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Fast Photo-driven Electron Spin Coherence Transfer: A Quantum Gate based on a Spin Exchange *J*-Jump

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Supporting Information Placeholder

ABSTRACT: Photoexcitation of the electron donor (D) within a linear, covalent donor-acceptor-acceptor molecule (D-A₁-A₂) in which A₁ = A₂ results in sub-nanosecond formation of a spincoherent singlet radical ion pair state, ¹(D^{*}-A₁^{*}-A₂), for which the spin-spin-exchange interaction is large: $2J = 79 \pm 1$ mT. Subsequent laser excitation of A₁^{*} during the lifetime of ¹(D^{*}-A₁^{*}-A₂) rapidly produces ¹(D^{*}-A₁-A₂^{*}), which abruptly decreases 2J 3600-fold. Subsequent coherent spin evolution mixes ¹(D^{*}-A₁-A₂^{*}) with ³(D^{*}-A₁-A₂^{*}) resulting in mixed states which display transient spin-polarized EPR transitions characteristic of a spincorrelated radical ion pair. These photo-driven J-jump experiments show that it is possible to use fast laser pulses to transfer electron spin coherence between organic radical ion pairs and observe the results using an essentially background-free timeresolved EPR experiment.

Controlling the spin dynamics of complex multi-spin molecular systems is a major goal in spintronics and quantum information processing.¹ Fast photo-initiated electron transfer within covalently-linked organic donor-acceptor molecules having specific donor-acceptor (D-A) distances and orientations results in the formation of spin-entangled electron-hole pairs (i.e. radical ion pairs, RPs) having well-defined initial spin configurations, while time-resolved electron paramagnetic resonance (TREPR) techniques provide an important means of manipulating and controlling these coherent spin states.² Organic RPs display coherent spin motion for up to ~100 ns,³ which makes it possible that this coherence may provide the basis for new quantum information processing strategies based on organic molecules.

We have previously demonstrated that the RP populations within linear and branched D-A₁-A₂ arrays can be controlled using one wavelength-selective laser pulse to generate D⁺·A₁⁻·A₂ and a second, subsequent wavelength-selective laser pulse to excite A₁⁻ resulting in the thermodynamically uphill reaction D⁺·A₁⁻·A₂ \rightarrow D⁺·A₁-A₂⁻.⁴ Because of the close proximity of D⁺ and A₁⁻, the exponentially distance-dependent Heisenberg spin-spin exchange coupling (2) between D⁺ and A₁⁻ is necessarily large,⁵ while that between D⁺ and A₂⁻ is much smaller. Here we show that laser excitation of the A₁⁻ radical ion results in coherent transfer of the initial D⁺·A₁⁻·A₂ RP spin state to D⁺·A₁-A₂⁻.

The synthesis of **1** and **2** are described in the Supporting Information. All synthetic intermediates and final products were characterized by ¹H and ¹³C NMR, MALDI-TOF, MS-ESI, and UV-vis spectroscopy. The attachment of the 2,3,5,6-



tetramethylbiphenyl group (B₁) to perylene (PER) in 1 and 2 shifts the 438 nm absorption maximum of PER in toluene slightly to 446 nm (Figure 1). This is consistent with the expected molecular geometry where the durene π system should be nearly orthogonal to that of PER due to steric effects of its methyl groups. The absorption spectra of both naphthalene-1,8:4,5-bis(dicarboximide) (NDI) acceptors in 1 and the single NDI acceptor in 2 are not perturbed by their attachment to the 2,5-dimethylphenyl group (B₂).⁶ The ground state spectra of both 1 and 2 indicate that the electronic coupling between PER and NDI is weak.

Cyclic voltammetry on 1 and 2 at a Pt electrode in butyronitrile containing 0.1 M Bu₄NPF₆ (Figures S1A,B) shows two reversible one-electron NDI reduction waves at $E_{red} = .0.53$ and -1.02 V vs. SCE,⁶ and a single reversible one-electron PER oxidation wave at $E_{ox} = 1.06$ V vs. SCE.⁷ The reduction potentials of the two NDIs in 1 are indistinguishable; however, using differential pulse voltammetry (Figure S1C), the second reduction peak of 1 is somewhat asymmetric. The NDI reduction waves of 1 have about twice the current as the PER oxidation wave, so that they result from independent reduction of each NDI within 1. Using the Weller equation (see Supporting Information), the estimated energies of PER⁺⁺·B₁·NDI₁⁺⁺·B₂·NDI₂ and PER⁺⁺·-B₁·NDI₁⁺⁺ for 1 and 2 in toluene are both 2.46 eV, while that of



Figure 1. Normalized UV-vis spectra of 1 (black) and 2 (red) in toluene.



Figure 2. Transient absorption spectra of **1** in toluene at 295K. A) following a 416 nm, 120 fs laser pulse. Inset: transient kinetics monitored at 520 nm. B) following a 416 nm, 7 ns laser pulse. Inset: transient kinetics monitored at 480 nm.

PER⁺⁺·B₁·NDI₁·B₂·NDI₂⁻⁺ for 1 is 2.62 eV. Since the ¹⁺PER energy is 2.76 eV, the free energies for photogenerating all RPs are favorable. However, the significantly longer RP distance of PER⁺⁺·B₁·NDI₁·B₂·NDI₂⁻⁺ (29.0 Å) relative to that of PER⁺⁺·B₁·NDI₁·B₂·NDI₂ (16.6 Å) results in an additional 0.16 eV Coulombic energy change making electron transfer to NDI₂ energet-ically less favorable than that to NDI₁.

The transient absorption spectra of 1 in toluene at 295K following selective photoexcitation of PER with a 416 nm, 120 fs laser pulse (Figure 2A) show the initial formation of a strong ^{1*}PER absorption band at 720 nm,⁸ which decays with the simultaneous appearance of a broad PER^{+•} absorption centered around 550 nm⁹ and two NDI^{*} absorption bands at 480 nm and 610 nm.⁶ The charge separation (CS) kinetics are fit at 520 nm to a time constant of τ_{CS} = 277 ± 3 ps. Given that the ^{1*}PER lifetime is 4.6 ns,¹⁰ the resultant quantum yield of charge separation is 94%. At later times, the corresponding nanosecond transient absorption spectra (Figure 2B) show that the PER** and NDI* absorptions decay with a charge recombination (CR) time constant of τ_{CR} = 603 ± 12 ns. The residual long-lived absorption near 500 nm results from ^{3*}PER produced by CR in a 45% yield.¹¹ Corresponding data acquired for control dyad 2 (Figures S2A and S2B) give τ_{CS} = 300 ± 3 ps and τ_{CR} = 680 ± 3 ns. The similarity between the time constants for both charge separation and recombination in 1 and 2 indicates that 416 nm excitation produces only PER^{+•}-B₁-NDI₁^{••}-B₂-NDI₂ in 1, which is consistent with the fact that moving the electron from NDI₁ to NDI₂ requires a Coulomb energy penalty of 0.16 eV.

Rapid charge separation from the ^{1*}PER precursor state results in formation of the singlet RP: ¹(PER⁺⁺-B₁-NDI₁⁻⁺-B₂-NDI₂), which may undergo electron-nuclear hyperfine couplinginduced radical pair intersystem crossing (RP-ISC) to produce the triplet RP, ³(PER⁺⁺-B₁-NDI₁⁻⁺-B₂-NDI₂). The subsequent CR is spin selective; i.e. the singlet RP recombines to the singlet



Figure 3. A) Energy levels and electron transfer pathways D = PER, A = NDI. B) Expanded view of the RP energy levels as a function of magnetic field (2*J* > 0).

ground state and the triplet RP recombines to yield the neutral local triplet (Figure 3A). Application of a static magnetic field causes Zeeman splitting of the RP triplet sublevels, and varying the field strength modulates the efficiency of RP-ISC by adjusting the energies of triplet sublevels relative to that of the singlet level (Figure 3B). When the Zeeman splitting of the triplet RP sublevels equals the intrinsic singlet-triplet splitting, 2J, of the RP, there is an increase in the RP-ISC rate. This increase translates into a maximum in triplet RP production and therefore a maximum in neutral local triplet yield upon CR. By monitoring the yield of local triplet production as a function of applied magnetic field, the magnitude of 2J can be measured directly.¹² The value of 2J within PER**-B1-NDI1**-B2-NDI2 was measured using the effect of a magnetic field on the ^{3*}PER yield monitored at 480 nm and 4 μ s following the laser pulse. The ^{3*}PER yield for 1 exhibits a resonance at $2J = 79 \pm 1$ mT (Figure 4), while a similar resonance is observed for 2 at $2J = 82 \pm 1$ mT (Figure S3). The similarity of the 2J values for 1 and 2 provides additional evidence that PER**-B1-NDI1**-B2-NDI2 is primarily populated within 1. Since 2J depends exponentially on distance, moving the electron to NDI2 should result in a large decrease in 2J.

TREPR spectra were acquired using continuous microwave irradiation in a ~350 mT magnetic field (see Supporting Information), so that the Zeeman split triplet RP sublevels are best described by the T_{+1} , T_0 , and T_{-1} eigenstates that are quantized along the applied magnetic field, while the singlet RP energy



Figure 4. Relative triplet yield monitored at 480 nm as a function of magnetic field strength for 1 in toluene at 295 K following a 416 nm, 7 ns laser pulse.



Figure 5. TREPR spectra of 1 in toluene at 295 K at the indicated times following a single 416 nm, 7 ns laser pulse at $t_{416} = 0$ (red traces), and following the two-pulse sequence: 416 nm, 7 ns laser pulse at $t_{416} = 0$; 480 nm, 7 ns laser pulse at $t_{480} = 15$ ns (black traces).

level (S) is unaffected (Figure 3B).^{2b,2d,13} RP-ISC depends on both the spin-spin exchange interaction (2J) and the dipolar interaction (D) between the two radicals that comprise the RP. The magnitude of 2J depends exponentially on the distance (r) between the two radicals, and is assumed to be isotropic, while D depends on $1/r^3$ and is anisotropic. In fluid solution, however, D is rotationally averaged to zero for small molecules such as 1 and 2.

When 2J is large, such as the \sim 80 mT values observed for PER**-B1-NDI1*-B2-NDI2 and PER**-B1-NDI1*, S-T0 mixing is generally weak.¹⁴ However, when 2*J* is generally <10 mT, coherent S-T₀ mixing occurs,^{2b,2d,13} and the two resulting mixed states are preferentially populated due to the initial population of S, so that the four EPR transitions that occur between these mixed states and the initially unpopulated T_{+1} and T_{-1} states are spin polarized.^{14a,15} The TREPR spectrum consists of two anti-phase doublets, centered at the g-factors of the individual radicals that comprise the pair, in which the splitting of each doublet is determined by 2J. The electron spin polarization pattern from low field to high field of the EPR signal, i.e. which transitions are in enhanced absorption (a) or emission (e), is determined by the sign rule:^{2d,16} $\Gamma = \mu \cdot \text{sign}(2J) = (-)$ gives e/a or = (+) gives a/e, where μ is -1 or +1 for a singlet or triplet excited state precursor, respectively. Thus, if 2J > 0, singlet excited state precursors yield an (e,a,e,a) line pattern. If the g-factors of the two radicals are similar and are split by hyperfine couplings, the two doublets overlap strongly, and appear as a distorted (e,a) signal. The spectra are simulated by applying the spin-correlated radical pair model using 2J along with the g-factors and the hyperfine coupling constants of D^{+} and A^{-} .^{14-15,17}

The TREPR spectra of 1 and 2 in toluene at 295 K following selective 416-nm photoexcitation of PER show only a very weak signal for 1 (Figure 5) and no signal for 2. This is consistent

with the very large 2J value measured directly by the magnetic field effect on the ^{3*}PER yield. The large 2J value inhibits $S-T_0$ mixing resulting in a greatly decreased transition probability between these states and $T_{\pm 1}$.^{2g,14,17b} The weak signal observed for 1 most likely results from generation of a small population of NDI₂.⁻ that is strongly spin-polarized.

Our previous results have shown that photoexcitation of NDI[•] at 480 nm produces its excited doublet state (^{2*}NDI[•]) that has a 260 ps lifetime.⁶ This lifetime is sufficiently long to allow electron transfer from ^{2*}NDI[•] to nearby electron acceptors.⁴ The presence of the short-distance B₂ bridging molecule between the two NDI molecules in 1 makes electron transfer from ^{2*}NDI₁[•] to NDI₂ kinetically favorable. In principle, fast electron transfer from NDI₁^{*} to NDI₂ should not perturb the coherence of the two spins within the initial RP, but transfer it intact to the second RP. Selective 416-nm photoexcitation of PER within 1 at t = 0 followed by selective 480-nm photoexcitation of NDI₁[•] at t = 15 ns results in the appearance of a strong spin-polarized RP signal (Figure 5). Irradiation of 1 and 2 with a single laser pulse at 480 nm, which is not absorbed by their ground states does not result in any EPR signals (Figure S4). Simulation of the experimental spin-polarized RP spectra using the model of Till and Hore^{17b} yields 2J = 0.022 mT (Figure S5). Thus, rapid photo-driven electron transfer from the initial RP to the secondary RP results in a nearly 3600-fold decrease in 2J.

The spin-polarized RP signal that appears following photoexcitation of 1 with an initial 416 nm laser pulse at $t_{416} = 0$ and a second, subsequent 480 nm laser pulse at t_{480} shows an interesting dependence on t_{480} - t_{416} , the time delay between the 416 nm and 480 nm laser pulses (Figure 6). The times of the laser pulses are measured at the maximum intensity of each pulse. The data is fit to the convolution of a Gaussian function with a width of 10 ± 1 ns and a single exponential decay of 11 ± 1 ns. Since the 416 nm and 480 nm laser pulse widths (FWHM) are both 7 ns, the slow rise of the spin-polarized RP EPR signal results from the build-up of the initial PER^{+•}-B₁-NDI₁^{••}-B₂-NDI₂ population during the 416 nm pulse convolved with the electron transfer from $ND1_1^{\bullet}$ to NDI_2 induced by the second 480 nm pulse. Rapid photogeneration of PER**-B1-NDI1**-B2-NDI2 using 416 nm excitation results in zero quantum coherence (ZQC) between the S and T_0 energy levels.^{3c,17a,18} Rapid dephasing of the ZQC results from the interaction of the electron spins with their environment, and only a very small amount of S-T₀ mixing occurs because 2J is large.¹⁴ If the 480 nm pulse is applied prior to dephasing, then the ZQC is transferred from PER**-B1-NDI₁[•]-B₂-NDI₂ to PER^{*}•-B₁-NDI₁-B₂-NDI₂[•], wherein the abrupt



Figure 6. Intensity of the spin-polarized EPR signal of 1 in toluene at 295 K and 100 ns as a function of the time delay, $t_{480} - t_{416}$ between the 416 nm, 7 ns laser pulse at $t_{416} = 0$ and the second 480 nm, 7 ns laser pulse at t_{480} .

reduction in 2J greatly increases ST_0 mixing and the transition probability from the mixed states to $T_{\pm 1}$ resulting in the appearance of the spin-polarized EPR signal.¹⁴ In contrast, when the 480 nm pulse is applied after dephasing in PER^{**}-B₁-NDI₁^{**}-B₂-NDI₂ is complete, 2J is still dramatically reduced, but coherent S-T₀ mixing does not occur. The small amount of S-T₀ mixing generated in PER^{**}-B₁-NDI₁^{**}-B₂-NDI₂ is insufficient to produce an observable spin-polarized EPR signal in PER^{**}-B₁-NDI₁-B₂-NDI₂^{**}. In fact, no spin-polarized EPR signal is observed when t_{480} - t_{416} > 50 ns. Thus, the observed 11 ± 1 ns decay time of the EPR signal most likely reflects the ZQC dephasing time of PER^{**}-B₁-NDI₁^{**}-B₂-NDI₂.

Our data illustrate how laser manipulation of coherent spin states can control the magnetic interactions between the spins offering new opportunities to design molecular systems for studying quantum information processing.

ASSOCIATED CONTENT

Supporting Information Available: Experimental details including synthesis, electrochemistry, and additional transient optical and EPR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1)(a)Gershenfeld, N. A.; Chuang, I. L. Science 1997, 275, 350; (b)Mehring, M. Appl. Magn. Res. 1999, 17, 141; (c)Harneit, W. Phys. Rev. A 2002, 65, 032322; (d)Morton, J. J. L.; Tyryshkin, A. M.; Ardavan, A.; Porfyrakis, K.; Lyon, S. A.; Briggs, G. A. D. Los Alamos National Laboratory, Preprint Archive, Quantum Physics 2004, 1; (e)Mehring, M.; Mende, J. Phys. Rev. A: At., Mol., Opt. Phys. 2006, 73, 052303/1; (f)Salikhov, K. M.; Golbeck, J. H.; Stehlik, D. Appl. Magn. Res. 2007, 31, 237; (g)Sato, K.; Nakazawa, S.; Rahimi, R.; Ise, T.; Nishida, S.; Yoshino, T.; Mori, N.; Toyota, K.; Shiomi, D.; Yakiyama, Y.; Morita, Y.; Kitagawa, M.; Nakasuji, K.; Nakahara, M.; Hara, H.; Carl, P.; Hoefer, P.; Takui, T. J. Mater. Chem. 2009, 19, 3739; (h)Wesenberg, J. H.; Ardavan, A.; Briggs, G. A. D.; Morton, J. J. L.; Schoelkopf, R. J.; Schuster, D. I.; Molmer, K. Phys. Rev. Lett. 2009, 103, 070502/1; (i)Nakahara, M.; Ota, Y.; Rahimi, R.; Kondo, Y.; Tada-Umezaki, M., Eds. Molecular Realizations of Quantum Computing 2007; World Scientific Publishing: Singapore, 2009; Vol. 2; (j)Kandrashkin, Y. E.; Salikhov, K. M. Appl. Magn. Res. 2010, 37, 549; (k)Morita, Y.; Yakiyama, Y.; Nakazawa, S.; Murata, T.; Ise, T.; Hashizume, D.; Shiomi, D.; Sato, K.; Kitagawa, M.; Nakasuji, K.; Takui, T. J. Am. Chem. Soc. 2010, 132, 6944; (I)Yoshino, T.; Nishida, S.; Sato, K.; Nakazawa, S.; Rahimi, R. D.; Toyota, K.; Shiomi, D.; Morita, Y.; Kitagawa, M.; Takui, T. J. Phys. Chem. Lett. 2011, 2, 449; (m)Brown, R. M.; Tyryshkin, A. M.; Porfyrakis, K.; Gauger, E. M.; Lovett, B. W.; Ardavan, A.; Lyon, S. A.; Briggs, G. A. D.; Morton, J. J. L. Phys. Rev. Lett. 2011, 106, 110504/1.

(2)(a)Hasharoni, K.; Levanon, H.; Greenfield, S. R.; Gosztola, D. J.; Svec, W. A.; Wasielewski, M. R. J. Am. Chem. Soc. **1995**, *117*, 8055; (b)Carbonera, D.; DiValentin, M.; Corvaja, C.; Agostini, G.; Giacometti, G.; Liddell, P. A.; Kuciauskas, D.; Moore, A. L.; Moore, T. A.; Gust, D. J. Am. Chem. Soc. **1998**, *120*, 4398; (c)Shaakov, S.; Galili, T.; Stavitski, E.; Levanon, H.; Lukas, A.; Wasielewski, M. R. J. Am. Chem. Soc. **2003**, *125*, 6563; (d)Dance, Z. E. X.; Mi, Q.; McCamant, D. W.; Ahrens, M. J.; Ratner, M. A.; Wasielewski, M. R. J. Phys. Chem. B **2006**, *110*, 25163; (e)Miura, T.; Carmieli, R.; Wasielewski, M. R. J. Phys. Chem. A **2010**, *114*, 5769; (f)Miura, T.; Scott, A. M.; Wasielewski, M. R. J. Phys. Chem. C **2010**, *114*, 20370; (g)Colvin, M. T.; Ricks, A. B.; Scott, A. M.; Smeigh, A. L.; Carmieli, R.; Miura, T.; Wasielewski, M. R. J. Am. Chem. Soc. **2011**, *133*, 1240; (h)Miura, T.; Wasielewski, M. R. J. Am. Chem. Soc. **2011**, *133*, 2844.

(3)(a)Kothe, G.; Weber, S.; Ohmes, E.; Thurnauer, M. C.; Norris, J. R. J. Phys. Chem. **1994**, *98*, 2706; (b)Laukenmann, K.; Weber, S.; Kothe, G.; Oesterle, C.; Angerhofer, A.; Wasielewski, M. R.; Svec, W. A.; Norris, J. R. J. Phys. Chem. **1995**, *99*, 4324; (c)Hoff, A. J.; Gast, P.; Dzuba, S. A.; Timmel, C. R.; Fursman, C. E.; Hore, P. J. Spectrochim. Acta, Part A **1998**, *54A*, 2283.

(4)(a)Debreczeny, M. P.; Svec, W. A.; Marsh, E. M.; Wasielewski, M. R. J. Am. Chem. Soc. **1996**, *118*, 8174; (b)Lukas, A. S.; Miller, S. E.; Wasielewski, M. R. J. Phys. Chem. B **2000**, *104*, 931; (c)Lukas, A. S.; Bushard, P. J.; Wasielewski, M. R. J. Am. Chem. Soc. **2001**, *123*, 2440.

(5)Heisenberg, W. Z. Phys. 1926, 38, 411.

(6)Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. J. Phys. Chem. A 2000, 104, 6545.

(7)Kubota, T.; Miyazaki, H.; Ezumi, K.; Yamakawa, M. Bull. Chem. Soc. Jap. 1974, 47, 491.

(8) Pagès, S.; Lang, B.; Vauthey, E. J. Phys. Chem. A 2003, 108, 549.

(9)Shida, T. Electronic Absorption Spectra of Radical Ions; Elsevier: New York, 1988.

(10)Katoh, R.; Sinha, S.; Murata, S.; Tachiya, M. J. Photochem Photobiol. A 2001, 145, 23.

(11)(a)Bensasson, R.; Land, E. J. Trans. Faraday Soc. **1971**, 67, 1904; (b)Rachford, A. A.; Goeb, S.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2008**, 47, 4348.

(12)(a)Anderson, P. W. Phys. Rev. **1959**, 115, 2; (b)Shultz, D. A.; Fico, R. M., Jr.; Bodnar, S. H.; Kumar, R. K.; Vostrikova, K. E.; Kampf, J. W.; Boyle, P. D. J. Am. Chem. Soc. **2003**, 125, 11761; (c)Scott, A. M.; Miura, T.; Ricks, A. B.; Dance, Z. E. X.; Giacobbe, E. M.; Colvin, M. T.; Wasielewski, M. R. J. Am. Chem. Soc. **2009**, 131, 17655.

(13)(a)Hasharoni, K.; Levanon, H.; Greenfield, S. R.; Gosztola, D. J.; Svec, W. A.; Wasielewski, M. R. J. Am. Chem. Soc. **1996**, 118, 10228; (b)Kobori, Y.; Yamauchi, S.; Akiyama, K.; Tero-Kubota, S.; Imahori, H.; Fukuzumi, S.; Norris, J. R., Jr. Proc. Natl. Acad. Sci. U. S. A. **2005**, 102, 10017.

(14)(a)Closs, G. L.; Forbes, M. D. E.; Norris, J. R. J. Phys. Chem. 1987, 91, 3592; (b)Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. Chem. Phys. Lett. 1987, 135, 307.

(15)Hore, P. J.; Hunter, D. A.; Mckie, C. D.; Hoff, A. J. Chem. Phys. Lett. 1987, 137, 495.

(16)Hore, P. J. In Advanced EPR in Biology and Biochemistry; Hoff, A. J., Ed.; Elsevier: Amsterdam, 1989, pp 405.

(17)(a)Norris, J. R.; Morris, A. L.; Thurnauer, M. C.; Tang, J. J. Chem. Phys. **1990**, 92, 4239; (b)Till, U.; Hore, P. J. Molec. Phys. **1997**, 90, 289.

(18)(a)Salikhov, K. M.; Bock, C. H.; Stehlik, D. Appl. Magn. Reson. 1990, I, 195; (b)Bittl, R.; Kothe, G. Chem. Phys. Lett. 1991, 177, 547; (c)Zwanenburg, G.; Hore, P. J. Chem. Phys. Lett. 1993, 203, 65; (d)Kothe, G.; Weber, S.; Ohmes, E.; Thurnauer, M. C.; Norris, J. R. J. Phys. Chem. 1994, 98, 2706.

