Supplementary Information

W-band transient EPR and photoinduced absorption on spin-labeled fullerene derivatives

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S1: CW EPR spectra and simulations of MRP and MRC in toluene at room temperature
S2: 2D plots of the field dependent TREPR signals of MRP and MRC
S3: time evolution of MRP at different magnetic field values
S4: time evolution of the MRC ground state
S5: 500 ns integration of TREPR spectrum of MRP
S6: microwave power dependence of the TREPR signal of MRP
S7: ground state absorption spectra and spectral dependence of the PIA signals
S8: PIA spectra for MRP and MRC probed at 700 nm
S9: concentration dependence of the decay time constants for PIA decays in MRP, MRC and C_{60}

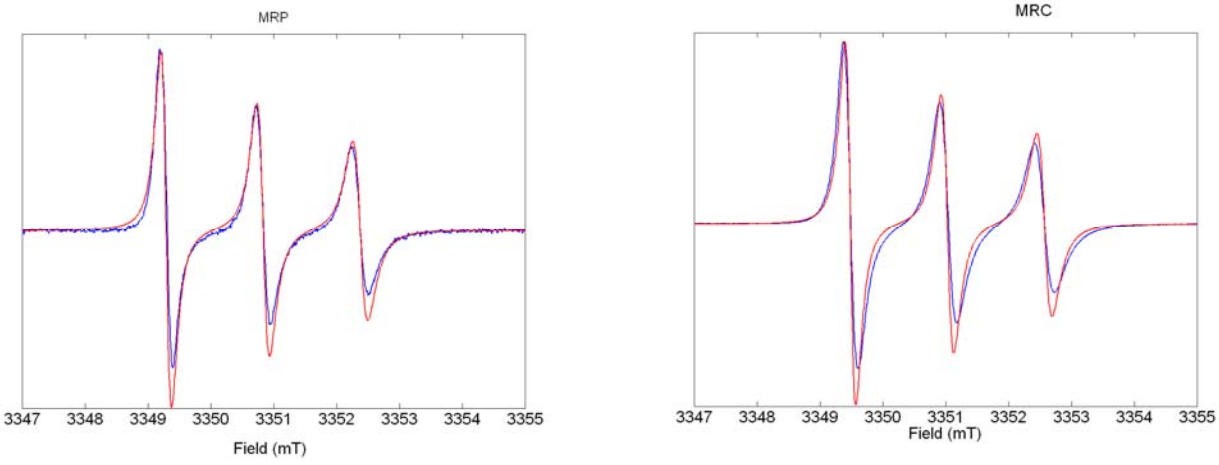

Figure S1: CW spectrum of MRP (left) and MRC (right) in toluene (1 mM) at room temperature (blue lines) together with their simulations (red lines). The "garlic" module of Easyspin is used to simulate the spectra, resulting in a rotational correlation time of $\tau_c = 0.40 \times 10^{-10}$ s

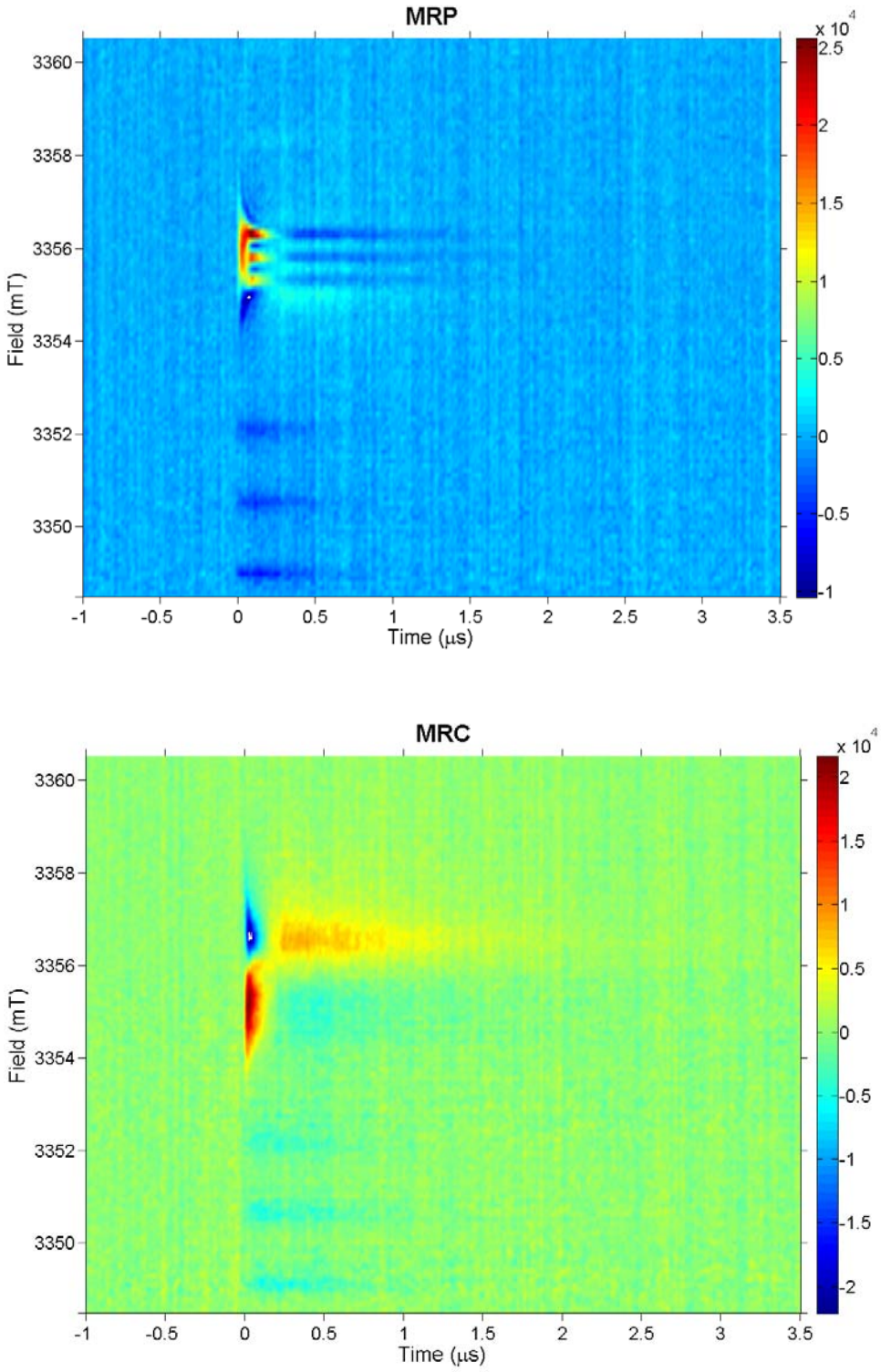

Figure S2: 2D plots of the field dependent TREPR signals for MRP (upper, 500 averages per field value) and MRC (lower, 250 averages per field value) in toluene solution (1 mM). Both are recorded with the video amplifier at 20 MHz.

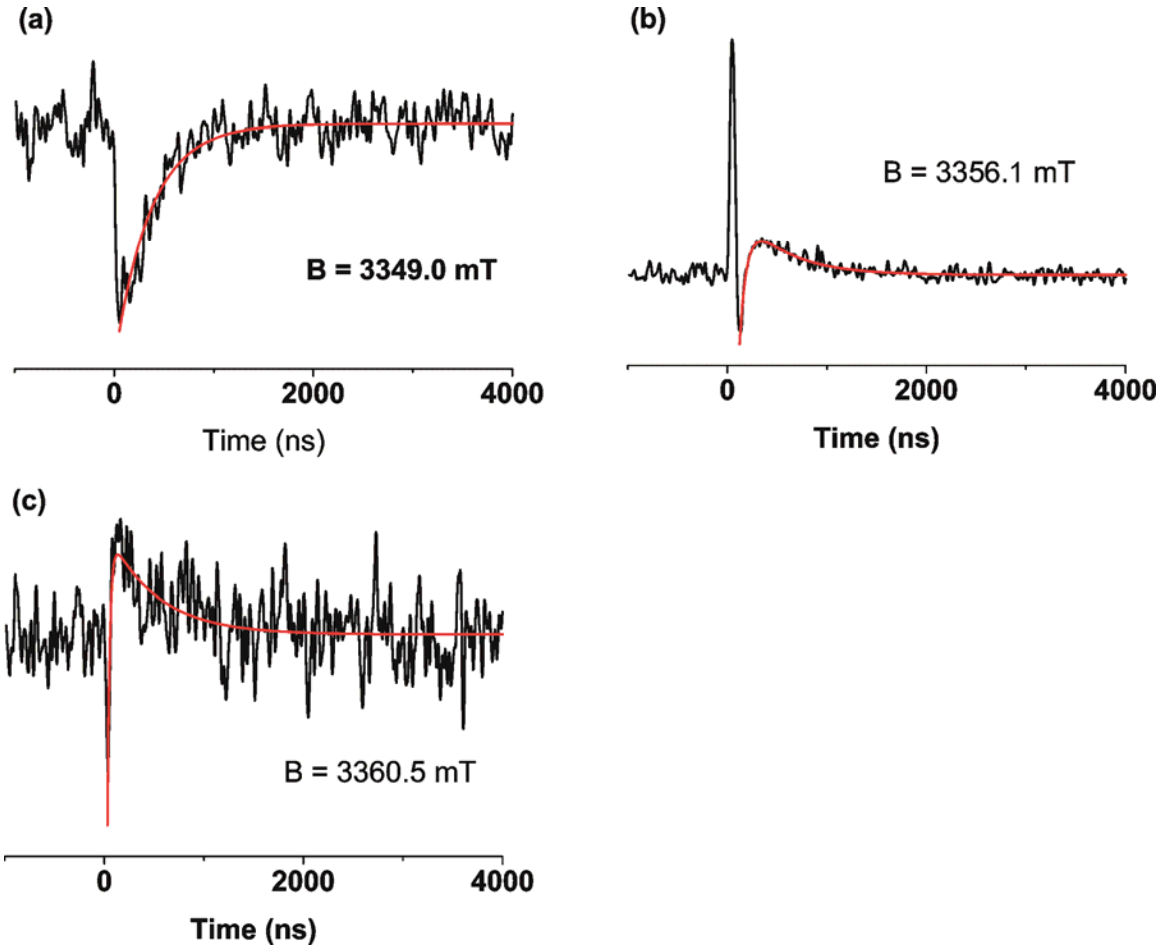

Figure S3: Time evolution of the spin polarization of MRP (black) at different magnetic field values corresponding to the open triangles in Figure 1. (a) B = 3349.0 mT, D_0 (m_I = -1) , (b) B = 3356.1 mT, Q_1(-1/2,-3/2) (m_I = +1) and Q_1(+3/2,+1/2) (m_I = 0), (c) B = 3360.5 mT, D_1. For the fitting of the signals (red), a mono-exponential decay (a) or a bi-exponential decay (b and c) is used. In (b), the fitting starts after the initial broad signal which is shortly discussed in the main article.

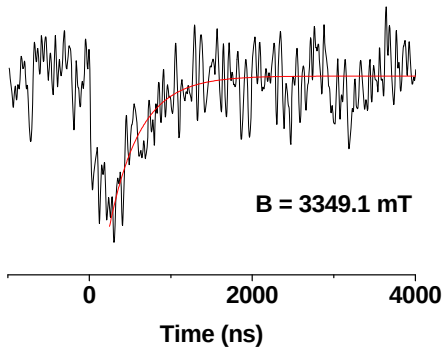

Figure S4: Time evolution of the spin polarization of the MRC ground state (B = 3349.1 mT, D_0 (m_I = -1)) together with the mono-exponential fitting (red).

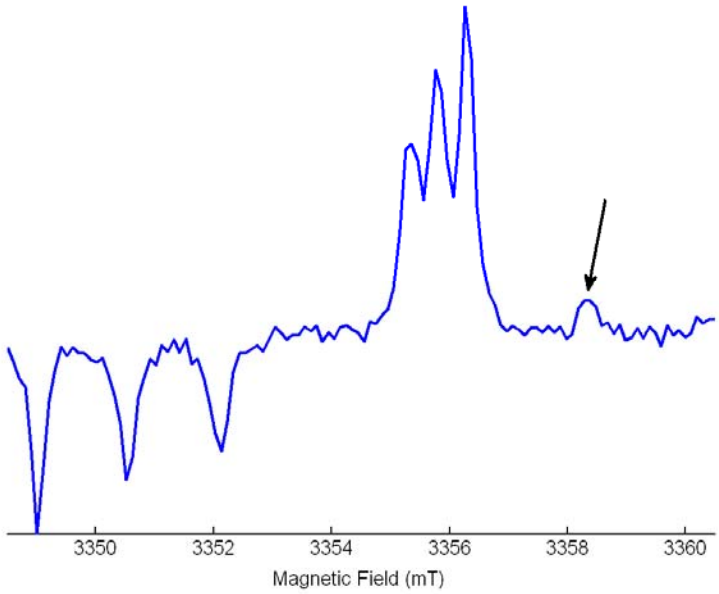

Figure S5: TREPR spectrum of MRP in toluene (1mM) obtained by integration from 0 to 0.5 μs in the time domain. The arrow indicates the position of the fullerene triplet line ($g_T = 2.0012$).

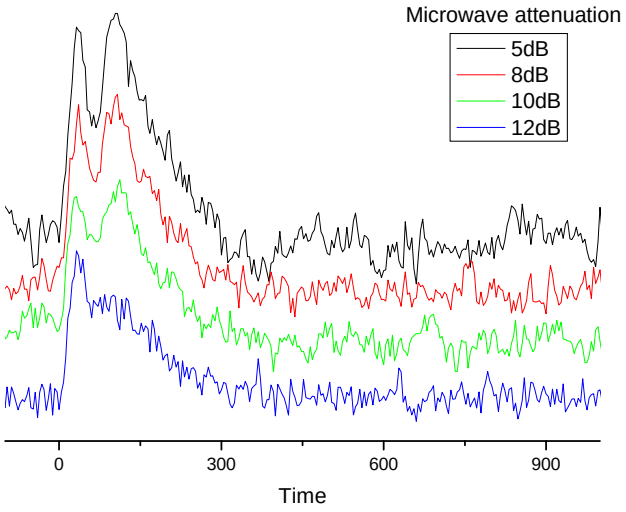

Figure S6: Microwave power dependence of the TREPR signal of MRP (trip-quartet line corresponding with fig. 3.b).The shape of the signal does not change in time, thus excluding an attribution of transient nutation to the initial broad signal observed (see main text). The video amplifier is set to a 200 MHz bandwidth and 1000 averages are taken per field trace.

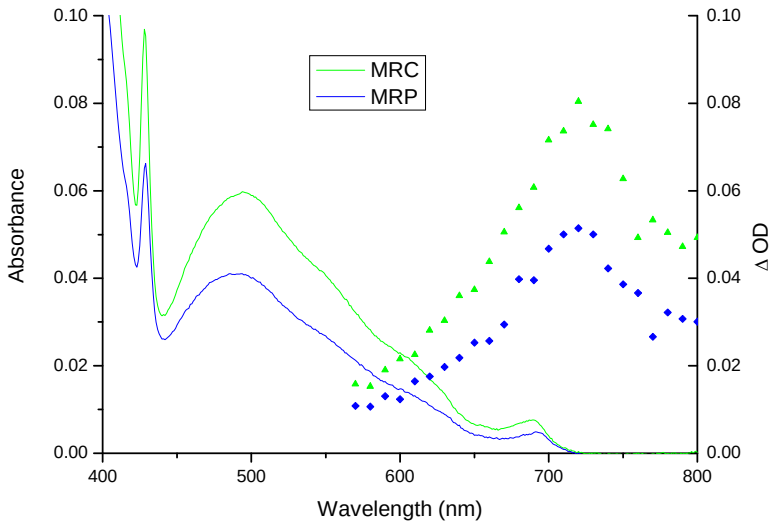

Figure S7: Ground-state absorption spectra (solid lines) of MRP (blue) and MRC (green) in toluene solution together with the spectral dependence of the PIA signals around 35 ns after the laser flash (triangles for MRC, diamonds for MRP). The difference in amplitude is due to a difference in the concentrations between the two samples ~ 0.1 mM.

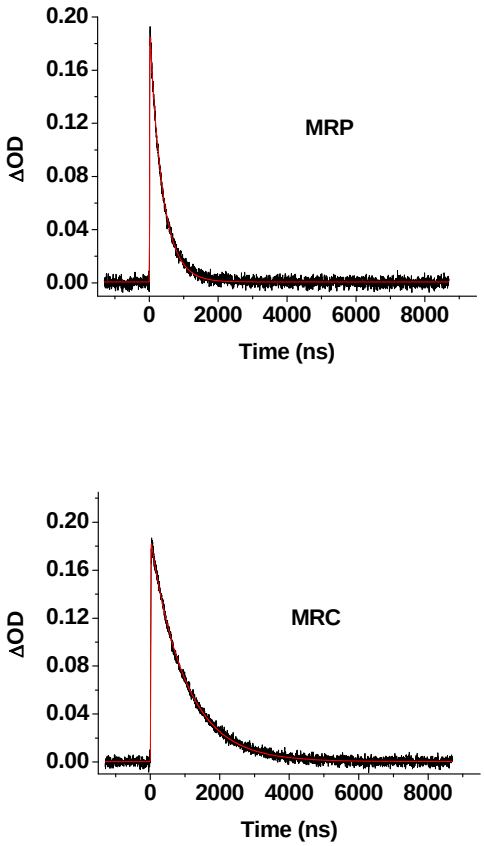

Figure S8: PIA decay curves (black) probed at 700 nm for MRP (upper) and MRC (lower), both in toluene solution with a concentration of 1 mM. The fitting (red) is performed by the convolution of a Gaussian response function (FWHM = 13 ns) with a mono-exponential decay. The time constants are (366 ± 4) ns for MRP and (984 ± 6) ns for MRC and can also be found in Table 1 of the main article.

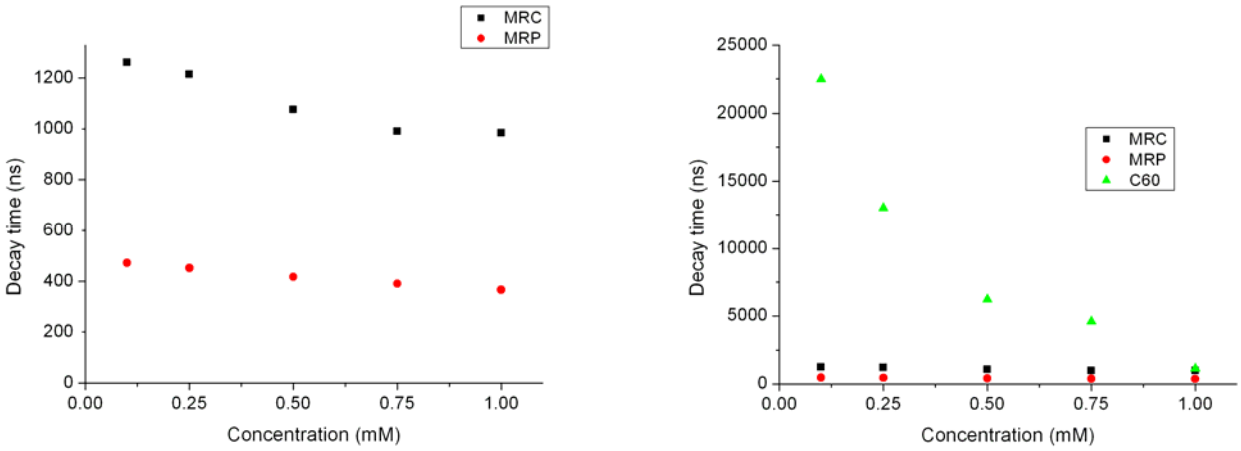

Figure S9: Concentration dependence of the decay time constants for PIA decays in MRP, MRC and C_{60}. The data in the figure correspond with the decay time obtained with a monoexponential decay of the PIA. For lower concentrations of MRP, a slightly better fit is obtained with a biexponential decay built with a fast and a slow component. The fast component corresponds to the one showed in this figure, while the slower decay time is on the order of the one for pristine C_{60} and thus attributed to a diamagnetic byproduct. This indicates the instability of the radical unit, probably caused by the longer exposure time to the laser light following from the longer integration times needed at these low concentrations and the successive dilutions to obtain the lower concentrations.