Supplementary information to

Tuning of Molecular Qubits: Very Long Coherence and Spin-Lattice-Relaxation Times

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1. Pulsed Q-Band EPR

All measurements were performed on a homebuilt pulsed Q-band EPR spectrometer, with an Oxford Instruments CF935 continuous Helium flow cryostat. The samples were filled in quartz tubes, degassed by three freeze-pump-thaw cycles (solutions), followed by flame sealing. In all cases, electron spin echo detected EPR spectra were simulated with the Matlab toolbox "EasySpin". Relaxation measurements were performed at field position of the most intense resonance line, marked with an asterisk in the spectra. Spin-lattice relaxation was measured by inversion recovery- and phase memory times via Hahn echo pulse sequences; both were fitted with exponential functions (mono-, bi- or stretched exponentials).

1.1. Solvent Dependence of Electron Spin Relaxation

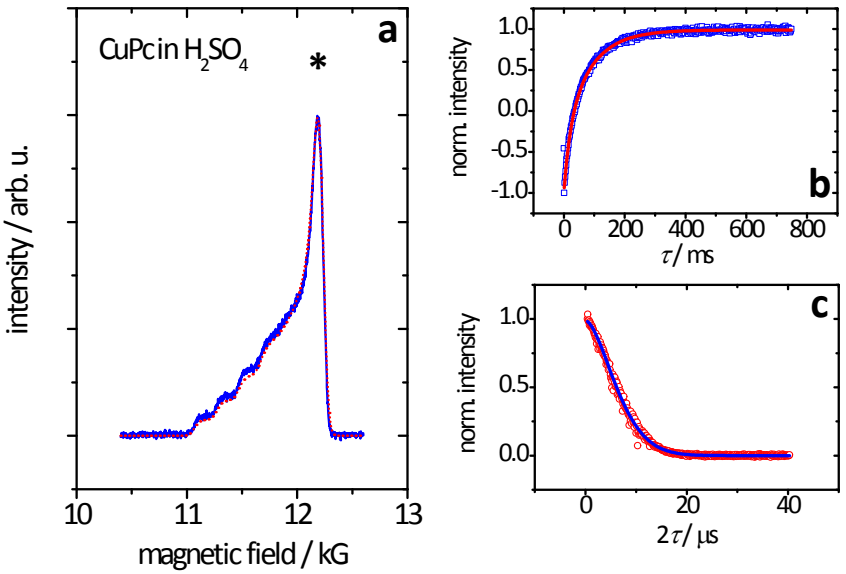

Figure S1: Pulsed Q-band EPR spectroscopy of CuPc in 0. m5 M solution (H_2SO_4) at 7 K. **(a)** ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S1-S3.

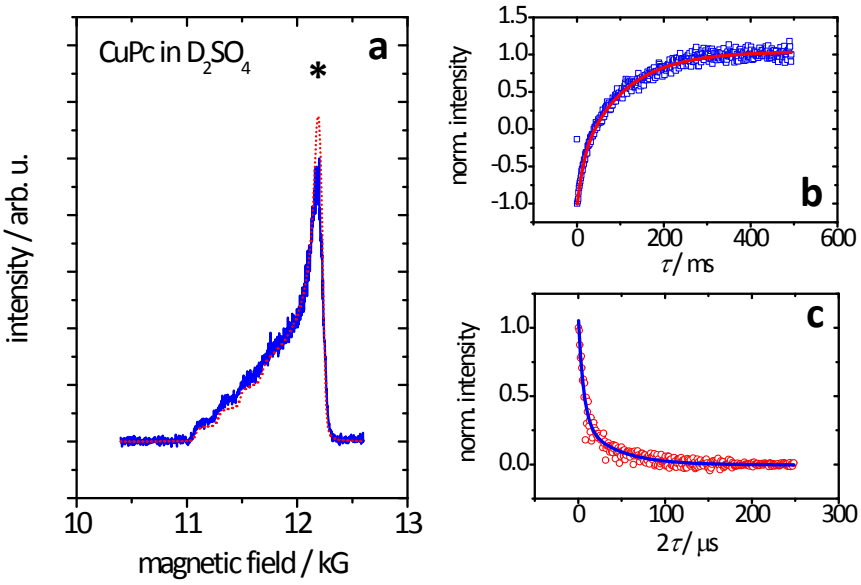

Figure S2: Pulsed Q-band EPR spectroscopy of CuPc in 0. 5 mM solution (D_2SO_4) at 7 K. (**a**) ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S1-S3.

Table S1: Simulation parameters for ESE-detected EPR spectra of CuPc in 0.5 mM solution (H_2SO_4, D_2SO_4) at 7 K and Q-band.

solvent	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$ / MHz	$A_\perp$ / MHz
H_2SO_4	2.1990 ± 0.0005	2.0496 ± 0.0005	630 ± 10	15 ± 10
D_2SO_4	2.1965 ± 0.0005	2.0502 ± 0.0005	610 ± 10	30 ± 10

Table S2: Parameters of biexponential fit functions for inversion recovery experiments of CuPc in 0.5 mM solution (H_2SO_4, D_2SO_4) at 7 K and Q-band.

solvent	A_f	$T_{1,f}$ / ms	A_s	$T_{1,s}$ / ms
H_2SO_4	-0.71 ± 0.03	20 ± 1	-1.29 ± 0.04	85 ± 2
D_2SO_4	-0.58 ± 0.04	14 ± 2	-1.52 ± 0.04	103 ± 3

Table S3: Parameters of bi- or stretched exponential fit functions for Hahn echo experiments of CuPc in 0.5 mM solution (H_2SO_4, D_2SO_4) at 7 K and Q-band.

solvent	A_f	$T_{M,f}$ / µs	A_s	$T_{M,s}$ / µs	k
H_2SO_4	-	-	0.999 ± 0.005	7.78 ± 0.04	1.66 ± 0.02
D_2SO_4	0,79 ± 0.03	6.1 ± 0.5	0.32 ± 0.03	41 ± 4	-

1.2.Ligand Dependence of Electron Spin Relaxation

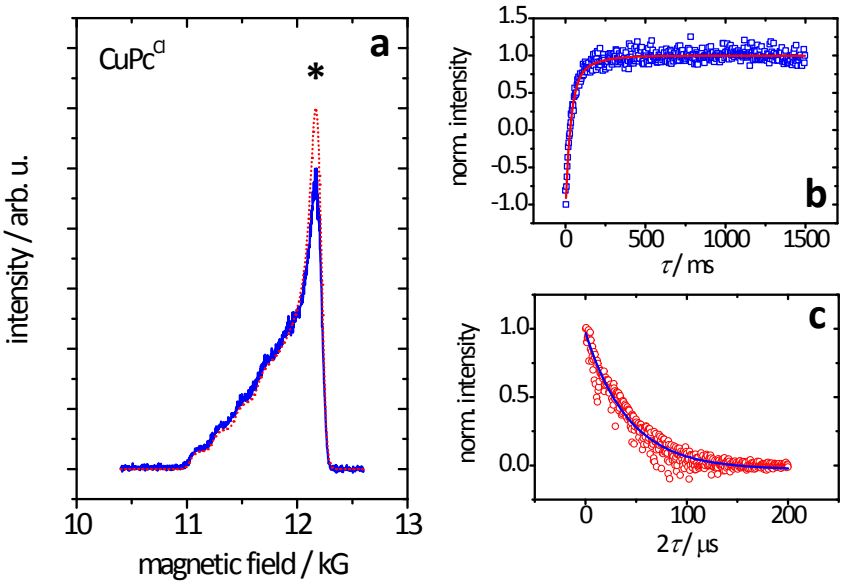

Figure S3: Pulsed Q-band EPR spectroscopy of $CuPc^{Cl}$ in 0.5 mM solution (D_2SO_4) at 7 K. **(a)** ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S4-S6.

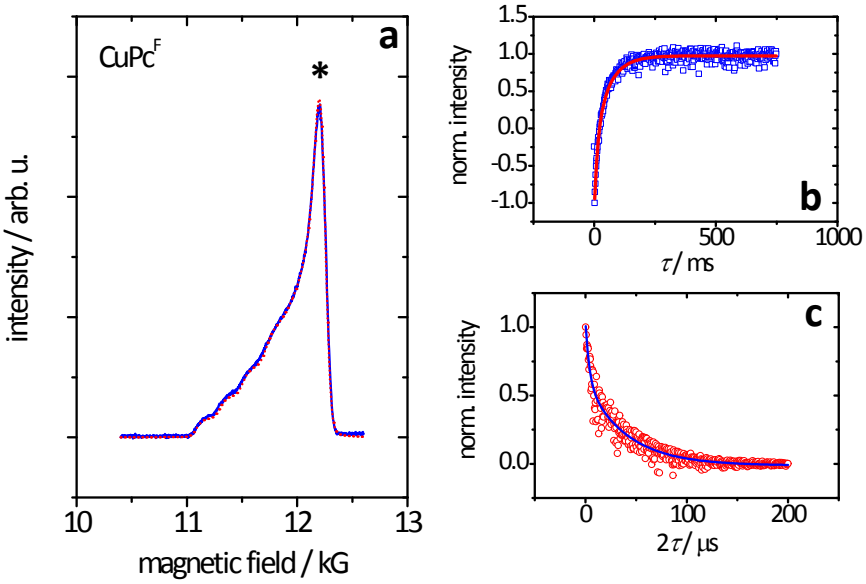

Figure S4: Pulsed Q-band EPR spectroscopy of $CuPc^F$ in 0.5 mM solution (D_2SO_4) at 7 K. **(a)** ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S4-S6.

Table S4: Simulation parameters for ESE-detected EPR spectra of $CuPc^{Cl}$ and $CuPc^F$ in 0.5 mM solution (D_2SO_4) at 7 K and Q-band.

compound	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$ / MHz	$A_\perp$ / MHz
$CuPc^{Cl}$	2.2050 ± 0.0005	2.0525 ± 0.0005	620 ± 10	30 ± 10
$CuPc^F$	2.1925 ± 0.0005	2.0470 ± 0.0005	630 ± 10	15 ± 10

Table S5: Parameters of biexponential fit functions for inversion recovery experiments of $CuPc^{Cl}$ and $CuPc^F$ in 0.5 mM solution (D_2SO_4) at 7 K and Q-band.

compound	A_f	$T_{1,f}$ / ms	A_s	$T_{1,s}$ / ms
$CuPc^{Cl}$	-1.7 ± 0.2	36 ± 4	-0.3 ± 0.2	140 ± 56
$CuPc^F$	-0.9 ± 0.1	14 ± 2	-1.1 ± 0.1	60 ± 4

Table S6: Parameters of biexponential fit functions for Hahn echo experiments of $CuPc^{Cl}$ and $CuPc^F$ in 0.5 mM solution (D_2SO_4) at 7 K and Q-band.

compound	A_f	$T_{M,f}$ / µs	A_s	$T_{M,s}$ / µs
$CuPc^{Cl}$	-	-	1.01 ± 0.01	43 ± 1
$CuPc^F$	0.45 ± 0.04	3.8 ± 0.6	0.62 ± 0.02	40 ± 2

1.3.Metal Dependence of Electron Spin Relaxation

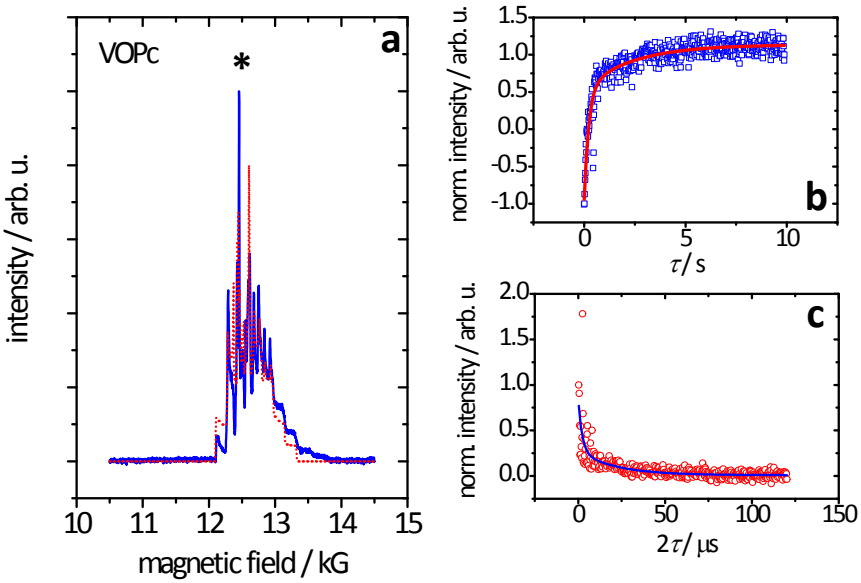

Figure S5: Pulsed Q-band EPR spectroscopy of VOPc in 0.5 mM solution (D_2SO_4) at 7 K. **(a)** ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S7-S9.

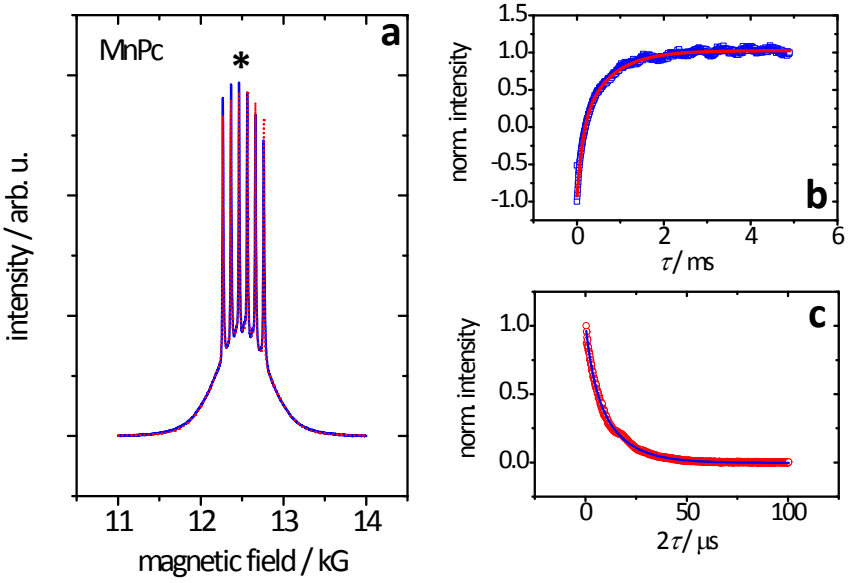

Figure S6: Pulsed Q-band EPR spectroscopy of MnPc in 0.5 mM solution (D_2SO_4) at 7 K. **(a)** ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S7-S9.

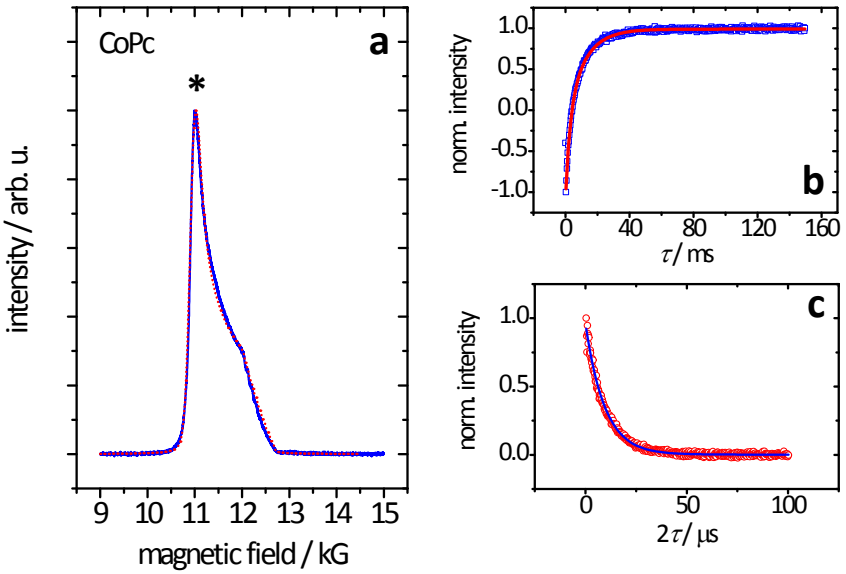

Figure S7: Pulsed Q-band EPR spectroscopy of CoPc in 0.5 mM solution (D_2SO_4) at 7 K. **(a)** ESE detected EPR spectrum (blue, solid line) and simulation (red, broken line). Asterisk indicates field position for relaxation measurements. **(b)** Inversion recovery data (blue, open squares) and biexponential fit (red, solid line). **(c)** Hahn echo data (red, open circles) and biexponential fit function (blue, solid line). All simulation and fit parameters are given in tables S7-S9.

Table S7: Simulation parameters for ESE-detected EPR spectra of VOPc, MnPc and CoPc in 0.5 mM solution (D_2SO_4) at 7 K and Q-band.

compound	g_z	g_y	g_x	A_z / MHz	A_y / MHz	A_x / MHz
VOPc	1.9975 ± 0.0005	1.9760 ± 0.0005	1.9760 ± 0.0005	85 ± 10	220 ± 10	480 ± 10
MnPc	2.0000 ± 0.0005	1.9978 ± 0.0005		n. a.	278 ± 10	
CoPc	2.0232 ± 0.0005	2.2830 ± 0.0005		259 ± 10	60 ± 10	

Table S8: Parameters of biexponential fit functions for inversion recovery experiments of VOPc, MnPc and CoPc in 0.5 mM solution (D_2SO_4) at 7 K and Q-band.

compound	A_f	$T_{1,f}$ / ms	A_s	$T_{1,s}$ / ms
VOPc	-1.49 ± 0.06	226 ± 18	-0.59 ± 0.04	2405 ± 268
MnPc	-0.93 ± 0.02	0.134 ± 0.005	-1.06 ± 0.02	0.69 ± 0.01
CoPc	-0.95 ± 0.03	2.7 ± 0.1	-1.13 ± 0.03	11.1 ± 0.2

Table S9: Parameters of biexponential fit functions for Hahn echo experiments of VOPc, MnPc and CoPc in 0.5 mM solution (D_2SO_4) at 7 K and Q-band.

compound	A_f	$T_{M,f}$ / µs	A_s	$T_{M,s}$ / µs
VOPc	0.61 ± 0.08	2.1 ± 0.5	0.27 ± 0.04	22 ± 5
MnPc	0.37 ± 0.01	4.1 ± 0.2	0.65 ± 0.01	14.0 ± 0.2
CoPc	-	-	0.961 ± 0.005	9.44 ± 0.07

1.4.Temperature Dependence of Electron Spin Relaxation

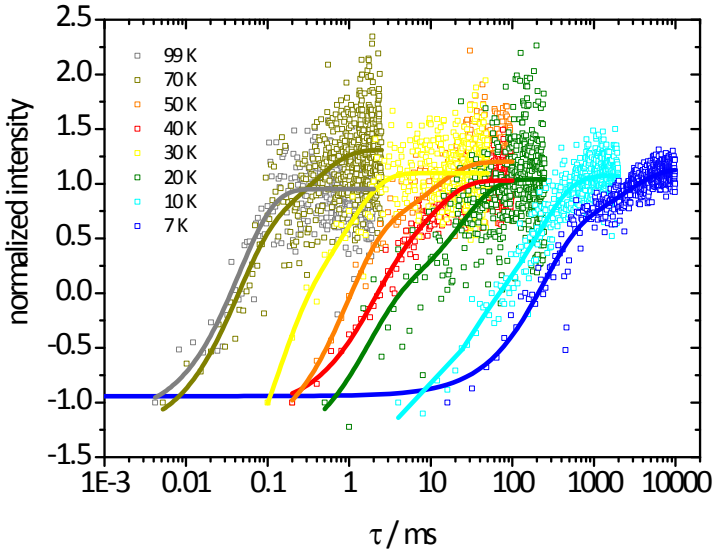

Figure S8: Inversion recovery data (open squares) and mono-/biexponential fits (solid lines) of VOPc in 0.5 mM D_2SO_4-solution measured at Q-band, 7-99 K. Fit parameters are given in table S10.

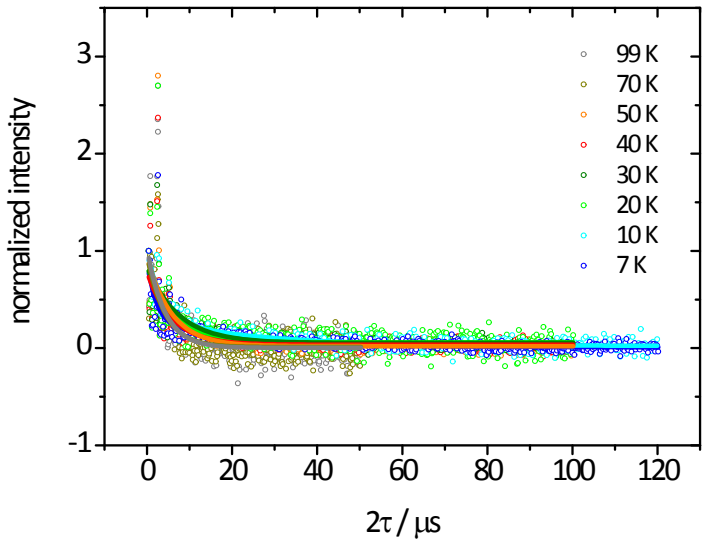

Figure S9: Hahn echo data (open circles) and bi-/monoexponential fit functions (solid lines) of VOPc in 0.5 mM D_2SO_4-solution measured at Q-band, 7-99 K. Fit parameters are given in table S11.

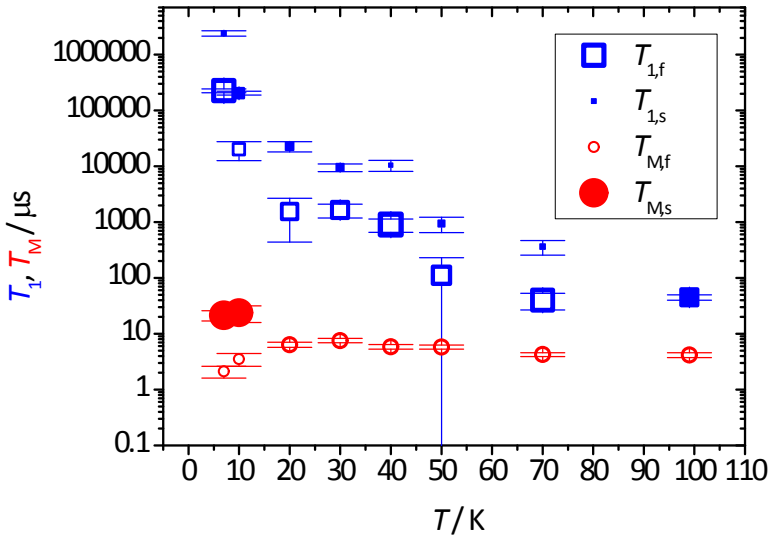

Figure S10: Temperature dependent relaxation data of VOPc in 0.5 mM D_2SO_4-solution measured at Q-band, 7-99 K. Fast and slow spin-lattice- (blue, open respectively filled squares) as well as fast and slow spin-spin relaxation times (red, open respectively filled circles) including standard deviation from fits, symbol size corresponds to contribution of process to echo decay. Parameters are given in tables S10-S11.

Table S10: Parameters of bi-/monoexponential fit functions for inversion recovery experiments of VOPc in 0.5 mM D_2SO_4-solution measured at Q-band, 7-99 K.

T / K	A_f	$T_{1,f}$/ ms	A_s	$T_{1,s}$ / ms
7	-1.49 ± 0.06	226 ± 18	-0.59 ± 0.04	2405 ± 268
10	-0.9 ± 0.2	20 ± 8	-1.5 ± 0.1	204 ± 6
20	-1.4 ± 0.6	2 ± 1	-1.1 ± 0.2	23 ± 5
30	-1.2 ± 0.2	1.6 ± 0.5	-0.9 ± 0.2	10 ± 2
40	-1.9 ± 0.3	0.9 ± 0.2	-0.7 ± 0.1	10 ± 2
50	-2 ± 2	0.1 ± 0.1	-1.4 ± 0.5	0.9 ± 0.3
70	-1.8 ± 0.3	0.04 ± 0.01	-0.8 ± 0.2	0.4 ± 0.1
99	-2.1 ± 0.2	0.045 ± 0.005	-	-

Table S11: Parameters of bi-/monoexponential fit functions for Hahn echo experiments of VOPc in 0.5 mM D_2SO_4-solution measured at Q-band, 7-99 K.

T / K	A_f	$T_{M,f}$/ µs	A_s	$T_{M,s}$ / µs
7	0.61 ± 0.08	2.1 ± 0.5	0.27 ± 0.04	22 ± 5
10	0.67 ± 0.09	3.5 ± 0.9	0.29 ± 0.08	24 ± 8
20	0.78 ± 0.06	6.4 ± 0.7	-	-
30	0.78 ± 0.05	7.6 ± 0.7	-	-
40	0.74 ± 0.05	5.9 ± 0.6	-	-
50	0.91 ± 0.05	5.8 ± 0.5	-	-
70	0.94 ± 0.05	4.2 ± 0.3	-	-
99	1.02 ± 0.07	4.2 ± 0.4	-	-