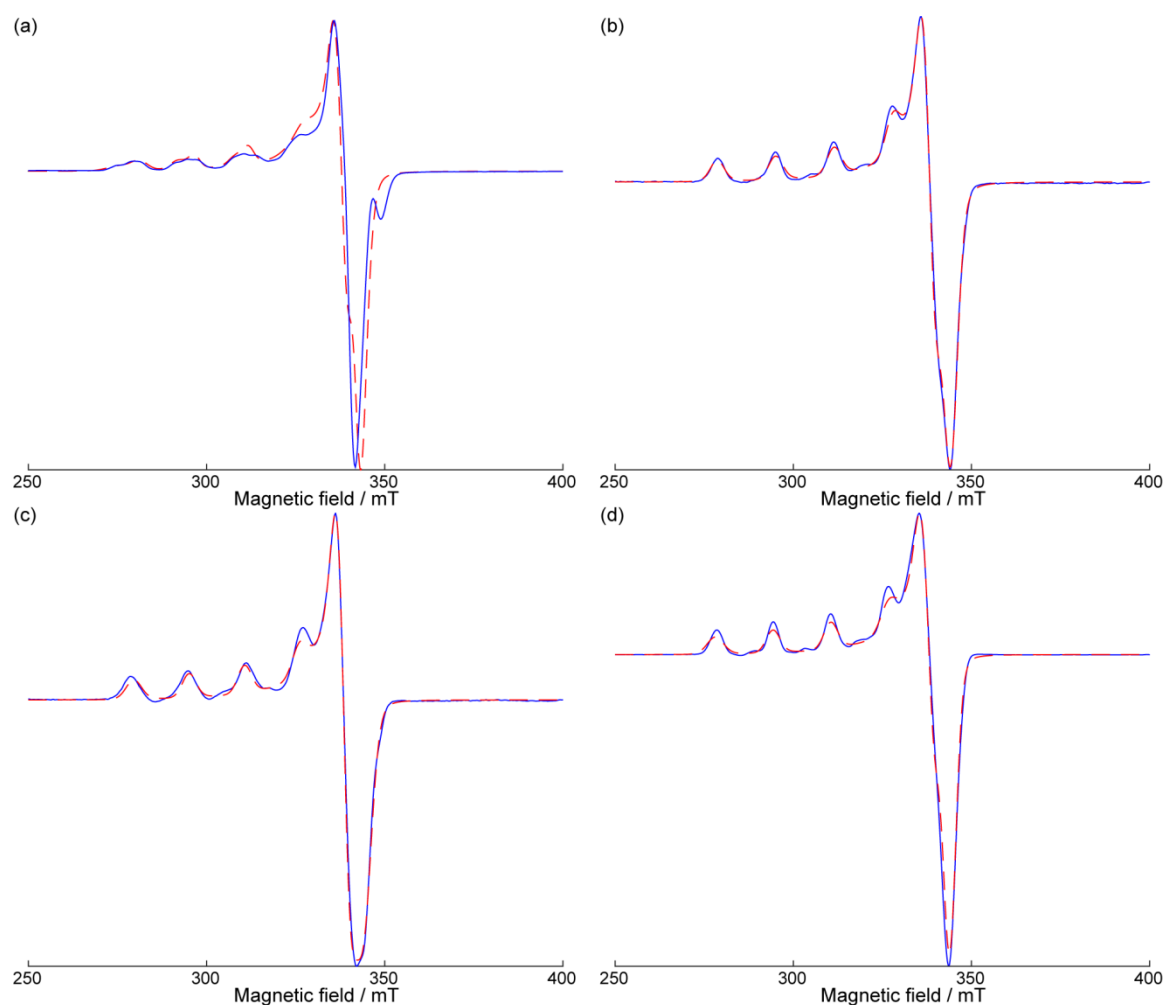


Figure S2. Experimental and simulated CW EPR spectra of powdered $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ complexes in SS state with $\text{R} = \text{Et}$ (a), i-Pr (b), n-Bu (c) and CP (d).

Interestingly, the compound $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ with $\text{R} = \text{Et}$ (Figure S2a) shows an additional spectral feature around 350 mT that is not reproduced in the simulation. One possibility to explain the origin of this line refers to so-called “extra-absorption”, which is a special feature of X-band EPR spectra of copper(II) compounds with appreciable ^{14}N hyperfine interaction constants; it arises due to an interplay between g - and A -anisotropies [S3]. Another option is that it arises due to weak intercluster/interchain couplings, as was previously observed for some other compounds of the breathing crystals family in high magnetic fields (unpublished results).

II. Photoswitching in reference compound with R = Me

Compound with R = Me was studied in detail in our previous research [S4]. In particular, almost complete photoswitching from SS to WS state at 5 K has been evidenced [S4]. However, for fair comparison with other compounds of the studied series in this work, we have reproduced photoswitching in R = Me complex using all the same illumination and other parameters as for the complexes with R = Et, i-Pr, n-Bu and CP. Figure S3 shows the effect of photoswitching for the compound with R = Me at 5 K. There are some deviations of spectra shape from symmetric Voigtian profile; however, similar minor deviations were present also in our previous work [S4], to be attributed to the quality of the sample. The hyperfine splitting lines at g_{\parallel} component of the Cu(II) ion (in $\sim 260\text{-}330$ mT region) are invisible in photoinduced spectrum, confirming that photoswitching is nearly complete.

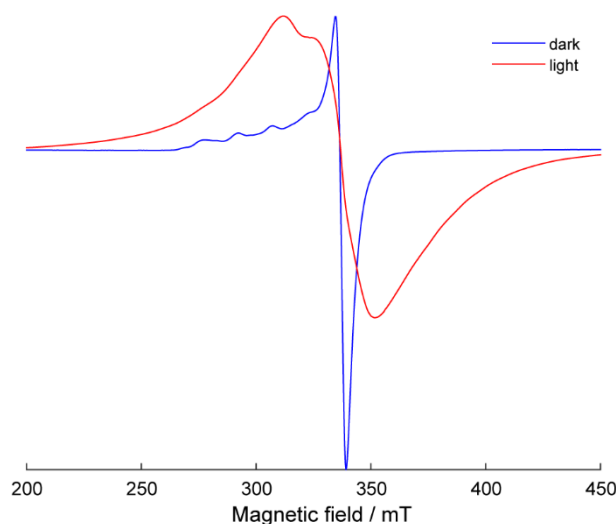


Figure S3. Photoswitching in $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ complex with R = Me at 5 K. Blue – CW EPR spectrum before light illumination (SS state), red – after illumination (nearly pure WS state).

Relaxation studies for this complex with R = Me were performed in our previous work [S4]. For convenience, Figure S4 shows some example data; the full dataset can be found in Ref. [S4].

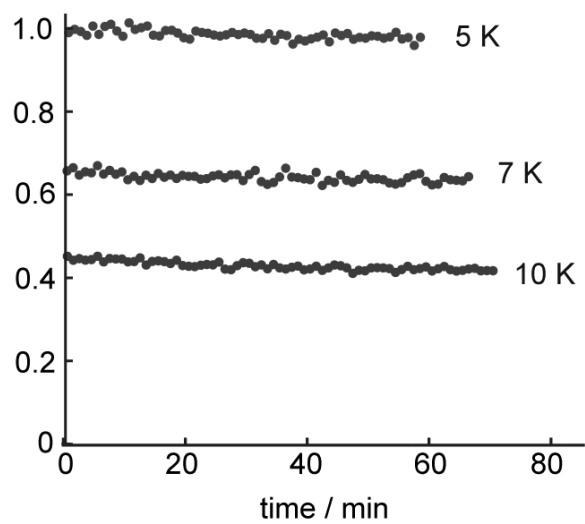


Figure S4. WS→SS relaxation in $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ complex with R = Me at 5 K. Adopted from Ref.[S4]

III. Simulations of self-decelerating relaxation curves

The WS→SS relaxation process in breathing crystals has an unusual temporal dependence that is well approximated by self-decelerating curve [S5]. Such self-decelerating dependence originates from distribution of paramagnetic centers with different potential barrier between WS and SS state potential wells. We assume that these barrier heights are normally distributed. Therefore, similar to the previous studies [S5], experimental dependences were least-square fitted using the function $\exp(-kt)$ with the rate constant k . This rate constant, in turn, is given by expression $k=k_0\exp(-\delta E/k_B T)$, where δE is the energy offset normally distributed around zero with the standard deviation parameter σ . In other words, the probability to find energy barrier with the offset δE is assumed to obey Gaussian distribution law $p(\delta E) = (1/\sqrt{2\pi}\sigma)\exp(-\delta E^2/2\sigma^2)$, and the integration over all δE realizations is accomplished. Two parameters were varied in simulation: k_0 and σ .

Figure S5 shows the relaxation curves for compounds with R = Et and R = i-Pr fitted using self-decelerating dependences. Most of the data were obtained and fitted in time range from 0 to 1 hour, but the data collected at T = 5 K span from 0 to 2 hours. It is evident that the values of γ_{WS} decrease by no more than 12-15% after two hours of relaxation. Table S1 lists the parameters that were used in simulations.

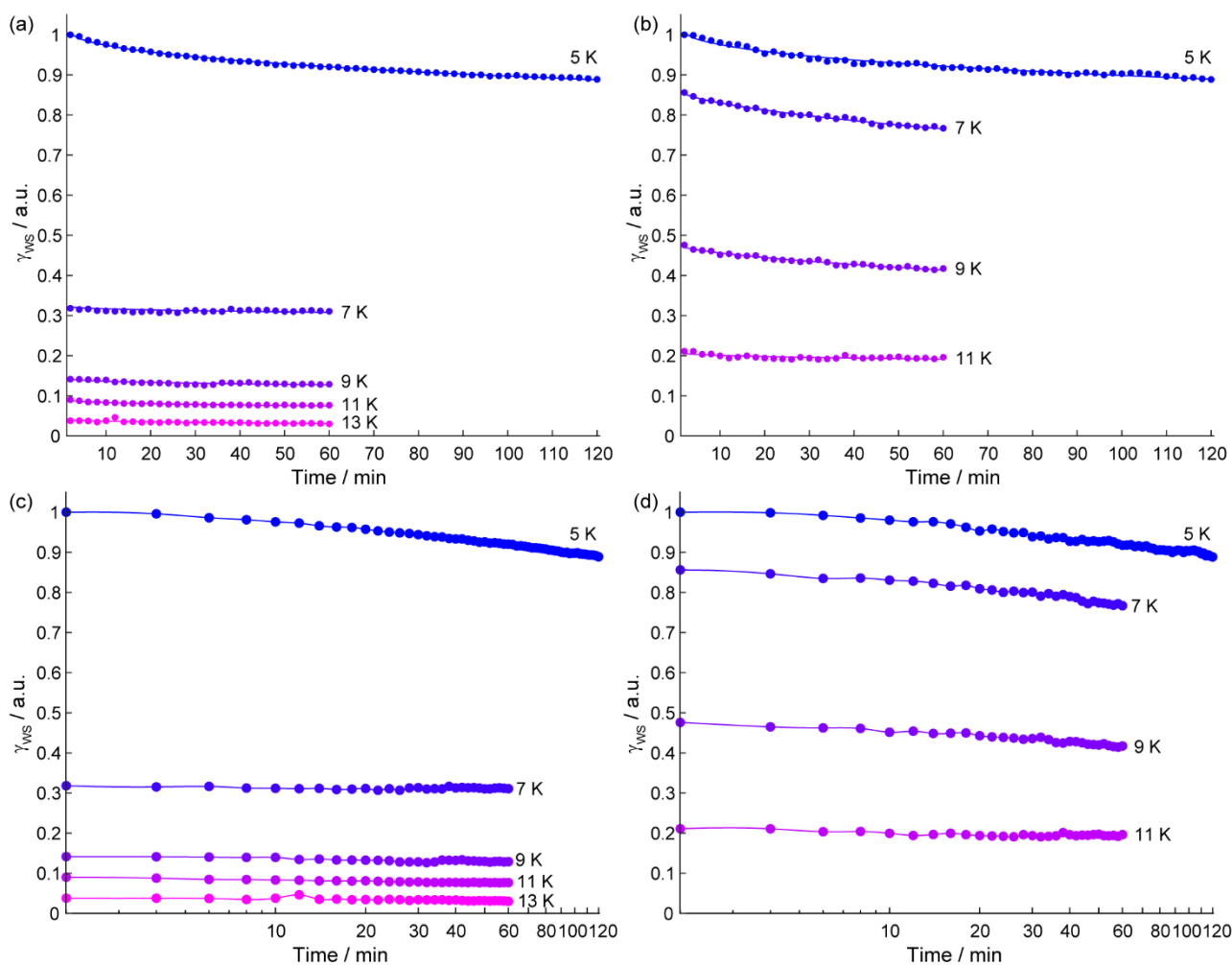


Figure S5. WS→SS relaxation in $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ complexes with $\text{R} = \text{Et}$ (a,c) and $\text{R} = \text{i-Pr}$ (b,d) at 5 – 13 (11) K. The data at 5 K are shown and fitted on the scale of 2 hours. Plots (a,b) are shown on linear scale, (c,d) – on logarithmic scale.

Table S1. Parameters used for simulations of self-decelerating dependences. Errors correspond to standard deviations obtained during fitting.

R =	T = 5 K		T = 7 K		T = 9 K		T = 11 K		T = 13 K	
	k_0 / min^{-1} $\cdot 10^{-3}$	σ / cm^{-1}	k_0 / min^{-1}	σ / cm^{-1}	k_0 / min^{-1}	σ / cm^{-1}	k_0 / min^{-1}	σ / cm^{-1}	k_0 / min^{-1}	σ / cm^{-1}
Et	0.031 ± 0.004	13.5 ± 0.30	0.003 ± 0.012	20.5 ± 13.4	0.06 ± 0.05	26.5 ± 6.1	0.46 ± 0.14	21.0 ± 4.0	0.71 ± 0.42	24.8 ± 11.5
i-Pr	0.025 ± 0.005	14.3 ± 0.76	0.120 ± 0.024	14.8 ± 1.0	0.16 ± 0.03	19.7 ± 1.5	0.09 ± 0.09	29.5 ± 9.5	-	-

Note that, except for the data at 5 K, the obtained parameters (Table S1) have to be treated with care, because experimental dependences are too close to the linear ones and the accuracy is insufficient.

It is interesting to estimate how long does it take to achieve complete relaxation to the ground SS state by extrapolating the obtained theoretical curves to a longer time delays. Although such approach cannot be considered as rigorous basis for any solid conclusions, it gives some crude estimates of the orders of magnitudes. Figure S6 shows that for both compounds with R = Et and R = i-Pr complete relaxation from WS to SS state at 5 K requires around 100 days.

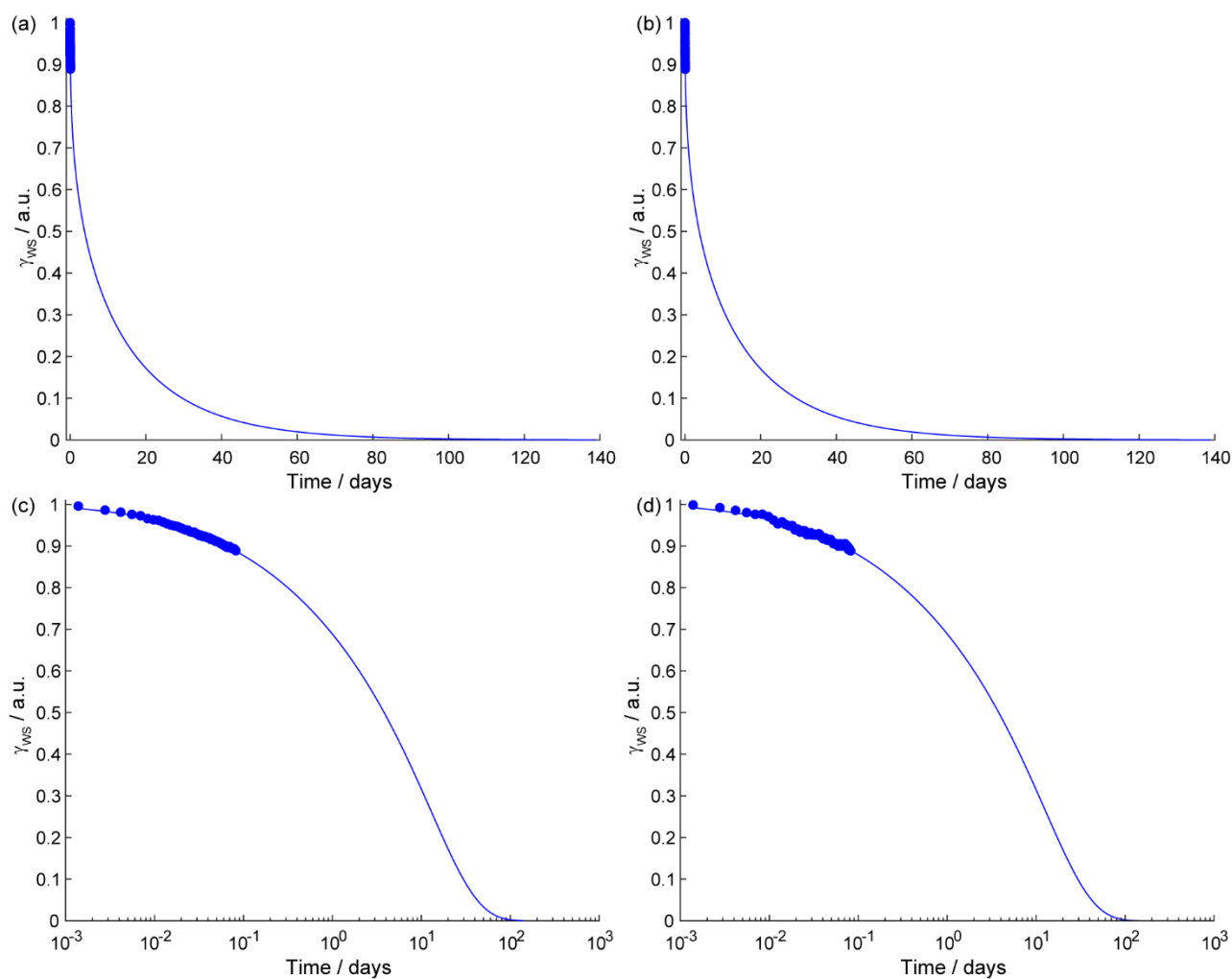


Figure S6. Theoretical extrapolation of WS→SS relaxation in $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2[\text{Cu}(\text{hfac})_2]$ complexes with R = Et (a,c) and R = i-Pr (b,d) at 5 K. Plots (a,b) are shown on linear scale, (c,d) – on logarithmic scale.

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