

# CIDEP from a Polarized Ketone Triplet State Incarcerated within a Nanocapsule to a Nitroxide in the Bulk Aqueous Solution

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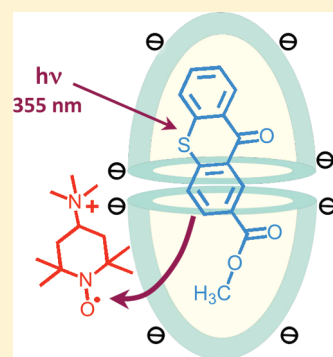
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 Supporting Information

**ABSTRACT:** Thioxanthone and benzil derivatives were incarcerated into an octa acid nanocapsule. Photoexcitation of these ketones generated electronic triplet excited states, which become efficiently quenched by positively charged nitroxides adsorbed outside on the external surface of the negatively charged nanocapsule. Although the triplet excited ketone and quencher are separated by a molecular wall (nanocapsule), quenching occurs on the nanosecond time scale and generates spin-polarized nitroxides, which were observed by time-resolved EPR spectroscopy. Because opposite signs of spin polarization of nitroxides were observed for thioxanthone and benzil derivatives, it is proposed that the electron spin polarization transfer mechanism of spin-polarized triplet states to nitroxides is the major mechanism of generating nitroxide polarization.

**SECTION:** Kinetics, Spectroscopy



Stable free radicals, such as nitroxides, are known to efficiently quench photoexcited triplet states of organic molecules.<sup>1</sup> Recently, we have shown that this quenching also occurs, although at a slower rate, if the photoexcited ketone is incarcerated inside of an organic container (octa acid) that separates the excited-state ketone and nitroxide by a molecular wall.<sup>2</sup> For this study, we used the cavitand termed “octa acid” (OA, Chart 1), which is known to incarcerate nonpolar molecules by forming a complex in aqueous solutions at basic pH.<sup>3</sup> It was established that relatively nonpolar ketones, such as 4,4′-dimethyl benzil (**1**, Chart 1), form a 2:1 complex with OA, where two OA molecules encapsulate one molecule of **1** (**1**@OA<sub>2</sub>).<sup>4</sup> The ketone **1** shows room-temperature phosphorescence with a lifetime of 596 μs when encapsulated inside of OA.<sup>2</sup> The phosphorescence of **1**@OA<sub>2</sub> was quenched efficiently by a positively charged nitroxide (T<sup>+</sup>, Chart 1) with a rate constant of  $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . We rationalized this high rate constant with the involvement of electrostatic attractions of the positively charged quencher (T<sup>+</sup>) and the negatively charged external surface of the OA capsule. No quenching of the phosphorescence of **1**@OA<sub>2</sub> was observed by the negatively charged nitroxide (T<sup>−</sup>, Chart 1) under our experimental conditions, which was rationalized by electrostatic repulsion between incarcerated **1** and T<sup>−</sup>. The upper limit for the rate constant of this quenching was estimated to be  $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , which is 4 orders of magnitude lower than the rate constant for quenching by T<sup>+</sup>.<sup>2</sup>

The quenching of triplet states of ketones by nitroxides often generates spin-polarized nitroxides, which had been observed by time-resolved electron paramagnetic resonance (TR-EPR) spectroscopy.<sup>5–7</sup> In these studies, the triplet quenching and spin polarization occurred during collisions of freely diffusing ketones and nitroxides or with the nitroxide that was covalently linked to

the ketone. In this Letter, we investigate whether spin polarization of nitroxides is also observable in quenching processes, where the triplet ketone and the nitroxide are separated by a molecular wall (OA).

As ketones, we selected 4,4′-dimethyl benzil (**1**) and the thioxanthone derivative **2** (Chart 1). Both ketones have been shown to form 2:1 complexes with OA.<sup>2,8</sup> Efficient triplet quenching of **1**@OA<sub>2</sub> by T<sup>+</sup> has been demonstrated by phosphorescence measurements.<sup>2</sup> Because **2**@OA<sub>2</sub> did not show measurable phosphorescence at room temperature, laser flash photolysis experiments were performed to establish the quenching efficiency of **2**@OA<sub>2</sub> triplet states by T<sup>+</sup>. Excitation of **2**@OA<sub>2</sub> with laser pulses (355 nm, 5 ns pulse width) generated the transient absorption spectrum shown in Figure 1 (left). This transient absorption with a maximum at 650 nm was assigned to the triplet state of **2** based on previous experiments in acetonitrile solution<sup>8</sup> and similarities with unsubstituted thioxanthone.<sup>9</sup> However, the triplet lifetime of **2** is strongly reduced (91 ns) in OA complexes compared to that in acetonitrile solutions (12 μs). This short triplet lifetime is assumed to be caused by quenching by the hydrogens present in the internal walls of OA.

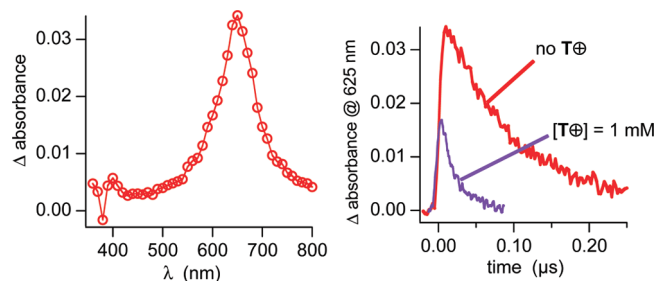
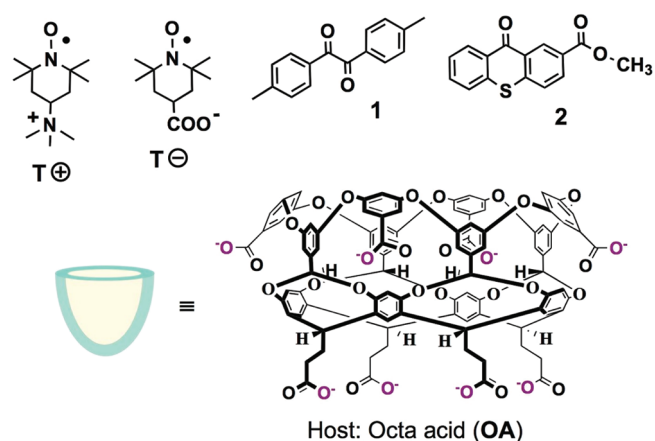
In the presence of two equivalents of T<sup>+</sup>, the absorbance of triplet states of **2** at the end of the laser pulse is reduced to approximately half of its value in the absence of T<sup>+</sup> (Figure 1, right). This indicates that **2**@OA<sub>2</sub> triplet states are quenched efficiently by T<sup>+</sup>. At a high enough ratio of T<sup>+</sup> to capsulepelexes (**2**@OA<sub>2</sub>), such as 20:1, the triplet quenching by T<sup>+</sup> dominates,

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Chart 1. Structures of Guest Molecules and Host



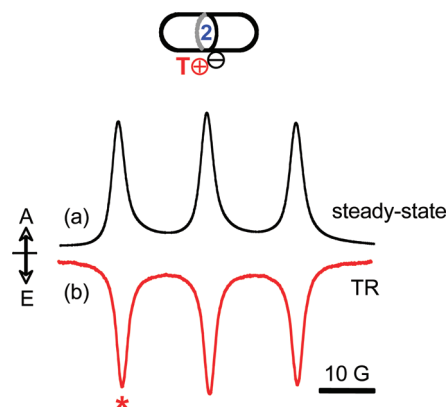
**Figure 1.** (Left) Triplet–triplet absorption spectrum of  $2@OA_2$  in deoxygenated aqueous buffer solution recorded at the end of the laser pulse (355 nm, 5 ns pulse width).  $[2] = 0.5$  mM;  $[OA] = 1$  mM; 10 mM borate buffer; pH = 9. (Right) Transient absorption decay traces at 625 nm in the absence and presence of  $T^+$  (1 mM).

and putative competing C–H quenching from OA should be negligible (see also Supporting Information, Figure S1).

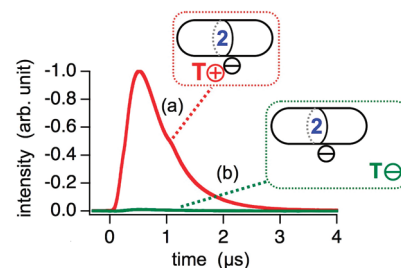
TR-EPR experiments were performed on aqueous solutions of complexes of  $2@OA_2$  in the presence of 20 equiv of  $T^+$  using pulsed laser excitation (355 nm). An emissive spin-polarized EPR spectrum was observed (Figure 2b). This observed TR-EPR spectrum is in good agreement with the steady-state EPR spectrum of the nitroxide (Figure 2a). TR-EPR experiments were performed at different concentrations of  $T^+$ . With increasing concentration of  $T^+$ , the TR-EPR signal increased and reached a plateau at an excess of above 20 equiv of  $T^+$  (see Supporting Information, Figure S2). A spin polarization lifetime of 650 ns was observed at low  $T^+$  concentrations (0.2 mM), which decreased slightly at higher  $T^+$  concentrations (550 ns, 10 mM  $T^+$ ; Figure 3a). The slight decrease in spin polarization lifetime is probably caused by spin–spin interactions at higher nitroxide concentrations.

TR-EPR experiments of  $2@OA_2$  in the presence of the negatively charged nitroxide ( $T^-$ ), in contrast to the positively charged  $T^+$ , generated no detectable spin-polarized EPR signal (Figure 3b). The absence of spin-polarized signals is consistent with inefficient triplet quenching caused by electrostatic repulsion of the negatively charged nanocapsule and negatively charged nitroxide.

The above experiments indicate that spin polarization of  $T^+$  is generated by static quenching of ketone triplet states by positively charged nitroxides adsorbed at the external surface of OA. A possible mechanism to generate spin polarization is the triplet



**Figure 2.** Steady-state EPR (a; integrated form) and TR-EPR (b) spectra of  $2@OA_2/T^+$  solutions recorded 300–500 ns after pulsed laser excitation (355 nm, 5 ns pulse width) in deoxygenated aqueous buffer solutions at room temperature.  $[2] = 0.5$  mM;  $[OA] = 1$  mM;  $[T^+] = 10$  mM; 10 mM borate buffer; pH = 9. The red star marks the field position for the kinetic trace shown in Figure 3.

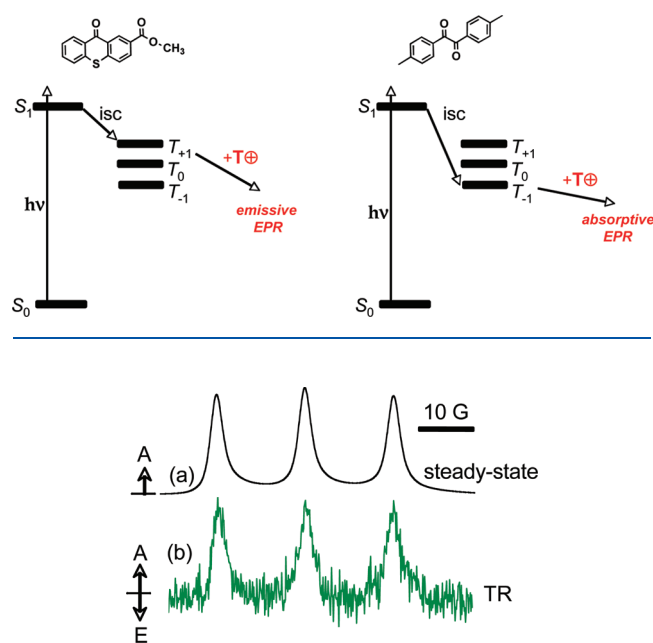


**Figure 3.** Transient EPR kinetic traces of  $2@OA_2/T^+$  (a, red) and  $2@OA_2/T^-$  (b, green) recorded after pulsed laser excitation.  $[2] = 0.5$  mM;  $[OA] = 1$  mM;  $[T^+] = 10$  mM;  $[T^-] = 10$  mM. For experimental details, see Figure 2. The field position for the traces are marked with a red star in Figure 2.

spin polarization transfer mechanism (Scheme 1),<sup>10</sup> where spin-polarized ketone triplet states are produced by triplet sublevel selective intersystem crossing from singlet excited states ( $S_1$ ). This polarization of ketone triplet states is transferred to the nitroxide by electron spin exchange and electron dipole–dipole interaction between the ketone triplet and the radical during the spin interaction process. Because the lifetime of spin polarization of triplet states is usually short (only several nanoseconds for ketones),<sup>11</sup> the observed fast static quenching of triplet states by positively charged  $T^+$  (observed by laser flash photolysis) and fast buildup of the spin-polarized EPR signal (Figure 3a) supports this mechanism. Because emissive spin-polarized triplet states are generated during intersystem crossing from singlet excited states of **2** (Scheme 1),<sup>12</sup> emissive spin-polarized nitroxides would be generated in this transfer mechanism. An alternative mechanism for generation of polarization is the radical–triplet pair mechanism. This mechanism involves the interaction of nonpolarized triplets and doublets (nitroxides), involving the zero-field splitting of the triplet and the hyperfine interaction-mediated mixing of quartet and doublet states.<sup>7</sup> Both mechanisms would generate emissive spin-polarized nitroxides for interaction with triplet states of **2**.

One can distinguish between the triplet spin polarization transfer mechanism and the radical–triplet pair mechanism by measuring TR-EPR of  $1@OA_2$  in the presence of  $T^+$ . In contrast to **2**,

**Scheme 1. Triplet Sublevel Selective Intersystem Crossing Generating Spin-Polarized Triplet States**



**Figure 4.** Steady-state EPR (a; integrated form) and TR-EPR (b) spectra of  $1@OA_2/T^+$  solutions recorded 100–300 ns after pulsed laser excitation (308 nm, 15 ns pulse width) in deoxygenated aqueous buffer solutions at room temperature.  $[1] = 0.5$  mM;  $[OA] = 1$  mM;  $[T^+] = 10$  mM; 10 mM borate buffer; pH = 9.

which generates emissive spin-polarized triplet states ( $T_{+1}$ ) during intersystem crossing from singlet excited states ( $S_1$ ), triplet states of **1** are absorptively polarized after photoexcitation ( $T_{-1}$ ) (Scheme 1).<sup>12</sup> If the triplet spin polarization transfer mechanism is active during quenching of triplet states of  $1@OA_2$  by  $T^+$ , absorptive spin-polarized nitroxides should be observed. If the radical–triplet pair mechanism dominates, emissive spin polarization of nitroxides should be observed. Figure 4 shows the TR-EPR spectrum after laser excitation of  $1@OA_2$  in the presence of  $T^+$ . Because the TR-EPR signal of the nitroxide is absorptively polarized, we conclude that the triplet spin polarization transfer mechanism is responsible. The significantly lower signal-to-noise ratio for  $1@OA_2/T^+$  (Figure 4b) compared to that of  $2@OA_2/T^+$  (Figure 2b) is caused by the poor excitation light absorption of **1** compared to that of **2**.

In summary, TR-EPR and transient absorption measurements demonstrate that triplet states of ketones (**1** and **2**) incarcerated in a nanocontainer (OA) are quenched efficiently by nitroxides in the bulk solution. This quenching of an incarcerated guest triplet state by molecules in the bulk solvent can be controlled by supramolecular factors such as Coulombic attraction and repulsion between the guest@host complex and charged quencher molecules in the bulk solvent phase. In the case of the positively charged nitroxide ( $T^+$ ) as the quencher, charge attraction to the negatively charged host surface causes efficient static quenching of incarcerated guest triplet states generating the TR-EPR signal of spin-polarized nitroxides. Because opposite signs of spin polarization of nitroxides were observed for thioxanthone and benzil derivatives, we conclude that the electron spin polarization transfer mechanism of spin-polarized triplet states to nitroxides is the major operating mechanism for generation of polarized nitroxides.

## EXPERIMENTAL SECTION

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

**TR-EPR.** TR-EPR experiments employed the pulses from a Spectra-Physics GCR 150-30 Nd:YAG laser (355 nm, 5 ns) or a Lambda Physik Lextra 50 excimer laser (308 nm, 15 ns), 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 ( $\sim 0.3$  mm optical path length) in the rectangular cavity of the EPR spectrometer. Further details are described elsewhere.<sup>13</sup>

**Laser Flash Photolysis.** Laser flash photolysis experiments employed the pulses from a Spectra-Physics GCR 150-30 Nd:YAG laser (355 nm, 5 ns) and a computer-controlled system, which has been described elsewhere.<sup>14</sup>

## ASSOCIATED CONTENT

**Supporting Information.** Origin of materials, experimental details, and additional TR-EPR and transient absorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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