Supplementary Information

A practical approach to calculate the time evolutions of magnetic field effects on photochemical reactions in nano-structured materials

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S1. Analysis by stochastic Liouville equation (SLE)

The matrix elements of $H(r)$ is represented by,

$$H(r) =$$

$$\begin{array}{cccc}
|S, I, m> & |T_{-}, I, m+1> & |T_0, I, m> & |T_{+}, I, m-1> \\
\left(\begin{array}{cccc}
J(r) & \frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m+1)} & \frac{m}{2}A+\frac{(g_{\mathrm{a}}-g_{\mathrm{b}})}{2}\mu_{\mathrm{B}}\hbar^{-1}B & -\frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m-1)} \\
\frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m+1)} & -g\mu_{\mathrm{B}_e}\hbar^{-1}B-\frac{m+1}{2}A-J(r) & \frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m+1)} & 0 \\
\frac{m}{2}A+\frac{(g_{\mathrm{a}}-g_{\mathrm{b}})}{2}\mu_{\mathrm{B}_e}\hbar^{-1}B & \frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m+1)} & -J(r) & \frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m-1)} \\
-\frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m-1)} & 0 & \frac{A}{2\sqrt{2}}\sqrt{I(I+1)-m(m-1)} & g\mu_{\mathrm{B}}\hbar^{-1}B+\frac{m-1}{2}A-J(r)
\end{array}\right) & & &
\end{array}
\tag{S1}$$

where I and m are the spin quantum number and the magnetic quantum number for a nuclei, respectively. For the single magnetic nuclei, values of I= 1/2 and m= ±1/2 are adopted. In the SLE analysis, the final results were calculated by summing the results calculated with the values of m= +1/2 and of m= -1/2. The matrix elements in eq S1 are essentially the same with that presented in the literatures[S1,S2] except the elements for the S-T_0 coherence. In our simulation, a term for the Δg effect is included.

In the cage model, the total transition-probability matrix elements of **W** is given as,

$$\mathbf{W}=\begin{pmatrix} \dfrac{-2D\left[1+\left(\Delta r_1/d\right)\right]}{\Delta r_1^{\,2}} & \dfrac{2D}{\Delta r_1^{\,2}} & & & & & & & \\ \dfrac{D}{\Delta r_1^{\,2}} & \dfrac{-2D}{\Delta r_1^{\,2}} & \dfrac{D}{\Delta r_1^{\,2}} & & & & & & \\ & \dfrac{D}{\Delta r_1^{\,2}} & \dfrac{-2D}{\Delta r_1^{\,2}} & \dfrac{D}{\Delta r_1^{\,2}} & & & & & \\ & & \bullet & \bullet & \bullet & & & & \\ & & & \bullet & \bullet & \bullet & & & \\ & & & & \bullet & \bullet & \bullet & & \\ & & & & & \dfrac{D}{\Delta r_3^{\,2}} & \dfrac{-2D}{\Delta r_3^{\,2}} & \dfrac{D}{\Delta r_3^{\,2}} & \\ & & & & & & \dfrac{D}{\Delta r_3^{\,2}} & \mathbf{W}_{L,L} & 0 \\ & & & & & & & \mathbf{W}_{L+1,L} & 0 \end{pmatrix} \tag{S2}$$

where the first row represents the condition of the reflecting wall at *d*. In matrix **W**, Δr value is switched from Δr_1 to Δr_2 at 16th row and from Δr_2 to Δr_2 at 32th row. In 16th row, the elements of **W** are given by,

$$\mathbf{W}_{16,15}=\left(\frac{2}{1+f}\right)\left(\frac{D}{\Delta r_1^{\,2}}\right)$$

$$\mathbf{W}_{16,16}=-\left(\frac{2}{f}\right)\left(\frac{D}{\Delta r_1^{\,2}}\right)$$

$$\mathbf{W}_{16,17}=\left(\frac{2}{(1+f)f}\right)\left(\frac{D}{\Delta r_1^{\,2}}\right) \tag{S3a}$$

$$f=\frac{\Delta r_2}{\Delta r_1} \tag{S3b}$$

In 32th row, similarly, the elements of **W** are given by,

$$\mathbf{W}_{32,31}=\left(\frac{2}{1+f}\right)\left(\frac{D}{\Delta r_2^{\,2}}\right)$$

$$\mathbf{W}_{32,32}=-\left(\frac{2}{f}\right)\left(\frac{D}{\Delta r_2^{\,2}}\right)$$

$$\mathbf{W}_{32,33} = \left(\frac{2}{(1+f)f}\right)\left(\frac{D}{\Delta r_2{}^2}\right) \tag{S4a}$$

$$f = \frac{\Delta r_3}{\Delta r_2} \tag{S4b}$$

In the cage model, the terms of $\mathbf{W}_{L,L}$ and $\mathbf{W}_{L+1,L}$ determine the escape rate of RPs from the cage and represented as[S3]

$$\mathbf{W}_{L,L} = \frac{-\left\{k_{\mathrm{out}}(1+\Delta r_3/r)+k_{\mathrm{in}}(1-\Delta r_3/r)\right\}}{\Delta r_3{}^2}$$

$$\mathbf{W}_{L+1,L} = \frac{k_{\mathrm{out}}}{\Delta r_3{}^2} \tag{S5}$$

where $k_{\mathrm{in}} = D$. In the simulation, the RP is collected at the last segments (L+1) and cannot diffuse back. This means that once the radicals escape from the cage, they cannot diffuse back to the inside of the cage.

The radial weighting factors for r_jth position are represented as,

$$V(0) = \frac{d\Delta r_1}{2}$$

$$V(j) = r_j f\Delta r$$

$$V(L) = \frac{r_L f\Delta r_3}{2} \tag{S6}$$

f takes the value of 1 in the region where the Δr_1 value is used. The Δr value is switched from Δr_1 to Δr_2 at 16th row and from Δr_2 to Δr_2 at 32th row. In these rows, $V(j)$ are given by,

$$V_{16} = \frac{r_1(1+f)\Delta r_2}{2}$$

$$V_{32} = \frac{r_2(1+f)\Delta r_3}{2} \tag{S7}$$

The form of the spin relaxation matrices used in SLE is described in the literature.[S4] We used the following matrix elements to describe the spin relaxations,

$$\mathbf{R} = \frac{1}{2}\mathbf{R}_1 + \frac{1}{4}\mathbf{R}_2 + \frac{1}{3}\mathbf{R}_3 \tag{S8a}$$

$$\mathbf{R}_1 = \begin{array}{c} \begin{array}{cccccc} \rho_{SS} & \rho_{ST_0} & \rho_{T_0S} & \rho_{T_0T_0} & \rho_{T_+T_+} & \rho_{T_-T_-} \end{array} \\ \begin{pmatrix} -\frac{1}{T_2} & 0 & 0 & \frac{1}{T_2} & 0 & 0 \\ 0 & -\frac{1}{T_2} & \frac{1}{T_2} & 0 & 0 & 0 \\ 0 & \frac{1}{T_2} & -\frac{1}{T_2} & 0 & 0 & 0 \\ \frac{1}{T_2} & 0 & 0 & -\frac{1}{T_2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \tag{S8b}$$

$$\mathbf{R}_2 = \begin{array}{c} \begin{array}{cccc} \rho_{SS} & \rho_{T_0T_0} & \rho_{T_+T_+} & \rho_{T_-T_-} \end{array} \\ \begin{pmatrix} -3\left(\frac{1}{T_1}\right)_{\text{radical}} & \left(\frac{1}{T_1}\right)_{\text{radical}} & \left(\frac{1}{T_1}\right)_{\text{radical}} & \left(\frac{1}{T_1}\right)_{\text{radical}} \\ \left(\frac{1}{T_1}\right)_{\text{radical}} & -\left(\frac{1}{T_1}\right)_{\text{radical}} & 0 & 0 \\ \left(\frac{1}{T_1}\right)_{\text{radical}} & 0 & -\left(\frac{1}{T_1}\right)_{\text{radical}} & 0 \\ \left(\frac{1}{T_1}\right)_{\text{radical}} & 0 & 0 & -\left(\frac{1}{T_1}\right)_{\text{radical}} \end{pmatrix} \end{array} \tag{S8c}$$

$$\mathbf{R}_3 = \begin{array}{c} \begin{array}{ccc} \rho_{T_0T_0} & \rho_{T_+T_+} & \rho_{T_-T_-} \end{array} \\ \begin{pmatrix} -2\left(\frac{1}{T_1}\right)_{\text{TT}} & \left(\frac{1}{T_1}\right)_{\text{TT}} & \left(\frac{1}{T_1}\right)_{\text{TT}} \\ \left(\frac{1}{T_1}\right)_{\text{TT}} & -\left(\frac{1}{T_1}\right)_{\text{TT}} & 0 \\ \left(\frac{1}{T_1}\right)_{\text{TT}} & 0 & -\left(\frac{1}{T_1}\right)_{\text{TT}} \end{pmatrix} \end{array} \tag{S8d}$$

$$\left(\frac{1}{T_1}\right)_{\text{TT}} = \left(\frac{1}{T_1}\right)_{\text{radical}} + \left(\frac{1}{T_1}\right)_{\text{RP}} \tag{S8e}$$

Here we assumed that the longitudinal spin relaxations do not contribute to the decoherences between the S and T_0 states.

S2. Parameters used for stochastic Liouville equation (SLE) analysis

Table S2-1 Physical Parameters Used for the SLE analysis

Parameters for Calculation	abbreviation	Used Values
Exchange interaction in contacted RP	J_0	-1×10^{11} rad s^{-1}
Exponential decay constant in r for $J(r)$	γ	20 nm^{-1}
Radius of radical a	d_a	0.4 nm
Radius of radical b	d_b	0.4 nm
The closest distance in radical pair	d	0.6 nm
Hyperfine coupling constant	A	-0.4 mT
Anisotropy of the hyperfine coupling constant	δA	1.3 mT
g-factor for radical a	g_a	2.0033[S5]
g-factor for radical b	g_b	2.0033[S5]
Anisotropy of the g-factor for radical a	δg_a	0.002
Anisotropy of the g-factor for radical b	δg_b	0.002
Rate constant of the hydrogen abstract reaction	k_{gen}	3×10^{6} s^{-1} [S6]

Table S2-2 Mathematic Parameters Used for the Inverse Laplace Transformation

Figure	Method	β	k	δ	Δt
Figure 2	**1**	0	12	2×10^{7}	-
	2			8×10^{9}	1.25×10^{-9} s
Figure 4a	**1**	0	12	2×10^{10} or 2×10^{9}	-
Figure 4c	**1**	0	12	2×10^{9}	-
	2			2×10^{11}	1×10^{-11} s
Figure 5	**1**	0	12	2×10^{7}	-
	2			8×10^{9}	1.25×10^{-9} s
Figures 7-9	**1**	0	12	1×10^{7} or 1×10^{6}	-
	2			5×10^{8}	5×10^{-8} s

S3. References

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(S2) F. Ito, T. Ikoma, K. Akiyama and A. Watanabe S. Tero-Kubota *J. Phys. Chem. B*, 2006, **110**, 5161-5162.

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(S4) M. J. Hansen and J. B. Pederson B, *Riken Review*, 2002, **44**, 34-37.

(S5) K. Maeda, M.Terazima, T. Azumi, and Y. Tanimoto, *J. Phys. Chem*., 1991, **95**, 197-204.

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