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Electron Spin Polarization Transfer from a Nitroxide Incarcerated within a Nanocapsule to a Nitroxide in the Bulk Aqueous Solution

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ABSTRACT A thioxanthone derivative containing a covalently attached ^{15}N-labeled nitroxide was incarcerated into an octaacid nanocapsule. Photoexcitation of the thioxanthone chromophore generated electron spin polarization of the nitroxide. This spin polarization of the ^{15}N-labeled nitroxide was transferred through the walls of the carcerand to a ^{14}N-labeled nitroxide in external bulk solvent, a process that was directly observed by time-resolved EPR spectroscopy. The efficiency of the communication between the incarcerated guest and molecules in the bulk solvent was shown to be controlled by supramolecular factors such as Coulombic attraction and repulsion between the guest@host complex and charged molecules in the bulk solvent phase.
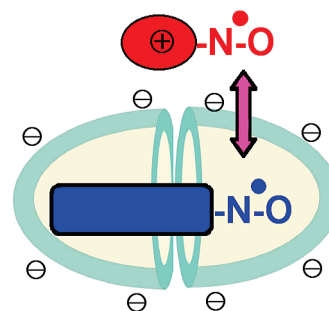
SECTION Kinetics, Spectroscopy
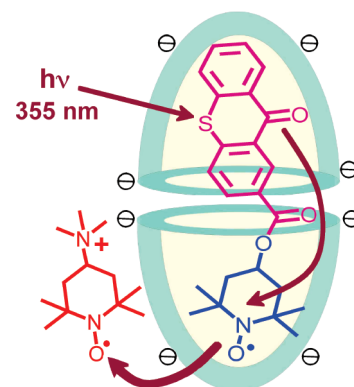
In pioneering work Balzani,[1] Deshayes,[2,3] and Piotrowiak[2,3] demonstrated by studying electronic energy transfer and electron transfer processes that electronically excited states of guest molecules incarcerated in hemicarcerands can communicate through the walls of the host with molecules in bulk solvent. As expected, the interactions of the incarcerated guest with molecules in the bulk solvent outside the host occur with rate constants considerably smaller than those found for the free guest in solution. The fact that interactions occur at all is the result of overlap of the orbitals of the guest with the orbitals of external molecules in the bulk solvent through the orbitals of the carcerand (host). Orbital interactions that occur through bonds are termed "superexchange". The superexchange phenomenon is well established in nuclear and electronic spin spectroscopy.[4]

Previously, we reported an investigation of the electron spin–spin "superexchange" between an incarcerated nitroxide and a nitroxide in the external bulk aqueous phase (Scheme 1).[5] For this study, we employed a ^{15}N-labeled incarcerated nitroxide (Bz-^{15}T, Chart 1) and a ^{14}N-labeled free nitroxide (^{14}T⊕) in the external phase (Chart 1). By using different nuclear spins for incarcerated and free nitroxides, the simultaneous observation of both radicals by EPR spectroscopy can be achieved. As host, we selected a cavitand termed "octa acid" (OA, Chart 1), which is known to incarcerate nonpolar molecules by forming a capsuleplex under basic conditions in aqueous solutions.[6,7] It was established that the nonpolar benzophenone derivative containing a ^{15}N-labeled nitroxide substituent forms a 2:1 capsuleplex with OA, where two OA molecules encapsulate Bz-^{15}T.[5] In the presence of a positively charged ^{14}N-labeled free nitroxide in solution, a broadening of Bz-^{15}T and ^{14}T⊕ signals was observed by steady-state EPR spectroscopy. We interpreted this signal

Scheme 1. Spin–Spin Communication between an Incarcerated Nitroxide (Blue) and a Positively Charged Nitroxide (red) through the Walls of a Carcerand (Green)

broadening to be spin–spin communication between the incarcerated nitroxide with the free nitroxide in solution caused by "superexchange" through the walls of the host.[5]
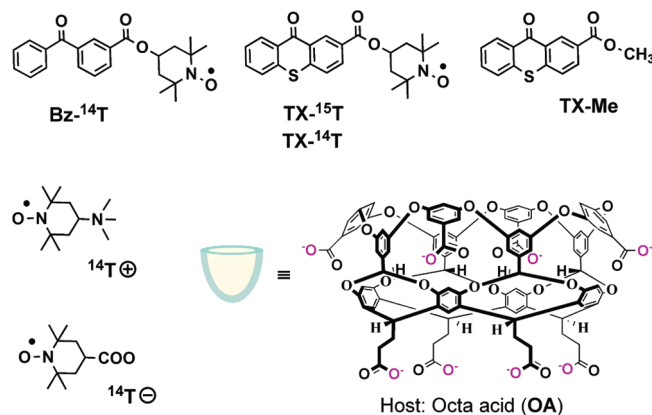
A more direct method to investigate spin–spin interactions between an incarcerated nitroxide with a free nitroxide in the bulk solution would be time-resolved observation of spin-polarization transfer between the two nitroxides by time-resolved EPR spectroscopy (TR-EPR). Spin-polarized nitroxides can be generated by chemically induced dynamic electron polarization (CIDEP) by quenching of triplet excited states with nitroxides.[8–10] High triplet quantum yields, fast intersystem crossing, and high triplet energies favor aromatic ketones, such as benzophenone derivatives as triplet sensitizers in CIDEP experiments. If the aromatic ketone and the

Chart 1. Structures of Guest Molecules and Host

Figure 1. Triplet−triplet absorption spectra of TX-Me and TX-^{14}T in acetonitrile recorded 0.5 to 2 μs (TX-Me) or 0−20 ns (TX-^{14}T) after pulsed laser excitation (355 nm, 5 ns pulse width) in deoxygenated acetonitrile solutions at room temperature.

nitroxide are covalently linked, then the observed spin-polarization of the nitroxide is optimized.[11] It is believed that for covalently linked systems the triplet electron spin polarization transfer mechanism is dominant in generating spin-polarized nitroxides. In this mechanism, spin-polarized triplet states, produced by triplet sublevel selective intersystem crossing, transfer their polarization to the nitroxide.[12] Because the lifetime of spin polarization of triplet states is usually short (only several nanoseconds for ketones),[13] covalently linked systems are most favorable for the electron spin polarization transfer mechanism to produce significant polarization.

In our previous steady-state EPR studies of spin−spin communication between incarcerated nitroxides with free nitroxides in solution, we used a nitroxide-tethered benzophenone (Bz-^{15}T; Chart 1) as incarcerated guest.[5] However, benzophenone shows only poor optical absorption at 355 nm, the preferred excitation wavelength for our TR-EPR experiments, which use a Nd/YAG laser. To improve the absorption and signal-to-noise ratio of our measurements at 355 nm, we selected thioxanthone as a chromophore to replace the benzophenone chromophore (Chart 1). The thioxanthone derivative TX-^{15}T has similar dimensions as Bz-^{15}T from our previous study;[5] therefore, it is expected that similar host−guest complexes are formed involving two OA and one TX-^{15}T. Steady-state EPR experiments (Supporting Information, Figure S1) on TX-^{14}T showed that the rotational correlation time (τ_c)[5] increased from 0.14 ns in solution to 2.1 ns in the presence of OA. This increase is an indication of reduced mobility, which is consistent with incarceration of TX-^{14}T in OA. In addition, the coupling constant (a_N)[5] decreased from 16.7 G in solution to 16.0 G in the presence of OA. The decreased coupling constant indicates a decreased polarity of the environment surrounding the nitroxide, which is consistent with incarceration in the nonpolar interior of OA.

In this report, we demonstrate by TR-EPR that spin polarization of incarcerated nitroxides, TX-^{15}T@(OA)$_2$, can be generated by photoexcitation of the incarcerated thioxanthone chromophore. Furthermore, this spin polarization can then be transferred to a nitroxide (^{14}T⊕) in the bulk solution, and the kinetics of this transfer process can be directly followed by TR-EPR. In addition, we also show how this communication between an incarcerated guest and molecules in
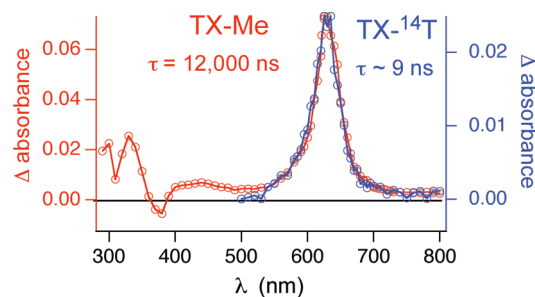
the bulk solvent can be controlled by supramolecular factors such as Coulombic attractions and repulsions between a charged guest@host complex and charged nitroxides in the bulk phase.

We performed transient triplet−triplet absorption measurements to determine the rate constant of intramolecular quenching of thioxanthone triplets by the covalently linked nitroxide. Figure 1 shows the transient absorption spectrum after excitation of TX-^{14}T in acetonitrile solutions with laser pulses at 355 nm (blue spectrum). This spectrum was assigned to triplet−triplet absorption of TX-^{14}T because of the nearly identical spectral shape compared with the triplet−triplet absorption spectrum of the related thioxanthone derivative (TX-Me, Chart 1), which does not contain the nitroxide quencher (Figure 1, red spectrum). In addition, unsubstituted thioxanthone shows a similar triplet−triplet absorption.[14,15] The diamagnetic TX-Me shows a triplet lifetime of 12 000 ns under our experimental conditions. However, the observed triplet lifetime of paramagnetic TX-^{14}T is three orders of magnitude shorter (∼9 ns). Fast intramolecular quenching of the TX triplet by the nitroxide clearly occurs.

Fast intramolecular quenching is required to produce significant strong spin-polarized TR-EPR signals. TR-EPR experiments were performed on TX-^{14}T in acetonitrile solutions using pulsed laser excitation (355 nm, 5 ns). An emissive spin-polarized nitroxide signal was observed with a polarization lifetime of 0.48 μs (Supporting Information, Figure S2). This emissive spin polarization of the nitroxide is expected by the spin polarization transfer mechanism,[9,10,13] where spin polarized triplet states of TX are generated by photoexcitation and intersystem crossing from the singlet excited state selectively to the highest of the three triplet state sublevels. The short-lived spin polarized triplet states of TX can transfer their spin polarization to nitroxides if the quenching process occurs within the lifetime of spin-polarized triplet states. The observed emissive spin polarization of nitroxides is consistent with the emissive spin polarization of triplet states of most aromatic ketones, such as benzophenone derivatives.[16]

TR-EPR experiments were performed on aqueous solutions of complexes of TX-^{15}T@(OA)$_2$ using pulsed laser excitation. The emissive spin-polarized ^{15}N-nitroxide spectrum (Figure 2b) is in good agreement with the steady-state spectrum (integrated form, Figure 2a). A relatively long spin polarization lifetime of 1.7 μs was observed in OA compared
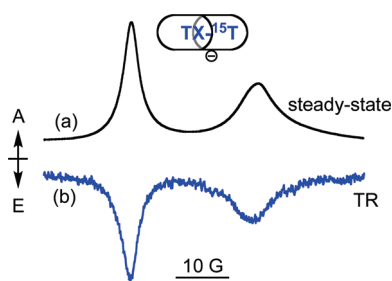
Figure 2. (a) Steady-state EPR (integrated form) and (b) TR-EPR spectra of TX-^{15}T@OA solutions recorded 0.8 to 1.3 μs after pulsed laser excitation (355 nm, 5 ns pulse width) in deoxygenated aqueous buffer solutions at room temperature. [TX-^{15}T] = 0.5 mM; [OA] = 1 mM; 10 mM borate buffer; pH 9.
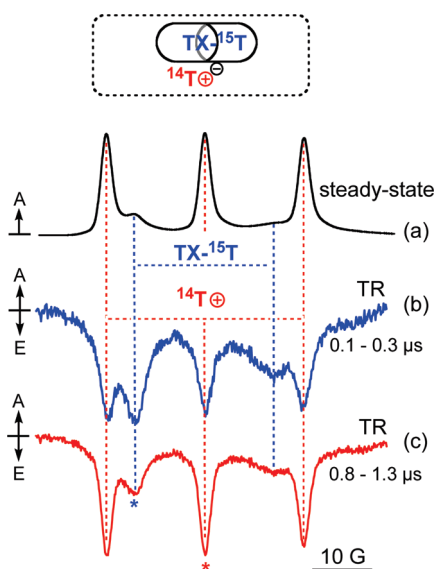

Figure 3. (a) CW-EPR (integrated form) and (b,c) TR-EPR spectra of TX-^{15}T@OA/^{14}T⊕ solutions recorded (b) 0.1 to 0.3 μs and (c) 0.8 to 1.3 μs after pulsed laser excitation (355 nm, 5 ns pulse width) in deoxygenated aqueous buffer solutions (pH 9) at room temperature. [^{14}T⊕] = 1 mM; [TX-^{15}T] = 0.5 mM; [OA] = 1 mM.

with acetonitrile solutions (0.48 μs), which is probably caused by the confinement of the nitroxide inside the OA cavity.

The addition of a positively charged external guest (^{14}T⊕) to the TX-^{15}T@(OA)$_2$ solution generated very different TR-EPR spectra. Figure 3b,c show the TR-EPR spectra at different observation time windows. At the earliest time window (0.1 to 0.3 μs after the laser pulse), the two-line signal of the internal guest, TX-^{15}T, is more significant (Figure 3b), whereas on later time scales (0.8 to 1.3 μs), the three-line signal of spin-polarized external guest, ^{14}T⊕, is more significant (Figure 3c). Figure 4 shows the kinetic traces of spin polarization of both internal and external guests. The rise time of the signal of the internal guest reflects the time it takes to generate spin polarization of TX-^{15}T by intramolecular triplet quenching in addition to the instrument's response time. The rise time of spin polarization of the external guest, ^{14}T⊕, is significantly delayed compared with that of TX-^{15}T. This delay is an indication of spin-polarization transfer from TX-^{15}T to ^{14}T⊕. In addition, the lifetime of TX-^{15}T spin polarization is shorter
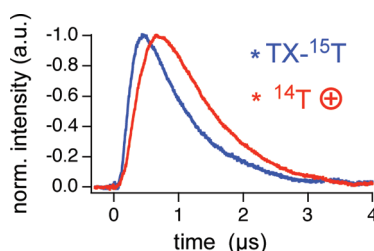

Figure 4. Transient EPR kinetic traces of TX-^{15}T@OA/^{14}T⊕ solutions recorded after pulsed laser excitation. For experimental details, see Figure 3. The field positions for the traces are marked with blue and red stars in Figure 3.
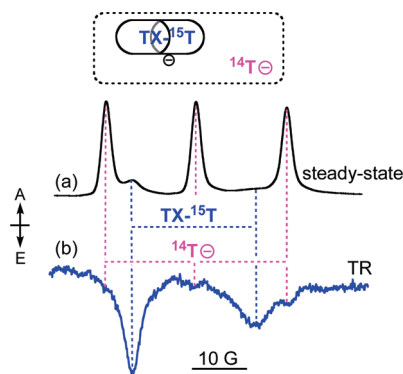

Figure 5. (a) CW-EPR (integrated form) and (b) TR-EPR spectra of TX-^{15}T@OA/^{14}T⊖ solutions recorded 0.8 to 1.3 μs after pulsed laser excitation (355 nm, 5 ns pulse width) in deoxygenated aqueous buffer solutions (pH 9) at room temperature. [^{14}T⊖] = 1 mM; [TX-^{15}T] = 0.5 mM; [OA] = 1 mM.

(0.76 μs) in the presence of ^{14}T⊕ compared with the absence of ^{14}T⊕ (1.7 μs) (Supporting Information, Figure S3a,c). This reduced lifetime shows that spin polarization of an incarcerated guest can be quenched by a nitroxide adsorbed on the outside of the OA capsuleplex.

Because OA capsuleplexes have a negatively charged external surface and ^{14}T⊕ is positively charged, Coulombic attraction increases the interaction of the external guest with the walls of the OA capsuleplexes. Previous steady-state EPR studies[5] showed a significant increase in rotational correlation time for ^{14}T⊕ in the presence of OA capsuleplexes (0.10 ns) compared with ^{14}T⊕ in water (0.025 ns). This increased correlation time is an indication of significant interactions of ^{14}T⊕ with the OA capsuleplex, which should increase spin-polarization transfer. However, if a negatively charged external guest (^{14}T⊖) is used, then Coulombic repulsion should prevent spin polarization transfer by repelling the ^{14}T⊖ from the capsuleplex wall. Figure 5 shows the EPR experiments of TX-^{15}T@(OA)$_2$ in the presence of 2 equiv of (^{14}T⊖). Whereas in the steady-state spectrum, the three-line spectrum of ^{14}T⊖ dominates (Figure 5a), almost exclusively the two-line spectrum of TX-^{15}T is detected in TR-EPR experiments (b). The near absence of the three-line component of ^{14}T⊖ in Figure 5b demonstrates that spin-polarization transfer from TX-^{15}T to ^{14}T⊖ is strongly inhibited by Coulombic repulsion. In addition, the spin polarization decay kinetics of TX-^{15}T are experimentally identical in the presence and absence of ^{14}T⊖ (Supporting

Information, Figure S3a,b), showing that quenching is insignificant. The above experiments demonstrate that spin—spin interactions can be enhanced by supramolecular binding resulting from Coulombic attractions or inhibited by Coulombic repulsions that prevent bonding.

Another way to inhibit spin—spin interactions is possible by substitutional entrapment of $^{14}T\oplus$ into another host. Previously, we have shown that $^{14}T\oplus$ forms supramolecular complexes with cucurbit[8]uril (CB8).[17] EPR experiments were performed of aqueous solutions of TX-$^{15}T@(OA)_2$, $^{14}T\oplus$, and CB8. The steady-state EPR spectrum is dominated by a broad signal probably caused by clustered complexes of $^{14}T\oplus@CB8$ (Supporting Information, Figure S4a). In contrast, the TR-EPR spectra show exclusively the two-line spectrum of spin-polarized TX-^{15}T (Supporting Information, Figure S4b,c). This two-line spectrum is experimentally indistinguishable from the TR-EPR spectrum in the absence of $^{14}T\oplus$ (Figure 2b). In addition, the spin-polarization lifetimes of the two systems are almost identical (TX-$^{15}T@(OA)_2$/$^{14}T\oplus@CB8$, $\tau = 1.6\ \mu s$; TX-$^{15}T@(OA)_2$, $\tau = 1.7\ \mu s$). The unchanged lifetime demonstrates that spin polarization transfer from TX-^{15}T to $^{14}T\oplus$ is inhibited by entrapment of $^{14}T\oplus$ in CB8 and removal from the OA surface.

In summary, TR-EPR experiments demonstrate that electron spin polarization from an incarcerated nitroxide can be transferred through the walls of the carcerand to a nitroxide in external bulk solvent. This communication between an incarcerated guest and molecules in the bulk solvent can be controlled by supramolecular factors such as Coulombic attraction and repulsion between the guest@host complex and charged molecules in the bulk solvent phase. In addition, this communication can be controlled by a secondary host (CB8) that traps external nitroxides from the bulk solvent and prevents communication with incarcerated nitroxides in OA capsuleplexes.

EXPERIMENTAL SECTION

Materials. For, origin and synthesis procedures, see the Supporting Information.

TR-EPR. TP-EPR experiments employed the pulses (355 nm, 5 ns) from a Spectra-Physics GCR 100 Nd/YAG laser, a Bruker ESP 300 X-band EPR spectrometer, and a PAR boxcar averager and signal processor (Models 4420 and 4402) to record time-resolved spectra or a Tektronics digitizer (TDS 360) to record polarization decay traces. Argon-saturated solutions were passed through a quartz flow cell (~0.3 mm thick) in the rectangular cavity of the EPR spectrometer. Further details are described elsewhere.[11]

Laser Flash Photolysis. Laser flash photolysis experiments employed the pulses from a Spectra-Physics GCR 100 Nd/YAG laser (355 nm, 5 ns) and a computer-controlled system that has been described elsewhere.[18] Solutions of TX-^{14}T and TX-Me were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength employed. We recorded transient absorption spectra by employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse.

SUPPORTING INFORMATION AVAILABLE
Synthesis procedures and analyses, experimental details, TR-EPR spectra of TX-^{14}T in acetonitrile, TR-EPR spectra of spectra of TX-$^{15}T@(OA)_2$/$^{14}T\oplus@CB8$. This material is available free of charge via the Internet at http://pubs.acs.org.

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