Supporting Information for

Classical and quantum kinetics interpretation of nanoviscosity effect on the spinchemistry of an electron donor/Pt-complex/electron acceptor triad

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1 Solvent-data and handling of pTHF

 Table S1
 Characteristic solvent-parameters of THF and pTHF.

| | Т | poly-THF 650 (Sigma) | THF |
|---|-------|----------------------|-------------|
| Molecular weight | - | 625-675 g/mol | 77.21 g/mol |
| Degree of polymerisation | - | ~9 | - |
| Density (ρ) | 25°C | 0.978 g/ml | 0.889 g/ml |
| Refractive index (n20/D) | 20°C | 1.465 | 1.407 |
| Dielectric constant (ε _r) | | 5.0 ^ª | 7.52 |
| Pekar-factor ($\Upsilon = 1/(nD20)^2 - 1/\epsilon_r$) | | 0.27 | 0.37 |
| | 25°C | 443 mPa s | 0.518 mPa s |
| Dynamic viscosity | 40°C | 170 mPa s | |
| | 60°C | 75 mPa s | |
| | 100°C | 22 mPa s | |

All values, except for ^a provided by the suppliers Sigma-Aldrich for THF and BASF for pTHF ^avalue taken from Ref [1]

During the handling of the solvent, especially the sample preparation, pTHF was heated with a hot water bath to reduce the viscosity and to speed up the work-process.

2 Synthesis

The target compound was synthesized following an established routine[2,3] outlined in scheme S1 starting from commercially available precursors. All reactions were carried out under an atmosphere of nitrogen (dried with Sicapent from Merck, oxygen was removed with a cupric oxide catalyst R3-11 from BASF) using standard Schlenk techniques.[4] Solvent for oxygen and/or moisture sensitive reactions were freshly distilled under nitrogen from the appropriate dehydrating agent (sodium/benzophenone "ketyl blue" for THF, CaH₂ for 1,2-dichloroethane and Mg/I₂ for MeOH) and degassed by purging with dry nitrogen before use. Solvents for chromatography and work-up procedures were technical grade and distilled prior to use. Flash chromatography was performed on silica gel (Macherey-Nagel "Silica 60 M", 40–63 μ m) wet-packed in glass columns. Pyrrole was purified by slow filtration over a short column of alumina directly prior to use. All other chemicals were obtained commercially and were used without further purification.

Compounds 1[5], 2[6], 3[2,7], 4[8], 5[9], 6[10], 7[2], meso-phenyldipyrromethane[9] were synthesized according to literature.



Scheme S1 Synthesis of the target triad DPtA from commercially available precursors.

Synthesis of [DPtCl]₂ based on lit.[11-13]

Under nitrogen, K_2PtCl_4 (170 mg, 4 µmol) and compound **4** (200 mg, 410 µmol) were added to 10 ml of a degassed mixture of 2-ethoxyethanole and deionized water (3/1 by volume). The reaction mixture was stirred at 80°C for 18 h. After the suspension cooled down to rt, distilled water (40 ml) was added and the precipitate was filtered of with a sintered glass funnel (P4) and washed with water (3 x 10 ml). The crude product was then dried under reduced pressure and was used without further purification due to its insolubility in most conventional organic solvents.

Yield: 0.27 g (0.19 mmol, 92 %) of a grey solid.

 $C_{64}H_{65}Cl_2N_6O_4Pt_2$ [1434.26 g/mol]

Synthesis of DPtA based on lit.[14,15]

Under nitrogen compound **7** (250 mg, 418 µmol) was dissolved in dry THF (30 ml) and DDQ (104 mg, 460 µmol) was added before the mixture was stirred at rt for 2 h. Then, finely powdered K₂CO₃ (580 mg, 4.18 mmol) was added and the mixture was stirred for 15 min before [DPtCI]₂ (300 mg, 209 µmol) and triethylamine (2 ml) were added. The reaction was then stirred at rt for 18 h before DCM (20 ml) and celite (aprox. 10 g) were added. The resulting mixture was filtered through a small plug of celite which was rinsed with DCM until the eluent was colorless. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography on silica (eluent: DCM \rightarrow DCM/MeOH = 100/0.2), a second flash column chromatography on silica (eluent: DCM/PE/THF = 60/40/1) and preparative recycling GPC (THF, 4 ml/min) to yield the product as a red powder which was precipitated from DCM into MeOH. The obtained solid was again precipitated from DCM into n-pentane. The red solid was analytically pure after drying under high vacuum (approx, 10⁻⁵ mbar) for 24 h.

Yield: 52.0 mg (38.0 µmol, 9 %) of a red solid.

C₇₅H₆₃N₇O₆Pt [1353.46 g/mol]

¹**H-NMR** (400 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 8.88-8.84 \ (-, 4\text{H}), 8.16-8.15 \ (\text{m},1\text{H}), 8.07-8.04 \ (-, 2\text{H}), 7.91 \ (\text{d}, {}^{3}J_{\text{H},\text{H}} = 2.3 \ \text{Hz}, 1\text{H}), 7.75 \ (\text{AA}', 2\text{H}), 7.63 \ (\text{d}, {}^{3}J_{\text{H},\text{H}} = 8.6 \ \text{Hz}, 1\text{H}), 7.52 \ (\text{dd}, {}^{3}J_{\text{H},\text{H}} = 8.6 \ \text{Hz}, {}^{4}J_{\text{H},\text{H}} = 2.2 \ \text{Hz}, 1\text{H}), 7.46 \ (\text{BB}', 2\text{H}), 7.09-7.04 \ (-, 3\text{H}), 7.01-6.96 \ (-, 5\text{H}), 6.94 \ (\text{d}, {}^{3}J_{\text{H},\text{H}} = 8.3 \ \text{Hz}, 1\text{H}) \ 6.82-6.76 \ (-, 6\text{H}), 6.70 \ (\text{dd}, {}^{3}J_{\text{H},\text{H}} = 8.2 \ \text{Hz}, {}^{4}J_{\text{H},\text{H}} = 2.4 \ \text{Hz}, 1\text{H}), 6.63 \ (\text{dd}, {}^{3}J_{\text{H},\text{H}} = 4.4 \ \text{Hz}, {}^{4}J_{\text{H},\text{H}} = 1.4 \ \text{Hz}, 1\text{H}), 6.61 \ (\text{dd}, {}^{3}J_{\text{H},\text{H}} = 2.7 \ \text{Hz}, {}^{3}J_{\text{H},\text{H}} = 2.5 \ \text{Hz}, 1\text{H}), 6.55 \ (\text{dd}, {}^{3}J_{\text{H},\text{H}} = 4.5 \ \text{Hz}, {}^{3}J_{\text{H},\text{H}} = 1.6 \ \text{Hz}, 1\text{H}), 3.96 \ (\text{s}, 2\text{H}), 3.76 \ (\text{s}, 6\text{H}), 3.20-3.09 \ (-, 4\text{H}), 1.33 \ (\text{s}, 9\text{H}), 1.26 \ (\text{s}, 9\text{H}). \end{split}$$

¹³C-NMR (100 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 164.3 \text{ (C)}, 163.3 \text{ (C)}, 155.9 \text{ (C)}, 152.6 \text{ (CH)}, 151.3 \text{ (CH)}, 151.0 \text{ (C)}, 147.09 \text{ (C)}, 147.06 \text{ (C)}, \\ 144.6 \text{ (C)}, 143.6 \text{ (C)}, 141.8 \text{ (C)}, 139.90 \text{ (CH)}, 139.86 \text{ (C)}, 138.9 \text{ (C)}, 137.1 \text{ (C)}, 137.0 \text{ (CH)}, \\ 136.7 \text{ (CH)}, 136.2 \text{ (C)}, 136.1 \text{ (C)}, 135.7 \text{ (C)}, 135.3 \text{ (C)}, 133.0 \text{ (C)}, 132.4 \text{ (C)}, 131.9 \text{ (CH)}, 131.7 \\ \text{ (CH)}, 131.4 \text{ (CH)}, 130.8 \text{ (CH)}, 129.5 \text{ (CH)}, 129.3 \text{ (CH)}, 128.6 \text{ (C)}, 128.2 \text{ (CH)}, 128.1 \text{ (CH)}, \\ 127.8 \text{ (C)}, 127.7 \text{ (C)}, 127.6 \text{ (C)}, 127.5 \text{ (C)}, 126.9 \text{ (CH)}, 126.6 \text{ (CH)}, 126.4 \text{ (CH)}, 122.2 \text{ (CH)}, \\ 120.3 \text{ (CH)}, 117.9 \text{ (CH)}, 117.4 \text{ (CH)}, 114.9 \text{ (CH)}, 111.4 \text{ (CH)}, 107.2 \text{ (CH)}, 55.8 \text{ (CH}_3), 41.0 \\ \text{ (CH}_2), 35.9 \text{ (C)}, 34.6 \text{ (C)}, 33.0 \text{ (CH}_2), 32.4 \text{ (CH}_2), 31.8 \text{ (CH}_3), 31.3 \text{ (CH}_3). \end{split}$$

| Microanalysis (CHN): | calc. for $C_{75}H_{63}N_7O_6Pt$ | C-%: 66.56, | H-%: 4.69, | N-%: 7.24 |
|---------------------------|---|------------------|------------|------------|
| | found for $C_{75}H_{63}N_7O_6Pt$ | C-%: 66.18, | H-%: 4.67, | N-%: 7.09. |
| ESI-MS (pos., high res.): | $[M^{**}] = C_{75}H_{63}N_7O_6Pt; c$ $\Delta = 0.55 ppm$ | alc.: 1353.45042 | 2, found: | 1353.45117 |

Synthesis of [ppzPtCl]₂ based on lit.[11-13]

Under nitrogen, K_2PtCl_4 (1.00 g, 2.41 mmol) and 1-phenylpyrazole (350 mg, 320 µl, 2.41 mmol) were added to 30 ml of a degassed mixture of 2-ethoxyethanole and deionized water (3/1 by volume). The reaction mixture was stirred at 80°C for 18 h. After the suspension cooled down to rt, distilled water (80 ml) was added and the precipitate was filtered of with a sintered glass funnel (P4) and washed with water (3 x 10 ml). The crude product was then dried under reduced pressure and was used without further purification due to its insolubility in most conventional organic solvents.

Yield: 620 mg (830 $\mu mol,$ 69 %) of a slightly grey solid.

 $C_{18}H_{14}Cl_2N_4Pt_2$ [747.41 g/mol]

Synthesis of Pt based on lit.[14,15]

Under nitrogen *meso*-phenyldipyrromethane (890 µg, 402 µmol) was dissolved in dry THF (10 ml) and DDQ (100 mg, 442 µmol) was added before the mixture was stirred at rt for 2 h. Then, finely powdered K_2CO_3 (560 mg, 4.02 mmol) was added and the mixture was stirred for 15 min before [ppzPtCl]₂ (150 mg, 201 µmol) and triethylamine (2 ml) were added. The reaction was then stirred at rt for 18 h before DCM (20 ml) and celite (aprox. 10 g) were added. The resulting mixture was filtered through a small plug of celite which was rinsed with DCM until the eluent was colorless. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography on silica (eluent: DCM/PE = $1/3 \rightarrow 1/1$) to yield the product as a red powder which was precipitated from DCM into MeOH. The obtained solid was again precipitated from DCM into n-pentane. The red solid was analytically pure after drying under high vacuum (approx, 10⁻⁵ mbar) for 24 h.

Yield: 450 μg (80.0 μmol , 20 %) of a red solid.

 $C_{24}H_{18}N_4Pt$ [557.52 g/mol]

¹H-NMR (400 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 8.12-8.11 \text{ (m, 1H)}, 8.10 \text{ (dd, }{}^{3}J_{\text{H,H}} = 2.9 \text{ Hz}, \, {}^{4}J_{\text{H,H}} = 0.6 \text{ Hz}, 1\text{H}), 8.03-8.02 \text{ (m, 1H)}, 7.92 \text{ (d,} \\ {}^{3}J_{\text{H,H}} = 2.4 \text{ Hz}, 1\text{H}), 7.53-7.44 \text{ (-, 5H)}, 7.35-7.33 \text{ (m, 1H)}, 7.29-7.27 \text{ (m, 1H,)}, 7.18-7.10 \text{ (-,} \\ 2\text{H}), 6.86 \text{ (dd, }{}^{3}J_{\text{H,H}} = 4.3 \text{ Hz}, \, {}^{3}J_{\text{H,H}} = 1.2 \text{ Hz}, 1\text{H}), 6.63-6.61 \text{ (-, 2H)}, 6.57 \text{ (dd, }{}^{3}J_{\text{H,H}} = 4.3 \text{ Hz}, \, {}^{4}J_{\text{H,H}} = 1.5 \text{ Hz}, 1\text{H}), 6.47 \text{ (dd, }{}^{3}J_{\text{H,H}} = 4.4 \text{ Hz}, \, {}^{3}J_{\text{H,H}} = 1.7 \text{ Hz}, 1\text{H}). \end{split}$$

¹³C-NMR (100 MHz, CD₂Cl₂):

$$\begin{split} \delta \, [\text{ppm}] = & 152.3 \, (\text{CH}), \, 150.9 \, (\text{CH}), \, 148.5 \, (\text{C}), \, 145.4 \, (\text{C}), \, 140.2 \, (\text{CH}), \, 138.1 \, (\text{C}), \, 137.3 \, (\text{C}), \, 136.4 \, (\text{C}), \\ & 135.7 \, (\text{CH}), \, 131.8 \, (\text{CH}), \, 131.4 \, (\text{CH}), \, 131.3 \, (\text{C}), \, 130.9 \, (\text{CH}), \, 128.9 \, (\text{CH}), \, 127.7 \, (\text{CH}), \, 126.9 \\ & (\text{CH}), \, 125.6 \, (\text{CH}), \, 124.2 \, (\text{CH}), \, 117.5 \, (\text{CH}), \, 117.1 \, (\text{CH}), \, 111.0 \, (\text{CH}), \, 107.3 \, (\text{CH}). \end{split}$$

| Microanalysis (CHN): | calc. for $C_{24}H_{18}N_4Pt$ | C-%: 51.70, | H-%: 3.25, | N-%: 10.05 |
|---------------------------|--|-----------------|------------|-------------|
| | found for $C_{24}H_{18}N_4Pt$ | C-%: 51.67, | H-%: 3.45, | N-%: 10.07. |
| ESI-MS (pos., high res.): | $[M^{**}] = C_{24}H_{18}N_4Pt;$ $\Delta = 0.81 \text{ ppm}$ | calc.: 557.1175 | 7, found: | 557.11712 |

3 Analytical Methods

3.1 NMR-Spectroscopy

¹H and ¹³C NMR spectra were measured on a Bruker Avance III HD 400 FT-Spectromenter (¹H: 400.03 MHz, ¹³C: 100.59 MHz) in deuterated dichloromethane (CD_2Cl_2). At 300 K, CD_2Cl_2 was used after rinsing over basic alumina. Samples were filtered and placed in frequency-matched 5 mm glass sample tubes. Chemical shifts are given in ppm relative to the residual nondeuterated CH_2Cl_2 signal (in ppm: ¹H: CH_2Cl_2 : 5.32; ¹³C: CH_2Cl_2 : 53.84).[16]

The abbreviations used for assigning the spin multiplicities are: s = singlet, d = doublet, dd = doublet of doublet; p = primary, s = secondary, t = tertiary, q = quaternary. Multiplet signals or overlapping signals in proton NMR spectra that could not be assigned to first order couplings are given as (-).

3.2 Mass-Spectrometry

Mass spectra were recorded with a Bruker Daltonic microTOF focus (ESI). Mass spectrometry peaks are reported as m/z. For calculation of the respective mass values of the isotopic distribution, the software module "Bruker Daltonics IsotopePattern" from the software Compass 1.1 from Bruker Daltonics GmbH, Bremen was used. Calculated (calc.) and measured (found) peak values correspond to the most intense peak of the isotopic distribution.

3.3 Elemental Analysis (CHN)

Elemental analyses were performed with a vario MICRO cube CHNS instrument for non-halogenated compounds from Elementar at the Institut für Anorganische Chemie, Universität Würzburg.

3.4 Steady State UV/Vis-absorption Spectroscopy

• JASCO V-670 UV/Vis/NIR spectrometer (software SpectraManager v. 2.08.04)

The used solvent, DCM was spectroscopic grade and was used without further purification. Absorption spectra were recorded in 1 cm quartz cuvettes from Starna (Pfungstadt, Germany) at rt. Absence of aggregation of the complex could be proven by a concentration independent behaviour $(10^{-6}-10^{-4} \text{ M})$.

3.5 fs-Transient Absorption Spectroscopy

- Newport-Spectra-Physics Solstice one box chirped pulse amplified ultrafast Ti:Sapphir laser system (CPA) with a fundamental wavenumber of 12 500 cm⁻¹ (800 nm), a pulse length of 100 fs and a repetition rate of 1 kHz
- Newport-Spectra-Physics TOPAS-optical parametric amplifier as the source for the pump pulses with a pulse length shorter than 150 fs
- Ultrafast Systems Helios transient absorption spectrometer with a CMOS sensor (1.5 nm intrinsic resolution, 200–1000 nm sensitivity range)

All experiments were performed in quartz cuvettes from Spectrocell (Oreland, PA) with an optical path length of 2 mm equipped with a micro-stirrer to allow stirring during the measurement. All samples were dissolved in freshly distilled THF, filtered and degassed for at least 15 min before each measurement. The stability of the samples was verified by recording the steady-state absorption spectra before and after the time-resolved measurements.

The output of the CPA was split into two parts. One part was used to seed an optical parametric amplifier (Newport-Spectra-Physics, TOPAS) to generate the pump pulse with a pump energy of 100–250 nJ at the wavenumber of excitation and a pulse length shorter than 150 fs. The second part was used to generate the horizontally polarized probe beam by focusing onto a moving calcium fluoride-plate to produce a white light continuum between 29 400 cm⁻¹ (340 nm) and 11 800 cm⁻¹ (850 nm). The measurements were carried out under magic angle conditions and the pump and probe beam met under an angle of 6°. The pump beam was collimated to a spot, which was at least two times larger than the diameter of the spatially overlapping probe pulse. The temporal delay of the probe pulse relative to the pump pulse was varied over a maximum range of 8 ns using a motorized, computer-controlled linear stage. The first 4 ps had a delay interval between two consecutive data points of 20 fs and the interval was increased in logarithmic steps up to 200 ps for very large delay times. After passing the sample, the probe pulses were detected by a CMOS with 4 nm resolution in a range of 400–800 nm. The instrument response function (IRF) was ca. 100 fs wide and was determined by fitting of the coherent artefact. Part of the probe light pulse was used to correct for intensity fluctuations of the white light continuum. A mechanical chopper, working at 500 Hz, blocked every second pulse, in order to measure *I* and *I*₀.

The time resolved spectra were analyzed by global fitting with GLOTARAN (v. 1.2).[17] For this purpose a sequential (i. e. unbranched unidirectional model) was applied to model the Gaussian type IRF, the coherent artefact at time zero, and to yield the evolution associated difference spectra (EADS) with the minimum number of exponential functions producing a satisfying fit. The white light dispersion (chirp) was corrected by fitting a third order polynomial to the cross phase modulation signal of the pure solvent under otherwise identical experimental conditions.

3.6 ns-Transient Absorption Spectroscopy

- Edinburgh LP 920 laser flash spectrometer with a 450 W ozone-free Xe arc lamp including a photomultiplier (Hamamatsu R955), digital storage oscilloscope (Tektronix TD3012B) and software (L900 v. 7.3.5)
- Continuum Minilite II Nd:YAG laser operating at 10 Hz, 3-5 ns pulse duration, pulse energy 8 mJ at 28200 cm⁻¹ (355 nm)
- H₂-Raman shifter (~50 bar)
- EKS-PLA NT 342A Nd:YAG laser operating at 10 Hz, 3-5 ns pulse duration, pulse energy 59 mJ at 28 200 cm⁻¹ (355 nm)
- OPO BBO II optical parametric oscillator for generating photon energies between 28200 cm⁻¹ (355 nm) and 14 300 cm⁻¹ (700 nm)

All measurements were carried out in a 1 cm quartz cell (Starna, Pfungstadt, Germany). THF was destilled prior to use. THF and p-THF were degassed by freeze pump thaw cycles and stored in a glovebox under nitrogen atmosphere with an oxygen-amount of < 1ppm in which sample-preparation was done. White light was provided by a pulsed Xe flash lamp for meassurements on timescales shorter than 100 μ s. For longer timescales, the Xe flash lamp had to be used in continuos wave (cw) mode to provide a a stable light intensity. All measurements were carried out with activated fluorescence correction implemented in the L900 software and the time range was chosen such that the decay profile was completely back to zero or at least parallel to the abscissa. Measurements were performed at different concentrations ($10^{-6}-10^{-5}$ M) and pulse energies (0.2–1.2 mJ) to check for the absence of bimolecular deactivation processes. For all measurements a long pass (LP) filter (> 400 nm) was placed in front of the detector slit to avoid signals of higher order. The instrument response (ca. 7 ns) of the set-up was determined by measuring the scattered excitation pulse using a LUDOX AS-30 colloidal silica suspension

Zero-field (B = 0)

in water.

The samples were excited with 5 ns laser pulses from a Continuum Minilite II Nd:YAG laser. The excitation energy of 24000 cm⁻¹ (416 nm) was achieved by shifting the third harmonic generation of the fundamental at 9400 cm⁻¹ (1024 nm) to lower energy with a raman-shifter charged with hydrogen (~50 bar) and selecting the desired energy with a Pellni-Broca prism. Transient maps were obtained by

measuring temporal decay profiles in 4 nm steps between 12 500 and 25 000 cm⁻¹ (800–400 nm) and were at least averaged 64 times. For selected wavelengths the signals were averaged 10–20 times depending on the signal-to-noise ratio. Using the corresponding spectrometer software function decay curves with a lifetime shorter than 100 ns were deconvoluted with the IRF while longer decays were only tail-fitted. Residuals and autocorrelation function (without any significant structure) served as the main criteria in the evaluation of the fit.

The quantum yield of CS state formation was estimated by actinometry at 24 000 cm⁻¹ (416 nm) vs. Ru(bpy)₃Cl₂[18] (in H₂O) using equation (S1).

$$\Phi_{\rm CS} = \Phi_{\rm ref} \times \frac{\Delta OD_{\rm CS} \times \varepsilon_{\rm ref}}{\Delta OD_{\rm ref} \times \varepsilon_{\rm CS}}$$
(S1)

A value of 11 300 L mol⁻¹ cm⁻¹ [18] was used for the Ru(bpy)₃Cl₂ transient signal at 22 300 cm⁻¹ (448 nm). The triplet state quantum yield for the references is close to unity according to literature[19-21], therefore $\Phi_{ref} = 1$. The ε_{cs} values for the CS state were extracted from spectroelectrochemistry measurements of similar complexes with equivalent donor and acceptor moieties.[2] The ΔOD_{cs} and ΔOD_{ref} values were determined by an average of four different measurements at four different laser intensities to ensure a linear dependence of the ΔOD with the laser intensity. The determined quantum yield of charge seperation was 0.23 for DPtA in THF.

Non-zero Field (B > 0)

- GMW Associates C-frame electromagnet 5403 (pole diameter = 76 mm, pole face = 38 mm, axial hole in poles 6.35 mm, pole gap = 12 mm), Sorensen (DLM40-75E) power supply
- Hall-Sensor (Single-Axis Magnetic Field Transductor YM12-2-5-5T, SENIS GmbH)

For the field-dependent measurements the aforementioned laser flash spectroscopy set-up was equipped with an electromagnet. The samples were excited with ca. 5 ns laser pulses from the 28200 cm⁻¹ output of an EKS-PLA NT 342A Nd:YAG shifted to the desired wavenumber by an OPO BBO II optical parametric oscillator. In any case the excitation pulse had an energy of around 1.2 mJ. The pump and flash beams were aligned perpendicularly to each other, with the pump beam being focused through the poles and the white light being directed through the open faces of the C-frame. The magnetic field strength was controlled by a Hall-sensor which was placed at the side of the pole face. The field difference between the positions of the Hall sensor at the pole face and the position where pump and flashlight met within the cuvette, was corrected by a previously determined calibrating curve. The stepsize between different fields was 0.1-1.0 mT at low magnetic fields (between 0.0-10 mT) and was further increased to 1.0-10 mT steps (between 10-100 mT), 10-50 mT steps (between 100-400 mT), and 100-500 mT steps (between 400-1800 mT). The error of determining the magnetic field was assigned to ± 0.02 mT. Since traces of O_2 in the solution reduce the MFE drastically the transient signals at selected magnetic fields, e.g. at 0, 300, 1000 and 1800 mT were tested repeatedly to prove gas-tight conditions.

4 Complementary Results



4.1 ns-Transient Absorption Spectroscopy of DPtA in pTHF

Figure S1 ns-transient absorption spectroscopy of **DPtA** in pTHF at rt after excitation at 24000 cm⁻¹. Spectra are depicted in blue to green at early and green to red at later times a) transient Absorption spectra between 0.50 μ s and 0.59 μ s and b) 0.6 μ s and 2.98 μ s c) kinetic of the decay at 19900 cm⁻¹ and d) 21100 cm⁻¹.



4.2 fs-Transient Absorption of DPtA in THF

Figure S2 a) chirp corrected fs-transient absorption spectra of DPtA in THF at rt after excitation at 19800 cm⁻¹. Spectra are depicted in blue to green at early, and in yellow to red at later times. The grey shaded area is strongly influenced by scattered pump light b) evolution associated decay spectra (EADS) obtained from a global deconvolution c) time traces and fit at selected wavelengths.

Figure S2 a) shows the transient absorption spectra of **DPtA** in THF while the evolution associated spectra obtained by global deconvolution of the data are given in Figure S2 b). The first EADS (black) shows ground state bleaching (GSB) which is strongly superimposed by the coherent artefact but is necessary for a satisfying fit. It evolves with a lifetime of 104 fs to a second EADS (red) which in turn S11

evolves with a lifetime of 129.3 ps to the third transient (blue). Both EADS show small absorption contributions in addition to the GSB, but none which are characteristic for either the NDI radical anion at 21100 cm⁻¹ (474 nm) and 16600 cm⁻¹ (602 nm)[22] or the TAA radical cation at 13600 cm⁻¹ (735 nm).[23] The first three EADS are therefore assigned to processes associated only with the central Pt(II) dipyrrinato complex. In accordance to comparable complexes of Ir(III) the decay of the first transient with τ = 104 fs is assigned to the inter system crossing from the singlet excited state to a triplet excited state.[24] The second process (τ = 120 ps) is a relaxation of the triplet excited state. The third process shows a lifetime of 10 ns and leads to the fourth and final EADS which shows, albeit very weakly, the signals characteristic for both radical ions mentioned above. It is therefore assigned to the electron transfer from donor to acceptor in a pseudo concerted manner as described before.[2,3] We assume that first an electron is transferred from the excited central Pt(II) complex to the NDI with a rate constant of around 1/(10 ns) to yield a **DPt⁺A⁻** state. This process is followed by a relatively fast subsequent hole transfer from the oxidised Pt-dipyrrin chromophore to the TAA to give D⁺PtA⁻. This process cannot be observed directly as the intermediate concentration of **DPt⁺A⁻** is very low. The difference of the rate constants of charge separation deduced from transient absorption measurements on the ns-timescale 1/(26 ns), see main text, Figure 1) and the fs-timescale (10 ns) is caused by the short time range of the fsexperiment which is only about 7 ns and therefore shorter than the lifetime of the observed process. This leads to significant errors in the determination of long lifetimes in the fs-transient absorption.

5 Data Analysis

To prepare the acquired data for further analysis, the decays at all magnetic fields were backextrapolated to the rise of the excitation pulse to account for the width of the laser pulse, the finite response time of the instrument and especially the slow population of the CS-state. This time was then defined as time zero. The back-extrapolation was done by deconvolution of the decays with the instrument response function (IRF), and addition of the noisy residuals of the fit to the decay trace of the deconvolution as shown in Figure S3. In this procedure, the time zero, the IRF and the population-time were kept constant for all magnetic fields while the lifetime of the decay was variable.

Furthermore, the intrinsic offset of the decay curves at very late times, which is caused by the set-up, was subtracted and all decay curves were normalized to 1 to compensate for laser intensity fluctuations. The corrected traces were reduced in their amount of data-points by selecting around 250 points, with a high data point density at early times and continuously lower density towards later times. The data prepared thereby were imported into the MatLab program and fitted to the model established by Hayashi and Nakagura[25] which is shown in Scheme S2 and described by equation (S2).



Figure S3 Back-extrapolation of the early part of the transient absorption signal. The first 0.5 μ s after the signal onset (time zero) are deconvoluted with the IRF and a rise time of the CS-state of 26 ns (red). The theoretical decay without IRF and rise time is shown in blue. Inset: To generate a proper noise for the back-extrapolated decay, the residual of the deconvolution fit is added to the theoretical decay between 0.5 μ s and time zero (green).



Scheme S2 Model for the charge-recombination of radical pairs with negligible exchange interaction and a finite *Zeeman* splitting. The rate constant k_{T} of triplet recombination, is assumed to be zero because the process is spin-forbidden. Magnetic field dependent processes are depicted in red.

$$d[S]/dt = -(k_{S} + 2k_{\pm} + k_{ST_{0}})[S] + k_{ST_{0}} + [T_{0}] + k_{\pm}([T_{+}] + [T_{-}])$$

$$d[T_{0}]/dt = k_{ST_{0}}[S] - (k_{T} + 2k_{\pm} + k_{ST_{0}})[T_{0}] + k_{\pm}([T_{+}] + [T_{-}])$$

$$d[T_{+}]/dt = k_{\pm}[S] + k_{\pm}[T_{0}] - (k_{T} + 2k_{\pm})[T_{+}]$$

$$d[T_{-}]/dt = k_{\pm}[S] + k_{\pm}[T_{0}] - (k_{T} + 2k_{\pm})[T_{-}]$$
(S2)

Here k_{STO} , k_{S} and the initial singlet population p_{S} are magnetic field independent values. k_{STO} is fixed to 4.0 E7 s⁻¹ based on a classical approximation of the semi classical model by *Schulten* and *Wolynes*.[3,26] p_{S} and k_{S} are determined by a global fit of the decays at 16 representative magnetic fields using script 1 given in the Section 11. As the only field dependent parameter, k_{\pm} can subsequently be determined by individually fitting the decay at each magnetic field using script 2 given in Section 11. The initial singlet character pS was determined to be 0.07 for **DPtA** in THF, while k_{S} was found to be variable to some degree while still giving satisfying fits. This can be explained by the fact that in kinetic systems such as the one described by scheme S2 and equation (S2) two rate-constants k may compensate each other to yield nearly identical decay curves for different combinations of values. This is the case for k_{S} and k_{\pm} at low fields. As shown in Figure S4, higher values of k_{S} give lower values of $k_{\pm}(0)$ and *vice versa*. The effect is especially pronounced for the fast decays at low magnetic field values, and is reduced for the slow decays at high magnetic field which are predominantly determined by the processes associated with k_{\pm} and therefore less sensitive to variations of k_{S} .



Figure S4 Influence of k_s on the behavior of k_{\pm} . Lower values of k_s (black and green circles) lead to higher values of k_{\pm} . The best fit to a double lorentzian with $k_{hfc,0} = 4.0 \text{ E7 s}^{-1}$ (black curve) is achieved for values of $k_s = 1.048 \text{ E7 s}^{-1}$ (orange circles).

To decide which pair of k_s and $k_{\pm}(0)$ values is the most plausible, the different sets of k_{\pm} -values were fitted to a double Lorentzian function (equation (S3)).

$$k_{\pm}(B) = \frac{k_{\rm hfc,0}}{1 + (B_0 / B_{\rm 1/2, hfc})^2} + \frac{k_{\rm rel,0}}{1 + (B_0 / B_{\rm 1/2, rel})^2} + k_{\rm rel,\infty}$$
(S3)

If the two steps of the curve are sufficiently separated, the first Lorentzian describes the coherent spin flip, caused by isotropic hyper fine coupling to the nuclei involved in the radicals. The second Lorentzian describes incoherent spin relaxation processes which should be mostly determined by the rotational modulation of the anisotropic hyper fine coupling.[3] In THF, at low magnetic fields the coherent processes are significantly faster than the incoherent ones. Here, the first Lorentzian is the dominant term. If one takes into account that at B = 0 the triplet sublevels are degenerate and therefore k_{\pm} should be equal to k_{ST0} , then one can determine the optimal k_{s} -value by comparison with a fit to equation (S2) where $k_{hfc,0}$ is kept equal to $k_{ST0} = 4.0 \text{ E7 s}^{-1}$ as done in Figure 4. Although in pTHF the contributions of coherent and incoherent mechanism of spin mixing at low fields are less clearly separated in their orders of magnitude, the same approach as in THF was applied. The optimum values determined for k_s and p_s can be found in Table 1 of the main text.

6 Comparison of B_1 and $B_{hfc,1/2}$

The coefficient B_1 in equation (2) in the main text represents the field value at which the coherent contribution to k_{\pm} has dropped to half its value at zero field. This value should be distinguished from the "half field" value $B_{hfc,1/2}$ usually quoted to characterize spin chemical magnetic field effect, and often represented by relations like equation (3). Usually it is measured by means of the field dependent effect on some product yield.

Table S2 Examples of decay functions for selected fields calculated for DPtA in THF according to equations (1).



Figure S5 a) Field dependence of k_{\pm} and of $k_{eff, 2}$, the slowest rate constant of the triexponential function describing the charge recombination kinetics (cf. the examples in Table S2). The graphical significance of the parameters B_1 and $B_{hfc,1/2}$ is indicated. b) Set of charge recombination curves in THF at low fields c) detail of b) with pertinent field values indicated in units of mT.

Considering product yields at some intermediate time, these are approximately linearly related to effective rate constants of product formation. Hence, in our case, we can consider the magnetic field effect on the effective rate constant of recombination, which can be extracted from the tri-exponential decay function, appearing as the solution to reaction scheme (1). In Table S2 this tri-exponential function is given for some values of the magnetic field *B*.

The weight of the three exponentials is very different. At fields below 8-10 mT, the region of coherent magnetic field effects, the decay is practically monoexponential. At higher fields it becomes practically bi-exponential, with the smaller one of the decay constants decreasing continuously from zero field to high field. The second highest rate constant converges quickly to a value of about two times the zero field value of the smallest rate constant as soon as the pertinent exponential adopts sizeable contributions which in no case exceed a maximum value of about 1/3. Therefore, to assess the half field value of the kinetics in the coherent regime we can concentrate on the smallest of the three rate constants, which we will denote as $k_{eff,2}$. It is plotted as a function of the magnetic field *B* in a double log plot in Figure S5a. Its limiting value at zero field comes close to the value of $k_s/4$, corresponding to a situation of perfectly established spin equilibrium. Assuming the coherent region to extend between 0 and 8 mT, the half-field value of $k_{eff,2}$ between these limits ($k_{eff,2}$ (0 mT) = $2.50 \times 10^6 \text{ s}^{-1}$, $k_{eff,2}(8 \text{ mT}) = 1.72 \times 10^6 \text{ s}^{-1}$), is $2.11 \times 10^6 \text{ s}^{-1}$, which occurs at $B_{hfc,1/2} = 3.4 \text{ mT}$. About the same value is also obtained by assessing the middle of the decay signals at about 0.5 µs between 0 and 8 mT (cf. Figure S2b and c)

7 Fitting the magnetic field dependence of k_{\pm} in pTHF



 $pTHFa = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.953604, k2 \rightarrow 6.65462 *10^{6}, B2 \rightarrow 0.9, k0 \rightarrow 24511.7\}, 2.11323\}; \\ pTHFb = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.960648, k2 \rightarrow 6.67726 *10^{6}, B2 \rightarrow 0.85, k0 \rightarrow 24515.6\}, 2.11541\}; \\ pTHFc = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.948316, k2 \rightarrow 6.50045 *10^{6}, B2 \rightarrow 0.948316, k0 \rightarrow 24504.2\}, 2.11253\}; \\ pTHFd = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.93, k2 \rightarrow 0., B2 \rightarrow 0.001, k0 \rightarrow 23000.1\}, 2.46346\}; \\ pTHFe = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.953604, k2 \rightarrow 6.65462 *10^{6}, B2 \rightarrow 0.9, k0 \rightarrow 24511.7\}, 2.11323\}; \\ pTHFf = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.953604, k2 \rightarrow 6.65462 *10^{6}, B2 \rightarrow 0.9, k0 \rightarrow 24511.7\}, 2.11323\}; \\ pTHFf = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.943932, k2 \rightarrow 5.34372 *10^{6}, B2 \rightarrow 1.1, k0 \rightarrow 24464.5\}, 2.11869\}; \\ pTHFg = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.968957, k2 \rightarrow 6.54431 *10^{6}, B2 \rightarrow 0.8, k0 \rightarrow 24515.\}, 2.11898\}; \\ pTHFn = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.987903, k2 \rightarrow 5.74221 *10^{6}, B2 \rightarrow 0.7, k0 \rightarrow 24400.5\}, 2.12935\}; \\ pTHFi = \{\{k1 \rightarrow 4. *10^{7}, B1 \rightarrow 0.944609, k2 \rightarrow 6.20877 *10^{6}, B2 \rightarrow 1.1, k0 \rightarrow 24492.8\}, 2.11331\}; \end{cases}$

Figure S6 Examples of theoretical curves with different parameter sets for lg[k± (lg[B])] for pTHF according to equation (2). All data sets, except for set pTHFd (red curve), corresponding to the extreme of a pure single Lorentzian step, lead to practically indistinguishable curves. The last number in each parameter line denotes the sum of square deviations over all experimental data points.

8 Demonstration of Fit Quality



Figure S7 Comparison of fit of decay kinetics in THF according to classical model with k_{\pm} given be equation (2) in the main text, using the parameters in Table 1. Black curves: experimental data, red curves: simulation.



Figure S8 Comparison of fit of decay kinetics in pTHF according to classical model with k_{\pm} given be equation (2) in the main text, using the parameters of Set c in Table 1. Black curves: experimental data, red curves: simulation.

9 Dipole-dipole relaxation matrix and triplet-triplet dephasing

In a RP with the electron spins at a fixed distance R, the zero field splitting parameter is given by

$$D = -\frac{3}{2} \frac{g^2 \mu_B^2}{R^3}$$
(S4)

The characteristic parameter *Dip* used in the program code is

$$DIP = \frac{g^2 \mu_B^2}{R^3} = \frac{18548}{(R/Å)^3} G = \frac{326.4}{(R/Å)^3} ns^{-1}$$
(S5)

For a separation of R = 20 Å, $DIP = 4.08 \times 10^7 \text{ s}^{-1} \triangleq 2.32 \text{ G}$.

The rate constant k_{dd} for transitions between T₀ and T_± is given by[25]

$$k_{\rm dd} = \frac{1}{\hbar} \frac{3}{10} \frac{g^2 \mu_{\rm B}^2}{R^6} \frac{\tau_{\rm c}}{1 + \omega_0^2 \tau_c}$$
(S6)

To derive the relaxation matrix for the density matrix treatment, we followed the method employed in previous work [27,28] for the analogous case of anisotropic hyperfine coupling. Within Redfield theory the relaxation operator (Redfield matrix) is defined by the equation:

$$\left(\frac{d\rho_{\alpha\alpha'}(t)}{dt}\right)_{\rm rel} = \sum_{\beta\beta'} R_{\alpha\alpha',\beta\beta'} \rho_{\beta\beta'}(t)$$
(S7)

where the indices α , α' , β , β' refer to the eigenstates of the time-independent spin Hamiltonian of the system comprising hyperfine couplings, Zeeman interaction of electron spins with the external magnetic field, and exchange interaction.

The relaxation operator R in equation (S7) is given by [29]

$$R_{\alpha\alpha',\beta\beta'} = \frac{1}{2\hbar^2} \left[J_{\alpha\beta\alpha'\beta'}(\alpha'-\beta') + J_{\alpha\beta\alpha'\beta'}(\alpha-\beta) - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\gamma\beta\gamma\alpha}(\gamma-\beta) - \delta_{\alpha\beta} \sum_{\gamma} J_{\gamma\alpha'\gamma\beta'}(\gamma-\beta') \right]$$
(S8)

Here, for the sake of simplicity, the arguments α , α' , β , β' of the functions $J(\omega)$ denote angular frequencies in rad/s defined as $\alpha = E_{\alpha} / \hbar$ and so on. The quantities $J_{\alpha\alpha',\beta\beta'}(\omega)$ are defined through correlation functions of the stochastic Hamiltonian of dipole-dipole interaction H₁(t):

$$J_{\alpha\alpha',\beta\beta'}(\omega) = \int_{-\infty}^{+\infty} \overline{(\alpha | \mathbf{H}_1(t) | \alpha')(\beta' | \mathbf{H}_1(t+\tau) | \beta)} e^{-i\omega\tau} d\tau$$
(S9)

Where the stochastic Hamiltonian of dipole-dipole interaction of electron spins is as follows:

$$\begin{split} H_{1}(t) &= \\ \left(\hat{s}_{1z}\cdot\hat{s}_{2z} - \frac{1}{4}(\hat{s}_{1+}\cdot\hat{s}_{2-} + \hat{s}_{1-}\cdot\hat{s}_{2+})\right)F_{0}(t) + (\hat{s}_{1+}\cdot\hat{s}_{2z} + \hat{s}_{1z}\cdot\hat{s}_{2+})F_{1}(t) + (\hat{s}_{1-}\cdot\hat{s}_{2z} + \hat{s}_{1z}\cdot\hat{s}_{2-})F_{1}^{*}(t) + \\ (\hat{s}_{1+}\cdot\hat{s}_{2+})F_{2}(t) + (\hat{s}_{1-}\cdot\hat{s}_{2-})F_{2}^{*}(t); \end{split}$$
(S10)

Here \hat{s}_{1z} etc. are the operators of either donor or acceptor electron spin; $F_0(t)$, $F_1(t)$, $F_2(t)$ are stochastic functions, the overline means averaging over the different realizations of the stochastic Hamiltonian $H_1(t)$ in time.

The correlation functions of the stochastic quantities $F_0(t)$, $F_1(t)$, $F_2(t)$ are given by:

$$\overline{F_0(t)F_0(t+\tau)} = \frac{4}{5}DIP^2 e^{-\tau/\tau_c}; \quad \overline{F_1(t)F_1^*(t+\tau)} = \overline{F_2(t)F_2^*(t+\tau)} = \frac{3}{10}DIP^2 e^{-\tau/\tau_c}; \quad (S11)$$

with τ_c as the correlation time of the perturbation. Equations (S7-S11) represent the basis for programming the relaxation operator R.

Numerical values of the relaxation matrices for dipolar relaxation under various conditions are given in Table **S3**. The matrix elements referring to population transfer from T_0 to T_{\pm} are in good agreement with the results derived from equation (S6).

Miura and Murai[30] suggested the following operator for triplet-triplet dephasing by dipolar interaction:

$$R_{\text{TTD}} = w_{\text{TTD}} \sum_{j=+1,-1} \left(\left| \mathbf{T}_{j} \mathbf{T}_{0} \right\rangle \left\langle \mathbf{T}_{j} \mathbf{T}_{0} \right| + \left| \mathbf{T}_{0} \mathbf{T}_{j} \right\rangle \left\langle \mathbf{T}_{0} \mathbf{T}_{j} \right| \right)$$
(S12)

In the matrices shown in Table S3, the corresponding matrix elements are marked in pink. At zero field, they are of a similar order of magnitude as the matrix elements representing the population trasnfer from T_0 to T_{\pm} , but they show a weaker magnetic field dependence at higher fields (not shown in the table). **Table S3** Dipole-Dipole Relaxation matrices. The value of k_{dd} was calculated using equation (S3). Marked in yellow are the matrix elements connecting the populations of T_0 with T_+ and T_- . The matrix elements marked in pink refer to the triplet-triplet-dephasing matrix elements specified in equation (S12).

| τ_{c} = 0.2 ns | | B = 0 mT | | | | | | | | |
|---------------------|---------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----------------|
| | тото | T+T0 | T-T0 | T0T+ | T+T+ | T-T+ | T0T- | T+T- | T-T- | k _{dd} |
| тото | -0,00019981 | 0 | 0 | 0 | 9,99E-05 | 0 | 0 | 0 | 9,99E-05 | 1,00E-04 |
| T+T0 | 0 | -0,00039962 | 0 | 0 | 0 | 0 | -9,99E-05 | 0 | 0 | |
| T-T0 | 0 | 0 | -0,00039962 | -9,99E-05 | 0 | 0 | 0 | 0 | 0 | |
| T0T+ | 0 | 0 | -9,99E-05 | -0,00039962 | 0 | 0 | 0 | 0 | 0 | |
| T+T+ | 9,99E-05 | 0 | 0 | 0 | -0,00029972 | 0 | 0 | 0 | 0,00019981 | |
| T-T+ | 0 | 0 | 0 | 0 | 0 | -0,00029972 | 0 | 0 | 0 | |
| TOT- | 0 | -9.99E-05 | 0 | 0 | 0 | 0 | -0.00039962 | 0 | 0 | |
| T+T- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0,00029972 | 0 | |
| T-T- | 9,99E-05 | 0 | 0 | 0 | 0,00019981 | 0 | 0 | 0 | -0,00029972 | |
| | | | | | | | | | | |
| , | τ _c = 0.2 ns | 5 | B =20 mT | | | | | | | |
| | тото | T+T0 | T-T0 | T0T+ | T+T+ | T-T+ | TOT- | T+T- | T-T- | Kaa |
| тото | -0.0001336 | 0 | 0 | 0 | 6.68E-05 | 0 | 0 | 0 | 6.68E-05 | 6.69E-05 |
| T+T0 | 0 | -0.00028356 | 0 | 0 | 0 | 0 | -6 68F-05 | 0 | 0 | 0,002.00 |
| T-T0 | 0 | 0 | -0.00028356 | -6.68E-05 | 0 | 0 | 0 | 0 | 0 | |
| TOT+ | 0 | 0 | -6 68E-05 | -0.00028356 | 0 | 0 | 0 | 0 | 0 | |
| T+T+ | 6 68F-05 | 0 | 0 | 0 | -0.00013379 | 0 | 0 | 0 | 6 70E-05 | |
| T-T+ | 0,002 05 | 0 | 0 | 0 | 0,00013373 | -0.00013379 | 0 | 0 | 0,702.05 | |
| TOT- | 0 | -6 68F-05 | 0 | 0 | 0 | 0 | -0.00028356 | 0 | 0 | |
| T+T- | 0 | 0,002 05 | 0 | 0 | 0 | 0 | 0,00020550 | -0.00013379 | 0 | |
| T.T. | 6 68E-05 | 0 | 0 | 0 | 6 70E-05 | 0 | 0 | 0,00013373 | -0.00012279 | |
| 1-1- | 0,081-03 | 0 | 0 | 0 | 0,702-05 | 0 | 0 | 0 | -0,00013373 | |
| | $\tau_{c} = 4 \text{ ns}$ | | B = 0 mT | | | | | | | |
| | тото | T+T0 | T-T0 | T0T+ | T+T+ | T-T+ | T0T- | T+T- | T-T- | k _{dd} |
| тото | -0,00399623 | 0 | 0 | 0 | 2,00E-03 | 0 | 0 | 0 | 2,00E-03 | 2,00E-03 |
| T+T0 | 0 | -0,00799247 | 0 | 0 | 0 | 0 | -2,00E-03 | 0 | 0 | |
| T-T0 | 0 | 0 | -0,00799247 | -2,00E-03 | 0 | 0 | 0 | 0 | 0 | |
| T0T+ | 0 | 0 | -2,00E-03 | -0,00799247 | 0 | 0 | 0 | 0 | 0 | |
| T+T+ | 2,00E-03 | 0 | 0 | 0 | -0,00599435 | 0 | 0 | 0 | 0,00399623 | |
| T-T+ | 0 | 0 | 0 | 0 | 0 | -0,00599435 | 0 | 0 | 0 | |
| T0T- | 0 | -2,00E-03 | 0 | 0 | 0 | 0 | -0,00799247 | 0 | 0 | |
| T+T- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0,00599435 | 0 | |
| T-T- | 2,00E-03 | 0 | 0 | 0 | 0,00399623 | 0 | 0 | 0 | -0,00599435 | |
| | | | | | | | | | | |
| | τ_{c} = 4 ns | | B = 2 mT | | | | | | | |
| | тото | T+T0 | T-T0 | T0T+ | T+T+ | T-T+ | T0T- | T+T- | T-T- | k _{dd} |
| тото | -0,00133991 | 0 | 0 | 0 | 6,70E-04 | 0 | 0 | 0 | 6,70E-04 | 6,71E-04 |
| T+T0 | 0 | -0,00422586 | 0 | 0 | 0 | 0 | -6,70E-04 | 0 | 0 | |
| T-T0 | 0 | 0 | -0,00422586 | -6,70E-04 | 0 | 0 | 0 | 0 | 0 | |
| T0T+ | 0 | 0 | -6,70E-04 | -0,00422586 | 0 | 0 | 0 | 0 | 0 | |
| T+T+ | 6,70E-04 | 0 | 0 | 0 | -0,00111747 | 0 | 0 | 0 | 0,00044751 | |
| T-T+ | 0 | 0 | 0 | 0 | 0 | -0,00111747 | 0 | 0 | 0 | |
| T0T- | 0 | -6,70E-04 | 0 | 0 | 0 | 0 | -0,00422586 | 0 | 0 | |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00111747 | 0 | |
| T+T- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0,00111747 | 0 | |

10 Quantum dynamical simulations



Figure S8 Results of quantum dynamical simulations at seven characteristic fields for low viscous solvents, characteried by the rotational correlation time τ_{cr} in comparison to experimental results in THF.



Figure S9 Results of quantum dynamical simulations at seven characteristic fields for highly viscous solvents, characteried by the rotational correlation time τ_c , in comparison to experimental results in pTHF.

10.1 Quantum dynamical simulation of spin evolution under hfc and ahfc



Figure S10 Extension of Figure 7 in the text to more fields.

10.2 Quantum dynamical simulation of rigid medium



Figure S11 Comparison of decay signals. Left: experiment, right: quantum calculation for rigid solution, adopting an anisotropy value of $\Delta A = 1.75$ mT

11 Report on Spin Probe Experiments in THF and pTHF

Research Report on Polymer Effect on EPR Probe Spectra

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The following probe molecules **1** and **2**, provided by Prof. Godt, were investigated in THF and poly-THF.



Experimental

The probe molecules **1** and **2** (Figure 1) were prepared in Adelheid Godt's laboratory as published previously^[1] and stored under N_2 gas at -20 °C until further use.

For CW-EPR measurements each probe molecule was dissolved either in THF or polyTHF (125 μ M). For EPR measurements, the samples were transferred into quartz capillaries (50 μ l Hirschmann ringcaps). CW-EPR measurements were performed on a Miniscope MS5000 X-Band EPR spectrometer (Freiberg instruments GmbH) at room temperature. The parameters of the measurements were chosen as follows in order not to distort the spectral shape: 0.113 mW Microwave power; 100 kHz modulation frequency; 0.108 mT and 0.09 mT modulation amplitude for THF and polyTHF, respectively; 60 s scan time; 10 scans. The spectra in THF were simulated using the function garlic of the MATLAB toolbox Easyspin^[2] (Figures 1), the spectra in pTHF using the function chili (Figure 2). For the sake of simplicity, we used a Spin S=1/2 system containing one spectral component featuring an isotropic rotational diffusion in order to obtain an effective rotational correlation time in THF and polyTHF, respectively. Models that give better fits would include several components and anisotropic rotational diffusion. However the present evaluation was only aimed at obtaining rough estimates of the correlation times in the two solvents.

Results

The resulting cw spectra of the two probes in the two solvents are shown in Figures 1 and 2.



Figure 1 Experimental CW-EPR spectra (black) and corresponding spectral simulation (red) of probe molecule **1** in (a) THF and (b) polyTHF.



Figure 2 Experimental CW-EPR spectra (black) and corresponding spectral simulation (red) of probe molecule **2** in (a) THF and (b) polyTHF.

Table 1. Parameters used in fitting the spectra in Figure 1 and 2^a

| Probe molecule | Solvent | A-tensor, MHz | g-tensor | τ _{corr} , ps |
|----------------|---------|---------------|------------------|------------------------|
| 1 | THF | [17 85] | | 163 |
| | polyTHF | [19 100] | [2.00906 2.00687 | 1259 |
| 2 | THF | [17 85] | 2.00300] | 269 |
| | polyTHF | [18 100] | | 1585 |

^a The g-tensor was taken from literature ^[3], the A-tensor and τ_{corr} (see Table 1) were found using least-square fits.

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12 Friction Coefficients

Friction coefficients λ were determined for the following structures from solvent viscosity η , and hydrodynamic Radius V_h (Connolly solvent excluded volume) according to equation (S13) of the extended Stokes-Einstein-Debye model, neglecting the correlation time of free rotation τ_0 . The parameters used and the results for λ are given in Table S4.

$$\tau_c = \frac{\lambda V_{\rm h}}{6kT} \eta + \tau_0 \tag{S13}$$

DPtA DIrA
$$\begin{array}{c} & & & & \\ & & & & \\ & & & \\ & & & \\ &$$

Spin Probe 1

Spin Probe 2



 Table S4
 Parameters of extended Stokes-Einstein-Debye model

| Probe | Solvent | $	au_{c}$, ns | η , mPa s | $V_{\rm h}^{\rm a}$, Å ³ | λ |
|-------------------|---------|----------------|----------------|--------------------------------------|-------|
| DIrA ^b | MeCN | 0.23 | 0.343 | 1162 | 12.4 |
| DPtA | THF | 0.2 | 0.518 | 993 | 9.6 |
| DPtA | pTHF | 4 | 443 | 993 | 0.22 |
| Spin probe 1 | THF | 0.163 | 0.518 | 642 | 12.1 |
| Spin probe 1 | pTHF | 1.26 | 443 | 642 | 0.11 |
| Spin probe 2 | THF | 0.27 | 0.518 | 943 | 13.6 |
| Spin probe 2 | pTHF | 1.58 | 443 | 943 | 0.093 |

^a Connolly solvent excluded volume ^b from Ref. [31]

13 Matlab Scripts

MatLab-script 1

(for the determination of global parameters p_s , k_s and k_{sto} for 16 representative magnetic field strengths)

Parts which demand an input are marked red and explained in green.

```
function [x,resnorm,residual,exitflag,output] = Difg(xo,Mx,My)
options = optimset('Display', 'iter','TolFun',2E-30,'TolX',2E-30,'Algorithm',{'levenberg-
marquardt',.001},'MaxIter',1000,'MaxFunEvals',50000);
  [x,resnorm,residual,exitflag,output] = lsqcurvefit(@nestedfun1,xo,Mx,My,[],[],options);
                                     function output = nestedfun1(x,Mx)
                                                                      x(1:16,2)=4e7; k^2 = k_{ST0} = ! 4.0 E7 s^{-1}
                                                                      x(2:16,3)=x(1,3); %k3 = ks has to be determined once for all 16 decays
                                                                         x(1:16,4)=0; \&k4 = k_T = ! 0
                                                                         k=x;
                                                                         o=length(Mx(1,:));
                                                                         for b=1:o
                                                                                                          l(b) = find(Mx(:,b)>0,1,'last');
                                                                         end
                                                                         function dy = ode1(t,y)
                                                                                                            dy = zeros(4,1);
                                                                                                            k(1,2)*y(1)+k(1,2)*y(2);
                                                                                                          dy(2) = -k(1,4) * y(2) - k(1,1) * y(2) - k(1,1) * y(2) + k(1,1) * y(3) + k(1,1) * y(4) - k(1,1) * y(4) + k(1,1) * y(1) + k(1
k(1,2)*y(2)+k(1,2)*y(1);
                                                                                                            dy(3) = -k(1,4)*y(3)-k(1,1)*y(3)-k(1,1)*y(3)+k(1,1)*y(2)+k(1,1)*y(1);
                                                                                                            dy(4) = -k(1,4) * y(4) - k(1,1) * y(4) - k(1,1) * y(4) + k(1,1) * y(2) + k(1,1) * y(1);
                                                                         end
                                                                         function dy = ode2(t, y)
                                                                                                             dy =zeros(4,1);
                                                                                                             dy(1) = -k(2,3)*y(1)-k(2,1)*y(1)+k(2,1)*y(4)+k(2,1)*y(3)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)*y(1)-k(2,1)+k(2,1)*y(1)-k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+k(2,1)+
k(2,2)*y(1)+k(2,2)*y(2);
                                                                                                          dy(2) = -k(2,4) * y(2) - k(2,1) * y(2) - k(2,1) * y(2) + k(2,1) * y(3) + k(2,1) * y(4) - k(2,1) * y(4) + k(2
k(2,2)*y(2)+k(2,2)*y(1);
                                                                                                            dy(3) = -k(2,4)*y(3)-k(2,1)*y(3)-k(2,1)*y(3)+k(2,1)*y(2)+k(2,1)*y(1);
                                                                                                          dy(4) = -k(2,4)*y(4) - k(2,1)*y(4) - k(2,1)*y(4) + k(2,1)*y(2) + k(2,1)*y(1);
                                                                         end
                                                                         function dy = ode3(t,y)
                                                                                                          dy =zeros(4,1);
                                                                                                          dy(1) = -k(3,3) * y(1) - k(3,1) * y(1) + k(3,1) * y(4) + k(3,1) * y(3) - k(3,1) * y(1) - k(3,1) * y(1) - k(3,1) * y(1) + k(3
k(3,2)*v(1)+k(3,2)*v(2);
                                                                                                            dy(2) = -k(3,4)*y(2)-k(3,1)*y(2)-k(3,1)*y(2)+k(3,1)*y(3)+k(3,1)*y(4)-k(3,1)*y(3)+k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)*y(4)-k(3,1)+k(3,1)*y(4)-k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1)+k(3,1
k(3,2)*y(2)+k(3,2)*y(1);
                                                                                                             dy(3) = -k(3,4)*y(3)-k(3,1)*y(3)-k(3,1)*y(3)+k(3,1)*y(2)+k(3,1)*y(1);
                                                                                                             dy(4) = -k(3,4)*y(4) - k(3,1)*y(4) - k(3,1)*y(4) + k(3,1)*y(2) + k(3,1)*y(1);
                                                                         end
                                                                         function dy = ode4(t, y)
                                                                                                            dy = zeros(4,1);
                                                                                                            dy(1) = -k(4,3)*y(1) - k(4,1)*y(1) + k(4,1)*y(4) + k(4,1)*y(3) - k(4,1)*y(1) - k(4,1) - k(4,1)*y(1) - k(4,1) + k(4,1)*y(1) - k(4,1) + k(4,1)*y(1) - k(4,1) + k(4,
k(4,2)*y(1)+k(4,2)*y(2);
                                                                                                            dy(2) = -k(4,4) * y(2) - k(4,1) * y(2) - k(4,1) * y(2) + k(4,1) * y(3) + k(4,1) * y(4) - k(4,1) * y(4) + k(4,1) * y(4,1) * y(4) + k(4,1) * y(4) + k(4,1) * y(4) + k(4,1) * y
 k(4,2)*y(2)+k(4,2)*y(1);
                                                                                                            dy(3) = -k(4,4)*y(3)-k(4,1)*y(3)-k(4,1)*y(3)+k(4,1)*y(2)+k(4,1)*y(1);
                                                                                                            dy(4) = -k(4,4)*y(4) - k(4,1)*y(4) - k(4,1)*y(4) + k(4,1)*y(2) + k(4,1)*y(1);
                                                                         end
                                                                         function dy = ode5(t,y)
                                                                                                            dv = zeros(4,1);
                                                                                                          dy(1) = -k(5,3) * y(1) - k(5,1) * y(1) + k(5,1) * y(4) + k(5,1) * y(3) - k(5,1) * y(1) - k(5,1) * y(1) + k(5
k(5,2)*y(1)+k(5,2)*y(2);
                                                                                                          dy(2) = -k(5,4) * y(2) - k(5,1) * y(2) - k(5,1) * y(2) + k(5,1) * y(3) + k(5,1) * y(4) - k(5,1) * y(4) + k(5,1) * y(5) + k(5
k(5,2)*y(2)+k(5,2)*y(1);
                                                                                                          dy(3) = -k(5,4) * y(3) - k(5,1) * y(3) - k(5,1) * y(3) + k(5,1) * y(2) + k(5,1) * y(1);
                                                                                                          dy(4) = -k(5,4) * y(4) - k(5,1) * y(4) - k(5,1) * y(4) + k(5,1) * y(2) + k(5,1) * y(1);
```

```
end
                                                                                               function dy = ode6(t,y)
                                                                                                                                          dy = zeros(4,1);
                                                                                                                                           dy(1) = -k(6,3)*y(1) - k(6,1)*y(1) + k(6,1)*y(4) + k(6,1)*y(3) - k(6,1)*y(1) - k(6,1) - 
k(6,2)*v(1)+k(6,2)*v(2);
                                                                                                                                           dy(2) = -k(6,4) * y(2) - k(5,1) * y(2) - k(6,1) * y(2) + k(6,1) * y(3) + k(6,1) * y(4) - k(6,1) * y(4) + k(6,1) * y(6) + k(6
 k(6,2)*y(2)+k(6,2)*y(1);
                                                                                                                                           dy(3) = -k(6,4) * y(3) - k(6,1) * y(3) - k(6,1) * y(3) + k(6,1) * y(2) + k(6,1) * y(1);
                                                                                                                                             dy(4) = -k(6,4) * y(4) - k(6,1) * y(4) - k(6,1) * y(4) + k(6,1) * y(2) + k(6,1) * y(1);
                                                                                               end
                                                                                               function dy = ode7(t,y)
                                                                                                                                           dv = zeros(4,1);
                                                                                                                                           dy(1) = -k(7,3)*y(1)-k(7,1)*y(1)+k(7,1)*y(4)+k(7,1)*y(3)-k(7,1)*y(1)-k(7,1)*y(3)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)*y(1)-k(7,1)+k(7,1)*y(1)-k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)+k(7,1)
k(7,2)*y(1)+k(7,2)*y(2);
                                                                                                                                          dy(2) = -k(7,4) * y(2) - k(7,1) * y(2) - k(7,1) * y(2) + k(7,1) * y(3) + k(7,1) * y(4) - k(7,1) * y(4) + k(7,1) * y(7,1) * y(7,1) * y(7,1) * y(7,1) * y(7,1) * y(7,1) * y(7,
 k(7,2)*y(2)+k(7,2)*y(1);
                                                                                                                                           dy(3) = -k(7,4)*y(3)-k(7,1)*y(3)-k(7,1)*y(3)+k(7,1)*y(2)+k(7,1)*y(1);
                                                                                                                                             dy(4) = -k(7,4) * y(4) - k(7,1) * y(4) - k(7,1) * y(4) + k(7,1) * y(2) + k(7,1) * y(1);
                                                                                               end
                                                                                               function dy = ode8(t,y)
                                                                                                                                           dv = zeros(4,1)i
                                                                                                                                             dy(1) = -k(8,3)*y(1) - k(8,1)*y(1) + k(8,1)*y(4) + k(8,1)*y(3) - k(8,1)*y(1) - k(8,1) - k(8,1)*y(1) - k(8,1) + 
 k(8,2)*y(1)+k(8,2)*y(2);
                                                                                                                                          dy(2) = -k(8,4) * y(2) - k(8,1) * y(2) - k(8,1) * y(2) + k(8,1) * y(3) + k(8,1) * y(4) - k(8,1) * y(4) + k(8,1) * y(6) + k(8,1) * y(6) + k(8,1) * y(6) + k(8
k(8,2)*v(2)+k(8,2)*v(1);
                                                                                                                                           dy(3) = -k(8,4) * y(3) - k(8,1) * y(3) - k(8,1) * y(3) + k(8,1) * y(2) + k(8,1) * y(1);
                                                                                                                                           dy(4) = -k(8,4) * y(4) - k(8,1) * y(4) - k(8,1) * y(4) + k(8,1) * y(2) + k(8,1) * y(1);
                                                                                               end
                                                                                               function dv = ode9(t,v)
                                                                                                                                          dy = zeros(4,1);
                                                                                                                                             k(9,2)*y(1)+k(9,2)*y(2);
                                                                                                                                          dy(2) = -k(9,4) * y(2) - k(9,1) * y(2) - k(9,1) * y(2) + k(9,1) * y(3) + k(9,1) * y(4) - k(9,1) * y(4) + k(9,1) * y(6) + k(9,1) * y(6) + k(9,1) * y(6) + k(9,1) * y(6) + k(9
 k(9,2)*v(2)+k(9,2)*v(1);
                                                                                                                                             dy(3) = -k(9,4) * y(3) - k(9,1) * y(3) - k(9,1) * y(3) + k(9,1) * y(2) + k(9,1) * y(1);
                                                                                                                                             dy(4) = -k(9,4)*y(4) - k(9,1)*y(4) - k(9,1)*y(4) + k(9,1)*y(2) + k(9,1)*y(1);
                                                                                               end
                                                                                               function dy = odel0(t,y)
                                                                                                                                           dv = zeros(4,1);
                                                                                                                                           dy(1) = -k(10,3) * y(1) - k(10,1) * y(1) + k(10,1) * y(4) + k(10,1) * y(3) - k(10,1) * y(1) - k(10,1) * y(1) + k(10,1) * y(
 k(10,2)*y(1)+k(10,2)*y(2);
                                                                                                                                           dy(2) = -k(10,4) * y(2) - k(10,1) * y(2) - k(10,1) * y(2) + k(10,1) * y(3) + k(10,1) * y(4) - k(10,1) * y(4) - k(10,1) * y(4) + k(10,1) * y(
 k(10,2)*y(2)+k(10,2)*y(1);
                                                                                                                                             dy(3) = -k(10,4) * y(3) - k(10,1) * y(3) - k(10,1) * y(3) + k(10,1) * y(2) + k(10,1) * y(1);
                                                                                                                                             dy(4) = -k(10,4) * y(4) - k(10,1) * y(4) - k(10,1) * y(4) + k(10,1) * y(2) + k(10,1) * y(1);
                                                                                               end
                                                                                               function dv = odell(t, v)
                                                                                                                                           dy = zeros(4,1);
                                                                                                                                           dy(1) = -k(11,3) * y(1) - k(11,1) * y(1) + k(11,1) * y(4) + k(11,1) * y(3) - k(11,1) * y(1) - k(11,1) * y(1) - k(11,1) * y(1) + k(1) * y(1) * y(1) + k(1) + k(1) + k(1) + k(1) + k(1) + k(1) + 
 k(11,2)*v(1)+k(11,2)*v(2);
                                                                                                                                          dy(2) = -k(11, 4) * y(2) - k(11, 1) * y(2) - k(11, 1) * y(2) + k(11, 1) * y(3) + k(11, 1) * y(4) - k(11, 1) * y(4) + k(1) * y(4) + k(11, 1) * y(4) + k(1) + k(1) * y(4) + k(
 k(11,2)*y(2)+k(11,2)*y(1);
                                                                                                                                           dy(3) = -k(11,4) * y(3) - k(11,1) * y(3) - k(11,1) * y(3) + k(11,1) * y(2) + k(11,1) * y(1);
                                                                                                                                             dy(4) = -k(11,4) * y(4) - k(11,1) * y(4) - k(11,1) * y(4) + k(11,1) * y(2) + k(11,1) * y(1);
                                                                                               end
                                                                                               function dv = ode12(t,v)
                                                                                                                                           dy = zeros(4,1);
                                                                                                                                           dy(1) = -k(12,3) * y(1) - k(12,1) * y(1) + k(12,1) * y(4) + k(12,1) * y(3) - k(12,1) * y(1) - k(12,1) * y(1) + k(12,1) * y(
 k(12,2)*y(1)+k(12,2)*y(2);
                                                                                                                                          dv(2) = -k(12, 4) * v(2) - k(12, 1) * v(2) - k(12, 1) * v(2) + k(12, 1) * v(3) + k(12, 1) * v(4) - k(12, 1) * v(4) + k
k(12,2)*y(2)+k(12,2)*y(1);
                                                                                                                                             dy(3) = -k(12, 4) * y(3) - k(12, 1) * y(3) - k(12, 1) * y(3) + k(12, 1) * y(2) + k(12, 1) * y(1);
                                                                                                                                             dy(4) = -k(12,4) * y(4) - k(12,1) * y(4) - k(12,1) * y(4) + k(12,1) * y(2) + k(12,1) * y(1);
                                                                                               end
                                                                                               function dy = odel3(t,y)
                                                                                                                                           dy = zeros(4,1);
                                                                                                                                             dy(1) = -k(13,3) * y(1) - k(13,1) * y(1) + k(13,1) * y(4) + k(13,1) * y(3) - k(13,1) * y(1) - k(13,1) * y(1) - k(13,1) * y(1) + k(13,1) * y(
 k(13,2)*y(1)+k(13,2)*y(2);
                                                                                                                                          dv(2) = -k(13, 4) * v(2) - k(13, 1) * v(2) - k(13, 1) * v(2) + k(13, 1) * v(3) + k(13, 1) * v(4) - k(13, 1) * v(4) + k
k(13,2)*y(2)+k(13,2)*y(1);
                                                                                                                                             dy(3) = -k(13,4) * y(3) - k(13,1) * y(3) - k(13,1) * y(3) + k(13,1) * y(2) + k(13,1) * y(1);
                                                                                                                                           dy(4) = -k(13,4)*y(4) - k(13,1)*y(4) - k(13,1)*y(4) + k(13,1)*y(2) + k(13,1)*y(1);
                                                                                               end
                                                                                                                                                                 function dv = odel4(t,v)
                                                                                                                                          dv = zeros(4,1);
                                                                                                                                           dy(1) = -k(14,3) * y(1) - k(14,1) * y(1) + k(14,1) * y(4) + k(14,1) * y(3) - k(14,1) * y(1) - k(14,1) * y(1) - k(14,1) * y(1) + k(14,1) * y(
 k(14,2)*y(1)+k(14,2)*y(2);
                                                                                                                                          dy(2) = -k(14, 4) * y(2) - k(14, 1) * y(2) - k(14, 1) * y(2) + k(14, 1) * y(3) + k(14, 1) * y(4) - k(14, 1) * y(4) + k(14, 1) * (14, 1) * y(4) + k(14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (14, 1) * (1
 k(14,2)*y(2)+k(14,2)*y(1);
```

```
dy(3) = -k(14,4) * y(3) - k(14,1) * y(3) - k(14,1) * y(3) + k(14,1) * y(2) + k(14,1) * y(1);
                                                                 dy(4) = -k(14,4)*y(4) - k(14,1)*y(4) - k(14,1)*y(4) + k(14,1)*y(2) + k(14,1)*y(1);
                                            end
                                            function dv = ode15(t,v)
                                                                 dy =zeros(4,1);
                                                                 dy(1) = -k(15,3) * y(1) - k(15,1) * y(1) + k(15,1) * y(4) + k(15,1) * y(3) - k(15,1) * y(1) - k(15,1) * y(1) + k(15,1) * y(
k(15,2)*y(1)+k(15,2)*y(2);
                                                                 dy(2) = -k(15,4) * y(2) - k(15,1) * y(2) - k(15,1) * y(2) + k(15,1) * y(3) + k(15,1) * y(4) - k(15,1) * y(4) + k(15,1) * y(
k(15,2)*y(2)+k(15,2)*y(1);
                                                                  dy(3) = -k(15,4) * y(3) - k(15,1) * y(3) - k(15,1) * y(3) + k(15,1) * y(2) + k(15,1) * y(1);
                                                                 dy(4) = -k(15,4) * y(4) - k(15,1) * y(4) - k(15,1) * y(4) + k(15,1) * y(2) + k(15,1) * y(1);
                                            end
                                            function dy = odel6(~,y)
                                                                 dy =zeros(4,1);
                                                                 dy(1) = -k(16,3) * y(1) - k(16,1) * y(1) + k(16,1) * y(4) + k(16,1) * y(3) - k(16,1) * y(1) - k(16,1) * y(1) - k(16,1) * y(1) + k(16,1) + k(
k(16,2)*y(1)+k(16,2)*y(2);
                                                                 dy(2) = -k(16,4) * y(2) - k(16,1) * y(2) - k(16,1) * y(2) + k(16,1) * y(3) + k(16,1) * y(4) - k(16,1) * y(4) + k(16,1) + k(
k(16,2)*y(2)+k(16,2)*y(1);
                                                                 dy(3) = -k(16,4)*y(3) - k(16,1)*y(3) - k(16,1)*y(3) + k(16,1)*y(2) + k(16,1)*y(1);
                                                                 dy(4) = -k(16,4) * y(4) - k(16,1) * y(4) - k(16,1) * y(4) + k(16,1) * y(2) + k(16,1) * y(1);
                                            end
                                            ode_options = odeset('OutputFcn',@odeplot,'Stats', 'on');
odes = {@ode1, @ode2, @ode3, @ode4, @ode5, @ode6, @ode7, @ode8, @ode9, @ode10, @ode11,
@ode12, @ode13, @ode14, @ode15, @ode16};
                                            output = zeros(size(Mx));
                                            parfor a = 1:length(odes)
                                                                 [t,y] = ode23(odes{a},Mx(:,a),[0.07 0.31 0.31 0.31]);
                                                                                                       %initial population of [singulet triplet triplet]
                                                                 output(:,a) = sum(y, 2);
                                            end
                     end
Eo=nestedfun1(x,Mx);
for q=1:16
p(q) = length(Eo(:,q));
 end
display(p)
display(1)
figure
cmap=colormap(jet(o))
 for w=1:16
plot(Mx(:,w),My(:,w),'color',cmap(w,:),'Marker','.');
hold on
plot(Mx(:,w),Eo(:,w),'color',cmap(w,:),'LineWidth',1);
end
xlabel('t/s')
ylabel('intensity a.u.')
axis([0 1E-4 0 1])
hold off
 for u=1:16
                      AusgabeD(:,u*2-1)=Mx(:,u);
                      AusgabeD(:, u*2) = My(:, u);
end
 for u=1:16
                      AusgabeF(:,u*2-1)=Mx(:,u);
                      AusgabeF(:,u*2)=Eo(:,u);
 end
dlmwrite('xo.txt',x,',')
dlmwrite('Datensatz.txt',AusgabeD,',')
dlmwrite('Fit.txt',AusgabeF,',')
display(resnorm)
display(output)
```

MatLab-script 2

(for the individual determination of k_{\pm} at all magnetic field strengths) Parts which demand an input are marked red and explained in green.

```
function [x,resnorm,residual,exitflag,output] = Difg(xo,Mx,My)
options = optimset('display','iter','TolFun',2E-50,'TolX',2E-50,'Algorithm',{'levenberg-
marquardt',.001},'MaxIter',500,'MaxFunEvals',120000);
[x,resnorm,residual,exitflag,output] = lsqcurvefit(@nestedfun1,xo,Mx,My,[],[],options);
          function output = nestedfun1(x,Mx)
                   x(1,2)=4e7; k^2 = k_{st0} = ! 4.0 E7 s^{-1}
                   x(1,3)=0.986 e7; k^3 = k_s use value from global fit
                    x(1,4)=0; \&k4 = k_T = ! 0
                    k=x;
                   o=length(Mx(1,:));
                    for b=1:0
                             l(b) = find(Mx(:,b)>0,1,'last');
                    end
                    function dy = odel(t,y)
                             dy = zeros(4,1);
                             k(1,2)*y(1)+k(1,2)*y(2);
                             dy(2) = -k(1,4) * y(2) - k(1,1) * y(2) - k(1,1) * y(2) + k(1,1) * y(3) + k(1,1) * y(4) - k(1,1) * y(4) + k(1
k(1,2)*y(2)+k(1,2)*y(1);
                             dy(3) = -k(1,4) * y(3) - k(1,1) * y(3) - k(1,1) * y(3) + k(1,1) * y(2) + k(1,1) * y(1);
                              dy(4) = -k(1,4) * y(4) - k(1,1) * y(4) - k(1,1) * y(4) + k(1,1) * y(2) + k(1,1) * y(1);
                    end
                    ode_options = odeset('OutputFcn',@odeplot,'Stats', 'on');
                    odes = {@ode1};
                    output = zeros(size(Mx));
                    parfor a = 1:length(odes)
                              [t,y] = ode23(odes{a},Mx(:,a),[0.07 0.31 0.31 0.31]);
                                     %initial population of [singulet triplet triplet triplet] (values from global
fit)
                             output(:,a) = sum(y, 2);
                    end
          end
Eo=nestedfun1(x,Mx);
for q=1:1
p(q) = length(Eo(:,q));
end
figure
cmap=colormap(jet(o));
for w=1:1
plot(Mx(:,w),My(:,w),'color',cmap(w,:),'LineStyle','.');
hold on
plot(Mx(:,w),Eo(:,w),'color',cmap(w,:),'LineWidth',1);
end
xlabel('t/s')
ylabel('intensity a.u.')
axis([0 1E-4 0 1])
hold off
```

end

```
for u=1:1
   AusgabeD(:,u*2-1)=Mx(:,u);
   AusgabeD(:,u*2)=My(:,u);
end
for u=1:1
   AusgabeF(:,u*2-1)=Mx(:,u);
   AusgabeF(:,u*2)=Eo(:,u);
```

end

display(resnorm)

end

14 References

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