Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information For

Electron Spin Polarization Transfer Induced by Triplet-Radical Interactions in the Weakly Coupled Regime

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The simulation of the triplet spectra was carried out using routines provided by the Easy Spin simulation package. To include both the effects of magneto-photoselection and D-, E-strain, the resonance fields and linewidths were calculated on a grid of orientations using the *resfields* function. The resulting line positions were then converted to a spectrum convoluted with a Gaussian lineshape using the *makespec* and *convspec* functions and summed with a weighting factor to take the magneto-photoselection into account. Since the Q_x and Q_y transition dipole moments of porphyrins lie in the plane of the molecule, excitation of the molecules with the electric field of the light plane polarized perpendicular to the magnetic field selects molecules with their z-axes parallel to the field. Because the excitation probability follows $\sin^2\alpha$ where α is the angle between the electric field of the light and the transition dipole moment, the photoselection scales with $\cos^2\theta$ where θ is the angle between the porphyrin z-axis and the magnetic field. Thus, the amplitudes were scaled by a factor $f_p\cos^2\theta + (1 - f_p)$. The parameter f_p takes into account the fact that frozen aqueous protein solutions do not form clear glasses and hence a considerable degree of light scattering occurs, which leads to loss of the polarization of the light. The fraction f_p is the portion of the light that retains its polarization. The parameters used for the triplet simulations are given in Tables S1 and S2.

Table S1 Simulation Parameters for protoporphyrin IX triplet state

Parameter	Value
Zero field splitting	D = 37.38 mT = 3.494x10^{-2} cm^{-1}, E = –5.72 mT = 5.34x10^3 cm^{-1}
g-tensor	$g_{xx} = g_{yy} = g_{zz}$ = 2.0023
Linewidth	1.0 mT
D-Strain, E-Strain	70.4 MHz, 98.8 MHz
Population rates	$p_x : p_y : p_z$ = 0.128 : 0.114 : 758
Polarized fraction of photoexcitation, f_p	0.680

Table S2 Simulation Parameters for free base triplet state

Parameter	Value
Zero field splitting	D = 41.2 mT = 3.86x10^{-2} cm^{-1}, E = –6.4 mT = 8.0x10^3 cm^{-1}
g-tensor	$g_{xx} = g_{yy} = g_{zz}$ = 2.0023
Linewidth	1.5 mT
D-Strain, E-Strain	27.1 MHz, 4 MHz
Population rates	$p_x : p_y : p_z$ = 0.284 : 0.716 : 0
Polarized fraction of photoexcitation, f_p	0.597

The spectrum of the nitroxide radical was calculated using the Easy Spin function *pepper* and the following parameters. No orientation dependence of the signal intensity was included.

Table S3 Simulation Parameters for MTSSL radical

Parameter	Value
g-tensor	g_{xx} = 2.00800 g_{yy} = 2.00586 g_{zz} = 2.00199
^{14}N hyperfine coupling	$A_{xx} = A_{yy}$ = 16 .1 MHz A_{zz} = 108.4 MHz
Linewidth	1.3 mT